

Fig. 2. The unit cell of photoadduct (2).

121.5 (2), C(9)—C(4)—O(1) = 127.2 (2)°. The irregular geometry of the six-membered pyrimidine ring is very similar in both molecules; corresponding bond lengths and endocyclic bond angles are within 0.014 Å and 2.2° respectively (Table 2). However, there are marked differences in bond angles in the five-membered pyrazole ring moieties, reflecting the alternative tautomeric distribution of the  $\pi$  electrons. In particular, the sum of the endocyclic angles at C(3) and N(1) is 11° smaller in the photoadduct than in allopurinol, while the N(2) angle is 6° larger.

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## Structure of Dicyanodurene\*

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**Abstract.** C<sub>12</sub>H<sub>12</sub>N<sub>2</sub>,  $M_r = 184.24$ , monoclinic,  $C2/c$ ,  $a = 17.176$  (9),  $b = 5.055$  (2),  $c = 12.460$  (8) Å,  $\beta = 113.27$  (5)°,  $Z = 4$ ,  $V/Z = 248.5$  (4) Å<sup>3</sup>,  $D_x = 1.231$  (2) g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 0.69$  cm<sup>-1</sup>,  $F(000) = 392$ ,  $T = 183$  (3) K,  $R = 0.055$  for 977 reflections. The bond lengths and angles are normal. The molecule is slightly puckered into a chair form owing to the crowding of the substituents.

\* 2,3,5,6-Tetramethyl-1,4-benzenedicarbonitrile.

The hydroxyalkyl side chain on N(2) is fully extended with a terminal methyl group, and all substituents are in staggered conformations.

The water molecule of crystallization [O(3)] is involved in hydrogen bonding to three different molecules of the photoadduct, using its own H atoms to bond to the carbonyl O atom [O(1) at  $x, y, z$ ] and to N(1) at  $1-x, -y, 1-z$  as well as bonding, *via* the hydroxyl H atom, to O(2) at  $1-x, -\frac{1}{2}+y, 1\frac{1}{2}-z$ . The hydroxyl O atom, O(2), in turn hydrogen bonds *via* H(5) to N(5) at  $1-x, 1-y, 1-z$ . Thus, each formula unit is involved in seven hydrogen bonds leading to the network illustrated in Fig. 2.

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A further consequence of the crowding is that the CH<sub>3</sub> groups are rotated away from the eclipsed orientation found in durene by 8 (2) and 15 (3)°. Adjacent methyl groups rotate in the same direction in order to minimize the H···H contacts. There are no special intermolecular interactions apparent from the packing.

**Introduction.** The crystal structure of dicyanodurene was originally determined (van Rij, 1976) as

part of a comparison of the packing of this molecule with those of terephthalonitrile (van Rij & Britton, 1977; Drück & Littke, 1978; Colapietro, Domenicano, Portalone, Schultz & Hargittai, 1984) and tetrafluoroterephthalonitrile (van Rij & Britton, 1981; Dunitz, Schweizer & Seiler, 1982; Seiler, Schweizer & Dunitz, 1984). The original determination, at room temperature, did not lead to well defined positions for the H atoms, but difference Fourier maps through the expected plane of the H<sub>3</sub> positions were best interpreted on the assumption that the CH<sub>3</sub> groups were ordered and rotated 10–15° away from the arrangement with *mmm* symmetry, with the methyl H atoms nearest to the ring H atom coplanar with the ring. This arrangement is found in durene (Stam, 1972; Prince, Schroeder & Rush, 1973; Abovyan, Alyasnikova & Kitai-gorodskii, 1977; see also *Discussion*). To resolve this question we have redetermined the structure of dicyanodurene at 183 K.

**Experimental.** Dicyanodurene was prepared from durene in two steps by Dr W. B. Gleason. Durene was converted to diiododurene (Suzuki, Nakamura & Goto, 1966) which was converted to dicyanodurene (Friedman & Shechter, 1961). The product was recrystallized from absolute ethanol [m.p. 477–478 K, uncorrected, *cf.* 481–482 K reported by Grundmann & Frommelt (1965)].

