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The Crystal Structure of the Molecular Complex Formed by Acetonitrile and Bromine in the Mole Ratio 2:1

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The crystal structure of the molecular complex formed by two molecules of acetonitrile and one molecule of bromine (melting point $-41\cdot5°C$) has been determined from three-dimensional X-ray data obtained at $-70°C$. The monoclinic unit cell of dimensions: $a=13\cdot94$, $b=6\cdot19$, $c=5\cdot14$ Å and $\beta=114\cdot9°$ contains two molecules of bromine and four molecules of acetonitrile. The space group is $C2/m$. The structure exhibits linear, centrosymmetric groups of nitrogen–halogen–halogen–nitrogen atoms. The interhalogen bond length is $2\cdot328$ Å, and the nitrogen–halogen distance is $2\cdot84$ Å. The complex is apparently weakly bonded, and in this respect it differs from the complexes formed by halogen and aliphatic amines or other nitrogen containing compounds. Bond properties are discussed. Nuclear magnetic resonance spectra taken at $77°K$ agree with a model wherein the methyl group rotates about its threefold axis. The X-ray data requires this rotation to be associated with preferential orientations of the methyl group and is thus restricted.

Introduction

The crystal structures of molecular 1:1 complexes formed by amines and halogen molecules so far reported in the literature exhibit a common feature in that the nitrogen atom of the organic molecule forms, with the attached halogen molecule, an approximately linear grouping in the solid (Hassel & Rømming, 1962).

In these compounds the nitrogen atom is believed to acquire a formal positive charge, whose counterpart, to the extent of say roughly half a unit, is transferred by delocalization of the σ electrons of the group in the bond formation to the outer halogen atom. The latter is always the more electronegative in cases of hetero-halogen molecular acceptors. The central halogen atom is further believed to become only slightly charged.

These complexes are all 'strong' charge transfer complexes. This is indicated by the short nitrogen–halogen bond distances compared with the accepted van der Waals distances; the elongated halogen–halogen bond distances compared with the corresponding gas phase values; the high values of the heats of formation and melting points; *etc.* Many complexes involving sulphur compounds show similar relationships (Hassel & Rømming, 1962; Briegleb, 1961).

Weaker complexes containing ethers, ketones, alcohols or benzene as donors, and homo-halogen mol-

ecules as acceptors, have in all cases hitherto investigated been shown to form linear centrosymmetric bridges of donor–halogen–halogen–donor groupings in the solid state (Hassel & Rømming, 1962; Groth & Hassel, 1964).

As described above, although to a lesser extent, electronic charge is believed to be transferred from the donor molecules to the acceptors by delocalization of the bonding electrons under bond formation. It can be qualitatively understood therefore, that the halogen molecule, which forms 1:1 complexes with strong donor molecules such as trimethylamine *etc.*, can in less favourable cases make two weaker bonds to the donor molecules.

In support of this interpretation we outline here the results of a structure investigation of a 2:1 complex between acetonitrile and bromine, which is the first example to be found of a structure of the second kind involving a nitrogen donor. There are reasons for believing that a similar, isomorphous complex exists between acetonitrile and chlorine. Acetonitrile is for example considered to be a much weaker donor than trimethylamine.

Experimental

Commercial acetonitrile which had been freshly distilled over phosphorus pentoxide was mixed with commercial bromine of reagent grade in the mole ratio 2:1 at a temperature close to the melting point, $-41 \cdot 5 \, ^\circ C$, which was determined by a method of Reilly & Rae (1954).

A small amount of the resulting dark brown mixture was drawn into a glass capillary of 0·2 mm diameter to be sealed off while the sample was kept at $-78 \, ^\circ C$ by the use of solid carbon dioxide.

The sample tube was then quickly mounted on a Weissenberg goniometer in a stream of precooled air. Yellow single crystals, having their c axes coinciding approximately with the direction of the capillary tube and the rotation axis, were grown by the conventional low-temperature technique.

Weissenberg and oscillation diagrams were taken with Cu $K\alpha$ radiation at a sample temperature of $-70 \, ^\circ C$. The reflexion intensities were determined photometrically from four multiple-film Weissenberg diagrams for each of the first four layers, using the equi-inclination method. Higher order Weissenberg diagrams could not be obtained with Cu $K\alpha$ radiation. The crystal was rotated through approximately 200°.

Intensities reduced to a common scale were as usual corrected for Lorentz–polarization factor effects. In the case of reflexions particularly close to the base line in upper layers it was necessary to allow for spot area variation in determining intensities, since these reflexions were recorded on only one side of the film. No other corrections were made to the experimental data.

The number of possible reflexions amounts to 346, of which 22 are non-observable. These were given intensity values equal to half the minimum observed intensity.

Proton nuclear magnetic resonance spectra were taken of the solid polycrystalline material at 77 °K with a Varian broadline spectrometer operating at 60 MHz.

Determination of the structure

The crystal is monoclinic with cell dimensions: $a = 13 \cdot 94 \pm 0 \cdot 07$, $b = 6 \cdot 19 \pm 0 \cdot 03$, $c = 5 \cdot 14 \pm 0 \cdot 03$ Å, $\beta = 114 \cdot 9 \pm 0 \cdot 5 \, ^\circ$.

