

ellipsoids. Inspection of the result indicates that the carbon atoms which are not involved in the crowding around the central Si atom undergo stronger vibration; they are C( $\alpha$ , 3), C( $\alpha$ , 4), C( $\alpha$ , 6), C( $\alpha$ , 7) and the three outside carbon atoms in the phenyl ring. The directions of the maximum amplitudes are almost in the ring planes. The characteristics of the thermal motion in the two crystals are quite similar and the *F* compound has larger amplitude than the *H* compound; this is reasonable in view of the stability of these two compounds.

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## The Crystal Structure of Tetraphenylarsonium 3-Fluoro-1,1,4,5,5-pentacyano-2-azapentadienide

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One of the two carbanions produced by the reaction of sodium or potassium cyanide with 1,2-dichlorohexafluorocyclopentene has been identified by X-ray diffraction as 3-fluoro-1,1,4,5,5-pentacyano-2-azapentadienide. The crystal structure analysis of the tetraphenylarsonium salt was completed without any chemical assumptions.

Tetraphenylarsonium 3-fluoro-1,1,4,5,5-pentacyano-2-azapentadienide forms deep red orthorhombic crystals with  $a = 9.789$ ,  $b = 24.601$ ,  $c = 23.918$  Å. The space group is *Pcab* with 8 molecules per unit cell. The structure was refined by least-squares methods and the final residual (*R*) was 5.7% for the 2835 reflections included in the analysis.

In the cation the arsenic atom is bonded to four carbon atoms at the corners of a tetrahedron with an average As-C bond distance of  $1.897 \pm 0.009$  Å. The cation's ideal  $\bar{4}$  symmetry is destroyed by rotation of the four planar phenyl groups around the As-C bond. The average C-C bond distance in the four phenyl groups is  $1.389 \pm 0.012$  Å.

The deep red carbanion is nonplanar, probably the result of internal steric effects. The average of the five C $\equiv$ N bonds is  $1.146 \pm 0.012$  Å, in agreement with other reported cyano compounds.

### Introduction

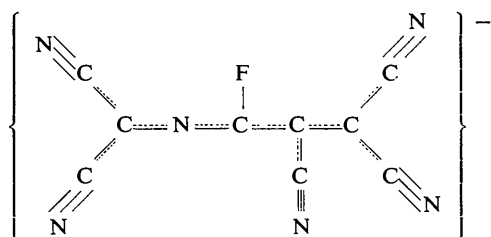
The reaction of sodium or potassium cyanide with an excess of 1,2-dichlorohexafluorocyclopentene produces deeply colored solutions. From this reaction mixture, Carpenter (1965) found that two strongly colored carbanions could be isolated as the tetraalkylammonium, -phosphonium or -arsonium salts. The microanalyses indicated that the red carbanion had an approximate

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empirical formula of C<sub>9-11</sub>N<sub>6</sub>OF. The magenta carbanion was formulated as C<sub>11</sub>N<sub>6</sub>F. Since the chemical and physical properties did not suggest a structure, an X-ray crystal structure determination appeared essential. The tetraphenylarsonium salt of the red anion (henceforth TPAS<sup>+</sup> RD<sup>-</sup>) was chosen for the X-ray investigation since it was the most unusual of the two carbanions. The presence of the tetraphenylarsonium cation suggested that the structure of the anion could

be ascertained with a minimum of chemical assumptions. The results of our study showed that the anion was 3-fluoro-1,1,4,5,5-pentacyano-2-azapentadienide:



Experimental

The TPAS<sup>+</sup> RD<sup>-</sup> crystallizes from acetone as deep red surfboard-shaped crystals. Weissenberg photographs taken about the  $\bar{a}$  axis indicated orthorhombic symmetry with no evidence of twinning or disorder. The systematic absences were:

$hkl$	no absences
$0kl$	absent if $l=2n+1$
$h0l$	absent if $h=2n+1$
$hk0$	absent if $k=2n+1$

The space group is uniquely determined to be  $Pcab$  ( $D_{2h}^{15}$ ).

A crystal was cleaved to give a parallelepiped  $0.05 \times 0.09 \times 0.21$  mm, dipped in liquid nitrogen, and then mounted on a General Electric single-crystal orienter. The long dimension of the crystal (the  $\bar{a}$  axis) was parallel to the  $\phi$  axis of the orienter. The unit-cell dimensions were determined with a narrow beam of copper radiation ( $\alpha_1 = 1.54050$  and  $\alpha_2 = 1.54434$  Å) with a narrow slit at the counter window. The averages of these measurements are given below:

$$a = 9.789 \pm 0.003, \quad b = 24.601 \pm 0.006, \\ c = 23.918 \pm 0.006 \text{ \AA}.$$

The density of TPAS<sup>+</sup> RD<sup>-</sup> was determined by flotation in a potassium iodide solution to be  $1.368 \text{ g. cm}^{-3}$ . The molecular weight of the anion was calculated to be 205.0 g, indicating that the microanalyses were probably in error. The density calculated for eight molecules of tetraphenylarsonium 3-fluoro-1,1,4,5,5-pentacyano-2-azapentadienide per unit cell is  $1.371 \text{ g. cm}^{-3}$ .

Intensity measurements were made using a proportional counter with a linear amplifier-pulse height selector combination. The stationary-crystal stationary-counter technique was employed in measuring the 4278 reflections with  $2\theta \leq 120.0^\circ$ . The 285  $0kl$  reflections with  $l=2n+1$  were also surveyed and were used to calculate a background correction. The 2850 reflections which were greater than 1.2 times the background count at that particular value of  $2\theta$  were considered to be observed reflections. A correction for the  $\alpha_1 - \alpha_2$  splitting was calculated by comparing selected stationary crystal intensities with the corresponding values measured by the moving crystal-moving counter technique.

### Determination and refinement of the trial structure

A sharpened three-dimensional Patterson synthesis with the origin peak removed was calculated. The arsenic-arsenic vectors were easily identified in the Harker sections. The value of the  $x$  coordinate for the arsenic atom is approximately  $\frac{1}{4}$ , introducing an ambiguity in the  $z$  coordinate between  $z$  and  $\frac{1}{4} - z$ . By comparing a minimum function based on the arsenic-arsenic vector with a series of low-resolution Fourier syntheses computed using only the terms with  $l=2n$ , the orientations of the four phenyl groups were determined. Structure factors were computed for all the observed reflections, using the two choices for the  $z$  coordinate of the arsenic atom. The agreement between the observed and calculated values was better for  $z=0.142$  than for  $z=0.108$  and the former value was used in all subsequent calculations.

