

TABLE I
ACTIVATION PARAMETERS FOR REACTIONS OF PHENOXIDE
AND HYDROXIDE IONS WITH SULFONIUM IONS^a

Reactants	ΔF^* at 80°, kcal. mole ⁻¹	ΔH^* kcal. mole ⁻¹	ΔS^* , 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

^a 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 π -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.⁴ 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, π -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 π -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.¹ 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.² 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).

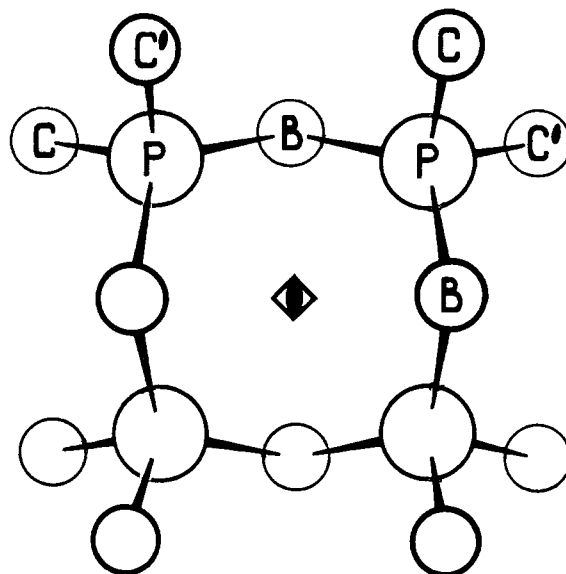


Figure 1.

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 ± 1 , P-B-P = 104 ± 2 , C-P-C = $103 \pm 2^\circ$; P-B = 2.08 ± 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 (5×10^6 to 50×10^6), have not been studied by the standard equilibrium method. Since a value for the molecular weight, M , in the equilibrium sedimentation equation¹

$$M = \frac{2RT \ln(f_2c_2/f_1c_1)}{(1 - \bar{v}\rho)4\pi^2N^2(x_2^2 - x_1^2)}$$

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

revolutions per second, it is clear that an accurate measurement of the instantaneous speed is essential at very low field strengths. In this equation, \bar{v} is the partial specific volume of the virus, ρ the density of the solution, f the activity coefficient at concentration c in g./100 ml., x the distance in centimeters of a position in the solution from the center of rotation, T the absolute temperature and R the molar gas constant.

The magnetically suspended ultracentrifuge² fulfills the requirement for very low speeds without rotor hunting. Accordingly, a detailed study of several viruses has been initiated. Results with southern bean mosaic virus (SBMV) and with bushy stunt virus (BSV) are here presented to establish applicability of this method.

Sedimentation was carried out in 3 mm. columns of solution by the two-speed method for rapid attainment of equilibrium.³ For SBMV, the initial speed was held at 15.0 rps. for 24 hours before decelerating to 10.5 rps. Equilibrium was attained within 5 hours after cutback in speed; the experiment was allowed to continue longer, but no change in the Jamin interference fringe pattern was observed. A plot of the logarithm of the concentration *versus* the square of the distance from the center of rotation was linear to the bottom of the cell. Using a value of $\bar{v} = 0.696$ ml./g.,⁴ $\rho = 1.0049$ g./ml. for the virus in 0.075 *M* KCl-0.005 *M* phosphate (K), pH 7.0 (total ionic strength = 0.10) and an initial virus concentration, c_0 , of 0.35% from an assumed specific refractive increment of 0.0019 ml./0.01 g. at 546 m μ , the apparent molecular weight of this preparation at 20.00 \pm 0.01° is 6.3×10^6 .

Linear $\ln c$ vs. x^2 plots at this temperature also were obtained with BSV in the same solvent. The apparent molecular weight, both at $c_0 = 0.12\%$ and 0.32% was 7.8×10^6 where \bar{v} was assumed to be 0.739 ml./g.⁵ In these experiments, the initial speed was held at 20.0 rps. for 22 hours for the lower concentration before decelerating to 13.9 rps., whereas for the higher concentration the same initial speed was held for 21 hours before decelerating to 12.4 rps.