On a basis of four acetonitrile units and two molecules of bromine per unit cell, this leads to a density of 2·0 g.cm^{-3} at $-70 \, ^\circ C$ [*cf.* an estimate of 1·8 g.cm^{-3} based on the density of liquid acetonitrile at 20 °C and solid bromine at $-70 \, ^\circ C$ (Hawes, 1959)].

Possible space groups for the structure are $C2/m$, $C2$ or Cm. The present determination is based on the first, which requires all except 8 hydrogen atoms in the unit cell to be placed in mirror planes, leaving two free position parameters for each of the heavier atoms.

The (001) projection was first calculated, and the approximate positions of the bromine atoms were easily found from the Patterson projection. Subsequent Fourier analysis showed that all structure factor signs were determined by the bromine contributions. Although the heavy atoms are well resolved in mirror planes perpendicular to the reference plane, effects due to series termination are quite marked in the two-dimensional electron density map.

A partial difference synthesis was then performed with subtraction of the contributions from all except the hydrogen atoms. In the corresponding electron density map only the out-of-plane hydrogen atoms were evident, whereas the in-plane hydrogen atom overlaps too much with one of the carbon atoms in the projection. The R index from this zone was found to be less than 8%, using isotropic individual temperature factors and recently published form-factor values (Hanson, Herman, Lea & Skillman, 1964).

Assuming a linear arrangement of CH$_3$CN–Br$_2$–NCCH$_3$ and a bromine–bromine distance of 2·3 Å, approximate values of the z parameters of the heavier atoms could be determined. Since, however, the a and c axes are not at right angles, two different possible sets of z parameter values resulted. Of these, a model with the atoms situated along the shortest diagonal of the mirror plane could be rejected for geometrical reasons in favour of one based on a linear arrangement of the atoms on the longest diagonal.

Except in the case of hydrogen the parameters, including the scale factors, were refined by least-squares techniques applied to the reflexions of each layer separately, using individual isotropic B values. The values of the sets of bromine parameters thus obtained showed only small individual variations from layer to layer, whereas fluctuations, especially of the values of the carbon and nitrogen z parameters, were naturally more pronounced.

The mean parameter values were used as basis in a full-matrix least-squares refinement with the complete experimental material included, apart from a few reflexions obviously suffering from extinction. Only the bromine atoms were given symmetry restricted temperature factors. Based on the resulting parameter values, the individual scale factors were subsequently adjusted before repeating this whole process. On completion, the value $R = 8.2\%$ was obtained. Unobserved reflexions were included in the calculation of R, whereas a few reflexions suffering from secondary extinction were excluded. Resulting parameter values are given in Table 1, where anisotropic temperature factors are computed according to the formula:

$$\exp\left[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)\right].$$

Checking showed that the individual scale factors needed no further adjustment. The comparatively high value of the thermal parameter for nitrogen may be due, in part, to the triply bonded atom being more electron deficient than has been assumed.

The structure was then refined using anisotropic temperature coefficients for all except the hydrogen atoms. The R value dropped to 7.8%. Resulting parameter values are presented in Table 2. By comparison with Table 1 it will be seen that corresponding coordinate values differ only slightly.

Table 3 lists observed and calculated structure factor values.

In the above refinements, all y parameters were kept fixed along with the hydrogen parameters. Position parameter values of the hydrogen atoms were easily found, with use of the gas phase values of the intrinsic molecular data of the acetonitrile group (Thomas, Sherrard & Sheridan, 1955). Since, however, this in principle affords two possible positions for the methyl group, the previous two-dimensional partial difference electron density map was consulted to decide between the two possibilities.

The individual weights attached to the reflexions were determined from the standard weighting scheme:

$$F_o \le FB, \quad WTG = A1(F_o)^{B1}$$
$$F_o > FB, \quad WTG = A2(F_o)^{B2}$$

with $A1 = 0.1$, $B1 = 0.5$, $FB = 6.0$, $A2 = 0.4$ and $B2 = 0.5$.

Subsequently, a three-dimensional Fourier analysis was computed. The atomic peaks appeared in positions as expected, with peak heights equal to 70.2, 8.3, 7.8,

Table 1. *Positional and thermal parameters*

(a) Positional parameters; estimated standard deviations in parentheses ($\times 10^4$). Values are fractional.

	x	y	z
Br	0.43121 (0.2)	0.0	0.5717 (1)
N	0.2604 (3)	0.0	0.7405 (11)
C(1)	0.2037 (2)	0.0	0.8484 (9)
C(2)	0.1284 (3)	0.0	0.9690 (10)

(b) Thermal parameters. The anisotropic temperature factor coefficients for the bromine atom are multiplied by 10^5. The isotropic temperature factors for the light atoms are in $Å^2$. Estimated standard deviations in parentheses.

