HAMMETT–TAFT CONSTANTS OF sym-TRIAZINYL AND PYRIMIDINYL GROUPS

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The great amount of data on the reactivities of sym-triazine and pyrimidine derivatives indicate the electron-acceptor character of the triazinyl and pyrimidinyl groups. However, except for the σ_p^- constants of the triazinyl group [1], the quantitative characteristics of their electronic effects have not been reported. We have determined the Hammett–Taft constants of these groups using data from the ^{19}F NMR spectra of m- and p-fluorophenyl-sym-triazines and 2-, 4-, and 5-(m- and p-fluorophenyl)pyrimidines. We obtained these compounds by known methods; the data on their elementary compositions and the spectral characteristics confirm their structures. The δ^F chemical shifts (Table 1) were measured with an HX-90 spectrometer at 84.66 MHz under pulse conditions for dilute solutions (0.5–1 mole %) in inert solvents with different polarities (with C_6F_6 as the internal standard). The average chemical shift relative to fluorobenzene was determined for each compound. The σ_I and σ_R^0 constants of the indicated groups were calculated by means of correlation equations [2]. It follows from the data presented that the nature of the solvent has an appreciable influence on the inductive effects of the investigated groups but virtually no influence on the mesomeric effects.

TABLE 1

Substituent R in the $R-C_6H_4F$ series	δ^F, ppm, relative to C_6H_5F				δ_{av}, F	Constants	
	CCl_4	$CHCl_3$	acetone	DMSO		σ_I	σ_R^0
m-(2-Pyrimidinyl)	0,40	0,11	0,17	−0,24	0,08	0,07	0,09
p-(2-Pyrimidinyl)	−2,40	−2,71	−2,34	−2,52	−2,52		
m-(4-Pyrimidinyl)	−0,75	−1,14	−0,67	−0,62	−0,88	0,21	0,09
p-(4-Pyrimidinyl)	−3,49	−3,84	−3,29	−3,32	−3,57		
m-(5-Pyrimidinyl)	−1,66	−1,76	−1,15	−1,00	−1,38	0,28	−0,04
p-(5-Pyrimidinyl)	−0,38	−0,62	0,19	0,21	−0,20		
m-Triazinyl	−0,72	−0,90	−1,09	−0,82	−0,90	0,21	0,20
p-Triazinyl	−6,76	−7,22	−6,52	−6,50	−6,86		

LITERATURE CITED

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