of platinum gauze that was centered in the cell window, the auxiliary electrode was a platinum wire, and the reference electrode was an aqueous SCE. In control experiments this procedure did allow the successful recording of the ESR spectra of electrogenerated nitrobenzene and fluorenone azine anion radicals.

Chemicals. Aliquots (1-L) of DMF (Burdick and Jackson) were purified by passage through a column of alumina (500 g, 80–200 mesh, Brockman activity 1, activated at 600 °C overnight) and were collected over a mixture of Davison 4-Å molecular sieves and alumina. This procedure was carried out in a dry, nitrogen-filled glovebag. After purification, the solvent was transferred immediately to the vacuum line. Acetonitrile (Burdick and Jackson) was purified according to the procedure of Walter and Ramaley, method B.[22] This procedure involves four reflux–distillation steps using, successively, anhydrous Al_2Cl_6, $KMnO_4/LiCO_3$, $KHSO_4$, and CaH_2. The purified solvent was then stored on the vacuum line over CaH_2. Fl=NNHTs was synthesized by refluxing an equimolar mixture of fluorenone and tosylhydrazine in ethanol for 30 min. After the solvent was removed, the precipitate was recrystallized twice from ethanol [mp 180–184 °C (lit. mp 180–182 °C[23]). Fluorenone hydrazone[24] and fluorenone imine[25] were synthesized according to known procedures. All other compounds were commercially available. Purities and identities of all compounds were verified electrochemically and chromatographically (HPLC) and by melting point determination, when appropriate.

Acknowledgment. Financial support of this work by the National Science Foundation is gratefully acknowledged.

Registry No. Fl=NNHTs, 52341-51-2; $Fl{=}NNTs^{\cdot 2-}$, 102073-69-8; fluorenone, 486-25-9; tosylhydrazine, 1576-35-8.

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Dependence of ^{13}C NMR Chemical Shifts in Arylcyclopropanes on Conformation and Electron Demand

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The ^{13}C NMR spectra of conformationally rigid arylcylopropanes have been examined in order to determine the strength and conformational dependence of the benzene–cyclopropane interaction. Previous work with conformationally flexible arylcyclopropanes has implicated both conjugative and hyperconjugative interactions between the aromatic π-system and the bonding orbitals of cyclopropane. The substituent-induced chemical shifts are inconsistent with *either* mechanism being dominant. Replacement of the two hydrogen atoms on a cyclopropane methylene carbon with chlorine causes a reversal of the normal SCS response imposed by substitution on the aromatic ring. The model systems used were spiro[cyclopropane-1,9′-[9*H*]-fluorene], 1,1-diphenylcyclopropane, and 1,1a,6,6a-tetrahydrocycloprop[*a*]indene.

The use of ^{13}C NMR chemical shifts as a probe for changes in electron density produced by substitution has a long and checkered history.[2] The method has been most successful (as judged by the criteria of the quality of correlation between chemical shifts and σ-values,[3] calculated electron densities,[4] or chemical intuition[5]) in evaluating the chemical shifts of carbons in conjugated molecules. It is clear that in the majority of cases studied resonance structures provide an adequate model to explain the observed shifts.[6] Similar success has not been forthcoming in the analyses of aliphatic and saturated cyclic hydrocarbons.[2c,3a] It is in the fusion of a saturated hydrocarbon to a group with varying π-electron demand that the most unusual behavior of substituent-induced chemical shifts (SCS values) have been observed. Through-space, through-bond, conjugative, and hyperconjugative explanations have been invoked to explain the "normal", "inverse", and "random" behavior of SCS values in response to π-electron demand.

Our work with the conjugative properties of cyclopropane[7] required an interpretation of a number of the physical properties of the cyclopropane ring as a function of the conformation of an attached aromatic π-system. Current wisdom holds that cyclopropane is an effective π-donor,[8] utilizing one of its highest occupied, bonding orbitals (usually an e′ orbital drawn from either the Förster–Coulson–Moffitt[9] (FCM) or Walsh[10] sets). The

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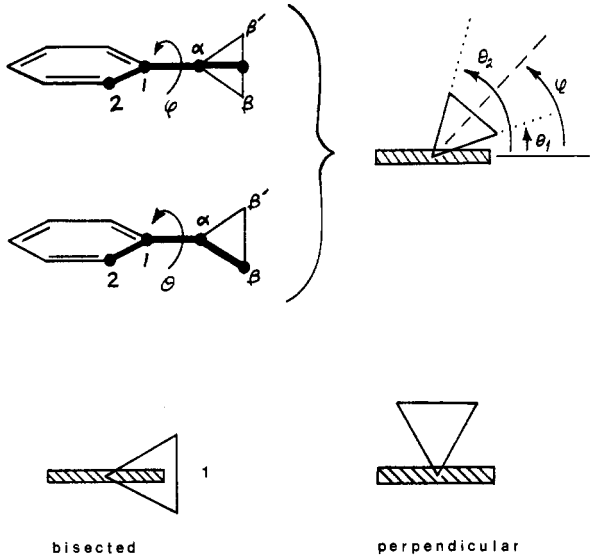
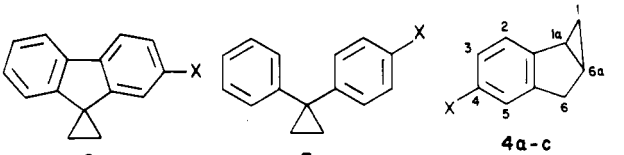