The absence of upward curvature in the $\ln c$ vs. x^2 plots attests to the purity of the samples.⁶ Also, the schlieren patterns by velocity sedimentation in the Spinco Model E ultracentrifuge gave no indication of polydispersity. For the purpose of identification, the sedimentation coefficient corrected to that in water at 20° of SBMV (0.35%) was 117×10^{-13} sec. and that of BSV (0.12%) was 136×10^{-13} sec.

These data indicate that the magnetically suspended ultracentrifuge is very well suited for further thermodynamic studies on viruses and large polymers.

(2) J. W. Beams, R. D. Boyle and P. E. Hexner, *Rev. Sci. Instr.*, **32**, 645 (1961).

(3) P. E. Hexner, L. E. Radford and J. W. Beams, *Proc. Nat. Acad. Sci.*, **47**, 1848 (1961).

(4) G. L. Miller and W. C. Price, *Arch. Biochem.*, **10**, 467 (1946).

(5) A. S. McFarlane and R. A. Kekwick, *Biochem. J.*, **32**, 1607 (1938).

(6) H. K. Schachman, "Ultracentrifugation in Biochemistry," Academic Press Inc., New York, N. Y., 1959, p. 203.

It might be noted that for rotor speeds much below 10 rps. where the ratio of the gravitational to the centrifugal field no longer is small the centrifuge cell can be so hinged in the rotor that the flat surfaces of the cell windows automatically are approximately parallel to the resultant of the two fields in the cell.

We are indebted to Dr. Russell L. Steere of the U. S. Department of Agriculture, Beltsville, Maryland, for these samples of purified virus and to Mr. T. E. Dorrier for special assistance. This work was supported by a Grant (A-3118) from the U. S. Public Health Service; H. G. K. is an American Machine and Foundry Fellow, and R. F. B. is a postdoctoral fellow of the U. S. Public Health Service.

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RECEIVED APRIL 13, 1962

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COMMENTS ON THE SIGNS OF PROTON COUPLING CONSTANTS

Sir:

A number of recent papers¹ concerned with the spin-spin coupling of non-bonded protons have contained experimental results that appear to be inconsistent with certain quantitative aspects of the approximate valence-bond theory.² The essential point is that in the compounds studied the relative signs of the geminal (1,1) and vicinal (1,2) proton coupling constants were determined to be of opposite sign,³ while the simple fragment-model theory indicates that the constants should be of like sign if reasonable values for the bond angles are assumed.

Although a detailed comparison of theory and experiment is complicated by a number of uncertain factors (*e.g.*, effect of substituents, lack of knowledge of bond angles) the most important problem is that only *relative* signs are provided by the available data, in contrast to the absolute signs obtained from the calculations. Thus, the observed difference in relative signs for the geminal and vicinal couplings does not show which theoretical results are in disagreement with experiment. In this Communication, we wish to suggest a method for obtaining an indication of the absolute sign of a proton coupling constant

(1) R. R. Fraser, R. V. Lemieux and J. D. Stevens, *J. Am. Chem. Soc.*, **83**, 3901 (1961) (dioxolanes); C. A. Reilly and J. D. Swalen, *J. Chem. Phys.*, **35**, 1522 (1961) (epichlorohydrin); F. Kaplan and J. D. Roberts, *J. Am. Chem. Soc.*, **83**, 4668 (1961) (diethyl sulfite); R. Freeman, K. McLauchlan, K. Pachler and J. Musher, private communication (2,3-dibromopropionic acid); S. Manatt, private communication (alkyl ethers); H. S. Gutowsky, private communication (bridge in 2,2-metacyclophane).

(2) (a) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959); (b) H. Gutowsky, M. Karplus and D. M. Grant, *ibid.*, **31**, 1278 (1959); (c) S. Alexander, *ibid.*, **34**, 106 (1961).

(3) The opposite relative sign is in agreement with that found for the coupling between an atom X (X = Sn, P, Hg, etc.) and geminal *versus* vicinal protons. See, for example, P. T. Narasimhan and M. Rogers, *J. Chem. Phys.*, **31**, 1430 (1959); for X = F, the constants apparently have been shown to be of the same sign by S. L. Stafford and J. D. Baldeschwieler, *J. Am. Chem. Soc.*, **83**, 4478 (1961).