Some features of the packing modes of carboxylic acids are discussed. Monocarboxylic acids R–CO₂H, containing residues R, which are either nonchiral or racemic, almost invariably form cyclic hydrogen-bonded pairs. If the R group is small, the molecules may interlink by single O–H⋯O bonds to form a chain motif in which the O–H⋯O(carboxyl) bond is almost linear, the C–O⋯(H)O angle ≈ 130°, and the O–H proton donor lies in the plane of the carbonyl system O=C<, to which it is hydrogen-bonded. Monocarboxylic acids with chiral residues and which are enantiomeric show some tendency to form a hydrogen-bonded chain motif along a twofold screw axis. The angular geometry of this O–H⋯O bond shows considerable variation and seems to be dependent upon the van der Waals contacts between the R groups along the hydrogen-bonded chain. Dicarboxylic acids HO₂C–R–CO₂H form extended chains, the carboxyl groups being interlinked by O–H⋯O bonds into cyclic pairs. This arrangement is adopted, almost without exception, for all types of R groups. Carboxylic acids, in which the intramolecular environments of the two carboxyl O atoms are identical, may show orientational disorder of the carboxyl group in the crystal. This depends on the intermolecular environment of the carboxyl dimer. Belonging to this category are p-substituted benzoic acids, which almost invariably adopt the packing motif in which the carboxyl dimers lie side by side with a neighbouring phenyl ring on the same plane and are separated from each other by C–H⋯O contacts of ≈ 3.5 Å. This arrangement is conducive to disorder of the carboxyl dimer. The benzoic acids, and indeed many planar acids, form stacks in which the direction of offset between the carboxyl groups lies either along the carbonyl C=O bond or the hydroxyl C–OH bond. The carboxyl group in these two stacking types may show disorder of the carboxyl dimer, suggesting that the energy difference between the two stacking types is small. Carboxylic acids also form interplanar contact via an antiparallel arrangement of C–O bonds which may be either C=O or C–OH bonds or a disordered combination thereof. Intramolecular forces probably favour the synplanar C=C=C=C=O conformation in the α,β-unsaturated acids R–CH=CH–CO₂H. The antiplanar C=C=C=C=O form may be induced by intermolecular forces. Orientational disorder between the syn- and antiplanar C=C=C=C=O conformations may be induced by the stacking forces of the carboxyl dimers. The observed antiplanar C=C=C=C=O conformation in a number of acids has been associated with a motif containing a lateral C–H⋯O(carboxyl) contact ≈ 3.5 Å. The few known crystal structures of carboxylic acids containing an acetylenic C–H proton donor have not shown acetylenic C–H⋯O(carboxyl) interactions which are strikingly short. Indeed, but-3-ynoic acid shows only a ≈ C=H⋯C≡C contact. The minimum van der Waals distance between carboxyl O atoms appears to be dependent upon their direction of approach. Hydroxyl O atoms which make contact so that their C–O(H) bonds are almost collinear (C–O⋯C–O), may approach each other to within 2.9 Å. Carbonyl and hydroxyl O atoms which are arranged so that their electron lone-pair lobes are directed at each other do not make contact less than 3.5 Å.

1. Introduction

This work is part of a programme concerned with the systematics of packing of hydrogen-bonded groups. The scope of this paper encompasses principal features of the molecular packing modes of carboxylic acids R–CO₂H in the crystalline state. Much information of chemical interest is hidden in crystal structures because they represent minimum energy arrangements, and whereas little can be inferred from a single structure, certain trends become apparent if enough structures are available. Our precise purpose, therefore, lies in the detection of the primary molecular interactions present in carboxylic acid structures. The paper is divided into three sections. Firstly, we consider the geometry of the carboxyl group, and its conformational properties with respect to the attached residue R. Secondly, we describe the various modes of interlinking carboxylic acids by hydrogen bonds and finally we consider the packing environment about the hydrogen-bonded carboxyl dimer.

2. The carboxyl group

2.1. Geometry of the carboxyl group

Major geometric features of the carboxyl group in a number of crystal structures are listed in Table I. The molecules chosen were those in which there is no ori-
entational disorder of the carboxyl group in the crystal. The average bond lengths and angles are C=O 1.21, C-O(H) 1.31, O-H (neutrons) 1.00 Å, O=C–O 123°. The O–H angle lies between 110–114.5° (neutrons). The O–H group has been observed, in the crystalline phase, to adopt either a synplanar (1a) or antiplanar (1b) O=C–O–H conformation. According to the infra-red spectrum of gaseous monomeric formic acid (Miyazawa & Pitzer, 1959), the synplanar structure is the more stable conformer by 2 kcal mole−1; indeed, microwave studies (Lide, 1964) have indicated this difference to be at least 4 kcal mole−1. These findings are consistent with the observation that the antiplanar O=C–O–H form (1b) occurs only when the O–H bond participates in an intramolecular O–H⋯O bond, particularly in 1,2-disubstituted dicarboxylic acids as shown in (2). The crystal structure of o-methoxybenzoic acid (Gopalakrishna & Cartz, 1972) is a rare excep-

Table 1. Bond lengths (Å) and angles (°) of carboxyl groups with no orientational disorder

<table>
<thead>
<tr>
<th>Compound</th>
<th>C=O</th>
<th>C-OH</th>
<th>O-H</th>
<th>O=C–O</th>
<th>C-O–H</th>
<th>Method*</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formic acid (formic acid: formamide)</td>
<td>1.202</td>
<td>1.320</td>
<td>125.4</td>
<td></td>
<td></td>
<td>X</td>
<td>Nahrungbauer &amp; Larsson (1968)</td>
</tr>
<tr>
<td>Acetic acid at -140°C</td>
<td>1.206</td>
<td>1.321</td>
<td>121.9</td>
<td>110.5</td>
<td></td>
<td>N</td>
<td>Jönsson (1971)</td>
</tr>
<tr>
<td>Acetic acid (acetic acid: phosporic acid)</td>
<td>1.226</td>
<td>1.319</td>
<td>121.3</td>
<td></td>
<td></td>
<td>X</td>
<td>Jönsson (1970)</td>
</tr>
<tr>
<td>β-Tetronic acid</td>
<td>1.230</td>
<td>1.302</td>
<td>0.99</td>
<td>121.5</td>
<td>110.0</td>
<td>N</td>
<td>Jönsson (1972)</td>
</tr>
<tr>
<td>Oxalic acid dihydrate</td>
<td>1.234</td>
<td>1.303</td>
<td>121.4</td>
<td></td>
<td></td>
<td>X</td>
<td>Jönsson (1972)</td>
</tr>
<tr>
<td>Oxalic acid (oxalic acid: acetamide)</td>
<td>1.204</td>
<td>1.310</td>
<td>122.9</td>
<td></td>
<td></td>
<td>X</td>
<td>Benghiat &amp; Leiserowitz (1972a)</td>
</tr>
<tr>
<td>Oxalic acid (oxalic acid: furamide)</td>
<td>1.212</td>
<td>1.291</td>
<td>1.03</td>
<td>126.6</td>
<td>114.4</td>
<td>N</td>
<td>Delaplane &amp; Ibers (1969)</td>
</tr>
<tr>
<td>Fumaric acid</td>
<td>1.212</td>
<td>1.298</td>
<td>126.2</td>
<td></td>
<td></td>
<td>X</td>
<td>Leiserowitz &amp; Nader (1972)</td>
</tr>
<tr>
<td>Maleic acid</td>
<td>1.201</td>
<td>1.301</td>
<td></td>
<td>126.2</td>
<td></td>
<td>X</td>
<td>Huang, Leiserowitz &amp; Schmidt (1973)</td>
</tr>
<tr>
<td>o-Chlorobenzoic acid</td>
<td>1.202</td>
<td>1.312</td>
<td>1.00</td>
<td>123.2</td>
<td>110.2</td>
<td>N</td>
<td>Ellison, Johnson &amp; Levy (1971)</td>
</tr>
<tr>
<td>(-)-o-Carboxyphenyl methyl sulphoxide</td>
<td>1.202</td>
<td>1.314</td>
<td></td>
<td>123.2</td>
<td></td>
<td>X</td>
<td>Pipper (1971)</td>
</tr>
<tr>
<td>(+)-o-Carboxyphenyl methyl sulphoxide</td>
<td>1.209</td>
<td>1.310</td>
<td>124.0</td>
<td></td>
<td></td>
<td>X</td>
<td>Benghiat et al. (1972)</td>
</tr>
<tr>
<td>o-Ethoxybenzoic acid</td>
<td>1.208</td>
<td>1.295</td>
<td>124.5</td>
<td></td>
<td></td>
<td>X</td>
<td>Okaya, Stemple &amp; Kay (1966)</td>
</tr>
<tr>
<td>2,3-Dimethylbenzoic acid</td>
<td>1.214</td>
<td>1.318</td>
<td></td>
<td>122.0</td>
<td></td>
<td>X</td>
<td>Ringertz (1971)</td>
</tr>
<tr>
<td>(-)-o-Carboxyphenyl methyl sulphoxide</td>
<td>1.214</td>
<td>1.332</td>
<td></td>
<td>118.3</td>
<td></td>
<td>X</td>
<td>James &amp; Williams (1974)</td>
</tr>
<tr>
<td>(++)-o-Carboxyphenyl methyl sulphoxide</td>
<td>1.214</td>
<td>1.313</td>
<td></td>
<td>121.7</td>
<td></td>
<td>X</td>
<td>Ferguson &amp; Sim (1961)</td>
</tr>
</tbody>
</table>

* X = X-ray diffraction, N = neutron diffraction.
assumed by Leiserowitz & Schmidt (1965) that the preferred conformation was determined by the non-bonded interactions between C\(\beta\) and its attached H atoms on the one hand, and the hydroxyl or carbonyl O atoms on the other. Mainly because of the difference between the angles C\(^\alpha\)-C-O and C\(^\gamma\)-C-O(H) the non-bonded distances C\(^\alpha\)···O and H\(^\beta\)···O are 0.1-0.2 Å larger for the usual synplanar than for the alternative antiplanar conformation (4\(b\)). The synplanar rule does not apply to the \(\alpha,\beta\)-unsaturated acids R-CH=CH-CO\(\_\)OH, there are several molecules showing the antiplanar C\(^\alpha\)=C-C=O form. Dunitz & Strickler (1968) accounted for the observed antiplanar C=C-C=O conformation by regarding the double bonds as being deformed into two bent bonds. Thus the antiplanar C=C-C=O conformation, i.e. the synplanar C=C-COH conformer, would correspond to the energetically favoured staggered disposition of bonds. Dunitz & Strickler concluded that these two factors, non-bonded interactions and the preference for staggered rather than eclipsed disposition of bonds, are both operating in favour of the synplanar conformation C=C-C=O in saturated systems. If C\(^\alpha\)-C\(^\beta\) is a double bond, then the first factor favours synplanarity, the second antiplanarity. The correctness of this approach of taking into account interaction between bonds is borne out by a comparison of the conformational properties of \(\beta\)-substituted trans-unsaturated acids R-CX=CH-CO\(\_\)H as a function of the size of the atom substituent X on the \(\beta\)-carbon. In allenedicarboxylic acid HO\(\_\)C-CH=CH-CO\(\_\)H, where the X substituent is absent, the molecule exhibits an antiplanar C=C-C-O conformation, both in its own structure (Leiserowitz & Nader, 1973) [C-O 1.22, C-O(H) 1.29 Å] and in its complex with acetamide (Nader, 1976). Molecules containing \(\beta\)-substituents such as Cl, e.g. \(\beta\)-chloro-trans-cinnamic acid (Filippakis, Leiserowitz, Rabinovich & Schmidt, 1972), or CH\(_3\), e.g. vitamin A acid (Stam, 1972), exhibit the synplanar C=C-C=O conformation.

All the unsaturated carboxy-esters R-CH=CH-CO\(\_\)CH\(_3\) listed in Table 2 exhibit the synplanar C=C-C=O arrangement. This feature must be due primarily to intramolecular forces only since the packing environments about the carboxy-ester groups in these crystal structures differ from each other. This point is highlighted by the stacking arrangements of monomethyl fumarate (Leiserowitz & Tang, 1976) and monomethyl trans,trans-muconate (Rabinovich & Schmidt, 1967) (Figs. 1 and 2); in the fumarate the carboxy-ester groups are stacked with an offset mainly along the carbonyl C=O bonds (5a) whereas in the muconate the offset is along the C-O(CH\(_3\)) bond (5b).

