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The Structures of the Isomer C of the Macrobicyclic Polyether (21S,26R,29S,34R)-21,22,23,24,25,26,29,30,31,32,33,34-Dodecahydro-1,4,7,14,17,20,28,35-octaoxa-[2³,²⁹anti.2¹⁸,³⁴anti][7.7]orthocyclophane at 295 K and of its Methanol Complex at 295 and 123 K

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Abstract

Crystals of the title compound, $C_{28}H_{42}O_8$, have cell dimensions $a = 14.832$ (4), $b = 12.806$ (2), $c = 14.555$ (2) Å, $\beta = 103.88$ (1)°, $V = 2683.8$ (9) Å³; $P2_1/a$, $Z = 4$. $R = 0.036$ for 2546 reflections. Its 1:1 methanol complex crystallizes with $a = 14.520$ (2), $b = 15.391$ (3), $c = 12.754$ (2) Å, $\beta = 95.02$ (2)°, $V = 2839.3$ (9) Å³ at 295 K, and $a = 14.353$ (3), $b = 15.279$ (2), $c = 12.659$ (5) Å, $\beta = 95.00$ (2)°, $V = 2765.3$ (13) Å³ at 123 K; space group $P2_1/n$, $Z = 4$. $R = 0.040$ for 2071 reflections at 295 K and 0.033 for 2060 reflections at 123 K. The structures were solved by direct methods and refined with anisotropic vibration for O and C atoms. The macrobicyclic molecule consists of a dicyclohexano-14-crown-4 ring bridged by an $OCH_2CH_2OC_6H_4OCH_2CH_2O$ group. In isomer C the four cis H atoms at the cyclohexano ring junctions are on the same side of the 14-crown-4 entity as the bridge. The conformation of the molecule is essentially unchanged in the methanol complex where the methanol hydroxy group forms a weak bifurcated hydrogen bond to the O atoms on the aromatic ring.

Introduction

Three isomeric macrobicyclic polyethers, A, B and C, differing only in the configurations of the ring-junction C atoms of the cyclohexano groups, have been synthesized and found to have greatly different formation constants for complexation with alkali metals. Although they had diagnostically different infrared spectra, the relative configurations were established only by crystal structure determination of all three isomers (Bandy, Parsons & Truter, 1981). The structural formula and numbering of the atoms in these molecules are shown in Fig. 1. The hydrogenation of aromatic rings to form the cyclohexyl groups at an early stage of the synthesis gives mainly cis addition at the ring junctions, and the H atoms on C(21) and C(26) are therefore on the same side of the molecule; they can be either on the same side as, or on the opposite side to, the bridge atoms O(4) and O(17). The situation is the same for the H atoms on C(29) and C(34).

In the present paper we describe the crystal structure of the isomer C, having all four H atoms |H(21), H(26), H(29), and H(34)| on the same side as O(4) and O(17). This isomer has the lowest formation constant (although the value of $|KL|/|K||L|$ in methanol at 298 K is 10^4 l mol⁻¹) and has not yielded suitable crystalline complexes with metal salts. The unsolvated compound crystallizes from ethanol. From methanol, solvated crystals are obtained with stoichiometry 1:1; they show a sharp band in the IR spectrum at 3555 cm⁻¹, instead of the broad bands at lower frequencies usually found in hydrogen-bonded compounds. This appears to be an example of 'molecular recognition' by the guest, methanol, of the host macrobicyclic com-
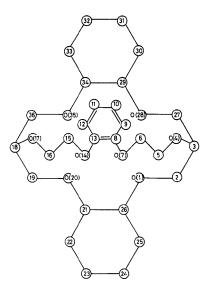
Fig. 1. Numbering scheme of the macrobicyclic molecule. The H atoms on the bridgehead C atoms |H(3) and H(18)|, on the ring junctions |H(21), H(26), H(29) and H(34)|, and in the benzene ring |H(9), H(10), H(11) and H(12)| are numbered to correspond to the C atoms. H atoms in methylene groups or in cyclohexane rings are further distinguished by A and B, e.g. H(2)A, H(2)B or H(22)A, H(22)B.

pound, isomer C; in contrast, isomers A and B form no such adducts. To establish the nature of the bonding in the 1:1 entity we have determined its crystal structure at 295 and at 123 K.

Experimental

Colourless crystals of the two samples were supplied by D. G. Parsons. Crystals of the unsolvated isomer C were obtained from ethanol. The methanol complex became opaque in air so the crystal was coated in Araldite. This was not necessary for isomer C itself.

Preliminary photographs were taken at room temperature to establish the approximate unit-cell dimensions and space groups, and to check on the quality of the crystals. Accurate unit-cell dimensions were obtained from 25 high-θ reflections centred on an Enraf–Nonius CAD-4 diffractometer. This instrument was used for measurement of intensities with ω–2θ scans. For the low-temperature study the crystal was kept in a stream of nitrogen by means of the Nonius cryostat with local modifications. For each crystal three orientation-control reflections were checked after every 100 reflections and two intensity-control reflections after every 3600 s exposure. Experimental details are given in Table 1. Scans were made in the bisecting position, with a maximum time of 90 s per reflection. With the CAD-4 processing program (Hursthouse, 1976), Lorentz and polarization corrections were applied; observations for which $|F| \leq 4\sigma_{(F)}$ were rejected.

Structure determination

The crystal structure of the unsolvated compound was solved by direct methods with *SHELX* (Sheldrick, 1976). An E map obtained from 520 signs with $E \geq 1.3$ revealed all the non-hydrogen atoms. One cycle of isotropic least-squares refinement with unit weights gave $R = 0.12$. 35 H atoms, including those at the ring junctions, appeared in the difference map. These were close to positions obtained geometrically assuming C–H $= 0.98$ Å. Inclusion of H atoms in calculated positions with a common vibration parameter and anisotropic refinement for the O atoms reduced R to 0.062. Parallel refinements were then carried out. In one, with reflections equally weighted and individual vibration parameters allowed for H, R

Table 1. *Additional crystal data and experimental conditions*

	Isomer C	Isomer C:CH$_3$OH	Isomer C:CH$_3$OH
Temperature (K)	295	295	123
D_m (Mg m^{-3})	1.25	1.26	
D_c (Mg m^{-3})	1.254	1.260	1.294
M_r	506.6	538.7	538.7
$F(000)$	1096	1168	1168
λ (Mo $K\alpha_1$) (Å)	0.70926	0.70926	0.70926
μ(Mo $K\alpha_1$) (mm^{-1})	0.085	0.085	0.086
Crystal dimensions (mm)	0.46 × 0.36 × 0.25	0.18 × 0.20 × 0.33	0.20 × 0.25 × 0.30
ω scan (°)	1.20 + 0.35 tan θ	0.75 + 0.35 tan θ	0.80 + 0.35 tan θ
Aperture (mm)	1.60 + 1.5 tan θ	1.3 + 1.5 tan θ	1.3 + 1.5 tan θ
θ range (°)	1.50 to 22.5	1.5 to 22	1.5 to 20°
Indices of intensity-control reflections	311, 145	126, 132	321, 271
N_i*	3493	3484	2563
N_t†	2546	2074	2060

* Number of independent reflections measured.
† Number of reflections with $F > 4\sigma_{(F)}$.

