in these assemblies leads to rather inefficient isomerization with $\phi \leq 0.0015$.[25] The products recovered included *cis*-**1** and the phenanthrene derivative **2**, which was formed in other media only upon prolonged irradiation. Evidently in this medium, the quantum yield for formation of **2** from *cis*-**1** is higher than that for *trans*-**1** to *cis*-**1**. Phenanthrenes are known to form from *cis*-stilbenes by way of the photogenerated dihydrophenanthrene in the presence of an oxidizing agent.[26] Usually this occurs with a quantum yield much lower than that for trans to cis isomerization. With the assumption that photoisomerization of *cis*- to *trans*-**1** is more hindered than that of *trans*- to *cis*-**1**, the likelihood of *cis*-**1** cyclizing is probably high enough to prevent much of the intermediate *cis*-**1** from being seen in the analysis.

We have measured quantum yields for both fluorescence and trans to cis isomerization of **1** in a variety of media.[27,28] Table I shows that in homogeneous solution these values are very similar to those of *trans*-stilbene. Generally, photoisomerization of **1** decreases from CH_2Cl_2 solution to CTAB micelles to lipid vesicles above T_c to lipid vesicles below T_c, while fluroescence increases over the same range. This trend is expected since the range of media investigated represents an increase in viscosity seen by the stilbene group. In general, the observation that isomerization quantum yields are much higher in all the "liquid" media than for the supported multilayers is in accord with other evidence that suggests even for "well-organized" bilayer systems there is little order or alignment of the terminal ends of the alkyl chains above T_c.

The fluorescence and photoisomerization quantum yields obtained in liquid media (CH_2Cl_2) were used to calculate a decay ratio, (R), that is, the fraction of twisted intermediate states which isomerize to the cis form. The values of R show somewhat more complex behavior. In solution, micelles, and vesicles above T_c, R is the same within experimental error. In vesicles below T_c, R decreases noticeably. There are two possible explanations for this. First, the effective viscosity of the highly organized medium in vesicles below T_c may slow the motion of the stilbene to the twisted state to the extent that radiationless decay occurs before it has reached the totally twisted configuration. This would favor decay to the starting material. Alternatively, the excited stilbene may reach the twisted configuration, but then be forced back to the trans form by the more organized alkyl chains of the host surfactant which had been deformed by the twisting.

The results suggest that in vesicles above T_c the orderliness, or degree of alignment, of surfactant alkyl groups in the bilayer midsection near the alkyl terminus is similar to that in micelles. Little order is present, but there is sufficient viscosity to noticeably increase the fluorescence of **1**. Below T_c, this region appears to become considerably more highly ordered. That this is not simply a temperature effect can be seen by examination of the results for vesicles of DDAB/DCP, which at room temperature are similar to those for the other vesicles at 0 °C. This mixed vesicle is composed of surfactants, one containing a cationic and the other an anionic head group. Such a vesicle would be expected to have very tightly packed alkyl chains, and should be in the "gel" phase even at relatively high temperatures.

The results of this work are consistent with those of Czarniecki and Breslow,[15] who photolyzed a series of surfactant benzophenones in vesicle solutions. They found patterns of hydrogen abstractions from the surfactant alkyl chains which suggested considerable disorder in the vesicles above T_c. We feel, however, that due to the smaller perturbational effects and lower concentrations used, our probe is more appropriate for investigating conditons in vesicle solutions. We are currently engaged in further investigtions with shorter chain homologues of **1**, which should provide information about conditions at various positions along the surfactant chain, as well as in the central region. We hope to use this information to develop an order parameter similar to that found with deuterium quadrupole splitting studies.[29]

Acknowledgments. We are grateful to the National Science Foundation (Grant CHE 7823126) for support of this work.

---

[24] Fromherz, P. *Rev. Sci. Instrum.* **1975**, *46*, 1380.

[25] This represents the combied yield of *cis*-**1** and **2**. The maximum quantum yield for disappearance of *trans*-**1** is 0.007, which probably includes dimer formation as the major reaction.

[26] See, for example: Mallory, F. B.; Wood, C. S.; Gordon, J. T.; Lindquist, L. C.; Savitz, M. L. *J. Am. Chem. Soc.* **1962**, *84*, 4361, and references therein.

[27] Stockton, G. W.; Polnaszek, C. F.; Tulloch, A. P.; Hasan, F.; Smith, I. C. P. *Biochemistry* **1976**, *15*, 954.

