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The Crystal Structures of Fluorene Derivatives. II. 2-Bromodiazofluorene

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2-Bromodiazofluorene ($C_{13}H_7N_2Br$) crystallizes in the monoclinic system, space group $C2/c$, with a unit cell of dimensions $a=22{\cdot}51\pm0{\cdot}03$, $b=5{\cdot}60\pm0{\cdot}01$, $c=20{\cdot}24\pm0{\cdot}03$ Å, $\beta=120{\cdot}0\pm0{\cdot}2°$, containing eight molecules. The crystal structure was determined by the heavy-atom technique and refined by electron-density and difference syntheses and finally by least-squares methods using three-dimensional data.

Introduction

The reason for this crystal-structure determination has been discussed in part I of this series. The main interest lies in the cyclopentadiene ring which Parry & Warren (1965) have suggested has greater aromatic character in 2-bromodiazofluorene than in 2-bromoketofluorene, and for which Warren (1966) has calculated bond lengths. The currently available intensity data allow the determination of the principal features of the crystal structure only. These are described here.

Experimental

2-Bromodiazofluorene ($C_{13}H_7N_2Br$; Fig. 1) crystallizes from benzene as thin translucent red plates having rhombohedral cross section elongated parallel to [010]. The plane of the plate is (001)*.

Oscillation and Weissenberg photographs determined the space group as Cc or $C2/c$ with principal axial lengths $a=22{\cdot}51\pm0{\cdot}03$, $b=5{\cdot}60\pm0{\cdot}01$, $c=20{\cdot}24\pm0{\cdot}03$ Å, $\beta=120{\cdot}0\pm0{\cdot}2°$, $\varrho_o=1{\cdot}62\pm0{\cdot}02$ g.cm^{-3}, ϱ_c (eight molecules per unit cell)$=1{\cdot}63$ g.cm^{-3}.

The centrosymmetric space group was assumed; subsequent work soon showed this assumption to be correct.

The linear absorption coefficient for Cu $K\alpha$ radiation$=46$ cm^{-1}. The crystals melt with gas evolution (nitrogen) at 123 °C.

The intensities used were collected by photometric measurement from integrated zero and upper-layer equi-inclination Weissenberg photographs taken about [010]. The accuracy of the intensity measurements and range of $\sin^2\theta$ obtainable were limited by radiation damage to the crystals, which showed after about 100 hours, and by the high mean-temperature factor. The numerical magnitudes of the temperature factors obtained must partly reflect the radiation damage. Two carfully measured crystals were used for the data collection: one for layers $k=0$ and 1, the other for $k=2$ and 3. In this way the intensities of 595 reflexions were measured. They were corrected for absorption by calculation from the known crystal dimensions (Busing & Levy, *ORABS* program). Because of the very high mean-temperature factor these reflexions are mainly

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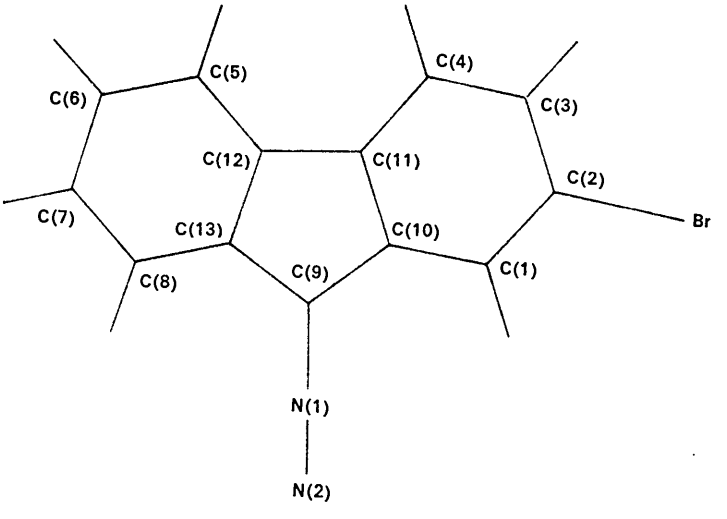

Fig. 1. Schematic diagram of the molecule showing the atom numbering.

low and middle order. They were therefore supplemented by visually estimated high-order terms. These were collected from equi-inclination Weissenberg photographs, corrected for absorption, and scaled to the previously collected integrated data.

Solution of the structure

The crystal structure was solved by conventional heavy-atom methods starting with the (010) projection. Refinement in projection was by two electron-density

Table 1. *Final parameters*

Coordinate standard deviations are enclosed in brackets.

	x (Å)	*y* (Å)	*z* (Å)	*B* (Å²)
C(1)	2·332 (0·020)	1·522 (0·019)	11·802 (0·022)	7·82
C(2)	1·609 (0·022)	0·564 (0·017)	12·332 (0·028)	8·76
C(3)	8·837 (0·020)	2·269 (0·022)	17·145 (0·028)	8·13
C(4)	7·376 (0·022)	2·026 (0·021)	16·781 (0·038)	8·61
C(5)	3·755 (0·020)	2·141 (0·021)	16·265 (0·026)	8·97
C(6)	2·402 (0·022)	2·432 (0·019)	16·196 (0·026)	9·39
C(7)	9·182 (0·020)	0·734 (0·020)	13·508 (0·026)	9·52
C(8)	7·833 (0·020)	1·523 (0·019)	12·678 (0·024)	12·74
C(9)	4·909 (0·020)	1·931 (0·019)	11·863 (0·024)	7·70
C(10)	3·802 (0·022)	1·231 (0·022)	12·152 (0·022)	6·95
C(11)	4·628 (0·020)	0·152 (0·022)	13·081 (0·028)	7·58
C(12)	6·224 (0·020)	0·156 (0·020)	13·292 (0·026)	8·15
C(13)	6·379 (0·022)	1·282 (0·022)	12·541 (0·022)	6·85
N(1)	6·773 (0·020)	0·184 (0·023)	19·422 (0·022)	9·10
N(2)	7·104 (0·022)	1·078 (0·023)	20·208 (0·022)	9·92
BrO	−0·412 (0·004)	0·901 (0·004)	11·911 (0·002)	ANISO

Final heavy atom anisotropic *B* values

B(1,1)	0·0059
B(2,2)	0·0982
B(3,3)	0·0087
B(1,2)	0·0028
B(1,3)	0·0045
B(2,3)	0·0019

Calculated hydrogen positions

	x	*y*	*z*
H(1)	9·391 Å	5·020 Å	19·098 Å
H(3)	9·398	1·559	16·714
H(4)	6·908	1·328	16·240
H(5)	3·887	1·309	15·726
H(6)	0·167	1·945	15·716
H(7)	0·109	3·725	16·779
H(8)	3·271	5·155	18·222

Table 2. *Molecular geometry of 2-bromodiazofluorene*

Standard deviations are enclosed in brackets.

