Crystal Structures of Condensation Products of Malononitrile. V.

2,4-Diamino-3,5-dicyano-6-cyanomethylpyridine*

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2,4-Diamino-3,5-dicyano-6-cyanomethylpyri-dine, a trimer of malononitrile, crystallizes in space group $P\bar{1}$ with lattice parameters $a = 4.947(1)$, $b = 9.546(2)$, $c = 10.675(2)$ Å, $\alpha = 69.91(2)$, $\beta = 80.94(2)$, $\gamma = 76.36(2)°$. 770 X-ray reflections were recorded as observed on an automatic four-circle diffractometer. The structure was refined by full-matrix least squares methods ($R_w = 6.0$ %, $R = 5.8$ %). The molecule is essentially planar apart from the cyano group and hydrogen atoms of the $CH_2(CN)$ group; the dihedral $N-C-C-(CN)$ angle is $53°$. The hydrogen atoms of the amino groups are engaged in hydrogen bonding to cyano nitrogen atoms and the ring nitrogen atom of neighbouring molecules, the $N\cdots N$ contacts ranging from 3.00 to 3.16 Å.

Three trimers of malononitrile, called I, II, and III, were described by Schenk and Finken [1] in 1928 and several structures for the trimers have since then been proposed. Trimer II, obtained by the reaction of malononitrile with gaseous ammonia in benzene, has been shown independently by Atkinson and Johnson [2] and Taguchi and Matsuura [3] to be ammonium 2-cyanomethyl-1,1,3,3-tetracyanopropenide and the crystal structure of the corresponding potassium salt has been determined.[4] Trimer I was synthesized by reaction of malononitrile with sodium ethanolate. From considerations based on IR-, NMR-, and mass spectra Taguchi and Matsuura [3] and Takeshima et al.[5] proposed the structure to be 2,4-diamino-3,5-dicyano-6-cya-nomethylpyridine, a finding which is confirmed by the present X-ray investigation. Trimer III which is obtained by pyrolysis of II, shows close chemical similarity to I. The formula 2,6-diamino-3,5-dicyano-4-cyanomethylpyridine

seemed reasonable from IR- and NMR-spectra [5] and an X-ray structure investigation of this compound has been initiated in our laboratory.

Ducker and Gunter [7] have recently discussed and summarized different structures postulated earlier for the three trimers. According to Ducker and Gunter an unambiguous distinction between such complex structures cannot be made on the spectral evidence reported. By performing alternative syntheses they have shown that trimer I and III are in fact 2,4-diamino-3,5-dicyano-6-cyanomethylpyridine and 2,6-diamino-3,5-dicyano-4-cyanomethylpy-ridine, respectively.

EXPERIMENTAL

Trimer I was synthesized as described by Schenk and Finken [1] and crystallized from water as transparent brown platy needles. The crystals showed a curved appearance and the reflections on Weissenberg diagrams (Laue symmetry $\bar{1}$) were elongated. It was found difficult to obtain crystals suitable for an investigation of high accuracy and accordingly a rapid data collection routine was applied. Several crystals were rejected when examined in the X-ray beam. Finally, a crystal cut to a rhomb shaped plate ($0.35 \times 0.14 \times 0.05$ mm^3) and mounted in a general orientation on a Syntex $P\bar{1}$ diffractometer gave narrow peaks by ω scan for several reflections. This crystal was used for all measurements.

Intensity data were collected using graphite-monochromated MoKα radiation and utilizing the ω scan technique with a scan range of $1°$ and a scan speed of $2°$ min^{-1}. Background counts were registered for a total time of 0.5 of the integration time $\pm 1°$ off the peak position. Three standard reflections were monitored after every 50 reflections and their intensities showed no decrease with time. One half of the reciprocal sphere was examined out to $2\theta = 45°$. All data

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Table 1. Final atomic parameters. Fractional coordinates ($\times 10^4$), thermal parameters ($\times 10^4$), and the principal values for the r.m.s. amplitudes of vibration ($\text{Å} \times 10^2$) are listed for the heavy atoms. The temperature factor is given by $\exp - (B11h^2 + B22k^2 + B33l^2 + B12hk + B13hl + B23kl)$. Fractional coordinates ($\times 10^3$) and isotropic temperature factors (Å^2) are listed for the hydrogen atoms. For numbering of atoms, see Fig. 1.

