It can readily be shown that the excess atom fraction of oxygen-18 of a single position to which all enrichment is attributed, y, can be related to the observed mass spectrometer ratios by the following equation:

$$y = (n + 1)\left[\frac{c_2}{2 + c_2} - \frac{c_1}{2 + c_1}\right]$$

where c_1 = $CO^{16}O^{18}/CO^{16}O^{16}$ ratio in tank carbon dioxide as measured on the mass spectrometer

c_2 = $CO^{16}O^{18}/CO^{16}O^{16}$ ratio in enriched carbon dioxide as measured on the mass spectrometer

and n = the number of atoms of oxygen of normal isotopic composition which are added to the single enriched atom during analysis.

Using this equation and the values of n, c_1, and c_2 determined experimentally, the results given in Table I were calculated.

FAYETTEVILLE, ARK.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF OREGON]

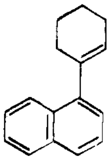
Coplanarity and Chromatographic Adsorbability of Some Isomeric Naphthylcycloalkenes and Polycyclic Aromatic Hydrocarbons[1,2]

L. H. KLEMM, DAVID REED,[3] AND C. D. LIND[4]

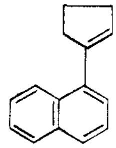
Received January 21, 1957

Binary mixtures (dissolved in isooctane) of (a) isomeric α- and β-substituted naphthalenes bearing phenyl, cyclohexenyl (I and IV), and cyclopentenyl (II and III) groups; (b) II and IV, and; (c) anthracene and phenanthrene, were investigated by down-flow frontal analysis for relative chromatographic adsorbability on silicic acid impregnated with picric acid or 2,4,7-trinitrofluorenone. In cases (a) and (b) the more nearly coplanar β-substituted naphthalene was adsorbed more tenaciously while in (c) little difference in adsorbability was evident. Results were consistent with data for displacement analysis of binary mixtures from alumina. The characteristics of impregnated silicic acid as an adsorbent are described. In particular it is proposed that adsorption of the substrate occurs principally *via* a steady-state process in which the impregnant molecules serve as "active sites" for molecular compound formation on the surface of the ground mass, silicic acid.

A survey of published observations reveals that coplanarity factors may play an important part in chromatographic adsorbabilities of conjugated isomeric biaryls and arylalkenes on alumina. Thus Orchin and Reggel[5] found that 2,2′-binaphthyl (effectively coplanar) was held more tenaciously than the more twisted 1,2′-binaphthyl. For mixtures of the geometric isomers of stilbene, 4,4′-dimethylstilbene, and 4,4′-dimethoxystilbene the coplanar *trans* form was adsorbed more strongly in every case.[6] A mixture of the three possible 1,4-diphenylbutadienes, moreover, showed the order of adsorbability *trans-trans* (coplanar) > *trans-cis* > *cis-cis* (noncoplanar).[7] Also indicative of such an effect are the findings of Orchin and coworkers[5,8] that adsorbabilities of certain conjugated iso-π-electronic (though not isomeric) aromatic hydrocarbons fall in the orders: fluoranthene > mixed 1- and 2-phenylnaphthalenes > 1-phenylnaphthalene; benzofluoranthene > 1,2′-binaphthyl;[9] and perylene > 1,1′-binaphthyl.[10] The authors report herewith semiquantitative studies on the relative adsorbabilities of various other such pairs of hydrocarbons (usually isomeric substituted naphthalenes) on alumina, silicic acid impregnated with picric acid (TNP) or 2,4,7-trinitrofluorenone (TNF),[11] and silicic acid alone.



I



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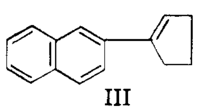
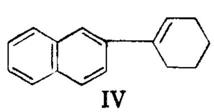


III



IV

In studies with alumina, limited approximately equimolar amounts of the isomeric pairs I plus IV

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[1] Supported (in part) by the Petroleum Research Fund of the AMERICAN CHEMICAL SOCIETY and (in part) through sponsorship by the Office of Ordnance Research, U. S. Army, contract number DA-04-200-ORD-176.

