benzene, but is difficultly soluble in petroleum ether. It gives a yellow color with sulfuric acid and is insoluble in aqueous sodium hydroxide solution.

Anal. Calcd. for $C_{13}H_8N_2O$: C, 75.00; H, 3.84; N, 13.46. Found: C, 74.59; H, 3.65; N, 13.12.

The corresponding phenazine derivative was obtained by refluxing a solution of 0.6 g. of I and 0.6 g. of o-phenylenediamine in 50 ml. of glacial acetic acid for half an hour. The product was recrystallized from glacial acetic acid in pale yellow crystals, m.p. 221°, yield *ca.* 91%. It gives a red color with sulfuric acid and is sparingly soluble in common organic solvents.

Anal. Calcd. for $C_{19}H_{11}N_3$: C, 81.13; H, 3.91; N, 14.94. Found: C, 81.19; H, 3.80; N, 14.63.

5,6-Diacetoxybenzo(h)quinoline (IIIb).—5,6-Dihydroxybenzo(h)-quinoline (IIIa) was obtained after the procedure described by Badger, Pearce and Pettit[4] by the action of phenylhydrazine on 1 g. of I; IIIa formed colorless crystals from ethyl alcohol, m.p. 207°, yield *ca.* 57%. It gave no color with aqueous ferric chloride solution and was soluble in aqueous sodium hydroxide solution with green color.

Anal. Calcd. for $C_{13}H_9NO_2$: C, 73.93; H, 4.26; N, 6.63. Found: C, 73.71; H, 3.61; N, 6.53.

A solution of 0.8 g. of IIIa in 15 ml. of acetic anhydride[4] was refluxed for half an hour. The cooled reaction mixture gave colorless crystals (0.65 g.) which were recrystallized from acetic anhydride, m.p. 194°; IIIb is insoluble in cold aqueous sodium hydroxide solution and gives no color with ferric chloride.

Anal. Calcd. for $C_{17}H_{13}NO_4$: C, 69.15; H, 4.40; N, 4.74. Found: C, 68.75; H, 4.21; N, 4.29.

Photochemical Reactions with I and IV in Sunlight. General Remarks.—The photochemical reactions were carried out as described in the previous publications.[1]

Photochemical Reaction of VIII with p-Methoxybenzaldehyde.—One gram of VIII and 0.8 g. fo p-methoxybenzaldehyde in 45 ml. of benzene were exposed to sunlight for 27 days (October). The deposit that separated during exposure was crystallized from ethanol into colorless crystals, m.p. 225°, yield *ca.* 89%. The photo-product gave a yellow color with concentrated sulfuric acid, and developed a green color with ferric chloride. It was partially soluble in cold aqueous sodium hydroxide solution with a yellow color.

When the photo-product (0.8 g.) was heated at 260° (bath-temp.), under reduced pressure (oil-pump) for 15 minutes, a sublimate was obtained which upon crystallization from ethanol proved to be (VII, R = $C_6H_4OCH_3$-p) (m.p. and mixed m.p.).

Action of Sulfuric Acid on II (Ar = $C_6H_4OCH_3$-p).—Compound II (Ar = $C_6H_4OCH_3$-p) (0.8 g.) was dissolved in 5 ml. of concentrated sulfuric acid, and the reaction mixture was allowed to stand at room temperature overnight. It was then poured into cold water and neutralized with sodium carbonate. The yellow substance that separated was crystallized from benzene and identified as I (m.p. and mixed m.p. and the formation of the corresponding phenazine derivative). Acidification of the alkaline solution, gave p-methoxybenzoic acid.

Thermal Decomposition of XIa.—One gram of XIa was heated at 265–270° (bath-temp.) for 1.5 hours under reduced pressure. The colorless sublimate on the cooled parts of the reaction vessel was collected and crystallized from ethanol (*ca.* 0.23 g.) and was identified as stilbene (m.p. and mixed m.p.). The contents of the reaction vessel were recrystallized from benzene (0.34 g.) and identified as I (m.p. and mixed m.p.).

Action of Aromatic Aldehydes on IV in the Dark. General Procedure.—A mixture of 0.01 mole of IV, 0.03 mole of the appropriate aldehyde and few drops of piperidine in 50 ml. of absolute ethanol was refluxed (steam-bath) for two hours. The product which separated on cooling was recrystallized from ethanol into colorless crystals (VII) (*cf.* Table IV). The resulting oxazoles are insoluble in aqueous sodium hydroxide solution and their alcoholic solutions give no color when treated with ferric chloride.

Giza, Egypt, U.A.R.

