Cyclopropane Anisotropy. Effects of Systematically Varied Cyclopropane Geometries in Aromatic Systems[1]

Roger C. Hahn* and Philip H. Howard

Contribution from the Department of Chemistry, Syracuse University, Syracuse, New York 13210. *Received July 26, 1971*

Abstract: Pmr spectra have been obtained for all aryl nitro derivatives of 1,1a,6,6a-tetrahydrocycloprop[*a*]indene (F5), spiro[cyclopropane-1,1′-indan] (S5), 1a,2,3,7b-tetrahydro-1*H*-cyclopropa[*a*]naphthalene (F6), spiro[cyclopropane-1,1′-tetralin] (S6), 1,1a,2,3,4,8b-hexahydrobenzo[*a*]cyclopropa[*c*]cycloheptene (F7), spiro[cyclopropane-1,1′-benzosuberan] (S7), and the corresponding parent systems. For F and S series members having an α proton (β-, β'-, and α'-nitro isomers), the chemical shift of that proton was determined relative to a comparable proton in the parent series. The bond anisotropy theory and the cyclopropane group anisotropy theory both correctly predict cyclopropane deshielding (effect on α proton) for F5 and F6 systems and shielding for S5 and S6. However, bond anisotropy theory predicts cyclopropane shielding for F7 and S7, while group anisotropy theory predicts deshielding for both systems. The experimental data agree completely with the predictions of the group anisotropy theory, strongly indicating the superiority of this concept in the present applications.

Over the last decade, the magnetic anisotropy effects of the cyclopropane ring have received attention from a number of investigators. The high-field shift of protons directly attached to cyclopropane has been attributed to a ring current effect,[2,3] but it was concluded that available data did not leave this theory firmly established.[3] Long-range cyclopropane anisotropy effects,[4] consistent with the measured, large diamagnetic susceptibility of cyclopropane,[5] also have been explained in terms of a ring current.

More recently, interest has arisen in a semiquantitative treatment of long-range anisotropy effects of cyclopropane rings.[6-8] Two of the methods of calculating the shielding effects of a cyclopropane ring depend on the general equation derived by McConnell[9] (eq 1).

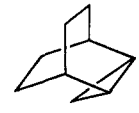
$$\Delta\tau = \frac{\Delta\chi}{3}\frac{(3\cos^2\theta - 1)}{R^3} \qquad (1)$$

The utility of this expression rests on the assumption that the shielding field of a specific group of electrons can be represented by an infinitesimally small magnet (point dipole). This approximation is most reasonable when R, the distance (in Å) between the shielded proton and the center of the cyclopropane ring, is fairly large ($R \gg r$, where r is the atomic radius of the proton). In eq 1, $\Delta\tau$ is the additional shift value of an affected proton due to the cyclopropane ring, $\Delta\chi$ is the molecular susceptibility and is empirically determined, and θ is the acute angle which the line R makes with the plane of the cyclopropane ring.

Tori and Kitahonoki[6] suggested that the concept of bond anisotropy[10] could be used instead of group anisotropy to explain the long-range shielding effects of a cyclopropane ring. They used a modified McConnell equation (2), in which $\Delta\tau$ and $\Delta\chi$ are the same as for eq 1, R_i is the distance (in Å) between the midpoint of a C–C single bond of the cyclopropane ring and the affected proton, and θ_i is the acute angle which line R_i makes with the C–C single bond. This treatment is still an approximation because a C–C bond is represented as a point dipole and does not take into account the electron cloud volume.

$$\Delta\tau = \frac{\Delta\chi}{3}\sum_{i=1}^{3}\frac{(3\cos^2\theta_i - 1)}{R_i^3} \qquad (2)$$

Tori and Kitahonoki[6] compared the two methods for a series of substituted tricyclo[3.2.2.0^{2,4}]nonanes (I). They concluded that calculated values are closer to observed values when eq 2 (bond anisotropy) is used.



I

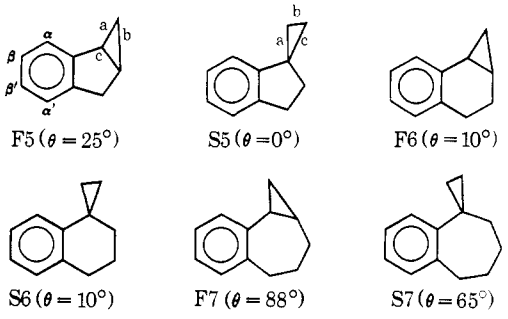
However, their study dealt with a single skeletal framework.

Other investigators[3,11] have assumed cyclic σ-electron delocalization in cyclopropane and have calculated shielding effects using the empirical ring-current treatment of Johnson and Bovey.[12] This method avoids sources of error inherent in the point dipole approximation, but was considered tedious[6] until recent development of a convenient cyclopropane shielding map.[11]

Previous studies in this laboratory[1b,13] provided many nitro derivatives of 1,1a,6,6a-tetrahydrocycloprop[*a*]indene (F5), spiro[cyclopropane-1,1′-indan]

