

- fairs Division and by the United States Atomic Energy Commission.
- (3) Scarborough College, University of Toronto, West Hill, Ontario, M1C 1A4, Canada.
 - (4) NASA fellow 1964–1967, Illinois Institute of Technology.
 - (5) University College, Dublin.
 - (6) A. J. Kresge, *J. Pure Appl. Chem.*, **8**, 243 (1964).
 - (7) For recent reviews, see (a) W. J. Albery in "Proton Transfer Reactions", E. F. Caldin and V. Gold, Ed., Chapman and Hall, London, 1975; (b) R. L. Schowen, *Prog. Phys. Org. Chem.*, **9**, 275 (1972); (c) V. Gold, *Adv. Phys. Org. Chem.*, **7**, 259 (1959).
 - (8) S. Olsson, *Ark. Kemi*, **9**, 85 (1959); V. Gold, R. W. Lambert, and D. P. N. Satchell, *J. Chem. Soc.*, 2461 (1960); A. J. Kresge and Y. Chiang, *J. Am. Chem. Soc.*, **84**, 3976 (1962); J. L. Longridge and F. A. Long, **89**, 1292 (1967).
 - (9) A. J. Kresge and Y. Chiang, *J. Am. Chem. Soc.*, **89**, 4411 (1967).
 - (10) C. G. Swain, E. C. Stivers, J. F. Renwer, Jr., and L. J. Schaad, *J. Am. Chem. Soc.*, **80**, 5885 (1958); E. S. Lewis and J. K. Robinson, **90**, 4337 (1968); M. J. Stern and R. E. Weston, *J. Chem. Phys.*, **60**, 2815 (1974).
 - (11) W. J. Albery and M. H. Davies, *J. Chem. Soc., Faraday Trans. 1*, **68**, 167 (1972).
 - (12) B. D. Batts and J. Kilford, *J. Chem. Soc., Faraday Trans. 1*, **69**, 1033 (1973).
 - (13) A. J. Kresge and W. J. Albery, *J. Chem. Soc., Chem. Commun.*, 507 (1974).
 - (14) J. Schulze and F. A. Long, *J. Am. Chem. Soc.*, **86**, 331 (1964).
 - (15) F. A. Long and E. A. Walters, personal communication.
 - (16) A. J. Kresge and Y. Chiang, *J. Am. Chem. Soc.*, **83**, 2877 (1961).
 - (17) W. J. Albery and A. N. Campbell-Crawford, *J. Chem. Soc., Perkin Trans. 2*, 2190 (1972).
 - (18) V. Gold and S. Grist, *J. Chem. Soc., Perkin Trans. 2*, 89 (1972).
 - (19) A. J. Kresge and Y. Chiang, *J. Chem. Phys.*, **49**, 1439 (1968).
 - (20) When corrections for deviations from the rule of the mean are applied the values become 0.655 ± 0.011 (Batts and Kilford) and 0.697 ± 0.014 (present data).
 - (21) A. J. Kresge, D. P. Onwood, and S. Slae, *J. Am. Chem. Soc.*, **90**, 6982 (1968).
 - (22) L. C. Gruen and F. A. Long, *J. Am. Chem. Soc.*, **89**, 1287 (1967).
 - (23) R. A. More O'Ferrall, G. W. Koeppel, and A. J. Kresge, *J. Am. Chem. Soc.*, **93**, 9 (1971).
 - (24) V. Gold, *Trans. Faraday Soc.*, **56**, 255 (1960).
 - (25) J. Bigeleisen, *J. Chem. Phys.*, **23**, 2264 (1955); **28**, 694 (1958).
 - (26) W. A. Van Hook, *J. Chem. Soc., Chem. Commun.*, 479 (1972); J. W. Pyper, R. S. Newburg, and G. W. Barton, Jr., *J. Chem. Phys.*, **46**, 2253 (1967).
 - (27) V. Gold, *Trans. Faraday Soc.*, **64**, 2770 (1968).
 - (28) W. J. Albery and M. H. Davies, *Trans. Faraday Soc.*, **65**, 1059 (1969).
 - (29) Note that $\phi^{\circ}/\phi^{\infty} = [\text{HDO}]^2/4[\text{HDO}][\text{D}_2\text{O}] = 0.945$.
 - (30) H. J. Bernstein, *J. Chem. Phys.*, **20**, 263 (1952); J. Bigeleisen and P. Goldstein, *Z. Naturforsch. A*, **18**, 205 (1963).
 - (31) For the important case of fractionation at a single isotopic position, the identity of ϕ and the true fractionation factor $([X-D]/[X-H])(1-x)/x$ in a 50–50 $\text{H}_2\text{O}-\text{D}_2\text{O}$ mixture provides an alternative means of measurement.²⁸
 - (32) A. J. Kresge and R. A. More O'Ferrall, calculations to be published.
 - (33) A minority of authors use n for x . The present use can hardly cause confusion and takes advantage of the affinity of n and x .
 - (34) Without the assumption of no coupling between reacting and nonreacting hydrogens, the contribution to k_r/k_H from all three hydrogens is $\{(1-n)^3 + (\phi_1^{\pm}\gamma_2^2 + 2\phi_2^{\pm}\gamma_1\gamma_2)n(1-n)^2 + (\phi_2^{\pm2}\gamma_2^2 + 2\phi_1^{\pm}\phi_2^{\pm}\gamma_1\gamma_2)n^2(1-n) + n^3\phi_1^{\pm}\phi_2^{\pm2}\}$ where γ is now γ_1 and $\gamma_2 = [\text{D}_2\text{O}-\text{H}-\text{S}]^{1/2}[\text{H}_2\text{O}-\text{D}-\text{S}]^{1/2}/[\text{D}_2\text{O}-\text{D}-\text{S}][\text{H}_2\text{O}-\text{H}-\text{S}]^{1/2}$.
 - (35) J. W. Pyper, R. S. Newburg, and G. W. Barton, Jr., *J. Chem. Phys.*, **47**, 1179 (1967).
 - (36) Comparisons based on similar methods of measurement and calculation should be more reliable than absolute values.
 - (37) A. J. Kresge, S. Slae, and D. W. Taylor, *J. Am. Chem. Soc.*, **92**, 6309 (1970).
 - (38) A. J. Kresge, S. G. Mylonakis, Y. Sato, and V. P. Vitullo, *J. Am. Chem. Soc.*, **93**, 6181 (1971).
 - (39) A. J. Kresge in "Proton Transfer Reactions", V. Gold and E. F. Caldin, Ed., Chapman and Hall, London, 1975.
 - (40) R. J. Thomas and F. A. Long, *J. Am. Chem. Soc.*, **86**, 4770 (1964).
 - (41) Calculated in ref 38 from the data of B. C. Challis and F. A. Long, *J. Am. Chem. Soc.*, **87**, 1196 (1965).
 - (42) J. M. Williams and M. M. Kreevoy, *Adv. Phys. Org. Chem.*, **6**, 63 (1968).