	x	y	z	B11(B)	B22	B33	B12	B13	B23	u1,u2,u3
C1	1864(10)	7600(5)	1142(5)	495(32)	97(8)	84(7)	-24(23)	-172(24)	-80(11)	26,19,16
C2	3339(10)	6106(5)	1786(4)	450(29)	72(7)	66(6)	-6(21)	-77(22)	-60(10)	24,18,16
C3	5185(9)	5887(5)	2715(5)	339(27)	75(7)	81(6)	-3(22)	-55(21)	-54(11)	21,20,16
C4	5348(10)	7166(5)	3048(5)	397(28)	90(7)	90(6)	-8(22)	-125(22)	-79(11)	24,18,18
C5	3734(11)	8573(5)	2421(5)	525(32)	79(8)	128(7)	5(24)	-229(27)	-95(12)	29,20,16
C6	2955(10)	4869(6)	1412(6)	386(28)	96(8)	76(6)	-54(22)	-38(21)	-47(12)	22,20,19
C7	7227(11)	7009(5)	4013(5)	440(29)	77(7)	111(7)	5(22)	-117(26)	-81(11)	25,21,16
C8	3799(14)	9951(6)	2809(7)	604(39)	111(8)	197(11)	99(29)	-384(33)	-167(15)	36,20,18
C9	933(16)	10684(6)	3160(6)	828(48)	97(8)	135(9)	24(33)	-354(34)	-93(14)	35,20,19
N1	2083(9)	8800(4)	1485(4)	600(28)	84(6)	127(6)	35(19)	-315(22)	-94(10)	31,18,17
N2	187(11)	7883(5)	186(5)	778(33)	85(7)	125(7)	17(24)	-364(25)	-84(10)	34,19,17
N3	2622(10)	3885(5)	1110(4)	788(33)	111(7)	112(6)	-185(23)	-73(21)	-101(11)	30,24,18
N4	6716(10)	4516(5)	3290(5)	487(29)	91(7)	123(7)	54(22)	-192(21)	-81(11)	28,21,17
N5	8776(10)	6829(5)	4769(5)	563(30)	148(8)	144(7)	39(23)	-287(25)	-112(12)	32,23,19
N6	-1290(13)	11260(6)	3408(6)	796(41)	150(9)	213(9)	32(29)	-164(30)	-201(14)	35,30,21
H1	-83(11)	891(6)	-20(5)	4.9(0.7)						
H2	0(11)	728(6)	-14(5)	*						
H3	662(11)	370(6)	304(5)	*						
H4	794(11)	439(6)	374(5)	*						
H5	511(14)	984(7)	355(7)	8.7(1.3)						
H6	524(14)	1069(8)	207(6)	*						

Table 2. Bond distances, bond angles, hydrogen bond distances, and hydrogen bond angles.

BOND DISTANCES (A)

N1-C1	1.348(6)	C5-N1	1.318(5)	C3-N4	1.338(6)	C8-C9	1.478(10)	N4-H3	0.92(5)
C1-C2	1.426(6)	C1-N2	1.332(6)	C4-C7	1.441(7)	C9-N6	1.143(7)	N4-H4	0.79(5)
C2-C3	1.383(6)	C2-C6	1.430(7)	C7-N5	1.143(6)	N2-H1	0.97(5)	C8-H5	1.06(6)
C3-C4	1.406(6)	C6-N3	1.144(6)	C5-C8	1.517(7)	N2-H2	0.80(6)	C8-H6	1.14(7)
C4-C5	1.391(6)								

BOND ANGLES (°)

C5-N1-C1	118.6(4)	C2-C3-C4	117.1(4)	C4-C5-C8	120.1(4)	C1-N2-H1	120(3)
N1-C1-C2	121.2(4)	C2-C3-N4	121.7(4)	C8-C5-N1	116.3(4)	C1-N2-H2	126(4)
•N1-C1-N2	116.6(4)	N4-C3-C4	121.3(4)	C5-C8-C9	110.2(5)	H2-N2-H1	114(5)
N2-C1-C2	122.1(4)	C3-C4-C5	119.5(4)	C2-C6-N3	179.3(5)	C3-N4-H3	120(3)
C1-C2-C3	119.8(4)	C3-C4-C7	119.6(4)	C4-C7-N5	177.1(5)	C3-N4-H4	123(4)
C1-C2-C6	118.8(4)	C7-C4-C5	120.9(4)	C8-C9-N6	178.8(6)	H4-N4-H3	116(5)
C6-C2-C3	121.3(4)	C4-C5-N1	123.6(4)				

