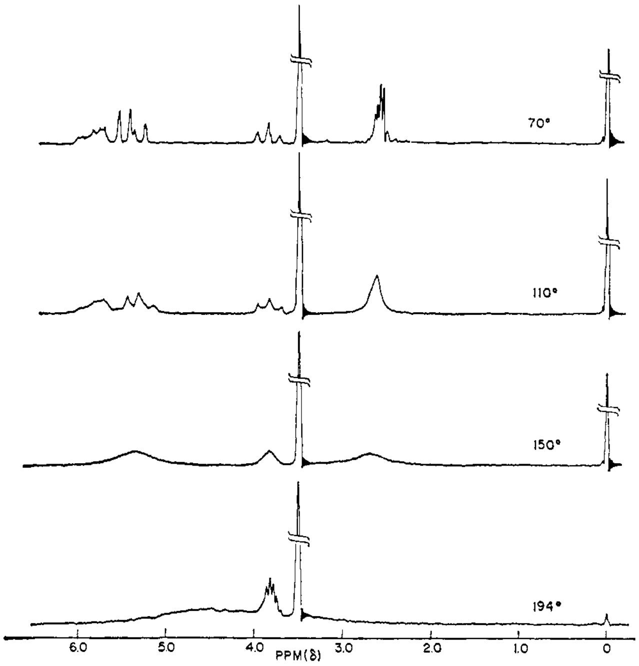
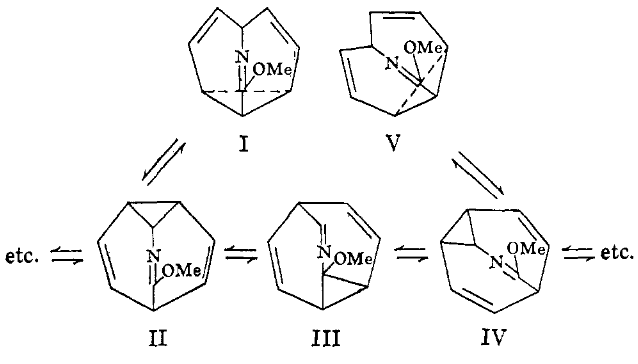


Figure 2. Nmr spectra of I in $Cl_2C{=}CCl_2$ solution at 70, 110, 150, and 194°.

tion which restricts the number of possible structures (21) to I. Spin-decoupling studies (Figure 1) demonstrated that the olefinic protons centered at $\delta \sim 5.8$ are strongly coupled to the cyclopropyl protons, whereas the protons giving the more well-resolved vinyl absorption at $\delta \sim 5.5$ interact substantially with the bridgehead proton. The bridgehead and cyclopropyl protons do not appear to be spin coupled.

When a sample of I in tetrachloroethylene solution is heated above 150° (Figure 2), the proton signals from different regions are seen to coalesce, the sole exception being the 3.8-ppm signal which, apart from coupling constants,[4] does not seem to be affected.[5]

The only averaging process that can produce this behavior is the combination of the two Cope rearrangements illustrated in I through V below. The two-step



conversion of II to the equivalent structure IV amounts formally to a rotation of the inner "spoke" on the outer "rim" by $2\pi/7$ radians, it being evident that repetition of such a process would average the rim positions and exclude the spoke.[6] Each of the seven equivalent structures thus generated is connected by a second Cope rearrangement of the type I $\rightleftarrows$ II to a more stable isomer whose structure corresponds to I, the unique proton in the averaging process thereby appearing in the bridgehead position.

The reason that such a relatively simple averaging process occurs is apparently the strong preference of the nitrogen atom for participation in a double bond. By precluding any rearrangement path that places the heteroatom in the three-membered ring, this maintains the integrity of the three skeletal atoms constituting the "spoke" above and limits the number of accessible structural arrangements to 28, seven each of types I, II, III, and seven apparently incidental ones related to III in the same way as I is to II.

**Acknowledgment.** We wish to express our gratitude to the National Institutes of Health and the Lilly Research Laboratories for their generous financial support of this work. We are grateful to Mr. H. Gisler for assistance in recording the spectra.

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(4) At 194° all other protons are scrambled at a rate about equal to that of the frequency separation between the vinyl and cyclopropyl regions. This is fast compared to any couplings to the bridgehead proton, so that it should appear as an eight-line pattern with the same total spread as the low-temperature triplet.

(5) When the sample is subsequently cooled to room temperature, the previous spectrum reappears without modification. The identical result was observed on returning the −90° sample to room temperature.

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(7) Alfred P. Sloan Foundation Fellow, 1965–1967; author to whom inquiries should be directed.

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## The Structure of a Dicarbonium Ion in the Crystalline State[1]

*Sir:*

There has been considerable controversy surrounding claims for the detection of dicarbonium ions in solution.[2,3] A report[4] of a tetraphenylcyclobutenium dicarbonium ion in solution was not substantiated by an X-ray study[5] on the crystal. More recently, Volz and Volz de Lecea[6] have reported the identification and isolation of a number of di- and tricarbonium ions as crystalline hexachloroantimonate salts. Hart and co-workers[7] have also reported studies on similar systems. As definite crystallographic evidence for the presence of a dicarbonium ion in the solid state would be of great value, we have undertaken an X-ray study of the compound reported to be I.[6] In the course of the later stages of our investigation, the crystal structure of the tetra-*p*-anisylethylene dication was described.[8]

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(1) Work supported in part by U. S. Public Health Service Grant GM 12470-03 and GM 722-05.

