

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

Chemical Structure and Chromatographic Adsorbability of Aromatic Hydrocarbons on Alumina^{1,2,3}

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An investigation of structural factors involved in the relative chromatographic adsorbabilities of binary mixtures of aromatic hydrocarbons on alumina was made using elution of the components with petroleum ether or petroleum ether-benzene and analysis of the effluent fractions by evaporation and m.p. determination on the residues. The Law of Inequalities—*i.e.*, if (in adsorbability) $A > B$ and $B > C$, then $A > C$ —was found to hold. Moreover, adsorbability was found to increase with increasing (a) number of double bonds, (b) approach to coplanarity, (c) symmetry number, (d) extent of conjugation, and (e) number of sterically unhindered methyl or alkylene groups. In two alkylarene series R-Zr, the effect of R in fostering adsorbability was found to be Me (unhindered) $> Et \approx H > i\text{-Pr}$, *tert*-Bu. From the fact that the adsorbability relationships are closely analogous to those found for fostering stability in *bona fide* 1:1 π -type molecular compounds in solution it is proposed that adsorption on alumina also involves π -type complexation where the "active spots" on the alumina are relatively broad electron-attracting areas on to which the electron-donating hydrocarbon substrate is held monomolecularly and preferentially (where such arrangement is sterically possible) in a planar configuration parallel to the surface.

Despite the fact that alumina is a favorite adsorbent for use in chromatographic separations and purifications of aromatic hydrocarbons, the only extensive systematic study which has been reported in an effort to correlate structure or physico-chemical properties of the compounds used with chromatographic adsorbability thereon is the classical research of Winterstein and Schön.⁵ These authors, who investigated the diphenylpolyene series and miscellaneous parent arenes of 2-9 rings, concluded that, in general, adsorbability (1) increases with the number of double bonds present (Unsaturation Rule),⁶ (2) is greater for an *acene* (a linearly condensed arene) than for an isomeric *phene* (an angularly condensed arene) or a *cata*-condensed compound with the same number of rings (Acene Rule) and (3) is greater for a colored isomer than for a white one. More recently Klemm, Reed, and Lind⁷ have noted that of conjugated isomeric biaryls and arylalkenes or of conjugated iso- π -electronic⁸ (though not isomeric) aromatic hydrocarbons the most nearly coplanar compound of the group is adsorbed most tenaciously (Coplanarity Rule). We have now undertaken studies on the

relative adsorbabilities of various types of aromatic hydrocarbons in an effort to test some of the preceding generalizations further, to search for additional correlations, and to develop, if possible, a rationale for the observed behaviors. In this regard the present paper constitutes a preliminary experimental survey of various series of compounds selected on the bases of ease of handling, availability, and pertinence as well as an interpretative account of other cases described in the literature.⁸

The general procedure was essentially that used by Winterstein and Schön⁵ whereby a solution in petroleum ether or benzene-petroleum ether of a mixture of two compounds is added to a column of alumina. The components are subsequently eluted into arbitrary fractions by means of the same solvent, and compositions of the residues remaining from evaporation of these fractions are investigated by melting point determination. The order of increasing adsorbability (same as the order of appearance in the effluent) and a semi-quantitative estimate of the degree of separation of the components are thus obtained. The analytical method, to be sure, has the limitation that it operates best for mixtures of solid components with rather widely separated melting points and, of course, is inapplicable to mixtures of liquid components. To avoid possible difficulties due to the overriding of one component by another or to flooding of the column, the ratio of the weights of the components used was kept close to 1:1 and the total combined weights of adsorbates charged to the column was kept small. At least under such circumstances (deviations therefrom were not investigated) orders of adsorbability were reproducible. The

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(2) Part II in the series on Correlation of Structure with Chromatographic Adsorbability. For part I see ref. 7. For part III see L. H. Klemm and D. Reed, *J. Chromatography*, in press.

(3) Abstracted (in part) from the M.S. theses of L. A. Miller and B. T. Ho, University of Oregon, June, 1959.

(4) Research assistant, 1957-1959.

(5) A. Winterstein and K. Schön, *Zeit. physiol. chemie*, **230**, 146 (1934).

(6) The same generalization has been noted for carotenoids on various adsorbents. See P. Karrer and E. Jucker, *Carotinoide*, Birkhäuser, Basel, 1948, p. 31.

(7) L. H. Klemm, D. Reed, and C. D. Lind, *J. Org. Chem.*, **22**, 739 (1957).

(8) No exhaustive survey of recent literature is claimed. On the other hand, all apparently potential leads gleaned from the common chromatographic books and reviews have been carefully followed. Especially useful in this regard were ref. 20 and L. Zechmeister, *Progress in Chromatography* 1938-1947, Chapman and Hall, London, 1950.