An observed and a difference Fourier synthesis were then computed with the contribution of the tetraphenylarsonium group to determine the phases. Only sixteen peaks ranging in heights from 2.4 to 6.6  $\text{e. \AA}^{-3}$  were found which could be assigned to the anion. The identification of the atom peaks was based on chemical considerations; for example, three collinear terminal atoms were assumed to be a cyano group attached to a carbon atom. The mean carbon atom peak height was 3.8  $\text{e. \AA}^{-3}$ , and the mean nitrogen atom peak height was 3.9  $\text{e. \AA}^{-3}$ . The fluorine atom peak height was 6.6  $\text{e. \AA}^{-3}$ . An observed and a difference Fourier synthesis using all 41 atoms for determining the phases revealed no additional peaks. Since a nitrogen atom in the chain was unexpected, N(40) was assumed to be a carbon atom in the initial refinement. The initial parameters for the least-squares refinement were obtained from the 41 atom-observed Fourier synthesis. The starting value of  $R$ , the usual residual, was 19.1%.

Because of the large number of variables involved in the refinement, the block approximation to the full matrix was employed. A  $3 \times 3$  block was used for the positional parameters and a  $6 \times 6$  block for the anisotropic thermal parameters. The quantity minimized was  $\sum w(\Delta F)^2$ , where  $\Delta F = |F_o| - |F_c|$  and the weighting scheme was:

$$\begin{aligned} \text{if } F(\text{obs}) < 100 & \quad |w = F(\text{obs})/100 \\ \text{if } 100 < F(\text{obs}) \leq 400 & \quad |w = 1.0 \\ \text{if } 400 < F(\text{obs}) & \quad |w = 400/F(\text{obs}). \end{aligned}$$

Partial shifts of 0.75 and 0.375 were used for the positional and thermal parameters respectively. The scale factor  $G$  was shifted by 0.20 times the amount calculated by dividing  $\sum w \Delta F (\partial |F_c| / \partial G)$  by  $\sum w (\partial |F_c| / \partial G)_2$ .

A total of four least-squares cycles reduced the residual  $R$  to 8.5%. A comparison of the thermal parameters for atom 40 (which had been refined as a carbon atom to this point) with those of carbons 30–33 in the chain indicated that atom 40 was a nitrogen and not a carbon atom. The subsequent refinements all used

atom 40 as a nitrogen atom. Five more least-squares cycles reduced the residual  $R$  to 6.7%.

At this point a careful study of the observed and calculated structure factors, the original data, and some Weissenberg photographs revealed a few errors in the observed amplitudes. These errors were corrected where feasible. Three reflections for which a setting error had been made were removed from the data and are noted by an asterisk in Table 4.

A difference Fourier synthesis was calculated in an attempt to locate the 20 hydrogen atoms of the four phenyl groups. Positions for all the hydrogen atoms

were obtained from the difference synthesis. An isotropic temperature factor (the average of the isotropic equivalent of its respective carbon atom) was assigned to each hydrogen atom. The contribution of the hydrogen atoms was included in the subsequent least-squares refinement, but their positional and thermal parameters were not varied.

Six additional least-squares cycles were computed before the refinement was terminated. On the final cycle the average shift in the positional parameters for the carbon and nitrogen atoms was 0.0004 Å. The largest shift was 0.0022 Å [for the  $y$  coordinate of N(39)], which is one-third of the standard deviation for that

Table 1. *Final positional parameters and their estimated deviations for the heavy atoms*

Atom	From final least squares ( $\times 10^4$ )			After correction for libration ( $\times 10^4$ )		
	$x$	$y$	$z$	$x$	$y$	$z$
C(1)	2283	0346	2185	2282	0345	2186
C(2)	1605	0694	2543	1602	0694	2546
C(3)	1549	0567	3116	1546	0567	3119
C(4)	2172	0108	3313	2170	0107	3317
C(5)	2839	-0236	2957	2839	-0237	2960
C(6)	2905	-0114	2380	2906	-0115	2382
C(7)	3026	-0097	1029	3028	-0098	1028
C(8)	2252	-0574	1059	2252	-0575	1058
C(9)	2728	-1038	0790	2730	-1041	0789
C(10)	3960	-1030	0503	3965	-1032	0501
C(11)	4699	-0560	0478	4706	-0562	0477
C(12)	4247	-0090	0741	4252	-0091	0740
C(13)	0775	0797	1123	0771	0797	1122
C(14)	0002	0484	0756	-0004	0484	0755
C(15)	-1205	0690	0536	-1214	0690	0535
C(16)	-1626	1214	0680	-1637	1215	0678
C(17)	-0865	1522	1048	-0874	1524	1047
C(18)	0341	1316	1270	0335	1317	1270
C(19)	3745	1094	1345	3748	1095	1344
C(20)	4764	1160	1740	4770	1161	1740
C(21)	5683	1588	1699	5691	1590	1699
C(22)	5567	1946	1253	5574	1949	1253
C(23)	4582	1883	0849	4588	1885	0848
C(24)	3657	1455	0893	3660	1457	0892
C(25)	-1816	2783	2560	-1827	2788	2556
C(26)	-0366	3352	3127	-0372	3358	3123
C(27)	-0716	1841	3004	-0719	1840	3003
C(28)	2873	2267	4525	2881	2264	4528
C(29)	2705	1311	4380	2716	1303	4384
C(30)	-0771	2812	2989	-0778	2817	2986
C(31)	-0213	2349	3222	-0216	2350	3220
C(32)	0782	2319	3634	0782	2319	3634
C(33)	2255	1830	4221	2262	1825	4224
$\sigma$	7	3	2			
F(34)	1228	2805	3829	1228	2807	3829
$\sigma$	4	1	2			
N(35)	-2646	2772	2231	-2660	2778	2226
N(36)	-0104	3796	3213	-0111	3805	3209
N(37)	-1157	1455	2816	-1161	1452	2815
N(38)	3421	2595	4780	3430	2593	4783
N(39)	3087	0892	4525	3100	0882	4530
N(40)	1298	1869	3823	1302	1865	3825
$\sigma$	7	2	2			
*As(41)	24400	05314	14186	24400	05314	14186
$\sigma$	6	2	2			

\* Values times  $10^5$ .

