The Structure of 2-Amino-1,3-oxazole*

BY A. ALBINATI† AND M. G. MARCON

Istituto di Chimica del Politecnico, Piazza L. da Vinci 32, 20133 Milano, Italy and Istituto di Chimica Farmaceutica dell'Università, Milano, Italy

P. TRALDI

Centro di Studio per le Sostanze Organiche Naturali, CNR, c/o Istituto di Chimica del Politecnico, Milano, Italy

AND P. CAVOLI

Istituto di Chimica Generale, Via Loredan 2, 35100 Padova, Italy

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Abstract. C₃H₄N₂O, \( M_r = 84.08 \), monoclinic, \( P2_1/c \), \( Z = 4 \), \( a = 10.093 (4) \), \( b = 3.972 (2) \), \( c = 10.081 (4) \) Å, \( \beta = 78.98 (2)° \) (from a least-squares refinement of 20 values of 20 reflections), \( V = 396.7 \) Å³, \( D_x = 1.407 \) Mg m⁻³. 714 independent reflections up to \( \sin \theta/\lambda = 0.5947 \) Å⁻¹ (Mo K\( \alpha \) radiation) were collected. The structure was solved by direct methods and refined to a final \( R \) of 0.042 for 455 observed reflections. The molecule is planar and the geometry is consistent with that expected for oxazoles.

Introduction. Oxazole derivatives constitute an interesting class of substances with a wide range of applications, for example as pharmaceuticals, optical-sensitizing dyes and scintillants (for reviews see Traldi, Vettori & Clerici, 1980; Lakhan & Ternai, 1974).

Mass-spectral studies have been extensively used, beside X-ray crystallography, to determine the structure of various complex oxazoles (Traldi et al., 1980). In mass-spectrometric studies, MO calculations based on various approximations have been widely used (Levsen, 1978) to describe the EI mass-spectrometric behaviour and to clarify and confirm mechanistic hypotheses; in particular simple molecules have been successfully used as model compounds.

The starting point for the calculations of the electronic distribution, both of the neutral species and the ionic moiety, is usually the X-ray-determined geometry, so accurate data on simple 'model' compounds are needed.

As part of a systematic study of some five-membered-ring heterocyclic compounds, it seemed interesting to determine and study the structure of one such 'model compound': 2-amino-1,3-oxazole. Moreover, the title compound is particularly interesting because its mass-spectrometric behaviour, which has been studied in some detail (Selva, Traldi, Rapi, Ginanneschi & Chelli, 1979), differs strongly from that of other substituted oxazoles, being influenced by the electron-donating property of the amino group.

Data were collected on an automated PW 1100 four-circle diffractometer using an \( \omega/2\theta \) scan mode, up to \( \sin \theta/\lambda = 0.5947 \) Å⁻¹ (graphite-monochromated Mo K\( \alpha \) radiation, \( \lambda = 0.71069 \) Å).

The scan speed was 0.05° s⁻¹ and a constant scan width of 1.40° was used. Background was measured for 10 s at each side of the peak and the values were subsequently averaged. Out of the 714 independent reflections collected, 455 were considered as observed having \( \omega_{\text{net}} \geq 3\sigma(I) \). Three standard reflections were measured every hour to check the stability of the experimental conditions and the decay of the crystal; no significant variation was detected.

Table 1. Final positional coordinates and temperature factors, \( B_{\text{eq}} \) or \( B_{\text{iso}} \), with e.s.d.'s in parentheses

