

# The Crystal and Molecular Structure of 1,1,2,3,3,4,5-Heptamethyl-spiro[4.5]-6,9-diene-1-phosphetanium Bromide

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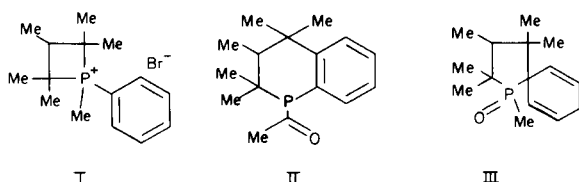
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Sir:

In recent years there has been controversy in the literature regarding the structure assignment of the rearrangement product obtained from a phosphetanium bromide (I). Cremer (1) assigned the fused aromatic structure II to the rearrangement product and Trippett (2) assigned the spiro-fused system III. In a later communication Cremer (3) concluded the product was III by a definitive labelling experiment. It was anticipated that the rearrangement product, whatever structure assignment was correct, would possess rather unusual molecular parameters because of the large number of methyl substituents, and therefore the crystal structure of the phosphonium bromide analogue, kindly supplied by Dr. Cremer, was undertaken.



The space group was unambiguously assigned as  $P2_1/c$  and least-squared lattice constants were determined on a General Electric XRD-5 diffractometer as  $a = 8.418(1)$ ,  $b = 12.768(1)$ ,  $c = 16.309(1)\text{\AA}$ , and  $\beta = 103.20(1)^\circ$ . Data were collected on a General Electric XRD-490 diffractometer using the stationary-counter, stationary-crystal method, balanced Ni and Co filters, and Cu radiation. Because the crystal decayed rapidly when irradiated, counting times were limited to 2 seconds per filter. A total of 1284 observed reflections, from 2026 measured to a  $2\theta$  limit of  $100^\circ$ , were corrected for  $\alpha_1$ - $\alpha_2$  splitting, absorption, and Lorentz-polarization in the usual manner.

The heavy atom coordinates were determined by Patterson methods and the remainder of the structure from

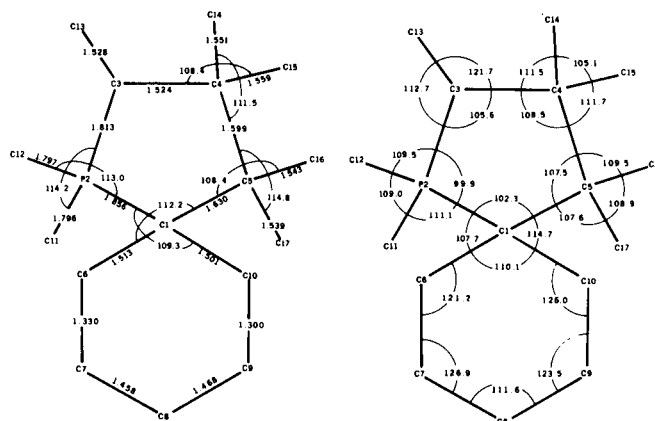


Figure 1

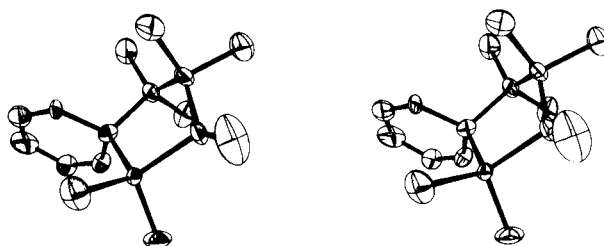


Figure 2

standard electron density syntheses. Using block-diagonal least-squares, with  $\frac{1}{2}$  weights, refinements were carried out assuming isotropic temperature factors for the hydrogen atoms and anisotropic temperature factors for the non-hydrogen atoms. Refinement continued until convergence at  $R = 0.05$ .

Figure 1 is a schematic drawing of the molecule indicating distances and angles. Figure 2 is an ORTEP stereo drawing. The molecule is indeed the spiro-fused system

but the previous assignment of methyl group positions was incorrect. Rather than the 2,2,3... arrangement, the 2,3,3... arrangement is shown to be correct. The fact that the six-membered ring is a diene and not an aromatic highly delocalized structure is obvious from the C6-C7 and C9-C10 bond distances of 1.33Å and 1.30Å, respectively. Some delocalization does seem apparent if one considers the other C-C distances within this ring which are significantly shorter than the standard C-C single bond distance, 1.54Å.

It was anticipated that the methyl substitution would cause the structure to possess unusual bond distances and angles. Indeed, Figure 1 does show that this is true but it is difficult to assess what portion of these distortions is due to the methyl groups and not to the x-ray data (as

previously mentioned, the crystal decayed rapidly and irregularly when irradiated). The average C-C external methyl distances are normal  $1.54 \pm 0.01\text{Å}$  but the internal ring C-C distances 1.52, 1.60, and 1.63Å are not those anticipated. The P-C distances are normal except P2-Cl, 1.86Å as opposed to the accepted literature value 1.80Å.

The crystal packing is such that no contact distances exist between non-hydrogen atoms less than 3.5Å.

#### REFERENCES

- (1) S. E. Cremer and R. J. Chorvat, *Tetrahedron Letters*, 413 (1968).
- (2) S. Trippett, W. Hawes, S. E. Fishwick, and J. Flint, *Chem. Commun.*, 1113 (1967).
- (3) S. E. Cremer, *Chem. Commun.*, 1133 (1968).