[2] Part of this material was presented at the Symposium on Polycyclic Hydrocarbons at the Atlantic City Meeting of the AMERICAN CHEMICAL SOCIETY, September, 1956. Part IX in the series on Chemical Reactivities of Arylcycloalkenes. For paper VIII see L. H. Klemm, J. W. Sprague, and E. Y. K. Mak, *J. Org. Chem.*, 22, 161 (1957).

[3] Research assistant, 1955–56.

[4] Research associate, 1956.

[5] M. Orchin and L. Reggel, *J. Am. Chem. Soc.*, **69**, 505 (1947).

[6] L. Zechmeister and W. H. McNeely, *J. Am. Chem. Soc.*, **64**, 1919 (1942).

[7] Alumina containing 25% of celite was used; J. H. Pinckard, B. Wille, and L. Zechmeister, *J. Am. Chem. Soc.*, **70**, 1938 (1948).

[8] M. Orchin and R. A. Friedel, *J. Am. Chem. Soc.*, **68**, 573 (1946).

[9] *Cf.* M. Orchin and L. Reggel, *J. Am. Chem. Soc.*, **73**, 436 (1951).

[10] In the last of these cases the alumina was diluted with the apparently relatively inactive Super-Cel.

[11] The use of silica gel impregnated with a polynitroaromatic complexing agent for gross separation of hydrocarbon mixtures into aromatic, hydroaromatic and alkenic, and saturated hydrocarbons was reported by M. Goldewicz, *Nature*, **164**, 1132 (1949).

and 1-phenylnaphthalene (V) plus 2-phenylnaphthalene (VI) were first adsorbed on the column and then eluted with an appropriate solvent (isooctane in the former case, 2 volume % acetone in isooctane in the latter). Spectral investigation of the effluent showed that in both cases the column was virtually, if not completely, depleted of 1-isomer before the 2-isomer began to appear.

For adsorption on impregnated silicic acid a down-flow frontal analysis method was used wherein standard isooctane influent solution approximately equimolar in each of the two components to be compared was allowed to percolate continuously through the column under gravity. Combinations of substituted naphthalenes used as solutes (α and β, respectively) were the isomeric pairs I and IV, II and III, and V and VI (adsorbed on columns of both TNF- and TNP-impregnated silicic acid) as well as the nonisomeric pair II and IV (adsorbed on the former column only). Through periodic ultraviolet spectrophotometric analysis of the effluent values were obtained for the retention ratio, Q (ratio of moles of β-compound retained on the column to moles of α-compound retained), as a function of cumulated volume of influent. Though not all experiments were pursued to the same relative degree of completeness, the typical resultant curve (Fig. 1) had a sigmoid shape and incorporated the features of (a) an initial horizontal portion (all α and β retained on column) where the retention ratio equals the ratio of concentrations of β to α in the standard influent; (b) a region of continuous and relatively rapid rise due to greater adsorbability of β than of α; and (c) a region wherein the curve levels off rapidly and attains a constant maximum value (corresponding to a steady state in the system). However, inasmuch as the present exploratory research was designed only for qualitative checking of the relationship between coplanarity and adsorbability, we record herewith (Table I) simply the maximum retention ratio ($Q_{\max}$) observed in each case, irrespective of whether a steady state was attained or not.

