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Packing Studies in Cyano-Aromatic Compounds: The Structure of 1,4-Benzenedicarbonitrile

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Abstract. $C_8H_4N_2$, $M_r = 128\cdot13$; $P\bar{1}$; $a = 3\cdot839\ (4)$, $b = 6\cdot579\ (9)$, $c = 7\cdot333\ (60)$ Å, $\alpha = 114\cdot48\ (20)$, $\beta = 93\cdot59\ (29)$, $\gamma = 96\cdot97\ (11)°$; $Z = 1$; $D_m = 1\cdot286$, $D_c = 1\cdot281$ g cm^{-3}; $V = 166$ Å^3; μ(Mo $K\alpha$) $= 0\cdot8757$ cm^{-1}; $F(000) = 66$. This structure was solved by direct methods and refined by least-squares analysis to an R of 0·058 including 362 reciprocal points. 1,4-Benzenedicarbonitrile shows a method of intermolecular charge compensation similar to that in 4-pyridinecarbonitrile.

Introduction. X-ray structure determinations of benzenehexacarbonitrile (Littke, 1967; Littke & Wallenfels, 1978) and pyridinepentacarbonitrile (Littke, 1972; Littke & Weber, 1978) have shown that the strong intramolecular interactions between the π-system of the aromatic ring and the very electrophilic cyano groups give rise to intermolecular charge compensation which leads to interesting packing principles. To complete these studies, X-ray structure determinations of 1,3,5-benzenetricarbonitrile (Littke & Drück, 1978), and 1,4-benzenedicarbonitrile were undertaken. Results for the last substance are reported in this paper.

1,4-Benzenedicarbonitrile was crystallized from acetonitrile as colourless prisms, with the crystal data shown above. A single crystal was ground to a sphere of radius 0·4 mm and mounted on a Nonius CAD-4 diffractometer. The intensities of 1657 independent reflexions were collected in the range $3 < \theta < 40°$ with Mo $K\alpha$ radiation and the $\omega/2\theta$ scan mode. Of these, 362 were considered 'observed' according to the criterion $I > 2\sigma(I)$ and used in the refinement step. Scattering factors for neutral atoms were taken from Hanson, Herman, Lea & Skillman (1964). The structure was solved by the symbolic addition procedure using the programs *SIGMA*2 (Ammon, Dickinson, Chastain, Boonstra & Stewart, 1970) and *PHASE* (Boonstra, Chastain & Stewart, 1970) and including 168 phases with $E > 1\cdot3$. The reflexions $1\bar{3}6$, $\bar{2}\bar{1}2$ and $2\bar{5}1$ were arbitrarily assigned phases of 180°. The developed phases gave the correct solution. The corresponding E map showed all the non-hydrogen atoms of the asymmetric unit.

Several refinement cycles assuming unit weights and isotropic temperature factors gave an R of 0·132. The subsequent introduction of anisotropic temperature factors resulted in a further reduction to $R = 0\cdot088$. A difference synthesis calculated with the observed reflexions with $\sin\theta/\lambda < 0\cdot5$ Å^{-1} showed the H atoms as the most prominent peaks. Further full-matrix refinement (C, N anisotropic, H isotropic) gave $R = 0\cdot058$. The final positional parameters are given in Table 1.* Fig. 1 shows the atomic numbering scheme.

Discussion. The bond lengths and angles (Table 2) and also the results from a calculation of a least-squares plane (Table 3) show no such distortion of the benzene ring as reported for 1,2,4,5-benzenetetracarbonitrile (Prout & Tickle, 1972). The small shortening of the bond lengths C(1)–C(6) and C(3)–C(4) is perhaps due

Table 1. *Fractional atomic coordinates of heavy atoms* ($\times10^4$) *and hydrogen atoms* ($\times10^3$) *with standard deviations in parentheses*

	x	y	z
C(1)	1337 (15)	3683 (9)	861 (7)
C(2)	1242 (14)	5963 (9)	2029 (7)
C(3)	−102 (14)	7283 (9)	1166 (7)
C(7)	2569 (16)	6987 (10)	4164 (8)
N(1)	3635 (15)	7797 (9)	5834 (7)
H(1)	230 (17)	284 (10)	147 (9)
H(2)	−4 (17)	887 (10)	201 (9)

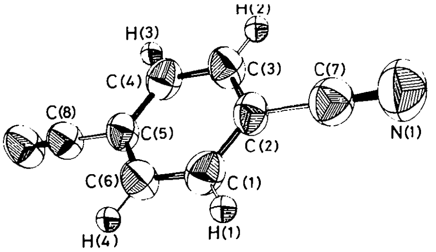

Fig. 1. Molecule of 1,4-benzenedicarbonitrile. Thermal ellipsoids of the non-hydrogen atoms are scaled to the 50% probability level; the hydrogen-atom radius is 0·1 Å.

