

Tableau 5. Distances interatomiques (Å) et angles (°) caractérisant les liaisons hydrogène

Code de symétrie

(i)	$1+x, -1+y, z$	(iv)	$1-x, 1-y, 1-z$
(ii)	$1+x, y, z$	(v)	$-x, 1-y, -z$
(iii)	$1-x, -y, -z$	(vi)	$-1-x, 1-y, -z$

O(1)–H(O1)···O(2 ^{iv})	2,653 (11)	H(O1)···O(2 ^{iv})	1,712
N–H(N)···I(1 ⁱ)	3,738 (4)	H(N)···I(1 ⁱ)	2,947
N–H'(N)···I(1 ⁱⁱⁱ)	3,624 (4)	H'(N)···I(1 ⁱⁱⁱ)	2,645
N–H(N)···I(2 ⁱⁱⁱ)	3,723 (5)	H(N)···I(2 ⁱⁱⁱ)	3,068
N–H''(N)···I(3 ⁱ)	3,688 (6)	H''(N)···I(3 ⁱ)	2,777
O(1)–H(O1)–O(2 ^{iv})	165	N–H(N)–I(2 ⁱⁱⁱ)	124
N–H(N)–I(1 ⁱ)	136	N–H''(N)–I(3 ⁱ)	152
N–H'(N)–I(1 ⁱⁱⁱ)	166		

Distances intermoléculaires I···I inférieures à 4,300 Å

I(1)···I(1 ⁱⁱⁱ)	4,276 (2)	I(1)···I(2 ^v)	4,178 (2)
I(1)···I(2 ⁱⁱ)	4,265 (2)	I(2)···I(2 ^{vi})	3,961 (2)

Liaisons hydrogène

La cohésion de l'édifice cristallin est assurée par des interactions de type ionique et des liaisons de faible énergie. Le Tableau 5 indique les distances interatomiques et les angles caractérisant l'existence de liaisons hydrogène intermoléculaires ainsi que les contacts de van der Waals I···I inférieurs à 4,30 Å.

Chaque atome d'iode est accepteur d'un proton du groupement amine protoné NH₃⁺, les distances les plus courtes se trouvant entre N–H'(N)···I(1) (3,624 Å) et N–H''(N)···I(3) (3,688 Å). L'atome d'hydrogène du groupement OH participe à des liaisons hydrogène entre molécules organiques.

Dans ce complexe le cation organique n'a aucune influence sur la régularité des octaèdres TeI₆²⁻ et comme dans les composés analogues la stabilité de l'édifice cristallin est assurée par un réseau de liaisons hydrogène et des contacts de van der Waals.

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The Crystal and Molecular Structure of the Tetrafluoroborate, Hexafluoroantimonate and Hexafluorophosphate Salts of the Bicyclo[5.4.1]dodecapentaenylium Ion

BY RICCARDO DESTRO AND MASSIMO SIMONETTA

Istituto Chimica Fisica Università e Centro CNR, Via Golgi 19, 20133 Milano, Italy

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Abstract

The molecular and crystal structures of three salts of the bicyclo[5.4.1]dodecapentaenylium cation, C₁₂H₁₁⁺, namely the tetrafluoroborate, BF₄⁻, the hexafluoro-

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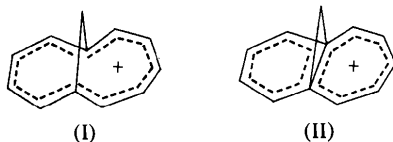
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unequivocally to the classification of the cation as a perturbed [11]annulenium system.

