Acta Cryst. (1979). B**35**, 2605–2609

The Crystal Structure of the Inclusion Compound between Cycloveratril, Benzene and Water

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(*Received* 18 *April* 1979; *accepted* 12 *June* 1979)

Abstract

A monoclinic phase of the 1:0·5:1 inclusion compound between cycloveratril, benzene and water crystallizes in space group $C2/c$, with $a = 33{\cdot}908$ (9), $b = 9{\cdot}629$ (3), $c = 22{\cdot}748$ (5) Å, $\beta = 134{\cdot}02$ (1)°, $Z = 8$. The cycloveratril:benzene ratio was confirmed by gas chromatography. The structure was refined to a final R of 0·057. The host molecules have an umbrella shape with their methyl groups approximately coplanar with the benzene rings and are stacked along **b**. The guest molecules occupy the cavities of cages formed by methyl groups. The water molecules probably form bifurcated hydrogen bonds with the O atoms of cycloveratril.

Introduction

Oliverio & Casinovi (1952) obtained a compound with a cyclic structure from a reaction between formaldehyde and veratrol. X-ray studies distinguished two monoclinic crystalline phases and suggested firstly that this substance, which forms clathrates with a large variety of organic molecules, was a cyclic hexamer and subsequently, from considerations based on Fourier transform calculations, that it could be a cyclic trimer (Bertinotti, Carelli, Liquori & Nardi, 1952; Caglioti, Liquori, Gallo, Giglio & Scrocco, 1958; Gallo, Giglio & Liquori, 1958). The last hypothesis was later supported by mass spectrometry, chemical evidence and molecular-weight determinations (Lindsey, 1963; Goldup, Morrison & Smith, 1965). Thus this compound was recognized as 2,3,7,8,12,13-hexamethoxy-5,10-dihydro-15*H*-tribenzo[*a*,*d*,*g*]cyclononene (cycloveratril, CVT), for which steric requirements favour a crown conformation for the cyclononatriene ring (Fig. 1).

As part of a research programme which employs clathrates as systems in which to perform photochemical and polymerization reactions and to include drugs we have determined the crystal structure of the title compound. The present investigation establishes the detailed crystal packing and geometry of the host molecule as well as the size and shape of the cavity.

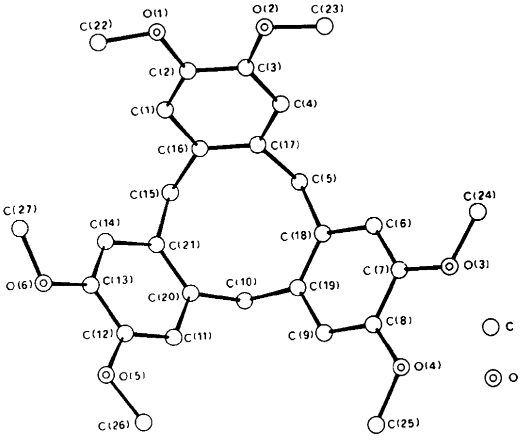

Fig. 1. Atomic numbering of CVT.

Experimental

Colourless prisms of the inclusion compound (CVTBW) were grown by slow evaporation from benzene at room temperature. Crystal data are collected in Table 1.

Differential scanning calorimetry showed that the crystals lose benzene, and probably water, within a range of temperature centred at 355 K by an endothermic process and subsequently melt at 504 K.

The composition of CVTBW was checked by gas-chromatography, X-ray and density measurements. The observed density (1·24 Mg m^{-3}) was obtained by the gradient method, which, however, is inadequate to determine the CVT:benzene:water ratio, owing to the small contribution of one guest molecule to the density.

The ratio CVT:benzene was found to be 1:0·5 by gas chromatography at 393 K accomplished with a Hewlett–Packard model 7620 A apparatus equipped with a Hewlett–Packard 3380 A integrator and a 6 ft × $\frac{1}{8}$ in (1·8 m × 3 mm) internal diameter column packed with Chromosorb 108.

