CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* A24, 321–324.

CYGLER, M., PRZYBYLSKA, M. & EDWARDS, O. E. (1982). *Acta Cryst.* B38, 479–482.

GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* A27, 368–376.

PELLETIER, S. W., DeCAMP, W. H., FINER-MOORE, J. & ICHINOHE, Y. (1979). *Cryst. Struct. Commun.* 8, 299–304.

PELLETIER, S. W. & KEITH, L. H. (1970). *Chemistry of the Alkaloids*, edited by S. W. PELLETIER, pp. 503–505. New York: Van Nostrand–Reinhold.

PRZYBYLSKA, M. (1961). *Acta Cryst.* 14, 424–429.

PRZYBYLSKA, M. (1976). *Acta Cryst.* B32, 1638–1642.

PRZYBYLSKA, M. & MARION, L. (1956). *Can. J. Chem.* 34, 185–187.

STEWART, J. M. (1976). XRAY 76. Tech. Rep. TR-466. Computer Science Center, Univ. of Maryland, College Park, Maryland.

Structure of 13-Methyl-2,10-dioxatricyclo[4.4.4.0^{1,6}]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. $C_{13}H_{22}O_2$, $M_r = 210 \cdot 3$, is triclinic, space group $P\bar{1}$: $a = 6 \cdot 420\ (3)$, $b = 8 \cdot 734\ (4)$, $c = 11 \cdot 520\ (5)$ Å, $\alpha = 68 \cdot 59\ (3)$, $\beta = 82 \cdot 37\ (3)$, $\gamma = 80 \cdot 27\ (3)°$, $V = 590 \cdot 95$ Å^3, $\mu(\text{Mo } K\alpha) = 0 \cdot 083$ mm^{-1} at RT; $a = 6 \cdot 347\ (3)$, $b = 8 \cdot 685\ (2)$, $c = 11 \cdot 336\ (3)$ Å, $\alpha = 68 \cdot 47$, $\beta = 82 \cdot 37\ (4)$, $\gamma = 80 \cdot 09\ (3)°$, $V = 572 \cdot 05$ Å^3, $\mu(\text{Mo } K\alpha) = 0 \cdot 086$ mm^{-1} at 96 K; $Z = 2$, $D_c = 1 \cdot 182$ (RT) and $1 \cdot 221$ Mg m^{-3} (96 K). The low-temperature data extend to sin $\theta/\lambda = 0 \cdot 86$ Å^{-1} and include 5988 independent reflexions. The structure was solved by direct methods and refined to $R = 0 \cdot 033$ 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 $0 \cdot 026\ (1)$ Å, and other pairs of chemically equivalent bonds do not differ by more than $0 \cdot 003$ 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[4.4.4.0^{1,6}]tetradecane, $C_{12}H_{20}O_2$, is briefly described. At 103 K the orthorhombic unit cell has $a = 12 \cdot 26\ (1)$, $b = 12 \cdot 22\ (1)$, $c = 13 \cdot 79\ (1)$ 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.

(1)   (2)
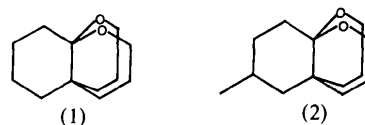
Details of the analysis

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 $0 \cdot 15 \times 0 \cdot 3 \times 0 \cdot 55$ mm) was grown by sublimation in an evacuated capillary tube and a new, more extensive, data set (sin θ/λ limit

Table 1. *Fractional atomic coordinates* ($\times 10^5$) *and vibrational parameters* ($\times 10^4$ Å^2) *for* C *and* O *atoms* (*e.s.d.'s in parentheses*)