Table 2. *Final thermal parameters and their estimated standard deviations for the heavy atoms*

All values have been multiplied by  $10^5$ .  
The temperature factor for an atom is of the form  $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$

Atom	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
C(1)	01033	00162	00116	00118	-00028	00031
C(2)	01455	00179	00119	00253	00069	00022
C(3)	01732	00237	00115	00237	00081	-00012
C(4)	01417	00230	00129	00075	-00015	00042
C(5)	01597	00236	00151	00354	00108	00097
C(6)	01665	00217	00127	00262	00099	00070
C(7)	01271	00147	00097	-00069	-00013	-00007
C(8)	02012	00158	00162	-00177	00110	-00001
C(9)	02581	00147	00194	-00013	-00089	00043
C(10)	02403	00175	00149	00381	-00231	-00027
C(11)	01771	00257	00170	00430	00089	00017
C(12)	01239	00204	00136	00159	00062	-00006
C(13)	00983	00192	00113	-00041	00076	00059
C(14)	01056	00250	00136	00106	-00072	-00035
C(15)	01209	00374	00158	00087	-00144	-00090
C(16)	01389	00347	00185	00338	-00224	00012
C(17)	01359	00229	00280	00294	-00145	00041
C(18)	01009	00168	00221	-00023	-00135	00051
C(19)	00841	00161	00139	-00008	00074	-00019
C(20)	01045	00196	00198	-00044	-00031	-00066
C(21)	01065	00236	00275	-00200	00028	-00067
C(22)	01259	00190	00316	-00296	00340	-00028
C(23)	01483	00211	00236	-00105	00192	00068
C(24)	01359	00180	00154	-00118	00082	00062
C(25)	01106	00186	00200	-00129	00020	00032
C(26)	01310	00201	00183	-00037	-00226	-00024
C(27)	01234	00171	00176	00006	00094	-00011
C(28)	01805	00255	00203	-00128	-00319	00035
C(29)	01669	00210	00170	-00059	-00188	00071
C(30)	00995	00187	00157	-00081	00007	-00032
C(31)	00978	00192	00139	-00109	00050	-00026
C(32)	01261	00172	00149	-00159	-00054	-00040
C(33)	01315	00216	00163	-00145	-00175	00008
$\sigma$ (C)	00086	00073	00011	00055	00051	00020
F(34)	01989	00170	00272	-00184	-00622	-00031
$\sigma$ (F)	00062	00007	00008	00036	00038	00012
N(35)	01454	00291	00279	-00161	-00472	00038
N(36)	02198	00213	00318	-00169	-00755	-00013
N(37)	01751	00222	00302	-00168	-00147	-00118
N(38)	03671	00287	00418	-00327	-01504	00028
N(39)	02144	00293	00298	00041	-00575	00025
N(40)	01235	00209	00151	-00026	00035	00003
$\sigma$ (N)	00099	00013	00015	00060	00062	00022
As(41)	00975	00146	00120	-00019	00035	00023
$\sigma$ (As)	00006	00001	00001	00005	00004	00002

parameter. The final value of  $R$  was 5.7% for the 2835 observed reflections. The final positional parameters for the heavy atoms are given in Table 1 and their final thermal parameters in Table 2. The standard deviations quoted are the average values obtained from the inverse of the appropriate block matrix.

A final difference synthesis was computed and a new set of hydrogen positions was obtained. The hydrogen parameters are given in Table 3 and do not differ significantly from the earlier set used in the least-squares refinement. The final set of structure factors calculated using the parameters given in Tables 1, 2 and 3 are listed in Table 4.

Table 3. Probable hydrogen positions

The hydrogen atom is given followed by the atom to which it is bonded, the position parameters times  $10^3$ , the bond distance, and the peak height on the second difference map

Atom	$x$	$y$	$z$	Distance (Å)	Peak height (e.Å <sup>-3</sup> )
H(2)–C(2)	119	104	241	1.00	0.5
H(3)–C(3)	081	083	340	1.18	0.4
H(4)–C(4)	208	005	373	1.00	0.4
H(5)–C(5)	335	–059	315	1.10	0.3
H(6)–C(6)	350	–035	207	1.11	0.5
H(8)–C(8)	109	–046	124	1.25	0.4
H(9)–C(9)	245	–133	083	0.78	0.4
H(10)–C(10)	440	–142	030	1.16	0.5
H(11)–C(11)	561	–060	027	1.03	0.4
H(12)–C(12)	478	026	072	1.01	0.4
H(14)–C(14)	040	011	073	0.99	0.5
H(15)–C(15)	–175	054	020	1.03	0.3
H(16)–C(16)	–245	135	046	1.01	0.4
H(17)–C(17)	–107	190	115	0.99	0.3
H(18)–C(18)	087	153	144	0.84	0.4
H(20)–C(20)	480	086	207	1.09	0.3
H(21)–C(21)	649	163	202	1.10	0.4
H(22)–C(22)	620	232	131	1.10	0.3
H(23)–C(23)	424	214	043	1.24	0.4
H(24)–C(24)	287	143	064	0.98	0.4

The scattering factors used in all the calculations were hydrogen and carbon-graphite from McWeeny (1951), nitrogen from Hoerni & Ibers (1954), and arsenic (uncorrected for dispersion) from *International Tables for X-ray Crystallography* (1962).

## Results and discussion

### The tetraphenylarsonium cation (TPAS<sup>+</sup>)

An analysis of the rigid-body translational and librational motions of TPAS<sup>+</sup> was carried out by the method of Cruickshank (1956, 1961). The arsenic atom was assumed to be the center of mass. The results of the rigid-body analysis are given in Table 5. The r.m.s. difference between the observed and calculated  $U_{ij}$  is 0.0082 Å<sup>2</sup>, the poor agreement probably due to an oscillation of the phenyl groups around the As–C bond. The use of the rigid-body approximation for TPAS<sup>+</sup>, however, is questionable. Therefore, the treatment of each phenyl group and the arsenic atom as a separate rigid-body with the arsenic atom as the origin was also

tried. In this case the four sets of  $T-\omega$  values were not interpretable in terms of the geometry of the phenyl groups. Consequently, although the rigid-body approximation is a crude model, the position parameters for TPAS<sup>+</sup> were corrected in this manner. The libration-corrected positional parameters are given in Table 1. Using these parameters the intramolecular distances and angles in TPAS<sup>+</sup> were calculated and are illustrated in Fig. 1, with the nonbonded distances tabulated in Table 6.

The least-squares planes for the four phenyl groups were calculated and are summarized in Table 7. There is no significant nonplanarity in any of the four phenyl groups. The average value of the 24 carbon-carbon bond distances in the four groups is 1.389 Å, in good agreement with the distances in benzene of 1.397 Å reported by Stoicheff (1954) and 1.393 Å found by Cox,