Table 2. Conformations of \(\alpha,\beta\)-trans unsubstituted carboxylic acids and esters about the carboxyl carbon–carbon bond and their C=O bond lengths (Å)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Conformation</th>
<th>C=C-O</th>
<th>C-OH</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monomethyl fumarate, ester group</td>
<td>syn</td>
<td>1.98</td>
<td>1.328</td>
<td>Leiserowitz &amp; Tang (1976)</td>
</tr>
<tr>
<td>acid group</td>
<td>anti+ disorder</td>
<td>1.246</td>
<td>1.276</td>
<td></td>
</tr>
<tr>
<td>Monomethyl trans,trans-muconate</td>
<td>syn</td>
<td>1.17</td>
<td>1.38</td>
<td>Rabinovich &amp; Schmidt (1967)</td>
</tr>
<tr>
<td>ester group</td>
<td>anti</td>
<td>1.23</td>
<td>1.31</td>
<td>Filippakis, Leiserowitz &amp; Schmidt (1967)</td>
</tr>
<tr>
<td>acid group</td>
<td>syn</td>
<td>1.203</td>
<td>1.338</td>
<td>Leiserowitz &amp; Schmidt (1965)</td>
</tr>
<tr>
<td>Dimethyl trans,trans-muconate</td>
<td>syn</td>
<td>1.19</td>
<td>1.41</td>
<td>Leiserowitz &amp; Schmidt (1965)</td>
</tr>
<tr>
<td>Methyl m-bromocinnamate</td>
<td>syn</td>
<td>1.19</td>
<td>1.32</td>
<td>Leiserowitz &amp; Schmidt (1965)</td>
</tr>
<tr>
<td>Methyl p-bromocinnamate</td>
<td>syn</td>
<td>1.24†</td>
<td>1.30</td>
<td>Higgs &amp; Sass (1963), Chatani, Sakata &amp; Nitta (1963)</td>
</tr>
<tr>
<td>Acrylic acid</td>
<td>syn</td>
<td>1.237</td>
<td>1.297</td>
<td>Robertson &amp; Sutherland (1964)</td>
</tr>
<tr>
<td>Crotonic acid</td>
<td>syn</td>
<td>1.240</td>
<td>1.310</td>
<td>Robertson &amp; Sutherland (1964)</td>
</tr>
<tr>
<td>Sorbic acid</td>
<td>syn</td>
<td>1.24</td>
<td>1.30</td>
<td>Filippakis &amp; Schmidt (1967)</td>
</tr>
<tr>
<td>trans-(\beta)-2-Furylacrylic acid</td>
<td>syn</td>
<td>1.22</td>
<td>1.31</td>
<td>Block, Filippakis &amp; Schmidt (1967)</td>
</tr>
<tr>
<td>trans-(\beta)-2-Thienylacrylic acid, (\beta)-form</td>
<td>syn+ disorder</td>
<td>1.25</td>
<td>1.29</td>
<td>Block, Filippakis &amp; Schmidt (1967)</td>
</tr>
<tr>
<td>trans-(\beta)-2-Thienylacrylic acid, (\gamma)-form</td>
<td>syn+ disorder</td>
<td>1.22</td>
<td>1.30</td>
<td>Koch (1972)</td>
</tr>
<tr>
<td>trans-(\beta)-Ionylidene crotonic acid</td>
<td>syn+ disorder</td>
<td>1.256</td>
<td>1.287</td>
<td>Schenk (1972)</td>
</tr>
<tr>
<td>3-(1,1,5-Trimethyl-5-cyclohexen-6-yl)-proenoic acid</td>
<td>syn+ disorder</td>
<td>1.257</td>
<td>1.275</td>
<td>Bernstein &amp; Leiserowitz (1972)</td>
</tr>
<tr>
<td>trans,trans-Muconic acid, molecule A</td>
<td>syn+ syn</td>
<td>1.236</td>
<td>1.294</td>
<td></td>
</tr>
<tr>
<td>trans,trans-Muconic acid, molecule B</td>
<td>syn+ syn</td>
<td>1.297</td>
<td>1.275</td>
<td></td>
</tr>
<tr>
<td>trans,trans-Muconic acid*</td>
<td>syn</td>
<td>1.209</td>
<td>1.310</td>
<td>Benghiat et al. (1972)</td>
</tr>
<tr>
<td>Fumaric acid</td>
<td>syn</td>
<td>1.245</td>
<td>1.283</td>
<td>Martuscelli (1969)</td>
</tr>
<tr>
<td>Octa-2,6-(\beta)-trans,trans-dienedioic acid</td>
<td>syn+ disorder</td>
<td>1.261</td>
<td>1.261</td>
<td>Martuscelli &amp; Mazzarella (1969)</td>
</tr>
<tr>
<td>Octa-2,6-(\beta)-cis,trans-dienedioic acid at the trans end of the molecule</td>
<td>disorder</td>
<td>1.22</td>
<td>1.29</td>
<td>Brown (1966)</td>
</tr>
<tr>
<td>Fumaric acid, monoclinic form</td>
<td>anti</td>
<td>1.22</td>
<td>1.29</td>
<td>Bednowitz &amp; Post (1966)</td>
</tr>
<tr>
<td>Fumaric acid, triclinic form</td>
<td>anti</td>
<td>1.228</td>
<td>1.290</td>
<td></td>
</tr>
<tr>
<td>Fumaric acid (fumaric acid: (\beta)-picoline N-oxide)</td>
<td>syn</td>
<td>1.19</td>
<td>1.33</td>
<td>Gorres, McAfee &amp; Jacobson (1975)</td>
</tr>
<tr>
<td>trans-Cinnamic acid</td>
<td>anti</td>
<td>1.22</td>
<td>1.30</td>
<td>Ladell, McDonald &amp; Schmidt (1956)</td>
</tr>
<tr>
<td>(p)-Chloro-trans-cinnamic acid</td>
<td>disorder</td>
<td>1.263</td>
<td>1.264</td>
<td>Glusker, Zacharias &amp; Carrell (1975)</td>
</tr>
</tbody>
</table>

* The C=C-C=O conformation in trans,trans-muconamic acid is shown to be synplanar in §3.2.3.
† The C-O bond lengths were averaged from two crystal structure analyses.
In the \(\alpha,\beta\)-unsaturated carboxylic acids \(R-CH=CH-CO_2H\) the picture does not appear to be clear-cut. Of the 21 acids listed in Table 2, 13 lie in the synplanar form, 5 in the antiplanar form, and 3 show pronounced orientational disorder of the carboxyl group. These results indicate that the conformation of the carboxyl group is determined by a combination of inter- and intramolecular forces. The questions arising from these observations are, firstly, which conformation is preferred by intramolecular forces only and secondly, what are the intermolecular forces which play a role in determining the conformation of the carboxyl group?

As regards the first question, there is little doubt that intramolecular forces lead to a preference for the synplanar conformation \(C=C-C=O\) in the esters \(R-CH=CH-CO_2CH_3\). Let us then compare the molecular geometries of the fragment \(-CH=CH-CO_2\) in analogous ester and acid molecules. The acid and ester fragments were chosen from fumaramic acid (Benghiet, Kaufman, Leiserowitz & Schmidt, 1972) and monomethyl fumarate (Leiserowitz & Tang, 1976), respectively. The bond lengths and angles are shown in Fig. 3(a) and (b).

The average scatter from the mean of 0.005 Å in bond length and 0.7° in angle between the two fragments indicates that their intramolecular force fields are similar to each other. This similarity is consistent with the fact that most of the carboxylic acid molecules listed in Table 2 are in the synplanar \(C=C-C=O\) conformation, implying that intramolecular forces show a preference, albeit slight, for the synplanar conformer. Moreover we shall show later that all the molecules listed in Table 2 which exist in the antiplanar form have similar packing environments about their carboxyl groups and that their antiplanar \(C=C-C=O\) conformations are probably induced by intermolecular forces.

In the \(o\)-substituted benzoic acids (6) the \(o\)-substituent \((=F, CH_3, Cl, Br)\) makes contact with the carbonyl O atom except for \(o\)-fluorobenzoic acid (Krausse & Dunken, 1966). Its C-O lengths of 1.255 and 1.280 Å indicate a pronounced measure of disorder of the carboxyl group. Obviously the relatively bulky substituents Br, Cl and CH_3 in (6) preclude disorder of the carboxyl groups. That this disorder in \(o\)-fluorobenzoic acid is enhanced by intermolecular forces will be brought out later.

\[
\begin{align*}
X=F \quad \text{(Krausse & Dunken, 1966)}
\quad &
X=CH_3 \quad \text{(Smith, Florencio & Garcia-Blanco, 1971)}
\quad &
X=Cl \quad \text{(Ferguson & Sim, 1961)}
\quad &
X=Br \quad \text{(Ferguson & Sim, 1962)}
\end{align*}
\]
3. Modes of interlinking carboxyl groups via the O–H⋯O bond

Carboxylic acid molecules R–CO₂H may be interlinked to form either the cyclic hydrogen-bonded dimer (7), which is the most commonly observed motif in the solid state, or the rarely encountered catemer* motif (8) in which each carboxyl group is linked to two neighbours via single O–H⋯O(carbonyl) bonds. We shall analyse in this section the various ways in which carboxyl groups may be linked to form the catemer as well as account for its rare occurrence in the solid.

3.1. The catemer motif

The catemer motif (8) consists of carboxylic acid molecules related to each other in the crystal by space symmetry. We shall make use of only those symmetry elements which occur most frequently in molecular crystals, namely translation, the twofold screw axis, and the glide, and neglect n-fold screw axes (n=3,4,6) which are rarely encountered.

Catemer motifs may be constructed for both the syn- as well as the antiplanar O=C–O–H conformer. Two postulated arrangements incorporating the antiplanar O=C–OH conformer are shown in (9a) and (9b). The O–H⋯O=C bond in (9a) is approximately collinear, in (9b) the C=O⋯O angle is variable. While similar packing modes occur in the crystal structures of secondary amides, RCONHX, as shown in motifs (10a) and (10b), the catemer motifs (9) have not been encountered in carboxylic acid structures, presumably because of the unfavourable antiplanar O=C–OH conformer.

Assuming the synplanar O=C–O–H conformer we may formulate three distinct hydrogen-bonding packing modes shown in (11a), (11b) and (11c). The molecules are related by 2₁ axes (or glides) in all three arrangements. Motif (11a) is a hydrogen-bonded coplanar system in which the O–H proton donor points almost at the carbonyl O acceptor atom with a C=O⋯O(H₂O) angle close to 120° yielding a translation axis of ~5 Å. At first sight this arrangement does not appear unreasonable. Indeed amide groups in the crystal structures of adipamide (Hospital & Housty, 1966) and of the β-form of o-chlorobenzamide (Kato, Takaki & Sakurai, 1974) are arranged in a very similar pattern as shown in (12) with the primary difference that along the 5 Å twofold screw axis of adipamide and o-chloro-
benzamide the amide groups are linked by N-H-..O bonds of ~2.95 Å, which are replaced in the carboxylic acid motif (11) by a van der Waals contact of similar length between the carbonyl and hydroxyl O atoms.

This short O-..O distance of 2.95 Å would not be unusual; distances in the range 2.9-3.1 Å have been observed in the crystal structures of fumaric acid (Brown, 1966; Bednowitz & Post, 1966), furane-α,α'-dicarboxylic acid (Martuscelli & Pedone, 1968), and maleic acid (James & Williams, 1974) between hydroxyl O atoms, as shown in (13). The electron lone-pair lobes of these hydroxyl O atoms (assuming sp³ hybridization) are not directed at each other.

