Both the *p*- and *m*-nitro-substituted phenolate anions at m/e 138 decompose further by loss of NO to form ions at m/e 108. This decomposition is substantiated in both compounds by the observation of a flat-top metastable ion at m/e 85 (calcd m/e 84.6). Our calculations of the kinetic energy released in these processes indicate that these daughter ions at m/e 108 are structurally different. The energy change in formation of the *p*-semiquinone anion radical is greater (0.3 ± 0.03 eV) than for the meta radical anion (0.13 ± 0.01 eV). Independent evidence for the stability of the *p*-semiquinone anion radical in the gas phase was found in our observation that in the negative-ion mass spectrum of benzoquinone the only ion formed is at m/e 108.[12,13] On the other hand, the proposed *m*-semiquinone anion radical decomposes further by loss of CO to go to an ion m/e 80. The observation that no peak at m/e 80 is found in the case of the para compound supports the view that the *p*-semiquinone anion radical is particularly stable. In fact, this is perhaps the most obvious difference between the two spectra. A proposed structure for this ion at m/e 80 is a cyclopentadienone ketyl. This process is substantiated by the observation of a flat-top metastable ion at m/e 59 (calcd m/e 59.2). The excess kinetic energy released in this process was found to be 0.15 ± 0.02 eV.

Finally, in both compounds ions are observed at m/e 122 due to loss of NO_2 from the parent ion. The ion at m/e 92 may be formed by the loss of NO from the m/e 122 ion. However, no metastable peak was observed for this process. The ion of greatest abundance in all the nitroaromatic compounds investigated is at m/e 46 due to the NO_2^- anion. This ion was extremely useful in calibration of our modified mass marker.[14]

Aplin, *et al.*, have concluded for a wide range of organic compounds including nitrobenzene that negative-ion mass spectrometry is "of limited value" for the determination of structure and molecular weight.[2] Our experience with nitroaromatics at least indicates that negative ion mass spectroscopy can provide complementary structural information to that obtained in positive ion mass spectrometry.

Acknowledgments. We wish to acknowledge a National Science Foundation grant for purchase of the mass spectrometer. C. L. B. wishes to thank the California State College at Los Angeles Foundation for partial support and W. P. W. thanks the Research Corporation. Both C. L. B. and W. P. W. wish to thank the Caltech President's Fund and NASA Contract No. NAS 7-100 for support.

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[13] P. M. Collins, L. G. Christophorou, E. L. Chaney, and J. G. Carter, *Chem. Phys. Lett.*, 4, 646 (1970).

[14] We thank Mr. H. Ouchi of the Hitachi Perkin-Elmer Co. for help in modifying our instrument.

* Address correspondence to this author.

Costello L. Brown
Department of Chemistry, California State College at Los Angeles
Los Angeles, California 90032

William P. Weber*
Department of Chemistry, University of Southern California
Los Angeles, California 90007

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Nucleic Acid Analogs. The Interaction of Poly-9-vinyladenine with Polyuridylic Acid

Sir:

The formation of complementary base-paired complexes between both ribo- and deoxypolynucleotides is a well-known phenomena.[1,2]

We now wish to report that base-paired complex formation can also occur between poly-9-vinyladenine[3] (PVAd) and polyuridylic acid (Poly U) even though the backbones of these polymers are considerably different. Continuous variation[4a–c] mixing experiments (Figure 1) at neutral pH in both 0.01 *M* Na^+ and 0.1 *M* Na^+ have shown that PVAd[4d] (M_n, 106,000) and Poly U[4e] (S_{20}, 6.06) form a stable complex with 1:1 stoichiometry in bases.

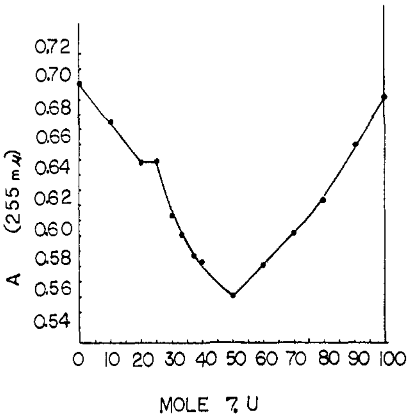

Figure 1. Continuous variation mixing curve for PVAd and Poly U in 0.01 *M* Tris buffer, pH 7.4, 0.01 *M* NaCl after 3 days at 25°.

The absorbance–temperature profile (Figure 2) indicated some cooperative character to the transition but it was not reversible. In the range of 0.005 *M* Na^+–0.1 *M* Na^+ the thermal transition curves remained monophasic and the dissociation temperature (T_m) varied linearly with the logarithm of the salt concentration. The slope of this plot (Figure 3) was 0.32 that of the double-stranded Poly U–Poly A[2] complex suggestive of a lower charge density[5,6] for the hybrid complex.

