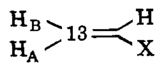
methyl), 182 (2-fluoro), 178 (3-fluoro), 175.5 (4-fluoro), 182.5 (2-bromo), 177.5 (3-bromo), 180 (2-methoxyl), 175.5 (3-methoxy), and 173 (4-methoxy). (c) In system I, when X = C_6H_5, $J_{^{13}CH_A}$ = 156 and $J_{^{13}CH_B}$ = 162 c.p.s.; when X = Cl, $J_{^{13}CH_A}$ = 160 and $J_{^{13}CH_B}$ =



I

161 c.p.s.[6] When X = Br, $J_{^{13}CH_A}$ = 163.8 and $J_{^{13}CH_B}$ = 159.6 c.p.s.[7] This change in the $J_{^{13}CH_A}/J_{^{13}CH_B}$ ratio from styrene to vinyl bromide is also consistent with contributions from the spin-dipole and/or electron-orbital terms.[8]

On the basis of these arguments, it is evident that s-characters calculated from $J_{^{13}CH}$ are unreliable and misleading. Values calculated from the long-range coupling are meaningless even when expressed in one significant figure; those calculated from the short-range coupling are probably equally meaningless whenever two or more heteroatoms are bonded to the ^{13}C.

Acknowledgment.—We thank the United States Atomic Energy Commission for financial support (Grant CCO-1189-11).

(6) E. B. Whipple, W. E. Stewart, G. S. Reddy, and J. H. Goldstein, *J. Chem. Phys.*, **34**, 2136 (1961).
(7) R. M. Lynden-Bell, *Mol. Phys.*, **6**, 537 (1963).
(8) The validity of our suggestion that spin-dipole and electron-orbital terms contribute to proton-^{13}C coupling certainly requires further experimental scrutiny, in view of theoretical predictions by J. A. Pople, *ibid.*, **1**, 216 (1958) that "coupling *via* currents induced on a third atom will always be negligible."
(9) Fellow of the Alfred P. Sloan Foundation.
(10) National Science Foundation Predoctoral Cooperative Fellow, 1962–1964.

KEDZIE CHEMICAL LABORATORY
MICHIGAN STATE UNIVERSITY
EAST LANSING, MICHIGAN

GERASIMOS J. KARABATSOS[9]
CHESTER E. ORZECH, JR.[10]

RECEIVED APRIL 27, 1964

Substituent Effects. III.[1] Correlation of ^{13}C–F and ^{29}Si–H Couplings by Pairwise Interactions

Sir:

A "direct" additivity rule for J_{CH} for substituted methanes of the type CHXYZ was first observed by Malinowski[2]; namely, $J_{CH} = \zeta_x + \zeta_y + \zeta_z$, where ζ_x is a parameter associated with substituent x. Significant departures from this simple additivity rule have been reported[3–5] for compounds which contain highly electronegative substituents. Recently, Douglas[6] introduced pairwise interaction terms as corrections for departures from "direct" additivity. Essentially, his equation can be written as $J_{CH} = \zeta_x + \zeta_y + \zeta_z + \zeta_{xy} + \zeta_{xz} + \zeta_{yz}$, where ζ_{xy} is an interaction parameter associated with substituents x and y, and is independent of substituent z.

Recently it has been reported that J_{CF}[3,7] and J_{SiH}[8,9] do not obey the "direct" additivity rule. We wish to report here that J_{CF} and J_{SiH} can be correlated by pairwise interactions. For simplicity, we will redefine the interaction parameter by $\eta_{xy} = \zeta_{xy} + 0.5(\zeta_x + \zeta_y)$, so that the equation above becomes $J(xyz) = \eta_{xy} + \eta_{xz} + \eta_{yz}$, where J(xyz) is a coupling constant for a compound containing substituents x, y, and z. The parameters shown in Tables I and II have been evaluated in a straightforward manner; namely, $\eta_{xx} = J(xxx)/3$ and $\eta_{xy} = [J(xxy) - \eta_{xx}]/2$, respectively.

