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The Molecular and Crystal Structure of Hydrogen Cyanide Tetramer (Diaminomaleonitrile)

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A three-dimensional crystal structure analysis of hydrogen cyanide tetramer has led to a location of all atoms with average standard deviations of 0·0025 Å for carbon and nitrogen atoms and 0·04 Å for hydrogens. The diaminomaleonitrile structure is proved. In its crystal setting the molecule has no symmetry. The two amino groups have different configurations, one being planar and one tetrahedral while both being involved in intermolecular N–H · · · N hydrogen bonds. An analysis is made of the anisotropic nature of the atomic thermal vibrations. Molecular orbital calculations have been made for this molecule and for tetracyanoethylene leading to π bond orders for all bonds. Order/length relationships for the carbon–carbon bonds are discussed in some detail.

1. Introduction

This investigation was undertaken with the object of establishing with certainty the molecular structure of hydrogen cyanide tetramer in the solid state. The history of chemical investigation of this compound is a long one, dating from its preparation by Lange (1873). Its molecular structure was in considerable doubt until Webb *et al.* (1955) showed by infrared absorption measurements and dipole moment measurements that the molecule is almost certainly diaminomaleonitrile (Fig. 1). Their conclusions have been supported by the subsequent work of Bredereck *et al.* (1956*a*, *b*) and of Robertson & Vaughan (1958) which involved infrared absorption measurements of some derivatives and some further study of the chemical properties of the tetramer. Wadsten & Andersson (1959), on the basis of a limited X-ray diffraction study of single crystals, proposed that the compound is a dimer of HCN in the solid state but their conclusions can be shown to be based on an incorrect interpretation of the Patterson function. Our results, providing conclusive proof for the diamomaleonitrile structure have been reported briefly (Penfold & Lipscomb, 1960).

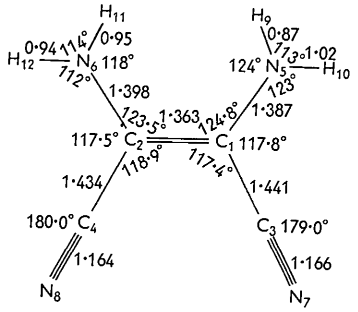

Fig. 1. The molecule of diaminomaleonitrile showing observed bond lengths and angles.

2. Experimental

Almost colourless needle shaped crystals elongated along the *c* axis were grown from aqueous ethanolic solution. The crystals slowly turned brown in sunlight but with no observable change in the X-ray diffraction pattern.

Crystallographic data

Unit cell parameters, assuming $\lambda = 1{\cdot}5418$ Å for Cu $K\alpha$ radiation were observed as follows:

$$a = 6{\cdot}44 \pm 0{\cdot}01,\ b = 18{\cdot}24 \pm 0{\cdot}03,\ c = 5{\cdot}22 \pm 0{\cdot}01\ \text{Å},\ \beta = 122{\cdot}0^\circ \pm 0{\cdot}5^\circ .$$

These are in agreement with the values reported by Sass & Donohue (1957) and Wadsten & Andersson (1959). Density observed (by flotation) 1·373 g.cm.$^{-3}$; calculated 1·378 for four tetramer molecules per unit cell. Linear absorption coefficient for Cu $K\alpha$ radiation 9·4 cm.$^{-1}$. Absent spectra: $0k0$ for k odd, and $h0l$ for l odd, indicating $P2_1/c$ as the space group, which was confirmed by the structure analysis.

Relative intensities of 899 distinct X-ray reflections were measured by visual estimation of equi-inclination Weissenberg photographs of the $hk0$, 1, 2, 3, and 0, 1, 2, 3, $4kl$ levels of the reciprocal lattice. The crystals were chosen so that the crystal path length of the X-ray beam was never more than 0·4 mm. No corrections for absorption were made.

3. The structure determination

Preliminary inspection of the X-ray diffraction photographs showed that the 041 reflection was by far the most intense. The structure factor graph for this

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reflection projected on to (100) consists of 16 approximately square shaped areas whose sides are of length $b/8$ and $c/2$. It was apparent that in order to satisfy this intense reflection, while not violating any of the packing requirements of the space group, the molecular centers should be close to $z=0$ or $\frac{1}{2}$ and $y=\frac{1}{8}, \frac{3}{8}, \frac{5}{8}, \frac{7}{8}$. However, many and varied attempts to proceed from this point and to determine the structure by considering $hk0$ and $0kl$ data only were unsuccessful.

Three-dimensional Patterson function

Two distinct three-dimensional vector distributions were evaluated, the first P, the familiar Patterson function, sharpened, and with its origin peak removed by suitable modification of the coefficients. The second was $P'=P+XQ$ where

$$Q = \int \nabla\varrho(x, y, z) \cdot \nabla\varrho(x+u, y+v, z+w)\,d\tau$$

is the gradient Patterson function, and X is a fraction chosen here as 0·04. Jacobson *et al.* (1961) have shown that Q is readily evaluated as

$$16\pi^2 \sum_h \sum_k \sum_l (\sin\theta/\lambda)^2 |F_{hkl}|^2 \cos 2\pi(hx+ky+lz)$$

and that its use in the structure analysis of cellobiose significantly increased the resolution of vector maps. In this investigation also, it led to considerably improved resolution and the distribution P' was used in all subsequent analysis.

It has been shown (e.g. Buerger, 1959) that in a centrosymmetrical structure, if an identification can be made of a single vector between an atom at x, y, z and the symmetry related atom at $\bar{x}$, $\bar{y}$, $\bar{z}$ (an inversion vector) then the structure may in principle be solved. The requirements in practice are that the atom chosen represents a sufficient proportion of the scattering matter of the asymmetric unit. The procedure is to superpose the vector map on itself with a displacement of the origin by $2x$, $2y$, $2z$ in order to locate an image of the true structure in the vector distribution and referred to an origin at x, y, z. Atom positions are then points of coincidence of peaks in the two maps. In practice there will also be a number of spurious peaks due mainly to non-resolution of the original vector distribution. Buerger has shown that the unwanted background is reduced most effectively by taking the minimum of the two superposed maps, to produce the 'minimum function'. A program for evaluating the minimum function at all points in the unit cell for any chosen superposition point was written for the I.B.M. type 704 data processing machine and is described further in the Appendix.