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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 33629 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond lengths* (Å) *and angles* (°) *with standard deviations in parentheses*

C(1)–C(2); C(4)–C(5)	1·392 (8)
C(2)–C(3); C(5)–C(6)	1·395 (11)
C(3)–C(4); C(6)–C(1)	1·376 (13)
C(2)–C(7); C(5)–C(8)	1·451 (13)
C(7)–N(1); C(8)–N(2)	1·138 (12)
H(1)–C(1); H(3)–C(4)	0·935 (80)
H(2)–C(3); H(4)–C(6)	0·965 (60)

C(1)–C(2)–C(3)	120·6 (0·7)	H(1)–C(1)–C(2)	118·9 (3·2)
C(2)–C(3)–C(4)	119·5 (0·5)	H(1)–C(1)–C(6)	121·2 (3·2)
C(2)–C(1)–C(6)	119·9 (0·7)	H(2)–C(3)–C(2)	118·1 (4·5)
C(1)–C(2)–C(7)	119·9 (0·7)	H(2)–C(3)–C(4)	122·4 (4·5)
C(3)–C(2)–C(7)	119·5 (0·5)		
C(2)–C(7)–N(1)	179·4 (0·7)		

Table 3. *Deviations* (Å) *of the atoms from the least-squares plane of the molecule* (*the atoms marked with an asterisk were not included in the computation of the plane*)

A = 3·48931	C(1)	0·000	C(8)*	−0·010
B = 1·64180	C(2)	0·000	N(1)*	0·028
C = −2·91264	C(3)	0·000	N(2)*	−0·028
D = 0·82090	C(4)	0·000	H(1)*	0·019
	C(5)	0·000	H(2)*	0·036
	C(6)	0·000	H(3)*	−0·019
	C(7)*	0·010	H(4)*	−0·036

to a stronger double-bonding character between the atoms involved in each of these bonds. The bond length between the ring C atom C(2) and the C atom of the cyano group shows greater similarity with the sp^3–sp bond type (1·459 Å) than with the sp^2–sp type (1·419 Å).

The packing of the molecules in the crystal can be seen in Fig. 2. One molecular layer is displaced with respect to the next layer in such a way that the neighbouring cyano groups link together. The perpendicular from the negatively charged N atom to the bond of the neighbouring cyano group lies nearer to the positively charged C atom of this group (0·4123 Å) than to the N atom (0·7257 Å). The intermolecular distances are: N(1)–C(8) 3·626, N(1)–N(2) 3·675 and C(7)–C(8) 3·921 Å. A similar packing principle is also described for 4-pyridinecarbonitrile (Laing, Sparrow & Sommerville, 1971). This kind of intermolecular charge compensation gives rise to the high melting and sublimation point of the compound (222°C) and explains why it was possible to obtain single crystals only in polar solvents.

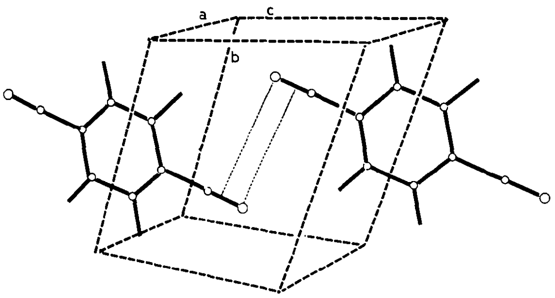

Fig. 2. Schematic representation of the unit cell of 1,4-benzene-dicarbonitrile showing the intermolecular contacts.

All calculations were made with the XRAY 70 system (Stewart, Kundell & Baldwin, 1970) on the Univac 1106 computer of the University of Freiburg, Germany. We gratefully acknowledge the financial support given to us by the 'Deutsche Forschungsgemeinschaft'.

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