While the present paper was being prepared, Dr Edshammar sent the author the structural parameters he had obtained from his study of crystals of Mg_6Rh ($a_o=20{\cdot}1$ Å). He also stated that these parameters did not explain the intensity data his colleague had collected from crystals of Mg_6Pd, and that the latter structure had not yet been solved.

Comparison of his parameters with those obtained here show that Mg_6Rh is isostructural with Na_6Tl. All rhodium atoms are in place of thallium and all magnesium atoms in place of sodium, the Laves–Friauf polyhedron, again, being empty.

Since the noble metals have metallic radii differing by no more than about 2%, the lack of isostructural behavior of Mg_6Rh and Mg_6Pd is surprising, especially since rhodium and palladium are adjacent to each other in the periodic table of the elements. Also, the increased number of magnesium atoms (352 in Mg_6Rh as compared to 340 in Mg_6Pd) results in Mg–Mg bonds that are still shorter than those observed here (see also the Refinement section).

It seems at this stage impossible to predict the type of structure that might be represented by Mg_6Ir and Mg_6Pt or possibly by Mg_6Ru and Mg_6Os (if these two also exist). Each of these will have to be investigated separately with the use of single-crystal data. As stated in the Refinement section, the crystal of Mg_6Pt ($a_o=20{\cdot}083$ Å) investigated here is still believed to be twinned, but the possibility of the existence of a third and a fourth structure type will, as yet, have to be taken into account.

An important lesson to be learned from the present experience is that one should not draw conclusions from visual inspection of powder photographs as to whether or not intermetallic compounds are isostructural. Unfortunately, this has been done quite frequently in the past and is sometimes still practised today.

I am very thankful to Mr Benes Trus and Mrs Jean Westphal for having provided valuable help with computing problems. I also thank my wife, Mrs Lalli Samson, for having prepared the stereo pictures (Figs. 2 and 3). I am grateful for Mr Anthony Wong's successful efforts to prepare the single crystals.

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The Crystal Structures of 2,4,6-Trichlorobenzonitrile and 2,4,6-Tribromobenzonitrile

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2,4,6-Trichlorobenzonitrile crystallizes in the monoclinic space group $P2_1/c$ with $a=3{\cdot}97$ (1), $b=16{\cdot}06$ (3), $c=12{\cdot}84$ (2) Å, and $\beta=91{\cdot}0$ (3)°. 2,4,6-Tribromobenzonitrile crystallizes in the monoclinic space group $P2_1/m$ with $a=8{\cdot}82$ (2), $b=10{\cdot}34$ (2), $c=4{\cdot}89$ (1) Å, and $\beta=95{\cdot}8$ (2)°. The structures of both compounds were determined from three-dimensional film data and were refined to conventional R values of 0·134 and 0·089, respectively. Neither molecular structure contains any unusual features. The packing of the molecules in the crystals is dominated by weak Lewis acid-base interactions, CN···X, between the cyanide groups and *ortho* halogen atoms in a manner reminiscent of the dimerization of carboxylic acids. In the chloro compound these interactions lead to dimers, with CN···Cl distances of 3·22 Å. In the bromo compound these interactions lead to infinite chain-like polymers, with CN···Br distances of 3·06 Å.

Introduction

Short intermolecular N···X distances are well known in the cyanogen halides (ClCN, Heiart & Carpenter, 1956; BrCN, Geller & Schawlow, 1955; ICN, Ketelaar & Zwartsenberg, 1939) and have recently been found in the halocyanoacetylenes (ClCCCN and BrCCCN, Bjorvatten, 1968; ICCCN, Borgen, Hassel & Rømming, 1962). These short distances have been interpreted as indicating donor–acceptor or acid–base interactions between adjacent molecules. A study of *p*-halobenzonitriles and isonitriles, looking for the same phenomenon (*p*-iodobenzonitrile, Schlemper & Britton, 1965; preliminary results quoted in Britton, 1967), has been in progress in this laboratory. In the course of this work, it seemed to us that two partially completed structural studies involving related compounds should be finished. Gol'der, Zdanov & Umanskij (1952) determined the structure of 2,4,6-trichlorobenzonitrile in projection, and it appeared possible that short N···Cl distances might be present, although not with a linear CN···Cl arrangement. Bredig (1930) determined the space group and unit cell of 2,4,6-tribromobenzonitrile; from the size, shape, and symmetry of the unit cell is seemed to us that a linear alignment of molecules, and specific intermolecular interactions, were a distinct possibility. Accordingly, we report here more complete structure determinations for both these compounds.

Experimental

Both compounds were prepared by Mr Henry Grote from the corresponding aniline *via* the Sandmeyer reaction. Recrystallization from benzene gave crystals suitable for X-ray diffraction studies. The unit-cell dimensions were determined from Weissenberg and precession photographs (Cu $K\alpha$, $\lambda = 1{\cdot}5418$ Å; Mo $K\alpha$, $\lambda = 0{\cdot}7107$ Å). These dimensions, along with previous results, are reported in Table 1. For the chloro compound, the systematic extinctions ($0k0$, $k=2n+1$; $h0l$, $l=2n+1$) indicate a $P2_1/c$ space group. For the bromo compound, systematic extinctions ($0k0$, $k=2n+1$) indicate the space group to be either $P2_1$ or $P2_1/m$. Bredig concluded that $P2_1/m$ is the correct choice, based on morphology and etch figures; the final solved structure confirms this choice. To avoid slow sublimation, both crystals were sealed in capillaries for intensity-data collection.

