

Planar packing of tetrachlorodicyanobenzene isomers

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Ortho-, *meta*- and *para*-tetrachlorodicyanobenzene (TDB, tetrachlorobenzenedicarbonitrile) form 1/1 complexes with hexamethylbenzene (HMB). Seven polymorphic forms of the crystals, one of *o*-TDB, two of *m*-TDB and four of *p*-TDB, have been found. All of the complexes involve layers of two-dimensional arrays, and in six of the complexes the layers are homogeneous, alternate layers being entirely TDB or entirely HMB. The layers can be described in terms of an hexagonal tiling and in five of the homogeneous layers the TDB are ordered so that one CN and two Cl come together at each corner of the tiles. In the sixth the *m*-TDB is disordered, but a plausible arrangement can still be found with one CN and two Cl coming together in the same fashion.

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1. Introduction

In the crystal structure of 3,4,5,6-tetrachlorodicyanobenzene, *o*-TDB (Britton, 1981*b*) planar layers with the packing arrangement shown in Fig. 1 were found. This pattern can be approximated by a regular hexagonal tiling, as outlined in the figure. Each CN group points halfway between Cl atoms on two adjacent molecules. Fig. 1 may be represented as in Fig. 2(*d*) by hexagons with circles at the corners corresponding to the CN groups, thus indicating the orientation of the molecules (*see below*). If, for all isomers, one CN is in contact with two Cl, then there is necessarily only one CN at each vertex of the tile. With only these restrictions, planar tiling and one circle per vertex, it is possible to draw an unlimited number of tilings.

In Fig. 2 four possibilities are shown that are regular in two dimensions and that have no more than one tile in the asymmetric unit. For each tiling, the plane group is indicated and the unit cell is shown. So far we have considered the isomer with the CN groups *ortho* to each other. In Fig. 3 three tilings are shown for the *meta* isomer, with no more than one molecule in the asymmetric unit, and in Fig. 4 two tilings are shown for the *para* isomer, with no more than half a molecule in the asymmetric unit.

This paper describes attempts to grow crystals with planar packings of the sort depicted in Figs. 2, 3 and 4; that is, to see whether the intermolecular arrangement of one CN group and two Cl atoms might occur often enough to be regarded as an intermolecular synthon. The general approach is to grow or attempt to grow crystals of charge-transfer complexes *A*:*B*,

where *A* is one of the three isomers of $\text{Cl}_4\text{C}_6(\text{CN})_2$ (all of which are π -electron acceptors) and *B* is a π -electron donor of approximately the same planar area as the *A* molecule. More generally, this work represents an attempt to see whether π complexing can be used to align molecules for intermolecular σ interactions.

The effective area of *o*-TDB can be calculated to be 69.7 \AA^2 from the molecular volume (V_{cell}/Z) of 247.8 \AA^3 and the average interlayer distance of 3.554 \AA (Britton, 1981*b*). The molar volumes of *m*- and *p*-TDB are only slightly smaller, namely 243.2 and 243.1 \AA^3 (Britton, 1981*a*), respectively, and all three isomers require approximately the same area. For the electron donor, the most obvious choice was hexamethylbenzene (HMB), which has a very similar molecular volume, 254 \AA^3 (Lonsdale, 1929; Brockway & Robertson, 1939), and which packs by itself into hexagonal layers.¹ This proved to be a good choice and the structures of complexes of all three isomers of TDB with HMB are reported here.² Reddy, Goud *et al.* (1993) have used the same approach to form planar layers of 1,3,5-tricyanobenzene with linear $\text{CN} \cdots \text{H} - \text{C}$ intermolecular interactions.

2. Experimental

2.1. Syntheses

Approximately equimolar mixtures of HMB and each one of the TDB isomers were dissolved in solvent and crystals grown by evaporation at room temperature. After polymorphs were found, a variety of solvents were used. A list of the solvents, the polymorphs found from each, and the crystal habits observed, is included in the supplementary material.³

For the *ortho* isomer, only one crystal form of the 1/1 complex was found. A needle-like crystal, grown from acetonitrile, was used for the structure determination and is reported as ORTHO below.

For the *meta* isomer, two crystalline modifications of the 1/1 complex were found. A needle of META-I cut from a thick needle grown from acetonitrile was used for the structure determination. Crystals of META-II,⁴ showing frequent twinning, were obtained from benzene. These crystals deformed very easily and most attempts to cut or cleave them ruined the crystal for diffraction purposes. Eventually, five data sets were collected from four different crystals. The data

¹ The HMB layers in the room-temperature form of the crystal are metrically close to hexagonal, but the crystal is only triclinic since the sixfold axes in successive layers do not coincide. For more complex examples of the same phenomenon, see Britton (2000). In the low-temperature form (Santarsiero *et al.*, 1985), similar layers occur with symmetry $\bar{3}$.

² Attempts were also made to prepare similar complexes with 1,3,5-triethylbenzene, anthracene, phenanthrene, pyrene and 2,6-dimethylnaphthalene. Complexes could only be isolated in a few cases, and these did not show a layered arrangement of the TDB molecules. Such results as there are will be reported elsewhere.

³ Supplementary material for this paper is available from the IUCr electronic archives (Reference: BK0105). Services for accessing these data are described at the back of the journal.

⁴ The labels for the two polymorphs, as well as for the *para* polymorphs below, do not relate to the stability but only to the order in which they were discovered.

reported come from an obvious twin that was cut in half along the twin line.

With the *para* isomer, four crystalline modifications of the 1/1 complex were found. For PARA-I, a sword-shaped crystal grown from acetonitrile was used for the structure determination. For PARA-II and PARA-III, the same plate, grown from acetonitrile, was used for the structure determinations. The transformation of PARA-II is discussed later. For PARA-IV, a needle grown from methylene chloride was used for the structure determination. PARA-II and PARA-III could be prepared easily, but in the most recent crystallizations, neither I nor IV could be prepared. This is surprising but not unheard of; Dunitz & Bernstein (1995) describe examples of similar behavior.

Attempts were made to measure the melting points of the various complexes on a Fisher-Johns Apparatus. These were unsuccessful. In every case, sublimation began between 400 and 450 K and continued to about 500 K, at which point the sample had either disappeared or a small amount of liquid remained. The temperatures of the various changes were not reproducible to better than *ca* 25 K. For reference, the melting points of the starting materials are: HMB, 439–441 K; *o*-TDB, 520–522 K; *m*-TDB, 523–524 K; *p*-TDB, 576–578 K.

2.2. X-ray analysis: general

Experimental data are given in Table 1. Scattering factors and corrections for anomalous dispersion were taken from the *International Tables for X-ray Crystallography*.

