Shielding Effects of a Cyclopropane Ring[1]

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Abstract: A ring-current model has been used to calculate the magnetic anisotropy of a cyclopropane ring. This method has proved to be convenient and rapid for estimating the shielding contribution of a cyclopropane ring to the total chemical shifts of neighboring protons with only the aid of molecular models. Shift contributions calculated on the basis of a ring-current model are applied to over 40 different compounds of known geometry.

Cyclopropane rings possess a wide variety of unique chemical and physical properties as a result of bond angle deformation. It has been reported that cyclopropane has a molar susceptibility of -39.9×10^{-6},[3] while the value predicted from Pascal's numbers is *ca.* -32×10^{-6}. The enhanced susceptibility has been attributed to a ring current. The ability of cyclopropane to sustain a ring current is also consistent with Coulson and Moffit's valence bond description of bonding in the strained three-membered ring where resonance structures leading to cyclic σ-electron delocalization are important.[4] However, changes in hybridization of carbon can alter local contributions to diamagnetic susceptibility,[5] and it is not yet possible to determine whether or not ring currents play a significant role with regard to the enhanced susceptibility for cyclopropane. The magnitude of $^{13}C-^{1}H$ coupling in cyclopropane[6] does suggest a rather large deviation from normal sp^3 hybridization of saturated carbon.

It has been recognized for several years that a cyclopropane ring can exert considerable influence on the chemical shifts of neighboring protons. The ^1H shift of cyclopropyl protons (0.22 ppm)[7,8] occurs at unusually high field compared to normal methylene protons, and anomalous shifts are noted for other protons in molecules containing cyclopropane rings. Several methods have been used to estimate the shielding contribution of a three-membered ring. Wiberg and Nist[9] attempted to explain cyclopropane shieldings with the point dipole approximation and carbon–carbon bond anisotropies derived from unstrained, saturated hydrocarbons. While in qualitative agreement, the predicted shifts were only one-fourth the observed magnitude. Tori and Kitahonoki[10] obtained better agreement of experimental and calculated shifts for a limited number of compounds using the same procedure and an empirically deduced carbon–carbon bond anisotropy. Norin and Forsen[11] assigned a group anisotropy to the cyclopropane ring using the point dipole approximation. All of these approaches suffer from inherent inadequacies of the point dipole approximation[12] as well as the fact that the approximation assumes an axially symmetric electron distribution,[13] which is certainly not the case for either cyclopropane carbon–carbon bonds or a cyclopropane ring.

Several workers have noted that qualitatively the anisotropy of a cyclopropyl group can be explained by assuming a ring current involving cyclic σ-electron delocalization among the three carbon atoms.[9–11,14] Patel, Howden, and Roberts[8] used the semiclassical ring current model of Johnson and Bovey[15] to calculate the shielding effect of a three-membered ring, assuming either four or six mobile electrons precessing in the plane of the ring. The calculated values were reported to be in no more than qualitative agreement with observed shift differences for the limited number of compounds considered. Burke and Lauterbur[16] used our calculations to explain ^1H and ^{13}C shieldings in cyclopropane relative to the central methylene groups of long-chain alkanes. They were also able to account for the enhanced molar susceptibility of cyclopropane from the ring current model, although local contributions due to unusual carbon hybridization were not considered.

Since the chemistry of cyclopropyl derivatives has received much attention in recent years, it is desirable to have available a convenient procedure with which to accurately predict the shielding effects of a cyclopropane ring. The point dipole approximation has severe limitations for even the most simple cases,[12]

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[3] J. R. Lacher, J. W. Pollock, and J. D. Park, *J. Chem. Phys.*, 20, 1047 (1952).

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[7] All chemical shifts are expressed as δ, parts per million, relative to tetramethylsilane.

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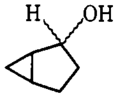
Chart I. Experimental[a] ^1H Shifts and Calculated[b] Cyclopropane Contribution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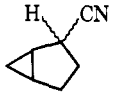
cis, 4.40^c (−0.11)
trans, 4.14^c (0.07)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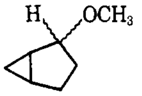
cis, 2.96^d (−0.11)
trans, 2.87^d (0.07)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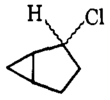
cis, 4.10^e (−0.11)
trans, 3.72^e (0.07)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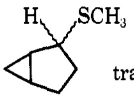
cis, 4.35^e (−0.11)
trans, 4.29^e (0.07)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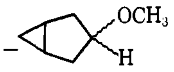
cis, 3.19^f (−0.11)
trans, 3.04^f (0.07)


