

might be regarded as an incipient second Lewis acid-base interaction, but the geometry at the chlorine atom, where C-Cl...N is approximately 90°, makes it unlikely. Returning to the bromo compound, if we make the same calculation, but with a CN...Br distance of 3.06 Å between the cyanide group and the bromine atom in the *para* position on the next molecule, and further require that all Br...Br distances be 4.00 Å or greater, with interlayer spacing of 3.45 Å, thus shifting the CN...Br interaction from the *ortho* to the *para* bromine atom, we find a molecular volume of 230 Å<sup>3</sup>, about 3% larger than in the actual structure. Presumably, the actual structure occurs because its greater packing efficiency, and therefore greater van der Waals energy, more than offsets the failure to make the best (linear) CN...Br contact.

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## The Crystal Structures of BrC(CN)<sub>3</sub>, ClC(CN)<sub>3</sub>, and CH<sub>3</sub>C(CN)<sub>3</sub>

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Bromotricyanomethane, BrC(CN)<sub>3</sub>, is orthorhombic, space group *Pbca* (*D*<sub>2h</sub><sup>15</sup>), with *a* = 6.09 (1), *b* = 11.49 (2), and *c* = 17.62 (3) Å; there are eight molecules in the unit cell. The structure has been determined from three-dimensional Weissenberg film data and refined by least-squares methods to a conventional *R* of 0.15. The structure contains tetrahedral BrC(CN)<sub>3</sub> molecules with normal bond distances and angles. The packing is dominated by a short intermolecular N...Br distance of 3.03 Å and two short N...C distances of 3.18 and 3.20 Å. Chlorotricyanomethane, ClC(CN)<sub>3</sub>, and 1,1,1-tricyanoethane, CH<sub>3</sub>C(CN)<sub>3</sub>, are isomorphous, both hexagonal, space group *P6<sub>3</sub>/m* (*C*<sub>6h</sub><sup>2</sup>), with identical cell constants *a* = 10.23 (2) and *c* = 9.95 (2) Å; there are six molecules in the unit cell. Both structures were solved from three-dimensional Weissenberg data and were refined by least-squares methods: ClC(CN)<sub>3</sub> to an *R* of 0.088, CH<sub>3</sub>C(CN)<sub>3</sub> to an *R* of 0.155. The structures contain tetrahedral molecules with required mirror symmetry; these molecules also have normal bond distances and angles. Short intermolecular distances were found between a nitrogen atom on one molecule and three cyanide carbon atoms on the next; N...C is approximately 3.10 Å in all cases. These interactions lead to the formation of weakly bound trimers. Orthorhombic and monoclinic modifications of ClC(CN)<sub>3</sub> were also found.

### Introduction

As part of a continuing study of weak Lewis acid-base interactions (see the preceding paper for a more extensive introduction) we have determined the crystal structures of bromo-, chloro-, and methyltricyanomethane, XC(CN)<sub>3</sub>, where X = Br, Cl, or CH<sub>3</sub>, to deter-

### References

- BJORVATTEN, T. (1968). *Acta Chem. Scand.* **22**, 410.  
 BORGEN, B., HASSEL, O. & RØMMING, C. (1962). *Acta Chem. Scand.* **16**, 2469.  
 BREDIG, M. A. (1930). *Z. Kristallogr.* **74**, 56.  
 BRITTON, D. (1967). *Perspect. Struct. Chem.* **1**, 109.  
 CHRISTENSEN, T. A. & STRØMME, K. O. (1969). *Acta Cryst.* **B25**, 657.  
 GELLER, S. & SCHAWLOW, A. L. (1955). *J. Chem. Phys.* **23**, 779.  
 GOL'DER, G. A., ZDANOV, G. S. & UMANSKIJ, M. M. (1952). *Z. Fiz. Khim. SSSR*, **26**, 1434, *per Struct. Rep.* **16**, 510.  
 HEIART, R. B. & CARPENTER, G. B. (1956). *Acta Cryst.* **9**, 889.  
*International Tables for X-ray Crystallography* (1962). Vol. III, p. 201. Birmingham: Kynoch Press.  
 KETELAAR, J. A. A. & ZWARTSENBERG, J. W. (1939). *Rec. Trav. chim. Pays-Bas*, **58**, 448.  
 SCHLEMPER, E. O. & BRITTON, D. (1965). *Acta Cryst.* **18**, 419.  
 SILVERMAN, J., YANNONI, N. & KRUKONIS, A. P. (1969). *Acta Cryst.* **A25**, S139.

mine whether any unusual intermolecular interactions are present. These compounds are all unstable and volatile so that low-temperature measurements would be required for accurate structure determinations. However, since our main interest is in the packing, we have used the available equipment to determine the structures at room temperature.

