Electrical, Magnetic, and Structural Characterisation of 4-Cyano-1,3,6-triazacycl[3.3.3]azine

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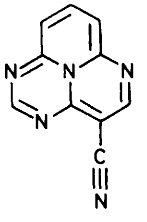
4-Cyano-1,3,6-triazacycl[3.3.3]azine crystallises in the monoclinic system, space group $P2_1/c$, with a = 6.411(4), b = 15.366(6), c = 9.211(5) Å, β = 104.30(5)°, U = 879.3 Å^3, Z = 4, D_c = 1.48 Mg m^{-3}. The structure was solved by direct methods and refined to a final R of 0.045 for 737 observed reflections. The molecules are arranged in distorted columns, parallel to c, with two types of overlap and interplanar spacings of 3.09 and 3.31 Å which alternate. The crystals show semiconductive behaviour with $\rho = 2 \times 10^9\ \Omega$ cm at 300 K, the properties arising from charge transfer interactions between the acceptor atoms of the cyano group and the donor atoms of the ring. The closest intermolecular non-hydrogen contacts are C(3a)–C(10′) = 3.153(6), C(4)–C(10′) = 3.293(6), and N(9b)–N(11′) = 3.159(5) Å. In contrast, 1,3,4,6-tetra-azacycl[3.3.3]azine and its 2,5-dimethyl analogue have $\rho_{300\,K} > 10^{14}\ \Omega$ cm and all intermolecular contacts are of the van der Waals type.

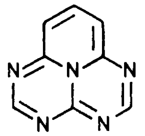
Organic charge transfer complexes may be classified into two distinct groups based upon the degree of charge transfer.[1] The non-bonding complexes have room temperature conductivities of 10^{-8} S cm^{-1} or less and, in general, their structures are characterised by mixed stacks in which the donors and acceptors alternate. In contrast the dative complexes have higher conductivities, with σ_{rt} 10^{-7}—10^{3} S cm^{-1}, and in this group the criteria for high conductivity are partial charge transfer[2] and segregated stacking. The less conductive complexes, in this category, also exhibit mixed stacks along which the interplanar distances reflect the degree of charge transfer. Thus in TMPD–TCNQ,[3] which has an ionic ground state, the interplanar spacing is 3.27 Å whereas in DPE–TCNQ,[4] which has a neutral ground state, the spacing is 3.45 Å. The spacings are also influenced by other considerations such as the planarity of the molecules and steric effects.

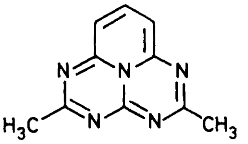
In contrast, the homomolecular crystals from which the complexes are formed are insulators[5] and, in these, the molecules are held together by weak van der Waals forces. Self charge transfer interactions may, however, elevate the conductivity. The most common type of self transfer occurs in molecules which contain a π-electron-donor system separated by a non-conjugated bridge from a π-electron-acceptor system and charge transfer may take place *via* either intramolecular[6] or intermolecular interaction.[7] Urbanski[8] has considered the possibility of self transfer between the electron-donor and electron-acceptor substituents of conjugated systems, the simplest example considered being nitroaniline, but cyanuric chloride[9] and halogenocyanoacetylenes[10] also fall into this category. Iodocyanoacetylene forms linear chain structures (**1**) in which the intermolecular N···I contact is 2.93 Å. For comparison, the N···I contact in pyrazine–tetraiodoethylene[11] is 2.98 Å and the van der Waals distance[12] is 3.65 Å. Short intermolecular contacts have also been found in the crystal structure of 4-cyano-1,3,6-triazacycl[3.3.3]azine reported in this paper and electron-donor–acceptor interactions between the ring and the cyano group give rise to semiconductive behaviour.

$\mathrm{I{-}C{\equiv}C{-}C{\equiv}N \cdots I{-}C{\equiv}C{-}C{\equiv}N}$

(**1**)


(**2**)


(**3**)


(**4**)

Experimental

Crystal Data.—$C_{10}H_5N_5$ (**2**), M_r = 195.2, monoclinic, space group $P2_1/c$, a = 6.411(4), b = 15.366(6), c = 9.211(2) Å, β = 104.30(5)°, U = 879.3 Å^3, Z = 4, D_c = 1.48 Mg m^{-3}, $F(000)$ = 400, Mo-K_α (λ = 0.710 59 Å), μ = 0.059 mm^{-1}.