A Generalized Gauche NMR Effect in ^{13}C , ^{19}F , and ^{31}P Chemical Shifts and Directly Bonded Coupling Constants. Torsional Angle and Bond Angle Effects

David G. Gorenstein¹

Contribution from the Department of Chemistry, University of Illinois at Chicago Circle, Chicago, Illinois 60680. Received August 9, 1976

Abstract: The ^{31}P , ^{13}C , or ^{19}F chemical shifts of atoms arranged in a gauche conformation are upfield from the shifts of atoms in a trans conformation. In contrast to earlier explanations for the γ effect, these shifts are attributed to bond angle changes which arise from a coupling of bond angles to torsional angles. Conformationally dependent, directly bonded coupling constants are also attributed to the bond angle deformation resulting from torsional bond angle changes.

The steric theory of Grant and Cheney^{2a} has been widely accepted^{2b,c} as a basis for understanding the γ shift (the upfield ^{13}C shift of a γ carbon resulting from substitution on the γ carbon of a hydrocarbon chain). Thus, the ^{13}C chemical shifts of the γ -methylene carbon and the methyl carbon in axially substituted methylcyclohexane are shifted 3–5 ppm upfield relative to the signals in equatorially substituted methylcyclohexane.³ These shifts are proposed to result from polarization of the electrons due to steric interactions. In the case of the axial methylcyclohexane, the methyl hydrogens and the axial γ -methylene hydrogens sterically interact, leading to an increase in the electron density on carbon.

We wish to argue against this explanation of the γ effect and to propose that the γ effect follows, at least in part, from a generalized "gauche" NMR effect applicable to ^{13}C as well as ^{19}F , ^{31}P , and other heavy-atom chemical shifts. In addition we wish to point out that the conformational sensitivity of heavy-atom chemical shifts and directed bonded coupling

constants are related and originate from a bond angle distortion dependent upon the torsional conformation.

Results and Discussion

We have recently shown that ^{31}P chemical shifts of phosphate esters are primarily determined by the RO-P-OR bond angle⁴ and the RO-P-OR torsional angles.⁵ Thus, a decrease in the RO-P-OR bond angle leads to a downfield shift in the ^{31}P signal. In addition, the ^{31}P chemical shift of an ester in a gauche, gauche (g,g) conformation is upfield from the chemical shift of an ester in a non-g,g conformation, such as gauche, trans (g,t).

We have also observed that ester torsional angles and bond angles are strongly "coupled".⁶ Thus, rotation about the O-P bond from a gauche to a trans conformation results in ca. a $\sim 5^\circ$ reduction in the RO-P-OR bond angle. As a result of this coupling, ^{31}P shifts in acyclic phosphate esters are largely determined by the torsional conformation, with bond angle

distortions following the conformational changes.⁵ The temperature dependence of the ³¹P chemical shifts of nucleic acids,⁷ empirical correlations,⁴ and CNDO and ab initio molecular orbital calculations^{5,6,8} support these conclusions.

