

**1,4,11,14,21,30-Hexaoxa[4](1,2)benzeno[4](1,2)benzeno[2](2,6)pyridino[2](1,2)-
benzenophane,* C₂₉H₂₇NO₆, (1), and its Hydrated Dimethanol Complex,
C₂₉H₂₇NO₆·2CH₃OH·H₂O, (2)**

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(Received 7 June 1983; accepted 18 July 1983)

Abstract. (1): $M_r = 485.54$, triclinic, $P\bar{1}$, $a = 9.804$ (4), $b = 12.155$ (5), $c = 12.373$ (5) Å, $\alpha = 62.91$ (4), $\beta = 70.10$ (5), $\gamma = 73.06$ (5)°, $V = 1217.8$ (9) Å³, $Z = 2$, $D_x = 1.324$ (1) Mg m⁻³, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 0.087$ mm⁻¹, $F(000) = 512$, $T = 291$ K, $R = 0.064$ for 3448 observed [$F > 3\sigma(F)$] diffractometer data. (2): $M_r = 567.64$, monoclinic, $P2_1/n$, $a = 18.147$ (5), $b = 8.535$ (3), $c = 20.477$ (6) Å, $\beta = 102.71$ (6)°, $V = 3093.8$ (16) Å³, $Z = 4$, $D_x = 1.218$ (1) Mg m⁻³, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 0.084$ mm⁻¹, $F(000) = 1208$, $T = 293$ K, $R = 0.063$ for 4026 observed [$I > 2\sigma(I)$] diffractometer data. On the uptake of methanol, the macrocycle (1) changes its conformation to facilitate one strong O··N hydrogen bond of 2.873 (5) Å, with one methanol molecule (*M1*) accommodated in the host cavity. The second methanol (*M2*) and the (disordered) water link this unit to a symmetry-related one to give a dimer via N··O(*M1*)··O(*M2*)··O(*W*)··O(*W*)'··O(*M2*)'··O(*M1*)'··N' interactions.

Introduction. The title ligand (1) (Fig. 1) was reported to form crystalline stoichiometric adducts with lower *n*-alcohols (Weber & Vögtle, 1980). More recently, macrocycles analogous to (1) were designed, displaying high selectivities towards various branched or linear alcohols (Weber, Vögtle, Josel, Newkome & Puckett, 1983). However, the nature of the binding forces in these compounds remained uncertain. Only one complex between a (bicyclic) polyether and methanol has been structurally investigated so far (Bandy, Hughes & Truter, 1982). It thus seemed worthwhile to determine the structures of (1) and its methanol adduct (2).

Experimental. Methanol complex (2) kindly provided by Professor F. Vögtle and Dr E. Weber, University of Bonn, D-5300 Bonn, Federal Republic of Germany, and recrystallized from methanol, uncomplexed macrocycle (1) obtained on crystallization of (2) from

* Nomenclature according to Weber, Vögtle, Josel, Newkome & Puckett (1983).

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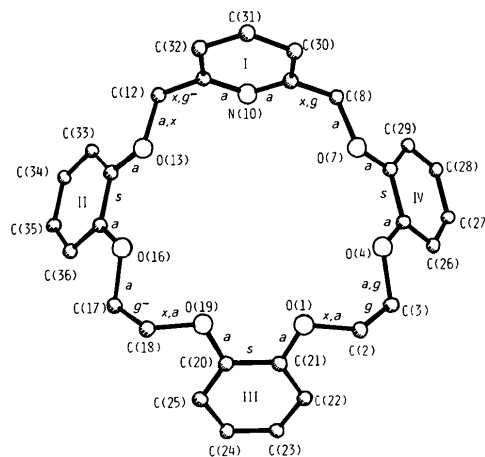


Fig. 1. The chemical structure of (1), showing the numbering scheme and the designation of aromatic nuclei. Endocyclic torsion angles [$a = anti$, $g^{(-)}$ = ($-$) *gauche*, $s = syn$, $x = 185^\circ$ to 1100°] are also indicated; the second symbol, where present, stands for a torsion angle in (2) different from that in (1).