In attempts to find a particular polymorph or to understand generally what was happening, a large number of crystals were

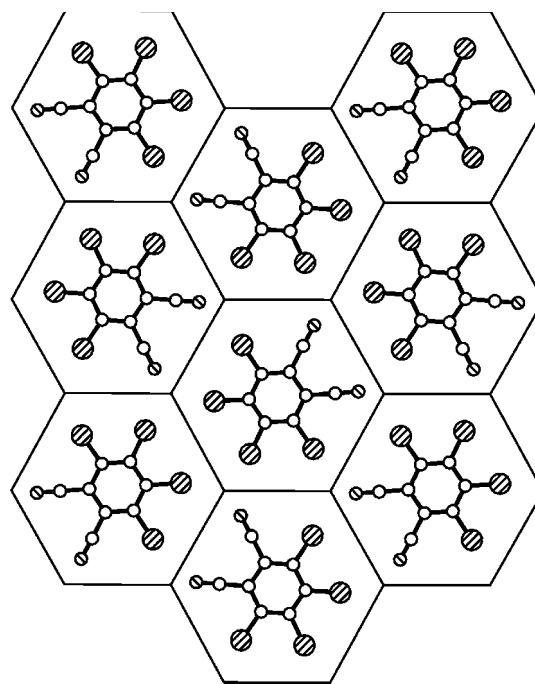


Figure 1

A two-dimensional layer from the structure of *o*-tetrachlorodicyanobenzene, showing how this can be viewed as a hexagonal tiling.

Table 1

Experimental details.

The Niggli cell constants for META-II are $a = 8.9554$ (13), $b = 14.064$ (2), $c = 15.939$ (2) Å, $\alpha = 83.395$ (2), $\beta = 88.790$ (2), $\gamma = 76.460$ (2)°. They have been converted to those listed in the table by the matrix 0, -1, 0/-1, 0, 0/1, 0, -1 so that the similarity between META-I and META-II can be seen more readily.

	ORTHO	META-I	META-II
Crystal data			
Chemical formula	C ₈ Cl ₄ N ₂ ·C ₁₂ H ₁₈	C ₈ Cl ₄ N ₂ ·C ₁₂ H ₁₈	C ₈ Cl ₄ N ₂ ·C ₁₂ H ₁₈
Chemical formula weight	428.16	428.16	428.16
Cell setting, space group	Monoclinic, <i>C2/c</i>	Triclinic, <i>P</i> $\bar{1}$	Triclinic, <i>P</i> $\bar{1}$
a, b, c (Å)	15.824 (3), 9.1501 (15), 13.894 (2)	7.5290 (12), 8.9503 (14), 9.0513 (11)	14.064 (2), 8.9554 (13), 18.117 (3)
α, β, γ (°)	90, 102.879 (3), 90	118.425 (3), 109.414 (3), 95.139 (3)	118.407 (2), 90.832 (3), 76.460 (2)
V (Å ³)	1961.1 (6)	482.80 (12)	1938.8 (5)
Z	4	1	4
D_x (Mg m ⁻³)	1.450	1.473	1.467
Radiation type	Mo <i>K</i> α	Mo <i>K</i> α	Mo <i>K</i> α
No. of reflections for cell parameters	1872	776	3897
θ range (°)	3–27	2.7–27.4	2.7–27.2
μ (mm ⁻¹)	0.610	0.620	0.617
Temperature (K)	173 (2)	173 (2)	173 (2)
Crystal form, colour	Needle, yellow	Thick plate, yellow	Prism, yellow
Crystal size (mm)	0.45 × 0.15 × 0.10	0.50 × 0.35 × 0.10	0.45 × 0.40 × 0.35
Data collection			
Diffractometer	Siemens SMART system	Siemens SMART system	Siemens SMART system
Data collection method	ω scans	ω scans	ω scans
Absorption correction	Multi-scan	Multi-scan	Multi-scan
T_{\min}	0.90	0.76	0.76
T_{\max}	0.94	0.94	0.81
No. of measured, independent and observed parameters	6155, 2242, 1604	4996, 2197, 1784	19 454, 8698, 5502
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
R_{int}	0.0494	0.0245	0.0586
θ_{\max} (°)	27.52	27.51	27.49
Range of h, k, l	-18 → h → 20 -11 → k → 11 -16 → l → 18	-9 → h → 9 -11 → k → 11 -11 → l → 11	-18 → h → 18 -11 → k → 11 -23 → l → 23
Refinement			
Refinement on	F^2	F^2	F^2
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.043, 0.1129, 0.952	0.0378, 0.1137, 1.041	0.0715, 0.2249, 1.002
No. of reflections and parameters used in refinement	2242, 121	2197, 185	8698, 542
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.062P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0720P)^2 + 0.0590P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.153P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$	0.004	0.006	0.027
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ⁻³)	0.29, -0.234	0.267, -0.236	1.265, -0.63
Extinction method	None	<i>SHELXTL</i>	None
Extinction coefficient	-	0.037 (8)	-

	PARA-I	PARA-II	PARA-III	PARA-IV
Crystal data				
Chemical formula	C ₈ Cl ₄ N ₂ ·C ₁₂ H ₁₈	C ₈ Cl ₄ N ₂ ·C ₁₂ H ₁₈	C ₈ Cl ₄ N ₂ ·C ₁₂ H ₁₈	C ₈ Cl ₄ N ₂ ·C ₁₂ H ₁₈
Chemical formula weight	428.16	428.16	428.16	428.16
Cell setting, space group	Triclinic, <i>P</i> $\bar{1}$	Triclinic, <i>P</i> $\bar{1}$	Monoclinic, <i>C2/m</i>	Triclinic, <i>P</i> $\bar{1}$
a, b, c (Å)	7.513 (3), 8.615 (3), 9.029 (3)	7.5567 (11), 8.8956 (11), 8.9921 (11)	9.754 (2), 15.410 (3), 7.5550 (15)	7.4982 (1), 9.0371 (3), 15.4538 (6)
α, β, γ (°)	114.24 (3), 113.30 (2), 91.92 (3)	116.697 (3), 112.099 (3), 92.101 (3)	90, 116.88 (3), 90	85.080 (2), 81.795 (2), 71.168 (2)
V (Å ³)	475.8 (3)	484.66 (11)	1012.9 (4)	980.10 (5)
Z	1	1	2	2
D_x (Mg m ⁻³)	1.494	1.467	1.404	1.451
Radiation type	Mo <i>K</i> α	Mo <i>K</i> α	Mo <i>K</i> α	Mo <i>K</i> α
No. of reflections for cell parameters	24	876	799	1500
θ range (°)	11–28	4.5–27.5	2.6–26.9	2–25
μ (mm ⁻¹)	0.629	0.617	0.591	0.611
Temperature (K)	189 (2)	174 (2)	297 (2)	174 (2)
Crystal form, colour	Sword-shaped, yellow	Plate, yellow	Plate, yellow	Deformed needle, yellow

Table 1 (continued)