TABLE I. RELATIVE CHROMATOGRAPHIC ADSORBILITIES OF AROMATIC HYDROCARBONS ON ALUMINA COLUMNS

Run No.	Name	M.P., °C.	Wt. of each (mg.)	Size of Column ^b	Length of Run (Hr.)	Melting Ranges (°C.) of Selected Fractions of Effluent ^c			Extent of Separation ^e
						First fraction ^d	Intermediate fraction ^e	Last fraction ^f	
1	9-Phenylanthracene	151.5-152.5	150	A	16	149-152	117-141	105-110	Fair
	1-Phenylanthracene	113-114.5							
2 ^h	1-Phenylanthracene	113-114.5	100	A	(8)	111-113.5	— [†]	209-212	Complete
	2-Phenylanthracene	211.5-212.5							
3	1,1'-Binaphthyl	157-158	100	A	4.2	156.5-157.5	100-128	70-73	Good
	1,2'-Binaphthyl	74.5-76							
4	1-(1-Naphthyl)cyclopentene (III)	<25	200	A	3.7	<25	51-73	83-85.5	Fair
	1-(2-Naphthyl)cyclopentene (I)	85-86							
5	1-Vinylnaphthalene	<25	200	A	4.0	<25	45-57	59-62	Fair
	2-Vinylnaphthalene	66-67							
6	Biphenyl	69-71	100	A	3.4	70-71	(Faint film)	114-116	Complete
	Fluorene	113.5-115							
7	Naphthalene	80.5-81.5	75	A	12.6	80.5-81.5	63.5-66	96-98	Very good
	2-Vinylnaphthalene	66-67							
	Phenanthrene	97.5-99							
8	Anthracene	210-211	80	A	15	206-209	128-173	142-148	Fair
	Pyrene	149-150							
9	1,2,3,4-Tetrahydronaphthalene	<25	100	A	1.8	<25	<25	79-81	Complete
	Naphthalene	80-81							
10	Naphthalene	80-81	150	A	(2.6)	79-81	— [†]	156-157	Complete
	1,1'-Binaphthyl	157-158							
11	Naphthalene	80-81	150	A	2.4	78-81	<25	<25	Very good
	1-Phenylnaphthalene	<25							
12	Anthracene	209-210	130	A	15	206-210	138-174	140-150	Fair
	9-Phenylanthracene	151.5-152.5							
13	1-(1-Naphthyl)cyclopentene (III)	<25	150	A	3.7	<25	(Oily solid) [†]	101-102	Good
	2-Phenylnaphthalene	101.5-102							
14	1-(1-Naphthyl)cyclopentene (III)	<25	150	A	3.2	<25	47-55	58-60	Fair
	1-(2-Naphthyl)cyclohexene (IV)	60-61							
15 ^g	Benzo[<i>c</i>]phenanthrene	67-68.5	50	A	(3.4)	52-59	50-135	194-195	{ Virtually none Very good Complete
	Pyrene	149-150							
	Triphenylene	195-196							
16	Chrysene	247-248	30	A	52	— ^k	—	— ^k	Complete
	Naphthacene	324-328	15						
17	Triphenylene	195-196	75	A	58	190-193.5	172-209	214-232	Fair
	Chrysene	247-248							
18	Benz[<i>a</i>]anthracene ^r	158.5-159.5	50	A	64	168-184	175-199	182-208	Poor
	Chrysene	247-248							
19	Benz[<i>a</i>]anthracene	158.5-159.5	15	A	55	— ^k	—	— ^k	Complete
	Naphthacene	324-328							
20	3-(2-Naphthyl)cyclopentene (II)	<25	200	B	5	<25	68-78	82-85	Good
	1-(2-Naphthyl)cyclopentene (I)	84.5-86							
21	3-(2-Naphthyl)cyclohexene (V)	<25	200	B	4	<25	(Oily solid) [†]	57.5-59	Good
	1-(2-Naphthyl)cyclohexene (IV)	56-58							

TABLE I (Continued)

Run No.	Components Used in Mixture ^a			M.P., °C.	Wt. of each (mg.)	Size of Column ^b	Length of Run (Hr.)	Melting Ranges (°C.) of Selected Fractions of Effluent ^c			Extent of Separation ^d
	Name	M.P., °C.	Intermediate fraction ^e					First fraction ^d	Last fraction ^f		
22	Pentamethylbenzene	53-55	100	C	4.6	45-49	55-91	160-164	Poor		
23	Hexamethylbenzene	163-165	300	C	5.5	76-80	101-150	162-164	Fair		
24	Durene	163-165	100	C	3.8	68-77	43-49	53.5-57	Fair		
25	Pentamethylbenzene	53-55	300	C	2.2	<25	<25	79-80	Good		
26	Durene	79-81	100	A	2.3	78-81	91.5-94	92.5-94	Good		
27	Naphthalene	80-81	100	A	3.3	65-67	59-68	78-83	Fair		
28	Acenaphthene	66-67	100	A	2.3	78-80.5	<25	32.5-34	Fair		
29	1-(2-Naphthyl)cyclopentene (I)	85-86	140	B	2.3	<25-53	<25	<25	Poor		
30	Naphthalene	80-81	100	B	2.3	<25	<25-35	63-80	Poor		
31	2-tert-Butylnaphthalene	80-81	100	C	2.6	<25	46.5-52	55-56	Fair		
32	Naphthalene	80-81	100	A	2.5	80-81	55-57	46-49	Complete		
33	2-Bromonaphthalene	56-57	100	A	(6.6)	78-80	— [†]	47-50	Complete		
34 ^g	2-Bromonaphthalene ^m	56-57	100	A	(1.8)	210-212	75-176	74-78	Good		
35 ^h	2-Acetonaphthone	53.5-55	100	A	13	56-58	<25	76.5-79	Good		
36	Naphthalene	80-81	100	A	16	191-206	120-186	45-161	Poor		
37 ^h	2-Acetonaphthone	53.5-55	100	B	8.5	74-76	147-205	210-212	Fair		
38 ^h	Anthracene	211-212	100	A	5.2	71.5-74	(Trace)	54.5-57.5	Good		
39 ^h	9-Methylanthracene	79-80	50	A	29	144-156	100-123	110-118	Poor		
40	9-Ethylanthracene	56-58	25	A	60	117-160	120-160	107-160	None		
41 ^h	6-Methylbenz [a]anthracene	125-128	9.5	A	30	143-146	146-152	176-179	Fair		
42 ^h	4-Methylbenz [a]anthracene	139-140	25	A	72	132-135	—	186-192	Very good		
43	7-Methylbenz [a]anthracene	149-150.5	150	A	4	58.5-60.5	67-73	71-76	Poor		
	10-Methylbenz [a]anthracene	180-181.5									
	12-Methylbenz [a]anthracene	136-138									
	4-Methylbenz [a]anthracene	194.5-195									
	1-(2-Naphthyl)cyclohexene (IV)	60-61									
	1-(2-Naphthyl)cyclopentene (I)	85-86									

^a Unless otherwise designated the components were added to the column as a solution in the minimum volume of reagent grade petroleum ether (30–60°) and eluted with the same solvent. Other solvents used are listed as % (by vol.) reagent grade benzene in petroleum ether. Where separation of components occurred, names given in the table for each particular run are listed in order of appearance of the compounds in the effluent—*i.e.*, in order of increasing adsorbability. ^b The column of alumina used was as follows: Size A, 1.9 × 30 cm. (av. 105 g.); size B, 1.9 × 40 cm. (av. 140 g.); size C, 1.6 × 80 cm. (av. 250 g.). ^c Determined on the residue from evaporation of the solvent. ^d First fraction which contained more than a trace of residue. ^e Usually taken as the middle fraction, the fraction of widest melting range, or the one which best illustrates the degree of separation of the components. ^f In most (but not all) cases the last fraction collected represented virtually complete removal of hydrocarbon substrate from the column. ^g As based on general observations of the melting ranges of the various fractions. ^h Components dissolved in 50% benzene-petroleum ether, but eluted with petroleum ether only. ⁱ The less strongly adsorbed component was completely eluted in the first fractions. Intermediate fractions contained little, if any, residue. Acetone was added to the petroleum ether developer to help elute the more strongly adsorbed component. ^j Only a trace was present. ^k Separation was readily observed on the column because of characteristic fluorescences. Naphthalene (yellow fluorescence) was more strongly adsorbed than chrysene or benz[*a*]anthracene (blue fluorescence). ^l That chrysene was not eluted so readily as benz[*a*]anthracene was confirmed by comparison of the melting ranges of the effluent fractions with a standard m.p. *vs.* composition curve for the mixed components. ^m Because of the proximity of the melting points of the components, the identities of the eluted fractions were established by m.m.p. with *bona fide* samples, by Beilstein tests (positive on first fractions, negative on later ones), and by the fact that 2-acetonaphthone fluoresces (light blue) when adsorbed on alumina while 2-bromonaphthalene does not fluoresce. ⁿ Run with 2% benzene. ^o Run with 4% benzene. ^p Run with 5% benzene. ^q Run with 50% benzene.

