

- (3) M. M. Crutchfield, C. H. Dungan, J. H. Letcher, V. Mark, and J. R. Van Wazer, "Topics in Phosphorus Chemistry", Vol. 5, M. Grayson and E. J. Griffith, Ed., Interscience, New York, N.Y., 1967.
- (4) M. Murray and R. Schmutzler, "Techniques of Chemistry", Vol. 4, Part 1, K. W. Bentley and G. W. Kirby, Ed., Wiley-Interscience, New York, N.Y., 1972.
- (5) G. Mavel, "Annual Reports on NMR Spectroscopy", Vol. 5b, F. Mooney, Ed., Academic Press, New York, N.Y., 1973.
- (6) S. O. Grim, E. F. Davidoff, and T. J. Marks, *Z. Naturforsch.*, **266**, 184 (1971), and references therein.
- (7) L. D. Quin and J. J. Breen, *Org. Magn. Reson.*, **5**, 17 (1973).
- (8) E. Fluck, J. Lorenz, *Z. Naturforsch.*, **226**, 1095 (1967).
- (9) All chemical shifts reported in this paper are positive if they are deshielded with respect to the reference (85% H_3PO_4).
- (10) D. Purdela, *Rev. Roum. Chim.*, **13**, 1415 (1968); D. Purdela, *J. Magn. Reson.*, **5**, 23 (1971).
- (11) Reference 3, p 216.
- (12) M. Haemers, R. Ottinger, D. Zimmerman, and J. Riese, *Tetrahedron*, **29**, 3539 (1973); see also, G. M. Blackburn, J. S. Cohen, and I. Weatherall, *ibid.*, **27**, 2903 (1971).
- (13) S. O. Grim, W. McFarlane, E. F. Davidoff, and T. J. Marks, *J. Phys. Chem.*, **70**, 581 (1966).
- (14) The effect of $d\pi-p\pi$ overlap is considered elsewhere: T. A. Albright, W. J. Freeman, and E. E. Schweizer, submitted for publication.
- (15) That an electronegative group produces a downfield chemical shift in ^{13}C NMR by withdrawal of electrons through the σ framework is well known. According to the Van Wazer-Letcher theory substitution of a group more electronegative than carbon is expected to cause an upfield chemical shift.¹⁶ But in fact, amino and alkoxy substituted phosphonium salts have resonances that are shifted to much lower fields compared to their alkyl analogs. This is a consequence, in part, of their assumption that $\langle r^{-3} \rangle_{3p} / \Delta E$ does not change for a given coordination number on phosphorus.¹⁷ The ΔE has been shown not to change significantly for a large variety of molecules in ^{13}C chemical shift calculations; however, $\langle r^{-3} \rangle_{2p}$ does undergo significant changes.¹⁸
- (16) Reference 3, p 180.
- (17) Reference 3, p 114.
- (18) J. A. Pople, *Mol. Phys.*, **7**, 301 (1964); B. V. Cheney and D. M. Grant, *J. Am. Chem. Soc.*, **89**, 5319 (1967); A. B. Strong, D. Ikenberry, and D. M. Grant, *J. Magn. Reson.*, **9**, 145 (1973).
- (19) R. L. Lichter and J. D. Roberts, *J. Am. Chem. Soc.*, **94**, 2495 (1972).
- (20) J. B. Stothers, "Carbon-13 NMR Spectroscopy", Academic Press, New York, N.Y., 1972.
- (21) Reference 20, pp 284 and 297.
- (22) D. B. Boyd and R. Hoffmann, *J. Am. Chem. Soc.*, **93**, 1064 (1971).
- (23) W. T. Raynes in "Specialist Periodical Reports on Nuclear Magnetic Resonance", Vol. 2, R. K. Harris, Ed., The Chemical Society, London, 1973, pp 27 and 28.
- (24) Reference 20, pp 377 and 378.
- (25) K. D. Summerhays and G. E. Maciel, *J. Am. Chem. Soc.*, **94**, 8348 (1972).
- (26) H. A. Bent, *Chem. Rev.*, **61**, 275 (1961), in particular p 281.
- (27) T. A. Albright, W. J. Freeman, and E. E. Schweizer, unpublished results.
- (28) P. Beck in "Organic Phosphorus Compounds", Vol. 2, G. M. Kosolapoff and L. Maier, Ed., Wiley-Interscience, New York, N.Y., 1972, p 189.
- (29) C. S. Labow and E. E. Schweizer, unpublished results.