Introduction

The synthesis of stable salts (tetrafluoroborate and perchlorate) of the bicyclo[5.4.1]dodecapentaenylum cation (hereinafter BDP) was first reported by Grimme, Hoffmann & Vogel (1965). The structure of this ten π -electron system has been investigated on the basis of its electronic spectra by Grimme, Heilbronner, Hohlneicher, Vogel & Weber (1968), and by interpretation of the ^{13}C NMR chemical shifts by Kemp-Jones, Jones, Sakai, Beeman & Masamune (1973). The former authors have regarded the ion as a perturbed [11]-annulenium system (I), whereas the latter have suggested a benzohomotropenylium structure (II), where a significant electron overlap between C(1) and C(6) (*cf.* Fig. 2) is present. Using a perturbational molecular orbital approach, Haddon (1975) has considered the effect of a 1–6 transannular interaction on the annulene system, and evaluated the implied energy change. This treatment, however, cannot predict to what extent the molecule avails itself of the resulting extra stabilization. In the light of our preliminary account of the X-ray analysis of BDP hexafluorophosphate (Destro, Pilati & Simonetta, 1976), Haddon (1977) later reinvestigated the ion, focusing in particular on the experimental bond lengths. His study has suggested that the electronic structure of BDP is determined by a complex interplay of perturbations. We report here the complete and up-to-date results of the X-ray determination of the BDP geometry, a part of the systematic investigation of the conformation of bridged annulenes, which have long been a subject of interest in our laboratory (see, for example, Destro & Simonetta, 1977; Simonetta, 1974). Our work was initiated in 1969 with the analysis of BDP tetrafluoroborate. Some years later a second derivative, the hexafluoroantimonate salt, was available and analyzed. Recently, low-temperature and high-resolution data of a third salt, BDP hexafluorophosphate, were collected and a satisfactory description of the structure could be obtained. All the samples studied were kindly supplied by Professor E. Vogel, whom we deeply thank.



The BF_4^- salt

Most of the crystals, in the form of yellow-orange needles, were twinned and showed apparent ortho-

rhombic symmetry on preliminary Weissenberg photographs. Correct monoclinic symmetry was indicated by a thin crystal 0.2 mm long (cross section 0.1×0.05 mm), which was used to obtain cell parameters (Table 1) by film measurements, essentially following the Straumanis technique. Even after prolonged exposure, only a few intensities were detectable at $\sin \theta/\lambda > 0.42 \text{ \AA}^{-1}$. This fact, together with the appearance of diffuse streaks in the vicinity of strong reflexions, was indicative of possible structural disorder. The systematic absences, $h0l$ for l odd, $0k0$ for k odd, and hkl for $h+k$ odd, are common to three space groups, $C2$, Cm and $C2/m$. (The conventional C -centered unit cell was preferred to the I -centered cell with $a = 10.941$, $b = 9.965$, $c = 11.085 \text{ \AA}$, $\beta = 104.97^\circ$.)

Intensity data were collected from multiple-film equi-inclination Weissenberg photographs (layers 0–8 around b and 0–2 around a) with Ni-filtered $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). After processing of the data (Lorentz and polarization factors applied, no correction for absorption), only 552 reflexions out of 1135 explored had net intensities above background.

Several attempts to solve the structure based on the interpretation of the Patterson synthesis (program written by Filippini & Gramaccioli, 1969) or on direct methods, using first the computer program of Long (1965) and then the early version of programs written in our laboratory (Bianchi, Destro & Gavezzotti, 1972), were unsuccessful.

A possible reason for the failure of direct methods was the paucity of measurable intensities, especially at high $\sin \theta/\lambda$ values. Therefore, our efforts were devoted to the attainment of larger crystals, with the aim of increasing the number of reliable observations. Several crystallization procedures were tried with different mixtures of solvents (glacial acetic acid, ethanol and acetonitrile) at different temperatures. The best result consisted of a single crystal of dimensions $0.30 \times 0.18 \times 0.08$ mm, which was used to collect a second set of data on a General Electric diffractometer automated by Datex, with Ni-filtered copper radiation and a propor-

