

Crystal Structures of Condensation Products of Malononitrile

IV. 2-Amino-1,1,3-tricyanopropene ("Dimeric Malononitrile"), Space Group $P2_1$

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The crystals are monoclinic, space group $P2_1$, with cell dimensions $a = 5.28_1$ Å, $b = 5.42_0$ Å, $c = 11.56_6$ Å, and $\beta = 96.2_4^\circ$. 606 reflections were recorded as observed on an automatic four-circle diffractometer. The structure was refined by full-matrix least squares methods ($R_w = 4.0$ %, $R = 4.8$ %). Bond distances and angles in the molecule are essentially the same as those found in the crystal modification previously investigated. The dihedral angle $(H_2N) - C - CH_2 - (CN)$ is 12° . *Inter*-molecular hydrogen bonds between the amino group and nitrogen atoms of cyano groups form infinite two-dimensional networks parallel to the (001)-planes.

The present work was undertaken as part of a program of X-ray crystallographic studies on condensation products of malononitrile. The compounds so far investigated are the potassium salts of 2-cyanomethyl-1,1,3,3-tetracyanopropene¹ and 1,1,3-tricyanopropanone,² and 2-amino-1,1,3-tricyanopropene³ (space group $P2_1/c$). The last compound has also been studied by Zacharias.⁴ Refs. 3 and 4 will be referred to as $C_6N_4H_4(A)$ and $C_6N_4H_4(A')$, respectively. A comparison of these may be found in the discussion.

When $C_6N_4H_4$ synthesized by a base catalyzed dimerisation of malononitrile was recrystallized from an unpolar solvent (benzene or petroleum ether containing traces of acetone) two different crystal forms were obtained.⁵ One was slightly coloured (yellow to brownish) and had the space group $P2_1/c$; the other form was colourless with crystals of space group $P2_1$. The latter will be referred to as $C_6N_4H_4(B)$. Its crystal structure is described in the present paper.

DTA thermograms of $C_6N_4H_4(B)$ were found to be strongly dependent on the heating rate. The diagram obtained with high heating rate indicated combined melting and transformation to $C_6N_4H_4(A)$ at about $10^\circ C$ below the melting point of $C_6N_4H_4(A)$ ($171^\circ C$). Further cooling and heating gave thermograms identical to those of $C_6N_4H_4(A)$.⁵ The diagrams are consistent with $C_6N_4H_4(B)$ being the stable form at room temperature. However, a transforma-

tion in the solid phase may be impeded by the energy barrier between the modifications. The possibility of $C_6N_4H_4(B)$ being unstable at room temperature can thus not be excluded.

The major differences between the IR-spectra of the two crystal forms are found in the N-H stretching and N-H bending absorption bands.⁵

CRYSTAL DATA

The crystals of $C_6N_4H_4(B)$ showed typical dendritic growth and it was difficult to obtain crystals suitable for the data collection. The colourless thin plates (001) belong to the monoclinic system with space group $P2_1$. The cell dimensions determined on a manual four-circle diffractometer (CuK radiation), and estimated standard deviations, are: $a = 5.2809(8)$ Å, $b = 5.4204(8)$ Å, $c = 11.5668(26)$ Å, and $\beta = 96.24(2)^\circ$. The unit cell contains two molecules of one enantiomer ($\rho_{\text{calc}} = 1.332$ g cm⁻³, $\rho_{\text{obs}} = 1.32$ g cm⁻³).

About 810 reflections with $2\theta < 55^\circ$ were measured on an automatic four-circle diffractometer. (MoK α radiation, highly oriented graphite crystal monochromator, and $\omega/2\theta$ scan techniques were applied.) 606 reflections were recorded as observed, having intensities greater than twice their standard deviations obtained from counter statistics with a 2 % uncertainty in the measurements added. No absorption correction was made. An irregular elliptic plateformed crystal with maximum dimensions of $0.36 \times 0.15 \times 0.03$ mm³ was used for all X-ray measurements.

