Table I. Coupling Constants (in c.p.s.) of the Vinyl and Allylic Protons of Bicyclo[3.2.1]octene-2 Derivatives

	J_{AZ}[10]	J_{BC}	J_{AD}	J_{ZD}	$|J_{AE}|$	$|J_{ZG}|$	$|J_{BE}|$	$|J_{BZ}|$	$|J_{BA}|$
III	−17.0	+7.0	+2.0	+4.7	0.6	2.4	0.6	2.0	1.0
IV	−17.0	+7.0			0.6	2.2	0.6	2.0	1.4
V		+7.0			0.6		0.5		1.2

and the bridgehead proton (J_{AD} and J_{ZD}) accord well with those found in *exo-* and *endo*-allylic substituted derivatives of I.[3,11] This agreement is particularly reassuring since the stereochemistry of allylic protons in these structures cannot be predicted by the Karplus equation.[7,12]

It is interesting to note that the two pairs of W-disposed protons (ZG and AE) have apparently similar geometries, yet their coupling constants are appreciably different.

Similarly, the C-4–Z and C-4–A bonds appear to possess the same angular relationship to the plane described by C-2–C-3–C-4, but nonetheless the vinyl-allylic coupling constants $|J_{BZ}|$ and $|J_{BA}|$ are quite different in III and somewhat different in the 5-methyl compound IV. These inequalities suggest that III may be distorted so that the C-4–Z bond is more axial than the C-4–A bond with respect to the plane described by C-2–C-3–C-4. It is worth remembering that vinyl-allylic coupling constants are composed of two components, J^{σ} and J^{π}, which are opposite in sign, and consequently are quite sensitive to any alteration in the geometric relationship of the coupled protons.[13]

As we have already mentioned,[3] *exo* substitution at C-4 by bromine or hydroxyl (I and II) caused the coupling between B and A to vanish. This result may stem from an enhancement of the above-mentioned distortion on insertion of a polar substituent *exo* at C-4.[13,14] It is interesting to observe that *exo*-4-deuterio-5-methylbicyclo[3.2.1]octene-2 (V)[15] retains vinyl-allylic coupling (see Table I).

Nevertheless, although we believe that intramolecular flection exerts a determinative influence on vinyl-allylic coupling in the bicyclo[3.2.1]octene-2 skeleton, substituent effects should not be discounted. These matters are presently under active study, and our results and interpretations will be reported later.

Finally, we wish to draw attention to the striking parallel between the present long-range couplings of the vinyl proton and the long-range interactions experienced in the electron paramagnetic resonance spectra of radical anions which possess a bicyclo[3.2.1]-octene-2 skeleton.[16] Apparently, both kinds of coupling involve participation of the olefinic bond in inter-

(11) *exo*-1-Methyl-2,3-benzbicyclo[3.2.1]octanol-4 and its *endo* isomer had allylic coupling constants (^3J) of 2.8 and 5.0 c.p.s., respectively: W. Herz and G. Caple, *J. Am. Chem. Soc.*, **84**, 3517 (1962).
(12) M. Karplus, *ibid.*, **85**, 2870 (1963).
(13) Calculation predicts that the C-4–Z bond makes an angle of 67° to the plane described by C-2–C-3–C-4, whereas the corresponding angle for the C-4–A bond should be 55° (see E. W. Garbisch, *ibid.*, **86**, 5561 (1964)).
(14) A reasonable explanation is as follows. Repulsion between the dipoles associated with the C-4–Z (*e.g.*, when Z is Br) and C-3–Br bonds will cause the C-4–A bond to rotate into the null coupling sector which lies between 40 and 30° to the C-2–C-3–C-4 plane.
(15) C. W. Jefford, J. Gunsher, S. Mahajan, and B. Waegell, *Tetrahedron Letters*, No. 28, 2333 (1965).
(16) G. A. Russell, K. Y. Chang, and C. W. Jefford, *J. Am. Chem. Soc.*, **87**, 4383 (1965).

action mechanisms which have common stereochemical features.[17]

(17) However, coupling between the vinyl proton and an ethane bridge proton (which might be inferred from e.p.r. data) is not observed in the n.m.r. spectra of I–V.