Compound $Cl_3C_6H_2CN$

Multiple film Weissenberg data (Cu $K\alpha$ radiation) were collected for $0kl$–$2kl$ using an approximately cylindrical crystal 0·10 mm in diameter and 0·88 mm in length. Precession data, $hk0$ and $h0l$, were collected to scale the Weissenberg layers. Intensities were measured by visual comparison with a series of timed exposures of a selected reflection. There were 349 independent reflections of measurable intensity and 154 more, in the same region of reciprocal space, with intensities too faint to measure. The latter were included in the final least-squares calculations with F(unobserved) taken as $\frac{1}{2}F_o$(min). Lorentz and polarization corrections were made, but not absorption corrections; the linear absorption coefficient, μ, is 95·6 cm^{-1}.

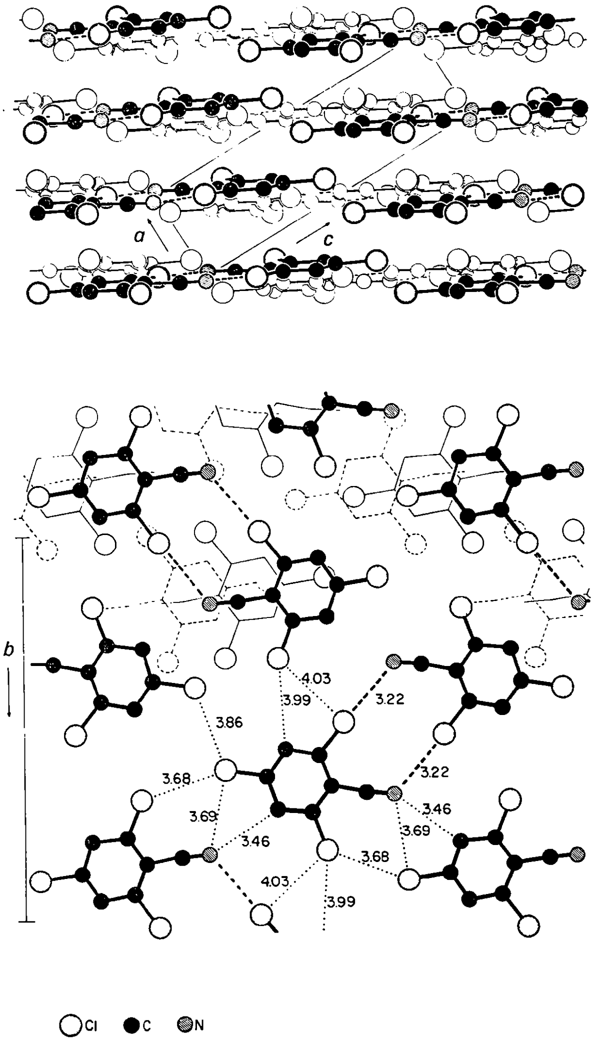

Fig. 1. Crystal structure of trichlorobenzonitrile. Top, projection along **b**, where the separation into layers is clearly seen. Bottom, projection perpendicular to layers. Displacement of successive layers is shown in the top half of this view; the in-plane contacts of a single molecule are shown in the bottom half. All numbers are distances in Å.

Table 1. *Crystal data*

	$Cl_3C_6H_2CN$		$Br_3C_6H_2CN$	
	This work	Gol'der	This work	Bredig
a	3·97 (1) Å	4·11 Å	8·82 (2) Å	8·77 Å
b	16·06 (3)	15·95	10·34 (2)	10·32
c	12·84 (2)	12·83	4·89 (1)	4·88
β	91·0 (3)°	91·5°	95·8 (2)°	96·0°
D_{obs}	–	1·67 g.cm^{-3}	–	–
D_{calc}	1·674 (5) g.cm^{-3}	1·64	2·540 (7) g.cm^{-3}	2·51 g.cm^{-3}
Z	4		2	
Volume	205 Å^3 per molecule		223 Å^3 per molecule	
Space group	$P2_1/c$		$P2_1/m$	

A three-dimensional Patterson map clearly showed the three chlorine atom positions. A Fourier synthesis was used to determine the light atom positions. Positions of the chlorine and carbon atoms in the benzene ring agreed approximately with the previously reported y and z parameters. The cyanide, however, was positioned differently, such that the nitrogen atom position was roughly that previously reported, but the carbon atom was attached to the other nearby benzene ring (Fig. 1).

Full-matrix least-squares refinement was carried out with all atoms ultimately given anisotropic thermal parameters. At every third cycle the Weissenberg layers were rescaled; consequently, anisotropic thermal parameters in the **a** direction are less meaningful due to this rescaling. The intense reflections appeared to be affected by extinction, and eight with $F_c > 58$ were omitted from the refinement (four others with $F_c > 58$ were inadvertently left in the last refinement; but for none of these four was the difference between F_o and F_c large, so the refinement was not repeated). In the final cycle, the weighted sum of residuals (r) was 0·027, the unweighted sum of residuals, (R) was 0·134, and F_w was 20·8 in the weighting scheme.* To check that the cyanide position was correct, (since it differed from the previously reported position), Fourier and difference Fourier maps were calculated based on all atoms having isotropic thermal parameters. The cyanide carbon atom peak had a height of 66 on an arbitrary scale in the Fourier map, while the height at the previously reported (incorrect) position, which also corresponded roughly to a hydrogen atom position, was 7 on the same scale. The highest peak on the difference map was of height 22, in the close vicinity of one of the chlorine atom positions and a consequence of anisotropic thermal motion. Final parameters are given in Table 2. Observed and calculated structure factors are listed in Table 3.