A single inversion peak was located as follows. There were, as has been mentioned, strong indications that the centre of one tetramer molecule was close to the point $x, \frac{1}{8}, 0$ or $x, \frac{1}{8}, \frac{1}{2}$. Whatever the molecular structure this will be a pseudo-centre of symmetry for the molecule and there should consequently be a

Table 1. *Atomic parameters*

Atom	x	y	z	X (Å)	$10^2\sigma_X$	Y (Å)	$10^2\sigma_Y$	Z (Å)	$10^2\sigma_Z$	$10^2\beta_{11}$	$10^2\beta_{22}$	$10^2\beta_{33}$	$10^2\beta_{12}$	$10^2\beta_{13}$	$10^2\beta_{23}$
C_1	0·7315	0·1055	−0·0825	4·740	0·20	1·924	0·15	−0·431	0·20	2·20	0·24	3·93	−0·04	1·54	0·03
C_2	0·7595	0·1564	0·1249	4·922	0·20	2·853	0·15	0·652	0·20	2·05	0·23	3·80	−0·01	1·58	0·06
C_3	0·5031	0·0675	−0·2451	3·260	0·23	1·231	0·17	−1·279	0·21	2·81	0·28	4·40	−0·12	1·85	−0·11
C_4	0·5626	0·1692	0·1684	3·646	0·22	3·087	0·17	0·879	0·22	2·40	0·27	4·58	−0·02	1·95	0·00
N_5	0·9019	0·0899	−0·1546	5·845	0·21	1·639	0·17	−0·807	0·21	2·65	0·34	5·82	−0·12	2·34	−0·45
N_6	0·9641	0·2010	0·2826	6·247	0·19	3·665	0·14	1·475	0·19	2·18	0·25	4·51	−0·06	1·76	−0·14
N_7	0·3202	0·0380	−0·3764	2·075	0·22	0·693	0·18	−1·965	0·23	3·18	0·40	6·44	−0·35	1·97	−0·37
N_8	0·4048	0·1794	0·2028	2·623	0·22	3·272	0·18	1·059	0·26	2·86	0·40	7·15	−0·03	2·94	−0·10
H_9	1·046	0·110	−0·067	6·78	3·9	2·01	2·9	−0·35	3·5						
H_{10}	0·878	0·050	−0·306	5·69	3·4	0·92	2·7	−1·60	3·4						
H_{11}	1·115	0·183	0·320	7·22	3·7	3·34	2·5	1·67	3·7						
H_{12}	0·974	0·222	0·452	6·31	3·6	4·06	3·1	2·36	3·6						

Table 2. *Observed and calculated structure factors* (*scaled by* 10)

h, k, l	F_o	F_c
0, 0,0		2240
2	62	61-
4	423	395-
6	118	113
8	481	441-
10	105	88
12	98	86
14	97	92-
16	66	59-
18	25	22
20	27	27
22	32	36-
0, 1,1	215	218
2	83	78-
3	393	392-
4	1056	1028
5	239	231
6	109	109-
7	71	72
8	198	183-
9	13	12
10	115	107
11	146	146
12	51	45-
13	73	67
14	16	16
15	70	66-
16	*	3
17	*	10
18	*	4
19	36	35
20	18	19-
21	9	8-
22	*	8
23	*	12-
0, 0,2	389	394-
1	65	67-
2	101	115-
3	84	87
4	9	3-
5	104	105
6	84	82-
7	328	331-
8	213	222
9	164	172-
10	38	38-
11	127	118
12	35	32-
13	13	11-
14	24	19-
15	9	9
16	31	30-
17	32	34
18	16	15
19	24	24-
20	9	11
21	13	13
0, 1,3	69	69-
2	71	75
3	131	143
4	37	34-
5	40	40
6	45	45
7	35	33-
8	60	60-
9	66	68
10	40	40
11	70	76-
12	103	106
13	69	70-
14	31	30-
15	54	53
16	20	21-
17	18	17-
18	27	25-
19	13	12-
0, 0,4	55	54-
1	31	27
2	27	27-
3	13	12
4	51	47
5	51	47-
6	31	29-
7	13	12
8	35	33-
9	16	15
10	28	29
11	16	13-
12	31	30-
13	43	43
14	37	34
15	16	17-
16	45	51
0, 1,5	*	1-
2	31	33
3	25	24
4	9	8-
5	13	10
6	18	17-
7	*	1
8	25	24
9	28	25-
10	25	27-
11	*	4-
1, 0,0	148	159-
1	281	300
2	130	138-
3	198	205
4	39	40
5	268	252
6	238	231-
7	277	260-
8	124	122
9	98	97-

h, k, l	F_o	F_c
1,10,0	228	217
11	46	41-
12	104	96-
13	64	57
14	64	65
15	70	66
16	45	44-
17	69	57-
18	65	66-
19	*	2-
20	60	64
21	52	55
22	*	4
23	9	4-
1, 1,1	70	68
2	360	366
3	183	190
4	*	6
5	18	18
6	224	219-
7	64	66
8	109	109
9	64	63-
10	85	82-
11	123	118-
12	84	85
13	37	36
14	152	150
15	13	10-
16	123	118-
17	53	55-
18	43	39-
19	*	6
20	*	5-
21	13	8-
22	13	11-
$\bar{1}$, 1,1	56	54
2	393	305-
3	155	163
4	297	293-
5	389	389-
6	181	188-
7	139	132-
8	48	46
9	159	157
10	125	125-
11	102	99
12	46	46
13	13	11-
14	58	62
15	*	4-
16	45	48-
17	*	4-
18	62	64
19	24	24-
20	35	36-
21	24	26
22	30	34-
23	*	9
1, 0,2	65	75-
1	202	195
2	80	79-
3	55	53
4	62	60-
5	45	43-
6	141	151
7	73	68
8	44	44-
9	66	66-
10	168	175-
11	13	15
12	134	129
13	77	76
14	64	60
15	13	11-
16	22	25
17	*	6-
18	42	42
19	*	1-
20	47	45-
21	*	14-
$\bar{1}$, 0,2	274	311
1	242	268
2	273	281
3	57	59
4	31	31-
5	18	21
6	164	158-
7	127	123
8	87	83-
9	101	100-
10	16	5
11	16	14-
12	31	30
13	47	41
14	86	85-
15	18	19
16	35	36
17	*	4-
18	18	18
19	18	18-
20	41	44-
21	16	18-
22	18	20
1, 1,3	16	12
2	31	29-
3	90	92-
4	*	0
5	153	154
6	49	50
7	40	39
8	84	88-
9	120	126-
10	20	19-
11	20	17-

h, k, l	F_o	F_c
1,12,3	20	19-
13	*	4
14	60	61-
15	*	6
16	49	47
17	20	18
18	25	28
$\bar{1}$, 1,3	20	21-
2	140	158
3	136	152-
4	74	77
5	54	59
6	49	52
7	37	37-
8	30	29-
9	36	36
10	48	44-
11	81	76
12	40	43-
13	52	51-
14	28	24
15	20	20
16	48	46
17	40	41
18	22	20-
19	9	9
20	18	17
1, 0,4	18	19-
1	100	99-
2	39	44-
3	13	12-
4	39	41
5	79	79
6	54	53
7	13	12-
8	*	0
9	40	41
10	13	11
11	16	18
12	25	27-
13	46	45-
14	*	4-
$\bar{1}$, 0,4	*	2
1	45	43-
2	41	41-
3	35	36
4	13	9
5	31	29-
6	55	47
7	77	66-
8	35	36
9	39	38
10	16	15
11	58	54-
12	45	45-
13	*	6-
14	40	41
15	25	28
16	18	17-
17	16	15-
18	*	25
1, 1,5	31	32-
2	64	65-
3	34	35
4	*	4-
5	27	29-
6	*	8-
$\bar{1}$, 3,5	16	14
4	13	8-
5	37	36-
6	22	22-
7	49	44
8	31	28
9	*	9
10	32	35
11	13	14-
12	13	12
13	9	8
2, 0,0	168	173
1	226	240
2	182	194-
3	127	132
4	103	91
5	144	139
6	18	18-
7	99	103
8	252	240-
9	85	85-
10	99	98
11	59	57
12	31	29
13	22	25
14	70	69
15	18	15
16	90	84
17	16	13
18	37	34-
19	47	48-
20	39	40-
21	13	15
22	*	3-
2, 1,1	110	112-
2	44	48-
3	*	11-
4	158	165
5	147	156
6	132	140-
7	39	39-
8	45	46-
9	50	52-
10	93	96-
11	9	10-
12	126	123-

