

1,3,5,7,9,11,13,15,17,19-eicosadecaene $[\lambda_{\text{max}}^{\text{isoctane}}]$
(principal bands) 376, 397, 420 and 447 $\text{m}\mu$.⁶

(6) F. Sondheimer, R. Wolovsky and D. A. Ben-Efraim, to be published.

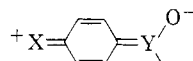
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RECEIVED DECEMBER 19, 1959

SOLVENT EFFECTS ON MESOMERIC CHARGE SEPARATION¹

Sir:

Reactivity² and dipole moment³ data have suggested that the contribution to the resonance hybrid of dipolar resonance structures, *e.g.*

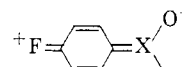


is enhanced by solvents which support ionization.

We report herein unequivocal evidence for such phenomena based upon the difference in the F^{19} n.m.r. shielding parameters for substituents in the *p*- and *m*-positions of fluorobenzene, $S_p^F - S_m^F$. This quantity (hereafter referred to as the meso-

tions to this behavior are the two $-R$ substituents, OH and NH_2 , for which the m.c.p. can be influenced by hydrogen bonding between the substituent and the hydroxylic solvents. Consistent with such an interpretation are the facts that the m.c.p. values for the proton donating OH group are more negative (greater electron density) and those for the proton accepting NH_2 group are less negative in hydroxylic than in the non-hydroxylic solvents.

In contrast, the m.c.p.'s for every $+R$ substituent show that the electron density at the F^{19} atom is decreased appreciably with increased ability of the solvent to support ionization. The nature of the present results is such that these solvent effects must be ascribed to the increased contribution to the resonance hybrid of the dipolar resonance form⁵



It is of interest to note in connection with the nearly solvent independent character of the m.c.p.'s

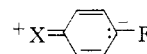
TABLE I
MESOMERIC CHARGE PERTURBATIONS (M.C.P.'s), $S_p^F - S_m^F = H_m^F - H_p^F$ (IN P.P.M.), FOR SUBSTITUTED FLUOROBENZENES

Subst.	Class	Solvent					Av.
		Cyclo-C ₆ H ₁₂	CCl ₄	CH ₃ OH	75% aq. CH ₃ OH		
NH ₂	-R	-13.8 ± 0.1	-13.8 ± 0.2	-13.4 ± 0.1	-12.9 ± 0.1	...	
OCH ₃	-R	-12.6 ± 0.1	-12.6 ± 0.1	-12.6 ± 0.2	-12.5 ± 0.1	-12.6	
OH	-R	-12.1 ± 0.1	-12.2 ± 0.1	-13.5 ± 0.2	-13.0 ± 0.2	...	
F	-R	-9.8 ± 0.1	-9.8 ± 0.3	-9.7 ± 0.1	-9.5 ± 0.0	-9.7	
OCOCH ₃	-R	-6.0 ± 0.1	-6.0 ± 0.1	-5.8 ± 0.1	-5.7 ± 0.1	-5.9	
Cl	-R	-5.1 ± 0.1	-5.1 ± 0.1	-5.1 ± 0.1	-4.9 ± 0.1	-5.1	
CO ₂ H	+R	(insol.)	(insol.)	6.4 ± 0.1	6.6 ± 0.1	...	
CO ₂ C ₂ H ₅	+R	5.8 ± 0.1	6.1 ± 0.1	6.5 ± 0.1	6.6 ± 0.1	...	
CH ₃ CO	+R	5.6 ± 0.1	5.9 ± 0.1	6.6 ± 0.1	7.3 ± 0.1	...	
NO ₂	+R	5.8 ± 0.1	5.8 ± 0.1	6.5 ± 0.1	7.2 ± 0.1	...	
CHO	+R	7.8 ± 0.1	8.1 ± 0.2	...	9.0 ± 0.1	...	

meric charge perturbation, m.c.p.) provides a quantitative measure of the order of electron densities in the immediate vicinity of the F^{19} nucleus produced by mesomeric interaction of the *para* substituent.^{2c,4}

Table I records m.c.p.'s for a variety of typical $-R$ and $+R$ substituents in four solvents at "infinite dilution." The m.c.p. values for most $-R$ substituents show a second order dependence on solvent which cannot with confidence be taken to appreciably exceed the limits of the present experimental error. Apparently the average m.c.p.'s listed for these substituents are therefore approximate intramolecular properties. The only excep-

tion for the $-R$ substituents that the contribution to the resonance hybrid of the dipolar canonical form



is apparently much less dependent upon solvent than that of the above type.^{2c}

Solutions 5% (by vol.) in the substituted fluorobenzene were employed and the shifts obtained^{2c} relative to the internal standard (2%) tetrafluorotetrachlorocyclobutane.⁶ We are much indebted to Dr. G. V. D. Tiers for suggesting and supplying a sample of this standard.

(1) This work was supported in part by the Office of Naval Research, Project NRO55-328.

(2) (a) B. Gutbezahl and E. Grunwald, *THIS JOURNAL*, **75**, 559 (1953); (b) M. M. Davis and H. B. Hetzer, *J. Res. Nat. Bur. Stand.*, **60**, 569 (1958); (c) R. W. Taft, Jr., S. Elrenson, I. C. Lewis and R. E. Glick, *THIS JOURNAL*, **81**, 5352 (1959).

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(5) R. W. Taft, Jr., *ibid.*, **79**, 1045 (1957).

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RECEIVED NOVEMBER 23, 1959