SHORT STRUCTURAL PAPERS

The Clathrate of Tri-*o*-thymotide (TOT) and Pyridine

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Abstract. $2C_{33}H_{36}O_6 \cdot C_5H_5N$, trigonal, $P3_121$, $a = 13.67$ (1), $c = 29.90$ (1) Å, $Z = 6$, $d_c = 1.16$ g cm^{-3}. TOT crystallizes in the ratio 2:1 to give a 'cavity-type' clathrate [Newman & Powell, *J. Chem. Soc.* (1952), pp. 3747–3751]. The pyridine molecule is located on the binary axes. A new triclinic ($P\bar{1}$) form of TOT clathrate (involving three channels) has been found.

Introduction. The structure of unsolvated tri-*o*-thymotide (TOT) has already been reported (Brunie & Tsoucaris, 1974). The crystal structure determination of this compound has been carried out as part of a general study of the TOT clathrates. During the course of this work, Williams & Lawton (1975) reported an independent determination of the structure of pure TOT, and also gave details of some previously deter-mined inclusion forms, with which this pyridine complex is isostructural. The solid-state conformation of TOT has also been reported by Ollis, Stoddart & Sutherland (1974).

2095 independent reflexions were collected up to $\theta = 55°$, with a Nonius CAD-4 diffractometer (Cu $K\alpha$, $\lambda = 1.5418$ Å). 319 of these are considered as unobserved ($I < 2\sigma$). The structure was solved by direct methods with *MULTAN* (Germain, Main & Woolfson, 1971). Fourier maps show that the pyridine molecule is located on the binary axes; the highest peak is attributed to the N atom. The refinement was carried out by the full-matrix least-squares method with anisotropic temperature factors to an R of 0.08.* H atoms have not been located. The final atomic coordinates are given in Table 1. The atoms of pyridine are labelled N(1), C(34), C(35) and C(36), and those of TOT according to Fig. 1.
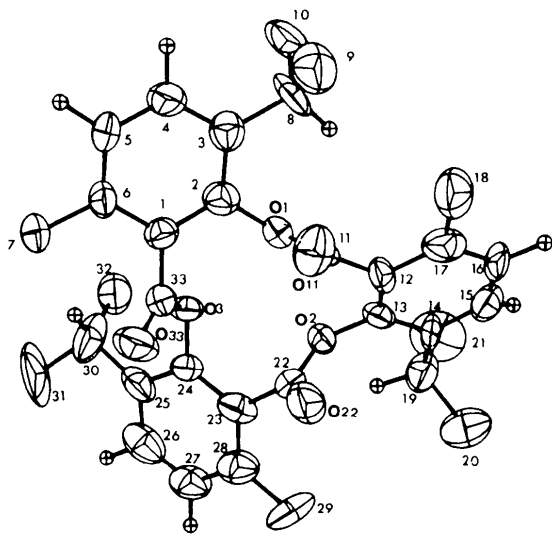

Fig. 1. *ORTEP* diagram of a molecule of TOT.

Discussion. Although the pyridine atoms have large temperature factors, they exhibit only a very limited disorder. We have shown in Fig. 2 only the six molecules of TOT related by point-group symmetry; the complete figure may be obtained by applying all the lattice translations indicated in the unit cell drawn.

The conformation of the TOT molecule is of the propeller type, as in pure TOT. Packing is determined by normal van der Waals contacts; the most significant are quoted in Tables 2 and 3 (one is particularly short, 3.10 Å). Fig. 3 shows the pyridine surrounded by eight molecules of TOT.