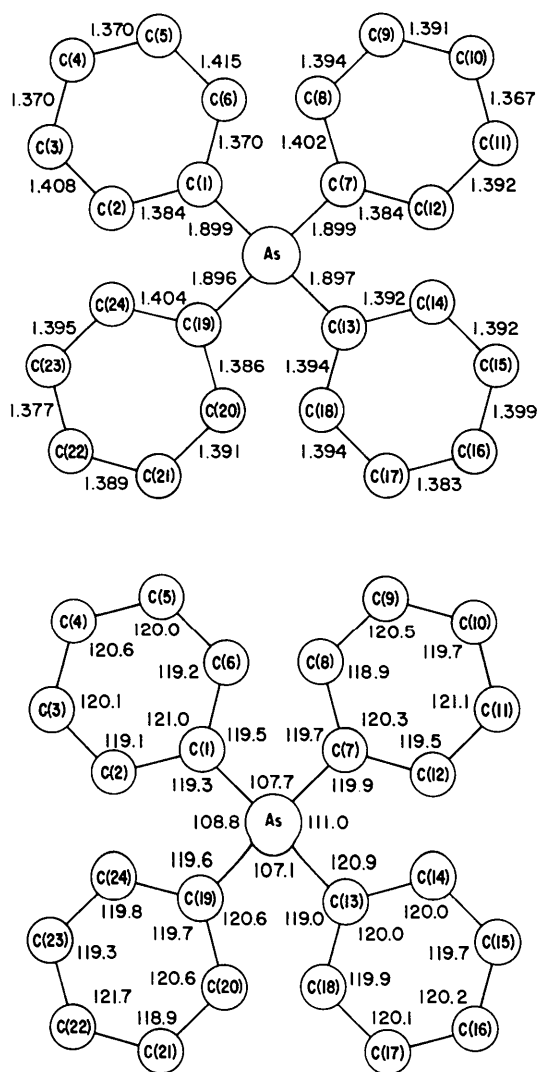


Fig. 1. The atomic numbering, distances and angles in the tetraphenylarsonium cation. The angles C(1)–As–C(13) of 112.0° and C(7)–As–C(19) of 110.2° are not shown.

Table 4. Observed and calculated structure factors

The values of h and k are given above each group with the values of I, IOF (observed) and 10F (calculated) given in that order. A negative F indicates an unobserved reflection. The reflections marked with an asterisk were not included in the least-squares and R-factor calculations.

Table with multiple columns containing numerical data for structure factors, including observed (I), observed of first order (IOF), and calculated (10F) values for various reflections. The table is organized into groups by h and k values.

Table 4 (cont.)

Table with multiple columns containing numerical data, likely representing crystallographic parameters or atomic coordinates. The table is organized into several sections, each starting with a header like 'Mn Atk=0' or 'Mn Atk=1'. Each section contains a list of rows with various numerical values and some text labels.

Table 5. Rigid-body thermal parameters for the tetraphenylarsonium cation (TPAS<sup>+</sup>)
$$T = \begin{pmatrix} 485 & 14 & -10 \\ & 465 & 6 \\ & & 346 \end{pmatrix} \times 10^{-4} \text{ \AA}^2$$

$$\omega = \begin{pmatrix} 53 & -24 & -15 \\ & 61 & -9 \\ & & 94 \end{pmatrix} \times 10^{-1} \text{ deg}^2$$

$$\sigma(T) = \begin{pmatrix} 22 & 18 & 19 \\ & 22 & 18 \\ & & 21 \end{pmatrix} \times 10^{-4} \text{ \AA}^2$$

$$\sigma(\omega) = \begin{pmatrix} 7 & 5 & 6 \\ & 8 & 6 \\ & & 8 \end{pmatrix} \times 10^{-1} \text{ deg}^2$$

Principal axes	Direction cosines ( $\times 10^4$ ) relative to			Eigenvalue	Direction cosines ( $\times 10^4$ ) relative to		
	<i>a</i>	<i>b</i>	<i>c</i>		<i>a</i>	<i>b</i>	<i>c</i>
Eigenvalue				$\omega$ 9.9 deg <sup>2</sup>			
T 0.0493 \AA <sup>2</sup>	8923	4495	-0415	8.2	2957	0345	-9546
0.0458	4450	-8913	-0871	2.8	5981	-7860	1568
0.0345	0761	-0592	9953		7449	6173	2531

Atom*	<i>U</i> <sub>11</sub>	<i>U</i> <sub>22</sub>	<i>U</i> <sub>33</sub>	<i>U</i> <sub>12</sub>	<i>U</i> <sub>13</sub>	<i>U</i> <sub>23</sub>
C(1)	501(-48)	497(-21)	336(-15)	72(30)	-17(-19)	46(25)
C(2)	706(76)	549(-33)	345(-12)	154(76)	41(16)	33(25)
C(3)	841(46)	727(4)	333(-26)	145(-3)	48(-6)	-18(-47)
C(4)	688(-185)	705(-85)	374(5)	46(-138)	-9(-61)	63(-28)
C(5)	775(-26)	724(21)	438(42)	216(52)	64(31)	145(32)
C(6)	808(172)	665(99)	368(-12)	160(71)	59(47)	104(43)
C(7)	617(39)	451(-33)	281(-97)	-42(-83)	-8(-10)	-10(-2)
C(8)	977(253)	484(5)	470(-5)	-108(-102)	65(63)	-2(34)
C(9)	1253(266)	451(-49)	562(-12)	-8(-45)	-53(-79)	64(144)
C(10)	1166(123)	537(-40)	432(-111)	232(48)	-137(-209)	-40(34)
C(11)	860(41)	788(146)	493(26)	262(54)	53(-34)	25(40)
C(12)	602(-13)	626(54)	394(-8)	97(-11)	37(-6)	-9(-17)
C(13)	477(-27)	589(29)	328(-59)	-25(-73)	45(68)	88(71)
C(14)	513(-21)	766(63)	394(-63)	65(51)	-43(40)	-52(-41)
C(15)	587(19)	1147(175)	458(-107)	53(-18)	-85(54)	-134(-139)
C(16)	674(66)	1064(29)	536(-52)	206(-18)	-133(-45)	18(-58)
C(17)	660(1)	702(-102)	812(291)	179(-69)	-86(-87)	61(-23)
C(18)	490(-101)	515(-80)	640(214)	-14(-144)	-80(-90)	76(35)
C(19)	408(-131)	494(-16)	403(-31)	-5(30)	44(44)	-28(-36)
C(20)	507(-64)	601(-38)	574(40)	-27(66)	-18(31)	-98(-70)
C(21)	517(-180)	724(-57)	797(30)	-122(111)	17(70)	-100(-51)
C(22)	611(-217)	582(-142)	916(40)	-181(100)	202(152)	-42(-56)
C(23)	720(-92)	646(52)	684(-28)	-64(79)	114(5)	101(20)
C(24)	660(12)	552(34)	446(-51)	-72(-38)	49(-7)	92(37)
As	473(-12)	448(-17)	348(2)	-12(-26)	21(31)	34(28)

\* The experimental values of *U*<sub>*ij*</sub> are given followed by *U*<sub>*ij*</sub>(obs) - *U*<sub>*ij*</sub>(calc) in parentheses.Table 6. Nonbonded distances in the tetraphenylarsonium (TPAS<sup>+</sup>) cation