However, a short contact of 3 Å between carbonyl and hydroxyl O atoms would be unfavourable in the catemer (11a). This is borne out by the crystal structure of the benzamide-succinic acid complex (Huang, Leiserowitz & Schmidt, 1973), from which it was deduced that O lone-pair-..O lone-pair interactions do not permit an approach less than 3.5 Å between two O atoms of neighbouring carboxyl groups arranged as in motif (11a), the lone-pair lobes of the carbonyl and hydroxyl O atoms being partially directed towards each other. Benzamide and succinic acid form a centrosymmetric 2:1 complex unit (Fig. 4) via the hydrogen-bond pairing of their carboxyl and amide groups. These complex units are interlinked, along a 5 Å axis, by N-H-..O bonds of 3.0 Å between the benzamide molecules. The carboxyl-amide pair is distorted; the twist angle between the planes of the carbonyl and amide groups is 20°. By means of this distortion a separation of 3.6 Å is achieved between the carbonyl and hydroxyl O atoms of the carboxyl groups related by the 5 Å axis. Were the carboxyl group coplanar with the amide group, then the separation between the O atoms would be 3.0 Å, i.e. the interpair N-H-..O distance.

The unfavourable O-..O separation of 3 Å in the planar motif (11a) may be increased by rotating the carboxyl group about its C-C bond by an angle of ~20° out of the hydrogen-bonding plane to achieve an arrangement of carboxyl groups as in the benzamide-succinic acid complex, as well as by changing the tilt of the carboxyl group about an axis perpendicular to its plane. However, these changes would reduce the linearity of the O-H-..O bond and increase the C=O-..(H)O angle. Nevertheless such a hydrogen-bond motif has been observed in the crystal structure of the enantiomeric 2-b-methyloctadecanoic acid (Abrahamsson, 1959a) in which the molecules are hydrogen-bonded along a 2₁ axis of 5.0 Å. Only the xz projection was reported, yet it clearly shows that the plane of the carboxyl group is appreciably tilted with respect to the 5 Å axis. On the other hand, the racemic 2-DL-methyloctadecanoic acid (Abrahamsson, 1959b) exists as hydrogen-bonded dimers (7). Its aliphatic chains are close-packed along a 5 Å axis as in the chiral structure which is indicative of the adjustment of the hydrogen bond of the enantiomeric structure to the requirements of close-packing of aliphatic chains along the 5 Å axis.

The poor contact between O atoms in motif (11a) may be improved while maintaining a planar hydrogen-bonded system and a linear O-H-..O bond by simply increasing the C=O-..O angle from the initial value, of ~130°, to 180°, yielding a collinear O-H-..O-C bond shown in motif (11b), which has a translation axis of ~6.3 Å. Although the collinear hydrogen bond is commonly observed in amides (N-H-..O-C),
quite the opposite is true for the O-H...O=C bond, particularly in carboxylic acids. An approximately collinear O-H...O=C hydrogen bond exists in the structure of enantiomeric (R)-(+)-2,2-diphenyl-1-methylcyclopropane carboxylic acid (Lin, Paul & Curtin, 1974), which forms the catemer motif (11b) along a 2_1 axis of 6.3 Å. Walborsky, Barash, Young & Impastato (1961) had originally deduced from infrared measurements that these enantiomeric 2,2-diphenylcyclopropane carboxylic acids (14) exist as hydrogen-bonded catemers in the crystal whereas the racemate exists as dimers. The enantiomer (-)-2-methyl-2-ethyl-

![Image](image_url)

forms cyclic hydrogen-bonded pairs with an O-H...O(carbonyl) distance of 2.674 Å. Derissen & Smit pointed out that despite the observation that the O-H...O distance is shorter in the β-modification (2.674 vs. 2.702 Å) and furthermore that the hydrogen-bonding angles in the β-form are more favourable, the α-form is nevertheless the more stable of the two. The reported heats of sublimation for α- and β-oxalic acid are 23.45 and 22.28 kcal mole^-1 (Bradley & Cotson, 1953). The preferred stability of α-oxalic acid may be due in part to its O-H...O(hydroxyl) interaction.

The third catemer motif (11c) contains a linear O-H...O bond with a C=O-HO angle of ~120° and a translation axis of ~7-0 Å. This motif has been observed in a limited number of monocarboxylic acids, namely formic acid (Holtzberg, Post & Fankuchen, 1953), acetic acid (Jönsson, 1971; Nahringbauer, 1970) and β-tetrolic acid (Benghiat & Leiserowitz, 1972a). Both formic and acetic acids appear in planar hydrogen-bonded arrays via glides of axial lengths 6.5 and 7.0 Å, respectively.

Table 3. Hydrogen-bond distances (Å) and angles (°) in formic, acetic and β-tetrolic acids

<table>
<thead>
<tr>
<th></th>
<th>O-H-O</th>
<th>C-O-H</th>
<th>C=O-(H)O</th>
<th>C-O(H)-O</th>
<th>Method*</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formic acid</td>
<td>2.58</td>
<td>122</td>
<td>114</td>
<td>X</td>
<td>X-rays</td>
<td>Holtzberg, Post &amp; Fankuchen (1953)</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>2.631</td>
<td>110.5</td>
<td>133.2</td>
<td>119.6</td>
<td>N</td>
<td>Jönsson (1971)</td>
</tr>
<tr>
<td>β-Tetrolic acid</td>
<td>2.655</td>
<td>111</td>
<td>136.7</td>
<td>121.4</td>
<td>X</td>
<td>Benghiat &amp; Leiserowitz (1972a)</td>
</tr>
</tbody>
</table>

* X = X-rays, N = neutrons
It is noteworthy that the hydrogen-bonding arrangement in acetic acid contains the cyclic 'dimer' (16).

This 'dimer' is almost coplanar so that a methyl C-H bond is directed at the carbonyl O atom forming a C-H-O contact of 3.4 Å (H-O 2.4 Å). Jönsson (1971) had pointed out in a neutron diffraction study of acetic acid that this C-H-O arrangement should not be regarded as constituting a C-H-O bond without conclusive spectroscopic evidence. The methyl group of acetic acid exhibits static disorder in its crystalline 1:1 complex with phosphoric acid (Jönsson, 1972) hinting that the synplanar H-C-C=O conformation in the acetic acid crystal may be additionally stabilized by the C-H-O 'interaction'.

Tetrolic acid is dimorphic. The molecules in the metastable α-modification (Benghiat & Leiserowitz, 1972a) are linked into hydrogen-bonded pairs whereas the stable β-tetronic acid exhibits the catemer motif (Fig. 6), the set of coplanar carboxyl groups being interlinked by single O-H-O bonds via a 2₁ axis of 7.1 Å.

There is an increasing distortion of the hydrogen bond comparing formic, acetic and β-tetronic acid in that order (Table 3). The O-H-O bond is somewhat lengthened, and the C=O-H(O)O and the C-O-O(aryl) angles are opened appreciably. This increasing distortion may be correlated with the relative sizes of the groups R in view of the close contact between R and the carbonyl O atom. Indeed this close R-O(aryl) contact severely restricts the size and nature of R and in fact rules out the catemer (11c) for the vast majority of carboxylic acids. We illustrate this by considering model compounds with progressively larger R groups.

(16)

Monofluoroacetic acid (Kanters & Kroon, 1972) with a residue CH₂F just slightly larger than the CH₃ group of acetic acid, does not appear in the catemer motif in the solid; it rather forms cyclic dimers. Assuming the observed synplanar C-C-C=O conformation and acceptable van der Waals contacts of F-O 3.1 and F-H 2.8 Å, the fluoro acid may be inserted into the catemer motif (11c) only with 'poor' hydrogen-bonding angles [C=O-·-O 155°, C-O(H)-·-O 126°] as shown in (17). This argument is applicable to molecules R-CH₂-CO₂H which exhibit a preference for the synplanar R-C-C=O conformation, e.g. bromoacetic acid (Vor der Bruck & Leiserowitz, 1976), trichloroacetic acid (Jönsson & Hamilton, 1972) and α,β-saturated acids R-CH₃-CH₂-CO₂H, a class which invariably appears in the synplanar C=C-C=O conformation, and which all form cyclic hydrogen-bonded dimers in the solid state.

(17)

These steric arguments are less convincing when applied to the α,β-trans unsaturated carboxylic acids R-CH=CH-CO₂H. The molecule may be inserted into the catemer (11c) provided the conformation of C=O-C=O is antiplanar as shown in (18). Since the less-favoured antiplanar C=C-C=O conformation does not occur infrequently (see § 2.2), the catemer (11c) cannot be discounted simply on the grounds that the synplanar C-C-C=O form is preferred.

It would seem that, by and large, better packing is achieved with cyclic hydrogen-bonded dimers than with the catemer (11) in view of the absence of constraints on the shape of the carboxy residue R in the formation of the cyclic dimer as compared to the catemer, as well as the greater degrees of freedom in the arrangement of the dimer units in the crystal to promote favourable intermolecular contacts.

These arguments promoting the cyclic hydrogen-bonded dimer (7) cannot be applied as forcefully to enantiomeric monocarboxylic acids R*-CO₂H. The chiral molecules forming the cyclic dimer would have to be related by either crystallographic or local two-fold symmetry. A crystallographic twofold axis, which would have to lie perpendicular to the cyclic dimer, could impose unnecessary constraints on the overall crystal structure; twofold symmetry localized to the dimer could result in different packing environments of the two molecules of the dimer. The crystal structures of the three chiral monocarboxylic acids discussed above which form catemer motifs show that the O-H-O hydrogen-bond geometry is sufficiently flexible to allow the 2₁ axes about which these molecules are hydrogen-bonded to vary in length from 5-8 Å in order to accommodate suitable packing. However, it may be assumed that if molecular packing cannot be accommodated within these limits then the chiral acids must form cyclic dimers. This is probably the case for levopimaric acid, C₂₉H₄₀O₂ (Karle, 1972), which forms the dimer between two independent molecules in the asymmetric unit. The molecule is very bulky and probably cannot pack suitably along a catemer axis lying within the limits of 5-8 Å.
The very fact that 'distorted' O–H···O systems have been found almost only in chiral acids, and that the catemer (11c), with C=O···(H)O and C–O(H)···O(carbonyl) angles close to 120°, has been observed to date only in formic, acetic and β-tartaric acid implies that there are preferred directional properties of the O–H···O(carbonyl) bond, namely the bond tends to be linear, the C=O···(H)O angle to be close to 120°, and the O–H bond to lie in the plane of the carbonyl system to which it is hydrogen-bonded.

3.2. Dicarboxylic acids

This discussion will be centred primarily on the various ways dicarboxylic acids form one-dimensional chains in which the carboxyl groups are linked to each other via cyclic pairs (7) of O–H···O bonds. The analysis will include 1,2-disubstituted acids which form intramolecular O–H···O bonds, chain-like dicarboxylic acids (19), followed by a detailed examination of monocarbonamide derivatives (20).

3.2.1. 1,2-Disubstituted acids with an intramolecular O–H···O bond. The 1,2-disubstituted carboxylic acids may be divided into two classes, one which contains an intramolecular O–H···O bond between the two neighbouring carboxyl groups and the other which does not. Molecules belonging to the first class may be interlinked via an O–H···O(carbonyl) bond between the available O–H proton donor and carbonyl O acceptor. This linkage may be achieved either by translation (21a), or along a 21 axis or glide (21b). The translation motif is possible if R1 and R2 are sufficiently small so as not to hinder each other, their intermolecular contact being governed by the length of the intramolecular O–H···O bond. Maleic acid (James & Williams, 1974) appears in this motif. The 21 axis (or glide) motif (21b) has the advantage that it does not depend on the sizes of R1 and R2. Furan-3,4-dicarboxylic acid (Williams & Rundle, 1964) exhibits this arrangement as well as cyclopropane-l,1-dicarboxylic acid (Meester, Schenk & MacGillavry, 1971), in which the interlinked molecules are related by a non-crystallographic glide plane. Motifs (21a) and (21b) are not the only modes in which these molecules may be interlinked, e.g. bicyclo[2,2,2]-octa-2,5-diene-2,3-dicarboxylic acid (Hechtfisher, Steigmann & Hoppe, 1970) does not contain the linear chains (21); rather the chains are helical with distorted fourfold screw axis symmetry.

3.2.2. Chain-like dicarboxylic acids. Dicarboxylic acids which contain carboxyl groups which are antiparallel to each other almost invariably achieve O–H···O hydrogen-bonded chains in which the molecules are interlinked by translation symmetry (22). The crystal structure of chiral (−)-chlorosuccinic acid (Kryger, Rasmussen & Danielsen, 1972) provides an example of this rule for, despite the asymmetric CI substituent, the two carboxyl groups are almost antiparallel to each other, yielding the hydrogen-bonded arrangement (22).

