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sym-Triphenylcyclopropenylium Hexabromotellurate(IV), $(C_{21}H_{15})_2[TeBr_6]$

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Abstract. $M_r = 1141·7$, monoclinic, $P2_1/c$, $a = 13·663\,(1)$, $b = 13·360\,(1)$, $c = 21·718\,(2)$ Å, $\beta = 93·612\,(7)°$, $V = 3956\,(1)$ Å^3, $Z = 4$, $D_m = 1·92$, $D_x = 1·912$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 67·85$ cm^{-1}, $F(000) = 2176$, room temperature, final $R = 0·026$ for 3500 independent observed reflections. The $TeBr_6^{2-}$ anion is nearly octahedral with the Te—Br bonds ranging from 2·69 to 2·72 Å and the Br—Te—Br angles ranging from 87·6 to 92·1°. The average cyclopropenylium C—C bond distance is 1·377 Å. The planes of the phenyl rings are twisted relative to the plane of the cyclopropenylium ring by *ca* 5°.

Introduction. The geometry of the hexahalotellurate dianion (TeX_6^{2-}) has provoked considerable interest (Clark, McWhinnie, Mallaki, Dance & Jones, 1980). A distorted octahedral configuration is predicted by valence shell electron pair repulsion (VSEPR) theory (Gillespie & Nyholm, 1957). However, work based on MO theory predicts regular octahedral geometry (Gillespie, 1970; Johnstone, Jones & Vasudev, 1972). Several 'undistorted' structures of the $TeBr_6^{2-}$ anion have been reported (Brown, 1964; Das & Brown, 1966; Dahan & Lefebvre-Soubeyran, 1976*a*; Berg & Nielsen, 1979); however, only in the most recent study were the data corrected for absorption. In each case the dianion possesses crystallographically imposed point symmetry: $\bar{1}$, $m3m$, 2, $\bar{3}$ respectively. Another structure (Dahan & Lefebvre-Soubeyran, 1976*b*) also locates the $TeBr_6^{2-}$ at a position with twofold symmetry; the dianion is slightly distorted possibly due to hydrogen bonding involving the Br atoms [Te—Br distances range from 2·642 (3) to 2·798 (3) Å; Br—Te—Br angles range from 85·7 (1) to 93·0 (1)°]. Several TeX_6^{2-} (X = Cl or I) structures have been reported but only one shows a clearly distorted $TeCl_6^{2-}$ anion (Russo, Valle & Calogero, 1980). This is also hydrogen-bonded to the cation.

The structure of the *sym*-triphenylcyclopropenylium cation (TPCP) has been reported by Sundaralingam & Jensen (1966). The short cyclopropenylium C—C distance observed in that structure [1·373 (5) Å] is in excellent agreement with the distance predicted for the $C_3H_3^+$ structure (1·377 Å) (Radom, Hariharan, Pople & Schleyer, 1976). However, the apparent distortion of the phenyl rings (C—C distances range from 1·338 to 1·444 Å in a single phenyl ring) is disturbing.

In this paper we report the structure of $(TPCP)_2[TeBr_6]$. By collecting a relatively high-angle data set, and by accounting for absorption effects, we hoped to generate superior structures for both the TPCP cation and the $TeBr_6^{2-}$ anion.

Experimental. Diffraction-quality crystals supplied by Mr Kenneth A. Smith of the Department of Chemistry, University of California, Berkeley. Crystal density measured by flotation in toluene/bromoform. Orange crystals, elongated parallelepipeds (0·25 × 0·21 × 0·18 mm) with bevelled corners.

Enraf–Nonius CAD-4 diffractometer. Cell dimensions determined using 24 well centered reflections with $28 < 2\theta < 40°$. All reflections with $0·037 < \sin\theta/\lambda < 0·583$ Å^{-1} ($0 \le h \le 15$, $0 \le k \le 15$, $-25 \le l \le 25$) measured using ω–2θ scans with following conditions: aperture, vertical 3·0 mm, horizontal $(0·55 + 0·35\tan\theta)$ mm; scan width, $(2·0 + 1·0\tan\theta)°$; background, 25% each side of peak scan; pre-scan rate 6·7° min^{-1}; additional scan if $0·015 < \sigma(I)/(I) < 1$,

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with rate calculated from pre-scan to give $\sigma(I)/I = 0{\cdot}015$, but not slower than *ca* 0·8° min^{-1}. Orientation checked every 250 reflections and maintained within 0·1° (one re-orientation required). Intensity standards (016, $\bar{1}4\bar{1}$, 400) measured every 2 h of exposure indicated a drop in intensity of *ca* 1% over 106 h; no corrections made. ψ scans yielded a range in normalized transmission factors of 25·4%.