Atoms	Distance
C(1)-C(7)	3.065 \AA
C(1)-C(19)	3.085
C(13)-C(19)	3.052
C(1)-C(13)	3.147
C(7)-C(13)	3.127
C(7)-C(19)	3.111
C(1)-C(20)	3.332
C(7)-C(6)	3.240
C(7)-C(14)	3.359
C(13)-C(24)	3.307
C(19)-C(12)	3.293
C(19)-C(18)	3.391
C(18)-C(24)	3.395
C(1)-H(20)	2.78
C(7)-H(6)	2.60
C(7)-H(14)	2.72
C(13)-H(24)	2.82
C(19)-H(12)	2.74
C(8)-H(14)	2.60

Table 7. Least-squares planes for the phenyl groups in the tetraphenylarsonium ion

Atom	Plane and deviations ( $\times 10^3$ ) (\AA)			
	I ( <i>i</i> =0)	II ( <i>i</i> =6)	III ( <i>i</i> =12)	IV ( <i>i</i> =18)
C(1+ <i>i</i> )	-002	001	003	-008
C(2+ <i>i</i> )	002	-002	001	006
C(3+ <i>i</i> )	-003	003	-006	002
C(4+ <i>i</i> )	003	-003	007	-009
C(5+ <i>i</i> )	-003	002	-003	006
C(6+ <i>i</i> )	003	000	-002	002
As(41)*	093	-087	044	-087

\* The arsenic atom was not included in the calculation of the plane.

Plane	Direction cosines ( $\times 10^4$ ) with respect to			Distance to origin
	<i>a</i>	<i>b</i>	<i>c</i>	
I	8456	5130	1475	3.098 \AA
II	-4849	2651	-8334	-3.552
III	5112	3790	-7714	-0.945
IV	6148	-5795	-5350	-1.018

Table 8. *Rigid-body thermal parameters for the anion (RD<sup>-</sup>)*

$T = \begin{pmatrix} 516 & -72 & 51 \\ & 580 & -40 \\ & & 375 \end{pmatrix} \times 10^{-4} \text{ \AA}^2$		$\omega = \begin{pmatrix} 155 & -88 & 119 \\ & 199 & -110 \\ & & 171 \end{pmatrix} \times 10^{-1} \text{ deg}^2$					
$\sigma(T) = \begin{pmatrix} 49 & 41 & 47 \\ & 45 & 41 \\ & & 49 \end{pmatrix} \times 10^{-4} \text{ \AA}^2$		$\sigma(\omega) = \begin{pmatrix} 28 & 19 & 23 \\ & 25 & 19 \\ & & 28 \end{pmatrix} \times 10^{-1} \text{ deg}^2$					
Principal axes	Direction cosines ( $\times 10^4$ ) relative to			Principal axes	Direction cosines ( $\times 10^4$ ) relative to		
Eigenvalue	<i>a</i>	<i>b</i>	<i>c</i>	Eigenvalue	<i>a</i>	<i>b</i>	<i>c</i>
T 0.0641 $\text{\AA}^2$	5532	-8019	2258	$\omega$ 38.7 deg <sup>2</sup>	5320	-5991	5984
0.0473	7886	5914	1684	9.5	5274	7873	3193
0.0358	2686	-0849	-9595	4.2	6624	-1457	-7349

Atom	<i>U</i> <sub>11</sub>	<i>U</i> <sub>22</sub>	<i>U</i> <sub>33</sub>	<i>U</i> <sub>12</sub>	<i>U</i> <sub>13</sub>	<i>U</i> <sub>23</sub>
C(25)	537(-207)	570(-163)	580(-54)	-79(-12)	12(186)	48(19)
C(26)	636(-107)	616(10)	520(-76)	-23(21)	-134(-43)	-36(-35)
C(27)	599(-197)	524(-102)	510(-114)	4(110)	56(251)	-16(30)
C(28)	876(52)	782(64)	588(-69)	-78(18)	-189(55)	52(62)
C(29)	810(68)	644(-46)	493(-152)	-36(-20)	-112(2)	106(66)
C(30)	483(-111)	573(-56)	455(-13)	-49(8)	4(18)	-48(-39)
C(31)	475(-76)	589(-9)	403(-9)	-66(9)	30(14)	-39(-4)
C(32)	612(94)	527(-54)	432(55)	-97(-24)	-32(-81)	-60(-20)
C(33)	638(22)	662(13)	472(-23)	-89(-30)	-104(-64)	12(13)
F(34)	966(295)	521(-70)	788(284)	-112(-30)	-369(-298)	-46(3)
N(35)	706(-244)	892(39)	809(-51)	-98(-14)	-280(111)	57(-13)
N(36)	1067(18)	653(57)	922(29)	-103(-56)	-448(-150)	-19(-28)
N(37)	850(-341)	681(18)	875(-91)	-102(45)	-87(434)	-176(-112)
N(38)	178(586)	880(84)	1211(256)	-200(-62)	-892(-321)	42(70)
N(39)	1041(106)	898(165)	864(11)	25(-7)	-341(-111)	37(-46)
N(40)	600(43)	641(49)	438(18)	-16(46)	21(-4)	4(34)

Table 9. *Least-squares planes for the anion*

Plane and deviations in $\text{\AA}$ ( $\times 10^3$ ) from the plane.					
Atom	I	II	III	IV	
C(25)	-18	-5			
N(35)	-44	1			
C(26)	55	2			
N(36)	103	-3			
C(30)	-8	11		-2	
C(31)	-18	-5		3	
C(27)	-14			0	
N(37)	-15			1	
C(32)	-17			-4	
F(34)	-24			3	
N(40)	16		6		
C(33)	14		-10		
C(28)	-55		4		
N(38)	-95		0		
C(29)	52		-9		
N(39)	66		8		

Plane	Direction cosines ( $\times 10^4$ ) with respect to			Distance to origin	Description of plane
	<i>a</i>	<i>b</i>	<i>c</i>		
I	-7122	-0078	7019	5.494 $\text{\AA}$	All atoms in anion
II	-7004	0262	7133	5.799	Dicyano group at one end
III	-7226	-0453	6898	5.175	Dicyano group at other end
IV	-7152	-0058	6989	5.498	Middle cyano group and F(34)



Cruickshank & Smith (1958). The standard deviation calculated on the basis of the 24 observed C–C distances is 0.012 Å. The value of 0.008 Å was computed from the least-squares standard deviations. The larger value is preferred since it more closely reflects the experimental deviations.

The average As–C bond distance is  $1.897 \pm 0.009$  Å, where the standard deviation is 1.5 times the value computed from the least-squares standard deviations. The values reported for the arsenic–carbon bond distance in various compounds range from 1.82 to 1.99 Å (*e.g.* see Cullen & Trotter (1963) and references therein) with large estimated standard deviations. Hedberg, Hughes & Waser (1961) reported the average As–C distance in arsenobenzene to be  $1.966 \pm 0.021$  Å. Using the criterion suggested by Cruickshank & Robertson (1953), the two bond lengths are significantly different ( $t_0 = 3.0$ ). Although the shortening of the As–C bond in TPAS<sup>+</sup> may be attributed to a formal charge effect,

precise values for other As–C bond distances are required before the presence of a formal charge effect can be ascertained.

