Structure of 13-Methyl-2,10-dioxatricyclo[4.4.4.01,6]tetradecane at 96 K

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Abstract

The structure of the title compound has been determined at room temperature (RT) and with improved accuracy at 96 K. \(\text{C}_{12}\text{H}_{22}\text{O}_2\), \(M_r = 210.3\), is triclinic, space group \(P\overline{1}\): \(a = 6.420 (3), b = 8.734 (4), c = 11.520 (5) \text{Å}, \alpha = 68.59 (3), \beta = 82.37 (3), \gamma = 80.27 (3)°, \ V = 590.95 \text{Å}^3, \ g(\text{Mo }K\alpha) = 0.083 \text{mm}^{-1}\) at RT; \(a = 6.347 (3), b = 8.685 (2), c = 11.336 (3) \text{Å}, \alpha = 68.47, \beta = 82.37 (4), \gamma = 80.09 (3)°, \ V = 572.05 \text{Å}^3, \ g(\text{Mo }K\alpha) = 0.086 \text{mm}^{-1}\) at 96 K; \(Z = 2, \ D_e = 1.182 \text{(RT)} \text{and } 1.221 \text{Mg m}^{-3} (96 \text{K})\). The low-temperature data extend to \(\sin \theta/\lambda = 0.86 \text{Å}^{-1}\) and include 5988 independent reflexions. The structure was solved by direct methods and refined to \(R = 0.033\) for 4080 reflexions with \(I \geq 3\sigma_I\). The bond-length difference between the two chemically equivalent, conformationally inequivalent, geminal C-O bonds in the \(sc, ap\) conformation is 0-026 (1) \text{Å}, and other pairs of chemically equivalent bonds do not differ by more than 0-003 \text{Å}. The molecule behaves as a rigid body with its main librational and translational axes nearly parallel to the principal molecular axis with the smallest moment of inertia. The disordered crystal structure of the unsubstituted propellane, \(2,10\)-dioxatricyclo[4.4.4.01,6]tetradecane, \(\text{C}_{12}\text{H}_{20}\text{O}_2\), is briefly described. At 103 K the orthorhombic cell has \(a = 12.26 (1), b = 12.22 (1), c = 13.79 (1) \text{Å}, Z = 8\), probable space group \(P2_1ca\).

Introduction

The two equivalent, geminal C-O bonds of the dioxapropellane (1) become conformationally non-equivalent in the expected chair-chair-chair form of the molecule. Our attempt to obtain experimental evidence for a difference in length between such bonds was thwarted by disorder in the crystal structure of (1) (see Appendix). The methylated title compound (2) was therefore prepared. Details of the synthesis will be given elsewhere; here we report on its crystal structure.

Details of the analysis

The substance (m.p. 319 K) was crystallized from ether at 258 K and a first data set collected with a Hilger & Watts Y290 diffractometer at room temperature. Although the structure could be solved by direct methods the data were not good enough to yield results of the desired accuracy. A single crystal of better quality (dimensions 0-15 × 0-3 × 0-55 mm) was grown by sublimation in an evacuated capillary tube and a new, more extensive, data set (\(\sin \theta/\lambda\) limit 0-567) was collected with a Philips PW 1100 diffractometer at 96 K.
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Table 2. Fractional atomic coordinates ($\times 10^3$) and vibrational parameters ($\times 10^4$ Å$^2$) for C and O atoms (e.s.d.'s in parentheses)

