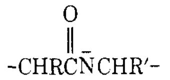
consequences of amino vs. amide proton ionization arise not only in the resultant stereochemistry of the metal ion,[1b,c] but also the conformation of the peptide. X-ray studies[20] have shown that deprotonated peptide groups usually contain planar



$$\text{-CHR}\overset{\overset{\text{O}}{\|}}{\text{C}}\overset{-}{\text{N}}\text{CHR}'\text{-}$$

iii

iii moieties. Deprotonated amine groups, on the other hand, may not require any great change in peptide conformation. Considering the relatively low pH value at which $[\mathrm{Co(DPA)(H_2O)_3}^{2+}]$ undergoes amine deprotonation, care probably should be exercised now in the assignment of metal ion induced deprotonation reaction in metal-peptide and -protein systems to amide proton ionization.

Acknowledgment. The authors gratefully acknowledge support of this work through West Virginia University Senate Grant 7740. We wish to thank Professor B. J. McCormick for valuable and stimulating discussions.

References and Notes

(1) (a) S. P. Datta and B. R. Rabin, *Trans. Faraday Soc.*, **52,** 1123 (1956); (b) M. K. Kim and A. E. Martell, *Biochemistry*, **3,** 1169 (1964); (c) R. B. Martin, M. Chamberlain, and J. T. Edsall, *J. Am. Chem. Soc.*, **82,** 495 (1960).
(2) C. C. McDonald and W. D. Phillips, *J. Am. Chem. Soc.*, **85,** 3736 (1963).
(3) J. K. Romary, J. D. Barger, and J. E. Bunds, *Inorg. Chem.*, 7, 1142 (1968), and D. W. Gruenwedel, *ibid.*, **7,** 495 (1968). Solutions of $\mathrm{Co(DPA)^{2+}}$ and $\mathrm{Co(DPA)^{2+}}$ are extremely oxygen sensitive forming reversible (to N_2) and irreversible oxygenation products, respectively, even at low O_2 pressures. Gruenwedel cited above acknowledges that in the basic solutions cobalt(II) complexes of ligands containing amino and pyridyl donor groups changed from a pink to a brown color, which, unknown at that time, is indicative of μ-peroxodicobalt(III) species. The reversible oxygenation properties of $\mathrm{Co(DPA)_2}^{2+}$ will be detailed in a future report.
(4) Potentiometric studies of $\mathrm{Co(AMP)_2}^{2+}$ formation have been reported previously, L. G. Sillén and A. E. Martell, *Chem. Soc. Spec. Publ.*, **No. 17,** 482 (1964); **No. 25,** 415 (1972). None of the papers listed apparently involved studies of these complexes at high pH. Perhaps oxygenation reactions were encountered (see ref 3).
(5) D. E. Goldberg and W. C. Fernelius, *J. Phys. Chem.*, **63,** 1246 (1959).
(6) $[\mathrm{Co^{2+}}] = 1.33 \times 10^{-3}$ M; the titrant was 0.121 M NaOH. All potentiometric measurements were made on a Corning Digital Research Model 112 pH meter equipped with Corning glass and calomel extension electrodes. The ionic strength of all solutions was maintained at 0.10 M ($\mathrm{KNO_3}$).
(7) Titrations of 2:1, DPA·3HCl to cobalt(II), solutions had an inflection at $a = 3.0$, indicating the formation of $[\mathrm{Co(DPA)_2}^{2+}]$. Above pH 8.8, a second buffer zone similar to that for the 1:1 system was observed. Log $K_{1a} = -10.13 \pm 0.02$ and $K_{2a} = -11.82 \pm 0.06$. The visible spectrum of the 2:1 DPA to cobalt(II) deprotonated species is very similar that of the deprotonated 1:1 *metal* chelate. *We are not at this time prepared to assign both* proton ionizations in $[\mathrm{Co(DPA)_2}^{2+}]$ to the formation of $[\mathrm{Co(H_{-1}DPA)_2}]$.
