(ϵ 34,000), 272 (5470), and 298 mμ (3690); λ_{min} 252 (ϵ 4280) and 286 mμ (3250)[8]; ν_{max}^{KBr} 3350, 819, and 802 cm.$^{-1}$; [α]D +225.[9] Demethylation of Ib with pyridine hydrochloride gave 3-hydroxy-1,11-iminoestra-1,3,5(10),9(11)-tetraen-17-one (Ia, 81% yield), m.p. 290–300° dec.; λ_{max} 229 (ϵ 32,000), 270 (5050), and 301 mμ (3530); ν_{max}^{KBr} 3380, 1725, and 828 cm.$^{-1}$; [α]D +331° (pyridine).

Further work is in progress on the synthesis of steroids containing an indole nucleus.

(8) The ultraviolet absorption spectrum of Ib compared very favorably with that of 2,3-dimethyl-6-methoxyindole: N. Neuss, H. E. Boaz, and J. W. Forbes, *J. Am. Chem. Soc.*, **76**, 2463 (1954).

(9) Additional support for the structure Ib as well as for IIIb and IV was obtained by mass spectrometric analysis, which will be discussed in the full length paper on this synthesis.

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Fig. 1.—Correlations of $\sigma(Y)$ with σ_I and σ for YC₆H₄SO₂.

Electronic Effects of the Sulfonyl Group in Aromatic Systems. Relationships between Inductive and d-Orbital Resonance Contributions[1]

Sir:

Recent reports[2] have discussed possible relationships between resonance and induction parameters of substituted benzenes. Although Taft[3] proposed σ_R and σ_I as independent parameters which in general are not directly interrelated, McDaniel's correlations[4] suggested that in benzoic acids a linear *meta–para* relationship may exist for *families* of substituents bonded to the ring through a common atom, e.g., SCH_3, SH, $SC(O)CH_3$, $S(O)CH_3$, SO_2NH_2, and SO_2CH_3. The corresponding phenols, however, deviated substantially from linearity. Subsequently, Taft[2a] demonstrated that better linearity is realized if comparison is restricted to series of more closely related substituents, e.g., m- and p-$FC_6H_4SO_2X$ (X is F, Cl, CH_3, C_2H_5, NH_2, O^-). Significantly, $S(O)CH_3$ and SF_5 did not qualify for the SO_2X line.

We now report that for acetic acids, benzoic acids, and phenols substituted with $SO_2C_6H_4Y$[1b,5,6] the parameters of SO_2X and relative influence of Y can be correlated for each series; other factors influencing the S–X bond remain virtually constant (*cf.* above). From the data (Table I)[7] several significant relationships become apparent.

(1) (a) Supported by grants from the Petroleum Research Fund and Army Research Office (Durham); (b) preceding paper: C. Y. Meyers, *Gazz. chim. ital.*, **93**, 1206 (1963).

(2) (a) R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Andersen, and G. T. Davis, *J. Am. Chem. Soc.*, **85**, 3146 (1963); (b) L. A. Cohen and W. M. Jones, *ibid.*, **85**, 3397, 3402 (1963); (c) D. R. Eaton and W. A. Sheppard, *ibid.*, **85**, 1310 (1963); (d) O. Exner, *Tetrahedron Letters*, 815 (1963).

(3) R. W. Taft, *J. Phys. Chem.*, **64**, 1805 (1960).

(4) D. H. McDaniel, *J. Org. Chem.*, **26**, 4692 (1961).

(5) C. Y. Meyers, G. Moretti, and L. Maioli, *ibid.*, **27**, 625 (1962); B. Cremonini, Doctoral Dissertation, University of Bologna, 1962.

(6) C. Y. Meyers, G. Lombardini, and L. Bonoli, *J. Am. Chem. Soc.*, **84**, 4603 (1962).