6

cis, 4.22^d (0.34)
4.27^c
trans, 3.85^d (0.68)
3.82^c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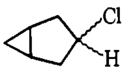
cis, 3.78^c (0.34)
trans, 3.42^c (0.68)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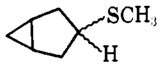
cis, 4.37^c (0.34)
trans, 3.83^c (0.68)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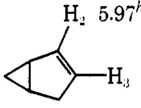
cis, 3.08^f (0.34)
trans, 2.50^f (0.68)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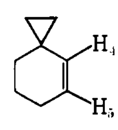
H_2 5.97^h (−0.03)
H_3 5.42^h (0.26)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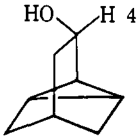
H_4 4.95^i (0.50)
H_5 5.57^i (−0.03)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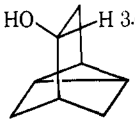
H 4.15^j (−0.22)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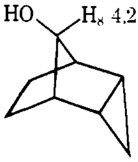
H 3.60^k (0.27)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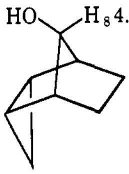
H_8 4.24^l (−0.16)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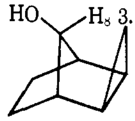
H_8 4.09^l (0.16)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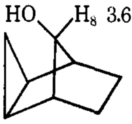
H_8 3.57^l (0.82)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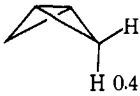
H_8 3.60^l (0.39)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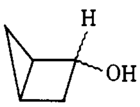
H 1.47^m (0.19)
H 0.44^m (1.39)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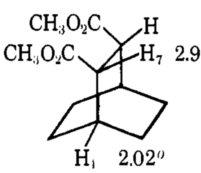
cis, 4.26^n (0.09)
trans, 3.73^n (0.61)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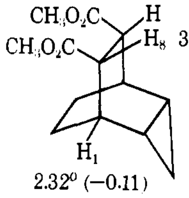
H_7 2.92^o
H_1 2.02^o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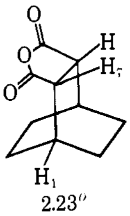
H_8 3.03^o (−0.16)
H_1 2.32^o (−0.11)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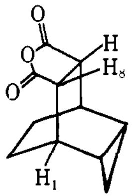
H_7 3.13^o
H_1 2.23^o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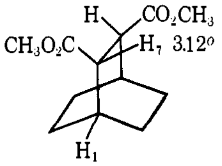
H_8 3.30^o (−0.16)
H_1 2.60^o (−0.11)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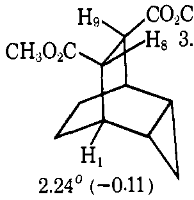
H_7 3.12^o
H_1 1.87^o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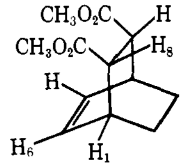
H_9 3.27^o (0.04)
H_8 3.18^o (−0.16)
H_1 2.24^o (−0.11)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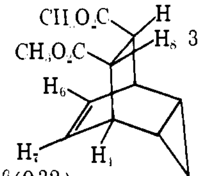
H_8 3.00^o
H_6 6.33^o
H_1 2.92^o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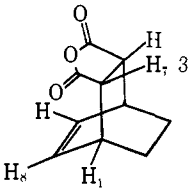
H_8 3.09^o (−0.16)
H_7 5.87^o (0.32)
H_1 3.15^o (−0.11)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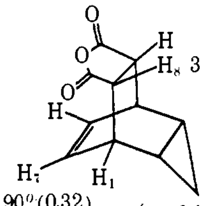
H_7 3.16^o
H_8 6.33^o
H_1 3.22^o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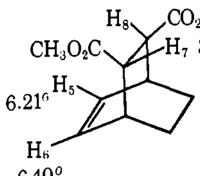
H_8 3.30^o (−0.16)
H_7 5.90^o (0.32)
H_1 3.45^o (−0.11)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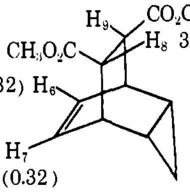
H_8 2.91^o
H_7 3.19^o
H_5 6.21^o
H_6 6.40^o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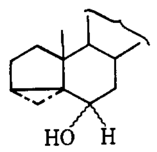
H_9 2.94^o (0.04)
H_8 3.33^o (−0.16)
H_6 5.71^o (0.32)
H_7 5.87^o (0.32)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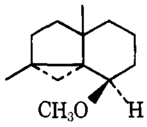
α-OH, 3.95^p (−0.17)
β-OH, 3.39^p (0.74)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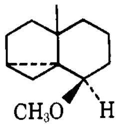
H 2.97^q (0.74)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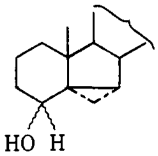
H 3.22^q (0.54)

Chart I (*Continued*)



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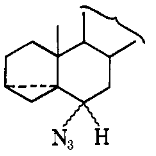
α, 4.08^r (−0.07)
β, 3.45^r (0.88)



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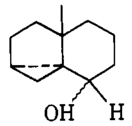
α, 3.72^s (−0.07)
β, 3.28^s (0.88)



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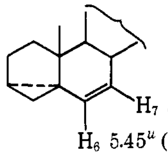
α, 5.07^t (0.88)
β, 4.47^t (−0.07)



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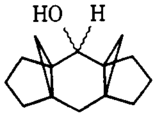
H_7 5.05^u (0.14)
H_6 5.45^u (0.73)