The computer programs used are described in Ref. 6.

STRUCTURE DETERMINATION

The structure was determined by a method analogous to that applied for $C_6N_4H_4(A)$. Three possible orientations of the planar part of the molecule were found from a sharpened Patterson synthesis. Next the model was moved stepwise through the cell, R -values for about 50 low-order reflections being calculated for each step. All but two sites corresponding to R -minima could be excluded by packing considerations. A Fourier synthesis for 270 low-order reflections with phases based on a parameter set with an R -minimum of 34 % revealed the remaining cyano group. The parameters of the heavy atoms were refined by the "minimum residual method"⁷ to an R -value of 4.5 %, including the 60 largest structure factors.

The parameters were further refined by full-matrix least squares techniques to a final R_w -value of 4.0 % for the 606 observed reflections ($R = 4.8$ %). Starting positions for the hydrogen atoms were calculated from geometrical considerations. Refinement of individual isotropic temperature factors for the hydrogen atoms gave unreasonable values, and a common temperature factor was eventually refined. The weight analysis based on the standard deviations in intensities showed negligible intensity dependence except for the smallest F -values. No secondary extinction effects was observed. The atomic form factors for carbon and nitrogen were those of Cromer and Waber,⁸ and that for hydrogen was taken from Stewart *et al.*⁹ A final difference Fourier map contained no larger density fluctuations than ± 0.20 e Å⁻³.

Table 1. Continued.

