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1,2-Dicyanobenzene. A Precursor of Phthalocyanines

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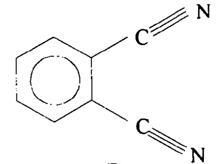
Abstract

The molecule of 1,2-dicyanobenzene, $C_8H_4N_2$, possesses mirror symmetry. The two cyano groups are bent slightly above the plane of the molecule. The six aromatic C—C bonds in the benzene ring have a mean value of 1.377 Å. The C—CN and C≡N bond lengths are 1.430 (7) and 1.149 (8) Å, respectively. The internal angles in the benzene ring differ slightly from 120°. The shortest intermolecular contact is N(1)···H(2) of 2.657 (16) Å.

Comment

We have used 1,2-dicyanobenzene as a precursor in the synthesis of phthalocyanines. Using a previously described preparation method (Kubiak & Janczak, 1993), we obtained several metallophthalocyanines (Janczak & Kubiak, 1993*a*,*b*, 1994*a*) and a new group of compounds, the bicyclic phthalocyanines (Janczak & Kubiak, 1994*b*).

Of the three isomers of dicyanobenzene, only the crystal structure of the 1,4-isomer has been published (Van Rij & Britton, 1977; Drück & Littke, 1978; Colapietro, Domenicano, Portalone, Schultz & Hargittai, 1984). This paper reports the crystal structure of the 1,2-isomer, (I).



(I)

The molecular geometry with the atomic numbering is shown in Fig. 1. The crystals are composed of isolated molecules of 1,2-dicyanobenzene. The two cyano groups are slightly bent above the benzene plane retaining molecular symmetry *m*. This plane is perpendicular to the benzene ring and bisects the C(1)—C(1$^{\rm i}$) and C(3)—C(3$^{\rm i}$) bonds [symmetry code: (i) $-x$, y, z]. The mean aromatic C—C bond length of 1.377 Å is comparable to analogous mean distances found in the 1,4-isomer (1.388 Å; Drück & Littke, 1978) and in 1,2,4,5-tetracyanobenzene [1.401 (8) Å; Prout & Tickle, 1978]. The C≡N bond length of 1.149 (8) Å is typical of cyano groups and comparable to C—N distances found in various cyano derivatives (Britton, 1981*a*,*b*; Casado, Nygaard & Sorensen, 1971; Colapietro, Domenicano, Marciante & Portalone, 1981). The C—CN distance of 1.430 (7) Å is comparable to C—CN distances of 1.451 (13) Å in the 1,4-isomer (Drück & Littke, 1978), 1.446 (8) Å in 1,2,4,5-tetracyanobenzene (Prout & Tickle, 1978) and 1.439 (6) Å in 4-cyanopyridine (Laing, Sparrow & Sommerville, 1971). This bond length is intermediate between the expected value of 1.419 Å for *sp*–*sp*^{2} C—C bond lengths and the value of 1.459 Å for *sp*–*sp*^{3} C—C bond lengths (Stoecheff, 1962).

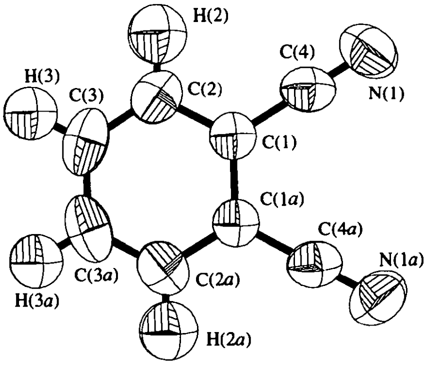


Fig. 1. View of the molecular structure of 1,2-dicyanobenzene with the atom-numbering scheme. Displacement ellipsoids are plotted at the 50% probability level.

The mutual arrangement of the 1,2-dicyanobenzene molecules is illustrated in Fig. 2. The structure is composed of linear stacks of parallel and overlapping molecules forming a quasi-herringbone bond array. The distance between two successive parallel benzene rings is 3.503 (14) Å. This value is a little larger than the

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van der Waals distance of 3.4 Å for aromatic C atoms (Pauling, 1960). The dihedral angle between two benzene ring planes from successive stacks is 128.2 (6)°. The intermolecular H···N contact distances are greater than 2.6 Å, with the closest distance being 2.657 (16) Å between atoms N(1) and H(2)($\frac{1}{2}-x$, $1-y$, $\frac{1}{2}+z$).