We were unable to obtain reliable results for water.

The possible space groups are $C2/c$ and Cc since the reflexions hkl and $h0l$ are absent for $h + k$ and l odd respectively. The inspection of the $h0l$ Patterson projection suggested the presence of a twofold rotation axis parallel to **b**, so that the correct space group seemed to be $C2/c$. This choice was supported by the results of the refinement.

A crystal 0·8 × 0·6 × 0·2 mm was mounted on a Syntex $P2_1$ diffractometer with a graphite monochromator and the lattice parameters were determined from 15 reflexions at high θ and with Mo $K\alpha$ radiation. Intensities were collected on the same diffractometer by the ω-scan mode along **b**. 3266 independent reflexions with $I > 3\sigma(I)$ were recorded up to $2\theta = 56°$. Each reflexion was scanned at a rate varying between 2 and 29° min^{-1}, depending on its intensity, over a range of 1·2°. Background counts were taken on both sides of a reflexion for a time equal to that of the peak recording. Three standard reflexions, monitored after every 100 reflexions, showed only the deviations from the mean predicted by counting statistics. Lorentz and polarization factors were applied taking into account the monochromator crystal (Azaroff, 1955). No correction was made for absorption.

Table 1. *Crystal data of CVTBW*

Cycloveratril, $C_{27}H_{30}O_6$, $M_r = 450{\cdot}54$
Benzene, C_6H_6, $M_r = 78{\cdot}11$
Water, H_2O, $M_r = 18{\cdot}02$
Monoclinic, space group $C2/c$
$Z = 8$, $F(000) = 2168$
$a = 33{\cdot}908\ (9)$, $b = 9{\cdot}629\ (3)$, $c = 22{\cdot}748\ (5)$ Å, $\beta = 134{\cdot}02\ (1)°$
$V = 5340{\cdot}9$ Å^3, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 9{\cdot}6$ m^{-1}
$D_m = 1{\cdot}24$, $D_x = 1{\cdot}26$ Mg m^{-3}

Structure solution and refinement

The structure was solved by *MULTAN* (Main, Woolfson, Lessinger, Germain & Declercq, 1974) from the 255 highest $|E|$ and the 47 lowest $|E|$.

The E map, computed from the best set of phases, showed all the non-hydrogen atoms of CVT and benzene and only one more peak, O(7), which later was attributed to an O atom of a water molecule. The benzene molecule lies on the crystallographic twofold axis. The structure was refined by isotropic then anisotropic block-diagonal least squares with all the observed reflexions, and programs of Cerrini & Spagna (1977).

Scattering factors were taken from *International Tables for X-ray Crystallography* (1974). The function minimized was $\sum w(|F_o| - |F_c|)^2$, with $w = (a + |F_o| + b|F_o|^2)^{-1}$.

All the H atoms, except for one on the water molecule, were located in a difference synthesis computed at the end of the isotropic refinement. All

Table 2. *Fractional coordinates of the non-hydrogen atoms, with e.s.d.'s in parentheses*