was reduced to 0·060; only for three of the atoms [H(5)A, H(10) and H(11)] was the value of $U_{iso} >$ 0·1 Å^2, the largest being 0·14 Å^2. At this stage, the 310 reflection had $|F_o| - |F_c|/\sigma = \Delta F/\sigma = 10\cdot4$. In the second refinement, (i) counting weights were used, (ii) H atoms were given a common isotropic vibration parameter and (iii) all other atoms were allowed anisotropic vibration; R fell to 0·036 and 310 had improved to $\Delta F/\sigma = 4\cdot1$. Further cycles of refinement and examination of various weighting analyses showed that $w = 0\cdot4458/\sigma^2_{(F)}$ gave the most uniform distribution of ΔF with F_o and $\sin\theta/\lambda$. Refinement was complete with the most significant shift 0·078 of the corresponding standard deviation, $R = 0\cdot036$ and $R' = 0\cdot038$. Final atomic coordinates with the equivalent isotropic vibration parameters are in Table 2.*

The crystal structure of the methanol complex was also solved by direct methods with *SHELX*; 523 planes with $E_{min} \geq 1\cdot3$ gave an E map in which all C and O positions of the polyether molecule and a further atom, possibly solvate, were revealed. A second solvate atom, confirming the presence of methanol, and some of the H atoms, including those at the ring junctions, were located in a difference map at $R = 0\cdot15$. All the H atoms on the bicyclic molecule were included in calculated positions, C—H = 0·98 Å, with a common isotropic vibration parameter. After further isotropic refinement, the O atoms were allowed anisotropic vibration parameters and the H atoms of the macrocyclic molecule individual isotropic vibration parameters. Refinement, after omission of the reflections $\overline{3}21$, 301 and 221 (for which $|F_o|$ and $|F_c|$ were respectively 274 and 291, 237 and 248, 202 and 220), led to $R = 0\cdot067$, all the H atoms having reasonable vibration parameters. The four H atoms of the methanol molecule were clearly revealed in a difference synthesis. In the final full-matrix refinement, counting weights were used (giving a satisfactory weighting analysis), and all C and O atoms were allowed anisotropic vibration; the H atoms of the macrocycle were in calculated positions with a common isotropic temperature factor. The H atoms of the methanol molecule were refined independently; there is some uncertainty in these H-atom positions and their final thermal parameters are rather high. Refinement converged at $R = 0\cdot040$ and $R' = 0\cdot036$ for 360 parameters.

Refinement of the low-temperature structure of the methanol solvate followed a course parallel to that of the room-temperature structure, except that no reflec-

* Lists of structure factors, anisotropic vibration parameters, H-atom coordinates and deviations of atoms from selected mean planes for all three structures have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36950 (49 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Atomic parameters for isomer C of the macrobicyclic polyether: fractional coordinates* $(\times 10^4)$ *and thermal parameters* $(Å^2 \times 10^3)$

$$U_{eq} = \tfrac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* (\mathbf{a}_i . \mathbf{a}_j).$$

	x	y	z	U_{eq}
O(1)	3041 (1)	−2970 (1)	1083 (1)	49·7 (6)
C(2)	3377 (2)	−2712 (2)	281 (1)	49·7 (9)
C(3)	4411 (2)	−2495 (2)	467 (1)	46·3 (9)
O(4)	4881 (1)	−3470 (1)	670 (1)	52·0 (6)
C(5)	5830 (2)	−3502 (2)	631 (2)	59 (1)
C(6)	6262 (2)	−4429 (2)	1188 (2)	59 (1)
O(7)	6286 (1)	−4206 (1)	2151 (1)	58·0 (7)
C(8)	6509 (1)	−4990 (2)	2804 (2)	48·5 (9)
C(9)	6771 (2)	−5988 (2)	2631 (2)	61 (1)
C(10)	6974 (2)	−6706 (2)	3366 (2)	73 (1)
C(11)	6916 (2)	−6435 (2)	4255 (2)	72 (1)
C(12)	6659 (2)	−5433 (2)	4439 (2)	59 (1)
C(13)	6461 (1)	−4709 (2)	3721 (2)	49 (1)
O(14)	6234 (1)	−3685 (1)	3816 (1)	59·1 (7)
C(15)	5988 (2)	−3367 (2)	4654 (1)	58 (1)
C(16)	5646 (2)	−2280 (2)	4497 (2)	58 (1)
O(17)	4885 (1)	−2245 (1)	3702·0 (9)	47·6 (6)
C(18)	4026 (2)	−1873 (2)	3845 (1)	43·3 (9)
C(19)	3262 (2)	−2351 (2)	3088 (1)	47·6 (9)
O(20)	3275 (1)	−3467 (1)	3095 (1)	51·5 (6)
C(21)	3787 (1)	−3958 (2)	2488 (1)	39·6 (8)
C(22)	3986 (1)	−5061 (2)	2860 (1)	48·4 (9)
C(23)	3106 (2)	−5695 (2)	2766 (1)	52 (1)
C(24)	2532 (2)	−5705 (2)	1755 (2)	55 (1)
C(25)	2337 (2)	−4600 (2)	1372 (2)	56 (1)
C(26)	3236 (1)	−4009 (2)	1462 (1)	43·2 (8)
C(27)	4767 (2)	−1731 (2)	1271 (1)	47·0 (9)
O(28)	4246 (1)	−790 (1)	1086 (1)	49·5 (6)
C(29)	4680 (2)	79 (2)	1632 (1)	44·9 (9)
C(30)	4084 (2)	1030 (2)	1309 (1)	55 (1)
C(31)	4506 (2)	2007 (2)	1840 (2)	60 (1)
C(32)	4695 (2)	1861 (2)	2905 (2)	54 (1)
C(33)	5295 (2)	906 (2)	3206 (1)	49·8 (9)
C(34)	4853 (1)	−80 (2)	2702 (1)	41·0 (8)
O(35)	3967 (1)	−279 (1)	2896 (1)	45·1 (6)
C(36)	3984 (2)	−687 (2)	3812 (1)	46·5 (9)

tions (other than those with $F_o \leq 4\sigma_F$) were omitted. Convergence was reached at $R = 0\cdot033$ and $R' = 0\cdot031$. The thermal parameters are, of course, much lower in the low-temperature study: the e.s.d.'s of the macrobicyclic parameters have been reduced by *ca* 25% and in the methanol molecule by up to 50%. The H atoms of the methanol molecule are now well defined.

The final atomic parameters for the methanol solvate structures at both temperatures are in Table 3.

The computer programs used were the CAD-4 processing program (Hursthouse, 1976) and *SHELX* (Sheldrick, 1976) for structure determination with the scattering factors for C, O and H included in that program. These were run on the ICL System 4 at Rothamsted Experimental Station. For molecular geometry, programs written by Owen (1981a) for the Prime 550 computer were used.