The intrinsic viscosities of the complex at neutral pH were 2.86 dl/g (0.1 *M* NaCl) and 4.35 dl/g (0.01 *M* NaCl). These values, because of their magnitude and low sensitivity to the change in salt concentration,[7] are consistent with a semirigid rod in analogy to DNA.

The circular dichroism[8] curve for this complex (λ_{max} 259 mμ, $R = +31.1 \times 10^{-40}$; λ_{min} 244 mμ, $R =$

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[1] G. Felsenfeld and H. T. Miles, *Annu. Rev. Biochem.*, **36**, 407 (1967).

[2] A. M. Michelson, J. Massoulie, and W. Gushlbauer, *Progr. Nucl. Acid Res. Mol. Biol.*, 6, 83 (1967).

[3] H. Kaye, *J. Polym. Sci., Part B*, 7, 1 (1969).

[4] (a) G. Felsenfeld and A. Rich, *Biochim. Biophys. Acta*, **26**, 457 (1957); (b) measured on a Cary 14 uv spectrophotometer; (c) equimolar (bases) solutions of PVAd and Poly U were prepared based on the dry weight of PVAd and the micromoles of phosphorus per milligram for the Poly U; (d) the molecular weight was determined with a Mechrolab osmometer; (e) the Poly U was purchased from Miles Laboratories, Inc., Elkart, Ind.

[5] L. Kotin, *J. Mol. Biol.*, 7, 309 (1963).

[6] C. Schildkraut and S. Lifson, *Biopolymers*, **3**, 195 (1965).

[7] J. Eigner and P. Doty, *J. Mol. Biol.*, **12**, 549 (1965).

[8] Measured on a Durrum Jasco J-20 ORD-CD spectropolarimeter.

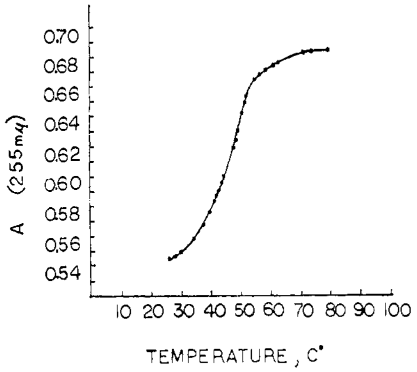

Figure 2. Absorbance–temperature profile for the 2 Poly U–PVAd complex in 0.01 *M* Tris buffer, pH 7.4, 0.01 *M* NaCl.

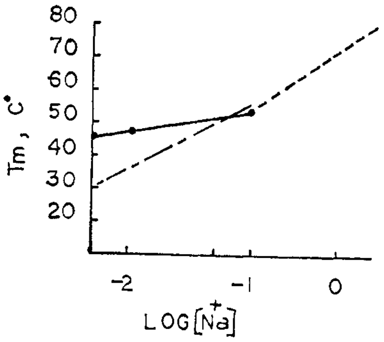

Figure 3. Melting temperature of the 2 Poly U–PVAd complex plotted as a function of log [Na⁺] (—). The data for the 2 Poly U–Poly A complex (- - - -) and the Poly U–Poly A complex (— — —) were taken from ref 2 (p 109) for comparison.

-3.3×10^{-40}; λ_{max} 222 mμ, $R = +3.6 \times 10^{-40}$; λ_{min} 204 mμ, $R = -3.9 \times 10^{-40}$) is nonconservative at the longer wavelengths and it is similar to that of the Poly U–Poly A complex[9] except for the more intense rotational strengths. These results may suggest that the base pairs are tilted and stacked in a helical array. In light of a recent paper by Johnson and Tinoco,[9] this interpretation must be viewed with caution, however.

If it is assumed that PVAd is largely syndiotactic,[10,11] then a triple-stranded structure (Figure 4a) with the uracils of two Poly U chains Watson–Crick base paired to every other adenine on the vinyl polymer is consistent with our results. Corey–Pauling models of this complex have shown that any base stacking distance between 3.4 and <5 Å is possible and that a helical conformation with about a 15-Å radius is likely. Base pairs tilted to the chain axis have also been shown to be possible with the models.

An alternative structure (Figure 4b), where one Poly U chain snakes along one side of the PVAd chain with alternating Watson–Crick and Hoogsten base pairs and alternating syn and anti uracils has also been constructed with Corey–Pauling models. This structure seems less likely than the first because of the destabilizing electrostatic repulsion of the phosphates, which are only ≈2.5 Å apart, and the unfavorable strain and entropy of a polynucleotide in a compressed snake conformation.

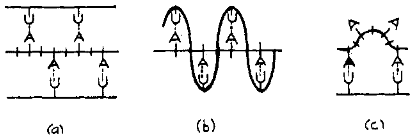

Figure 4. Schematic representations of (a) 2 Poly U–PVAd triple-stranded complex; (b) Poly U–PVAd double-stranded complex; and (c) double-stranded 25% uracil complex.