	x	y	z
C(1)	0·1463 (2)	0·4137 (5)	0·0936 (3)
C(2)	0·1326 (2)	0·5079 (5)	0·0365 (3)
C(3)	0·1715 (2)	0·5454 (5)	0·0343 (3)
C(4)	0·2233 (2)	0·4865 (5)	0·0898 (3)
C(5)	0·2959 (2)	0·3313 (5)	0·2064 (3)
C(6)	0·3681 (2)	0·5154 (5)	0·2679 (3)
C(7)	0·4102 (2)	0·6006 (5)	0·3300 (3)
C(8)	0·4262 (2)	0·5975 (5)	0·4056 (3)
C(9)	0·4002 (2)	0·5062 (5)	0·4170 (3)
C(10)	0·3325 (2)	0·3208 (5)	0·3735 (3)
C(11)	0·2958 (2)	0·4716 (5)	0·4172 (3)
C(12)	0·2542 (2)	0·5296 (5)	0·4075 (3)
C(13)	0·1995 (2)	0·5002 (5)	0·3369 (3)
C(14)	0·1879 (2)	0·4117 (5)	0·2793 (3)
C(15)	0·2121 (2)	0·2626 (5)	0·2172 (3)
C(16)	0·1995 (2)	0·3558 (5)	0·1520 (3)
C(17)	0·2381 (2)	0·3920 (5)	0·1493 (3)
C(18)	0·3408 (2)	0·4250 (5)	0·2781 (3)
C(19)	0·3573 (2)	0·4200 (5)	0·3543 (3)
C(20)	0·2842 (2)	0·3831 (5)	0·3575 (3)
C(21)	0·2297 (2)	0·3519 (5)	0·2878 (3)
C(22)	0·0461 (3)	0·5656 (7)	−0·0093 (5)
C(23)	0·1950 (3)	0·6888 (7)	−0·0236 (4)
C(24)	0·4249 (3)	0·6900 (10)	0·2485 (4)
C(25)	0·4877 (2)	0·6764 (7)	0·5452 (3)
C(26)	0·3173 (3)	0·6657 (7)	0·5311 (4)
C(27)	0·1070 (2)	0·5795 (8)	0·2504 (4)
C(28)	0·0218 (3)	0·5533 (9)	0·2927 (4)
C(29)	0·0428 (3)	0·6742 (9)	0·3345 (4)
C(30)	0·0224 (4)	0·8006 (9)	0·2942 (5)
O(1)	0·0824 (1)	0·5721 (4)	−0·0208 (2)
O(2)	0·1544 (1)	0·6417 (4)	−0·0247 (2)
O(3)	0·4396 (2)	0·6886 (5)	0·3247 (2)
O(4)	0·4687 (1)	0·6832 (4)	0·4650 (2)
O(5)	0·2619 (2)	0·6175 (4)	0·4622 (2)
O(6)	0·1604 (2)	0·5641 (4)	0·3305 (2)
O(7)	0·0625 (3)	0·1472 (7)	0·3958 (4)

these H atoms were included in the last cycles, keeping fixed their positional and thermal parameters. To each H atom was given approximately the B, reached at the end of the isotropic refinement, of the C atom to which it is bonded. The final R and R_w were 0·057 and 0·082 respectively. The final atomic coordinates are reported in Tables 2 and 3.*

The bond lengths and angles of CVT and benzene are given in Tables 4 and 5.

Discussion

The CVT bond distances and angles show good agreement with those of comparable structures. The values of equivalent bond lengths and angles in CVT do not differ significantly. It is possible to recognize two groups of C–C bonds in the benzene rings of CVT. The first includes bonds of the type C(1)–C(16), C(4)–C(17), C(2)–C(3) and C(16)–C(17), for which the average length is 1·40 Å. To the second belong the bonds C(1)–C(2) and C(3)–C(4), which have an average length of 1·38 Å. The cyclononatriene ring has a crown conformation (Table 6) with an average value

Table 3. *Fractional coordinates of the hydrogen atoms found in the final difference synthesis*