<i>h</i>	<i>k</i>	<i>l</i>	<i>F_o</i>	<i>F_c</i>	<i>h</i>	<i>k</i>	<i>l</i>	<i>F_o</i>	<i>F_c</i>	<i>h</i>	<i>k</i>	<i>l</i>	<i>F_o</i>	<i>F_c</i>	<i>h</i>	<i>k</i>	<i>l</i>	<i>F_o</i>	<i>F_c</i>
3	2	-2	41	43	3	5	4	21	28	4	2	3	54	52	5	1	-2	45	46
3	2	-1	69	69	3	5	5	22	17	4	2	4	52	47	5	1	-1	36	36
3	2	0	14	15	3	6	-3	25	27	4	2	5	30	25	5	1	0	35	36
3	2	2	58	59	3	6	-2	32	33	4	2	6	27	25	5	1	1	23	27
3	2	3	76	80	3	6	1	23	27	4	2	8	27	26	5	1	2	41	39
3	2	4	28	31	3	6	2	17	17	4	3	-9	28	25	5	1	3	51	49
3	2	5	20	19	3	6	3	21	27	4	3	-8	18	17	5	1	4	35	35
3	2	7	21	21	4	0	-12	53	50	4	3	-7	19	22	5	1	6	23	19
3	2	8	38	40	4	0	-10	44	43	4	3	-6	27	26	5	2	-10	16	3
3	3	-12	18	19	4	0	-9	15	17	4	3	-4	24	26	5	2	-6	29	25
3	3	-11	23	19	4	0	-8	57	56	4	3	-3	28	28	5	2	-6	14	14
3	3	-8	33	35	4	0	-7	98	97	4	3	-1	18	20	5	2	-7	16	15
3	3	-6	58	57	4	0	-6	142	147	4	3	0	45	43	5	2	-6	27	27
3	3	-5	62	62	4	0	-5	49	50	4	3	1	88	82	5	2	-4	17	13
3	3	-4	65	67	4	0	-4	57	58	4	3	2	50	49	5	2	-3	36	40
3	3	-3	51	54	4	0	-3	53	54	4	3	4	42	42	5	2	-1	18	22
3	3	-2	52	50	4	0	-1	60	79	4	3	5	15	12	5	2	-1	18	22
3	3	-1	37	34	4	0	0	37	36	4	3	6	29	28	5	2	2	68	64
3	3	0	121	124	4	0	1	57	60	4	3	7	20	20	5	2	3	39	35
3	3	1	53	59	4	0	2	44	45	4	4	-7	16	8	5	2	4	19	24
3	3	2	98	100	4	0	4	35	33	4	4	-6	33	37	5	3	-3	0	27
3	3	3	18	21	4	0	5	14	11	4	4	-4	23	23	5	3	-2	30	26
3	3	4	43	66	4	1	-10	31	28	4	4	-3	44	41	5	3	-1	19	22
3	3	5	72	77	4	1	-9	17	19	4	4	0	30	32	5	3	0	33	33
3	3	6	30	39	4	1	-8	48	44	4	4	1	22	25	5	4	-4	31	27
3	3	7	18	21	4	1	-7	53	50	4	4	2	34	30	5	4	-4	18	3
3	3	9	25	30	4	1	-6	27	29	4	4	3	32	28	5	4	-1	29	25
3	4	-10	26	22	4	1	-5	42	43	4	4	4	38	34	5	4	0	20	17
3	4	-9	17	18	4	1	-4	52	53	4	4	6	40	36	5	4	4	20	18
3	4	-8	31	25	4	1	-3	34	32	4	4	7	19	17	6	0	4	16	18
3	4	-7	33	26	4	1	-2	15	16	4	5	-5	17	12	6	0	-6	24	27
3	4	-6	19	14	4	1	-1	46	49	4	5	-4	34	29	6	0	-6	24	27
3	4	-5	44	41	4	1	0	62	63	4	5	-3	20	20	6	0	-3	22	24
3	4	-4	22	17	4	1	1	13	21	4	5	-2	17	14	6	0	-2	25	33
3	4	-3	24	26	4	1	2	14	13	4	5	-1	18	18	6	0	0	34	36
3	4	-2	21	24	4	1	4	30	34	4	5	2	20	20	6	0	2	26	26
3	4	-1	76	79	4	1	5	24	23	5	0	-11	28	32	6	0	5	24	25
3	4	0	70	69	4	1	10	19	13	5	0	-10	23	21	6	1	-7	22	18
3	4	1	25	38	4	1	9	17	16	5	0	-7	27	31	6	1	-6	19	20
3	4	3	18	34	4	2	-12	26	20	5	0	-6	65	67	6	1	-5	27	29
3	4	4	17	17	4	2	-9	26	27	5	0	-4	14	12	6	1	-5	27	29
3	4	5	32	34	4	2	-8	31	31	5	0	-3	21	22	6	1	0	17	15
3	5	-6	27	24	4	2	-7	22	18	5	0	-2	18	16	6	1	3	24	23
3	5	-7	19	21	4	2	-6	24	25	5	0	1	21	20	6	1	4	22	22
3	5	-6	32	33	4	2	-5	48	51	5	0	5	27	29	6	1	5	21	20
3	5	-5	49	45	4	2	-4	63	64	5	0	6	16	11	6	2	-4	38	39
3	5	-4	41	40	4	2	-3	33	35	5	1	-10	22	20	6	2	-3	26	21
3	5	-3	20	19	4	2	-2	64	63	5	1	-8	33	36	6	2	-2	39	38
3	5	-2	29	23	4	2	-1	39	36	5	1	-6	53	53	6	2	0	19	17
3	5	0	37	42	4	2	0	39	36	5	1	-5	39	37	6	3	-3	24	17
3	5	2	24	40	4	2	1	67	66	5	1	-4	66	65	6	3	0	20	18
3	5	3	19	15	4	2	2	83	80	5	1	-3	15	10	6	3	1	22	20

Observed and calculated structure factors are listed in Table 1 and atomic parameters in Table 2. The numbering of atoms is given in Fig. 1. The eigenvalues of the atomic vibration tensors are presented in Table 3.

