Organic and Biological Chemistry

The Electronic Properties of Three-Membered Rings. I. σ_I and σ_{R° Substituent Constants from F^{19} Nuclear Magnetic Resonance[1]

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Abstract: The F^{19} nmr spectra of *m*- and *p*-fluorophenylcyclopropanes, oxiranes, thiiranes, ethylenimines, and oxaziridines have been determined in dilute carbon tetrachloride solution. The inductive and resonance substituent constants have been calculated from the precise linear relationships developed by Taft and co-workers. The results of the present work are compared with the reported constants for structurally similar acyclic substituents and with the donor–acceptor properties of three-membered rings in the excited state.

The electronic properties of three-membered rings have received considerable attention in recent years. Since Walsh[3] concluded from molecular orbital calculations and from ultraviolet spectroscopy that cyclopropane and oxirane possessed "properties of unsaturation," many extensive studies have been carried out to determine if a three-membered ring can transmit or extend conjugation. Although most investigations have been directed toward an understanding of the cyclopropyl system, the electronic effects of the cyclopropyl ring are still a controversial issue. For example, Hammett ρ values are ambiguous over the ability of the cyclopropane ring to transmit conjugation.[4,5] This is also true for results obtained from ultraviolet spectroscopy.[6–8] Recently, Closs and Klinger[9] have concluded from the analysis of the H^1 nmr spectrum of phenylcyclopane that there is an electronic interaction between the cyclopropyl and aromatic rings.

The electronic interaction of the oxirane or the aziridine ring with an adjacent carbonyl group has been reported by Cromwell and co-workers.[10,11] The results of their investigation showed that the three-membered ring in *trans*-arylaroylethylenimines or oxides can transmit the electrical effect of a β-phenyl group to the α-carbonyl as measured by the ultraviolet absorption spectra. More recently Ketcham, *et al.*,[12] have shown that, in the excited state, oxirane and thiirane are electron withdrawing relative to benzene, whereas cyclopropane is electron donating. These results will be described further in the discussion part of this paper. In the present investigation, the ground-state donor–acceptor properties of three-membered rings have been determined relative to benzene by F^{19} nmr. A definitive answer to the ability of the cyclopropane, oxirane, thiirane, and aziridine rings to *transmit conjugation* in the ground state will be presented in a future publication on the F^{19} nmr shielding parameters in stilbene-type systems.

Results and Discussion

The extreme sensitivity of fluorine shielding in *m*- and *p*-fluorophenyl groups to small intramolecular perturbations produced by the ring substituents has been well established.[13–16] The precise linear relationships developed by Taft from the F^{19} nmr shielding parameters of *meta*- and *para*-substituted fluorobenzene permit the detection of and the separation of inductive and resonance effects. These correlations which are based on experimental work[13–16] as well as theoretical justification[17,18] are presented in the following equations where $\int_H^{p\text{-}X}$ and $\int_H^{m\text{-}X}$ are the fluorine chemical shifts in parts per million of *para*- and *meta*-substituted fluorobenzenes, respectively, relative to a fluorobenzene standard, and σ_I and σ_{R° are the inductive and resonance substituent constants.

$$\int_H^{p\text{-}X} - \int_H^{m\text{-}X} = -(29.5)\sigma_{R^\circ}$$

$$\int_H^{m\text{-}X} = -7.1\sigma_I + 0.60$$

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[1] Presented before the Division of Organic Chemistry, 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1966.

[2] Inquiries may be addressed to the Dow Chemical Co., Midland, Mich. 48640.

[3] A. D. Walsh, *Trans. Faraday Soc.*, **45**, 179 (1949).

[4] E. N. Trachtenberg and G. Odian, *J. Am. Chem. Soc.*, **80**, 4018 (1958).

[5] R. Fuchs, C. A. Kaplan, J. J. Bloomfield, and L. F. Hatch, *J. Org. Chem.*, **27**, 733 (1962).

[6] G. W. Cannon, A. A. Santilli, and P. Shenian, *J. Am. Chem. Soc.*, **81**, 1660 (1959).

[7] R. H. Eastman and S. K. Freeman, *ibid.*, **77**, 6642 (1955).

[8] R. J. Mohrbacher and N. H. Cromwell, *ibid.*, **79**, 401 (1957).

[9] G. L. Closs and H. B. Klinger, *ibid.*, **87**, 3265 (1965).

[10] N. W. Cromwell, R. E. Bambury, and J. L. Adelfang, *ibid.*, **82**, 4241 (1960).

[11] N. H. Cromwell, F. H. Schumacher, and J. L. Adelfang, *ibid.*, **83**, 974 (1961).