In both the iodide salt examined by Mooney (1940) and the tetrachloroferrate salt studied by Zaslow & Rundle (1957), TPAS<sup>+</sup> is required by the space group to have  $\bar{4}$  symmetry. In the present study the  $\bar{4}$  symmetry of TPAS<sup>+</sup> is destroyed by the rotation of the phenyl groups around the As–C bond. The observed asymmetry is apparently the result of crystal packing and is not an effect of intramolecular steric repulsion.

*The 3-fluoro-1,1,4,5,5-pentacyano-2-azapentadienide anion (RD<sup>-</sup>)*

An analysis of the rigid-body translational and libration motion for RD<sup>-</sup> was carried out by the method given by Cruickshank (1956, 1961). The center of mass was taken as the unweighted average of the positional parameters of the atoms in the anion. As expected, the

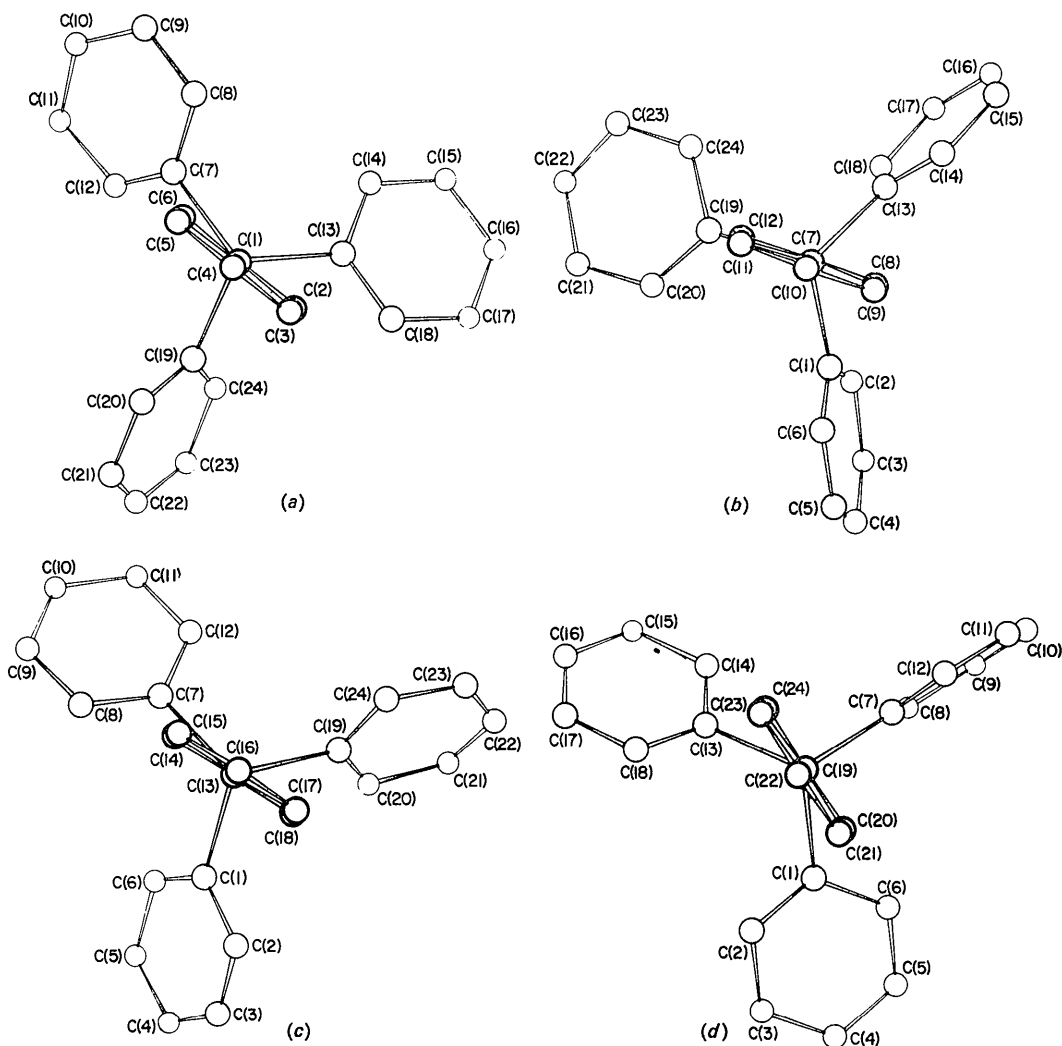


Fig. 2. Views down the four arsenic–carbon bonds in the cation: (a) down As–C(1); (b) down As–C(7); (c) down As–C(13) (d) down As–C(19).

center of mass at 0.0616, 0.2316, 0.3555 is close to C(32). The results of the rigid-body analysis are given in Table 8. The libration-corrected positional parameters are given in Table 1. The intramolecular distances and angles in the anion were calculated using the corrected parameters and are illustrated in Fig. 3.

The validity of using the rigid-body approximation for the anion is also questionable. The r.m.s. deviation between the observed and calculated  $U$ 's is 0.0131. This large value is probably due to wagging of the cyano groups. A similar effect was observed by Bekoe & Trueblood (1960) in tetracyanoethylene and by Long, Sparks & Trueblood (1965) in 7,7,8,8-tetracyanoquinodimethane. The average correction for the five  $C\equiv N$  bonds was 0.0045 Å, which is probably too small by a factor of two. However, since the standard deviation of a bond length is 0.012 Å, there is little merit in attempting to obtain a more accurate correction.

The five  $C\equiv N$  bond lengths, after the libration correction, average  $1.146 \pm 0.012$  Å, in agreement with other cyanocarbons [see Bekoe & Trueblood (1960) and Long, Sparks & Trueblood (1965)]. The average  $C-C\equiv N$  angle is  $176.8 \pm 1.1^\circ$ , significantly different from a linear bond angle of  $180.0^\circ$ . The nonlinearity is due to steric repulsion involving the fluorine atom and the cyano groups. The large angles of  $C(31)-C(30)-C(26)$  and  $N(40)-C(33)-C(28)$  are due to a repulsion between F(34) and C(26) and C(28). The resulting distortion equalizes the two fluorine intramolecular contacts:  $F(34)-C(26)$  is 2.672 Å and  $F(34)-C(28)$  is 2.682 Å.