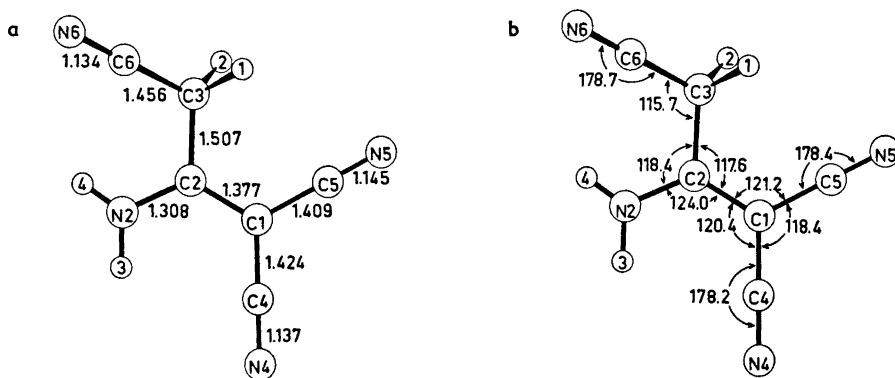


Fig. 1. Schematical drawing of the molecule showing bond distances (a) and angles (b) (uncorrected values). Small circles indicate hydrogen atoms.

Table 2. Fractional atomic coordinates and thermal parameters with estimated standard deviations ($\times 10^5$). The temperature factor is given by $\exp -(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)$. A common isotropic temperature factor (\AA^2) is given for the hydrogen atoms. For numbering of atoms, see Fig. 1.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C1	12384	-32	18509	2479	2519	582	1178	501	103
	57	91	26	136	139	28	267	98	124
C2	23402	-19632	24753	2472	2106	561	-256	563	-398
	57	93	26	137	132	26	259	94	106
C3	14864	-24650	36549	3667	2390	697	1263	1072	44
	76	96	30	172	148	33	305	121	123
C4	20783	6719	7652	3877	2780	725	1646	635	553
	62	89	32	167	164	31	290	116	125
C5	-7523	13651	22595	2956	2218	697	922	124	423
	65	100	28	146	128	30	279	107	118
C6	23633	-47801	41972	3470	2478	598	-535	945	-147
	71	91	33	153	141	28	283	103	125
N2	41233	-33604	21210	3989	2808	723	2343	1411	330
	60	91	26	160	129	31	266	104	118
N4	28121	11938	-906	6299	5416	906	2267	2103	1170
	61	105	27	180	191	31	346	118	137
N5	-23425	24744	26168	4404	3746	1119	3790	1136	344
	59	88	27	149	148	32	304	105	130
N6	30393	-65693	46353	5376	2683	949	426	811	807
	60	0	27	168	147	32	270	108	119
H1	-3260	-23635	35995	3.77					
	584	735	242	.44					
H2	20414	-13424	41914	»					
	666	733	309						
H3	46840	-30433	14634	»					
	600	762	275						
H4	48170	-44898	25625	»					
	635	763	280						

The root mean square discrepancy between "observed" atomic vibration components and those calculated from a rigid-body model¹⁰ is 0.0038 \AA^2 for the molecule. When the cyano group C6-N6 is omitted from the calculations the discrepancy is 0.0032 \AA^2 . In that case a negative eigenvalue of L as well as large standard deviations for the tensor elements of L results. This was also observed for the 2-cyanomethyl-1,1,3,3-tetracyanopropenide anion¹ when eight atoms in a similar geometrical arrangement were included in a TLS calculation, whereas analogous calculations for $C_6N_4H_4(A)$ and for the anion of 1,1,3-tricyanopropanone² resulted in reasonable eigenvalues.

"Riding" motion corrections¹¹ show that C1, C3, and N2 "ride" on C2, while C5 and C6 do not "ride" on C1 and C3, respectively.

Bond distances, bond angles, dihedral angles, and short contacts are listed in Table 4. Librational corrections correspond to the rigid-body calculation, except for $C\equiv N$ bonds which are corrected for "riding" motion. The "riding" corrected value for C2-N2 is 1.330 \AA . The standard deviations in bond lengths and angles have been calculated from the correlation matrix of the last least squares refinement cycle thus taking into account the positive correlation of about 0.5 between the y parameters of the heavy atoms. The estimated standard

Table 3. The root mean square amplitudes of vibration $(\bar{u}^2)^{\frac{1}{2}}$ (Å) and B -values (Å²) along the principal axes given by the components of a unit vector in fractional coordinates ($\times 10^3$).