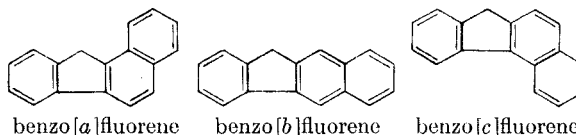
degree of separation seemed to be somewhat (though not markedly) dependent on the length of the column and the uniformity achieved in its packing. General results for all runs are summarized in Table I. Detailed information on the fractions obtained in two runs where successful separations of the components were attained under experimental conditions as nearly divergent from one another as any attempted in our studies are recorded in Tables III and IV in the experimental section.

As a check on the structural significance of the results we included a series of triads of adsorbates (taken two at a time) to ascertain if the experimentally determined adsorbabilities followed the Law of Inequalities—*i.e.* if (in adsorbability) A > B and B > C, then also A > C (where A, B, and C are three different substrates). The various cases in point are listed in Table II. The fact that no exceptions to this law have been observed in our studies is evidence in support of the belief that steady-state processes are occurring on the columns. Such is the situation even for runs 31–33 where the chemically different compounds naphthalene, 2-bromonaphthalene, and 2-acetonaphthone are compared. In a few test runs, results on relative adsorbabilities were found to be qualita-

tively the same with both petroleum ether alone and benzene-petroleum ether, though the mixed solvent sometimes gave a cleaner separation. On the basis of such results it will be assumed that the Law of Inequalities can be applied to all cases considered in this paper.

Runs 1–6 were made in an effort to check the Coplanarity Rule further. The first five involve isomeric biaryls and arylalkenes which differ from one another in angle of twist. The decreasing orders of adsorbability 2-phenylanthracene > 1-phenylanthracene > 9-phenylanthracene; 2,2'-binaphthyl⁹ > 1,2'-binaphthyl > 1,1'-binaphthyl; 2-alkenylnaphthalene > 1-alkenylnaphthalene (where the alkenyl group is vinyl, 1-cyclopentenyl, or 1-cyclohexenyl⁷); and 2-phenylnaphthalene > 1-phenylnaphthalene⁷, which follow increasing angles of twist in the molecules as well as the frequently noted more tenacious retention of *trans* (as compared to *cis*) isomers,⁷ constitute the main basis for this rule. Moreover, the rule holds in run 14, where the nearly coplanar (to the naphthalene ring) cyclohexenyl double bond fosters greater adsorbability than does the non-coplanar (also to the naphthalene ring) cyclopentenyl double bond, which is of greater inherent conjugative effect.¹⁰ In run 6 [fluorene (coplanar) > biphenyl (twisted in solution)] the components are iso- π -electronic, though the excellent degree of separation achieved is perhaps ascribable partially to the presence of an alkylene bridge *per se* in the fluorene (*vide infra*) as well as to differences in coplanarity. A similar consideration applies to the observation¹¹ that a mixture of benzo[*a* and *b*]fluorenes¹² is adsorbed more tenaciously than 2-phenylnaphthalene. The case of benzo[*b* or *c*]fluorene > 2-benzyl-naphthalene¹³ is free of the alkylene complication but involves instead the difficulty that the former is completely conjugated (*vide infra*), while the latter is not.

Operation of the Unsaturation Rule is apparent in runs 7 [phenanthrene (7 double bonds) > 2-vinylnaphthalene (6 double bonds) > naphthalene (5 double bonds)], 8 [pyrene (8 double bonds) >



anthracene (7 double bonds)], and 9 [naphthalene > 1,2,3,4-tetrahydronaphthalene], as well as in the

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

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

(11) M. Orchin and L. Reggel, *J. Am. Chem. Soc.*, **70**, 1245 (1948).

(12) I.U.P.A.C. 1957 Rules for nomenclature are used throughout this paper.

(13) M. Orchin, E. O. Woolfolk, and L. Reggel, *J. Am. Chem. Soc.*, **71**, 1126 (1949).

TABLE II
 TRIADS OF ADSORBATES WHICH CORROBORATE THE LAW OF INEQUALITIES
 FOR CHROMATOGRAPHIC ADSORBABILITY ON ALUMINA

Adsorbate Triad			Reference ^a
Strongest adsorbability	Intermediate adsorbability	Weakest adsorbability	
Anthracene	Phenanthrene	Naphthalene	W. and S., 7
Chrysene	Pyrene ^b	Anthracene ^b	W. and S., 8
Pyrene ^b	Anthracene ^b	Phenanthrene	W. and S., 8
Naphthacene	Benzo [a]pyrene	Chrysene	W. and S., 16
Chrysene	Triphenylene	Pyrene	W. and S., 15, 17
Naphthacene	Chrysene	Benz [a]anthracene	16, 18, 19
Hexamethylbenzene	Pentamethylbenzene	Durene	22, 23, 24
2-Acetonaphthone	2-Bromonaphthalene	Naphthalene	31, 32, 33
9-Methylanthracene	9-Ethylanthracene	Anthracene	34, 35, 36
9-Ethylanthracene	Anthracene	9-Isopropylanthracene	36, 37, 38
II	V	III	4, 14, 43

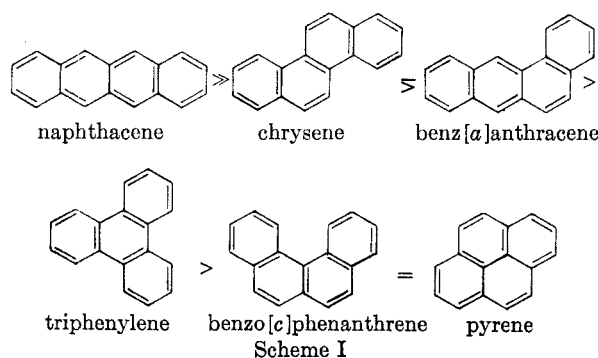
^a W. and S. refers to work of Winterstein and Schön, see ref. 5 in regular text. Numbers refer to particular runs as given in Table I. ^b Pyrene and anthracene separated readily in our experiment but were not separated by Winterstein and Schön.

cases of 2-phenylnaphthalene > naphthalene¹¹; 2-benzyl-naphthalene > naphthalene,¹³ and 6,12-dimethylbenz [a]anthracene > 6,12-dimethyl-1,2,3,4-tetrahydrobenz [a]anthracene.¹⁴ In our hands separation of the pyrene-anthracene mixture occurred readily though Winterstein and Schön did not succeed in their attempt at this.