2-propanol (Weber & Vögtle, 1980); data for (2) when deviating from those for (1) are given in square brackets in the following: crystal size ca $0.7 \times 0.65 \times 0.45$ [$0.75 \times 0.7 \times 0.6$] mm, Stoe-Siemens AED diffractometer, cell dimensions from 2θ angles for 34 reflections with $20 < 2\theta < 25^\circ$; 6926 [6728] profile-fitted (Clegg, 1981) data up to $2\theta = 50^\circ$, $-11[0] \leq h \leq 11[21]$, $-14[-10] \leq k \leq 14[5]$, $-14[-24] \leq l \leq 14[24]$, [406 systematically absent: $0k0$, $k = 2n + 1$; $h0l$, $h + l = 2n + 1$], 4288 [5430] unique ($R_{int} = 0.036$ [0.019]), 3451 [4036] intensities $> 1.5[2]\sigma(I)$, 3[10] erroneous reflections (machine fault) suppressed, no significant decline in intensity for 3 standard reflections, no absorption correction; structure solved by multisolution direct methods, blocked-cascade refinement on F , $w^{-1} = \sigma^2(F) + gF^2$ with $g = 4[10] \times 10^{-4}$, ligand H atoms in idealized positions ($C-H = 0.96$ Å) treated as 'riding atoms', all $U(H_i) = 1.2 U_{eq}$ of attached atoms, anisotropic temperature factors for non-H atoms [except for C(*M2b*), O(*Wa*),

O(*Wb*), O(*Wc*), 325 [380] parameters, $wR = 0.066$ [0.070], slope of probability plot = 1.71 [1.61], max. shift/e.s.d. = 0.045 [0.054], mean 0.010 [0.013], max. residual electron density 0.27 [0.58 and 0.51, close to disordered 'water'] e Å⁻³, minimum 0.25 [0.23] e Å⁻³; scattering factors from *International Tables for X-ray Crystallography* (1974), program for structure solution, refinement, graphical display and geometrical calculations (*SHELXTL*) written by Professor G. M. Sheldrick, for diffractometer control by Dr W. Clegg (both at Göttingen).

For (2) only: H-atom positions for *M1* taken from a difference map, hydroxyl H treated as 'riding atom', idealized methyl group (C—H = 1.04 Å) as 'rigid group'; three peaks of 1 to 1.5 e Å⁻³ considered as disordered water, their occupancy factors refined with one common isotropic temperature factor, then rescaled according to $\sum_{i=1}^3 f_i = 1$; f_i kept fixed during further refinement (to prevent correlation), isotropic *U* allowed to vary independently instead; one more peak of 1 e Å⁻³ close to *M2* taken as a second C-atom position *C(M2b)* with f identical to that of O(*Wc*) since *C(M2a)* and O(*Wc*) were mutually exclusive at that state of refinement; O(*M2*)—*C(M2a)* and O(*M2*)—*C(M2b)* restrained to be 1.45 Å with weights derived from $\sigma = 0.005$ Å.

Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters (Å² $\times 10^3$) (defined as one third of the trace of the orthogonalized U_{ij} tensor) for macrocycle (1)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i>
O(1)	10063 (2)	4725 (1)	2561 (1)	54 (1)
C(2)	9032 (2)	5321 (2)	3333 (2)	56 (1)
C(3)	7482 (2)	5483 (2)	3318 (2)	56 (1)
O(4)	7071 (2)	4268 (1)	3873 (1)	51 (1)
C(5)	5706 (2)	4247 (2)	3811 (2)	50 (1)
C(6)	5382 (2)	3056 (2)	4206 (2)	53 (1)
O(7)	6479 (2)	2078 (1)	4563 (2)	57 (1)
C(8)	6259 (3)	890 (2)	4744 (2)	64 (1)
C(9)	7657 (3)	-28 (2)	4856 (2)	55 (1)
N(10)	8434 (2)	-195 (2)	3810 (2)	49 (1)
C(11)	9668 (3)	-1033 (2)	3859 (2)	55 (1)
C(12)	10498 (3)	-1162 (2)	2653 (3)	68 (1)
O(13)	11514 (2)	-289 (2)	2004 (2)	64 (1)
C(14)	12172 (3)	-85 (2)	787 (2)	61 (1)
C(15)	13075 (3)	849 (2)	161 (2)	59 (1)
O(16)	13172 (2)	1409 (1)	870 (1)	60 (1)
C(17)	13945 (3)	2442 (2)	209 (2)	66 (1)
C(18)	13820 (3)	3031 (2)	1070 (2)	62 (1)
O(19)	12379 (2)	3624 (1)	1466 (1)	57 (1)
C(20)	11889 (2)	4832 (2)	722 (2)	49 (1)
C(21)	10612 (2)	5429 (2)	1313 (2)	48 (1)
C(22)	10014 (3)	6631 (2)	652 (2)	64 (1)
C(23)	10652 (3)	7245 (2)	-601 (3)	75 (1)
C(24)	11909 (3)	6664 (2)	-1180 (2)	76 (1)
C(25)	12540 (3)	5461 (2)	-517 (2)	66 (1)
C(26)	4664 (3)	5288 (3)	3396 (2)	67 (1)
C(27)	3334 (3)	5135 (3)	3360 (3)	84 (2)
C(28)	3011 (3)	3985 (3)	3755 (3)	92 (2)
C(29)	4024 (3)	2955 (3)	4173 (3)	76 (2)
C(30)	8073 (4)	-678 (3)	5970 (2)	77 (2)
C(31)	9333 (4)	-1538 (3)	6021 (3)	90 (2)
C(32)	10149 (3)	-1729 (2)	4953 (3)	78 (2)
C(33)	12014 (5)	-684 (3)	127 (3)	80 (2)
C(34)	12700 (4)	-385 (4)	-1120 (4)	99 (2)
C(35)	13557 (4)	520 (3)	-1721 (3)	94 (2)
C(36)	13784 (3)	1137 (3)	-1088 (3)	77 (1)

Discussion. Final atom parameters are given in Tables 1 and 2.* Bond distances and angles, as listed in Table 3, exhibit no anomalies and are (with few exceptions) identical within 3 σ in both compounds.

In the free macrocycle (1) a (non-crystallographic) mirror running through the pyridine atoms N(10) and C(31) and bisecting the opposite phenylene III implies

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, and torsion angles for (1) and (2) have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38739 (51 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH 1 2HU, England.

Table 2. Atomic coordinates ($\times 10^4$) and isotropic thermal parameters (Å² $\times 10^3$) for the hydrated methanol adduct (2)