Dicarboxylic acids containing carboxyl groups which are not antiparallel to each other cannot generate hydrogen-bonded chains by translation only. Rather, these molecules form chains (23) in which each carboxyl group participates in a hydrogen-bonded cyclic dimer. There are two principal modes of generating the chains (23) depending upon the molecular symmetry. If the two carboxyl groups are not related by molecular symmetry, they may each form cyclic hydrogen-bonded dimers about centres of inversion (assuming a racemic structure) and so generate the motif (23).

If the two carboxyl groups are related by molecular twofold symmetry, the hydrogen-bond motif (23) may be generated by a glide g (assuming a racemic structure) which is perpendicular to the molecular twofold axis and so forming a chain of (pseudo) 2/g symmetry, as shown in (24). The centres of the hydrogen-bonded...
dimers lie on the glide plane half-way between the two-fold axes. This motif encompasses a wide variety of molecules which may be subdivided into three classes. In one class the molecule itself possesses a twofold axis, which is part of the crystal symmetry. Structures belonging to this group include \(\beta\)-glutaric acid (Morrisson & Robertson, 1949a) and phthalic acid (van Schalkwyk, 1954). The second set comprises crystal structures in which the twofold symmetry is localized to the molecule and the hydrogen-bonding chain (24), i.e. is not part of the overall crystal symmetry. Crystal structures formed in this manner are 3,3-dimethylglutaric acid (Benedetti, Claverini & Pedone, 1972) and allene-dicarboxylic acid (Leiserowitz & Nader, 1973).

It is of interest that anhydrous acetylenedicarboxylic acid (Benghiat, Leiserowitz & Schmidt, 1972) forms this type of hydrogen-bonding chain shown in (25) by virtue of the dihedral angle of 58° between the planes of the two carboxyl groups. We are not able to state with certainty whether the non-planarity of anhydrous acetylenedicarboxylic acid is due primarily to intermolecular forces. The dihydrated form (Dunitz & Robertson, 1947), phenylpropionic acid (Rollett, 1955), and acetylenedicarbonamide (Leiserowitz & Tang, 1976) are all planar molecules, which seems to imply that the non-planarity of acetylenedicarboxylic acid is induced by crystal forces.

In molecules of the third class only the carboxyl groups are related by pseudo twofold symmetry, e.g. mesaconic acid (Gupta & Yadav, 1972). Its hydrogen-bonded chain (26) is propagated by a glide, the plane of which is almost perpendicular to that of the molecule. A chain similar to (24) may be formed via (pseudo) symmetry \(2/m\). Furane-\(\alpha,\alpha\)-dicarboxylic acid (Martuscelli & Pedone, 1968) and isophthalic acid (Alcala & Martinez-Carrera, 1972) fall into this class.

**Table 4. Cell constants of some acid-amide (HO\(\text{X}-\text{CONH}_2\)) crystal structures**

<table>
<thead>
<tr>
<th>Compound</th>
<th>(a) (Å)</th>
<th>(b) (Å)</th>
<th>(c) (Å)</th>
<th>(\beta) (°)</th>
<th>(Z)</th>
<th>Space group</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fumaramic acid</td>
<td>7.367</td>
<td>9.041</td>
<td>3.742</td>
<td>99.39</td>
<td>2</td>
<td>(P2_1)</td>
<td>Benghiat, Kaufman, Leiserowitz &amp; Schmidt (1972)</td>
</tr>
<tr>
<td>Succinamic acid</td>
<td>5.64</td>
<td>5.24</td>
<td>9.68</td>
<td>95.5</td>
<td>2</td>
<td>(Pc)</td>
<td></td>
</tr>
<tr>
<td>(trans,trans)-Muconamic acid*</td>
<td>7.1</td>
<td>10.1</td>
<td>9.6</td>
<td>107</td>
<td>4</td>
<td>(P2_1/2121)</td>
<td>Murakami &amp; Iitaka (1969)</td>
</tr>
<tr>
<td>((-))-2-Bromosuccinamic acid</td>
<td>7.70</td>
<td>9.23</td>
<td>8.88</td>
<td></td>
<td>4</td>
<td>(P2_1,2_2,2_1)</td>
<td></td>
</tr>
</tbody>
</table>

* The crystals of muconamic acid gave poor diffraction photographs.
We may anticipate that, in enantiomeric dicarboxylic acids containing carboxyl groups which are related by (pseudo) molecular twofold symmetry, the hydrogen-bond chain may be formed via a 2\_ axis generating a chain of (pseudo) symmetry 222\~ as shown in (27). The cyclic hydrogen-bonded dimers are formed about two-fold axes. These dimers are planar only if the planes of the carboxyl groups are parallel to the molecular twofold axis.

3.2.3. Monocarbonamide derivatives of dicarboxylic acids. Monocarbonamide derivatives of dicarboxylic acids (labelled here as carboxy-amide molecules) form hydrogen-bonded chains (28a) similar to (22), in which the amide and carboxyl groups are interlinked, via a pair of O--H...O(amide) and N--H...O(carboxyl) hydrogen bonds, into a cyclic dimer.

There is a second chain motif (28b) which comprises alternating hydrogen-bonded pairs of carboxyl groups and amide groups. Of these two chain motifs it would seem that the former is less favourable, for within the cyclic carboxy-amide pair (28a) there is a mismatch between the lengths of the O--H...O and N--H...O bonds (O--H...O 2.6, N--H...O 2.9 Å) and the C--N and C--O--H bond angles (C--N--H 120°, C--O--H 112°). Yet the molecules listed in Table 4 all appear in motif (28a). They form two-dimensional hydrogen-bonded networks, unlike dicarboxylic acids, by virtue of the additional N--H proton donor on the amide group. It is instructive to analyse the general features of their hydrogen-bond networks to determine the interplay between hydrogen-bonding interactions and intermolecular steric forces and, as a corollary thereof, to account for the preference of the motif (28a) over that of (28b). A clearer understanding of the packing characteristics of the carboxy-amides may be achieved by first reviewing some of the principal features of primary amide packing.

An analysis of the molecular packing modes of primary amides R--CONH\_2 (Leiserowitz & Schmidt, 1969) has shown that their hydrogen-bond structure tends to adopt, R permitting, the motif (29), achieved via interpair N--H...O bonds along a 2\_ axis (or glide) of 9.5 ± 0.3 Å. This hydrogen-bonding arrangement has been found in a number of structures including succindiamide (Davies & Pasternak, 1956) and acetylenedicarbonamide (Leiserowitz & Tang, 1976). The hydrogen-bonding arrangements of these two structures are shown in Fig. 7(a) and (b). The N--H...O motif (29) is coplanar, and contains linear N--H...O bonds symmetrically disposed about the carbonyl C=O bond with C=O...N angles ~120°.

This motif (29) is compatible with the electron density distribution of the carbonyl O as determined from the diffraction analyses of fumaramic acid (X-ray study at 20°C) (Hirshfeld, 1971), cyanuric acid (combined X-ray and neutron study at -170°C) (Verschoor & Keulen, 1971; Coppens & Vos, 1971), diketopiperazine (X-ray study at -150°C) (Harel & Hirshfeld, 1976), allenedicarboxylic acid acetamide (X-ray study at -160°C) (Berkovitch-Yellin, Leiserowitz & Nader, 1976). The electron density maps of these molecules, in particular the latter three as their diffraction data were measured at low temperatures, displayed the lonepair lobes of the carbonyl O; two peaks (L) in the plane of the carbonyl system with an O...L distance of ~0.6 Å and an L...O=C angle of ~110°. While these results indicate that the geometry of the N--H...O motif (29) is most favourable when the carbonyl O participates in two hydrogen bonds, the question arises...
whether this N–H⋯O geometry is preferred if the system contains only one N–H⋯O hydrogen bond. This question is answered in part by the structural and polarized infrared results on cyanuric acid as discussed by Leiserowitz & Schmidt (1969); and Coppens & Vos (1971). Its hydrogen-bonding network (Fig. 8) consists of cyclic hydrogen-bonded N–H⋯O pairs with an angular geometry shown in (30a), and collinear N–H⋯O=C bonds shown in (30b).

\[ (30a) \quad (30b) \]

Their respective N–H⋯O distances (Å) and corresponding N–H stretching frequencies \( v_s \) (cm\(^{-1}\)) are 2.805 and 3060, and 2.784 and 3210. These results seem to be in contradiction to the linear correlation between \( Av_s \) and N⋯O distance \( R \) given by Nakamoto, Margoshes & Rundle (1955) in which the slope, \( AR/Av_s \approx 8 \times 10^{-4} \) (Å cm). Clearly the difference in \( v_s \) between the two N–H⋯O geometries in cyanuric acid suggests that \( Av_s \) is dependent not only on the N⋯O distance but also on the angular geometry of the N–H⋯O bond, and furthermore, that motif (30a) is energetically preferred over that of (30b).

Within the crystal structure of fumaramic acid (Benghiat, Kaufman, Leiserowitz & Schmidt, 1972) the amide and carboxyl groups of molecules related by translation form hydrogen-bonded pairs (O–H⋯O 2.66, N–H⋯O 2.84 Å) generating chains (28a). These chains are interlinked, along a 2\_ axis of 9.04 Å (Table 4) by N–H⋯O bonds of 2.94 Å forming an arrangement shown in Fig. 9 similar to that of the primary amides discussed above. Naturally the hydrogen-bond motif about the carbonamide O in fumaramic acid, shown in (31), is similar to that of (29).

\[ (31) \]

The crystal structure of succinic acid HO₂C–(CH₂)₂–CONH₂ has not been determined. Yet its hydrogen-bond network is easily deduced from its cell constants (Table 4). The molecules are interlinked by translation via their amide and carboxyl groups to generate the hydrogen-bond chain (28a), as in fumaramic acid. This hydrogen-bond chain of succinic acid lies along the vector \( a + b = 7.7 \) Å, which matches in length the mean of the hydrogen-bonding translation axes of succindiamide (Davies & Pasternak, 1956) = 7.99 Å, and \( \beta \)-succinic acid (Morrison & Robertson, 1949b) = 7.61 Å. The hydrogen-bond chains of succinic acid are cross-linked via a \( c \) glide of 9.7 Å by N–H⋯O bonds between amide groups.

The amide group of succinic acid makes a shallow angle of \( \sim 43^\circ \) [= arcsin \((b/a + b)\)] with the \( c \) glide plane in a manner similar to that observed in the crystal structures of aliphatic primary amides CH₃–(CH₂)ₙ–CONH₂ (Turner & Lingafelter, 1955a, b), which leads to a somewhat distorted modification of the ‘ideal’ N–H⋯O bond motif (31). If so, the obvious question arises why does succinic acid not form a hydrogen-bond network similar to that of succindiamide (Fig. 7a) with its rather ideal interpair N–H⋯O bond arrangement. Insertion of succinic acid into the hydrogen-bond sheet structure of succindiamide would replace the NH₂ by an OH group. Hence the amide intrapair O⋯H⋯N would be substituted by the carboxy-amide pair (\( O\cdot\cdot\cdot H\cdot\cdot\cdot N \)), and the interpair N–H⋯O bond of 2.93 Å by an O(carbonyl)⋯O(hydroxyl) contact of \( \sim 2.9 \) Å. The geometry of this contact is such that the electron lone pair lobes of the two O atoms would be directed at each other. For this type of approach a separation of 2.9 Å is too short; an acceptable distance would be 3-6 Å as discussed earlier (§ 3.1). Hence it would hardly be possible to pack succinic acid into the more ideal hydrogen-bond network of succindiamide.

The chiral (−)-2-bromosuccinamic acid (Murakami & Itaka, 1969) also forms the chain motif (28a). These chains are not interlinked into a two-dimensional hydrogen-bond network as fumaramic and succinic acid. Rather, the chains are paired by N–H⋯O bonds between amide and carboxyl groups via a 2\_ axis parallel to the chain axis of 7.7 Å as shown in (32). The Br atoms are directed outwards from the pair of hydrogen-bonded chains and thus do not interfere sterically with the interchain N–H⋯O bond. Indeed were 2-bromosuccinamic acid to lie in an extended two-dimensional hydrogen-bond network similar to that of succinic acid, the structure would incorporate short intermolecular contacts involving the Br atoms. The motif (32) is only possible if the hydrogen-bond chain axis is \( \sim 8 \) Å long, i.e. twice the distance between the C atoms forming the carboxy-amide pair

\[ \text{which equals } 4 \text{ Å. In other words,} \]

\[ (32) \]
only succinamic or fumaramic acid derivatives may pack in such a manner.