Table 3. *Atomic parameters for the isomer C:methanol (1:1) complex: fractional coordinates (×10⁴), and thermal parameters (Å² ×10³)*

Thermal parameters are U_{iso} for the H atoms and U_{eq} for the C and O atoms. For each atom, the first row is for the structure at 295 K, the second row at 123 K.

$$U_{eq} = \tfrac{1}{3} \textstyle\sum_i \sum_j U_{ij} a_i^* a_j^* (\mathbf{a}_i \cdot \mathbf{a}_j).$$

	x	y	z	U_{iso}/U_{eq}
O(1)	4181 (2)	1570 (1)	1151 (2)	47·8 (9)
	4190 (1)	1539 (1)	1145 (1)	16·1 (7)
C(2)	3353 (3)	1111 (2)	1313 (3)	51 (2)
	3342 (2)	1089 (2)	1310 (2)	17 (1)
C(3)	2514 (3)	1675 (2)	1380 (2)	47 (1)
	2490 (2)	1662 (2)	1380 (2)	16 (1)
O(4)	2235 (2)	2012 (2)	359 (2)	53 (1)
	2216 (1)	2007 (1)	352 (1)	17·4 (7)
C(5)	1302 (3)	2282 (3)	184 (3)	55 (2)
	1268 (2)	2285 (2)	186 (2)	19 (1)
C(6)	1209 (2)	2804 (2)	−818 (3)	52 (1)
	1168 (2)	2815 (2)	−819 (2)	17 (1)
O(7)	1637 (2)	3620 (2)	−570 (2)	61 (1)
	1605 (1)	3638 (1)	−570 (1)	20·5 (7)
C(8)	1796 (2)	4179 (2)	−1367 (3)	44 (1)
	1772 (2)	4200 (2)	−1378 (2)	15 (1)
C(9)	1409 (3)	4123 (3)	−2391 (3)	53 (2)
	1391 (2)	4141 (2)	−2416 (2)	16 (1)
C(10)	1637 (3)	4754 (3)	−3110 (3)	57 (2)
	1627 (2)	4772 (2)	−3143 (2)	19 (1)
C(11)	2226 (3)	5415 (3)	−2808 (3)	58 (2)
	2237 (2)	5439 (2)	−2842 (2)	18 (1)
C(12)	2597 (2)	5477 (2)	−1767 (3)	51 (2)
	2610 (2)	5505 (2)	−1793 (2)	15 (1)
C(13)	2381 (2)	4863 (2)	−1050 (3)	41 (1)
	2373 (2)	4892 (2)	−1067 (2)	13 (1)
O(14)	2676 (2)	4865 (1)	−3 (2)	52 (1)
	2665 (1)	4893 (1)	−5 (1)	17·8 (7)
C(15)	3441 (2)	5394 (2)	359 (3)	49 (1)
	3448 (2)	5424 (2)	357 (2)	15 (1)
C(16)	3633 (2)	5193 (2)	1502 (3)	45 (1)
	3636 (2)	5210 (2)	1511 (2)	14 (1)
O(17)	3886 (2)	4310 (1)	1623 (2)	42·3 (9)
	3882 (1)	4309 (1)	1632 (1)	13·7 (7)
C(18)	4794 (2)	4144 (2)	2093 (2)	37 (1)
	4803 (2)	4142 (2)	2103 (2)	12 (1)
C(19)	5077 (2)	3255 (2)	1739 (2)	42 (1)
	5087 (2)	3241 (2)	1748 (2)	15 (1)
O(20)	5123 (2)	3198 (1)	629 (2)	44·6 (9)
	5132 (1)	3183 (1)	627 (1)	14·6 (7)
C(21)	4314 (2)	2852 (2)	32 (2)	38 (1)
	4307 (2)	2841 (2)	35 (2)	13 (1)
C(22)	4371 (2)	3127 (2)	−1099 (2)	46 (1)
	4356 (2)	3129 (2)	−1110 (2)	16 (1)
C(23)	5188 (2)	2698 (2)	−1581 (3)	49 (1)
	5178 (2)	2705 (2)	−1615 (2)	16 (1)
C(24)	5163 (3)	1723 (2)	−1477 (3)	54 (2)
	5160 (2)	1711 (2)	−1524 (2)	16 (1)
C(25)	5101 (3)	1446 (2)	−338 (3)	53 (2)
	5111 (2)	1427 (2)	−366 (2)	17 (1)
C(26)	4266 (2)	1861 (2)	91 (2)	41 (1)
	4262 (2)	1841 (2)	72 (2)	14 (1)
C(27)	2651 (2)	2429 (2)	2155 (2)	46 (1)
	2640 (2)	2420 (2)	2165 (2)	16 (1)
O(28)	3114 (2)	2119 (1)	3117 (2)	48·2 (9)
	3105 (1)	2100 (1)	3135 (1)	16·8 (7)
C(29)	3028 (2)	2681 (2)	3994 (2)	43 (1)
	3014 (2)	2667 (2)	4020 (2)	15 (1)

Table 3 (*cont.*)

	x	y	z	U_{iso}/U_{eq}
C(30)	3469 (2)	2221 (2)	4966 (2)	48 (1)
	3456 (2)	2207 (2)	4998 (2)	16 (1)
C(31)	3324 (3)	2744 (3)	5955 (3)	60 (2)
	3300 (2)	2736 (2)	5992 (2)	18 (1)
C(32)	3702 (3)	3661 (2)	5879 (3)	58 (2)
	3681 (2)	3665 (2)	5916 (2)	17 (1)
C(33)	3297 (3)	4109 (2)	4881 (2)	51 (1)
	3272 (2)	4112 (2)	4902 (2)	17 (1)
C(34)	3434 (2)	3587 (2)	3888 (2)	39 (1)
	3421 (2)	3584 (2)	3906 (2)	13 (1)
O(35)	4401 (1)	3488 (1)	3757 (2)	39·6 (8)
	4405 (1)	3484 (1)	3784 (1)	13·9 (7)
C(36)	4835 (2)	4202 (2)	3290 (2)	41 (1)
	4852 (2)	4204 (2)	3313 (2)	15 (1)
Methanol molecule				
O(50)	1456 (2)	4332 (2)	1686 (2)	78 (1)
	1485 (2)	4318 (1)	1698 (2)	24·7 (8)
C(51)	623 (5)	4748 (6)	1316 (6)	97 (3)
	653 (3)	4764 (3)	1328 (3)	31 (1)
H(50)	1758 (48)	4229 (43)	1139 (51)	203 (34)
	1764 (25)	4244 (23)	1214 (30)	47 (14)
H(51)A	342 (45)	4837 (42)	1881 (50)	164 (34)
	286 (23)	4822 (21)	1939 (28)	48 (11)
H(51)B	331 (44)	4357 (39)	826 (50)	177 (33)
	282 (23)	4417 (21)	764 (28)	50 (11)
H(51)C	706 (50)	5303 (44)	1170 (54)	193 (39)
	758 (23)	5378 (25)	1041 (27)	58 (12)

Results and discussion

Isomer *C* and its methanol complex are shown as stereopairs in Fig. 2. In these very similar polyether molecules, the ring-junction H atoms on C(21), C(26), C(29) and C(34) are on the same side of the mean 14-crown-4 plane as the bridge, atoms O(4) to O(17) inclusive. Because of the *cis* addition at the cyclohexano ring junctions, each chair-shaped ring has one axial and one equatorial O-atom substituent; O(1) and O(28) are the equatorial atoms.

The impression that the macrobicyclic molecule is unchanged on adduct formation is reinforced by comparison of the bond lengths, bond angles and torsion angles in Tables 4 and 5. Mean values for the various types of bonds, and their e.s.d.'s (calculated from the spread of the dimensions about the mean), are included in Table 4; these e.s.d.'s are about twice those obtained from inversion of the least-squares matrix.