(8) A. B. Blake and F. A. Cotton, *Inorg. Chem.*, **3,** 5 (1964).
(9) With a $d^7(\mathrm{Co^{2+}})$ ion, ligand field stabilization energies disfavor the tetrahedral relative to the octahedral configuration to a smaller extent than for any other d^{n+} ion: G. Wilkinson and F. A. Cotton, "Advanced Inorganic Chemistry", 2nd ed, Interscience, New York, N.Y., 1966, Chapter 29-F.
(10) The visible spectrum (320–650 nm) of deprotonated $[\mathrm{Co(DPA)^{2+}}]$ shows a strong absorption at 595 nm, which coupled with the large extinction coefficient (ϵ_{max} 1680 M^{-1} cm^{-1}) is typical of tetrahedral cobalt(II). However, the spectrum is more complex with weaker bands at 474 nm (800 M^{-1} cm^{-1}) and 380 nm (1280 M^{-1} cm^{-1}). These latter bands are shoulders on a very intense charge transfer band which tails into the visible. These latter bands are not yet understood and are probably not due to the presence of small amounts of oxygenated complexes. Molecular models indicate that $\mathrm{Co(H_{-1}DPA)OH}$ must be greatly distorted if indeed the geometry about Co is tetrahedral.
(11) Log $K_{1a} = -9.60 \pm 0.04$, $\mathrm{Co(DPA)^{2+} \rightleftharpoons Co(H_{-1}DPA)^+ + H^+}$; log $k_{2a} = -11.87 \pm 0.08$, $\mathrm{Co(H_{-1}DPA)^+ \rightleftharpoons Co(H_{-1}DPA)OH}$.
(12) Anal. Found: C, 44.06; H, 5.87; N, 12.86. Theoretical: C, 43.90; H, 5.83; N, 12.80. Crystals were obtained by adding 5 equiv of NaOH to a 1:1 DPA·3HCl to $\mathrm{Co(NO_3)·6H_2O}$ solution (10^{-2} M). The solution was placed in a vacuum dessicator over anhydrous $\mathrm{CaCl_2}$.
(13) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds", 2nd ed, Wiley, New York, N.Y. 1970.
(14) R. A. Nyquist and R. O. Kagel, "Infrared Spectra of Inorganic Compounds", Academic Press, New York, N.Y., 1971.
(15) Conductivity was determined at 25 °C on a Serfoss conductivity bridge Model RC M15, Arthur H. Thomas Co.
(16) $[\mathrm{Co^{2+}}] = 1.46 \times 10^{-3}$ M and the titrant was 0.121 M NaOH.
(17) $[\mathrm{Co^{2+}}] = 1.77 \times 10^{-3}$M and the titrant was 0.121 M NaOH.
(18) $\mathrm{Co(AMP)_2}^{2+} \rightleftharpoons \mathrm{Co(H_{-1}AMP)(AMP)^+ + H^+}$, log $K_{1a} = -9.94 \pm 0.10$; $\mathrm{Co(H_{-1}AMP)(AMP)^+ \rightleftharpoons Co(H_{-1}AMP)_2 + H^+}$, log $K_{2a} = -11.03 \pm 0.08$. The conductivity determined on a 2.1 × 10^{-3} M solution of $\mathrm{Co(H_{-1}AMP)_2·5.0H_2O}$ was 4.7 Ω cm^2/mol, indicating the presence of a neutral metal complex. Visible spectra of $\mathrm{Co(H_{-1}AMP)_2}$ are quite complex exhibiting λ_{max} values at 594 nm (1600 M^{-1} cm^{-1}), 473 nm (1030 M^{-1} cm^{-1}), and 371 nm (1750 M^{-1} cm^{-1}). The numbers in parentheses are extinction coefficients, and the latter two bands are shoulders on a very intense ultraviolet charge transfer band which tails into the visible. The spectrum is similar to that of $[\mathrm{Co(H_{-1}DPA)OH}]$.
(19) M. S. Michaildis and R. B. Martin, *J. Am. Chem. Soc.*, **91,** 4683 (1969): $\mathrm{Co(GG)_2 \rightleftharpoons Co(H_{-1}GG)(GG)^- + H^+}$, log $K_{1a} = -9.85$; $\mathrm{Co(H_{-1}GG)GG^- \rightleftharpoons Co(H_{-1}GG)_2{}^{2-} + H^+}$, log $K_{2a} = -10.15$.
(20) H. C. Freeman, *Adv. Protein Chem.*, **22,** 257 (1967).