| C(1)   | 33305 (10) | 15246 (8) | 71386 (6) | 93 (7) | 136 (7) | 145 (7) | -32 (2) | -9 (2) | -60 (3) |
| C(2)   | 31092 (12) | 28922 (9) | 77324 (7) | 156 (7) | 169 (7) | 191 (7) | -38 (2) | -27 (2) | -92 (3) |
| C(3)   | 14727 (13) | 26219 (10) | 88845 (7) | 218 (8) | 238 (7) | 188 (8) | -40 (3) | -5 (2) | -130 (4) |
| C(4)   | -62355 (12) | 23600 (10) | 85227 (8) | 171 (7) | 262 (8) | 211 (7) | -37 (3) | 46 (2) | -143 (4) |
| O(5)   | -3105 (8) | 9997 (6) | 80730 (5) | 138 (7) | 228 (7) | 177 (7) | -73 (2) | 50 (2) | -108 (3) |
| C(6)   | 10769 (10) | 12182 (8) | 69583 (6) | 96 (7) | 158 (7) | 136 (7) | -36 (2) | 3 (2) | -68 (3) |
| C(7)   | 45396 (11) | -983 (9) | 80213 (7) | 139 (7) | 156 (7) | 150 (7) | -27 (2) | -24 (2) | -50 (3) |
| C(8)   | 35729 (13) | -16418 (9) | 76671 (7) | 136 (7) | 157 (7) | 162 (7) | -11 (2) | -42 (3) |
| C(9)   | 22739 (12) | -19090 (9) | 76131 (7) | 150 (7) | 190 (7) | 167 (7) | -63 (2) | 1 (2) | -63 (3) |
| C(10)  | 10921 (11) | -3642 (9) | 66762 (7) | 120 (7) | 157 (7) | 142 (7) | -21 (2) | -11 (2) | -42 (3) |
| C(11)  | 46172 (10) | 21151 (8) | 58307 (7) | 105 (7) | 148 (7) | 163 (7) | -32 (2) | 8 (2) | -44 (3) |
| C(12)  | 33809 (11) | 31454 (9) | 47735 (7) | 156 (7) | 178 (7) | 153 (7) | -24 (2) | -24 (2) | -62 (3) |
| C(13)  | 11903 (11) | 31454 (9) | 47735 (7) | 156 (7) | 178 (7) | 153 (7) | -24 (2) | -24 (2) | -62 (3) |
| C(14)  | 58221 (15) | -31728 (10) | 85862 (8) | 297 (8) | 210 (7) | 12 (3) | -64 (3) | -31 (3) |
| C(15)  | 58221 (15) | -31728 (10) | 85862 (8) | 297 (8) | 210 (7) | 12 (3) | -64 (3) | -31 (3) |

Results and discussion

Bond lengths and angles obtained from the final coordinates are shown in Table 3; they have e.s.d.'s of about 0.001 Å and 0.1° respectively. A correction of +0.002 Å should be added uniformly to the bond lengths to allow for rigid-body libration motion (see later). Of the five pairs of chemically equivalent bonds

Table 3. Bond distances (Å), bond angles (°) and selected torsion angles (°)

| C-C | 1.551 | C(8)-C(15) | 1.524 |
| C-C | 1.545 | C(11)-C(12) | 1.526 |
| C-C | 1.529 | C(13)-C(14) | 1.516 |
| C-C | 1.516 | C(15)-O(5) | 1.432 |
| C-C | 1.412 | O(14)-C(6) | 1.438 |

0.86 Å$^{-1}$, 5988 independent reflections. 4080 with $I > 3\sigma(I)$ was collected at 96 K with an Enraf-Nonius CAD-4 diffractometer equipped with a graphite monochromator (Mo Ka radiation, $\lambda = 0.71069$ Å) and a low-temperature device. The structure was solved by direct methods and refined by full-matrix least-squares analysis with XRAY (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). The final $R$ was 0.039, with anisotropic vibration parameters for C and O, isotropic for H, and a modified weighting scheme (Dunitz & Seiler, 1973) with $r = 0.1°$. All bond lengths should be increased by 0.002 Å to allow for rigid-body libration correction.

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36524 (26 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
in the molecule, the only pair that shows an appreciable difference (>0.003 Å) in bond length is C(6)–O(5), 1.412 Å, and C(6)–O(14), 1.438 Å, difference 0.026 Å. The conformational inequivalence of these two bonds is imposed by the chair-chair-chair form of the molecule. As is clear from Fig. 1, which shows the molecular conformation, the longer bond C(6)–O(14) is synclinal (sc) to O(5)–C(4), and hence antiperiplanar (ap) to a tetrahedral lone pair on O(5), whereas the shorter bond C(6)–O(5) is ap to O(14)–C(13). Our observed difference of 0.026 Å is in pleasing agreement with results of calculations on methanediol and methoxymethanol in the sc, ap conformation which predict a relative lengthening by 0.025–0.030 Å of the C–O bond ap to a lone pair (Jeffrey, Pople & Radom, 1974; Lehn, Wipff & Bürgi, 1974; Williams, Scarsdale, Schäfer & Geise, 1981). Although bond-length differences between geminal C–O bonds have been observed in many molecules and may range up to 0.1 Å or more depending on various factors (Bürgi, Dunitz & Shelter, 1974; Chadwick & Dunitz, 1979; Jones, Kennard, Kirby & Martin, 1979; Jones & Kirby, 1979) we believe that this is the first example of an authentic bond-length difference between chemically equivalent geminal C–O bonds in the sc, ap conformation and attributable exclusively to the stereo-electronic factor.