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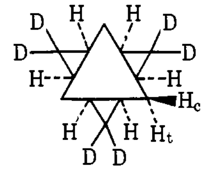
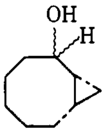
cis, 4.17^v (−0.48)
trans, 3.48^v (0.32)



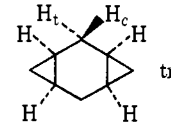
cis, cis-**40**-d_6

cis, ^{w}0.66 (1.28)
trans, ^{w}2.16 (−0.28)



41

cis, ^{x}4.12 (−0.14)
trans, ^{x}3.05 (0.75)



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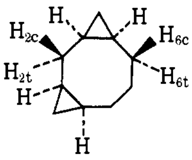
cis, 0.67 (1.27)
trans, 2.32 (−0.38)



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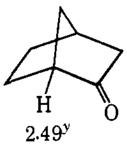
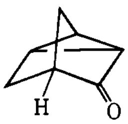
2-cis, 0.60 (1.96)
2-trans, 2.40 (−0.05)
6-cis, 0.60 (1.53)
6-trans, 2.20 (−0.20)



2.49^y

44



1.8^y (0.54)

45

[a] Chemical shifts are listed in δ (parts per million) relative to tetramethylsilane; cis, trans, α, and β refer to the substituent, if different from hydrogen. [b] Shift contributions of cyclopropane rings for a proton are in parentheses adjacent to the experimental chemical shift. Negative values are deshielding and positive values are shielding. [c] Reference 24. [d] Reference 23a. [e] Reference 23b. [f] Reference 23c. [g] Reference 22. [h] P. K. Freeman, private communication. [i] S. Nishida, I. Moritani, K. Ito, and K. Sakai, *J. Org. Chem.*, **32**, 939 (1967). [j] R. R. Saunders, J. A. Beisler, and H. Feilich, *ibid.*, **32**, 569 (1967). [k] J. A. Berson, D. Wege, G. M. Clark, and R. G. Bergman, *J. Amer. Chem. Soc.*, **91**, 5594 (1969). [l] J. S. Haywood-Farmer, R. E. Pincock, and J. I. Wells, *Tetrahedron*, **22**, 2007 (1966). [m] K. B. Wiberg and J. M. Lavanish, *J. Amer. Chem. Soc.*, **88**, 5272 (1966). [n] K. B. Wiberg and D. E. Barth, *ibid.*, **91**, 5124 (1969). [o] Reference 10. [p] G. Bauslaugh, G. Just, and E. Lee-Ruff, *Can. J. Chem.*, **44**, 2837 (1966). [q] W. G. Dauben, unpublished results. [r] P. G. Gassman and W. E. Hymans, *Tetrahedron*, **24**, 4437 (1968). [s] L. A. Freiberg, *J. Org. Chem.*, **30**, 2476 (1965). [t] Reference 14a. [u] S. R. Pathak and G. H. Whitham, *J. Chem. Soc. C*, 193 (1968). [v] L. Birladeanu, T. Hanafusa, and S. Winstein, *J. Amer. Chem. Soc.*, **88**, 2315 (1966). [w] R. S. Boikess and S. Winstein, *ibid.*, **85**, 343 (1963). [x] P. G. Gassman, E. A. Williams, and F. J. Williams, *ibid.*, **93**, 5199 (1971). [y] R. R. Sauers and P. E. Sonnet, *Chem. Ind.* (*London*), 786 (1963).

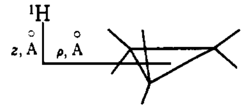
while application of ring current methods to individual structures is thought to be tedious.[10] We wish to report the use of a ring current model to construct a map which conveniently permits one to predict the shielding effect of a cyclopropane ring with surprising accuracy for a large number of cyclopropyl derivatives. The correlations which we present cannot be used to confirm or deny the existence of a ring current in cyclopropropane, although we did find that the anisotropy of a cyclopropane ring can be approximated with reasonable accuracy by applying the ring current model. Proof of a σ ring current in cyclopropane still awaits additional work.

Results and Discussion

The empirical model developed by Johnson and Bovey[15] has proved to be a reliable method for estimating the chemical shift arising from ring currents in aromatic molecules[17,18] and was employed in this study. The chemical shift, δ, due to an induced ring current was calculated by eq 1. The radius of the

$$\delta = \left(\frac{ne^2}{6\pi mc^2a}\right)([(1+\rho)^2+z^2]^{-1/2}) \times \left(K + \left[\frac{1-\rho^2-z^2}{(1-\rho)^2+z^2}\right]E\right) \quad (1)$$

ring, *a*, is expressed in ångströms, ρ and *z* are the distances from the center of the ring to the shielded nucleus in cylindrical coordinates (ångströms), and *K*



and *E* are complete elliptic integrals of the first and second kind, respectively. The modulus of the integrals, *k*, can be obtained from eq 2. The number of electrons

$$k^2 = \frac{4\rho}{(1+\rho)^2+z^2} \quad (2)$$

precessing in the ring is given by *n*, *e* is the electronic charge, *m* the mass of an electron, and *c* the speed of light. Computations were carried out on an IBM 7090 computer, and elliptic integrals were evaluated from polynomials given by Hastings.[19] Chemical shifts obtained from eq 1 are averaged for tumbling in the field.