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
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 (7)	−40 (3)	−5 (2)	−130 (4)
C(4)	−6235 (12)	23600 (10)	85327 (8)	171 (7)	262 (8)	211 (7)	−37 (3)	46 (2)	−143 (4)
O(5)	−3105 (8)	9996 (7)	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)	45729 (12)	−16418 (9)	76671 (7)	180 (7)	136 (7)	157 (7)	−16 (2)	−11 (2)	−42 (3)
C(9)	22739 (12)	−19090 (9)	76131 (7)	206 (7)	150 (7)	190 (7)	−67 (3)	1 (2)	−63 (3)
C(10)	10921 (11)	−3642 (9)	66627 (7)	144 (7)	169 (7)	180 (7)	−58 (2)	−8 (2)	−84 (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)	35712 (9)	48386 (7)	154 (7)	152 (7)	158 (7)	−39 (2)	1 (2)	−38 (2)
C(13)	11903 (11)	31454 (9)	47735 (7)	156 (7)	178 (7)	153 (7)	−24 (2)	−24 (2)	−62 (3)
O(14)	390 (8)	26429 (6)	59993 (5)	103 (7)	181 (7)	165 (7)	−9 (2)	−19 (2)	−68 (3)
C(15)	58221 (15)	−31728 (10)	85862 (8)	297 (8)	162 (7)	210 (7)	12 (3)	−64 (3)	−31 (3)

Table 2. *Fractional coordinates and isotropic vibrational parameters of* H *atoms* (*all* × 10^3)

	x	y	z	U (Å^2)
H(2,1)	268 (2)	399 (1)	712 (1)	207 (28)
H(2,2)	453 (2)	290 (1)	799 (1)	229 (29)
H(3,1)	123 (2)	358 (2)	915 (1)	271 (31)
H(3,2)	195 (2)	166 (1)	963 (1)	235 (28)
H(4,1)	−125 (2)	341 (1)	790 (1)	269 (30)
H(4,2)	−168 (2)	205 (1)	928 (1)	226 (28)
H(7,1)	606 (2)	11 (2)	803 (1)	256 (30)
H(7,2)	391 (2)	−33 (1)	892 (1)	227 (28)
H(8,1)	527 (2)	−143 (1)	679 (1)	203 (27)
H(9,1)	230 (2)	−289 (2)	739 (1)	238 (29)
H(9,2)	159 (2)	−215 (2)	845 (1)	258 (30)
H(10,1)	174 (2)	−21 (1)	581 (1)	213 (28)
H(10,2)	−42 (2)	−51 (1)	667 (1)	238 (29)
H(11,1)	600 (2)	241 (1)	596 (1)	215 (28)
H(11,2)	503 (2)	114 (1)	549 (1)	235 (28)
H(12,1)	317 (2)	458 (1)	504 (1)	178 (26)
H(12,2)	416 (2)	382 (1)	401 (1)	212 (27)
H(13,1)	25 (2)	415 (2)	422 (1)	267 (31)
H(13,2)	135 (2)	228 (1)	441 (1)	242 (29)
H(15,1)	526 (2)	−340 (2)	946 (1)	354 (35)
H(15,2)	738 (2)	−303 (2)	855 (1)	377 (36)
H(15,3)	582 (2)	−416 (2)	837 (1)	345 (34)

0·86 Å^{-1}, 5988 independent reflexions, 4080 with $I > 3\sigma_I$) was collected at 96 K with an Enraf–Nonius CAD-4 diffractometer equipped with a graphite monochromator (Mo $K\alpha$ radiation, $\lambda = 0\cdot71069$ 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 0·033, with anisotropic vibration parameters for C and O, isotropic for H, and a modified weighting scheme (Dunitz & Seiler, 1973) with $r = 1\cdot7$ Å^2. Atomic coordinates and vibration parameters are listed in Tables 1 and 2.*

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 librational motion (see later). Of the five pairs of chemically equivalent bonds

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

E.s.d.'s are about 0·001 Å for C—O and C—C bond lengths and about 0·1° for bond angles and torsion angles; e.s.d.'s in C—H distances are 0·01–0·02 Å. All bond lengths should be increased by 0·002 Å to allow for rigid-body librational correction.