[12] L. A. Strait, P. Ketcham, D. Jambotkar, and V. P. Shah, *ibid.*, **86**, 4628 (1964).

[13] R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Andersen, and G. T. Davis, *ibid.*, **85**, 709, 3146 (1963).

[14] R. W. Taft, Jr., S. Ehrenson, I. C. Lewis, and R. E. Glick, *ibid.*, **81**, 5132 (1959).

[15] R. W. Taft, Jr., *ibid.*, **79**, 1045 (1957).

[16] R. W. Taft, Jr., *J. Phys. Chem.*, **64**, 1805 (1960).

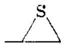
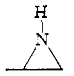
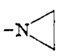
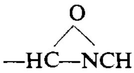
[17] F. Prosser and L. Goodman, *J. Chem. Phys.*, **38**, 373 (1963).

[18] R. W. Taft, Jr., F. Prosser, L. Goodman, and G. T. Davis, *ibid.*, **38**, 380 (1963).

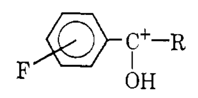
The high reactivity of oxiranes, thiiranes, and aziridines with acidic reagents[19] excludes any possibility for the determination of the inductive and resonance substituents constant in the usual manner.[20] F^{19} nmr is, therefore, a unique spectroscopic probe for such an investigation.

The chemical shifts and calculated substituent constants for the cyclopropane, oxirane, thiirane, aziridine, and oxaziridine are recorded in Table I. For purposes of comparison, values of σ_I and $\sigma_R°$, as determined by F^{19} nmr, have been included for substituent groups with similar structural features. The selection of a saturated aliphatic substituent for comparison with the cyclopropyl group can only approximate in structure the components of the three-membered ring since no saturated aliphatic substituent is comprised of three carbon–carbon and five carbon–hydrogen bonds. Fortunately, precise values of σ_I and σ_R have been determined from reactivity correlations for methyl, ethyl, isopropyl, and *t*-butyl and were found to differ by an average of only ±0.015 in both σ_I and σ_R, respectively.[21] The results from F^{19} nmr, which are summarized in Table I, show that the inductive and resonance substituent constants for the alkyl and vinyl groups are sufficiently different so that a definitive comparison can be made with the cyclopropyl group. The calculated values of σ_I and $\sigma_R°$ for the cyclopropyl group are −0.08 and −0.13, respectively, and thus are essentially the same as for the alkyl substituents. The present results provide strong support for the findings of Trachtenberg and Odian[4] who concluded, from a comparison of the Hammett ρ values for substituted *trans*-cinnamic, *trans*-2-phenylcyclopropanecarboxylic, and β-phenylpropionic acids, that the cyclopropane ring does not transmit conjugation.[22] This equivalence of electronic properties for the cyclopropyl and methyl groups in uncharged fluorobenzenes is noteworthy when compared with the results for the effect of the same substituents in the stabilization of carbonium ions. Taft and Tsuno[23] have found that the cyclopropyl and methyl substituents were decidedly different in their ability to stabilize the carbonium ion system

Table I. Shielding Parameters and Substituent Constants of Three-Membered Rings

Substituent	$\int_{H}^{m\text{-}X}$	σ_I	$\int_{H}^{p\text{-}X}$	$\sigma_{R°}$
	1.18	−0.08	5.11	−0.13
CH_2CH_3	0.96	−0.05	4.94	−0.13
CH_3[13]	1.18	−0.08	5.40	−0.15
$CH{=}CH_2$[13]	0.65	0.01	1.40	−0.03
	0.11	0.07	1.43	−0.04
	0.10	0.07	1.80	−0.06
OCH_3[13]	−1.05	0.25	11.50	−0.43
SCH_3[13]	−0.38	0.14	4.30	−0.17
	0.75	−0.02	3.26	−0.085
 [a]	0.10	0.07	8.52	−0.29
CH_2NH_2[13]	0.58	0.00	3.60	−0.15
NH_2	0.50	0.01	14.20	−0.48
 $-HC-NCH_3$	0.13	0.07	−1.55	0.05
$CONH_2$[13]	−0.18	0.11	−3.10	0.11

[a] V. F. Bystrov, O. A. Yuzhakova, and R. G. Kostyanovskii, *Dokl. Akad. Nauk SSSR*, **147**, 843 (1962).