h, k, l	F_o	F_c
2,13,1	37	36-
14	59	61
15	61	62
16	52	52
17	30	29
18	30	27
19	30	29-
20	*	3
$\bar{2}$, 1,1	142	163
2	83	86-
3	366	370
4	321	316
5	120	131-
6	85	88-
7	46	43-
8	105	105
9	97	89-
10	*	6
11	27	26-
12	148	147-
13	28	27
14	34	33
15	51	54-
16	*	6
17	13	11-
18	18	17
19	45	44-
20	25	25
21	9	6-
22	*	0
2, 0,2	180	182-
1	30	33-
2	46	48
3	*	3
4	81	79
5	34	34
6	58	60
7	60	61
8	90	91
9	70	73
10	73	72-
11	68	63-
12	50	48-
13	52	49-
14	31	30-
15	35	37
16	9	10-
17	*	1-
18	*	4-
19	13	15-
$\bar{2}$, 0,2	377	436-
1	208	232
2	*	5-
3	37	36
4	42	45-
5	47	49
6	81	81-
7	132	133
8	148	156
9	30	32-
10	*	1-
11	16	15
12	83	79
13	34	31-
14	30	30
15	47	45
16	43	42-
17	13	12
18	13	12-
19	54	56-
20	13	12-
21	9	12
22	22	28
2, 1,3	42	46-
2	34	32
3	20	20-
4	118	124-
5	20	20-
6	39	38
7	32	30
8	69	69
9	34	31
10	16	13
11	9	9-
12	13	10-
13	13	15
14	*	1
15	13	11
16	20	19
$\bar{2}$, 1,3	13	16
2	27	28
3	61	63-
4	202	218-
5	101	100
6	35	32-
7	37	36-
8	40	36-
9	20	17-
10	59	56-
11	9	12-
12	20	17
13	9	7-
14	31	31
15	45	45
16	52	52
17	37	37-
18	27	24-
19	9	5
20	24	25-
2, 0,4	96	95
1	*	7-
2	*	3
3	39	38-
4	27	29-

h, k, l	F_o	F_c
2, 5,4	30	30-
6	9	7-
7	25	25
8	20	20-
9	9	7
10	*	1-
$\bar{2}$, 0,4	117	116
1	42	44-
2	*	0
3	30	31
4	18	15
5	31	29
6	36	37
7	50	38
8	59	51-
9	54	48
10	41	44-
11	64	66-
12	20	20-
13	13	10
14	25	25
15	18	18
16	16	9
17	*	2
18	*	2
$\bar{2}$, 1,5	18	16-
2	28	25-
3	20	18-
4	22	21
5	38	33-
6	31	31
7	50	51
8	16	18
9	*	6-
10	27	27-
11	9	6-
12	32	31-
13	18	18
14	9	9-
3, 0,0	85	90
1	20	19-
2	46	41-
3	9	12
4	98	104
5	159	154
6	66	66
7	*	5
8	13	10
9	73	70-
10	60	61
11	*	8
12	111	112-
13	34	36-
14	55	54-
15	18	20
16	18	18-
17	22	23
18	24	26-
19	16	14-
20	24	26
21	20	24-
3, 1,1	102	106-
2	107	110-
3	9	12-
4	38	37
5	*	6-
6	27	29-
7	*	1
8	76	72
9	88	89
10	20	25
11	9	8
12	13	8
13	30	28-
14	47	47
15	27	25
16	22	23-
17	20	20
18	13	10
19	9	11
$\bar{3}$, 1,1	25	24
2	20	18
3	54	55-
4	25	20-
5	133	123-
6	111	105-
7	31	27
8	167	164
9	39	38-
10	119	111
11	55	53
12	36	32
13	52	52
14	34	33
15	13	13-
16	84	86-
17	9	10
18	46	46-
19	9	10-
20	9	10
21	16	16
3, 0,2	16	14-
1	16	16-
2	72	78
3	57	55-
4	22	18
5	56	56-
6	64	62-
7	*	5
8	13	15
9	13	6-
10	27	26-
11	28	31-
12	*	1

h, k, l	F_o	F_c
3,13,2	*	1-
14	32	31-
15	*	3-
16	20	22
$\bar{3}$, 0,2	156	172
1	118	121
2	83	85
3	9	13-
4	94	103-
5	96	98-
6	84	80-
7	115	119-
8	63	62-
9	84	81-
10	66	63-
11	42	42
12	99	105
13	9	5-
14	74	68
15	18	18
16	16	15-
17	22	23-
18	13	15-
19	*	1-
20	9	8-
21	43	45
3, 1,3	36	34
2	48	47
3	*	1-
4	9	9-
5	16	16-
6	46	46
7	9	5-
8	13	13
9	18	19
10	*	2
11	20	18
12	13	11-
$\bar{3}$, 1,3	75	84
2	145	166
3	20	18-
4	140	155
5	95	102
6	39	41
7	27	28-
8	71	75-
9	67	68-
10	37	36-
11	38	37-
12	20	16
13	32	32
14	13	9
15	24	23
16	*	4-
17	63	61-
18	*	1
19	*	5
20	9	9
$\bar{3}$, 0,4	140	137-
1	41	45-
2	101	98-
3	59	64
4	27	30
5	50	50
6	99	97
7	42	40-
8	18	19
9	18	16-
10	39	41-
11	13	14-
12	20	21
13	37	38
14	30	30
15	13	13-
16	9	9-
17	9	11
$\bar{3}$, 1,5	45	47-
2	76	76-
3	45	45
4	30	28-
5	30	30
6	9	8
7	35	35
8	27	27-
9	50	46-
10	*	9
11	27	25-
12	16	19
13	*	5
14	22	24-
$\bar{3}$, 0,6	9	12-
1	16	17-
2	9	9
3	39	37-
4	27	29
5	27	26
6	9	15-
7	27	26
8	18	21-
4, 0,0	94	95
1	53	55
2	20	18-
3	28	27-
4	50	46-
5	*	9-
6	13	14-
7	85	82-
8	*	10-
9	111	117-
10	22	23-
11	63	61
12	20	17-
13	9	6-

