The Molecular structure of $(C_{14}H_{18}P_2)^{+2}$ $2Br^-$

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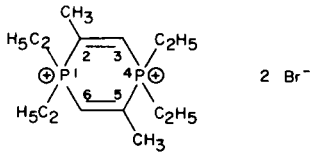
Sir:

The structure of the compound $(C_{14}H_{28}P_2)^{+2}$ $2Br^-$ has been shown to be 1,1,4,4-tetraethyl-2,5-dimethyl-1,4-diphosphoniacyclohexadiene-1,4-dibromide (I) by a single crystal x-ray diffraction study.



(I)

It has been predicted for the 1,1,2,4,4,5-hexaphenyl analogue of this compound (1,2) that delocalization of the π-electronic charge over the entire ring occurs. Support for this assumption is based upon ^{31}P nmr shifts which are positive (+3.5) indicating substantial shielding of the phosphorus nucleus whereas most simple phosphonium salts display ^{31}P shifts in the -20 to -30 cps region. (The ^{31}P nmr spectra are at 40.5 Mc/sec with the shifts in parts per million of methanol solution relative to an external standard of 85% phosphoric acid). Our x-ray data reported here, shows that this delocalization over the entire ring does not occur in the alkylated system (I).

This compound crystallizes in the space group $P2_1/c$ with two molecules in a unit cell of dimensions, a = 7.73, b = 14.76, c = 10.55 ± 0.02Å and β 124°55′ ± 5′. Refinement of the data from a single crystal of admittedly poor quality has reached a value of R = 0.16. A difference Fourier map at this stage shows no peaks greater than 1.5 e/Å^3 above background. The molecule has a center of symmetry and the six-membered ring is found to be planar within the estimated standard deviations of the atomic positions. The C_2-C_3 and C_5-C_6 distances are 1.30 ± 0.5Å proving that the ring is a diene. Phosphorus carbon distances within the ring are 1.82 ± 0.5Å whereas the phosphorus carbon distances outside the ring are 1.88 ± 0.05Å. All other carbon-carbon distances average to 1.55 ± 0.03Å. Bond angles throughout the structure conform to the expected values with the tetrahedral angles averaging 110 ± 2° and the angles around the sp^2 hybridized atoms averaging 120 ± 4°. Additional crystals of the compound, suitable for diffractometer studies, are now under preparation.

Acknowledgments.

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