The values, in parts per million, which were obtained for the mesomeric charge perturbation,[24] $\int_{m\text{-}X}^{p\text{-}X}$, are as follows: R = methyl = −27.5; R = cyclopropyl = −21.4; R = $CH{=}CHC_6H_5$ = −19.9. Similar results have been reported in the solvolysis of *para*-substituted phenyldimethylcarbinyl chlorides.[25,26] In this system, the cyclopropyl group is more effective than the isopropyl in stabilizing the electron-deficient center as evidenced by the rate enhancement and decrease in ΔH^* for the cyclopropyl when compared to the isopropyl substituent. It is clear from the above discussion that the substituent effect of the cyclopropyl group is strongly dependent on the electronic demand of the system. Furthermore, the stronger dependence of the substituent effect of the cyclopropyl group on its electronic environment affords an explanation for the larger pK_{R^+} value for the tricyclopropyl cation then is observed for either the trityl or *t*-butyl cations.[27]

Oxirane and thiirane exhibit the same inductive effect in the *meta* position. The sign of σ_I for these substituents is in agreement with that predicted on the basis of sign of the *m*-OCH_3 and *m*-SCH_3 groups. However, the magnitude of the inductive effect is considerably smaller than either *m*-SCH_3 or *m*-OCH_3. This decrease in electron-withdrawing ability may be attributed to the interposition of the methylene group between the heteroatom and the aromatic ring. The attenuation of the inductive effect by one methylene group has been calculated from Taft's σ^* values for the following pairs of substituents $ClCH_2CH_2/ClCH_2$, $CF_3CH_2CH_2CH_2/CF_3CH_2CH_2$, and $C_6H_5CH_2CH_2/C_6H_5CH_2$. The results[28] were 0.37, 0.27, and 0.37 or an average of 0.34. McGowan[29] has concluded from a discussion of various methods of estimating the attenuation of the inductive effect per CH_2– group that a value of 0.50

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(19) A. Weissberger, Ed., "Heterocyclic Compounds," Vol. 19, Interscience Publishers, Inc., New York, N. Y., 1964.

(20) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940.

(21) R. W. Taft, Jr., and I. C. Lewis, *Tetrahedron*, **5**, 210 (1959).

(22) Cromwell and Mohrbacher[8] concluded that the cyclopropyl ring can transmit conjugation in the excited state in 1-aroyl-2-arylcyclopropanes. Apparently, transmission of the phenyl ring unsaturation through the cyclopropane ring into the aroyl chromophore occurs, causing a smaller energy difference between the ground and the excited states of the 2-phenylcyclopropyl ketones as compared with the analogous energy difference in the unsubstituted cyclopropyl ketones.

(23) R. W. Taft and T. Tsuno, unpublished experiments. We wish to thank Professor Taft for making these results available to us.

(24) The mesomeric charge perturbation (mcp) $\int_{m\text{-}X}^{p\text{-}X} = (\delta_p^F - \delta_m^F)$, where δ_m^F refers to the F^{19} nmr shielding parameter of a *meta*-substituted fluorobenzene and δ_p^F refers to that for the corresponding *para* isomer.

(25) L. B. Jones and U. K. Jones, *Tetrahedron Letters*, 1493 (1966).

(26) H. C. Brown and J. D. Cleveland, *J. Am. Chem. Soc.*, **88**, 2051 (1966).

(27) N. Deno, H. G. Richey, Jr., J. S. Liu, D. N. Lincoln, and J. O. Turner, *ibid.*, **87**, 4533 (1965).

(28) J. E. Leffler and E. Grunwald, Ed., "Rates and Equilibria of Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1963, Chapter 7.

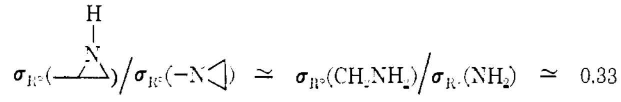
(29) J. C. McGowan, *J. Appl. Chem.* (London), **10**, 312 (1960).

gives better agreement in many cases. Therefore, the values of σ_I for oxirane and thiirane are in good agreement with theory. The direction of the resonance effect of the oxirane and thiirane substituent is the same as for the p-OCH_3 and p-SCH_3 groups. Direct conjugation of the heteroatom with the aromatic ring is inhibited by the methylene group and the magnitude of σ_{R° is reduced. The magnitude of σ_{R° for the three-membered rings appears to be directly related to the electronegativity effect of the heteroatom for the first-row elements, *i.e.*

The nature of this electronegativity effect on σ_{R° is the result of an "internal inductive" effect of the heteroatom on the carbon α to the aromatic ring. Since oxygen is more electronegative than carbon, the σ_{R° value of -0.04 for oxirane is less negative than the σ_{R° value of -0.13 for the cyclopropyl group. Although sulfur and carbon have the same electronegativity, the σ_{R° value for the thiirane substituent is considerably less negative than that for the cyclopropyl, group. This may indicate that a favorable geometry exists for the interaction of the d electrons on sulfur with the π system of the aromatic ring.