	PARA-I	PARA-II	PARA-III	PARA-IV
Crystal size (mm)	0.50 × 0.35 × 0.15	0.45 × 0.25 × 0.15	0.45 × 0.25 × 0.15	0.30 × 0.26 × 0.18
Data collection				
Diffractometer	Enraf–Nonius CAD-4	Siemens SMART system	Siemens SMART system	Siemens SMART system
Data collection method	ω -2 θ scans	ω scans	ω scans	ω scans
Absorption correction	Empirical	Multi-scan	Multi-scan	Multi-scan
T_{\min}	0.75	0.80	0.81	0.79
T_{\max}	0.91	0.91	0.91	0.90
No. of measured, independent and observed parameters	4293, 2775, 2324	5128, 2198, 1890	5342, 1204, 876	5453, 3354, 1520
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
R_{int}	0.074	0.0202	0.0323	0.066
θ_{max} (°)	29.98	27.47	27.49	25.13
Range of h, k, l	−10 → h → 4 −12 → k → 12 −12 → l → 12	−9 → h → 9 −11 → k → 11 −11 → l → 11	−12 → h → 12 −20 → k → 19 −9 → l → 9	−8 → h → 8 −10 → k → 10 −18 → l → 16
Refinement				
Refinement on	F^2	F^2	F^2	F^2
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.0737, 0.2115, 1.095	0.036, 0.107, 1.055	0.048, 0.149, 1.037	0.094, 0.247, 0.896
No. of reflections and parameters used in refinement	2775, 122	2198, 122	1204, 62	3354, 235
H-atom treatment	Mixed	Mixed	Mixed	Mixed
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.098P)^2 + 0.96P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.067P)^2 + 0.121P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.090P)^2 + 0.226P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.137P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\text{max}}$	0.001	0.003	0.001	0.001
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ^{−3})	0.571, −0.647	0.375, −0.311	0.322, −0.202	0.714, −0.971
Extinction method	SHELXTL	None	None	None
Extinction coefficient	0.09 (2)	—	—	—

Computer programs used: SMART and SAINT (Siemens, 1995), TEXSAN (Molecular Structure Corporation, 1985), MITHRIL (Gilmore, 1984), DIRDIF (Beurskens, 1984), SHELXTL (Sheldrick, 1994), CAD-4 Software (Enraf–Nonius, 1983), DIFABS (Walker & Stuart, 1983).

examined. In many cases, unit cells could not be found and the crystals were abandoned. The results for all of the crystals in which the cells were successfully measured are included in the supplementary material.

The H atoms in HMB were treated as part of ideally disordered methyl groups and then refined as riding on the attached C atom, with idealized bond lengths and angles, and with U values 50% larger than the U_{av} of the attached C atom. No attempt was made to sort out the actual disorder in the methyl groups. This procedure was used for all the structures.

2.3. X-ray analysis: specific

The determinations of the ORTHO, PARA-I and PARA-II structures were straightforward.

For META-I, the intensity statistics suggested a centric structure. With $Z = 1$ in $P\bar{1}$, however, the TDB molecule would lie on a center of symmetry and therefore must be disordered. This was resolved with disorder between two of the six possible orientations of the TDB. Further details of the solution and refinement of META-I, META-II and PARA-IV are available in the supplementary material.

Statistics for META-II suggested that the space group was $P\bar{1}$ and not $P1$, but this still required two TDB and two HMB

molecules in the asymmetric unit. A solution was found with two TDB molecules in general positions, one HMB in a general position and two HMB on inversion centers. The two TDB molecules are related by a pseudo-center of symmetry and all three HMB molecules are related by pseudo-translations. In addition, each of the TDB molecules proved to be disordered between two positions related by additional pseudo-centers. The META-I and META-II structures are very closely related (see §3 below). However, this close relationship was not recognized until both structures had been independently solved.

The structure of PARA-III was determined at room temperature only. Both molecules lie on sites of $2/m$ symmetry. The atomic displacement parameters of TDB were normal but those of HMB showed very large displacement amplitudes corresponding to rotation about the molecular sixfold axis. A model was tried with disordered HMB. This led to a lower R value, but the largest displacement amplitudes only decreased by ca 10%. The reported structure is the ordered model with the larger displacements.

When a crystal of PARA-III was cooled on the diffractometer, the crystal invariably changed, but in a variety of ways. Sometimes the change was only apparent when the cell was determined at low temperature. Other times the crystal

visibly shifted position or changed into two or three fragments. When they were visible, the transitions were abrupt. In all cases the crystals appeared to be transparent after the transition; they may have twinned or broken into several fragments, but they did not form a powder. The transition temperature was measured accurately for three different crystals using an Oxford Cryosystem for slow cooling. The transitions occurred at 249, 278 and 283 K. A pair of photographs showing a sample before and after a transition is available in the supplementary material. The results of the transitions varied. In one case, PARA-III transformed to PARA-I; in two cases, PARA-III transformed to PARA-II; and in one case, PARA-III became a mixture of PARA-II and PARA-I. Presumably both the temperature and the products of the transition were affected by the mounting process.

The crystal of PARA-IV, mentioned earlier, was mounted and a unit cell determined at room temperature. When the cell was recognized as belonging to a new polymorph, the crystal was cooled with the intention of collecting a low-temperature data set. The crystal, which had been a well shaped needle, changed to three connected segments, presumably twins, with

each segment still transparent. The crystal was moved so that, as far as possible, only the end segment was in the X-ray beam, at which point a data set was collected. As described above, no additional sample was found and the structure was solved from the data set obtained from the twinned crystal.

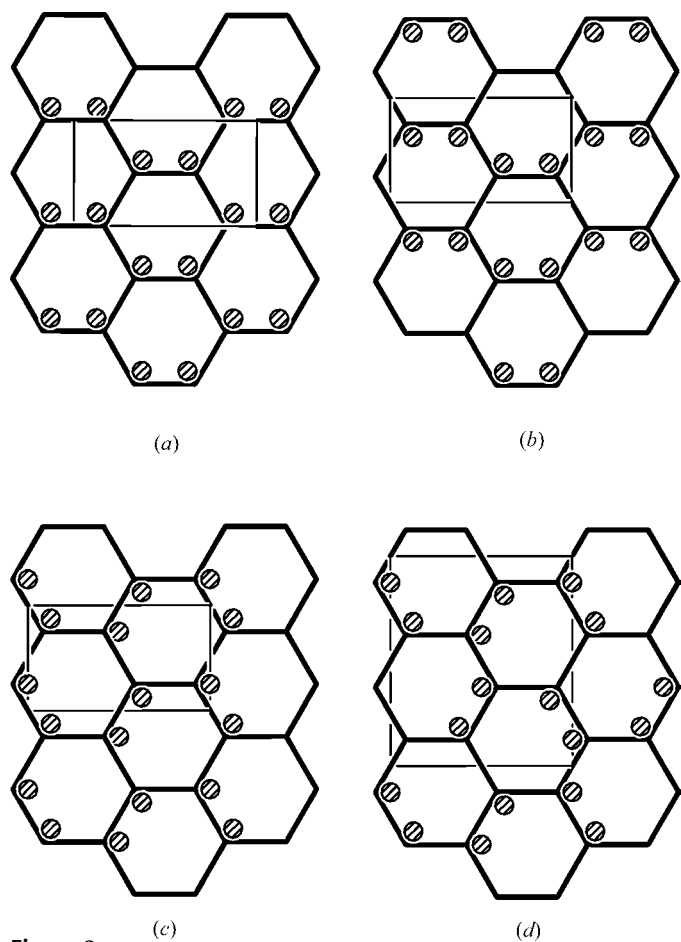


Figure 2 Possible tilings for *ortho*-tetrachlorodicyanobenzene. (a) Plane group *cm*, $Z = 2$, $\frac{1}{2}$ molecule in the asymmetric unit. (b) Plane group *pmg*, $Z = 2$, $\frac{1}{2}$ molecule in the asymmetric unit. (c) Plane group *pg*, $Z = 2$, 1 molecule in the asymmetric unit. (d) Plane group *pgg*, $Z = 4$, 1 molecule in the asymmetric unit.