Figure 1. Conformation definitions for arylcyclopropanes. The hashed rectangles represent a side-on-view of the aromatic ring. The bold lines in **1a** and **1b** are the line segments used to define the torsion angles ϕ and θ. The right-most segment in **1a** is drawn from α to the midpoint of the β–β' bond.

conformation required to maximize this interaction is referred to as "bisected" (see Figure 1). That cyclopropane is ineffective at accepting electron density from π-donors is also well-documented.[11] We have reported that if such an interaction were important to the total energy of the molecule, the "perpendicular" conformation (**1b**) would be a logical potential energy minimum.[7a] Recently, Heilbronner has challenged the equivalence between the FCM and the Walsh bases for the C–C orbitals of cyclopropane.[12] A consequence of using the FCM basis for qualitative evaluation of π-to-cyclopropane donation is that the "perpendicular" conformation might have to be abandoned in favor of a double minimum with p orbital and cyclopropane C–C bonds nearly colinear. In either case, the "bisected" conformation is *not* preferred for electron delocalization in cyclopropylcarbinyl anions and equivalent structures.

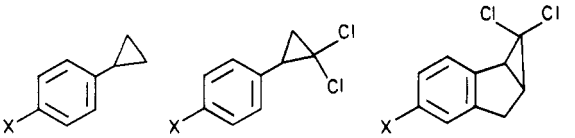
Our investigation of cyclopropane conjugation required a number of conformationally rigid arylcyclopropanes, spanning the range between the two limiting conformations. Among the compounds chosen were 2-substituted spiro[cyclopropane-1,9′-[9*H*]-fluorene][13] (**2**) and 4′-substituted 1,1-diphenylcyclopropane (**3**). The former rigidly



2a-c **3a-c** **4a-c**

a, X = H; **b**, X = NO_2; **c**, X = NH_2

maintains the "bisected" conformation; the latter has been shown by X-ray crystallography to be quite nearly "perpendicular".[14] A third rigid compound with neither of these two structures was also necessary to evaluate the distinction between conjugative and hyperconjugative interactions. The cyclopropindene **4**[15] was chosen for this comparison. Previous analyses of cyclopropylbenzenes, **5**,[2a] and (β,β-dichlorocyclopropyl)benzenes, **6**,[2b] have also been included. The unusual behavior of **6** upon substitution indicated that **7** would be useful to link compounds **4**, **5** and **6**.

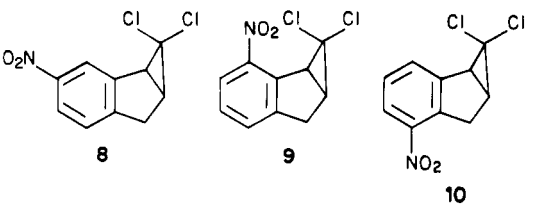


5a-c **6a-c** **7a,b**

a, X = H; **b**, X = NO_2; **c**, X = NH_2

Assignment of Isomer Structure. The requirement that the aromatic substituent be placed para to the cyclopropane ring demands care in assigning the regiochemistry of the appropriate derivative. The structure of 4-nitro-1,1a,6,6a-tetrahydrocycloprop[*a*]indene, **4b**, was proposed by Hahn and his co-workers on the basis of ^{1}H NMR spectroscopic studies.[15]

The nitration of **4a** gave a mixture of two mononitro derivatives. One was incompletely characterized, but is assumed to be the 2-nitro isomer of **4b**, based on the ^{1}H NMR spectrum and regiochemical preferences shown by arylcyclopropanes. The major isomer, **4b**, was obtained pure by repetative crystallization. Nitration of **7a**, on the other hand, provides at least three isomeric mononitro derivatives. These isomers were partially separated by liquid chromatography and finally isolated in pure form by recrystallization (see the Experimental Section). The three isomers were shown to be primary reaction products by comparison of the ^{1}H NMR spectrum of the crude product with those of the individual components. The three isomers, A, B, and C, have been assigned the structures, **7b**, 8, and 9, respectively.



