The Geometry of the [15]Annulenium System in Tricyclo[9.4.1.1^{3,9}]heptadecaheptaenylium Tetrafluoroborate
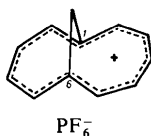
By Riccardo Bianchi, Riccardo Destro and Massimo Simonetta

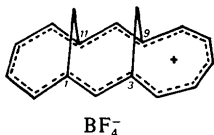*Istituto di Chimica Fisica e Centro CNR, Università, Via Golgi* 19, 20133 *Milano, Italy*

Abstract. $[C_{17}H_{15}]^+[BF_4]^-$, $M_r = 306 \cdot 1$, monoclinic, $P2_1/n$, $a = 9 \cdot 430$ (3), $b = 10 \cdot 239$ (4), $c = 15 \cdot 337$ (5) Å, $\beta = 100 \cdot 61$ (3)°, $Z = 4$, $D_c = 1 \cdot 397$, $D_m = 1 \cdot 395$ Mg m^{-3} (flotation), μ(Mo $K\alpha$) = $0 \cdot 125$ mm^{-1}, $F(000)$ = 632. Counter data collected with Mo $K\alpha$ radiation were used to derive the structure by direct methods. Usual refinement by a full-matrix least-squares method, based on 1451 reflexions with $I > 2\sigma(I)$, led to $R = 0 \cdot 049$ and $R_w = 0 \cdot 053$. Bond lengths along the ring perimeter of the cation indicate the aromatic character of the molecule. The two transannular distances C(1)–C(11) and C(3)–C(9) are $2 \cdot 322$ (5) and $2 \cdot 432$ (4) Å respectively; they prove the minimal nature of the corresponding C$\cdots$C overlap.

Introduction. The X-ray analysis of bicyclo[5.4.1]-dodecapentaenylium hexafluorophosphate (BDP; Destro, Pilati & Simonetta, 1976)

PF$_6^-$

has shown that the cation is best described as a perturbed [11]annulenium ion rather than in terms of a benzohomotropenylium ion. In fact, the value of $2 \cdot 30$ Å for the C(1)–C(6) distance – quite similar to that found in neutral bridged [10]annulenes – proves the minimal nature of the 1,6 overlap. Similar values for transannular distances are expected to occur in the 15π analog of BDP, which should hence possess a [15]-annulenium system.

BF$_4^-$

To confirm this expectation, we have undertaken the X-ray analysis of the title compound (hereinafter THDH), recently synthesized by Vogel (1977), who kindly supplied us with a sample of the substance.

Crystals of THDH are in the form of red-violet prisms. The cell parameters were obtained from a least-squares fit to the sin$^2 \theta$ values of 89 reflexions measured on a diffractometer. The space group $P2_1/n$ was indicated by absences $h0l$ with $h + l$ odd and $0k0$ with k odd. The density was measured by flotation in a dilute K_2HgI_4 solution. For the data collection a crystal $0 \cdot 30 \times 0 \cdot 30 \times 0 \cdot 20$ mm was mounted on a computer-controlled four-circle diffractometer using graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0 \cdot 71069$ Å) and a variable θ–2θ scan technique. The background was counted for half the total scanning time on each end of the scan range. Two standard reflexions were checked after each 48 intensity measurements; they showed no appreciable trend. In the range of measurements ($2\theta_{max} = 47°$) 2174 reflexions were measured, of which 1451 with $I > 2\sigma(I)$ were treated as observed. The variance $\sigma^2(I_{rel})$ was calculated as $[S + B + (0 \cdot 03 S)^2]v^2$, with S = scan count, B = total background and v = scan speed. Intensities and their standard deviations $\sigma(I_{rel})$ were corrected for Lorentz and polarization effects, but not for absorption ($\mu = 0 \cdot 125$ mm^{-1} for Mo $K\alpha$ radiation).

The structure was solved by direct methods (*MULTAN*; Germain, Main & Woolfson, 1971). The E map corresponding to the solution with the highest combined figure of merit clearly revealed 22 peaks with very little extraneous detail. For the refinement of the structure, the atomic coordinates derived from the map were adjusted to obtain a model (A) with exact m symmetry for the cation and tetrahedral symmetry for the BF$_4^-$ group. Rigid-body molecular motion was assumed for both ions and the H atoms were placed at calculated positions. Full-matrix least-squares refinement of model (A) was therefore carried out with shape (non-crystallographic symmetry) and **T L S** constraints. After a few least-squares cycles the B–F distance, until then kept fixed at $1 \cdot 38$ Å, was allowed to vary, always maintaining tetrahedral symmetry. Furthermore, the thermal parameters of the H atoms were no longer included in the **T L S** constraint. Thus, in the final cycles of refinement of this model 118 parameters were simultaneously adjusted: 53 atomic coordinates, 4 translational coordinates and 5 rotation angles for the two rigid groups, 20 + 20 components of the **T L S** tensors, 15 isotropic B values for the H atoms, and a scale factor. At the end of the refinement

the results were $R = 0.058$, $R_w = 0.065$ and goodness-of-fit $= 2.0$.