The  $C-C$  (cyano) bond distances average  $1.435 \pm 0.012$  Å and are not significantly different from com-

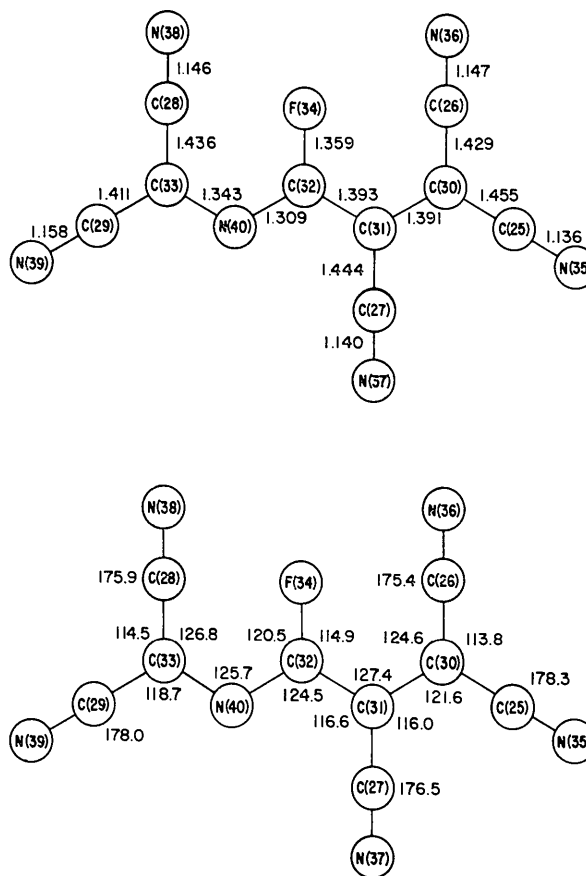


Fig. 3. The atomic numbering distances and angles in the 3-fluoro-1,1,4,5,5-pentacyano-2-azapentadienide anion.

Table 10. Intermolecular distances

The distance given is from atom  $I$  in the molecule specified by the parameters in Tables 1 and 2 to the atom  $J$  in the molecule specified by the letters  $A-G$ . Molecules  $A-G$  are located as follows:

$A$	$1+x, y, z$	$E$	$1-x, \frac{1}{2}-y, \frac{1}{2}+z$
$B$	$-x, -y, -z$	$F$	$\frac{1}{2}+x, \frac{1}{2}-y, z$
$C$	$1-x, -y, -z$	$G$	$x, \frac{1}{2}+y, \frac{1}{2}-z$
$D$	$\frac{1}{2}+x, -y, \frac{1}{2}-z$		

$I$	$J$	Molecule	Distance (Å)	$I$	$J$	Molecule	Distance (Å)
H(21)	N(35)	$A$	2.98	C(10)	N(40)	$D$	3.47
H(22)	N(35)	$A$	2.70	C(11)	C(29)	$D$	3.48
H(15)	C(9)	$B$	2.83	C(11)	N(39)	$D$	3.41
H(15)	C(10)	$B$	2.99	N(38)	C(23)	$E$	3.45
H(16)	C(10)	$B$	2.84	N(38)	H(23)	$E$	2.83
H(12)	C(11)	$C$	2.99	H(18)	N(35)	$F$	2.92
H(11)	C(12)	$C$	2.95	H(20)	N(36)	$F$	2.85
H(11)	H(12)	$C$	2.52	C(32)	C(25)	$F$	3.49
C(12)	C(11)	$C$	3.48	C(31)	N(35)	$F$	3.47
H(5)	C(13)	$D$	2.99	F(34)	H(9)	$G$	2.56
H(5)	C(18)	$D$	2.99	N(36)	H(8)	$G$	2.54
H(6)	N(37)	$D$	2.75	N(38)	H(10)	$G$	2.61
H(11)	C(29)	$D$	2.81	N(36)	C(8)	$G$	3.28
H(11)	N(39)	$D$	2.58	F(34)	C(9)	$G$	3.32
C(11)	H(3)	$D$	2.97	N(38)	C(10)	$G$	3.49
C(6)	N(37)	$D$	3.44				

parable bonds in tetracyanoethylene [ $1.449 \pm 0.009 \text{ \AA}$ , Bekoe & Trueblood (1960)], in 7,7,8,8-tetracyanoquinodimethane [ $1.440 \pm 0.004 \text{ \AA}$ , Long, Sparks & Trueblood (1965)], in pyridinium dicyanomethylide [ $1.41 \pm 0.01 \text{ \AA}$ , Bugg & Sass (1965)], and in ammonium tricyanomethide [ $1.40 \pm 0.01 \text{ \AA}$ , Desiderato & Sass (1965)]. The length of this C–C bond is discussed in some detail by Bekoe & Trueblood (1960). The small C–C–C angles of  $113.8$  and  $114.5^\circ$  in the dicyano groups are a consequence of intermolecular steric repulsion between F(34) and the atoms C(26) and C(28).

The average C–N bond distance in the chain is  $1.326 \pm 0.012 \text{ \AA}$  which is equivalent to the C–N bonds in an aromatic system (Sutton, 1958). The C–C bonds in the chain average  $1.392 \pm 0.012 \text{ \AA}$  and are close to the value in benzene (Sutton, 1958). These facts suggest that the bonds in the chain have about 50% double bond-character, in agreement with the resonance stabilized character of the anion.

The C–F distance of  $1.359 \pm 0.012 \text{ \AA}$  is slightly shorter than the average value of  $1.37 \text{ \AA}$  found in compounds

where there is only one fluorine bonded to a carbon atom (Sutton, 1958). When two or three fluorine atoms are bonded to the carbon atom the average distance is  $1.33 \text{ \AA}$  (Sutton, 1958). Karle, Karle, Owen & Hoard (1965) observed a similar effect in the dimer of hexafluorobutadiene where they found  $1.367$  and  $1.327 \text{ \AA}$  for the C–F distances in the two cases.

A number of least-squares planes were calculated for the anion and are tabulated in Table 9. As expected, the various cyano groups are planar. However, the entire anion, which is a highly resonance-stabilized system, is definitely nonplanar. Thus,  $\text{RD}^-$  provides an example of the fact that exact planarity is not a prerequisite to resonance stabilization.