8 **9** **10**

Differentiating between the two meta isomers (**7b**, 8) and the two ortho isomers (**9**, **10**) is easily accomplished by inspection of the ^{1}H NMR spectra. Compounds **9** and **10** have only one proton ortho to the nitro group. It is the

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Table I

	^{1}H NMR				^{13}C NMR				
	H_2	H_3	H_4	H_5	C_1	C_{1a}	C_6	C_{6a}	UV bands
4a	← 7.3–7.1 →				16.71	23.88	35.48	16.03	
4b	7.35	7.96		7.96	17.26	24.12	35.23	17.69	287 (9600)[a]
7a	7.35	7.2	7.2	7.2	66.18	42.89	34.11	35.48	
isomer A (**7b**)	7.50	8.10		8.02	64.96	42.30	33.92	36.45	385 (9400), 224 (sh)
isomer B (**8**)	8.20		8.10	7.30	65.01	42.15	34.26	35.96	278 (5700), 230 (sh), 217 (10000)
isomer C (**9**)		8.05	7.4	7.4	64.77	42.64	34.11	35.62	313 (2000), 269 (5300), 218 (9500)

[a] Data taken from ref 15.

distinction between **7b** and **8** that is ultimately critical. The assignments rest on the following arguments.

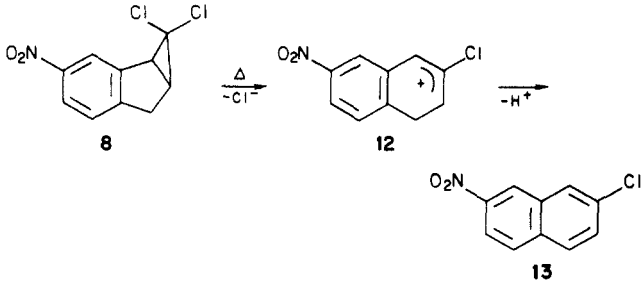
Hahn made use of the magnetic anisotropy of cyclopropane to determine the position of the nitro group in his synthesis of **4b**. According to Tori and Kitahanoki,[16] a proton fixed near the edge of a cyclopropane, such as the hydrogen on C_2 in **4a**, should experience a measurable shift downfield relative to the companion ortho hydrogen on C_5. Table I demonstrates that H_2 for isomer A is downfield of H_5 for isomer B and that H_2 for isomer B is downfield of H_5 for isomer A, consistent with the structural assignments of **7b** and **8** to A and B, respectively.

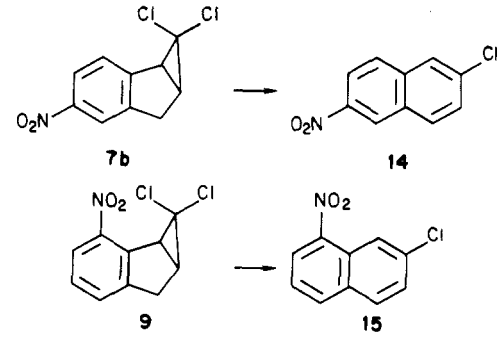
The assignment of isomer C as **9** is supported by the dramatic downfield shift of the hydrogen on C_{1a}. This hydrogen appears at δ 4.05, in contrast to the other isomers, in which this hydrogen is buried under the other two benzylic hydrogens (C_6) at $\delta \sim 3.4$. The hydrogen on C_{1a} lies within the deshielding region of the *o*-nitro substituent, consistent with assignment of **9** as isomer C.

The response of the benzylic carbon chemical shifts in **4a** to nitration producing **4b** is SCS > 0 for para substitution (C_{1a}) and SCS < 0 for meta substitution (C_6). This behavior is paralleled in numerous other studies. The SCS shifts for C_6 in **7b** and **8** are δ −0.19 and +0.15, the sign of the SCS values being consistent with the assigned structures. The C_{1a} SCS values are both negative, a feature most easily ascribed to the β,β-dichloro substitution in **7b** and **8** (vida infra).

The UV spectra of **4b** and **7b** are identical. Neither has the long wavelength shoulder seen in 3-nitro-1,1a,6,6a-tetrahydrocycloprop[*a*]indene (**11**), λ 310 nm, $\epsilon \sim 3000$.[15] The UV maximum is found at 275 nm, close to that for **8**. Thus the UV spectra are consistent with the pairs **4b** and **7b**, **8** and **11**, having the identical substitution patterns.

Finally, an unusual thermal reaction of **7b**, **8**, and **9** is observed upon heating the pure, molten compounds. As isomer B is heated to its melting point, the crystals first become translucent, then melt with the evolution of a volatile acid, certainly HCl, at 116–119 °C. The material that remains has a higher melting point than **8** and a ^{1}H NMR spectrum that consists entirely of aromatic protons. It is reasonable that the transformation of **8** to **13**, shown below, has occurred.[17] The other two isomers, A and C, lose HCl distinctly more slowly than does B. Very approximate half-lives are B, 2 min at 120 °C, A, 90 min at 140 °C, C, 90 min at 165 °C. The ranking B > A > C is certainly consistent with the formation of a carbocation such as **12** in the rate-determining step, provided the identity of the isomers are those given above. It is interesting to note that regardless of their structural simplicity, naphthalenes **13**, **14**, and **15** were previously unknown compounds. Resting upon this spectroscopic and chemical evidence, the assignment of **7b**, **8**, and **9** to isomers A, B, and C is quite secure.