Data reduction and structure refinement using standard heavy-atom methods performed on a PDP 11/60 computer using locally modified Nonius (1980) *SDP* software. Calculated absorption corrections based on measured crystal dimensions, orientation and absorption coefficient gave transmission coefficients between 0·25 and 0·35.* Weights assigned according to $w = 4F_o^2/\sigma^2(F_o^2)$ [where $F_o^2 = \omega(C-2B)/\text{Lp}$ and $\sigma^2(F_o^2) = \omega^2(C + 4B)/(\text{Lp})^2 + (pF_o^2)^2$; C = total counts in scan, B = sum of background counts, ω = scan speed in ° min^{-1}, Lp = Lorentz and polarization corrections] using a p factor of 0·03 representing a 3% uncertainty in intensity independent of counting statistics. Of the 7201 reflections measured, 6564 remained after deleting systematically absent reflections and redundant $0k\bar{l}$ reflections. 3500 reflections with $F_o^2 > 3\sigma(F_o^2)$ used in least-squares refinement.

Scattering factors from Cromer & Waber (1974). Values for f' and f'' from Cromer (1974). Te and Br atoms located from a Patterson map of the unique data. C atoms found in difference Fourier maps and inserted into structure model. Least-squares minimization of $D = \sum w(|F_o| - |F_c|)^2$, refining positions and isotropic thermal parameters gave $wR = (D/\sum wF_o^2)^{1/2} = 0{\cdot}10$. All H atoms located in difference Fourier maps as peaks of *ca* 0·40 e Å^{-3} and assigned idealized positions with a crystallographic C—H bond distance of 0·95 Å and isotropic thermal parameters of $B = 6{\cdot}5$ Å^2 (average B for phenyl C atoms plus one). 443 parameters in final refinement included 49 anisotropic non-H atoms, scale factor, and secondary-extinction coefficient [2·4 (2) $\times 10^{-8}$; Stout & Jensen, 1968]. Inclusion of the extinction coefficient is significant according to the R-factor-ratio test (Hamilton, 1965). At convergence (largest Δ/σ 0·13), $R = 0{\cdot}0259$, $wR = 0{\cdot}0300$, $S = 1{\cdot}23$ ($R = 0{\cdot}116$ including 3064 unobserved reflections). Two largest peaks in final difference Fourier map, located *ca* 1·1 Å from Br(6), 0·40 e Å^{-3}.

Discussion. The numbering scheme and bond lengths are shown in Fig. 1. Atomic coordinates and equivalent isotropic thermal parameters are given in Table 1. Bond angles and Br···Br distances for TeBr_6^{2-} are listed in Table 2. A stereo image of the unit cell is shown in Fig. 2.

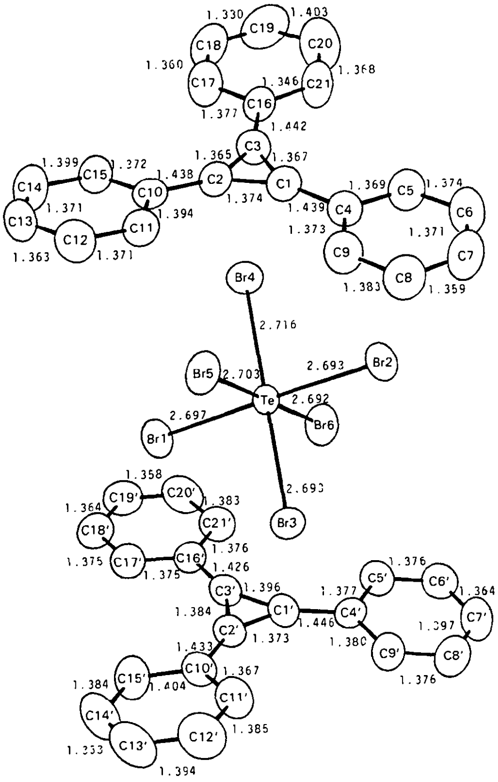

Fig. 1. Numbering scheme and bond lengths (Å) for $(\text{TPCP})_2[\text{TeBr}_6]$. Thermal ellipsoids are shown at 50% probability levels. H atoms have been omitted for clarity. E.s.d.'s of all Te—Br bond distances are 0·001 Å; C—C bond distances have e.s.d.'s of 0·008 to 0·010 Å.

