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Planar packing of tetrachlorodicyanobenzenes. II

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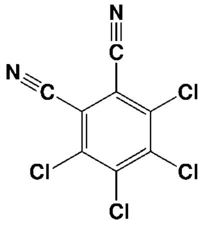
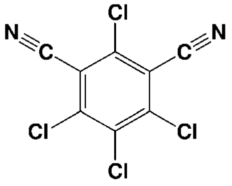
Equimolar mixtures of *ortho*- and *meta*-, or *ortho*- and *para*-, or *meta*- and *para*-tetrachlorodicyanobenzene, $C_6Cl_4(CN)_2$, form structures with disordered layers containing both kinds of molecules in rhombohedral or pseudo-rhombohedral cells. These structures are similar to the structure of the rhombohedral form of the *meta* isomer. The guiding force appears to be an intermolecular synthon, in which a nitrile group in one molecule interacts with Cl atoms in two adjacent molecules with N$\cdots$Cl distances of approximately 3.1 Å.

1. Introduction

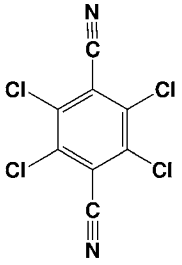
The crystal structures of the three isomers [abbreviated (O), (M-I), (P)] of tetrachlorodicyanobenzene (Britton, 1981*a*,*b*) all show short CCl$\cdots$NC contact distances of the order 3.1 Å. In (O) the molecules assemble into a planar arrangement with each N atom in contact with two Cl atoms. Fig. 1 shows an idealized version of a layer in (O). This arrangement raised the possibility of planar packing of (M) and (P) as well. A number of possible, ordered, planar, two-dimensional packings of the three isomers were suggested (Part I: Britton, 2002). These packings were based on the assumption that the molecules formed a planar array and that, where three molecules met, two Cl atoms and one cyano group were required at the meeting point. Co-crystals of (O), (M) and (P) with hexamethylbenzene were prepared and several of the suggested arrangements were found.



o-TDB



m-TDB



p-TDB

Other Cl$\cdots$NC contacts are well known. Desiraju & Harlow (1989) have looked at $X\cdots$NC interactions, where X = Cl, Br or I. Reddy *et al.* (1993) have pointed out the usefulness of CCl$\cdots$NC interactions in preparing molecular tapes. Desiraju (1995), in a general discussion of supramolecular synthons, discusses two types, both involving two C—Cl and two NC. Lommerse *et al.* (1996) used the Cambridge Structural Database (Allen *et al.*, 1991) to examine C—$X\cdots Y$ interactions, where X is any halogen and Y is N, O or S; they also used intermolecular perturbation theory to explore the nature of these interactions.

Recently, Tremayne *et al.* (2004) reported two new polymorphs of (M), (M-II) and (M-III), and referred to them as forms 2 and 3, respectively. Hu *et al.* (2004) reported two additional polymorphs, (M-IV) and (M-V), and referred to them as types II and III, respectively. (M-III) does not have a layered arrangement but does have a number of CCl···NC contacts. (M-IV) and (M-V) are similar to each other and to the suggested arrangement shown in Fig. 3(*c*) in Britton (2002). (M-II) is a disordered layered structure, in $R\bar{3}m$ with $z' = 1/6$, and is the focus of most of this paper.

(M-IV) and (M-V) bear further examination. If the observed unit-cell dimensions are multiplied by the matrix $[-\frac{1}{2},-\frac{1}{2},1\backslash 0,1,0\backslash -1,0,-1]$, the new cells are: (M-IV), a = 9.174 (2), b = 9.419 (2), c = 10.081 (2) Å, α = 90, β = 94.26 (1), γ = 120.89 (1)°; (M-V), a = 9.242 (1), b = 9.238 (1), c = 10.097 (1) Å, α = 90, β = 89.88 (1), γ = 119.99 (1)°. Both cells are similar to that of (M-II). The revised cell constants of (M-IV) are sufficiently different from those of (M-II) that (M-IV) may be a correct structure, related to that of (M-II) but ordered. The arrangement in one layer of (M-IV) corresponds to that suggested in Fig. 3(*c*) in Britton (2002). The cell constants of (M-V), on the other hand, agree closely with those of (M-II), and the powder diffraction pattern of (M-V) appears to be the same as that of (M-II), so that (M-V) and (M-II) appear to be the same, and the proposed, ordered structure for (M-V) is probably incorrect.