The model chosen considers the effect of electrons precessing in a circle which circumscribes the ring (a = 0.88 Å).[20] The previously mentioned Coulson–Moffitt description of bonding in cyclopropane[4] predicts cyclic σ-electron delocalization by resonance; however, resonance structures leading to σ delocalization are not equivalent in the "banana" bond-pairing scheme. Thus, based on this model, one might expect a "barrier" to electron mobility in cyclopropane

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(17) See ref 13, p 85.

(18) Farnum and Wilcox have developed a double-toroidal shell model which more accurately describes π-electron density in the benzene ring. However, we chose to use the simpler Johnson–Bovey treatment[15] because of experimental and theoretical limitations in applying ring-current models to cyclopropane: D. G. Farnum and C. F. Wilcox, *J. Amer. Chem. Soc.*, **89**, 5379 (1967).

(19) C. Hastings, "Approximations for Digital Computers," Princeton University Press, Princeton, N. J., 1955, pp 170–173.

(20) "Tables of Interatomic Distances and Configuration in Molecules and Ions," *Chem. Soc. Spec. Publ.*, No. **11** (1958).

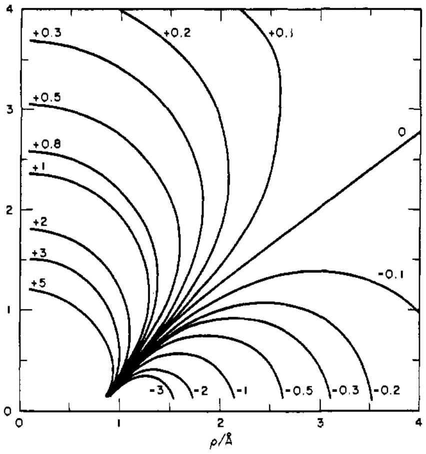

Figure 1. Shielding contours of a cyclopropane ring; ρ and Z are cylindrical coordinates expressed in ångströms.

Table I. Experimental and Calculated ^1H Shift Differences Due to Neighboring Cyclopropane[a]

Protons	$\Delta\delta_{exp}$[b]	$\Delta\delta_{calcd}$[c]	$(\Delta\delta_{exp} - \Delta\delta_{calcd})$[d]
(**1**-cis) − (**1**-trans)	0.26	0.18	0.08
(**2**-cis) − (**2**-trans)	0.09	0.18	−0.09
(**3**-cis) − (**3**-trans)	0.38	0.18	0.20
(**4**-cis) − (**4**-trans)	0.06	0.18	−0.12
(**5**-cis) − (**5**-trans)	0.15	0.18	−0.03
(**6**-cis[e]) − (**6**-trans[e])	0.37	0.34	0.03
(**6**-cis[f]) − (**6**-trans[f])	0.45	0.34	0.11
(**7**-cis) − (**7**-trans)	0.36	0.34	0.02
(**8**-cis) − (**8**-trans)	0.54	0.34	0.20
(**9**-cis) − (**9**-trans)	0.58	0.34	0.24
(**10**-H_2) − (**10**-H_3)	0.55	0.29	0.26
(**11**-H_5) − (**11**-H_4)	0.62	0.53	−0.09
(**12**) − (**13**)	0.55	0.49	0.06
(**14**) − (**15**)	0.15	0.32	−0.17
(**14**) − (**16**)	0.67	0.98	−0.31
(**14**) − (**17**)	0.64	0.55	0.09
(**15**) − (**16**)	0.52	0.66	−0.14
(**15**) − (**17**)	0.49	0.23	0.26
(**17**) − (**16**)	0.03	0.43	0.40
(**18**-exo) − (**18**-endo)	1.03	1.20	−0.17
(**19**-cis) − (**19**-trans)	0.53	0.52	0.01
(**21**-H_1) − (**20**-H_1)	0.30	0.11	0.19
(**21**-H_8) − (**20**-H_7)	0.11	0.16	−0.05
(**23**-H_1) − (**22**-H_1)	0.37	0.11	0.26
(**23**-H_8) − (**22**-H_7)	0.17	0.16	−0.01
(**25**-H_1) − (**24**-H_1)	0.37	0.11	0.26
(**25**-H_8) − (**24**-H_7)	0.06	0.16	−0.10
(**25**-H_9) − (**24**-H_7)	0.15	−0.04	0.19
(**27**-H_1) − (**26**-H_1)	0.23	0.11	0.12
(**26**-H_6) − (**27**-H_7)	0.46	0.32	0.14
(**27**-H_8) − (**26**-H_8)	0.09	0.16	0.07
(**29**-H_1) − (**28**-H_1)	0.23	0.11	0.12
(**28**-H_6) − (**29**-H_7)	0.43	0.32	0.11
(**29**-H_8) − (**28**-H_7)	0.14	0.16	−0.02
(**30**-H_5) − (**31**-H_6)	0.50	0.32	0.18
(**30**-H_6) − (**31**-H_7)	0.53	0.32	0.21
(**31**-H_8) − (**30**-H_7)	0.14	0.16	−0.02
(**31**-H_9) − (**30**-H_8)	0.03	−0.04	0.07
(**32**-α) − (**32**-β)	0.56	0.91	−0.35
(**32**-α) − (**32**-β)	0.56	0.51[g]	0.05
(**34**) − (**33**)	0.25	0.20	0.03
(**35**-α) − (**35**-β)	0.63	0.95	−0.32
(**35**-α) − (**35**-β)	0.63	0.55[g]	0.08
(**36**-α) − (**36**-β)	0.44	0.95	−0.54
(**37**-α) − (**37**-β)	0.60	0.95	−0.35
(**37**-α) − (**37**-β)	0.60	0.55[g]	0.05
(**38**-H_6) − (**38**-H_7)	0.40	0.59	−0.19
(**39**-cis) − (**39**-trans)	0.69	0.80	−0.11
(*cis*,*cis*-**40**-trans) − (*cis*,*cis*-**40**-cis)	1.50	1.56	−0.06
(**41**-cis) − (**41**-trans)	1.07	0.89	−0.18
(*cis*-**42**-trans) − (*cis*-**42**-cis)	1.65	1.65	0.00
(*cis*-**43**-2-trans) − (*cis*-**42**-2-cis)	1.80	2.01	−0.21
(*cis*-**43**-6-trans) − (*cis*-**43**-6-cis)	1.60	1.73	−0.13
(**44**) − (**45**)	0.70	0.54	0.16