	x	y	z
H(C1)	0·120	0·390	0·098
H(C4)	0·248	0·515	0·084
H1(C5)	0·292	0·235	0·220
H2(C5)	0·298	0·305	0·166
H(C6)	0·361	0·513	0·218
H(C9)	0·408	0·505	0·467
H1(C10)	0·365	0·300	0·443
H2(C10)	0·320	0·233	0·343
H(C11)	0·332	0·495	0·463
H(C14)	0·153	0·385	0·234
H1(C15)	0·182	0·210	0·195
H2(C15)	0·240	0·188	0·240
H1(C22)	0·012	0·625	−0·060
H2(C22)	0·042	0·475	−0·005
H3(C22)	0·070	0·595	0·055
H1(C23)	0·178	0·775	−0·058
H2(C23)	0·205	0·610	−0·043
H3(C23)	0·232	0·725	0·035
H1(C24)	0·445	0·770	0·257
H2(C24)	0·425	0·590	0·237
H3(C24)	0·382	0·725	0·197
H1(C25)	0·520	0·730	0·580
H2(C25)	0·505	0·580	0·578
H3(C25)	0·458	0·700	0·540
H1(C26)	0·325	0·715	0·577
H2(C26)	0·340	0·595	0·560
H3(C26)	0·328	0·705	0·505
H1(C27)	0·080	0·495	0·220
H2(C27)	0·115	0·620	0·223
H3(C27)	0·092	0·625	0·260
H(C28)	0·030	0·440	0·310
H(C29)	0·073	0·680	0·398
H(C30)	0·038	0·870	0·330
H(O7)	0·084	0·235	0·432

Table 4. *Bond distances* (Å) *of CVT and benzene, with e.s.d.'s in parentheses*

The primed atoms are related to the unprimed ones by a twofold rotation.

C(1)–C(2)	1·374 (11)	C(12)–C(13)	1·401 (17)
C(1)–C(16)	1·413 (15)	C(12)–O(5)	1·373 (9)
C(2)–C(3)	1·404 (9)	C(13)–C(14)	1·370 (11)
C(2)–O(1)	1·376 (13)	C(13)–O(6)	1·377 (9)
C(3)–C(4)	1·383 (15)	C(14)–C(21)	1·415 (10)
C(3)–O(2)	1·383 (10)	C(15)–C(16)	1·518 (11)
C(4)–C(17)	1·401 (11)	C(15)–C(21)	1·530 (12)
C(5)–C(17)	1·526 (14)	C(16)–C(17)	1·397 (9)
C(5)–C(18)	1·529 (14)	C(18)–C(19)	1·404 (11)
C(6)–C(7)	1·380 (14)	C(20)–C(21)	1·395 (16)
C(6)–C(18)	1·404 (7)	C(22)–O(1)	1·428 (9)
C(7)–C(8)	1·399 (12)	C(23)–O(2)	1·436 (10)
C(7)–O(3)	1·376 (7)	C(24)–O(3)	1·433 (14)
C(8)–C(9)	1·392 (7)	C(25)–O(4)	1·455 (12)
C(8)–O(4)	1·371 (12)	C(26)–O(5)	1·453 (17)
C(9)–C(19)	1·398 (13)	C(27)–O(6)	1·426 (19)
C(10)–C(19)	1·522 (7)	C(28)–C′(28)	1·405 (24)
C(10)–C(20)	1·531 (10)	C(28)–C(29)	1·351 (16)
C(11)–C(12)	1·383 (10)	C(29)–C(30)	1·386 (16)
C(11)–C(20)	1·409 (10)	C(30)–C′(30)	1·450 (29)

Table 5. *Bond angles* (°) *of CVT and benzene, with e.s.d.'s in parentheses*

The primed atoms are related to the unprimed ones by a twofold rotation.