Discussion

There are three concerns that must be addressed in order to make use of the ^{13}C NMR chemical shifts of arylcyclopropanes as a probe for electron transfer: 1. Are the SCS values "normal" or "inverse"? "Normal" implies that replacement of hydrogen by a π-electron donor on the aromatic ring should increase the electron density on an atom with which it is conjugated, giving rise to an upfield shift. "Inverse" would signal a downfield shift. 2. Are the magnitudes of the SCS values observed in substituted phenylcyclopropanes consistent with generous or meager delocalization of charge? 3. Do the magnitude and the sign of the SCS values depend on the aryl–cyclopropane torsional angle?

These three concerns are inextricably linked, and deconvolution will be more philosophical than mathematical. Question 3 shall be addressed within the context of the other two.

Cyclopropane Conformations. Most of the cyclopropanes used to address these concerns in the past displayed only slightly hindered rotation about the aryl–cyclopropane bond, making unequivocal statements concerning the relevant torsion angles impossible. One aspect of our work has been to construct arylcyclopropanes with well-defined geometries in order that the question of torsional dependence can be dealt with explicitly.

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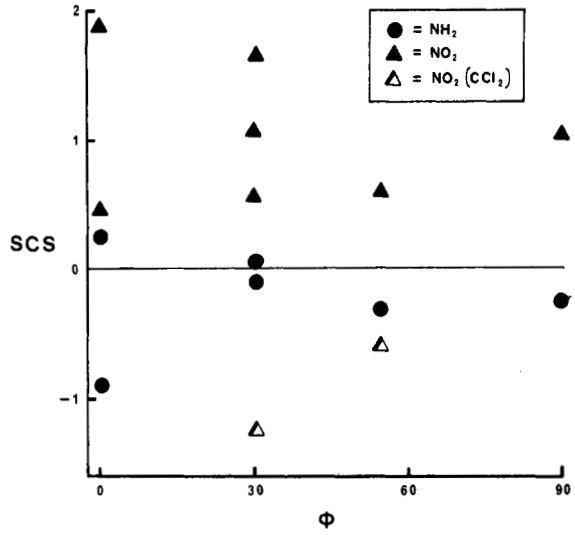

Figure 2. SCS values as a function of the torsion angle ϕ.

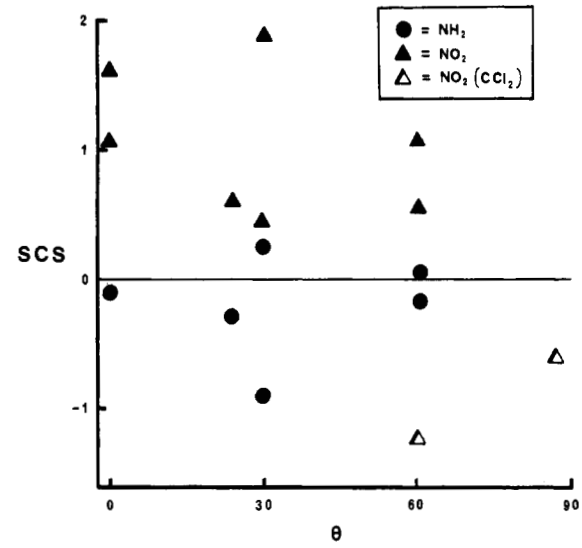

Figure 3. SCS values as a function of the torsion angle θ.

First let us define ϕ as the torsion angle involving carbons 2,1,α and the midpoint of the β–β' bond. In addition, let θ be the torsion angle 2–1–α–$\beta(\beta')$ (Figure 1). The angle θ is important to the discussion of hyperconjugation involving a single cyclopropane C–C bond. The values of ϕ and θ will be restricted to $0 \leq \phi,\theta \leq 90°$. Within this definition, the "bisected" conformation is characterized by $\phi = 0°$ and $\theta \simeq 30°$ for both cyclopropane β-carbons; "perpendicular" is characterized by $\phi = 90°$ and $\theta_1 = \theta_2 \simeq 60°$. Only approximate values of ϕ and θ are required because the change from one model to another will cause differences many times larger than those attributable to an uncertainty in the appropriate angle. It is assumed that the structure and therefore the torsion angles change little with substitution on the aromatic ring.

Normal vs. Inverse Chemical Shift Response to Substitution. Previous work by Roberts[2a] had indicated that the ^{13}C SCS values observed for 4-substituted cyclopropylbenzenes, **5**, were "normal". The explanation was advanced that a hyperconjugative interaction of the cyclopropane with the aromatic ring allowed for a π-electron charge reorganization, resulting in an increase in electron density at the cyclopropane β-carbons when the substituent was a good π-electron donor. Good π-electron acceptors were even more effective at producing a downfield shift corresponding to a decrease in electron density. Their report did not assess the sensitivity of the observed SCS values to conformational changes.