## Experimental

## Preparation

BrC(CN)<sub>3</sub> was prepared by the procedure of Dr H. D. Hartzler (1963) of E. I. du Pont de Nemours and Co., Central Research Department. A solution of 0.03 mole of bromine in 10 ml of benzene was added dropwise to a suspension of 0.03 mole AgC(CN)<sub>3</sub> in 30 ml benzene, under dry nitrogen at room temperature. After 30 minutes of stirring, the solution was decanted from the silver bromide precipitate and evaporated to dryness under vacuum. The pale yellow powder was sublimed at 50° to give small white needles of the desired product. The melting point, 74°, agrees with that of Hartzler (72–74.2°) and with that reported earlier by Birkenback & Huttner (1929) (74°). Crystals suitable for X-ray diffraction were grown by sublimation under reduced pressure at a few degrees above room temperature; it was necessary to coat the condensation surface with stopcock grease in order to be able to remove the crystals without serious damage. The crystals decomposed slowly on standing; crystals exposed to X-rays turned red in a few days, and decomposed to a powder in less than two weeks. This instability had a severe effect on the quantity and quality of the X-ray data.

A sample of ClC(CN)<sub>3</sub>, prepared by Dr S. Trofimenko, was supplied by Dr Hartzler (Trofimenko, Little & Mower, 1962). Crystals suitable for X-ray diffraction studies were grown by sublimation under reduced pressure at slightly above room temperature. The crystals (m.p. 47°) sublimed very readily and the problem was to avoid crystals that were too large. The heat of the hand provided better control than any other heating method found.

CH<sub>3</sub>C(CN)<sub>3</sub> was prepared from AgC(CN)<sub>3</sub> and CH<sub>3</sub>I by the method of Hantzsch & Osswald (1899). The m.p. (95°) and the analysis (C–56.92%, H–3.02%) agreed with the expected values of m.p. 93.5° and

C–57.13%, H–2.88%. Suitable crystals were grown by sublimation at reduced pressure.

In all cases, crystals were sealed in glass capillaries before being used for X-ray studies.

## Unit cells and space groups

The crystals were examined by precession photography (Mo K $\alpha$  radiation,  $\lambda=0.7107$  Å) and by Weissenberg and oscillation photography (Mo K $\alpha$  radiation and Cu K $\alpha$  radiation,  $\lambda=1.5418$  Å). Crystal data are listed in Table 1. Although individual photographs gave smaller errors, we regard the probable errors to be one part in 600 for the precession photographs and one part in 300 for the Weissenberg and oscillation photographs.

Systematic extinctions ( $0kl, k=2n+1; h0l, l=2n+1; hk0, h=2n+1$ ) for BrC(CN)<sub>3</sub> indicate the space group to be *Pbca*. Fensch & Wagner (1938) concluded that the space group was *Pbcm*, but their list of observed reflections agrees with ours and with space group *Pbca*.

The first crystal of ClC(CN)<sub>3</sub> examined appeared to be monoclinic; it decomposed during the third photograph taken, and no other monoclinic crystals were ever found. Nevertheless, it would appear from the molecular volume, that this was ClC(CN)<sub>3</sub> and no accidental impurity. Numerous orthorhombic crystals were found, all of which gave poor diffraction photographs and which were probably twinned. Systematic extinctions ( $0kl$ , none;  $h0l, h=2n+1; hk0$ , not determined;  $hkl$ , none) indicate the diffraction symbol to be *P-a?*. The dimensions and the part of the diffraction symmetry that could be determined, make it clear that this form of ClC(CN)<sub>3</sub> is not isomorphous with the bromo compound. No crystals of this form suitable for intensity photographs were found. A hexagonal third form, which was exactly isomorphous with the methyl compound, was also found. Systematic extinctions ( $00l, l=2n+1$ ) indicate the space group to be