Compound $Br_3C_6H_2CN$

Multiple-film Weissenberg data were collected for $h0l$–$h9l$ (Cu $K\alpha$ radiation) on a tabular $\{201\}$ crystal measuring $0·16 \times 0·18 \times 0·07$ mm and for $hk0$–$hk4$ (Mo $K\alpha$ radiation) data were collected on a prismatic crystal, elongated along **c**, measuring $0·15 \times 0·18 \times 0·45$ mm. On both crystals the developed forms were $\{201\}$ and $\{110\}$. Lorentz, polarization, and absorption corrections were made, the latter using the actual crystal shape. The linear absorption coefficients are 182 cm^{-1} for Cu $K\alpha$ radiation and 144 cm^{-1} for Mo $K\alpha$ radiation. Transmission factors ranged from 0·16 to 0·46 on the first crystal and from 0·10 to 0·19 on the second. The data were correlated and averaged. There were 304 independent reflections with measurable intensities.

The structure was solved from Patterson and Fourier maps and refined using full-matrix least-squares methods. After the initial refinement with anisotropic bromine atoms using all the data, the two sets of data were separated, refined independently, rescaled, and recombined. The structure was refined to this point with $F_w = 40$ in the weighting scheme; an examination of $||F_o| - |F_c||$ as a function of $|F_o|$ suggested that an F_w of 22 would be more nearly correct. Using this F_w value, and with only the bromine atoms anisotropic, the refinement converged at $r = 0·054$, $R = 0·089$.

Table 2. *Positional and thermal parameters**

	x	y	z	B_{11} or B	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Compound $Cl_3C_6H_2CN$									
Cl(2)	0·7481 (12)	−0·0156 (3)	0·1331 (3)	6·10 (34)	3·73 (22)	5·57 (27)	−0·04 (20)	1·22 (22)	−1·48 (19)
Cl(4)	0·2380 (12)	0·1041 (3)	0·4862 (3)	4·60 (34)	7·01 (31)	3·65 (24)	0·67 (21)	0·86 (22)	0·96 (19)
Cl(6)	0·7900 (12)	0·3131 (2)	0·2126 (4)	5·52 (32)	3·20 (21)	7·18 (28)	0·39 (21)	1·92 (23)	0·26 (21)
C(1)	0·7412 (41)	0·1476 (12)	0·1818 (12)	2·6 (10)	5·1 (11)	2·5 (8)	0·6 (8)	0·1 (8)	0·1 (8)
C(2)	0·6501 (48)	0·0678 (11)	0·2145 (16)	6·3 (14)	3·2 (10)	5·9 (13)	0·7 (8)	1·2 (10)	−2·1 (8)
C(3)	0·4894 (51)	0·0515 (11)	0·3068 (14)	6·2 (13)	7·1 (11)	1·4 (8)	1·0 (9)	0·1 (8)	1·1 (8)
C(4)	0·4278 (39)	0·1217 (12)	0·3696 (11)	3·5 (12)	6·0 (10)	1·6 (7)	2·0 (8)	1·2 (7)	−0·2 (9)
C(5)	0·5058 (45)	0·2047 (11)	0·3426 (15)	2·4 (10)	4·7 (11)	6·1 (12)	−0·0 (7)	0·3 (9)	0·7 (8)
C(6)	0·6805 (42)	0·2134 (9)	0·2490 (14)	3·3 (11)	3·3 (9)	3·6 (9)	−0·9 (7)	0·4 (8)	0·6 (7)
C(N)	0·9050 (47)	0·1644 (8)	0·0838 (17)	2·0 (12)	2·4 (8)	7·8 (14)	−0·3 (6)	3·0 (10)	−0·5 (8)
N	1·0464 (45)	0·1719 (8)	0·0097 (15)	7·3 (12)	4·5 (8)	8·3 (10)	−0·4 (7)	6·2 (9)	−0·4 (8)
Compound $Br_3C_6H_2CN$									
Br(2)	0·1868 (5)	0·5238 (4)	0·3307 (8)	3·29 (22)	2·52 (16)	4·02 (21)	0·44 (16)	−0·33 (15)	0·64 (14)
Br(4)	0·5785 (6)	$\frac{1}{4}$	1·1079 (11)	2·40 (28)	3·94 (28)	3·16 (27)	–	−0·38 (19)	–
C(1)	0·1853 (57)	$\frac{1}{4}$	0·3698 (94)	2·4 (10)					
C(2)	0·2565 (41)	0·3699 (38)	0·4839 (65)	2·8 (7)					
C(3)	0·3730 (40)	0·3712 (34)	0·7122 (61)	2·7 (6)					
C(4)	0·4393 (61)	$\frac{1}{4}$	0·7862 (101)	2·6 (10)					
C(N)	0·0955 (72)	$\frac{1}{4}$	0·1341 (117)	3·9 (12)					
N	−0·0163 (63)	$\frac{1}{4}$	−0·0334 (105)	5·1 (12)					

* Anisotropic temperature factors are of the form:
$\exp[-\frac{1}{4}(B_{11}h^2a^{*2} + \ldots + 2B_{12}hka^*b^* + \ldots)]$.
E.s.d.'s for the final significant figures are given in parentheses.