C. W. Jefford, J. Gunsher
Chemistry Department, Temple University
Philadelphia, Pennsylvania 19122

K. C. Ramey
Research Department, The Atlantic Refining Company
Glenolden, Pennsylvania

The Form of d Orbitals in Carbon–Sulfur π Bonds[1]

Sir:

Recently a substituent interference experiment on the intensity of the ^1L_b bands in substituted benzenes was proposed for ascertaining participation of d orbitals in a conjugation scheme.[2] Application of this experiment to phenylsilanes[2] and to the lower halogens[3] demonstrated that the Si 3d and the Cl, Br, I nd (or (n + 1)p) orbitals are in fact populated.[4] In divalent sulfur compounds there are two views: (1) that the sulfur 3p and 3d orbitals[4] are both utilized in S–C π bonding,[5,6] and (2) that use of 3d[4] is unimportant and that the bond involves only inclusion of sulfur 3p electrons in an olefinic or aryl π shell.[7] It is possible to decide between (1) and (2) by a substituent interference experiment.

In thiophenol the inflection band at 2800 Å. (Table I) can be assigned with little doubt as the benzene analog $^1L_b \leftarrow {}^1A$ transition.[8] If the sulfur 3d orbitals are utilized in π bonding to the ring, the intensity of the L_b band in *p*-methylthiophenol will have a destructive interference term resulting in the intensity being decreased from that of thiophenol itself. On the other hand, any 3pπ(S)–2pπ(C) bonding will lead to a constructive term causing the intensity to increase. The distinct decrease in the molar extinction coefficient of *p*-methylthiophenol (ϵ ∼300) from that for thiophenol (ϵ ∼700) establishes that the S d orbitals do importantly

(1) Supported in part by the Air Force Office of Scientific Research, Grant AF-AFOSR 742-65, and by the National Science Foundation.
(2) L. Goodman, A. Konstam, and L. H. Sommer, *J. Am. Chem. Soc.*, **87**, 1012 (1965).
(3) L. Goodman and L. J. Frolen, *J. Chem. Phys.*, **30**, 1361 (1959).
(4) The interference experiment does not distinguish between population of nd and (n + 1)p orbitals. A weak argument against utilization of (n + 1)p orbitals in halogens is given by J. R. Hoyland and L. Goodman, *J. Phys. Chem.*, **64**, 1816 (1960). This argument does not necessarily apply to SiH₃, however. We are in accord with a referee's suggestion that the main results of these papers do not distinguish between the 3d or 4p as the acceptor orbitals of sulfur. However, 3d seems to us to be more probable.
(5) D. P. Craig and C. Zauli, *Gazz. chim. Ital.*, **90**, 1700 (1960).
(6) See, *e.g.*, R. J. Gillespie, *Can. J. Chem.*, **33**, 818 (1960).
(7) See, *e.g.*, (a) G. Bergson, *Arkiv Kemi*, **16**, 315 (1960); **18**, 409, (1961); **19**, 181, 265 (1962); (b) A. Mangini and R. Passerini, *J. Chem. Soc.*, 4954 (1956).
(8) W. W. Robertson and F. A. Matsen, *J. Am. Chem. Soc.*, **72**, 5250 (1950). The more intense band at 2400 Å. is very probably a charge-transfer band S(3pπ) → ring (π*). The decrease in intensity in the series C₆H₅(Et)S, C₆H₅CH₂(Et)S, and C₆H₅(CH₂)₂(Et)S observed by E. A. Fehnal and M. Carmack, *ibid.*, **71**, 84 (1949), confirms this assignment.

take part in the π bonding. (Compare in contrast the increase in going from phenol to p-methylphenol.) Detailed consideration of the bonding and antibonding benzene orbitals which are involved requires this statement to hold for both the ground and excited states. The arguments against 4p orbital population are similar to those against $(n + 1)$p orbital population in the lower halogens.[4]

Craig and Zauli[5] calculated the approximate contraction deformation expected for S 3d orbitals engendered by neighboring Coulombic potentials. They concluded that the contracted d orbitals are still much "larger" than p valence shell orbitals, and as a consequence it is not as likely that the 3d orbitals will undergo as much angular deformation as the 3p orbitals (i.e., the d orbitals should not appreciably hybridize).[9a] However, Cruickshank, et al.,[9b] concluded from a formal Hartree–Fock calculation on the ^{7}I and ^{3}F terms of the S sp^{3}d^2 configuration that the d orbitals are compact.