Table 1. Crystal data for BrC(CN)<sub>3</sub>, ClC(CN)<sub>3</sub>, and CH<sub>3</sub>C(CN)<sub>3</sub>

	BrC(CN) <sub>3</sub>	BrC(CN) <sub>3</sub>	ClC(CN) <sub>3</sub>	ClC(CN) <sub>3</sub>	ClC(CN) <sub>3</sub>	CH <sub>3</sub> C(CN) <sub>3</sub>
	This work	Fensch & Wagner (1938)	This work	This work	This work	This work
<i>a</i>	6.09 (1) * Å	6.06† Å	6.55 (1) Å	5.57 (2)‡ Å	10.23 (2) Å	10.23 (2) Å
<i>b</i>	11.49 (2)	11.35†	9.45 (2)	9.26 (3)	—	—
<i>c</i>	17.62 (3)	17.20 (17.74)†	18.3 (1)	11.48 (4)	9.95 (2)	9.95 (2)
System	Orthorhombic	Orthorhombic	Orthorhombic	Monoclinic	Hexagonal	Hexagonal
Space group	<i>Pbca</i>	<i>Pbcm</i> †	<i>P-a?</i>	?	<i>P</i> 6 <sub>3</sub> / <i>m</i>	<i>P</i> 6 <sub>3</sub> / <i>m</i>
<i>Z</i>	8	8	8	4	6	6
<i>D</i> <sub>obs</sub>	—	1.8 g. cm <sup>-3</sup>	1.46 g. cm <sup>-3</sup>	—	—	1.18 g. cm <sup>-3</sup>
<i>D</i> <sub>cal</sub>	1.831 (6)	1.91 (1.84)	1.47	1.46	1.387 (4)	1.161 (4)
Volume per molecule	154 Å <sup>3</sup>	148 Å <sup>3</sup> (153)	142 Å <sup>3</sup>	143 Å <sup>3</sup>	150 Å <sup>3</sup>	150 Å <sup>3</sup>

\* Errors given are probable errors based on the method used for measurement.

† These are converted from kX units. It seems likely that  $c=17.17$  kX was a misprint for  $c=17.71$  kX, since they gave  $D_{cal}=1.82$  g. cm<sup>-3</sup>. See the text for a discussion of the space group.

‡ This is  $a/\sin \beta$ .  $\beta$  was not determined.

Table 2. Positional and thermal parameters

Form of the anisotropic temperature factor is: exp [ -1/4 ( B<sub>11</sub>h<sup>2</sup>a<sup>\*2</sup> + ... + 2B<sub>12</sub>hka\*b\* + ... ) ].

Table with 11 columns: Position, x, y, z, B or B<sub>11</sub>, B<sub>22</sub>, B<sub>33</sub>, B<sub>12</sub>, B<sub>13</sub>, B<sub>23</sub>. Rows are grouped by compound: BrC(CN)<sub>3</sub>, ClC(CN)<sub>3</sub>, and CH<sub>3</sub>C(CN)<sub>3</sub>.

P6<sub>3</sub> or P6<sub>3</sub>/m; the latter was shown to be correct by the complete structure determination.

Determination of the structures

BrC(CN)<sub>3</sub>

The original data, from which the structure was solved approximately using Patterson and Fourier maps, were visually estimated three-dimensional Weissenberg film data (Mo Kα radiation, 0kl-3kl) obtained with a rather large crystal. Layers were correlated with a small number of precession film intensities. Quality of these data was poor and a second set of Weissenberg film data was collected (Cu Kα radiation, h0l-h5l) using an acicular crystal, elongated along b and approximately cylindrical with a diameter of 0.1 mm. Oscillation data were also collected for layer correlation. Lorentz and polarization corrections were made, but not absorption corrections (μ=94.3 cm⁻¹ for Cu Kα radiation).\*

\* Most of the calculations were done using programs prepared at Princeton University by Professor R. A. Jacobsen. The final refinements in each case were carried out using programs prepared by Dr L. W. Finger. Group refinements were made using a local modification of an earlier modification by Doedens of the program ORFLS (Busing, Martin & Levy, 1962). All computer calculations were run on CDC 1604 or 6600 computers of the University of Minnesota Computer Center.