Magnetic Resonance Studies. II. Investigation of Phosphonium Salts Containing Unsaturated Groups by ^{13}C and ^{31}P Nuclear Magnetic Resonance¹

Thomas A. Albright, Walter J. Freeman,* and Edward E. Schweizer*

Contribution from the Department of Chemistry, University of Delaware, Newark, Delaware, 19711. Received July 26, 1974

Abstract: The β carbon in vinyltriphenylphosphonium bromide is found to be substantially deshielded in the ^{13}C NMR. Other phosphonium salts containing unsaturated groups adjacent to phosphorus also show this effect. The extent of the deshielding of the β carbon is interpreted to be a consequence of $d\pi-p\pi$ bonding between phosphorus and carbon. The β carbon of propynyltriphenylphosphonium bromide resonates at 121.8 ppm which is also consistent with $d\pi-p\pi$ bonding. A comparison of the ^{31}P chemical shifts of Ph_3P^+-R with the methyl ^{13}C chemical shifts of $Me-R$ shows a consistent increased shielding in the ^{31}P NMR of the title compounds and is interpreted in light of $d\pi-p\pi$ overlap.

Phosphonium salts have enjoyed a great deal of emphasis as useful intermediates in organic synthesis.² Therefore, a detailed account of the electronic structure of these compounds may provide clues to the nature of the reactions in which phosphonium salts, and by analogy other organophosphorus compounds, participate. Vinylphosphonium salts undergo facile Michael addition with a wide variety of nucleophiles,³ thus it is expected that the β vinyl carbon exhibits some degree of positive charge. A rationale for this fact is the overlap of the π orbital of the vinyl group with an empty d orbital on phosphorus. Utilization of d orbitals on phosphorus is still a matter of controversy with conflicting ideas often being presented.⁴ There have been no studies of the ^{13}C and ^{31}P NMR of phosphonium salts containing unsaturated groups to date. Since ^{13}C and ^{31}P NMR are sensitive probes for the electronic environment about molecules,^{5,6} it is expected that an examination of these parameters can shed light on the nature of $d\pi-p\pi$ interactions and the bonding in the title compounds.

Results and Discussion

The results of this NMR study of phosphonium salts having the general structure $Ph_3P^+-RX^-$, where R is an unsaturated group and X^- is either a bromide or chloride anion,

are presented in Tables I, II, and III. Table I lists the ^{31}P chemical shifts, Table II lists the ^{13}C chemical shifts, and Table III gives the ^{31}P - ^{13}C couplings taken from the carbon NMR. The values reported for **5** and **10** in the ^{13}C NMR agree with those reported by Gray.⁷ Table IV compares the ^{13}C chemical shifts of several unsaturated phosphonium salts to model analogs.

^{13}C NMR. The α effect has been related to the electronegativity of a group and has been interpreted to be largely due to inductive effects.^{8,9} In the previous work substitution of a triphenylphosphonium group for a hydrogen in compounds of the type $Ph_3P^+-CHRR^1$ has been shown to produce an α effect for the carbon directly bonded to the phosphorus of 4 ppm downfield. On this basis, the electronegativity of the triphenylphosphonium group is estimated to be between that of hydrogen and a methyl group.¹⁰ Inductive effects for the β position are much smaller than those for the α position. The β carbon in vinyltriphenylphosphonium bromide is found to be deshielded by 22.4 ppm as compared to ethylene (Table IV). An inductive effect can only account for a minor portion of this relatively large shift. Magnetic anisotropy effects can also be discounted in interpreting this shift since they contribute only a few parts per million.¹¹

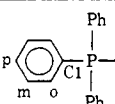
Table I. ^{31}P Chemical Shifts of Phosphonium Salts^a

No.	Compd	^{31}P	No.	Compd	^{31}P
1	$\text{Ph}_3\text{P}^+ - \text{CH}=\text{CH}_2 \text{Br}^-$	19.3	11	$\text{Ph}_3\text{P}^+ - \text{CH}_2\text{Ph Cl}^-$	23.2
2	$\text{Ph}_3\text{P}^+ - \text{CH}=\text{CH}-\text{Me Br}^-$ (trans)	18.7	12	$\text{Ph}_3\text{P}^+ - \text{CH}_2\text{C}_6\text{H}_4 - p\text{-Me Cl}^-$	22.7
3	$\text{Ph}_3\text{P}^+ - \text{CH}=\text{CMe}_2 \text{Cl}^-$	10.9	13	$\text{Ph}_3\text{P}^+ - \text{CH}_2\text{CH}=\text{CHPh Br}^-$	21.4
4	$\text{Ph}_3\text{P}^+ - \text{CH}=\text{C}=\text{CH}_2 \text{Br}^-$	18.7	14	$\text{Ph}_3\text{P}^+ - \text{CH}_2\text{C}\equiv\text{CH Br}^-$	21.3
5	$\text{Ph}_3\text{P}^+ - \text{Ph Br}^-$	22.5	15	$\text{Ph}_3\text{P}^+ - \text{CH}_2\text{C}\equiv\text{CH Br}^-$	22.0 ^a
6	$\text{Ph}_3\text{P}^+ - \text{C}\equiv\text{C}-\text{Me Br}^-$	5.3	16	$\text{Ph}_3\text{P}^+ - \text{CH}_2\text{OMe Cl}^-$	17.6
7	$(n\text{-Bu})_3\text{P}^+ - \text{Et Br}^-$	36.6 ^b	17	$\text{Ph}_3\text{P}^+ - n\text{-Bu Br}^-$	24.1
8	$(n\text{-Bu})_3\text{P}^+ - \text{CH}=\text{CH}_2 \text{Br}^-$	27.4	18	$\text{Ph}_3\text{P}^+ - n\text{-Bu Br}^-$	23.4
9	$(n\text{-Bu})_3\text{P}^+ - \text{CH}=\text{CHMe Br}^-$ (trans)	25.4	19	$(n\text{-Bu})_3\text{P}^+ - \text{Bu Br}^-$	33.9 ^b
10	$\text{Ph}_3\text{P}^+ - \text{CH}_2\text{CH}=\text{CH}_2 \text{Br}^-$	20.8	20	$(n\text{-Bu})_3\text{P}^+ - \text{CH}_2\text{CH}=\text{CH}_2 \text{Br}^-$	31.6