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* $r = \sum w(|F_o|^2 - |F_c|^2)^2 / \sum w|F_o|^4$; $R = \sum ||F_o| - |F_c|| / \sum |F_o|$; $w = (F_w/F_o)^4$ for $F_o > F_w$; $w = 1·0$ for $F_o \leqslant F_w$; $w = 0·5$ for F_o unobserved. The numerator of r was the function refined. Various calculations were made using local programs or programs supplied by Dr L. W. Finger of the Geology Department of the University of Minnesota, and were carried out on the CDC 1604 computer at the University Computer Center. Scattering factors used in the calculations were taken from *International Tables for X-ray Crystallography* (1962).

Results and discussion

The intramolecular bond lengths and angles for both compounds are given in Table 4. No unusual bond lengths exist in either compound, and, in view of the limited accuracy, a detailed discussion and comparison with other compounds is omitted. The bond angles also appear to be normal, including the increase in the ring angle at the carbon atoms attached to halogen atoms and the decrease of the remaining ring angles (for a closely related previous example of this phenomenon, see Christensen & Strømme, 1969). For least-squares planes through the molecules (with atoms weighted proportionally to their atomic numbers in determining the plane), the average deviation from the plane is 0·024 Å for the chloro compound and 0·06 Å for the bromo compound. These values are slightly greater than the average uncertainties in the atom positions, and we conclude that the molecules are slightly puckered. However, individual errors preclude any detailed discussion of the puckering.

The feature of most interest, and the reason for undertaking the study, is the packing of the molecules. The crystal structures are shown in Figs. 1 and 2. Both structures contain approximately planar layers of molecules. In the chloro compound, average distance between layers is 3·36 Å and the distance of closest approach between any pair of atoms in successive layers is 3·53 Å. In the bromo compound, the corresponding distances are 3·45 Å for the average distance and 3·57 Å for the distance of closest approach. However, within the planar layers both structures show the same surprising feature: the CN···X interactions, which we were hoping to find, do indeed occur, but between the nitrogen atoms and the *ortho* halogen atoms rather than the *para* halogen atoms. In both cases, this means that the angle C–N···X is nearer 120° than 180° (C–N···Cl angle is 122·4°, C–N···Br

Table 3. *Observed and calculated structure factors for* $X_3C_6H_2CN(\times 10)$

