

The yields of the alkazones are quite good from the three, four, and five carbon sugars. The yield from six carbon sugars is very poor, and the reaction in this case is quite slow. The reason for this difference between the five and six carbon sugars is not clear, but it appears to be associated with side reactions in the slower oxidations of the hexoses.

The complete oxidation of sugars by 1-methylphenylhydrazine explodes a myth based on intuition rather than fact. It also opens new vistas of theoretical and practical consequence and provides a facile synthetic entry to a unique class of highly unsaturated compounds.

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(10) Alfred P. Sloan Foundation Research Fellow.

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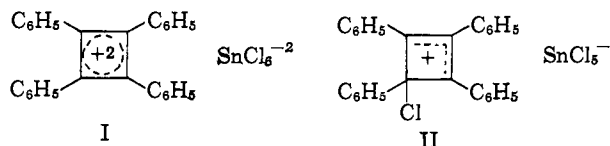
O. L. CHAPMAN<sup>10</sup>  
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RECEIVED DECEMBER 23, 1963

### The Crystal and Molecular Structure of a Carbonium Ion. 3-Chloro-1,2,3,4-tetraphenylcyclobutenium Pentachlorostannate

Sir:

The synthesis of the supposed dicarbonium ion salt, tetraphenylcyclobutenium hexachlorostannate (I), has recently been reported.<sup>1</sup> A three-dimensional structure analysis, by X-ray diffraction methods, of crystals of this material<sup>2</sup> has been carried out with the result that, at any rate in the solid state,<sup>3</sup> the compound in question is the isomeric monocation salt 3-chloro-1,2,3,4-tetraphenylcyclobutenium pentachlorostannate (II). Since, as far as the author is aware, the literature contains no reports of structure determinations either of carbonium ions<sup>4</sup> or of pentachlorostannate anions, some details of the structure of this salt may be of interest.



3-Chloro-1,2,3,4-tetraphenylcyclobutenium pentachlorostannate crystallizes in the orthorhombic system, in space group  $Pbca$ , with  $a = 19.50 \pm 0.03$ ,  $b = 27.42 \pm 0.05$ ,  $c = 10.55 \pm 0.02$  Å. There is one molecule per asymmetric unit containing 35 atoms, excluding hydrogen.

Some 3560 reflections, representing three-dimensional data to about  $1.1 \text{ \AA}^{-1}$ , were measured from a single crystal, sealed in a thin-walled glass capillary, with  $\text{Mo K}\alpha$  radiation. The intensity measurements were converted to structure amplitudes by means of a program specially written to handle the punched card output of the Hilger-Watts linear diffractometer used. No absorption corrections were applied.

The position of the tin atom in the unit cell was found from a study of the three-dimensional Patterson function and the rest of the structure determined from successive Fourier approximations to the electron density. The final electron-density distribution is shown in Fig. 1. Refinement was carried through in eight cycles of full matrix least-squares minimalization of the dif-

(1) H. H. Freedman and A. M. Frantz, *J. Am. Chem. Soc.*, **84**, 4165 (1962).

(2) Crystals suitable for X-ray work were kindly supplied by Dr. H. Freedman.

(3) H. H. Freedman and A. E. Young, *J. Am. Chem. Soc.*, **86**, 734 (1964).

(4) NOTE ADDED IN PROOF.—See, however, M. Sundaralingam and L. H. Jensen, *ibid.*, **85**, 3302 (1963).

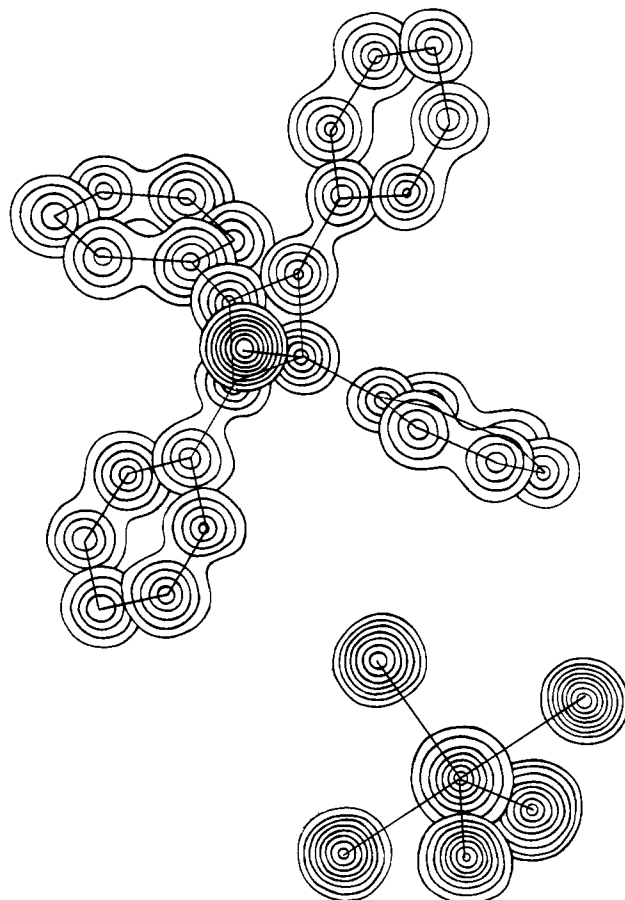


Fig. 1.—The electron density distribution over one formula unit in 3-chloro-1,2,3,4-tetraphenylcyclobutenium pentachlorostannate. The contours are at arbitrary, but equal, intervals for the various atomic species.