Table 3. Observed and calculated structure factors for BrC(CN)<sub>3</sub>(× 1)

Table with multiple columns for observed (O) and calculated (C) structure factors. Includes a grid of values for different h, k, l indices and a list of unobserved reflections at the bottom.

observable intensity. Full-matrix least-squares refinement, with all atoms isotropic, converged with  $r=0.216$ ;  $R=0.228$ .<sup>\*</sup> With the Br atom treated anisotropically, refinement converged at  $r=0.095$ ;  $R=0.148$ . A difference Fourier map at this point showed no peak higher than  $1.6 \text{ e.}\text{\AA}^{-3}$ . Final positional and thermal parameters are given in Table 2. Structure factors are given in Table 3.

CIC(CN)<sub>3</sub>

Weissenberg film data (Cu K $\alpha$  radiation,  $hk0-hk4$ ) were collected for the hexagonal modification of CIC(CN)<sub>3</sub>, using an acicular crystal elongated along  $c$ , approximately cylindrical of diameter 0.1 mm. Oscillation data were collected for layer correlation. There were 218 independent reflections of measurable intensity and 187 more reflections in the same region of reciprocal space with intensities too weak to measure; the latter were not included in the calculations. Lorentz and polarization corrections were made, but not absorption corrections ( $\mu=39.7 \text{ cm}^{-1}$  for Cu K $\alpha$  radiation). Atom positions were found from Patterson and Fourier maps.<sup>†</sup> Full-matrix least-squares refinement, with all atoms isotropic, converged at  $r=0.140$ ;  $R=0.198$ . Refinement converged at  $r=0.079$ ;  $R=0.109$ , with the Cl atom anisotropic and the light atoms isotropic. The highest peak on a difference Fourier map calculated at this point was  $0.6 \text{ e.}\text{\AA}^{-3}$ , compared with  $4.0 \text{ e.}\text{\AA}^{-3}$ , the height of the smallest atomic peak on the corresponding Fourier map. Although, as already mentioned, the quality of the data was not good (e.g. the C(2) and N(2) peaks were not resolved in the best Fourier map, and the amount of data was limited), it was decided to try refinement with all atoms anisotropic. Convergence was reached after three cycles with  $r=0.0514$ ,  $R=0.088$ . Hamilton's (1965) test gives  $R_{19,176,0.005}=1.15$  compared with  $(0.0790/0.0514)^{1/2}=1.24$ , so we report results of the final refinement.<sup>‡</sup> Parameters are given in Table 2. Structure factors are listed in Table 4.

<sup>\*</sup>  $R = \sum(|F_o| - |F_c|) / \sum|F_o|$ ,  $r = \sum w(|F_o|^2 - |F_c|^2) / \sum w|F_o|^4$ , where the numerator of  $r$  is the function refined,  $w = (F_w/F_o)^4$  for  $F_o > F_w$  and  $w=1$  for  $F_o \leq F_w$ ; in the final refinement cycles,  $F_w$  was 18.5 for BrC(CN)<sub>3</sub>, 8.6 for CIC(CN)<sub>3</sub>, and 6.9 for CH<sub>3</sub>C(CN)<sub>3</sub>. Scattering factors for all atoms were taken from *International Tables for X-ray Crystallography* (1962). No anomalous dispersion corrections were made.

<sup>†</sup> The calculations for both the CIC(CN)<sub>3</sub> and CH<sub>3</sub>C(CN)<sub>3</sub> were made by expanding the data and parameter lists to correspond to monoclinic symmetry, and all calculations were performed as if the crystal were monoclinic, since the program used does not handle hexagonal symmetry.

