

drocarbon.⁷ This ensures that the R⁺-R⁻ reaction is the predominant one. The other hydrocarbons were electrolyzed at constant applied voltage. The emission from the 9,10-dimethylantracene solution (Figure 1b), attributable to the R⁺-R⁻ reaction, clearly has a broad component to the red of the fluorescence.⁸ Anthracene (Figure 1c) yields mainly excimer emission. The difference between the latter two compounds is in accord with the expected destabilization of the excimer by the methyl groups, a steric effect which is of critical importance in 9,10-diphenylantracene and rubrene⁹; these two hydrocarbons give rise only to normal monomer fluorescence under all conditions. The absence of any chemiluminescence other than monomer fluorescence in these cases as well as in naphthacene is evidence against the intervention of an unknown reaction which might be responsible for the diffuse long wave length bands. Phenanthrene yields comparable amounts of monomer and excimer, while 3,4-benzpyrene gives only excimer fluorescence.

The presence of a broad structureless emission band which we have interpreted as excimer fluorescence is explicable only on the basis of the R⁺-R⁻ reaction. This implies strongly that the mechanism requires the close approach of R⁺ and R⁻ before electron transfer can take place and suggests that electron tunneling across appreciable distances is not a likely event.

The structure of an excimer and the possibility of isomeric excimers which may be separated by energy barriers is a point that we wish to consider in view of the data obtained from anthracene. Anthracene and phenanthrene are well known to undergo self-quenching *via* the interaction of ¹R* with R, whereas 9,10-diphenylantracene and rubrene fail to do so because of steric hindrance. The excimer of anthracene thus formed can revert to its components or undergo non-radiative decay to ground-state molecules.¹⁰ Triplet polyacenes undergo annihilation by both a collision process and by long-range interaction.¹¹⁻¹³ The latter leads only to normal fluorescence. The collision process, in the case of benzpyrene and pyrene, is the only explanation for the presence of delayed excimer fluorescence. There is evidence available to support the formation of at least one nonradiative excimer of anthracene, but there is no report of any excimer emission from anthracene. We have concluded that excimer emission predominates in R⁺-R⁻ annihilation, and we must conclude further that another excimer of anthracene (formed from R⁺ and R⁻) exists and that in contrast to those (or the one) formed from ¹R* + R or ³R* + ³R* it is capable of direct fluorescent emission. The simplest explanation is that the formation of the excimer as a charge-transfer state can yield a different excimer. It is puzzling that the collision of two triplets which eventually yields ¹R* does not yield some of this radiating excimer, for there is generally sufficient energy available (3.5 e.v. for anthracene). Apparently

(7) We have observed the e.s.r. spectrum of the radical cation.

(8) Short wave length emission is decreased by reabsorption of the fluorescence at the relatively high (0.01 M) concentration used.

(9) E. J. Bowen, *Trans. Faraday Soc.*, **50**, 100 (1954).

(10) The formation of dianthracene is a minor process: A. Dammers de Klerk, *Mol. Phys.*, **1**, 141 (1958).

(11) G. Porter and P. West, *Proc. Roy. Soc. (London)*, **A279**, 302 (1964).

(12) C. Tanaka, J. Tanaka, E. Hutton, and B. Stevens, *Nature*, **198**, 1192 (1963).

(13) C. A. Parker, *ibid.*, **200**, 331 (1963).

the charge-transfer state is of considerable importance for emission and may require an appreciable activation energy for its formation. These same arguments are applicable to 9,10-dimethylantracene and to phenanthrene.