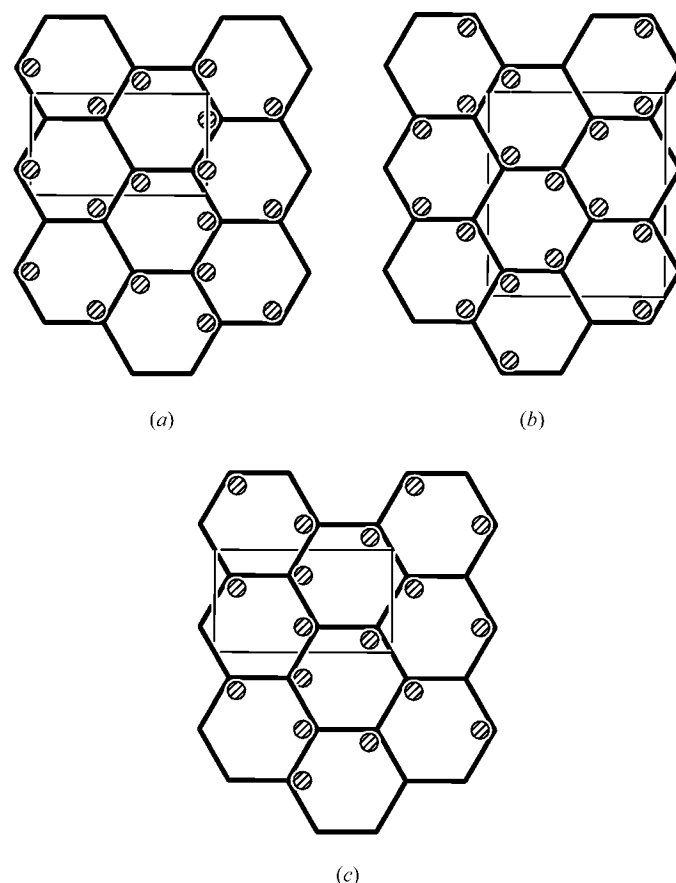


Figure 3 Possible tilings for *meta*-tetrachlorodicyanobenzene. (a) Plane group *p2*, $Z = 2$, 1 molecule in the asymmetric unit. (b) Plane group *pgg*, $Z = 4$, 1 molecule in the asymmetric unit. (c) Plane group *pg*, $Z = 2$, 1 molecule in the asymmetric unit.

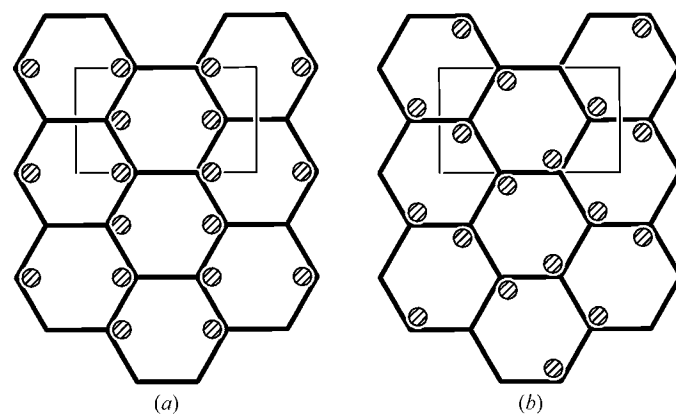


Figure 4 Possible tilings for *para*-tetrachlorodicyanobenzene. (a) Plane group *cmm*, $Z = 2$, $\frac{1}{2}$ molecule in the asymmetric unit. (b) Plane group *pgg*, $Z = 2$, $\frac{1}{2}$ molecule in the asymmetric unit.

3. Discussion

3.1. Bond lengths and angles

Figures showing the atom labelling and the anisotropic displacement ellipsoids are not necessary for a discussion of the packing. They have been omitted but are available in the supplementary material.

The bond lengths and angles for all three TDB isomers have been reported previously (Britton, 1981*a,b*). Those found here agree within experimental uncertainty. Similarly, the distances and angles in HMB are those expected. In previous work (Hamilton *et al.*, 1969) the methyl groups were oriented so that the molecule had D_{3d} symmetry. It is very likely true that the methyl groups in HMB are ordered in any particular molecule in these structures, but they appear to be disordered from molecule to molecule since a model with idealized disorder in the methyl groups gives a lower R value in each case than a model with idealized group geometry in which the torsion angle is allowed to vary.

3.2. Packing patterns: general

In all seven complexes layers of molecules occur. In six of the complexes, TDB layers alternate with HMB layers; in the sixth (PARA-I), the layers are composed of equal numbers of TDB and HMB. The latter is the only one of these seven structures that does not show the pattern that was being

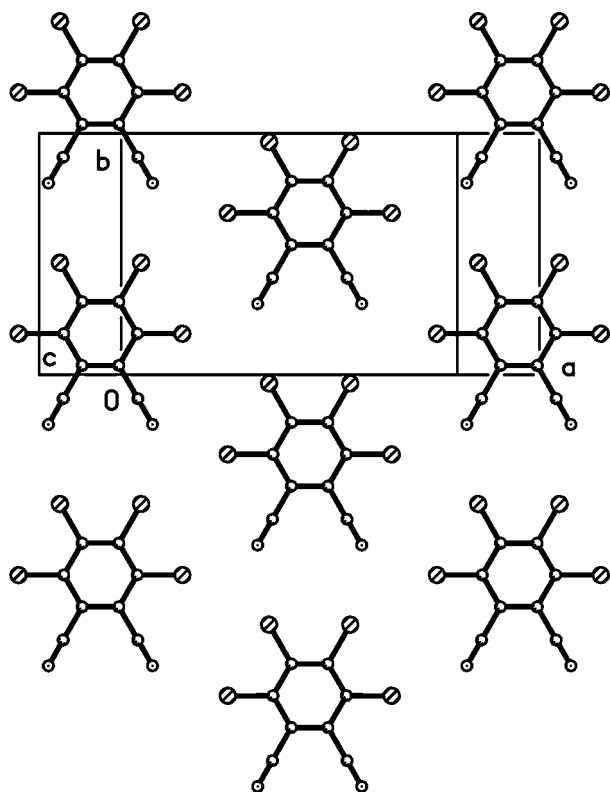


Figure 5
The packing of *o*-TDB in ORTHO. View perpendicular to (001). This should be compared with Fig. 2(*a*). The TDB molecules are tilted by 4.0° away from the mean plane. The HMB molecules in the next layer (not shown) are tilted by 4.8° away from the mean plane.

sought in this study. The packing of all of these compounds is described in the following subsections. In each case, a layer of TDB molecules (or TDB plus HMB in PARA-I) is shown from a viewpoint normal to the layer. The layer is oriented so that it matches one of the tilings in Figs. 2, 3 or 4. Wherever HMB is shown, for clarity, only one of the two sets of H-atom positions is shown.

The π stacking in these complexes is similar to that found in other HMB complexes (see, for example, Herbstein, 1971). In each case, one or two atoms in one ring lie approximately over the center of the next ring. The rings are $3.4\text{--}3.5\text{ \AA}$ apart in a perpendicular direction and are within $2\text{--}3^\circ$ of being parallel.

The packings of the PARA polymorphs are discussed before those of the META polymorphs because the results for the ORTHO and PARA polymorphs were used as a guide to sort out the disorder in META-I.