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Br	256 (2)	1654 (9)	5245 (39)	0	1046 (12)	0

	B
N	5.110 (0.080)
C(1)	2.458 (0.056)
C(2)	2.971 (0.060)

Table 2. *Positional and thermal parameters*

(a) Positional parameters; estimated standard deviations in parentheses ($\times 10^4$). Values are fractional.

	x	y	z
Br	0.43125 (0.2)	0.0	0.5720 (1)
N	0.2621 (3)	0.0	0.7414 (11)
C(1)	0.2036 (2)	0.0	0.8429 (10)
C(2)	0.1289 (2)	0.0	0.9696 (13)
H(1) (calc.)	0.1760	0.0	0.2218
H(2) (calc.)	0.0764	0.1465	0.9167

(b) Anisotropic temperature coefficients ($\times 10^5$). Estimated standard deviations in parentheses

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Br	252 (2)	1653 (10)	5358 (41)	0	1037 (12)	0
N	718 (27)	3935 (131)	7857 (408)	0	4386 (179)	0
C(1)	409 (20)	1642 (75)	3050 (273)	0	907 (122)	0
C(2)	146 (14)	2350 (86)	9026 (392)	0	1797 (124)	0

and 7·1 e.Å^{-3} for the bromine, nitrogen, cyanide carbon and methyl carbon respectively. The background variation about zero electron density is small, showing however, especially in the regions near the bromine atoms, distinct effects due to abrupt Fourier series termination.

Excluding a few reflexions suffering from extinction, a partial three-dimensional difference Fourier analysis was finally made, subtracting the contributions from all the atoms except hydrogen. Fig. 1 shows the resulting map at $y=0$ and $y=0.16$, with relatively distinct peaks for both the in-plane and the out-of-plane hydrogen atoms in the positions to be expected.

The coordinates of the hydrogen atoms obtained from these maps are $x=0.074$, $y=0.152$, $z=0.910$ and $x=0.162$, $y=0.0$, $z=0.190$ for the out-of-plane and in-

Table 3. *Observed and calculated structure factors*

The structure factor amplitudes of non-observed reflexions are put equal to zero.

h	k	F_o	F_c
l = 0			
2	0	42.2	45.0
4	0	11.9	-12.4
6	0	79.0	-88.8
8	0	62.5	-64.1
10	0	25.4	-24.2
12	0	17.1	15.4
14	0	41.8	41.0
16	0	33.0	28.9
1	1	78.8	-92.6
3	1	50.9	54.0
5	1	48.0	52.3
7	1	77.1	86.4
9	1	50.1	52.5
11	1	4.8	-4.6
13	1	41.6	-40.0
15	1	26.8	-25.8
0	2	123.0	158.2
2	2	37.5	38.3
4	2	11.1	-10.4
6	2	72.6	-73.3
8	2	57.7	56.7
10	2	22.9	-21.1
12	2	15.9	13.7
14	2	38.8	37.2
1	3	68.2	-71.4
3	3	35.3	-35.2
5	3	41.8	41.7
7	3	69.2	66.8
9	3	46.2	42.6
11	3	4.7	-4.0
13	3	36.4	-32.8
15	3	19.1	-21.8
0	4	91.6	88.5
2	4	31.0	31.0
4	4	11.5	-8.4
6	4	54.9	-49.0
8	4	46.6	-41.9
10	4	17.5	-14.7
12	4	13.5	10.1
14	4	25.5	28.2
1	5	49.4	-43.1
3	5	23.9	-20.0
5	5	30.1	26.6
7	5	48.2	41.8
9	5	32.5	28.4
0	6	36.3	48.1
2	6	21.0	19.8
4	6	4.9	-5.5
6	6	34.2	-28.6
8	6	26.4	-25.5
10	6	8.4	-9.6
1	7	25.2	-23.4
3	7	13.7	-23.4
5	7	15.3	15.1
7	7	21.3	22.7
0	8	16.6	24.0
l = 1			
0	0	73.7	-73.7
2	0	93.1	-93.1
4	0	40.4	39.3
6	0	41.6	44.6
8	0	63.8	62.7
10	0	40.3	37.8
12	0	0.0	-4.2
14	0	25.7	-24.3
1	1	137.8	155.9
3	1	31.8	31.8
5	1	0.0	-3.0
7	1	60.9	-57.0
9	1	51.2	-47.9
11	1	21.4	-18.5
13	1	7.8	10.4
0	2	63.5	-70.0
2	2	82.0	-84.0
4	2	32.8	-33.8
6	2	38.0	40.1
8	2	59.9	55.1
10	2	35.9	34.4
12	2	0.0	-3.9
14	2	21.1	-22.2
1	3	97.4	99.7
3	3	28.4	27.9
5	3	0.0	-3.8
7	3	48.2	-43.9
9	3	40.9	-38.9
11	3	20.4	-14.8
13	3	9.8	8.5
0	4	48.2	-48.8
2	4	58.3	-55.5
4	4	24.5	-22.4
6	4	28.5	28.6
8	4	44.7	40.2
10	4	27.8	25.9
12	4	0.0	3.0
1	5	55.4	58.3
3	5	20.5	20.3
5	5	0.0	3.4
7	5	34.4	28.7
9	5	29.0	-26.8
11	5	6.8	-9.8
0	6	27.1	-28.1
2	6	32.0	-31.6
4	6	13.5	-13.1
6	6	18.4	17.4
8	6	22.4	24.2
1	7	34.3	31.0
3	7	11.1	12.1
5	7	0.0	-2.1