For carbon as well as phosphorus, rotation about an O-X bond (X = C or P) from a gauche to a trans conformation results in a 5° reduction in the O-X-O bond angle.^{8a} Semiempirical and ab initio molecular orbital calculations on dimethoxymethane and analysis of x-ray structural data on related molecules confirms that the optimized O-C-O bond angle in dimethoxymethane is 112° for the g,g, conformation, 107° for the g,t conformation, and 102° for the t,t conformation.^{8a} Although smaller, similar coupled bond angle distortions are observed in acyclic alkanes.

Upfield shifts are observed for carbon,^{2,3,10-14} fluorine^{14,15} (and of course phosphorus^{5,7,16,17}) atoms arranged in a gauche conformation relative to a trans conformation. It should also be noted that as shown in Table I, relative to a trans conformation, a gauche conformation of atoms V_γ-X_β-Y_α-Z_{β'} leads to an upfield shift for all four atoms.^{18,19} We wish to propose in this paper that all of these upfield shifts are a general manifestation of a "gauche" NMR effect.¹⁸ Furthermore, we suggest that this gauche effect arises not from steric polarization of electron densities^{2a} but rather from a sensitivity of the heavy-atom chemical shifts to bond angle changes. The torsional conformation alters the bond angles which in turn results in changes in the chemical shifts. Specifically, the X-Y-Z bond angle is 2-6° larger in the gauche arrangement of atoms V-X-Y-Z than in the trans arrangement. It is this enlargement of the X-Y-Z bond angle in the gauche conformation that is largely responsible for the upfield shift of the atoms in this conformation.

In order to understand the possible physical mechanism(s) which is (are) responsible for this gauche NMR effect, we review briefly the theory of chemical shifts.

Theoretical Basis for Heavy-Atom Chemical Shifts

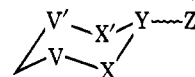
According to the Karplus and Pople²⁰ theory of ¹³C chemical shifts, the chemical shift of an atom A results from a diamagnetic contribution, σ_d^A, and a paramagnetic contribution, σ_p^A. In general, the major contribution to heavy-atom chemical shifts comes from the paramagnetic term:

$$\sigma_p^A = -\frac{e^2\hbar^2}{2m^2c^2} \langle r^{-3} \rangle_{2p} (\Delta E_{av})^{-1} \cdot \sum_B Q_{AB} \quad (1)$$

In this equation, $\langle r^{-3} \rangle_{2p}$ is the mean inverse cube radius for atom A 2p orbitals; ΔE_{av} is the average electronic excitation energy, and Q_{AB} is a function of the charge-bond order density matrix elements between atoms A and B. The chemical shift, if largely influenced by this paramagnetic term, will thus be affected by changes in bond overlap and hybridization (via the Q_{AB} term), changes in atomic charges (via mainly the $\langle r^{-3} \rangle$ term), as well as changes in ΔE_{av}. The often observed correlation of chemical shifts and charge densities^{5,21} probably derives from the expansion or contraction of the p orbitals with charge variations (hence altering $\langle r^{-3} \rangle$). Although the Karplus-Pople theory generally accounts for major trends in heavy-atom chemical shifts, small variations are frequently only poorly reproduced. In fact, we have earlier noted that ³¹P chemical shifts in phosphate diesters are just as well correlated with calculated phosphorus electron densities as the full paramagnetic term (eq 1).

In arguing our hypothesis that torsional-angle coupled bond angle changes are primarily responsible for these stereochemically dependent heavy-atom chemical shifts, we must at the very least demonstrate a bond angle sensitivity to heavy-atom shifts. It is encouraging, therefore, that both carbonyl ¹³C and phosphorus atom ³¹P signals are shifted 8-20

Table I. Chemical Shift Differences between Atoms in Axially and Equatorially Substituted Six-Membered Rings (ν_g-ν_t)



Compound	Chemical shift differences (ν _g -ν _t) ^a for atoms, ppm			
	V _γ	X _β	Y _α	Z _{β'}
Methylcyclohexane ^b (V, X, Y, Z = C)	5.4	3.7	4.6	3.9
Cyclohexanol ^c (V, X, Y = C; Z = O)	4.1	3.2	4.8	
4- <i>tert</i> -Butylcyclohexanol ^h (V, X, Y = C; Z = O)	5.4	2.4	3.3	
Nitrocyclohexane ^c (V, X, Y = C; Z = N)	3.1	2.8	3.6	
Fluorocyclohexane ^{d,g} (V, X, Y = C; Z = F)	3.8	2.4	3.4	Upfield
2,2-Difluoro- <i>trans</i> -decalin ⁱ (V, X, Y = C; Z = F, F)				11.6
D-Glucose ^e (V, X, Y, V' = C; X', Z = O)	2.9 (4.6) ^f	2.7	3.9	
D-Glucose methyl glycoside ^e (V, X, Y, V' = C; X' Z = O)	1.6 (2.6) ^f	2.5	3.8	
D-Xylose ^e (V, X, Y, V' = C; X', Z = O)	2.9 (3.9) ^f	1.4	4.5	
Methyl 2,3-DL-O-methyl- α-D-glucopyranoside-4,6- ethyl phosphate ^g (V, V' = C'; X, X' = O; Y = P (O); Z = O)				3.1
Methyl 2,3-DL-O-methyl-α-D- glucopyranoside 4,6-ethyl- thiol phosphate ⁱ (V, V' = C; X, X' = O; Y = P (S); Z = O (Et))				6.1
Methyl 2,3-DL-O-methyl-α- D-glucopyranoside-4,6- methyl phosphonate ^g (V, V' = C; X, X' = O; Y = P (O); Z = CH ₃)				6.0

^a Positive numbers indicate that the shifts of the axially substituted compounds (gauche conformation) are upfield from those in the equatorially substituted rings (trans conformation). ^b See ref 3.