#### Intermolecular distances

All the intermolecular distances less than  $3.5 \text{ \AA}$  were calculated. Distances involving a hydrogen atom which were less than  $3.0 \text{ \AA}$  are tabulated in Table 10, together with the heavy atom distances less than  $3.5 \text{ \AA}$ . As expected, the majority of the intermolecular contacts in-

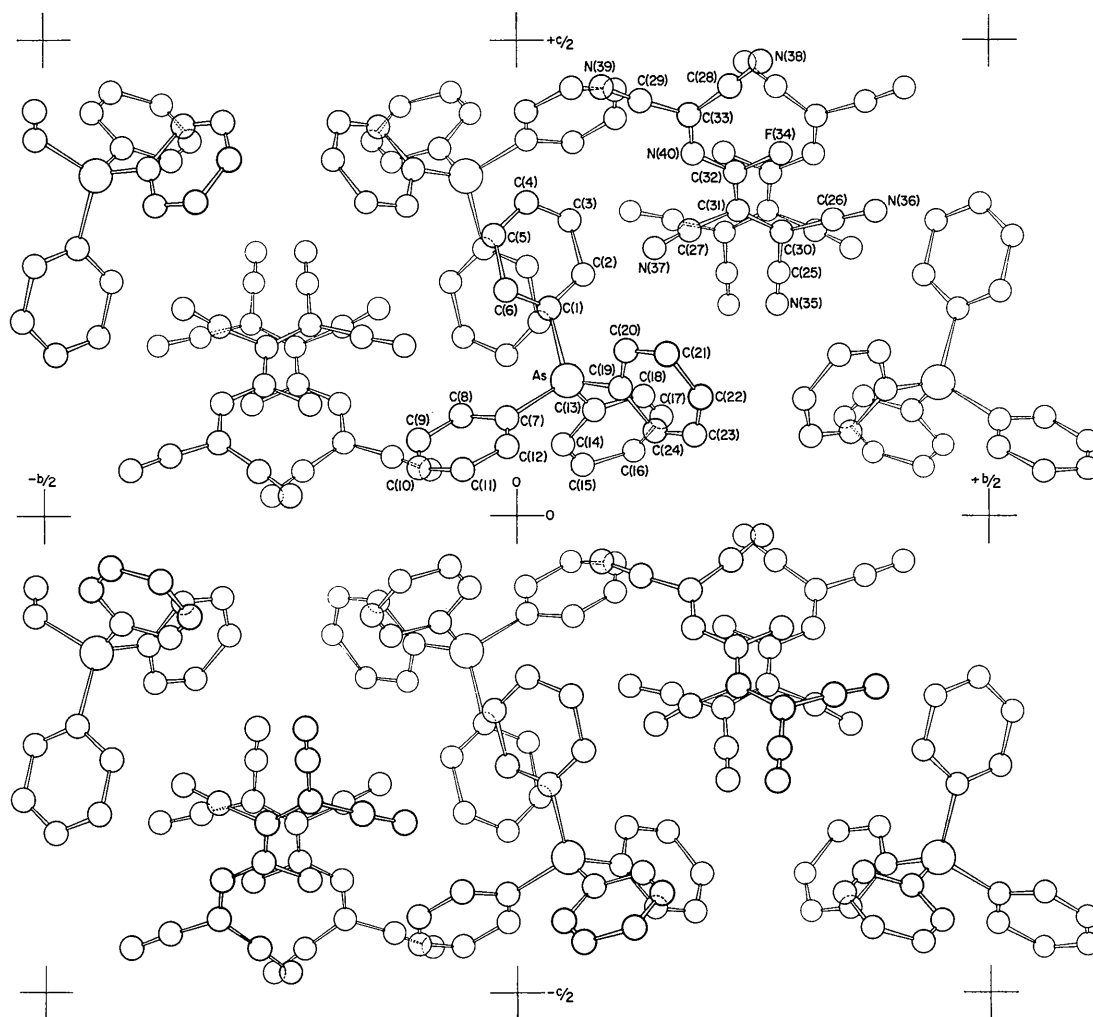


Fig. 4. A projection of the structure on the (100) plane illustrating the molecular packing.

volve the hydrogen atoms of the TPAS<sup>+</sup>. The three short N...H contacts of 2.54, 2.58 and 2.61 Å are close to the value of 2.6–2.7 Å expected for van der Waals contact. The F...H distance of 2.56 Å is the sum of the van der Waals radii. The shortest contacts between the heavier atoms are F(34)...C(9) (3.32 Å) and N(36)...C(8) (3.28 Å), both of which are van der Waals contacts.

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## Étude par Diffraction de Rayons X de Complexes d'Halogénures Alcalins et de Molécules Organiques. IV. Structure de NaBr.2CH<sub>3</sub>CONH<sub>2</sub>\*

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(Reçu le 29 juin 1965)

The structure of NaBr.2CH<sub>3</sub>CONH<sub>2</sub> has been determined by a three-dimensional X-ray analysis. Space group *P2<sub>1</sub>/c*, *Z*=4; *a*=9.11, *b*=6.49, *c*=17.72 Å, *β*=115.4°. Each sodium atom is octahedrally coordinated (2Br and 4O) and the structure consists of infinite chains of octahedra having one face in common. There are N–H...Br bonds between the chains. Distances Na–Br: 2.99 and 3.12. Mean distances: Na–O=2.35, N(H)–Br=3.50, C–O=1.22, C–N=1.31, C–C=1.50.

Le complexe NaBr.2CH<sub>3</sub>CONH<sub>2</sub> a été préparé par la méthode décrite par Titherley (1901): on dissout le bromure de sodium et l'acétamide dans l'éthanol anhydre et on refroidit la solution dans un exsiccateur au chlorure de calcium sous vide. Les cristaux se présentent sous forme d'aiguilles incolores très hygroscopiques (point de fusion: 145°C). Pour l'étude aux rayons X, nous les avons enfermés dans des tubes en verre de Lindemann.

#### Paramètres de la maille

Les dimensions de la maille-unité ont été mesurées sur des diagrammes de rotation (autour des axes *a* et *b*) et de Weissenberg. Le spectre d'un fil d'argent a servi

d'étalon (*a*=4,086 Å). Le groupe spatial est *P2<sub>1</sub>/c*, correspondant aux absences systématiques *h0l* pour *l*≠2*n* et *0k0* pour *k*≠2*n*. Les paramètres valent:

$$\begin{aligned} a &= 9,11 \pm 0,01 \text{ \AA} \\ b &= 6,49 \pm 0,01 \\ c &= 17,72 \pm 0,03 \\ \beta &= 115,4^\circ \pm 0,2^\circ \end{aligned}$$

Les résultats publiés précédemment (Gobillon & Piret, 1962) étaient basés sur une valeur légèrement erronée pour le paramètre *a* de l'argent. Il y a quatre 'molécules' de complexe par maille. La densité calculée, vérifiée expérimentalement, vaut 1,55.

#### Intensité des rayons diffractés

Les spectres de diffraction ont été obtenus à l'aide d'une caméra de Weissenberg, munie d'un dispositif intégrateur. La radiation incidente était Cu K $\alpha$  ( $\lambda$ =1,5418 Å). Les réflexions *hkl* ont été enregistrées par

\* Partie III: Structure de NaI.3CH<sub>3</sub>OH (Piret & Mesureur, 1965).

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