Fluorine-19 Nuclear Magnetic Resonance Study of Transmission of Electronic Effects through the Amide Linkage

By R. G. PEWS

(*Halogens Research Laboratory, The Dow Chemical Company, Midland, Michigan* 48640)

Summary It has been claimed that the amide linkage in benzanilides does not transmit electronic effects, but it is now shown by ^{19}F n.m.r. studies that the amide linkage does transmit electronic effects in the ground state.

RECENTLY, Menger[1] and his co-workers concluded from the pK_a values of the series of 4′-aminobenzanilides and 4′-hydroxybenzanilides that there is no conjugative transmission through the amide linkage in the ground state. These results were surprising since other linkages between diaryl rings are known to transmit electronic effects, *e.g.* azostilbenes,[2] stilbenes,[3] benzophenones,[4] diaryl ethers,[5] diaryl sulphides,[5] *trans*-stilbene oxides,[6] and *trans*-1,2-diarylcyclopropanes.[3]

We now report the transmission of electronic effects through the amide linkage from a series of 3- and 4-substituted-4′-fluorobenzanilides† (**1**). The shielding parameters were determined in tetrahydrofuran, acetone, and dimethylformamide and are recorded in the Table together with the shielding parameters in tetrahydrofuran for the 4-fluoro-3′- and 4′-substituted 1,2-diphenylethanes (**3**) and *trans*-4-fluoro-3′- and 4′-substituted stilbenes (**4**). The

† The amides reported in the Table gave satisfactory elemental analyses and i.r. spectra consistent with the suggested structure. The mp.'s were: (**1a**) 192—194°, (**1b**) 183—185°, (**1c**) 174—176°, (**1d**) 141–143°, (**1e**) 111—113°, (**1f**) 164—166°, (**1g**) 168—170°, (**2a**) 185—187°, (**2b**) 154—156.° The methods of preparation of the bibenzyls and stilbenes are described in ref. 3.

^{19}F *n.m.r. shielding parameters* (δ *p.p.m.*)[a] *relative to* 1,1,2,2-*tetrachloro*-3,3,4,4-*tetrafluorocyclobutane* (TCTFCB)

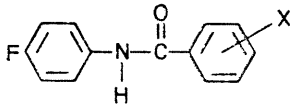
	Solvent	X = 4-OMe	H	4-Cl	3-Cl	3-CF_3	3-NO_2	4-NO_2	Slope (δ/σ°)
(1)	THF	6·48	6·02	5·65	5·55	5·36	5·12	4·98	−1·27
(1)	Me_2CO	6·55	6·11	5·71	5·62	5·51	5·26	5·11	−1·18
(1)	$HCONMe_2$	6·65	6·27	6·02	5·86	5·72	5·55	5·48	−0·99
(2)	THF	−3·73	—	—	—	—	—	−5·51	—
(2)	$HCONMe_2$	−3·56	—	—	—	—	—	−5·01	—
(4)	THF	4·43	4·33	4·13	4·08	4·01	3·85	3·83	−2·21
(3)	THF	1·95	1·21	0·76	0·46	0·28	−0·12	−0·69	−0·64

[a] The ^{19}F n.m.r. spectra were determined on a Varian A-56/60A. [b] All the data were corrected for δ (H)/(TCTFCB) = 0 in the least-square plots in the Figure.

effect of interchanging the carbonyl and amine portion of the amide relative to the fluorine detector was determined by comparison of the magnitude of

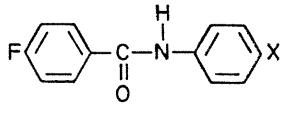
$$\int_{\text{TCTFCB}}^{\text{4-OMe}} - \int_{\text{TCTFCB}}^{\text{4-NO}_2}$$

in p.p.m. for amides (**1**) and (**2**) (tetrahydrofuran solution). The values of 1·50 and 1·78 p.p.m. for (**1**) and (**2**), respectively, show that the position of the amine and carbonyl moieties relative to the fluorine detector does not make an appreciable change in the substituent effect.



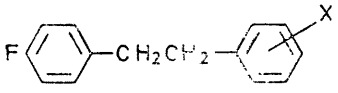
X

(1) a; 4′-OMe
b; H
c; 4′-Cl
d; 3′-Cl
e; 3′-CF_3
f; 3′-NO_2
g; 4′-NO_2

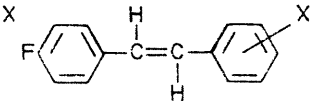


X

(2) a; OMe
b; NO_2

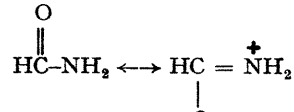


(3)



(4)

A quantitative measurement of transmission was obtained by plotting the shielding parameters against Taft's σ° constants (Figure). The slopes in p.p.m./σ° were obtained by least squares.‡,§ The transmissive effects for (**1**) decrease with an increase in solvent polarity. This may be attributed to an increase in neutralization of the amide dipolar with an increase in solvent polarity. If the transmission in the bibenzyls and stilbenes is considered to be 0 and 100%, respectively, the amide is *ca.* 40% as effective as a double bond in transmitting conjugation. Pauling[7] has estimated that (**5**) and (**6**) contribute 60 and 40%, respectively, corresponding to 40% double bond character for the C–N bond. The results of the present study support Pauling's estimate and substantiate the theory



(5) (6)

that the restricted rotation of the amide group is due to partial double bond character.

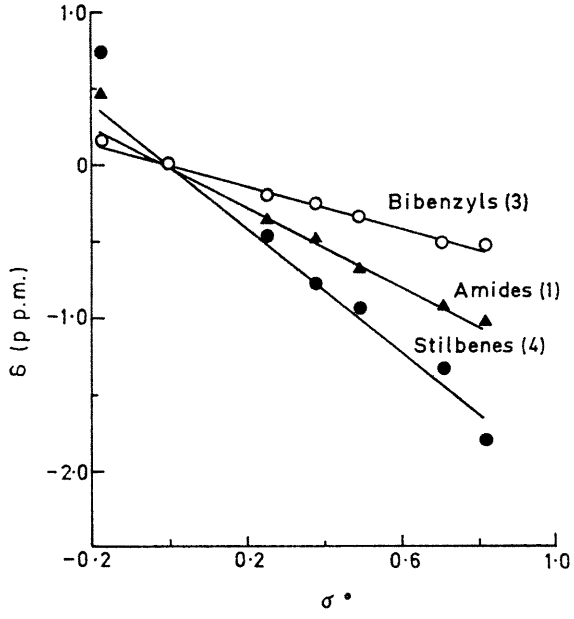


FIGURE. *Plot of Taft's* σ° *value* vs. ^{19}F *n.m.r. shielding parameters of bibenzyls, amides, and stilbenes in tetrahydrofuran solution.*

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‡ The 4-OMe derivatives were excluded from the least-squares calculations. See ref. 3.
§ The least-squares treatment gave correlation coefficients > 0·95.

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