Reduction of the temperature gave a 1/0·993 reduction in *b* and *c* and a greater reduction of 1/0·989 in *a* for the crystal of the methanol complex. There are changes in the atomic coordinates because the errors caused by libration are reduced at lower temperatures; the bond lengths increase (by about 0·005 Å) for the same reason. While the methanol C—H distances as found are now closer to the value obtained by neutron
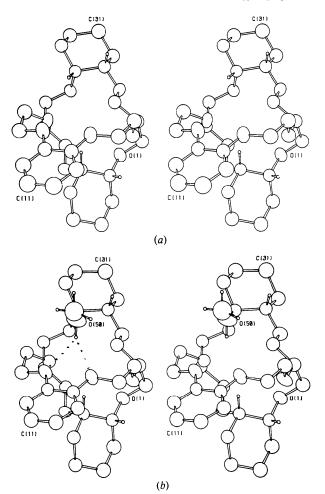
(a)

(b)

Fig. 2. (a) A stereoview of isomer C with the bridge containing the benzene ring towards the reader. O atoms are depicted as ellipsoids of vibration at the 50% confidence level. C as isotropic spheres. and H as spheres of arbitrary size. (b) A stereoview of the isomer C:methanol 1:1 complex in the same orientation as for isomer C in (a). O atoms are depicted as ellipsoids at the 50% confidence level. and C as isotropic spheres: H atoms on the ring junctions and the methanol molecule are spheres of arbitrary size. The dotted lines show the possible hydrogen bonding from H(50) to O(7) and O(14).

diffraction, 1·08 Å, the O—H distance has apparently, but not significantly, shortened; the corresponding neutron diffraction value is 0·96 Å. Even at 123 K, the C—C bond lengths are shorter than the standard values.

Methanol of solvation has usually been found in crystals with the O atom either coordinated to a cation or, more often, as a hydrogen-bond acceptor. Either interaction enhances the donor properties of the hydroxy H atom and the molecule is often part of a hydrogen-bonded network, which extends throughout the crystal. We have located methanol-containing structures in the files of the Cambridge Crystallographic Data Centre (searched in 1981; for a descrip-

Table 4. *Interatomic distances* (Å) *and angles* (°)

(i) Bond lengths in the macrobicyclic molecule

	Isomer C	Isomer C:CH$_3$OH 295 K	123 K
O(1)—C(2)	1·415 (3)	1·425 (4)	1·429 (3)
O(1)—C(26)	1·443 (3)	1·439 (4)	1·446 (3)
C(2)—C(3)	1·518 (3)	1·505 (5)	1·513 (4)
C(3)—O(4)	1·427 (3)	1·427 (4)	1·428 (3)
C(3)—C(27)	1·520 (3)	1·526 (4)	1·528 (4)
O(4)—C(5)	1·421 (3)	1·417 (4)	1·422 (3)
C(5)—C(6)	1·492 (3)	1·507 (4)	1·504 (4)
C(6)—O(7)	1·423 (3)	1·424 (4)	1·427 (3)
O(7)—C(8)	1·368 (3)	1·366 (4)	1·373 (3)
C(8)—C(9)	1·376 (4)	1·379 (4)	1·382 (4)
C(8)—C(13)	1·401 (3)	1·391 (5)	1·399 (4)
C(9)—C(10)	1·388 (4)	1·395 (5)	1·394 (4)
C(10)—C(11)	1·362 (5)	1·362 (5)	1·375 (4)
C(11)—C(12)	1·384 (4)	1·391 (5)	1·392 (4)
C(12)—C(13)	1·375 (4)	1·370 (5)	1·375 (4)
C(13)—O(14)	1·369 (3)	1·366 (4)	1·373 (3)
O(14)—C(15)	1·415 (3)	1·422 (4)	1·428 (3)
C(15)—C(16)	1·481 (3)	1·492 (4)	1·498 (4)
C(16)—O(17)	1·410 (4)	1·413 (4)	1·426 (3)
O(17)—C(18)	1·422 (3)	1·422 (4)	1·425 (3)
C(18)—C(19)	1·509 (3)	1·509 (4)	1·515 (4)
C(18)—C(36)	1·520 (3)	1·526 (4)	1·530 (4)
C(19)—O(20)	1·429 (3)	1·426 (3)	1·429 (3)
O(20)—C(21)	1·440 (3)	1·445 (4)	1·443 (3)
C(21)—C(22)	1·516 (3)	1·513 (4)	1·522 (4)
C(21)—C(26)	1·522 (3)	1·528 (4)	1·529 (4)
C(22)—C(23)	1·515 (3)	1·532 (5)	1·534 (4)
C(23)—C(24)	1·514 (3)	1·508 (5)	1·523 (4)
C(24)—C(25)	1·522 (3)	1·525 (5)	1·536 (4)
C(25)—C(26)	1·511 (3)	1·515 (5)	1·520 (4)
C(27)—O(28)	1·422 (3)	1·428 (4)	1·432 (3)
O(28)—C(29)	1·428 (3)	1·429 (4)	1·431 (3)
C(29)—C(30)	1·511 (3)	1·520 (4)	1·514 (4)
C(29)—C(34)	1·530 (3)	1·523 (4)	1·530 (4)
C(30)—C(31)	1·525 (3)	1·527 (4)	1·529 (4)
C(31)—C(32)	1·520 (3)	1·520 (5)	1·528 (4)
C(32)—C(33)	1·514 (3)	1·520 (4)	1·525 (4)
C(33)—C(34)	1·527 (3)	1·528 (4)	1·528 (4)
C(34)—O(35)	1·432 (2)	1·437 (4)	1·442 (3)
O(35)—C(36)	1·426 (2)	1·422 (4)	1·429 (3)
Mean C$_{sp^3}$–C$_{sp^3}$	1·523 (10)	1·518 (10)	1·523 (10)
Mean C$_{sp^3}$–O	1·432 (7)	1·427 (9)	1·431 (7)
Mean C$_{sp^2}$–C$_{sp^2}$	1·386 (10)	1·381 (13)	1·381 (12)
Mean C$_{sp^2}$–O	1·373	1·366	1·373

(ii) Bond angles in the macrobicyclic molecule

C(26)—O(1)—C(2)	116·9 (2)	115·7 (3)	115·0 (2)
O(1)—C(2)—C(3)	115·9 (2)	114·9 (3)	115·7 (2)
C(2)—C(3)—O(4)	107·4 (2)	108·9 (3)	108·7 (2)
C(2)—C(3)—C(27)	113·9 (2)	114·5 (3)	114·0 (2)
C(27)—C(3)—O(4)	110·0 (2)	108·9 (3)	108·9 (2)
C(3)—O(4)—C(5)	117·2 (2)	116·2 (3)	115·4 (2)
O(4)—C(5)—C(6)	107·6 (2)	107·6 (3)	107·8 (2)
C(5)—C(6)—O(7)	106·3 (2)	106·1 (3)	106·3 (2)
C(6)—O(7)—C(8)	118·8 (2)	119·3 (3)	119·3 (2)
O(7)—C(8)—C(9)	125·9 (2)	125·7 (3)	126·0 (3)
O(7)—C(8)—C(13)	114·5 (2)	113·6 (3)	114·0 (2)
C(13)—C(8)—C(9)	119·6 (2)	120·7 (3)	120·0 (3)
C(8)—C(9)—C(10)	119·5 (3)	118·6 (4)	119·0 (3)
C(9)—C(10)—C(11)	120·8 (3)	120·9 (3)	121·0 (3)
C(10)—C(11)—C(12)	120·2 (3)	120·1 (4)	120·1 (3)

Table 4 (cont.)