Substituent Effects on Naphthalene. II. Association Constants of Substituted Naphthalene–Picric Acid Complexes Determined Spectrophotometrically

By Pete D. Gardner, Richard L. Brandon,[1] N. Jane Nix and Ike Y. Chang

Association constants of twenty-two substituted naphthalenes have been measured using a spectrophotometric method. The values obtained are compared with values previously obtained using the partition method. A dependence of the value of the association constant on the wave length of measurement is noted and interpreted on the basis of "contact" charge-transfer or "solvent perturbation."

The formation of molecular complexes between polynitroaromatic hydrocarbons and aromatic compounds has been investigated quantitatively by the partition method[2] and by an adaptation of the spectrophotometric method described by Benesi and Hildebrand.[3] It has been frequently noted that the partition method, in which the partition coefficient of the polynitro compound between water and a non-polar solvent is measured with and without the donor in the non-polar phase, gives a higher value for the association constant than does the spectrophotometric method. Ross and Kuntz[4] have suggested that the partition method measures a number of interactions such as dipole–dipole interactions and intermolecular hydrogen

bonding while the spectrophotometric method measures only complexation due to charge-transfer bonding. In the theory of molecular-compound formation proposed by Mulliken,[5] the charge-transfer state, in which the aromatic donor compound has donated an electron to the polynitro acceptor compound, is responsible for the characteristic absorption of the complex.

A recent measurement of the association constant of naphthalene picrate in chloroform solution by Foster[6] has resulted in a value of $K = 2.4$ which is very near the value found using the partition method.[7] The difference from the value previously reported by Ross and Kuntz,[4] $K = 0.99$, was attributed to the large excess of donor compound. To minimize any effect due to excess

(1) Monsanto Chemical Co. Fellow, 1957–1958.

(2) T. S. Moore, F. Shephard and E. Goodall, *J. Chem. Soc.*, 1447 (1931).

(3) H. Benesi and J. H. Hildebrand, This Journal, **71**, 2763 (1949).

(4) S. D. Ross and I. Kuntz, *ibid.*, **76**, 74 (1954).

(5) R. S. Mulliken, *ibid.*, **74**, 811 (1952).

(6) R. Foster, *J. Chem. Soc.*, 5098 (1957).

(7) H. D. Anderson and D. L. Hammick, *ibid.*, 1089 (1950).

naphthalene, Foster used a 1:1 ratio of naphthalene to picric acid.

In the discussion, spectrophotometrically determined association constants of a number of substituted naphthalenes are compared with values previously obtained using the partition method.[8] It is noted with some of these that a dependence of the constant on wave length is found even with a 1:1 ratio of donor to acceptor. This dependence is particularly noticeable in the region of the overlap of picric acid and complex absorption.

Experimental

Spectrophotometric Method.—The procedure used is essentially the same as that described.[9] The spectrophotometric measurements were obtained using a Beckman model DU spectrophotometer equipped with Beckman "thermospacers" through which mineral oil was circulated to maintain a constant temperature of $28.50 \pm 0.05°$. The optical density of the complex was measured at from four to six concentrations of the complex and the association constant, equation 1, calculated using equation 2, a modified form of the Benesi and Hildebrand relation.[3]

$$K = [DA]/[D][A] \qquad (1)$$

$$\frac{A}{d} = \frac{1}{K\epsilon} B + \frac{1}{\epsilon} \qquad (2)$$

$$A = B[D]_0[A]_0, \quad B = \frac{1}{[D]_0 + [A]_0}$$

In equation 1, [D] and [A] represent the concentration of free donor and acceptor, respectively, and [DA] represents the concentration of the complex. In equation 2, $[D]_0$ and $[A]_0$ represent the initial concentration of donor and acceptor, K and ϵ are the association constant and extinction coefficient of the complex and d is the optical density of the complex. The association constants were calculated using the least squares method to determine the slope and intercept of the straight line represented by equation 2.

Except where otherwise noted, the association constants represent an average of values determined at a number of different wave lengths and were measured above 480 mμ, to avoid overlap with the absorption of picric acid. Below 480 mμ, a correction for the absorption due to picric acid was made from a plot of optical density *versus* wave length.

Reagents.—The solvent used in all cases was Baker Chemical Co. "reagent grade" chloroform containing 0.60% alcohol. All donor compounds were purchased or prepared using standard literature procedures. Solids were purified by recrystallization to constant m.p. and liquids fractionally distilled or purified by formation of the picric acid complex and recrystallization followed by decomposition of the complex and distillation. No significant discrepancies with literature values for the physical constants were found.