The azacycl[3.3.3]azines (**2**)—(**4**) were prepared by methods described previously[13,14] and the samples were purified successively by column chromatography, gradient sublimation, and recrystallisation. The space group and unit cell parameters of 4-cyano-1,3,6-triazacycl[3.3.3]azine (**2**) were obtained from precession and Weissenberg photographs. Intensity data were collected, in the range 1° < θ < 25.0°, from a crystal of approximate dimensions 0.40 × 0.25 × 0.10 mm, mounted with its c axis coincident with the ω-axis of a Stöe Stadi 2 two-circle diffractometer using Mo-K_α radiation and the background-ω scan-background technique. 1 331 unique reflections were measured of which 737 had significant counts [$I \geqslant 3\sigma(I)$]. The intensities were corrected for Lorentz and polarisation factors but not for absorption.

Multisolution direct methods using SHELX[15] enabled the positions of all non-hydrogen atoms to be readily located. The hydrogens were included in positions calculated from the molecular geometry (C–H = 1.08 Å). Common isotropic temperature factors were applied to the hydrogens and they were refined to a final value of U = 0.053(7) Å^2. Scattering factors were taken from ref. 16 and the weighting scheme $w = [\sigma^2(F_o) + 0.004\,07\,(F_o)^2]^{-1}$ adopted. Full matrix least-squares refinement with anisotropic temperature factors for the non-hydrogen atoms gave the final R = 0.045 and R_w = 0.050. The final difference map showed no peaks greater than 0.17 eÅ^{-3}.

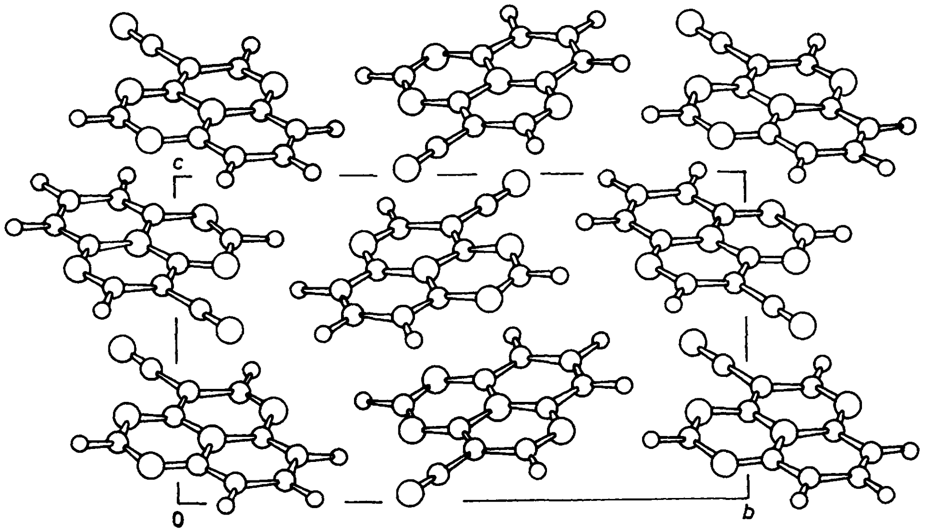


Figure 1. Crystal structure of 4-cyano-1,3,6-triazacycl[3.3.3]azine (**2**) projected along *a*

Table 1. Final fractional positional parameters (× 10^4) with e.s.d.s in parentheses

	x	*y*	*z*
N(1)	7 844(6)	−446(2)	1 205(6)
C(2)	6 937(7)	−1 008(3)	1 927(7)
N(3)	5 454(5)	−842(2)	2 708(5)
C(3a)	4 810(6)	−29(3)	2 710(6)
C(4)	3 162(6)	226(3)	3 397(6)
C(5)	2 656(7)	1 105(3)	3 443(7)
N(6)	3 554(6)	1 729(2)	2 833(6)
C(6a)	5 069(7)	1 503(3)	2 102(6)
C(7)	6 081(7)	2 135(3)	1 429(7)
C(8)	7 624(8)	1 904(3)	690(7)
C(9)	8 221(7)	1 044(3)	607(7)
C(9a)	7 275(6)	402(3)	1 258(6)
N(9b)	5 691(5)	639(2)	2 026(5)
C(10)	2 187(6)	−427(3)	4 221(6)
N(11)	1 397(6)	−937(3)	4 706(6)

Table 2. Details of molecular planes.