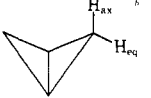
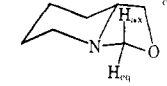
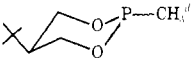
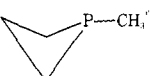
^c See ref 10. ^d H. J. Schneider and V. Hoppen, *Tetrahedron Lett.*, 7, 579 (1974). ^e See ref 11. ^f Chemical shift differences for atom Y'. ^g See ref 15. ^h See ref 14a. ⁱ D. B. Cooper, J. M. Harrison, T. D. Inch, and G. J. Lewis, *J. Chem. Soc., Perkin Trans. 1*, 1049 (1974). ^j J. T. Gerig and J. D. Roberts, *J. Am. Chem. Soc.*, **88**, 2791 (1966).

ppm downfield in five-membered rings relative to shifts in six-membered rings.^{4,14,23} Changes in hybridization resulting from bond angle changes in the cyclic compounds could be responsible for this ring effect.²⁴ It is also possible that this ring effect results from a change in the average excitation energy since a good correlation of ¹³C chemical shifts and λ_{max} for the n→π* transition in some cyclic carbonyl compounds has been demonstrated for this narrow class of compounds.²⁵

Unfortunately, the effect of bond angle (or ring size) on ³¹P and ¹³C chemical shifts is not as direct as implied by the comparison of shifts in six- and five-membered rings. Thus, while downfield ³¹P and ¹³C shifts are indeed associated with decreases in C-X-C (X = carbonyl or phosphorus) bond angles (comparing the six- and five-membered rings), downfield shifts are also associated with *increases* in C-X-C bond angles (comparing chemical shifts in five- and four-membered rings).^{14,23} In addition, in the cycloalkane series, decreasing bond angles results in a monotonically varying upfield ¹³C shift.^{2b} (However, in contrast to the cycloalkanone series, additional eclipsing effects as well as bond angle effects likely complicate the ring size cycloalkane comparison.)

Theoretically, there is little question that bond angle changes should affect ¹³C and ³¹P chemical shifts.^{5,23,26-28} It appears,

Table II. One-Bond Coupling Constants in Stereochemically Defined Ring Systems

Compound	C-X bond type	Axial C-X	Equatorial C-X
D-Glucopyranose ^a	Anomeric C-H	169.5	160
D-Galactopyranose ^a	Anomeric C-H	169.5	159.5
Methyl D-glucopyranoside tetra-O-acetate ^a	Anomeric C-H	170	159
	Methylene C-H	169	153
	Methylene C-H	158	148
	P-C	-42.8	-32.2
	P-C	-37.9	-33.7

^a Reference 29. ^b Reference 30. ^c Reference 31. ^d Reference 32. ^e Reference 33.

unfortunately, that bond angle changes alter chemical shifts by influencing more than one term in eq 1 and the present theory is inadequate to quantitatively account for these changes. However, whatever the basis for the ring effect on ³¹P and ¹³C chemical shifts, both nuclei are affected similarly and it is possibly significant that large downfield ³¹P and ¹³C shifts are associated with reductions in C-X-C (X = carbonyl carbon or phosphorus) bond angles (comparing the six- and five-membered rings). This observation fits nicely with the proposed ³¹P and ³¹C downfield shifts in trans vs. gauche conformations since the bond angle will be reduced in the trans conformation.

A Generalized Gauche Effect in Directly Bonded Coupling Constants

The coupled bond angle-torsional angle gauche effect is also quite likely responsible for the conformational dependence to directly bonded coupling constants. As shown in Table II, the directly bonded heavy-atom coupling constants in molecules possessing gauche stereochemistry are 5-10 Hz smaller than in molecules possessing trans stereochemistry. Thus, in six-membered rings, the ¹³C-X (X = ¹H, ³¹P, or ¹⁹F) coupling constants are smaller in equatorially substituted rings (trans stereochemistry to the ring carbons) than in axially substituted rings (gauche stereochemistry). Pseudoaxial and equatorial positions in five-membered rings (Table II) show similar stereochemical dependence to the coupling constants. Although this stereochemical sensitivity has been noted previously,^{2b,c,29-34} explanations have generally been based upon interactions of electron lone pairs³⁵⁻³⁹ with the C-X bond.