Atom	$(\bar{u}^2)^{\frac{1}{2}}$	B	e_x	e_y	e_z
C1	.214	3.63	121	124	39
	.194	2.96	14	81	-77
	.164	2.12	-147	110	13
C2	.209	3.43	94	-83	69
	.178	2.51	161	84	-17
	.164	2.13	-39	142	50
C3	.247	4.83	154	52	52
	.201	3.19	54	107	-63
	.171	2.31	-98	141	29
C4	.254	5.08	143	96	42
	.214	3.63	-98	13	69
	.181	2.59	79	-157	32
C5	.222	3.91	-6	61	81
	.212	3.54	170	81	-2
	.165	2.15	86	-154	31
C6	.234	4.33	160	-43	50
	.189	2.83	30	179	18
	.180	2.57	99	15	-69
N2	.273	5.89	147	82	47
	.201	3.18	19	116	-66
	.166	2.17	-120	118	32
N4	.338	9.04	135	103	44
	.260	5.33	115	-147	8
	.205	3.30	69	44	-75
N5	.302	7.20	130	103	47
	.261	5.39	51	76	-73
	.174	2.40	-130	133	5
N6	.279	6.14	168	39	45
	.256	5.15	-89	64	66
	.185	2.71	5	-169	35

deviations of the cell parameters have been ignored. The standard deviations are 0.005 Å or less for bonds between heavy atoms and 0.3° and 0.4° for angles of 120° and 180°. When hydrogens are involved the standard deviations are 0.04 Å and 2.5° or 3.5°, the last value for angles defined by two hydrogen atoms. Uncorrected bond distances and angles may also be found in Fig. 1.

The deviations of atoms from various least squares planes are listed in Table 5. Fig. 2 is a schematical drawing of the structure viewed along b showing the hydrogen bonding system. Deviations from least squares planes, dihedral angles, *etc.* have been given signs for convenient comparison with corresponding data for C₆N₄H₄(A) rather than the values obtained when calculated from the parameters listed in Table 2.

Table 4. Bond distances, bond angles, dihedral angles of the molecule, short *intra*-molecular contacts, hydrogen bond lengths and corresponding angles, and other short contacts (equivalent position numbers in parentheses as defined below). Estimated standard deviations in bond lengths between heavy atoms are 0.005 Å, in C-C-C and C-C-NH₂ angles 0.3°, and in C-C≡N 0.4°. Distances in parentheses are corrected for anisotropic thermal motion (see text).

Bond distances			Bond angles (°)	
C1-C2	1.377	(1.380)	C4-C1-C2	120.4
C2-C3	1.507	(1.515)	C5-C1-C2	121.2
C1-C4	1.424	(1.429)	C4-C1-C5	118.4
C1-C5	1.409	(1.416)	C1-C2-C3	117.6
C3-C6	1.456	(1.458)	C1-C2-N2	124.0
C2-N2	1.308	(1.321)	C3-C2-N2	118.4
C4-N4	1.137	(1.181)	C2-C3-C6	115.7
C5-N5	1.145	(1.188)	C1-C4-N4	178.2
C6-N6	1.134	(1.167)	C1-C5-N5	178.4
C3-H1	.95		C3-C6-N6	178.7
C3-H2	.90		C2-C3-H1	109
N2-H3	.86		C2-C3-H2	113
N2-H4	.85		C6-C3-H1	110
			C6-C3-H2	103
			H1-C3-H2	105
			C2-N2-H3	119
			C2-N2-H4	120
			H3-N2-H4	120
<i>Intra</i> -molecular contacts (Å)			Dihedral angles (°)	
C4··N2	2.83		C4-C1-C2-C3	175.8
C6··N2	2.78		C5-C1-C2-C3	-4.8
C4··H3	2.52		C4-C1-C2-N2	-2.1
C5··H1	2.54		C5-C1-C2-N2	177.3
C6··H4	2.41		C1-C2-C3-C6	169.9
			N2-C2-C3-C6	-12.0
Hydrogen bond lengths (Å)			Hydrogen bond angles (°)	
N2··N4(1)	3.00		N2-H3··N4	152
N2··N5(2)	2.95		N2-H4··N5	143
H3··N4(1)	2.21		H3··N4-C4	163
H4··N5(2)	2.22		H4··N5-C5	154
Other contacts (Å)				
C6··C5(3)	3.36			
C6··N5(3)	3.28			
C6··N6(4)	3.17			
N6··C3(5)	3.30			
N6··C3(6)	3.35			
N6··H1(5)	2.65			
N6··H2(3)	2.68			
N6··H2(6)	2.80			
1: (1-x, -½+y, -z)			2: (1+x, -1+y, z)	
3: (x, -1+y, z)			4: (1-x, ½+y, 1-z)	
5: (-x, -½+y, 1-z)			6: (1-x, -½+y, 1-z)	