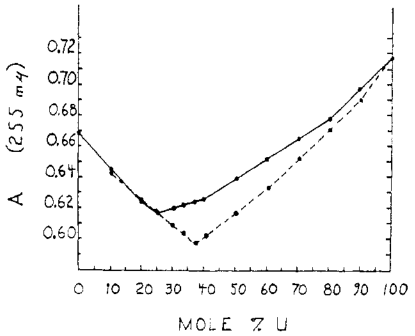

Figure 5. Continuous variation mixing curves for PVAd and Poly U in 0.001 *M* sodium cacodylate, pH 7.0 at 25° after 2 hr at 25° (—) and 24 hr at 4° (- - -).

Evidence for the formation of a second complex of PVAd with Poly U has been detected by observing a break at 25% uracil in the 0.01 *M* Na⁺ continuous variation mixing experiment (Figure 1). At lower salt concentration (0.001 *M* Na⁺) continuous variation mixing experiments[4a-c,e] (Figure 5) have clearly indicated formation of a second complex at 25% uracil. After standing for 24 hr at 4°, the 25% U complex was found to have changed into a stable apparent 37% U complex (Figure 5).

The CD for the 25% complex in 0.001 *M* Na⁺ is similar to that of 2 Poly U–PVAd except for a small positive shoulder at 276 mμ, λ_{max} 259.5 mμ, $R = +39.7 \times 10^{-40}$;[12] λ_{min} 244 mμ, $R = -10.6 \times 10^{-40}$; λ_{max} 222, $R = +9.8 \times 10^{-40}$; λ_{min} 204, $R = -21.3 \times 10^{-40}$. This shoulder is probably the same n–π* band observed in Poly dA.[13] A double-stranded structure (Figure 4c) containing PVAd loops is consistent with the experimental results. The nature of the apparent 37% complex[14] is a problem which will require further investigation.

Very recently a Japanese group of chemists has independently found that PVAd complexes with yeast RNA.[15] Our results, along with this fact, suggest that PVAd may be active in influencing replication and protein synthesis.

Acknowledgment. Grateful acknowledgement is given to the Texas A&M Research Council and the Robert A. Welch Foundation (Grant No. A-320) for partial support of this research. Acknowledgment

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(9) W. C. Johnson, Jr., and I. Tinoco, Jr., *Biopolymers*, 7, 727 (1969).

(10) This is a good assumption, as most free-radical polymerizations lead to a high percentage of syndiotactic placements.

(11) W. Cooper in "The Stereochemistry of Macromolecules," Vol. 2, A. D. Ketley, Ed., Marcel Dekker, New York, N. Y., 1967, p 219.

(12) The 276-mμ contribution was not subtracted from this transition.

(13) C. A. Bush and H. A. Scheraga, *Biopolymers*, 7, 395 (1969).

(14) Tentatively, this might be a mixture of structures **4a** and **4c** in the same complex.

(15) K. Kondo, H. Iwasaki, K. Nakatani, N. Ueda, K. Takemoto, and M. Imoto, *Makromol. Chem.*, 125, 42 (1969).

is also given to Dr. J. Nagyvary for the use of his Corey–Pauling models.

Howard Kaye
Department of Chemistry, Texas A&M University
College Station, Texas 77843

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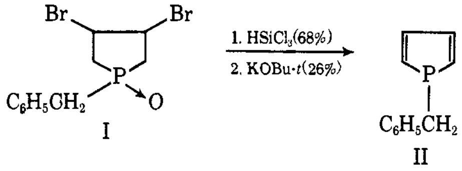
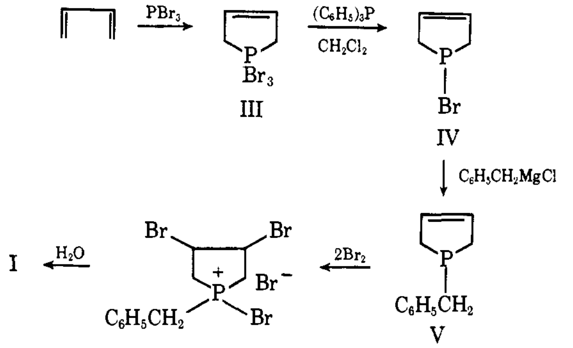
Molecular Structure of 1-Benzylphosphole by X-Ray Analysis[1]

Sir:

We wish to report the first determination of the molecular parameters of a phosphole. The synthesis of 1-benzylphosphole (II) resembled that already employed for 1-methylphosphole,[2] and made use of 1-benzyl-3,4-dibromophospholane oxide (I, mp 159–160°, analyzing correctly) as the key intermediate. As before, some of the corresponding 3-phospholene was formed but was removed on extraction with 2 *N* hydrochloric acid. Several methods of obtaining I were devised; that which proved most successful is shown below.