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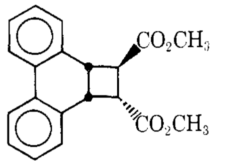
Interception of a Triplet Biradical by Paramagnetic Species. Enhancement of a Photocycloaddition

Sir:

The intervention of triplet 1,4 biradicals has long been suggested in Norrish II fragmentations[1] and [2 + 2] photocycloaddition reactions.[2-4] Evidence for their intermediacy in cycloadditions derives largely from the observation of virtually complete stereorandomization in photoproduct under conditions where reactants maintain stereochemical integrity.[3,4] There have been several observations of interception of biradicals.[5-15] Wagner[6] has estimated a lifetime of 300 ns for a 1,4 triplet biradical in the Norrish II reaction from an elegant intramolecular trapping experiment, and Scaiano[12] has directly determined the lifetime of a related biradical as 97 ± 15 ns in methanol[13] and 42 ns in benzene.[14] O'Neal has estimated a longer lifetime in the vapor phase.[7] We here report the interception of a 1,4-biradical intermediate in a [2 + 2] photocycloaddition. Di-*tert*-butyl nitroxide (N) and molecular oxygen interact efficiently with the 1,4 biradical and enhance its collapse to cyclobutanes.

The benzophenone (B) photosensitized reaction of phenanthrene (P) with dimethyl fumarate (F) affords the stereoisomeric cyclobutanes (T) and (C) and dimethyl maleate (M).[16,17] The mechanism is thought to involve a triplet exciplex, ^{3}(P···F), subsequent collapse of which to a biradical (^{3}SS) ultimately affords the photoproducts.[16,17] For both N and oxygen, small *increases* (5-20%) in the quantum yields for C + T occur on addition of small concentrations (10^{-2} M) of "quencher", while ϕ_M decreases. Further increase in [N] quenched both reactions owing to the known[18] quenching of ^{3}B and ^{3}P by N.



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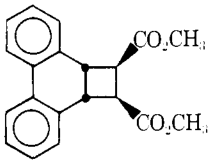

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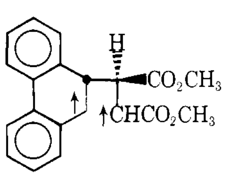


SS

We analyze the reaction in the presence of N as shown in Scheme I. A similar scheme applies for O_2.

For the first two terms, $\phi_{^3P}$ and $\phi_{^3SS}$, all necessary rate constants were either known[18] from competitive quenching of *trans*- to *cis*-stilbene isomerization or measured by the same technique. Concentrations employed minimized the effects of

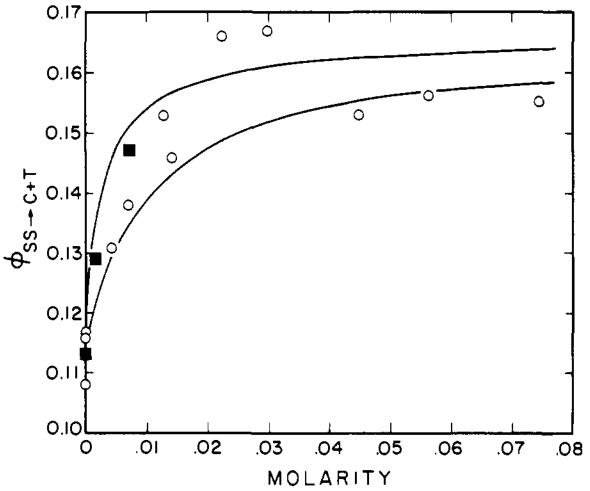


Figure 1, Apparent fraction of C + T from SS ($\phi_{SS\to C+T}$) in benzene as a function of N (○) or O_2 (■). Reactant concentrations varied, with $0.026 < P < 0.22$ M and $0.031 < F < 0.19$ M. Relevant kinetic data for O_2 quenching of ^{3}B and ^{3}P from A. Garner and F. Wilkinson, *Chem. Phys. Lett.*, **45**, 432, (1977), and O. L. J. Gijzeman, F. Kaufman, and G. Porter, *J. Chem. Soc., Faraday Trans. 2*, **69**, 708 (1973). Lines drawn are for the maximum and minimum values of $k_{SST}\tau_{SS}$ estimated in text.