Table 1. *Crystal data*

Anion	BF_4^-	SbF_6^-	PF_6^-	
T (K)	295	290	290	110
a (Å)	13.413 (5)	16.077 (3)	15.794 (4)	15.478 (4)
b	9.965 (3)	7.083 (2)	6.904 (1)	6.821 (2)
c	11.085 (5)	11.622 (2)	11.444 (3)	11.373 (3)
β ($^\circ$)	128.00 (6)	90	90	90
V (Å^3)	1167.6	1323.4	1247.9	1200.7
Space group	$C2/m$	$Pcam$	$Pcam$	$Pcam$
D_m (Mg m^{-3})	1.37	1.96	1.59	—
D_x	1.376	1.962	1.598	1.660
$\mu(\text{Cu K}\alpha)$	1.10	17.75	2.57	2.67
(mm^{-1})				
$\mu(\text{Mo K}\alpha)$	0.13	2.17	0.29	0.30
M_r	242.0	391.0	300.2	300.2
Z	4	4	4	4

tional counter. A θ - 2θ scan technique was used, the scan range including both the α_1 and α_2 peaks; background was counted for 20 s at each end of the scan, and the scanning rate was 0.5° in 2θ per min.

A single standard reflexion was checked after each 15 intensity measurements; it showed no significant drift in intensity. All the measured intensities, 1309 in number, were corrected for background and then for Lorentz and polarization factors; no correction for absorption was deemed necessary. Observational variances $\sigma^2(I)$ included, in addition to counting statistics for the scan and backgrounds, a term $(0.02 \times S)^2$, where S is the scan count.

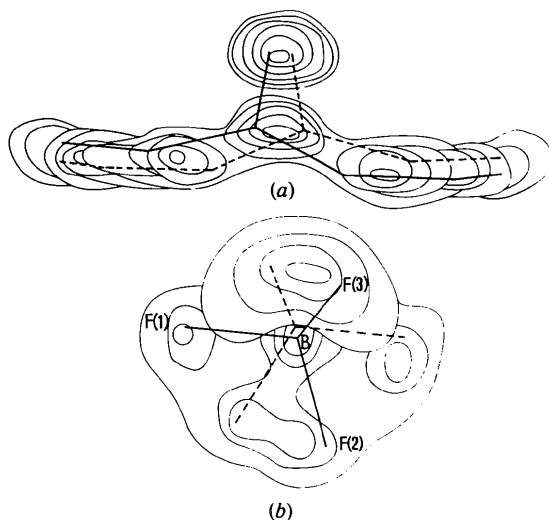


Fig. 1. Electron-density projections on (010) in (a) the cation and (b) the BF_4^- anion regions; contours are at arbitrary intervals. The superposition of the models adopted in describing the disorder is shown.

163 E 's > 1.5 were derived from the 702 reflexions with net intensities above background. The phase determination was again tried by symbolic addition. At the end of this process, which was carried out by hand, 76 phases were confidently assigned and subsequently used for the usual tangent-formula expansion. (It is worth noting that this starting set included 11 E 's, with $k > 8$, not measured on the Weissenberg photographs; moreover, eight reflexions, here with $E > 1.9$, had been assigned E values < 1.0 in the previous treatment.) A Fourier map based on the 163 phased E 's was then computed. Its main features were similar to those of the final electron-density map (Figs. 1 and 2) in the region of the cation, while only two peaks at $y=0$ were possibly related to the anion atoms. All attempts to interpret the map with ordered structures, both in centrosymmetric and non-centrosymmetric

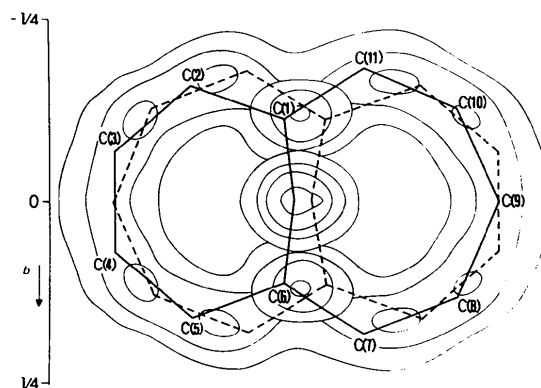


Fig. 2. BDP electron density in the BF_4^- salt. The map is viewed in the direction perpendicular to the ring plane. Besides the crystallographic mirror plane at $y=0$, a pseudo-mirror relates (statistically) one cation (full line) to the other (dotted line).