The reduction of the butadiene–phosphorus tribromide cycloadduct[3] (III) to form 1-bromo-3-phospholene [IV, 34%, bp 64–67° (27 mm), ^{31}P nmr signal −111.4 ppm relative to 85% phosphoric acid] is a new reaction of considerable synthetic value in phospholene chemistry; details on the procedure will be published elsewhere.[4] Compound V was identified by quaternization with methyl bromide to form the same salt obtained from 1-methyl-3-phospholene with benzyl bromide.[5]

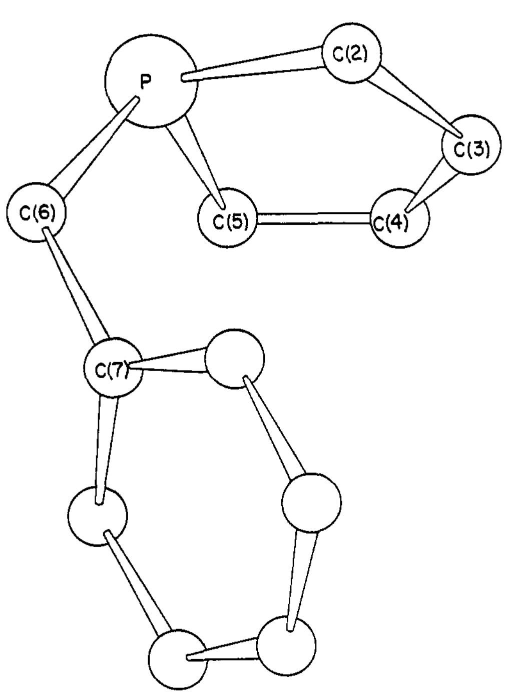


Figure 1. Molecular structure of 1-benzylphosphole. Molecular dimensions are $P-C_2 = 1.786$, $P-C_5 = 1.780$, $P-C_6 = 1.858$, $C_2-C_3 = 1.343$, $C_3-C_4 = 1.438$, $C_4-C_5 = 1.343$, $C_6-C_7 = 1.506$, mean phenyl $C-C = 1.382$ Å; $C_2PC_5 = 90.7°$, $C_2PC_6 = 106.1°$, $C_5PC_6 = 105.9°$, $PC_2C_3 = 109.9°$, $PC_5C_4 = 110.1°$, $C_2C_3C_4 = 114.1°$, $C_3C_4C_5 = 114.1°$, $PC_6C_7 = 116.4°$. Standard deviations of distances are ±0.005 Å for P–C bonds and ±0.006 Å for C–C bonds, while those for angles are ±0.2° for CPC angles and ±0.4° for CCC angles.

1-Benzylphosphole was considerably more stable than 1-methylphosphole and distilled without decomposition at 71–72° (0.2 mm); it had mp 34–34.5° and gave the correct analysis. It resembled 1-methylphosphole in having low basicity, a uv maximum in 95% ethanol at 286 mμ (log ε 3.65), and a ^{31}P nmr signal (−7.9 ppm) showing considerable deshielding relative to the corresponding 3-phospholene (V, +23.5 ppm). Its ring protons were similarly strongly deshielded (multiplet, δ 6.3–7.3 ppm, partly merged with phenyl protons), and the benzylic CH_2 group (δ 3.01 ppm) was not detectably coupled with phosphorus. Its mass spectrum confirmed its monomeric character (M^+ at *m/e* 174, 38.8% of $C_7H_7^+$ base peak). It is sensitive to oxygen and can be quaternized with alkyl halides.

Crystals of II obtained from a melt have cell dimensions $a = 17.62$, $b = 14.60$, $c = 7.67$ Å, and belong to the orthorhombic system with eight units of $C_{11}H_{11}P$ occupying general positions of space group *Pbca*. A total of 1351 independent structure amplitudes were derived from visually estimated intensities recorded by equiinclination Weissenberg photography of the *hk*0–7 layers. The structure was solved by the heavy-atom method and refined by full-matrix least-squares calculations[6] to the present conventional *R* of 0.073. The molecular dimensions are given in the legend of Figure 1.

Comparison of the phosphole dimensions with those of the heteroaromatics furan, pyrrole, and thiophene is of particular interest. The average $P-C_{sp^2}$ bond length 1.783 Å is significantly less[7] than the sum of the single-bond radii (1.10[8] and 0.74[9] Å, respectively), the

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[1] Supported in part by Public Health Service Research Grant No. CA-05507 from the National Cancer Institute.

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[6] Full details of the crystal structure analysis will be published elsewhere.

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[8] L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 224.

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