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Structure of 2-Amino-4,5-dicyanoimidazole

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Abstract. 2-Aminoimidazole-4,5-dicarbonitrile, $C_5H_3N_5$, $M_r = 133\cdot14$, monoclinic, $C2/m$, $a = 11\cdot764$ (4), $b = 9\cdot855$ (10), $c = 11\cdot656$ (4) Å, $\beta = 116\cdot54$ (3)°, $V = 1209$ (1) Å^3, $Z = 8$, $D_m = 1\cdot41$ (2), $D_x = 1\cdot46$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0\cdot7107$ Å, $\mu = 0\cdot66$ cm^{-1}, $F(000) = 544$, $T = 183$ K, $R(F) = 0\cdot064$ for 1425 independent reflections. There are two independent half molecules in the asymmetric unit, each of which lies perpendicular to a mirror plane. Each molecule forms six hydrogen bonds with neighboring molecules which may explain the unusually high decomposition temperature of 543 K. The molecules form hydrogen-bonded zigzag sheets about the $(\bar{2}02)$ planes.

Introduction. Cyanoimidazoles are important as intermediates in the formation of pyrimidine bases from hydrogen cyanide. They are also used in the preparation of ligands for stacked metal complexes as described by Rasmussen, Bailey & Bayón (1984) and Rasmussen, Bailey, Bayón & Butler (1984). The sample was prepared (Rasmussen, 1984) using the method of Sheppard & Webster (1973) who report a very high decomposition temperature of 543 K which is to be contrasted with a melting point of 363–364 K for imidazole (*The Merck Index*, 1976). This investigation is part of a continuing study of the properties of other imidazoles and their acid salts.

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Experimental. Powder was supplied by P. G. Rasmussen, recrystallized from ethanol–water mixture, a crystal $0\cdot80 \times 0\cdot25 \times 0\cdot10$ mm was mounted on a glass fiber, 25 reflections were scanned to obtain the unit-cell parameters, intensities of 1425 independent reflections were measured with a CAD-4 diffractometer in the ranges $0 \le \theta \le 28°$, $-15 \le h \le 15$, $0 \le k \le 13$, $0 \le l \le 15$. Density measured by flotation. No absorption corrections made. Three standard reflections measured periodically showed no significant deviations. 171 reflections with $F_o < 3\sigma$ were considered unobserved.

Structure solution using *MULTAN* (Germain, Main & Woolfson, 1971), full-matrix least-squares refinements on I_{obs} in *SHELX*76 (Sheldrick, 1976), amino hydrogens found from an $F_o - F_c$ synthesis and refined isotropically, C and N atoms refined anisotropically, and the half H atoms between N(3) atoms were fixed at $\frac{1}{3}$ and $\frac{2}{3}$ the distance between the ring N atoms of adjacent molecules. $R(F) = 0\cdot064$, $wR = 0\cdot081$, $S = 1\cdot07$, $w = 1\cdot000/[\sigma^2(F) + 0\cdot0070F^2]$, $\Delta/\sigma_{max} = 0\cdot07$, $\Delta\rho_{max} = 0\cdot45$, $\Delta\rho_{min} = -0\cdot31$ e Å^{-3}. Atomic scattering factors for non-H atoms were from *International Tables for X-ray Crystallography* (1968, Vol. III) and for hydrogens from Stewart, Davidson & Simpson (1965).‡

‡ An attempt was made to refine this structure in space group *C2*. The resulting parameters gave a structure with exceptionally large deviations between bond distances on opposite sides of the imidazole ring and thermal parameters for N(3′) which led to a non-positive-definite thermal ellipsoid.

Table 1. *Fractional positional parameters, B_{eq} values for non-H atoms and B_{iso} values for H atoms, with e.s.d.'s in parentheses*