(1) (a) Part III in a series on cyclopropylaromatic chemistry; (b) part II: R. C. Hahn, P. H. Howard, and G. A. Lorenzo, *J. Amer. Chem. Soc.*, **93**, 5816 (1971).
(2) K. B. Wiberg and B. J. Nist, *ibid.*, **83**, 1226 (1961).
(3) D. J. Patel, M. E. H. Howden, and J. D. Roberts, *ibid.*, **85**, 3218 (1963).
(4) (a) S. Forsén and T. Norin, *Acta Chem. Scand.*, **15**, 592 (1961); (b) J. Tadanier and W. Cole, *J. Org. Chem.*, **27**, 4610 (1962); (c) R. R. Sauers and P. E. Sonnet, *Chem. Ind. (London)*, 786 (1963); (d) T. Norin, *Acta Chem. Scand.*, **17**, 738 (1963).
(5) J. R. Lacher, J. W. Pollack, and J. D. Park, *J. Chem. Phys.*, **20**, 1047 (1952).
(6) K. Tori and K. Kitahonoki, *J. Amer. Chem. Soc.*, **87**, 386 (1965).
(7) S. Forsén and T. Norin, *Tetrahedron Lett.*, 2845 (1964).
(8) N. S. Bhacca, M. E. Wolff, and W. Ho, *ibid.*, 5427 (1968).
(9) H. M. McConnell, *J. Chem. Phys.*, **27**, 226 (1957).
(10) See L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd ed, Pergamon Press, New York, N. Y., 1969.
(11) C. D. Poulter, R. S. Boikess, J. I. Brauman, and S. Winstein, *J. Amer. Chem. Soc.*, **94**, 2291 (1972), and references therein. We are indebted to Professor Poulter for a preprint of this work.
(12) C. E. Johnson, Jr., and F. A. Bovey, *J. Chem. Phys.*, **29**, 1012 (1958).
(13) R. C. Hahn, P. H. Howard, S.-M. Kong, G. A. Lorenzo, and N. L. Miller, *J. Amer. Chem. Soc.*, **91**, 3558 (1969).

(S5), 1a,2,3,7b-tetrahydro-1*H*-cyclopropa[*a*]naphthalene (F6), spiro[cyclopropane-1,1′-tetralin] (S6), and 1,1a,-2,3,4,8b-hexahydrobenzo[*a*]cyclopropa[*c*]cycloheptene (F7).[14] This series contains a variety of cyclopropane orientations with respect to the benzene α proton (see below), which is close enough to the cyclopropane ring to be under considerable anisotropic influence. (The angle θ may be considered to be the angle made by the plane of the benzene ring with the cyclopropyl methine C–H bond for F series compounds, or with the corresponding C–C bond for S series compounds.) Comparison of chemical shifts of α protons (β-, β'-, and α'-nitro isomers) in these compounds with suitable reference protons was undertaken in the hope of providing a useful extended test of the relative merits of the bond and group anisotropy theories of cyclopropane anisotropy. Considerations to be enumerated later prompted inclusion of nitro derivatives of spiro[cyclopropane-1,1′-benzosuberan] (S7) in the study.



The nitro derivatives, in addition to other uses,[1b,13,15] usually have the aromatic proton resonances spread so that chemical shift values are readily assigned; they also provide sources of internal comparison for cyclopropane anisotropy effects (*e.g.*, comparison of the α proton in β-NO_2-F5 with the α' proton in β'-NO_2-F5).

Results and Discussion

Pmr chemical shift values[16] for the aryl protons in indan, tetralin, benzosuberan, and the β-, β'-, and α'-nitro isomers of F5, S5, F6, S6, F7, and S7, keyed to partial structures A, B, and C, are shown in Table I; aryl regions of these spectra are reproduced in Appendix I (microfilm edition).[17]

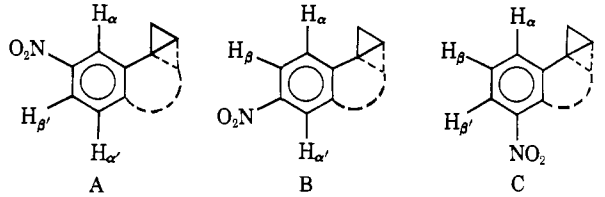


Table I. Chemical Shifts[a–c] (τ, $CDCl_3$) of Nitroaromatics

Compound	H_α	H_β	$H_{\beta'}$	$H_{\alpha'}$
α-Nitroindan		2.08 dd	2.76 t	2.49 dd
β-Nitroindan	1.99 d		2.03 dd	2.71 d
β-NO_2-F5[d]	*1.99 d*		2.14 dd	2.85 d
β'-NO_2-F5[d]	*2.67 d*	2.05 dd		2.07 d
α'-NO_2-F5	*~2.48*	2.80	~2.12	
β-NO_2-S5	*2.53 d*		2.02 dd	2.74 d
β'-NO_2-S5	*3.30 d*	~2.02		~1.96
α'-NO_2-S5	*3.12 dd*	2.74 t	2.10 d	
α-Nitrotetralin[e]		2.40 dd	2.84 t	2.72 dd
β-Nitrotetralin	2.13 d		2.15 dd	2.86 d
β-NO_2-S6	*1.92 d*		2.14 dd	2.89 d
β'-NO_2-F6	*2.65 d*	2.06 dd		2.15 d
α'-NO_2-F6	*2.54 dd*	2.84 t	2.45 dd	
β-NO_2-S6	*2.52 d*		2.21 dd	2.88 d
β'-NO_2-S6	*3.29 d*	~2.13		~2.09
α'-NO_2-S6	*3.17 dd*	2.83 t	2.49 dd	
α-Nitrobenzosuberan		2.57 dd	2.89 t	2.68 dd
β-Nitrobenzosuberan	2.03 d		2.07 dd	2.77 d
β-NO_2-F7	*1.83 d*		2.01 dd	2.82 d
β'-NO_2-F7	*2.56 d*	2.00 dd		2.11 d
α'-NO_2-F7	*~2.45*	2.80 t	~2.35	
β-NO_2-S7	*~1.99 d*		2.08 dd	2.81 d
β'-NO_2-S7	*2.69 d*	2.08 dd		2.08 d
α'-NO_2-S7[e]	*~2.57 dd*	2.86 t	~2.55	

[a] Spectra were taken at room temperature with a Varian A-60 spectrometer on ~10% (w/w) solutions in deuteriochloroform with tetramethylsilane as internal reference, unless otherwise noted. Accuracies are within ±0.02 ppm unless otherwise indicated (~); instrumental variations were determined to be less than ±0.01 ppm over the duration of the project. [b] For signal assignments, see microfilm edition.[17] Peak multiplicities are indicated by d (doublet), t (triplet), and dd (doublet of doublets). [c] Shifts affected by cyclopropane anisotropy are in italics. Designation of protons (α, β, β', α') in nitro reference compounds is necessarily based on the position of the nitro function (α or β only), while proton designation in cyclopropyl systems is based on the position of the cyclopropyl group. As a consequence, protons in β-nitrocyclopropyl aromatic systems are comparable with identically designated protons in the parent systems (*e.g.*, α *vs.* α), but protons in β'- and α'-nitrocyclopropyl aromatics *are not*. In evaluating cyclopropane anisotropy effects in the latter systems, α, β, and β' protons must be compared with α', β', and β protons, respectively, in the parent compounds. An alternative proton nomenclature proved indecipherable to referees. [d] Methylene chloride was used as an internal standard. [e] Recorded on a Japan Optics JMN-4H-100 spectrometer.