Scheme I

$$\begin{tikzcd}
B + {}^3F & & & \alpha^\circ(C + T) + (1 - \alpha^\circ)P + F + M \\
{}^3B \arrow[u, "F"', "k_{BF}"] \arrow[r, "k_{BP}"'] \arrow[d, "N"', "k_{BN}"] & {}^3P \arrow[r, "k_{PF}"] \arrow[d, "N"', "k_{PN}"] & {}^3(P\cdots F) \arrow[r] & {}^3SS \arrow[u, "\tau_{SS}^{-1}"'] \arrow[d, "k_{SSN}"', "N"] \\
B + N & P + N & & \alpha_N(C + T) + (1 - \alpha_N)(P + F + M)
\end{tikzcd}$$

$$\phi_{C+T} = \underset{\phi_{^3P}}{\frac{k_{BP}(P)}{k_{BP}(P) + k_{BF}(F) + k_{BN}(N)}} \times \underset{\phi_{^3SS}}{\frac{k_{PF}(F)}{k_{PF}(F) + k_{PN}(N)}} \times \underset{\phi_{SS\to C+T}}{\frac{\alpha^\circ + \alpha_N k_{SSN}\tau_{SS}(N)}{1 + k_{SSN}\tau_{SS}(N)}}$$

N on ^{3}B and ^{3}P, thus minimizing experimental error in $\phi_{^3P}$ and $\phi_{^3SS}$ and allowing calculation of $\phi_{SS\to C+T}$ to ±10%. Figure 1 shows the plot of $\phi_{SS\to C+T}$ vs. N. The increase to a plateau value of α_N ~45% above α° shows convincingly that N intercepts an intermediate subsequent to ^{3}P and enhances its probability of forming cyclobutane. We made no measurements with $[O_2]$ 7.25×10^{-3} M ($P_{O_2} = 1$ atm), and consequently did not achieve a plateau.

Several processes must be considered. N or O_2 could interact with either ^{3}SS or ^{3}(P···F). Each interaction could be spin exchange to give the corresponding singlet species or could be bond or complex formation. For reasons which follow, we explain enhancement of ϕ_{C+T} as spin exchange via eq 1.

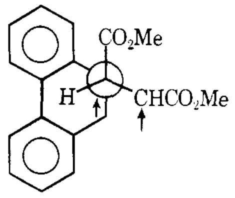
$$N\uparrow + {}^3SS \rightarrow N\downarrow + {}^1SS \xrightarrow{\text{fast}} \text{products} \qquad (1)$$

First, it is difficult to see how bond formation can enhance cycloaddition. Yields of new products are not large in the presence of oxygen in any case. GC analyses of aerated reaction mixtures at ~50% conversion show minimal quantities of new products (<4% of C + T). Published[19] chemical yields in the presence of oxygen indicate that >80% of the product is C + T. Second, the rates of reaction of O_2 and N with free radicals in solution, while rapid, appear to be substantially less than diffusion controlled,[20] while Heisenberg spin exchange rates between N radicals in organic solvents are nearly diffusion controlled.[21] We feel that these are fair models for the chemical trapping and spin exchange rates with ^{3}SS, respectively. The data do not speak to complex formation.