C(2)–C(1)–C(16)	121·5 (6)	C(1)–C(16)–C(15)	117·4 (6)
C(1)–C(2)–C(3)	119·7 (9)	C(1)–C(16)–C(17)	118·9 (7)
C(1)–C(2)–O(1)	125·2 (6)	C(15)–C(16)–C(17)	123·6 (1·0)
C(3)–C(2)–O(1)	115·1 (7)	C(4)–C(17)–C(5)	117·3 (6)
C(2)–C(3)–C(4)	119·2 (7)	C(4)–C(17)–C(16)	119·0 (9)
C(2)–C(3)–O(2)	115·8 (9)	C(5)–C(17)–C(16)	123·7 (7)
C(4)–C(3)–O(2)	125·0 (6)	C(5)–C(18)–C(6)	118·1 (7)
C(3)–C(4)–C(17)	121·7 (6)	C(5)–C(18)–C(19)	123·0 (5)
C(17)–C(5)–C(18)	114·8 (5)	C(6)–C(18)–C(19)	118·9 (8)
C(7)–C(6)–C(18)	122·1 (8)	C(9)–C(19)–C(10)	118·1 (7)
C(6)–C(7)–C(8)	119·1 (5)	C(9)–C(19)–C(18)	118·6 (5)
C(6)–C(7)–O(3)	125·0 (8)	C(10)–C(19)–C(18)	123·3 (8)
C(8)–C(7)–O(3)	115·8 (9)	C(10)–C(20)–C(11)	118·2 (1·0)
C(7)–C(8)–C(9)	119·3 (9)	C(10)–C(20)–C(21)	122·6 (6)
C(7)–C(8)–O(4)	116·3 (5)	C(11)–C(20)–C(21)	119·2 (7)
C(9)–C(8)–O(4)	124·4 (8)	C(14)–C(21)–C(15)	117·5 (1·0)
C(8)–C(9)–C(19)	121·9 (8)	C(14)–C(21)–C(20)	118·6 (7)
C(19)–C(10)–C(20)	113·4 (5)	C(15)–C(21)–C(20)	123·8 (7)
C(12)–C(11)–C(20)	121·3 (1·0)	C(2)–O(1)–C(22)	117·6 (8)
C(11)–C(12)–C(13)	119·5 (7)	C(3)–O(2)–C(23)	116·3 (9)
C(11)–C(12)–O(5)	125·1 (1·1)	C(7)–O(3)–C(24)	116·6 (9)
C(13)–C(12)–O(5)	115·4 (7)	C(8)–O(4)–C(25)	117·1 (5)
C(12)–C(13)–C(14)	119·6 (7)	C(12)–O(5)–C(26)	117·6 (7)
C(12)–C(13)–O(6)	116·3 (7)	C(13)–O(6)–C(27)	117·0 (7)
C(14)–C(13)–O(6)	124·1 (1·0)	C′(28)–C(28)–C(29)	120·5 (1·1)
C(13)–C(14)–C(21)	121·8 (1·1)	C(28)–C(29)–C(30)	121·0 (1·6)
C(16)–C(15)–C(21)	109·4 (5)	C(29)–C(30)–C′(30)	118·5 (1·2)

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34539 (26 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

for the C—C methylene bond distances of 1·53 Å. The bonds of the C(2)—O(1) and C(22)—O(1) type, involving the methoxy substituents, have average values of 1·38 and 1·44 Å respectively.

The situation can be summarized for the bond angles by giving the average values for groups indicated by one angle of the group: C(16)—C(1)—C(2) = 121·7, C(1)—C(16)—C(17) = 118·9, C(1)—C(2)—C(3) = 119·4, C(1)—C(16)—C(15) = 117·8, C(15)—C(16)—C(17) = 123·3, C(16)—C(15)—C(21) = 112·5, C(3)—C(2)—O(1) = 115·8, C(1)—C(2)—O(1) = 124·8 and C(2)—O(1)—C(22) = 117·0°.

All the bond distances and angles vary within narrow ranges in each group except those of the group formed by C(16)—C(15)—C(21), C(17)—C(5)—C(18) and C(19)—C(10)—C(20), which are very different and are mainly responsible for the lack of a threefold molecular axis. The angles at C(5) and C(10) are nearly equal and may reflect the strain of CVT, caused by the closure of the cyclononatriene ring, which gives rise to a widening of these angles. Thus a pseudomirror plane, passing approximately through C(15) and the mid-points of C(18)—C(19) and C(7)—C(8), is present. This symmetry is further disturbed by the positions of the methyl groups which lie near the least-squares planes which are each defined by a benzene ring and the O atoms linked to it (Table 6).