*trans,trans*-Muconamic acid (HO₂C-CH=CH-CH=CH-CO₂H) also forms the hydrogen-bond chain motif (28a) along b since its length of 10.1 Å is the mean between the lengths of the hydrogen-bonding translation axes of mucondiamide (Leiserowitz & Schmidt, 1969) = 10.3 Å, and muconic acid (Bernstein & Leiserowitz, 1972) = 9.9 Å. These muconamic chains are interlinked via a c glide of 9.6 Å by N-H...O bonds in a manner similar to fumaramic acid. The hydrogen-bonding translation axis of 10.1 Å also indicates that the conformation of C=C-C=O at the carboxyl end of muconamic acid must be synplanar, since only a synplanar conformation can be accommodated into the hydrogen-bonding motif (33) with b of 10.1 Å. We naturally assume that the C=C-C=O conformation at the amide end is synplanar. We are not aware of any exceptions to this rule.

As mentioned earlier, the translation motif (28b) comprising hydrogen-bonded amide and carboxyl pairs has not been observed. One drawback of this motif lies in the two-dimensional hydrogen-bonded networks which may be constructed therefrom. The only possible modes of interlinking the chains (28b) by N-H...O bonds are by translation as shown in motifs (34a) and (34b); the interpair N-H...O bond links amide groups in motif (34a) and links amide and carboxyl groups in (34b). However, both arrangements would contain the poor O(carbonyl)...O(hydroxyl) contact of ~2.9 Å discussed earlier (§ 3.1). Therefore we tend to rule out such an arrangement.

4. The carboxyl dimer and its environment

4.1. *The disordered carboxyl dimer*

In this section we shall examine the systematics of packing environment about the carboxyl dimer and the effect of environment on the carboxyl group. We begin with symmetric molecules where the intramolecular environment about the carboxyl and hydroxyl O atoms are identical. In this class of molecules X-CO₂H there exist two equivalent orientations (35a) and (35b) of the carboxyl dimer mutually indistinguishable unless incorporated into the crystal.

Therefore the observed degree of orientational disorder of the carboxyl dimer, i.e. the random incorporation of (35a) or (35b) at a point in the crystal, must be due to intermolecular forces. The disorder manifests itself in the observed lengths of the C-O bonds and the (disordered) locations of the hydroxyl H atom. Currie, Speakman & Curry (1967) had noted that the difference between C-O(carbonyl) and C-OH(hydroxyl) distances ranges widely from 0.04-0.12 Å, for which they accounted by assuming orientational disorder between (35a) and (35b).

Dunitz & Strickler (1968) pointed out that if the hydrogen-bonded pairs of aromatic carboxylic acids interact only weakly with one another in the solid, the arrangement in one pair must be largely independent of the arrangement in the other pairs, and so they predicted the possibility of disorder of the carboxyl group.

Recently Dieterich, Paul & Curtin (1974) pointed out a linear correlation between the difference in C-O lengths (Δr) and the difference in C-C-O angles (Δθ) in aromatic carboxylic acids. They showed that there is a continuum of these values from completely ordered (with large values of Δr and Δθ) to those which show disorder.

A carboxyl dimer containing C-O bonds equal in length exists in a state of disorder, either static or dynamic. Static disorder involves the existence of the two dimer orientations (35a) or (35b) and no proton transfer across the O-H...O bond. In dynamic disorder the hydroxyl proton is delocalized; either the proton is centrally situated in a symmetric O-H-O bond and the C-O bonds of the carboxyl group are in a state of resonance, or the proton undergoes rapid oscillations across the O-H...O bond accompanied by interconversion between the carboxyl C=O and hydroxyl C-O(H) bonds. As we shall observe later there
is no correlation between the difference in length between the C-O bonds and the length of the O-H···O hydrogen bond. This is strikingly so for identical molecules in different packing environments. This fact seems to be incompatible with dynamic disorder for we should expect a decrease in the length of the O-H···O bond with increased delocalization of the proton. Moreover, infrared spectra of carboxylic acids containing C-O bonds of equal length show the presence of the carbonyl C=O stretching mode, so we at least disqualify the symmetric O-H···O bond.

Complete static disorder implies that the crystal co-ordinates of the two disordered O atoms are separated by approximately 0-1 Å. Treating these two half-occupancy O atoms as a single atom should induce artificially high temperature factors in a least-squares structure-factor computation. Thus this effect should be evident in a comparison between ordered and disordered carboxyl groups which have the same thermal motion. This condition is well satisfied if the two carboxyl groups lie in the same crystal and are related by molecular symmetry. These demands are ideally fulfilled in trimesic acid, discussed below, where it is found the more equal in length the carboxyl C-O bonds, the higher the temperature factors of its O atoms.

The question then arises as to how intermolecular forces determine the degree of disorder of the carboxyl dimer. On the reasonable assumption that its orientation is determined primarily by nearest-neighbour interactions, we envisage a tendency towards disorder based on the following two criteria: (i) the neighbouring contacts of the carbonyl and hydroxyl O atoms are of a similar nature; (ii) the surroundings of the carbonyl and hydroxyl O atoms may be dissimilar, yet the lattice energy difference between the two orientations (35a) and (35b) of the carboxyl dimer is negligible. That the intermolecular environment of the carbonyl and hydroxyl O atoms may be identical is illustrated by the crystal structures of mellitic and trimesic acids, in which the two carboxyl O atoms are related to each other by crystallographic symmetry.

Mellitic acid (Darlow, 1961) contains two crystallographically independent molecules, each lying on a twofold axis (Fig. 10). Of the four independent hydrogen-bonded dimers (labelled A, B, C, D), two, A and B, lie on twofold axes while C and D have no symmetry constraints. The carboxyl dimers are not planar, the dihedral angles between the planes of the carboxyl groups of the dimers A, B, C, and D are 37°, 4°, 20° and 31°, respectively. It is unlikely that the O-H···O bonds in the dimers A and B are symmetric, since their O-H···O distances of 2.68 and 2.66 Å are no shorter than the O-H···O distances of 2.66 and 2.64 Å in dimers C and D in which the carboxyl C=O bonds are quite distinct.

The crystal structure of trimesic acid (Duchamp & Marsh, 1969) contains carboxyl dimers showing a wide spread in C-O bond length. The hydrogen-bonding motif (Fig. 11) is a two-dimensional network formed by six molecules bound together through pairs of O-H···O bonds. The networks are not planar, pleats involving dihedral angles of about 70° being formed by means of a twisting of some of the carboxyl groups out of the planes of their benzene rings. The carboxyl groups were classified by Duchamp & Marsh into three groups (Fig. 11). Group (I) comprises carboxyl groups which lie on the 70° pleat and are severely twisted out of the plane of their benzene rings (average twist 23°). Their average C=O, C-OH and O-H···O distances are 1.218, 1.319 and 2.652 Å. The second category (II) are the carboxyl groups which lie on planar sections...
of the layer and are approximately coplanar with their benzene rings (average twist 3°). For these the C=O, C−OH and O−H−...O distances are 1.245, 1.279 and 2.631 Å. The third category (III) comprises the carboxyl groups which form disordered O−H−...O bonds about a twofold axis (C=O 1.255, O−H−...O 2.645 Å) as well as the carboxyl groups (C=O 1.244, C−OH 1.275, O−H−...O 2.632 Å) in which the hydroxyl H atoms are partially disordered. Duchamp & Marsh were of the opinion that the O−H−...O bond of (III) cannot be symmetric as the O−H−...O distances are too long. On the other hand, they suggested that the bond lengths of the carboxyl group of (II) are indicative of considerable resonance. We could as well assume that these carboxyl groups are also disordered as in (III). Indeed the H peaks of (II) appear on the difference map (Fig. 11) to be more diffuse than those of (I); the average temperature factors $U_H$ of these H atoms are 0.07 and 0.04 Å², respectively. The values of the principal magnitudes of the thermal ellipsoids $U_1 > U_2 > U_3$ (listed by Duchamp & Marsh) of the O atoms averaged for each of (I), (II), (III) [i.e., $\langle U_1 \rangle$, $\langle U_2 \rangle$, $\langle U_3 \rangle$ for each category] are [0.070, 0.039, 0.030 Å²], [0.090, 0.044, 0.032 Å²] and [0.121, 0.062, 0.036 Å²] respectively. These results are indicative of disorder; the more equal in length the carboxyl C−O bonds, the higher the 'thermal motion'.

We may rationalize that dimers of (I), which lie at the 70° pleat have very different force fields at their carbonyl and hydroxyl O atoms prohibiting disorder. On the other hand, the dimers of (II) lie in the planar section of the layer structure so that the force fields at their carbonyl and hydroxyl O atoms are, perhaps, more equal, resulting in partial disorder.

While it appears difficult to decipher the complex packing of trimesic acid, there are crystal structures showing order/disorder of their carboxyl dimers which lend themselves more easily to analysis by virtue of their relatively simple packing motifs. Molecules which fall into this class include benzoic acid and propionic acid derivatives.

4.1.1. Benzoic acids. Some of the packing features of substituted benzoic acids have been discussed by Miller, Curtin & Paul (1974), in particular their stacking characteristics. They had observed that the carboxyl groups form interplanar contacts with each other, either via the stacking motif (36a) or an antiparallel arrangement of C−O bonds (36b).

In this discussion we shall confine ourselves primarily to the systematics of the packing environment about the carboxyl group in the $p$-substituted benzoic acids ($p = \text{H, CH}_3, \text{Cl, Br, CO}_2\text{H, C}_6\text{H}_5$), $o$-halogenated acids and 2,6-disubstituted acids.

The C−O bond lengths of $p$-toluic acid (Takwale & Pant, 1971) are almost equal (1.272, 1.275 Å) indicating pronounced disorder. The molecules are interlinked by methyl−methyl contacts. These chains make lateral contact with each other, forming a layer structure (Fig. 12). This lateral contact incorporates a motif (37) in which the $m$- and $o$-substituted C−H bonds make symmetric and edge-on contacts with the O−H−...O bond of the carboxyl dimer. In the interlayer contact the carboxyl dimer is sandwiched between the methyl groups which lie at almost equal distances from the two O atoms forming the O−H−...O bond. As might be expected, this symmetric environment about the O atoms induces disorder.
Terephthalic acid (Bailey & Brown, 1967) crystallizes in two triclinic modifications. The structure of the more stable \( \alpha \)-form was determined with an extensive set of X-ray intensities while only partial X-ray data were collected for the less stable \( \beta \)-form. The C-O bond lengths were found to be almost equal in the \( \alpha \)-form (1.262, 1.272 Å), less so in the \( \beta \)-form (1.25, 1.28 Å) indicating carboxyl disorder which is pronounced in the \( \alpha \) and partial in the \( \beta \)-form. In both modifications the molecules pack in chains of cyclic hydrogen-bonded dimers, which make lateral contact with each other to form layer structures [Fig. 12(a) and (b)]. These two-layer structures are identical with each other and incorporate the lateral C-H-O contacts of motif (37). The difference between the \( \alpha \) and \( \beta \)-modifications lies in their interlayer arrangements. In the \( \alpha \)-form the carboxyl dimers are closely stacked, the carboxyl groups being offset along the direction of the shorter ‘C=O’ bond of 1.262 Å. In the \( \beta \)-form the contact between the carboxyl dimers is characterized by an antiparallel arrangement of ‘C-O(H)’hydroxyl bonds of 1.28 Å as shown in (38).

We therefore attribute the almost complete disorder of the carboxyl group of the \( \alpha \)-form and the partial disorder of the carboxyl group of the \( \beta \)-form on the one hand to the similar environment of both O atoms within the layer and, on the other hand we infer, at least for the \( \alpha \)-form, that the interlayer interactions permit pronounced disorder despite differences in interstack environment of the two carboxyl O atoms. The C-O bond lengths of the \( \alpha \)-form do suggest a slight preference for the stacking arrangement (39a), where the carboxyl groups are offset along their C=O bonds, over that of (39b).