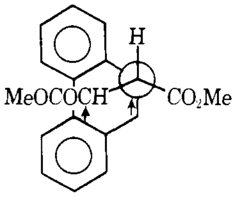
That the species intercepted is ^{3}SS and not ^{3}(P···F) follows from cycloadduct quantum yields,[16,17,22] which are an order of magnitude greater from ^{3}(P···F) than from ^{1}(P···F). Spin exchange with ^{3}(P···F) would consequently *quench* ϕ_{C+T}. Since[22b] 96% of the unperturbed ^{3}P + F interactions produce ^{3}SS, the enhancement cannot result from acceleration of that process. The constancy of the T/C ratio at 1.80 ± 0.05, independent of the concentration of N or O_2, suggests moreover that the interaction occur with a stereorandomized species such as ^{3}SS. We would not expect stereorandomization in ^{3}(P···F) itself.

Because of the smallness of the effect that we observe, quantitative dissection of our results is imprecise. A plot[14] of $\phi^\circ/\phi\text{-}\phi^\circ$ vs. $[N]^{-1}$ (for $\phi_{SS\to C+T}$) shows $\phi_N = 0.16_5 \pm 0.01$ and $k_{SSN}\tau_{SS}$ between 90 and 350 M^{-1}. Assuming $k_{SSN} \sim 5 \times 10^9$ M^{-1}, similar both to Heisenberg exchange rates[21] and to Small and Scaiano's value of interception of a type II biradical by oxygen,[14] we estimate $20 \lesssim \tau_{SS} \lesssim 70$ ns. It appears that ^{3}SS at least roughly resembles type II biradicals in lifetime.

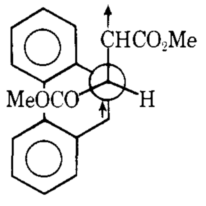
Enhancement of cyclobutane formation suggests that interception of ^{3}SS occurs preferentially in a structure predisposed to cyclobutane formation, e.g., conformation i below. Note that ii, with one more gauche interaction, may be sterically hindered from collapse to cyclobutane, while iii can only give fragmentation to P + F or P + M.



i



ii



iii

If conformational equilibration is rapid, enhancement of C + T production must result from some intrinsic bias toward collapse to cyclobutane in the N- or O_2-induced intersystem crossing, perhaps through some kind of complex.[14] In this view, τ_{SS}^{-1} is presumably the spontaneous spin inversion rate of ^{3}SS. Although we find this a thought-provoking speculation, it may alternatively simply be that ^{3}SS is initially formed in conformation i and is being intercepted before equilibration to ii and iii can occur.[23] On this basis τ_{SS}^{-1} measures the rate of equilibration of i with ii and iii. Interestingly, i is readily derived from a "sandwich" ^{3}(P···F) structure with the reacting double bonds overlaid.

Fragmentation, as measured by $\phi_{SS\to M}$, is diminished by a factor of 1.6 on O_2 saturation and by a factor of 1.4 at [N] = 0.056 M. Unfortunately, a detailed interpretation is not possible without further experiments. Both enhanced cycloadduct formation and new chemistry will dimish $\phi_{SS\to M}$. Since the dominant fragmentation is to the reactants P + F, $\phi_{SS\to M}$ is sensitive in any case to the M/F ratio produced on fragmentation, which may differ among i, ii, and iii. The contrast with type II biradicals, in which fragmentation is enhanced by O_2,[10-15] is nonetheless qualitatively apparent.

In summary, the present results point out that interception of a biradical by N or O_2 can enhance its probability of forming cyclobutane.[10,24] Interception is a viable kinetic probe by which these intermediates can be studied. We underscore the need for a much better understanding of the factors influencing intersystem crossing in biradicals and of the rates for conformational equilibration in such species. Finally, we note the potential synthetic utility of interception in altering product yields in reactions with biradical intermediates.