<table>
<thead>
<tr>
<th>( B_{\text{eq}} ) or ( B_{\text{iso}} ) (Å²)</th>
<th>( x )</th>
<th>( y )</th>
<th>( z )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C(1) )</td>
<td>0.8099 (2)</td>
<td>0.8784 (6)</td>
<td>0.3508 (2)</td>
</tr>
<tr>
<td>( C(2) )</td>
<td>0.6174 (3)</td>
<td>1.1040 (7)</td>
<td>0.3364 (3)</td>
</tr>
<tr>
<td>( C(3) )</td>
<td>0.6987 (3)</td>
<td>1.1146 (8)</td>
<td>0.2184 (3)</td>
</tr>
<tr>
<td>( N(1) )</td>
<td>0.8243 (2)</td>
<td>0.9681 (5)</td>
<td>0.2255 (2)</td>
</tr>
<tr>
<td>( N(2) )</td>
<td>0.8982 (2)</td>
<td>0.7225 (7)</td>
<td>0.4142 (3)</td>
</tr>
<tr>
<td>( O )</td>
<td>0.6870 (2)</td>
<td>0.9479 (4)</td>
<td>0.4269 (2)</td>
</tr>
<tr>
<td>( H(C2) )</td>
<td>0.524 (3)</td>
<td>1.154 (8)</td>
<td>0.371 (3)</td>
</tr>
<tr>
<td>( H(C3) )</td>
<td>0.684 (3)</td>
<td>1.195 (8)</td>
<td>0.132 (3)</td>
</tr>
<tr>
<td>( H(N2) )</td>
<td>0.986 (3)</td>
<td>0.659 (8)</td>
<td>0.367 (3)</td>
</tr>
<tr>
<td>( H'(N2) )</td>
<td>0.874 (3)</td>
<td>0.705 (9)</td>
<td>0.500 (4)</td>
</tr>
</tbody>
</table>

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Table 2. Bond lengths (Å) and angles (°) with e.s.d.'s in parentheses

<table>
<thead>
<tr>
<th></th>
<th>Calculated*</th>
<th>Calculated*</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(1)-O</td>
<td>1.356 (3)</td>
<td>1.35</td>
</tr>
<tr>
<td>C(1)-N(1)</td>
<td>1.294 (3)</td>
<td>1.31</td>
</tr>
<tr>
<td>C(1)-N(2)</td>
<td>1.343 (4)</td>
<td>0.91 (5)</td>
</tr>
<tr>
<td>C(2)-O</td>
<td>1.399 (4)</td>
<td>1.36</td>
</tr>
<tr>
<td>C(1)-N(1)-C(3)</td>
<td>103.0 (2)</td>
<td>107.5</td>
</tr>
<tr>
<td>C(1)-O-C(2)</td>
<td>114.6 (2)</td>
<td>113.1</td>
</tr>
<tr>
<td>O-C(1)-N(1)</td>
<td>110.7 (2)</td>
<td>116.0</td>
</tr>
<tr>
<td>C(2)-C(3)-N(1)</td>
<td>110.7 (2)</td>
<td>116.0</td>
</tr>
</tbody>
</table>

* According to Roche et al. (1971).
† Average value.

Fig. 1. A schematic view of the molecule showing numbering of the atoms.

Discussion. The oxazole ring is planar, the maximum deviation from the least-squares plane (defined by the ring atoms) being 0.009 Å.

The bond lengths in the ring show a certain amount of shortening consistent with some aromatic character. For example the C(3)-N(1) bond length [1.343 (4) Å] is shorter than the expected value of 1.475 Å when N is sp2 hybridized (Sutton, 1965) and comparable with the value 1.380 (5) Å found in 3-(p-aminophenyl)-5-phenyl-1,2,4-oxadiazole (Albinati & Brückner, 1978), or 1.403 (5) Å in 4-(p-chlorobenzylidene)-1,3-diphenyl-5-pyrazolone (Bovio & Locchi, 1972).

The C(1)-N(2) bond is also shorter than expected [1.343 (4) Å] and somewhat consistent with a multiple-bond character (Allman, 1975).

On the other hand the presence of two localized double bonds [C(2)–C(3) and C(1)–N(1)] is consistent with the not fully aromatic nature of the oxazole (e.g. facile Diels–Alder reactions, singlet oxygen auto-oxidation, etc.); the C(2)–C(3) bond [1.310 (4) Å] is shorter than the value of 1.351 (3) Å for a similar bond in 2-methyl-4-nitroimidazole (Kalman, van Meurs & Toth, 1980), and 1.36 (1) Å in pyrazole (La Cour & Rasmussen, 1973), where a high degree of π delocalization is present. Another example of extensive double-bond character for the C–C and C–N bonds is found in the related compound 2,2'-p-phenylenebis-(5-phenyl-1,3-oxazole) (Ambats & Marsh, 1965) where values of 1.347 (4) Å and 1.294 (4) Å are found.