The final set of parameters of model (A) was then submitted to the usual unconstrained refinement (model B), which included 259 parameters in a single matrix: coordinates and anisotropic temperature factors for the 22 heavy atoms, coordinates and isotropic B values for the 15 H atoms, and a scale factor. Convergence was assumed after three least-squares cycles, when no parameter shift was as large as 10% of its standard deviation. The final values of the residuals were $R = 0.049$ and $R_w = 0.053$, with a goodness-of-fit $= 1.7$. The final atomic parameters are given in Table 1.*

Refinement on all 1451 observed reflexions was accomplished by minimization of the quantity $\sum w(|F_o| - k|F_c|)^2$, with weights $w = 4F_o^2/\sigma^2(F_o^2)$. The program

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34130 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Final positional parameters* ($\times 10^4$; *for* H $\times 10^3$)

	x	y	z
B	6568 (4)	6034 (4)	8032 (3)
F(1)	7870 (2)	6275 (3)	8530 (2)
F(2)	6685 (3)	5129 (2)	7410 (2)
F(3)	5654 (3)	5607 (2)	8564 (2)
F(4)	6019 (3)	7149 (2)	7614 (2)
C(1)	7121 (3)	7343 (3)	3692 (2)
C(2)	8161 (4)	6673 (4)	3348 (2)
C(3)	8340 (3)	5328 (4)	3296 (2)
C(4)	9630 (4)	4840 (5)	3113 (2)
C(5)	10157 (4)	3586 (5)	3220 (3)
C(6)	9913 (5)	2549 (5)	3741 (4)
C(7)	9250 (5)	2401 (5)	4469 (4)
C(8)	8351 (5)	3179 (4)	4864 (3)
C(9)	7463 (3)	4195 (3)	4486 (2)
C(10)	6901 (4)	5062 (4)	5031 (3)
C(11)	6259 (3)	6256 (4)	4817 (2)
C(12)	6198 (4)	7205 (6)	5485 (3)
C(13)	6274 (4)	8514 (6)	5363 (4)
C(14)	6807 (4)	9179 (5)	4688 (4)
C(15)	7352 (4)	8652 (4)	3996 (3)
C(16)	5784 (4)	6730 (4)	3890 (2)
C(17)	7271 (4)	4343 (4)	3497 (2)
H(2)	890 (3)	718 (3)	322 (2)
H(4)	1015 (4)	548 (4)	283 (2)
H(5)	1086 (4)	341 (4)	287 (2)
H(6)	1039 (4)	175 (4)	365 (3)
H(7)	952 (4)	166 (4)	477 (3)
H(8)	825 (4)	298 (3)	547 (2)
H(10)	704 (3)	487 (3)	563 (2)
H(12)	617 (4)	687 (4)	603 (3)
H(13)	612 (4)	907 (4)	584 (2)
H(14)	695 (4)	1010 (4)	476 (2)
H(15)	795 (3)	911 (3)	374 (2)
H(16A)	540 (3)	601 (3)	349 (2)
H(16B)	508 (3)	738 (3)	389 (2)
H(17A)	630 (3)	456 (3)	321 (2)
H(17B)	745 (3)	345 (3)	324 (2)

used for the constrained refinement has been recently reported (Bianchi, Pilati & Simonetta, 1978), that for the unconstrained refinement was a modified version of *ORFLS* (Busing, Martin & Levy, 1962). Form factors for heavy atoms were from Cromer & Waber (1965) and for H atoms from Stewart, Davidson & Simpson (1965).

Discussion. For the cation the maximum difference between the individual geometrical values of model (B) and the corresponding ones of model (A) is twice the e.s.d.; hence only the geometrical values concerning model (A) are reported in Fig. 1 and Table 2. A slightly less satisfactory agreement between the two models is observed for the BF_4^- group. The B–F bond length in the tetrahedrally constrained ion is 1.355 (2) Å, while the distances in model (B) are: B–F(1) $= 1.344$ (4),
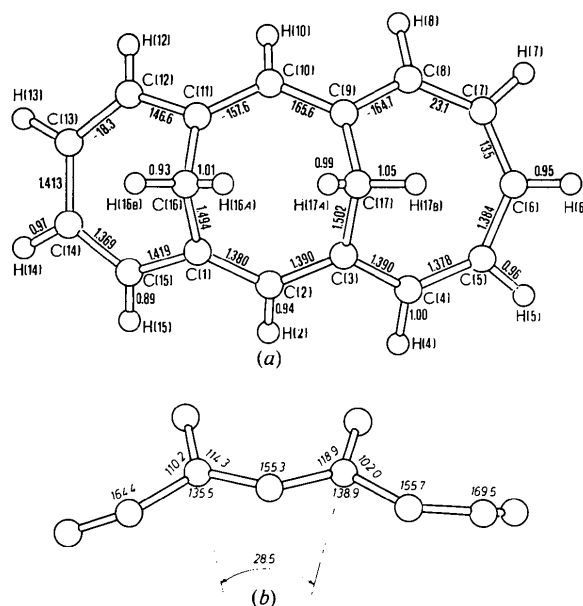

