THIN-LAYER CHROMATOGRAPHY OF MONOALKYL- AND POLYMETHYLARENES ON ALUMINA

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On the basis of earlier qualitative studies on relative adsorbabilities of arenes and their alkyl and alkylene derivatives in liquid–solid column chromatography (LSC), we[1] proposed that the arene system is adsorbed preferentially flatwise on to the surface of the chromatographic alumina adsorbent used. We ascribed the adsorption process to an interaction between the electron-attracting (polarizing) alumina surface and the π-electronic system of the arene. Although we suggested that *bona-fide* π-complexation is involved, it has been shown by SNYDER[2] that, at least in most arenes thus far studied, the interaction is better described simply as a polarization phenomenon (without attendant or significant aspects of electron-transfer, as is implied in the term "π-complex"). The effect of an alkyl or alkylene substituent in altering adsorbability of the parent arene was ascribed[1] to the operation of two opposing factors, namely (1) donation of electronic charge to the aromatic ring, and (2) steric hindrance to adsorption. It was noted that, when steric hindrance is negligible (e.g. for a methyl group with its carbon atom effectively coplanar with the arene system), the substituent enhances adsorbability, while when steric hindrance is appreciable (e.g. for a methyl substituent which projects out of the plane of the ring to a considerable extent or for a bulky substituent (such as *tert.*-butyl) factor (1) may be nullified or overwhelmed by factor (2), with a resultant lack of change or with a resultant decrease in adsorbability (respectively). SNYDER[3] reported quantitative data (relative retention volumes in linear elution adsorption chromatography) for adsorbabilities of various alkyl benzenes. Limited studies on other systems have been made. The present paper is a report of our quantitative results from thin-layer chromatography (TLC) on alumina of alkylarenes in the naphthalene, anthracene, phenanthrene, and azulene series. Included are data on polymethylarenes in the first and second of these systems. Correlation of our data with those reported by others is also presented. It should, however, be noted that we limit the scope of this correlation and discussion to the use of alumina as adsorbent and of a hydrocarbon as solvent.

EXPERIMENTAL

Starting materials

Most of the adsorbate hydrocarbons used were available in purified form from previous studies[1,4,5]. 9-n-Butyl- and 9-isobutylphenanthrenes were gifts from ANET

AND BAVIN[6]. Several polymethylated naphthalenes (1,2,3- and 1,2,4-trimethyl, 1,2,4,7- and 1,2,3,4-tetramethyl, 1,2,3,4,6-pentamethyl, and 1,2,3,4,6,7-hexamethyl) were available from current research in our laboratory[7]. 4,5-Methylene- and the three methylphenanthrenes, as well as the azulenes of Table VIII, were purchased from Aldrich Chemical Co. Six substituted phenanthrenes and 1-isopropylnaphthalene (as follow) were synthesized especially for this work.

9-n-Nonylphenanthrene. 9-Bromophenanthrene* was converted to 9-cyanophenanthrene by the method of MOSETTIG AND VAN DE KAMP[9] except that the crude product was extracted into benzene (rather than ethanol), average yield 85%, m.p. 108–110°. A solution of 20.3 g of the cyano compound in 200 ml of benzene was added dropwise to the Grignard reagent prepared from 26 ml of *n*-octyl bromide, 3.65 g of magnesium, and 175 ml of ether. The mixture was stirred and refluxed for 24 h and then poured into excess, ice-cold 20% aqueous ammonium chloride solution. The organic phase (combined with ether extracts of the aqueous phase) was extracted with eight 100-ml portions of conc. hydrochloric acid. Combined acid extracts were diluted with 1.2 l of water, heated in a beaker on a steam bath (to evaporate organic solvents), refluxed for 2 h (to hydrolyze the ketimine salt), cooled, and extracted with ether. The residue from evaporation of the ether extract was recrystallized from methanol (with charcoal treatment) to give 25.8 g (81%) of *9-n-nonanoylphenanthrene*, obtained as yellow needles, m.p. 63–65° (changed to 64–65° on recrystallization), I.R. absorption (in Nujol) at 6.0 μ. Analysis: Calcd. for $C_{23}H_{26}O$: C, 86.74; H, 8.23. Found*, C, 86.96; H, 8.47.