The electronic properties of aziridines are of special interest in that the heteroatom may be attached directly, α, or one carbon removed, β, to the aromatic ring. The results in Table I show a change in the sign of the inductive substituent constant, σ_I, with a change in position of the nitrogen in the aziridine ring. This change of sign for σ_I for the aziridines is due to the increased effect of the more electronegative nitrogen, compared to carbon, when placed in a position α to the aromatic ring. In the series

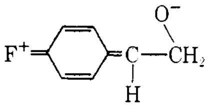
σ_I becomes increasingly positive (see Table I). The trend in this series is in good agreement with the previous observation that the first atom of the substituent plays a predominant role in determining the σ_I parameter for the substituent as a whole.[13] The resonance parameter σ_{R° is larger for the N-arylaziridine than for the isomeric 2-arylaziridine. This is in agreement with the larger value of p-fluoroaniline when compared with p-fluorobenzylamine. The equality of the ratios of the following σ_{R° parameters indicates that the aziridine



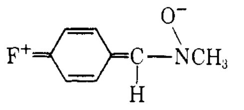
$$\sigma_{R^\circ}(\text{aziridinyl})/\sigma_{R^\circ}(-N\lhd) \simeq \sigma_{R^\circ}(CH_2NH_2)/\sigma_{R^\circ}(NH_2) \simeq 0.33$$

ring does not posses any donor–acceptor properties akin to an olefinic group.

The introduction of two heteroatoms into the three-membered ring to form an oxaziridine produces an electron-withdrawing effect in both the *meta* and *para* positions. The value of σ_I for the oxaziridine is more positive than any of the above-mentioned three-membered rings with the combined electronegativity effect of the two heteroatoms. It should also be noted that the oxaziridines are isomeric with the monomethylamides. Although the σ_I and σ_{R° values are not available for the monomethylamide, the electron-withdrawing property of the amide substituent in both *meta*- and *para*-substituted benzenes is well documented.[13] The opposite sign of σ_{R° for the oxirane and the oxaziridine indicates that the oxygen bridge between carbons permits very little, if any, contribution from resonance structure I, whereas structure II must make a measurable contribution to the resonance parameter of the oxaziridine.

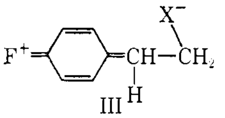


I



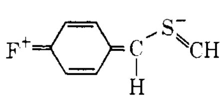
II

A comparison of the donor or acceptor properties in the ground state of the three-membered rings with the results obtained from ultraviolet spectroscopy (excited state) is instructive. From the ultraviolet spectra of a series of *para*-substituted phenylcyclopropanes, styrene oxides, and styrene sulfides, Ketcham, *et al.*,[12] showed that, relative to benzene, oxirane and thiirane are electron withdrawing, whereas cyclopropane is electron donating. The change of oxirane and thiirane from donor to acceptor species in going from the ground state to the excited state may be attributed, firstly, to a large contribution of the quininoid structures III and IV in the excited state, and secondly, to the absence of any such contribution in the ground state. Since substituent constants are determined in the ground state, the inversion of the donor–acceptor properties of oxirane and thiirane provide some explanation for the lack of any really good relationship between $\Delta\lambda$ and any parameter measuring the resonance effect of a substituent.[30]



III

X = O or S



IV

Experimental Section

Materials. The m- and p-fluorostyrene oxides were prepared by the epoxidation of the corresponding olefins with m-chloroperbenzoic acid.[31] The oxaziridines were prepared by oxidation of the corresponding Schiff bases with m-chloroperbenzoic acid. The styrene sulfides were prepared from the oxides by the procedure described by Guss.[32] The m- and p-fluorostyrenimines were prepared by the Wenker synthesis by the procedure described by Brois.[33] The m- and p-fluorocyclopropanes were prepared from olefin *via* the intermediate *gem*-dibromocyclopropanes as described by Ketcham.[34]

In addition to the elemental analysis recorded in Table II, the compounds were further characterized by their proton nuclear

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(30) H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1962, p 259.

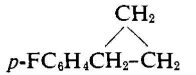
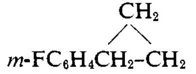
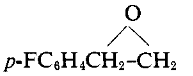
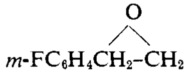
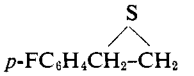
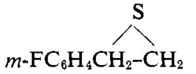
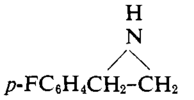
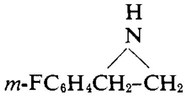
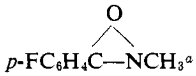
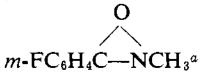
(31) N. N. Schwartz and J. H. Blumbergs, *J. Org. Chem.*, **29**, 1976 (1964).