O(*M1*), C(*M1*) and H(1*M1*) to H(4*M1*) belong to methanol (1), O(*M2*) to C(*M2b*) belong to methanol (2) and O(*Wa*) to O(*Wc*) stand for the disordered water molecule. Occupancy factors for C(*M2a*) = 0.75, C(*M2b*) = 0.25, O(*Wa*) = 0.38, O(*Wb*) = 0.37 and O(*Wc*) = 0.25 were kept fixed during the last cycles of refinement.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i>
O(1)	4499 (1)	310 (2)	1529 (1)	62 (1)*
C(2)	4432 (2)	-481 (4)	2129 (1)	65 (1)*
C(3)	5202 (2)	-657 (3)	2567 (1)	57 (1)*
O(4)	5489 (1)	763 (2)	2895 (1)	53 (1)*
C(5)	5252 (1)	1206 (3)	3462 (1)	50 (1)*
C(6)	5613 (1)	2527 (3)	3787 (1)	54 (1)*
O(7)	6158 (1)	3191 (2)	3502 (1)	57 (1)*
C(8)	6455 (2)	4657 (3)	3764 (1)	60 (1)*
C(9)	7036 (1)	5181 (3)	3391 (1)	50 (1)*
N(10)	6776 (1)	5548 (2)	2741 (1)	47 (1)*
C(11)	7278 (1)	6056 (3)	2392 (1)	44 (1)*
C(12)	6966 (2)	6436 (3)	1674 (1)	53 (1)*
O(13)	6669 (1)	5092 (2)	1280 (1)	54 (1)*
C(14)	7117 (1)	4350 (3)	918 (1)	47 (1)*
C(15)	6730 (1)	3463 (3)	377 (1)	48 (1)*
O(16)	5961 (1)	3423 (2)	296 (1)	58 (1)*
C(17)	5551 (2)	2376 (3)	-192 (1)	60 (1)*
C(18)	4741 (2)	2476 (4)	-158 (1)	62 (1)*
O(19)	4654 (1)	1739 (2)	448 (1)	58 (1)*
C(20)	3943 (1)	1739 (3)	570 (1)	53 (1)*
C(21)	3854 (1)	934 (3)	1143 (1)	57 (1)*
C(22)	3148 (2)	822 (4)	1285 (2)	80 (1)*
C(23)	2531 (2)	1567 (5)	867 (2)	98 (2)*
C(24)	2626 (2)	2405 (5)	320 (2)	85 (1)*
C(25)	3329 (2)	2470 (4)	176 (1)	67 (1)*
C(26)	4706 (2)	450 (4)	3724 (1)	62 (1)*
C(27)	4523 (2)	1000 (4)	4301 (2)	78 (1)*
C(28)	4877 (2)	2285 (4)	4622 (2)	83 (1)*
C(29)	5427 (2)	3055 (4)	4365 (2)	74 (1)*
C(30)	7778 (1)	5326 (3)	3706 (1)	53 (1)*
C(31)	8292 (2)	5906 (3)	3356 (1)	56 (1)*
C(32)	8031 (1)	6282 (3)	2689 (1)	52 (1)*
C(33)	7893 (1)	4440 (3)	1044 (1)	59 (1)*
C(34)	8292 (2)	3664 (4)	635 (2)	68 (1)*
C(35)	7910 (2)	2806 (4)	98 (1)	67 (1)*
C(36)	7129 (2)	2702 (3)	-33 (1)	59 (1)*
O(<i>M1</i>)	5186 (1)	5633 (3)	2150 (1)	93 (1)*
C(<i>M1</i>)	4976 (2)	4349 (4)	1720 (2)	100 (2)*
O(<i>M2</i>)	822 (3)	1035 (7)	2016 (3)	228 (3)*
C(<i>M2a</i>)	1132 (5)	-468 (10)	1894 (7)	276 (8)*
C(<i>M2b</i>)	1328 (8)	2169 (17)	1826 (8)	114 (5)
O(<i>Wb</i>)	2810 (5)	7485 (11)	2326 (4)	134 (3)
O(<i>Wc</i>)	2572 (7)	6168 (17)	1743 (7)	200 (5)
O(<i>Wc</i>)	2448 (10)	5463 (25)	2187 (9)	198 (7)
H(1 <i>M1</i>)	5741	5565	2340	104
H(2 <i>M1</i>)	5300	4157	1367	113
H(3 <i>M1</i>)	4414	4504	1477	113
H(4 <i>M1</i>)	5021	3388	2038	113

* Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor.

a highly symmetrical molecular geometry (Figs. 1 and 2) with five hetero-atoms (plane V) being coplanar to within $\pm 0.04 \text{ \AA}$ [O(1) deviating $0.48 (1)$, and O(19) $0.54 (1) \text{ \AA}$]. Endocyclic torsion angles deviate from the usual *anti* (for C–X–C–C, X = O, N), \pm *gauche* (for O–C–C–O) and *syn* (at 1,2-disubstituted benzene) about two C–O and two C–C bonds (Fig. 1), the observed values of 185° to 195° being common in benzo-crowns (*e.g.* Mercer & Truter, 1973; Hughes, Mortimer & Truter, 1978).

In this conformation, the lone pairs of the O atoms might be in suitable positions for an attack by an H-bond donor [indeed the complex of a bicyclic polyether containing only O hetero-atoms is formed without conformational changes (Bandy, Hughes & Truter, 1982)], but the more basic pyridine N appears well shielded. Accordingly, on the uptake of methanol, one of the 'hindering' benzene moieties rotates away (Fig. 3) [dihedral angles II/IV $87.2 (5)^\circ$ in (1), $40.8 (7)^\circ$ in (2); II/V $47.5 (4)$, IV/V $48.1 (4)^\circ$ in (1); II/V $63.5 (6)$, IV/V $28.0 (6)^\circ$ in (2)]. In the resulting non-symmetric conformation of the host in (2) (Fig. 3),

the five hetero-atoms are still coplanar [$\pm 0.12 (1) \text{ \AA}$, plane V] but only one irregular torsion of $ca 100^\circ$ [and one of $80.3 (3)^\circ$ about C(3)–O(4)] is required (Fig. 1).