C(1)—C(2)	1·452 (0·039) Å	C(7)—C(8)	1·407 (0·033) Å
C(2)—C(3)	1·385 (0·036)	C(8)—C(13)	1·429 (0·036)
C(3)—C(4)	1·339 (0·036)	C(13)–C(12)	1·404 (0·036)
C(4)—C(11)	1·431 (0·031)	C(13)–C(9)	1·429 (0·036)
C(11)–C(12)	1·501 (0·036)	C(9)—C(10)	1·456 (0·038)
C(12)–C(5)	1·384 (0·039)	C(10)–C(11)	1·393 (0·033)
C(5)—C(6)	1·349 (0·035)	C(10)–C(1)	1·362 (0·040)
C(6)—C(7)	1·404 (0·032)	C(2)—Br	1·876 (0·031)
N(1)—N(2)	1·124 (0·031)	C(9)—N(1)	1·323 (0·032)
C(1)—C(2)—C(3)	121·1 (2·4)°	C(12)–C(5)—C(6)	120·8 (2·9)°
C(2)—C(3)—C(4)	121·7 (2·4)	C(5)—C(6)—C(7)	127·5 (2·7)
C(3)—C(4)—C(11)	118·6 (2·3)	C(6)—C(7)—C(8)	109·9 (2·2)
C(4)—C(11)–C(10)	119·6 (2·3)	C(7)—C(8)—C(13)	125·9 (2·8)
C(11)–C(10)–C(1)	122·7 (2·2)	C(8)—C(13)–C(12)	117·9 (2·4)
C(10)–C(1)—C(2)	115·9 (2·1)	C(11)–C(12)–C(5)	117·8 (2·7)
C(11)–C(12)–C(13)	108·7 (2·2)	C(13)–C(9)—N(1)	126·2 (2·2)
C(12)–C(13)–C(9)	104·8 (2·2)	C(10)–C(9)—N(1)	102·5 (2·1)
C(13)–C(9)—C(10)	112·9 (1·9)	C(9)—N(1)--N(2)	178·2 (2·6)
C(9)—C(10)–C(11)	104·4 (2·1)	C(1)—C(2)—Br	118·5 (1·8)
C(10)–C(11)–C(12)	109·0 (2·2)	C(3)—C(2)—Br	120·3 (2·0)
C(4)—C(11)–C(12)	133·4 (2·5)	C(5)—C(12)–C(11)	131·2 (2·2)

syntheses followed by two difference syntheses. There was no indication in the difference syntheses of any significant anisotropic thermal motion for any atom. The final refinement was by six cycles of three-dimensional full-matrix least-squares (Busing, Martin & Levy *ORFLS* program). During the first three cycles atomic coordinates and individual isotropic temperature factors for all atoms, except hydrogen, and the layer scale factors were refined. For the final three cycles the layer-scale factors were fixed and the heavy-atom temperature factor refined anisotropically. 17 low-order reflexions which appeared to show extinction were given zero weight. The final R value for the observed terms was 0·09. The final parameters are listed in Table 1 and the intramolecular geometry in Tables 2 and 3. The observed and calculated structure factors are listed in Table 4.

Table 3. *Deviations of atoms from the best plane*

Best plane through all atoms

$$-0{\cdot}119x-0{\cdot}569y-0{\cdot}814z+4{\cdot}751=0\,.$$

Deviations from this plane

C(1)	−0·054 Å
C(2)	−0·001
C(3)	+0·043
C(4)	+0·077
C(5)	+0·050
C(6)	−0·009
C(7)	−0·095
C(8)	−0·068
C(9)	−0·026
C(10)	+0·019
C(11)	+0·021
C(12)	+0·048
C(13)	−0·001
N(1)	+0·030
N(2)	+0·080
Br	−0·112