Tremayne (2004) has proposed, and then rejected (on the basis of poor intermolecular contact distances), a structure for (M-II) with ordered layers combined with disordered orientations in the stacking. Tremayne *et al.* (2004) offered a similar explanation with an ordered layer and disordered stacking, but the details of the proposed layer were not given. It is proposed here that a better explanation is disorder within each layer, with the disorder constrained by the requirement that each N atom be in contact with two Cl atoms. Fig. 2 shows one such possible disordered arrangement; it is not difficult to continue the disorder indefinitely.

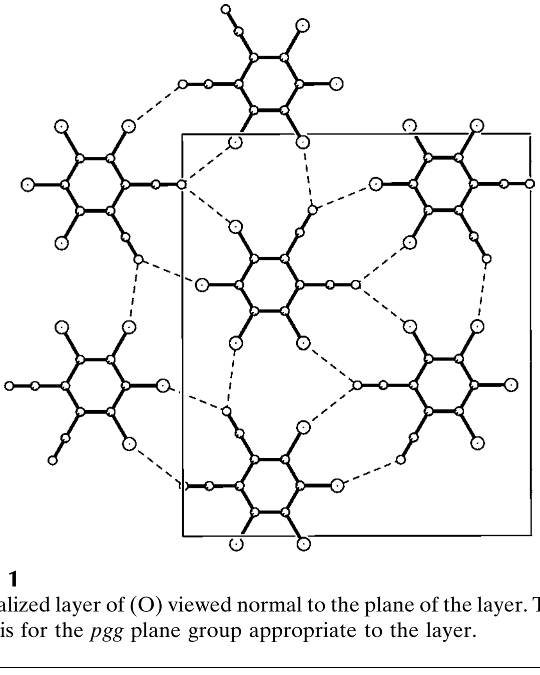


Figure 1
An idealized layer of (O) viewed normal to the plane of the layer. The cell shown is for the *pgg* plane group appropriate to the layer.

The two alternative explanations cannot be distinguished by ordinary diffraction methods, although it is quite possible that a study of the diffuse scattering might decide the question. See Welberry & Goossens (2008) for an overview of diffuse scattering calculations.

However, if a disordered arrangement, such as that in Fig. 2, is correct, then it might be possible to form similar disordered arrangements by the co-crystallization of mixed crystals involving more than one of the isomers. The results of these co-crystallizations are reported here.

2. Experimental

2.1. Syntheses

2.1.1. Crystals of the pure isomers. Samples of the three isomers had been provided previously by Dr Robert Battershell of the Diamond Shamrock Corporation.

The original structure determinations of (O), (M-I) and (P) were made on crystals grown from acetonitrile; no attempt was made to look for polymorphs. With the discovery of the polymorphs of (M) described above an attempt was made to find polymorphs by recrystallizing the compounds from six solvents: acetone, benzene, methylene chloride, chloroform, carbon tetrachloride and acetonitrile. All three compounds formed cocrystals with benzene, which was shown by the rapid decomposition of the crystals when exposed to air; the structures of these complexes will not be pursued here. With (O) and (P) the other five solvents all gave crystals with the previously reported structures, although a variety of crystal habits was found. With (M) the results were more varied. Crystals from methylene chloride, chloroform and acetonitrile gave (M-I). Crystallization from acetone gave mostly (M-II) with a few crystals of (M-III). Crystallization from carbon tetrachloride gave (M-II).

2.1.2. Crystals of the solid solutions. Approximately equimolar mixtures of the three possible pairs of isomers were

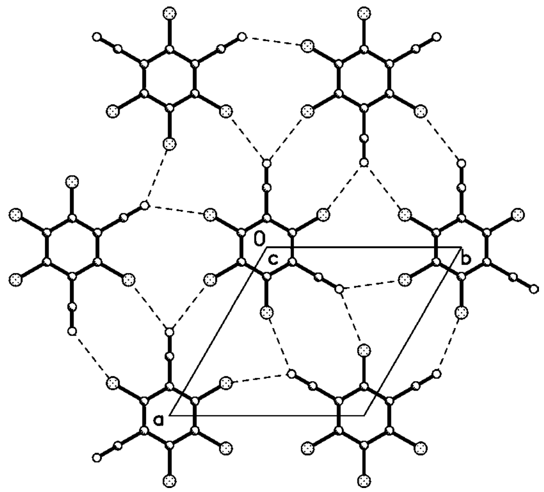


Figure 2
A possible arrangement of one layer of (M-II), viewed along the *c* axis. Each molecule can be in one of six orientations, subject to the constraint that each CN group points between Cl atoms on adjacent molecules.

Table 1
Experimental details.