Examination of Fig. 1 and Table I shows that in every instance the β-substituted naphthalene is adsorbed more strongly than the corresponding α-derivative, in accordance with the inherent smaller angle of twist and the decreased restriction to attainment of coplanarity in the former. This occurs even for the pair II and IV, where the difference in conjugative effect[12] of the cyclopentenyl and cyclohexenyl groups is still insufficient to offset the factor of twist.[13] However, in view of the suggestion[14] that the strength of adsorption should increase with increasing melting point it seems pertinent to inquire if the relationship found here might not fundamentally be associated with relative melting points rather than with relative angles of twist. In this regard there are recorded in Table I melting points of the hydrocarbons themselves as well as of their corresponding TNP and TNF molecular compounds. Included are also data on the phenanthrene-anthracene pair, selected for study because the components are both iso-π-electronic and planar and because their analogous TNP and TNF molecular compounds have essentially identical melting points. Examination of Table I shows that no consistent correlation of melting point and adsorbability prevails. Thus the orders of adsorbability IV > I on TNP-impregnated silicic acid, IV > II on TNF-impregnated silicic acid, and anthracene $\cong$ phenanthrene on plain silicic acid are inconsistent with the respective orders of melting points I.TNP > IV.TNP, IV.TNF $\cong$ II.TNF, and anthracene >> phenanthrene.

For the substrate mixtures I–IV and anthracene-phenanthrene experiments were conducted, under otherwise identical conditions, with adsorbents of both plain and impregnated silicic acids. Comparison of the results showed that (1) the presence of the complexing agent on the column serves to increase the total quantity of hydrocarbon adsorbed and (2) the molar ratio of hydrocarbon adsorbed to complexing agent present on the column is considerably less than 1 in all cases, but is closer to 1 for TNF as an impregnant than for TNP as an impregnant. Observation (2) is consistent with the generalization that TNF displays greater potency as a complexing agent than does TNP.

Pending further investigation, the authors tentatively propose the following as characteristics of these impregnated silicic acid columns: (a) The polynitro complexing agent, A, is adsorbed flatwise and monomolecularly at selected spots on the surface of the silicic acid ground mass. (b) Each such molecule of A constitutes an "active site" (designated as P) upon which only one molecule (in the usual case) of hydrocarbon substrate, B, may be adsorbed. (c) Adsorption of B on A is identifiable with molecular compound formation, of a type essentially like that which occurs in solution rather than like that which occurs in a crystalline solid.

It follows from characteristic (b) that the number of active sites of type P can be varied at will and in a quantitatively calculable fashion by varying the amount of complexing agent used for impregnation. Unfortunately silicic acid may fall short of ideality

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[12] L. H. Klemm, W. Hodes, and W. B. Schaap, *J. Org. Chem.*, **19**, 451 (1954).

[13] The close similarity of the ultraviolet spectra of the various 1-substituted napthhalenes used here (*cf.* ref. 36) precludes studies on mixtures such as I and II by our analytical procedure. Though the ultraviolet spectra of III and IV differ to a larger extent analysis of such a mixture by this method would still present difficulties.

[14] A discussion of this will be found in H. G. Cassidy, *Adsorption and Chromatography*, Interscience Publishers, Inc., New York, N. Y., 1951, pp. 128–9. It seems to us, however, that the example of the diphenylpolyenes cited there is a poor choice since the adsorbabilities also fall in the order expected on the basis of relative extents of the conjugated systems present.

TABLE I

Relative Chromatographic Adsorbabilities on Plain and Impregnated Silicic Acid Columns