Table 4. *Final observed and calculated structure factors*

H	K	L	|FO|	FC
0	0	2	89.0	91.5
0	0	4	312.0	-309.9
0	0	6	74.0	-72.6
0	0	8	27.0	-25.7
0	0	10	84.0	80.0
0	0	12	59.0	58.7
0	0	16	24.0	-24.8
0	0	18	8.0	-5.5
0	0	20	8.0	6.7
-2	0	2	77.0	81.1
-2	0	4	34.0	21.5
-2	0	6	261.0	-243.5
-2	0	8	18.0	-14.7
-2	0	10	66.0	62.6
-2	0	12	46.0	38.7
-2	0	14	22.0	22.5
-2	0	16	25.0	-21.5
-2	0	18	17.0	-15.1
-4	0	0	76.0	94.5
-4	0	2	52.0	49.5
-4	0	4	168.0	-172.5
-4	0	6	257.0	-232.0
-4	0	10	98.0	94.7
-4	0	12	42.0	40.1
-4	0	14	38.0	-36.7
-4	0	16	27.0	-24.3
-4	0	20	11.0	7.1
-4	0	22	8.0	4.6
-6	0	0	125.0	134.0
-6	0	2	35.0	29.0
-6	0	4	98.0	-103.9
-6	0	6	54.0	-36.7
-6	0	8	89.0	83.6
-6	0	10	149.0	154.0
-6	0	12	31.0	35.5
-6	0	14	45.0	-45.7
-6	0	16	20.0	-16.9
-6	0	18	11.0	-10.8
-6	0	22	8.0	10.9
-8	0	0	8.0	-5.7
-8	0	2	125.0	-138.9
-8	0	4	247.0	-247.7
-8	0	6	102.0	-97.8
-8	0	8	88.0	83.8
-8	0	10	76.0	74.0
-8	0	12	39.0	43.9
-8	0	14	23.0	-25.5
-8	0	16	57.0	-61.8
-8	0	18	8.0	-3.4
-8	0	20	17.0	19.2
-10	0	0	111.0	122.0
-10	0	2	84.0	-54.2
-10	0	4	133.0	-137.1
-10	0	6	42.0	47.2
-10	0	8	68.0	66.7
-10	0	10	54.0	54.7
-10	0	14	36.0	-34.9
-10	0	16	21.0	-19.9
-10	0	20	11.0	6.9
-10	0	22	8.0	5.2
-12	0	0	20.0	21.4
-12	0	2	57.0	-60.7
-12	0	4	87.0	-88.5
-12	0	6	24.0	-14.9
-12	0	8	121.0	121.4
-12	0	10	127.0	125.9
-12	0	12	21.0	-18.2
-12	0	14	58.0	-64.1
-12	0	16	17.0	-17.8
-12	0	18	20.0	19.7
-12	0	20	14.0	16.4
-12	0	22	11.0	11.2
-14	0	0	8.0	-7.2
-14	0	2	65.0	-73.9
-14	0	4	74.0	-71.7
-14	0	6	27.0	-16.6
-14	0	8	76.0	74.8
-14	0	10	17.0	15.9
-14	0	12	48.0	-49.1
-14	0	14	48.0	-49.1
-14	0	16	17.0	-17.8
-14	0	18	18.0	21.4
-14	0	20	11.0	10.2
-16	0	0	25.0	-30.6
-16	0	2	34.0	-33.9
-16	0	4	14.0	-16.1
-16	0	6	50.0	53.5
-16	0	8	76.0	77.6
-16	0	10	44.0	46.6
-16	0	12	37.0	-39.9
H	K	L	|FO|	FC
-16	0	14	62.0	-66.4
-16	0	18	17.0	19.0
-16	0	20	16.0	16.6
-18	0	2	37.0	-34.3
-18	0	4	37.0	-43.2
-18	0	6	20.0	14.2
-18	0	8	38.0	34.9
-18	0	10	26.0	32.5
-18	0	12	12.0	-9.0
-18	0	14	39.0	-42.5
-18	0	16	20.0	-22.3
-18	0	18	24.0	24.3
-18	0	20	25.0	25.3
-20	0	0	11.0	-10.9
-20	0	2	21.0	-18.7
-20	0	6	25.0	18.5
-20	0	8	31.0	27.8
-20	0	10	21.0	-26.1
-20	0	12	39.0	-43.5
-22	0	0	8.0	-9.2
-22	0	2	11.0	-8.2
-22	0	6	25.0	22.0
-22	0	8	21.0	23.6
-22	0	12	21.0	-18.4
-22	0	14	18.0	-17.4
-22	0	16	11.0	13.1
-22	0	18	20.0	21.9
-24	0	2	8.0	-9.0
-24	0	6	11.0	13.5
-24	0	8	8.0	7.2
-24	0	10	8.0	-11.5
-24	0	12	26.0	-17.9
-24	0	14	8.0	11.4
-24	0	16	15.0	13.5
-24	0	18	14.0	14.5
-26	0	8	8.0	7.6
-26	0	10	8.0	-3.4
-26	0	12	18.0	-13.9
-26	0	16	8.0	6.7
-26	0	18	8.0	6.8
2	0	2	30.0	38.0
2	0	4	150.0	-137.1
2	0	6	132.0	-132.9
2	0	8	68.0	-66.1
2	0	10	48.0	49.0
2	0	12	44.0	37.6
2	0	14	12.0	-16.8
4	0	2	175.0	188.4
4	0	4	14.0	-7.8
4	0	6	68.0	-67.9
4	0	8	11.0	-8.8
4	0	10	12.0	-13.9
4	0	12	27.0	21.9
4	0	14	21.0	18.3
6	0	2	115.0	123.0
6	0	4	20.0	20.5
6	0	6	79.0	-83.6
6	0	8	35.0	-36.6
6	0	10	15.0	16.0
6	0	12	15.0	8.5
6	0	14	8.0	4.5
8	0	2	95.0	91.7
8	0	4	39.0	48.7
8	0	6	47.0	-46.8
8	0	8	43.0	-47.6
8	0	10	11.0	-8.8
8	0	12	15.0	6.3
8	0	14	26.0	10.8
10	0	2	105.0	114.8
10	0	4	24.0	24.6
10	0	6	25.0	-26.7
10	0	8	28.0	-25.2
10	0	12	12.0	13.6
10	0	14	11.0	6.2
12	0	2	27.0	18.6
12	0	4	23.0	22.6
12	0	8	26.0	-28.7
14	0	2	47.0	50.0
14	0	4	11.0	-12.3
16	0	2	21.0	26.6
-1	1	0	-	84.6
-1	1	1	-	43.0
-1	1	2	169.0	163.2
-1	1	3	245.0	-233.6
-1	1	4	310.0	-268.7
-1	1	5	281.0	-249.9