We propose instead that these torsional effects are once again a manifestation of the bond angle distortion in the various torsional conformations. It has been recognized for some time now that ¹J_{13C-H} is sensitive to the C-H bond hybridization. Bond angle and steric effects on ¹J_{13C-H} coupling constants have been explained on this basis.^{4,14} These bond angle changes can be rationalized on the basis of eq 2, proposed⁴³ for calculating Fermi-contact coupling constants:

$$J_{13C-X} = \frac{Aa_C^2 \cdot a_X^2}{1 + S_{C-X}} + B \quad (2)$$

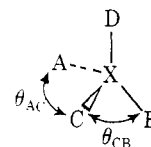
Table III. Calculated C-H Coupling Constant Changes, ΔJ, as a Function of Bond Angle Distortion, Δθ

Distortion, deg Δθ _{CA} = -Δθ _{CB}	% s ^a	ΔJ, Hz
0	25	0
±1	25.93	+6.6
±2	25.78	+5.5
±4	25.19	+3
±6	24.15	-6.0

^a % s character in C-X bond (other bond angles tetrahedral).

where A and B are constants, a_C² and a_X² are the percent s character, and S_{C-X} is the overlap integral for the C-X bond.

According to eq 2, as the bond angle incorporating a C-X bond increases, the percent s character should increase, thus increasing ¹J_{C-X} (reasonably assuming that the overlap integral increases with percent s character much slower than the percent s character).⁴³ However, just the opposite trend is evident from inspection of Table II. Thus, the gauche structures with larger angles actually have smaller coupling constants than the trans structures. The reason for this discrepancy is that in a roughly tetrahedral atom, hybridization and geometry arguments require that distortion of one bond angle must lead to distortion in one or more other bonds. Thus in a tetrahedral atom



keeping all bond angles except θ_{AC} and θ_{CB} fixed requires that an increase in θ_{AC} must lead to a decrease in θ_{CB} (of course, other bonds will rehybridize and other bond angles will change as well, though these will be ignored for simplicity). The hybridization of bond X-C will be related to bond angles θ_{AB}, θ_{AC}, and θ_{CB} by the relationship⁴⁴

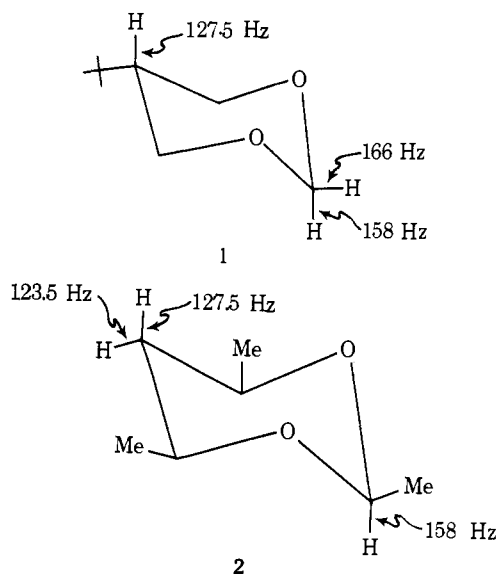
$$\delta^2 = - \frac{\cos \theta_{AB}}{\cos \theta_{AC} \cos \theta_{CB}}$$

where δ is the mixing constant determining the percent s character in the s,p hybrid, X-C bond

$$a^2 = \% s = \frac{1}{1 + \delta^2}$$

Assuming that θ_{AB} is constant and that Δθ_{AC} = -Δθ_{CB}, it is possible to calculate the change in coupling constant, ΔJ, in the X-C bond using eq 2 for small bond angle distortions Δθ_{AC}. Table III shows that C-H coupling constants (using constants A and B of ref 43) may either increase or decrease as distortion from tetrahedral symmetry occurs. The range of ΔJ (~12 Hz) very nicely fits the observed variation in conformationally dependent coupling constants, for which bond angle distortions up to 5-6° are expected.⁸

Although directly bonded coupling constants in structures possessing gauche conformations are nearly always 7-10 Hz smaller than in trans related conformations, significant exceptions do exist, such as in molecules 1 and 2. In 1, the axial C-H on the acetal carbon is ~8 Hz smaller than the equatorial (or trans) C-H. In contrast, the axial C-H on the methylene carbon in 2 is 4 Hz larger than the equatorial or trans hydrogen (viewing along H-C-C-O). As shown in Table III, only large distortions (>4°) should decrease the coupling constants for the gauche conformation. Small distortions (<4°) should increase the coupling constants for the gauche conformation.

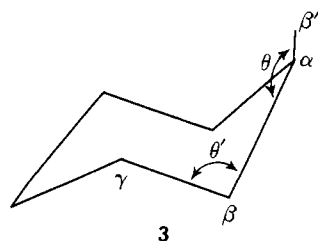


This also agrees very nicely with our observation that bond angle distortions are largest for tetrahedral atoms possessing directly bonded heteroatoms such as the acetal carbon in **2** or dimethoxymethane ($\Delta\theta \sim 5^\circ$). In *n*-butane, the C-C-C bond angle is only $\sim 1^\circ$ larger in the gauche vs. the trans conformation.