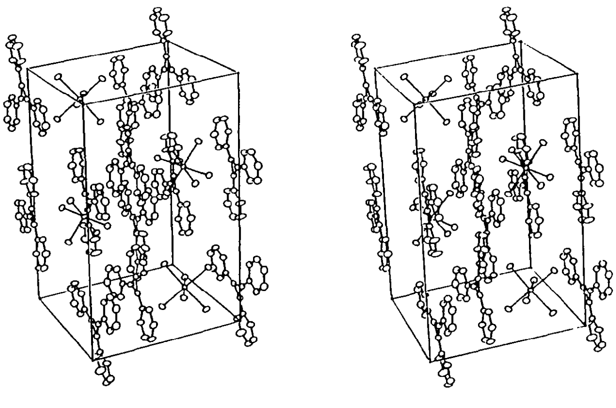

Fig. 2. Stereoscopic *ORTEP* view (Johnson, 1965) of the unit-cell contents of $(\text{TPCP})_2[\text{TeBr}_6]$. The c axis is vertical and the a axis is approximately horizontal.

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* Absorption-correction parameters, anisotropic thermal parameters, H-atom parameters, bond angles and least-squares planes in the TPCP cations, and structure factors have been deposited with the British Library Lending Division as Supplementary Publiction No. SUP 39862 (34 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

sym-Triphenylcyclopropenylium cation

The average bond distance, 1·377 (12) Å (the number in parentheses indicates a variance for individual distances of 0·012 Å), of the cyclopropenylium moiety confirms the value predicted by calculations and found in earlier work (see above). The exocyclic bonds [*e.g.* C(1)—C(4)] are shorter than the expected value for a C—C σ bond. This is in agreement with positive-charge delocalization throughout the π-aromatic system imparting some double-bond character to the exocyclic bonds. The planes of the phenyl rings are twisted relative to the plane of the cyclopropenylium ring by *ca* 5°. The bond lengths and angles of the phenyl rings are normal, except for the bond lengths between C(18), C(19), C(20), and C(12'), C(13'), C(14'), which show large deviations from the rest of the phenyl-ring C—C bonds. The large thermal ellipsoids of these atoms suggest disorder. However, inspection of the Fourier map did not reveal any alternative peaks for the C atoms in question. A search for hydrogen–bromine contacts less than 3 Å revealed no correlation with the observed deviations.

Hexabromotellurate(IV) *dianion*

The average Te—Br bond distance of 2·699 (9) Å agrees with the values found previously. In contrast to previous studies, this structure is based on data corrected for absorption and locates the $TeBr_6^{2-}$ at a general position, a condition met by the only $TeCl_6^{2-}$ structure with evident distortions from octahedral geometry (Russo *et al.*, 1980). The packing of the TPCP counterion precludes O_h point symmetry for the dianion (see Fig. 2). Moreover, the present structure is not subject to hydrogen bonding such as that observed in the distorted TeX_6^{2-} structures mentioned above.

Inspection of the Te—Br bond lengths reveals some deviations from regular octahedral geometry of the dianion. The difference between the longest and shortest Te—Br bond lengths is 0·024 Å, while the standard deviation in any one bond length is only 0·001 Å. The three longest bonds are directed toward the single face of the octahedron [Br(1), Br(4) and Br(5)] which exhibits the two longest Br···Br distances and most obtuse Br—Te—Br angles. The observed distortions could be a consequence of packing forces, or they may indicate the location of the tellurium lone electron pair at the capped position of the distorted octahedral face. We feel that the degree of distortion found here, regardless of its interpretation, places an upper limit on the magnitude of the stereochemical effect of the putative lone electron pair in $TeBr_6^{2-}$.

This crystal structure was solved at the Chexray Facility of the Department of Chemistry, University of California, Berkeley. We wish to thank E. J. Wucherer, Dr F. L. Hollander, and Professors S.-H. Kim and K. N. Raymond for their guidance.

Table 1. *Atomic coordinates and* B_{eq} *for non-*H *atoms of* (*TPCP*)$_2$[TeBr$_6$]

The e.s.d. of the last digit is shown in parentheses.