The conformational change of (1) facilitates a strong O(M1)···N(10) hydrogen bond of $2.873 (5) \text{ \AA}$ [O(M1)–H(1M1)···N(10) = $175.9 (4)^\circ$] with the N···H vector [$1.877 (5) \text{ \AA}$] coincident with the direction of the lone pair and the H atom deviating by only $0.24 (2) \text{ \AA}$ from the aromatic plane I (Fig. 3), a geometry very similar to that previously found in a glucitol/pyridine adduct (Kim, Jeffrey & Rosenstein, 1971). However, the overall host/guest arrangement, *i.e.* the accommodation of methanol into the cavity of the macrocycle (Fig. 4), contrasts with the 'sandwich configuration' usually observed in adducts of crown ethers with neutral H-bond donors (*e.g.* von Deuten, Knöchel, Kopf, Oehler & Rudolph, 1979; Bandy, Truter & Vögtle, 1981; Weber, 1982), whilst 'encapsulated complexes' are only found with cationic guest molecules (*e.g.* Uiterwijk, Harkema, Geevers & Reinhoudt, 1982; Reinhoudt, den Hertog & de Jong, 1981).

Table 3. Bond lengths (\AA) and angles ($^\circ$) for (1) and (2)

	(1)	(2)		(1)	(2)
O(1)–C(2)	1.415 (3)	1.431 (3)	O(1)–C(21)	1.381 (2)	1.369 (3)
C(2)–C(3)	1.480 (4)	1.493 (3)	C(3)–O(4)	1.432 (3)	1.428 (3)
O(4)–C(5)	1.374 (3)	1.378 (3)	C(5)–C(6)	1.398 (4)	1.396 (4)
C(5)–C(26)	1.386 (3)	1.385 (4)	C(6)–O(7)	1.366 (3)	1.376 (3)
C(6)–C(29)	1.387 (4)	1.377 (4)	O(7)–C(8)	1.427 (4)	1.420 (3)
C(8)–C(9)	1.496 (3)	1.499 (4)	C(9)–N(10)	1.333 (3)	1.348 (3)
C(9)–C(30)	1.376 (4)	1.364 (3)	N(10)–C(11)	1.334 (3)	1.347 (3)
C(11)–C(12)	1.492 (4)	1.491 (3)	C(11)–C(32)	1.390 (4)	1.381 (3)
C(12)–O(13)	1.435 (3)	1.437 (3)	O(13)–C(14)	1.355 (3)	1.369 (3)
C(14)–C(15)	1.410 (4)	1.397 (3)	C(14)–C(33)	1.384 (6)	1.378 (4)
C(15)–O(16)	1.372 (4)	1.370 (3)	C(15)–C(36)	1.382 (4)	1.384 (4)
O(16)–C(17)	1.421 (3)	1.422 (3)	C(17)–C(18)	1.489 (5)	1.488 (4)
C(18)–O(19)	1.419 (3)	1.431 (3)	O(19)–C(20)	1.376 (2)	1.367 (3)
C(20)–C(21)	1.399 (3)	1.400 (4)	C(20)–C(25)	1.376 (3)	1.372 (4)
C(21)–C(22)	1.374 (3)	1.378 (4)	C(22)–C(23)	1.382 (3)	1.402 (4)
C(23)–C(24)	1.371 (4)	1.371 (5)	C(24)–C(25)	1.385 (3)	1.373 (5)
C(26)–C(27)	1.387 (5)	1.379 (5)	C(27)–C(28)	1.350 (6)	1.365 (5)
C(28)–C(29)	1.363 (4)	1.392 (5)	C(30)–C(31)	1.365 (5)	1.387 (4)
C(31)–C(32)	1.376 (4)	1.381 (4)	C(33)–C(34)	1.375 (5)	1.389 (4)
C(34)–C(35)	1.356 (6)	1.376 (4)	C(35)–C(36)	1.406 (6)	1.385 (4)
O(M1)–C(M1)		1.406 (5)	O(M2)–C(M2a)		1.445 (11)
O(M2)–C(M2b)		1.446 (17)	O(M1)–H(1M1)		0.999
C(2)–O(1)–C(21)	119.8 (2)	117.1 (2)	O(1)–C(2)–C(3)	114.7 (3)	108.5 (2)
C(2)–C(3)–O(4)	108.2 (2)	113.2 (2)	C(3)–O(4)–C(5)	115.4 (2)	118.7 (2)
O(4)–C(5)–C(6)	115.3 (2)	114.9 (2)	O(4)–C(5)–C(26)	125.7 (2)	125.5 (2)