Laszlo[18a] has shown that for structural studies to be valid they may need to be obtained in several solvents.[18b] Pmr spectra therefore were taken of β-nitrotetralin, β'-NO_2-F6, and β'-NO_2-S6 in carbon tetrachloride, since this solvent is known to give minimal differential solvation effects.[18a] The new solvent produced a uniform upfield shift of 0.05 ± 0.02 ppm for the α-proton resonance in all three compounds; it was concluded that the magnitude of differential solvent shift effects would not change any of the conclusions derived from spectra taken in deuteriochloroform. Laszlo's concern was based partly on problems introduced on attempting to compare systems containing greatly different functional groups, *e.g.*, compounds containing a heteroatom *vs.* compounds lacking one. The possibility of differential solvation effects clearly is great in such a case. The present compounds all have the nitrobenzene moiety in common, and large differential solvation effects were not anticipated.

(14) Compound codings used here and henceforth (F5, S6, etc.) conveniently recall skeletal features: F stands for a fused cyclopropane ring, S for a spirocyclopropane; 5, 6, or 7 refers to the size of ring fused to the benzene ring.

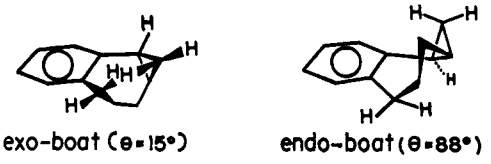
(15) Complete isomer distributions and partial rate factors from nitration of F5, *et al.*, a study of nitro group anisotropy effects, and mass spectral behavior in these systems will appear in separate papers.

(16) Many of these values vary slightly from those reported previously[13] as a result of being redetermined for the present purposes (*i.e.*, better resolved spectra were obtained, and calibrations were rechecked).

(17) Appendix I will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number JACS-72-3143. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

(18) (a) P. Laszlo, *Bull. Soc. Chim. Fr.*, 2658 (1964); (b) *Progr. Nucl. Magn. Resonance Spectrosc.*, 3, 317 (1967).

Preferred conformations of molecular frameworks were determined initially from consideration of Dreiding models. These models allow only one conformation of indan, F5, and S5. The preferred conformation for tetralin and for S6 is a distorted chair;[19] two such equivalent conformations exist in each case. For F6, the two possible distorted chair conformations (θ = 10 and 50°) are made nonequivalent by the presence of bond oppositions in the 50° conformation.[20] Nmr signal coalescence studies of benzosuberan and selected methyl and deuterio derivatives[21,22] show that the chair form (two identical conformations) predominates; the same conformational preference was assumed for S7. However, fusion of a cyclopropane ring into the benzosuberan system to form the F7 skeleton reduces the allowed conformations (*according to a Dreiding model*) to only the "exo-boat" and the "endo-boat" forms shown below. The model indicates severe hydrogen–hydrogen opposition in the exo-boat, thus allowing *a priori* the choice of the 88° conformation as



the favored one.

For each of the above cyclopropyl systems the selected preferred conformation was supported by the nitration behavior of the hydrocarbon (predominant nitration ortho and para to the cyclopropyl group in F5, S5, F6, and S6; predominant nitration meta to the cyclopropyl in F7 and S7)[15] and by the uv spectral characteristics of the nitro derivatives.[1b,13] For the F series compounds the contribution of the "ordinary" C–C bond replaced by bond C (see above) in the fused cyclopropane ring was subtracted, making measurements necessary for indan, tetralin, and benzosuberan. The value of -5.5×10^{-30} cm^3/molecule chosen for the ordinary $\Delta\chi^{C-C}$ is the same as that used by Tori and Kitahonoki.[6] Values from -5.5 to -25 have been suggested,[10] but Bothner-By and Pople[23] have calculated a limiting value of -7.5×10^{-30}. By this criterion, a value near the small end of the reported range appears more reasonable.

Although $\Delta\chi^{C-H}$ appears not to be negligibly small,[10] and it has been recommended that screening effects of all bonds displaced or introduced be considered,[24] C–H bond effects have been omitted from the present treatment. This omission is based on the assumption that the net screening effect of the C–H bonds in a parent compound is not appreciably different from that in a cyclopropyl derivative, and is not likely to outweigh the cyclopropane anisotropy effect.[25]

(19) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill, New York, N. Y., 1962.
(20) A. L. Goodman and R. H. Eastman, *J. Amer. Chem. Soc.*, **86**, 908 (1964).
(21) S. Kabuss, H. Friebolin, and H. Schmid, *Tetrahedron Lett.*, 469 (1965).
(22) (a) H. Hart and J. L. Corbin, *J. Amer. Chem. Soc.*, **87**, 3135 (1965); (b) E. Grunwald and E. Price, *ibid.*, **87**, 3139 (1965).
(23) A. A. Bothner-By and J. A. Pople, *Annu. Rev. Phys. Chem.*, **16**, 43 (1965).
(24) J. W. ApSimon, W. G. Craig, P. V. Demarco, D. W. Mathieson, L. Saunders, and W. B. Whalley, *Tetrahedron*, **23**, 2339, 2357 (1967).
(25) Just as increased p character of a cyclopropane C–C bond appears to change the magnitude of molecular anisotropy from that of an ordinary C–C bond,[6] so a cyclopropane C–H bond, with its increased s character, probably does not exert an anisotropy effect equal to that of an ordinary C–H bond. Attempts to account for such a difference, taking into consideration the deficiencies of the point dipole approximation, do not appear worthwhile in the present context. Modifications which assign finite dipole lengths also do not notably improve reported calculated bond anisotropies.[10,24]