Fig. 1. The cation of THDH viewed along a principal axis of inertia. (a) Numbering scheme, bond lengths (bottom: e.s.d.'s for C–C bond lengths 0.004–0.006 Å and for C–H bond lengths 0.02–0.03 Å) and torsional angles (top: e.s.d.'s 0.4–1.0°) along the annulene ring. (b) Dihedral angles between least-squares planes. The values refer to the constrained model (A), where m symmetry was imposed.

Table 2. *Bond angles* (°) *between heavy atoms in model* (A) (*constrained*)

C(2)–C(1)–C(15)	121·1 (3)		C(4)–C(5)–C(6)	133·8 (3)
C(2)–C(1)–C(16)	123·7 (3)		C(5)–C(6)–C(7)	134·9 (4)
C(15)–C(1)–C(16)	114·7 (3)		C(1)–C(15)–C(14)	124·7 (3)
C(1)–C(2)–C(3)	128·3 (3)		C(15)–C(14)–C(13)	127·8 (4)
C(2)–C(3)–C(4)	119·2 (3)		C(1)–C(16)–C(11)	102·2 (2)
C(2)–C(3)–C(17)	124·1 (3)		C(3)–C(17)–C(9)	108·3 (3)
C(4)–C(3)–C(17)	116·5 (3)		F(1)–B–F(2)	109·5 (1)
C(3)–C(4)–C(5)	128·4 (3)			

B—F(2) = 1·349 (5), B—F(3) = 1·364 (4), and B—F(4) = 1·364 (5) Å.

Besides the already mentioned BDP cation (Destro et al., 1976), two molecules are particularly convenient for comparison with the THDH geometry: syn-4,13:6,11-dimethano[15]annulenone (SYNO; Wagemann, Müllen, Vogel, Pilati & Simonetta, 1977) and syn-5,7-diformyltricyclo[9.4.1.1^{3,9}]heptadeca-2,4,7,9,-11,13,15-heptaene (DIAL; Pilati & Simonetta, 1977). For the four compounds we have evaluated (see Table 3) the quantities $\bar{r} = \langle r_i \rangle$, $\rho = \langle (r_i - \bar{r})^2 \rangle^{1/2}$, and $\tau = \langle \tau_i^2 \rangle^{1/2}$, where r_i are the observed bond lengths in the ring, and τ_i the torsion angles in the annulene perimeter (if $\tau_i > 90°$, it is replaced by $180° - |\tau_i|$). As already evidenced by calculation of the same quantities for several bridged annulenes (Gavezzotti & Simonetta, 1976; Destro & Simonetta, 1977), values of ρ greater than 0·03 Å are usually observed for cyclopolyolefins (SYNO and DIAL in Table 3), while the aromatic character of the molecules corresponds to a significantly smaller degree of dispersion around the mean value $\bar{r}$. Interestingly, according to Fig. 1 the variation of bond lengths along the annulene perimeter of the THDH cation is more marked in the outer six-membered ring defined by atoms C(1), C(11), C(12), C(13), C(14) and C(15) (ring A) than in the central six-membered and the outer seven-membered rings (B and C respectively). Moreover, the average C—C bond length $\bar{r}$ is 1·398 Å for ring A while in rings B and C it is shortened to 1·385 and 1·384 Å respectively. It has been reported that in ions where C bears a formal positive charge, such as in the triphenylcyclopropenium (Sundaralingam & Jensen, 1966), 1,2,3-tris-dimethylaminocyclopropenium (Ku & Sundaralingam, 1972), chlorotetraphenylcyclobutenium (Bryan, 1964) and methyloxocarbonium (Boer, 1968) cations, bond lengths for these C atoms are almost universally shortened beyond the amounts required by hybridization alone. Whether this applies also in the present case, i.e. that in THDH the positive charge might be mainly localized on rings B and C, is open to speculation. On the other hand, in the six-membered ring of the BDP cation, the dispersion o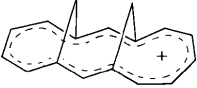f C—C bond lengths around the 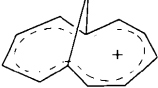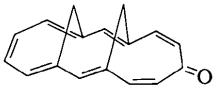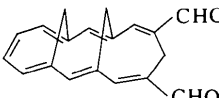mean coincides with that observed in the seven-membered ring; hence, dispersion of the charge on the whole perimeter was proposed for that system.