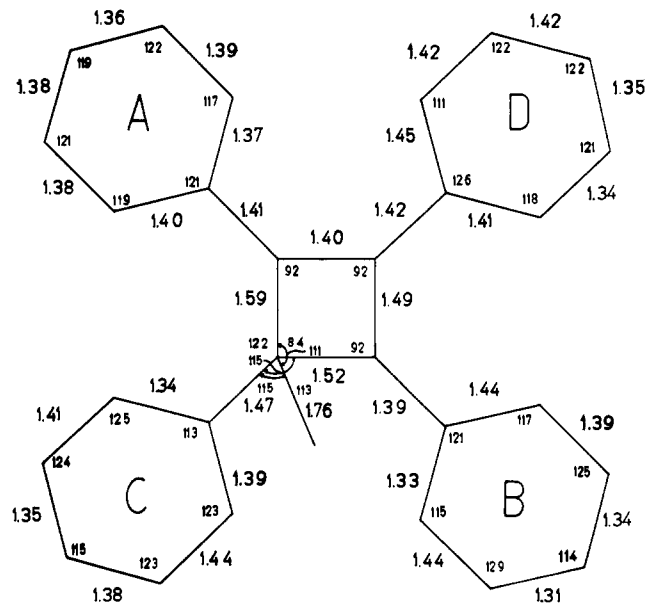


Fig. 2.—Bond lengths and angles in the cation of 3-chloro-1,2,3,4-tetraphenylcyclobutenium pentachlorostannate.

ferences between observed and calculated structure amplitudes. All 105 positional parameters, 35 isotropic thermal parameters, and 3 scale factors were varied in alternate cycles to give a value for  $R$  of 0.202 for all reflections. The values of the bond lengths and angles derived from the final positional coordinates of the cation are shown in Fig. 2. The standard deviation in

the position of a carbon atom, as calculated by the least-squares program ORFLS, is 0.04 Å., giving a standard error in a C-C bond length of about 0.06 Å. This high value, although not exceptional for a molecule of this complexity, is disappointing since it means that little significance attaches to the actual values found for the bond lengths in the cyclobutenium moiety. The observed values, however, do coincide closely with what might be expected in such an arrangement. Further refinement, now in progress, using anisotropic thermal parameters may well allow a more precise definition of the geometry of the molecule. At the present stage it is better to consider only the over-all structure of the molecule as significant.

The carbon atoms of the phenyl group A and the attached carbon atom of the four-membered ring lie in a plane given by the equation

$$0.6579X - 0.2730Y - 0.7018Z - 0.8697 = 0$$

Those of group B and the attached carbon atom lie in a plane of equation

$$0.6601X - 0.2545Y - 0.7067Z - 0.9817 = 0$$

effectively parallel to the first but separated from it by 0.11 Å. The phenyl group C and the corresponding carbon atom lie in a plane inclined at 83° to the previous two. The 3-chloro atom lies some 0.12 Å. from this plane. The corresponding group D forms a plane inclined at 57° to planes A and B and at 26° to ring C. The average deviation of atoms from these mean planes is 0.03 Å., the greatest 0.05 Å. There is no significant distortion of any of the phenyl groups from regular planar hexagons of side 1.39 Å.

The molecular shape implies that the delocalization of the positive charge in the cation takes place primarily over the two rings A and B. The tilt of ring D is that commonly found where overcrowding of phenyl rings is avoided by free rotation. The inclination of ring C is remarkable in that no free rotation has occurred about the single C-C bond linking it to the four-membered ring. It may be that this is dictated by the crystal packing or there may be some electronic interaction between the chlorine atom and the ring.

All the angles in the cyclobutenium ring are reduced from strain-free values by equal amounts. The bonds from the ring to the phenyl groups A, B, and D effectively bisect the external angles (C-C-C = 134 ± 7°).

The pentachlorostannate anion is in the form of a regular trigonal bipyramid. The Sn-Cl bond lengths are, in-plane, 2.30, 2.40, and 2.38 Å., perpendicular, 2.37 and 2.39 Å. ( $\sigma = 0.025$  Å.). The in-plane Cl-Sn-Cl angles are 114, 120, and 126°. The other angles lie in the range 90 ± 4°.