^a This represents a calculated value for CDCl_3 which was obtained by taking the difference of the chemical shifts for $\text{Ph}_3\text{P}^+ - n\text{-Bu}$ in CDCl_3 and CDCl_3 -trifluoroacetic acid solutions (17 and 18) and obtaining a solvent correction that was added to 14. ^b Values taken from S. O. Grim et al., *J. Phys. Chem.*, 70, 581 (1966).

Table II. ^{13}C Chemical Shifts of Phosphonium Salts^a

Compd	No.	Carbon chemical shift, ppm										
		1	2	3	4	5	6	Cl	o	m	p	
$\text{Ph}_3\text{P}^+ - \text{CH}=\text{CH}_2 \text{Br}^-$	1	119.2	145.2						117.2	133.9	130.7	135.5
$\text{Ph}_3\text{P}^+ - \text{CH}=\text{CH}-\text{Me Br}^-$ (trans)	2	110.1	159.5	21.7					118.0	133.7	130.5	135.2
$\text{Ph}_3\text{P}^+ - \text{C}(\text{Me})_2 \text{Cl}^-$	3	102.4	172.0	29.9	24.8				119.4	133.2	130.6	134.8
$\text{Ph}_3\text{P}^+ - \text{CH}=\text{C}=\text{CH}_2 \text{Br}^-$	4	75.3	218.3	80.3					118.2	133.9	130.4	135.4
$\text{Ph}_3\text{P}^+ - \text{Ph Br}^-$	5								117.4	134.7	130.9	135.9
$\text{Ph}_3\text{P}^+ - \text{C}\equiv\text{C}-\text{Me Br}^-$	6	60.4	121.8	7.4					118.3	133.1	130.4	135.9
$(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2)_3\text{P}^+ - \text{CH}=\text{CH}_2 \text{Br}^-$	8	119.0	141.2	19.3	23.6	24.0	13.6					
$\text{Ph}_3\text{P}^+ - \text{CH}_2\text{CH}=\text{CH}_2 \text{Br}^-$	10	28.6	126.3	123.1					117.7	133.9	130.4	135.1
$\text{Ph}_3\text{P}^+ - \text{CH}_2\text{C}\equiv\text{C}-\text{H Br}^-$	14	17.0	70.1	77.0					117.5	134.3	131.3	136.8

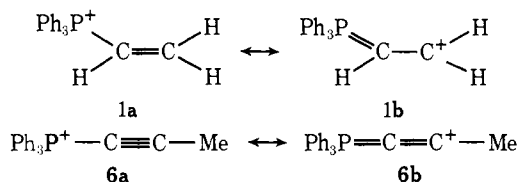
^a The numbering system is as follows:  except as noted. All compounds were run in CDCl_3 except 14 which was run in

trifluoroacetic acid- CDCl_3 solution and referenced to internal TMS.

Although the electronegativities of a triphenylphosphonium group and a methyl group are comparable, the effects of the two substituents on the chemical shift of a β vinyl carbon are quite different. As can be seen in Table IV, the β carbon of propene resonates at 115 or 7.8 ppm upfield from that of ethylene, whereas the β carbon of vinyltriphenylphosphonium bromide is found at 145.2 or 22.4 ppm downfield from ethylene. In the absence of $d\pi$ - $p\pi$ overlap between phosphorus and carbon, the triphenylphosphonium group could be expected to show an effect similar to that of a methyl group. Charge polarization via hyperconjugation is expected to be important for compounds such as propene,¹² leading to increased electron density at the β carbon. The large downfield shift found for the β carbon of vinyltriphenylphosphonium bromide serves to point out that while such effects may be operative in vinylphosphonium salts, they are not dominant.