Previous to this report, Reynolds and co-workers evaluated the ^{13}C SCS values of 4-substituted (2',2'-dichlorocyclopropyl)benzenes, **6**, and found that the response of the CCl_2 (β) carbon to aromatic substitution (inverse) was *opposite* that observed for the CH_2 (β') carbon (normal).[2b] The experimentally determined minimum energy conformation displays $\theta(\beta) = 86°$ and $\theta(\beta') = 23°$. Reynolds' explanation for this behavior required a change from normal SCS values in conformations having θ near 0° to inverse SCS values for θ near 90°. Because the Reynolds and Roberts explanations were inconsistent and given our own interest in the conformationally dependent properties of cyclopropanes, we offer the following resolution.

In Table II is collected the chemical shift, SCS, and torsion angle data for the cyclopropanes **2–7**. An inspection of the table quickly reveals that the cyclopropane β-carbon SCS values are all "normal", *regardless of the torsion angles ϕ and θ*, with the exception of CCl_2 (β) carbons in **6** and **7**. Figures 2 and 3 also demonstrate the lack of a consistent angular dependence for the SCS values.

Table II

compd	carbon	substit	shift	SCS	ϕ, deg	θ, deg
2	α	H	29.43		0	
		NH_2	29.24	−0.19		
		NO_2	30.07	0.64		
	β	H	18.32			
		NH_2	18.57	0.25		30
		NO_2	18.76	0.45		
3	α	H	29.92		90	
		NH_2	*a*			
		NO_2	30.12	0.20		
	β	H	16.42			
		NH_2	16.28	−0.14		60
		NO_2	17.54	1.12		
4	α	H	23.88		30	
		NH_2	23.05	−0.83		
		NO_2	24.12	0.24		
	β	H	16.71			
		NH_2	16.76	0.05		60
		NO_2	17.26	0.55		
	β'	H	16.03			
		NH_2	15.93	−0.10		0
		NO_2	17.69	1.66		
5[b]	α	H	34.12		0	
		NH_2	33.27	−0.85		
		NO_2	34.29	0.17		
	β	H	9.10			
		NH_2	8.20	−0.90		30
		NO_2	10.98	1.88		
6[c]	α	H	35.07		54	
		NH_2	34.79	−0.28		
		NO_2	34.92	−0.15		
	β	H	60.17			
		NH_2	60.66	0.49		86
		NO_2	59.58	−0.59		
	β'	H	25.64			
		NH_2	25.34	−0.30		23
		NO_2	26.23	0.59		
7	α	H	42.89		30	
		NO_2	42.30	−0.59		
	β	H	66.18			60
		NO_2	64.96	−1.22		
	β'	H	35.48			0
		NO_2	36.55	1.07		

[a] Not observed. [b] Data from ref 2a. [c] Data from ref 2b.

What emerges from this overview is the following judgment: the β-carbons of 4-substituted cyclopropylbenzenes display normal SCS values if the cyclopropane carbons bear only hydrocarbon functionality. Compare the values for **4** and **7**. They differ only in the dichloro substitution of one of the β-carbons. The effect is pro-

found; only the sign of the SCS for carbon β' is preserved. It is reasonable that the conformational dependence observed by Reynolds et al. is an artifact of the model chosen.

There are two concerns that arise from the previous discussion. The first is whether there *is* in fact a dependence of β-carbon SCS values upon ϕ (or θ). The "hyperconjugative" (Roberts) and similar molecular orbital explanations of SCS values would be difficult to substantiate if the answer were "no". Figures 2 and 3 fail to show expected minima at θ near 90° or θ near 0°, as required by conjugative or hyperconjugative interactions, respectively. It is conceivable the shifts are the result of conformationally independent mechanisms (inductive, through-space); however, the observed β-shifts are consistently larger than α-shifts for any series of compounds. Inductive transmission typically results in an alternation in the sign of observed SCS values.[3a] Such is not the case for cyclopropanes. A reasonable though not satisfying explanation follows from de Meijere's observation that cyclopropane is a respectable π-electron donor for any value of ϕ except those perilously close to 90° ("perpendicular").[18]

Of some interest is the origin of the seemingly anomalous behavior of dichloro-substituted carbons. Similar inverse shifts have been observed for 2-substituted ethylbenzenes.[3a] It would be convenient to ascribe the inverse shifts to the electronegativity difference between hydrogen or carbon and chlorine. However, Krabbenhoft has observed quite normal SCS values for β,β-dichlorostyrenes and used simple resonance forms to rationalize the data and the positive value of ρ derived from a single-parameter Hammett plot.[3d] An alternative explanation for the dichlorocyclopropane shifts again involves a conformationally dependent interaction. Hyperconjugation between the aromatic π-system and the C_α–CCl_2 bond would increase the apparent electronegativity of the CCl_2 carbon. The resultant change in the electron distribution in the C–Cl bonds would produce a net increase in electron density at the CCl_2 carbon. The geometries of **6** and **7** are reasonably well suited to support such hyperconjugation.