$$B_{eq} = 8\pi^2(U_{11} + U_{22} + U_{33} + 2U_{13}\cos\beta).$$

	x	y	z	B_{eq}/B_{iso} (Å²)	Occupancy
N(1A)	0·6901 (3)	0·0	0·0669 (3)	1·93	1·0
C(2A)	0·7418 (3)	0·0	0·1946 (3)	1·25	1·0
N(3A)	0·7706 (2)	0·1131 (2)	0·2668 (2)	1·22	1·0
C(4A)	0·8208 (2)	0·0697 (2)	0·3931 (2)	1·27	1·0
C(5A)	0·8683 (2)	0·1614 (2)	0·4985 (2)	1·38	1·0
N(6A)	0·9091 (2)	0·2363 (2)	0·5824 (2)	1·81	1·0
H(1A)	0·6695 (19)	0·0932 (22)	0·0218 (19)	2·4 (2)	1·0
H(3A*)	0·7558	0·2044	0·2515	3·6	0·5
N(1B)	0·4238 (3)	0·0	0·2907 (3)	2·13	1·0
C(2B)	0·2972 (3)	0·0	0·2461 (3)	1·24	1·0
N(3B)	0·2262 (2)	0·1130 (2)	0·2204 (2)	1·26	1·0
C(4B)	0·1020 (2)	0·0695 (2)	0·1747 (2)	1·21	1·0
C(5B)	−0·0025 (2)	0·1613 (2)	0·1324 (2)	1·33	1·0
N(6B)	−0·0856 (2)	0·2363 (2)	0·0959 (2)	1·80	1·0
H(1B)	0·4660 (21)	0·0537 (2)	0·3181 (22)	5·0 (2)	1·0
H(3B)*	0·2410	0·2044	0·2361	3·6	0·5

* These half hydrogens were not refined.

Table 2. *Selected bond distances (Å), bond angles (°) and hydrogen-bond parameters (Å, °), with e.s.d.'s in parentheses*

	Molecule A	Molecule B
N(1)—H(1)	1·03 (2)	0·70 (3)
N(1)—C(2)	1·334 (4)	1·341 (4)
C(2)—N(3)	1·347 (2)	1·343 (2)
N(3)—C(4)	1·386 (2)	1·381 (2)
C(4)—C(4')	1·373 (4)	1·371 (4)
C(4)—C(5)	1·423 (3)	1·423 (3)
C(5)—N(6)	1·145 (3)	1·147 (3)
H(1)—N(1)—H(1')	126 (5)	98 (5)
H(1)—N(1)—C(2)	117 (3)	128 (5)
N(1)—C(2)—N(3)	124·1 (1)	124·0 (1)
N(3)—C(2)—N(3')	111·7 (3)	112·2 (3)
C(2)—N(3)—C(4)	106·0 (2)	105·8 (2)
N(3)—C(4)—C(4')	108·0 (3)	108·0 (3)
N(3)—C(4)—C(5)	122·4 (2)	122·5 (2)
C(4')—C(4)—C(5)	129·4 (5)	129·4 (4)
C(4)—C(5)—N(6)	178·1 (2)	178·1 (2)

	N—N	N—H	H···N	∠N—H···N
N(1A)—H(1A)···N(6B)	3·127 (2)	1·03 (2)	2·11 (2)	167 (5)
N(1B)—H(1B)···N(6A)	3·195 (3)	0·70 (3)	2·50 (2)	172 (5)
N(3A)—H(3A)···N(3B)	2·756 (2)			

Discussion. There are two half molecules of 2-amino-4,5-dicyanoimidazole in the asymmetric unit which lie perpendicular to mirror planes. Table 1 lists the atomic coordinates and equivalent isotropic temperature factors. Bond distances and angles are listed in Table 2. The labels of the atoms are shown in Fig. 1.* Unsubstituted imidazole does not have mirror symmetry since one of the ring N atoms has an H

* Lists of structure factors, anisotropic thermal parameters and least-squares-molecular-planes data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. 53197 (9 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
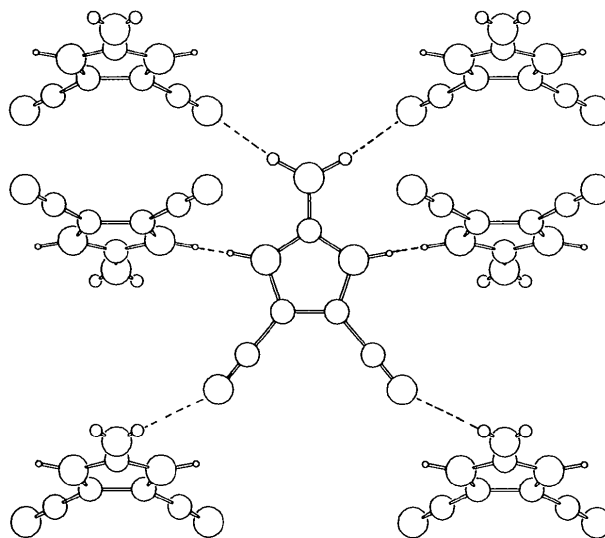

Fig. 2. Hydrogen bonding around one molecule.