[28] Incorporation into micelles was done by slowly dropping an appropriate amount of benzene stock solution of **1** into a warm stirred solution of 0.05 M CTAB. The solution was stirred overnight to evaporate the benzene. Incorporation into vesicles was done by mixing appropriate amounts of stock solutions of **1** and surfactant in benzene to give a ratio of 1:100. The mixture was evaporated to form a film on the sides of a vial, triply distilled water was added, and the mixture was sonicated with the immersible probe of a Heat Systems Model 220-F ultrasonicator until a clear solution resulted. This was centrifuged to remove titanium particles. Monolayers and multilayer assemblies were prepared by the method of Kuhn.[23] Solutions were degassed by passing N_2 purified by bubbling through chromous solution over stirred samples of the solution in an absorbance cell fitted with a stopcock. Irradiations were with a Schoeffel 1000-W Hg-Xe lamp fitted with a Bausch and Lomb monochromator set at 313 nm. Actinometry was with an Aberchrome reversible actinometer previously calibrated by ferrioxalate actinometry. Absorbance and fluorescence spectroscopy were performed with a Perkin-Elmer model 576 ST UV-vis spectrophotometer and a Hitachi MPF 2A spectrofluorimeter. Quantum yields were determined by analysis of the absorbance spectra before and after irradiation and supported by high-pressure liquid chromatography by using a Whatman 10/25 PAC column and Varian Varichrome UV-vis detector set at the isosbestic point for the trans to cis conversion of **1**.

[29] Fulbright Fellow, 1979; present address: Centro de Quimica Estrutural, Complexo Interdisciplinar, Instituto Superior Technico, Lisboa 1, Portugal.

John C. Russell, Silvia B. Costa,[29] Reginald P. Seiders
David G. Whitten*
Department of Chemistry, University of North Carolina
Chapel Hill, North Carolina 27514

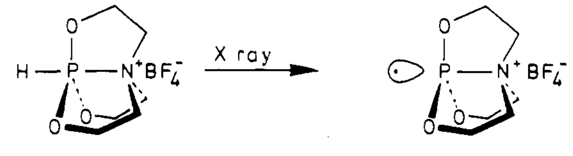
Received May 7, 1980

ESR Study of X-Irradiated $[HP(OCH_2CH_2)_3N]BF_4$: Phosphorus in a Trigonal-Bipyramidal Configuration with the Unpaired Electron in Apical Position

Sir:

Numerous studies concerning the structure of phosphoranyl radicals in solution have been published. Usually, a trigonal-bipyramidal (TBP) structure with the unpaired electron in an equatorial position has been assigned. However, these assignments cannot be conclusive since they are based on isotropic hyperfine coupling constants and theoretical predictions. The studies dealing with oriented phosphoranyl radicals in solid matrixes are very scarce, and from these studies conflicting ideas arise about the location of the unpaired electron. For $Ph_3\dot{P}Cl$, the unpaired electron is assumed to reside in an antibonding P–Cl orbital.[1] On the other hand, for $\dot{P}F_4$ and $Cl_3\dot{P}O^-$, a TBP structure has been found with the unpaired electron located in the axial axis.[2,3]

We now report the single-crystal study of the radical derived from $[HP(OCH_2CH_2)_3N]BF_4$ (**1**). In this compound, the



(1) (2)

phosphorus atom possesses a TBP configuration with the adjacent

---

[1] Berclaz, T.; Geoffroy, M.; Ginet, L.; Lucken, E. A. C. *Chem. Phys. Lett.* **1979**, *62*, 515–518.

[2] Hasegawa, A.; Ohnishi, K.; Sogabe, K.; Miura, M. *Mol. Phys.* **1975**, *30*, 1367–1375.

[3] Gillbro, T.; Williams, F. *J. Am. Chem. Soc.* **1974**, *96*, 5032–5038.

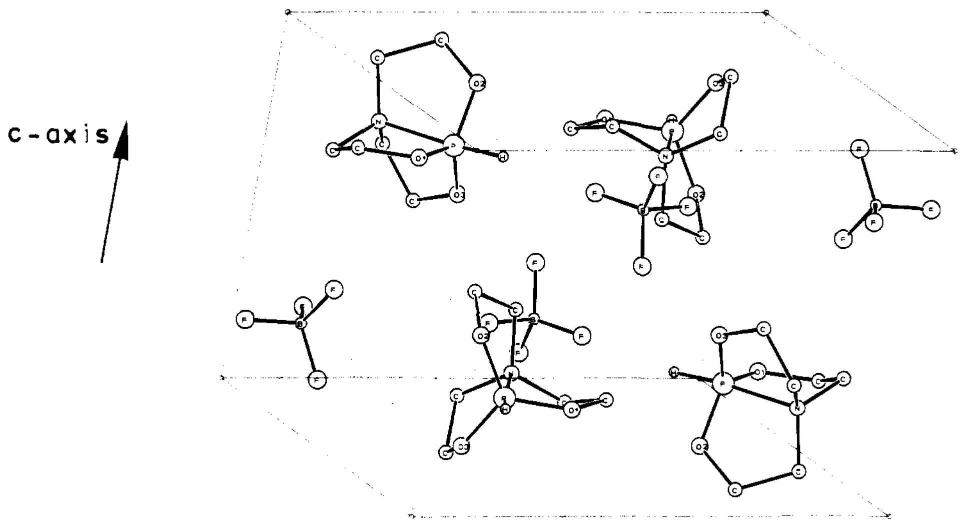


Figure 1.