A comparison between observed and predicted coupling constants is shown in Table III. Considering that the evaluation of the interaction parameters does not take into account the inherent error in the measured coupling constants, we conclude that the agreement between experiment and prediction is very good. Obviously a trial-and-error or a least-squares

TABLE I

INTERACTION PARAMETERS, η_{xx}, FOR J_{CF} AND J_{SiH}, CALCULATED BY $\eta_{xx} = J(xxx)/3$

Interaction parameter	^{13}C–F couplings, c.p.s.	^{29}Si–H couplings,[d] c.p.s.
H,H	52.6[a]	67.5
F,F	86.0[a]	127.2
Cl,Cl	112.2[b]	121.0
Br,Br	124.0[c]	107.9

[a] Calculated from an average of values found by N. Muller and D. J. Carr, *J. Phys. Chem.*, **67**, 112 (1963), and in ref. 5. [b] Calculated from an average of values found by Muller and Carr[a] and in ref. 7. [c] Calculated from an average of values found by R. K. Harris, *J. Mol. Spectry.*, **10**, 309 (1963), and by P. C. Lauterbur in "Determinations of Organic Structures by Physical Methods," Vol. 2, edited by F. C. Nachod and W. D. Phillips, Academic Press, Inc., New York, N. Y., 1962, p. 505. [d] Data taken from ref. 8.

TABLE II

INTERACTION PARAMETERS, η_{xy}, FOR J_{CF} AND J_{SiH}, CALCULATED BY $\eta_{xy} = [J(xxy) - \eta_{xx}]/2$

Interaction parameters	^{13}C–F couplings, c.p.s.	^{29}Si–H couplings,[e] c.p.s.
Cl,H	90.8[a]	83.5
F,H	93.6[b]	77.4
F,Br	119.0[c]	
F,Cl	106.5[c]	
F,CN	89.0[d]	
H,CN	59.7[d]	

[a] Data taken from G. V. D. Tiers, *J. Am. Chem. Soc.*, **84**, 3972 (1962). [b] Calculated from an average of values found by Muller and Carr, footnote *a*, Table I, and in ref. 5. [c] Data taken from Muller and Carr, footnote *a*, Table I. [d] Data taken from ref. 3. [e] Data taken from ref. 8.

TABLE III

COMPARISON BETWEEN CALCULATED AND OBSERVED COUPLING CONSTANTS

Compound	J_{calcd}, c.p.s.		J_{obsd}, c.p.s.	Difference calcd. − obsd., c.p.s.
	J_{Si-H}			
SiH_3Cl	$\eta_{H,H} + 2\eta_{Cl,H}$	= 234.5	238.1[a]	+3.6
SiH_3F	$\eta_{H,H} + 2\eta_{F,H}$	= 222.3	229.0[a]	+6.7
	J_{C-F}			
CH_2F_2	$\eta_{H,H} + 2\eta_{H,F}$	= 239.7	233.4[b]	+6.3
CF_2Br_2	$\eta_{Br,Br} + 2\eta_{F,Br}$	= 362.0	357.8[c]	+4.2
CF_2Cl_2	$\eta_{Cl,Cl} + 2\eta_{F,Cl}$	= 325.2	324.7[d]	+0.5
CF_2HCN	$\eta_{H,F} + \eta_{H,CN} + \eta_{F,CN}$	= 242.3	243.5[e]	−1.2

[a] Data taken from ref. 8. [b] An average of values found by Muller and Carr, footnote *a*, Table I, and in ref. 5. [c] An average of value found by Muller and Carr,[b] and by Harris, footnote *c*, Table I. [d] An average of values found by Muller and Carr,[b] and by Lauterbur, footnote *c*, Table I. [e] Data taken from ref. 3.