C(6)–C(5)–C(26)	119.0 (3)	119.5 (3)	C(5)–C(6)–O(7)	115.7 (2)	115.9 (2)
C(5)–C(6)–C(29)	118.8 (2)	119.7 (3)	O(7)–C(6)–C(29)	125.5 (3)	124.4 (2)
C(6)–O(7)–C(8)	115.7 (2)	116.9 (2)	O(7)–C(8)–C(9)	110.0 (2)	108.8 (2)
C(8)–C(9)–N(10)	114.9 (2)	116.1 (2)	C(8)–C(9)–C(30)	122.1 (2)	121.1 (2)
N(10)–C(9)–C(30)	123.0 (2)	122.8 (2)	C(9)–N(10)–C(11)	117.8 (2)	117.8 (2)
N(10)–C(11)–C(12)	115.2 (2)	116.0 (2)	N(10)–C(11)–C(32)	122.4 (2)	122.1 (2)
C(12)–C(11)–C(32)	122.4 (2)	121.9 (2)	C(11)–C(12)–O(13)	107.9 (3)	113.2 (2)
C(12)–O(13)–C(14)	117.0 (3)	118.6 (2)	O(13)–C(14)–C(15)	115.0 (3)	115.2 (2)
O(13)–C(14)–C(33)	126.2 (2)	125.3 (2)	C(15)–C(14)–C(33)	118.8 (2)	119.5 (2)
C(14)–C(15)–O(16)	115.6 (2)	115.4 (2)	C(14)–C(15)–C(36)	119.5 (3)	119.8 (2)
O(16)–C(15)–C(36)	124.9 (3)	124.8 (2)	C(15)–O(16)–C(17)	115.6 (2)	117.5 (2)
O(16)–C(17)–C(18)	109.3 (2)	107.5 (2)	C(17)–C(18)–O(19)	114.2 (2)	108.3 (2)
C(18)–O(19)–C(20)	119.8 (2)	116.6 (2)	O(19)–C(20)–C(21)	115.0 (2)	116.2 (2)
O(19)–C(20)–C(25)	125.4 (2)	124.7 (2)	C(21)–C(20)–C(25)	119.6 (2)	119.1 (3)
O(1)–C(21)–C(22)	114.9 (2)	115.7 (2)	O(1)–C(21)–C(22)	125.1 (2)	124.6 (3)
C(20)–C(21)–C(22)	119.9 (2)	119.7 (2)	C(21)–C(22)–C(23)	120.2 (2)	119.6 (3)
C(22)–C(23)–C(24)	119.9 (2)	120.6 (3)	C(23)–C(24)–C(25)	120.4 (2)	119.0 (3)
C(20)–C(25)–C(24)	120.0 (2)	121.9 (3)	C(5)–C(26)–C(27)	119.8 (3)	120.0 (3)
C(26)–C(27)–C(28)	121.3 (3)	120.7 (3)	C(27)–C(28)–C(29)	119.3 (3)	119.8 (3)
C(6)–C(29)–C(28)	121.7 (3)	120.2 (3)	C(9)–C(30)–C(31)	119.2 (3)	119.6 (2)
C(30)–C(31)–C(32)	118.8 (3)	118.1 (2)	C(11)–C(32)–C(31)	118.9 (3)	119.5 (3)
C(14)–C(33)–C(34)	121.8 (3)	120.5 (2)	C(33)–C(34)–C(35)	119.2 (5)	119.9 (3)
C(34)–C(35)–C(36)	121.3 (3)	120.2 (3)	C(15)–C(36)–C(35)	119.3 (3)	120.2 (2)
C(M1)–O(M1)–H(1M1)		108.0 (2)			

The methanol CH_3 group points towards phenylene III (Figs. 3 and 4) and the hydroxyl O can thus accept an H bond from a second methanol ($M2$) at an $O(M1) \cdots O(M2)$ distance of $2.782(8) \text{ \AA}$, which enhances the donor property of the hydroxyl H of $M1$. The ligand $\cdots M1 \cdots M2$ unit is probably linked to a symmetry-related unit *via* a third, at least threefold disordered, molecule $O(Wa)$, $O(Wb)$, $O(Wc)$ at distances typical of H bonds (Fig. 5). $O(W)$ was taken as water since the solvent used for crystal growing had not been specially dried, but might also be a third methanol. The latter assumption would be supported by the additional volume per asymmetric unit occupied in (2) [as compared to that in (1)] of 165 \AA^3 which (when divided by three) corresponds to that of methanol (55 \AA^3 at 163 K with $O \cdots O = 2.66 \text{ \AA}$) (Tauer & Lipscomb, 1952).