Table II. Observed and Calculated Chemical Shift Changes, α Protons

Compd	Nitro isomer	Shift due to cyclopropane, ppm: Internal comparison[a,b]	Parent comparison[a,c]	Calcd by group anisotropy[d]	Calcd by bond anisotropy[e]
F5	β	−0.08	−0.13	−0.15	−0.10
	β'	−0.18	−0.09	−0.15	−0.10
	α'		−0.05	−0.15	−0.10
S5	β	+0.57	+0.54	+0.25	+0.54
	β'	+0.56	+0.61	+0.25	+0.54
	α'		+0.63	+0.25	+0.54
F6	β	−0.23	−0.22	−0.21	−0.22
	β'	−0.24	−0.17	−0.21	−0.22
	α'		−0.20	−0.21	−0.22
S6	β	+0.43	+0.35	+0.40	+0.87
	β'	+0.41	+0.46	+0.40	+0.87
	α'		+0.41	+0.40	+0.87
F7	β	−0.28	−0.20	−0.29	+0.09
	β'	−0.26	−0.21	−0.29	+0.09
	α'		−0.07	−0.29	+0.09
S7	β	−0.09	−0.06	−0.23	+0.18
	β'	−0.12	−0.11	−0.23	+0.18
	α'		−0.09	−0.23	+0.18

[a] Errors caused by second-order spin–spin interactions were assumed to be negligible since a difference was determined. [b] The α proton in a β- (β'-) nitro isomer was compared with the α' proton in the β'- (β-) nitro isomer. [c] Determined relative to the corresponding nitro isomer of indan, tetralin, or benzosuberan and adjusted for cyclopropane shift effects other than anisotropy (see Discussion). [d] $\Delta\chi$ was taken to be -19×10^{-30} cm^3/molecule. [e] $\Delta\chi$ was taken to be -15×10^{-30} cm^3/molecule. These values are of the same order of magnitude as those previously derived or measured (ref 5–7).

Observed and calculated chemical shift changes attributed to cyclopropane anisotropy are given in Table II. Two sets of experimental values are shown and are of themselves significant. Internal comparison values were obtained by subtracting (for example) the $H_{\alpha'}$ value for β'-NO_2-S5 (τ 1.96, Table I) from the H_α value for β-NO_2-S5 (2.53), and by subtracting the $H_{\alpha'}$ value for β-NO_2-S5 (2.74) from the H_α value for β'-NO_2-S5 (3.30). The constancy of matched pairs of values speaks for minimal ground state conjugative interaction between nitro and cyclopropyl groups in the β'-nitro isomers, even where cyclopropane geometry may be favorable for such interaction. The parent comparison values were obtained by subtracting shift values of parent protons from values of corresponding derivative protons and adjusting for shift effects (other than anisotropy) attributable to incorporation of a cyclopropane ring. For instance, H_α (β-NO_2-S6) minus H_α (β-nitrotetralin) gives a gross $\Delta\tau$ of 0.39 ppm; the other two aryl protons of β-NO_2-S6, presumed to be unaffected by cyclopropane anisotropy, differ from the corresponding β-nitrotetralin protons by an average of 0.04 ppm (Table I), so that the net anisotropy effect on H_α is 0.35 ppm. The close agreement between internal comparison values and net parent comparison values (Table II) increases confidence in the usefulness of the latter. Internal comparisons between α'- and α-nitro isomers were precluded by intrusion of severe steric effects into the spectra of the latter.[1b,13,15]

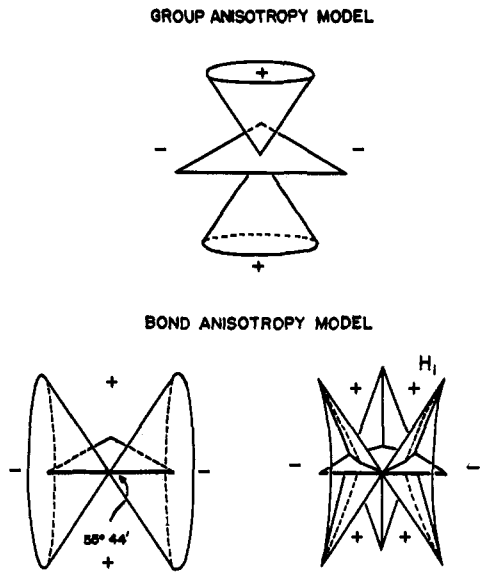


Figure 1.

For the F5, S5, F6, and S6 systems there is agreement in sign between the observed and calculated anisotropy shift values for both models. Nitro isomer assignments (β *vs.* β', α *vs.* α') in these systems, made on the basis of nmr differences, are clearly consistent with the nitration behavior of the hydrocarbons and with pertinent uv and mass spectral features;[1b,13,15] more rigorous structure proofs were deemed unnecessary. However, application of the two anisotropy models to the F7 and S7 frameworks revealed in each case a divergence in the sign of the predicted cyclopropane anisotropy effects. Because uv and mass spectral features are almost identical for β- and β'-NO_2-F7[1b,13,15] and for β- and β'-NO_2-S7,[15] independent syntheses of β-NO_2-F7 and β-NO_2-S7 were performed (see Experimental Section). These confirmed the structure assignments and the superiority of the group anisotropy model; the α-proton shifts for all F7 and S7 nitro isomers conform to the predictions of this model (Table II). Although the possibility cannot be ruled out that factors (*e.g.*, inductive effects) other than anisotropy effects produce the rather small downfield shifts seen for S7 isomers, the consistent success of the group anisotropy model in the systems under discussion encourages an interpretation which neglects such factors.