K	L	FO	FC
X=CL			
H=0			
4	0	235	-250
6	0	651	624
8	0	221	-223
10	0	444	426
12	0	62*	75
1	1	66	-33
2	1	422	-448
3	1	364	382
4	1	303	-283
5	1	667	777
6	1	254	254
7	1	391	425
8	1	250	230
9	1	327	-280
10	1	43*	-43
11	1	49*	21
12	1	436	442
13	1	244	224
0	2	409	-452
1	2	105	-106
2	2	317	321
3	2	338	334
4	2	568	-604
5	2	462	496
6	2	290	-261
7	2	103	-64
8	2	462	455
9	2	295	275
10	2	44*	18
11	2	357	329
12	2	133	134
13	2	51*	74
1	3	476	-528
2	3	381	-386
3	3	597	-657
4	3	619	565
5	3	496	516
6	3	244	210
7	3	337	-325
8	3	39*	37
9	3	356	-362
10	3	274	272
11	3	47*	2
12	3	168	-153
13	3	173	-159
0	4	338	352
1	4	284	285
2	4	493	-528
3	4	54*	48
4	4	505	-522
5	4	221	-214
6	4	350	-343
7	4	38*	-61
8	4	402	-394
9	4	239	-245
10	4	112	92
11	4	49*	2
12	4	51*	-29
13	4	52*	15
1	5	487	-532
2	5	32*	-48
3	5	78	51
4	5	335	-306
5	5	224	-203
6	5	142	-141
7	5	41*	44
8	5	43*	-64
9	5	171	-160
10	5	168	-149
11	5	261	-262
12	5	52*	-92
13	5	159	150
14	5	187	-187
0	6	478	518
1	6	397	-389
2	6	274	206
3	6	123	101
4	6	263	-252
5	6	110	108
6	6	41*	-68
7	6	397	-377
8	6	147	131
9	6	48*	-3
10	6	116	82
11	6	141	-131
12	6	52*	-29
13	6	105	-98
1	7	39*	47
2	7	264	-227
3	7	217	207
4	7	173	-159
5	7	558	630
6	7	45*	58
7	7	46*	96
8	7	48*	-26
9	7	137	-128
10	7	51*	16
11	7	122	127
0	8	343	347
1	8	380	351
2	8	174	159
3	8	139	132
4	8	45*	22
5	8	46*	9
6	8	48*	9
7	8	134	94
8	8	256	266
9	8	154	-142
10	8	216	219
11	8	138	121
1	9	47*	-95
2	9	144	-139
3	9	223	235
4	9	152	149
5	9	153	133
6	9	129	117
7	9	51*	-10
8	9	275	287
9	9	53*	-35
0	10	175	173
1	10	50*	70
2	10	50*	2
3	10	203	202
4	10	208	-192
5	10	52*	-50
6	10	52*	-28
7	10	127	-152
8	10	53*	-68
9	10	134	134
1	11	136	-136
2	11	52*	-107
3	11	224	-225
4	11	228	-235
0	12	53*	-62
1	12	53*	26
2	12	53*	-104
2	13	129	-109
H=1			
2	0	255	-238
3	0	(520)	-737
4	0	194	-157
5	0	302	-302
6	0	359	345
7	0	468	454
8	0	44*	-82
9	0	385	-374
10	0	51*	-11
11	0	283	-282
12	0	190	197
13	0	214	-214
1	1	(433)	603
1	-1	158	-131
2	1	(567)	879
2	-1	134	113
3	1	178	182
3	-1	(584)	-913
4	1	159	176
4	-1	228	201
5	1	181	182
5	-1	138	128
6	1	235	-228
6	-1	600	-708
7	1	302	280
7	-1	179	-154
8	1	395	-383
8	-1	198	-208
9	1	48*	62
9	-1	252	-254
10	1	52*	-28
10	-1	52*	-57
11	1	177	-168
11	-1	211	184
12	1	54*	-51
12	-1	58*	-65
13	1	238	245
13	-1	234	-248
14	1	123	-126
0	2	(756)	1565
0	-2	(422)	-582
1	2	(757)	-1316
1	-2	465	-539
2	2	294	308
2	-2	355	-337
3	2	273	-273
3	-2	251	-225
4	2	127	109
4	-2	213	-188
5	2	295	267
5	-2	95	64
6	2	381	382
6	-2	393	-396
7	2	121	-89
7	-2	123	123
8	2	46*	-7
8	-2	237	-205
9	2	358	336
9	-2	329	332
10	2	53*	109
10	-2	229	-231
11	2	156	-160
11	-2	56*	-96
12	2	65*	101
12	-2	118*	-78
1	3	29*	32
1	-3	266	-265
2	3	181	193
2	-3	563	621
3	3	73	-17
3	-3	153	-138
4	3	184	169
4	-3	35*	-6
5	3	515	541
5	-3	401	-414
6	3	41*	-23
6	-3	341	327
7	3	256	266
7	-3	157	-135
8	3	164	-143
8	-3	47*	-9
9	3	167	-173
9	-3	50*	-57
10	3	226	207
10	-3	54*	-5
11	3	283	293
11	-3	129	-121
12	3	381	371
12	-3	369	376
0	4	135	-156
0	-4	(537)	710
1	4	182	172
1	-4	33*	17
2	4	35*	9
2	-4	271	-284
3	4	300	-282
3	-4	290	-275
4	-4	38*	-75
4	4	188	-178
5	4	323	307
5	-4	124	113
6	4	172	-162
6	-4	356	373
7	4	443	486
7	-4	409	432
8	4	196	174
8	-4	219	-216
9	4	53*	19
9	-4	154	113
10	4	56*	67
10	-4	56*	99
11	4	202	210
11	-4	58*	51
1	5	367	-380