A crystal 0.35 × 0.40 × 0.40 mm was used for the data collection. *D<sub>m</sub>* was not measured. Data were collected on an Enraf–Nonius CAD-4 diffractometer equipped with a graphite monochromator. 25 reflections with 10 < θ < 17° were used to determine the cell parameters. Systematic extinctions (*hkl*, *h + k* odd; *h0l*, *l* odd) confirmed the space group *C2/c* found in the earlier determination. Data were collected, using ω–2θ scans, in the range 0 < θ < 32° for one hemisphere (ranges: *h* – 25 to 25; *k* 0 to 7; *l* – 18 to 18). 3443 reflections were measured and combined to give 1726 independent reflections (*R<sub>int</sub>* = 0.044) of which 977 with *I* > 3σ(*I*) were used in the calculations. Three check reflections measured every 4500 s of exposure time showed no systematic change with time. No absorption correction was made. The trial structure was taken from the room-temperature determination (which had been solved from the Patterson map) and refined with full-matrix least squares on *F*<sup>2</sup>s. The center of the molecule lies on a center of symmetry at  $\frac{1}{4}, \frac{1}{4}, 0$ . The heavy atoms were given anisotropic thermal parameters. The H atoms were located from a difference Fourier map and both positions and isotropic thermal parameters were refined. Refinement converged with *R* = 0.055, *wR* = 0.068 and *S* = 1.74; *w* = 1/σ<sup>2</sup>(*F*) was calculated from σ<sup>2</sup>(*I*) = σ<sup>2</sup>(*I*)<sub>cs</sub> + (0.05*I*)<sup>2</sup>, where σ(*I*)<sub>cs</sub> is the standard deviation in *I* based on counting statistics alone.

Table 1. Fractional atomic coordinates and equivalent isotropic temperature factors

$$B_{eq} = (1/3) \sum_i \sum_j B_{ij} a_i^* a_j^* a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B<sub>eq</sub></i> (Å <sup>2</sup> )
N1	0.4042 (1)	0.6776 (4)	0.2630 (1)	3.14 (6)
C1	0.3035 (1)	0.3985 (3)	0.0893 (1)	1.77 (5)
C2	0.3390 (1)	0.2189 (3)	0.0361 (1)	1.78 (5)
C3	0.2843 (1)	0.0638 (3)	–0.0550 (1)	1.77 (5)
C4	0.3598 (1)	0.5560 (4)	0.1855 (1)	2.21 (5)
C5	0.4335 (1)	0.1956 (4)	0.0741 (2)	2.50 (6)
C6	0.3177 (1)	–0.1372 (4)	–0.1152 (2)	2.36 (6)
H51	0.448 (2)	0.210 (5)	0.005 (2)	3.6 (5)
H52	0.452 (2)	0.024 (6)	0.107 (2)	4.7 (6)
H53	0.465 (2)	0.332 (5)	0.127 (2)	4.3 (6)
H61	0.362 (2)	–0.242 (5)	–0.060 (3)	5.5 (7)
H62	0.277 (2)	–0.271 (6)	–0.158 (3)	6.7 (8)
H63	0.345 (2)	–0.057 (6)	–0.165 (2)	5.4 (7)

Table 2. Bond lengths (Å) and angles (°)

N1–C4	1.145 (2)	C5–H52	0.96 (3)
C1–C2	1.399 (2)	C5–H53	0.96 (3)
C1–C3'	1.409 (2)	C5–H51	1.00 (3)
C1–C4	1.445 (2)	C6–H61	0.96 (3)
C2–C3	1.394 (2)	C6–H62	0.97 (3)
C2–C5	1.504 (3)	C6–H63	0.99 (3)
C3–C6	1.505 (2)		
C2–C1–C3'	124.0 (1)	H52–C5–H51	106 (2)
C2–C1–C4	118.5 (1)	H52–C5–C2	110 (2)
C3'–C1–C4	117.5 (1)	H53–C5–H51	107 (2)
C3–C2–C1	118.1 (1)	H53–C5–C2	113 (2)
C3–C2–C5	120.6 (1)	H51–C5–C2	110 (1)
C1–C2–C5	121.3 (1)	H61–C6–H62	102 (3)
C2–C3–C1'	117.9 (1)	H61–C6–H63	103 (2)
C2–C3–C6	121.2 (1)	H61–C6–C3	112 (2)
C1'–C3–C6	120.9 (1)	H62–C6–H63	111 (2)
N1–C4–C1	178.8 (2)	H62–C6–C3	114 (2)
H52–C5–H53	111 (2)	H63–C6–C3	113 (2)

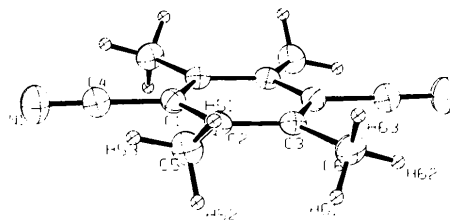


Fig. 1. *p*-C<sub>6</sub>(CH<sub>3</sub>)<sub>4</sub>(CN)<sub>2</sub>. Thermal ellipsoids are shown at the 50% probability level. H atoms are shown with arbitrary size.