Table 2. Fractional coordinates ($\times 10^4$) for the BF_4^- salt structure

No e.s.d.'s are given, since the ions were refined as rigid groups (see text). Non-primed and primed atoms define the four distinct groups used to interpret the disordered structure.

	x	y	z		x	y	z
B	3390	0	1983	B'	3321	0	1870
F(1)	2312	0	1832	F(1')	3414	0	3153
F(2)	4395	0	3483	F(2')	4491	0	2253
F(3)	3427	1106	1308	F(3')	2689	1106	1036
C(1)	1959	-1152	5552	C(1')	1589	1152	4869
C(2)	2502	-1595	7046	C(2')	561	1595	3400
C(3)	3207	-698	8260	C(3')	-26	698	2180
C(9)	-191	0	2180	C(9')	3037	0	8278
C(10)	103	-1268	2814	C(10')	2661	1268	7648
C(11)	906	-1814	4324	C(11')	1861	1814	6138
C(12)	2514	0	5312	C(12')	2362	0	5039
H(2)	2377	-2484	7287	H(2')	195	2484	3186
H(3)	3691	-1132	9277	H(3')	-618	1132	1169
H(9)	-856	0	1100	H(9')	3524	0	9367
H(10)	-375	-1945	2218	H(10')	2824	1945	8261
H(11)	809	-2665	4682	H(11')	1399	2665	5809
H(12A)	3390	0	6067	H(12A')	2411	0	4235
H(12B)	2339	0	4334	H(12B')	3207	0	5982

space groups, were unsuccessful, and disorder had to be introduced. The fitting of the electron density necessitated, for the cation, the superposition of two annulene systems, as depicted in Figs. 1 and 2, and corresponds physically to a random reversal of direction of successive BDP ions in the crystal. Two BF_4^- groups with their boron atoms almost coincident, and rotated with respect to each other by 60° around an axis parallel to \mathbf{b} , completed the interpretation of the disordered structure.

The positional and thermal parameters of the model were settled by successive difference Fourier syntheses; this procedure led to $R = 0.28$ for the 437 reflexions with $I > 2\sigma(I)$.

High interactions between the parameters of pairs of atoms less than 1.0 \AA apart (statistically) prevented any further refinement by usual least-squares techniques. In any case, the correctness of the interpretation of the structure was confirmed when a more reliable geometry for the cation became available, *i.e.* after the solution of the structure of the hexafluorophosphate salt (see below). From the isotropic refinement of the cation atoms of that structure, a rigid model with exact m symmetry was derived for BDP, and placed in the cell of the BF_4^- salt in such a way as to roughly coincide with one of the two models illustrated in Fig. 2. From this model, the second one was obtained by a 180° rotation around the inertial axis perpendicular to the ring plane, and constrained refinement was performed with the program written by Bianchi, Pilati & Simonetta (1978). The following parameters were varied simultaneously: the scale factor, the $2 + 2$ coordinates of the center of mass of the two cations, the two angles of rotation (one for each cation) of the rigid groups around the inertial axis

Table 3. *Rigid-body-motion parameters for the BF_4^- salt*

	BF_4^-	BDP
$T_{11} (\text{\AA}^2)$	1017 (74)	351 (48)
T_{22}	654 (60)	956 (53)
T_{33}	906 (55)	1140 (70)
T_{12}	-143 (58)	0
T_{13}	0	-21 (35)
$L_{11} (\text{rad}^2)$	707 (56)	135 (31)
L_{22}	947 (83)	124 (15)
L_{33}	492 (56)	41 (23)
L_{12}	-252 (59)	0
L_{13}	0	24 (21)
Eigenvalues of \mathbf{L} (rad^2)	0.109	0.014
	0.057	0.013
	0.048	0.003