The strong disorder of the \( \alpha \)-form seems to suggest that either the interactions between the stacked dimers

Fig. 12. \( \rho \)-Toluic acid (Takwale & Pant, 1971). Intra- and interlayer arrangement. Distances: C-O 1.272, 1.275, O-H-O 2.63, C-H-O 3.59, 3.47 Å. Offset between adjacent molecules in the layer is 1.35 Å.

Fig. 13. (a) \( \alpha \)-Terephthalic acid (Bailey & Brown, 1967). Intra- and interlayer packing. Distances: O-H-O 2.608, C-O2 1.262, C-O1 1.272, C-H-O 3.48, 3.60 Å. Offset from coplanarity between adjacent hydrogen-bonded chains is 0.6 Å. (b) \( \beta \)-Terephthalic acid (Bailey & Brown, 1967). Intra- and interlayer packing. Distances: O-O 2.58, C-O, 1.25, C-O2 1.28, C-H-O 3.46, 3.48 Å. Offset from coplanarity between adjacent hydrogen-bonded chains is 0.6 Å.
may be weak (Dunitz & Strickler, 1968) or that the energy difference between the two carboxyl dimer orientations (39a) and (39b) in their stacks is small. The first suggestion is perhaps ruled out on the basis that carboxylic acids show a tendency to crystallize in stacks.

Regarding the interlayer motif (38) of β-terephthalic acid, it is noteworthy that benzoic acid (Sim, Robertson & Goodwin, 1955), which also exhibits the intralayer arrangement (37), shows an interplanar arrangement (40) which, at first sight, is similar to that of β-terephthalic acid (38). The crystal structure of benzoic acid was determined from two-dimensional X-ray data so that the error in its C–O lengths of 1.24 and 1.29 Å must be at least 0.02 Å. Comparing the interlayer motifs of β-terephthalic acid and benzoic acid shows an antiparallel pairing of ‘C–OH’ bonds in terephthalic acid, whereas in benzoic acid the ‘C=O’ bonds are paired antiparallel. It is difficult to reconcile this difference unless we assume effective long-range interactions which are different in the two structures. This point is substantiated by the crystal structures of the analogous p-bromobenzoic acid (Ohkura, Kashino & Haisa, 1972) and p-chlorobenzoic acid (Miller, Paul & Curtin, 1974). The C–O bonds of the bromo acid are distinct with lengths of 1.225 and 1.307 Å, unlike the chloro acid with lengths of 1.253 and 1.273 Å. Both acids display the intralayer motif (37) common to benzoic acids and the carboxyl-stacking motif (38a), yet the bromo acid shows no evidence of carboxyl disorder. We, therefore, conclude that the extent of order/disorder of the carboxyl group is also dependent on fairly long-range interactions.

The crystal structures of some substituted biphenyl-4-carboxylic acids also show the packing features found in the 4-substituted benzoic acids. 2-Chlorobiphenyl-4-carboxylic acid (Sutherland & Hoy, 1969) (Fig. 14) and the iodo derivative (Sutherland, 1970) both show the layer motif (37) and the carboxyl stacking motif (39b). The C–O bond lengths in both structures (2'-Cl, 1.261, 1.289; 2'-I, 1.250, 1.264 Å) indicate appreciable disorder. The stacking of their carboxyl groups, which are offset along the direction of the ‘C–O(H)’ bonds, is unlike that of the disordered carboxyl groups of α-terephthalic acid, where the offset is along the ‘C=O’ bond, providing further evidence of the small energy difference between the stacks (39a) and (39b).

The crystal structure of 2-chlorobiphenyl-4-carboxylic acid (Sutherland & Hoy, 1969) (Fig. 15) does not contain the lateral C–H⋯O contacts of the layer motif (37), as such an arrangement would incur very short contacts involving the Cl atom. The carboxyl groups are stacked as in motif (39a), i.e. they are offset along the direction of the C=O bond. The C–O lengths of 1.205 and 1.315 Å indicate no disorder which may be correlated with the asymmetric lateral environment of the carboxyl dimer.

The lateral C–H⋯O contacts of motif (37) are also present in the o-halogenated benzoic acids (F, Cl, Br). The carboxyl bonds of the Cl (Ferguson & Sim, 1961) and Br (Ferguson & Sim, 1962) derivatives show distinct carbonyl and hydroxyl character in keeping with the asymmetric intramolecular environment of the carboxyl group (§ 2.2). On the other hand, the C–O lengths of 1.255 and 1.280 Å in o-fluorobenzoic acid (Krausse & Dunken, 1966) tend to be equal: the stacking pattern of its carboxyl groups (Fig. 16) resembles motif (39a). Despite the asymmetric intramolecular environment of the carboxyl group introduced by the F substituent, its relative smallness compared with CH₃, Cl and Br obviously permits some orientational disorder.

The common occurrence in benzoic acids of the intralayer motif (37) with its C–H⋯O contacts of ~3.5 Å raises the question whether the motif is induced by close-packing or weak C–H⋯O interactions, or a combination of these two effects. A similar question was recently raised by Kvick, Koetzle, Thomas & Takusagawa (1974) in their discussion of the lateral
C-H\cdots O contacts (H\cdots O 2.40, 2.30 Å) in pyridine-2,3-dicarboxylic acid shown in (41), which is similar to motif (37).

That close-packing plays a dominant role in the formation of (37) is confirmed by the crystal structure of pentafluorobenzoic acid (Benghiat & Leiserowitz, 1972b), which exhibits an arrangement similar to the intralayer motif (37) in which the (C)H\cdots O contacts are replaced by (C)F\cdots O contacts of 3.2 Å. The pentafluorobenzoic acid molecule is not planar, unlike the unsubstituted benzoic acids already described; the carboxyl group is twisted out of the plane of the ring by 30°. Its C-O lengths of 1.228 and 1.278 Å and the presence of the hydroxyl H atom on a difference map indicated that the carboxyl pair does not exhibit appreciable disorder. This lack of disorder was attributed to the packing normal to the plane of the carboxyl dimer which revealed that it is sandwiched between C-F bonds and differences in environment about the carboxyl and hydroxyl O atoms.

We conclude that benzoic acids which appear in the layer motif (37) may show disorder of their carboxyl dimers which is compatible with the lateral symmetric environment about the two O atoms of the carboxyl group. Regarding the interlayer motif, an almost symmetric environment, as observed in \( p \)-toluic acid, permits disorder. Stacked carboxyl dimers may be offset along the C-O bond, which may be either the C=O bond or the C-O(H) bond or a disordered combination thereof. Medium-range interactions obviously play a role in determining the extent of C-O order/disorder in this structure type, as demonstrated by the crystal structure of \( p \)-bromobenzoic acid. Carboxyl groups also form interplanar antiparallel arrangements of C-O bonds, either C=O or C-OH.

We now consider the symmetrically substituted benzoic acids in which the lateral C-H\cdots O contacts of motif (37) would be precluded, i.e. molecules with di-o or di-m-substituted phenyl rings. Molecules belonging to this class are 3,4,5-trimethylbenzoic acid, 2,4,6-trimethylbenzoic acid (mesitoic acid) and 2,6-dimethylbenzoic acid.

In 3,4,5-trimethylbenzoic acid (Cano, Martinez-Carrera & Garcia-Blanco, 1970) the carboxyl pair is sandwiched edge-on by the \( m \)-substituted methyl C atoms lying opposite the midpoints of the O-H\cdots O bonds. The contacts above the plane of the carboxyl dimer with the Me groups are not symmetrically disposed with respect to the carboxyl group, yet the C-O lengths of 1.251 and 1.287 Å show evidence of disorder. The carboxyl pairs of mesitoic acid (Florencio & Smith, 1970; Benghiat & Leiserowitz, 1972c) display disorder according to their C-O lengths of 1.248 and 1.275 Å and to the fact that the difference map shows disordered hydroxyl H atoms. This effect may be due to the presence of the \( o \)-methyl groups which are related by molecular twofold symmetry, and which would provide similar contact geometry for the carboxyl group in its two equivalent orientations. Furthermore, the O atoms are partially shielded from intermolecular contacts by the \( o \)-methyl groups. The extent of shielding is dependent upon the degree of coplanarity of the carboxyl group with the benzene ring; the larger the angle of twist the more exposed are the O atoms. The angle of twist in mesitoic acid is 48.5° versus 53.5° in 2,6-dimethylbenzoic acid (Anca, Martinez-Carrera & Garcia-Blanco, 1967) which has C-O lengths of 1.226 and 1.276 Å, indicating less disorder than in mesitoic acid.

4.1.2. Propiolic acids. In the propiolic acid series \( R-C-C-CO_{2}H \), the (room temperature) orthorhombic form of phenylpropionic acid (Rollett, 1955) has C-O bonds which are equivalent by virtue of crystallographic symmetry. Both anhydrous acetylenedicarboxylic acid and \( \alpha \)-tetrolic acid display pronounced disorder of their carboxyl dimers not imposed by crystallographic symmetry. The crystal structure of acet...
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ylenedicarboxylic acid (Benghiat, Leiserowitz & Schmidt, 1972) (Fig. 17) does show a measure of packing symmetry about the carboxyl O atoms which perhaps accounts for the disorder as indicated by the C-O lengths (1.261, 1.248, 1.262, 1.244 Å) and the location of 'split' H atoms on a difference map. A symmetric hydrogen bond is ruled out as the O-H· · ·O distance of 2.668 Å is 0.01 Å longer than the unsymmetric O-H· · ·O(carbonyl) bonds of both propiolic acid (Leiserowitz & Olovsson, 1976) and β-tetronic acid (Benghiat & Leiserowitz, 1972a). Furthermore, the infrared spectrum of crystalline anhydrous acetylenedicarboxylic acid (Leiserowitz, 1975, unpublished results) shows the band at 1700 cm⁻¹, due to the carbonyl stretching mode. We infer from the disorder of the carboxyl dimers that the intramolecular separation of the two carboxyl groups by the acetylene bond is sufficient to permit the existence of both conformers (42a) and (42b).

α-Tetronic acid (Benghiat & Leiserowitz, 1972a) forms cyclic hydrogen-bonded pairs. The C-O bonds are almost equal in length (1.252, 1.265 Å) and disordered hydroxyl H atoms were located on a difference map. A symmetric O-H· · ·O bond is incompatible with the O· · ·O distance of 2.649 Å, being only 0.006 Å shorter than that of the unsymmetric O-H· · ·O bonds of both propiolic acid and β-tetronic acid. Furthermore, the infrared spectra of both forms of tetronic acid (Leiserowitz, 1975, unpublished results) show a band at 1690 cm⁻¹ due to the carbonyl C=O stretching mode. [The spectrum of the β-form shows an additional band at 1630 cm⁻¹ which may be associated with the catemer O-H· · ·O bond (Walborsky et al., 1961).] In α-tetronic acid the hydrogen-bonded pairs are linked by Me· · ·Me contacts generating linear chains. These chains are interconnected to form an approximate layer structure. Neither the intra- nor the interlayer contacts are symmetrically disposed about the disordered carboxyl group. The interlayer arrangement of α-tetronic acid does not include closely stacked groups, as in β-tetronic acid which exhibits the carboxyl stacking motif (39a). Rather, it includes an antiparallel arrangement of disordered C-O bonds similar to that observed in benzoic acid (40) and β-terephthalic acid (38).

Propiolic acid (Leiserowitz & Olovsson, 1976) H-C≡C-CO₂H, in contrast to α-tetronic acid and acetylenedicarboxylic acid, forms hydrogen-bonded dimers, which show distinct carbonyl and hydroxyl character (C-O 1.218, 1.310 Å). As this structure will be discussed later, suffice it to say that an acetylenic C-H· · ·O(carbonyl) contact of 3.3 Å may be responsible for stabilizing the fixed orientation of its carboxyl group.

4.2. The carboxyl dimer and possible C-H· · ·O interactions

The carbonyl O atom, which participates in the O-H· · ·O bond of the carboxyl dimer, is capable of accepting another acid proton donor, X-H, where X is N or O, as shown in (43). There are numerous carboxylic acid structures which demonstrate the principle that, if the molecule contains an additional proton donor, the structure adopted will satisfy the full complement of two hydrogen bonds to the carbonyl O atom. The question we wish to raise is whether a C-H bond is a proton donor sufficiently strong to form a C-H· · ·O(carbonyl) interaction and thus induce its existence in motif (43).