C(1)—C(6)	1·551		C(8)—C(15)	1·524
C(1)—C(2)	1·545		C(1)—C(11)	1·547
C(2)—C(3)	1·529		C(11)—C(12)	1·526
C(3)—C(4)	1·514		C(12)—C(13)	1·516
C(4)—O(5)	1·432		C(13)—O(14)	1·432
O(5)—C(6)	1·412		O(14)—C(6)	1·438
C(1)—C(7)	1·541		C—H	0·95–1·04
C(7)—C(8)	1·530			
C(8)—C(9)	1·529			
C(9)—C(10)	1·527			
C(10)—C(6)	1·528			

|				
O(5)—C(6)—C(1)	111·8		O(14)—C(6)—C(1)	111·0
O(5)—C(6)—C(10)	104·4		O(14)—C(6)—C(10)	110·2
C(2)—C(1)—C(6)	109·9		C(11)—C(1)—C(6)	109·5
C(2)—C(1)—C(7)	109·1		C(11)—C(1)—C(7)	109·6
C(6)—O(5)—C(4)	115·0		C(6)—O(14)—C(13)	115·5
O(5)—C(4)—C(3)	110·9		O(14)—C(13)—C(12)	111·6
C(4)—C(3)—C(2)	109·1		C(13)—C(12)—C(11)	109·9
C(3)—C(2)—C(1)	113·3		C(12)—C(11)—C(1)	112·8
C(10)—C(6)—C(1)	113·8		C(7)—C(8)—C(15)	111·0
O(5)—C(6)—O(14)	105·1		C(9)—C(8)—C(15)	112·1
C(7)—C(1)—C(6)	110·0			
C(2)—C(1)—C(11)	108·7		C(4)—O(5)—C(6)—O(14)	−62·8
C(6)—C(10)—C(9)	112·7		O(5)—C(6)—O(14)—C(13)	178·2
C(10)—C(9)—C(8)	110·5			
C(9)—C(8)—C(7)	109·5			
C(8)—C(7)—C(1)	115·1			
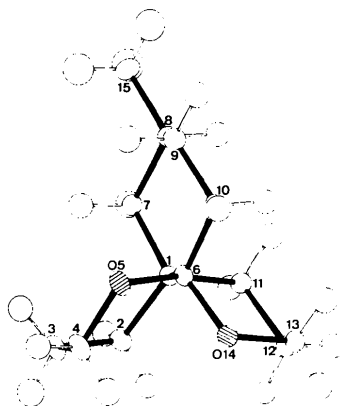
Fig. 1. Molecular structure showing atomic numbering and vibration ellipsoids (96 K) at the 50% probability level.

Fig. 2. Explanation of symbols defining the geometry of the two geminal C—O bonds.

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 & Shefter, 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 stereoelectronic factor.

In this connexion it is noteworthy that this structure does not fit at all well with the empirical correlation $\Delta\beta(^\circ) = +173\Delta d(\text{Å})$ 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 $\Delta\beta = -5.0^\circ$, $\Delta d = +0.026$ Å, so that even the sign is wrong. The most likely explanation of the discrepancy is that the empirical correlation is

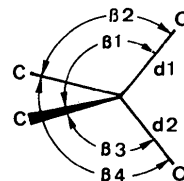based mainly on structures showing large Δd values which tend to occur in molecules where the geminal C—O bonds are very different in their chemical reactivity, and in such molecules the ground-state structures may already show distortions pointing along the reaction pathway [see Chadwick & Dunitz (1979) 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 overweighed 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) 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)°] of the four bridgehead O—C—C angles. On the other hand, the small OCO angle of 105·1 (1)° 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 $\Delta_{A,B} = z^2_{A,B} - z^2_{B,A}$ (where $z^2_{A,B}$ 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 $15 \times 14/2 = 105$ pairs of heavy atoms in the molecule we find $\langle\Delta^2\rangle^{1/2} = 7.5 \times 10^{-4}$ Å^2 with $\Delta_{max} = 22 \times 10^{-4}$ Å^2; for the 17 bonded pairs the corresponding values are 5×10^{-4} Å^2 and 9×10^{-4} Å^2. As the e.s.d.'s of the Δ's are approximately $(2)^{1/2}\sigma(U)$ or about 10×10^{-4} 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 *THMB* (Trueblood, 1978) gave the following results for the T, L and S tensors (referred to a molecular inertial coordinate system):