The cyano group in acrylonitrile provides a better model for the effect of a triphenylphosphonium group, since the deshielding of the β carbon is a result of the interaction between the π orbitals of the vinyl and cyano groups. In an analogous fashion, the π bonds in **1** through **6** and **8** (Table II) donate electron density into empty d orbitals on phosphorus and are therefore responsible for the large downfield shift seen for the β carbons. Thus, $d\pi$ - $p\pi$ conjugation contributes significantly to the ground state for these compounds with resonance structures **1b** and **6b** considered to be important.

C2 in **6b** should also exhibit a low field chemical shift relative to C2 in **6a**. Inspection of the ^{13}C chemical shifts for propynyl substituted compounds in Table IV, provides a dramatic illustration of this phenomena with the β carbon



of propynyltriphenylphosphonium bromide deshielded 42.6 ppm from C2 of propyne. The methyl group in **6** is deshielded compared to that of propyne (Table IV). This is seen to be consistent with the contribution of resonance structure **6b**, since the ring current of a double bond deshields relative to that of a triple bond.¹³ It is also seen from Table II that both the ortho and para resonances are shifted to lower fields in the triphenylphosphonium groups. Thus $d\pi$ - $p\pi$ bonding with the phenyl substituents is significant for triphenylphosphonium salts.

Comparing the β vinyl ^{13}C chemical shifts in **1** and **8** (Table II), it is seen that $d\pi$ - $p\pi$ overlap of the vinyl substituent with phosphorus is similar. This also supports the notion that anisotropy of the phenyl groups in **1** does not produce the deshielding of the β vinyl carbon. The β vinyl carbon in 1-phenyl-2-phospholene 1-oxide is also found to be shifted to low fields relative to the α vinyl carbon.¹⁴

Phosphorus-Carbon Coupling. An examination of the ^{31}P - ^{13}C coupling constants in Table III shows that $^1J_{^{31}\text{P}-^{13}\text{C}}$ for sp^2 substituents is larger than that for sp^3 hybridized substituents, e.g., compare **1** and **10**. Also in **6** where the hybridization of one of the ligands is sp , the coupling constant increases dramatically. There are also many reversals in the magnitude of the couplings making a correlation to $^1J_{^{13}\text{C}-\text{H}}$ appear to be fruitless as shown in the pre-

Table III. ^{31}P - ^{13}C Coupling Constants^a

Compd	No.	^{31}P - ^{13}C coupling constants ^a										
		1	2	3	4	5	6	C1	o	m	p	
$\text{Ph}_3\text{P}^+-\text{CH}=\text{CH}_2 \text{ Br}^-$	1	80.3	<i>b</i>					90.3	10.5	12.9	3.2	
$\text{Ph}_3\text{P}^+-\text{CH}=\text{CHMe} \text{ Br}^-$	2	86.1	2.6	19.9			90.7	10.5	12.9	2.9		
$\text{Ph}_3\text{P}^+ \begin{matrix} \text{C}=\text{C} \\ \text{H} \quad \text{Me} \\ \text{Me} \end{matrix} \text{ Cl}^-$	3	89.4	1.2	18.6	7.7		89.5	10.6	12.8	2.4		
$\text{Ph}_3\text{P}^+-\text{CH}=\text{C}=\text{CH}_2 \text{ Br}^-$	4	93.3	1.3	14.7			91.4	10.6	13.2	2.8		
$\text{Ph}_3\text{P}^+-\text{Ph} \text{ Br}^-$	5						89.8	10.2	12.8	2.9		
$\text{Ph}_3\text{P}^+-\text{C}\equiv\text{C}-\text{Me} \text{ Br}^-$	6	191.7	33.0	3.8			100.5	12.4	14.2	3.0		
$(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2)_3\text{P}^+-\text{CH}=\text{CH}_2 \text{ Br}^-$	8	72.6	<i>b</i>	48.8	1.8	9.0	<i>b</i>					
$\text{Ph}_3\text{P}^+-\text{CH}_2\text{CH}=\text{CH}_2 \text{ Br}^-$	10	49.7	13.4	9.8			85.9	9.8	12.4	2.6		
$\text{Ph}_3\text{P}^+-\text{CH}_2\text{CHC}\equiv\text{C}-\text{H} \text{ Br}^-$	14	58.6	12.8	9.6			88.4	10.1	13.2	3.0		

^a The numbering system is the same as in Table I. The digital resolution was ± 0.1 Hz. ^b Unresolved coupling.