Rather conclusive crystallographic and spectroscopic evidence for C-H· · ·A interactions exists where A is a strong proton acceptor and C-H is a constituent of the halo-forms, hydrogen cyanide, and acetylene derivatives as discussed by Sim (1967). Donohue (1968) has discussed the evidence for the C-H· · ·O interaction in the solid state, particularly those C-H groups

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Fig. 18. Benzoquinone (Trotter, 1960a). Layer structure. The C-H· · ·O contacts are marked.
which do not appear to be under the influence of activating groups tending to promote ionization of the H atom. The existence of these C-H...O interactions has been claimed by a number of workers, notably Sutor (1963), on the basis of short C-H...O distances of approximately 3.2 Å. Donohue presented arguments that an O...H distance of 2.4 Å is not presumptive evidence of hydrogen-bond formation and doubted whether many of the short C-H...O distances (H...O 2.2 Å) can be regarded as hydrogen bonds in the same sense that the term is used for O-H...O, N-H...O and N-H...N systems.

What then is an essential yardstick for an acceptable C-H...O interaction in the solid state? It is not unreasonable to base ourselves partially on the stereochemical considerations deduced from the packing modes of O-H...O and N-H...O systems, i.e. that the C-H bond be directed towards the O atom, lies in the plane of the carbonyl system, makes, if possible, an angle close to 120° with the C=O bond, and last, but not least, that the C-H...O distance be short. There is a general tendency to regard a C-H...O contact as not being a significant interaction if the C-H...O distance is greater than 3.3 Å. In this context we comment on the hydrogen-bonding structure of β-pyrazincarboxamide (Rø & Sørum, 1972a) shown in (44a).

![Diagram](44a)

The N-H...O distance in the hydrogen-bonded pair in (44a) is 2.92 Å, while the N-H...O distance along the 10-7 Å glide is as long as 3.24 Å. The C-H...N contacts of 3.38 Å along the glide prevent a closer approach between N and O. Thus it appears that packing forces have induced a pronounced stretch of the interpair N-H...O bond of pyrazincarboxamide. By analogy we shall not, a priori, regard a C-H...O interaction as insignificant if its C...O distance is greater than 3.2 Å.

There remains, however, of how we may be further assured whether a given C-H...O contact, which satisfies the stereochemical conditions stated above, plays a determining role in forming the crystal structure. To resolve this question we may query whether the motif involving the C-H...O contact repeats itself in a number of different structures and secondly, whether the molecule in question could not have adopted a more favourable arrangement, but for the C-H...O contact. We illustrate this approach by analysing relevant aspects of the crystal structures of pyrazincarboxamide, uracil and benzoquinone.

Pyrazincarboxamide crystallizes in four modifications, α, β, γ, δ (Tamura, Kuwano & Sasada, 1961), of which the α-, β-, and δ-forms have been reported. The α-form (Takaki, Sasada & Watanabe, 1960) contains two types of cyclic hydrogen-bonded pairs, N-H...O bonds of 2.90 Å and N-H...N bonds of 3.14 Å. The hydrogen-bonding structure of the β-form (44a), just discussed, contains N-H...O bonds of 2.92 and 3.24 Å.

The δ-form (Rø & Sørum, 1972b) contains only the NH...O bond of 2.90 Å involved in the cyclic amide pair. These pairs are related along a 5-73 Å axis to form an extended ribbon (44b) which is approximately coplanar. The contacts along the ribbon are N-H...O 3.48 Å and C-H...N 3.40 Å. These results seem to suggest that C-H...N interactions as well as weak N-H...O interactions stabilize the structure. In the β-form (44a) the relatively short interpair N-H...O bond (3.24 Å) is achieved since the pairs, being interlinked by a glide, do not form a coplanar set, and thus permit a closer approach between pairs.

![Diagram](44b)

In the structure of uracil (Parry, 1954; Stewart & Jensen, 1967) one carbonyl O atom participates in two N-H...O hydrogen bonds (45), and the other makes short contacts of 3.25 and 3.32 Å with two C-H bonds (46).

![Diagram](45) (46)

A more homogeneous hydrogen-bonded structure could be formed were both carbonyl O atoms to participate in N-H...O bonds, as in 5-fluorouracil (Fallon, 1973) or 6-azauracil (Singh & Hodgson, 1974) suggesting that the observed hydrogen-bond structure of uracil is compensated by the motif (46) containing the two C-H...O contacts.

Bernstein, Cohen & Leiserowitz (1974), in a review on the structural features of quinones, attributed C-H...O interactions of 3.5 Å to account for the layer structure of 1,4-benzoquinone (Trotter, 1960a) (Fig. 18). The argument was reinforced by the observation.
that in the 1:1 crystal complex of thymine with benzoquinone (Sakurai & Okunuki, 1971) in which each component occupies alternate layers, the benzoquinone layer is identical with that of its mono-component structure. The different interlayer environments of benzoquinone in the two structures indicate that its layer arrangement must be primarily determined by intra- and not interlayer forces. It may, however, be argued that the layer structure of benzoquinone corresponds to a very close-packed system. It is noteworthy that tetrafluoro-p-benzoquinone (Meresse, Courseille & Chanh, 1974) does not form a layer motif as in benzoquinone; rather the molecules pack in such a way that a C=O bond points towards the C atom of a C=O of a neighbouring molecule inclined at a steep angle to the first and with an O...C separation of 2.9 Å. This C=O...C interaction, which is not uncommon, has been discussed by Bolton (1964).

The above examples do seem to present evidence, albeit tenuous, for the existence of C-H...O and C-H...N interactions. At this point we pass on to C-H...O contacts in carboxylic acid structures considering C(sp)-H and C(sp2)-H bonds in turn.

4.2.1. The carboxyl dimer and the C(sp)-H...O contact. The crystal structure of but-3-ynoic acid (Benghiat & Leiserowitz, 1972c) does not contain intermolecular C-H...O contacts. Rather, the acetylenic C-H bond points at the C-C triple bond (Fig. 19). The H...C-C (midpoint) distance is 3.0 Å. A C(sp3)-H bond is directed towards the carbonyl O atom (C-H...O 3.45, H...O 2.6 Å).

Benghiat & Leiserowitz (1972c) argued that the specific and attractive nature of this C-H...C=C interaction be gauged from the fact that the crystal structure of butynoic acid does not incorporate C-H...O contacts. Whether butynoic acid can indeed form an acceptable structure with C-H...O contacts was considered by examining the hydrogen-bonding structure (47) of an analogous compound, cyanoacetamide (Chieh & Trotter, 1970). The structure consists of hydrogen-bonded dimers where the available N-H bond is linked to a cyano group. Were butynoic acid to adopt either of the isostructural arrangements (48a) or (48b), the group C=N-H-N with an N-H...N distance of 3.1 Å would be replaced by a C-H...O contact of 3.2-3.4 Å. The hypothetical arrangement
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(48a) contains a C-H...O(carbonyl) interaction but requires an antiplanar conformation of the O=C-C-C group. The preferred synplanar conformation embodies a C-H...O(hydroxyl) interaction (48b). In the absence of either (48a) or (48b) it was concluded, tentatively, that the ≏C-H...C≡C(midpoint) and the C(sp²)-H...O(carbonyl) interactions in the observed structure override the acetylenic C-H...O forces in the hypothetical arrangements (48).

The structure of propiolic acid (Leiserowitz & Olovsson, 1976), in contrast to butynoic acid, should permit an acetylenic ≏C-H...O(carbonyl) interaction. The crystal structure (Fig. 20) shows hydrogen-bonded dimers interlinked by a ≏C(-H)...C≡C contact of 3.76 Å (H...C-C 2.85 Å) and a non-linear ≏C(-H)...O(carbonyl) contact of 3.3 Å (H...O 2.8 Å). The C-O lengths of 1.218 and 1.310 Å are distinct indicating little or no disorder, unlike α-tetrolic acid or acetylenedicarboxylic acid. This suggests that the C-H...O(carbonyl) contact plays a role in fixing the orientation of the carbonyl group. It may be argued that but for the C-H...O(carbonyl) interaction, the molecules could have adopted a structure similar to that of β-tetrolic acid (Fig. 6), incorporating the hydrogen-bond catemer motif (11c) and an acetylenic C-H...C≡C contact but not a C-H...O(carbonyl) contact. However, it is difficult to reconcile the non-linear C-H...O contact of propiolic acid with the convincing C-H...O(carbonyl) interaction of 3.2 Å in the crystal structure of the analogous \( N \)-methylpropiolamide (Leiserowitz & Tuvval, 1976) shown in (49). This C-H...O system is linear, the C≡O...H angle is 123° and the C-H bond is almost coplanar with the carbonyl system.

Regarding the ≏C-H...C≡C motif found in butynoic and propiolic acids, it is noteworthy that a (≡C-)D...C≡C(midpoint) contact of 2.68 Å occurs in the low-temperature phase of solid acetylene-d₂ (Koski & Sandor, 1975). These contacts are analogous to the ≏C-I...C≡C(midpoint) contacts found in diiodoacetylene (Dunitz, Gehrer & Britton, 1972). These I...C≡C contacts of about 3.4 Å were interpreted by the authors as being donor...acceptor interactions.

4.2.2. \( \alpha,\beta \)-trans-Unsaturated acids and the C(sp²)-H...O contact. The packing arrangements about the carboxyl dimer of an \( \alpha,\beta \)-unsaturated acid, \( R-CH=CH-CO_2H' \) participating in a lateral C(sp²)-H...O(carbonyl) contact with a C=O...H angle of ~130° are shown in (50) and (51), for syn- and antiplanar C=C-C=O conformations, respectively. Of these two arrangements, in...

Fig. 22. Fumaric acid (Brown, 1966). Interlayer structure of the monoclinic form.
termolecular H⋯H repulsion is certainly more severe in (50); thus (51) containing the antiplanar C=C–C=O conformer should be preferred. While intramolecular forces favour the synplanar C=C–C=O conformation in α,β-unsaturated acids, the acids which exhibit the antiplanar C=C–C=O conformation, i.e. α- and β-fumaric acid, monomethyl muconate, monomethyl fumarate and α-trans-cinnamic acid, pack in the motif (51). Bernstein & Leiserowitz (1972) had pointed out that the crystal structures of fumaric acid (Brown, 1966; Bednowitz & Post, 1966), and trans,trans-monomethylmuconate (Rabinovich & Schmidt, 1967) involve C–H⋯O contacts of about 3.5 Å incorporating motif (51). Fumaric acid is dimorphic (PT, Z=1; P21/c, Z=6); in both modifications the molecular structures contain carboxyl groups with distinct carbonyl and hydroxyl character (average values C=O 1.225, C–OH 1.292 Å) and exhibit the antiplanar C=C–C=O conformation. Fumaric acid lies in layers in its two crystal forms; moreover, these layers are isostructural (Fig. 21). In the monoclinic structure (Fig. 22), the layers are related by 21 axes; in the triclinic structure (Fig. 23) the layers are related by translation. Since intramolecular forces favour the synplanar C=C–C=O conformation, the antiplanar C=C–C=O conformation of fumaric acid must be due primarily to intralayer forces, i.e. C–H⋯O(carbonyl) forces; the interlayer interactions are probably ruled out, since the packing of the layers is different in the two structures. Indeed, the synplanar C=C–C=O conformation is adopted by fumaric acid (C–O 1.19, 1.33 Å) in the adduct β-picoline N-oxide:fumaric acid (Gorres, McAfee & Jacobson, 1975).

The packing features of the higher analogue trans-trans-muconic acid (Bernstein & Leiserowitz, 1972) differ from those of fumaric acid in both the intra- and interlayer structures. Muconic acid is triclinic (PT), containing two molecules, say A and B, per unit cell, each of which forms hydrogen-bonded chains. These chains constitute a layer structure (Fig. 24) in which the two independent molecules A and B are related to each other by a pseudo 21 axis. Within the layer all the C–H bonds are directed approximately at the O atoms with an average C–H⋯O distance of 3.5 Å. The C–O lengths of 1.257 and 1.275 Å in A tend to be equal while those in B are unlike in length (1.236, 1.294 Å), indicating specific carbonyl and hydroxyl bond character. The equal O–H⋯O distances of 2.605 and 2.614 Å for A and B and the infrared spectrum (Bernstein & Leiserowitz, 1972), which exhibits a carbonyl stretching band at 1680 cm⁻¹, indicate that the near equality of the C–O lengths of A is due to disorder of its carboxyl dimer. The conformation of C=C–C=O is synplanar in B, and shows a slight preference for synplanarity in A.