In this connexion it is noteworthy that this structure does not fit at all well with the empirical correlation \( \Delta \beta (\text{°}) = +173 \Delta d (\text{Å}) \) found by Bürgi et al. (1974) between geminal C–O bond-length differences \( \Delta d = d_2 - d_1 \) and OCC angle differences \( \Delta \beta = \beta_1 + \beta_2 - \beta_3 - \beta_4 \); see Fig. 2 for explanation of symbols). This correlation says that as one C–O bond lengthens and the other shortens, the shorter bond tends to move towards the CCC plane and the longer bond tends to move away from it. In our case this tendency is not observed: we have \( \Delta \beta = -5.0^\circ, \Delta d = +0.026 \text{ Å} \), so that even the sign is wrong. The most likely explanation of the discrepancy is that the empirical correlation is based mainly on structures showing large \( \Delta d \) values which tend to occur in molecules where the geminal C–O bonds are very different in their chemical reactivity, and in such molecules the ground-state structures may already show distortions pointing along the reaction pathway [see Chadwick & Dunitz (1979) and Jones & Kirby (1979) for examples]. In our case, with chemically equivalent C–O bonds, any such motion along the reaction coordinate for heterolytic rupture of one bond to give an oxocarbonium ion at C(6) must be minimal and outweighed by other factors. Among these, the most important is probably the steric compression between the axial H atoms H(10, 1) and H(13, 2), \( d = 2.16 (2) \text{ Å} \). This should tend to open the angle C(14)–C(6)–C(10) at the expense of O(5)–C(6)–C(10), which is by far the smallest \([104.4 (1)^\circ]\) of the four bridgehead O–C–C angles. On the other hand, the small OOC angle of 105.1 (1)^\circ follows directly from Bent’s (1961) rule.

The remaining molecular parameters do not seem to call for any special comments. They agree reasonably well with those found in the symmetrical, unsubstituted 2,10,11-trioxatricyclo[4.4.4.0^1,6]tetradecane (Banyard & Dunitz, 1976). However, it seems futile to try to make a detailed comparison since the latter structure was determined at room temperature and shows much higher vibrational parameters and indications of disorder.

**Thermal-motion analysis**

For a completely rigid body \( \Delta A_{A,B} = z_{A,B}^2 - z_{B,A}^2 \) (where \( z_{A,B}^2 \) is the mean-square vibration amplitude of atom A in the direction B) should be zero for every pair of atoms A, B in the molecule (Rosenfield, Trueblood & Dunitz, 1978). For the 15 x 14/2 = 105 pairs of heavy atoms in the molecule we find \( \langle \Delta A^2 \rangle^{1/2} = 7.5 \times 10^{-4} \text{ Å}^2 \) with \( \Delta A_{\text{max}} = 22 \times 10^{-4} \text{ Å}^2 \); for the 17 bonded pairs the corresponding values are 5 \times 10^{-4} \text{ Å}^2 and 9 \times 10^{-4} \text{ Å}^2. As the e.s.d.'s of the \( \Delta A's \) are approximately \( (2)^{1/2} \sigma(U) \) or about 10 \( \times 10^{-4} \text{ Å}^2 \) (see Table 1), the agreement with the rigid-body model is as good as can be expected – or even a little better. Calculation of the rigid-body motions with \( \text{THMB} \) (Trueblood, 1978) gave the following results for the \( T, L \) and \( S \) tensors (referred to a molecular inertial coordinate system):
In this coordinate system both \( \mathbf{L} \) and \( \mathbf{T} \) are approximately diagonal, with the main libration axis and also the main translational direction along \( X \), the principal axis of the molecule corresponding to the smallest moment of inertia. This is approximately along the \( \text{C}(8)-\text{C}(15) \) bond. The agreement between observed and calculated \( U_{ij} \) values is good, as expected from the result of the rigid-body test: \[ \frac{(AU_{ij})^2}{\sigma^2} = 6 \times 10^{-4} \] This is much better agreement than was obtained in our low-temperature structure of 18-crown-6 (Maverick, Seiler, Schweizer & Dunitz, 1980) even though that analysis was based on more extensive experimental data and yielded more accurately determined \( U_{ij} \) values than the present analysis. This shows that, in some cases at least, discrepancies between observed and calculated \( U_{ij} \) values may be attributable more to failure of the underlying rigid-body model than to errors in the experimental vibration amplitudes.