Table 1. *Positional parameters*

	x		y		z	
N(1)	0.0000		0.2513	(21)	0.1667	
C(34)	0.0000		0.4368	(20)	0.1667	
C(35)	-0.0939	(15)	0.3411	(23)	0.1781	(07)
C(36)	-0.0953	(21)	0.2411	(22)	0.1782	(12)
O(1)	0.3399	(06)	0.8304	(06)	0.1723	(02)
O(2)	0.3429	(06)	0.9950	(07)	0.1047	(02)
O(3)	0.4771	(07)	0.8951	(06)	0.0944	(02)
O(11)	0.1741	(08)	0.7101	(08)	0.1395	(04)
O(22)	0.2206	(07)	0.9060	(08)	0.0483	(03)
O(33)	0.3774	(09)	0.7337	(07)	0.0561	(02)
C(1)	0.4112	(10)	0.7216	(10)	0.1332	(03)
C(2)	0.3700	(09)	0.7451	(10)	0.1725	(04)
C(3)	0.3613	(11)	0.6903	(12)	0.2130	(04)
C(4)	0.3989	(12)	0.6097	(13)	0.2130	(04)
C(5)	0.4403	(12)	0.5886	(12)	0.1741	(05)
C(6)	0.4475	(11)	0.6424	(11)	0.1340	(04)
C(7)	0.4958	(15)	0.6171	(14)	0.0933	(04)
C(8)	0.3156	(13)	0.7184	(14)	0.2557	(04)
C(9)	0.2143	(13)	0.6022	(15)	0.2754	(04)
C(10)	0.4090	(14)	0.7772	(14)	0.2906	(04)
C(11)	0.2357	(12)	0.8019	(11)	0.1558	(04)
C(12)	0.2083	(11)	0.8936	(10)	0.1625	(04)
C(13)	0.2592	(10)	0.9863	(11)	0.1342	(04)
C(14)	0.2357	(11)	1.0730	(11)	0.1362	(04)
C(15)	0.1602	(12)	1.0657	(13)	0.1709	(05)
C(16)	0.1115	(12)	0.9775	(14)	0.1986	(05)
C(17)	0.1317	(10)	0.8868	(13)	0.1950	(04)
C(18)	0.0736	(13)	0.7820	(13)	0.2271	(04)
C(19)	0.2858	(14)	1.1709	(13)	0.1023	(05)
C(20)	0.3388	(13)	1.2870	(12)	0.1290	(05)
C(21)	0.1918	(15)	1.1561	(14)	0.0708	(05)
C(22)	0.3155	(11)	0.9527	(10)	0.0620	(03)
C(23)	0.4218	(11)	0.9850	(10)	0.0370	(03)
C(24)	0.4998	(12)	0.9579	(10)	0.0543	(03)
C(25)	0.6044	(12)	0.9915	(12)	0.0350	(04)
C(26)	0.6277	(12)	1.0581	(11)	-0.0050	(04)
C(27)	0.5495	(13)	1.0837	(11)	-0.0231	(04)
C(28)	0.4463	(13)	1.0487	(11)	-0.0025	(04)
C(29)	0.3625	(13)	1.0812	(13)	-0.0228	(04)
C(30)	0.6940	(13)	0.9683	(13)	0.0538	(04)
C(31)	0.7242	(18)	0.9030	(19)	0.0202	(05)
C(32)	0.8013	(14)	1.0815	(16)	0.0679	(06)
C(33)	0.4158	(10)	0.7809	(10)	0.0901	(03)

Table 2. *Shortest* TOT–TOT *intermolecular distances* $<3 \cdot 90$ Å

Symmetry code

None	x, y, z		(v)	$1 - x, 1 + y - x, -z + \frac{1}{3}$
(i)	$x - 1, y - 1, z$		(vi)	$1 - x, y - x, -z + \frac{1}{3}$
(ii)	$x, y - 1, z$		(vii)	$-x, y - x, -z + \frac{1}{3}$
(iii)	$1 - y, x - y + 1, z + \frac{1}{3}$		(viii)	$-x, y - x - 1, -z + \frac{1}{3}$
(iv)	$y - 1, x, -z$			

C(5)–O(2^vi)	3·10	C(20)–C(2^v)	3·66
C(16)–C(16^vii)	3·26	C(9)–C(28^iii)	3·67
O(2)–C(4^v)	3·31	C(17)–C(16^vii)	3·67
C(9)–O(33^iii)	3·47	C(17)–C(18^vii)	3·74
C(16)–C(15^vii)	3·50	C(23)–C(4^v)	3·77
C(10)–O(33^iii)	3·51	C(18)–C(12^vii)	3·78
C(18)–O(11^vii)	3·52	C(9)–C(23^iii)	3·80
O(22)–C(26^iv)	3·55	C(15)–C(15^vii)	3·80
C(17)–C(17^vii)	3·55	C(4)–O(3^vi)	3·85
C(24)–C(4^v)	3·60	C(9)–C(26^iii)	3·86
O(3)–C(5^v)	3·62	O(22)–C(32^iv)	3·87
C(13)–C(5^v)	3·64	C(5)–O(1^vi)	3·87
O(33)–C(27^iv)	3·65	C(5)–C(20^ii)	3·88