	(M-II)	(O/P)	(M/P-II)
Crystal data			
Chemical formula	$C_8Cl_4N_2$	$C_8Cl_4N_2$	$C_8Cl_4N_2$
M_r	265.90	265.90	265.90
Cell setting, space group	Rhombohedral, $R\bar{3}m{:}H$	Hexagonal, $R\bar{3}m{:}H$	Monoclinic, $C2/m$
Temperature (K)	173 (2)	173 (2)	173 (2)
a, b, c (Å)	9.2171 (14), 9.2171 (14), 9.935 (2)	9.2473 (8), 9.2473 (8), 9.9590 (13)	7.9237 (9), 9.4546 (11), 6.5157 (7)
α, β, γ (°)	90.00, 90.00, 120.00	90.00, 90.00, 120.00	90.00, 93.106 (2), 90.00
V (Å^3)	731.0 (2)	737.52 (13)	487.41 (9)
Z	3	3	2
D_x (Mg m^{-3})	1.812	1.796	1.812
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	1.17	1.16	1.17
Crystal form, color	Prism, colorless	Prism, colorless	Prism, colorless
Crystal size (mm)	0.50 × 0.35 × 0.25	0.45 × 0.35 × 0.30	0.35 × 0.35 × 0.30
Data collection			
Diffractometer	Bruker 1X CCD area detector	Bruker 1K CCD area detector	Bruker 1K CCD area detector
Data collection method	ω scans	ω scans	ω scans
Absorption correction	Multi-scan†	Multi-scan†	Multi-scan†
$T_{\min}$	0.64	0.64	0.58
$T_{\max}$	0.75	0.71	0.70
No. of measured, independent and observed reflections	2730, 226, 216	1227, 176, 167	2825, 589, 562
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
$R_{\rm int}$	0.031	0.038	0.016
$\theta_{\max}$ (°)	27.5	25.0	27.5
Refinement			
Refinement on	F^2	F^2	F^2
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.031, 0.086, 1.24	0.029, 0.086, 1.28	0.031, 0.080, 1.08
No. of reflections	226	176	589
No. of parameters	21	22	53
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.045P)^2 + 0.495P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.058P)^2 + 0.025P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.039P)^2 + 0.594P]$, where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$	0.001	0.001	0.001
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å^{-3})	0.21, −0.27	0.22, −0.22	0.40, −0.46
Extinction method	None	*SHELXTL*	None
Extinction coefficient	–	0.036 (10)	–

Computer programs used: *SMART*, *SAINT* (Siemens, 1995), *SHELXTL* (Sheldrick, 2008). † Based on symmetry-related measurements.

prepared as mixtures (O/M), (O/P) and (M/P). Each mixture was recrystallized from each of the six solvents mentioned above. The crystallization was carried out by dissolving the mixture and allowing the solution to evaporate to dryness, all at room temperature. In each case, except with benzene, there were a number of well formed crystals plus some more finely divided material. The latter was not examined further.

Not unexpectedly, solvates were found using benzene; these were not considered further. In the remaining solvents the crystals were identified by unit-cell determinations. For each combination of solvent and mixture the unit cell of at least one crystal was determined, more if there were significantly different habits. Crystallization of (O/P) and (O/M) gave the same result, crystals in the space group $R\bar{3}m$, similar to those of (M-II), from all solvents. One of the crystals of (O/M) was large enough that the single crystal could be dissolved and used to determine a ^{13}C NMR (chloroform-d) spectrum; this showed approximately equal amounts of both components. Recrystallization of (M/P) gave variable results: crystallization from carbon tetrachloride or acetonitrile produced (M/P-I), which was similar to (M-II); crystallization from methylene chloride or chloroform gave crystals of (M/P-II), a disordered structure in space group $C2/c$; crystallization from acetone gave crystals of both (M/P-I) and (M/P-II).

2.2. X-ray analysis

In each of the disordered structures the C—Cl, C—CN and C—N distances were restrained to be 1.713 (1), 1.445 (1) and 1.142 (1) Å, respectively, based on the averages of the distances in (O), (M) and (P) at 173 K (Britton, 2007, 2008). The Cl and C (in CN) were constrained to have the same ADPs.

Complete data were collected for at least one structure of each kind (see Table 1).[1] For all of the $R\bar{3}m$ structures the data are virtually identical. Table 2 shows the cell constants for all the $R\bar{3}m$ structures that were determined completely. Complete data are only given for two of these, (M-II) and (O/P). There are no significant differences in any of the others. Complete data are also given for (M/P-II), which is also disordered, but in the space group $C2/c$ rather than $R\bar{3}m$. Fig. 3

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[1] Supplementary data for this paper are available from the IUCr electronic archives (Reference: BS5066). Services for accessing these data are described at the back of the journal.