Results and Discussion

The values of association constants of various substituted naphthalenes with picric acid in chloroform obtained spectrophotometrically are compared with the values obtained using the partition method[8] in Table I. The data are graphically represented in Fig. 1. As was expected, the partition method gave in all cases a higher value for the association constant. However, the relative order of stability, as determined by the partition method, was maintained. Thus, the increase in stability of the complex in the order: 2-halo < 1-halo < 1-alkyl < 2-alkyl < 2-alkoxy < 1-alkoxy indicates that the same arguments used in explaining the results of the partition method may be invoked to explain the present results. The relative

(8) P. D. Gardner and W. E. Stump, This Journal, **79**, 2759 (1957).

(9) S. D. Ross, M. Bassin, M. Finkelstein and W. A. Leach, *ibid.*, **76**, 69 (1954); see also J. Landauer and H. McConnell, *ibid.*, **74**, 1221 (1952).

order of the association constants within the individual groups was the same except for the halogenonaphthalenes and 2-alkoxynaphthalenes.

Table I

Association Constants for the Interaction of Substituted Naphthalenes with Picric Acid in Chloroform Solution (28.5°)

Donor	Source[b]	K, l.-mole^{-1} (spectrophotometric)	K_s, l.-mole^{-1} (partition)[8]
Naphthalene	P	1.13 ± 0.11	2.31
1-Methyl-	P	$1.47 \pm .04$	3.16
1-Ethyl-	L	$1.41 \pm .06$	2.61
1-Isopropyl-	L	$0.97 \pm .05$	1.87
2-Methyl-	P	$1.76 \pm .01$	3.50
2-Ethyl-	L	$1.45 \pm .06$	2.77
2-Isopropyl-	L	$1.35 \pm .08$	2.51
2-t-Butyl-	L	$1.16 \pm .20$	
1-Fluoro-	P	$0.55 \pm .02$	1.49
1-Chloro-	P	$.43 \pm .02$	1.87
1-Bromo-	P	$.51 \pm .05$	2.06
2-Fluoro-	P	$.33 \pm .01$	1.28
2-Chloro-	L	$.34 \pm .01$	1.50
2-Bromo-	P	$.43 \pm .03$	1.57
1-Methoxy-	P	$2.78 \pm .23$	4.89
1-Ethoxy-	P	$3.76 \pm .32$	5.78
1-Isopropoxy-	L	$2.87 \pm .01$	4.81
2-Methoxy-	P	$1.48 \pm .09$	3.30
2-Ethoxy-	P	$2.11 \pm .21$	3.01
2-Isopropoxy-	L	$1.66 \pm .23^a$	3.09
1-Vinyl-	L	$2.13 \pm .10^a$	
2-Vinyl-	L	$1.79 \pm .12^a$	

^{a} The picrate was used in the measurement of the association constants. In all other cases, a large excess of the donor compound was present. ^{b} P, purchased. L, prepared as described in the literature.

Halogenonaphthalenes.—As is expected these compounds have the lowest association constants of any of the groups measured. This behavior is consistant with the electron-withdrawing nature of the substituent. However, the regular increase of the association constant with decrease in the electronegativity of the substituent as found by the partition method is not evident. The association constants for the iodonaphthalenes are lower than any of the other halogen derivatives. However, the variation in the association constant with change in wave length is so marked that an average value becomes meaningless.

Alkylnaphthalenes.—As with the values determined by the partition method, the order of the association constants seems to be dictated mainly by steric effects. This is evident in the order: methyl > ethyl > isopropyl > t-butyl as well as in the fact that the 1-substituted naphthalenes have lower association constants than the 2-substituted compounds. This order agrees very satisfactorily with the results found by the partition method.

Alkoxynaphthalenes.—The order of association constants for the 1-substituted series parallels the order obtained by the partition method, but no such parallel is found for the 2-substituted naphthalenes. The order in which the ethoxy substituted compounds have the highest association constants is not easily explained without invoking

a complicated interaction of steric and resonance effects.

Vinylnaphthalenes.—In the case, no comparison with results of the partition method may be made. However, the high value of the association constant is consistant with the electron-donating effect of the vinyl group.[10] The association constants were determined using the picric acid complexes since both 1-vinyl- and 2-vinylnaphthalene polymerize upon standing.

Variation with Wave Length.—An examination of the data summarized in Table I indicates a dependence of the association on the wave length of measurement. Since the wave length range covered was only 30 to 40 mμ, two compounds were chosen for more detailed study. The results are summarized in Table II. In the region above 480 mμ, only 1-isopropyl-, 2-isopropyl-, 2-t-butyl-, 1-ethoxy-, 2-isopropoxy-, 1-iodo- and 2-iodonaphthalene showed this wave length dependence. The association constant increased with increasing wave length at the rate of 0.01 to 0.02 K per mμ. It is evident that those compounds showing a wave length dependence contain substituents having a large steric requirement. In this connection, it should be noted that in neither this study nor in the previous work of Ross and Kuntz[4] was naphthalene picrate found to exhibit such a wave length dependence above 480 mμ.