3.3. ORTHO

The packing of the TDB in ORTHO is shown in Fig. 5; the arrangement is that shown in Fig. 2(*a*). This is different from the two-dimensional packing in *o*-TDB itself, which corresponds to Fig. 2(*d*).

The complexes 1,3,5-tricyanobenzene/HMB (Reddy, Goud *et al.*, 1993), 3,5-dicyano-1-nitrobenzene/HMB and 3,5-dinitro-1-cyanobenzene/HMB (Bock *et al.*, 1996) have structures that are closely related to that of ORTHO. All four compounds crystallize in the same space group with similar cell dimen-

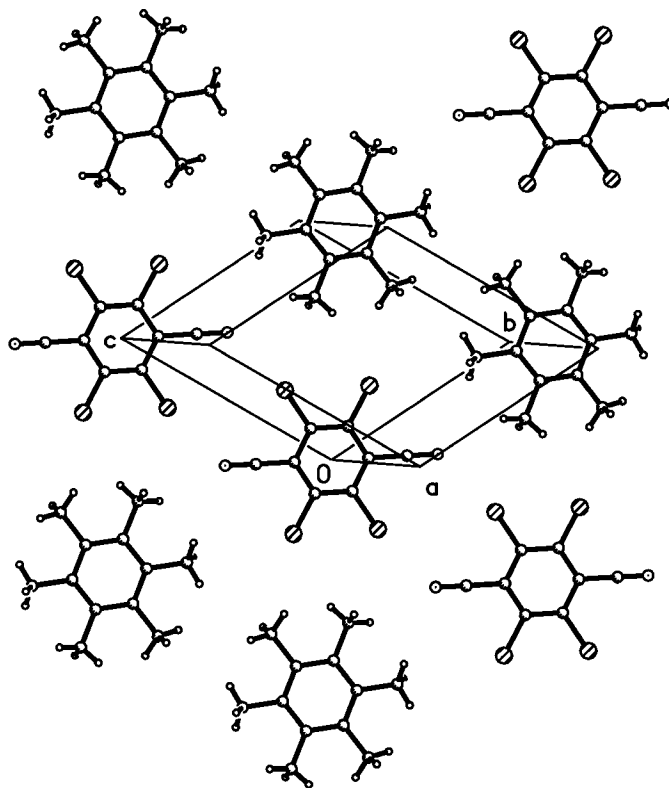


Figure 6
A layer of PARA-I viewed normal to the $(2\bar{1}0)$ plane. This is the hexagonally tiled layer. The TDB molecules are tilted by 4.7° and the HMB molecules by 2.0° with respect to the mean plane.

sions. In every case there are columns, held together by π complexing, with the two molecules alternating in the column. In every case there are approximately planar layers of HMB alternating with approximately planar layers of the complexing partner. The difference between them is that in ORTHO the CN groups have bifurcated intermolecular interactions with Cl atoms on two different molecules, while in the other three the CN groups have linear interactions with H atoms on the adjacent molecules.

3.4. PARA-I

The packing of PARA-I is shown in Fig. 6. This is the only complex that does not have the alternating layers of TDB and HMB. Here the TDB molecules form ribbons with $\text{CN}\cdots\text{Cl}$ contacts similar to those in the two-dimensional layers, but with only one intermolecular Cl interaction with each CN. These interactions occur in pairs across centers of symmetry to form the ribbons. Very similar two-dimensional ribbons and layers occur in the structure of the 1,3,5-trichlorotricyanobenzene/HMB complex (Britton, 1988), although the three-dimensional packings are different. Similar paired $\text{CN}\cdots\text{Cl}$ interactions also occur in the crystal structures of 2,4,6-trichlorobenzonitrile (Pink *et al.*, 2000) and the complex 1,3,5-trichlorotricyanobenzene/mesitylene (Britton, 1997). The distances and angles for these interactions are given in Table 2. It can be seen that the $\text{N}\cdots\text{Cl}$ distance increases as the

$\text{N}\cdots\text{Cl}-\text{C}$ angle deviates further from being linear, as has been discussed by Nyburg & Faerman (1985).

An alternative view of PARA-I is shown in Fig. 7. Here a layer of TDB is shown in which the TDB molecules are tilted by 22.2° with respect to the mean plane. This view will be of use in §3.6 where PARA-I, PARA-II and PARA-III are compared.

Reddy, Panneerselvam *et al.* (1993) have shown that substituted 2,3-dicyano-5,6-dichlorobenzenes can be used to form molecular tapes held together by pairs of $\text{CN}\cdots\text{Cl}$ interactions involving both CN groups on one molecule and both Cl on the next. The work here suggests that substituted 2,5-dicyano-3,6-dichlorobenzenes could form tapes at least as well.

3.5. PARA-II

The packing of TDB in PARA-II is shown in Fig. 8. The arrangement is similar to that shown in Fig. 4(a). It differs in that the mirror planes in Fig. 4(a) have been lost.

3.6. PARA-III plus a comparison with PARA-I and PARA-II

The packing of TDB in PARA-III is shown in Fig. 9. This is the same as that shown in Fig. 4(a) and is similar to that found for PARA-II.

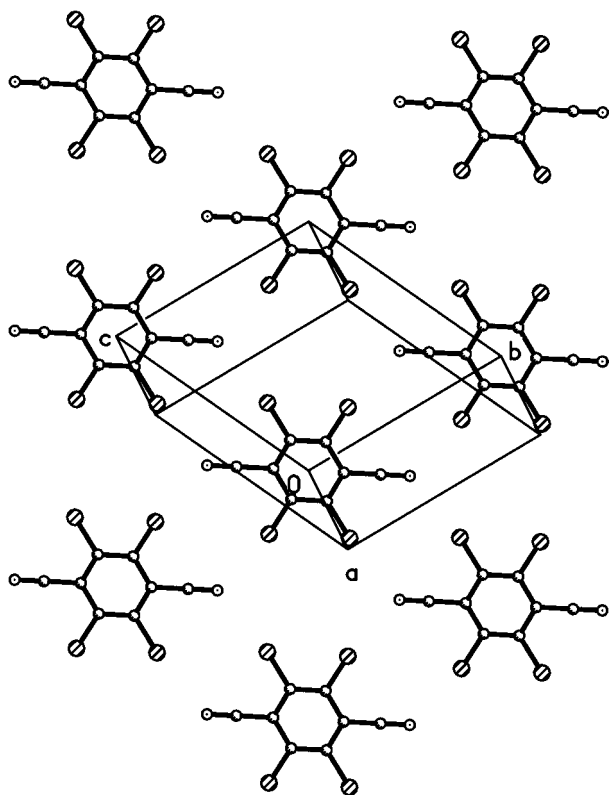


Figure 7

A layer of PARA-I viewed normal to the (100) plane. This is not the hexagonally tiled layer; the TDB molecules are tilted by 22.2° with respect to the mean plane. This drawing should be compared with Figs. 4(a), 6, 8 and 9.