It is now pertinent to inspect more closely the two anisotropy models to see why they give rise to divergent predictions in only two of the six skeletons studied, and why sign differences are considered to be more important than magnitude differences in determining the relative merits of the two models. Figure 1 shows the magnetic field shapes created by the group anisotropy theory and the bond anisotropy theory. The shape of the magnetic field in the latter case is due to the summation of the fields of the three cyclopropane C–C bonds. According to the group anisotropy model, a proton on any line which makes an angle less than 55° 44′ with the plane of the cyclopropane ring at its center experiences anisotropic deshielding. In the bond anisotropy model, any proton on a line which makes an angle greater than 55° 44′ with the center of the nearest cyclopropane C–C bond is shielded. Only a proton which satisfies both of the above requirements (*e.g.*, H_i in Figure 1) is in that critical region for which the predictions of the two models differ in sign. Compounds containing such a proton (derivatives of F7 and S7 in this study) appear to be a minority of reported cyclopropane systems; no comment on these differences in the two models was found in prior literature.

The *magnitudes* of the differences between the shifts predicted for F7 and S7 by the two methods are less than the difference calculated for S6 (Table II). However, the magnitude of difference is susceptible to changes in choices of the empirical $\Delta\chi$ values, whereas the *sign* of Δ_{ppm} is not, since this is determined by the value(s) of θ. The latter feature thus is taken as a more critical indication of the relative merits of the models.

It then becomes important to consider, for the F7 and S7 derivatives, the sensitivities of the signs of the calculated Δ_{ppm} values to changes in measured θ values. Assuming that a Dreiding model accurately represents the F7 molecule, θ's can be measured readily to within $\pm 5°$. Application of the group anisotropy method to F7 involves a measured θ value of 25°, which is 30° away from the "crossover value" (Figure 1) of 55° 44′, where the sign of the calculated shift would change. Application of the bond anisotropy method to F7 reveals that most of the anisotropy effect comes from the bond closest to the affected proton, since Δ_{ppm} varies with $1/R_i^3$ (eq 2). Values of 79, 52, and 35°, measured for θ_a, θ_b, and θ_c, respectively, indicate that only the anisotropy of bond a (the nearest bond) contributes to the net shielding effect calculated for the α proton, and that an error of over 15° would be needed to reduce the shielding effect of bond a to where it would be overbalanced by the deshielding effects of bonds b and c. Errors in R values also conceivably could affect the sign of Δ_{ppm} as calculated by the bond anisotropy method, but again the magnitude of the errors needed to do this seems beyond the limits of measuring accuracy. A parallel situation exists for the S7 system.

Additional evidence favoring the group anisotropy model appears in the aliphatic region of the pmr spectra of F7 and its α-, β-, and β'-nitro derivatives. The benzylic protons for each of these isomers (shown for parent F7 in Appendix I, microfilm edition[17]) appear as two distinct multiplets separated by almost 0.8 ppm, indicating an overwhelming preference for a single conformation. This is assumed to be the endo-boat form (see above). A pronounced deshielding anisotropy effect on the downfield (axial) proton ($\sim$0.5 ppm) is apparent on comparison with the benzylic protons of benzosuberan and its aryl nitro derivatives.[1b,13] This proton also is in the "critical" cyclopropane anisotropy region; deshielding is predicted only by the group anisotropy model.

The results of the present study cast doubts on the ability of the bond anisotropy model to predict cyclopropane shielding effects for a wide variety of structures. Previous examples of superior correlations using this model[6] included no protons in the critical anisotropy region, and may be attributable to effects of other structural features. On the other hand, the group anisotropy model, despite the inherent limitations of the point dipole approximation,[10] rather accurately predicts the sign and size of cyclopropane

shielding in the systems at hand. Comparison of this model with the successful Johnson–Bovey ring current model[12] now is in progress, but structures which provide a definitive evaluation of relative merits may be hard to find. Finally, it is noted that while positive proof still is lacking, the group anisotropy model (like the ring current model) provides correlations consistent with the presence of a ring current in cyclopropane.

Experimental Section[26]

Melting points and boiling points are uncorrected. Proton magnetic resonance spectra were obtained with a Varian A-60 or a Jeolco J-100 (100 MHz); ultraviolet spectra were recorded on a Perkin-Elmer Model 202. Mass spectra were obtained from a Perkin-Elmer RMU-6E; infrared spectra were recorded on a Perkin-Elmer Infracord Model 137. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn., and Scandinavian Microanalytical Laboratory, Herlev, Denmark.

Preparation of 6-Nitro-1a,2,3,7b-tetrahydro-1*H*-cyclopropa[*a*]naphthalene (β-NO_2-F6). 7-Nitrotetrahydronaphth-1-ol. 7-Nitro-1-tetralone[27] (1.0 g, 5.24 mmol) in 30 ml of 95% ethanol was reduced by sodium borohydride (869 mg, 23 mmol) to yield 884 mg (88%) of 7-nitrotetrahydronaphth-1-ol, mp 108–110°: pmr [$(D_3C)_2C{=}O$] τ 1.70 (1 H, d, 8-H), 2.09 (1 H, dd, 6-H), and 2.74 (1 H, d, 5-H); ir (KBr) 3280, 1510, 1330, 908, 860, 820, 797, and 738 cm^{-1}.

6-Nitro-1,2-dihydronaphthalene. This nitroalkene was prepared by dehydration of the above alcohol as described for 8-nitro-1,2-dihydronaphthalene;[1b] work-up and hexane recrystallization yielded pale yellow crystals, mp 36.0–36.5°: pmr ($CDCl_3$) τ 7.4–7.8 (2 H, multiplet, allylic CH_2), 6.9–7.3 (2 H, m, benzylic CH_2), 3.47 (1 H, d, benzylic vinylic H), 3.83 (1 H, dt, other vinylic H,) 2.78 (1 H, d, α'-(H), 2.17 (1 H, d, α-H), and 2.04 (1 H, dd, β'-H); uv λ_{max}^{EtOH} 275 mμ (ϵ 25,400); λ_{max}^{hexane} 249 mμ (ϵ 25,100); ir (neat, NaCl) 1620, 1580, 1520, and 1340 (NO_2), 1085, 900, 835, 805, 778, and 740 cm^{-1}.