h	k	F_o	F_c
l = 1			
-2	0	47.1	-45.0
-4	0	46.2	52.7
-6	0	92.0	97.5
-8	0	63.5	63.9
-10	0	0.0	0.2
-12	0	51.4	-58.4
-14	0	32.6	-34.9
-16	0	18.6	-16.6
-1	1	56.1	34.0
-3	1	12.3	-12.4
-5	1	102.6	-106.3
-7	1	67.9	-71.1
-9	1	20.2	-22.8
-11	1	18.9	21.5
-13	1	40.6	45.9
-15	1	31.8	38.4
-2	2	35.1	-35.6
-4	2	45.9	48.8
-6	2	85.8	85.8
-8	2	35.7	56.8
-10	2	0.0	-0.5
-12	2	52.9	-52.3
-14	2	30.2	-32.0
-16	2	15.3	-15.0
-1	3	40.8	40.0
-3	3	7.5	-10.2
-5	3	70.6	-71.9
-7	3	55.3	-66.1
-9	3	15.3	-17.3
-11	3	13.8	15.8
-13	3	39.2	37.8
-15	3	29.8	31.4
-2	4	23.2	-22.2
-4	4	38.2	34.5
-6	4	54.6	57.8
-8	4	38.5	40.4
-10	4	0.0	-1.1
-12	4	37.7	-37.8
-14	4	21.4	-24.6
-1	5	25.2	27.0
-3	5	8.2	-8.3
-5	5	44.0	-42.9
-7	5	39.3	-38.1
-9	5	13.1	-10.7
-11	5	11.2	11.2
-13	5	24.1	25.3
-2	6	11.5	-12.9
-4	6	21.2	20.6
-6	6	36.8	33.0
-8	6	25.9	24.4
-10	6	6.5	-1.0
-1	7	15.4	15.5
-3	7	4.5	-5.1
-5	7	25.6	-22.7
-7	7	21.9	-22.1
l = 2			
2	0	47.0	44.4
4	0	89.8	97.2
6	0	26.5	27.0
8	0	0.0	0.3
10	0	39.7	-36.2
12	0	33.4	-32.4
1	1	12.4	-12.3
3	1	53.2	-35.0
5	1	71.1	-57.8
7	1	22.6	-22.2
9	1	28.0	28.8
11	1	38.5	36.6
13	1	32.0	23.0
0	2	0.0	-2.1
2	2	58.9	38.5
4	2	79.1	80.7
6	2	24.2	24.2
8	2	5.4	0.2
10	2	34.3	-32.3
12	2	28.8	-29.3
1	3	10.5	-11.1
3	3	45.0	-44.6
5	3	55.4	-55.3
7	3	15.8	-17.9
9	3	22.2	23.6
11	3	31.6	29.9
0	4	18.4	19.2
2	4	29.3	28.2
4	4	56.3	53.9
6	4	18.0	18.3
8	4	0.0	-0.3
10	4	25.3	-23.8
12	4	19.1	-22.2
1	5	28.8	-28.3
3	5	36.6	-34.0
5	5	12.4	-11.7
7	5	13.3	15.0
9	5	17.3	20.2
2	6	16.6	17.6
4	6	28.9	31.7
6	6	9.7	11.8
8	6	0.0	-0.3
1	7	12.1	-13.7
3	7	13.2	-19.0
-2	0	0.0	-10.1
-4	0	104.9	-97.7
-6	0	79.3	-74.4
-8	0	16.1	-20.8
-10	0	30.3	30.9
-12	0	45.8	45.9
-14	0	39.3	43.3