h, k, l	F_o	F_c
4,14,0	39	39
15	13	11
16	*	2
17	31	31
18	27	27
19	16	20-
4, 1,1	34	36
2	18	16
3	*	5-
4	99	106
5	48	56
6	16	13
7	*	3
8	18	21-
9	13	7
10	13	7-
11	41	38-
12	*	6
13	43	43-
14	30	26-
15	9	7
16	30	26-
17	*	12-
$\bar{4}$, 1,1	30	28
2	48	43-
3	48	44-
4	63	58-
5	154	157-
6	13	10-
7	126	121
8	18	18
9	*	3
10	66	66-
11	24	22
12	34	36-
13	71	72
14	30	27-
15	77	79-
16	24	21
17	16	13
18	61	60
19	36	35
20	20	24
$\bar{4}$, 0,2	207	244
1	75	79
2	35	32
3	76	77-
4	93	95-
5	41	42
6	32	34
7	43	37
8	22	19
9	81	84-
10	24	23
11	127	133
12	35	34
13	18	18-
14	97	102-
15	55	55-
16	74	70-
17	35	32
18	20	20
19	13	14-
20	9	12
4, 1,3	*	6-
2	*	1-
3	20	24
4	34	37-
5	9	7-
6	9	12-
7	*	13-
$\bar{4}$, 1,3	56	57
2	40	41-
3	126	142-
4	94	100
5	9	12
6	31	31-
7	101	105-
8	103	111-
9	53	55
10	97	100
11	111	109
12	94	94
13	39	35-
14	27	26-
15	27	25
16	16	14-
17	9	8-
18	32	28-
19	*	5-
$\bar{4}$, 0,4	28	23-
1	75	74-
2	71	73
3	99	103
4	49	49
5	28	22
6	101	102-
7	161	177-
8	28	29-
9	16	11-
10	20	19
11	13	7
12	32	28-
13	35	33
14	28	25
15	16	13
16	49	42
17	22	18-
18	18	19-
$\bar{4}$, 1,5	74	70-
2	102	102
3	127	124
4	53	49

h, k, l	F_o	F_c
$\bar{4}$, 5,5	27	24-
6	9	9
7	*	2
8	13	10-
9	16	12
10	28	28-
11	59	48-
12	*	2-
13	*	6-
14	20	15
15	22	24
$\bar{4}$, 0,6	76	70-
1	76	66
2	39	35-
3	*	3-
4	38	32
5	48	40-
6	34	32
7	49	37
8	9	10
9	13	10-
5, 0,0	45	44-
1	136	129
2	135	128-
3	25	25
4	18	18
5	45	40-
6	141	133
7	53	56
8	13	11-
9	*	10-
10	*	0
11	*	8
12	9	7
13	22	23
14	*	6-
15	9	10
16	9	10
5, 1,1	*	4
2	53	52-
3	69	68-
4	24	24-
5	80	84
6	70	67-
7	20	19
8	9	11
9	60	59-
10	22	21
11	9	9-
12	13	12-
13	13	13
$\bar{5}$, 1,1	*	15-
2	243	248-
3	109	119
4	13	12
5	20	15-
6	*	7-
7	30	27
8	*	3
9	24	22-
10	96	101
11	45	46-
12	18	18-
13	27	23-
14	34	37-
15	13	12-
16	30	29
17	18	19
$\bar{5}$, 0,2	79	83-
1	35	32-
2	89	98
3	103	101-
4	13	10
5	67	61
6	184	200-
7	91	98
8	25	28
9	30	31
10	65	62
11	37	34
12	35	32-
13	79	77-
14	45	41
15	9	9-
16	32	32
17	22	21
18	13	14-
$\bar{5}$, 1,3	31	34
2	54	59
3	42	39
4	70	81-
5	74	85-
6	*	3
7	102	108-
8	46	48
9	121	129
10	85	97-
11	37	36
12	42	42-
13	46	43-
14	25	24
15	25	21
16	9	8-
17	37	34-
18	25	27
6, 0,0	65	66-
1	*	4-
2	49	46
3	37	38-
4	78	74
5	24	19
6	37	35-
7	27	27

h, k, l	F_o	F_c
6, 8,0	9	7-
9	9	6
10	16	15-
11	9	10
12	45	49-
6, 1,1	31	30
2	*	4
3	16	14
4	22	24-
5	*	3
6	*	18
$\bar{6}$, 1,1	93	94-
2	103	98
3	62	60
4	34	32-
5	18	18
6	49	47
7	30	25
8	63	63
9	34	31-
10	45	45-
11	20	22-
12	*	3-
13	9	8
14	*	5
$\bar{6}$, 0,2	13	13-
1	56	54
2	100	98-
3	96	94-
4	30	25
5	85	83-
6	107	111
7	61	63
8	43	37-
9	13	5-
10	9	5
11	18	18-
12	25	23
13	30	26-
14	22	22-
15	9	10
$\bar{6}$, 1,3	69	78
2	93	107-
3	54	66-
4	*	8-
5	70	76
6	40	33-
7	27	28-
8	59	67
9	49	53-
10	62	66
11	20	21
12	48	44-
13	*	3-
14	13	10
15	9	7-
16	*	13
7, 0,0	9	10
1	9	2
2	18	19-
$\bar{7}$, 1,1	36	32-
2	*	3
3	20	16
4	*	1
5	25	21-
6	51	49-
7	48	44
8	30	29-
9	*	3-
$\bar{7}$, 0,2	9	8
1	49	42
2	30	26
3	16	12-
4	30	26
5	20	16-
6	9	5-
7	9	6
8	*	1-
9	9	10-
10	43	41-
11	39	38
$\bar{7}$, 1,3	13	11-
2	30	30
3	31	33-
4	9	9
5	25	27
6	13	15
7	9	6-
8	31	28
9	*	2-
10	16	15-
11	*	7-
12	9	5
13	*	14
$\bar{8}$, 0,2	25	26
1	*	2
8, 1,3	9	8
2	59	65-
3	20	21-
4	*	16

large Patterson peak at $2x, \frac{1}{4}, 0$ of weight about 6 (Patterson, 1949). Only one such peak was found along the line $u, \frac{1}{4}, 0$ and so the approximate centre of the molecule was fixed in space. By exploring vector space in the neighborhood of this peak it was possible to find two peaks of single weight separated by twice the length of a carbon–carbon double bond and which did in fact prove to be inversion peaks of the central carbon atoms. It was also possible by working from these to locate further possible inversion peaks corresponding to atoms attached to the two central carbons.

The two best resolved inversion peaks were chosen and the minimum function $M2$ (Buerger, 1959) was computed for each. Both of the $M2$ distributions possessed many more peaks than there were atoms, but after superposition of these two to produce $M4$ there remained only two small spurious peaks readily distinguishable because of their chemically unreasonable positions. The set of carbon and nitrogen coordinates, assigned directly from $M4$ was used as the starting point of a three-dimensional least-squares refinement. The initial assignments were on an average, displaced by 0·13 Å from the final positions.

Refinement of atomic parameters

Three-dimensional least-squares refinement of parameters was carried out, using the program ORXLS written by William R. Busing and Henri A. Levy for the I.B.M. 704, weighting factors being derived from individually assigned standard errors of the observed intensities. For three successive preliminary cycles, carbon and nitrogen atoms only were considered and were treated isotropically. Finally for three further cycles hydrogen atoms, located from a difference Fourier synthesis, were included with fixed isotropic temperature factors while all carbon and nitrogen atoms were treated anisotropically. The 85 parameters adjusted comprised one scale factor, three positional parameters for each of the twelve atoms of the asymmetric unit and six thermal parameters for each of the eight carbon and nitrogen atoms. Atomic scattering factors used were those of McWeeny (1951) for nitrogen and hydrogen and of Hoerni & Ibers (1954) for carbon.