Table IV. Comparison of the ^{13}C Chemical Shifts for Unsaturated Model Compounds

Compd	X	Carbon		
		1	2	3
$\text{X}-\text{CH}=\text{CH}_2$	H ^a	122.8	122.8	
	Me ^a	133.1	115.0	
	CN ^a	107.7	137.8	
	P ⁺ Ph ₃	119.2	145.2	
$\text{X}-\text{CH}=\text{CHMe}$ (trans)	Me ^b	125.8	125.8	
	CN ^c	102.1	150.8	
	P ⁺ Ph ₃	110.1	159.5	
	H ^d	66.9	79.2	-1.9
$\text{X}-\text{C}\equiv\text{C}-\text{Me}$	Me ^d	72.6	72.6	-0.8
	C(O)Me ^e	87.0	97.4	
	P ⁺ Ph ₃	60.4	121.8	7.4

^a Reference 5, p 184. ^b Reference 5, p 70. ^c Reference 5, p 187. ^d A. B. Strong, D. Ikenberry, and D. M. Grant, *J. Magn. Reson.*, 9, 145 (1973). ^e D. D. Traficante and G. E. Maciel, *J. Phys. Chem.*, 69, 1348 (1965), for *n*-BuC \equiv CC(O)Me.

vious paper of this series.¹ This has also been noted by Gray in an NMR study of another series of phosphonium salts.⁷ Further insight into the nature of phosphorus coupling constants is hindered as there has been no theoretical study for the coupling of phosphorus where the use of d orbitals has been included.

It is noted that there is much more of a change in $^1J_{^{31}\text{P},^{13}\text{C}}$ for the coupling of the C1 phenyl carbon of the triphenyl substituents (Table III) in this series of compounds (14.6 range) than previously reported for compounds of the type $\text{Ph}_3\text{P}^+-\text{CH}_2\text{RX}^-$.⁷

Alkyltriphenylphosphonium salts have a coupling between phosphorus and the C1 phenyl carbon of 80.1 to 88.6 Hz.¹ However, vinyl substituted triphenylphosphonium salts exhibit $^1J_{^{31}\text{P},^{13}\text{C1 phenyl}} = 89.5$ -91.4 Hz and propynyltriphenylphosphonium bromide (6) has the largest $^1J_{^{31}\text{P},^{13}\text{C1 phenyl}}$ (100.5 Hz). The trend toward a larger phosphorus C1 phenyl coupling with increasing unsaturation of the substituent being varied is noted. However, a simple explanation based on increased electronegativity of the substituent and hence an increased effective nuclear charge on phosphorus leading to larger P-C coupling¹⁵ does not adequately explain both the phosphorus-C1 phenyl couplings and the couplings of the phosphorus to the directly bonded carbon of the other substituent.

^{31}P NMR. In Figure 1 the ^{31}P chemical shifts of the triphenylphosphonium salts are plotted against the ^{13}C chemical shifts of compounds in which the triphenylphosphonium group is replaced by a methyl group. The plotted data fall onto three distinct lines. Line A is drawn for triphenylphosphonium salts where R is a saturated alkyl group. The data for this line are taken from the previous paper in this se-

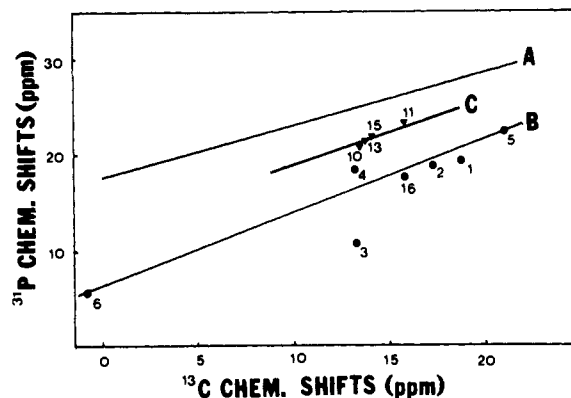


Figure 1. Comparison of ^{31}P chemical shifts of $\text{Ph}_3\text{P}^+-\text{RX}^-$ versus ^{13}C chemical shifts of Me-R. Numbers refer to compounds listed in Table I and lines drawn for A, B, and C correspond to those obtained by linear regression analysis.

ries.¹ The correlation between the phosphorus and carbon chemical shift data for these simple alkyl analogs is seen to be good (correlation coefficient, $r = 0.969$). This agreement demonstrates clearly that the same factors which affect the carbon chemical shift of a methyl group are also operative for the ^{31}P chemical shifts for alkyl substituted triphenylphosphonium salts.