The dimer can be described as an $N(\text{ligand}) \cdots O(M1) \cdots O(M2) \cdots O(Wa) \cdots O(Wc) \cdots O(M2)' \cdots O(M1) \cdots N(\text{ligand})'$ sequence (Fig. 5). However, dis-

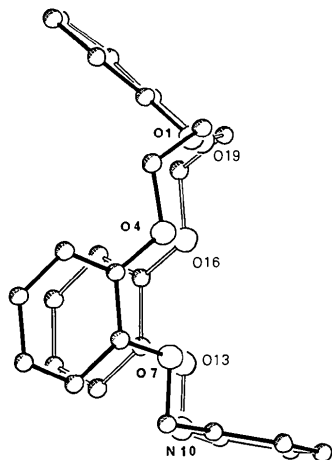


Fig. 2. A perspective view of the macrocycle (1); radii are arbitrary.

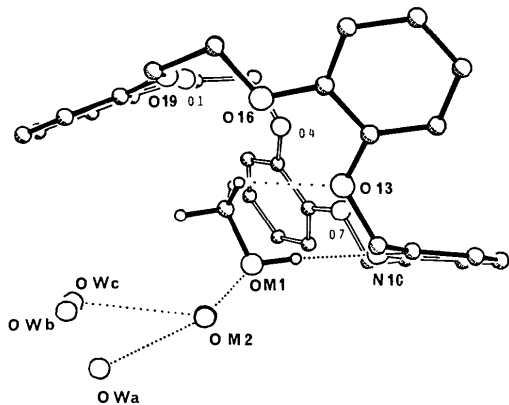


Fig. 3. A perspective view of the methanol adduct (2); radii are arbitrary. Dotted lines indicate probable hydrogen bonds; the contact of $2.652(6) \text{ \AA}$ between $H(2M1)$ and $O(13)$ may not be significant.

tances of $2.95(2)$ and $3.03(3) \text{ \AA}$ between each of the two C positions of $M2$ and $O(Wc)$ [*cf.* $O(M2) \cdots O(Wc) = 3.24(2) \text{ \AA}$, *i.e.* by far the weakest link in the H-bond chain] indicate an even more severe, but irresolvable disorder, as is confirmed by the relatively low U of $C(M2b)$ and by two residual densities of about 0.5 to 0.6 e \AA^{-3} close to $O(Wc)$ and $O(Wb)$ in the final map. The latter atom is probably not involved in the H-bond system [closest contact $O(Wb) \cdots O(M2) = 3.42(2) \text{ \AA}$] but fills lattice spaces. It seems that the region occupied by $O(W)$ could also be occupied by larger molecules, in accordance with the joint uptake of methanol and ethanol (Weber & Vögtle, 1980); the relatively free motion of guests in these positions may be responsible for the rapid decomposition of (2) when not sealed in a capillary, which in turn might explain the diverse stoichiometries reported by Weber & Vögtle (1980) and in the present study.

The recovery of the free macrocycle (1) from its methanol adduct (2) on recrystallization from 2-propanol is possibly facilitated by a *ca* 40% overlap of pyridine nuclei (related by inversion at $1, 0.5, 0$) at $3.38(2) \text{ \AA}$ in the lattice of (1).

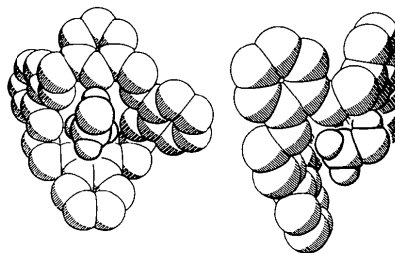


Fig. 4. The accommodation of macrocycle (1) to the guest molecule methanol illustrated by a space-filling model (top and side views).