$$L = \begin{bmatrix} 155 & 4 & -2 \\ & 121 & -19 \\ & & 98 \end{bmatrix} \text{rad}^2 \times 10^{-5}$$

$$T = \begin{bmatrix} 155 & -9 & 3 \\ & 119 & -6 \\ & & 89 \end{bmatrix} \text{Å}^2 \times 10^{-4}$$

$$S = \begin{bmatrix} -27 & -16 & -50 \\ -76 & 11 & 36 \\ 106 & -13 & 16 \end{bmatrix} \text{rad Å} \times 10^{-5}.$$
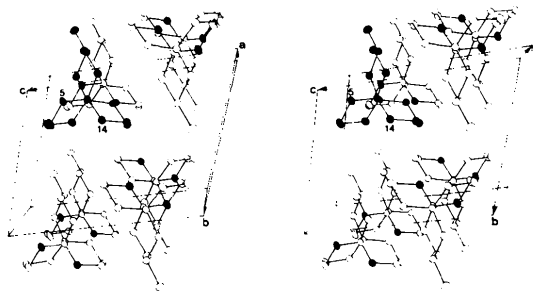

Fig. 3. Stereoscopic view of the packing in the crystal. The atoms of the reference molecule and the O atoms of symmetry-related molecules are indicated by filled circles.

In this coordinate system both **L** and **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 C(8)—C(15) bond. The agreement between observed and calculated U_{ij} values is good, as expected from the result of the rigid-body test: $\langle(\Delta U_{ij})^2\rangle^{1/2} = 6 \times 10^{-4}$ Å². 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.

Packing

The packing is rather loose with no intermolecular H···H distances less than 2·4 Å; there are about 20 such distances between 2·45 and 2·60 Å, all between molecules of opposite chirality. The shortest C—H···O distances, however, occur between translation-related molecules: O(5)···H(7)[Ī00], 2·57 Å and O(14)···H(11)[Ī00], 2·61 Å, both pointing nearly along the 'equatorial' lone-pair orbitals of the O atoms (see Fig. 3). In addition, O(14) interacts with a second H atom on the opposite side of the COC plane: O(14)···H(13′)[011], 2·68 Å, but here the H atom is not so close to the plane bisecting the COC angle. The next shortest O···H distances are >2·8 Å. In the structure of 18-crown-6 (Maverick *et al.*, 1980) all six O atoms were involved in C—H···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 O atoms are thus involved, but the two resulting C—H···O contacts seem to be the principal feature of the crystal packing along **a**.

APPENDIX

Crystal structure of (1) (2,10-dioxatricyclo[4.4.4.0¹·⁶]tetradecane, $C_{12}H_{20}O_2$)

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: $a = 12\cdot26$ (1), $b = 12\cdot22$ (1), $c = 13\cdot79$ (1) Å, $Z = 8$. Systematic absences ($hk0$, $h = 2n$ only; $h0l$, $l = 2n$ only) were compatible with the space groups $P2_1ca$ or $Pmca$, but, in addition, all reflections with l odd were very weak, and there was also a conditional absence: ($0kl$, if l even then $2k + l = 4n$ only), indicating that the subcell with $c' = c/2$ can be described in terms of the space groups $Pn2_1a$ or $Pnma$.