The uncorrected bond distances of C₆N₄H₄(A), C₆N₄H₄(A'), and C₆N₄H₄(B) as well as the arithmetic mean values are given in Table 6.

Table 5. Deviations of atoms from some least squares planes (Å). Plane No. 1 is through all heavy atoms but the cyano group of $-\text{CH}_2(\text{CN})$, plane No. 2 is through the $\text{C}(\text{CN})_2$ group, and plane No. 3 through the remaining heavy atoms defining plane No. 1. Deviations of atoms not defining the planes in parentheses.

Atom	1	2	3
C1	0.006	-0.006	(-0.041)
C2	0.012	(-0.018)	0.000
C3	-0.073	(-0.128)	0.000
C4	-0.005	0.007	(-0.132)
C5	0.022	0.007	(0.019)
N2	0.050	(0.022)	0.000
N4	-0.034	-0.003	(-0.226)
N5	0.016	-0.003	(0.050)
H3	(0.057)		(-0.042)
H4	(-0.003)		(-0.029)

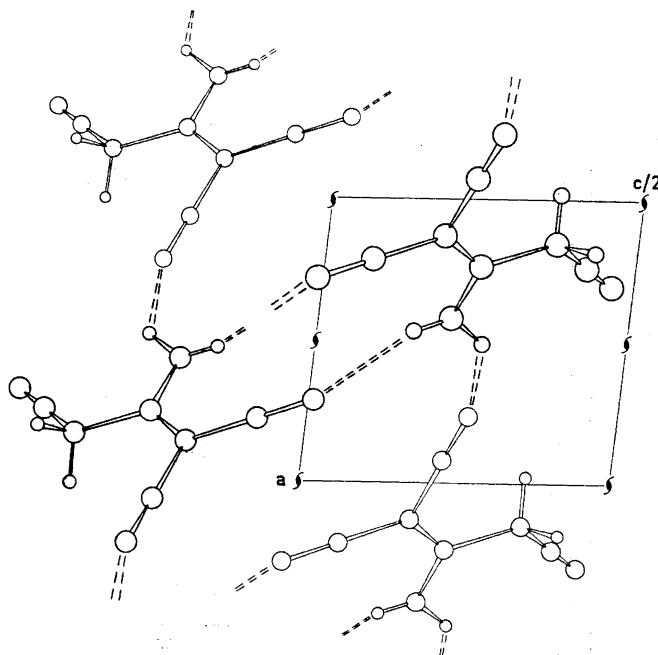


Fig. 2. Schematical drawing of the structure viewed along the b axis showing the packing and the hydrogen bond system.