(32) C. O. Guss and D. L. Chamberlain, Jr., *J. Am. Chem. Soc.*, **74**, 1342 (1952).

(33) S. J. Brois, *J. Org. Chem.*, **27**, 3532 (1962).

(34) R. Ketcham, R. Cavestri, and D. Jambotkar, *ibid.*, **28**, 2139 (1963).

Table II

Compound	Formula	Bp, °C (mm)	$n^{25}D$	C, % Calcd	C, % Found	H, % Calcd	H, % Found	F, % Calcd	F, % Found	S or N, % Calcd	S or N, % Found
 p-$FC_6H_4CH_2$-CH_2	C_9H_9F	90(45)	1.5051	79.38	79.71	6.66	7.00	13.95	13.30		
 m-$FC_6H_4CH_2$-CH_2	C_9H_9F	85(40)	1.5049	79.38	79.84	6.66	6.71	13.95	13.0		
 p-$FC_6H_4CH_2$-CH_2	C_8H_7FO	92(14)	1.5074	69.56	69.94	5.11	4.68	13.75	13.5		
 m-$FC_6H_4CH_2$-CH_2	C_8H_7FO	89(13)	1.5078	69.56	69.95	5.11	5.41	13.75	13.3		
 p-$FC_6H_4CH_2$-CH_2	C_8H_7FS	52–56(0.5)	1.5610	62.31	63.08	4.58	4.97	12.32	12.5	20.75	19.47
 m-$FC_6H_4CH_2$-CH_2	C_8H_7FS	60–65(1–2)	1.5601	62.31	63.02	4.58	4.72	12.32	13.4	20.75	19.10
 p-$FC_6H_4CH_2$-CH_2	C_8H_8FN	132–138(6–8)	1.5310	70.05	69.38			13.85	14.5	10.22	10.15
 m-$FC_6H_4CH_2$-CH_2	C_8H_8FN	127–129(6)	1.5330	70.05	69.93			13.85	14.0	10.22	9.81
 p-FC_6H_4C—NCH_3[a]	C_8H_8FON	45(0.05)	1.5080	62.74	62.85	5.24	4.98				
 m-FC_6H_4C—NCH_3[a]	C_8H_8FON	45(0.05)	1.5076	62.74	62.24	5.24	5.41				

[a] Active oxygen by iodometric analysis was >90%.

magnetic resonance spectrum. The chemical shift of the aliphatic protons were found in every case to be identical with that observed in the spectrum of the corresponding nonfluorinated compound.

Procedure. Fluorine nmr spectra were obtained with Varian Associates high-resolution nmr spectrometer operating at 56.4 Mcps. Approximately 5% (volume) solutions of the fluorobenzenes were used with either 1,1,2,2-tetrachloro-3,3,4,4-tetrafluorocyclobutane or o-difluorobenzene as the internal reference. The chemical shifts were then related to fluorobenzene as described previously.[13]

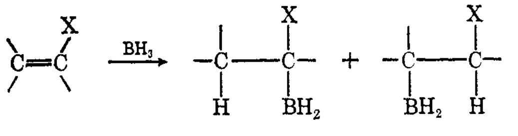
Transfer Reactions Involving Boron. XIV. The Stereochemistry of α-Transfer Reactions[1]

Daniel J. Pasto and James Hickman[2]

Contribution from the Department of Chemistry, University of Notre Dame, Notre Dame, Indiana 46556. *Received April 21, 1967*

Abstract: The stereochemistry of the rearrangement of α-chloroorganoboranes, formed in part in the hydroboration of vinyl chlorides, to alkylchloroboranes is shown to proceed with complete inversion of stereochemistry at carbon.

The addition of borane to a heterosubstituted olefin (**1**) results in the formation of both α- and β-heterosubstituted organoboranes (**2** and **3**, respectively), the relative amounts of the two isomers depending on the heterofunctional group X. Previous investigations in our laboratories have shown that **2** undergoes spontaneous rearrangement to **4**,[3–5] termed an α transfer,[3] that this rearrangement occurs prior to the basic oxidation–hydrolysis work-up procedure, and that **2** does



1 2 3 (1)

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[2] Reilly Research Fellow, 1965–1966; National Institutes of Health Predoctoral Fellow (1-F1-GM-31, 055-01A1), 1966 to present.

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[5] D. J. Pasto and R. Snyder, *J. Org. Chem.*, **31**, 2773 (1966).