h	k	F_o	F_c
l = 2			
-16	0	0.0	2.0
-1	1	27.4	-26.1
-3	1	54.0	48.3
-5	1	92.6	82.1
-7	1	57.6	54.0
-9	1	8.0	7.3
-11	1	68.3	-64.2
-13	1	37.9	-39.4
-15	1	18.9	-18.3
-2	2	9.7	-9.0
-4	2	79.8	-78.2
-6	2	68.3	-64.1
-8	2	15.5	-17.8
-10	2	24.5	25.4
-12	2	41.0	41.4
-14	2	37.0	38.9
-1	3	20.3	-19.1
-3	3	36.0	38.7
-5	3	63.8	63.6
-7	3	41.8	43.3
-9	3	6.9	3.8
-11	3	52.5	-50.9
-13	3	34.4	-33.0
-15	3	16.0	-14.8
-2	4	9.2	-8.4
-4	4	48.7	-50.1
-6	4	44.1	-46.2
-8	4	12.1	-11.6
-10	4	18.0	18.2
-12	4	29.4	31.2
-14	4	27.2	28.7
-1	5	12.1	-12.2
-3	5	23.8	24.5
-5	5	40.1	39.0
-7	5	28.9	28.4
-9	5	0.0	1.6
-11	5	34.4	-32.9
-13	5	19.4	-23.0
-2	6	6.1	-6.1
-4	6	30.4	-28.5
-6	6	28.8	-28.8
-8	6	7.5	-6.4
-10	6	14.8	10.8
-1	7	5.5	7.0
-3	7	10.5	13.9
-5	7	19.1	21.2
-7	7	12.8	16.1
l = 3			
0	0	14.5	-14.6
2	0	34.5	-34.7
4	0	45.4	-43.2
6	0	14.0	-11.6
8	0	14.8	16.5
10	0	12.8	19.4
1	1	29.5	28.9
3	1	49.5	49.3
5	1	17.4	17.2
7	1	0.0	2.1
9	1	15.1	-20.0
0	2	14.9	-12.9
2	2	36.2	-31.6
4	2	42.9	-39.1
6	2	14.6	-10.6
8	2	15.2	15.1
10	2	13.1	17.7
1	3	27.4	23.2
3	3	45.7	38.6
5	3	16.9	14.1
7	3	0.0	1.6
9	3	14.6	-16.6
0	4	11.4	-9.4
2	4	27.5	-23.1
4	4	33.1	-28.6
6	4	12.2	-7.9
8	4	12.1	11.4
1	5	19.5	15.8
3	5	29.3	25.6
5	5	11.3	9.9
7	5	8.3	-6.0
0	6	11.7	-14.1
2	6	8.4	-17.7
-2	0	32.3	35.8
-4	0	35.2	60.8
-6	0	34.4	37.8
-8	0	11.3	10.2
-10	0	53.9	-59.2
-12	0	43.3	-37.7
-14	0	23.2	-20.5
-16	0	17.4	20.1
-1	1	9.4	-9.3
-3	1	53.5	-50.0
-5	1	53.4	-53.5
-7	1	15.6	-16.0
-9	1	32.7	31.7
-11	1	38.8	37.8
-13	1	40.0	33.4
-15	1	0.0	0.8
-17	1	19.2	-20.7
-2	2	36.2	32.8
-4	2	61.4	54.2
-6	2	36.1	34.3
-8	2	8.7	7.6
-10	2	50.3	-32.7
-12	2	40.3	-34.7
-14	2	21.9	-18.2
-16	2	18.8	18.0

h	k	F_o	F_c
l = 3			
-1	3	10.1	-7.8
-3	3	53.2	-43.9
-5	3	62.8	-44.7
-7	3	15.4	-11.7
-9	3	25.8	23.9
-11	3	33.0	31.1
-13	3	34.4	30.9
-2	4	26.8	23.8
-4	4	35.1	37.8
-6	4	24.7	25.2
-8	4	0.0	4.1
-10	4	35.5	-37.2
-12	4	30.1	-26.6
-14	4	13.0	-13.0
-1	5	0.0	-6.0
-3	5	28.8	-27.5
-5	5	30.9	-30.5
-7	5	8.2	-5.9
-9	5	18.3	15.2
-11	5	23.1	21.8
-13	5	22.8	20.9
-2	6	14.1	14.6
-4	6	16.6	22.3
-6	6	14.2	15.5
-8	6	0.0	1.9
-10	6	19.4	-22.2
-3	7	11.7	-14.9
-5	7	12.4	-17.8

plane hydrogen atoms respectively. The former figures compare especially well with the calculated values given in Table 2.

The lattice multiplicity of the out-of-plane hydrogen atom is twice that of any other atom, and leads to these being better defined in the map. Significant evidence of the methyl group being in the alternative position could not be found.

The resulting distribution of the electron density is generally rather sensitive to the approximations inherent in the basic computations. Thus it is seen in Fig. 1 that the variation of the background electron density is much more pronounced in regions not far from the original positions of the subtracted atoms than outside, where the density has been found to reach extreme values of ± 0.4 e.Å^{-3} in some points, but is mostly much closer to zero.

Results and discussion

In Fig. 2, a model of the lattice structure is shown, and in Table 4, molecular data values are presented together with some standard values of bond lengths. Errors due to uncertainties in cell dimensions have not been taken into account. Correction of the halogen bond length due to the thermal motion of the bromine

Fig. 1. Three-dimensional difference electron density map at $y=0$ (upper) and $y=0.16$. Contours at intervals of 0.30 e.Å^{-3}. Zero and negative contours broken.

atoms cannot be estimated accurately according to standard methods owing to the weak nature of the nitrogen–halogen bond.

The addition compound clearly consists of two organic groups added to one molecule of bromine to obtain a linear centrosymmetric grouping consisting of nitrogen–bromine–bromine–nitrogen. This is in principle as observed in the oxygen–homohalogen complexes. The significant departure from linearity of the whole molecule is considered to be due to lattice interactions. This is not a strong complex, a fact which is reflected in the relatively long addition bond distance of 2.84 Å, compared with the observed nitrogen–halogen bond distance in complexes involving strong donors (2.2–2.3 Å) (Hassel & Rømming, 1962). However, the interhalogen bond has been slightly weakened upon complexing. The observed increase in bond length is 0.05 Å, which is much less than that observed in the strong complex formed by hexamethylene and bromine (0.15 Å) or in complexes with iodine chloride (Hassel & Rømming, 1962). In these respects also, the present structure resembles more closely those of oxygen–halogen complexes. It may in addition be worth noting that the structures of the four-atom halogen groups in the mutually isomorphous complexes formed by dimethylammonium chloride and iodine (2:1), and dimethylammonium bromide and bromine (2:1), are in principle rather similar to the four-atom grouping of the present structure (Strømme, 1959).