Magnitude of Cyclopropane SCS Values. The often-quoted judgment about cyclopropane, that it is a good electron donor and a poor electron acceptor, can also be evaluated with the help of the appropriate SCS values. Again, the question of whether or not the values show a conformational dependence becomes important. In Figures 2 and 3 it is difficult to detect a consistent variation of SCS with either ϕ or θ. For that reason, all SCS values will be treated as equal, regardless of cyclopropane conformation. This situation is in distinct contrast to that observed in the case of 4-substituted styrenes.[4a,b] The observed insensitivity is in part the result of the differences between the models **2–7** in addition to any inherent properties of cyclopropane.

The average β-SCS values for NH_2-substituted compounds is −0.30. When the substituent is NO_2, the average shift is +1.15. The fact that the two differ by a factor of almost 4 is not instantly useful for two reasons: first, NH_2 and NO_2 need not be "equal-but-opposite" perturbations;[19] second, the through-space and solvent-reorganization effects need not parallel any hyperconjugative interaction. Without a theoretical method for disentangling the SCS values, comparison with a model provides the most economical solution. The two most appropriate models are 4-substituted styrenes, to judge conjugative effects, and 4-substituted phenylalkanes, to judge the effect on a saturated hydrocarbon.

The β-carbon SCS values for the 4-(dimethylamino)-styrene and 4-nitrostyrene are −4.27 and 4.70,[4a] respectively. The ratios between these and the average cyclopropane SCS values are 14:1 and 4:1, respectively. The comparison reaffirms the near-equality between π-donor capabilities of olefins and cyclopropanes and the disparity between their π-acceptor qualitites. Although the preferred conformation necessary to maximize cyclopropane's π-acceptor properties is a question not yet resolved, it is conceivable that the best conformation is not adequately represented by the compounds **2–7**. The structure of **3** should be nearest the "perpendicular", but **3c** displays only a very modest SCS (δ −0.14), particularly in contrast to **5c** (δ −0.90).

There have been several ^{13}C NMR studies of 4-substituted alkylbenzenes.[2a,3a,b] In each case, the β-carbon SCS is *inverse*. No explanation other than hyperconjugation has been given to explain this unusual behavior. One of these reports demonstrated that the inverse character is independent of substituents on the β-carbon (–H, –Br, $-S^+Me_2$).[3b] This result is at odds with the rationalization given above for the β,β-dichlorocyclopropane inverse SCS values. We offer no solution for this inconsistency; indeed, our work sheds more darkness than light on the interpretation of nonconjugatively transmitted substituent effects. What can emerge from this comparison of cyclopropylbenzene and alkylbenzene β-carbon SCS values is the similarity between cyclopropane and an alkene and its dissimilarity with alkanes.

Conclusions

It has been shown that the anomalous SCS behavior observed by Reynolds can be ascribed to the chlorine substitution and not to the geometry of the molecule. In fact, it is difficult to extract any angular dependence from the SCS values of compounds **2–7**. Although it can be argued that the inconsistency stems from the structural diversity of the models, it is clear that the function that relates SCS values to either ϕ or θ cannot be purely trigonometric, as Reynolds has suggested for cyclopropane and demonstrated for styrene. It has been reaffirmed that cyclopropane is an effective π-donor and at best a mediocre π-acceptor.

Experimental Section

All melting points are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 710B instrument. NMR (^1H and ^{13}C) were recorded on a JEOL FX-100 spectrometer as solutions in deuteriochloroform (0.5–1.0 M). Proton spectra were referenced to Me_4Si and carbon spectra to the center of the deuteriochloroform triplet (δ 77.0). All shifts are reported in ppm relative to Me_4Si = 0. Microanalyses were obtained from the University of Massachusetts Analytical Services. IR bands are reported in cm^{-1}. UV spectra are given as λ in nm (ϵ).

All commercial materials were reagent grade or better and used as received. Most solvents were used without prior distillation. Preparative liquid chromatography was performed on a system similar to the Myers design,[21] utilizing Michel–Miller columns from Ace Glass and Woelm silica gel (40–60-μm particle size). The hexane and ethyl acetate solvents were distilled prior to use. Gas chromatography utilized a Varian 90-P equipped with either a 2 m, 10% SE-30 column or a 2 m, AN-600 column operating isochratically.

(18) de Meijere, A.; Schallner, O.; Weitemeyer, C.; Spielmann, W. *Chem. Ber.* **1979**, *112*, 908–935.

(19) A reasonable comparison one can make is between $\sigma^+(NH_2) = -1.3$ and $\sigma^-(NO_2) = 1.24$.[20] The similarity in these two values argues for a rough equivalence between the effects of NO_2 and NH_2.

(20) Ritchie, C. D.; Sager, W. F. *Prog. Phys. Org. Chem.* **1964**, *2*, 323.