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Direct Infrared Determination of the Resonance Interaction in Monosubstituted Benzenes

Sir:

An important consideration in aromatic chemistry is the amount of electronic interaction between various substituents and the nucleus. The usual method of estimation involves the measurement of reaction rates, position of equilibria, or physical constants of a series of disubstituted benzenes containing one fixed substituent chosen for this purpose. Unfortunately, the fixed substituent employed as a probe may itself affect the required interaction between the other substituent and the ring. Nevertheless, measurements can be made in cases where such further perturbation is restricted and the results are usually expressed as σ^0 values.¹ The interaction can be considered to be made up of inductive and resonance contributions as shown in the equation $\sigma^0 = \sigma_I + \sigma_R^0$, where σ_I represents the inductive effect and σ_R^0 the resonance effect arising from the substituent in the ground state. Values of σ_I are well established for many substituents and can be estimated from aliphatic or aromatic reactivities or from the fluorine n.m.r. shielding parameters for *meta*-substituted fluorobenzenes. The σ_R^0 values for certain substituents have been found^{1,2} both from the difference $\sigma^0 - \sigma_I$, where σ^0 values have been derived from reactivities, and from the difference in fluorine n.m.r. shielding parameters for *para*- and *meta*-substituted fluorobenzenes. Values for substituents capable of conjugative electron withdrawal are found to be solvent dependent and may also be exalted as a result of conjugation with the *para*-substituted fluorine atom, when determined by the n.m.r. method. The values obtained for such substituents are designated $\bar{\sigma}_R$. Recent work³ has shown that the carbon-13 chemical shifts of the *para* carbons in monosubstituted benzenes, especially when corrected by the amount of the corresponding *meta* shift, correlate closely with σ_R^0 values. This represents the only reported method of measuring such interactions directly.

Although intensities of substituent vibrations have been correlated with σ or σ^+ values,⁴ no quantitative relationship for the intensities of the skeletal modes of aromatic molecules has hitherto been established. Katritzky has previously predicted⁵ that the intensities of the ring stretching bands in six-membered aromatic

(1) R. W. Taft, Jr., *J. Phys. Chem.*, **64**, 1805 (1960), and references given therein.

(2) R. W. Taft, Jr., E. Price, I. R. Fox, I. C. Lewis, K. K. Andersen, and G. T. Davis, *J. Am. Chem. Soc.*, **85**, 3146 (1963).

(3) G. E. Maciel and J. J. Natterstad, *J. Chem. Phys.*, **42**, 2427 (1965), and references given therein.

(4) See, for example, T. L. Brown, *J. Phys. Chem.*, **64**, 1798 (1960).

(5) A. R. Katritzky, *J. Chem. Soc.*, 4162 (1958); *Quart. Rev. (London)*, **13**, 353 (1959).

Table I. Calculation of σ_R^0 Values from the Integrated Intensities (A) of the ν_{16} Bands in Monosubstituted Benzenes

Substituent	$A^{1/2a}$	$\pm\sigma_R^0$ (calcd.)	$-\sigma_R^0$ (n.m.r.) ^c	$-\sigma_R^0$ (reactivity) ^c	$\bar{\sigma}_R$ (n.m.r.) ^d	$\bar{\sigma}_R$ (reactivity) ^f
NMe ₂	71.4	0.53	0.54	0.52
OMe	57.7	0.425	0.43	0.41
OH	54.2	0.40	0.43	0.40
F	46.4	0.345	0.32	0.35
OCOMe	32.7	0.24	0.21
Br	32.3	0.24	0.163	0.19
Cl	30.5	0.225	0.18	0.20
COMe	30.7 ^b	0.225 ^b	0.19	0.12
CO ₂ Et	25.9 ^b	0.19 ^b	0.195	0.08
NO ₂	25.2	0.185	0.19	0.14
CF ₃	17.8	0.135	0.10 ^e	0.02
Et	17.0	0.125	0.14	0.09
Me	16.6	0.125	0.146	0.10
CN	15.1	0.11	0.21	0.08
CH ₂ Cl	9.5	0.07	0.03
CCl ₃	0	0.00

^a Precision better than ± 1 (A in l. mole⁻¹ cm.⁻²). ^b May be exalted; see text. ^c Reference 2. ^d Reference 2; calculated from figures for dilute solutions in cyclohexane using the formula given therein. ^e Calculated from figures in L. M. Yagupol'ski, V. F. Bystrov, A. V. Stepanyants, and Yu. A. Fialkov, *Zh. Obshch. Khim.*, **34**, 3682 (1964). ^f Values are $2.0\sigma_R^m$: R. W. Taft, Jr., and I. C. Lewis, *J. Am. Chem. Soc.*, **81**, 5343 (1959).