HYDROGEN BOND LENGTHS (A)				HYDROGEN BOND ANGLES (°)		EQUIV. POS.	
N2•••N1(1)	3.09	H1•••N1(1)	2.15	N2-H1•••N1(1)	163	1: -x,2-y,-z	
N2•••N3(2)	3.16	H2•••N3(2)	2.42	N2-H2•••N3(2)	155	2: -x,1-y,-z	
N4•••N6(3)	3.00	H3•••N6(3)	2.24	N4-H3•••N6(3)	139	3: 1+x,-1+y,z	
N4•••N5(4)	3.03	H4•••N5(4)	2.28	N4-H4•••N5(4)	160	4: 2-x,1-y,1-z	

were collected within 24 h. 770 of the 1204 independent reflections were recorded as observed ($I_{count} > 2\sigma(I_{count})$). A 4 % uncertainty because of experimental fluctuations was included in the estimated standard deviations in the net intensities; the uncertainties calculated from the standard reflections were 1.1, 0.6, and 3.5 %. No absorption correction was applied.

The cell dimensions were obtained by a least squares calculation based upon the 2θ values of 24 reflections. The computations have been carried out on a CYBER 74 with programs described elsewhere.[8] Figures have been prepared by ORTEP.[9] Atomic form factors were those of Doyle and Turner [10] except for hydrogen.[11] $\lambda(MoK\alpha) = 0.71069$ Å.

CRYSTAL DATA

2,4-Diamino-3,5-dicyano-6-cyanomethylpyridine, $C_9H_6N_6$, M.W. 198.0
Space group $P\bar{1}$, $Z = 2$, $F(000) = 204$.
$a = 4.947(1)$, $b = 9.546(2)$, $c = 10.675(2)$ Å, $\alpha = 69.91(2)$, $\beta = 80.94(2)$, $\gamma = 76.36(2)°$, $U = 458.5$ Å^3, $D_x = 1.434$ g cm^{-3}, a is the needle axis.

STRUCTURE DETERMINATION AND REFINEMENT

The reflections recorded as unobserved were scaled assuming the space group to be $P\bar{1}$. The $N(Z)$ plot and the Wilson ratio showed a hypercentric intensity distribution and the Wilson plot was far from linear. An assumed value of 3.0 Å^2 for the temperature factor was used in deriving the unitary structure factors. Application of symbolic addition procedures did only reveal molecular fragments. An essentially planar molecule was indicated by the high U-value of ($10\bar{2}$) (0.86) and from inspection of a sharpened Patterson map. The peaks close to the origin gave a good fit to the molecule, which was assumed to be the substituted pyridine as proposed from spectroscopical studies.[3,5] By moving the planar part of the molecule through the cell, and calculating the R value for 40 low-order reflections for each step, an R minimum of 42 % was obtained. The remaining cyano group was located by Fourier techniques.

Full-matrix least squares refinement of $M = \sum w\Delta F^2$ with $w = 1/\sigma^2(F_o)$ proceeded to an R_w index of 6.0 % for the observed reflections ($R = 5.8$ %). Initial positions of the hydrogen atoms were calculated from geometrical con-
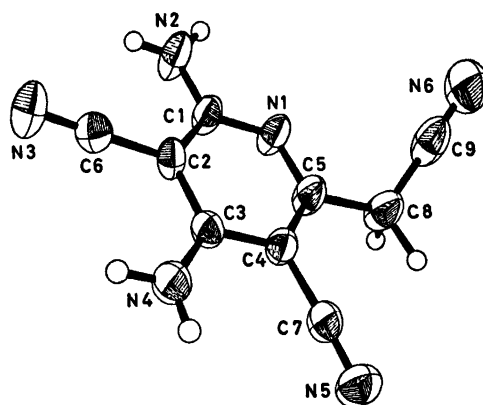
Fig. 1. A drawing of the molecule (50 % probability thermal motion ellipsoids for the heavy atoms).

siderations; positional parameters and a common thermal parameter for the amino and the methylene hydrogen atoms, respectively, were refined. The weight analysis indicated that the estimated standard deviations for the low angle data (sin $\theta/\lambda < 0.3$) might have been slightly underestimated.

