

from the relative sizes of the H, COOEt, and C(CH₃)₂-OH groups. The negative entropy of activation (Table I) is also in agreement with a planar transition state for bond shift.

The transition state for ring inversion is most likely the planar form A (Fig. 1) that has alternate single and double bonds; on the other hand, the planar transition state B for bond shift has equal bond lengths. From the rate data, it follows that the free-energy difference at -2° between A and B amounts to 2.4 kcal./mole, with A the more stable form.

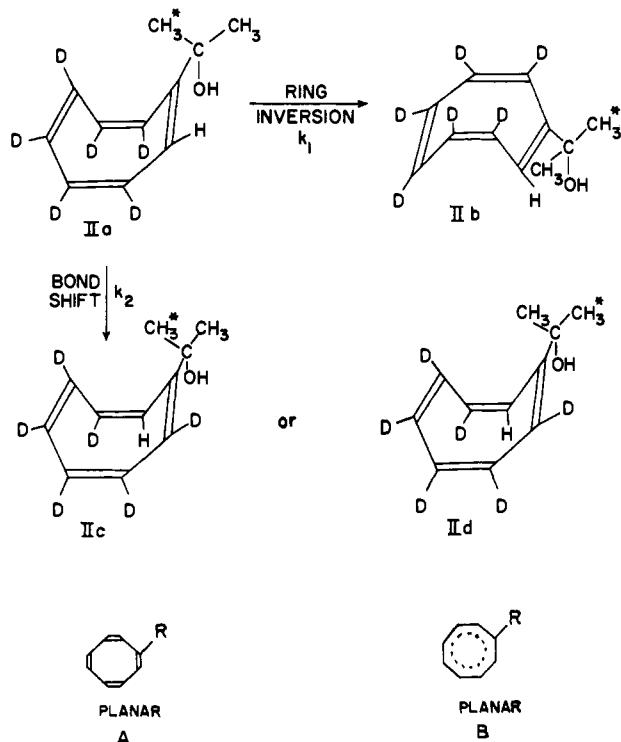


Figure 1.

Structure B has an orbitally degenerate π -electron system and, according to the Jahn-Teller theorem,⁹ a distortion of the molecule to make the carbon-carbon bonds alternately shorter and longer will result in stabilization. This stabilization energy can therefore be equated with the energy difference between A and B. Theoretical calculations of the difference in (potential) energy between A and B are rather discordant, although they all show that A should be the more stable state. The values are 44,¹⁰ 0.02,¹¹ and 1.31¹² kcal./mole. The last of these is in good agreement with the value obtained from the n.m.r. measurements.

The n.m.r. spectrum of I in carbon tetrachloride solution at -30° showed bands of equal intensities at τ 3.09 and 4.11 which are assigned to the ring protons in IIa and IIc (C(CH₃)₂OH replaced by COOEt in both cases), respectively. The two bands broadened at higher temperatures and coalesced at +40°. The rate constant for bond shift was obtained over the temperature range -15 to +75°. Values of ΔH^* and ΔS^* are given in Table I.

Further work on the n.m.r. spectra of cyclooctatetraene derivatives is in progress.

- (9) H. A. Jahn and E. Teller, *Proc. Roy. Soc. (London)*, **A161**, 220 (1937).
 (10) N. L. Allinger, *J. Org. Chem.*, **27**, 443 (1962).
 (11) C. A. Coulson and W. T. Dixon, *Tetrahedron*, **17**, 215 (1962).
 (12) L. C. Snyder, *J. Phys. Chem.*, **66**, 2299 (1962).