		Isomer C:CH$_3$OH	
	Isomer C	295 K	123 K
C(11)–C(12)–C(13)	119·8 (3)	119·8 (4)	119·4 (3)
C(12)–C(13)–C(8)	120·0 (2)	119·9 (3)	120·6 (3)
C(8)–C(13)–O(14)	114·4 (2)	114·6 (3)	113·9 (2)
C(12)–C(13)–O(14)	125·6 (2)	125·5 (3)	125·5 (2)
C(13)–O(14)–C(15)	118·9 (2)	119·2 (3)	118·7 (2)
O(14)–C(15)–C(16)	106·7 (2)	105·8 (3)	105·0 (2)
C(15)–C(16)–O(17)	109·5 (2)	109·3 (3)	109·7 (2)
C(16)–O(17)–C(18)	117·3 (2)	116·2 (2)	115·4 (2)
O(17)–C(18)–C(19)	107·4 (2)	107·7 (3)	107·7 (2)
O(17)–C(18)–C(36)	111·1 (2)	111·4 (3)	111·5 (2)
C(36)–C(18)–C(19)	111·4 (2)	111·3 (3)	111·3 (2)
C(18)–C(19)–O(20)	113·2 (2)	113·0 (3)	112·8 (2)
C(19)–O(20)–C(21)	116·2 (2)	116·0 (2)	115·6 (2)
O(20)–C(21)–C(22)	105·9 (2)	106·8 (3)	106·6 (2)
O(20)–C(21)–C(26)	112·5 (2)	112·4 (3)	112·4 (2)
C(26)–C(21)–C(22)	108·8 (2)	109·4 (3)	108·9 (2)
C(21)–C(22)–C(23)	112·2 (2)	111·7 (3)	112·0 (2)
C(22)–C(23)–C(24)	111·3 (2)	111·7 (3)	111·8 (2)
C(23)–C(24)–C(25)	111·2 (2)	111·5 (3)	110·9 (2)
C(24)–C(25)–C(26)	110·4 (2)	110·0 (3)	109·6 (2)
C(21)–C(26)–O(1)	110·3 (2)	111·4 (3)	110·8 (2)
C(25)–C(26)–O(1)	109·7 (2)	110·1 (3)	109·6 (2)
C(25)–C(26)–C(21)	111·2 (2)	111·2 (3)	111·5 (2)
C(3)–C(27)–O(28)	109·1 (2)	109·0 (3)	109·1 (2)
C(27)–O(28)–C(29)	113·8 (2)	113·8 (2)	113·4 (2)
O(28)–C(29)–C(30)	107·6 (2)	107·3 (3)	107·4 (2)
O(28)–C(29)–C(34)	113·9 (2)	115·1 (3)	114·8 (2)
C(34)–C(29)–C(30)	111·5 (2)	111·1 (3)	111·4 (2)
C(29)–C(30)–C(31)	111·4 (2)	110·4 (3)	110·3 (2)
C(30)–C(31)–C(32)	111·6 (2)	111·2 (3)	111·1 (2)
C(31)–C(32)–C(33)	110·3 (2)	111·0 (3)	110·8 (2)
C(32)–C(33)–C(34)	112·0 (2)	112·8 (3)	112·8 (2)
C(33)–C(34)–C(29)	109·0 (2)	109·2 (3)	108·9 (2)
C(29)–C(34)–O(35)	106·7 (2)	107·6 (3)	107·4 (2)
C(33)–C(34)–O(35)	111·2 (2)	110·5 (3)	110·7 (2)
C(34)–O(35)–C(36)	116·0 (2)	116·1 (2)	116·2 (2)
O(35)–C(36)–C(18)	112·8 (2)	113·2 (3)	112·7 (2)

(iii) Bond and hydrogen-bonding dimensions of the methanol molecule in the isomer C:methanol complex, at 295 and 123 K

	295 K	123 K
(a) Bond lengths		
O(50)–H(50)	0·87 (7)	0·77 (4)
O(50)–C(51)	1·412 (7)	1·419 (4)
C(51)–H(51)A	0·87 (6)	0·98 (4)
C(51)–H(51)B	0·94 (6)	1·00 (4)
C(51)–H(51)C	0·88 (7)	1·02 (4)
(b) Valence angles		
H(50)–O(50)–C(51)	107 (5)	107 (3)
O(50)–C(51)–H(51)A	104 (4)	106 (2)
O(50)–C(51)–H(51)B	105 (4)	111 (2)
O(50)–C(51)–H(51)C	112 (5)	114 (2)
H(51)A–C(51)–H(51)B	116 (6)	109 (3)
H(51)A–C(51)–H(51)C	96 (6)	108 (3)
H(51)B–C(51)–H(51)C	123 (6)	109 (3)
(c) Hydrogen-bonding contacts		
H(50)···O(7)	2·37 (7)	2·43 (4)
O(50)···O(7)	3·113 (4)	3·072 (3)
H(50)···O(14)	2·28 (7)	2·32 (4)
O(50)···O(14)	3·020 (4)	2·988 (3)
O(50)–H(50)···O(7)	144 (6)	142 (4)
O(50)–H(50)···O(14)	143 (6)	146 (3)

Table 4 (cont.)

	295 K	123 K
(d) Torsion angles		
H(50)–O(50)–C(51)–H(51)A	180 (6)	177 (4)
H(50)–O(50)–C(51)–H(51)B	58 (6)	58 (4)
H(50)–O(50)–C(51)–H(51)C	–78 (7)	–65 (4)

Table 5. Torsion angles (°)