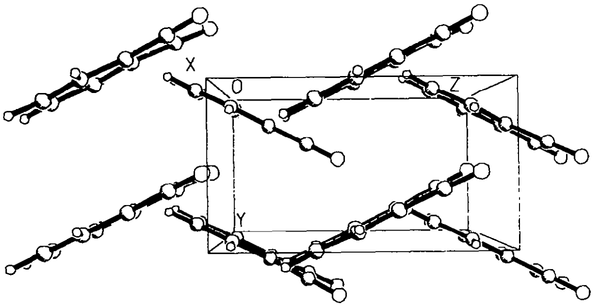

Fig. 2. The molecular arrangement of 1,2-dicyanobenzene in the unit cell.

Experimental

The sample of 1,2-dicyanobenzene was purchased from the Aldrich Chemical Co. The colourless single crystals used for the X-ray measurements were obtained by sublimation at 383 K in an evacuated and sealed glass ampoule. The density D_m was measured by flotation.

Crystal data

$C_8H_4N_2$
$M_r = 128.1$
Orthorhombic
$Pmn2_1$
$a = 12.584$ (3) Å
$b = 3.894$ (1) Å
$c = 6.955$ (1) Å
$V = 340.8$ (2) Å^3
$Z = 2$
$D_x = 1.249$ Mg m^{-3}
$D_m = 1.244$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 20 reflections
$\theta = 6$–$10°$
$\mu = 0.073$ mm^{-1}
$T = 295$ K
Prism
0.45 × 0.40 × 0.25 mm
Colourless

Data collection

Kuma KM-4 computer-controlled four-circle κ-axis diffractometer
$\omega/2\theta$ scans
Absorption correction: none
636 measured reflections
355 independent reflections
259 observed reflections $[F > 4\sigma(F)]$

$R_{\rm int} = 0.0296$
$\theta_{\rm max} = 26°$
$h = -15 \rightarrow 15$
$k = 0 \rightarrow 4$
$l = 0 \rightarrow 8$
2 standard reflections monitored every 50 reflections
intensity decay: none

Refinement

Refinement on F
$R = 0.0501$
$wR = 0.0614$
$S = 0.61$
259 reflections
54 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F) + 0.01F^2]$
$(\Delta/\sigma)_{\rm max} = 0.021$

$\Delta\rho_{\rm max} = 0.19$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.16$ e Å^{-3}
Extinction correction: $F_{\rm corr} = F_o/[1 + (0.002 \times \chi F^2/\sin\theta)]^{1/4}$
Extinction coefficient: $\chi = 0.0899$ (9)
Atomic scattering factors from *SHELXTL/PC* (Sheldrick, 1990)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
C(1)	0.0557 (3)	0.1996 (9)	0.1545 (8)	0.0564 (10)
C(2)	0.1096 (3)	0.0633 (12)	0	0.0733 (13)
C(3)	0.0555 (5)	−0.0663 (11)	−0.1519 (8)	0.0830 (16)
C(4)	0.1120 (3)	0.3421 (10)	0.3142 (8)	0.0690 (12)
N(1)	0.1578 (3)	0.4550 (13)	0.4424 (10)	0.0934 (15)

Table 2. *Selected geometric parameters* (Å, °)

C(1)—C(1$^{\rm i}$)	1.401 (6)	C(3)—C(3$^{\rm i}$)	1.397 (11)
C(1)—C(2)	1.378 (6)	C(4)—N(1)	1.149 (8)
C(1)—C(4)	1.430 (7)	C(2)—H(2)	1.00 (10)
C(2)—C(3)	1.354 (6)	C(3)—H(3)	1.00 (3)
C(1)—C(2)—C(3)	120.3 (4)	C(4)—C(1)—C(1$^{\rm i}$)	119.7 (2)
C(1)—C(4)—N(1)	179.5 (4)	C(1)—C(2)—H(2)	116 (3)
C(2)—C(1)—C(4)	120.7 (3)	C(2)—C(3)—H(3)	120 (2)
C(2)—C(1)—C(1$^{\rm i}$)	119.5 (2)	H(3)—C(3)—C(3$^{\rm i}$)	120 (2)
C(2)—C(3)—C(3$^{\rm i}$)	120.2 (3)	C(3)—C(2)—H(2)	123 (3)

Symmetry code: (i) $-x, y, z$.