1	-5	389	396
2	5	39*	53
2	-5	341	340
3	5	40*	-10
3	-5	228	229
4	5	488	483
4	-5	419	456
5	5	44*	-59
5	-5	242	220
6	5	205	-198
6	-5	321	-314
7	5	230	-207
7	-5	168	174
8	5	52*	-75
8	-5	52*	-88
9	5	128	-94
9	-5	55*	41
10	5	160	168
10	-5	242	224
11	5	183	-188
11	-5	59*	136
0	6	105	101
0	-6	281	-273
1	6	258	-245
1	-6	348	-316
2	6	352	-310
2	-6	333	364
3	6	127	-131
3	-6	300	-266
4	6	323	-303
4	-6	340	345
5	6	48*	-95
5	-6	48*	-32
6	6	162	-148
6	-6	139	128
7	6	105	-71
7	-6	184	180
8	6	230	-258
8	-6	353	357
9	6	57*	68
9	-6	57*	24
10	-6	59*	-30
11	-6	169	-178
1	7	173	-132
1	-7	276	282
2	7	244	240
2	-7	266	262
3	7	218	-190
3	-7	149	-123
4	7	50*	-118
4	-7	238	-221
5	7	52*	-10
5	-7	144	127
6	7	54*	-87
6	-7	221	-223
7	7	56*	32
7	-7	56*	-80
8	7	182	-187
8	-7	291	-288
9	7	52*	-117
9	-7	152	158
10	-7	60*	-85
11	-7	143	141
0	8	52*	53
0	-8	51*	12
1	8	217	-204
1	-8	232	-221
2	8	252	251
2	-8	185	-168
3	8	251	-232
3	-8	280	-282
4	8	54*	-25
4	-8	118	78
5	8	56*	55
5	-8	111	114
6	8	57*	-134
6	-8	138	149
7	8	59*	48
7	-8	57*	-22
8	8	130	116
8	-8	289	-319
9	8	61*	-50
1	9	56*	-20
2	9	113	59
3	9	146	162
3	-9	181	-199
4	9	58*	85
4	-9	302	309
5	9	297	273
5	-9	346	-397
6	9	165	-159
6	-9	60*	-73
7	9	61*	78
8	9	62*	-128
9	9	62*	29
0	10	272	289
1	10	59*	-21
2	10	60*	21
7	10	179	177
2	11	143	159
H=2			
2	0	193	-189
3	0	33*	-35
4	0	38*	-0
5	0	231	-189
6	0	156	-129
7	0	52*	114
8	0	142	-111
9	0	60*	13
10	0	312	-295
11	0	67*	18
1	1	84	-50
1	-1	102	119
2	1	217	-210
2	-1	191	193
3	1	234	-242
3	-1	403	-447
4	1	135	126
4	-1	102	-116
5	1	417	-427
5	-1	152	-146
6	1	321	-299
6	-1	309	298
7	1	52*	32
7	-1	257	-276
8	1	113	-102
8	-1	157	120
9	1	61*	16
9	-1	61*	-49
10	1	64*	-19
10	-1	64*	-20
11	1	67*	48
11	-1	159	148
12	1	206	-226
12	-1	204	217
0	2	91	73
0	-2	90	86
1	2	195	174
1	-2	245	-270
2	2	357	-386
2	-2	224	-215
3	2	38*	-104
3	-2	142	119
4	2	198	180
4	-2	164	140
5	2	46*	-53
5	-2	284	259
6	2	421	433
6	-2	303	270
7	2	54*	-55
7	-2	68*	-55
8	2	284	-291
8	-2	163	-162
9	2	124	-105
9	-2	242	233
10	2	65*	-39
10	-2	65*	-30
11	-2	68*	35
12	2	201	-230
1	3	526	652
1	-3	443	430
2	3	175	181
2	-3	105	100
3	3	187	-154
3	-3	254	240
4	3	46*	-14
4	-3	133	108
5	3	49*	-20
5	-3	236	-220
6	3	53*	5
6	-3	52*	-16
7	3	56*	69
7	-3	204	199
8	3	60*	-117
8	-3	59*	35
9	3	150	134
9	-3	220	245
10	3	169	-157
10	-3	132	132
11	-3	68*	-32
0	4	191	-191
0	-4	262	-274
1	4	392	-441
1	-4	291	258
2	4	342	344
2	-4	227	221
3	4	176	-137
3	-4	46*	-49
4	4	279	287
4	-4	424	433
5	4	53*	81
5	-4	131	-128
6	4	171	166
6	-4	336	326
7	4	59*	-26
7	-4	175	166
8	-4	62*	83
9	-4	178	-180
10	4	153	-155
10	-4	67*	-53
11	-4	68*	9
1	5	132	137
1	-5	405	386
2	5	51*	40
2	-5	294	-278
3	5	52*	-41
3	-5	250	-250
4	5	232	212
4	-5	53*	-12
5	5	57*	16
5	-5	55*	92
6	5	59*	3
6	-5	201	-205
7	5	62*	79
7	-5	62*	-42
8	-5	64*	-49
9	-5	189	193
10	5	210	225
11	-5	213	229
0	6	55*	-48
0	-6	206	-212
1	6	55*	47
1	-6	190	-173
2	6	219	-181
2	-6	119	-117
3	6	57*	-79
3	-6	56*	32
4	6	59*	128
4	-6	257	223
5	6	145	116
5	-6	60*	48
6	6	63*	73
6	-6	62*	27
7	6	228	231
7	-6	406	-385
8	-6	189	-189
1	7	60*	-54
1	-7	59*	-3
2	7	145	130
2	-7	120	-118
3	7	62*	-2
3	-7	103*	-114
4	7	56*	56
4	-7	62*	-48
5	7	251	-233
5	-7	478	-425
6	-7	298	276
0	8	189	-203
1	8	129	-116
2	-8	350	-346
3	-8	186	181
2	-9	146	-158
3	-9	264	-267