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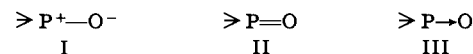
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The Amount of π -Bonding in Phosphorus-Oxygen and Sulfur-Oxygen Bonds

Sir:

The amount of π -bonding in phosphorus-oxygen bonds has remained questionable,¹ with various investigators preferring forms I, II, or III. A similar



question applies to sulfur-oxygen bonds. Use of 3d-orbitals in π -bonding at tetrahedral phosphorus seems hard to avoid in ylids considering qualitatively the unusual stability of certain Wittig reagents² and quantitatively the analysis of base-catalyzed hydrogen-exchange rates in onium ions of 2nd, 3rd, 4th, and 5th row elements.³ The dependence of C¹³-H coupling constants on the electronegativity of attached groups⁴ offers an ideal way to detect the amount of positive charge on phosphorus or sulfur and therefore the amount of p-d π -bonding in compounds with PO or SO bonds. Table I shows our results most important for the resolution of this problem for phosphine oxides, sulfones, and sulfoxides.

TABLE I
 C¹³-H COUPLING CONSTANTS

Compound	Solvent ^a	J^b	Compound	Solvent ^a	J^b
(CH ₃) ₃ N	Neat	131	(CH ₃) ₃ P:	Neat	127
(CH ₃) ₄ N ⁺ Cl ⁻	D ₂ O or CF ₃ CO ₂ H	145	(CH ₃) ₃ P ⁺	D ₂ O	134
(CH ₃) ₃ NH	D ₂ O or CF ₃ CO ₂ H	143	(CH ₃) ₂ P ⁺ H	CF ₃ CO ₂ H	135
(CH ₃) ₃ NO	D ₂ O	143	(CH ₃) ₂ PO	D ₂ O	129
(CH ₃) ₃ NOH	CF ₃ CO ₂ H	144	(CH ₃) ₂ P ⁺ OH	CF ₃ CO ₂ H	131
CH ₃ NO ₂	Neat	148	(CH ₃) ₂ S	Neat	138 ^c
			(CH ₃) ₂ S ⁺ I ⁻	CF ₃ CO ₂ H	146
CH ₃ CON(CH ₃) ₂	Neat	138	(CH ₃) ₂ SO	Neat	138 ^c
CH ₃ CON(CH ₃) ₂	D ₂ O	139	(CH ₃) ₂ SO ₂	D ₂ O	139 ^c

^a Where protonated onium ions were studied in CF₃CO₂H we may not have complete protonation; these samples were prepared by addition of 1 mole of the neutral substrate to at least 3 moles of CF₃CO₂H. ^b Coupling constants determined by linear measurement on an A-60 spectrometer at 250 c.p.s. sweep width; a check of some coupling constants using a frequency counter indicates that these values are probably good to ± 0.5 c.p.s. ^c The coupling constants for some of the compounds containing sulfur had been reported previously [N. Muller, *J. Chem. Phys.*, **36**, 359 (1964)], but these values are from our measurements.

The large increase in coupling constant in (CH₃)₄N⁺ over (CH₃)₃N is due to the greater electronegativity of N⁺ compared to >N:; when the nitrogen is more electronegative, it pulls more p-character into the carbon atomic orbital involved in the CN bond, leaving more s-character in the CH bonds leading to a larger C¹³-H coupling constant.⁴ A simple calculation based on the nearly linear relation of s-character to C¹³-H coupling constants⁵ indicates that the amount of

- (1) R. F. Hudson in "Advances in Inorganic and Radiochemistry," Vol. 5, Academic Press, New York, N. Y., 1963, pp. 368-377.
 (2) U. Schoellkopf, *Angew. Chem.*, **71**, 260 (1960).
 (3) W. von E. Doering and A. K. Hoffman, *J. Am. Chem. Soc.*, **77**, 521 (1955).
 (4) N. Muller and D. E. Pritchard, *J. Chem. Phys.*, **31**, 1471 (1959).
 (5) N. Muller and D. E. Pritchard, *ibid.*, **31**, 768 (1959).

p-character in the carbon atomic orbital of the CN bonds is 79% in $(\text{CH}_3)_3\text{N}$ and 87% in $(\text{CH}_3)_4\text{N}^+$. As expected, the $\text{C}^{13}\text{-H}$ coupling constant for trimethylamine N-oxide shows that the electronegativity of N^+ in the N-oxide is nearly the same as the electronegativity of N^+ in quaternary ammonium salts so that the NO bond in N-oxides must be almost completely $\text{N}^+\text{-O}^-$.