Comparison of Gauche NMR Effect Theories

In contrast to the polarization theory of Grant and Cheney the coupled torsional-bond angle, gauche effect explains the relative magnitude of the upfield shifts ($\nu_g - \nu_t$) for the V, X, Y, Z atoms in the gauche vs. trans conformations. For both pyranoses and substituted cyclohexanes, the $\nu_g - \nu_t$ shift differences in Table I are largest in the α and γ positions. If polarization of electron densities resulting from steric interactions is solely responsible for these upfield shifts, then the $\nu_g - \nu_t$ shift difference should be larger for the directly interacting atoms (V $_{\gamma}$ -Z $_{\beta}$). This is clearly not supported by the shifts in Table I. Additionally, the steric theory fails to explain why similar shifts are observed in fluorocyclohexane, cyclohexanol, and methylcyclohexane, for which significantly different steric interactions of the substituent and the γ axial hydrogens would be expected. In contrast, since the origin of the bond angle distortion is likely 1,4-bond-bond repulsion,⁸ which should be fairly independent of the substituent (C, O, F, N), the sterically very different substituents will give rise to similar $\nu_g - \nu_t$ shift differences.

The observed variation of the $\nu_g - \nu_t$ shift differences at the α , β , γ , and β' positions is, however, consistent with our torsional angle-bond angle hypothesis. Bond angles θ and θ' in **3**



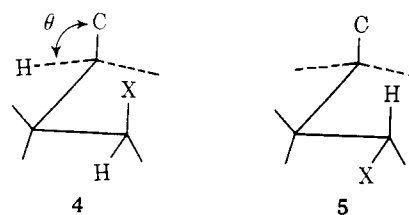
should be the angles primarily sensitive to conformational variations about the α - β bond.⁸ The six-membered ring likely moderates the bond angle distortion in θ' and energy minimization of the molecules in the gauche conformation is largely achieved through an increase of the θ angle (see ref 8 for x-ray crystallographic data supporting this conclusion). This would explain why $\nu_g - \nu_t$ is larger at the α position than at the β' or β position. That the γ shift difference is also larger than the β'

or β shift difference is likely due to a charge alternation effect;⁴⁵ the magnitude of the charge perturbations alternates along a hydrocarbon chain rather than monotonically decreasing with increasing distance from the center of the perturbation.

Additionally, in contrast to the steric polarization theory, the bond angle-torsional angle theory nicely accounts for subtle variations in the gauche effect chemical shifts. Thus, the $Y_{\gamma'}$ shift difference is larger than the Y_{γ} shift difference in D-glucose, D-glucose methyl glycoside, and D-xylose (Table I). This follows directly from our bond angle-torsional angle coupling hypothesis since the bond angle distortion is greater in a C_{γ} -O $_{\beta}$ -C $_{\alpha}$ -O structural fragment than a C_{γ} C $_{\beta}$ C $_{\alpha}$ -O structural fragment.

The recent data of Schneider and Hoppen⁴⁶ very effectively demonstrate the inadequacy of the steric polarization theory. In the monohalogen-substituted cyclohexanes ($C_6H_{11}X$; X = F, Cl, Br, or I) the ^{13}C chemical shift differences between axially and equatorially substituted conformers varies only moderately for the α carbon ($\nu_g - \nu_t = 3.8$ -6.9 ppm) and β carbon (2.4 to 4.6 ppm). However, the $\nu_g - \nu_t$ chemical shift differences for the γ carbons are 3.4 (X = F), 0.0 (X = Cl), -3.0 (X = Br), and -7.1 (X = I). Thus, in the bromo- and iodocyclohexanes, the axial (gauche) conformers have γ - ^{13}C shifts *downfield* from the equatorial (trans) conformers. No correlation of shift differences and conformer energy differences (presumably reflecting steric interactions) is observed.⁴⁶ These results suggest that mechanisms other than steric polarization of electrons (or for that matter bond angle-torsional angle changes) influence the gauche NMR effect.

Finally, the Grant theory fails to satisfactorily account for the δ effect.^{2b,c,47,48} In compounds with structural fragments **4** and **5** the δ syn-axial orientation of C and X in **4** is sterically



more crowded than the δ gauche-trans orientation in **5**, yet the syn-axial orientation results in a 2-3 ppm downfield shift for the δ - ^{13}C .⁴⁷ It is possible to rationalize these downfield shifts within the framework of our bond angle hypothesis if it is assumed that bond angle distortion in **4** alleviates the 1,5-steric interaction. Presumably decreasing bond angle θ in **4** would minimize the steric interaction and possibly explain the downfield shift in **4**. The increase in the downfield δ syn-axial effect in more rigid ring systems⁴⁹ supports this interpretation since this constrains other modes of geometry distortion and thus requires even larger decreases in θ to minimize the torsional strain.

In conclusion, our bond angle distortion hypothesis can potentially eliminate a number of deficiencies in the Grant steric polarization model for ^{13}C (and likely other heavy atom) chemical shift. It is likely, however, that a number of different effects are responsible for these shifts, and until a more exact theoretical understanding of heavy-atom chemical shifts is achieved, all reasonable models must be considered. In contrast, a very simple model based upon our bond angle-torsional angle gauche effect now can semiquantitatively explain the stereochemical dependence to directly bonded coupling constants. The importance of bond angle distortion will likely also be recognized as a potential explanation for "irregularities" in Karplus-type relationships in three-bond coupling constants.^{2b,c,50}

Acknowledgment. Support of this research by the National Science Foundation (GP 38763) and the National Institutes of Health (GM-17575) is gratefully acknowledged.