-1	1	6	130.0	-113.9
-1	1	7	111.0	98.0
-1	1	8	60.0	53.8
-1	1	9	135.0	132.6
H	K	L	|FO|	FC
-1	1	10	11.0	6.4
-1	1	11	11.0	-11.9
-1	1	12	18.0	19.5
-1	1	13	32.0	-34.7
-1	1	14	0.0	2.5
-1	1	15	25.0	-27.6
-3	1	0	134.0	148.1
-3	1	1	112.0	-124.6
-3	1	2	95.0	85.8
-3	1	3	139.0	-121.3
-3	1	4	26.0	-23.3
-3	1	5	68.0	42.7
-3	1	6	45.0	-45.4
-3	1	7	79.0	75.7
-3	1	8	35.0	-35.5
-3	1	9	10.0	15.8
-3	1	10	59.0	67.5
-3	1	11	10.0	8.3
-3	1	12	26.0	26.7
-3	1	13	28.0	-27.7
-3	1	14	10.0	-14.3
-3	1	15	10.0	-9.9
-3	1	16	14.0	12.7
-5	1	0	45.0	38.9
-5	1	1	98.0	-102.7
-5	1	2	58.0	-60.8
-5	1	3	112.0	-109.6
-5	1	4	86.0	-85.5
-5	1	5	120.0	103.0
-5	1	6	84.0	-85.9
-5	1	7	100.0	101.8
-5	1	8	22.0	22.8
-5	1	9	44.0	48.3
-5	1	10	62.0	72.3
-5	1	11	10.0	9.5
-5	1	12	18.0	13.2
-5	1	13	39.0	-48.7
-5	1	14	0.0	-0.2
-5	1	15	21.0	-20.6
-5	1	16	14.0	-12.3
-5	1	17	14.0	18.0
-7	1	0	82.0	83.2
-7	1	1	157.0	-159.5
-7	1	2	25.0	-23.8
-7	1	3	74.0	-67.3
-7	1	4	60.0	-56.2
-7	1	5	15.0	14.0
-7	1	6	48.0	-48.5
-7	1	7	90.0	90.9
-7	1	8	25.0	-27.9
-7	1	9	41.0	48.0
-7	1	10	29.0	28.3
-7	1	11	67.0	-80.9
-7	1	12	31.0	33.4
-7	1	13	57.0	-63.9
-7	1	14	26.0	-25.7
-7	1	15	10.0	-7.5
-7	1	16	21.0	-21.6
-7	1	17	14.0	11.9
-9	1	0	0.0	1.6
-9	1	1	81.0	-78.3
-9	1	2	62.0	-62.8
-9	1	3	30.0	-25.4
-9	1	4	0.0	1.9
-9	1	5	91.0	86.9
-9	1	6	24.0	21.8
-9	1	7	113.0	115.8
-9	1	8	58.0	60.2
-9	1	9	49.0	49.7
-9	1	10	41.0	43.2
-9	1	11	34.0	-33.7
-9	1	12	0.0	-1.6
-9	1	13	44.0	-50.3
-9	1	14	10.0	-10.8
-9	1	15	0.0	-5.7
-9	1	16	14.0	-13.0
-9	1	17	14.0	12.5
-11	1	0	20.0	17.9
-11	1	1	86.0	-81.1
-11	1	2	32.0	-37.9
-11	1	3	32.0	-33.5
-11	1	4	112.0	-118.2
-11	1	5	70.0	74.8
-11	1	6	36.0	-37.8
-11	1	7	95.0	99.3
-11	1	8	68.0	70.8
-11	1	9	11.0	-12.6
-11	1	10	19.0	24.8
-11	1	11	71.0	-77.2
-11	1	12	10.0	-13.7
H	K	L	|FO|	FC
-11	1	13	15.0	-18.5
-11	1	14	15.0	-22.0
-11	1	15	18.0	18.1
-11	1	16	10.0	-8.4
-11	1	17	14.0	17.8
-13	1	0	10.0	6.4
-13	1	1	49.0	-53.0
-13	1	2	10.0	10.0
-13	1	3	14.0	15.7
-13	1	4	30.0	-26.8
-13	1	5	38.0	39.5
-13	1	6	14.0	14.5
-13	1	7	34.0	35.1
-13	1	8	42.0	40.5
-13	1	9	22.0	-18.7
-13	1	10	36.0	34.4
-13	1	11	53.0	-56.4
-13	1	12	15.0	-13.5
-13	1	13	31.0	-32.8
-13	1	14	37.0	-41.6
-13	1	15	0.0	-0.7
-13	1	16	10.0	-7.4
-13	1	17	25.0	23.4
-15	1	0	0.0	8.1
-15	1	1	14.0	-12.5
-15	1	2	36.0	-34.8
-15	1	3	10.0	7.1
-15	1	4	36.0	-37.6
-15	1	5	63.0	69.3
-15	1	6	0.0	4.8
-15	1	7	41.0	42.8
-15	1	8	42.0	47.9
-15	1	9	32.0	-34.4
-15	1	10	35.0	38.8
-15	1	11	36.0	-31.2
-15	1	12	19.0	-16.6
-15	1	13	15.0	-16.4
-15	1	14	15.0	-13.2
-15	1	15	28.0	28.9
-15	1	16	0.0	-8.7
-15	1	17	29.0	35.7
-17	1	0	0.0	-1.6
-17	1	1	29.0	-33.3
-17	1	2	21.0	-21.5
-17	1	3	10.0	5.3
-17	1	4	0.0	1.0
-17	1	5	46.0	55.4
-17	1	6	0.0	-1.6
-17	1	7	23.0	23.6
-17	1	8	0.0	2.9
-17	1	9	34.0	-37.9
-17	1	10	10.0	8.9
-17	1	11	62.0	-62.1
-17	1	12	11.0	-7.8
-17	1	13	10.0	-13.2
-17	1	14	34.0	-31.6
-17	1	15	28.0	30.7
-19	1	6	21.0	23.3
-19	1	7	0.0	7.7
-19	1	8	31.0	30.3
-19	1	9	0.0	2.1
-19	1	10	0.0	-4.0
-19	1	11	22.0	-20.7
-19	1	12	10.0	-4.1
1	1	1	122.0	-126.8
1	1	2	47.0	-46.2
1	1	3	122.0	-125.6
1	1	4	38.0	34.9
1	1	5	40.0	37.8
1	1	6	42.0	-39.1
1	1	7	97.0	90.8
1	1	8	0.0	-8.3
1	1	9	68.0	71.8
1	1	10	27.0	23.7
1	1	11	0.0	0.3
1	1	12	23.0	30.1
3	1	1	66.0	-59.9
3	1	2	36.0	46.8
3	1	3	144.0	-151.7
3	1	4	14.0	8.7
3	1	5	37.0	-37.0
3	1	6	74.0	-82.3
3	1	7	18.0	21.0
3	1	8	24.0	-19.3
3	1	9	24.0	18.7