		Isomer C:CH$_3$OH	
	Isomer C	295 K	123 K
C(26)–O(1)–C(2)–C(3)	–75·7 (2)	–77·9 (4)	–76·7 (3)
C(21)–C(26)–O(1)–C(2)	121·0 (2)	117·4 (3)	116·2 (2)
C(25)–C(26)–O(1)–C(2)	–116·2 (2)	–118·7 (3)	–120·3 (2)
O(1)–C(2)–C(3)–O(4)	72·8 (2)	71·4 (4)	70·9 (3)
O(1)–C(2)–C(3)–C(27)	–49·3 (3)	–50·8 (4)	–50·9 (3)
C(2)–C(3)–O(4)–C(5)	164·5 (2)	157·7 (3)	158·1 (2)
C(27)–C(3)–O(4)–C(5)	–71·0 (2)	–76·7 (3)	–77·2 (3)
C(2)–C(3)–C(27)–O(28)	–55·4 (2)	–45·6 (4)	–46·0 (3)
O(4)–C(3)–C(27)–O(28)	–176·1 (2)	–167·8 (3)	–167·6 (2)
C(3)–O(4)–C(5)–C(6)	159·8 (2)	166·6 (3)	166·8 (2)
O(4)–C(5)–C(6)–O(7)	–68·3 (2)	–73·9 (3)	–73·9 (3)
C(5)–C(6)–O(7)–C(8)	169·4 (2)	169·3 (3)	168·3 (2)
C(6)–O(7)–C(8)–C(13)	–176·4 (2)	–167·4 (3)	–167·1 (2)
O(7)–C(8)–C(13)–O(14)	–2·4 (3)	–1·3 (4)	–1·7 (3)
C(8)–C(13)–O(14)–C(15)	167·7 (2)	164·6 (3)	164·6 (2)
C(12)–C(13)–O(14)–C(15)	–14·1 (3)	–17·1 (5)	–16·7 (4)
C(13)–O(14)–C(15)–C(16)	–171·7 (2)	–175·4 (3)	–174·7 (2)
O(14)–C(15)–C(16)–O(17)	58·4 (2)	62·7 (3)	62·4 (3)
C(15)–C(16)–O(17)–C(18)	120·5 (2)	117·4 (3)	116·8 (2)
C(16)–O(17)–C(18)–C(19)	–154·1 (2)	–156·0 (3)	–155·9 (2)
C(16)–O(17)–C(18)–C(36)	83·8 (2)	81·7 (3)	81·7 (3)
O(17)–C(18)–C(19)–O(20)	58·1 (2)	62·6 (3)	62·8 (3)
C(36)–C(18)–C(19)–O(20)	180·0 (2)	–175·0 (3)	–174·6 (2)
O(17)–C(18)–C(36)–O(35)	66·8 (2)	72·6 (3)	72·2 (3)
O(35)–C(36)–C(18)–C(19)	–52·9 (2)	–47·6 (4)	48·1 (3)
C(18)–C(19)–O(20)–C(21)	–92·6 (2)	–96·3 (3)	96·0 (3)
C(19)–O(20)–C(21)–C(26)	–80·6 (2)	–78·8 (3)	80·3 (3)
O(20)–C(21)–C(26)–O(1)	63·4 (2)	63·3 (3)	63·6 (3)
O(20)–C(21)–C(26)–C(25)	–58·5 (2)	–60·0 (4)	–58·7 (3)
O(1)–C(26)–C(21)–C(22)	–179·6 (2)	–178·2 (3)	–178·5 (2)
C(25)–C(26)–C(21)–C(22)	58·5 (2)	58·6 (4)	59·2 (3)
C(3)–C(27)–O(28)–C(29)	–162·7 (2)	–161·6 (3)	160·9 (2)
C(27)–O(28)–C(29)–C(34)	–59·8 (2)	–61·4 (4)	–60·8 (3)
O(28)–C(29)–C(34)–C(33)	–178·6 (2)	–179·6 (3)	179·9 (2)
O(28)–C(29)–C(34)–O(35)	–58·5 (2)	–59·6 (3)	–60·2 (3)
C(30)–C(29)–C(34)–O(35)	63·6 (2)	62·5 (3)	62·1 (3)
C(29)–C(34)–O(35)–C(36)	166·0 (2)	159·0 (3)	159·3 (2)
C(33)–C(34)–O(35)–C(36)	–75·3 (2)	–81·8 (3)	–81·9 (3)
C(34)–O(35)–C(36)–C(18)	–88·8 (2)	–89·7 (3)	–88·8 (3)

tion see Allen *et al.*, 1979) and checked on the environment of the methanol molecules found. Apart from the clathrate compounds, discussed later, we found no examples of methanol acting only as a donor. However, it may be doing so in three recently published crystal structures. In one (de Wit, Trompenaars, Pennings, Reinhoudt, Harkema & van Hummel, 1981) the methanol site is partially occupied (*ca* 0·75) and the O···O distance is 2·7 Å (Harkema, 1981). In the second (Messerschmidt & Werner, 1981), our calculation of the O···O distance gives 2·85 Å. In the third (Weber, 1981), the methanol is a donor to the N atom of an uncoordinated isothiocyanate ion with

O···N 2·768 (9) Å. None of the crystallographic papers quoted, nor preceding papers on the syntheses of the compounds, quotes infrared spectra.

In our structures, the methanol molecule is held by a weak bifurcated hydrogen bond. At 123 K the methanol hydroxy group has O···O contacts of 3·072 (3) and 2·988 (3) Å to O(7) and O(14); the corresponding H(50)···O distances are 2·43 (4) and 2·32 (4) Å, and the O(50)–H(50)···O angles are 142 (3) and 146 (3)°. As the H atom was located only 0·77 (4) Å from the O atom, the H···O distances are maximum values. This hydrogen bonding makes no significant difference to C—O bond lengths of the acceptor atoms O(7) and O(14). Its main effect is shown in Table 6; atoms C(6) and C(15) are further from the plane of the aromatic ring in the direction away from H(50).

The use of neutron diffraction to locate H atoms unequivocally has confirmed the existence of bifurcated hydrogen bonds. Ceccavelli, Jeffrey & Taylor (1981) quoted 25 such examples and gave the average H···O distance as 2·03 (13) Å with O—H···O angles of 151 (15)°; theoretical calculations have shown these results to be energetically favourable (Taylor, 1981).

A bifurcated hydrogen bond has previously been reported in a complex with a macrobicyclic ether, 1,5,12,16,23,26,29-heptaoxa[7^{3,14}][5.5]orthocyclophane (Herbert & Truter, 1980). In this example the donor molecule was a water molecule which was itself a hydrogen-bond acceptor. One of the donor H atoms formed a symmetrical bifurcated hydrogen bond with dimensions which are not significantly different from those found in isomer C:CH_3OH; in addition, the other H atom formed an unsymmetrical bifurcated bond with O(water)···O 3·036 (5) and 2·883 (5) Å. The effect on the ligand was a significant change in two torsion angles |18 (1) and 33 (1)°| compared with the uncomplexed molecule (Owen, 1981b).

The weak bonding shown in the present complex results in an IR spectral shift in the hydroxy stretching frequency of 89 cm⁻¹, which is of the same order as that shown by a dilute solution of methanol in carbon tetrachloride on the addition of ethers, e.g. diphenyl ether 34 cm⁻¹, anisole 77 cm⁻¹, or dihydropyran 94 cm⁻¹ (Bellamy & Pace, 1969). For linear hydrogen bonds, Bellamy & Owen (1969) have given a relation between the change in hydroxy stretching frequency and the O···O distance; for $\Delta v = 89$ cm⁻¹ the distance would be 3·004 Å.
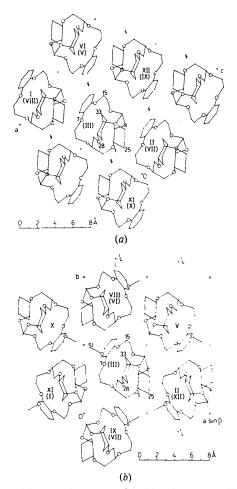

(a)

(b)

Fig. 3. (a) The crystal structure of the bicyclic compound isomer C projected down b. Some of the atoms of the crystal-chemical unit are numbered. O atoms are shown as circles. Roman numerals denote the equivalent positions relative to the coordinates in Table 2: (I) ½ + x, −½ − y, z; (II) −½ + x, − ½ − y, z; (III) x, − 1 + y, z; (IV) x, 1 + y, z; (V) ½ − x, −½ + y, 1 − z; (VI) ½ x, ½ + y, 1 − z; (VII) −½ + x, − ½ − y, z; (VIII) ½ + x, −½ · y, z; (IX) 1 − x, −1 − y, 1 − z; (X) ½ − x, −½ + y, −z; (XI) ½ − x, ½ + y, −z; (XII) 1 − x, −y, 1 − z. Parentheses indicate the molecule one unit cell below that shown. IV is one unit cell above the crystal chemical unit. (b) The crystal structure of the methanol solvate projected down c. Some of the C atoms of the crystal-chemical unit are numbered. Roman numerals denote equivalent positions relative to the coordinates in Table 3: (I) −½ + x, ½ − y, −½ + z; (II) ½ + x, ½ − y, ½ + z; (III) x, y, z − 1; (IV) x, y, z + 1; (V) 1 − x, 1 − y, −z; (VI) ½ − x, ½ + y, − ½ − z; (VII) ½ − x, − ½ + y, −½ − z; (VIII) ½ − x, ½ + y, ½ − z; (IX) ½ − x, −½ + y, ½ − z; (X) − x, 1 − y, −z; (XI) − ½ + x, ½ − y, ½ + z; (XII) ½ + x, ½ − y, −½ + z.