Runs 10-12 represent examples where coplanarity and unsaturation effects should tend to counteract one another. Though cases involving more subtle differences in degree of unsaturation would be desirable, the general gross dominance of the Unsaturation Rule over the Coplanarity Rule is noteworthy. Though it is not clear that the conditions of the experiment justify comparison here, the observation¹⁵ that dianthracene (formed *in situ* by chromatography of anthracene in the presence of light) > anthracene may also illustrate the point. Run 13, on the other hand, shows the additivity of effects in the good separation of 2-phenylnaphthalene from 1-(1-naphthyl)cyclopentene.

Interpretation of the relative adsorbabilities of condensed polynuclear arenes appears more difficult. In this regard the experimentally determined (runs 15-19) relationships among the six possible

benzenoid tetracyclic compounds (Scheme I) are instructive. Thus the strong adsorption of naphthacene is consistent with the Acene Rule and the weak adsorption of pyrene (one less double bond than in the others) with the Unsaturation Rule. Though quantitative evaluation of these factors is not yet possible, it is proposed that the entire Scheme I may be rationalized in terms of three rules, *viz.* (a) the forementioned Unsaturation Rule, (b) an expanded Coplanarity Rule and (c) a Symmetry Rule. Briefly, the Symmetry Rule states that adsorbability increases with increasing symmetry number¹⁶ (S.N.) of the molecule. For practical application of this rule one considers condensed molecules as two-dimensional only. If such rule were completely dominant, Scheme I ought to have the order triphenylene (S.N. 6) > naphthacene = pyrene (S.N. 4) > chrysene = benzo [c]phenanthrene (S.N. 2) > benz [a]anthracene (S.N. 1). The expanded Coplanarity Rule, then, takes cognizance of the fact that "intramolecular overcrowding"¹⁷ will cause distortion of four of these tetracyclic compounds out of coplanar configurations.¹⁸ For complete dominance of coplanarity effects the expected order of adsorbability would be naphthacene = pyrene (both coplanar) > benz [a]anthracene (bumping of "phene hydrogens" in the 1- and 12-positions) > chrysene (two sets of phene hydrogens) > triphenylene (three sets of phene hydrogens) > benzo [c]phenanthrene (over-



(14) L. F. Fieser and R. N. Jones, *J. Am. Chem. Soc.*, **60**, 1940 (1938).

(15) W. J. Levy and N. Campbell, *J. Chem. Soc.*, 1442 (1939).

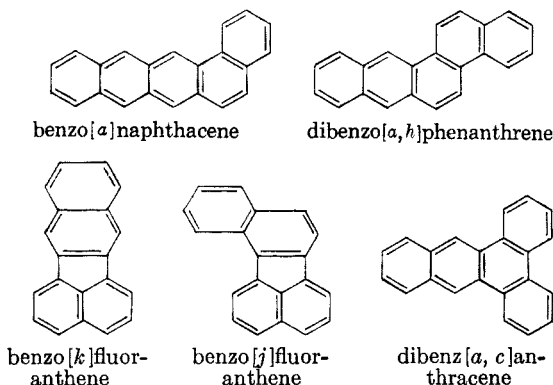
(16) Symmetry number as used here represents the number of equivalent orientations possible for flatwise adsorption of the substrate molecule onto a surface.

(17) A discussion of intramolecular overcrowding is given by J. C. Speakman in W. Klyne and P. B. D. de la Mare, *Progress in Stereochemistry*, Butterworths, London, Vol. 2, 1958, pp. 22-31.

(18) For comparison of phenanthrene-type distortions with the more conventional type of molecular overcrowding noted in ref. 17 see C. A. Coulson, "Molecular Geometry and Steric Deformation," presented at the Kekule Symposium on Theoretical Organic Chemistry, London, Sept., 1958, in press.

crowding of carbons and hydrogens at the 1- and 12-positions). The observed order might reasonably follow from an order of precedence for these rules of (a) > (b) > (c). It is then apparent that the Acene Rule may be considered a corollary of these other three.

For more complicated arenes, cases accounted for by rule (a) have been considered elsewhere.⁵ Rule (b) may be invoked to account for the order benzo[*a*]naphthacene > dibenzo[*a,h*]phenanthrene > dibenz[*a,c*]anthracene;⁵ a combination of rules (a), (b), and (c), to account for the observations^{11,13} that benzo[*a*]fluorene and benzo[*b*]fluorene (equivalent in terms of the three rules) are not separated but are more strongly adsorbed than the isomeric benzo[*c*]fluorene (*phene*-type hydrogen bumping); and rule (c), to account for the greater



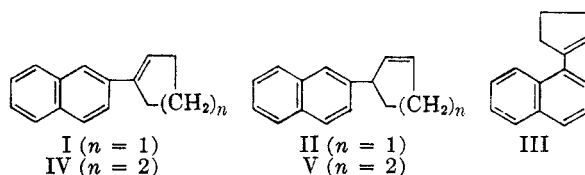
adsorbability⁹ of benzo[*k*]fluoranthene over that of benzo[*j*]fluoranthene.¹⁹ The order anthracene > phenanthrene⁵ is accounted for by rules (b) and (c). A variety of other cases investigated by Winterstein and Schön⁵ may be rationalized, but would not be predictable on the basis of these qualitative rules.

The greater adsorbability of conjugated (as compared to isomeric unconjugated) polyenes on alumina has been noted by previous investigators.²⁰ Runs 20 and 21 confirm the presumption that conjugation *per se* is also of pertinence in naphthylcycloalkenes. However, rule (a) is dominant over effects of conjugation in determining the order of adsorbability 9,10-dihydroanthracene (6 double bonds) > 1,2,3,4-tetrahydroanthracene (5 double bonds).²¹ Tentatively, we propose a Conjugation Rule to the effect that of isomeric unsaturated hydrocarbons which differ from one another only in degree of conjugation, the most extensively conjugated isomer will be adsorbed most tenaciously on alumina.