<sup>‡</sup> To test the possibility that the proper space group is  $P6_3$  rather than  $P6_3/m$ , data were refined with an idealized molecular geometry in  $P6_3/m$  (starting as close to the final parameters given in Table 2 as possible) and in  $P6_3$  (starting with the molecule rotated  $3.3^\circ$  away from coincidence with the mirror plane). After three cycles of refinement, the molecule in  $P6_3$  had moved back toward the  $P6_3/m$  positions to the extent that no corresponding pair of atom positions differed by as much as one standard deviation; therefore,  $P6_3/m$  was accepted as the correct space group.

Table 4. Observed and calculated structure factors for CIC(CN)<sub>3</sub> and CH<sub>3</sub>C(CN)<sub>3</sub> ( $\times 10$ )

CHLORO		METHYL	
L	F <sub>o</sub>	L	F <sub>o</sub>
1	121	1	87
2	107	2	329
3	431	3	329
4	121	4	249
5	75	5	319
6	121	6	114
7	121	7	121
8	121	8	121
9	121	9	121
10	121	10	121
11	121	11	121
12	121	12	121
13	121	13	121
14	121	14	121
15	121	15	121
16	121	16	121
17	121	17	121
18	121	18	121
19	121	19	121
20	121	20	121
21	121	21	121
22	121	22	121
23	121	23	121
24	121	24	121
25	121	25	121
26	121	26	121
27	121	27	121
28	121	28	121
29	121	29	121
30	121	30	121
31	121	31	121
32	121	32	121
33	121	33	121
34	121	34	121
35	121	35	121
36	121	36	121
37	121	37	121
38	121	38	121
39	121	39	121
40	121	40	121
41	121	41	121
42	121	42	121
43	121	43	121
44	121	44	121
45	121	45	121
46	121	46	121
47	121	47	121
48	121	48	121
49	121	49	121
50	121	50	121
51	121	51	121
52	121	52	121
53	121	53	121
54	121	54	121
55	121	55	121
56	121	56	121
57	121	57	121
58	121	58	121
59	121	59	121
60	121	60	121
61	121	61	121
62	121	62	121
63	121	63	121
64	121	64	121
65	121	65	121
66	121	66	121
67	121	67	121
68	121	68	121
69	121	69	121
70	121	70	121
71	121	71	121
72	121	72	121
73	121	73	121
74	121	74	121
75	121	75	121
76	121	76	121
77	121	77	121
78	121	78	121
79	121	79	121
80	121	80	121
81	121	81	121
82	121	82	121
83	121	83	121
84	121	84	121
85	121	85	121
86	121	86	121
87	121	87	121
88	121	88	121
89	121	89	121
90	121	90	121
91	121	91	121
92	121	92	121
93	121	93	121
94	121	94	121
95	121	95	121
96	121	96	121
97	121	97	121
98	121	98	121
99	121	99	121
100	121	100	121

\* INDICATES UNOBSERVED REFLECTIONS

CH<sub>3</sub>C(CN)<sub>3</sub>

Weissenberg film data (Cu K $\alpha$  radiation,  $hk0-hk4$ ) were collected using an acicular crystal elongated along  $c$ , approximately cylindrical with a diameter of 0.1 mm. Oscillation data were collected for layer correlation and 54 reflections in the same region of reciprocal space with intensities too weak to measure; the latter were included in the eventual refinement with intensities equal to half the minimum observable intensity. Lorentz and polarization corrections were made, but not absorption corrections ( $\mu=6.7 \text{ cm}^{-1}$  for Cu K $\alpha$  radiation). The compound was assumed to be isostructural with the chloro compound, and initial parameters were chosen on this basis. Full-matrix least-squares refinement, with all atoms isotropic, converged at  $r=0.130$ ,  $R=0.171$ . With all atoms anisotropic, refinement converged at  $r=0.103$ ,  $R=0.154$ . As with the chloro compound, the same objections to anisotropic refinement apply, but again a comparison of  $R_{22,203,0.005}=1.07$ , with  $(0.130/0.103)^{1/2}=1.12$ , leads us

to report the results of the anisotropic refinement. The final parameters are given in Table 2; the structure factors are listed in Table 4. A final difference Fourier map showed the highest peak to be  $0.4 \text{ e.}\text{\AA}^{-3}$ , compared with  $5.4 \text{ e.}\text{\AA}^{-3}$  for the lowest atomic peak in the corresponding Fourier map. No attempt was made to include the hydrogen atoms.