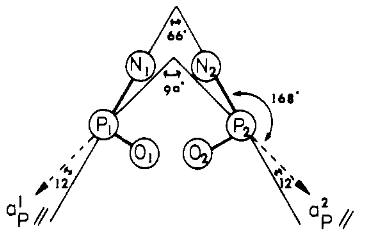


Figure 2.

hydrogen and nitrogen atoms in the apical positions as revealed by X-ray crystallography.[4] The ESR spectra of an X-irradiated single crystal[5] of **1** show that two identical radicals with an angle between their $a_{\mathrm{P}\parallel}$ components of 90 ± 2° are present on rotation about the crystallographic *c* axis. The occurrence of differently oriented radicals is consistent with the X-ray analysis of precursor **1**, which also shows two orientations in the unit cell (Figure 1).[6] However, in the latter case, the angles between the P–N linkages are 66°. Taking into account that two such molecules are mirror images (Figure 1), we may indicate the direction of the $a_{\mathrm{P}\parallel}$ components as shown in Figure 2. Thus, the structure of **2** can be decribed as a slightly deformed TBP configuration in which the unpaired electron and the nitrogen atom occupy the apical sites.

From the anisotropic contributions of the phosphorus hyperfine splittings, $a_{\mathrm{P}\parallel} = 888$ G and $a_{\mathrm{P}\perp} = 753$ G, one calculates[7] $a_{\mathrm{P,iso}} = 798$ G. These values indicate a phosphorus 3s spin density of 0.21 and a 3p spin density of 0.43, which gives a total spin density of 0.64 on phosphorus. The nearly isotropic ^{14}N splitting of 22 G indicates a spin density of 0.05 in its 2s orbital, a value which probably has a negative sign since it is the result of spin polarization in the P–N linkage. Apparently, the remaining spin density is distributed over the equatorial oxygen ligands.

The value of the ^{31}P isotropic coupling constant and the spin-density distribution in **2** are very similar to those observed for nonrigid phosphoranyl radicals.[8] Invariably, in the latter cases, a TBP structure is assigned in which the unpaired electron occupies an equatorial position. This structure seems to be supported by the p/s ratio, ~2, which is frequently observed. However, in spite of similar spectral data for **2**, this compound shows a quite different geometry, probably as a result of the molecular and crystal constraints.

The C_{3v} structure observed for **2** has also been found by Lucken et al.[1] for $\mathrm{Ph_3\dot{P}Br}$ and $\mathrm{Ph_3\dot{P}Cl}$. However, in these cases, the electron density is assumed to reside in the P–halogen σ^* orbital as inferred from the observed high spin density on the halogen. It is not clear whether the difference between these σ^*-C_{3v} structures and the present C_{3v} structure with the unpaired electron as the fifth apical ligand is the result of the electron-withdrawing character of the halogen in the former structures or the molecular constraints of the latter.

Recently, Roberts et al.[9] suggested that the relatively high rate of ligand exchange in $\mathrm{Me_2N\dot{P}(OEt)_2OBu}$-*t* can be explained by assuming a C_{3v} intermediate with the unpaired electron in an antibonding P–N orbital. However, we show here that radical **2** is the cyclic analogue of the intermediate mentioned, which has to be described as trigonal bipyramidal with the unpaired electron and nitrogen in the apical positions.

Acknowledgments. This investigation has been supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for the Advancement of Pure Research (ZWO).

---

(4) Clardy, J. C.; Milbrath, D. S.; Springer, J. P.; Verkade, J. G. *J. Am. Chem. Soc.* **1976**, *98*, 623-624.

(5) The single crystal of **1** was a gift from Dr. D. van Aken, Department of Organic Chemistry, Eindhoven University of Technology, The Netherlands.

(6) The ORTEP drawing of the unit cell of **1** was kindly delivered by Dr. G. J. Visser, Computing Centre of the Eindhoven University of Technology, The Netherlands.

(7) Symons, M. C. R. "Chemical and Biological Aspects of Electron-Spin Resonance Spectroscopy", Van Nostrand-Reinhold: New York, 1978; pp 26-30.

(8) Dennis, R. W.; Roberts, B. P. *J. Organomet. Chem.* **1973**, *47*, C8.

(9) Hay, R. S.; Roberts, B. P. *J. Chem. Soc., Perkin Trans. 2* **1978**, 770-778.

(10) For **2**, $g_\perp = 2.005$ and $g_\parallel = 1.988$.

J. H. H. Hamerlinck,* P. Schipper, H. M. Buck
Department of Organic Chemistry
Eindhoven University of Technology
Eindhoven, The Netherlands

Received March 3, 1980

A Three-Carbon Condensative Expansion. Application to Muscone

Sir:

Multicarbon ring expansions represent a relatively rare family of reactions. Recent emphasis on macrocyclic compounds heightens the interest in adjusting ring sizes by more than one carbon. We report (1) a simple approach to three-carbon ring expansions[1,2] involving a silyl-mediated fragmentation of β-keto

---

(1) Carlson, R. G.; Biersmith, E. L. *J. Chem. Soc. D* **1969**, 1049. Gutsche, C. D.; Redmore, D. "Carbocyclic Ring Expansion Reactions", Academic Press: New York, 1968; Chapter 10.