The tensors are referred to a Cartesian coordinate system coincident with the principal inertial axes L , M and N . For the anion, N was assumed parallel to the crystallographic b axis. All components of the tensors have been multiplied by 10^4 .

parallel to \mathbf{b} , the non-zero components of \mathbf{T} and \mathbf{L} tensors (assumed equal for both cations),* and the corresponding parameters for the two BF_4^- rigid tetrahedra ($\text{B-F} = 1.35 \text{ \AA}$). The population factor was kept fixed at 0.5 for both ions.

Convergence was assumed when no parameter shift was greater than 5% of its standard deviation. The corresponding R was 0.13 and the R_w index 0.14 for the 437 reflexions [with $I > 2\sigma(I)$] on which the refinement of the 29 parameters was based ($R = 0.17$ including all reflexions with $I > 0$). A difference map revealed residues up to 0.43 e \AA^{-3} in the vicinity of the BF_4^- groupings. This could suggest a possible third orientation of the anion or, more likely, simply reflect the inadequacy of describing the thermal anisotropy by an ellipsoidal motion. Further pursuit of model fitting did not seem economical. The final coordinates are given in Table 2, while Table 3 reports the rigid-body-motion parameters.†

The $\text{C}(1)\cdots\text{C}(6)$ transannular distance, 2.30 \AA , is worth mentioning, since it indicates that the correct way of describing the BDP system is as an annulenium ion, rather than a benzohomotropylum cation.

The packing arrangement of the ions in the structure is shown in Fig. 3. The disorder does not lead to any unusual approach distances between ions; the closest $\text{F}\cdots\text{C}$ contact is 3.16 \AA , and there are no $\text{C}\cdots\text{C}$ distances below 3.4 \AA .

* In the program used for constrained refinement, the TLS tensors are referred to the system defined by the inertial axes. All components of the tensor \mathbf{S} are zero owing to symmetry requirements of the space group.

† Lists of structure factors and anisotropic thermal parameters for the tetrafluoroborate and hexafluorophosphate salt structures have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34369 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

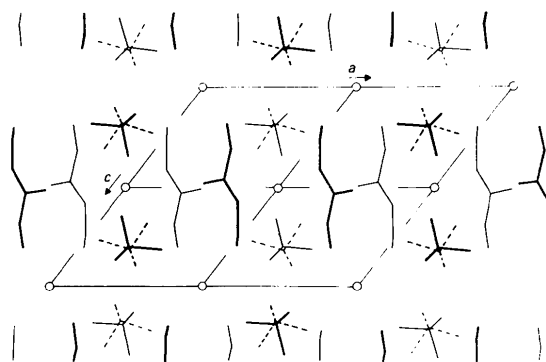


Fig. 3. Packing arrangement in the tetrafluoroborate salt. For the sake of clarity, only one model for the BDP cation has been reported.

The SbF_6^- salt

Crystals of BDP hexafluoroantimonate are well-formed, square-based bipyramids. A small sample, $0.15 \times 0.15 \times 0.12$ mm, was used to derive cell dimensions (Table 1) and counter data. Accurate unit-cell parameters were obtained by the fitting of $\sin^2 \theta$ values of 60 counter reflexions. Systematic absences $h0l$, $h \neq 2n$ and $0kl$, $l \neq 2n$ indicate the space groups $Pcam$ or $Pca2_1$.