X=BR

H	K	FO	FC
L=0			
2	0	628	-560
3	0	905	-936
5	0	981	1082
8	0	430	-504
2	1	305	-301
3	1	458	414
4	1	512	-470
5	1	211	192
1	2	773	863
2	2	1198	-1178
3	2	919	-808
5	2	302	274
6	2	739	726
7	2	434	-430
2	3	828	878
3	3	567	-533
5	3	322	-321
6	3	272	180
7	3	311	305
0	4	1156	1336
3	4	826	-790
5	4	670	722
1	5	797	795
4	5	624	-671
1	6	466	434
2	6	580	-550
3	6	406	-336
6	6	469	416
1	7	548	515
2	7	585	593
3	7	457	-428
4	7	328	-277
5	7	284	-261
6	7	272	277
0	8	577	651
3	8	188	-182
5	8	297	289
1	9	411	424
2	9	194	194
4	9	554	-494
L=1			
		265	-224
1	0	1082	-1235
1	0	226	258
2	0	373	-353
3	0	1087	1193
3	0	388	-290
4	0	284	266
4	0	695	-602
5	0	314	288
5	0	491	-452
6	0	705	-771
7	0	729	735
0	1	157	-132
1	1	415	468
1	1	219	-164
2	1	602	-615
2	1	259	244
3	1	332	315
3	1	289	-256
4	1	285	-179
4	1	330	325
5	1	229	191
5	1	328	-278
6	1	220	199
6	1	290	266
7	1	244	-278
0	2	932	-1071
1	2	793	-879
1	2	886	1047
2	2	338	-242
2	2	199	151
3	2	344	304
3	2	470	374
4	2	966	1043
4	2	884	-817
5	2	432	-434
5	2	646	-533
6	2	289	-196
6	2	285	304
7	2	353	-445
8	2	320	369
0	3	652	805
1	3	410	-408
1	3	244	226
2	3	280	-272
3	3	547	-568
4	3	364	300
4	3	696	-639
5	3	328	322
5	3	513	466
0	4	247	202
1	4	864	-992
1	4	217	195
2	4	284	-263
2	4	1016	1077
3	4	749	734
4	4	294	250
4	4	292	-285
5	4	387	351
5	4	401	-421
6	4	652	-745
7	4	460	514
0	5	179	167
1	5	149	171
1	5	559	560
2	5	659	-794
3	5	779	-750
4	5	250	189
5	5	335	308
6	5	465	411
0	6	488	-516
1	6	300	-326
1	6	543	535
2	6	153	-120
3	6	247	213
4	6	516	561
4	6	493	-404
5	6	296	-240
5	6	368	-250
7	6	298	-277
0	7	571	621
1	7	317	-304
1	7	462	499
2	7	276	-279
2	7	289	-248
3	7	486	-480
3	7	415	-375
4	7	370	352
4	7	491	-411
5	7	330	340
5	7	420	404
8	7	322	-329
1	8	193	-246
2	8	205	-121
2	8	555	554
3	8	298	273
3	8	222	-143
0	9	257	308
1	9	264	280
2	9	499	-566
3	9	466	-430
6	9	338	316
0	11	446	369
L=2			
0	0	412	-377
1	0	795	837
1	0	977	-1032
2	0	472	455
3	0	471	454
3	0	300	327
4	0	774	-847
4	0	1139	1139
5	0	237	-278
5	0	351	-278
6	0	448	-464
7	0	368	479
8	0	350	327
0	1	529	-544
1	1	356	355
1	1	369	366
2	1	408	-372
3	1	379	340
3	1	265	-192
4	1	180	152
4	1	279	261
5	1	264	-245
5	1	283	-263
6	1	308	240
0	2	583	-542
1	2	266	223
1	2	552	-592
2	2	977	1053
2	2	611	-599
3	2	293	-247
3	2	879	825
5	2	689	-687
6	2	440	-422
7	2	323	256
1	3	592	-663
1	3	193	-190
2	3	397	351
2	3	486	488
3	3	267	230
3	3	250	197
4	3	317	-330
6	3	425	-417
6	3	360	-367
0	4	298	-277
1	4	503	485
1	4	719	-841
2	4	398	357
2	4	374	376
3	4	535	512
3	4	226	193
4	4	840	-815
4	4	560	607
6	4	309	-288
0	5	577	-673
1	5	232	218
2	5	277	267
3	5	468	445
3	5	301	245
4	5	227	193
5	5	250	-220
5	5	509	-520
0	6	308	-279
1	6	205	-207
2	6	544	542
2	6	380	-335
3	6	170	-145
3	6	526	449
5	6	372	-403
0	7	219	-192
1	7	517	-583
2	7	341	329
2	7	464	471
3	7	338	303
3	7	392	353
4	7	347	-331
6	7	438	-436
1	8	184	170
1	8	228	-233
3	8	185	220
4	8	377	346
0	9	490	-472
2	9	325	310
3	9	417	421
L=3			
0	0	457	472
1	0	480	460
1	0	350	323
2	0	644	-651
2	0	307	-261
3	0	265	-250
3	0	615	-654
4	0	308	-253
4	0	233	207
5	0	512	502
6	0	446	393
6	0	528	477
7	0	275	-240
0	1	405	-406
1	1	382	354
1	1	303	279
2	1	318	-339
3	1	217	214
4	1	256	203
6	1	305	237
0	2	676	725
2	2	510	-556
3	2	764	-729
3	2	254	-256
4	2	263	-238
5	2	469	494
6	2	307	167
0	3	333	292
1	3	460	-539
2	3	248	223
4	3	415	-414
0	4	323	345
1	4	452	506
2	4	690	-643
2	4	221	-195
3	4	483	-537
4	4	250	310
0	5	227	-196
1	5	438	430
2	5	366	-406
4	5	254	229
5	5	296	-261
6	5	295	327
0	6	382	365
2	6	307	-301
3	6	473	-417
0	7	219	229
1	7	455	-502
2	7	224	232
4	7	428	-432
1	8	200	181
2	8	219	-148
1	9	410	368
2	9	313	-287
L=4			
0	0	384	-344
1	0	330	320
2	0	396	-363
2	0	305	346
3	0	397	425
4	0	357	345
1	1	265	265
2	1	283	-307
1	2	590	-572
2	2	349	345
0	3	276	263
2	3	305	-304
3	3	299	-327
1	5	301	297
3	5	217	-267
4	5	265	283
1	6	315	-312
2	7	319	-316
3	7	285	-316
5	7	272	273
L=5			
1	0	269	271
0	3	268	-164
1	5	270	-202

Unobserved reflections are indicated by *
Reflections weighted zero are indicated by (FO)

angle is 130°). The normal triple-bond arrangement for the cyanide group would lead us to expect an angle near 180° for the intermolecular bond angle in cases like this. We can rationalize the 120° bond angle based on resonance forms that place a double bond between the carbon and nitrogen atoms and two unshared pairs of electrons on the nitrogen atom; but this is an *ad hoc* argument and is not supported by the bond lengths in the chloro compound, which is by far the more accurately determined of the two. Here, interactions are at least as strong, *i.e.* distances are at least as short, as in the linear cases involving aromatic compounds, although they are not as short as in the XCN and XC_2CN structures. For *p*-chlorobenzonitrile, the CN···Cl distance has been estimated at 3·3 Å (Britton, 1967) compared with 3·22 (2) Å here. In *p*-bromobenzonitrile, the CN···Br distance has been estimated at 3·2 Å (Britton, 1967); in 9-dicyanomethylene-2,7-dibromofluorene (Silverman, Yannoni, & Krukonis, 1969) it has been found to be 3·18 and 3·23 Å; in this study the distance is found to be 3·06 (4) Å. This is surprising since each cyanide group is involved in two CN···Br contacts here, compared with only one in the other compounds mentioned. It is difficult to imagine that an increase in the number of contacts per group is also accompanied by an increase in strength for each contact.