Anal. Calcd for $C_{10}H_9NO_2$: C, 68.56; H, 5.18; N, 8.00. Found: C, 68.86; H, 5.18; N, 8.12.

β-NO_2-F6. Reaction of 6-nitro-1,2-dihydronaphthalene (2.0 g, 11.4 mmol) with iodomethylzinc iodide (80 mmol) and work-up as for synthesis of α'-NO_2-S5[1b] yielded 200 mg (9%) of β-NO_2-F6, mp 31.5–32.0°; pmr ($CDCl_3$) τ 8.9–9.2 (2 H, m, cyclopropyl CH_2), 7.2–7.6 (2 H, m, benzylic CH_2), 7.6–8.9 (4 H, m, remaining nonaromatic H's), 2.89 (1 H, d, α'-H), 2.14 (1 H, dd, β'-H), and 1.92 (1 H, d, α-H); uv λ_{max}^{EtOH} 282 mμ (ϵ 8400); λ_{max}^{hexane} 273 mμ (ϵ 8240); ir (neat, NaCl) 1520 and 1340 (NO_2), 928, 906, 877, 861, 830, 795, 745, and 736 cm^{-1}.

Anal. Calcd for $C_{11}H_{11}NO_2$: C, 69.82; H, 5.86; N, 7.40. Found: C, 70.02; H, 5.68; N, 7.27.

Preparation of 7'-Nitrospiro[cyclopropane-1,1'-tetralin] (β-NO_2-S6). 7-Nitro-1-methylenetetralin. A Wittig reaction between triphenylphosphonium methylide (74 mmol) and 7-nitro-1-tetralone (9.0 g, 47 mmol) was conducted and worked up as reported for 4-nitro-1-methyleneindan[1b] to yield 1.88 g (21%) of 7-nitro-1-methylenetetralin, mp 53.5–54.0°; pmr ($CDCl_3$) τ 4.42 and 4.90 (1 H each, s's, vinyl H's), 7.11 (2 H, t, benzylic CH_2), 7.3–7.6 (2 H, m, allylic H's), 7.8–8.3 (2 H, m, remaining nonaromatic H's), 2.81 (1 H, d, α'-H), 2.10 (1 H, dd, β'-H), and 1.60 (1 H, d, α-H); uv λ_{max}^{EtOH} 259 mμ (ϵ 19,800); λ_{max}^{hexane} 254 mμ (ϵ 18,400); ir (KBr) 1510 and 1330 (NO_2), 900, 885, 867, 819, 792, 750, and 733 cm^{-1}.

Anal. Calcd for $C_{11}H_{11}NO_2$: C, 69.83; H, 5.86; N, 7.40. Found: C, 69.92; H, 5.73; N, 7.43.

β-NO_2-S6. 7-Nitro-1-methylenetetralin (1.8 g, 9.5 mmol) in 10 ml of ether was added dropwise to Simmons–Smith reagent (100 mmol) prepared the same way as for synthesis of α'-NO_2-S5.[1b] Work-up yielded 0.6 g (31%) of β-NO_2-S6, mp 46.5–47.0°: pmr ($CDCl_3$) τ 7.09 (2 H, t, benzylic CH_2), 9.06 (2 H, dt, cyclopropyl CH_2's), 7.9–8.5 (4 H, m, remaining nonaromatic H's), 2.88 (1 H, d, α'-H), 2.52 (1 H, d, α-H), and 2.21 (1 H, dd, β'-H); uv λ_{max}^{EtOH} 284 mμ (ϵ 8000); ir (KBr) 1510, 1330, 1105, 1070, 1040, 1015, 952, 900, 888, 849, 810, and 742 cm^{-1}.

Anal. Calcd for $C_{12}H_{13}NO_2$: C, 70.92; H, 6.45; N, 6.89. Found: C, 71.03; H, 6.60; N, 6.67.

Independent Synthesis of 7-Nitro-1,1a,2,3,4,8b-hexahydrobenzo[*a*]cyclopropa[*c*]cycloheptene (β-NO_2-F7). 2-Nitro-6,7-dihydro-5*H*-benzocycloheptene. Dehydration of 3-nitrobenzosuberan-5-ol (8.0 g, 38.6 mmol)[28] as described for preparation of 8-nitro-1,2-dihydronaphthalene[1b] and work-up afforded 6.2 g (85%) of the desired nitroalkene, mp 42–45°; pmr ($CDCl_3$) τ 2.04 (1 H, d, α-H), 2.09 (1 H, dd, β'-H), 2.81 (1 H, d, α'-H), 3.57 (1 H, dt, benzyl vinyl H), 3.99 (1 H, dt, other vinyl H), 7.10 (2 H, m, benzyl), 7.55 (2 H, m, allylic), and 8.0 (2 H, m, remaining CH_2); λ_{max}^{EtOH} 252 mμ (ϵ 25,500); ir (neat, NaCl) 1520, 1340, 902, 838, 829, 770, 741, and 675 cm^{-1}.