Equation to the plane
$0.5136X + 0.1258Y + 0.8488Z - 3.3062 = 0$

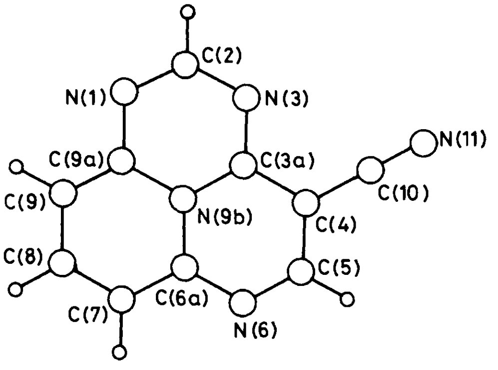
Distances and e.s.d.s from the plane (in Å)

N(1)	0.038(5)	C(7)	−0.024(6)
C(2)	−0.018(6)	C(8)	−0.015(6)
N(3)	−0.062(4)	C(9)	0.008(6)
C(3a)	0.011(4)	C(9a)	0.027(5)
C(4)	−0.045(5)	N(9b)	0.011(4)
C(5)	0.012(6)	C(10)	0.028(5)*
N(6)	−0.014(5)	N(11)	0.012(5)*
C(6a)	0.000(5)		

* Denotes atoms not defining the plane.

The final atomic co-ordinates are listed in Table 1 and the results of least-squares-planes calculations are in Table 2. Lists of thermal parameters and hydrogen atomic co-ordinates are in Supplementary Publication No. SUP 56 153 (2 pp.).*

Table 3. Bond distances (Å) and angles (°) with e.s.d.s in parentheses



(a) Distances

N(1)–C(2)	1.311(6)	N(6)–C(6a)	1.357(7)
N(1)–C(9a)	1.356(5)	C(6a)–C(7)	1.396(7)
C(2)–N(3)	1.351(6)	C(6a)–N(9b)	1.393(5)
N(3)–C(3a)	1.316(5)	C(7)–C(8)	1.379(7)
C(3a)–C(4)	1.415(6)	C(8)–C(9)	1.383(6)
C(3a)–N(9b)	1.394(6)	C(9)–C(9a)	1.371(7)
C(4)–C(5)	1.392(6)	C(9a)–N(9b)	1.421(6)
C(4)–C(10)	1.431(7)	C(10)–N(11)	1.138(6)
C(5)–N(6)	1.313(7)		

(b) Angles

C(2)–N(1)–C(9a)	117.2(4)	N(6)–C(6a)–N(9b)	121.2(4)
N(1)–C(2)–N(3)	127.3(4)	C(7)–C(6a)–N(9b)	118.1(4)
C(2)–N(3)–C(3a)	116.2(4)	C(6a)–C(7)–C(8)	120.6(4)
N(3)–C(3a)–C(4)	122.2(4)	C(7)–C(8)–C(9)	121.0(5)
N(3)–C(3a)–N(9b)	122.4(4)	C(8)–C(9)–C(9a)	120.4(5)
C(4)–C(3a)–N(9b)	115.4(4)	N(1)–C(9a)–C(9)	121.5(4)
C(3a)–C(4)–C(5)	119.2(4)	N(1)–C(9a)–N(9b)	119.7(4)
C(3a)–C(4)–C(10)	118.3(4)	C(9)–C(9a)–N(9b)	118.7(4)
C(5)–C(4)–C(10)	122.3(4)	C(3a)–N(9b)–C(6a)	121.7(4)
C(4)–C(5)–N(6)	124.4(5)	C(3a)–N(9b)–C(9a)	117.1(3)
C(5)–N(6)–C(6a)	117.9(4)	C(6a)–N(9b)–C(9a)	121.2(4)
N(6)–C(6a)–C(7)	120.7(4)	C(4)–C(10)–N(11)	179.0(5)

Results and Discussion

The crystal structure of 4-cyano-1,3,6-triazacycl[3.3.3]azine, projected along *a*, is shown in Figure 1 and the molecular geometry is in Table 3. The planarity, bond lengths and angles are similar to those of the tetra-azacycl[3.3.3]azine analogues.[17,18] The molecule is nearly planar, the maximum deviation from the plane being 0.062(4) Å, and it stacks, in the direction of *c*, with

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* See Instructions for Authors in *J. Chem. Soc., Perkin Trans. 2*, 1985, Issue 1.

Table 4. Close intermolecular contacts (in Å) with e.s.d.s in parentheses.