Preliminary rotation and Weissenberg photographs indicated space group $Pmn2_1$. The structure was solved by direct methods. A difference map showed maxima in positions consistent with the expected locations of the H atoms. The positional and displacement parameters for the H atoms were refined. Data collection: Kuma KM-4 diffractometer software (Kuma, 1989). Cell refinement and data reduction: Kuma KM-4 diffractometer software. Program used to solve and refine structure: *SHELXTL/PC* (Sheldrick, 1990). Molecular graphics: *SHELXTL/PC*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and least-squares-planes data have been deposited with the IUCr (Reference: KA1110). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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The Relative Basicities of Tris(pyrazol-1-yl)-1,3,5-triazine (TPT), Water and the Picrate Anion in the Solid State

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Abstract

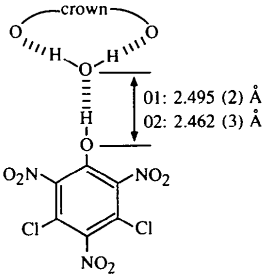
In the solid state, the picrate of tris(pyrazol-1-yl)-1,3,5-triazine (TPT) containing water and chloroform, exists as an oxonium picrate solvated by TPT and chloroform, $H_3O^+.C_6H_2N_3O_7^-.C_{12}H_9N_9.CHCl_3$. The compound shows the shortest $H_3O^+\cdots O^-$ distance ever reported. All H atoms of the oxonium cation are involved in strong hydrogen bonds joining the TPT molecule and the picrate anion. The TPT molecule mimics the crown ethers in stabilizing the H_3O^+ cation.

Comment

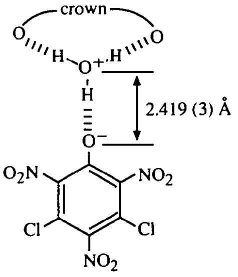
Proton transfer between an acid and a base, both neutral, to produce two charged species (A—H$\cdots B \rightarrow A^-\cdots$H—$B^+$) has never been observed in the gas phase (Abboud, Notario & Botella, 1994), although an appreciable degree of proton transfer has been recently found to exist in the case of the very strong complex $(CH_3)_3N\cdots HCl$ (Legon & Rego, 1989). The situation is completely different in the solid state where the salt-like structures are common (for instance, all NH_4^+ salts). The difference in energy is provided by the lattice, especially by the hydrogen bonds.

The question of proton transfer in crystals arises when the difference in basicity between A^- and B increases, for instance when AH is an organic acid and B is water. Here, we shall examine the case where AH is picric acid (2,4,6-trinitrophenol). Picric acid was the strongest gas acid known (higher acidity than HCl, HBr and HI) (Dzidic, Carrol, Stillwell & Horning, 1974) until very recently (Koppel *et al.*, 1994). Since the solid state compares better with the gas phase than with solution, the situation $C_6H_2(NO_2)_3$—$OH\cdots H_2O$ would be expected to be quite favourable to observe the transfer of the proton to the water, $C_6H_2(NO_2)_3$—$O^-\cdots H_3O^+$, in the crystal.

An examination of the structures reported in the Cambridge Structural Database [CSD; October 1993; $R \leq 0.075$ (Allen *et al.*, 1991)] concerning crystals containing both picric acid (or very close derivatives) and water, shows two situations, (I) (water–picric acid) and (II) (oxonium picrate).



(I) CIRTECT01 and 02



(II) KEPNEY

In bis(water–dichloropicric acid)–18-crown-6, (I), two polymorphs CIRTEC01 and CIRTEC02, (Britton, Chantooni, Wang & Kolthoff, 1984; Britton, Chantooni & Kolthoff, 1988), the O$\cdots$O distance is longer than in bis(oxonium dichloropicrate)–dicyclohexano-18-crown-6, (II) (Peiju, Ming & Wenji, 1990) [note that dichloropicric acid is stronger than picric acid in solution (Pearce & Simpkins, 1968)]. The situation

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