[a] α, β, cis, and trans refer to substituents if different from protons. [b] $\Delta\delta_{exp}$ represents the chemical-shift difference for protons listed in column 1 [$(H_A) - (H_B)$]. By convention, high-field shifts were subtracted from low-field shifts. [c] $\Delta\delta_{calcd}$ is the calculated value for $(H_A) - (H_B)$, assuming that $H_A = H_B$ in the absence of cyclopropane shielding, where by definition $\delta_{calcd} > 0$ represents upfield shifts and $\delta_{calcd} < 0$ represents downfield shifts. [d] The standard deviation of $\Delta\delta_{exp}$ from $\Delta\delta_{calcd}$ is 0.20 ppm; however, simply correcting for the expected axial–equatorial shift difference gives a standard deviation of 0.14 ppm. [e] Reference 22. [f] Reference 23. [g] For comparison, $\Delta\delta_{calcd}$ has been corrected for the expected axial–equatorial shift difference (see Discussion).

and consequently a smaller resulting current. Because of the form of eq 1 (*vide supra*), it is convenient to diminish the current by simply decreasing the number of electrons (n). We found an optimization of experimental and calculated shift differences for $n = 4.5$. Our values for n and a can be compared with those used by Roberts[8] ($a = 0.88$ Å, $n = 6$ or $a = 1.01$ Å, $n = 4$) and Lauterbur[16] ($a = 1.10$ Å, $n = 3.5$). The former sets were chosen on the basis of Coulson–Moffitt[4] *vs.* Walsh[21] models of cyclopropane, while the latter was empirically determined to reproduce the $^{13}C/^1H$ shielding ratio of cyclopropane relative to "normal" methylene values. The equivalent dipole of our 4.5-electron 0.88-Å current is approximately 20% smaller than that of the 3.5-electron 1.10-Å current. In view of the difficulties in separating cyclopropane shieldings from other effects (*vide infra*) and the hybridization problems involved in Burke and Lauterbur's assumptions, we can see no justification for further refinement of our model.

Figure 1 is a shielding map for a cyclopropane ring. Contour lines were constructed from chemical shifts calculated by eq 1. Positive contours represent upfield shifts due to cyclopropane shielding, and negative contours represent downfield shifts due to deshielding. Values for ρ and z can be conveniently measured from molecular models by constructing a right angle (similar to a carpenter's square) of the appropriate scale, calibrated in ångströms. The calculated shieldings reported in Chart I represent the shielding contribution of the cyclopropane ring, estimated from values of ρ and z obtained from either Dreiding or molecular framework models.

The compounds listed in Table I represent a rather extensive test of the ability of a ring current model to predict cyclopropane shielding. Experimental $\Delta\delta$ values represent shift differences (intramolecular or intermolecular) between the designated pair of protons. Calculated $\Delta\delta$ values represent the expected chemical-shift separation based on the cyclopropane shielding map, assuming identical shifts in the absence of the cyclopropane ring. Only systems with known geometries, established by considerations other than chemical shift and with easily identifiable ^1H shifts, were used. Intramolecular and intermolecular ^1H shift comparisons were made so as to minimize anisotropies due to groups other than cyclopropane. Predicted shielding values ranged from 1.39 to −0.22 ppm (per cyclopropane) with a standard deviation of 0.14 ppm. The agreement between ex-

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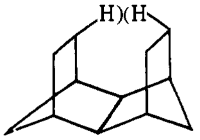
(21) A. D. Walsh, *Trans. Faraday Soc.*, 45, 179 (1949).

periment and theory is very good when one considers that the major deviations are obviously due to shieldings (σ electron or steric) not involving the cyclopropane "ring current" (*vide infra*) and that no correction was made for these perturbations. In spite of these limitations, relative positions of ^{1}H shifts for related pairs were, with two exceptions, predicted correctly.