$B_{eq} = \frac{4}{3}(a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab\beta_{12}\cos\gamma + ac\beta_{13}\cos\beta + bc\beta_{23}\cos\alpha)$.

	x	y	z	B_{eq}(Å^2)
Te	0·25993 (3)	0·25412 (3)	0·12140 (2)	2·666 (7)
Br(1)	0·35284 (5)	0·07675 (5)	0·13552 (3)	4·33 (2)
Br(2)	0·17282 (5)	0·43415 (5)	0·10708 (3)	4·30 (2)
Br(3)	0·36893 (5)	0·32376 (5)	0·21982 (3)	4·10 (2)
Br(4)	0·14476 (5)	0·18544 (5)	0·02398 (3)	4·72 (2)
Br(5)	0·12149 (5)	0·19528 (5)	0·19728 (3)	4·44 (2)
Br(6)	0·39949 (5)	0·30823 (5)	0·04583 (3)	4·64 (2)
C(1)	0·1045 (4)	0·2812 (5)	0·0731 (3)	3·8 (1)
C(2)	−0·1111 (4)	0·1803 (4)	0·0845 (3)	3·7 (1)
C(3)	−0·1119 (4)	0·2145 (5)	0·0252 (3)	3·8 (1)
C(4)	0·0965 (4)	0·3826 (4)	0·0952 (3)	3·6 (1)
C(5)	−0·0970 (5)	0·4609 (5)	0·0546 (3)	4·7 (2)
C(6)	0·0929 (5)	0·5585 (5)	0·0744 (3)	5·7 (2)
C(7)	0·0862 (6)	0·5763 (5)	0·1367 (3)	5·9 (2)
C(8)	−0·0836 (5)	0·5007 (5)	0·1787 (3)	5·2 (2)
C(9)	0·0894 (5)	0·4034 (5)	0·1572 (3)	4·7 (2)
C(10)	−0·1195 (4)	0·0984 (5)	0·1268 (3)	3·6 (1)
C(11)	0·1286 (5)	0·1149 (5)	0·1896 (3)	4·4 (2)
C(12)	0·1381 (5)	0·0355 (5)	0·2287 (3)	5·5 (2)
C(13)	0·1363 (5)	0·0603 (5)	0·2073 (3)	5·5 (2)
C(14)	−0·1258 (6)	−0·0782 (5)	0·1459 (3)	6·1 (2)
C(15)	−0·1175 (5)	0·0020 (5)	0·1051 (3)	4·7 (2)
C(16)	−0·1224 (4)	0·1965 (4)	−0·0403 (3)	3·8 (1)
C(17)	0·1269 (5)	0·0999 (5)	−0·0624 (3)	5·3 (2)
C(18)	−0·1363 (5)	0·0796 (5)	−0·1238 (3)	5·9 (2)
C(19)	−0·1419 (6)	0·1554 (6)	−0·1635 (3)	7·1 (2)
C(20)	0·1409 (8)	0·2545 (6)	−0·1421 (4)	9·0 (3)
C(21)	−0·1282 (6)	0·2737 (5)	−0·0803 (3)	6·4 (2)
C(1')	0·6184 (4)	0·2891 (5)	0·1817 (3)	3·8 (1)
C(2')	0·6097 (4)	0·2205 (4)	0·2281 (3)	3·6 (1)
C(3')	0·6150 (4)	0·1870 (5)	0·1681 (3)	3·7 (1)
C(4')	0·6317 (4)	0·3911 (4)	0·1616 (3)	3·7 (1)
C(5')	0·6409 (5)	0·4117 (5)	0·1001 (3)	4·8 (2)
C(6')	0·6547 (5)	0·5089 (5)	0·0815 (3)	5·7 (2)
C(7')	0·6601 (5)	0·5838 (5)	0·1243 (4)	6·2 (2)
C(8')	0·6536 (5)	0·5645 (5)	0·1871 (3)	5·9 (2)
C(9')	0·6378 (5)	0·4672 (5)	0·2046 (3)	5·0 (2)
C(10')	0·6009 (4)	0·1997 (4)	0·2923 (3)	3·8 (1)
C(11')	0·5845 (6)	0·2751 (5)	0·3329 (3)	5·4 (2)
C(12')	0·5750 (6)	0·2524 (6)	0·3945 (3)	6·7 (2)
C(13')	0·5829 (6)	0·1540 (6)	0·4154 (3)	6·2 (2)
C(14')	0·6008 (5)	0·0804 (5)	0·3761 (3)	5·6 (2)
C(15')	0·6083 (5)	0·1009 (5)	0·3141 (3)	5·0 (2)
C(16')	0·6197 (4)	0·1073 (4)	0·1246 (3)	3·6 (1)
C(17')	0·6175 (5)	0·0100 (5)	0·1451 (3)	4·6 (2)
C(18')	0·6238 (5)	0·0671 (5)	0·1037 (3)	5·4 (2)
C(19')	0·6308 (5)	0·0495 (5)	0·0422 (3)	5·6 (2)
C(20')	0·6324 (5)	0·0467 (5)	0·0222 (3)	5·7 (2)
C(21')	0·6275 (5)	0·1261 (5)	0·0628 (3)	4·8 (2)

Table 2. *Bond angles and* Br···Br *distances for the* $TeBr_6^{2-}$ *anion*

The e.s.d. of the last digit is shown in parentheses.