	Binary Substrate Mixture[a]									
	α-Component				β-Component					
Impregnant, A on Silicic Acid	Compound B_1	M. p. of B_1 °C.	M. p. of $A \cdot B_1$ °C.	Conc. in influent[b]	Compound B_2	M. p. of B_2 °C.	M. p. of $A \cdot B_2$ °C.	Conc. in influent[b]	Molar ratio influent (β/α)	Retention Ratio, Q_{max}[c] (β/α)
None	I	48	...	10.0	IV	61	...	10.0	1.00	1.21[d]
	Phenanthrene	98	...	10.0	Anthracene	215	...	10.0	1.00	1.02[d]
4.4% TNP	I	48	127[e]	5.64	IV	61	82[e]	5.53	0.98	1.62[d]
	II	<25[f]	76[e]	4.61	III	86	104[e]	4.59	1.00	2.1[g]
	V	<25[h]	...[i]	6.36	VI	103	...[j]	6.41	1.00	>1.03[k]
	Phenanthrene	98	133[l]	10.0	Anthracene	215	138[l]	10.0	1.00	0.92[d]
0.66% TNF	I	48	...[m]	3.37	IV	61	129[m]	4.86	1.44	4.0[g]
4.0% TNF	II	<25[f]	125[m]	4.61	III	86	149[m]	4.59	1.00	2.7[n]
	II	<25[f]	125[m]	9.21	IV	61	129[m]	7.38	0.80	1.8[n]
0.66% TNF	V	<25[h]	...[i]	6.01	VI	103	171[o]	5.72	0.95	2.2[g]
4.0% TNF	Phenanthrene	98	197[o]	10.0	Anthracene	215	194[o]	10.0	1.00	1.05[d]

[a] Dissolved in spectral grade isooctane. [b] In units of $10^{-4}M$. [c] Uncorrected for effect of layers of plain silicic acid in the cases of the impregnated columns. [d] Column apparently in a steady-state condition. [e] See ref. 17. [f] B.p. 121–122.5°/0.4 mm. [g] System not yet in a steady state. [h] B.p. 121–126°/0.5 mm. [i] It has been reported[5] that V fails to form a crystalline complex with either TNP or TNF. [j] M. Orchin and R. A. Friedel [*J. Am. Chem. Soc.*, **71**, 3002 (1949)] reported that the picrate of VI "is so unstable as to elude isolation." *Cf.* R. A. Friedel, M. Orchin, and L. Reggel, *J. Am. Chem. Soc.*, **70**, 199 (1948). [k] Quantitative measurements were conducted only so far as to be sure V was appearing in the filtrate considerably earlier than VI could be detected therein. From semiquantitative data, however, one can estimate a Q_{max} of 1.3 for steady state. [l] O. L. Baril and E. S. Hauber, *J. Am. Chem. Soc.*, **53**, 1087 (1931). [m] No crystalline TNF compound forms for I. See L. H. Klemm and J. W. Sprague, *J. Org. Chem.*, **19**, 1464 (1954). [n] Essentially in a steady-state condition. Value given is an average taken over fluctuations in the upper asymptotic part of the curve. [o] M. Orchin and E. O. Woolfolk, *J. Am. Chem. Soc.*, **68**, 1727 (1946).

as a ground mass since it exhibits active sites (designated as G) for adsorption of B[15] in the absence of any molecules of A. Lending credence to the identity of molecular compound formation and adsorption (characteristic c) is the fact that in three cases a colored zone formed at the top of the impregnated adsorbent and gradually expanded downward as the experiment continued. From (c) it appears that one might be able to obtain relative steady-state constants for molecular compound formation on impregnated silicic acid which should be directly comparable to the corresponding relative equilibrium constants for the same reactions occurring in solution.

Efforts are underway in our laboratory to investigate further the characteristics of chromatographic columns impregnated with polynitroaromatic complexing agents and to develop, if possible, quantitative relationships thereon.