3	1	10	22.0	26.7
3	1	11	10.0	9.4
5	1	1	17.0	-13.3
5	1	2	0.0	1.4
5	1	3	54.0	-66.7
H	K	L	|FO|	FC
5	1	4	21.0	-18.5
5	1	5	75.0	-83.6
5	1	6	10.0	-10.8
5	1	7	0.0	-2.7
5	1	8	31.0	-34.1
5	1	9	39.0	39.5
5	1	10	0.0	3.7
5	1	11	17.0	19.0
7	1	1	46.0	55.3
7	1	2	86.0	86.6
7	1	3	30.0	-35.8
7	1	4	10.0	8.7
7	1	5	25.0	-22.2
7	1	6	18.0	-17.7
7	1	7	10.0	-11.9
7	1	8	15.0	-12.8
7	1	9	10.0	11.9
7	1	10	0.0	-0.7
7	1	11	17.0	17.3
9	1	1	41.0	45.7
9	1	2	57.0	63.5
9	1	3	45.0	-47.9
9	1	4	0.0	-2.6
9	1	5	67.0	-71.6
9	1	6	25.0	-25.6
9	1	7	18.0	-20.4
9	1	8	10.0	-8.6
9	1	9	15.0	17.0
9	1	10	0.0	-5.2
9	1	11	14.0	18.5
11	1	1	36.0	36.1
11	1	2	27.0	30.7
11	1	3	23.0	-21.2
11	1	4	14.0	12.5
11	1	5	28.0	-30.8
11	1	6	0.0	-1.9
11	1	7	0.0	6.1
11	1	8	10.0	-13.5
11	1	9	10.0	10.3
13	1	1	40.0	44.5
13	1	2	25.0	23.8
13	1	3	10.0	-10.7
13	1	4	18.0	22.2
13	1	5	18.0	-14.3
13	1	6	15.0	-19.2
13	1	7	14.0	-13.2
15	1	1	14.0	9.2
17	1	2	14.0	15.3
17	1	3	0.0	2.8
17	1	4	0.0	-1.9
0	2	1	23.0	-30.2
0	2	2	71.0	-78.7
0	2	3	147.0	-152.0
0	2	4	60.0	57.3
0	2	5	28.0	-32.7
0	2	6	103.0	98.2
0	2	7	82.0	80.4
0	2	8	20.0	-18.0
0	2	9	20.0	22.7
0	2	10	64.0	-61.3
0	2	11	0.0	-0.9
0	2	12	26.0	-25.9
0	2	13	20.0	-23.9
-2	2	0	44.0	-54.0
-2	2	1	91.0	-105.7
-2	2	2	0.0	-2.6
-2	2	3	89.0	-89.5
-2	2	4	37.0	37.6
-2	2	5	0.0	1.9
-2	2	6	17.0	-9.9
-2	2	7	53.0	57.8
-2	2	8	82.0	70.3
-2	2	9	155.0	133.7
-2	2	10	57.0	48.3
-2	2	11	0.0	-6.2
-2	2	12	30.0	-30.9
-2	2	13	50.0	-59.6
-2	2	14	19.0	-13.4
-4	2	0	15.0	-14.6
-4	2	1	184.0	-159.5
-4	2	2	0.0	0.1
-4	2	3	96.0	-104.3
-4	2	4	11.0	12.9
-4	2	5	12.0	-10.1
-4	2	6	40.0	35.0
-4	2	7	49.0	-46.4
-4	2	8	24.0	-21.1
-4	2	9	55.0	53.5
-4	2	10	62.0	-66.1
-4	2	11	11.0	-10.6
H	K	L	|FO|	FC
-4	2	12	0.0	8.9
-4	2	13	25.0	-29.9
-4	2	14	19.0	20.2
-4	2	15	16.0	-21.3
-6	2	0	72.0	-75.5
-6	2	1	47.0	-56.5
-6	2	2	60.0	51.7
-6	2	3	81.0	-87.6
-6	2	4	94.0	95.4
-6	2	5	0.0	8.9
-6	2	6	16.0	13.8
-6	2	7	151.0	145.6
-6	2	8	51.0	-42.7
-6	2	9	33.0	31.2
-6	2	10	32.0	-32.7
-6	2	11	35.0	-34.9
-6	2	12	11.0	-11.9
-6	2	13	22.0	-27.3
-6	2	14	0.0	-2.7
-6	2	15	19.0	-24.7
-8	2	0	0.0	-15.9
-8	2	1	56.0	-54.9
-8	2	2	15.0	15.8
-8	2	3	66.0	-54.0
-8	2	4	50.0	47.0
-8	2	5	40.0	38.8
-8	2	6	52.0	50.2
-8	2	7	80.0	70.3
-8	2	8	35.0	-30.4
-8	2	9	36.0	33.9
-8	2	10	35.0	-31.5
-8	2	11	27.0	-17.2
-8	2	12	0.0	2.7
-8	2	13	22.0	-27.3
-8	2	14	16.0	23.1
-8	2	15	0.0	-4.4
-8	2	16	19.0	26.2
-10	2	0	15.0	10.6
1	101.0	-97.8		
-10	2	2	24.0	28.7
-10	2	3	28.0	-27.1
-10	2	4	36.0	32.1
-10	2	5	91.0	80.2
-10	2	6	0.0	8.8
-10	2	7	71.0	64.7
-10	2	8	41.0	-37.4
-10	2	9	42.0	-36.8
-10	2	10	39.0	-38.4
-10	2	11	58.0	-58.3
-10	2	12	0.0	-13.2
-10	2	13	30.0	-36.4
-10	2	14	0.0	5.5
-10	2	15	0.0	6.2
-10	2	16	0.0	-1.0
-10	2	17	26.0	25.5
-12	2	0	15.0	-18.0
-12	2	1	43.0	-41.9
-12	2	2	15.0	11.6
-12	2	3	0.0	-4.8
-12	2	4	26.0	24.4
-12	2	5	64.0	63.3
-12	2	6	11.0	-6.9
-12	2	7	75.0	69.6
-12	2	8	0.0	-0.2
-12	2	9	11.0	13.6
-12	2	10	12.0	-12.5
-12	2	11	49.0	-43.6
-12	2	12	12.0	-12.8
-12	2	13	36.0	-43.0
-12	2	14	25.0	27.3
-12	2	15	11.0	14.1
-12	2	16	11.0	15.5
-12	2	17	15.0	22.2
-14	2	0	18.0	13.9
-14	2	1	51.0	-58.9
-14	2	2	28.0	16.6
-14	2	3	0.0	8.1
-14	2	4	15.0	10.3
-14	2	5	63.0	63.2
-14	2	6	22.0	16.8
-14	2	7	22.0	16.8
-14	2	8	41.0	-35.7
-14	2	9	11.0	-5.0
-14	2	10	0.0	-9.1
-14	2	11	54.0	-52.3
-14	2	12	33.0	33.8
-14	2	13	28.0	-29.8
-14	2	14	11.0	11.9
-14	2	15	23.0	26.4
-14	2	16	0.0	-4.4