Compounds **1–9** serve to illustrate some of the problems which arise even for closely related structures. Winstein's[22] and Freemen's[23] groups have shown that bicyclo[3.1.0]hexane derivatives **1–9** prefer a boat conformation. On this basis one might expect $\Delta\delta_{exp}$ to be relatively constant for **1–5** and **6–9** (see Table I); however, this is not the case. In addition, chemical shifts reported for *cis*-**6** and *trans*-**6** by separate laboratories[22,24] gave a variation in $\Delta\delta$ of 0.08 ppm.[25]

It has been demonstrated that protons which experience strong nonbonded interactions with other protons, for example in hydrocarbon **46**, show a pronounced deshielding.[26] Steric deshielding undoubtedly accounts for the large negative deviations seen for comparisons involving **16**, where H_8 experiences a large nonbonding interaction with the endo proton at C_3. Steric interactions may also be responsible for low experimental shift differences between cis and trans protons in *cis,cis*-**40** and *cis*-**43**. The designated cis protons of both hydrocarbons are in a crowded environment.



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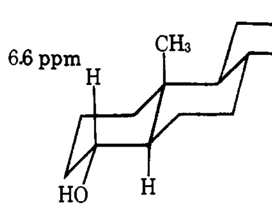
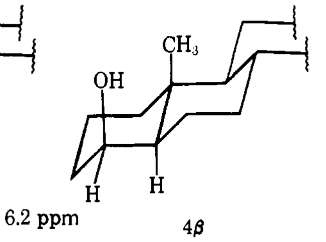
Major deviations are also seen for comparisons of axial and equatorial protons in steroids **32**, **35**, **36**, and **37**. Normally, axial protons appear at higher field than their equatorial counterparts by 0.3–0.8 ppm, with the exact magnitude of the separation being substituent dependent.[27] However, a comparison of α and β epimers for **32**, **35**, **36**, and **37** indicates that shielding by the cyclopropane ring reverses the normal shift positions of axial and equatorial protons. Since $\Delta\delta_{calcd}$ did not include the normal difference between axial and equatorial shifts, the large negative deviations seen for $\Delta\delta_{exp} - \Delta\delta_{calcd}$ are expected. If one makes the reasonable assumption that the chemical-shift difference between the protons at C_4 of 5α-cholestan-4α-ol and 5α-cholestan-4β-ol[28] is a good model for "normal" axial–equatorial separations in **32**, **35**, and **37**, then $\Delta\delta_{exp} - \Delta\delta_{calcd}$ for these cyclosteroids is 0.05, 0.08, and 0.05 ppm, respectively (see Table I). Decalins **33** and **34** have equatorial C_6 protons in different shielding regions of the three-membered ring. In this case the calculated and experimental shift differences are in excellent agreement.



4α



4β

In summary, the ring-current model offers an accurate, convenient method by which to estimate the shielding effect of a cyclopropane ring. Structure assignments based on chemical-shift data are often tenuous; however, the magnitudes of $\Delta\delta_{exp}$ and $\Delta\delta_{calcd}$ for an isomeric pair are often (see Table I) significantly greater than ($\Delta\delta_{exp} - \Delta\delta_{calcd}$). Thus, with reasonable precautions our model appears quite useful in this regard.[29]

Experimental Section

General. Nmr spectra were obtained on a Varian A-60 spectrometer with chemical shifts (δ, parts per million) measured relative to tetramethylsilane ($\delta = 0$) or hexamethyldisiloxane ($\delta = 0.06$).

Cyclopropanation of 1,4-Cyclohexadiene. Following the usual procedure,[30] 48.0 g of zinc–copper couple and 174.0 g of diiodomethane in 150 ml of diethyl ether were treated with 16.0 g of 1,4-cyclohexadiene for 11 days. At the end of this time, the entire reaction mixture was added to more iodozinc methylene iodide, which had been perpared from 48.8 g of zinc–copper couple and 174.0 g of diiodomethane in 150 ml of diethyl ether. The mixture was stirred under reflux for an additional 9.5 days and worked up in the usual way. The reaction was monitored by glpc ($^1/_4$ in. × 2 m 25% Apiezon L, 60–80 Chromosorb W). It was observed that although the monoadduct, Δ^3-norcarene, was formed fairly rapidly, the desired diadducts were slow to appear. After work-up the starting diene had almost completely disappeared, but only *ca.* 30% of Δ^3-norcarene had been converted to diadducts *cis*- and *trans*-tricyclo[5.1.0.0^{3,5}]octane (*cis*- and *trans*-**42**).