### Results and discussion

The interatomic distances in the molecules are given in Table 5. In view of the instability of the crystals and the consequent low quality of the data we believe that the error estimates are optimistic, and that there are no demonstrated deviations from normal geometry and bond lengths in these molecules. Similarly, the anisotropic thermal parameters do not warrant any extensive rationalization.

Table 5. Bond lengths and angles in  $\text{XC}(\text{CN})_3$

	$\text{BrC}(\text{CN})_3$	$\text{ClC}(\text{CN})_3$	$\text{CH}_3\text{C}(\text{CN})_3$
X—C(4)	1.95 (2) Å	1.78 (1) Å	1.57 (2) Å
C(4)—C(1)	1.37 (3)	1.51 (2)	1.50 (2)
C(4)—C(2)	1.46 (4)	1.42 (2)	1.45 (2)
C(4)—C(3)	1.43 (3)	—	—
C(1)—N(1)	1.15 (3)	1.15 (2)	1.15 (2)
C(2)—N(2)	1.19 (4)	1.29 (3)	1.20 (2)
C(3)—N(3)	1.20 (3)	—	—
X—C(4)—C(1)	108.6 (16)°	108.9 (10)°	110.8 (13)°
X—C(4)—C(2)	105.6 (16)	110.7 (6)	111.0 (7)
X—C(4)—C(3)	111.7 (17)	—	—
C(1)—C(4)—C(2)	110.6 (20)	109.3 (10)	107.7 (7)
C(2)—C(4)—C(3)	108.1 (20)	108.0 (21)	108.5 (21)
C(3)—C(4)—C(1)	112.0 (15)	—	—
C(4)—C(1)—N(1)	179.6 (30)	179.7 (16)	174.9 (14)
C(4)—C(2)—N(2)	173.7 (22)	174.0 (20)	175.3 (12)
C(4)—C(3)—N(3)	176.3 (30)	—	—

Table 6. Intermolecular distances in  $\text{ClC}(\text{CN})_3$  and  $\text{CH}_3\text{C}(\text{CN})_3$

Distance*		$\text{ClC}(\text{CN})_3$	$\text{CH}_3\text{C}(\text{CN})_3$
a	N(1)—C(1)	3.09 Å	3.09 Å
b	N(1)—C(2)	3.09	3.11
c	N(1)—C(3)	3.27	3.31
d	N(1)—N(1)	3.42	3.48
e	N(1)—N(2)	3.55	3.49
f	N(1)—X	3.39	3.58
g	N(2)—C(1)	3.14	3.29
h	N(2)—N(1)	3.30	3.43
i	N(2)—C(2)	3.45	3.49
j	N(2)—X	3.49	3.48
k	N(2)—X	3.65	3.78
l	X—X	4.03	4.07

\* See Fig. 2.

The point of interest for which these studies were undertaken, and which we believe is demonstrated in the results, is the packing of the molecules (Figs. 1 and 2). The short intermolecular distances in  $\text{BrC}(\text{CN})_3$  are shown in Fig. 1; all  $\text{N}\cdots\text{Br}$  and  $\text{Br}\cdots\text{Br}$  distances less than  $4.0 \text{ \AA}$ , and all  $\text{N}\cdots\text{N}$  and  $\text{N}\cdots\text{C}$  distances

less than  $3.5 \text{ \AA}$ , are indicated, as well as a few additional distances. The short intermolecular distances in  $\text{ClC}(\text{CN})_3$  and  $\text{CH}_3\text{C}(\text{CN})_3$  are given in Table 6 (with reference to Fig. 2) for the same range of values.