When the atomic coordinates are corrected for libration, they yield bond lengths that are uniformly about 0.002 Å longer than the uncorrected values shown in Table 3.

### APPENDIX

**Crystal structure of (1) (2,10-dioxatricyclo[4.4.4.0^{1,6}]tetradecane, \( \text{C}_{12}\text{H}_{20}\text{O}_{2} \))**

Crystals (m.p. 325 K) prepared by sublimation from a sample kindly provided by Professor P. Deslongchamps were soft and pliable at room temperature. Diffraction measurements at 103 K gave an orthorhombic unit cell: \( a = 12.26 (1), b = 12.22 (1), \) \( c = 13.79 (1) \) Å, \( Z = 8 \). Systematic absences \( (h0l, h = 2n \text{ only}; 0kl, l = 2n \text{ only}) \) were compatible with the space groups \( P2_{1}ca \) or \( Pmca \), but, in addition, all reflections with \( l \) odd were very weak, and there was also a conditional absence: \( (0kl, \text{ if } l \text{ even then } 2k + l = 4n \text{ only}), \) indicating that the subcell with \( c' = c/2 \) can be described in terms of the space groups \( Pn2_{1}a \) or \( Pnma \).

Although the crystal used was not unduly small (dimensions \( \sim 0.3-0.35 \) mm) only 572 reflections out of 1969 measured had \( I > 3\sigma \). An attempt to solve the subcell structure by direct methods in the latter space group was successful in that it led to an interpretable \( E \) map in which atoms 1, 3, 4, 6 lay on the pseudo mirror plane bisecting the COC angle. The next shortest \( \text{C-H} \cdots \text{O} \) distances are \( >2.8 \) Å. In the structure of 18-crown-6 (Maverick et al., 1980) all six \( \text{O} \) atoms were involved in \( \text{C-H} \cdots \text{O} \) interactions at distances of \( 2.45-2.8 \) Å roughly along the tetrahedral lone-pair directions. In the present structure only the 'equatorial' lone pairs on the \( \text{O} \) atoms are thus involved, but the two resulting \( \text{C-H} \cdots \text{O} \) contacts seem to be the principal feature of the crystal packing along \( \text{a} \).
with the pseudo symmetry of the subcell. However, all attempts to refine trial structures in the expanded cell led to apparent disorder at one of the two molecular sites. Since it was clear that accurate C–O distances would not be obtainable with this crystal the analysis was not pursued further.

References


A 1:2 Host–Guest Complex Formed Between 1,4,7,10,13,16-Hexaoxaaclooctadecane (18-Crown-6) and Phenyl Carbamate

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Abstract

C_{12}H_{24}O_{6}.2C_{7}H_{7}NO_{2}, M_r = 538.60, monoclinic, 
P_{2_1}/c, a = 10.053(2), b = 11.893(3), c = 12.359(3) Å, \(\beta = 105.51\) (2)°, \(V = 1423.8\) (5) Å³, \(Z = 2\), \(d_r = 1.26\) Mg m⁻³, \(\mu(Cu K\alpha) = 0.817\) mm⁻¹.

Full-matrix least-squares refinement (non-hydrogen atoms anisotropic, H atoms isotropic) based on 1518 reflections led to a final \(R\) of 0.040. The 18-crown-6 ether sits on a center of symmetry and exhibits approximate \(D_{3d}\) symmetry. The six oxygen atoms are alternately 0.24 (1) Å above and below the mean plane and form a nearly planar hexagon with averaged sides of 2.86 (1) Å. The two guest molecules are related by a center of symmetry and each forms hydrogen bonds with H–O distances of 2.12 (3) and 2.39 (3) Å.

Introduction

The weak interactions between crown ethers and neutral organic molecules are of chemical and biological interest. The study of such interactions may lead to the design of specific host molecules for small neutral biologically active compounds, as well as to a better understanding of secondary interactions that occur at biological receptors or enzyme pockets. These weak interactions may be of importance in stereoselective recognition by receptors and substrates. Although a number of structures of 18-crown-6 ethers with charged species have been described, only the neutral complexes with dimethyl acetylenedicarboxylate (1:1) (Goldberg, 1975), dimethyl sulfone (1:1) (Weber & Vögtlé, 1980), urea (1:5) (Harkema, Van Hummel, Daasvatn & Reinhoudt, 1981) and benzenesulfonamide (1:2) (Knochel, Kopf, Oehler & Rudolph, 1978) have been reported. We would like to describe the