	Angle (°)	Br···Br (Å)
Br(1)–Te–Br(2)	178·15 (3)	5·389 (1)
Br(1)–Te–Br(3)	88·88 (2)	3·774 (1)
Br(1)–Te–Br(4)	92·13 (2)	3·898 (1)
Br(1)–Te–Br(5)	91·00 (2)	3·851 (1)
Br(1)–Te–Br(6)	87·64 (2)	3·731 (1)
Br(2)–Te–Br(3)	90·08 (2)	3·811 (1)
Br(2)–Te–Br(4)	88·95 (2)	3·789 (1)
Br(2)–Te–Br(5)	90·52 (2)	3·832 (1)
Br(2)–Te–Br(6)	90·84 (2)	3·835 (1)
Br(3)–Te–Br(4)	178·17 (3)	5·408 (1)
Br(3)–Te–Br(5)	89·41 (2)	3·796 (1)
Br(3)–Te–Br(6)	90·78 (2)	3·833 (1)
Br(4)–Te–Br(5)	89·05 (2)	3·799 (1)
Br(4)–Te–Br(6)	90·78 (3)	3·850 (1)
Br(5)–Te–Br(6)	178·63 (3)	5·394 (1)

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Structure of the β Phase of 4-Aminopyridinium Hemiperchlorate, $[H(C_5H_6N_2)_2]ClO_4$*

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Abstract. $M_r = 288{\cdot}5$, $P2_1/c$, $a = 7{\cdot}030\,(2)$, $b = 12{\cdot}924\,(4)$, $c = 14{\cdot}442\,(3)$ Å, $\beta = 97{\cdot}04\,(2)°$, $V = 1302{\cdot}2\,(6)$ Å^3, $Z = 4$, $D_x = 1{\cdot}472\,(1)$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0{\cdot}229$ mm^{-1}, $F(000) = 600$, $T = 193$ K, $R = 0{\cdot}064$ for 2445 reflections. Two NH_2py moieties are hydrogen bonded to form an $(NH_2py)_2H^+$ cation; these cations are hydrogen bonded *via* the amino groups to perchlorate anions. As in the α phase at 295 K, the N—H···N bond is asymmetric and nearly linear with an N···N distance of 2·697 (4) Å. The dihedral angle between the planes of the bridged pyridine rings is 89·8 (5)°.

Introduction. This work is a contribution to the study of strong N—H···N hydrogen bonds. Such hydrogen bonds have been observed in $(BHB)^+$ species with a captive proton between two heterocyclic bases B, such as pyridine or substituted pyridines (Dean & Wood, 1975; Grech, Malarski & Sobczyk, 1976). Geometrical parameters such as the asymmetry and angle of the hydrogen bridge were correlated to spectroscopic data in order to find a suitable form for a potential which would describe the dynamic behaviour of the proton in these bonds. A survey of diffraction studies of several homoconjugated cations reveals N—H···N geometries ranging from an asymmetric hydrogen bond, as in benzimidazole hemitetrafluoroborate [N···N = 2·787 (4) Å] (Quick, Williams, Borah & Wood, 1974), to a very short, symmetrical linear bond [2·635 (2) Å] in hydrogen diquinuclidin-3-one perchlorate (Rozière, Belin & Lehmann, 1982). These studies show that the geometry of the N—H···N bridge can be related to the N···N distance and to the environment around the bridging atoms.

Recently the crystal structure of the α phase of 4-aminopyridinium hemiperchlorate was determined by neutron diffraction at 295 K by Rozière, Williams, Grech, Malarski & Sobczyk (1980). The hydrogen bridge in the $(NH_2py)_2H^+$ cation was found to be asymmetric and nearly linear. Infrared spectra in the N—H···N region exhibited an anomalous temperature effect. A subsequent differential thermal analysis of this solid indicated a first-order phase transition at 290 K. A determination of the structure of the low-temperature β phase presently has been undertaken in order to elucidate the nature of the temperature effect attributed to the N—H···N bond.

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* Hydrogen Bond Studies. 148. Part 147: Hermansson, Thomas & Olovsson (1984).

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