Table 2
Unit cell and R-factor data for the $R\bar{3}m$ structures.

Structure	Temperature (K)	a (Å)	c (Å)	R
(M-II)	297	9.2304 (13)	10.089 (2)	0.017
(M-II)	173	9.2171 (14)	9.935 (2)	0.031
(O/M)	173	9.2200 (13)	9.931 (2)	0.019
(O/P)	173	9.2473 (8)	9.9590 (13)	0.029
(M/P-I)	297	9.2330 (13)	10.091 (2)	0.022

Table 3
Unit-cell data for the pseudo-$R\bar{3}m$ structures.

Structure	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)
(M-II)	9.217	9.217	9.935	90	90	120
(O)†	9.124	9.416	9.945	90	94.91	121.06
(M-IV)‡	9.174	9.419	10.081	90.0	94.26	120.89
(M/P-II)§	9.169	9.169	10.107	85.52	94.48	118.47

† The unit cell given in Britton (2007) was transformed by the matrix $[-1, \frac{1}{4}, \frac{1}{2}\backslash 0, -\frac{1}{2}, 0\backslash 1, 0, 1]$. ‡ The unit cell given in Hu *et al.* (2004) was transformed by the matrix $[-\frac{1}{2}, -\frac{1}{2}, 1/0, 1, 0/-1, 0, -1]$. § The unit cell given in Table 1 was transformed by the matrix $[\frac{1}{2}, \frac{1}{2}, -1/-\frac{1}{2}, \frac{1}{2}, 1/1, 0, 1]$.

shows the atom labeling and displacements for (M-II), (O/P) and (M/P-II). One layer of (M-II) was shown earlier in Fig. 2. Fig. 4 shows one layer of (O/P). The corresponding pictures for (O/M) and (M/P-I) would be similar. Fig. 5 shows one layer of (M/P-II). In the latter the disorder is not complete. The occupancies are 0.430 (4) for Cl1 and 0.785 (2) for Cl2 in the 173 K structure. In the same structure at 298 K, based on a different crystal, the occupancies are 0.479 (7) and 0.761 (3).

If the cell constants of (M/P-II) are multiplied by the matrix $[\frac{1}{2},\frac{1}{2},-1\backslash-\frac{1}{2},\frac{1}{2},1\backslash1,0,1]$ the resulting cell has a = 9.169, b = 9.169, c = 10.107 Å, α = 85.52, β = 94.48, γ = 118.47°. Clearly the (M/P-II) structure is similar to the $R\bar{3}m$ structure.

3. Summary

The disorder in the four solid solutions must include disorder within the layers as well as between them. However, this disorder within the layers is still possible even if it is required that the Cl···CN···Cl synthon forms at every possible opportunity. In view of the number of ordered structures containing this synthon, it seems a reasonable conclusion that it prevails in the disordered structures as well. The simplest explanation of the structure of (M-II) is that the same kind of disorder occurs within the layers there. The layers are ordered with respect to each other as far as possible given that there is disorder within the layers.

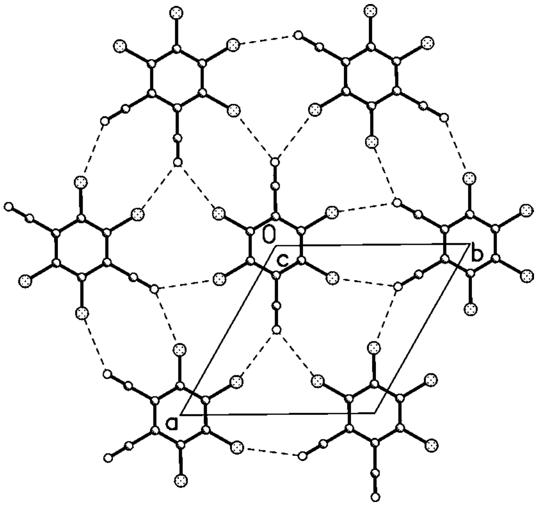
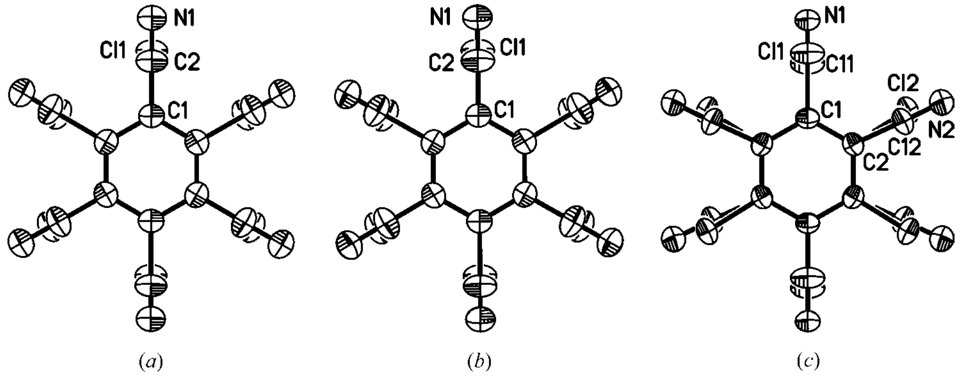