β-NO_2-F7. Reaction of the above nitroalkene (3.0 g, 15.9 mmol) with iodomethylzinc iodide (100 mmol) and work-up as for preparation of α'-NO_2-S5[1b] gave 120 mg (4%) of nearly pure β-NO_2-F7. Pmr and ir absorptions matched those reported for the product from nitration of F7.[13]

1-Methylenebenzosuberan. Triphenylphosphonium methylide (from 0.23 mol of phosphonium salt and 0.24 mol of sodium *tert*-amyloxide) in benzene (500 ml) was allowed to react with 1-benzosuberone (36.3 g, 0.23 mol) according to the procedure of Conia and Limasset.[29] The reaction mixture was filtered, and the filtrate washed with water until the aqueous portion was nearly colorless. Removal of solvent from the dried solution (sodium sulfate–magnesium sulfate) and distillation of the partly spilled residue at aspirator pressure gave 17.2 g of colorless liquid which showed no ir C=O absorption, and a strong C=CH_2 band at 945 cm^{-1}. The pmr spectrum ($CDCl_3$), in addition to terminal vinyl =CH_2 absorptions at τ 4.94 and 5.04, showed a strong methyl singlet at τ 7.92 and a vinylic triplet at 4.07, demonstrating the presence of ~65% 1-methyl-1-benzosuberene. This mixture was used without further separation in the subsequent reaction.

Spiro[cyclopropane-1,1'-benzosuberan] (S7). Reaction of a 35/65 mixture of 1-methylenebenzosuberan and 1-methyl-1-benzosuberene (15.8 g, 100 mmol) with iodomethylzinc iodide (350 mmol) and work-up as for synthesis of spiro[cyclopropane-1,1'-tetralin][1b] gave 14.1 g (81.7%) of a mixture consisting of ~90% cyclopropanated material (nmr and vpc analysis). Preliminary distillation showed S7 to be significantly higher boiling than other mixture components; fractionation through a Todd column gave 2.86 g of 98% pure S7 as a colorless liquid, bp 90–91° (2.0 mm): ir (neat, NaCl) 1440, 1088, 1041, 1018, 912, 758, and 747 cm^{-1}; pmr ($CDCl_3$) τ 2.92 (4 H, m, aromatic), 7.12 (2 H, m, benzylic), 8.37 (6 H broad m, $(CH_2)_3$), and 9.25 (4 H, dd, cyclopropyl CH_2's). An analytically pure sample was obtained by preparative gas chromatography.

Anal. Calcd for $C_{13}H_{16}$: C, 90.64; H, 9.36. Found: C, 90.65; H, 9.47.

Nitration of S7.[30] A chilled solution of acetyl nitrate (made from 0.86 g (13.7 mmol) of 100% nitric acid and a twofold excess of acetic anhydride) in 10 ml of methylene chloride was added dropwise to a chilled, stirred solution of hydrocarbon S7 (1.074 g, 6.25 mmol) in methylene chloride (10 ml). The mixture was kept at 0–5° for 18 hr and stirred 3 hr with 20 ml of water. The washed and dried organic layer was stripped of solvent and washed through 1 in. of silica gel with 25% benzene–hexane (200 ml). Vpc analysis of the pale yellow residue (1.36 g, ~100%) on a QF-1 column (190°; 5 ft × 1/8 in.) showed two peaks (1 and 2) with relative areas of 2 and 6 (in order of increasing retention time), and two overlapping peaks (3 and 4) with total area of 92. Chromatography on silica gel (hexane elution) afforded fractions greatly enriched in peak 2. Further purification *via* preparative vpc gave a pale yellow oil identified as α'-NO_2-S7, mp ~19°; ir (CS_2) 1355, 950 (weak), 818, 743, and 711 cm^{-1}; nmr ($CDCl_3$) τ 2.45–2.67 (2 H, m, α- and β'-H's), 2.86 (1 H, t, β-H), 7.02 (2 H, m, benzylic), 8.35 (6 H, broad m, $(CH_2)_3$), and 9.14 (4 H, broad s, cyclopropyl H's); mass spectrum (70 eV) *m/e* 200 (M − 17; 100%)[15] (compare α-NO_2 isomer).

Anal. Calcd for $C_{13}H_{15}NO_2$: C, 71.86; H, 6.96; N, 6.45. Found: C, 72.25; H, 6.98; N, 6.51.

Preparative vpc (collecting the front side of peak 3) and recrystallization from hexane afforded β-NO_2-S7 as pale yellow crystals, mp 46–47.5°. Ir peaks (CS_2) include diagnostic peaks at 1217, 909, and 832 cm^{-1}. See Discussion for pmr data.

(26) Syntheses not described here appear elsewhere.[1b,13]

(27) J. von Braun and H. Jungmann, *Justus Liebigs Ann. Chem.*, **451**, 40 (1926).

(28) P. A. S. Smith and W. L. Berry, *J. Org. Chem.*, **26**, 27 (1961).

(29) J.-M. Conia and J.-C. Limasset, *Bull. Soc. Chim. Fr.*, 1936 (1967).

(30) This procedure is a modification of that used by L. M. Stock and P. E. Young. We are indebted to Professor Stock for providing the information.

Anal. Calcd for $C_{13}H_{15}NO_2$: C, 71.86; H, 6.96; N, 6.45. Found: C, 71.98; H, 7.03; N, 6.40.

Similar manipulation of peak 4 (backside) gave β'-NO_2-S7 as a pale yellow solid, mp 65–66.5°; ir (CS_2, diagnostic peaks) 917, 901, and 839 cm^{-1}. See Discussion for pmr data.

Anal. Calcd for $C_{13}H_{15}NO_2$: C, 71.86; H, 6.96; N, 6.45. Found: C, 71.66; H, 6.80; N, 6.69.

In addition to pmr features noted in the Discussion, β- and β'-NO_2-S7 have nonaromatic pmr absorptions very similar to those described for α'-NO_2-S7.

Repeated preparative vpc (collection of peak 1) provided 5 mg of α-NO_2-S7 as a pale yellow oil: ir (CS_2, diagnostic peaks) 783, 748, and 732 cm^{-1}; nmr ($CDCl_3$) τ 2.63 (1 H, dd, β-H), ~2.78 and 2.89 (2 H, distorted dd and overlapped t, α'-H and β'-H, respectively), 7.02 (2 H, m, benzylic), 8.35 (6 H, broad m, $(CH_2)_3$), 9.20 and 9.42 (2 H each, broad s's, cyclopropyl H's); mass spectrum (70 eV) *m/e* 217 ($M\cdot^+$) and 189 (M − 28, 100%)[15] (compare α'-NO_2 isomer).