EXPERIMENTAL

Materials used. Alcoa grade F-20 alumina and Mallinckrodt reagent grade 100-mesh silicic acid were used as obtained. All solvents for recrystallization and chromatography were reagent or spectral grade. TNP (practical grade) was purified by recrystallization once from ethanol, air-drying, and then recrystallization from benzene–petroleum ether (30–60°), m.p. 120–121°. TNF (Dajac Laboratories[16]) was freed of a more strongly adsorbed brown impurity by elution chromatography using chloroform and silicic acid and was then recrystallized from chloroform, m.p. 172–173°. Naphthylcycloalkenes I–IV were prepared and purified as previously described.[17] 1-Phenylnaphthalene[18] was refluxed 4 hr. with Raney nickel[19] in ethanol, distilled *in vacuo*, heated with 30% palladium-on-charcoal for 4 hr. at 350°,[5] and redistilled, b.p. 121–126°/0.5 mm., $n_D^{25.5}$ 1.6637, log ε = 4.74 at 225 mμ in isooctane solution; reported[5] n_D^{20} 1.6646, log ε = 4.78 at 225 mμ in cyclohexane solution. 2-Phenylnaphthalene was prepared by dehydrogenation of IV (7 g.) by heating at 300–350° with 30% palladium-on-charcoal (0.4 g.) for 2.5 hr., extraction into benzene, and recrystallization from absolute ethanol to constant m.p., 101–102.5°, yield 80–90%.[20] C.p. anthracene was purified further by the method described by Fieser,[21] m.p. 214–215°. Technical grade phenanthrene was treated as described by Phillips[22] and then chromatographed as for anthracene, m.p. 97–98°.

Impregnation of silicic acid. Method A. Through a wet (with chloroform) column of 100 g. of silicic acid was percolated approximately 2. l. of 0.01*M* solution of TNP or TNF in chloroform (sufficient to ensure saturation of the column). The column was allowed to drain for 12 hr. and then the upper and lower sections were dug out and discarded. The central portion (50–60% of total length) was dried in air for a day and then at 100° for 2–3 hr., pulverized with a mortar and pestle, and stored in a brown bottle. Microanalysis for

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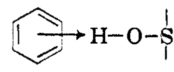
(15) It has been proposed that adsorption of aromatic hydrocarbons on silica gel may involve a π-complex of the type  $\rightarrow \mathrm{H{-}O{-}Si{-}}$; see A. V. Kiselev, *Doklady Akad. Nauk S. S. S. R.*, 106, 1046 (1956).

(16) To which we are indebted for a gift of this chemical.

(17) L. H. Klemm and W. Hodes, *J. Am. Chem. Soc.*, **73**, 5181 (1951).

(18) R. Weiss, *Org. Syntheses*, **Coll. Vol. III**, 729 (1955).

(19) R. Mozingo, *Org. Syntheses*, **Coll. Vol. III**, 181 (1955); A. A. Pavlic and H. Adkins, *J. Am. Chem. Soc.*, **68**, 1471 (1946).

(20) We are indebted to Dr. Herman Ziffer for this preparation.

(21) L. F. Fieser, *Experiments in Organic Chemistry*, 2nd ed., D. C. Heath and Co., New York, N. Y., 1941, p. 344.

(22) D. D. Phillips, *Org. Syntheses*, **34**, 31 (1954).