Attention must be paid in using τ values to differentiate aromatic compounds from cyclopolyolefins. For molecules listed in Table 3 a rather clear distinction can be made on the basis of this parameter, but values of τ larger than 20° have also been observed in some aromatic [14]annulenes, e.g. syn-1,6:8,13-dimethano[14]annulene (Destro, Pilati & Simonetta, 1977), where τ is 23·4°, and 1,6:8,13-butane-1,4-diylidene[14]annulene (Gramaccioli, Mugnoli, Pilati, Raimondi & Simonetta, 1972), with $\tau = 24·8°$.

The conformation of THDH, as described by bond angles and dihedral angles between least-squares planes, is very similar to that of SYNO and DIAL. The largest differences occur in the geometrical parameters involving atom C(6): the internal angle at this atom is 122·7° in SYNO and 115·2° in DIAL (to be compared with 134·9° in THDH); the dihedral angle between the plane defined by atoms C(5), C(6) and C(7) and the plane defined by atoms C(4), C(5), C(7) and C(8) is 148·1° in the former and 132·7° in the second cyclopolyolefin. The value of this dihedral angle in THDH, 169·5°, on the other hand, is close to the corresponding one in BDP, 173·2°. Of particular relevance is the resemblance of the dihedral angle between the bridges in the three structures: 28·5° here in THDH vs 27·5° in SYNO and 28·4° in DIAL. A similar value, 26·6°, was also found for this angle in the above mentioned syn-1,6:8,13-dimethano[14]-annulene. Consequently, the contact between the two inner bridge H atoms H(16A) and H(17A) has a value well below the sum of van der Waals radii: 1·81 Å in THDH, 1·84, 1·83 and 1·78 Å, respectively, in the other molecules.

Bond distances and angles involving atoms C(16) and C(17) are virtually identical in the three [15]-annulene compounds, with the possible exception of the bridgehead ∠C—C—C angles, where differences of up to 1·4° are observed. Consequently, the transannular distances C(1)···C(11) and C(3)···C(9) show similar values: 2·322 and 2·432 Å in THDH, 2·313 and 2·445 Å in SYNO, 2·314 and 2·423 Å in DIAL. As in the

Table 3. *Comparison of geometrical parameters of the annulene ring in related compounds*

	THDH	BDP	SYNO	DIAL
Compound				
$\bar{r}$ (Å)	1·389	1·397	1·404	1·411
ρ (Å)	0·016	0·024	0·042	0·052
τ (°)	20·4	18·7	26·2	30·2

case of BDP, where $C(1) \cdots C(6)$ is 2·30 Å, these values prove the minimal nature of the corresponding C—C overlap.

All F atoms are involved in $H \cdots F$ distances <2·50 Å, an approximate value of the sum of the van der Waals radii. Two of these rather short contacts concern both H atoms at C(16), while no $H \cdots F$ distances below 2·80 Å are observed for the H atoms of the other bridgehead C atom.

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α-L-Sorbopyranose: A Neutron Diffraction Refinement*

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Abstract. $C_6H_{12}O_5$, $M_r = 180\cdot16$, $P2_12_12_1$, $a = 6\cdot545$ (2), $b = 18\cdot062$ (7), $c = 6\cdot310$ (2) Å, $D_x = 1\cdot604$, $D_m = 1\cdot607$ Mg m⁻³, $V = 745\cdot94$ Å³. More accurate dimensions were obtained and the disorder in the orientation of the primary alcohol group, observed in the previous X-ray study [Kim & Rosenstein (1967). Acta Cryst. 22, 648–656], is confirmed and better defined. The gauche/trans orientation of the primary alcohol hydroxyl group has 0·625 occupancy and the gauche/gauche 0·375. The major component forms a normal hydrogen bond with an $H \cdots O$ distance of 1·867 Å; the minor component forms a bifurcated hydrogen bond having two interactions with $H \cdots O$ distances of 2·151 and 2·209 Å at an angle of 81°.

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Introduction. The X-ray crystal structure of α-L-sorbose (Kim & Rosenstein, 1967) revealed disorder in the orientation of the primary alcohol group between two of the three possible 'staggered' positions for the hydroxyl group. This implies two possible hydrogen-bonding arrangements of comparable energy. The purpose of this neutron diffraction study was to determine the precise hydrogen-bond geometry associated with these two arrangements. Suitable transparent crystals of good optical quality were obtained by slow evaporation from an ethanol–water solution. One hkl octant and part of an hkl octant of neutron diffraction