Fig. 1.

TABLE II

VARIATION OF THE ASSOCIATION CONSTANT WITH
WAVE LENGTH AND CONCENTRATION FOR THE INTERACTION
OF PICRIC ACID WITH NAPHTHALENE AND
2-t-BUTYLNAPHTHALENE IN CHLOROFORM

Wave length, mμ	Association constant, l.-mole^{-1}			
	Naphthalene^a	Naphthalene^b	2-t-Butyl-naphthalene^a	2-t-Butyl-naphthalene^b
530			1.6	
520			1.5	1.3
510			1.5	1.2
500			1.4	1.2
490				1.0
480			1.4	0.9
470	1.5		1.5	
460	1.5		2.0	
450	2.4		2.8	
440	3.4			
430	3.4	1.5		
420		1.6		
410		1.3		
400		1.2		
390		1.3		
385		2.2		

^{a} Solutions were prepared using the picric acid complex of the donor. ^{b} Solutions were prepared using an excess of the donor.

Ross and Labes,[11] in their study of the s-trinitrobenzene–naphthalene complex did not find a variation of association constant with either change in wave length or change in the ratio of donor to acceptor concentrations. The t-butylnaphthalene picrate association constant, however, was found

(10) F. G. Bordwell and K. Rohde, THIS JOURNAL, **70**, 1191 (1948).

(11) S. D. Ross and M. M. Labes, *ibid.*, **79**, 76 (1957); it should be noted that these authors found a dependence of K upon λ for the TNB-N.N-dimethylaniline complex.
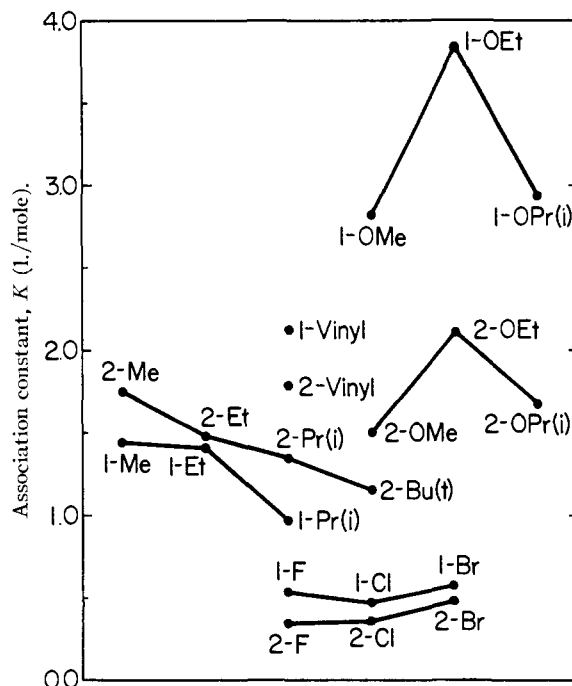
to be wave length dependent over the entire region studied. Moreover, the data of Foster[6] for the association constant of the naphthalene–picric acid complex indicate a similar variation in the region below 480 mμ. In view of this variability, one must not conclude that the partition method and the spectrophotometric method will give comparable results.

A solution comprised of equimolar concentrations of naphthalene and picric acid shows a rather well-defined absorption maximum (due to complex) at 388 mμ. A similar solution but with a tenfold increase in naphthalene concentration gives a spectrum with the same maximum but it is broad and indistinct. If picric acid is in excess, the absorption maximum is again sharp but shifted toward the visible, λ_{max} 395 mμ. This change in maximum with change in the relative concentration of naphthalene suggests that more than one complex type may be present. However, if the Benesi and Hildebrand relation is applicable, one necessity being that only 1:1 complexes are present, then the measured association constant should be the sum of the association constants of the various complex types and should be independent of wave length.[12] Thus this new absorption must be attributed to complex types other than 1:1. A 2:1 or 1:2 complex must also be rejected since absorption due to such species would be repressed in a solution of equimolar concentrations of donor and acceptor. This is, in fact, the only criterion for the existence of this type of complexation in the spectrophotometric method.

The possibility of interference by absorption due to interactions other than charge-transfer interaction has been considered by Orgel and Mulliken[12] and by Bayliss.[13] The wave length dependence

(12) L. E. Orgel and R. S. Mulliken, *ibid.*, **79**, 4839 (1957).