Some atoms of the methyl groups generate close contacts with the H atoms of the benzene rings, so that the widening of the angles of the C(1)—C(2)—O(1) type may be attributed to a repulsive interaction.

The O atom of the water molecule has three neighbours, O(1), O(2) and O(3), at 3·10, 3·05 and 3·28 Å respectively (Table 7). These distances are too long for hydrogen bonds. However, a bifurcated hydrogen bond with O(1) and O(2) can be assumed since one H atom of the water molecule lies approximately on the bisector of O(1)—O(7)—O(2). The O(1)···H and O(2)···H contacts are about 2·2 Å and the C(2)—O(1)···H and C(3)—O(2)···H angles are nearly tetrahedral.

The benzene plane contains **b** and is perpendicular to **a**.

The benzene molecules lie on twofold axes and are stacked above each other in channels parallel to **b** with waists formed by methyl groups and water molecule pairs, the C···C and O···O distances being about 5·0 and 4·7 Å. Thus the cage has an approximate hourglass shape with minimum and maximum extension along directions almost parallel and perpendicular to **a** respectively (Fig. 2).

There is evidence that CVTBW crystals can release the benzene molecules when immersed in a liquid such as chlorobenzene, in which CVT is scarcely soluble at room temperature, and that the chlorobenzene molecules replace those of benzene. By inspection of the CVTBW molecular packing it is clear that some methyl groups prevent the benzene molecules from

Table 7. *Relevant intermolecular contacts* (Å) *between non-hydrogen atoms, with e.s.d.'s in parentheses*

C(8)—C(25)^{I}	3·49 (1)	C(23)—C(23)^{V}	3·30 (2)
C(11)—C(23)^{II}	3·51 (1)	C(23)—C(24)^{V}	3·89 (2)
C(22)—C(22)^{III}	3·66 (1)	C(24)—C(27)^{VI}	3·91 (1)
C(22)—C(25)^{II}	3·84 (1)	O(1)—O(7)^{VII}	3·10 (1)
C(22)—C(25)^{IV}	3·88 (1)	O(2)—O(7)^{VII}	3·05 (1)
C(22)—O(4)^{IV}	3·31 (1)	O(3)—O(7)^{VIII}	3·28 (2)

Symmetry code

(I)	$1-x, 1-y, 1-z$	(V)	$\frac{1}{2}-x, \frac{3}{2}-y, -z$
(II)	$\frac{1}{2}-x, -\frac{1}{2}+y, \frac{1}{2}-z$	(VI)	$\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$
(III)	$-x, 1-y, -z$	(VII)	$x, 1-y, -\frac{1}{2}+z$
(IV)	$-\frac{1}{2}+x, \frac{3}{2}-y, -\frac{1}{2}+z$	(VIII)	$\frac{1}{2}+x, \frac{1}{2}+y, z$

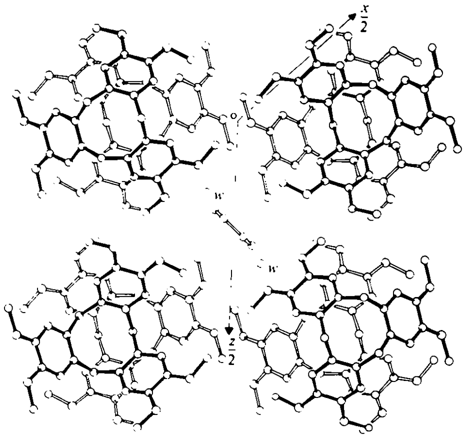

Fig. 2. A view of the molecular packing of CVTBW along **b**.

Table 6. *Some relevant torsion angles* (°) *of CVT, with e.s.d.'s in parentheses*

The convention of Klyne & Prelog (1960) is used.