C(3a^{i})–C(10^{ii})	3.153(6)	C(2^{i})–N(11^{iv})	3.336(7)	N(1^{i})–N(9b^{v})	3.278(5)
C(4^{i})–C(4^{ii})	3.364(6)	C(3a^{i})–N(11^{ii})	3.305(7)	N(9b^{i})–N(11^{ii})	3.159(5)
C(4^{i})–C(10^{ii})	3.293(6)	C(6a^{i})–N(11^{ii})	3.353(7)		
C(5^{i})–C(9^{iii})	3.354(8)	C(9^{i})–N(3^{v})	3.379(6)		
		C(10^{i})–N(1^{iii})	3.358(6)		

Equivalent positions are as follows:

(i)	x	y	z
(ii)	$1 - x$	$-y$	$1 - z$
(iii)	$x - 1$	y	z
(iv)	$x + 1$	y	z
(v)	$1 - x$	$-y$	$-z$

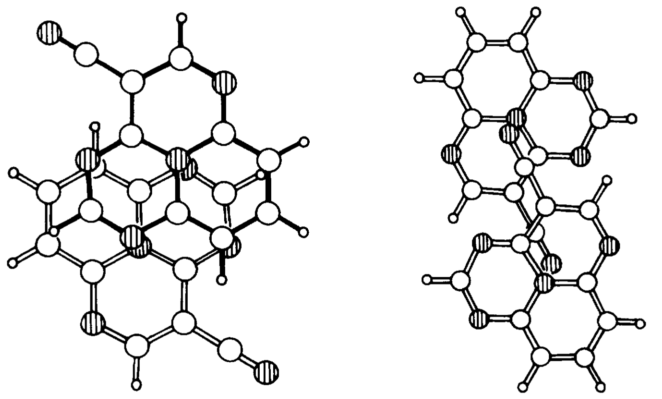

Figure 2. Molecular overlaps in 4-cyano-1,3,6-triazacycl[3.3.3]azine (**2**)

two types of overlap and two different spacings which alternate. The mean perpendicular spacings between the molecular planes are shorter than expected for a homomolecular crystal and correspond to 3.09 Å for the cyano group to ring overlap and 3.31 Å for the ring to ring overlap (Figure 2). The first of these overlaps is similar to the electron-donor–acceptor overlap in pyrene–TCNE[19] but surprisingly the intermolecular contacts and the interplanar separation are longer in the 1 : 1 complex. In 4-cyano-1,3,6-triazacycl[3.3.3]azine the intermolecular distances C(3a)–C(10′) = 3.153(6) Å and C(4)–C(10′) = 3.293(6) Å are considerably shorter than the sum of the van der Waals radii[12] which corresponds to 3.4 Å. Other close contacts are listed in Table 4. It is of interest to note that the C(3a)–C(10′) distance is the shortest intermolecular *carbon–carbon* contact reported for a homomolecular crystal and it corresponds closely with the closest carbon–carbon contacts found in heteromolecular salts.[20] The short spacings are attributed to intermolecular charge transfer between the electron-acceptor atoms of the cyano group and the electron-donor atoms of the peripheral ring.

The charge transfer interaction is analogous to that depicted by Urbanski *et al.*[8] for *o*-, *m*-, and *p*-nitroaniline. However, whereas nitroaniline is paramagnetic, 4-cyano-1,3,6-triazacycl[3.3.3]azine is diamagnetic, the magnetic susceptibility being $-1.1(2) \times 10^{-4}$ e.m.u. mol^{-1} and independent of temperature in the range 20—400 K investigated. The susceptibility is in close agreement with the value of -1.01×10^{-4} e.m.u. mol^{-1} calculated from Pascal's constants.

The resistivity of 4-cyano-1,3,6-triazacycl[3.3.3]azine at 300 K is 2×10^{9} Ω cm and, for comparison, the electrical properties of two related materials are reported. 1,3,4,6-Tetra-azacycl[3.3.3]azine (**3**) and the dimethyl analogue, 2,5-dimethyl-1,3,4,6-tetra-azacycl[3.3.3]azine (**4**) are insulators. In these systems, the molecules stack in a plane-to-plane manner, in infinite columns, parallel to the single-crystal needle axis.[17,18] The spacing and type of overlap within the stacks are analogous to those in graphite[21] and the intermolecular contacts are of the van der Waals type. The resistivities of the 1,3,4,6-tetra-azacycl[3.3.3]azines at 300 K are greater than 10^{14} Ω cm, the values being typical of homomolecular organic crystals (*cf.*, for example, $\rho_{300\mathrm{K}} = 10^{20}$ Ω cm for pyrene[22] and 10^{16} Ω cm for metal-free phthalocyanine[23]). In comparison the lower resistivity of 4-cyano-1,3,6-triazacycl[3.3.3]azine is anomalous and may be attributed to self charge transfer as indicated by the close intermolecular contacts. The value is characteristic of heteromolecular charge transfer complexes in which the electron donors and acceptors alternate.

Acknowledgements

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