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References and Notes

(1) P. J. Wagner, *Adv. Photochem.*, **4**, 168 (1971), and references therein.
(2) G. S. Hammond, N. J. Turro, and A. Fischer, *J. Am. Chem. Soc.*, **83**, 4674 (1961).
(3) (a) D. R. Arnold, *And. Photochem.*, **6**, 301 (1968); (b) E. J. Corey, J. D. Bass, R. LeMahieu, and R. B. Mitra, *J. Am. Chem. Soc.*, **86**, 5570 (1964); (c) W. L. Dilling, T. E. Tabor, F. P. Boer, and P. P. North, *ibid.*, **92**, 1399 (1970); (d) P. D. Bartlett, *Quart. Rev.*, **4**, 473 (1970), and references therein.
(4) R. A. Caldwell, *J. Am. Chem. Soc.*, **95**, 1690 (1973).
(5) R. M. Wilson and S. Wunderly, *J. Am. Chem. Soc.*, **96**, 7350 (1974).
(6) P. J. Wagner and K. C. Liu, *J. Am. Chem. Soc.*, **96**, 5952 (1974).
(7) H. E. O'Neal, R. G. Miller, and E. Gunderson, *J. Am. Chem. Soc.*, **96**, 3351 (1974).
(8) P. J. Wagner and R. G. Zepp, *J. Am. Chem. Soc.*, **94**, 287 (1972).
(9) S. Farid, *Chem. Commun.*, 73 (1971).
(10) J. Grotewold, C. M. Previtali, D. Soria, and J. C. Scaiano, *J. Chem. Soc., Chem. Commun.*, 207 (1973).
(11) R. D. Small and J. C. Scaiano, *J. Photochem.*, **6**, 453 (1977).
(12) J. C. Scaiano, *J. Am. Chem. Soc.*, **99**, 1494 (1977).
(13) R. D. Small and J. C. Scaiano, *J. Phys. Chem.*, **81**, 828 (1977).
(14) R. D. Small and J. C. Scaiano, *Chem. Phys. Lett.*, **48**, 354 (1977).
(15) Y. Kubokawa and M. Anpo, *J. Phys. Chem.*, **79**, 2225 (1975).
(16) S. Farid, S. E. Hartman, J. C. Doty, and J. L. R. Williams, *J. Am. Chem. Soc.*, **97**, 3697 (1975).
(17) R. A. Caldwell, *J. Am. Chem. Soc.*, **95**, 1690 (1973).
(18) R. E. Schwerzel and R. A. Caldwell, *J. Am. Chem. Soc.*, **95**, 1382 (1973).
(19) G. Kaupp, *Angew. Chem., Int. Ed. Engl.*, **12**, 765 (1973).
(20) (a) C. H. Bamford and M. J. S. Dewar, *Proc. R. Soc. London, Ser. A*, **198**, 252 (1949); see also C. Walling, "Free Radicals in Solution", Wiley, New York, N.Y., 1957, p 418 ff. for reaction with O_2. (b) Reaction rate constants for nitroxide radicals with alkyl radicals are 4–7 × 10^8 M^{-1} s^{-1} in benzene: P. Schmid and K. U. Ingold, *J. Am. Chem. Soc.*, **99**, 6434 (1977).
(21) M. P. Eastman, R. G. Kooser, M. R. Das, and J. H. Freed, *J. Chem. Phys.*, **51**, 2690 (1969); J. C. Lang, Jr., and J. H. Freed, *ibid.*, **56**, 4103 (1972). See also W. Plachy and D. Kivelson, *ibid.*, **47**, 3312 (1967).
(22) (a) D. Creed and R. A. Caldwell, *J. Am. Chem. Soc.*, **96**, 7369 (1974); (b) R. A. Caldwell and D. Creed, unpublished work.
(23) This idea derives from external heavy-atom effects on coumarin dimerization, which apparently enhance cycloadduct quantum yields: R. Hoffman, P. Wells, and H. Morrison, *J. Org. Chem.*, **36**, 102 (1971).
(24) Enhanced quantum yields of cycloaddition in the presence of N (R. Hoffman, Ph.D. Dissertation, Purdue University, 1970) and O_2 (S. W. Wunderly, Ph.D. Dissertation, University of Cincinnati, 1974) have been noted previously. We thank Professors Morrison and Wilson, respectively, for private communications.