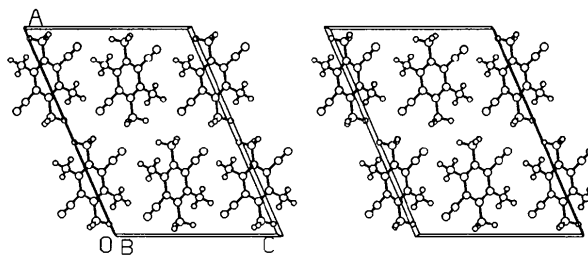


Fig. 2. The packing of C<sub>6</sub>(CH<sub>3</sub>)<sub>4</sub>(CN)<sub>2</sub> viewed down the *b* axis.

$(\Delta/\sigma)_{\max}$  in the final cycle of refinement was 0.02.  $(\Delta\rho)_{\max} = 0.25$ ,  $(\Delta\rho)_{\min} = -0.24 \text{ e } \text{Å}^{-3}$ . Atomic scattering factors and anomalous-dispersion corrections for all atoms were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). The computer programs used were from *TEXSAN* (Molecular Structure Corporation, 1985).

**Discussion.** The final positional parameters are given in Table 1.\* The thermal ellipsoids and the labelling of the atoms are shown in Fig. 1. Bond lengths and angles are given in Table 2; they are all normal within experimental error. The molecule deviates slightly but significantly from planarity. Ring atoms are alternately 0.0045 (15) Å above and below the mean plane of the C<sub>6</sub> ring, and the attached C atoms are further out of the plane in the same direction as the ring atoms to which they are attached [distances: C4 0.026 (2); C5 0.045 (2); C6 0.021 (2); N1 0.065 (2) Å]. Presumably, this is a consequence of the overcrowding of the attached groups. A second consequence of the overcrowding is that the methyl groups are rotated away from eclipsing the ring bond to C1 by 8 (2)° for the C5 methyl group and by 15 (3)° for the C6 methyl group. The displacements of the H atoms closest to the plane of the ring are in the opposite direction from the displacement of the CN group. In the structural studies of durene itself, Stam (1972) and Prince, Schroeder & Rush (1973) treated the molecule as if it had *mmm* symmetry, without going into detail, but Abovyan, Alyasnikova & Kitaigorodskii (1977), who were particularly interested in the rotation of the CH<sub>3</sub> groups, say that one group is rotated by 3° and the other, adjacent to the first, is rotated by -7°, that is, that they are rotated in opposite directions. However, their drawing shows that the rotations are in the same direction, and they give no estimate of the accuracy of these rotations. In the latter case, Abovyan *et al.* expected to find rotations near 15° for both groups based on the theoretical calculations of Mirskaya & Ivanova (1973). In a table in the supplementary material we have calculated the torsion angles for each H atom in both CH<sub>3</sub> groups in all three structure determina-

tions; in every case the *mmm* description for durene is adequate within the experimental error.

As mentioned in the *Introduction*, this structure determination was originally undertaken to compare the packing with that in two other *p*-dinitriles. In *p*-C<sub>6</sub>F<sub>4</sub>(CN)<sub>2</sub> (van Rij & Britton, 1981), the predominant feature of the packing appears to be an interaction between the basic lone pair on the CN group and the acidic ring C atom *ipso* to the CN group. In *p*-C<sub>6</sub>H<sub>4</sub>(CN)<sub>2</sub> (van Rij & Britton, 1977), the predominant feature of the packing appears to be antiparallel contacts between CN groups on adjacent molecules. In dicyanodurene the CN groups do not appear to play any significant role in the packing, which is shown in Fig. 2. The overall packing is a herringbone arrangement of the sort found in many planar molecules with no special interactions. The closest contact between CN groups is an N1...N1 contact of 3.43 Å across a twofold axis. To the extent that the energy of the CN...CN interaction is determined by the bond dipoles, the orientation is such that the energy is small and slightly repulsive.

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\* Lists of anisotropic thermal parameters, torsion angles, distances from the mean plane, torsion angles in previous durene structure determinations, and observed and calculated structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53355 (19 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.