The reaction mixture was separated into its components by two preparative glpc passes, $^5/_{16}$ in. × 2 m 35% tris(2-cyanoethoxy)propane on 60–80 Chromosorb W, at 51°. The chromatogram indicated that the diadduct portion was a mixture of two components (81:19, in order of increasing retention time). Examination of the two diadduct fractions, collected after the second chromatography, on a $^1/_4$ in. × 2 m 25% tris(2-cyanoethoxy)propane on 60–80 Chromosorb W column at 50° indicated that they were of 99.9% purity.

(a) *trans*-Tricyclo[5.1.0.0^{3,5}]octane (*trans*-42). The infrared spectrum of the major component was consistent with the structure *trans*-**42** and was identical with that of the major diadduct component obtained on biscarbenation of cyclohexadiene with diazomethane and cuprous chloride,[31] as well as with the infrared spectrum of the hydrocarbon obtained on dehalogenation of the trans bisdibromocarbenated 1,4-cyclohexadiene.[32] This fraction was obtained as a colorless liquid, n^{25}D 1.4751, bp 140.6°, nmr (CCl_4) −0.02 (2, endo H at C_4 and C_8), 0.50 (6, H at C_1, C_3, C_5, and C_7, and exo H at C_4 and C_8), and 1.70 ppm (4, H at C_2 and C_6).

Anal. Calcd for C_8H_{12}: C, 88.82; H, 11.18. Found: C, 88.52; H, 11.05.

(b) *cis*-Tricyclo[5.1.0.0^{3,5}]octane (*cis*-42). The infrared spectrum of the minor component was consistent with the structure *cis*-**42**, and was identical with that of the minor product obtained on biscarbenation of 1,4-cyclohexadiene with diazomethane and cuprous

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[22] S. Winstein, E. C. Friedrich, R. Baker, and Y. I. Lin, *Tetrahedron, Suppl.*, 8 (Part II), 621 (1966).

[23] (a) P. K. Freeman, F. A. Raymond, J. C. Sutton, and W. R. Kindley, *J. Org. Chem.*, 33, 1448 (1968); (b) P. K. Freeman, F. A. Raymond, and M. F. Grostic, *ibid.*, 30, 771 (1965); (c) P. K. Freeman, F. A. Raymond, and M. F. Grostic, *ibid.*, 36, 905 (1971).

[24] F. A. Raymond, Ph.D. Dissertation, University of Idaho, 1965.

[25] Chemical-shift accuracy to within ±0.10 ppm (or less) would require careful measurements extrapolated to infinite dilution. Such data are not available for a wide variety of cyclopropyl compounds.

[26] S. Winstein, P. Carter, F. A. L. Anet, and A. J. R. Bourn, *J. Amer. Chem. Soc.*, 87, 5247 (1965).

[27] See ref 12, p 239.

[28] C. W. Shoppee, R. E. Lack, and S. C. Sharma, *J. Chem. Soc. C*, 2083 (1968).

[29] (a) C. D. Poulter, E. C. Friedrich, and S. Winstein, *J. Amer. Chem. Soc.*, 92, 4274 (1970); (b) C. D. Poulter and S. Winstein, *ibid.*, 92, 4282 (1970).

[30] R. D. Smith and H. E. Simmons, *Org. Syn.*, 41, 72 (1961).

[31] W. von E. Doering and W. R. Roth, private communication.

[32] W. G. Kumler, R. S. Boikess, P. Bruck, and S. Winstein, *J. Amer. Chem. Soc.*, 86, 3126 (1964).

chloride.[31] It was obtained as a colorless liquid: $n^{25}\mathrm{D}$ 1.4703; bp 143–144°; nmr (CCl_4) −0.26 (2, endo H at C_4 and C_8), 0.67 (8, H at C_1, C_3, C_5, and C_7, exo H at C_4 and C_8, and cis H at C_2 and C_6), and 2.32 (2, trans H at C_2 and C_6).

Anal. Calcd for C_8H_{12}: C, 88.82; H, 11.18. Found: C, 88.80; H, 11.30.

cis-**Tricyclo[7.1.0.0^{3,5}]decane** (*cis*-**43**). A sample of *cis*-**43** was made available by Radlick:[33] nmr −0.22 (2, endo H at C_4 and C_{10}), 0.60 (9, exo H at C_4 and C_{10}, H at C_1, C_3, C_5, and C_9, and cis H at C_2, C_6, and C_8), 2.20 (2, trans H at C_6 and C_8).