Intensity data were collected on a Syntex $P\bar{1}$ diffractometer, using Nb-filtered $\text{Mo } K\alpha$ radiation. Essentially the same procedure described for the counter-data collection of the BF_4^- salt (see above) was followed. Owing to the small dimensions of the crystal, no absorption correction was applied during the processing of the data, the linear absorption coefficient of $\mu = 2.17 \text{ mm}^{-1}$ for $\text{Mo } K\alpha$ radiation suggesting that absorption factors range between 1.15 and 1.35. After the usual corrections for background, Lorentz and polarization factors were applied, the final set ($2\theta < 55^\circ$) consisted of 1600 reflexions, of which only 183 had negative net intensities. The overall B temperature factor derived by a Wilson (1949) plot had a value of 4.5 \AA^2 , which falls in the usual range. Intensity statistics did not allow a safe choice of the space group; tests based on the Wilson (1949) statistics indicated a distribution midway between centric and non-centric, with perhaps a slight predominance of the latter. A three-dimensional sharpened Patterson function was computed, from which a preliminary structure consistent with space group $Pcam$ could be readily assigned to the anion group. The structure was checked by computation of an electron density map calculated from phases based on the antimony atom alone. Since there are four molecules of $\text{C}_{12}\text{H}_{11}\text{SbF}_6$ in the unit cell, and there are eight equivalent positions in the centrosymmetric space group $Pcam$, the molecule should lie on the mirror plane. Hence, the BDP cation was expected to appear in the map with atoms C(9) and C(12) on the mirror plane. In contrast, as illustrated

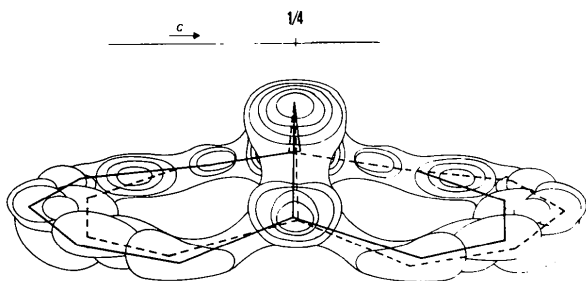


Fig. 4. Projection down the b axis of the electron density of BDP in the hexafluoroantimonate salt; contours are at arbitrary intervals. Two plausible models for the interpretation of the disorder are shown; they are related by the crystallographic mirror plane at $z = 0.25$.

in Fig. 4, the electron density corresponded to a BDP ion with its longest direction parallel to c , with the bridge atoms C(1), C(6) and C(12) lying almost exactly on the mirror plane. None of the possible ordered structures in the space group $Pca2_1$ was found to be correct, although least-squares refinement with anisotropic atoms for the SbF_6^- group and isotropic C atoms led to R values as low as 0.05. Rather unrealistic bond distances (1.30 to 1.56 Å) along the annulene perimeter, exceedingly high values of the B 's of the C atoms (up to 12 \AA^2), and large residues (up to 0.79 e \AA^{-3}) systematically occurring between pairs of atoms of the ring were indicative of a disordered structure in the space group $Pcam$. However, since the contribution to structure factor amplitudes of 'half' carbon atoms relative to that of the Sb atoms would be similar to that of H atoms in ordinary light-atom structures, any extensive search for plausible models of BDP did not seem worthwhile.*

Thermal-motion analysis of the SbF_6^- group did not give any evidence of disordering for the fluorine atoms; the Sb—F distances are in the range 1.79 (2)–1.87 (2) Å, and the bond angles vary between 87 (1) and 94 (1)°. The transannular C(1)···C(6) distance in BDP, in the range 2.3–2.5 Å depending on the various models tested, is in agreement with an annulene structure, and confirms the value found in the BF_4^- salt.

The PF_6^- salt

The close similarity of the cell dimensions of this compound with those of the hexafluoroantimonate salt (Table 1) and the identity of the systematic absences in

* Lists of structure factors and atomic parameters for this salt have not been deposited. They are available from the authors on request.