(13) N. S. Bayliss and C. J. Brackenridge, *ibid.*, **77**, 3957 (1955).

shown in Table II is best interpreted by what Mulliken describes as "contact" charge-transfer interactions; interactions in which van der Waal forces are not contributing to bonding. The effect of absorption due to "contact" charge-transfer interference is to give a low value for the association constant while giving too high a value for the extinction coefficient. The same may be said for the effect of what Bayliss calls "solvent perturbation." If similar wave length regions are compared, it is found that, within a given series, the extinction coefficients of compounds exhibiting a dependence of association constant on wave length have the higher extinction coefficients.

It might be expected that sterically hindered donor molecules for which association constants are low should be especially susceptible to "contact" interactions. It is seen from the data in Table II that 2-*t*-butylnaphthalene exhibits this behavior. While the primary charge-transfer process necessitates a close proximity of donor and acceptor, the "contact" process should require neither a tight nor inflexible geometry. This perhaps also explains why comparable substituent effects were not observed in the spectrophotometric and partition methods for the halogenonaphthalenes. Thus, while the results of the spectrophotometric method parallel those obtained by the partition method for the stronger complexes, values for the less tightly bound halogen compounds cannot be considered a reliable indication of the extent of complexation but only of relative order of complex strength. The two iodonaphthalenes showed such a dependence of K on λ that their values were deemed unworthy of reporting.

It appears inevitable that association "constants" measured spectrophotometrically will be lower than the true association constants as a result of interactions of the type described above. Indeed, these values are association constants only to the extent that donor and acceptor species are bound by the charge-transfer energy and might best be labeled K_{c-t} if they must be expressed as association constants at all. While this method gives what is probably the lowest possible value for an association constant, the partition method must give the largest value. The latter, which sums *all* forces tending to unite donor and acceptor molecules, is technically a more accurate representation of association as the constant is mathematically defined. By the choice of method, then, one either measures association constants or studies charge-transfer spectroscopy (including environmental effects); the choice is that simple.

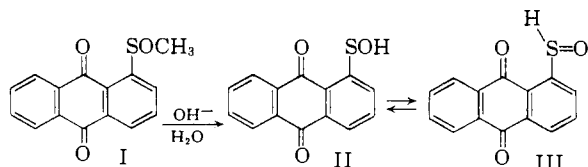# The Structure of Anthraquinone-1-sulfenic Acid (Fries' Acid) and Related Compounds

BY THOMAS C. BRUICE[1] AND ANNE B. SAYIGH

Quantitative infrared spectra for the carbonyl bands of methyl anthraquinone-1-sulfenate, dimethyl anthraquinone-1,4-disulfenate and methyl fluorenone-1-sulfenate are reported and compared to those for anthrone, anthraquinone, fluorenone and the 1-hydroxy- and 1,4-dihydroxyanthraquinones. The conclusion is reached that the –SOCH$_3$ group causes splitting of the quinone absorption, because of dissymmetry, just as does the 1-hydroxy, 1- and 2-amino and the 1-dimethyl amino groups. The various postulated structures for Fries' acid (anthraquinone-1-sulfenic acid) as well as its derivatives are discussed and evaluated in view of the spectroscopic evidence. It is concluded that the original structure of Fries is correct.

When methyl anthraquinone-1-sulfenate (I) is hydrolyzed under prescribed conditions, a bright red, crystalline compound forms. On the basis of the empirical formula, means of preparation, acid nature and reformation of I on treatment with methanol, Fries[2] assigned structure II to this substance noting also that the product behaved in some of its reactions as though II were in equilibrium with III. In the forty-five years since the investigations of Fries all other attempts to prepare sulfenic acids failed, although hundreds of references to sulfenic acids as postulated transitory intermediates appeared in the literature.[3]

The peculiar stability of Fries' acid was reconsidered by Kharasch,[3] who postulated a possible stabilization of the sulfenic acid group *via* hydrogen bonding, as in IV. Structure IV was proposed to account for the known instability of 2-anthraquinonesulfenic acid (V), as well as the inability

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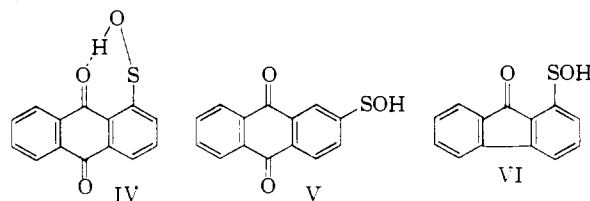
(3) N. Kharasch, S. J. Potempa and H. L. Wehrmeister, *Chem. Revs.*, **39**, 276 (1946).