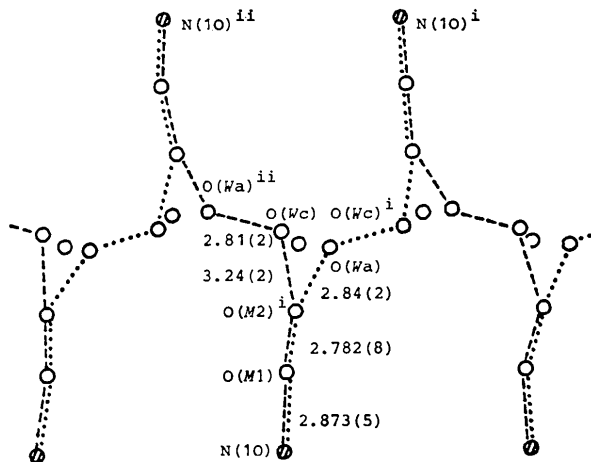


Fig. 5. Schematic presentation of hydrogen bonds (distances in \AA) viewed along c , demonstrating the alternative possibilities (\cdots and $- - -$) of dimer formation in (2). Symmetry codes [(i) $0.5 - x, 0.5 + y, 0.5 - z$; (ii) $0.5 - x, -0.5 + y, 0.5 - z$] refer to coordinates given in Table 1.

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Structure of the Mesoionic Compound *N*-[1-Methyl-3-(*p*-tolyl)-4-(1,2,3-triazolio)]acetamidate (MMTAT), $C_{12}H_{14}N_4O$

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(Received 7 April 1983; accepted 21 July 1983)

Abstract. $M_r = 230.28$, triclinic, $P\bar{1}$, $a = 11.940$ (18), $b = 7.642$ (9), $c = 7.378$ (9) Å, $\alpha = 79.76$ (1), $\beta = 108.17$ (1), $\gamma = 106.78$ (1)°, $Z = 2$, $V = 609.5$ Å³, $D_x = 1.254$, $D_m = 1.250$ Mg m⁻³, m.p. = 492–494 K, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.091$ mm⁻¹, $F(000) = 244$, $T = 298$ K. Final $R = 0.067$ for 641 independent non-zero reflexions. The planar mesoionic triazolio ring forms an almost coplanar conjugated system with the acetamidate group. The bond lengths found are in good agreement with CNDO2 calculations of π -bond order and π -charge densities. The possibility of the existence of an open-chain structure is excluded.

Introduction. Interest in mesoionic compounds has been intense during the past three decades due to the fact that some of these participate in chemical reactions providing new methods for the synthesis of a large variety of heterocyclic compounds while others show important pharmacological activity.

The crystal-structure analysis of the mesoionic title compound MMTAT was undertaken because of the need to know the exact form of the molecule in order to explain its chemical reactivity.

Experimental. Transparent, colourless, needle-like crystals prepared by one of us (Tsoleridis, 1983), $0.08 \times 0.10 \times 0.36$ mm. D_m by flotation in a mixture of CCl_4 and petroleum ether. Computer-controlled Philips PW 1100 four-circle single-crystal diffractometer, three-dimensional data, graphite-monochromated $\text{Mo } K\alpha$, ω scan mode. Cell parameters and standard deviations by least-squares analysis of measured θ angles of 196 strongest reflexions. Intensity statistics indicated $P\bar{1}$. Three standard reflexions without significant intensity variation. 2267 measured reflexions, $\theta = 3$ –22°, max. $hkl = 11, \pm 7, \pm 8$, $R_{\text{int}} = 0.07$, 2127 unique reflexions, 641 with $I > 2\sigma(I)$. No absorption correction. Direct methods with *MULTAN77* (Main, Lessinger, Woolfson, Germain & Declercq, 1977), phases of 140 reflexions with $E > 1.754$, all non-H atoms located on E map. Full-matrix least squares using F magnitudes, *XRAY76* (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976). H atoms located on difference Fourier map, included with isotropic temperature coefficients but not refined. $w = (F_{\text{obs}}/A)^2$ if $F_{\text{obs}} \leq A$, otherwise $w = (A/F_{\text{obs}})^2$ with $A = 14.0$; $R = 0.067$, $R_w = 0.063$, $S = 0.66$. $\Delta/\sigma_{\text{max}}$