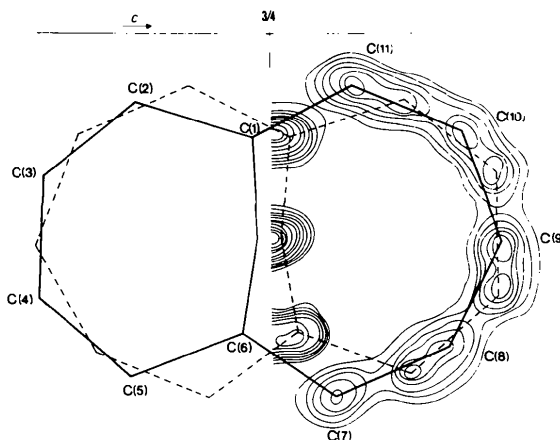


Fig. 5. BDP electron density from low-temperature data of the hexafluorophosphate salt. Comparison with Fig. 2 shows the improvement in resolution.

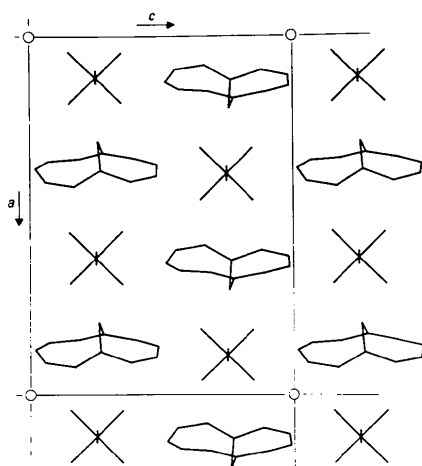


Fig. 7. The packing of the PF_6^- salt. Only ordered models for BDP are shown.

Table 5. Rigid-body-motion parameters for the PF_6^- salt

The tensors are referred to a Cartesian coordinate system coincident with the principal inertial axes L , M and N of the two ions. All components of the tensors have been multiplied by 10^4 .

	PF_6^-	BDP
T_{11} (\AA^2)	339 (2)	139 (7)
T_{22}	182 (2)	160 (5)
T_{33}	199 (2)	266 (10)
T_{12}	0	13 (4)
T_{23}	-30 (1)	0
L_{11} (rad^2)	74 (2)	175 (4)
L_{22}	111 (3)	21 (1)
L_{33}	169 (2)	36 (3)
L_{12}	0	4 (3)
L_{23}	-31 (2)	0
S_{11} (\AA rad)	0	0
S_{12}	6 (1)	0
S_{13}	-9 (1)	-41 (4)
S_{21}	-4 (2)	0
S_{22}	0	0
S_{23}	0	-10 (3)
S_{31}	-13 (2)	4 (2)
S_{32}	0	8 (2)
S_{33}	0	0
Eigenvalues of L (rad^2)	0.0186 0.0095 0.0074	0.0176 0.0036 0.0021

The final positional coordinates are reported in Table 4, and the corresponding geometry for BDP in Fig. 6. Rigid-body-motion parameters are listed in Table 5. A view of the structure, as seen down the b axis, is shown in Fig. 7.

A final density map showed some relatively high residuals (maximum value 0.5 e \AA^{-3}) in the proximity of both ions; they may be due to errors in the data and/or in the models. In any event the geometry of the cation, as extracted from our treatment, can be considered sufficiently accurate to distinguish the preferred structure of this system, which can be safely considered an annulanium ion [$\text{C}(1) \cdots \text{C}(6) = 2.293 \text{ \AA}$].

In spite of the disorder, two contacts between ions are below the sum of van der Waals radii. They are $\text{C}(3)_{xyz} \cdots \text{C}(10)_{-x, 1-y, \frac{1}{2}+z} = 3.355 \text{ \AA}$ and $\text{C}(10)_{xyz} \cdots \text{C}(10)_{-x, 1-y, 1-z} = 3.350 \text{ \AA}$.

Useful suggestions on the interpretation of the disorder in the BF_4 salt were made by Dr R. E. Marsh, at the California Institute of Technology. Drs R. Bianchi and T. Pilati were of valuable help in performing some computations, and Mr M. Bandera in preparing the drawings. Our thanks go to all of them.

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