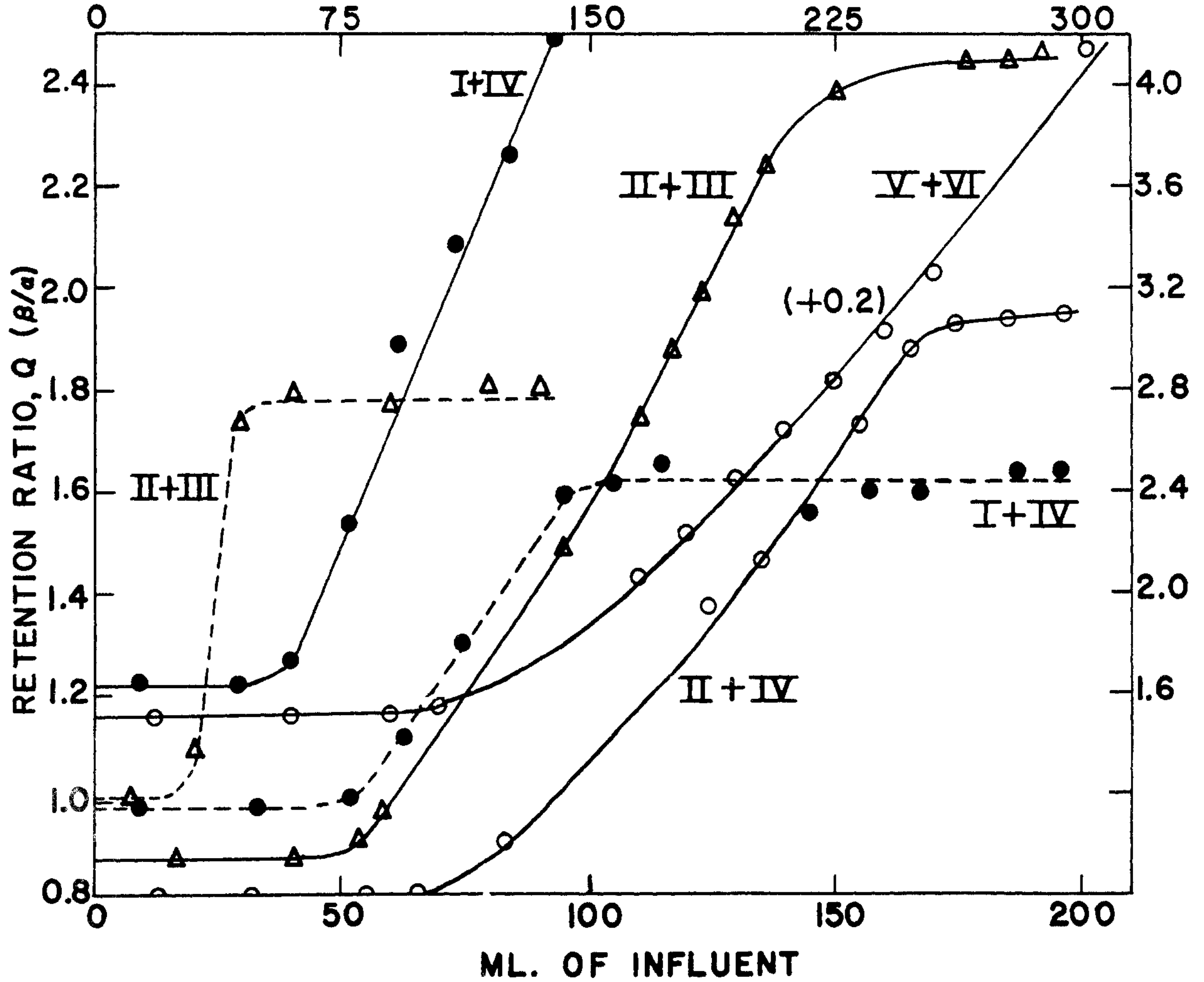


FIG. 1. RELATIVE CHROMATOGRAPHIC ADSORBABILITIES OF PAIRS OF α- AND β-MONOSUBSTITUTED NAPHTHALENES. Q is given in terms of total cumulated moles of β-compound adsorbed on the column to total cumulated moles of α-compound so adsorbed. Solid lines represent data for TNF-impregnated silicic acid as the adsorbent; broken lines, for TNP-impregnated silicic acid. The upper scale refers only to the run for II + III on TNF-silicic acid. The right hand scale refers only to the run for I + IV on TNF-silicic acid

carbon[23] indicated that the samples contained 4.4% (by weight) of TNP (1.9×10^{-4} moles of TNP per g.) and 4.0% of TNF (1.3×10^{-4} moles of TNF per g.), respectively.

Method B. This differed from method A only in that the TNF solution (TNP not used here) was *ca.* 0.085M and the impregnated silicic acid was dried only in air (but for several days) and then diluted by admixture with ten times its weight of plain silicic acid; found by analysis[23] to contain 0.66% (by weight) TNF (1.9×10^{-5} moles of TNF per g.).