In the case of increasing nonplanarity of a π-electron system (e.g., in sterically twisted anisoles), there is rapid loss of conjugation since the removal of one 2p orbital of the oxygen atom from the conjugation scheme is not compensated by another taking its place. The effect requires sufficient angular deformation of the in-plane p orbitals (as a consequence of the Σ framework hybridization) so that these orbitals are incapable of providing compensating overlap. It is important to note that this conclusion is experimentally rather than theoretically based.

By application of a twisting experiment it should be possible to ascertain whether the sulfur d orbitals in, say, thioanisole remain angularly atomic as predicted by Craig and Zauli, or whether they are substantially deformed in Σ framework hybridization. If they remain angularly undeformed, then as the SCH$_3$ group is twisted out of the ring plane by bulky ortho substituents, when one d orbital is removed from the conjugation scheme, another will take its place. The kind of intensity experiment described above (in this case requiring the intensity of the L$_b$ band in sterically hindered thioanisoles) could settle this question, but because intensity measurements are difficult in the case of inflection bands we have turned to measurements of the intramolecular F n.m.r. shielding effect, f_H^{p-X}, engendered by the p-SCH$_3$ substituent in fluorobenzene. This is approximately $+4.7$ p.p.m., a sharply reduced figure compared to that $(+11.5$ p.p.m.) for a p-OCH$_3$ substituent.[10] A positive shielding effect requires an increased ground-state electron density in the region of the F–C bond relative to unsubstituted fluorobenzene.[11]

We find the effect of twisting OCH$_3$ and SCH$_3$ from ring coplanarity produces F n.m.r. shielding effects which are dramatic in their qualitative differences.

I II III
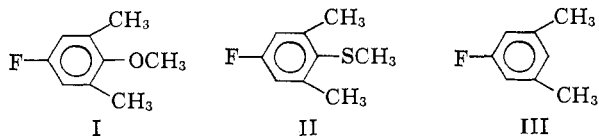
(9) (a) D. P. Craig, J. Chem. Soc., 997 (1959); (b) D. W. J. Cruickshank, et al., J. Chem. Phys., 40, 3733 (1964).
(10) R. W. Taft, et al., J. Am. Chem. Soc., 85, 3146 (1963).
(11) M. Karplus and T. P. Das, J. Chem. Phys., 34, 1683 (1961); F. P. Prosser and L. Goodman, ibid., 38, 374 (1963).

Under the same conditions as utilized above, the shielding of I relative to III, $f_{III}^I = +5.2$ p.p.m., indicates that the twisting effect of the 3,5-dimethyl groups does greatly reduce the increased density effect of p-OCH$_3$. On the other hand, the shielding of II relative to III, $f_{III}^{II} = -1.3$ p.p.m., indicates that in the twisted conformation the density is reduced to magnitudes less than that for fluorobenzene itself. This result means the twisted SCH$_3$ group has become a weak electron-accepting substituent.

The F n.m.r. shielding result clearly requires that there is population of the S 3d orbitals in the twisted conformation and hence establishes that the d orbitals are not severely angularly deformed.

Table I. Intensities of ^{1}L$_b$ $\leftarrow$ ^{1}A Bands in Thiophenols and Thioanisoles

Compound	Ref.	ϵ^a	λ, mμ
⟨○⟩–SH	b	700	269
CH$_3$–⟨○⟩–SH	c	300	275
⟨○⟩–OH	d	1320	269
CH$_3$–⟨○⟩–OH	e	1840	277
⟨○⟩–SCH$_3$	f	400	280
CH$_3$–⟨○⟩–SCH$_3$ (CH$_3$, CH$_3$)	g	(2200)^h	265
F–⟨○⟩–SCH$_3$ (CH$_3$, CH$_3$)	i	1600	263
F–⟨○⟩–SCH$_3$	i	900	290