The two C–O bonds are non-equivalent, the shorter being that bonded to the carbon substituted with the electron-donating NH2 group; both fall in the expected range for heterocyclic compounds [e.g. 1.371 (5) Å in furan].

The NH2 group lies in the plane of the ring but shows a significant distortion of the bond angles O–C–N and N–C–N [116.3 (2) and 129.0 (1)°] that may be due to non-bonding interactions.

The packing distances are in the range 3.60–4.20 Å. Several MO calculations have been carried out for oxazole and it may be interesting to compare the calculated geometry for this molecule (Roche, D’Amato & Benard, 1971) with that found for the present compound (cf. Table 2).

There is good overall agreement between the calculated values for oxazoles and the geometry found here, it being possible to ascribe the differences to the presence of the NH2 substituent.

References


Structure of Alnusenone (D:B-Friedoolean-5-en-3-one)

BY MINORU OHKI, KOHICHI TACHIBANA AND TOSHIRO KURODA

Research Institute, Wakamoto Pharmaceutical Co. Ltd., Kanate, Ohimachi, Ashigarakamigun, Kanagawa 258, Japan

AND AKIO TAKENAKA AND YOSHIOSASADA

Laboratory of Chemistry for Natural Products, Tokyo Institute of Technology, Nagatsuta, Midori-ku, Yokohama 227, Japan

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Abstract. C₃₀H₄₈O, Mᵣ = 424.71, triclinic, P1, a = 7.338(1), b = 14.856(1), c = 6.267(1) Å, α =
97.10(1), β = 113.60(1), γ = 93.20(1)°, Z = 1, Dx =
1.10 Mg m⁻³, μ(Cu Kα) = 4.9 cm⁻¹. The structure
was refined by a block-diagonal least-squares method.
The final R value was 0.037 for 1904 reflexions. The cis
fusion at the D/E junction and the axial α-methyl
group at C(13) cause the D and E rings to be in the
twist-boat and boat conformations respectively.

Introduction. Alnusenone (D:B-friedoolean-5-en-3-one, I), a naturally occurring triterpene (Chapon &
David, 1953), was isolated from Trogopterum Faeces
(Akamatsu, 1970).

Prismatic crystals were obtained from an ace-
tone–methanol solution at room temperature. Oscil-
lation and Weissenberg photographs indicated the
crystal to be triclinic. As the compound is optically
active, the space group should be P1. A crystal, 0.4 ×
0.5 × 0.65 mm, was mounted on a Rigaku automated
four-circle diffractometer. The unit-cell dimensions
were determined by least-squares refinement of 28
values for 22 high-angle reflexions. Intensity data were collected on the diffractometer
by the use of Ni-filtered Cu Kα radiation (λ =
1.54184 Å), with an ω/2θ scanning technique (2θ ≤
122°). Five reference reflexions showed no significant
intensity deterioration during the course of data
collection. Corrections were made for Lorentz and
polarization factors, but not for absorption. A total of
1904 independent reflexions were obtained, of which 7
reflexions had zero intensities [I ≤ σ(1)]. The standard
deviations were estimated by the equation σ²(Fᵦ) =
σᵦ²(Fᵦ) + qFᵦ; here σᵦ²(Fᵦ) was evaluated by counting
statistics and q (1.689 × 10⁻⁵) was derived from the
variations of the monitored reflexions.

Many peaks corresponding to cyclohexane rings
appeared on an E map calculated with MULTAN 78
(Main, Hull, Lessinger, Germain, Declercq & Woolf-
sion, 1978). One of the least-squares trials among
several possible models gave a promising low R value,