(1) Part II: E. R. Malinowski, L. Z. Pollara, and J. P. Larmann, *J. Am. Chem. Soc.*, **84**, 2649 (1962).
(2) E. R. Malinowski, *ibid.*, **83**, 4479 (1961).
(3) G. P. van der Kelen and Z. Eeckhaut, *J. Mol. Spectry.*, **10**, 141 (1963).
(4) N. Muller and P. I. Rose, *J. Am. Chem. Soc.*, **84**, 3973 (1962).
(5) S. G. Frankiss, *J. Phys. Chem.*, **67**, 752 (1963).
(6) A. W. Douglas, *J. Chem. Phys.*, **40**, 2413 (1964).
(7) R. K. Harris, *J. Phys. Chem.*, **66**, 768 (1962).
(8) E. A. V. Ebsworth and J. J. Turner, *J. Chem. Phys.*, **36**, 2628 (1962).
(9) H. S. Gutowsky and C. S. Juan, *ibid.*, **37**, 2198 (1962).

technique would yield an improved correlation. In particular, we wish to point out that this type of correlation indeed accounts for the peculiar variation in $^{13}C-F$ coupling constants[7] for the series CFH_3 (157.4 c.p.s.), CF_2H_2 (234.8 c.p.s.), CF_3H (274.3 c.p.s.), and CF_4 (259.2 c.p.s.).

This empirical correlation should be useful in the development of theories concerning nuclear magnetic dipole interactions and molecular wave functions. At the present time we are investigating these theoretical aspects. Also, we are investigating other systems in the light of this correlation.

Acknowledgment.—The authors gratefully acknowledge the support of the U. S. Army Research Office (Durham), Contract No. DA-31-124-ARO(D)-90.

(10) National Defense Fellow, Department of Health, Education, and Welfare.

DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING
STEVENS INSTITUTE OF TECHNOLOGY
HOBOKEN, NEW JERSEY
EDMUND R. MALINOWSKI
THEODORE VLADIMIROFF[10]

RECEIVED MAY 28, 1964

Ring Inversion and Bond Shift in Cyclooctatetraene Derivatives

Sir:

In order to obtain further information on the ring inversion[1] and bond shift processes[2] in cyclooctatetraene and its derivatives, we have examined the proton n.m.r. spectra,[3] with double irradiation at the deuteron frequency, of ethyl cyclooctatetraene-2,3,4,-5,6,7-d_6-carboxylate (I) and of cyclooctatetraenyl-2,3,4,5,6,7-d_6-dimethylcarbinol (II). Compound I was prepared by photochemical addition[4] of ethyl propiolate to benzene-d_6. Compound II was obtained by the reaction[5] of I with excess methylmagnesium iodide. These compounds were chosen because they were expected to give particularly simple spectra.[6]

At low temperatures (−35°) the ring proton of II (CS_2 solution) gave rise to two sharp lines of equal intensities separated by 2.6 c.p.s. The high-field band (τ 4.24) is assigned to the proton in IIa and IIb and the low-field band (τ 4.20) to the proton in IIc and IId because only the high-field band remained sharp in the absence of deuterium decoupling. The proton in IIa or IIb should[2] show a negligible coupling to the adjacent deuteron whereas the proton in IIc or IId should[2] show an appreciable coupling. The methyl protons also gave two bands (τ 1.16 and τ 1.21, separation = 3.3 c.p.s.), as expected[7] from a structure such as IIa, in which the two methyl groups are chemically nonequivalent. These two bands are not very sharp and it appears that the methyl groups are slightly coupled to one another.

As the temperature was increased the methyl doublet broadened, then coalesced (at −2°), and finally became a single sharp line. The doublet arising from the ring proton showed a similar behavior except that the coalescence temperature was much higher (+41°). Since the separation of the ring proton doublet is actually slightly smaller than that of the methyl doublet, the specific rate[8] at which the ring proton changes its environment (*e.g.*, IIa to IIb) must be very much smaller at the same temperature than the specific rate at which the methyl groups exchange their environments.