Table 6. *Angles* (°) *between normals to planes through various groups of atoms* (e.s.d.'s 0·1–0·2°)

Plane (i):   14-crown-4 O atoms |O(1)O(20)O(28)O(35)|
Plane (ii):   benzene ring C(8)–C(13)
Plane (iii): cyclohexane ring C(21)–C(26)
Plane (iv):   cyclohexane ring C(29)–C(34)

	Isomer C			Isomer C:CH_3OH 295 K			123 K		
	(ii)	(iii)	(iv)	(ii)	(iii)	(iv)	(ii)	(iii)	(iv)
(i)	36·9	48·3	39·8	39·0	50·1	42·4	38·3	49·9	42·1
(ii)		65·8	26·4		70·3	30·7		70·1	31·5
(iii)			43·2			44·2			43·4

Table 7. *Principal intermolecular contacts* (Å)

Contacts involving H atoms in calculated positions are shown without e.s.d.'s. Atoms a and b are in the crystal-chemical unit, a_j and b_i are in equivalent positions given by the Roman numerals defined in the legends to Fig. 3(a) and (b).

(a) Isomer C

a/a_j	b_i/b	$a \cdots b_i$ or $a_j \cdots b$	i	j
C(8)	C(36)	3·715 (3)	I	II
C(10)	C(32)	3·763 (4)	III	IV
C(11)	C(16)	3·794 (4)	V	VI
C(13)	C(36)	3·748 (3)	I	II
O(7)	H(19)B	2·80	I	II
C(8)	H(36)B	3·00	I	II
C(10)	H(32)B	3·05	III	IV
C(11)	H(16)A	3·12	V	VI
C(12)	H(36)B	3·06	I	II
C(13)	H(36)B	2·85	I	II
O(14)	H(19)B	2·70	I	II
C(23)	H(10)	2·96	VII	VIII
C(23)	H(15)B	3·12	IX	IX
C(24)	H(2)B	3·05	X	XI
C(32)	H(16)B	3·03	XII	XII
C(32)	H(23)B	3·07	IV	III
H(10)	H(23)B	2·33	VIII	VII
H(11)	H(18)	2·41	IX	IX
H(24)A	H(31)A	2·42	III	IV
H(25)A	H(27)A	2·44	II	I
H(25)B	H(30)A	2·38	X	XI

(b) Isomer C:CH$_3$OH

a/a_j	b_i/b	$a \cdots b_i$ or $b \cdots a_j$ 295 K	123 K	i	j
(i) Contacts not involving the methanol molecule					
C(5)	O(35)	3·384 (4)	3·294 (3)	I	II
C(6)	C(19)	3·764 (5)	3·697 (4)	I	II
C(6)	O(35)	3·300 (4)	3·221 (3)	I	II
C(10)	C(32)	3·763 (6)	3·686 (4)	III	IV
C(15)	O(20)	3·330 (4)	3·267 (3)	V	V
C(16)	C(23)	3·667 (5)	3·608 (4)	V	V
C(6)	H(19)B	3·06	3·01	I	II
C(10)	H(32)B	3·09	3·01	III	IV
C(11)	H(24)A	3·16	3·09	VI	VII
C(15)	H(23)A	3·01	2·95	V	V
C(15)	H(30)A	3·06	2·97	VIII	IX
C(16)	H(3)	3·14	3·07	VIII	IX
C(16)	H(23)A	3·07	3·00	V	V
C(19)	H(12)	3·06	2·97	V	V
O(20)	H(15)A	2·86	2·80	V	V
O(20)	H(15)B	2·93	2·86	V	V
C(23)	H(16)B	2·87	2·82	V	V
C(23)	H(31)A	3·14	3·05	III	IV
C(25)	H(10)	3·11	3·05	II	I
C(30)	H(15)B	3·15	3·07	IX	VIII
O(35)	H(5)A	2·68	2·59	II	I
O(35)	H(6)A	2·70	2·64	II	I
C(36)	H(5)A	3·07	2·99	II	I
H(3)	H(16)A	2·46	2·39	IX	VIII
H(6)B	H(19)B	2·42	2·34	I	II
H(11)	H(26)	2·57	2·47	VI	VII
H(15)B	H(23)A	2·42	2·36	V	V
H(15)B	H(30)A	2·35	2·29	VIII	IX
H(22)A	H(31)A	2·56	2·48	III	IV

Table 7 (*cont.*)

a/a_j	b_i/b	$a \cdots b_i$ or $b \cdots a_j$ 295 K	123 K	i	j
(ii) Contacts involving the methanol molecule (other than by hydrogen bonding)					
C(51)	C(2)	3·868 (9)	3·789 (5)	VIII	IX
C(51)	C(9)	3·784 (9)	3·743 (5)	X	X
C(51)	C(24)	3·718 (9)	3·648 (5)	XI	XII
C(51)	C(51)	3·753 (16)	3·775 (8)	X	X
O(50)	H(24)B	2·67	2·58	XI	XII
C(51)	H(2)B	2·93	2·85	VIII	IX
C(51)	H(24)B	3·12	3·04	XI	XII
C(51)	H(51)B	3·26 (6)	3·13 (3)	X	X
H(50)	C(16)	3·10 (7)	3·06 (4)	—	—
H(51)A	C(9)	3·12 (7)	2·99 (3)	X	X
H(51)A	C(24)	3·21 (6)	3·06 (3)	XI	XII
H(50)	H(16)A	2·64	2·59	—	—
H(51)A	H(24)B	2·72	2·59	XI	XII
H(51)B	H(51)C	2·89 (9)	2·64 (5)	X	X

The sharp hydroxy stretching frequency did suggest that the methanol molecule might be bound through the CH$_3$ group [by analogy with the 18-crown-6 complexes of dimethyl sulphone (Bandy, Truter & Vögtle, 1981) and of dimethylacetylene dicarboxylate (Goldberg, 1975)] but there is no evidence of this in the crystal structure. The sharpness (width 20 cm^{-1}) appears to be an example of the narrower band width found for weaker hydrogen bonds (Novak, 1974). In addition to the v_{OH}, the methanol complex also shows a band at 1028 cm^{-1} attributable to the COH bending frequency.

Table 5 shows that several torsion angles differ by more than 30° from the favourable ±60 or 180°. This might be a result of intramolecular C—H$\cdots$O bonding or of intermolecular interactions. The existence of C—H$\cdots$O bonding is still controversial. Maverick, Seiler, Schweizer & Dunitz (1980) redetermined the structure of 18-crown-6 at 100 K and considered the intramolecular C—H$\cdots$O contacts as possible hydrogen bonds holding the observed conformation. They found one H atom to make two intramolecular contacts of 2·46 and 2·64 Å with O atoms but their calculated consistent-force-field structure gives shorter distances than observed and does not include hydrogen-bonding considerations. On the other hand, in a recent paper on non-bonded potential functions for crystalline oxo-hydrocarbons, Cox, Hsu & Williams (1981) found it necessary to allow in some cases for C—H$\cdots$O hydrogen bonds. The sum of the van der Waals radii of H and O is 2·6 Å, so distances less than this, particularly if C_{sp^2}—H rather than C_{sp^3}—H is the donor, were considered as potential hydrogen bonds.