Table 4 (*cont.*)

H	K	L	|FO|	FC	H	K	L	|FO|	FC	H	K	L	|FO|	FC	H	K	L	|FO|	FC	H	K	L	|FO|	FC	H	K	L	|FO|	FC
-14	2	17	15.0	20.9	4	2	2	11.0	-8.4	-3	3	4	90.0	94.7	-9	3	4	44.0	42.0	-15	3	7	13.0	15.6	1	3	13	13.0	-9.4
-16	2	0	19.0	13.6	4	2	3	68.0	-65.6	-3	3	5	30.0	-28.7	-9	3	5	0.0	-0.4	-15	3	8	34.0	-31.6	3	3	2	39.0	-45.7
-16	2	1	19.0	-14.1	4	2	4	0.0	-7.8	-3	3	6	98.0	96.6	-9	3	6	34.0	36.0	-15	3	9	0.0	-11.2	3	3	3	39.0	-45.8
-16	2	2	33.0	38.8	4	2	5	11.0	-12.3	-3	3	7	14.0	9.2	-9	3	7	0.0	5.7	-15	3	10	34.0	-32.2	3	3	4	13.0	-13.6
-16	2	3	0.0	-1.5	4	2	6	33.0	32.6	-3	3	8	33.0	-34.7	-9	3	8	39.0	-33.3	-15	3	11	19.0	14.1	3	3	5	0.0	6.9
-16	2	4	0.0	-0.2	4	2	7	11.0	11.7	-3	3	9	19.0	16.8	-9	3	9	0.0	-0.3	-15	3	12	30.0	30.1	3	3	6	45.0	40.5
-16	2	5	31.0	21.1	4	2	8	27.0	29.4	-3	3	10	56.0	-69.7	-9	3	10	51.0	-47.4	-15	3	13	13.0	-8.2	3	3	7	0.0	2.0
-16	2	6	33.0	-34.8	4	2	9	30.0	25.3	-3	3	11	13.0	6.9	-9	3	11	35.0	23.9	-15	3	14	50.0	40.8	3	3	8	34.0	26.4
-16	2	7	49.0	44.9	6	2	1	32.0	29.0	-3	3	12	25.0	-23.0	-9	3	12	13.0	12.4	-15	3	15	19.0	-15.2	3	3	9	0.0	-6.6
-16	2	8	24.0	-18.9	6	2	2	66.0	-56.6	-3	3	13	49.0	-42.1	-9	3	13	13.0	-7.9	-17	3	2	21.0	24.2	3	3	10	37.0	-33.9
-16	2	9	31.0	-22.6	6	2	3	69.0	-81.9	-3	3	14	34.0	-23.8	-9	3	14	22.0	17.1	-17	3	3	0.0	-9.0	3	3	11	19.0	11.1
-16	2	10	0.0	4.1	6	2	4	0.0	-12.7	-3	3	15	0.0	-9.8	-11	3	0	13.0	-12.6	-17	3	4	21.0	18.8	3	3	12	35.0	-25.9
-16	2	11	56.0	-52.5	6	2	5	68.0	-76.1	-3	3	16	0.0	5.8	-11	3	1	0.0	-5.9	-17	3	5	18.0	-13.9	5	3	1	43.0	-34.3
-16	2	12	0.0	6.4	8	2	1	0.0	6.7	-3	3	17	25.0	24.9	-11	3	2	63.0	59.6	-17	3	6	28.0	-23.0	5	3	2	77.0	-88.9
-16	2	13	0.0	-5.1	8	2	2	37.0	-32.6	-3	3	18	18.0	12.3	-11	3	3	13.0	10.6	-17	3	7	0.0	-2.3	5	3	3	0.0	9.9
-16	2	14	0.0	6.3	8	2	3	0.0	-7.1	-5	3	0	63.0	-68.7	-11	3	4	57.0	59.0	-17	3	8	36.0	-29.9	5	3	4	13.0	11.3
-16	2	15	0.0	3.9	8	2	4	0.0	-4.1	-5	3	1	0.0	9.0	-11	3	5	0.0	1.6	-17	3	9	25.0	21.2	5	3	5	21.0	23.8
-16	2	16	0.0	3.9	8	2	5	28.0	-33.7	-5	3	2	43.0	40.3	-11	3	6	21.0	19.9	-17	3	10	0.0	-1.1	5	3	6	33.0	36.9
-16	2	17	16.0	16.1	8	2	6	0.0	8.2	-5	3	3	76.0	-66.8	-11	3	7	0.0	1.9	-17	3	11	0.0	1.2	5	3	7	18.0	15.0
-18	2	5	31.0	18.8	8	2	7	11.0	-10.9	-5	3	4	81.0	78.9	-11	3	8	66.0	-56.4	-17	3	12	19.0	15.5	5	3	8	34.0	38.6
-18	2	6	15.0	9.8	10	2	1	50.0	51.8	-5	3	5	22.0	15.1	-11	3	9	0.0	7.9	-17	3	13	14.0	-8.9	5	3	9	0.0	0.6
-18	2	7	19.0	24.1	10	2	2	39.0	-35.3	-5	3	6	73.0	67.0	-11	3	10	71.0	-62.3	-17	3	14	19.0	17.8	5	3	10	19.0	13.1
-18	2	8	31.0	-27.3	10	2	3	26.0	-20.3	-5	3	7	23.0	22.8	-11	3	11	0.0	-2.1	-17	3	15	19.0	16.2	5	3	11	0.0	1.4
-18	2	9	27.0	-20.8	10	2	4	24.0	-19.8	-5	3	8	0.0	3.7	-11	3	12	13.0	14.7	-17	3	16	0.0	4.7	5	3	12	14.0	-14.5
-18	2	10	19.0	-15.1	10	2	5	39.0	-38.7	-5	3	9	0.0	0.2	-11	3	13	0.0	8.0	-17	3	17	0.0	1.3	7	3	2	51.0	-46.7
-18	2	11	20.0	-25.0	10	2	6	11.0	19.8	-5	3	10	56.0	-49.0	-11	3	14	60.0	49.8	-17	3	18	13.0	-8.9	7	3	3	0.0	-1.1
