

TABLE I  
ACTIVATION PARAMETERS FOR REACTIONS OF PHENOXIDE  
AND HYDROXIDE IONS WITH SULFONIUM IONS<sup>a</sup>

Reactants	$\Delta F^\ddagger$ at 80°, kcal. mole <sup>-1</sup>	$\Delta H^\ddagger$ , kcal. mole <sup>-1</sup>	$\Delta S^\ddagger$ , e.u.
$C_6H_5O^- + C_6H_5CH_2S(CH_3)_2^+$	26.5	25.0	-4.4
$HO^- + C_6H_5CH_2S(CH_3)_2^+$	27.4	25.9	-4.3
$C_6H_5O^- + (CH_3)_3S^+$	30.1	28.5	-4.6
$HO^- + (CH_3)_3S^+$	29.6	26.8	-7.9

<sup>a</sup> 60-80° for  $C_6H_5CH_2S(CH_3)_2^+$ , 80-100° for  $(CH_3)_3S^+$ .

is again more reactive than phenoxide ( $1.7 \times 10^{-6} M^{-1} \text{ sec.}^{-1}$ ). Heats and entropies are listed in Table I.

No  $\pi$ -complexing was detected between the initial reactants in solution. No maximum was observed in the ultraviolet or visible spectrum above 305  $m\mu$  with 0.12  $M$  phenoxide and 0.08  $M$  benzyl-dimethylsulfonium ion in 0.1 mm. cells. The region below 305  $m\mu$  was obscured by strong absorptions characteristic of the separate reactants.

Ross and Kuntz found that molecular complex formation retarded the reaction of aniline with 1-chloro-2,4-dinitrobenzene.<sup>4</sup> Perhaps the initial-state complexing is stronger than the extra interaction in the transition state because amino and nitro groups are closer together. On the other hand,  $\pi$ -complexing between phenoxide and benzyl-dimethylsulfonium ions might be expected to be stronger at the transition state, where the reactants are already bonded by one O...C bond and necessarily in close proximity.

Our results have no bearing on the question of whether a  $\pi$ -complex distinct from the transition state may be a discrete intermediate in the reaction.

(4) S. D. Ross and J. Kuntz, *J. Am. Chem. Soc.*, **76**, 3000 (1954).

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RECEIVED APRIL 10, 1962

#### STRUCTURE OF DIMETHYL PHOSPHINOBORINE TETRAMER

Sir:

The trimer and the tetramer of  $(CH_3)_2PBH_2$  have been prepared by Burg.<sup>1</sup> They exhibit unusual stability. It has been suggested that this stability of the boron-phosphorus bond arises in large part from the availability of  $d$  orbitals on the phosphorus atoms. The deviation of the B-P-B angle from a tetrahedral value in the structure of the trimer determined by Hamilton seems to support such a view.<sup>2</sup> Similar results now have been obtained for  $[(CH_3)_2PBH_2]_4$  by single crystal X-ray diffraction.

The tetramer crystallizes in the monoclinic space group Cc with four molecules per unit cell. The unit cell parameters are  $a = 21.49$ ,  $b = 6.04$ ,  $c = 17.89 \text{ \AA}$ . and  $\beta = 125^\circ 24'$ .

The coordinates of the phosphorus atoms were found from Patterson projections by hand-superposition techniques. Use of these positions in

(1) A. B. Burg and R. I. Wagner, *J. Am. Chem. Soc.*, **75**, 3872 (1953).

(2) W. C. Hamilton, *Acta Cryst.*, **8**, 199 (1955).

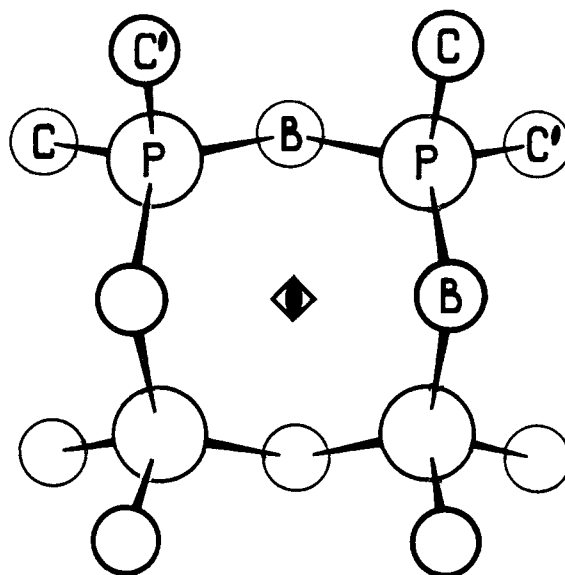


Figure 1.

conjunction with  $hkl$  data to construct a three-dimensional electron density map gave the coordinates of the remaining atoms. The hydrogen positions are still to be determined.

The molecule consists of an eight-membered ring with alternating boron and phosphorus atoms and two methyl groups on each phosphorus. The ring itself is puckered and exhibits  $D_{2d}$  symmetry (Fig. 1). At the present stage of refinement, with all atoms except hydrogen included, the agreement factor  $R = \Sigma ||Fo| - |Fc|| / \Sigma |Fo|$  is 0.18 for 528 observed reflections. Further refinement is still in progress on the CDC 1604 computer. Present values for some of the average bond angles and distances are B-P-B =  $125 \pm 1$ , P-B-P =  $104 \pm 2$ , C-P-C =  $103 \pm 2^\circ$ ; P-B =  $2.08 \pm 0.05$ , P-C =  $1.84 \pm 0.04 \text{ \AA}$ .

We wish to thank Dr. A. B. Burg for supplying us with samples of the tetramer and the Army Research Office for financial aid in the investigation. We are also indebted to the National Science Foundation for a fellowship to Paul Goldstein.

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RECEIVED MAY 16, 1962

#### MOLECULAR WEIGHT OF VIRUS BY EQUILIBRIUM ULTRACENTRIFUGATION

Sir:

In the past, viruses, because of their high molecular weight ( $5 \times 10^6$  to  $50 \times 10^6$ ), have not been studied by the standard equilibrium method. Since a value for the molecular weight,  $M$ , in the equilibrium sedimentation equation<sup>1</sup>

$$M = \frac{2RT \ln (f_2 c_2 / f_1 c_1)}{(1 - \bar{v} \rho) 4\pi^2 N^2 (x_2^2 - x_1^2)}$$

is inversely proportional to the square of the angular velocity,  $4\pi^2 N^2$ , where  $N$  is the number of

(1) T. Svedberg and K. O. Pedersen, "The Ultracentrifuge," Oxford University Press, New York, N. Y., 1940, p. 51.