Pauling has concluded⁶ from the structural data on amides that the dipolar form, $\text{-C}=\text{N}^+\text{O}^-$, contributes 40% of the total structure of amides. A linear dependence of $\text{C}^{13}\text{-H}$ coupling constant on the amount of positive charge on nitrogen would therefore predict a coupling constant in N,N-dimethylamides of 138–139 c.p.s. depending on the $\text{C}^{13}\text{-H}$ coupling constant one uses for N^+ ; this is consistent with the data in Table I. Therefore, $\text{C}^{13}\text{-H}$ coupling constants can be used as an experimental measure of the amount of positive charge on atoms bonded to methyl groups; this, in turn, can give information concerning bonding and structure.

We therefore have used this method on simple compounds containing PO and SO bonds. Trimethylphosphine shows a lower coupling constant than trimethylamine, and the increase on quaternization is smaller, as might be expected, because the C-P bond should be about 0.4 Å. longer than the C-N bond. The $\text{C}^{13}\text{-H}$ coupling constant for trimethylphosphine oxide in D_2O solution (Table I) indicates that the phosphorus atom in $(\text{CH}_3)_3\text{PO}$ more closely resembles a neutral P than a P^+ . We conclude that the phosphorus atom in $(\text{CH}_3)_3\text{PO}$ is nearly neutral, and the PO bond is best described as a double bond.^{7,12}

Considerations of solvation and changes in hybridization at phosphorus reinforce this conclusion. (1)

(6) L. Pauling in "Symposium on Protein Structure," A. Neuberger, Ed., John Wiley and Sons, Inc., New York, N. Y., 1958.

(7) The conclusions in this paper are in agreement with some previous comments⁸ on P=O and S=O bonds but do not agree with the results of a recent paper⁹ on molecular orbital calculations on phosphoryl compounds. Our conclusion from experimental values should be more reliable. However, it may be useful to record S_{dpp} overlap integrals^{10,11} for P=O and S=O bonds: S_{dpp} (P=O, phosphine oxide) = 0.06; S_{dpp} (S=O, sulfoxide) = 0.06; S_{dpp} (S=O, sulfone) = 0.17. These values can be compared with S_{pp} (C=O, ketone) = 0.23. Overlap integrals using Slater orbitals are always approximate and are undoubtedly especially crude here because of the sensitivity of the integral to a small amount of positive charge on phosphorus or sulfur: e.g., S_{dpp} (P=O, phosphine oxide) = 0.11 if the P-O bond is one-fourth dipolar. Also, there is undoubtedly mixing of orbitals so that the phosphorus orbitals used in π -bonding will actually have some p-character.

(8) J. R. Van Wazer, *J. Am. Chem. Soc.*, **78**, 5709 (1956); D. P. Craig, A. Maccoll, R. S. Nyholm, L. E. Orgel and L. E. Sutton, *J. Chem. Soc.*, 332 (1954).

(9) E. L. Wagner, *J. Am. Chem. Soc.*, **85**, 161 (1963).

(10) H. H. Jaffé, *J. Chem. Phys.*, **21**, 258 (1953); interpolation makes the S values quite approximate but the error is undoubtedly no worse than the errors in the approximate descriptions of the wave functions.

(11) R. S. Mulliken, *J. Am. Chem. Soc.*, **72**, 4493 (1950).