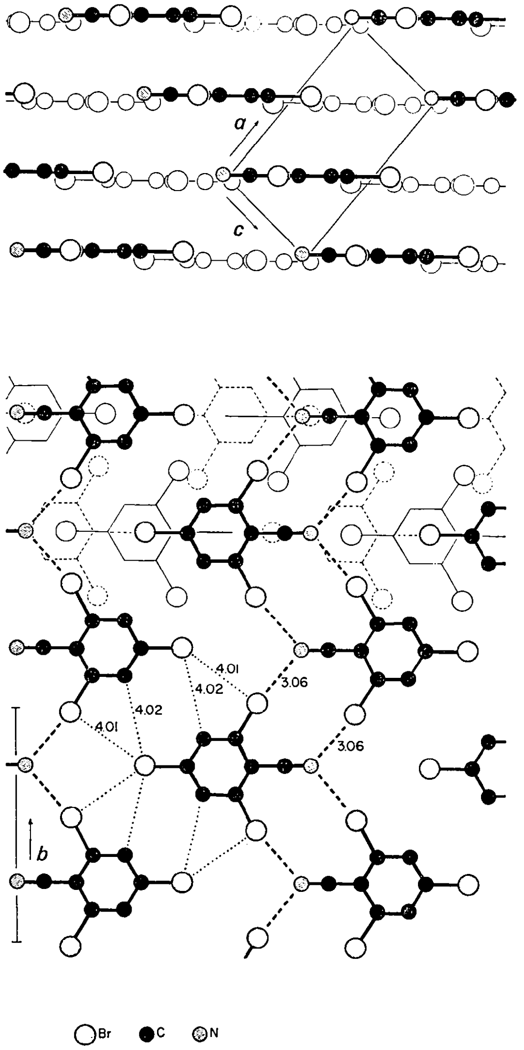

Fig. 2. Crystal structure of tribromobenzonitrile. The arrangement is as in Fig. 1.

Table 4. *Bond lengths and angles in* $Cl_3C_6H_2CN$ *and* $Br_3C_6H_2CN$

	$Cl_3C_6H_2CN$	$Br_3C_6H_2CN$
X(2)–C(2)	1·75 (2) Å	1·84 (4) Å
X(4)–C(4)	1·71 (2)	1·89 (5)
X(6)–C(6)	1·73 (1)	–
C(1)–C(2)	1·40 (2)	1·47 (6)
C(2)–C(3)	1·38 (2)	1·43 (5)
C(3)–C(4)	1·41 (2)	1·41 (6)
C(4)–C(5)	1·41 (2)	–
C(5)–C(6)	1·41 (2)	–
C(6)–C(1)	1·39 (2)	–
C(1)–C(N)	1·45 (2)	1·33 (8)
C(N)–N	1·12 (2)	1·21 (8)
C(6)–C(1) –C(2)	117·6 (15)°	115 (4)°
C(1)–C(2) –C(3)	123·9 (15)	123 (4)
C(2)–C(3) –C(4)	115·2 (15)	116 (4)
C(3)–C(4) –C(5)	125·1 (13)	125 (4)
C(4)–C(5) –C(6)	114·6 (14)	–
C(5)–C(6) –C(1)	123·3 (15)	–
C(1)–C(2) –X(2)	117·4 (15)	118 (4)
C(3)–C(2) –X(2)	118·7 (15)	119 (4)
C(3)–C(4) –X(4)	116·7 (15)	115 (4)
C(5)–C(4) –X(4)	118·2 (14)	–
C(5)–C(6) –X(6)	116·9 (14)	–
C(1)–C(6) –X(6)	119·5 (14)	–
C(N)-C(1) –C(2)	123·7 (15)	121 (5)
C(N)-C(1) –C(6)	118·7 (16)	–
N——C(N)-C(1)	174·4 (18)	163 (6)

Model calculations perhaps shed some light on the structures. As a reference, we estimate the molecular volume of the bromo compound, assuming that the structure is essentially that shown in Fig. 2. Also, we assume that it is idealized so that all bond lengths are normal, all bond angles are exactly 120° or 180° as appropriate (including the C–N···Br angle), and that important intermolecular contact distances are those actually found, *i.e.* 3·06 Å for N···Br, 4·01 Å for Br···Br, and 3·45 Å for the average interlayer spacing, Then, we find that unit-cell dimensions shift about 5 %, but the molecular volume stays at 223 $Å^3$. If we make the same hypothetical calculation for the chloro compound in the same arrangement, with N···Cl 3·22 Å, Cl···Cl 3·70 Å, and the interlayer distance 3·36 Å, the molecular volume is 206 $Å^3$ compared with the 205 $Å^3$ found in the actual structure. This says, in effect, that the actual structure of the chloro compound involves no more efficient packing than the hypothetical one; and it suggests that perhaps the reason for the difference in the structures is that chlorine, being a weaker acid than bromine, cannot accommodate two cyanide groups simultaneously. Fig. 1 shows that there is another chlorine atom close to the nitrogen atom; CN···Cl is 3·69 Å and C–N···Cl is 106·3°. This 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^3, about 3% larger than in the actual stiucture. 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 $BrC(CN)_3$, $ClC(CN)_3$, and $CH_3C(CN)_3$

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Bromotricyanomethane, $BrC(CN)_3$, is orthorhombic, space group $Pbca$ (D_{2h}^{15}), with $a=6{\cdot}09$ (1), $b=11{\cdot}49$ (2), and $c=17{\cdot}62$ (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 $BrC(CN)_3$ 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, $ClC(CN)_3$, and 1,1,1-tricyanoethane, $CH_3C(CN)_3$, are isomorphous, both hexagonal, space group $P6_3/m$ (C_{6h}^2), with identical cell constants $a=10{\cdot}23$ (2) and $c=9{\cdot}95$ (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: $ClC(CN)_3$ to an R of 0·088, $CH_3C(CN)_3$ 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 $ClC(CN)_3$ 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, $XC(CN)_3$, where $X=Br$, Cl, or CH_3, to determine 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.