We had expected in this study that  $\text{N}\cdots\text{X}$  interactions might be stronger than the usual van der Waals interactions for  $\text{X}=\text{Cl}$  and  $\text{Br}$ , but not for  $\text{X}=\text{CH}_3$ . The results do, indeed, show such an  $\text{N}\cdots\text{Br}$  interaction, as evidenced by the  $3.03 \text{ \AA}$  distance and the approximately linear  $\text{CN}\cdots\text{Br}$  geometry. This dis-

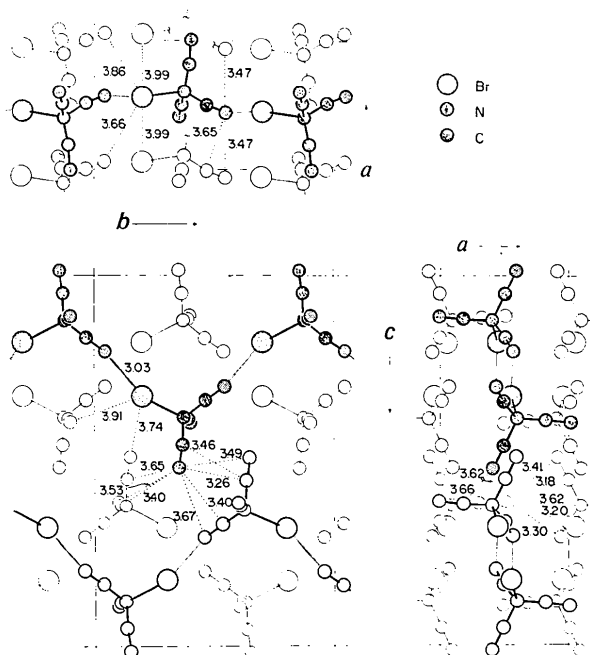


Fig. 1. The crystal structure of  $\text{BrC}(\text{CN})_3$ . Top, view down  $c$ ; lower left, view down  $a$ ; lower right, view into  $b$ . The same chain of molecules held together by  $\text{N}\cdots\text{Br}$  interactions is emphasized in all three views. Intermolecular distances (in Å) are given for all short contacts.

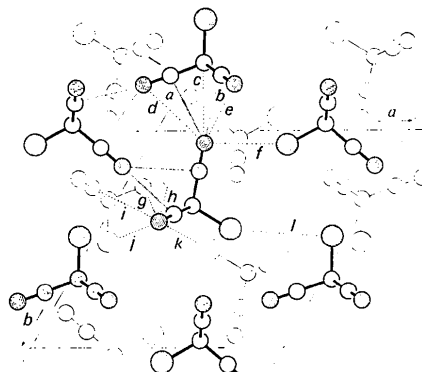


Fig. 2. The crystal structures of  $\text{ClC}(\text{CN})_3$  and  $\text{CH}_3\text{C}(\text{CN})_3$ . The view is down the  $c$  axis. The molecules centered at  $z=\frac{1}{2}$  are emphasized. The distances corresponding to the intermolecular contacts indicated by the letters are given in Table 6.

tance may be compared with the sum of the usual van der Waals radii, 3.45 Å (Pauling, 1960; see also the discussion in the preceding paper). On the other hand, there is no unusual N...Cl contact in  $\text{ClC}(\text{CN})_3$ , a conclusion that might have been drawn from the isomorphism with  $\text{CH}_3\text{C}(\text{CN})_3$ .

Before continuing to the next type of interaction we need to discuss the van der Waals radius of nitrogen. Pauling (1960) suggests 1.5 Å and Kitaigorodskii (1961) suggests 1.57 Å for this radius. However, Donohue (1961), in refining the structure of  $\alpha$ -nitrogen, pointed out that the N...N distance of 3.60 Å did not agree with Pauling's value for the radius. Pursuing his argument with more recent data, we find in  $\alpha$ -nitrogen (Jordan, Smith, Streib & Lipscomb, 1964) a shortest N...N distance of 3.42 Å, and in the structure of  $\gamma$ -nitrogen a shortest N...N distance of 3.275 Å at 20.5°K and 4015 atm (Schuch & Mills, 1970). If we use the expansion of  $\beta$ -nitrogen between 4015 and 0 atm to predict the corresponding expansion of  $\gamma$ -nitrogen, then we should correct the 3.275 Å value to 3.44 Å, to agree with the  $\alpha$ -nitrogen distance. From these results we conclude that 1.7 Å is a more reasonable value to use for the van der Waals radius for nitrogen, and that the smaller values given previously probably result from the frequent occurrence of weak but specific N...X interactions in crystals. This conclusion leads us to 3.4 Å as the van der Waals distance for a N...C contact with no acid-base character. Similarly, Klug (1965) has suggested that the usual O...C van der Waals distance of 3.10 Å should be replaced by 3.3–3.4 Å, and that a distance of 3.10 Å is abnormally short, *i.e.* it indicates an acid-base interaction.