The bond distances and angles are regular, and are not significantly different from those of pure TOT. The angles between the normals to the least-squares planes of the phenyl rings are 27, 43 and 43° (30, 37 and 48° for pure TOT); the difference between the respective orientation of the phenyl rings of the clathrate of pyridine and the pure TOT accounts for the *flexibility* of the molecule, as Williams & Lawton (1975) observed for ethanol and *n*-acetyl alcohol complexes. This flexibility suggested the possibility of the inclusion of large molecules. The unexpected result is the successful inclusion of molecules as cumbersome as *cis*-stilbene, *trans*-stilbene or the alanine–dinitrobenzene derivative (I) for which a new triclinic crystalline form occurs. Microanalysis confirms a host/guest ratio of 2:1. The unit-cell parameters are given in Table 4. The structure of the *cis*-stilbene compound is under investigation (Brunie, Knossow & Mauguen, 1977). Two
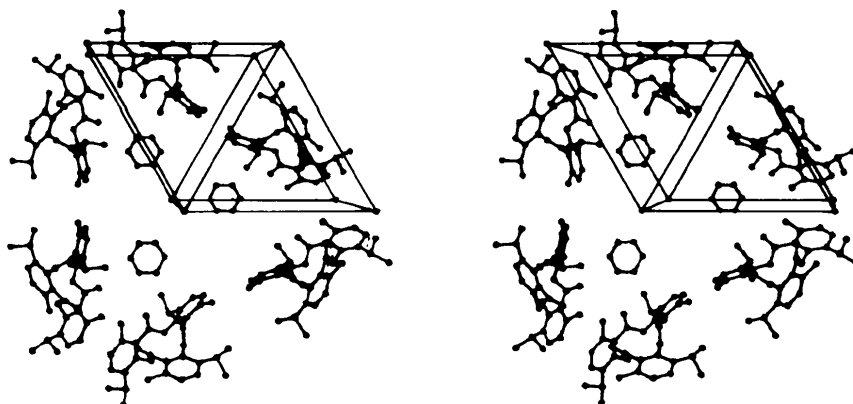

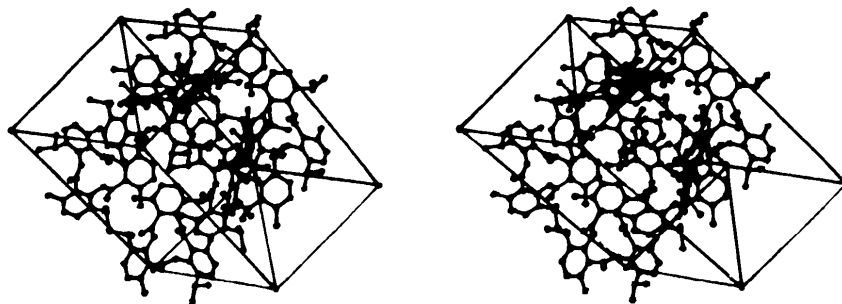Fig. 2. Stereoscopic view of TOT and pyridine molecules related by point-group symmetry.

Fig. 3. Stereoscopic view of the TOT molecules surrounding the pyridine.

Table 3. *Nearest neighbours of pyridine atoms and their interatomic distances* (<4 Å)

C(34)–O(11^{vii})	3·37	C(36)–C(32^i)	3·81
C(35)–O(11^{vii})	3·38	N(1)–C(32^i)	3·90
C(36)–C(20^{vii})	3·79		

Table 4. *Unit-cell parameters of three triclinic clathrates*

	a (Å)	b (Å)	c (Å)	α(°)	β(°)	γ(°)
cis-Stilbene	11·32	13·17	24·86	95·52	103·70	86·40
trans-Stilbene	11·64	13·02	24·41	96·89	103·28	84·71
(I)	11·36	13·79	23·36	90·24	90·02	89·18

important preliminary results are: first, the TOT is racemic ($P\bar{1}$, $Z = 2$) and second, the packing exhibits three channels, *two of which cross each other*.

$$CH_3 > CH-CH-NH-\langle O \rangle-NO_2$$
$$|$$
$$COOCH < ^{CH_3}_{CH_3}$$

(I)
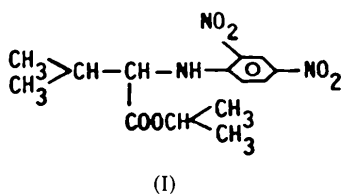
One could take advantage of the flexibility of the molecule of TOT and the very large size of the channels to study chemical and photochemical reactions of appropriate molecules within the cages or channels. Thus the clathrate channels or cages constitute a new medium in which to study reactions whose products, or reaction paths, may differ from those in solution: further work on these lines has been undertaken.

The calculations were performed on the IBM 370/168 computer of CIRCE (Orsay).

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