Line B as drawn in Figure 1 for compounds containing an unsaturated group α to the phosphorus falls below line A. Thus it is seen that the phosphorus resonances making up line B are consistently shielded with respect to saturated groups. The equation for line B is given by

$$\delta_{^{31}\text{P}} = 0.75(\delta_{^{13}\text{C}}) + 6.48$$

with a correlation coefficient $r = 0.978$. The ^{31}P chemical shifts for the vinyl triphenylphosphonium salts are consistent with the notion that increased shielding is produced by increased electron density on phosphorus via means of $d\pi-\pi$ bonding. This view is in contradiction to the conclusion of an early theoretical study of ^{31}P chemical shifts by Letcher and Van Wazer.^{16,17} The vinyl substituted compounds are shielded by approximately 8 ppm compared to alkyl substituted triphenylphosphonium salts. In addition the shielding of phosphorus in propynyltriphenylphosphonium bromide (6) by 12 ppm follows from the fact that an additional shielding effect due to circulating π electrons of the propynyl group is also present. A similar upfield shift of the phosphorus resonance is noted for vinyltri-*n*-butylphosphonium bromide; compare 7 with 8 and 9 in Table I. Thus an upfield shift of 9.2 ppm on going from ethyl- to vinyltri-*n*-butylphosphonium bromide illustrates well the effect of $d\pi-\pi$ overlap. It should be noted that the absolute values

Table V. Comparison of the ^{13}C Chemical Shifts for Allyl and Propargyl Substituted Model Compounds

Compd	Carbon			Compd	Carbon		
	X	1	2		X	1	2
$\text{X}-\text{CH}_2\text{CH}=\text{CH}_2$	H^a	133.1	115.0	$\text{X}-\text{CH}_2\text{C}\equiv\text{CH}$	H^c	79.2	66.9
	Me^b	140.2	113.3		Me^b	86.4	68.7
	P^+Ph_3	126.3	123.1		P^+Ph_3	70.1	77.0

^a Reference 5, p 184. ^b G. E. Maciel et al., *J. Phys. Chem.*, 76, 1466 (1972). ^c A. B. Strong, D. Ikenberry, and D. M. Grant, *J. Magn. Reson.*, 9, 145 (1973).

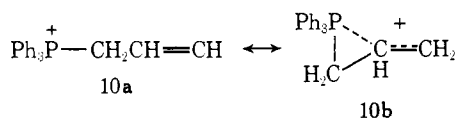
for the ^{31}P chemical shifts of tri-*n*-butylphosphonium salts are greater than those for the corresponding triphenylphosphonium salts. This result shows that $d\pi$ - $p\pi$ bonding from the phenyl substituents increases the shielding of the ^{31}P chemical shift, even though a phenyl group would be expected from carbon NMR to produce a downfield shift (e.g., the methyl group of toluene is deshielded from that in pentane).

The point for 1-(2-methylpropenyl)triphenylphosphonium chloride (**3**) is seen to fall below line B in Figure 1. This deviation is due to a larger upfield shift of the phosphorus than for the corresponding methyl group in the model carbon compound used to plot the abscissa. Such behavior is reasonable in view of the greater steric bulk of a triphenylphosphonium as compared to a methyl group. The greater upfield shift for the phosphorus atom in **3**, 10.9 ppm (Table I), than for *trans*-1-propenyltriphenylphosphonium bromide (**2**) (18.7 ppm) is also seen to be a result of steric compression of the phosphorus with the *cis*-methyl group in **3**. This shift is also observed both in the ^{13}C NMR and in the ^1H NMR¹⁸ for the *cis*-methyl group of **3**. The ^{13}C chemical shift of the *cis*-methyl in **3** is thus 24.8 ppm, whereas the *trans*-methyl in **3** is found at 29.9 ppm (Table II).

Line C in Figure 1 is drawn for compounds having an electron rich unsaturated group β to the phosphorus. The equation for line C is given by

$$\delta_{31\text{P}} = 0.66(\delta_{13\text{C}}) + 12.20$$

with the correlation coefficient $r = 0.953$. It is seen that these allyl, benzyl, and propynyl substituted triphenylphosphonium salts are consistently shielded by approximately 4 ppm from what would be expected on the basis of the ^{13}C chemical shifts of their methyl analogs. Again changing the triphenylphosphonium group for a tri-*n*-butylphosphonium group also shows this effect. On the basis of the ^{13}C NMR tetra-*n*-butyl- and 3-propenyltri-*n*-butylphosphonium bromide (**19** and **20**) should have nearly identical ^{31}P chemical shifts; however, **20** is shielded compared to **19**. These effects are presumably a consequence of overlap of a filled π orbital with an empty d orbital on phosphorus with the following resonance structures considered to be important:



Interaction of remote π bonds with phosphorus on the basis of ^{31}P NMR has been intimated for a series of allyl substituted phosphine oxides.¹⁹ Compound methoxymethyltriphenylphosphonium chloride (**16**) also shows this effect; however, compounds where the β carbon is electron deficient such as $\text{Ph}_3\text{P}^+-\text{CH}_2\text{C}(\text{O})\text{R}$ and $\text{Ph}_3\text{P}^+-\text{CH}_2\text{CN}$ as well as compounds containing an electron rich atom three bonds away such as $\text{Ph}_3\text{P}^+-\text{CH}_2\text{CH}_2\text{OMe}$ are not expected to overlap as efficiently with empty d orbitals on phosphorus. Therefore, these compounds fall on line A, drawn for alkyl substituted triphenylphosphonium salts.¹