Chromatography on impregnated silicic acid. Using the suction of a water aspirator a 2.5-cm. (diameter) column was packed dry with successive layers of 1 g. of plain silicic acid (to prevent possible elution of complexing agent), 4 g. of impregnated silicic acid, 0.5 g. of plain silicic acid, and a small wad of glass wool. The apparatus was all glass with nonlubricated ground joints[24] whereby were attached a receiver for effluent and a reservoir for influent. The column was prewashed with isooctane (50–300 ml.) until the effluent was spectrophotometrically clear. The experiment proper was conducted by continuous percolation under gravity of a standard isooctane solution, 4×10^{-4} to $1 \times 10^{-3}M$ in each of two hydrocarbon substrates, through the column and periodic spectrophotometric analysis (Beckman DU instrument) of cumulated samples (usually 10 ml. in size) of effluent at 2 to 4 selected wave lengths (I–IV, 224, 246, 282 $m\mu$; II–III, 225, 249; II–IV, 225, 246; V–VI, 225, 250, 280; phenanthrene-anthracene, 274, 292, 356, 375).[25] Spontaneous evaporation of solutions during chromatography was kept as low as reasonably possible but could not be entirely eliminated. The measured cumulated volume of effluent was assumed equal to the cumulated volume of influent. About 9 ml. of solution was required to fill the interstices of the column. No control of temperature (room) or rate of flow (average 3.3–7.5 ml./hr.) was attempted.

The total quantity of each substrate retained on the column was calculated by difference and used to ascertain the retention ratio Q as a function of the total cumulated volume of solution passed. Pertinent data in this regard are recorded in Table I and plotted in Fig. 1. The column gradually became orange-red in color for the systems anthracene-phenanthrene-TNP (light color), anthracene-phenanthrene-TNF (very dark), and II-III-TNF (dark). In a few cases plots of concentration of one substrate *vs.* cumulated

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(23) Conducted by Clark Microanalytical Laboratories, Urbana, Ill.

(24) Efforts to use rubber or neoprene stoppers or variously lubricated glass joints always produced extraneous chromophoric impurities in the effluent.

(25) L. H. Klemm, H. Ziffer, J. W. Sprague, and W. Hodes, *J. Org. Chem.*, 20, 190 (1955); R. A. Friedel and M. Orchin, *Ultraviolet Spectra of Aromatic Compounds*, John Wiley and Sons, Inc., New York, N. Y., 1951.

total volume of effluent showed transient maxima, presumably as a result of displacement of the less strongly adsorbed substrate by the more strongly adsorbed one.[26]

Chromatography on plain silicic acid. The procedure was the same as with impregnated silicic acid except that a total of 5.5 g. of plain adsorbent was used instead. Data are also to be found in Table I.

Chromatography on alumina. Into a 2.5 × 11.5 cm. column of alumina (packed and prewashed as for silicic acid) was passed 200 ml. of isooctane solution *ca.* $5 \times 10^{-5}M$ in each of V and VI. The column was then eluted with 2% (by volume) acetone in isooctane and the effluent was analyzed as previously. Nearly all of V had been eluted before VI began to appear.

This procedure was repeated for use of I and IV except that the size of the column was 2.5 × 20 cm., 10 ml. of solution *ca.* $5 \times 10^{-3}M$ in each substrate was used, and elution was conducted with 300 ml. of isooctane. I attained a maximum concentration in the effluent at a cumulative volume of 150 ml. and dropped to an immeasurably low value at 250 ml. Meanwhile no concomitant effusion of IV was evident.

EUGENE, ORE.

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[26] Ref. 14, pp. 225-6.