Reduction of the preceding ketone (12.7 g) was effected by refluxing it with a mixture of sodium hydroxide (5.6 g), hydrazine hydrate (12.5 ml), and triethylene glycol (100 ml) according to the general procedure of HUANG-MINLON[10]. The residue from evaporation of the ether extract of the acidified reaction mixture was crystallized from ethanol (with charcoal treatment) to yield 8.6 g (71%) of yellow 9-n-nonylphenanthrene, m.p. 79–81°. White, fibrous needles (m.p. 81–82°) were obtained by passing a solution of this crude product in petrol (40–50°) through a column of Alcoa F-20 alumina, evaporation of the effluent, and recrystallization of the residue. Analysis: Calcd. for $C_{23}H_{28}$: C, 90.73; H, 9.27. Found: C, 90.59; H, 9.40.

9-n-Heptadecylphenanthrene. The foregoing procedure was followed except that the Grignard reagent (from *n*-hexadecyl bromide) was stirred and refluxed with the cyano compound for 48 h. However, very little intermediate ketone (3.5%) was isolated from the extract of the organic phase with conc. hydrochloric acid. Most of the ketone remained in the organic phase, which was washed with water, dried, and evaporated to leave a yellow residue. Recrystallization of the residue from ethanol gave a 92% yield (total) of *9-n-heptadecanoylphenanthrene*, obtained as cream-colored, fine needles, m.p. 79–81° (raised to 82–83° on recrystallization), I.R. absorption (in Nujol) at 6.0 μ. Analysis: Calcd. for $C_{31}H_{42}O$: C, 86.45; H, 9.83. Found: C, 86.56; H, 10.04.

After reduction of this ketone and chromatographic purification of the resultant hydrocarbon there was obtained a 43% yield of white fluffy needles, m.p. 78–79.5° (raised to 83–84° on recrystallizations from ethanol and then from ethyl acetate). Analysis: Calcd. for $C_{31}H_{44}$: C, 89.36; H, 10.64. Found: C, 88.94; H, 10.88.

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* Elemental analyses by Micro-Tech Laboratories, Skokie, Ill.

2-Ethylphenanthrene (m.p. 65–66°, yield 50 %) and 9-ethylphenanthrene (m.p. 58–60°, yield 71 %) were obtained from the corresponding acetylphenanthrenes (Aldrich Chemical Co.) by Wolff-Kishner reductions in the preceding fashion. 9-Isopropenylphenanthrene (yellow liquid, b.p. 147–150°/0.3 mm, 50 % overall yield, positive test with aqueous permanganate) was synthesized and purified in a manner analogous to that previously reported for the synthesis of 9-(2-butenyl)phenanthrene[11]. Hydrogenation of the isopropenyl derivative to 9-isopropylphenanthrene (yellow liquid, b.p. 141–144°/0.5 mm, 65 % yield, negative test with aqueous permanganate) was effected at room temperature and one atm pressure of hydrogen gas by means of Raney nickel catalyst[12] in ethyl acetate solution.

1-Isopropylnaphthalene[13] (b.p. 138–145°/15 mm) was converted to its *1,3,5-trinitrobenzene adduct*, obtained as yellow needles (after recrystallization from ethanol) m.p. 101–101.5°. Analysis: Calcd. for $C_{19}H_{17}N_3O_6$: C, 59.53; H, 4.47; N, 10.96. Found: C, 59.27; H, 4.61; N, 11.13. Dissociation of the molecular compound by means of alumina and then distillation gave purified hydrocarbon, b.p. 122–124°/10 mm; n_D^{15} 1.5979 (lit. n_D^{15} 1.5728).

Cyclohexane (reagent grade) was distilled from P_2O_5, stored over Na wire, and used as the main chromatographic solvent. *tert.*-Butylbenzene (reagent grade) was distilled and used directly.