^{a} Molar extinction coefficient. ^{b} K. Bowden, E. A. Braude, and E. R. H. Jones, J. Chem. Soc., 948 (1946); solvent, n-hexane. ^{c} Y. Minoura, J. Chem. Soc. Japan, 73, 244 (1952); solvent, n-heptane. ^{d} Smoothed extinction coefficient, A.P.I. no. 99; solvent, isooctane. ^{e} Smoothed extinction coefficient, A.P.I. no. 322; solvent, isooctane. ^{f} A.P.I. spectrum no. 561; solvent, isooctane. An earlier spectrum determined by A. Mangini and R. Passerini, J. Chem. Soc., 4954 (1956), gives a higher value. ^{g} C. C. Price and S. Oae, "Sulfur Bonding," Ronald Press Co., New York, N. Y., 1962, p. 181; solvent, ethanol. ^{h} Extinction coefficients in parentheses are determined from not clearly resolved shoulder bands. ^{i} This work; solvent, 3-methylpentane.

Even though we cannot place much reliance on the accuracy of the measured intensity of the L$_b$ band, it is worth pursuing the expected effects of steric twisting as anticipated by the conclusion above. The intensity for complete twisting $I(90°)$ is expected to be M_d^2 where M_d is the spectroscopic moment[9] arising from the d orbital perturbation. In the unhindered case $I(0°) \sim (M_d + M_p)^2$ where M_p is the spectroscopic moment arising from the p-orbital perturbation and has opposite sense to M_d.[2] Therefore $I(90°) - I(0°) = +2M_pM_d - M_p^2$. Since the interference experiment on thiophenol demonstrates that $M_d > M_p$, $I(90°) - I(0°)$ is predicted to be >0. Thus if the d orbitals conjugate at 90° to the same extent as at 0°, the intensity of the L$_b$ band should increase upon steric twisting. If the d orbitals do not conjugate,

the intensity should tend toward zero, as in sterically twisted anisole.[12]

The first expectation is qualitatively confirmed in the observed spectra (Table I).[13] We do wish, however, to emphasize that no reliance can be placed on the magnitude of the observed increase because of the overlapping band problem.

Acknowledgment. The authors thank Dr. Edward Gregorek for the intensity measurements of the ^1L_b bands in the fluorothioanisoles and Mr. Joseph Rakshys for the F n.m.r. measurements. We are indebted to Professor G. Illuminati for supplying samples of compounds I–III.

(12) L. J. Frolen and L. Goodman, *J. Am. Chem. Soc.*, **83**, 3405 (1961).

(13) On the other hand, the CT band (shifted to ~2500 Å. in thioanisole) decreases in intensity upon steric twisting.

(14) John Simon Guggenheim Fellow, University College, London.

(15) Department of Chemistry, University of California, Irvine, Calif.

Lionel Goodman,[14] Robert W. Taft[15]

Whitmore Chemical Laboratory, The Pennsylvania State University
University Park, Pennsylvania

Concerning Linear Relationships between the σ and π Electron Effects of Unshared Pair Substituents. The Role of π(p–d) Conjugation[1]

Sir:

Evidence that both donor 3p and acceptor 3d (or 4p) orbitals of sulfur are utilized in the interaction of the thiomethoxy group with the benzene ring is presented in the companion paper.[2] This conclusion is further confirmed and extended by the comparison of the ground-state σ and π electronic properties of the methyl derivatives of the first- and second-row elements of groups IV-B to VII-B. We report herein these electronic properties as determined by the F^{19} n.m.r. shielding effects in *m*- and *p*-fluorophenyl derivatives. The evidence is timely in connection with current interest in linear relationships between substituent σ and π electron effects (*i.e.*, linear σ_I–σ_R or $\sigma_{(m)}$–$\sigma_{(p)}$ relationships).[3,4]

The F n.m.r. shielding parameter, f_H^{m-X} (for the *m*-X substituted fluorobenzene relative to internal fluorobenzene) is directly related to σ_I, the inductive reactivity parameter based upon substitution at carbon having only σ bonds, *i.e.*, –CH_2–X.[5] For this reason it has been proposed that the predominating contribution to f_H^{m-X} results from changes in the C–F σ bond moment produced by the polarization imposed by the $C_{(Ar)}$–X σ bond[6]; that is, f_H^{m-X} may be regarded as essentially a σ electron effect parameter.