Since the intralayer environments of A and B are essentially identical, the difference in orientational order/disorder of their carboxyl groups must be associated with interlayer environment. The direction of offset between successive layers is such that the interlayer contacts of A and B are not alike; this is evident particularly along the 4 Å stack axis. The stacking patterns of carboxyl dimers of A assuming synplanar and antiplanar C=C–C=O conformations, are shown in (53a) and (53b), respectively.
Regarding the monomethyl derivatives of fumaric acid (Leiserowitz & Tang, 1976) and muconic acid (Rabinovich & Schmidt, 1967), both structures (Figs. 2 and 3) exhibit the motif (51) with intralayer C—H···O distances of 3.54 and 3.49 Å, respectively. The carboxyl group of the fumarate shows a measure of disorder (1.246, 1.276 Å) with a slight preference for the antiplanar C=C—C=O conformation; on the other hand, the carboxyl group of the muconate shows distinct carbonyl C=O and hydroxyl C—OH bonds (1.228, 1.308 Å), the conformation of C=C—C=O being antiplanar. This difference in carboxyl disorder between these two structures must be due primarily to differences in their stacking arrangements. The stacking geometry of the C=C—CO₂H groups of the fumarate (Fig. 2) resembles that of the B molecules (52) of muconic acid. However, the conformation of the C=C—C=O group is antiplanar and partially disordered in the fumarate, and is synplanar in the B molecules of muconic acid. Similarly, while the stacking arrangement of the C=C—CO₂H groups of the muconate resembles that of the A molecules of muconic acid (53), the antiplanar carboxyl group of the muconate exhibits little or no disorder while the carboxyl group of A shows pronounced disorder.

We may resolve this apparent incongruity as follows. The tendency towards the antiplanar C=C—C=O conformation in the fumarate is consistent with a balance between the stacking and intramolecular forces on one hand, which would favour the synplanar C=C—C=O conformation like the B molecules of muconic acid, and, on the other hand, the lateral C—H···O contact of the fumarate which would favour the antiplanar C=C—C=O conformation. Similarly, the antiplanar C=C—C=O conformation in the muconate is possibly stabilized by a balance between the C—H···O interaction which would favour the antiplanar C=C—C=O conformation, and the stacking arrangement which favours a disordered carboxyl group as in the A molecular stack in muconic acid.

\[ \text{Fig. 25. Furane-\(\alpha,\alpha'\)-dicarboxylic acid (Martuscelli \\& Pedone, 1968). Intralayer packing. Distances: C—O 1.315, C=O 1.205, O—H···O 2.66 and C—H···O 3.32 Å. Adjacent molecules within the layer are offset by 0.8 Å.} \]

\[ \text{Fig. 26. Acrylic acid (Higgs \\& Sass, 1963; Chatani, Sakata \\& Nitta, 1963). Packing arrangement seen along [001]. Distances: C—H···O 3.3 and 3.6 Å.} \]

\[ \alpha\text{-trans-Cinnamic acid (Ladell, McDonald \\& Schmidt, 1956) exists in the antiplanar C=C—C=O conformation in the solid state. The carbonyl and hydroxyl bonds are distinct (1.22, 1.30 Å). The structure (54) shows a lateral C—H···O(carbonyl) contact of 3.66 Å. The carboxyl dimers are not stacked along a short axis, rather the molecules form plane-to-plane contact across the centre of inversion, so that the carboxyl pairs are sandwiched between benzene rings.} \]
Acids, crystallizes in a layer structure, but does not exhibit motif (51). Nevertheless, the lateral environment (Fig. 26) about the carboxyl pairs does comprise C-H⋅⋅⋅O(carbonyl and hydroxyl) contacts of 3.32 and 3.56 Å, very similar to the intralayer motif (37) of the benzoic acid derivatives.

We deduce from the packing motifs of the α,β-ununsaturated acids discussed above, which exist in the antiplanar C=C=C=O form, that molecules R-CH=CH-CO₂H which do not, or cannot, form C-H⋅⋅⋅O(carbonyl) contacts exist either in the synplanar C=C=C=O conformation or show some disorder of their carboxyl groups depending upon the nature of their stacking arrangements. In terms of these arguments, we may account for the conformational properties of fumaric (Benghiz, Kaufman, Leiserowitz & Schmidt, 1972) and muconic acids (see § 3.2.3). Fumaramic acid, an analogue of fumaric acid and monomethyl fumarate, displays a synplanar C=C=C=O conformation at the carboxyl end of the molecule; the synplanar C=C=C=O conformation at the amide end is consistent with the conformational pattern of amides. Assuming the antiplanar C=C=C=O conformation (55), it is possible to construct a hydrogen-bonding scheme similar to that of the observed crystal structure (Fig. 9). However, such a packing scheme would not include a C-H⋅⋅⋅O(carbonyl) contact; nor is it possible to devise a packing scheme from (55) containing the full complement of hydrogen bonds as well as a C-H⋅⋅⋅O(carbonyl) contact. In a similar manner we may account for the synplanar C=C=C=O conformation in muconamic acid.

4.3. Intralayer contacts between carboxyl dimers

The lateral contacts between carboxyl groups observed in the layer structures of fumaric acid, monomethyl fumarate and furane-α,α’-dicarboxylic acid all include the motif (56) which incorporates the contact geometry between hydroxyl O atoms (⋯O⋅⋅⋅O) dis-

cussed earlier (§ 3.1). The distance between the hydroxyl O atoms lies in the range 2.96-3.13 Å. This type of contact is also present in the layer structure of mesaconic acid (Gupta & Yadav, 1972) shown in (57). The distance between the hydroxyl O atoms is 2.88 Å.

According to Gupta & Yadav, this short O⋅⋅⋅O contact represents an O-H⋅⋅⋅O hydrogen bond, i.e. the hydroxyl O-H bond participates in a bifurcated O-H⋅⋅⋅O hydrogen bond. While it is possible that this short contact is stabilized by an electrostatic interaction between the O-H proton donor and the lone pair lobe of the neighbouring hydroxyl O atom, it is difficult to describe it as a hydrogen bond; the O-H bond in no way points towards the hydroxyl O atom.

Lateral contact between carboxyl dimers as shown in (58), in which there is no offset between the two dimers parallel to the O-H⋅⋅⋅O line, i.e. the angle O-(H)-O is ~90°, has not been encountered. This arrangement is unfavourable and does not permit close intermolecular contact as demonstrated by the crystal structure of benzamide-succinic acid discussed earlier (§ 3.1).

4.4. Interlayer contact between carboxyl dimers

The two principal modes of interplanar contact between carboxyl dimers are shown in (59) and (60).
Molecules which pack in this manner are listed in Table 5. The dimers which appear in motif (59) may be offset along either the C=O bond (59a), the C-OH bond (59b) or a disordered combination thereof, as is evident from Table 5. Thus the energy difference between the two modes (59a) and (59b) must be small. A very similar situation arises in (60) where the carboxyl groups interact via an antiparallel arrangement of C-O bonds, which may have either carbonyl (60a) or hydroxyl character (60b), or a disordered combination of the two.

This paper has demonstrated evidence favouring the role of O-H...O lone pair geometry in the hydrogen-bonding of carboxylic groups. The hydrogen-bonding modes of carboxylic acids have been discussed, in particular monocarboxylic acids R-CO$_2$H as a function of the size and chirality of R. The study has revealed some of the systematics of benzoic acid packing, the primary stacking features of carboxyl groups, the layer structures of some $\alpha,\beta$-unsaturated carboxylic acids in terms of C=C=O(carbonyl) contacts and the antiplanar conformation of the C=C=O system. It is hoped that this paper has shown the need for further studies, e.g. crystal structure analyses of monocarboxylic acids containing chiral residues to correlate the hydrogen-bonding motifs and the nature of the chiral residues; a more detailed knowledge of the energy of the O-H...O(carbonyl) bond as a function of angular geometry and of the possible role played by C-H...O(carbonyl) contacts in determining overall crystal structure.

I am indebted to the late G. M. J. Schmidt for his support, advice and criticism of this work. I am grateful to V. Benghiat, J. Bernstein, C.-P. Tang and O. Vor der Bruck who were engaged in structure analyses. I wish to thank F. Nader, M. Lahav and A. Hagler for stimulating discussions, and J. D. Dunitz for various suggestions. Lastly I wish to express my sincere thanks to I. Olovsson and members of his laboratory for their kindness, assistance, and for the working facilities they placed at my disposal during my stay in Uppsala. Partial support from a MINERVA grant is acknowledged.

References


Table 5. The two modes (59) and (60) of interplanar contact between carboxyl groups

<table>
<thead>
<tr>
<th>Compound</th>
<th>Length (Å) of C-O$_1$ bond in motif (59)</th>
<th>Length (Å) of C-O$_1$ bond in motif (60)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\beta$-Tetrolic acid</td>
<td>1.204</td>
<td>1.205</td>
<td>Benghiat &amp; Leiserowitz (1972a)</td>
</tr>
<tr>
<td>$\alpha$-Tetrolic acid</td>
<td>1.204</td>
<td>1.205</td>
<td>Benghiat &amp; Leiserowitz (1972a)</td>
</tr>
<tr>
<td>Furan-$\alpha,\alpha'$-dicarboxylic acid</td>
<td>1.204</td>
<td>1.205</td>
<td>Martuscelli &amp; Pedone (1968)</td>
</tr>
<tr>
<td>Fumaramic acid</td>
<td>1.204</td>
<td>1.205</td>
<td>Benghiat, Kaufman, Leiserowitz &amp; Schmidt (1972)</td>
</tr>
<tr>
<td>Triclinic fumaric acid</td>
<td>1.204</td>
<td>1.205</td>
<td>Bednowitz &amp; Post (1966)</td>
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<tr>
<td>Monomethyl fumarate</td>
<td>1.204</td>
<td>1.205</td>
<td>Leiserowitz &amp; Tang (1976)</td>
</tr>
<tr>
<td>$\alpha$-Terephthalic acid</td>
<td>1.204</td>
<td>1.205</td>
<td>Bernstein &amp; Leiserowitz (1972)</td>
</tr>
<tr>
<td>$\beta$-Terephthalic acid</td>
<td>1.204</td>
<td>1.205</td>
<td>Rabinovich &amp; Schmidt (1967)</td>
</tr>
<tr>
<td>$\alpha$-Terephthalic acid</td>
<td>1.204</td>
<td>1.205</td>
<td>Sim, Robertson &amp; Goodwin (1955)</td>
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<tr>
<td>p-Chlorobenzoic acid</td>
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<td>1.205</td>
<td>Bailey &amp; Brown (1967)</td>
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<td>p-Bromobenzoic acid</td>
<td>1.204</td>
<td>1.205</td>
<td>Miller, Paul &amp; Curtin (1974)</td>
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<td>p-Nitrobenzoic acid</td>
<td>1.204</td>
<td>1.205</td>
<td>Ohkura, Kashimo &amp; Haisa (1972)</td>
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<tr>
<td>2-Chlorobiphenyl-4-carboxylic acid</td>
<td>1.204</td>
<td>1.205</td>
<td>Tavale &amp; Pant (1971)</td>
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<tr>
<td>2'-Chlorobiphenyl-4-carboxylic acid</td>
<td>1.204</td>
<td>1.205</td>
<td>Sutherland &amp; Høy (1969)</td>
</tr>
<tr>
<td>2-Chlorobiphenyl-4-carboxylic acid</td>
<td>1.204</td>
<td>1.205</td>
<td>Sutherland (1969)</td>
</tr>
<tr>
<td>2'-Chlorobiphenyl-4-carboxylic acid</td>
<td>1.204</td>
<td>1.205</td>
<td>Sutherland (1970)</td>
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<td>2-Chlorobiphenyl-4-carboxylic acid</td>
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<td>Krausse &amp; Dunkel (1966)</td>
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<td>2-Chlorobiphenyl-4-carboxylic acid</td>
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<td>1.205</td>
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<td>1.205</td>
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<td>1.205</td>
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</tr>
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</table>

* The two C-O lengths of 1.33 and 1.37 in 2-naphthoic acid are obviously unreliable
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