References and Notes

- (1) Fellow of the Alfred P. Sloan Foundation, 1975–1977.
- (2) (a) D. M. Grant and B. V. Cheney, *J. Am. Chem. Soc.*, **89**, 5315 (1967); (b) see reviews, J. B. Stothers, "Carbon-13 NMR Spectroscopy", Academic Press, New York, N.Y., 1972; (c) and G. C. Levy and G. Nelson "Carbon-13 NMR Spectroscopy for Organic Chemists", Wiley-Interscience, New York, N.Y., 1972.
- (3) D. K. Dalling and D. M. Grant, *J. Am. Chem. Soc.*, **94**, 5318 (1972).
- (4) D. G. Gorenstein, *J. Am. Chem. Soc.*, **97**, 898 (1975).
- (5) D. G. Gorenstein and D. Kar, *Biochem. Biophys. Res. Commun.*, **65**, 1073 (1975).
- (6) D. G. Gorenstein, D. Kar, B. A. Luxon, and R. K. Momii, *J. Am. Chem. Soc.*, **98**, 1668 (1976).
- (7) D. G. Gorenstein, J. B. Findlay, R. K. Momii, B. A. Luxon, and D. Kar, *Biochemistry*, **15**, 3796 (1976).
- (8) (a) D. G. Gorenstein and D. Kar, *J. Am. Chem. Soc.*, **99**, 672 (1977). (b) D. G. Gorenstein, B. Luxon, and J. Findlay to be published in *Biochim. Biophys. Acta*.
- (9) L. Radom and J. A. Pople, *J. Am. Chem. Soc.*, **92**, 4786 (1970).
- (10) O. A. Subbotin and N. M. Sergeev, *J. Chem. Soc., Chem. Commun.*, 141 (1976).
- (11) H. J. Koch and A. S. Perlin, *Carbohydr. Res.*, **15**, 403 (1970).
- (12) T. Pehk and E. Lippmaa, *J. Magn. Reson.*, **3**, 679 (1971).
- (13) A. J. Jones, E. L. Eliel, D. M. Grant, M. C. Knoeber, and W. F. Bailey, *J. Am. Chem. Soc.*, **93**, 4772 (1971).
- (14) J. D. Roberts, F. J. Weigert, J. I. Krosschwitz, and H. J. Reich, *J. Am. Chem. Soc.*, **92**, 1338 (1970).
- (15) J. B. Dence and J. D. Roberts, *J. Am. Chem. Soc.*, **91**, 1542 (1969).
- (16) D. B. Cooper, T. D. Inch, and G. J. Lewis, *J. Chem. Soc., Perkin Trans. 1*, 1043 (1974).
- (17) (a) J. A. Mosbo and J. G. Verkade, *J. Am. Chem. Soc.*, **94**, 8224 (1972); (b) W. G. Bentrude and H.-W. Tan, *ibid.*, **95**, 4666 (1973).
- (18) (a) H. Eggert and C. Djerassi, *J. Am. Chem. Soc.*, **95**, 3710 (1973); (b) E. L. Eliel, W. F. Bailey, L. D. Kopp, R. L. Willer, D. M. Grant, R. Bertrand, K. A. Christensen, D. K. Dalling, M. W. Duch, E. Wenkert, F. M. Schell, and D. W. Cochran, *ibid.*, **97**, 322 (1975).
- (19) D. K. Dalling, D. M. Grant, and E. G. Paul, *J. Am. Chem. Soc.*, **95**, 3718 (1973), have also previously pointed out that the gauche interactions result in upfield shifts for these atoms.
- (20) (a) M. Karplus and J. A. Pople, *J. Chem. Phys.*, **38**, 2803 (1963); (b) M. Karplus and T. P. Das, *ibid.*, **34**, 1683 (1961).
- (21) (a) J. M. Sichel and M. A. Whitehead, *Theor. Chim. Acta*, **5**, 35 (1966); (b) A. Velenik and R. M. Lynden-Bell, *Mol. Phys.*, **19**, 371 (1970).
- (22) T. A. Albright, W. J. Freeman, and E. E. Schweizer, *J. Am. Chem. Soc.*, **97**, 2942 (1975).
- (23) (a) V. Mark, C. H. Dungan, M. M. Crutchfield, and J. R. Van Wazer, "31P Nuclear Magnetic Resonance", Wiley-Interscience, New York, N.Y., 1967; (b) G. M. Blackburn, J. S. Cohen, and I. Weatherall, *Tetrahedron*, **27**, 2903 (1971).
- (24) A. S. Perlin and H. J. Koch, *Can. J. Chem.*, **48**, 2639 (1970).
- (25) G. B. Savitsky, K. Namikawa, and G. Zweifel, *J. Phys. Chem.*, **69**, 3105 (1965).
- (26) N. Muller, P. C. Lauterbur, and J. Goldenson, *J. Am. Chem. Soc.*, **78**, 3557 (1956); J. R. Parks, *ibid.*, **79**, 757 (1957).
- (27) D. Purdela, *J. Magn. Reson.*, **5**, 23, 37 (1971); D. Purdela, *Rev. Roum. Chim.*, **13**, 1415 (1968).
- (28) J. H. Letcher and J. R. Van Wazer, *J. Chem. Phys.*, **44**, 815 (1966).
- (29) K. Bock, I. Lundt, and C. Pedersen, *Tetrahedron Lett.*, **13**, 1037 (1973).
- (30) Reference 2b, p 335.
- (31) Y. Takeuchi, P. J. Chivers, and T. A. Crabb, *J. Chem. Soc., Chem. Commun.*, **20**, 1274 (1974).
- (32) W. G. Bentrude, K. C. Yee, R. D. Bertrand, and D. M. Grant, *J. Am. Chem. Soc.*, **93**, 797 (1971).
- (33) G. A. Gray and S. E. Cremer, *J. Org. Chem.*, **37**, 3470 (1972).
- (34) K. Bock and L. Wiebe, *Acta Chem. Scand.*, **27**, 2676 (1973).
- (35) P. Laszlo, *Bull. Soc. Chim. Fr.*, **2**, 558 (1966).
- (36) W. B. Jennings, D. R. Boyd, C. G. Watson, E. D. Becker, R. B. Bradley, and D. M. Jerina, *J. Am. Chem. Soc.*, **94**, 850 (1972).
- (37) V. M. S. Gil and J. J. C. Teixeira-Dias, *Mol. Phys.*, **15**, 47 (1968).
- (38) J. P. Albrand, A. Cogne, D. Gagnaire, and J. B. Robert, *Tetrahedron*, **27**, 2453 (1971).
- (39) T. Yonezawa, I. Morishima, K. Fukuta, and Y. Ohmori, *J. Mol. Spectrosc.*, **31**, 341 (1969).
- (40) N. Muller and D. E. Pritchard, *J. Chem. Phys.*, **36**, 359 (1962).
- (41) S. L. Manatt, M. A. Cooper, C. W. Mallory, and F. B. Mallory, *J. Am. Chem. Soc.*, **95**, 975 (1973).
- (42) K. L. Servis, W. P. Weber, and A. K. Willard, *J. Phys. Chem.*, **74**, 3960 (1970).
- (43) Z. B. Maksic, M. Eckert-Maksić, and M. Randić, *Theor. Chim. Acta*, **22**, 70 (1971).
- (44) C. A. Coulson, "Valence", Oxford University Press, London, 1953, pp 194 and 195.
- (45) J. A. Pople and M. S. Gordon, *J. Am. Chem. Soc.*, **89**, 4253 (1967).
- (46) H. J. Schneider and V. Hoppen, *Tetrahedron Lett.*, **7**, 579 (1974).
- (47) S. H. Grover, J. P. Guthrie, J. B. Stothers, and C. T. Tan, *J. Magn. Reson.*, **10**, 227 (1973).
- (48) J. G. Batchelor, *J. Magn. Reson.*, **18**, 212 (1975).
- (49) J. B. Stothers, C. T. Tan, and K. C. Teo, *J. Magn. Reson.*, **20**, 570 (1975).
- (50) Work in progress.