(7) I-effects from *meta* and *para* positions were considered equivalent; by definition, R-effects reflect *all* influences of π-interaction between the substituent and the system into which it is introduced: *cf.* ref. 2b, 2d. 3, R. W. Taft and I. C. Lewis, *Tetrahedron*, **5**, 210 (1959), and M. J. S. Dewar and P. J. Grisdale, *J. Am. Chem. Soc.*, **84**, 3529 (1962), *et seq.*
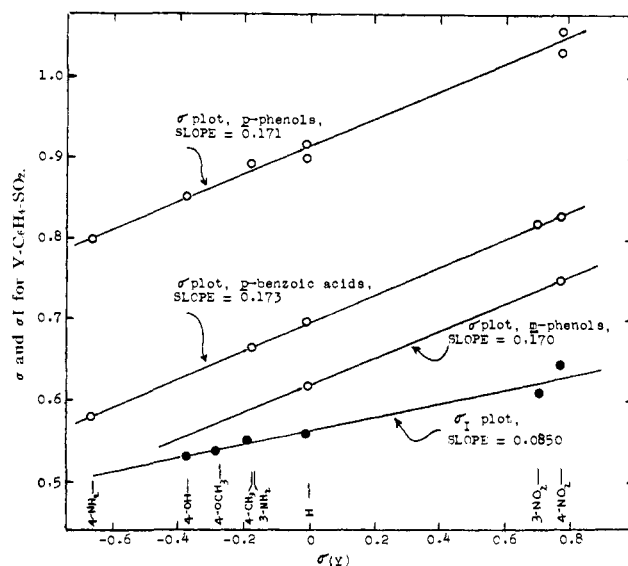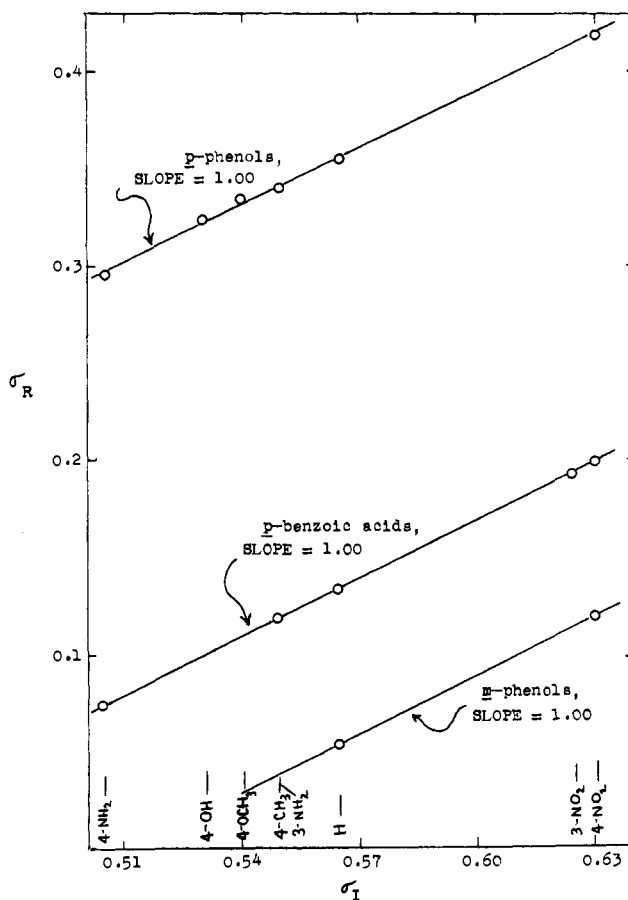

Fig. 2.—Correlations of σ_R with σ_I for YC₆H₄SO₂ (Y substituents as indicated).

The linear relationships between $\sigma(Y)$[8] and, respectively, σ_I and σ for YC₆H₄SO₂ in each series are shown in Fig. 1. The slopes indicate that σ increases at the same rate for p-benzoic acids and m- and p-phenols, and σ increases *twice* as fast as σ_I. From this and the relationship $\sigma = \sigma_R + \sigma_I$ it follows that *in each of the series R- and I-effects increase at the same rate* (Fig. 2.). Expressions derived from these relationships may be

(8) Hammett substituent constants (ionization of benzoic acids): J. Hine, "Physical Organic Chemistry," 2nd Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 87.

TABLE I

SUBSTITUENT CONSTANTS FOR BENZENESULFONYL-SUBSTITUTED PHENOLS AND BENZOIC ACIDS[a]

| Y Group | p-Benzoic acids | | | Phenols | | | |
| | | | | σ | | σ_R | |
	σ_I	σ	σ_R	meta	para	meta	para
4-NH$_2$	(.505)	0.58[b]	0.075	(0.51)	0.80[c]	0.005	0.295
					(.80)		
4-OH	.53	(.635)	.105	(.56)	.86	.03	.325
	(.53)				(.855)		
4-OCH$_3$	.54	(.65)	.11	(.575)	.87[c]	.035	.335
	(.54)				(.875)		
4-CH$_3$	.55	(.67)	.12	(.59)	.90[c]	.04	.34
	(.55)				(.89)		
3-NH$_2$	(.55)	.67	.12	(.595)	(.895)	.045	.345
H	.56	.70	.135	.62	.90	.055	.355
	.55[d]				.92[c]		
	(.565)				(.92)		
3-NO$_2$	.61	.82	.195	(.74)	(1.035)	.115	.41
	(.625)						
4-NO$_2$	.65	.83[e]	.20	.75	1.03	.12	.42
	(.63)				1.06[c]		
					(1.05)		