Looking at our structures with the idea that N...C distances less than 3.4 Å are suggestive of acid-base contacts, we find several situations where there are such short distances. In each molecule there is one of these contacts that is also supported by the rest of the geometry. In the bromo compound, the CN group approximately parallel to the *a* axis points halfway between the two close CN groups in the next molecule, with N...C distances of 3.18 and 3.20 Å. In the chloro and methyl compounds, the mirror-plane CN group points toward the central carbon atom of the next molecule, so that all of the N...C distances to the cyanide carbon atoms are approximately equal at 3.10 Å in both compounds. This leads to weakly bonded cyclic trimers about the *c* axis.

For comparison the following are some of the short N...C distances previously reported: cyanogen,

3.18 and 3.26 Å (Parkes & Hughes, 1963); tetracyanoethylene, 3.09, 3.12, 3.20, and 3.23 Å (Bekoe & Trueblood, 1960); 1,2,3-tricyanopropane, 3.10 Å (Hartman & Hirshfeld, 1966); 1,2,3,4-tetracyanocyclobutane, 3.07, 3.16, 3.18, and 3.19 Å (Greenberg & Post, 1968); tetracyanothiophene, 2.98 and 3.07 Å (Rychnovsky & Britton, 1968); tetracyano-1,4-dithiin, 3.13, 3.15, 3.15, 3.18, and 3.19 Å (Dollase, 1965); tetracyanoquinodimethane, 3.18 and 3.22 Å (Long, Sparks & Trueblood, 1965).

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### References

- BEKOE, D. A. & TRUEBLOOD, K. N. (1960). *Z. Kristallogr.* **113**, 1.
- BIRKENBACK, L. & HUTTNER, K. (1929). *Ber. dtsh. chem. Ges.* **62B**, 153.
- BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS, A Fortran Crystallographic Least-Squares Program*. Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tennessee.
- DOLLASE, W. A. (1965). *J. Amer. Chem. Soc.* **87**, 979.
- DONOHUE, J. (1961). *Acta Cryst.* **14**, 1000.
- FENSCH, W. & WAGNER, G. (1938). *Z. Phys. Chem.* **B41**, 1.
- GREENBERG, B. & POST, B. (1968). *Acta Cryst.* **B24**, 918.
- HAMILTON, W. C. (1965). *Acta Cryst.* **18**, 502.
- HANTZSCH, A. & OSSWALD, G. (1899). *Ber. dtsh. chem. Ges.* **32**, 641.
- HARTMAN, A. & HIRSHFELD, F. L. (1966). *Acta Cryst.* **20**, 80.
- HARTZLER, H. D. (1963). Private communication.
- International Tables for X-ray Crystallography* (1962). Vol. III, pp. 202 & 215. Birmingham: Kynoch Press.
- JORDAN, T. H., SMITH, H. W., STREIB, W. E. & LIPSCOMB, W. N. (1964). *J. Chem. Phys.* **41**, 756.
- KITAIGORODSKII, A. I. (1961). *Organic Chemical Crystallography*, p. 7. New York: Consultants Bureau.
- KLUG, H. P. (1965). *Acta Cryst.* **19**, 983.
- LONG, R. E., SPARKS, R. A. & TRUEBLOOD, K. N. (1965). *Acta Cryst.* **18**, 932.
- PARKES, A. S. & HUGHES, R. E. (1963). *Acta Cryst.* **16**, 734.
- PAULING, L. (1960). *The Nature of the Chemical Bond*, 3rd Ed. p. 260. Ithaca: Cornell Univ. Press.
- RYCHNOVSKY, V. & BRITTON, D. (1968). *Acta Cryst.* **B24**, 725.
- SCHUCH, A. F. & MILLS, R. L. (1970). *J. Chem. Phys.* **52**, 6000.
- TROFIMENKO, S., LITTLE, E. L. & MOWER, H. F. (1962). *J. Org. Chem.* **27**, 433.