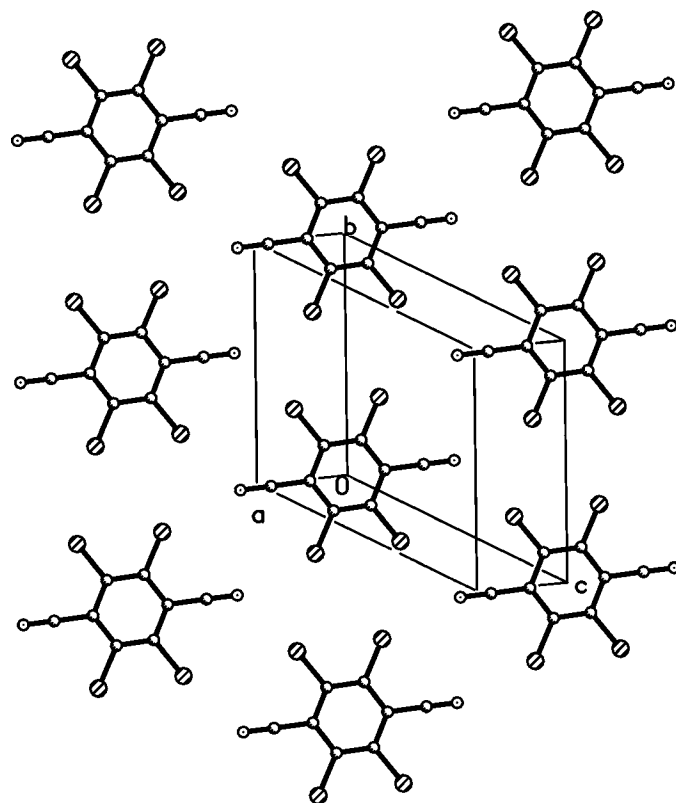


Figure 8

A layer of PARA-II viewed normal to the (100) plane. The TDB molecules are tilted by 3.0° with respect to the mean plane. The HMB molecules in the next layer (not shown) are tilted by 4.5° away from the mean plane. This drawing should be compared with Figs. 4(a), 7 and 9.

Recalling the results from the experimental section (§2.3), PARA-I, PARA-II and PARA-III could all be found at room temperature, but only PARA-I and PARA-II could be cooled to 173 K. When PARA-III was cooled, it transformed to either PARA-I or PARA-II, or both at the same time, at a temperature, which was not reproducible, between 250 and 300 K. Dunitz (1995) has pointed out that, usually, the denser polymorph should be the more stable. A comparison of the room-temperature values of V/Z , 495, 500 and 506 Å³ for PARA-I, PARA-II and PARA-III, respectively, would suggest that PARA-III is the high-temperature form, which agrees with the observed transformations. The transformation of PARA-III to PARA-II is easily understood by comparing Figs. 9 and 8; a small in-plane rotation of the TDB molecules is all that is required. This motion is small enough that the crystals remain single crystals through the transformation, at least on some occasions. The transformation of PARA-III to PARA-I is less obvious, but a comparison of Figs. 9 and 7 shows that the two structures are closer together than would appear from the layers for PARA-I shown in Fig. 6. A larger and out-of-plane motion is required to get from PARA-III to PARA-I, but again this is small enough that some of the crystals remain single crystals through the change. The volumes would suggest that PARA-I is more stable than PARA-II at low temperature, but no PARA-II to PARA-I transformation was ever observed.

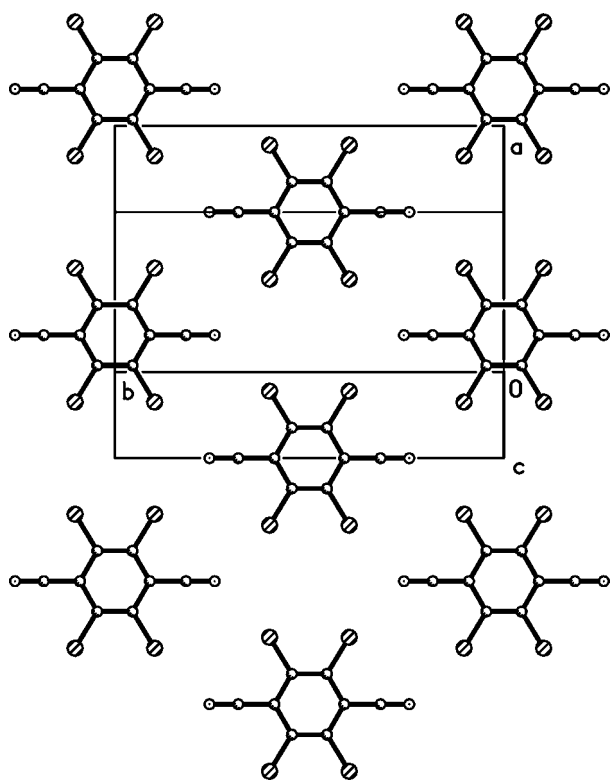


Figure 9
A layer of PARA-III viewed normal to the (001) plane. The TDB molecules are tilted by 7.5° away from the mean plane. The HMB molecules in the next layer (not shown) are tilted by 8.5° away from the mean plane. This drawing should be compared with Figs. 4(a), 7 and 8.

3.7. PARA-IV

The packing of PARA-IV is shown in Fig. 10. This is similar to the pattern shown in Fig. 4(b). It differs in that there are two independent TBD half-molecules in the unit cell rather than the one expected in the idealized arrangement. The glide planes in Fig. 4(b) are replaced by a pseudo- n -glide in the real triclinic structure. This shows up in the intensities also, where the $h0l$ reflections with $h + l$ odd have an average intensity that is less than 10% of the average intensity of the entire data set. V/Z for PARA-IV at room temperature is 511 Å³. Comparison with the volumes of PARA-I, PARA-II and PARA-III, given earlier, suggests that this is probably the highest-temperature form of PARA.

3.8. The Cl···CN···Cl contacts in the *ortho*- and *para*-TDB layers

In all the structures described above in which there are layers of TDB there is one CN group and two Cl atoms in the region of contact among three adjoining TDB. A general picture of this pattern is shown in Fig. 11 and the distances and angles for the contacts are given in the first half of Table 3. In each group there is one short N···Cl distance of 3.05 ± 0.10 Å. There is a second N···Cl distance that may be equally short or may be up to 0.3 Å longer. Finally, there is a Cl···Cl distance

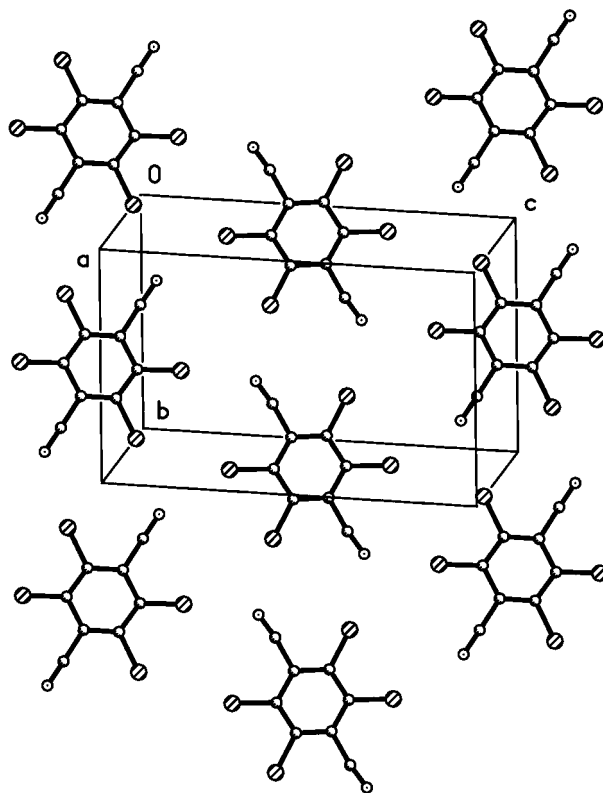


Figure 10
A layer of TBD in PARA-IV viewed normal to the (101) plane. The two independent TBD molecules are tilted by 4.5 and 6.3° with respect to the mean plane. The two HMB molecules in the next layer (not shown) are tilted by 5.8 and 7.2° away from the mean plane. This drawing should be compared with Fig. 4(b).