-18	2	12	0.0	20.5	10	2	7	11.0	-15.9	-5	3	11	22.0	21.7	-11	3	15	0.0	0.0	-19	3	2	13.0	10.8	7	3	4	0.0	9.4
-18	2	13	0.0	0.7	12	2	1	36.0	28.2	-5	3	12	25.0	-23.6	-11	3	16	28.0	26.7	-19	3	3	0.0	9.3	7	3	5	13.0	-8.3
-18	2	14	16.0	22.4	12	2	2	15.0	-13.1	-5	3	13	28.0	-15.5	-13	3	0	0.0	-5.2	-19	3	4	0.0	1.0	7	3	6	40.0	42.3
-18	2	15	16.0	19.6	12	2	3	24.0	-31.3	-5	3	14	49.0	38.0	-13	3	1	28.0	-25.5	-19	3	5	0.0	3.9	7	3	7	0.0	-13.9
-18	2	16	0.0	3.2	12	2	4	0.0	-3.2	-5	3	15	18.0	-15.8	-13	3	2	33.0	36.2	-19	3	6	22.0	-14.9	7	3	8	19.0	10.7
-18	2	17	16.0	17.8	12	2	5	29.0	-26.9	-5	3	16	31.0	23.8	-13	3	3	0.0	-7.2	-19	3	7	0.0	3.1	9	3	2	57.0	-53.7
-20	2	6	19.0	-14.2	14	2	1	22.0	15.8	-7	3	0	73.0	-70.1	-13	3	4	63.0	60.7	-19	3	8	25.0	-19.1	9	3	3	0.0	-12.6
-20	2	7	0.0	-7.7	-1	3	0	62.0	-106.4	-7	3	1	0.0	3.5	-13	3	5	0.0	4.0	-19	3	9	0.0	-1.5	9	3	4	44.0	-35.5
-20	2	8	0.0	0.6	-1	3	1	34.0	-45.9	-7	3	2	18.0	13.2	-13	3	6	21.0	-20.6	-19	3	10	0.0	-6.6	9	3	5	0.0	-4.0
-20	2	9	0.0	-15.4	-1	3	2	28.0	-27.0	-7	3	3	21.0	14.3	-13	3	7	33.0	32.1	-19	3	11	0.0	-16.8	9	3	6	0.0	0.5
-20	2	10	0.0	10.4	-1	3	3	34.0	31.6	-7	3	4	120.0	108.3	-13	3	8	80.0	-69.1	-19	3	12	0.0	15.5	9	3	7	18.0	17.9
-20	2	11	0.0	-15.2	-1	3	4	80.0	76.5	-7	3	5	0.0	-5.3	-13	3	9	0.0	1.6	-19	3	13	0.0	4.5	9	3	8	19.0	13.3
-20	2	12	0.0	1.6	-1	3	5	0.0	12.0	-7	3	6	34.0	36.1	-13	3	10	22.0	-17.9	-19	3	14	22.0	20.9	11	3	1	13.0	15.9
-20	2	13	0.0	-9.6	-1	3	6	55.0	59.5	-7	3	7	26.0	-20.8	-13	3	11	26.0	-22.2	-19	3	15	22.0	26.7	11	3	2	50.0	-54.3
-20	2	14	16.0	-16.6	-1	3	7	40.0	37.5	-7	3	8	55.0	-36.4	-13	3	12	0.0	4.7	-21	3	8	19.0	-13.7	11	3	3	0.0	9.4
-20	2	15	16.0	17.1	-1	3	8	0.0	5.9	-7	3	9	0.0	4.7	-13	3	13	0.0	-10.0	1	3	1	21.0	23.4	11	3	4	13.0	-13.9
-22	2	6	11.0	-8.1	-1	3	9	0.0	-3.3	-7	3	10	58.0	-57.1	-13	3	14	0.0	9.3	1	3	2	53.0	-52.6	11	3	5	0.0	-9.9
2	2	1	67.0	-65.5	-1	3	10	44.0	-39.7	-7	3	11	13.0	8.8	-13	3	15	13.0	6.4	1	3	3	28.0	-24.9	11	3	6	18.0	22.8
2	2	2	30.0	-33.3	-1	3	11	26.0	-28.2	-7	3	12	46.0	-40.6	-13	3	16	0.0	11.8	1	3	4	44.0	47.5	11	3	7	0.0	-2.9
2	2	3	145.0	-139.7	-1	3	12	47.0	-35.3	-7	3	13	25.0	14.2	-13	3	17	18.0	15.6	1	3	5	19.0	-14.2	11	3	8	19.0	16.1
2	2	4	19.0	11.9	-1	3	13	29.0	22.6	-7	3	14	0.0	13.5	-15	3	0	33.0	35.6	1	3	6	107.0	91.9	13	3	2	18.0	-18.0
2	2	5	46.0	-58.4	-1	3	14	19.0	15.3	-7	3	15	13.0	8.2	-15	3	1	18.0	-13.5	1	3	7	0.0	1.8	13	3	3	28.0	-26.8
2	2	6	35.0	34.9	-1	3	15	28.0	28.5	-7	3	16	21.0	19.5	-15	3	2	45.0	32.5	1	3	8	26.0	20.9	13	3	4	21.0	-18.4
2	2	7	57.0	59.7	-3	3	0	79.0	-102.7	-9	3	0	13.0	-14.3	-15	3	3	28.0	-33.1	1	3	9	14.0	15.4	15	3	2	28.0	-23.0
2	2	8	0.0	5.4	-3	3	1	0.0	-5.9	-9	3	1	0.0	-4.2	-15	3	4	18.0	15.9	1	3	10	19.0	-16.1	15	3	3	0.0	-8.3
2	2	9	28.0	31.7	-3	3	2	53.0	-48.4	-9	3	2	62.0	53.8	-15	3	5	21.0	20.1	1	3	11	30.0	-23.2					
4	2	1	22.0	-29.8	-3	3	3	22.0	-13.8	9	3	3	0.0	-1.0	-15	3	6	18.0	-19.1	1	3	12	0.0	-3.0					