(12) A referee has objected to our reasoning on the basis of Juan and Gutowsky's theory¹³ that unshared electron pairs on an atom bonded to C has a large effect on the $\text{C}^{13}\text{-H}$ coupling constant. This argument was advanced to explain data such as the change in $\text{C}^{13}\text{-H}$ coupling constant from 126 c.p.s. in ethane to 151 c.p.s. in methyl iodide despite the similarity of the electronegativities of iodine and carbon. However, it appears to us that Muller and Pritchard⁴ had a more reasonable explanation for this data; they attributed the larger-than-expected $\text{C}^{13}\text{-H}$ coupling constant in methyl iodide to the longer bond length which would allow more s-character to be in the C-H bonds. Muller and Pritchard's explanation is substantiated by the nearly linear dependence of $\text{C}^{13}\text{-H}$ coupling constants on electronegativity within any one row of the periodic table.¹⁴ Therefore our reasoning should be valid since it only involves comparisons of closely related compounds. The data for amides also substantiate our arguments.

(13) C. Juan and H. Gutowsky, *J. Chem. Phys.*, **37**, 2203 (1962);

(14) D. Tyssee, unpublished results.

Solvation: since the phosphine oxide spectrum was run in D_2O , H-bonding would tend to enhance the contribution of the polar form I. (2) Hybridization: one would expect a change in the hybridization of the atomic orbitals of phosphorus in the CP bonds from very little s-character in $(\text{CH}_3)_3\text{P}^{15}$ to about 25% s in $(\text{CH}_3)_3\text{PO}$. This would cause a change in orbital electronegativity which should lead to an increase in the $\text{C}^{13}\text{-H}$ coupling constant for $(\text{CH}_3)_3\text{PO}$ compared to $(\text{CH}_3)_3\text{P}$; the change from 25% s, $(\text{CH}_3)_4\text{C}$, to about 33% s, $(\text{CH}_3)_2\text{C}=\text{CH}_2$, is accompanied by an increase of about 2 c.p.s. in the $\text{C}^{13}\text{-H}$ coupling constants for the methyl groups.⁵

Although analogous compounds of the second row are not available for comparison with dimethyl sulfoxide and dimethyl sulfone, the conclusion seems clear; SO bonds are best described as double bonds.^{7,12} The results clearly show that the electronegativity of the sulfur atom in sulfoxides and sulfones closely resembles that in sulfides and is quite different from sulfonium salts. The result for dimethyl sulfone in D_2O is especially convincing.

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(15) The C-P-C angles in trimethylphosphine are about 100°: H. D. Springall and L. O. Brockway, *J. Am. Chem. Soc.*, **60**, 996 (1938).

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Acidity of Hydrocarbons. XV. Relative Stabilities of Triphenylmethyl and Bridgehead Triptycyl Carbanions¹

Sir:

As part of our continuing study of base-catalyzed proton-exchange reactions between hydrocarbons and cyclohexylamine we have found that cesium cyclohexylamide (CsCHA) is some $10^3\text{-}10^4$ times more reactive than lithium cyclohexylamide (LiCHA). Despite this large difference in reactivity, relative rates of exchange of different hydrocarbons are closely similar with both catalysts; for example, tritium exchange rates relative to benzene-*t* are given as follows for LiCHA at 50° and CsCHA at 25°, respectively: cumene- α -*t*, 0.84, 1.34; 2-phenylbutane-2-*t*, 0.31, 0.39°; toluene-2-*t*, 0.12, 0.20; toluene-3-*t*, 0.54, 0.57; toluene-4-*t*, 0.46, 0.48.³ Note that both benzylic C-T and aromatic C-T bonds are being compared. With the CsCHA catalyst we are able to study C-T bonds that exchange with LiCHA at inconveniently slow rates.

(1) This work was supported in part by grants from the Petroleum Research Fund of the American Chemical Society and by the Air Force Office of Scientific Research. Paper XIV: A. Streitwieser, Jr., and C. Perrin, *J. Am. Chem. Soc.*, in press.

(2) 0.43 at 50°.

(3) The LiCHA rates are based largely on work of R. G. Lawler, to be published soon.