[a] From ionization data in ref. 1b, 5, and 6, except where otherwise indicated; values in parentheses are interpolated from Fig. 1; σ_I determined from the corresponding acetic acid, and σ_R calculated as $\sigma - \sigma_I$ (see ref. 7). [b] Also reported by H. H. Szmant and G. Suld. *J. Am. Chem. Soc.*, **78**, 3400 (1956). [c] From the combined ionization data reported in ref. b and 2b. [d] O. Exner and J. Jonas, *Collection Czech. Chem. Commun.*, **27**, 2296 (1962). [e] The previously reported value (0.54, ref. b) was found to be in error (see ref. 5).

used to calculate and correlate other parameters for systems containing series of ArSO$_2$ substituents. For the YC$_6$H$_4$SO$_2$ substituent of (a) acetic acid, (b) p-benzoic acid, (c) m-phenol, and (d) p-phenol

For (a)

$$\sigma_I = a\sigma(Y) + b$$
$$a = 0.085$$
$$b = 0.565$$

For (b), (c), and (d),

$$\sigma = 2a\sigma(Y) + c \qquad \text{(b) (c) (d)}$$
$$\sigma_I = [\sigma + (2b - c)]/2 \qquad c = 0.70 \; 0.62 \; 0.92$$
$$\sigma_R = [\sigma - (2b - c)]/2 \qquad 2b - c = 0.43 \; 0.51 \; 0.21$$
$$\sigma_R = \sigma_I - (2b - c)$$

The last expression describes the relationship between resonance and inductive effects of YC$_6$H$_4$SO$_2$. Fig. 2 illustrates the linearity for the series[9] and also indicates that resonance becomes significant only when induction is appreciable, and that I-effects are always greater than R-effects for these groups even in p-phenols.

Consistent relationships like these are not usually observed with series of −R substituents.[2,3,7] Moreover the linear *meta–para* relationships exhibited by there sulfonylphenols, *viz.*

$$\sigma_R(p) - \sigma_R(m) = \sigma(p) - \sigma(m) = {\sim}0.30$$

are not shown by phenols substituted with NO$_2$, CN, CH$_3$CO, etc. With these, on the other hand, a fairly constant resonance ratio[10] is exhibited but the R-ratio

$$R(m)/R)p) = \alpha \; ({\sim}0.10)$$

for the sulfonylphenols varies regularly with σ_I (Fig. 3).[11]

(9) These relationships are linear over the range of Y groups generally investigated. Reasonably, σ_R approaches zero as σ approaches σ_I (cf. Fig. 1 and 2). Calculations based on the above expressions should be valid until σ_I is very close to or less than $2b - c$.

(10) R. W. Taft and I. C. Lewis, *J. Am. Chem. Soc.*, **80**, 2436 (1958); **81**, 5343 (1959).

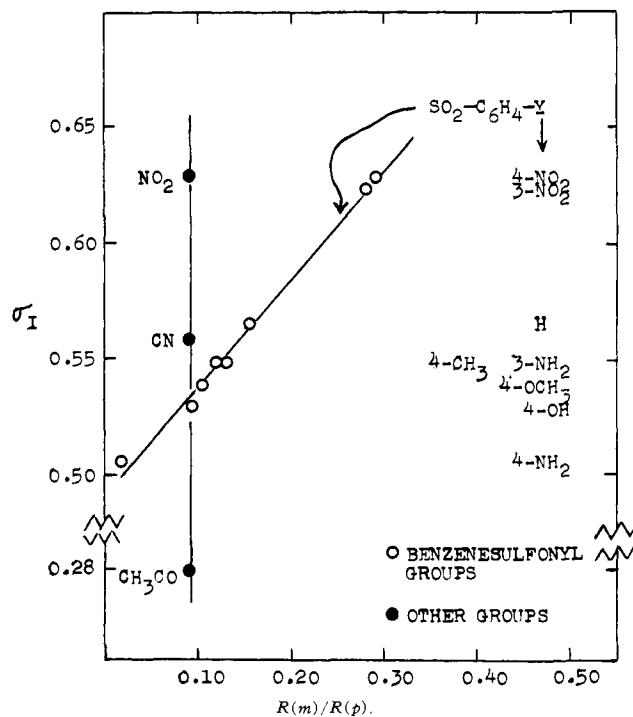(11) $R(m)/R(p)$ calculated as $[(\sigma(m) - \sigma_I)]/[(\sigma(p) - \sigma_I)]$.

Fig. 3.—Correlation of $R(m)/R(p)$ with σ_I for substituted phenols.

These relationships between resonance and inductive contributions of benzenesulfonyl functions suggest that d-orbital resonance and electronegativity are closely related. Resonance arising mainly from p-orbital interactions apparently is much more associated with other factors.

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