C(5)—C(18)—C(19)—C(10)	0·3 (8)	C(16)—C(17)—C(5)—C(18)	−100·3 (7)	C(8)—C(7)—O(3)—C(24)	178·2 (6)
C(18)—C(19)—C(10)—C(20)	−92·4 (7)	C(17)—C(5)—C(18)—C(19)	90·8 (7)	C(9)—C(8)—O(4)—C(25)	0·4 (8)
C(19)—C(10)—C(20)—C(21)	101·5 (6)	C(1)—C(2)—O(1)—C(22)	14·9 (8)	C(7)—C(8)—O(4)—C(25)	−177·0 (5)
C(10)—C(20)—C(21)—C(15)	−5·1 (9)	C(3)—C(2)—O(1)—C(22)	−164·9 (5)	C(11)—C(12)—O(5)—C(26)	7·3 (9)
C(20)—C(21)—C(15)—C(16)	−93·6 (6)	C(4)—C(3)—O(2)—C(23)	−4·0 (8)	C(13)—C(12)—O(5)—C(26)	−172·2 (6)
C(21)—C(15)—C(16)—C(17)	92·1 (7)	C(2)—C(3)—O(2)—C(23)	175·4 (5)	C(12)—C(13)—O(6)—C(27)	157·2 (6)
C(15)—C(16)—C(17)—C(5)	6·1 (8)	C(6)—C(7)—O(3)—C(24)	−0·3 (9)	C(14)—C(13)—O(6)—C(27)	−22·9 (9)

leaving the crystal. However, by rotating around the bonds of the C(2)–O(1) type, the methyl groups can open the cage and release the benzene.

Table 7 collects the most relevant intermolecular contacts. Some short methyl–methyl and carbon–methyl distances are present so that it is reasonable to assume the occurrence of strong van der Waals interactions in each pile of CVT molecules and between piles, as the CVT melting point indicates.

Of the two monoclinic α and β phases previously characterized by infrared and X-ray measurements (Caglioti, Liquori, Gallo, Giglio & Scrocco, 1958) for the CVT clathrates, the α phase seems to be formed, as in the case of CVTBW, when aromatic or bulky molecules are occluded, whereas the β phase allows the accommodation of thread-like molecules. The cell parameters of the compounds investigated so far show that b, and hence the arrangement of the molecules in a pile, is nearly constant. On the other hand, a and c can vary, probably because of the different sizes of the cavities, which are adapted to the guest molecules.

These clathrates may be used as suitable systems for photochemical reactions and as carriers of drugs. Further work is needed to establish whether more bulky molecules can be occluded.

As far as the inclusion of monomers is concerned it is necessary to investigate if the monomer mobility in the crystal is sufficient to promote polymerization reactions.

We thank Mr V. Mignini for assistance with the gas-chromatographic measurements.

One of the authors (EG) acknowledges the Consiglio Nazionale delle Richerche for financial support.

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Structure Cristalline du Thiocyanate de Tétraméthyltétrathiafulvalène (TMTTF)$_2$SCN

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(*Reçu le* 19 *janvier* 1979, *accepté le* 19 *juin* 1979)

Abstract

The organic conductor $(C_{10}H_{12}S_4)_2SCN$ [(TMTTF)$_2$ SCN] crystallizes in the triclinic system, space group $P\bar{1}$, with the following parameters $a = 7{\cdot}053\,(5)$, $b = 7{\cdot}598\,(5)$, $c = 12{\cdot}75\,(1)$ Å, $\alpha = 89{\cdot}08\,(5)$, $\beta = 92{\cdot}61\,(5)$, $\gamma = 108{\cdot}05\,(5)^\circ$, $V = 648{\cdot}8\,(4)$ Å^3. Intensities of 2483 reflexions were collected on an automated diffractometer. All the compounds (TMTTF)$_2$-X, with X = Br, BF$_4$, SCN, ClO$_4$, PF$_6$, NO$_3$, have the

0567-7408/79/112609-05$01.00