(21) Meyers, A. I.; Slade, J.; Smith, R. K.; Mihelich, E. D.; Hershenson, F. M.; Liang, C. D. *J. Org. Chem.* **1979**, *44*, 2247–2249.

Most reactions were worked up in the following way: the compound, dissolved in a suitable organic solvent (typically diethyl ether), was washed with water, 5% sodium bicarbonate solution, and brine. The organic layer was dried over magnesium sulfate and rotary evaporated. Deviations from this procedure occur as noted.

The syntheses of the spirofluorenes **2a–c** have been reported elsewhere.[13] The cycloprop[*a*]indenes **4a**,[22] **4b**,[15] and **7a**[23] were prepared by literature procedures.

Synthesis of 4-Amino-1,1a,6,6a-tetrahydrocycloprop[*a*]indene (4c). A solution of 71.4 mg (0.41 mmol) of **4b** in 5 mL of ethanol was brought to reflux under nitrogen. Anhydrous hydrazine, 85 μL, was added to the stirred solution followed by a small amount (1–2 mg) of 10% Pd/C. The solution was refluxed for 30 min. Progress of the reaction was checked by TLC in 90% toluene–10% petroleum ether. The reaction mixture was diluted with ethanol and filtered through Celite, and the solvent was removed on a rotary evaporator. The light yellow crystalline material obtained was recrystallized from ethanol/water to give 21 mg (36% yield) of off-white crystalline plates, mp 64.5–65 °C. These crystals rapidly decomposed on exposure to air, becoming ultimately black in color: We were unable to obtain satisfactory elemental analyses of this compound. ^1H NMR δ 7.05 (1 H, d, J = 7.6 Hz), 6.45 (2 H, d, J = ~7.6 Hz), 3.4 (2 H, br m), 3.12 (1 H, dd, J = 6.3, 17 Hz), 3.28 (1 H, d, J = 17 Hz), 2.22 (1 H, m), 1.75 (1 H, m) 0.96 (1 H, m), 0.00 (1 H, dd, J = 7.6, 3.9 Hz); ^{13}C NMR 144.09δ, 143.46, 137.42, 123.63, 112.96, 112.71, 35.43 (t), 23.05 (d), 16.76 (t), 15.93 (d).

Synthesis of 1,1-Dichloro-4-nitro-1,1a,6,6a-tetrahydrocycloprop[*a*]indene (7b). A solution of 3 mL of 70% nitric acid in 10 mL of acetic anhydride was stirred under nitrogen for 30 min to pre-form the acetyl nitrate. The mixture was diluted with 50 mL of methylene chloride and cooled to −40 °C. A solution of 2.0 g (0.01 mol) of dichlorocyclopropane **7a** in 10 mL of methylene chloride was added rapidly with stirring. The mixture was stirred at −30 to −40 °C for 30 min and then warmed slowly to room temperature over the period of 1 h. The reaction was quenched by adding carefully 25 g of potassium carbonate followed by 50 mL of water. The mixture was stirred for 30 min. The aqueous layer was separated and washed with several portions of methylene chloride. The organic layer was subjected to a normal workup. The reaction produced 2.38 g of a light yellow oil which was percolated over 40 g of alumina, using hexane to elute the mobile products. Combination and evaporation of the 500 mL of hexane fractions gave 1.94 g (80%) of a pale yellow oil. ^1H NMR revealed the oil to be a mixture of isomers.

The mixture of nitroaromatics was chromatographed on the low-pressure LC using hexane to 96% hexane/4% ethyl acetate as an eluent. Separation was not perfect, requiring several of the fractions to be recrystallized from heptane.

At least four distinct compounds eluted in the fractions surrounding the desired product, **7b**. The first compound off the column was not completely characterized. It displayed an acetyl methyl group in the ^1H NMR spectrum (δ 2.08) and a carbonyl group in the IR spectrum (1735 cm^{-1}). That it still bore the cycloprop[*a*]indene structure was revealed by the ^1H and ^{13}C NMR spectra. The next three compounds eluted were isomers of **7b**. The justification for the structural assignments is given in the Discussion.[24]

Isomer A. Structure assigned: 1,1-dichloro-4-nitro-1,1a,6,6a-tetrahydrocycloprop[*a*]indene (**7b**): ^1H NMR ($CDCl_3$) δ 8.10 (1 H, m), 8.02 (1 H, br s), 7.50 (1 H, d, J = 8 Hz), 3.30 (3 H, m), 2.75 (1 H, m); ^{13}C NMR 147.67 (s), 146.60 (s), 145.67 (s), 125.54 (d), 122.33 (d), 119.50 (d), 64.96 (s), 42.30 (d), 36.55 (d), 34.01 (t); IR ($CHCl_3$) 3040, 2940, 1525, 1350, 1080, 985, 790; UV (CH_3CN) 285 (9400), 224 (sh); mp 82–82.5 °C.