DISCUSSION

In the following the results of the present study will be compared with those obtained for the $P2_1/c$ form. The two investigations of this form, $\text{C}_6\text{N}_4\text{H}_4(\text{A})$ and $\text{C}_6\text{N}_4\text{H}_4(\text{A}')$, give similar results. All bond lengths and angles agree within three times the estimated standard deviations, see Table 6, and

Table 6. Uncorrected bond distances (Å) of dimeric malononitrile from three crystal structure determinations and the arithmetic mean values. The estimated standard deviations are about 0.002, 0.004, and 0.005 Å for $C_6N_4H_4(A)$, $C_6N_4H_4(A')$, and $C_6N_4H_4(B)$, respectively.

Bond	$C_6N_4H_4(A)$	$C_6N_4H_4(A')$	$C_6N_4H_4(B)$	Mean
C1-C2	1.382	1.394	1.377	1.384
C2-C3	1.501	1.504	1.507	1.504
C1-C4	1.422	1.424	1.424	1.423
C1-C5	1.421	1.429	1.409	1.420
C3-C6	1.458	1.470	1.456	1.461
C2-N2	1.313	1.317	1.308	1.313
C4-N4	1.141	1.141	1.137	1.140
C5-N5	1.151	1.146	1.145	1.147
C6-N6	1.133	1.139	1.135	1.134

the atomic thermal parameters also correspond quite closely. However, the cell parameter values for b and c differ by nearly 1 %. The authors are not aware of systematical errors in their data. In neither case were any precautions taken to avoid impurities and the difference in unit cell dimensions may partly be due to differences of purity of the samples used. An even better agreement obtained between the bond lengths of one of the investigations of the $P2_1/c$ form and those calculated by using the cell parameters of one and atomic positions of the other may, however, indicate some systematical errors in the unit cell dimensions. The final R -values were 4.6 (A) and 7.3 % (A'), and the R_w -values were 4.1 and 9.7 %. Since the studies were based on diffractometer and photographic data, respectively, one would expect $C_6N_4H_4(A)$ to be the more accurate determination. The findings of the present investigation will therefore be compared with those of $C_6N_4H_4(A)$, which are given in parentheses.

The most striking difference between the conformations of the molecule in the two polymorphs occurs in the dihedral angle $(NH_2)-C-CH_2-(CN)$, which has values of 12° (B) and 27° (A). The torsional strain about C2-C3 is rather small, however, and whereas the amino hydrogen-carbon repulsion ($H4 \cdots C6$) decreases when the dihedral angle changes from 12° to 27° , the methylene hydrogen-carbon repulsion ($H1 \cdots C5$) increases. The energy differences between torsional conformers based on CNDO/2 calculations¹² are small. The energy varies less than 2 kcal/mol for $(NH_2)-C-CH_2-(CN)$ angle values from 0 to 150° . A flat minimum at about 60° and a maximum of 16 kcal/mol for 180° is obtained. The remaining atoms of the molecule were fixed coplanar with the amino group and C2 and C3 during these calculations. While π bond orders obtained by CNDO/2 may not be quantitatively accurate, the trends in these parameters usually offer some insight into the factors responsible for the trends in total energy. In agreement with the calculated energies the π bond orders and atomic charges of the planar part of the molecule remain nearly constant when the dihedral angle varies from 0 to 150° . The value of the dihedral angle is most probably determined by packing effects and the corresponding cyano group C6-N6 is indeed involved in all short *inter*-molecular contacts for both crystal forms.

The largest deviation of atoms from a least squares plane through the "planar" part of the molecule is 0.073 Å (0.063 Å) for C3 (Table 5, plane 1). The deviation from planarity is mainly caused by a bending of the C2–C3 bond out of the plane through the planar C(CN)₂ group (plane 2). A bending of the C(CN)₂ group about the C1–C2 bond which was found for C₆N₄H₄(A) is not observed. A small twist of the C(CN)₂ group about the C1–C2 bond from an ideally planar configuration is indicated by the deviations of N2 and C3 from plane 1 or by the deviations of C4, N4 and C5, N5 from plane 3 (through C2, C3, and N2). The angle between the planes 2 and 3 is 4.2° (6.2°) and C2 is 0.13 Å (0.16 Å) above the plane through C1, C3, and N2.