(19) Cf. M. Orchin and L. Reggel, *J. Am. Chem. Soc.*, **73**, 436 (1951), for proofs of structures of these compounds.

(20) L. Zechmeister and L. Cholnoky, *Principles and Practice of Chromatography*, John Wiley, New York, 1941, p. 26.

(21) M. Orchin, *J. Am. Chem. Soc.*, **66**, 535 (1944).



From runs 28–30 [2-methylnaphthalene > 2-ethylnaphthalene \leq naphthalene > 2-*tert*-butylnaphthalene] and runs 34–38 [9-methylantracene > 9-ethylantracene \leq anthracene > 9-isopropylantracene] it is noted that adsorbability of the 2-naphthyl and 9-anthryl moieties is affected by the presence of an alkyl substituent in the order Me > Et \leq H > *i*-Pr, *tert*-Bu. The enhanced adsorbability of a methylarene (as compared to the parent arene) is also noted in the only benz[*a*]anthracene case so studied (run 39). This reversal in trend for the effect of an alkyl group on adsorbability as a function of increasing size of the group might result from the operation of two opposing factors, namely (1) donation of electronic charge to the aromatic ring and (2) steric hindrance to adsorption. One would expect any alkyl group to enhance adsorbability through operation (1). On the other hand, factor (2) should increase with the bulkiness of the substituent, especially if flatwise adsorption of the arene ring onto the alumina surface were preferred so that projection of a substituent in a direction perpendicular to the plane of the aryl moiety would interfere with the adsorption process. Conceivably, the reversal in trend might be a consequence merely of the increasing molecular weight of the substrate without simultaneous increase in the π -electronic system, rather than as a result of factor (2). That this latter alternative is not particularly pertinent, however, is indicated by the data from runs 22–25 where one finds the order of adsorbability hexamethylbenzene > pentamethylbenzene > durene > mesitylene.^{22,23} The good separation (run 26) of acenaphthene (dimethylene group coplanar with the naphthalene ring) from naphthalene (less strongly adsorbed) as compared to the poor separation of 2-ethylnaphthalene from naphthalene (run 29) supports these views, as does also the stronger adsorption (run 27) of I (a virtually coplanar,²⁴ trimethylene derivative of 2-vinylnaphthalene) as compared to its parent, 2-vinylnaphthalene (also essentially coplanar).²⁴

A check on the consequences of having a sterically hindered methyl group was attempted in runs 40 and 42 where one has the order 7-methylbenz-

(22) One might also note that these results are inconsistent with edgewise adsorption of the benzene ring, *cf.* ref. 31.

(23) Evidence that hexamethylbenzene and durene are coplanar in the crystalline state is surveyed by E. Harnik, F. H. Herbstein, G. M. J. Schmidt, and F. L. Hirschfeld, *J. Chem. Soc.*, 3288 (1954).

(24) L. H. Klemm, H. Ziffer, J. W. Sprague, and W. Hodes, *J. Org. Chem.*, **20**, 190 (1955).

[a]anthracene (uncrowded methyl group) = 4-methylbenz[a]anthracene (likewise uncrowded methyl group) > 12-methylbenz[a]anthracene (overcrowding of the methyl group and the 1-hydrogen atom,²⁵ essentially complete separation from the 4-isomer). However, overcrowding in the 12-isomer may well cause both out-of-plane bending of the C_{Ar}—C_M bond and twisting of the aromatic system (in opposite directions).¹⁷ The fair separation (run 41) of the 2- and 10-isomers (both uncrowded) indicates that electronic factors may also be of some significance in considerations of adsorbability in the series. A more definitive case would seem to be the observation of Wieland and Probst²⁶ that 9-methylfluorene (uncrowded, but sidewise-projecting methyl group) is adsorbed less tenaciously than fluorene.

From the foregoing observations we draw the following tentative alkyl-alkylene rule: Substitution of an alkyl or alkylene group on a parent arene increases adsorbability of the compound on alumina, provided that such substitution does not bring about increased steric hindrance to flatwise adsorption of the arene moiety. Where this substitution increases steric hindrance sufficiently, adsorbability will be lessened.

It has been suggested by Basu²⁷ that chromatographic adsorption of non-polar organic compounds involves auxiliary valence types or molecular complex formation. Our results on adsorbability seem readily interpretable in terms of such a model, whereby the hydrocarbon substrate functions as an electron donor (D) of relatively limited planar extent which is adsorbed preferentially flatwise (where this is sterically possible) onto broader areas of the electron acceptor (A), alumina,²⁸ by π -type complex formation. If such a model is appropriate and if steady state conditions do exist in the chromatographic column, our adsorbabilities should be directly correlatable with equilibrium data for stabilities (as measured in inert solvents) of *bona fide* molecular compounds of the same substrates with planar acceptors *provided that* either (1) the other acceptors are of sufficiently extensive areas so as to cover the entire substrate molecule or (2) they are geometrically so disposed as to "sense" all out-of-plane projections and the entire π -electronic system of the substrate molecule.

Let us consider some cases which ought to satisfy either condition (1) or (2). Measurements by Anderson and Hammick²⁹ on the picrates of the

methylbenzenes in chloroform solution³⁰ showed the order of stability hexamethylbenzene > durene > mesitylene > xylenes > toluene > benzene, and, on the picrates of the monoalkylbenzenes, the order in fostering stability by a substituent of Me (K = 0.51) > Et (0.45) > H (0.43) > *i*-Pr (0.36) > *tert*-Bu (0.31). For tetracyanoethylene complexes measured in methylene chloride solution Merrifield and Phillips³¹ found the stability constant increased by a factor of 1.9–3.1 for each additional methyl group substituted on the benzene nucleus. The order Me > Et > H in fostering stability was found for the series hexamethylbenzene (K = 263) > hexaethylbenzene (5) > benzene (2). Also of interest are their findings that fluorene > biphenyl; naphthalene > benzene; and pyrene > naphthalene.³² A methyl group on naphthalene has been found to enhance TNF complexation in glacial acetic acid.^{30,33} These results are in remarkably good agreement with our data on adsorbabilities of alkylarenes (runs 23, 25, 28–30, 34–39).³⁴ On the basis of the proposed geometries of overlap,³⁵ the order of stability of TNF complexes³³ I > 2-vinylnaphthalene > naphthalene is likewise correlatable with adsorbabilities (runs 7, 27).³⁶

Though the benz[a]anthracene molecule is too large to ensure complete overlap of its π -electronic system by TNF one notes that the relative adsorbabilities found in runs 39–41, involving only sterically uncrowded methyl substituents (in the 2-, 4-, 6-, 7-, and 10-positions) are consistent³⁷ with the data of Takemura, Cameron, and Newman³⁸ on the dissociation constants of TNF com-

(30) See also data of T. S. Moore, F. Shepherd, and E. Goodall [*J. Chem. Soc.*, 1447 (1931)] for stabilities of picrates as based on water-chloroform partition studies.