Although the crystal used was not unduly small (dimensions ~0·3–0·35 mm) only 572 reflections out of 1969 measured had $I > 3\sigma_I$. 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 perpendicular to the b axis, the remaining atoms being duplicated on both sides of this plane. This arrangement corresponds to a superposition of the two possible enantiomeric conformations at each molecular site. It seemed likely, therefore, that in the actual structure molecules displaced by the pseudo translation $c/2$ are enantiomeric rather than translationally equivalent as in the subcell. The expanded cell would then belong to the space group $P2_1ca$ with two sets of molecules in the unit cell, one set lying close to the plane $y = 0$, the other lying close to the plane $y = \frac{1}{2}$ and appropriately displaced in the **c** direction in accordance

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

BANYARD, S. H. & DUNITZ, J. D. (1976). *Acta Cryst.* B32, 318–320.

BENT, H. A. (1961). *Chem. Rev.* 61, 275–311.

BÜRGI, H. B., DUNITZ, J. D. & SHEFTER, E. (1974). *Acta Cryst.* B30, 1517–1527.

CHADWICK, D. J. & DUNITZ, J. D. (1979). *J. Chem. Soc. Perkin Trans.* 2, pp. 276–284.

DUNITZ, J. D. & SEILER, P. (1973). *Acta Cryst.* B29, 589–595.

JEFFREY, G. A., POPLE, J. A. & RADOM, L. (1974). *Carbohydr. Res.* 38, 81–95.

JONES, P. G., KENNARD, O., KIRBY, A. J. & MARTIN, R. J. (1979). *Acta Cryst.* B35, 755–757.

JONES, P. G. & KIRBY, A. J. (1979). *J. Chem. Soc. Chem. Commun.* pp. 288–289.

LEHN, J. M., WIPFF, G. & BÜRGI, H. B. (1974). *Helv. Chim. Acta*, 57, 493–496.

MAVERICK, E., SEILER, P., SCHWEIZER, W. B. & DUNITZ, J. D. (1980). *Acta Cryst.* B36, 615–620.

ROSENFIELD, R. E., TRUEBLOOD, K. N. & DUNITZ, J. D. (1978). *Acta Cryst.* A34, 828–829.

STEWART, J. M., KRUGER, G. J., AMMON, H. L., DICKINSON, C. & HALL, S. R. (1972). The XRAY system – version of June 1972. Tech. Rep. TR-192. Computer Science Center, Univ. of Maryland, College Park, Maryland.

TRUEBLOOD, K. N. (1978). *Acta Cryst.* A34, 950–954.

WILLIAMS, J. O., SCARSDALE, J. N., SCHÄFER, L. & GEISE, H. J. (1981). *J. Mol. Struct.* 76, 11–28.

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

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Abstract

$C_{12}H_{24}O_6 \cdot 2C_7H_7NO_2$, $M_r = 538 \cdot 60$, monoclinic, $P2_1/c$, $a = 10 \cdot 053$ (2), $b = 11 \cdot 893$ (3), $c = 12 \cdot 359$ (3) Å, $\beta = 105 \cdot 51$ (2)°, $V = 1423 \cdot 8$ (5) Å^3, $Z = 2$, $d_c = 1 \cdot 26$ Mg m^{-3}, μ(Cu $K\alpha$) = $0 \cdot 817$ mm^{-1}. Full-matrix least-squares refinement (non-hydrogen atoms anisotropic, H atoms isotropic) based on 1518 reflections led to a final R of $0 \cdot 040$. The 18-crown-6 ether sits on a center of symmetry and exhibits approximate D_{3d} symmetry. The six oxygen atoms are alternately $0 \cdot 24$ (1) Å above and below the mean plane and form a nearly planar hexagon with averaged sides of $2 \cdot 86$ (1) Å. The two guest molecules are related by a center of symmetry and each forms hydrogen bonds with H$\cdots$O distances of $2 \cdot 12$ (3) and $2 \cdot 39$ (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 & Vögtle, 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

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