Figure 4
A possible arrangement for one layer of (O/P) viewed along the c axis. Each (O) molecule can be in one of six orientations; each (P) molecule can be in one of three orientations. The disorder is subject to the constraint that each CN group points between Cl atoms on two adjacent molecules.

There are four different structures in which there are layers of molecules, (M-II), (O), (M-IV) and (M/P-II). The mixtures that crystallize in $R\bar{3}m$ are not regarded as essentially different structures. (M-II) has been described in a hexagonal cell in $R\bar{3}m$. If the orientations of the CN and Cl substituents in the other three structures are ignored, a pseudo-hexagonal cell can be found in each case. The cell constants for these pseudo-cells are given in Table 3. While the stacking of the layers in these four structures are not the same, they are very similar, that is to say, there is very little difference among the inter-layer interactions.

The structures of (O), (M-II) and (M-IV), the hexamethylbenzene complexes of all of the isomers, and the disordered solid solutions all have structures with approximately planar-hexagonal tiling. However, it should be noted that (M-I), (M-III) and (P) do not form planar-hexagonal structures. The occurrence of the Cl···CN···Cl synthon leads to planar arrangements, but it does not always occur; it is not a dominating synthon to the extent that hydrogen



(*a*) (*b*) (*c*)

Figure 3
Atom labeling and displacement ellipsoids (50% probability) for (*a*) (M-II), (*b*) (O/P) and (*c*) (M/P-II).

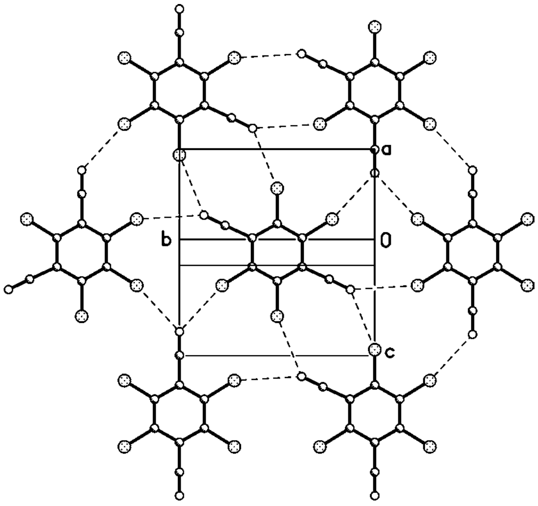


Figure 5
A possible arrangement for one layer in (M/P-II) viewed normal to the plane of the layer. This picture would be similar to that for (M/P-I) except that this structure is in the space group *C*2/*c* so that the vertical and approximately horizontal substituent positions are not equally disordered. A CN group is slightly more likely to occur in the vertical position than in the horizontal.

bonds are. It is not clear what factors lead to the occurrence of planar structures. Hexamethylbenzene (Le Magueres *et al.*, 2001) packs in a planar-hexagonal arrangement, although the $CH_3\cdots CH_3\cdots CH_3$ arrangement, geometrically similar to the $Cl\cdots CN\cdots Cl$ arrangement, would not be thought of as a useful synthon. On the other hand, hexachlorobenzene (Reddy *et al.*, 2006) does not form a planar-hexagonal structure even though Jetti *et al.* (2000) have shown that the $Cl\cdots Cl\cdots Cl$ synthon can be used to form planar host molecule packings based on 2,4,6-tris(4-chlorophenoxy)-1,3,5-triazine. A possible packing with planar layers for hexachlorobenzene, based on the bond distances, intermolecular $Cl\cdots Cl$ distances, and ring-to-ring distances found in the actual structure has the same molecular volume as the actual structure. The predictability of planar structures appears to be an open question.

One additional aspect of this project that might be worthy of further study (although there is no intention to do it here) is to find the smallest proportion of polymorph *A* that will lead to the disordered rhombohedral structure in polymorph *B*. This is more or less a phase diagram problem except that the answer may well vary from solvent to solvent.

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