Isomer B. Structure assigned: 1,1-dichloro-3-nitro-1,1a,6,6a-tetrahydrocycloprop[*a*]indene (**8**): ^1H NMR ($CDCl_3$) δ 8.20 (1 H, br s), 8.10 (1 H, m), 7.30 (1 H, d, J = 8 Hz), 3.31 (3 H, m), 2.72 (1 H, m); ^{13}C NMR ($CDCl_3$) 151.62 (s), 147.33 (s), 141.24 (s), 124.86 (d), 123.35 (d), 120.38 (d), 65.01 (s), 42.15 (d), 35.96 (d), 34.26 (t); IR ($CHCl_3$) 3050, 2940, 1530, 1355, 1080, 990, 835; UV (CH_3CN) 278 (5700), 230 (sh), 217 (10 000); mp 116–119 °C with decomposition (gas evolution).

Isomer C. Structure assigned: 1,1-dichloro-2-nitro-1,1a,6,6a-tetrahydrocycloprop[*a*]indene (**9**): ^1H NMR ($CDCl_3$) δ 8.05 (1 H, dd, J = 7, 2.2 Hz), 7.4 (2 H, m), 4.07 (1 H, dd, J = 7.3, 1.7 Hz), 3.3 (2 H, m), 2.65 (1 H, m); ^{13}C NMR ($CDCl_3$) 147.82 (s), 146.21 (s), 135.24 (s), 130.12 (d), 128.71 (d), 122.28 (d), 64.77 (s), 42.64 (d), 35.62 (d), 34.11 (t); IR ($CHCl_3$) 3080, 2970, 1555, 1375, 1020, 840; UV (CH_3CN) 313 (2000), 269 (5300), 218 (9500); mp 109–110 °C.

Ring Opening and Aromatization of 7b, 8, and 9. For each compound, one or two single crystals of the appropriate nitrocyclopropindene were placed in a melting point capillary. The capillary was placed in a melting point apparatus and heated until the melting point was reached. At its melting point (119 °C), **8** liberated HCl rapidly, as evidenced by the formation of bubbles in the melt. The acidic nature of the gas was confirmed with a piece of moistened pH indicating paper. Isomers **7b** and **9** had to be heated well beyond their melting points (to 140 °C and 165 °C, respectively) before HCl evolution could be detected visually. The ^1H NMR spectra were obtained by dissolving the product, obtained after prolonged heating, in 40 μL of deuteriochloroform. The spectra were recorded by using a 1-mm H/C dual probe. ^{13}C NMR spectra could not be obtained because of the low concentrations available. The ^1H NMR spectra of the naphthalenes are given below:

13 (2-nitro-7-chloronaphthalene): H_1 8.68, d, J = 2.0 Hz; H_3 8.23, dd, J = 9.03, 2.0 Hz; H_8 7.98, br s; H_4 7.94, d, J = 9.03 Hz; H_5 7.89, d, J = 8.8 Hz; H_6 = 7.62, dd, J = 8.8, 2.2 Hz.

14 (2-nitro-6-chloronaphthalene): H_1 8.75, br s; H_3 8.26, dd, J = 9.0, 2.4 Hz; H_4 7.94, d, J = 9 Hz; H_5 7.91, br s; H_8 7.86, d, J = 9; H_7 7.57, dd, J = 8.7, 2.1 Hz.

15 (1-nitro-7-chloronaphthalene): The spectrum has not been assigned because of the inability to resolve the meta couplings, δ 8.65, d, J = 1 Hz, 1 H; 8.31, d, J = 7.8 Hz, 1 H; 8.11, d, J = 8 Hz, 1 H; 7.9, d, J = 8.8 Hz, 1 H; 7.6, m, 2 H.

Registry No. **2a**, 167-02-2; **2b**, 81056-00-0; **2c**, 81055-96-1; **3a**, 3282-18-6; **3b**, 42932-08-1; **3c**, 102233-63-6; **4a**, 15677-15-3; **4b**, 25178-97-6; **4c**, 102233-64-7; **7a**, 56485-66-6; **7b**, 102233-65-8; **8**, 102233-66-9; **9**, 102233-67-0; **13**, 56961-38-7; **14**, 56961-37-6; **15**, 607-37-4.

Supplementary Material Available: A table of the ^{13}C NMR shifts of the compounds in Table II is available (2 pages). Ordering information can be found on any current masthead page.

(22) Goodman, A. L.; Eastman, R. H. *J. Am. Chem. Soc.* **1964**, *86*, 908–911.

(23) Billups, W. E.; Buynak, J. D.; Butler, D. *J. Org. Chem.* **1980**, *45*, 4636–4641.

(24) The nitrocyclopropindenes **7b**, **8**, and **9** were isolated in very low theoretical yield. After repeated crystallizations, insufficient material was obtained for elemental analysis. The conversions of **7b** to **14**, **8** to **13**, and **9** to **15** were performed with one or two single crystals. Elemental analyses were not attempted on these six compounds.