Table 2
Intermolecular Cl—N···Cl—C2 distances (Å) and angles (°) in 1/1 CN···Cl contacts.

Complex or compound	Cl—N···Cl	N···Cl	N···Cl—C2	Reference
PARA-I	130.9	3.051	167.5	This work
1,3,5-Trichlorobenzonitrile	119.2	3.153	176.1	Pink <i>et al.</i> (2000)
1,3,5-Trichlorotricyanobenzene/mesitylene	128.5	3.274	163.9	Britton (1997)
	157.7	3.535	130.1	
1,3,5-Trichlorotricyanobenzene/HMB	136.5	3.380	149.2	Britton (1988)

that ranges from 3.6 to 4.5 Å. The larger variation of the Cl···Cl distances suggests that the Cl···Cl contacts are weaker than the N···Cl contacts. If the N···Cl distances are compared with the N···Cl—C angles, it will be seen that the distance increases as the angle becomes further from being linear. This trend agrees with the conclusion of Nyburg & Faerman (1985) that the van der Waals radius of Cl is shortest, 1.58 Å, along the C—Cl bond direction, and increases to 1.78 Å at 90° away from the bond direction. However, if their N radius, 1.60 Å, is combined with their Cl radius, the shortest N···Cl distance would be 3.18 Å, which is considerably larger than many of the observed distances.

This can be interpreted as a shortening from the van der Waals distance as a result of a more specific Lewis acid–base interaction. See Price *et al.* (1994) and Lommerse *et al.* (1996) for further work on these types of intermolecular interactions.

In the crystal structures of 1,3,5-trichlorotrifluorobenzene (Chaplot *et al.*, 1981) and hexachloroborazine (Gopinathan *et al.*, 1974) there are Cl···Cl···Cl contacts that are very similar to the Cl···CN···Cl contacts, with one Cl···Cl—C angle near linear and the other nearer 120°. In this case, where each Cl would have to act both as a Lewis acid and a Lewis base, although the angles are suggestive, there is no shortening of the Cl···Cl distances, which are near 3.6 Å in both compounds.

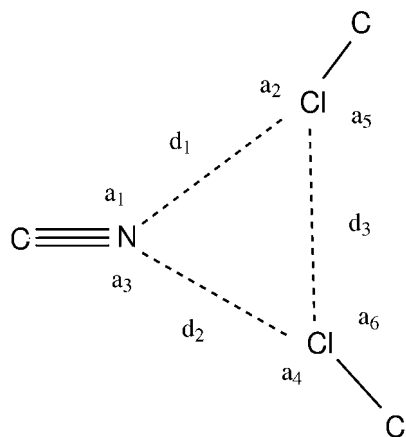


Figure 11
The generalized Cl···CN···Cl arrangement. The results are summarized in Table 3. They have been arranged so that d_1 is always less than d_2 .

3.9. META-I

As described above, the TDB molecules in META-I were disordered between two of the six possible orientations of the molecule. The TDB molecules are in planar layers, which alternate with planar layers of ordered HMB. In all the structures described above, in which there are layers of TDB, there is one CN group and two Cl atoms in the region of contact among three adjoining TDB molecules. This is the pattern described in the previous section. Assuming that this pattern is also true in META-I, then the TDB must alternate between the two observed orientations as we proceed along the [011] direction. With this restriction, there are only three patterns for three adjacent chains parallel to [011]: one pattern (shown in Fig. 12) with molecules related by translation along the **b** direction, a second pattern with molecules related by translation along the **c** direction, and a third with no translational relationship along **b** or **c** (these patterns are presented in the supplementary material). There are two different possible pairs of N···Cl and Cl···Cl contact distances, which are listed in Table 3. Of these, one pair involves sets of N···Cl distances and angles that do not fit the pattern found above, and one Cl···Cl distance that is impossibly short. If patterns with this set of distances are not allowed, only the pattern shown in Fig. 12

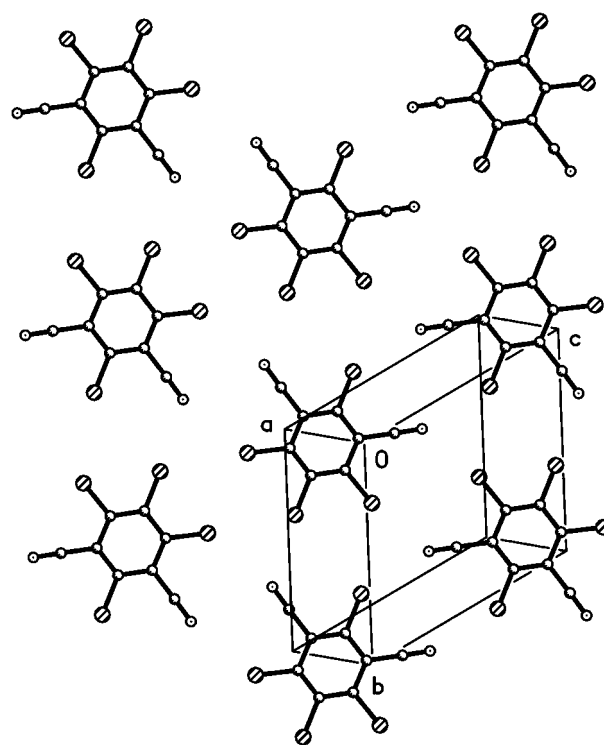


Figure 12
A layer of META-I viewed normal to the (100) plane. The TDB molecules are tilted by 3.1° with respect to the mean plane. The HMB molecules in the next layer (not shown) are tilted by 4.5° away from the mean plane. This drawing should be compared with Figs. 3(a) and 11.

Table 3

Distances and angles in the CN···Cl···Cl contacts.

See Fig. 11; d_1 is the shorter of the two CN···C distances. Room-temperature values are shown in *italic*.