rings which appear at about 1600 and 1585 cm.⁻¹ (ν_{16a} and ν_{16b} using Herzberg's notation) should be a function of the charge disturbance in the ring. An approximate relationship between the apparent extinction coefficients of these bands for monosubstituted benzenes and the mesomeric moments of the substituents was shown at that time. We now find that the square roots of the total integrated areas of these absorption bands correlate closely with reported σ_R^0 values. Figure 1 shows the correlation with σ_R^0 for eight substituents for which such values were available² from both reactivity and n.m.r. measurements. That the rate of change of dipole moment with the normal coordinate at the equilibrium position ($\partial\mu/\partial Q$), which is proportional to $A^{1/2}$, should be affected only by the resonance interaction of the substituent is reasonable as $\partial\mu/\partial Q$ for this vibration might be expected to be determined mainly by the π -electrons of the ring. The negligible influence of inductive effects is confirmed by the low intensity ($A < 2$) of the vibration for benzo-trichloride, which has a relatively high dipole moment. Further discussion of these matters is reserved for a forthcoming paper.

We have used the empirical equation, $\sigma_R^0 = 0.0074 \cdot A^{1/2}$, derived from the figure by inspection, to calculate values for a total of sixteen substituents, and these values are compared with previously reported σ_R^0 and $\bar{\sigma}_R$ values in Table I.

The intensities were measured on a Perkin-Elmer 125 spectrometer using the solvent-compensation technique, the samples being made up as dilute solutions in carbon tetrachloride. The two ν_{16} bands were integrated together partly for convenience and partly because it is probably not valid to separate them if the substituent is not of C_{2v} or higher symmetry (as will be discussed in the full paper). The benzene derivatives were purified by standard techniques and their purity checked by gas chromatography.

The procedure offers a simple method of determining solvent and temperature effects on resonance interactions in monosubstituted benzenes. In addition, unlike the methods discussed above, it is potentially applicable to such interactions in more complex systems. We are currently investigating these matters using a range of mono- and disubstituted benzenes

and monosubstituted pyridines. Other skeletal modes are also being studied. The only limitations appear to be that no sign can be given to the σ_R^0 values in monosubstituted benzenes and that values for compounds

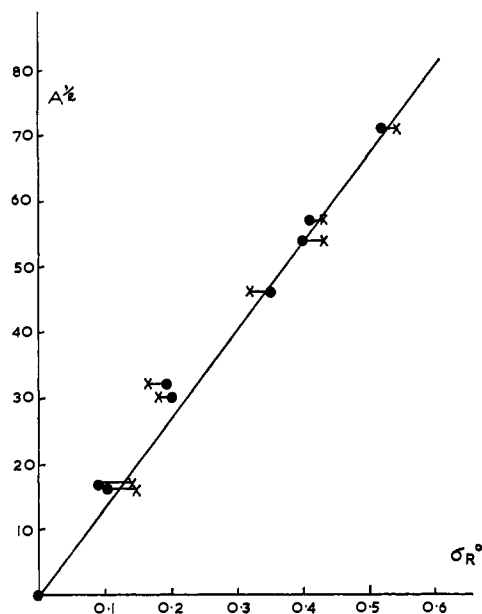


Figure 1. Plot of $A^{1/2}$ (A in l. mole⁻¹ cm.⁻²) vs. σ_R^0 values (reactivity, \bullet ; fluorine n.m.r., \times).

having another strong band near 1600 cm.⁻¹ (e.g., those with an α carbonyl group) may be exalted by coupling.

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Photodimerization of Metal-Complexed Olefins

Sir:

We wish to report the first clear-cut example of a new type of dimerization reaction, the light-induced cyclo-addition of olefins in the presence of certain metal