Before the final cycle of refinement, an empirical correction was made to the observed intensities for the effects of secondary extinction, the observed values for the strongest group of reflections being systematically too low. Corrected values for F^2 were calculated from the empirical expression

$$F^2_{\text{corr.}} = F_o^2 + F_c^2 \{\exp(-X/|F_c|)\}$$

a value of 70 being assigned to the single parameter X. This correction was applied to all of the 32 reflections for which F_c^2 was ≥ 500 the correction for $F^2 = 500$ being 0·043 F_c^2. In Table 2 are listed final values for F_o and F_c after such corrections had been made. The values of

$$R = \Sigma||F_o| - |F_c||/\Sigma|F_o| \quad \text{and} \quad r = \Sigma w(F_o^2 - F_c^2)^2/\Sigma w F_o^4$$

are 0·057 and 0·019 respectively for all observed reflections. All atomic parameters are listed in Table 1, in the case of positional parameters, with standard deviations.

4. Discussion

From the representation of the crystal structure as viewed down the c axis, shown in Fig. 2 it may be observed that the crystal owes its cohesion to a system of N–H · · · N hydrogen bonds. These bonds are fairly weak (see e.g. Pimentel & McClellan, 1960), ranging in length from 3·13 to 3·22 Å. Three of the four bonds connect a nitrile and an amino group while the unique fourth bond connects two amino groups and, on repetition by the two-fold screw axis links molecules into an endless helix. Consequently, all four nitrogen atoms are distinct as regards their intermolecular environment. The two nitrile nitrogens are linked to one and two amino groups respectively, as the acceptor atom in each case. One amino group is linked as donor to two nitrile groups while the other is linked as donor

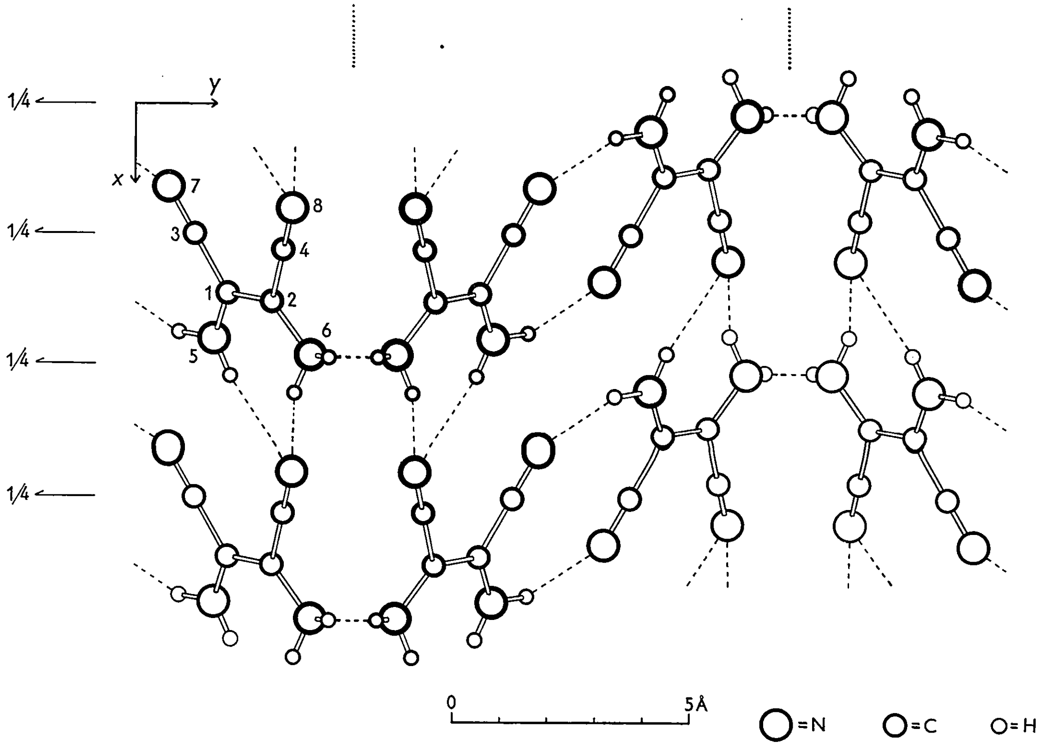


Fig. 2. The crystal structure viewed down the c axis. Hydrogen bonds are represented as broken lines.

to two nitrile groups and as acceptor to another amino group. Data relating to these hydrogen bonds are collected in Table 3. Shortest non-bonded distances are 3·30 Å for $C \cdots N$, 2·97 Å for $N \cdots H$, 2·99 Å for $C \cdots H$ and 2·37 Å for $H \cdots H$, none of which are significantly less than sums of van der Waals radii.

Errors in molecular dimensions

The standard deviations listed for atomic coordinates in Table 1 lead to standard deviations for interatomic distances of $\leq$ 0·0032 Å where no hydrogen is involved, and $\leq$ 0·040 Å for bonds involving hydrogen. From the detailed knowledge available of the vibration amplitudes of all the atoms except hydrogens, corrections were made to these distances to give the values actually shown in Fig. 1 where final bond angles are also inserted. These values represent the true equilibrium distances between bonded atoms, the assumption being made in each case that the atom furthest from the central C=C bond is riding on the other atom. Justification for this assumption is given below in a more detailed discussion of the molecular thermal vibrations. Approximate calculations show that the standard deviations of these corrections due to the uncertainty in the thermal parameters is close to 0·15 of the magnitude of the correction. With these errors must be included those due to uncertainties in unit cell parameters. In Table 4 are listed molecular bond lengths, before and after correction for thermal vibration, and the total estimated standard deviations. The mean standard deviations in bond angles are 0·30° for ∠ C–C–C and ∠ C–C–N, 2·3° for ∠ C–N–H, and 3·3° for ∠ H–N–H. We may now proceed to discuss the details of the molecular dimensions.