Compound	T (K)	a_1 (°)	d_1 (Å)	a_2 (°)	a_3 (°)	d_2 (Å)	a_4 (°)	a_5 (°)	d_3 (Å)	a_6 (°)
<i>o</i> -TDB	297	<i>140</i>	<i>3.04</i>	<i>164</i>	<i>131</i>	<i>3.06</i>	<i>169</i>	<i>147</i>	<i>4.28</i>	<i>145</i>
<i>o</i> -TDB	297	<i>142</i>	<i>3.15</i>	<i>162</i>	<i>146</i>	<i>3.38</i>	<i>147</i>	<i>139</i>	<i>3.71</i>	<i>160</i>
<i>o</i> -TDB	173	140	3.00	165	129	3.03	170	146	4.29	145
<i>o</i> -TDB	173	142	3.12	162	146	3.36	147	138	3.69	161
ORTHO	173	142	3.05	159	140	3.08	156	149	3.79	149
PARA-II	297	<i>132</i>	<i>3.08</i>	<i>168</i>	<i>153</i>	<i>3.28</i>	<i>144</i>	<i>134</i>	<i>3.74</i>	<i>163</i>
PARA-II	174	129	3.02	171	157	3.27	140	130	3.65	167
PARA-III	297	<i>134</i>	<i>3.13</i>	<i>162</i>	<i>134</i>	<i>3.13</i>	<i>162</i>	<i>145</i>	<i>4.50</i>	<i>145</i>
PARA-IV	174	133	2.96	169	132	3.01	162	141	4.38	151
PARA-IV	174	129	3.07	170	152	3.33	146	134	3.86	158
META-I	173	130	3.02	167	156	3.23	143	134	3.68	165
META-I	173	126	3.04	176	164	3.40	133	124	3.60	171
META-I†	173	164	2.93	134	130	3.02	167	166	3.10	133
META-I†	173	164	3.40	133	128	3.60	174	165	3.79	132
META-II	173	130	3.03	166	155	3.24	144	134	3.68	165
META-II	173	126	3.03	176	165	3.39	133	123	3.61	171
META-II	173	130	3.03	167	155	3.25	144	134	3.68	165
META-II	173	126	3.02	176	164	3.39	133	123	3.60	171

† This set of distances and angles corresponds to the rejected arrangement. See text.

remains. The most reasonable explanation of the results would be that layers of TCB with the pattern shown in Fig. 13 alternate with layers of HMB, but the orientations of the TCB

layers are completely disordered between the orientation shown and its centric inverse.

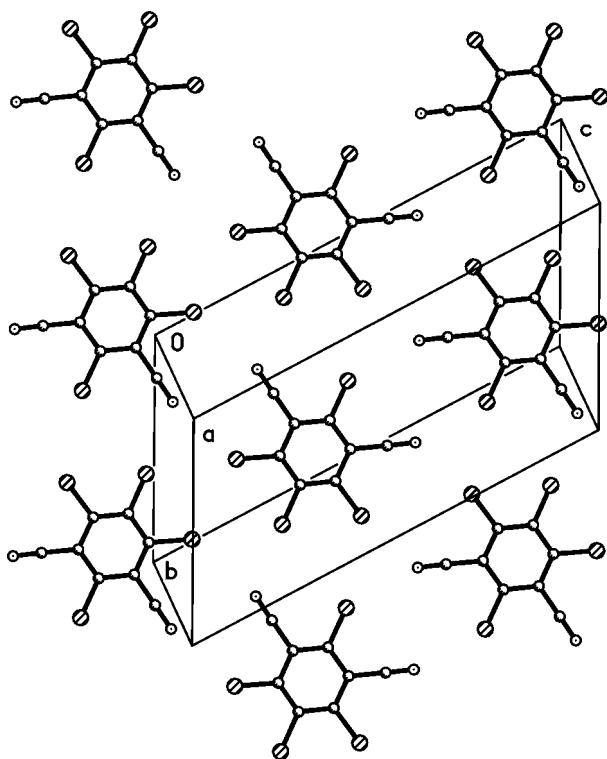


Figure 13

A layer of META-II viewed normal to the (100) plane. The TDB (at $x \approx 0.25$) molecules are tilted by 3.0 and 3.1° with respect to the mean plane. The HMB molecules located on centers at $x \approx 0$ (not shown) are tilted by 4.8 and 4.5° away from the mean plane. The HMB molecules in general positions at $x \approx 0.5$ (not shown) are tilted by 4.4° away from the mean plane. This drawing should be compared with Figs. 3(a) and 12.

3.10. META-II plus a comparison with META-I

The packing of META-II is shown in Fig. 13. A comparison with Fig. 12 shows the similarity between the TDB layers in the two structures. The values of b and α for META-I and META-II are the same and c for META-II is twice that of META-I within experimental uncertainty. In fact, the similarity extends much further than just the TDB layers: the two structures are virtually identical. The only real difference between them is the degree of disorder in the TDB layers: 0.50/0.50 in META-I and 0.85/0.15 in META-II. The two benzene molecules located on centers of symmetry and the third located in a general position in META-II coalesce to a single molecule located on a center in META-I. The two independent TDB molecules, which are related by a pseudo-center of symmetry in META-II, become two molecules across a real center of symmetry in META-I. The difference in coordinates between disordered pairs of TDB is the same within experimental uncertainty in META-I and META-II as well as between the two independent TDB molecules in META-II.

As a final demonstration of the similarity, if the $F_{\text{obs}}(hkl)$ values for META-II are converted to $F'_{\text{obs}}(h'k'l')$ values corresponding to the cell for META-I, and only those F'_{obs} are kept where h' , k' and l' are all integers, then the F'_{obs} data set leads to a META-I' structure that is identical to the real one within experimental uncertainty. This procedure, which discards three-fourths of the data, is equivalent to going back to the SMART frames and only reaping those reflections that correspond to the META-I cell. It is not surprising that this gives a 0.50/0.50 disordered arrangement of TDB since the omitted reflections are just those that arise from the greater order in META-II.

4. Summary

The original goal, to use π complexing to obtain crystal structures with two-dimensional arrays of all three isomers of TDB, has been achieved. Six of the seven structures reported here show such arrays and the seventh has layers that could be regarded as such an array with the molecules rotated by 22° out of the layer. This shows, as Reddy, Goud *et al.* (1993) have shown earlier, that three-dimensional charge-transfer complexes can be constructed to produce the desired two-dimensional arrangements. From the success with HMB and the failure with all the other π donors tried, it appears that the two components of the complex must match in shape as well as area for this approach to work.

In two of the structures, ORTHO and PARA-III, the symmetry of the TBD layers is that shown in Figs. 2 and 4. However, in PARA-II and PARA-IV, and META-I and META-II, the symmetries are lower than those shown in Figs. 3 and 4. In the latter cases, the symmetry elements required for the idealized arrangements of the TBD are lost when they do not coincide with symmetry elements in the HMB layers.

The common feature of these layers, the Cl \cdots CN \cdots Cl contacts, would appear to be a useful solid-state synthon. The interpretation that this involves interactions between the Lewis base CN and the Lewis acids Cl1 and Cl2, rather than only non-specific van der Waals interactions, seems a reasonable one.

The preparation of polymorphs was not part of the original question. Their occurrence suggests that the various arrangements shown in Figs. 2, 3 and 4 have similar energies, which would not be surprising. There are, however, three features of the various polymorphs that are surprising. First, it has not been possible in the past few years to prepare PARA-I, and PARA-IV has only been seen on one occasion. Similar behavior is known (see Dunitz & Bernstein, 1995), but is rare. Second, PARA-III, on cooling, transforms to PARA-I or PARA-II unpredictably. It would be interesting to know if there are other examples of such behavior. Third, the two polymorphs of META, which have recognizably different unit cells, are essentially the same structure, differing only in the degree of ordering of the stacking of the TBD layers. A difference between complete disorder, as in META-I, and complete order would be more understandable, rather than the 0.85/0.15 disorder that is actually found in META-II.

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