The final atomic parameters together with the eigenvalues of the vibration tensors are listed in Table 1. The numbering of the atoms may be seen from Fig. 1. Bond distances and angles are given in Table 2. The standard deviations have been calculated from the correlation matrix of the last refinement cycle. The observed and calculated structure factors are available from the authors upon request.

DISCUSSION

Molecular orbital calculation of π-electron densities of 2,4-diamino-3,5-dicyanopyridine has been carried out by Lofthus, using a method [12] based on extended HMO theory. The calculated π-bond orders for the bonds within the ring starting from $N1 - C1$ were as follows: 0.488, 0.543, 0.548, 0.491, 0.673, and 0.571. If these values are applicable for the present molecule one would expect asymmetry within the ring. However, the accuracy of this investigation prevents a detailed discussion of the bond length values. By a conservative estimation of the standard deviations given in Table 2 all distances must be considered as normal.
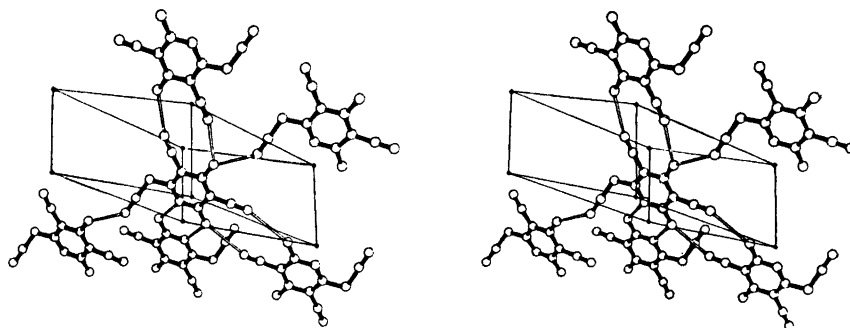
Fig. 2. One molecule and its hydrogen bonded neighbours. (The origin at the upper left corner; right handed crystal system; the *a* axis parallel to the plane of the paper.)

Table 3. Deviations (in Å) of atoms from a least squares plane through the ring. The distances from this plane to the centres of symmetry between hydrogen bonded neighbours are also given.

Atoms defining the plane		Other atoms and centres of symmetry			
C1	− 0.015	N2	− 0.051	C8	0.088
C2	0.028	C6	0.062	C9	1.217
C3	− 0.018	N3	0.097	N6	2.078
C4	− 0.005	N4	− 0.049	$0,\frac{1}{2},0$	0.205
C5	0.019	C7	− 0.047	0,1,0	− 0.325
N1	− 0.007	N5	− 0.100	$1,\frac{1}{2},\frac{1}{2}$	− 0.188

The crystal packing is presented in Fig. 2. All hydrogen atoms of the amino groups are engaged in hydrogen bonding (Table 2). Three pairs of hydrogen bonds between molecules related by centres of symmetry result in an infinite roughly planar arrangement of molecules in the (10$\bar{2}$) planes. The fourth hydrogen atom links translational related molecules of parallel layers by forming a bond to the nitrogen atom of the cyanomethyl group. The torsion of the cyanomethyl group is probably determined by these forces. The dihedral angle N1 − C5 − C8 − C9 is 52.9(7)°. The hydrogen bond lengths to the cyano nitrogen atoms are quite typical, as is the bond to the nitrogen atom of the ring (Refs. 13 − 16 and references therein).

The deviations of atoms from the least squares plane through the ring is presented in Table 3. The slight indication of a boat shaped ring becomes pronounced if the atom of the substituents are considered. The parallel planes are 3.46 Å apart and form an angle of 6.4° with (10$\bar{2}$) ($d_{10\bar{2}} = 3.32$ Å). The shortest *inter*-molecular contacts between heavy atoms are C···C of 3.32 Å and C···N of 3.22 Å.

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