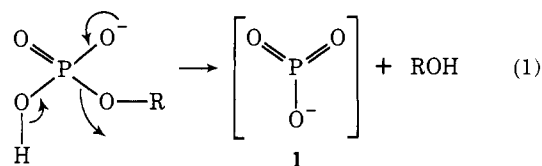
Nucleophilic Catalysis in the Hydrolysis of 2,4-Dinitrophenyl Dibenzy Phosphate

David G. Gorenstein*¹ and Yue-Guey Lee

Contribution from the Department of Chemistry, University of Illinois at Chicago Circle, Chicago, Illinois 60680. Received September 20, 1976

Abstract: The reaction of oxyanions with 2,4-dinitrophenyl dibenzyl phosphate involves nucleophilic catalysis in the cleavage of the P–O(aryl) bond. This conclusion is based upon irregularities in a Brønsted plot of the second-order rate constants for reaction of oxyanions and fluoride ion and observation of negligible solvent deuterium isotope effects. Inhibition of the reaction by organic solvents (1,4-dioxane and even the free acid component of formate and acetate buffers) is observed. Curved second-order plots with acetate, formate, and phosphate buffers are ascribed to a specific salt effect of the NaClO₄ electrolyte added to keep the ionic strength constant.

Our present understanding of the reactions of tetravalent phosphorus (particularly phosphate esters) may be discussed in the context of two limiting general mechanisms.^{2–4} The first of these may be called the S_N1(P) reaction,^{2a} which involves the unimolecular decomposition of a phosphate monoester to generate an unstable monomeric metaphosphate ion intermediate, **1**. The phosphorus–leaving group bond would be substantially broken in the transition state. At the other extreme, the phosphorus–leaving group bond is not broken at all in the transition state and this would be analogous to an



addition-elimination mechanism,⁵ proceeding through an unstable pentacovalent intermediate, **2**.

Of course, between these two extremes of elimination-