The acetonitrile group has been found to be linear in accordance with observations in the vapour phase. The triple bond distance of 1.138 (0.006) Å is somewhat shorter than that observed in the free molecule (1.157 Å) (Thomas, Sherrard & Sheridan, 1955). The shortening is probably too large to be explained as a vibration effect. Similar results have been obtained for other charge transfer complexes involving cyanide groups as donors (Bjorvatten, 1967). Also, in a number of cases observed, the corresponding CN-bond stretching frequencies increase upon complex formation (Gerrard, Lappert, Pyszora & Wallis, 1960; Filimonov & Bystrov, 1962; Augdahl & Klæboe, 1963).

The most probable explanation of this has been suggested to be that in the complexes the CN bond order is in fact higher than in the free nitriles (Gerrard et al., 1960; Purcell & Drago, 1966). This has further been thought to originate in an increased s character of the nitrogen term in the NC σ bond, since the corresponding increase in the p character to be associated with the lone-electron pair orbital on the nitrogen atom should strengthen the bond overlap with the orbitals of the relatively distant acceptor molecule (Filimonov & Bystrov, 1962).

The C(1)–C(2) distance has also been observed to be slightly shorter than in the free molecule. This may at least partly be due to molecular libration.

Intermolecular distances are found to be of the van der Waals type or longer. The complex is thus rather well-defined and of relatively high symmetry, apart
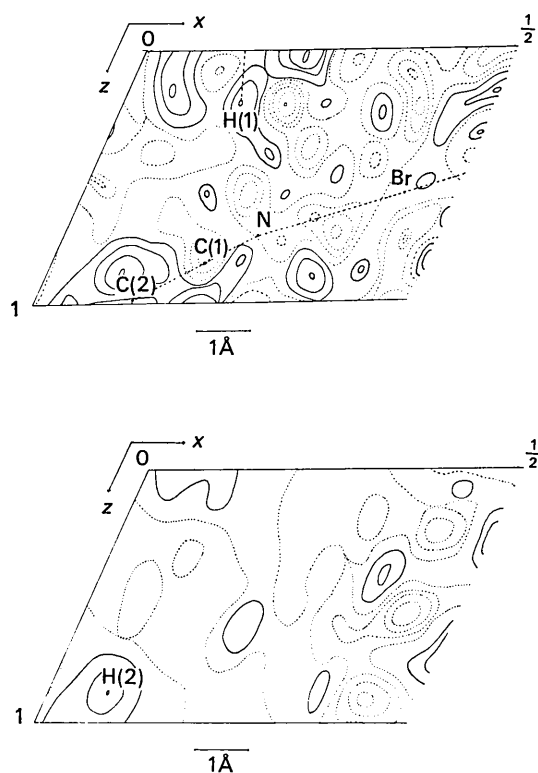
from a small distortion probably due to lattice inter-actions (Fig. 2).

The mechanism by which the bonds of the linear group are established is thought to depend on delocal-ization of the six axial electrons, of which four orig-inally constituted two lone pairs on the nitrogen atoms, whereas the remaining two were localized in the σ bond of the free halogen molecule.

This may well be represented by four-centre bonds with centres on the four atoms. As a result, small, excess negative charges would be expected to accumu-late at the halogen molecule. This can also be demon-strated by choosing some reasonable LCAO's, using for example Slater orbitals to represent the individual terms in a linear expansion, and computing the corre-sponding electron density along the chain axis.

More quantitative results may be obtained from analysis of nuclear quadrupole coupling constant data observed in the solid at the bromine and nitrogen nu-cleus sites. The values of these will probably be only slightly perturbed by lattice interactions. However, it is anticipated that in the halogen terms of the linear expansion, the axial p-orbital contribution plays the dominant role, considering the weakness of the addi-tion bond on one hand (Person, Gotton & Popov, 1963), and the high energy of the d_z orbital on the other. This is one advantage of this method over the older description of orthogonal two-centre bonds which needs a complete d orbital centred on each halogen atom.

The mechanism of bond formation discussed here seems to have a wider applicability than often re-cognized, and has in fact with modifications been used to explain bond properties of trihalides (Hach & Rundle, 1951; Pimentel, 1951; Rundle, 1961; Yama-saki & Cornwell, 1959; Carpenter, 1963; Müller, 1966).

A similar description should also in principle ac-count for bond properties observed in the strong addi-tion compounds involving halogens and aliphatic amines and others (Ginn & Wood, 1966).