cis,cis-**Tetracyclo[9.1.0.0^{3,5}.0^{7,9}]dodecane** (*cis,cis*-**40**). **(a)** When 2.00 g (17 mmol) of 1,4,7-cyclononatriene was treated with 45.56 g (170 mmol) of diiodomethane and 12.35 g (190 mmol) of zinc–copper couple in 200 ml of diethyl ether in the usual way[30] for 12 hr, glpc indicated complete disappearance of starting triene and the appearance of *ca.* 90% of one major component. Conventional work-up afforded a crude oil which solidified on cooling. Purification by fractional melting and sublimation at 65° (60 mm) yielded thin white needles, mp 54–57°. Vapor-phase chromatography of this material ($^1/_4$ in. × 2 m 25% XF1150 on 60–80 Chromosorb W) indicated it to be a mixture of two materials in the ratio of 97:3. Vapor-phase chromatographic separation of the main component, followed by resublimation, yielded white needles: mp 60–62°; nmr (CCl_4) −0.41 (3, endo H at C_4, C_8, and C_{12}), 0.66 (12, exo H at C_4, C_8, and C_{12}, H at C_1, C_3, C_5, C_7, C_9, and C_{11}, and cis H at C_2, C_6, and C_{10}), and 2.16 ppm (3, trans H at C_2, C_6, and C_{10}); $\mathrm{ir}_{\mathrm{KBr}}$ 3058, 2990, 2942, 2900, 2840, 1465, 1450, 1292, 1076, 1020, 1010, 848, and 728 cm^{-1}.

Anal. Calcd for $C_{12}H_{18}$: C, 88.82; H, 11.18; mol wt, 162. Found: C, 88.61; H, 11.11; *m/e* 162.

(b) An alternative synthetic route to *cis,cis*-**40** was also employed. To a stirred mixture of 1.0 g of 1,4,7-cyclononatriene and 13.8 g of potassium *tert*-butoxide in 50 ml of benzene, maintained under anhydrous nitrogen, was added over a period of 1 hr, 21 g of bromoform in 20 ml of benzene. The mixture was stirred overnight at room temperature and then poured into water. Petroleum ether was added and the organic layer separated, washed with water and saturated sodium chloride solution, and dried over anhydrous sodium sulfate. Evaporation of the petroleum ether yielded a dark residue which was then chromatographed on deactivated alumina. The solid petroleum ether eluant was recrystallized from chloroform–hexane to yield 2.5 g (48%) of white crystals: mp 240.0–246.0° dec; $\mathrm{ir}_{\mathrm{KBr}}$ 1465, 880, 770, 685, 515, and 490 cm^{-1}.

Anal. Calcd for $C_{12}H_{12}Br_6$: C, 22.67; H, 1.90; Br, 75.43. Found: C, 22.72; H, 1.97; Br, 75.11.

To a stirred mixture of 1.5 g of the hexabromide and 7.1 g of *tert*-butyl alcohol in 65 ml of anhydrous tetrahydrofuran, maintained under anhydrous nitrogen, was added 1.29 g of lithium, freshly cut into small pieces. After the initial exothermic reaction had ceased, the mixture was stirred and refluxed for 3 hr. The mixture was then cooled and poured through glass wool into 100 ml of water and the water was extracted with 200 ml of pentane. The organic layer was separated and extracted with two 150-ml portions of water and 150 ml of saturated sodium chloride solution. After drying over anhydrous sodium sulfate, the pentane solution was concentrated at reduced pressure. Glpc on $^1/_4$ in. × 2 m 25% XF-1150, 60–80 Chromosorb W, and on 25% Apiezon L, 60–80 Chromosorb W, revealed the presence of only one component. This product had the same glpc retention time and infrared spectrum as *cis,cis*-**40**.

Methylene-d_2 Iodide. In a 1-l. flask were placed 225 g of sodium iodide and 90 g of sodium methoxide and these solids were dried by pumping at 1 mm for 6 hr. To the solids were added 400 ml of anhydrous dioxane, 300 ml of deuterium oxide (99.8%), and 500 g of methylene iodide. The mixture was stirred at reflux for 10 hr and then extracted with four 500-ml portions of petroleum ether. The petroleum ether extracts were combined, extracted with three 150-ml portions of water and 150 ml of saturated sodium chloride solution, and dried over anhydrous magnesium sulfate. The bulk of the petroleum ether and dioxane was evapoated on a water aspirator and the residue was distilled, bp 75° (19 mm), affording 346 g of a light straw colored liquid. Infrared examination and comparison with the infrared spectrum of a sample of known composition revealed that 92% deuteration had occurred.

cis,cis-**Tetracyclo[9.1.0.0^{3,5}.0^{7,9}]dodecane-4,4,8,8,12,12-d_6** (*cis,cis*-**40**-d_6). The deuterated compound was prepared by the Simmons–Smith procedure,[29] using methylene-d_2 iodide and by dehalogenation of 4,4,8,8,12,12-hexabromo-*cis,cis*-tetracyclo[9.1.0.0^{3,5}.0^{7,9}]dodecane in *tert*-butyl-*O*-*d* alcohol; nmr (neat) 0.66 (9, H at C_1, C_3, C_5, C_7, C_9, and C_{11} and cis H at C_2, C_6, and C_{10}), and 2.16 ppm (3, trans H at C_2, C_6 and C_{10}).

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[33] P. Radlick and S. Winstein, *J. Amer. Chem. Soc.*, **86**, 1866 (1964).