Further evidence for homo $d\pi$ - $p\pi$ overlap is provided by Table V. In general, a methylene group deshields the α carbon on a vinyl or ethynyl group and shields the β carbon. However, both **10** and **14** have α and β carbons with approximately the same chemical shift. In **10** with the intervention of **10b** the α vinyl carbon should become more shielded than what would be expected in **10a**. Furthermore, the β vinyl carbon in **10b** should be deshielded compared to **10a** since electron density is being removed. These predictions are confirmed from the data in Table V. It is also seen from Table III that $^2J_{31\text{P},13\text{C}}$ for **10** and **14** are 13.4 and 12.8 Hz, respectively. These couplings are substantially larger than $^2J_{31\text{P},13\text{C}}$ for $\text{Ph}_3\text{P}^+-\text{CH}_2\text{CO}-\text{R}$ ($^2J_{31\text{P},13\text{C}} = 3.0$ to 5.2 Hz)⁷ and the other two bond couplings of phosphorus to the substituents reported in this paper. This may be due in part to the contribution of resonance structures similar to that of **10b**.

Experimental Section

Spectra were obtained on a Bruker HFX-90 spectrometer equipped for Fourier transform pulsed NMR with a Nicolet 1085 data system. The ^{31}P and ^{13}C data were taken at operating frequencies of 36.431 and 22.628 MHz, respectively. The ^{31}P chemical shifts are reported as referenced to external 85% H_3PO_4 with shifts occurring downfield from the reference taken as positive. The ^{13}C chemical shifts are reported with respect to internal TMS with downfield shifts again reported as positive. All samples except **14** and **18** were run as 0.1 to 0.05 M solutions of CDCl_3 at 28° with broad band ^1H decoupling. Spectral assignments were made with the aid of off-resonance decoupling and model compounds as appropriate. The assignments of the resonances for the *n*-butyl groups in **8** were made by the similarity to those reported for tetra-*n*-butylphosphonium bromide.⁵ The assignments for the acetylenic carbons in **6** rest upon the similar trend noted for the vinylphosphonium salts and the larger phosphorus-carbon coupling observed for C1 (191.7 Hz) compared to C2 (33.0 Hz) which conforms to the relative magnitudes of one- and two-bonded couplings in all phosphonium salts studied. Compounds **14** and **18** were run in a solution consisting of approximately 1:1 trifluoroacetic acid- CDCl_3 . The tabulated values reported in Table I represent the average chemical shift for each compound taken over several runs; no compound varied by more than ± 0.3 ppm with the average being ± 0.17 ppm.

All phosphonium salts were prepared according to standard methods.^{2b} Compounds **4** and **6** were prepared by previously reported procedures.²⁰

Acknowledgment. This work was supported in part by a U.S. Public Health Service Grant for which we are most grateful. We also wish to acknowledge helpful discussions with Dr. David L. Dalrymple.

References and Notes

- (1) T. A. Albright, W. J. Freeman, and E. E. Schweizer, previous paper in this issue.
- (2) (a) A. W. Johnson, "Ylid Chemistry", Academic Press, New York, N.Y., 1966; (b) P. Beck, "Organic Phosphorus Compounds", Vol. 2, G. M. Kosolapoff and L. Maier, Ed., Wiley-Interscience, New York, N.Y., 1972, p 189.
- (3) E. E. Schweizer, A. T. Wehman, and D. M. Nycz, *J. Org. Chem.*, **38**, 1583 (1973), and references therein.
- (4) See, for example, K. A. R. Mitchell, *Chem. Rev.*, **69**, 157 (1969); T. B. Brill, *J. Chem. Educ.*, **50**, 392 (1973); R. F. Hudson, *Rev. Pure Appl. Chem.*, **9**, 371 (1964), for reviews of differing viewpoints.

- (5) J. B. Stothers, "Carbon-13 NMR Spectroscopy", Academic Press, New York, N.Y., 1972.
- (6) J. R. Van Wazer, "Determination of Organic Structures by Physical Methods", Vol. 4, F. C. Nachod and J. J. Zuckerman, Ed., Academic Press, New York, N.Y., 1971, p 393.
- (7) G. A. Gray, *J. Am. Chem. Soc.*, **95**, 7736 (1973).
- (8) T. D. Brown, Ph.D. Thesis, University of Utah, 1966.
- (9) Reference 5, p 160.
- (10) Estimated from the data of ref 8, p 62.
- (11) Reference 5, p 104.
- (12) For a theoretical study of the mechanism of electron delocalization in vinyl groups, see L. Libit and R. Hoffmann, *J. Am. Chem. Soc.*, **96**, 1370 (1974).
- (13) D. Rosenberg and W. Drenth, *Tetrahedron*, **27**, 3893 (1971).
- (14) G. A. Gray and S. E. Cremer, *J. Org. Chem.*, **37**, 3458 (1972).
- (15) See, for example, the discussion in ref 5, p 375.
- (16) J. H. Letcher and J. R. Van Wazer, *J. Chem. Phys.*, **44**, 815 (1965).
- (17) It must be noted that several approximations were made in the Letcher-Van Wazer study; namely, $\langle r^{-3} \rangle$ for the p and d orbital contributions were held constant and terms resulting from interactions of the groups around phosphorus mixing into certain excited electronic states on the phosphorus atom through multiple bond interactions were neglected.
- (18) R. K. Howe, *J. Am. Chem. Soc.*, **93**, 3549 (1971).
- (19) A. I. Razumov et al., *J. Gen. Chem. USSR (Engl. Transl.)*, **40**, 1704 (1970).
- (20) W. P. Murray, M.S. Thesis, University of Delaware, 1973.