Independent Synthesis of β-NO_2-S7. 8-Nitro-1-methylenebenzosuberan. 8-Nitro-1-benzosuberone (8.6 g, 42 mmol) was subjected to reaction with triphenylphosphonium methylide (74 mmol) and work-up as reported for synthesis of 4-nitro-1-methyleneindan.[1b] The product (4.6 g, 54%) was a pale yellow oil: ir ($CHCl_3$, 1525, 1345, 910, 875, and 832 cm^{-1}; pmr ($CDCl_3$) τ 1.95 (1 H, d, 9-H), 2.03 (1 H, dd, 7-H), 2.79 (1 H, d, 6-H), 4.77 (1 H, d, syn vinyl), 4.92 (1 H, d, anti vinyl), 7.15 (2 H, m, benzylic), 7.60 (2 H, m, allylic), and 8.21 (4 H, m, other CH_2's).

β-NO_2-S7. Reaction of the above nitroalkene (2.74 g, 13.5 mmol) with iodomethylzinc iodide (135 mmol) and work-up as for synthesis of α'-NO_2-S5[13] afforded a mixture containing ~20% cyclopropanated material, which could not be separated on silver nitrate–silica gel chromatography. Enrichment *via* selective hexane extraction (−40°) and preparative vpc gave pure β-NO_2-S7, identical in all properties with the product isolated from nitration of S7 (see above).

Acknowledgment. Partial support of this work by the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

The Formation of Optically Active 1,2-Cyclononadiene from Two Different Cyclopropylidene Precursors[1]

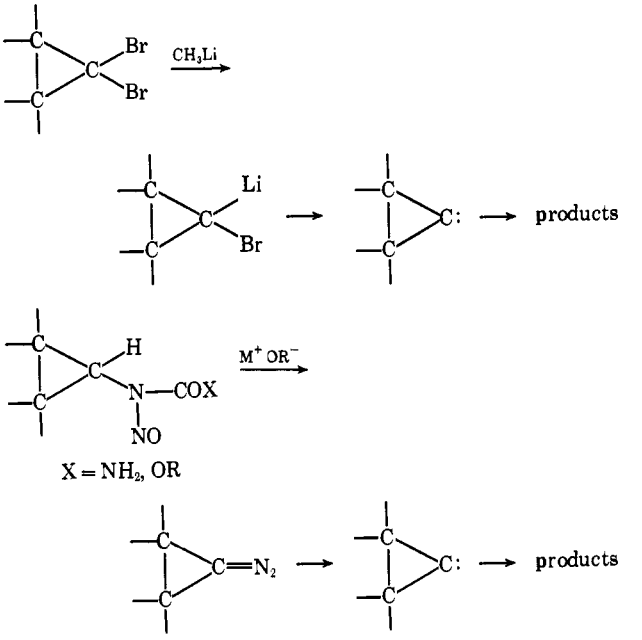
William R. Moore* and Robert D. Bach[2]

Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139. *Received June 18, 1971*

Abstract: Optically active 1,2-cyclononadiene (**7**) has been prepared by the opening of two different chiral cyclopropylidene precursors obtained by treatment of a *gem*-dibromocyclopropane with methyllithium and treatment of an *N*-nitrosourea (a diazocyclopropane precursor) with lithium ethoxide. At 0°, optically pure (1*R*,8*R*)-(−)-9,9-dibromo-*trans*-bicyclo[6.1.0]nonane (**2**) and (1*R*,8*R*)-(−)-*N*-nitroso-*N*-(9-*trans*-bicyclo[6.1.0]nonyl)urea (**6**) both give (*S*)-(−)-**7** having a high optical purity (slightly lower from **2**, which gives a higher optical purity at −78°). This result suggests that in the two cases, the transition states for ring opening are closely similar. The ring opening occurs by the equivalent of inward conrotation of the *trans*-methylene groups, a mode which reflects relief of strain. The possibility of the intervention of planar allene intermediates is considered. While such species are probably not important in this case, they may be in acyclic systems.

The formation of allenes by way of cyclopropylidene intermediates is an extremely useful reaction which has made a wide variety of cyclic and acyclic allenes readily available.[3,4] Two generally useful methods for generating cyclopropylidenes are outlined in Scheme I. Since α eliminations are often considered to give "carbenoids," while loss of nitrogen from a diazoalkane is regarded as giving a more or less "free" carbene, it is possible that cyclopropylidenes generated in these different ways would exhibit quite different re-

Scheme I



(1) Acknowledgment is made to the National Science Foundation for support of this research.

(2) National Institutes of Health Predoctoral Fellow, 1964–1967.

(3) (a) W. von E. Doering and P. M. Laflamme, *Tetrahedron*, **2**, 75 (1958); (b) W. R. Moore and H. R. Ward, *J. Org. Chem.*, **25**, 2073 (1960); (c) W. M. Jones, *J. Amer. Chem. Soc.*, **82**, 6200 (1960); (d) L. Skattebøl, *Tetrahedron Lett.*, 167 (1961); (e) W. R. Moore and H. R. Ward, *J. Org. Chem.*, **27**, 4179 (1962); (f) L. Skattebøl, *Acta Chem. Scand.*, 17, 1683 (1963); (g) L. Skattebøl, *Org. Syn.*, **49**, 35 (1969), and references therein.

(4) (a) The addition of singlet carbon, generated in an arc, to olefins at *ca.* 77° K appears to give cyclopropylidenes which in turn yield allenes; P. S. Skell and R. R. Engel, *J. Amer. Chem. Soc.*, **89**, 2912 (1967), and references therein. (b) Recoil carbon atoms (from nuclear reactions) also add to ethylene to give allene as a major product; J. Nicholas, C. MacKay, and R. Wolfgang, *ibid.*, **88**, 1610 (1966), and references therein.