(31) R. E. Merrifield and W. D. Phillips, *J. Am. Chem. Soc.*, **80**, 2778 (1958). Their comments on the relation of structures of the TCNE complexes to stabilities would seem to fit our adsorption complexes equally well (except, perhaps, for absolute distances between the adsorbate and the alumina surface layer).

(32) Though we did not measure benzene *vs.* naphthalene directly, common laboratory experience indicates that the latter is more strongly adsorbed. Cf. run 8 and ref. 5 for the pyrene-naphthalene relationship.

(33) L. H. Klemm, J. W. Sprague, and H. Ziffer, *J. Org. Chem.*, **20**, 200 (1955).

(34) Some discrepancies occur between orders of adsorbability and stabilities of complexes formed between alkylarenes and small inorganic molecules, where stereochemical interactions may be less definite [cf. L. J. Andrews, *Chem. Revs.*, **54**, 713 (1954), and especially L. J. Andrews and R. M. Keefer, *J. Am. Chem. Soc.*, **74**, 4500 (1952)].

(35) L. H. Klemm and J. W. Sprague, *J. Org. Chem.*, **19**, 1464 (1954).

(36) It is interesting to note that the order of adsorbability 2-acetonaphthone > 2-bromonaphthalene > naphthalene (runs 31–33) is opposite to that found for the stabilities of their TNF complexes (see ref. 33).

(37) This assumes that the ratio of stability constants of 1.5 for 6-Me/10-Me is too small to ensure separation by adsorption.

(38) K. H. Takemura, M. D. Cameron, and M. S. Newman, *J. Am. Chem. Soc.*, **75**, 3280 (1953).

(25) A diagram indicating the magnitude of this effect is given by M. Orchin, *J. Org. Chem.*, **16**, 1165 (1951).

(26) H. Wieland and O. Probst, *Ann.*, **530**, 274 (1937).

(27) S. Basu, *Chemistry and Industry*, 764 (1956).

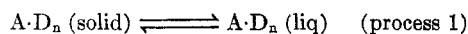
(28) The attraction of the alumina may be ascribed to polarization by the Al³⁺ ions. For suggestions on the action of γ -alumina as a Lewis acid see D. A. Dowden in W. E. Garner, *Chemisorption*, Butterworths, London, 1957, p. 15.

(29) H. D. Anderson and D. Hammick, *J. Chem. Soc.*, 1089 (1950).

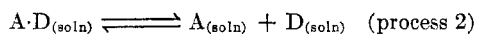
plexes of these compounds in chloroform. In run 42, however, where the sterically crowded 12-methyl derivative is run against the sterically uncrowded 4-isomer, the relative adsorbabilities found are opposite to the stabilities of the TNF complexes. The position occupied by the TNF moiety in its complex with the 12-isomer may be automatically adjusted so as to avoid the steric hindrance of the sidewise-projecting methyl group, whereas such adjustment cannot be made by the alumina surface.

In runs conducted by frontal analysis using TNF-impregnated silicic acid in the manner described by Klemm, Reed, and Lind⁷ it was found that the conjugated hydrocarbons I and IV were retained on the column more tenaciously than their unconjugated isomers II and V, respectively. The consistency of these results with the data from alumina results because the TNF molecule is too small to allow simultaneous maximum overlap of both the naphthyl and alkenyl π -electronic systems (as alumina might conceivably do) in II and V (and, hence, may be presumed to overlap only the naphthyl nucleus) but just large enough for such simultaneous overlap in I and IV.³⁵ Also the relationships 2-alkenylnaphthalene > isomeric 1-alkenylnaphthalene and 2-phenylnaphthalene > 1-phenylnaphthalene may be ascribed to a closer approach to coplanarity in the 2-isomer for the alumina adsorption process and to better overlap in the 2-isomer for polynitroarene complexation in solution³³ or on silicic acid.⁷

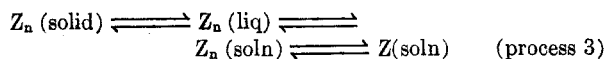
Stabilities in *crystalline* molecular compounds have been correlated directly with melting point by Orchin.³⁹ Such stability refers to the equilibrium process



while stabilities of molecular complexes in solution refer to a *different* equilibrium, *viz.*



where crystalline geometries and intermolecular forces (other than in the unit complex A·D) are not involved.⁴⁰ The lack of correlation between melting point and adsorbability on impregnated silicic acid has been noted previously,⁷ where it has been suggested that adsorption 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. Pursuing this same general theme, one also notes that if crystallites (Z_n) of adsorbate (Z) form on the alumina column and are pertinent to the final overall separation process, then one would be concerned primarily⁴¹ with the steady-state phenomena



If, on the other hand, adsorbate molecules are held monomolecularly and widely dispersed on the alumina surface, one would have the steady state



If process 3 is an appropriate representation of chromatography on alumina, then adsorbability ought to vary directly with melting point and/or inversely with solubility. If process 4 is appropriate, however, adsorbability should be independent (at least within wide limits)⁴² of both of these adsorbate properties. A check of the data in Table I shows that, in 40% of the binary mixtures run, stronger adsorption occurred for the lower melting component. Moreover, though only gross differences in relative solubilities have been noted in our experiments, in some cases (runs 3, 8, 12, 24, 28, 34, and 36) the more soluble component is more tenaciously adsorbed and in other cases (runs 10, 15, 16, 17, 19, and 37) it is less tenaciously adsorbed. On the basis of these considerations and the preceding correlations of adsorbability with stabilities of *bona fide* molecular compounds as measured in solution, we propose that separations on our alumina columns involve as the most pertinent process⁴³ a relatively rapidly reversible steady-state condition (process 4) occurring between molecules of hydrocarbon adsorbed monomolecularly on "active spots" of the alumina surface in a π -type (outer- or charge-transfer) complex and molecules of hydrocarbon dissolved in the eluting solvent.

Additional studies to test further the generalizations and proposals made in this paper are planned for the future.

EXPERIMENTAL

Syntheses and purification of substrates. Unless specifically noted otherwise, every substrate used in adsorbability studies was (a) obtained from Distillation Products Industries (white label grade), (b) chromatographed separately using alumina with petroleum ether (30–60°), benzene, or a mixture of the two solvents, and (c) recrystallized once or twice from ethanol.

