1245. *Applications of Proton Resonance Spectroscopy to Structural Problems. Part XXIII.*[1] *Determination of Hammett σ-Constants for Heterocycles*

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The chemical shifts of the α-proton of a series of β-arylacrylic acids are correlated by the Hammett equation; measurement of pyridine, pyridine 1-oxides, and pyridine derivatives gives σ-values for the heteroatom "substituents."

THE Hammett equation has become one of the most widely used relationships to correlate structure–reactivity in aromatic compounds. The application of the equation has been extended from benzenoid to heteroaromatic compounds, and the replacement of a heteroatom for CH or CH:CH in benzene considered as a "substitution" and assigned a σ-constant. However, as a recent review[2] shows, relatively little work has been carried out on heteroaromatic compounds, and often the available values of σ-constants for heteroatoms are not derived from reaction series which have been well studied and shown to be reliable for benzenoid derivatives. We thought that it would be instructive to apply a simple nuclear magnetic resonance (n.m.r.) method to this problem, and have accordingly studied a series of β-aryl- and β-heteroaryl-acrylic acids.

EXPERIMENTAL

N.m.r. spectra were recorded on a Perkin-Elmer 40 Mc. spectrometer, for 0·3M-solutions in dimethyl sulphoxide, and in trifluoroacetic acid, with tetramethylsilane as internal reference. Sodium salts were also measured as 0·3M-solutions in deuterium oxide, with acetonitrile (τ CH_3 8·1) as internal reference.

The compounds were recrystallised commercial specimens, or were prepared by literature methods,[3,4] and had melting points in agreement with published values. The sodium salts were prepared from the respective acids.

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[1] Part XXII, J. F. Cavalla, A. R. Katritzky, M. J. Sewell, and G. R. Bedford, *J.*, 1965, 4546.

[2] H. H. Jaffé and H. Lloyd Jones, *Adv. Heterocyclic Chem.*, 1964, **3**, 209.

[3] A. R. Katritzky and A. M. Monro, *J.*, 1958, 150.

[4] M. Hartmann and W. Bosshard, *Helv. Chim. Acta*, 1941, **24**, 28E.

DISCUSSION

The results are recorded in Table 1. The coupling constants of *trans*-ethylene have been discussed *inter alia* by Hogeveen *et al.*,[5] and Laszlo and Schleyer.[6] The last workers give the relations:

$$J_{trans} = 19{\cdot}0 - 3{\cdot}2\,(E_{\mathrm{R}} + E_{\mathrm{R}'} - 2E_{\mathrm{H}})$$

where E_{R} represents the electronegativity of substituent R. The electronegativity of substituted aryl groups varies little, and the almost constant value of J in Table 1 is expected.

The β-hydrogen atoms in β-arylacrylic acids had chemical shifts at lower field than the α-protons because of (a) the effect of the conjugated carbonyl group, and (b) the aromatic ring current. When the relative chemical shifts for the α- and β-protons for the substituted cinnamic acids were plotted against Hammett σ-constants, a good correlation ($r = -0{\cdot}973$) was found for the α-protons (see Figure; the point for NH_2 may be affected by solvation of the aminogroup) ($r = -0{\cdot}973$ for dimethyl sulphoxide solution, $r = -0{\cdot}912$ for trifluoroacetic acid), but less so for the β-protons ($r = -0{\cdot}850$). Steric and magnetic anisotropic (possibly including ring current) effects may account for the poor relationship for the β-protons. The anions show little regularity, possibly owing to hydration differences.

Using the Hammett plots for the α-protons in dimethyl sulphoxide, and the chemical shifts found for the pyridylacrylic acids and their 1-oxides, Hammett σ-constants were obtained for the pyridines and pyridine 1-oxides (Table 2). σ-Constants for the pyridinium ions were similarly obtained from the observations in trifluoroacetic acid.