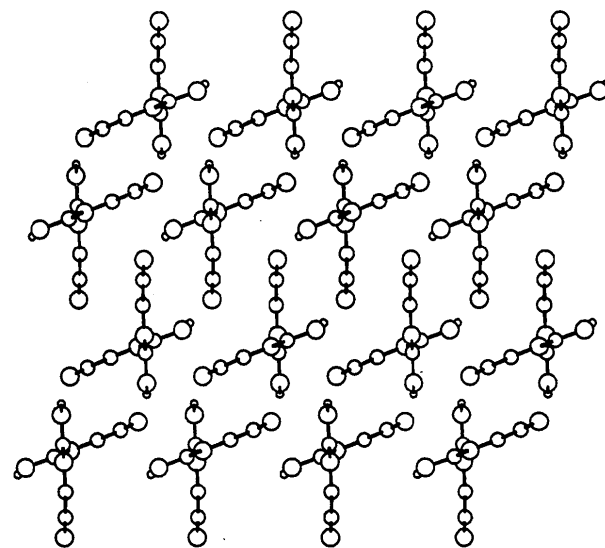Fig. 1. Thermal-ellipsoid plot of two independent molecules showing the numbering scheme.

Fig. 3. Packing diagram in the [010] direction.

atom attached, while the other does not (Craven, McMullan, Bell & Freeman, 1977). In order to compare the effects of substituents on the bond distances in 2-amino-4,5-dicyanoimidazole it is necessary to average the non-equivalent bonds in the low-temperature imidazole structure. Also comparison is best made with the bond distances uncorrected for thermal motion since no such corrections have been made in the present work. There are no significant differences in bond angles between the two structures. The average N(3)—C(4) bond distance of 1·384 (2) Å is significantly longer than the value of 1·365 Å reported for imidazole, and similarly the C(4)—C(4') distance of 1·372 (4) Å is significantly longer than the imidazole value of 1·359 Å. This may be due to the electron-withdrawing tendency of the cyano groups at this end of the molecule.

The high decomposition temperature of this compound may be due to the six hydrogen bonds formed by each molecule with its neighbors as illustrated in Fig. 2. There are strong hydrogen bonds of length 2·756 (2) Å between N(3) atoms in different molecules. Each molecule forms two weaker hydrogen bonds from amino N—H to cyano groups in neighboring molecules, of length 3·195 Å, and two additional non-equivalent hydrogen bonds from the cyano groups to the N—H groups in neighboring molecules, of length 3·127 Å. The extension of this pattern forms sheets of molecules in the (2̄02) crystal planes. This result is in agreement with the observed

infrared spectrum of the solid (Rasmussen, 1984) which shows several peaks in the N—H region. In order to accommodate this pattern of hydrogen bonding, both molecules A and B are bent significantly out of plane with C(4) 0·05 and 0·04 Å respectively, from the least-squares plane. In comparison, imidazole forms only two N—H···N hydrogen bonds per molecule (Craven et al., 1977).

The crystal packing is shown in Fig. 3.

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Structure of the 2:1 Complex of 2-[4,5-Bis(methylthio)-1,3-dithiol-2-ylidene]-1,3-dithiolo[4,5-d]dithiole (BMDMTF) and 7,7',8,8'-Tetracyano-p-quinodimethane (TCNQ)*

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Abstract. BMDMTFNTCNQ (2/1), $2C_9H_8S_8.C_{12}H_4N_4$, $M_r = 949.46$, triclinic, $P\bar{1}$, $a = 8.570$ (3), $b = 10.098$ (4), $c = 12.217$ (4) Å, $\alpha = 98.97$ (3), $\beta = 77.67$ (3), $\gamma = 107.14$ (3)°, $V = 982.09$ Å³, $D_x = 1.603$ g cm⁻³, $Z = 1$, $\lambda(Cu\ K\alpha) = 1.5418$ Å, $\mu = 80.84$ cm⁻¹, $F(000) = 484$, $T = 295$ K, $R = 5.5\%$ ($wR = 4.3\%$) for 2373 observed reflections. The generally planar BMDMTF (D) and TCNQ (A) molecules follow each other in ADDADD order in the [1̄20] direction with their molecular planes mutually arranged in a common plane parallel to (211); the

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* TCNQ is 2,2'-(2,5-cyclohexadiene-1,4-diylidene)bispropanedinitrile.