*Triphenylene.*⁴⁴ A mixture of 10 g. of dodecahydrotriphenylene⁴⁵ (m.p. 230–232°) and 1 g. of 30% palladium-on-charcoal (American Platinum Works) was heated in a 40 × 300-mm. Pyrex test tube fitted with a cork bearing a bent glass tube (to prevent loss of triphenylene through sublimation and entrainment by evolved hydrogen) for one hr. in a

(42) It is readily apparent that extremes of solubility may prevent process 4 from operating because of lack of adsorption or lack of dissolution.

(43) Though the systematic investigation of this point has not yet been made, there are indications that even in cases where the adsorbate components are observed to crystallize out of solution in the uppermost region of the column, use of a sufficiently long column ensures that the order of appearance of components in the effluent remains unchanged.

(44) Method developed by Dr. Herman Ziffer.

(45) C. Mannich, *Ber.*, **40**, 153 (1907).

(39) *Cf.* ref. in footnote 25.

(40) Discrepancies between stabilities of molecular compounds as measured by criteria of m.p. and equilibrium constant have been noted previously; see, for example, refs. 35 and 38.

(41) For the relatively few molecules adsorbed directly to the alumina surface in this case, process 4 would apply.

Wood's metal bath maintained at 240°. Over a period of 6 hr. the bath temperature was increased gradually to 310° where it was held for 11 hr. longer. The cooled benzene extract (after treatment with Nuchar) of the mixture deposited needles, m.p. 198–199° (first crop) and 196–199° (second crop), total av. yield 8.2 g. (86%). Percentage yields were lower for larger batches.

9-Ethylantracene. To the Grignard reagent from 20.3 g. (0.13 mole) of ethyl iodide, 3 g. of magnesium, and 70 ml. of anhydrous ether was slowly added a solution of 10 g. (0.051 mole) of anthrone⁴⁶ in 100 ml. of anhydrous benzene. The mixture was refluxed for 9 hr. and then poured onto ice and concentrated hydrochloric acid. Distillation of the dried organic layer gave 9.2 g. (87%) of liquid, b.p. 149–156°/1 mm. which solidified on cooling. This was recrystallized and chromatographed. The first fraction (3.6 g., m.p. 56–58°) was selected for further use; reported⁴⁷ m.p. 59°.

9-Isopropylantracene. In the foregoing manner there was obtained from 10 g. of anthrone and 22 g. of isopropyl iodide 8 g. (71%) of liquid, b.p. 153–160°/1.3 mm. The first fraction (3.4 g.) from chromatography was recrystallized from methanol, m.p. 75–76°; reported⁴⁸ m.p. 76°.

1-Phenylantracene. 1-Phenylantraquinone⁴⁹ was reduced according to published directions⁵⁰ except that the zinc was activated⁵¹ and the period of reflux was 58 hr. After chromatography and recrystallization, the product formed white needles, m.p. 113–114.5°; reported⁵⁰ yellow needles, m.p. 123°.

2-Phenylantracene.⁵² The black product resulting from refluxing (air condenser) 10 g. of 2-methyl-4'-phenylbenzophenone⁵³ for 7.5 hr. (whereupon evolution of water had ceased) was sublimed in portions of 1–3 g. at ca. 150°/0.5–1.0 mm. for periods up to 12 hr. Combined sublimates (4.1 g.) were recrystallized (Norit) from methyl ethyl ketone, yield 2.1 g. (22%) of pale yellow leaflets, m.p. 211.5–212.5° [reported⁵⁴ m.p. 207–207.5°, $\lambda_{\text{max}}^{\text{isoctane}}$ 229 m μ (log ϵ 4.41), 257 (4.80), 276 (4.90), 318 (3.24)—shoulder, 330 (3.52), 346 (3.75), 364 (3.87), 384 (3.73),⁵⁵ used without recrystallization.

Anal. Calcd. for C₂₀H₁₄: C, 94.45; H, 5.55. Found: C, 94.32; H, 5.56.

1,2'-Binaphthyl was prepared according to the method of Hooker and Fieser,⁵⁶ except that dehydrogenation of the intermediate was effected by heating with 1 g. of 30% palladium-on-charcoal at 280–290° for 3.5 hr. and finally at 350° momentarily. The product was chromatographed first with TNF-impregnated silicic acid⁷—Florasil (1:2 by vol.) and then with alumina, m.p. 74.5–76° (without recrystallization). 1,1'-Binaphthyl was prepared and purified likewise; yield 28%, m.p. 155–158° from the first chromatographic column; final m.p. 157–158° (without recrystallization). This sample did not exhibit the melting peculiarities

described by Orchin and Friedel.⁵⁷ 2-Ethynaphthalene,⁵⁸ prepared by Clemmensen reduction of 2-acetonaphthone, was distilled twice (b.p. 79–80°/0.8 mm.) and used directly. 2-*tert*-Butylnaphthalene^{59,60} (b.p. 96–99°/1.5 mm.) was converted to its picrate (m.p. 99–101°) which was dissociated on alumina. The sample used was obtained by evaporation (*sans* heating) of the first fraction of effluent.

For preliminary purification benzo[*c*]phenanthrene⁶⁰ was converted to its picrate which was dissociated on alumina. Pyrene (Matheson practical grade) was recrystallized from ethanol, treated with maleic anhydride to remove reactive impurities,⁶¹ and chromatographed. Chrysene was treated with maleic anhydride and recrystallized from benzene as white platelets. Benz[*a*]anthracene was converted to its picrate, which was recrystallized three times from glacial acetic acid and then dissociated on alumina. Chromatography twice gave white platelets (not recrystallized). Naphthacene (H. and M. Chemical Co., practical grade) was chromatographed using benzene and a column protected from light by means of an aluminum foil wrapping and was used without recrystallization. 9-Phenylantracene⁶² (Aldrich Chemical Co.) was chromatographed on 1:1 (by vol.) alumina-Celite using hexane as solvent and then recrystallized twice from absolute ethanol and once from acetonitrile. 9-Methylantracene was obtained from Aldrich Chemical Co.; durene, from Humble Oil and Research Co. 2-Bromonaphthalene was available from previous research.³³ 2-Acetonaphthone was purified merely by recrystallization from petroleum ether (30–60°); 2-methylnaphthalene, from methanol. Acenaphthene was given a preliminary treatment with decolorizing carbon in ethanol. The liquids 1,2,3,4-tetrahydronaphthalene and mesitylene were used directly after careful fractional distillation, b.p.'s 59–59.5°/1.8 mm. and 156–157°/1 atm., respectively. Naphthalene (Baker's analytical reagent) and samples (kindly supplied by Prof. M. S. Newman) of the methylbenz[*a*]anthracenes were used as obtained. Anthracene,⁷ phenanthrene,⁷ phenylnaphthalenes,⁷ and alkenylnaphthalenes^{33,63,64} were used directly in the purified forms described previously.