Table 3. *Atomic distances and angles related to hydrogen bonds*

$N_5 \cdots N_8'$	3·21 Å	$N_6 \cdots N_8'$	3·12 Å
$H_9 \cdots N_8'$	2·35 Å	$H_{11} \cdots N_8'$	2·26 Å
$\angle\ C_1\text{–}N_5\text{–}H_9$	124°	$\angle\ C_2\text{–}N_6\text{–}H_{11}$	118°
$\angle\ C_1\text{–}N_5\text{–}N_8'$	117°	$\angle\ C_2\text{–}N_6\text{–}N_8'$	120°
$\angle\ C_4'\text{–}N_8'\text{–}H_9$	120°	$\angle\ C_4'\text{–}N_8'\text{–}H_{11}$	170°
$\angle\ N_5\text{–}H_9\text{–}N_8'$	170°	$\angle\ N_6\text{–}H_{11}\text{–}N_8'$	150°
$N_5 \cdots N_7'$	3·12 Å	$N_6 \cdots N_6'$	3·16 Å
$H_{10} \cdots N_7'$	2·17 Å	$H_{12} \cdots N_6'$	2·24 Å
$\angle\ C_1\text{–}N_5\text{–}H_{10}$	123°	$\angle\ C_2\text{–}N_6\text{–}H_{12}$	112°
$\angle\ C_1\text{–}N_5\text{–}N_7'$	105°	$\angle\ C_2\text{–}N_6\text{–}N_6'$	114°
$\angle\ C_3'\text{–}N_7'\text{–}H_{10}$	144°	$\angle\ C_2'\text{–}N_6'\text{–}N_6$	108°
$\angle\ N_5\text{–}H_{10}\text{–}N_7'$	154°	$\angle\ N_6\text{–}H_{12}\text{–}N_6'$	166°
		$\angle\ N_8'\text{–}N_5\text{–}N_7'$	138°
		$\angle\ N_8'\text{–}N_6\text{–}N_6'$	125°

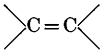
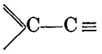
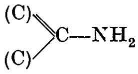
Table 4. *Molecular bond lengths*

Bond	Length (uncorrected)	Length (corrected for thermal vibration)	Total standard deviation
C_1–C_2	1·363 Å	1·363 Å	0·006 Å
C_1–C_3	1·436	1·441	0·007
C_2–C_4	1·430	1·434	0·007
C_1–N_5	1·372	1·387	0·008
C_2–N_6	1·393	1·398	0·007
C_3–N_7	1·142	1·166	0·010
C_4–N_8	1·144	1·164	0·010
N_5–H_9	0·87		0·04 excluding vibration corrections
N_5–H_{10}	1·02		
N_6–H_{11}	0·95		
N_6–H_{12}	0·94		

The molecule

Location of the twelve atoms with the accuracy indicated in Table 1 leaves the gross structure of the molecule in no doubt. It is diaminomaleonitrile (DAMN). However, because of strong intermolecular forces there is no molecular symmetry. The molecule possesses no mirror plane and is twisted by 6° about the central C=C bond. Of the amino groups, one (containing N_5) is planar within limits of error and the other is close to tetrahedral as indicated by the relevant bond angles. These observations raise the interesting question of the most likely configuration of these groups in the absence of strong intermolecular forces. On the grounds that three hydrogen bonds will

Table 5. *Carbon–carbon and carbon–nitrogen bond lengths*

Bond	Molecule	Length (Å)	References
	Ethylene	1·337 av.	(*a*)
	Vinyl cyanide	1·339	(*b*)
	Tetracyanoethylene	1·317	(*c*)
	Diaminomaleonitrile	1·363	(*d*)
	Propynal	1·446	(*e*)
	Vinyl cyanide	1·426	(*b*)
	Tetracyanoethylene	1·448 av.	(*c*)
	Diaminomaleonitrile	1·437 av.	(*d*)
—C≡N	Hydrogen cyanide	1·156	(*f*)
	Cyanoacetylene (microwave)	1·157	(*g*)
	Cyanoacetylene (X-ray)	1·14	(*h*)
	Vinyl cyanide	1·164	(*b*)
	Tetracyanoethylene	1·15 av.	(*c*)
	Diaminomaleonitrile	1·165 av.	(*d*)
	*p*-Nitroaniline	1·37	(*i*)
	p-Aminophenol	1·47	(*j*)
	4-Amino-2:6 dichloropyrimidine	1·34	(*k*)
	Diaminomaleonitrile	1·392 av.	(*d*)

(*a*) Costain & Stoicheff (1959) (Table IV).
(*b*) Costain & Stoicheff (1959).
(*c*) Bekoe & Trueblood (1960).
(*d*) This paper.
(*e*) Morton (1958).
(*f*) Nethercot *et al.* (1952) and Simmons *et al.* (1952).
(*g*) Westenberg & Wilson (1950).
(*h*) Shallcross & Carpenter (1958).
(*i*) Donohue & Trueblood (1956).
(*j*) Brown (1951).
(*k*) Clews & Cochran (1949).

Table 6. *π-Electron molecular orbitals and their energies*

(*a*) *DAMN*

Orbital	Symmetry	Energy (e.v.)
ψ_8	A_2	$\alpha_c+4{\cdot}65$
ψ_7	B_1	$\alpha_c+2{\cdot}90$
ψ_6	A_2	$\alpha_c+0{\cdot}91$
$\psi_5 = 0{\cdot}339\varphi(A+B)-0{\cdot}504\varphi(C+D)-0{\cdot}050\varphi(E+F)+0{\cdot}358\varphi(G+H)$	B_1	$\alpha_c-1{\cdot}52$
$\psi_4 = 0{\cdot}304\varphi(A-B)-0{\cdot}040\varphi(C-D)-0{\cdot}382\varphi(E-F)-0{\cdot}510\varphi(G-H)$	A_2	$\alpha_c-4{\cdot}24$
$\psi_3 = 0{\cdot}376\varphi(A+B)-0{\cdot}045\varphi(C+D)-0{\cdot}360\varphi(E+F)-0{\cdot}477\varphi(G+H)$	B_1	$\alpha_c-4{\cdot}26$
$\psi_2 = 0{\cdot}604\varphi(A-B)+0{\cdot}218\varphi(C-D)+0{\cdot}214\varphi(E-F)+0{\cdot}205\varphi(G-H)$	A_2	$\alpha_c-5{\cdot}22$
$\psi_1 = 0{\cdot}489\varphi(A+B)+0{\cdot}421\varphi(C+D)+0{\cdot}237\varphi(E+F)+0{\cdot}168\varphi(G+H)$	B_1	$\alpha_c-6{\cdot}22$

(*b*) *TCE*

Orbital	Symmetry	Energy (e.v.)
ψ_{10}	B_1	$\alpha_c+5{\cdot}35$
ψ_9	B_3	$\alpha_c+3{\cdot}36$
ψ_8	A_1	$\alpha_c+2{\cdot}09$
ψ_7	B_2	
$\psi_6 = 0{\cdot}312\varphi(A-B+I-J)-0{\cdot}254\varphi(C-D+G-H)-0{\cdot}419\varphi(E-F)$	B_1	$\alpha_c+0{\cdot}02$
$\psi_5 = 0{\cdot}369\varphi(A+B+I+J)+0{\cdot}017\varphi(C+D+G+H)-0{\cdot}477\varphi(E+F)$	B_3	$\alpha_c-2{\cdot}64$
$\left.\begin{matrix}\psi_4\\ \psi_3\end{matrix}\right\} = 0{\cdot}415\varphi(A-B-I+J)+0{\cdot}280\varphi(C-D-G+H)$	A_1	$\alpha_c-4{\cdot}59$
	B_2	
$\psi_2 = 0{\cdot}372\varphi(A-B+I-J)+0{\cdot}309\varphi(C-D+G-H)+0{\cdot}180\varphi(E-F)$	B_1	$\alpha_c-5{\cdot}08$
$\psi_1 = 0{\cdot}261\varphi(A+B+I+J)+0{\cdot}299\varphi(C+D+G+H)+0{\cdot}438\varphi(E+F)$	B_3	$\alpha_c-6{\cdot}02$

force a non-planar configuration on the group whereas two hydrogen bonds will allow planarity or non-planarity depending on the valence forces within the molecule, we conclude that the most stable configuration for a free molecule is one of complete planarity. The nitrogen valence shell electrons would then be in predominantly sp^2 hybrid orbitals.