The processes which average the environments of the two methyl groups are IIa → IIb and IIa → IId. On the other hand, the processes IIa → IIc and IIa → IId contribute to the averaging of the environments of the ring proton. Although the rates of these two latter processes could be different, they must be the same if the transition state for the bond shift is planar, as will be assumed in the following discussion. From the n.m.r. results mentioned above, it can be seen that $k_1 + k_2/2 \gg k_2$, so that $k_1 \gg k_2$, and therefore the rate constant obtained from the methyl protons is effectively k_1, the rate constant for ring inversion (without bond shift).

The enthalpy and entropy of activation for bond shift (Table I) were obtained[6,8] by measurements of the rate constant from 26 to 66°. Because of the broadened nature of the methyl bands below the coalescence temperature, corresponding parameters of meaningful accuracy for ring inversion have not yet been obtained.

TABLE I

KINETIC PARAMETERS FOR BOND SHIFT AND RING INVERSION IN CYCLOOCTATETRAENE DERIVATIVES

Compound	Temp., °C	Process	k (sec.$^{-1}$)	ΔF^* (kcal./mole)	ΔH^*	ΔS^* (e.u.)
I	40	Bond shift	126	15.3	12.8	−8.0
II	41	Bond shift	5.4	17.4	15.4	−6.3
II	−2	Bond shift	0.1[a]	17.1[a]		
II	−2	Ring inversion	7.8	14.7		

[a] Extrapolated.

Evidence for a planar (or nearly planar) transition state for bond shift comes from a comparison of the specific rates of bond shift in II (0.04 sec.$^{-1}$, extrapolated) and in cyclooctatetraene[2] itself (26 sec.$^{-1}$) at the same temperature (−10°). The lower specific rate of bond shift in II can be ascribed to greater repulsive interactions of the $C(CH_3)OH$ group with the adjacent CH and CD groups in the transition state than in the ground state. If the transition state were highly puckered, the reverse order would be expected. This, of course, does not rule out a slight amount of puckering in B. The specific rate of bond shift (2.6 sec.$^{-1}$, extrapolated) in I (see below) at −10° is intermediate between the two values above as expected

(1) The ring inversion process has only been studied quantitatively in dibenzcyclooctateraenedicarboxylic acid that is rather distantly related to the structure of cyclooctatetraene itself. The activation energy for inversion was found to be 27 kcal./mole [K. Mislow and H. D. Perlmutter, *J. Am. Chem. Soc.*, **84**, 3591 (1962)]. See also N. L. Allinger, W. Szkrybals, and M. A. DaRooge, *J. Org. Chem.*, **28**, 3007 (1963).

(2) F. A. L. Anet, *J. Am. Chem. Soc.*, **84**, 671 (1962); G. M. Whitesides and J. D. Roberts, D. E. Gwynn and J. D. Roberts, unpublished observations, quoted by J. D. Roberts, *Angew. Chem.*, **75**, 20 (1963).

(3) Spectra were measured on a Modified Varian HR60 at 60 Mc./sec. The modification consisted of a field-frequency control of the type used by R. Freeman and D. H. Whiffen, *Proc. Phys. Soc.* (London), **79**, 794 (1962). An NMR Specialties Model SD60 decoupler was used to provide the second radiofrequency (*ca.* 9.1 Mc. sec.) for double irradiation.

(4) D. Bryce-Smith and J. E. Lodge, *J. Chem. Soc.*, 695 (1963); E. Grovenstein and D. V. Rao, *Tetrahedron Letters*, **No. 4**, 148 (1961).

(5) A. C. Cope and R. M. Pike, *J. Am. Chem. Soc.*, **75**, 3320 (1953).

(6) F. A. L. Anet and J. S. Hartman, *ibid.*, **85**, 1204 (1963).

(7) P. M. Nair and J. D. Roberts, *ibid.*, **79**, 4565 (1957).

(8) H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1956), J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Company, Inc., New York, N. Y., 1959, p. 218.