The reason why acetonitrile forms weak complexes with halogens compared with complexes containing aliphatic amines for example, is mainly due to its lone electron pair, which is considered to be firmly attached to the relatively electron-poor triple bonded nitrogen atom in acetonitrile, and thus less available for bond formation than the lone pair of the relatively electron-rich nitrogen in aliphatic amines.

In Table 5, values of the principal root-mean-square amplitudes of oscillation of the heavier atoms have been listed along with values of the corresponding axial components. These are referred to Table 2. The cyanide carbon oscillations are nearly isotropic, where-as the motions of the others are anisotropic. For these atoms, amplitudes along the chain are smaller than amplitudes perpendicular to the chain.
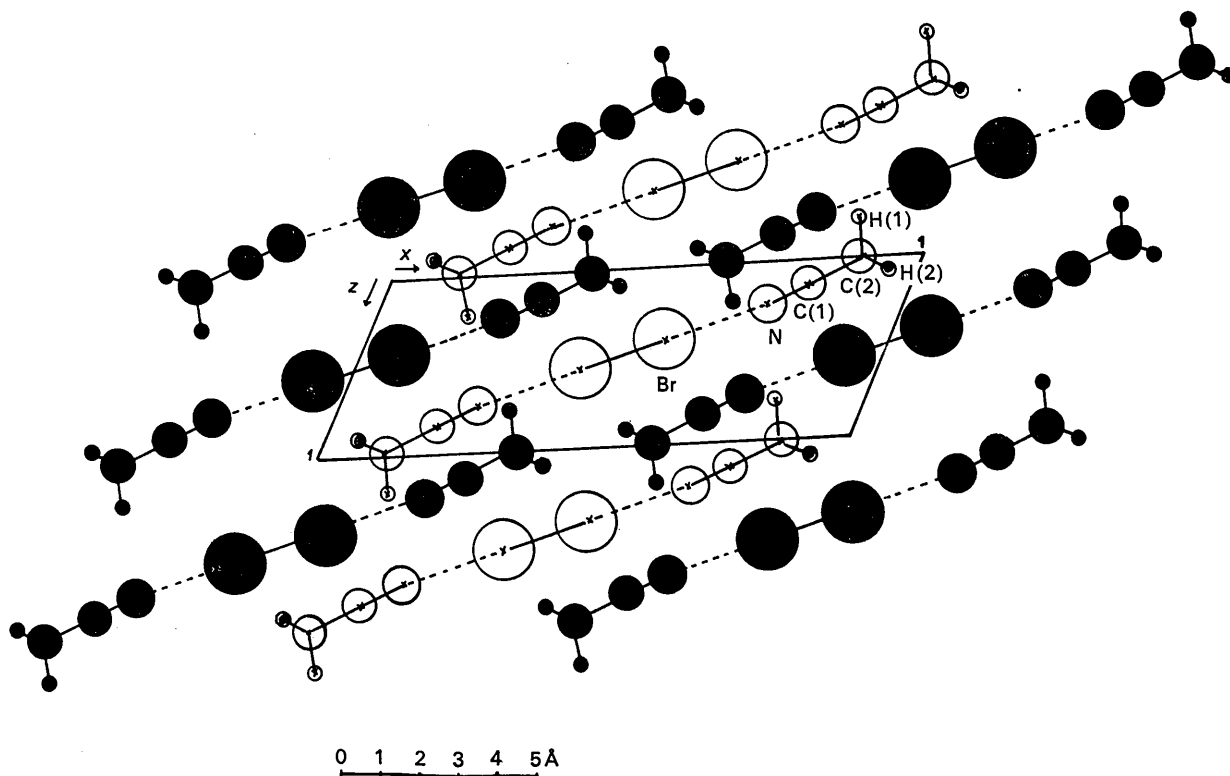

0 1 2 3 4 5Å

Fig. 2. The lattice structure as seen along the y axis. White circles represent atoms in molecules at $y=0$. Black circles represent atoms in molecules at $y=\pm\frac{1}{2}$. Addition bonds are represented by broken lines. Covalent bonds are represented by full lines.

Proton magnetic resonance spectra have been taken of the polycrystalline material at 77°K. The average value of the experimental second moment is $5\cdot35\pm0\cdot1$ g^2, suggesting that the hydrogen atoms undergo rotation about the threefold axis at an average rate of at least 10^5 cycles per second.

The corresponding computed value of an isolated methyl group based on molecular data obtained by microwave spectroscopy on acetonitrile in the gas phase (Thomas, Sherrard & Sheridan, 1955) is $5\cdot03$ g^2, which is one quarter of the rigid-body value. The figures compare well, the discrepancy being mainly due to the remaining intramolecular and intermolecular interactions, which are small.

However, the nuclear magnetic resonance data alone cannot discriminate between free rotation of the methyl groups about the threefold axes and the more natural restricted reorientation from one potential minimum position to another. The same second moment value of the isolated methyl group is obtained from both models.