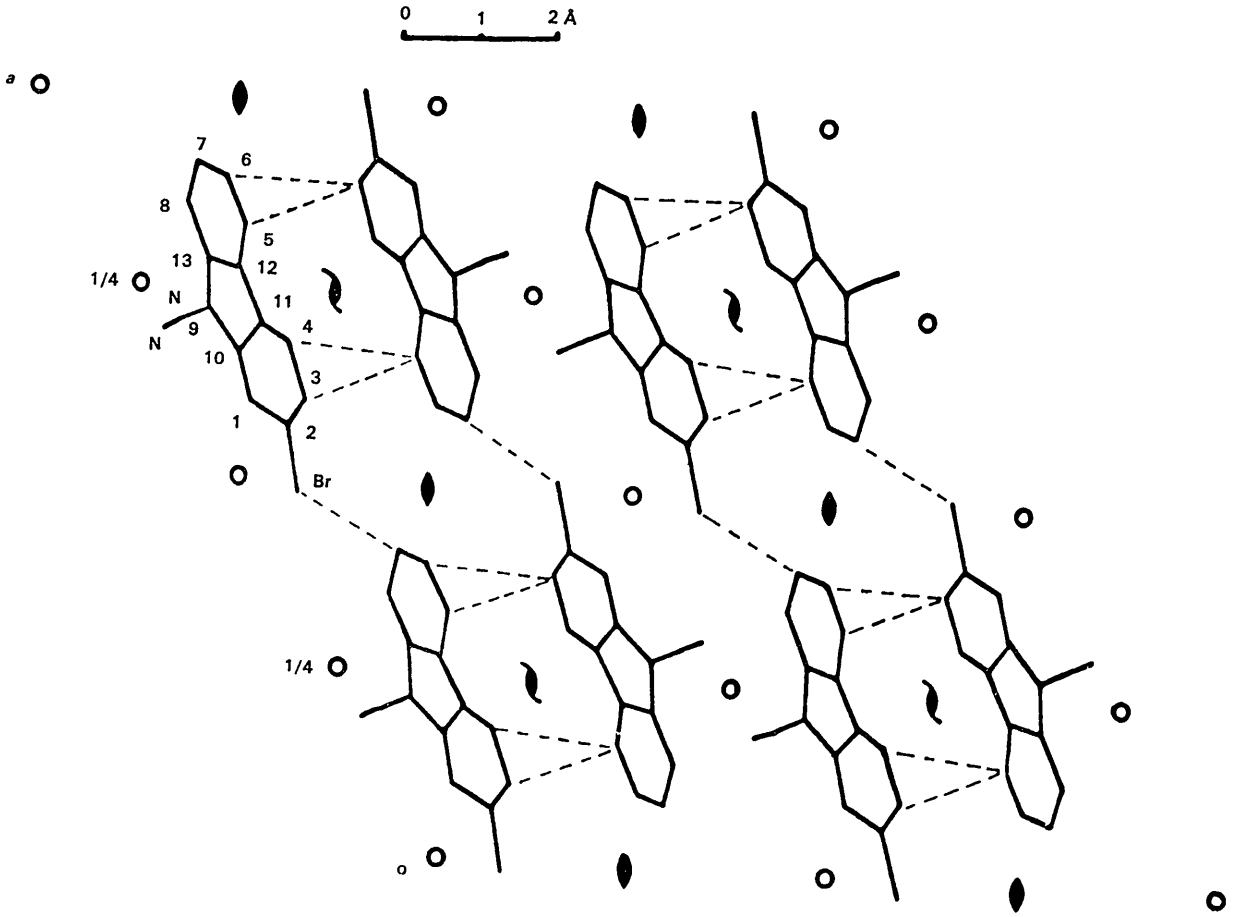

Fig. 2. Molecular arrangement viewed down [010]. Broken lines represent closest approaches.

The crystal structure

The structure consists of paired chains of molecules held together by van der Waals forces (Fig. 2). The planes of the molecules are at an angle of 55° to the (010) plane. In general the atoms lie, within experimental accuracy, on the best plane through the molecules (Table 3), but atoms Br, C(7) and N(2) appear to be displaced significantly from the plane, even at the rather large standard deviations obtained. With the exception of the angles in the cyclopentadiene ring at C(9), C(10) and C(13), where there is likely to be distortion from the values in fluorene, only three angles differ from the values in fluorene by more than two standard deviations. These are the angles at C(6), C(7) and C(8). Their standard deviations and temperature factors are no different from those of other atoms in the aromatic rings and there is no reason to suppose that any atom is misplaced. The distortion is presumably the result of interaction between atoms C(7) and Br in adjacent molecules. These atoms are separated by 3·86 Å which is the closest approach not involving hydrogen atoms between two adjacent molecules.

The only other difference of note between the geometry of this molecule and that of 2-bromoketofluorene (Griffiths & Hine, 1970) lies in the cyclopentadiene ring, where the bonds C(9)–C(10) and C(9)–C(13) are rather shorter in the present diazo compound than in the keto compound, and the angle C(10)–C(9)–C(13) is increased. These changes agree qualitatively with the calculations of Warren (1966). The accuracy of the present structure determination is, however, not great enough to establish the effect unequivocally.

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The Crystal Structure of $(NH_4)_4UF_8$*

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The crystal structure of $(NH_4)_4UF_8$ has been determined from counter measurements of 849 reflections and refined by full-matrix least squares with anisotropic thermal parameters to an R index of 0·048. The space group is $C2/c$ with four formula units in a unit cell with $a=13·126\pm0·005$, $b=6·692\pm0·003$, $c=13·717\pm0·005$ Å and $\beta=121°19'$. The calculated density is 2·982 g.cm^{-3} and the measured density is 2·96 g.cm^{-3}. The uranium atom has 8 fluorine neighbors at an average distance of 2·28 Å which form a distorted tetragonal antiprism. These discrete polyhedra are linked *via* the ammonium ions, presumably through N–H---F hydrogen bonds. The four fluorine atoms nearest each nitrogen atom are roughly tetrahedrally disposed. The structure is compatible with the observed morphology and cleavage. The crystals usually twin on (001). There are several possible twinning mechanisms which result in a minimum distortion of the packing at the twin boundary. This compound is isostructural with analogous Pa, Am, Np and Pu compounds.

Introduction

Complexes of ammonium fluoride and actinide(IV) fluorides in the ratio 4:1 have been prepared for americium (Asprey & Penneman, 1962), neptunium (Keenan, 1963; Penneman, Kruse, George & Coleman, 1964), uranium and plutonium (Benz, Douglass, Kruse & Penneman, 1963) and protactinium (Asprey, Kruse & Penneman, 1967). On the basis of X-ray powder diffraction patterns, these compounds are considered to be isostructural. Additional data on the preparation of, and a description of $(NH_4)_4UF_8$ including partial optical properties are given by Penneman *et al.* (1964).

The only alkali-metal actinide(IV) fluoride of this stoichiometry thus far prepared is Li_4UF_8, whose structure has been described by Brunton (1967). This compound is orthorhombic with a distinctly different structure from that of the ammonium compounds.

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