For –R *para* substituents, the F n.m.r. shielding parameter, f_{m-X}^{p-X} (for the *p*-X substituted fluorobenzene

relative to its *meta* isomer as internal reference), is directly related to σ_R^0, the resonance reactivity parameter which is presumably based upon the contribution of the net π electron effect to normal *para* σ values.[4] This shielding parameter is also directly related to MO theory ground-state π electron charge density at the *para* carbon atom (bonded to F).[7] Evidently the predominating contribution to f_{m-X}^{p-X} results from the localization of π electronic charge in the C–F region produced by a net delocalization of π electrons into the ring from X (f_{m-X}^{p-X} positive) or from the ring into X (f_{m-X}^{p-X} negative). Accordingly, f_{m-X}^{p-X} may be taken as the π electron effect parameter.

Compelling evidence for these assignments is provided by the following additional considerations. Values of f_{m-X}^{p-X} in general cover an order of magnitude greater range than values of f_H^{m-X}.[4,5] Nevertheless, there are recently obtained data available for 14 substituents for which $f_{m-X}^{p-X} = 0.0 \pm 0.4$ p.p.m., whereas the f_H^{m-X} values cover a range from −7.2 to +0.7 p.p.m.[4,5,8] The structures of these substituents[9] are such that it is reasonable to propose that in the ground state there is very little net flow of π charge either in or out of the benzene ring.

In Figure 1 the π electron effect parameter, f_{m-X}^{p-X}, is plotted *vs.* the σ electron effect parameter, f_H^{m-X}.

Figure 1. Relationship between π and σ electron effects of substituents on F n.m.r. shielding in *m*- and *p*-FC_6H_4X compounds (X is as indicated): ordinate, the π electron effect parameter; abscissa, the σ electron effect parameter.

The closed circles give the results (obtained in CCl_4 solutions by the previously reported method[5]) for the

(1) This work was supported in part by the National Science Foundation.

(2) L. Goodman and R. W. Taft, *J. Am. Chem. Soc.*, **87**, 4385 (1965).

(3) (a) N. L. Bauld, Abstracts, 139th National Meeting of the American Chemical Society, St. Louis, Mo., March 1961; (b) D. H. McDaniel, *J. Org. Chem.*, **26**, 4692 (1961); (c) C. Y. Meyers, *et al.*, *J. Am. Chem. Soc.*, **86**, 2944 (1964); C. D. Ritchie and W. F. Sager, *Progr. Phys. Org. Chem.*, **2**, 389 (1964).

(4) R. W. Taft, *et al.*, *J. Am. Chem. Soc.*, **85**, 3146 (1963).

(5) R. W. Taft, *et al.*, *ibid.*, **85**, 709 (1963), and earlier references.

(6) R. W. Taft, *et al.*, Abstracts, Meeting of the Society of Applied Spectroscopy, Cleveland, Ohio, Sept. 30, 1964, paper 91.

(7) (a) R. W. Taft, *et al.*, *J. Chem. Phys.*, **38**, 380 (1963); (b) G. E. Maciel and J. J. Natterstad, *ibid.*, **42**, 2427 (1965); (c) T. K. Wu and B. P. Dailey, *ibid.*, **41**, 2796; (d) and references therein.

(8) Unpublished results; G. E. Maciel, *J. Am. Chem. Soc.*, **86**, 1269 (1964); R. West, private communication; W. A. Sheppard, private communication.

(9) These substituents are $Sn(CH_3)_3$, $Ge(CH_3)_3$, $C(OCH_3)_3$, H, CH_2Cl, $P(C_6H_5)_2$, $CH_2NH_3^+$, CCl_3, $N(CF_3)_2$, $SOCH_3$, $N(COF)CF_3$, $N(COF)_2$, $C(CN)_3$, and ICl_2.