Chromatography on alumina. In general, a Pyrex chromatographic tube, fitted at the bottom end (*via* a non-lubricated ground-glass joint) with a fritted glass disc and constricted end, was filled with reagent grade petroleum ether (30–60°). Alcoa activated alumina (grade F-20 γ -alumina, used directly from the can) was gradually introduced while the tube was tapped vigorously with heavy rubber tubing until a column of adsorbent 30–80 cm. high (105–250 g.) resulted. A layer of purified sand, 1 cm. thick, was placed atop the alumina to protect the latter from disturbance by the solvent. The solvent was allowed to drain until its level reached the top of the sand. Thereupon, a mixture containing equal weights (10–300 mg.) of each component, dissolved in a minimum volume of either reagent grade⁶⁵ petroleum ether (30–60°) alone or admixed with reagent grade benzene (up to 50% by vol.), was added to the top of the column and the chromatogram was de-

(46) K. H. Meyer, *Org. Syntheses*, Coll. Vol. I, 60 (1941).

(47) F. Krollpfeiffer and F. Branscheid, *Ber.*, 56, 1617 (1923).

(48) E. B. Barnett and M. A. Matthews, *Ber.*, 59, 1429 (1926).

(49) E. Bergmann, L. Haskelberg, and F. Bergmann, *J. Org. Chem.*, 7, 303 (1942).

(50) C. Weizmann, E. Bergmann, and L. Haskelberg, *J. Chem. Soc.*, 391 (1939).

(51) E. L. Martin, *J. Am. Chem. Soc.*, 58, 1441 (1936).

(52) Synthesized by Dr. Roger H. Mann.

(53) W. E. Baehmann and F. H. Moser, *J. Am. Chem. Soc.*, 54, 1124 (1932).

(54) J. W. Cook, *J. Chem. Soc.*, 1087 (1930).

(55) Cf. Y. Hirshberg, *Trans. Faraday Soc.*, 44, 285 (1948).

(56) S. C. Hooker and L. F. Fieser, *J. Am. Chem. Soc.*, 58, 1216 (1936).

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

(58) Prepared by Dr. Jack T. Spence.

(59) N. G. Bromby, A. T. Peters, and F. M. Rowe, *J. Chem. Soc.*, 144 (1943).

(60) M. S. Newman, H. V. Anderson, and K. H. Takemura, *J. Am. Chem. Soc.*, 75, 347 (1953).

(61) E. Clar, *Ber.*, 65, 1425 (1932).

(62) Purified by Dr. C. Douglas Lind.

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

(64) L. H. Klemm, B. T. Ho, C. D. Lind, B. T. MacGowan, and E. Y. K. Mak, *J. Org. Chem.*, 24, 949 (1959).

(65) Of several brands tried only Mallinckrodt reagent grade (30–60°) petroleum ether was found to leave a sufficiently small amount of residue upon evaporation of a 1- to 2-l. sample as to be suitable for use as an eluent for the methylbenzanthracenes and other slightly soluble hydrocarbons.

TABLE III
FRACTIONS COLLECTED IN RUN 6

Total Wt. of Effluent Fraction ^a (g.)	Wt. of Residue (mg.)	M.p. of Residue (°C.)
150	None	—
64	50	70-71
85	50	65.5-69
62	None	—
92	5	104-110
87	50	114-115
115	20	114-116
107	20	113.5-115

^a Fractions are listed in order of appearance.

veloped and eluted at room temperature by gravity flow using, in general, the same solvent. The solvent and the size of the sample were determined by solubility and availability of the components. The rate of flow through the column was 150-300 ml./hr. for columns 30-40 cm. long and 75-150 ml./hr. for those 80 cm. long. Fractions of effluent were collected somewhat arbitrarily, weighed, evaporated rapidly almost to dryness in a stream of nitrogen on a steam bath and then slowly on a tared watchglass in air at room temperature. Any resultant residue was weighed and (if crystalline) was powdered, mixed thoroughly, and used for m.p. determination. Details of the individual runs are given in Table I and typical data for fractions collected in two runs where successful separations were obtained are given in Tables III and IV.

In test runs, samples of the unconjugated cycloalkenyl-naphthalenes II and V were passed through alumina individually and the effluents were checked for the possible presence of the conjugated isomers I and IV, respectively. No evidence of doublebond migration under the conditions of our experiments was found.

Chromatography on TNF-impregnated silicic acid. This was conducted in the manner previously described⁷ using adsorbent 4% by weight in TNF and spectral analysis of the effluent at 226 and 298 $m\mu$ for the mixture I-II and at 227 and 296 $m\mu$ for the mixture IV-V. In each case the conjugated isomer was more tenaciously adsorbed (retention ratios I/II = 2.4; IV/V = 2.0-2.5) and the concentration of the unconjugated isomer reached a transient maximum

TABLE IV
FRACTIONS COLLECTED IN RUN 42

Total Wt. of Effluent Fraction ^a (g.)	Wt. of Residue (mg.)	M.p. of Residue (°C.)
132	3	132-135
127	4	134-136
524	13	136-138
254	2	132.5-136
289	1	133.5-136
301	1	128-135
324	1	120-129
155	None ^b	—
315	1	180-188
272	2	188-192
211	2	190-192
949	4	183.5-190.5
218	3	185-192
307	3	186-190.5
210	2	186-192
242	3	181-188
ca. 1200 ^c	5	181-188

^a Fractions are listed in order of appearance. The first fractions, which yielded no residue, are not listed. ^b Separation of the two components was facilitated by the fact that two distinct, light blue fluorescent zones could be seen throughout the development process. ^c Eluted with 3% benzene-petroleum ether.

in the effluent which was slightly greater than that in the influent. With the mixture IV-V an orange zone preceded a red zone down the column until the former was eluted and the latter had expanded to occupy the entire column.⁶⁶ With the mixture I-II the column became red-orange. In a test run using only V in the influent the column became orange and no spectral evidence was found for the presence of IV in the effluent.

EUGENE, ORE.

(66) This spectacular phenomenon is readily interpreted in terms of a preceding zone containing essentially only V (forms an orange TNF complex) and a following expanding zone containing both V and IV (forms an orange red TNF complex, cf. ref. 35).