[CONTRIBUTION FROM THE CANCER RESEARCH LABORATORY, UNIVERSITY OF FLORIDA]

Physical Properties of Aminoazobenzene Dyes. VI. Intramolecular Hydrogen Bonding and Tautomerism in 4-Hydroxyazobenzene Derivatives and Higher Homologs[1]

EUGENE SAWICKI[2]

Received January 21, 1957

The phenylhydrazone ⇄ azo dye tautomerism of 2′-methyl-, 4′-methyl-, 2′-methoxycarbonyl-, 4′-ethoxycarbonyl-, and unsubstituted derivatives of 4-phenylazo-1-naphthol and 5-phenylazo-8-hydroxyquinoline has been studied in alcoholic solution. In 5-(2′-methoxycarbonylphenylazo)-8-hydroxyquinoline the intramolecular hydrogen bond between the methoxycarbonyl ketonic oxygen and the azonium hydrogen involved in the 6-membered ring of the phenylhydrazone tautomer was of the same order of energy as the intramolecular hydrogen bond between the heterocyclic nitrogen and the hydroxyl hydrogen in the 5-membered ring of the azo tautomer. The 2′- and 4′-electron donor and electron attractor substituents studied in this paper were found to have similar qualitative effects on the tautomerism of 4-phenylazo-1-naphthol in alcohol and the tautomerism of the monocationic salt of 4-dimethylaminoazobenzene.

4-Hydroxyazobenzene has been shown to exist in alcohol in the azo form, λ_{max} 350 mμ.[3] Shingu[4] has shown that electron attractor substituents in the benzene ring of 1-phenylazo-4-naphthols increase the relative proportion of the phenylhydrazone tautomer while electron donor substituents in the 4′-position of the benzene ring increase the proportion of the azo tautomer. Each of these tautomers has a characteristic absorption spectrum with the azo tautomer absorbing at shorter wavelengths.[3] In this respect the 2′,4′-dinitro derivative of 4-hydroxyazobenzene acts like the 2,4-dinitrophenylhydrazone of *p*-benzoquinone in that it shows evidence of quinonoid character by its ability to undergo the Diels-Alder reaction with cyclopentadiene.[5] The discovery of the existence of a tautomeric equilibrium in solution between 4-phenylazonaphthol (I) and naphthoquinone monophenylhydrazone (II) by Kuhn and Bär[3] has been confirmed spectrally by Burawoy and Thompson,[6] Ospenson,[7] Badger and Buttery,[8] and Hadzi.[9] Ospenson has also given spectral evidence that 4-phenylazo-1-anthrol exists in alcohol almost completely in the phenylhydrazone form. From a study of the spectrum of 9-phenylazo-10-anthrol and appropriate derivatives in alcohol, Shingu[4] has concluded that the compound exists in solution only as anthraquinone monophenylhydrazone. These results parallel the reduction potentials[10] in alcohol of *p*-benzoquinone, 0.71*v*; 1,4-naphthoquinone, 0.49*v*; 1,4-anthraquinone, 0.40*v*; and 9,10-anthraquinone, 0.15*v*. *p*-Benzoquinone is the least stable of the *p*-quinones and the equilibrium Ph—NH—N=Ar=O ⇄ Ph—N=N—Ar—OH is displaced completely to the right; 9,10-anthraquinone is the most stable of these quinones and the equilibrium is displaced completely to the left.

The spectral data of Badger and Buttery[8] indicate that 4-phenylazo-1-naphthol exists in absolute alcohol solution as an equilibrium mixture of the

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[1] This investigation was supported by research grant C-1308 from the National Cancer Institute of the National Institutes of Health, U. S. Public Health Service.

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[3] R. Kuhn and F. Bär, *Ann.*, **516,** 143 (1935).

[4] H. Shingu, *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, **35,** 78 (1938).

[5] W. Lauer and S. Miller, *J. Am. Chem. Soc.*, **57,** 520 (1935).

[6] A. Burawoy and A. Thompson, *J. Chem. Soc.*, 1443 (1953).

[7] J. Ospenson, *Acta Chem. Scand.*, **5,** 491 (1951).

[8] G. Badger and R. Buttery, *J. Chem. Soc.*, 614 (1956).

[9] D. Hadzi, *J. Chem. Soc.*, 2143 (1956).

[10] J. B. Conant and L. F. Fieser, *J. Am. Chem. Soc.*, **45,** 2194 (1923).