All intermolecular contacts are between anions and cations. The shortest intermolecular approach is between a chlorine atom of the  $\text{SnCl}_5^-$  anion and the 3-chloro atom where the separation is only 3.67 Å. This, however, is not significantly different from the sum of the van der Waals radii of the atoms concerned. The shortest C-Cl approach is 3.61 Å.

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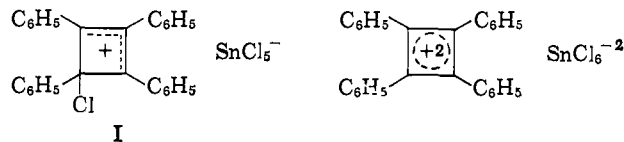
ROBERT F. BRYAN

RECEIVED OCTOBER 21, 1963

### Tetraphenylcyclobutenium Difluoroborate<sup>1</sup>

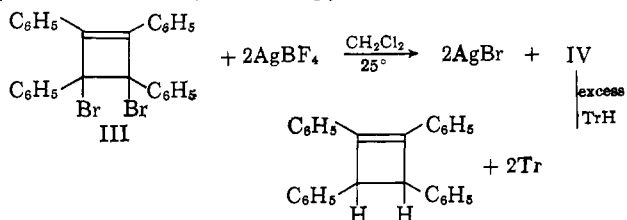
Sir:

The recent X-ray investigation by Bryan<sup>2</sup> leaves no doubt that the crystalline product obtained from 3,4-dibromotetraphenylcyclobutene (III) and tin tetrachloride is in fact the chloromonocation pentachlorostannate (I) and not the dication hexachlorostannate (II).<sup>3</sup> The possibility that solvation forces, absent

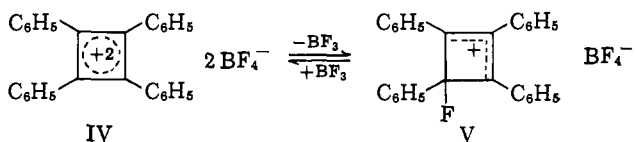


in the solid state, could be the decisive factor in the formation of the potential Hückel aromatic system II, coupled with the difficulties in clearly discriminating between penta- and hexacoordinate chlorostannate, led us to investigate fluoroborate as the stabilizing anion.

Reaction of III in methylene chloride solution with two moles of silver fluoroborate affords *two* moles of silver bromide (97%, >95% pure by X-ray) and a deep red solution (IV) which on treatment with excess tropilidene (TrH) yields tropylium fluoroborate (80%



of 2 equiv.) and tetraphenylcyclobutene<sup>3</sup> (70%). It is clear that both bromines have been displaced by fluoroborate and the transfer of hydride from two moles of tropilidene proves the absence of skeletal rearrangement and is consistent with the presence of the dication (IV).<sup>4</sup> However, this chemical evidence does not rule out the presence of the monofluorocation (V), formed at the expense of IV. The formation of V implies that IV is an exceedingly energetic species with a  $pK_R$  comparable to that of boron trifluoride, and in view of



the previous report that 3,4-dichlorotetramethylcyclobutene forms only the monocation in solution<sup>5</sup> and the present finding of Bryan,<sup>2</sup> it becomes obligatory to clearly demonstrate that dication IV is the major species present.

Experimental access to such a demonstration is available from the  $F^{19}$  n.m.r. spectrum of IV.<sup>6</sup> A methylene chloride solution of IV exhibits one singlet at +70.9 p.p.m. (relative to external  $\text{CF}_3\text{CCOH}$ ) and

(1) Presented in part at the 145th National Meeting of the American Chemical Society, New York, N. Y., Sept., 1963.

(2) R. F. Bryan, *J. Am. Chem. Soc.*, **86**, 733 (1964).

(3) H. H. Freedman and A. M. Frantz, Jr., *ibid.*, **84**, 4165 (1962).

(4) It has been established that hydride exchange with TrH occurs only with fully ionized carbonium ions, and we have verified this for the case of III, which undergoes no detectable exchange with TrH in  $\text{CH}_2\text{Cl}_2$  solution even after 3 days. However, structural evidence based on this hydride exchange reaction with the chlorostannate carbonium ion, which also forms cyclobutene in good yield,<sup>3</sup> becomes ambiguous inasmuch as the formation of (Tr)<sub>2</sub><sup>+</sup> $\text{SnCl}_6^{2-}$  from I requires the liberation of a mole of  $\text{SnCl}_4$ .

(5) T. J. Katz, J. R. Hall, and W. C. Neikam, *J. Am. Chem. Soc.*, **84**, 3199 (1962).

(6) We are greatly indebted to Dr. E. B. Baker, Physical Research Lab., The Dow Chemical Company, Midland, Michigan, for the  $F^{19}$  spectra.