According to X-ray data, the latter is definitely favoured, even at temperatures considerably higher than 77°K. This demonstrates the ability of X-rays to locate average potential minima of mobile groups in solids, i.e. when the Laue–Bragg diffraction is dominated by contributions from these regions. It presupposes that the time spent in points outside the minima is relatively short even in cases of 'flat' barriers as in the present example, where the interminimum distance is about 1·8 Å, and the mean barrier as low as of the order of one kcal per mole acetonitrile, as found in other compounds containing methyl groups, for example methyl alcohole (Nishikawa, 1956).

The full-matrix least-squares program used in the present calculations has been written by Chr. Rømming, Department of Chemistry, University of Oslo, Oslo, Norway. It represents a revised version of a program written by Gantzel, Sparks & Trueblood (I.U.C. World List No. 384).

The Fourier program has been written by Gantzel & Hope, Department of Chemistry, University of California, Los Angeles, California.

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Table 4. *Interatomic distances and angles*

Estimated standard deviations in parentheses.

	Observed in 2CH$_3$CN–Br$_2$	Dist. in free molecules	Van der Waals distances
Br——Br	2·3280 (0·0009) Å	2·284 Å	3·90 Å
Br——N	2·837 (0·0041)		3·45
N ≡ C(1)	1·138 (0·0056)	1·157	
C(1)–C(2)	1·442 (0·0051)	1·458	

	Observed angles
Br–Br— N	179·4 (0·11)°
Br–N——C(1)	171·6 (0·42)
N –C(1)–C(2)	179·6 (0·51)

Table 5. *Values of r.m.s. displacements along the principal axes of the vibration ellipsoid; and their components parallel to the crystallographic axes*

E.s.d.'s in parentheses.

	R.M.S. amplitudes	Ux	Uy	Uz
	0·248 (0·002) Å	0·050 Å	0 Å	0·265 Å
Br	0·138 (0·001)	0·149	0	0·038
	0·179 (0·0005)	0	0·179	0
	0·316 (0·003)	0·256	0	0·322
N	0·095 (0·002)	0·071	0	−0·040
	0·276 (0·024)	0	0·276	0
	0·185 (0·020)	0·073	0	−0·142
C(1)	0·181 (0·005)	0·187	0	0·144
	0·179 (0·006)	0	0·179	0
	0·320 (0·011)	0·091	0	0·347
C(2)	0·074 (0·015)	0·078	0	0·014
	0·214 (0·004)	0	0·214	0

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The Crystal and Molecular Structure
of N,N,N',N' -Tetramethyl-p-diaminobenzene–Chloranil, TMPD-Chloranil

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Crystalline TMPD–chloranil has been shown to be predominantly a molecular complex, although the presence of a minority (up to some 20%) of doubly charged $TMPD^{2+}$ and $chloranil^{2-}$ ions, as indicated by absorption spectra, could not be excluded from X-ray work. Electron spin resonance measurements have shown that the crystals do not contain $TMPD^{+}$, and that $chloranil^{-}$ ions are present only to a small extent (0·8%). The methyl groups of TMPD do not show free rotation about the $N-CH_3$ bonds.

Introduction

N,N, N',N'-Tetramethyl-p-diaminobenzene–chloranil, TMPD–chloranil,
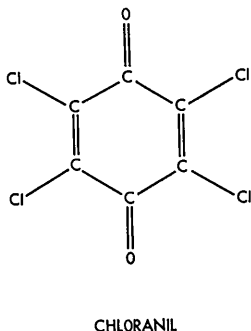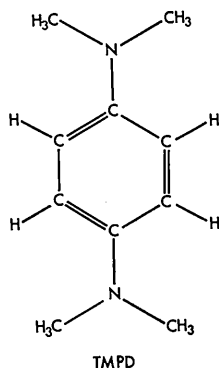
TMPD   CHLORANIL

has been studied as part of a program to obtain more information on compounds containing TMPD units (for another paper see de Boer, Vos & Huml, 1968). TMPD–chloranil is an interesting charge-transfer complex (Pott, 1966). At room temperature the compound is weakly paramagnetic. In accordance with electron spin resonance (e.s.r.) measurements, this paramagne-

tism has been ascribed to the presence of a small number of $chloranil^{-}$ ions (approximately 0·8%). A $TMPD^{+}$ signal is not observed. To check whether the absence of the signal is not due to somehow hampered recognition, Pott & Kommandeur (1967) also investigated some purposely made non-stoichiometric crystals (with a TMPD-excess of the order of 0·1%) and found that in these, as well as the $chloranil^{-}$, the $TMPD^{+}$ signal was readily observable. As the e.s.r. measurements thus give evidence for the absence of $TMPD^{+}$ ions in the pure crystals, the TMPD units are either neutral or doubly charged. Absorption spectra indicate the presence of $TMPD^{2+}$ and $chloranil^{2-}$ ions. However, the number of doubly charged ions is difficult to estimate from the spectra.

The compound undergoes a phase transition at lower temperatures, as may be noticed from a splitting of the $chloranil^{-}$ e.s.r. absorption signal below 250 °K. The splitting increases with decreasing temperature. X-ray pictures show that the crystals of the low temperature phase are twinned, presumably owing to a change in symmetry from monoclinic to triclinic during the transition.

According to Pott (1966) there are two different types of TMPD–chloranil, which may be distinguished