Homoallyl Interaction between the Nitrogen Lone Pair and the Nonadjacent π Bond. ^1H and ^{13}C Nuclear Magnetic Resonance Contact Shifts and the Orientation of the Lone Pair Electrons in 2-Azabicyclo[2.2.2]oct-5-enes^{1,2}

Isao Morishima* and Kenichi Yoshikawa

Contribution from the Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Kyoto, Japan. Received September 30, 1974

Abstract: The orientation of the nitrogen lone pair electrons in 2-azabicyclo[2.2.2]oct-5-ene and its *N*-methyl derivative has been studied with the aid of Ni(AA)₂ (nickel acetylacetonate) induced ^1H and ^{13}C NMR contact shifts and molecular orbital calculations in view of elucidation of nonbonded n,π interaction ($n-\pi$ transannular interaction) in azabicyclic molecules. Ni(AA)₂-induced ^1H and ^{13}C contact shifts for these molecules were plausibly explained by the spin density distributions obtained by INDO-UHF-MO calculation for the corresponding hydrocarbon σ radical, bicyclo[2.2.2]oct-5-en-2-yl, in which the radical lobe occupies exo and endo positions. This allowed us to conclude that the nitrogen lone pair for *N*-methyl derivative is preferentially oriented at the exo position while the exo and endo positions are equally favored for the *N*-H derivative. This was further confirmed by other NMR evidence. CNDO/2-MO calculations were also performed for above azabicyclic molecules to illuminate the factors that determine the nitrogen lone pair orientation. It is concluded that steric repulsion and $n-\pi$ transannular electronic stabilization energies are essentially important to determine the lone pair orientation in the title molecule.

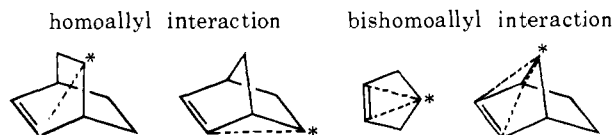
Neighboring group participation in the reaction intermediate or in the electronic and geometrical structures of ground or excited state of molecules constitutes an essential concept in the organic chemistry. As a part of our continuing investigations^{2,3} toward understanding neighboring group participation in the electronic structures of rigid σ -bonded molecules, we have studied here the stereospecific orientation of lone pair electrons and electronic structures in 2-azabicyclo[2.2.2]oct-5-ene derivatives. Much attention has been paid to the transannular interaction between nonbonded π electrons.⁴ However, quite limited studies have been available concerning the neighboring group effect on the stereospecific orientation of lone pair electrons which appears to be one of the interesting problems in the stereochemistry of organic molecules.

The specific orientation of the lone pair electrons on the C₇ carbon in 7-norbornenyl anion has been studied⁵ by stereospecific deuterium capture of anti and syn anion intermediates. The preference for anti 7-norbornenyl anion has been suggested and interpreted as resulting from bishomoantiaromatic character of this anion. Quantum chemical studies of this anion have also been performed. However,



semiempirical MO calculations failed to determine definitely the orientation of lone pair electrons in 7-norbornenyl anion.^{6,7} It may be readily accessible from this example that the problem on the transannular effect between lone pair electrons and the neighboring π bond in bicyclic molecule is still open to further experimental and theoretical studies.

We have recently carried out a photoelectron spectroscopic study of nonbonded n,π interaction involved in several cyclic and bicyclic amines containing nonadjacent π bonds.² It was revealed that the feature of the nonadjacent n,π interaction is quite different between homoallyl and bishomoallyl n,π interacting systems; for the homoallyl interaction, both n,π and n,π^* interactions contribute com-



petitively to the relative stability of the interacting system. It is, therefore, of interest to study the orientation of lone pair electrons in homoallyl n,π interacting molecules in relation to the bishomoconjugative system.⁸

In these circumstances, we have studied here the orientation of nitrogen lone pair electrons and electronic structures in 2-azabicyclo[2.2.2]oct-5-ene (**2**), its *N*-methyl derivative (**3**), and their saturated homologs (**4**, **5**) with the aid of