There have been a number of accurate bond length measurements on conjugated systems of similar complexity and these are listed in Table 5. Of the C≡N bonds it may be remarked that no systematic variation in length appears to accompany the attachment of a nitrile group to a conjugated system. Excluding from consideration the relatively uncertain X-ray value of 1·14 Å for the bond in cyanoacetylene, the conjugated bonds have an average length very close to that in HCN gas. The other bonds in DAMN are more difficult to classify. In an attempt to provide some theoretical basis for discussion of these bonds, we have carried out an LCAO MO treatment of the molecule and have calculated mobile bond orders for all bonds.

Bond order calculations

For the purposes of the MO calculations the molecule was regarded as having C_{2v} symmetry with all non-central bond lengths possessing their mean values and the π-electron approximation was invoked. Coulomb integrals were assigned in the manner suggested by Orgel *et al.* (1951), as a further approximation the two types of carbon atom being assigned the same value (α_c). Coulomb integrals α_N and α_N' for nitrogens in nitrile and amino groups respectively were then ($\alpha_c-2{\cdot}0$) e.V. and ($\alpha_c-4{\cdot}5$) e.V. Following Mulliken (1949) resonance integrals β were taken to be $10S$, where S is the $\pi-\pi$ overlap integral for the pair of atoms concerned for the observed interatomic distance. In Table 6 the bonding molecular orbitals are listed along with the energies of all orbitals, and the key to the mode of representation of the component atomic orbitals is to be found in Fig. 3. The first unoccupied molecular orbital ψ_6 with an energy of ($\alpha_c+0{\cdot}91$) e.V. was clearly anti-bonding. Mobile bond orders (Coulson, 1939) and atomic π-electron populations, calculated on the assumption that the five

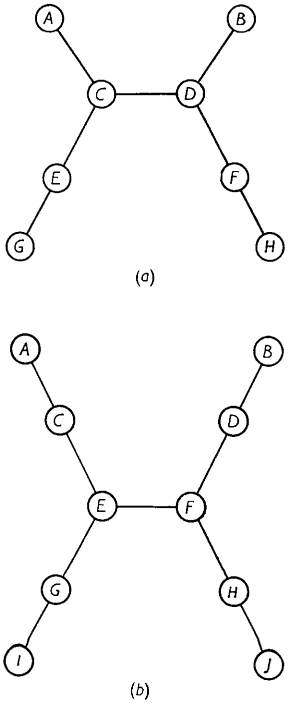


Fig. 3. Carbon–nitrogen skeletons of (*a*) diaminomaleonitrile and (*b*) tetracyanoethylene showing the labelling of atoms with respect to the molecular orbitals of Table 6. Nitrogen atoms are those labelled *A*, *B*, *G*, *H* in (*a*) and *A*, *B*, *I*, *J* in (*b*). The remainder are carbons.

bonding levels are filled by the 10 available electrons, are listed in Table 7. Similar calculations were carried out for tetracyanoethylene (TCE) for which accurate bond lengths are known (Bekoe & Trueblood, 1960). The symmetry assumed was D_{2h}. In this case bond order and electron population calculations were extended to include the singly and doubly charged anions (Webster *et al.*, 1960) assuming that the extra electrons will successively occupy the orbital ψ_6 which our calculations, in agreement with those of Phillips *et al.* (1960) show to be not significantly anti-bonding.

It is now of interest to examine the order/length relationship of the bonds in the two compounds. In Fig. 4 we show order-length curves for C–C bonds, presenting for comparison a single curve where the point for π bond order zero refers to sp^3 hybridization, and also three separate curves for sp^3, sp^2 and sp hybridization respectively (Coulson, 1948*). Points for the C–C bonds in DAMN and TCE, derived from observed bond lengths and calculated bond orders are inserted. The vertical lines indicate the limits of error i.e. their lengths are three times the standard deviation above and below each point.

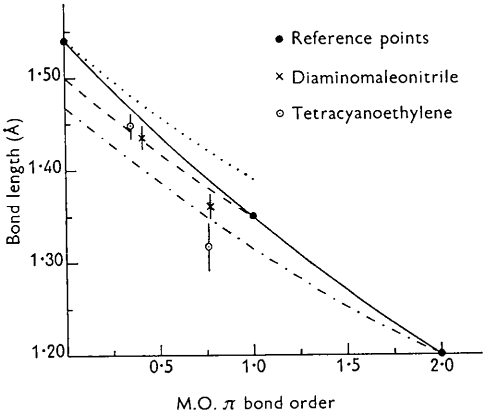


Fig. 4. Curves relating bond length to π bond order for carbon–carbon bonds where both σ orbitals are sp^3 hybrids (dotted line), sp^2 hybrids (dashed) and sp hybrids (dots and dashes) respectively. A single full line joins the three reference points for ethane, ethylene and acetylene. Vertical lines drawn through the experimental points for DAMN and TCE represent three times the standard deviation above and below.

Before examining the relationships of the experimental points to the various curves we must first decide which curve, if any, is appropriate to each type of bond. In other words we must determine as closely as we can the relative amounts of s and p character in each of the σ orbitals involved. As a first approximation we may regard all three orbitals about each central carbon atom as sp^2 hybrids and each of the orbitals about the nitrile as an sp hybrid. However, as has been shown by Coulson (1948), the hybridization ratio of p to s will be the same for all bonds formed by an atom *only* when all bond angles are equal. In the trigonal planar case this will be so only when all angles are 120°. When this condition does not hold for the trigonal case Coulson has shown that the hybridization ratios for the bonds directed to atoms A, B, C, are

$$\lambda_A^2 = -\cos\alpha/(\cos\beta\cos\gamma),\quad \lambda_B^2 = -\cos\beta/(\cos\gamma\cos\alpha)\,,\quad \lambda_C^2 = -\cos\gamma/(\cos\alpha\cos\beta)\,,$$

where α is the angle subtended at the central atom by atoms B and C, etc.

If the averages are taken of the corresponding angles about C_1 and C_2 of DAMN, average values of λ^2 for C–CN and C=C bonds are 2·6 and 1·75 respectively. The predicted σ bond radii are therefore 0·76 Å and 0·745 Å respectively. If we further assume that the σ bonds directed from the nitrile carbons are pure sp hybrids we would predict lengths for C–CN and C=C of 1·495 Å and 1·49 Å *in the absence of π bonding.* In other words the appropriate reference curves for the C–CN and C=C bonds lie below the sp^2 curve (which assumes a σ radius of 0·75 Å) by 0·005 Å and 0·01 Å respectively. Similar calculations for TCE show that the reference curves for C–CN and C=C both lie below the sp^2 curve by 0·013 Å.