No bond distances are significantly different from those of C₆N₄H₄(A). However, bond angle values for C4–C1–C2 or C4–C1–C5, being 120.4° (121.6°) and 118.4° (117.2°), differs more than three times the standard deviations. The differences may be real and are probably caused by the hydrogen bonding systems. This is supported by the fact that the C4–N4 group bends slightly towards the amino hydrogen atom engaged in hydrogen bonding for both crystal forms thus also making a significant difference between the C1–C4–N4 angles. On the contrary, the bending of the C5–N5 group, if real, is in both cases found to be away from the amino hydrogen atom.

The thermal motions are fairly similar in the two crystal modifications. All but three atoms of C₆N₄H₄(B), namely C2, C5, and C6, have their largest vibrational amplitudes roughly normal to plane 1, which was the case for all atoms of C₆N₄H₄(A). N4 with *B* of 9.0 Å² (10.5 Å²) has the largest eigenvalue. The qualitative description of the motion of the molecules based on the "riding" corrections are alike. The results of rigid-body calculations are also similar, ignoring the fact that the molecules cannot strictly be treated as rigid bodies. The small energy differences between torsional conformers and the results of the TLS analysis earlier referred to supports this point of view. It is also difficult to differentiate between a rigid-body motion and an internal torsional motion about the C1–C2 bond. For both crystal forms the axes of libration are roughly parallel to this bond, normal to plane 1, and in plane 1 normal to C1–C2. The corresponding r.m.s. values are 6.6 (6.8), 3.0 (3.1), and 2.2° (1.2°). The reduced r.m.s. translational amplitudes are 0.199 (0.199), 0.184 (0.171), and 0.161 Å (0.163 Å).

The hydrogen bonding schemes are quite dissimilar for the two crystal forms. However, planar single chains are formed by *inter*-molecular hydrogen bonds (N2–H4···N5) between translational equivalent molecules in both modifications. The chains run along *a* + *b* in (B) and along *b* in (A) corresponding to identity periods of 7.56₉ Å and 7.54₁ Å. Plane 1 coincides with the analogous plane through all molecules of a chain, the plane normals making an angle of only 0.2° (0.6°). In the *P*2₁/*c* form all molecules in one chain are hydrogen bonded (by N2–H3···N4) to molecules in one parallel, screw related chain. In the *P*2₁ form hydrogen bonds between screw related chains are also formed, the chains running along *a* + *b* and *a* – *b*, respectively. One molecule is hydrogen bonded (by N2–H3···N4) to two translational equivalent chains. Each chain is thus linked to one of the screw related chains by one hydrogen bond only and an infinite two-dimensional network along *a* and *b* is formed, leading to the growth of plateformed crystals.

The hydrogen bonding system is shown in Fig. 2. Hydrogen bond lengths and angles are listed in Table 4. $N\cdots N$ distances of 2.95 (2.96) and 3.00 Å (3.05 Å), and $H3-N2\cdots N4$ and $H4-N2\cdots N5$ angles of 20 (24) and 27° (20°) are quite normal.³ An $N\cdots N$ distance of 3.10 Å for a similar hydrogen bond has been reported for diaminofumaronitrile.¹³ The nitrogen atoms hydrogen bonded to one amino group deviate 0.11 and 0.05 Å from plane 1. They are situated on the same side of the plane as N2 (with deviation of 0.05 Å). The plane normal of 1 makes an angle of 51.7° with *b*, corresponding to a molecule thickness of 3.36 Å (3.42 Å), and all *inter*-molecular distances between atoms of the planar parts of molecules are longer than 3.4 Å.

It is reasonable to expect that the energies of the two crystal modifications are very nearly the same. The molecular volumes are 165.4, 168.5, and 164.5 Å³ for (A), (A') and (B), respectively. A phase transformation would involve a rather drastic rearrangement of the molecules and the hydrogen bonding systems.

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