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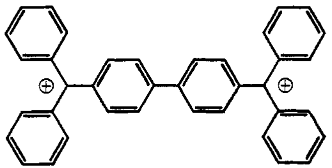

$2SbCl_6^{\ominus}$

I

The dark red crystals of $C_{38}H_{28}Sb_2Cl_{12}$ (mol wt 1153.2) belong to the monoclinic system, with $a = 16.67 \pm 0.03$, $b = 12.81 \pm 0.02$, $c = 21.52 \pm 0.02$ A; $\beta = 105°$. The space group is $P2_1/c$ with four $C_{38}H_{28}Sb_2Cl_{12}$ entities in the unit cell. Intensity data were obtained by visual estimates of equiinclination Weissenberg photographs (Cu $K\alpha$). A total of 3118 independent structure amplitudes was obtained. The structure was determined by the heavy atom method and, at the present stage of refinement, the crystallographic $R$ factor is 0.11 on all observed reflections. Further refinement is in progress, but the essential structural details are now evident and are summarized below. The estimated standard deviations in C–C bonds is 0.04 A and in C–C–C angles is 2.0°.

A drawing of the structure showing the atom numbering is given in Figure 1. The angles around atoms C(7) and C(26) range from 119 to 122°, with the sum of the angles around these atoms being 360.0° in each case. C(7) and C(26) each lie within 0.015 A from the plane defined by the three atoms to which they are bonded; these groups of four atoms must be considered planar within the accuracy of the analysis. A difference map shows no significant residual electron density at positions corresponding to bonding sites near C(7) and C(26). The foregoing evidence seems conclusively in favor of the existence of the dicarbonium ion species in the crystal.

The average C–C length involving either C(7) or C(26) is 1.44 A, shorter than the accepted C($sp^2$)–C($sp^2$) single bond distance of approximately 1.48 A.[9,10] Similar shortenings have been observed in the triphenylmethyl[11] and *sym*-triphenylcyclopropenium[12] cations. The angles of twist of the best planes of the phenyl rings A, B, and C (Figure 1) from the best plane through atoms C(1), C(7), C(8), and C(14) are 37, 27, and 30°, respectively, while the planes through the rings D, E, and F make angles of 36, 32, and 33° with the best plane through C(23), C(26), C(27), and C(33). These values compare with 31.8° reported for the triphenylmethyl cation[11] and 28.2° found in the tetra-*p*-anisylethylene dication,[8] but are considerably greater than the 7–21° range found in the *sym*-triphenylcyclopropenium system.[12]

The angle of twist between rings C and D is 40°, which is much greater than the value found in crystalline biphenyl (where the molecule is planar)[13] or the values (~20°) generally assumed[6,7,14] to prevail in solution, and may indicate that the dication in I behaves more as two separate triphenylmethyl cations than was hitherto anticipated.[6,7] It is interesting to note that a similarly large angle (41°) has been found between the two planes containing a central carbon atom and its bonded neighbors in the tetra-*p*-anisylethylene dicarbonium ion.[8]

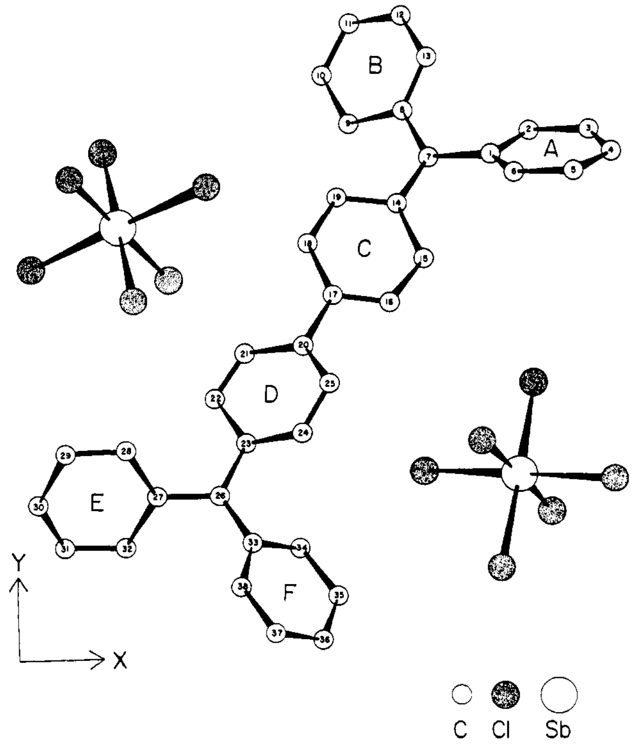

Figure 1. A view of the structure looking along the *c* direction.

The hexachloroantimonate anions are octahedral with a mean Sb–Cl distance of 2.355 A. The shortest contact between either C(7) or C(26) and a chlorine atom is 3.50 A involving C(7).

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## Stereospecific Exchange Reactions of Optically Active $R_3Si^*H(D)$ Catalyzed by Group VIII Metals[1]

*Sir:*

Recent studies of the silicon–hydrogen bond have shown that group VIII metal catalysts give two types of reactions that are highly stereospecific.[2,3] The hydro-

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(1) Current support of this work by the National Science Foundation, Grant GP-5662, is gratefully acknowledged. Preliminary studies were carried out at The Pennsylvania State University with support from Dow-Corning Corp.

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