We have found that within the macrobicyclic molecule there are five distances from C—H to an O at least four atoms away of <2·6 Å, but only one, H(19)A$\cdots$O(1) at 2·25 Å, is less than 2·40 Å: the C(19) to O(1) separation is 2·965 (3) Å. This is not

changed significantly in the methanol complex structure.

Heating at 373 K for 2 h does not drive off all the methanol; however, the methanol is lost on further heating to give the unsolvated compound which melts at 406 K, *i.e.* approximately the same temperature as that for the other two isomers *A* and *B*.

In their crystalline forms, the three isomeric molecules occupy equal volumes (*ca* 668 Å^3), and all intermolecular contacts are at van der Waals distances. In the packing diagrams for isomer *C* and the methanol complex (Fig. 3*a,b*), the view chosen to give the best resolution of the molecules shows the similarity of certain molecules in projection. The packing arrangements are, however, quite different.

The shorter intermolecular contacts are in Table 7. For the unsolvated compound there are 17 pairs of C···H contacts calculated to be <3·2 Å of which seven involve C atoms of the aromatic rings; those selected are the shortest about each symmetry element. The two shortest O···H contacts are included. The Roman numeral superscripts are defined in the legend to Fig. 3(*a*). There are shorter contacts between macrobicyclic ether molecules in the methanol complex, including three pairs of C···O distances <3·2 Å. 13 of the 19 pairs of C···H contacts <3·2 Å are given in Table 7(*b*)(i).

A listing of the distances involving the methanol molecule is in Table 7(*b*)(ii); the main contacts are to the methanol related by the centre of symmetry at 0,½,0. There is no evidence of CH···O hydrogen bonding. The C(51)···C(51^x) distance is not significantly different ($\Delta = 0.022$ Å, $\sigma = 0.018$ Å) at the two temperatures in contrast with the effect expected, and found, in Table 7(*b*)(i), that reduction in temperature reduces the intermolecular contacts (by 0·059–0·090 Å with e.s.d.'s of 0·005–0·007 Å).

The additional volume occupied per methanol molecule is 38·9 (3) Å^3. In the crystal structure of solid methanol (Tauer & Lipscomb, 1952), this volume is 54·5 (3) and 52·2 (5) Å^3 at 163 and 113 K respectively and the molecules are held in hydrogen-bonded chains, O···O 2·66 (3) Å. The difference in volumes indicates very efficient packing in our host–guest complex probably because the methyl groups pack together.

The relationship between the macrobicyclic ether and *n*-alcohols contrasts with that of tri-*o*-thymotide which gives isomorphous crystals when it contains alcohols up to 9·5 Å in length, in cavities. However, the methanol clathrate is anomalous in having a greater volume than the ethanol one and in being the least stable (Lawton & Powell, 1958); it is from methanol that the unsolvated compound can be crystallized (Baker, Gilbert & Ollis, 1952). Recently, Weber & Vögtle (1980) have suggested that the 2:1 compounds they obtained from non-branched alcohols from meth-

anol to 1-hexanol, with a novel pyridino crown compound are similar to the tri-*o*-thymotide inclusion compounds. No information was given about the IR spectra or the crystal structures.

The factors affecting weakly held complexes are very subtle. Co-crystallization may be the result of a specific guest–host relationship or, as in a clathrate compound, the host structure may be sufficiently rigid to accommodate a variety of non-bonded guests. For example, with Dianin's compound, 4-*p*-hydroxyphenyl-2,2,4-trimethylchroman, as the host, the ethanol guest is disordered and not close enough to the host to be hydrogen bonded (Flippen, Karle & Karle, 1970). In an α-cyclodextrin inclusion complex of methanol, the alcohol was found to be disordered, but some hydrogen bonding was postulated (Hingerty & Saenger, 1976), while with γ-cyclodextrin the included *n*-propanol could not be located (Lindner & Saenger, 1980).

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Structures of L-Phenylalanine Dimers, N-(tert-Butoxycarbonyl)-L-phenylalanyl-L-phenylalanine Benzyl Ester (Boc-Phe-Phe-OBzl) and L-Phenylalanyl-L-phenylalanine Ethyl Ester Trifluoroacetate (Phe-Phe-OEt.Tfa)

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Abstract

The crystal structures of the title compounds have been determined by the direct method and refined by the block-diagonal least-squares method. Boc-Phe-Phe-OBzl has space group $P2_1$, with $a = 14\cdot363$ (3), $b = 19\cdot016$ (5), $c = 5\cdot077$ (1) Å, $\beta = 97\cdot02$ (2)°, $V = 1376\cdot3$ (8) Å³, $Z = 2$, and $R = 0\cdot070$ for 1921 reflections; Phe-Phe-OEt.Tfa has space group $P2_12_12_1$, with $a = 16\cdot507$ (4), $b = 24\cdot927$ (7), $c = 5\cdot650$ (1) Å, $V = 2325$ (1) Å³, $Z = 4$, and $R = 0\cdot074$ for 1544 reflections. The former crystallizes in the parallel β pleated sheet. Deviation of the main-chain conformation from that of the typical β sheet due to the substitution of bulky terminal groups is observed. The latter molecule is not in the β sheet, but has a column structure with a hydrophilic core of hydrogen bonds and a hydrophobic shell.

Introduction

Difficulties in the crystallization of peptides often restrict X-ray conformational studies in the solid state. When the peptide to be studied has large hydrophobic side chains, it becomes more difficult to obtain crystals large enough for X-ray analysis. Crystal structure studies of peptides involving two successive phenyl-

alanine residues so far reported are limited to dipeptides and tripeptides. These crystal structures can be classified into either of the following two groups on the basis of intermolecular interactions: (1) parallel β pleated-sheet-type structures stabilized by a pair of intermolecular hydrogen bonds, and (2) salt type in which the crystal packing is determined by hydrogen bonds and electrostatic interactions between peptides and counter-ions. In both cases, however, clusters of the phenylalanine side chains are observed in the crystal structures.

We have been studying the solid-state structures of poly(α-amino acids), which carry large hydrophobic side chains, by X-ray diffraction and have found the coexistence of ω- and α-helices in poly(L-phenylalanine) on the basis of X-ray fiber photographs (Yamashita, Yamane, Ashida, Yamashita & Yamashita, 1979). In this case, the side-chain–side-chain interactions must play an important role in determining the type of helix. To reveal the role of phenyl groups in peptide conformations, some phenylalanine oligomers have been synthesized and their crystal structures studied. This report deals with the crystal structures of N-(tert-butoxycarbonyl)-L-phenylalanyl-L-phenylalanine benzyl ester (Boc-Phe^1-Phe^2-OBzl) and L-phenylalanyl-L-phenylalanine ethyl ester trifluoroacetate (Phe^1-Phe^2-OEt.Tfa), both of which have two phenylalanyl residues. The former belongs to the type (1) mentioned above, and the latter to (2).