Referring now to Fig. 4 we note that the C–CN and C=C points for DAMN lie off the correct reference curves by 0·010 Å (above) and 0·006 Å (below) respectively, neither distance being significant. Our conclusions, therefore, are that within our limits of error the C–C bond lengths in DAMN are consistent with the π bond orders, calculated as we have described, and σ bond radii calculated as described by Coulson having due regard to the state of hybridization of the orbitals.

Table 7

(*a*) Atomic π electron populations

	DAMN	TCE	TCE$^-$	TCE^{--}
Central C	0·97	0·89	0·98	1·07
Nitrile C	0·76	0·68	0·74	0·81
Nitrile N	1·37	1·38	1·48	1·57
Amino N	1·89	—	—	—

(*b*) Mobile bond orders

	DAMN	TCE	TCE$^-$	TCE^{--}
Central C=C	0·77	0·76	0·58	0·42
C–CN	0·41	0·35	0·46	0·56
Nitrile C–N	0·865	0·87	0·79	0·71
Amino C–N	0·275	—	—	—

In the case of TCE, the C–CN and C=C points lie respectively 0·020 Å above and 0·047 Å below their

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* Coulson's (1948) estimate of 0·75 Å for the sp^2 radius of carbon was based on the then assumed dimensions of ethylene i.e. 1·35 Å for the C=C bond and 120° for ∠ H–C–H. The most recent values of Dowling & Stoicheff (1959) are 1·339 Å and 117° 34′ indicating that the value of λ^2 for σ bonds between carbon atoms is 1·71, not 2·0. If we then take our primary reference point for the bond radius to be 0·745 Å for $\lambda^2 = 1·71$, Coulson's relationship predicts 0·75 Å for $\lambda^2 = 2·0$ (sp^2 hybridization) the same as the 1948 value.

correct reference curves, the first distance being just significant and the second one highly so. In seeking an explanation we note that each atom of the central bond is connected to two highly electronegative groups and we suggest that the apparently anomalous distances are due at least qualitatively to a withdrawal of σ electrons from the region of the central bond. This would lead to an initial decrease in repulsive forces, and a corresponding build up in the region of the C–CN bond with consequent initial increase in repulsive forces, then to be adjusted to the new equilibrium situation. Bekoe & Trueblood (1960) have also discussed this point but in assuming the π bond order of the central bond is unity they have compared its length with that in ethylene (1·339 Å), the difference being of possible significance only. The difference becomes definitely significant only when the effect of π bond order is taken into account as described above. It will be noted from Table 7 that our calculations predict that the most noticeable results of the addition of electrons to TCE to form negative ions will be a lengthening of the central bond and a shortening of the C–CN bonds by amounts given approximately by the slopes of the appropriate curves in Fig. 4, and the change in bond order in Table 7.

Costain & Stoicheff (1959) have shown that the length of a C–C bond tends to increase linearly as the total number of other atoms attached to the bond increases. This can be regarded as another way of stating the dependence of carbon radius on the hybridization state. However, in the molecules which are listed by these authors in deriving their linear plots no account has been taken of π bond orders and indeed the tacit assumption has been made that the π bond order is constant which is by no means necessarily so. It seems unprofitable, therefore, to discuss the bond lengths in DAMN and TCE relative to these linear plots. It would be most valuable to have reliable estimates of π bond orders in the molecules which Costain & Stoicheff use and, in particular, for comparison with the present work, in all the molecules listed in our Table 5.

Because of the lack of good reference points, particularly for π bond order unity, it is not possible to draw a reliable order/length curve for C–N bonds. The values obtained for C–NH_2 in DAMN may, however, be suggested as providing one such reference point for the construction of a complete curve.

Molecular thermal vibrations

The nature of the molecular vibrations may be understood by reference to Table 8 which lists the r.m.s. components of the displacements of all atoms, (*a*) along their principal vibration directions, (*b*) along the bonds in which they participate, and (*c*) normal to the mean molecular plane. There are only three markedly anisotropic atoms, the amino nitrogen N_5 and the nitrile nitrogens N_7 and N_8, and as a first approximation we may regard the molecular anisotropy as vibrations of these atoms normal to the bonds C_1–N_5, C_3–N_7 and C_4–N_8 respectively. N_5, of the planar amino group, has its anisotropic motion confined almost entirely to the single direction normal to the molecule and hence normal to each of the two hydrogen bonds for which it is donor. N_6 of the tetrahedral amino group is largely prevented from vibrating anisotropically by the three hydrogen bonds with which it is involved. N_7 and N_8 of the nitrile groups, while having a large vibration amplitude normal to the molecular plane, are not confined to this direction by the hydrogen bonds for which they are acceptors and it will be noted that their amplitudes of displacement are high in two of the principal vibration directions. There is no evidence for any anisotropy of the molecule as a whole considered as a rigid body. It is clear that the apparent positions of all the atoms except C_1 and C_2, and particularly of N_5, N_7, N_8, will be displaced from the true positions because in all cases the anisotropic atoms are vibrating radially about a bond, (Cruickshank, 1956; Cruickshank *et al.*, 1959). Corrections made to molecular bond lengths to allow for this effect ranged from 0·004 Å for C_2N_6 to 0·024 Å for C_3N_7 and are listed in Table 4. It is of significance that this range of magnitudes is closely similar to that calculated in the detailed treatment of Bekoe & Trueblood (1960) for TCE.

Table 8. *R.m.s. components of atomic thermal displacement*

Atom	Displacement in directions of 3 principal axes of vibration ellipsoid	Displacement in direction of indicated bond		Displacement normal to molecular plane
C_1	0·21, 0·20, 0·18 Å	C_1–C_2	0·20 Å	0·20 Å
		C_1–C_3	0·18	
		C_1–N_5	0·19	
C_2	0·20, 0·19, 0·17	C_2–C_1	0·20	0·19
		C_2–C_4	0·18	
		C_2–N_6	0·18	
C_3	0·23, 0·21, 0·20	C_3–C_1	0·20	0·22
C_4	0·21, 0·21, 0·18	C_4–C_2	0·18	0·21
N_5	0·28, 0·20, 0·19	N_5–C_1	0·19	0·27
N_6	0·22, 0·19, 0·18	N_6–C_2	0·18	0·22
N_7	0·28, 0·26, 0·19	N_7–C_3	0·19	0·28
N_8	0·27, 0·25, 0·19	N_8–C_4	0·19	0·27

APPENDIX

The program HASP written for the I.B.M. 704 data processing machine for evaluating the Buerger minimum function uses the magnetic tape binary output of MIFRI (Sly & Shoemaker, 1959) a Fourier summation program. HASP will evaluate the minimum function over the complete unit cell which may be divided into 30 or 60 sections, the grid intervals within a section being 60ths × 60ths or 30ths × 120ths.

The available grid intervals have been kept large to minimize computing time but the superposition point need not be a grid point, the program performing linear interpolations where necessary. Final output is in a coded form on a scale of 0 to 39, the number associated with each grid point being represented by a single character.

The program is written in FORTRAN and requires a minimum of 8,192 words of core storage. About 20 minutes of machine time is required to evaluate and output on magnetic tape a complete unit cell of 30 sections.

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