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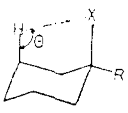
Steric Effects on Carbon-13 Nuclear Magnetic Resonance Shifts in Alkanes[1]

Sir:

Whereas the gross effects of substituents on α carbon shifts ($\Delta(C_\alpha)$) can be understood in terms of calculated electron densities,[2] the pronounced and stereoselective effects on more remote carbons have led to several conflicting proposals of shielding mechanisms. Most recently, Gorenstein[3] has connected the shielding observed in gauche fragments, as, e.g., in **1**, with increasing bond angles in such arrangements. Introduction of an axial substituent in cyclohexane, however, produces deshielding not only at C_β but in many cases also at C_α (C_γ in **1**, misread in ref 3, is always upfield from the e isomer **2**). Since no reliable and accurate spectroscopical structure determinations are available for heterosubstituted cyclohexanes, we have investigated steric distortions as possible sources of shielding variations using Allinger's molecular mechanics force field (FF).[4] For **1** and **2** (R = H or CH_3; X = F, Cl, Br, I, OH, CH_3, H) no correlation of changes of bond length ($\Delta l < 0.3\%$), bond angles ($\Delta\theta < 2\%$) and torsional angles ($\Delta\varphi < 16\%$)[5] with the observed ^{13}C shifts[6] are found. In fact, increasing $XC_\alpha C_\beta$ bond angles correspond to downfield C_α shifts, establishing a regular trend for secondary and tertiary cyclohexyl halides; other angles at C_α change to a significantly lesser degree. Furthermore, variation of the substituent X leads to $XC_\alpha C_\beta C_\gamma$ torsional angle changes, but the $C_{\beta'} C_\alpha C_\beta C_\gamma$ angles change simultaneously in the opposite direction. Only the widening of the $C_\alpha C_\beta C_\gamma$ bond angle in **1** as compared to **2** by up to 2.2° can be related to the smaller deshielding effects of X on C_β in gauche fragments. Hybridization changes for $C_\alpha X$ bonds, as obtained from FF calculated bond angles using Coulson's formula,[7] do not reproduce observed trends in cyclohexane shifts.[5] In the absence of recognizable steric distortions, electrical effects are expected to determine the observed shifts.[8]



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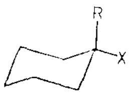

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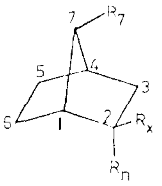
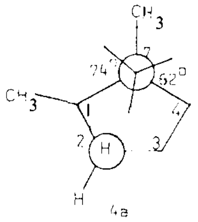
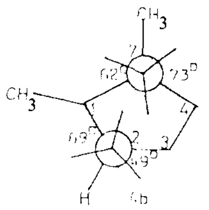


3a (R7=Rx=Rn=H)
3b (R7=CH_3, Rx=Rn=H)
3c (Rx=CH_3, R7=Rn=H)
3d (Rn=CH_3, R7=Rx=H)



4a



4b

The most clearly defined shielding mechanism by a steric perturbation, proposed by Grant and Cheney,[9] relates the shift at C_i to the force vector exerted on a C_i–H bond. It should apply also to deshielding situations, to interactions with heteroatoms, and to carbon atoms not in γ position. In defining the shielding force vector on the C_i–H bond, an equation is proposed which is derived from a potential[10] for nonbonded interactions:

$$F = 0.6952 \times 10^{-5}(18\epsilon/r^*)[(r^*/r)^{10} - (r^*/r)^7] \cos\theta \quad (1)$$

Equation 1 applies to hydrogen-hydrogen interactions (ϵ = 0.004 109, r^* = 3.632) as well as to carbon-hydrogen interactions (ϵ = 0.026 102, r^* = 3.575);[10] r represents the distance between the hydrogen attached to C_i and the interacting H or C; θ is the angle between the force vector and the C_i–H bond. Since repulsive nonbonded interactions are extremely sensitive to small changes in r, we have applied eq 1 only to fully relaxed molecular structures as obtained by FF energy minimization. An illustrative example is the 1,3 diaxial interaction force in a methyl cyclohexane, which decreases by 80% in going from ideal "standard" to the relaxed geometry. In pioneering their correlation, Grant and Cheney[9] had used nonrelaxed geometries and moreover idealized conformer populations and geometries. The FF calculated geometries of hydrocarbons **1** (R = H; X = CH_3) and **3a–d**[5] and the observed syn-γ ^{13}C