TABLE 1

Chemical shifts and coupling constants

R	R′	Hβ(τ)	*H*α(τ)	*J* (c./sec.)	R	R′	Hβ(τ)	*H*α(τ)	*J* (c./sec.)
2py	CO_2H	2·39	3·17	15·9	*m*-MeO·C_6H_4	CO_2H	2·43	3·47	16·2
		(1·96) *	(2·84)	(16·1)			(2·06)	(3·46)	(16·2)
2py	CO_2Et	2·34	3·12	16·0	*m*-Cl·C_6H_4	CO_2H	2·47	3·39	16·6
2pyO	CO_2H	2·07	2·99	16·5			(2·10)	(3·48)	(16·0)
3py	CO_2H	2·36	3·32	16·3	*m*-NO_2·C_6H_4	CO_2H	2·29	3·29	16·2
		(1·97)	(2·93)	(16·5)			(1·96)	(3·28)	(16·1)
3py	CO_2Pr^n	2·32	3·22	16·2	*p*-Me_2N·C_6H_4	CO_2H	2·52	3·80	15·8
3py	CO_2Bu^i	2·31	3·23	16·2	*p*-MeO·C_6H_4	CO_2H	2·43	3·63	16·3
3py	$CONH_2$	2·53	3·27	16·3			(2·05)	(3·57)	(16·0)
3pyO	CO_2H	2·47	3·29	16·6	*p*-NH_2·C_6H_4	CO_2H	2·59	3·89	16·1
3pyO	CO_2Et	2·42	3·18	16·1	*p*-Me·C_6H_4	CO_2H	2·44	3·54	16·0
3pyO	CO_2Pr^n	2·41	3·17	16·0			(2·04)	(3·54)	(16·0)
3pyO	CO_2Bu^n	2·41	3·17	16·2	*p*-Cl·C_6H_4	CO_2H	2·44	3·46	16·2
3pyO	$CONH_2$	2·69	3·23	16·2	*p*-NO_2·C_6H_4	CO_2H	2·32	3·28	16·2
4py	CO_2H	2·44	3·24	16·2	C_6H_5	CO_2H	2·41	3·47	16·0
		(2·00)	(3·10)	(16·4)			(2·00)	(3·46)	(16·2)
4py	CO_2Me	2·37	3·13	16·3	*m*-MeO·C_6H_4	CO_2Na	2·83	3·67	16·2
4py	$CONH_2$	2·62	3·18	16·2	*p*-Me_2N·C_6H_4	CO_2Na	2·82	3·82	16·1
4pyO	CO_2H	2·47	3·39	16·2	*p*-MeO·C_6H_4	CO_2Na	2·82	3·78	16·2
4pyO	CO_2Et	2·42	3·30	16·0	*p*-Me·C_6H_4	CO_2Na	2·81	3·71	16·2
					p-Cl·C_6H_4	CO_2Na	2·82	3·76	16·2
					p-NO_2·C_6H_4	CO_2Na	2·89	3·63	16·2
					C_6H_5	CO_2Na	2·77	3·65	16·1

* The values in parentheses are the results obtained from measurements of the solutions in CF_3CO_2H.

These results show some resemblance to those given in ref. 2, but the latter show a wide variation in themselves. However, the present results show internal consistency, and lie in the order expected qualitatively for the general chemistry of pyridines and pyridine

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[5] H. Hogeveen, G. Maccagnani, and F. Taddei, *Rec. Trav. chim.*, 1964, **83**, 937.

[6] P. Laszlo and P. von Ragué Schleyer, *Bull. Soc. chim. France*, 1964, 87.

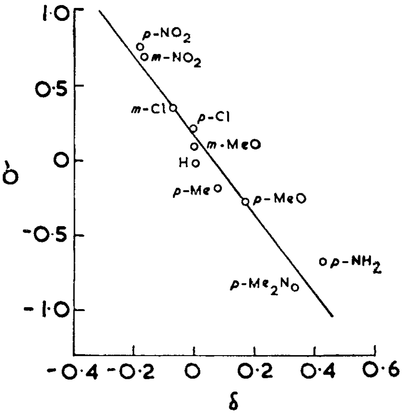
1-oxides. Infrared[7,8] and ultraviolet spectra,[9] and dipole moments,[10] indicate that the order of electron-donor ability of substituted rings is: phenyl > 4-pyridyl 1-oxide, 3-pyridyl > 3-pyridyl 1-oxide, 4-pyridyl. This order is apparent from the σ-values.

TABLE 2

Substituent constants for aza- and modified aza-substituents

Substituent	σ α	σ β	σ γ	S *
$\geqslant N$	1·0	0·6	0·8	0·12
$\geqslant \overset{+}{N}-O^-$	[1·5] †	0·7	0·4	0·12
$\geqslant \overset{+}{N}H$	2·2	1·9	1·3	0·14

* The standard deviation for the regression line. † Value suspect due to steric interaction.



Plot of Hammett σ-constants against δ for β-aryl-acrylic acids in dimethyl sulphoxide—H_α

In addition, the 2-substituted rings are both shown to be powerfully electron-attracting. Pyridinium rings are known to be strongly electron-attracting at all positions; it is of interest that in the present circumstances the inductive and/or field effects appear to be more important than the mesomeric effect, as σ is less for a 4-substituted pyridinium ring than for the 3-substituted analogue.

We plan to explore the apparent wide variation of Hammett σ-constants for heterocyclic compounds. Some of the possible reasons for apparent variations may be mentioned. (i) Some of the values are considerably more negative than those for electron-withdrawing groups such as NO_2, and consequently require moderate extrapolations from the graphs of benzene data. (ii) *ortho*-Values suffer from some of the same disadvantages that are found for *o*-substituted benzenes: although steric effects will be low for $N\colon$ and $N^+\colon H$ (not for *N*-oxides), direct field effects could be important, and, for n.m.r. work, anisotropic effects. (iii) Solvation effects will be particularly important in leading to variation in electron-withdrawing power of a hetero atom.

This work was carried out during the tenure (by F. J. S.) of a D.S.I.R. Research Studentship. We thank British Petroleum Ltd. for financial aid.

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[*Received, March* 10*th*, 1965.]

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[7] A. R. Katritzky, A. M. Monro, J. A. T. Beard, D. P. Dearnaley, and N. J. Earl, *J.*, 1958, 2182.
[8] A. R. Katritzky, *Rec. Trav. chim.*, 1959, **78**, 995.
[9] A. R. Katritzky, A. M. Monro, and J. A. T. Beard, *J.*, 1958, 3721.
[10] A. R. Katritzky, E. W. Randall, and L. E. Sutton, *J.*, 1957, 1769.