Chromatographic procedure

A humidity chamber was devised by adaptation of a dry-box to the purpose[14]. This chamber, 86 (long) × 58 × 58 cm (more than adequate in size), was fitted with glass windows on top and over the upper half of the front side, a pair of attached long rubber gloves for manipulations inside the chamber by the operator, a large outside door on one end and, on the other end, a cubic side chamber (27 cm on a side, fitted with an inner door to the main chamber and another door to the laboratory environment). The humidity chamber was prepared for use by placing therein a large, shallow tray of a saturated aqueous solution of an inorganic salt[15] (in order to give a relative humidity of ca. 10–30 % at room temperature[16]), glass TLC developing tanks with covers and containing cyclohexane or cyclohexane–*tert.*-butylbenzene as solvent, standard solutions (4·10⁻² M for naphthalene, 2·10⁻² M for all other substrates, in benzene as solvent) of adsorbates in stoppered flasks, wash solvent, and necessary utensils. Humidity equilibration was allowed to occur over a period of 10–24 h.

Meanwhile, pyrex glass plates (20 × 20 cm) were cleaned and coated with Aluminum Oxide G as previously described[17]. The plates (stacked in a rack) were heated at 130° for 3–12 h, then at 260 ± 5° for 24 h, and finally again at 130° for 3–12 h. They were immediately transferred to the humidity chamber where they were equilibrated for 24–48 h. Just before use a narrow zone of alumina was removed from along each edge of the plate and two spots (each made from a 1-μl aliquot of stock solution; except for naphthalene only, for which a 2-μl aliquot was used) for each of eight different compounds (including the parent arene as a reference) were deposited from a microsyringe at 1-cm intervals along the starting line (3 cm from the bottom edge of the plate). The order of the samples (from left to right) was the same on each half of the plate. The plate was conditioned for 30 min in the atmosphere of the TLC tank and then run until the solvent front reached 10 cm beyond the starting line. Plates were removed from the humidity chamber (to the room proper) by way of the

side chamber. Spots were detected as rapidly as possible by means of ultraviolet light (from a UVS-11 Mineralight, Ultra-Violet Products, Inc., San Gabriel, Calif.) for naphthalene, anthracene, and phenanthrene compounds or by spraying with a solution of $SbCl_5$ in CCl_4[18] (1:2 by vol.) and subsequent warming in an oven for 5–10 min for azulene compounds. Compounds investigated were divided into six sets, as given in Tables II, III and V–VIII. Specific experimental conditions used in each set are indicated in these tables. When one adsorbate appears in two different tables it was run in two separate, independent series of experiments. R_F values were obtained for the centers of the spots and were considered acceptable for any particular compound on the particular plate only if they agreed within 0.02. A batch of three to nine acceptable plates was produced for each substituted arene.

Selection of separability parameters

The separability of alkylarenes (as measured by the range of R_F values in a set of compounds) is a function of both the activity of the alumina and the eluting power of the solvent. In order to minimize competition between the solvent and the adsorbate in the absorption process, we first used the non-polar cyclohexane (devoid of un-saturation and non-bonding electrons) as solvent and adjusted the activity of the alumina by variation of the equilibrium atmospheric humidity until the range of R_F values found was maximal. For the naphthalene system (least strongly adsorbed of those investigated) 10 % relative humidity (the minimum practical percentage available for equilibration in our apparatus) was used. With the more strongly adsorbed anthracene and phenanthrene compounds, best separation was achieved with 30 % relative humidity. Various attempts to increase the eluting power of the solvent (*e.g.* by use of benzene, *tert.*-butylbenzene, chloroform, or carbon tetra-chloride—alone or in admixture with cyclohexane), without simultaneous increase in activity of alumina, decreased total R_F range. However, separability of alkylanthra-cenes and alkylphenanthrenes was tripled by a combination of 10 % relative humidity and 9:1 (by volume) cyclohexane–*tert.*-butylbenzene (most effective of all binary solvents tried). This same solvent pair (optimal ratio 11.5:1) nearly doubled sepa-rability of alkylnaphthalenes when *ca.* 0% humidity (*i.e.* when anhydrous $CaSO_4$, rather than a salt solution) was used in the chamber, but, at the same time, repro-ducibility of R_F values was markedly decreased. Efforts to improve separability of methylnaphthalenes and methylanthracenes (short of using anhydrous conditions) were unsuccessful.

Handling of data

Our method of handling the crude experimental data is illustrated by means of Table I for a typical system of compounds (the methylanthracenes). First the average of the observed R_F values for all acceptable spots of one compound on a particular plate (*e.g.* plate No. 1) was calculated and recorded as R_F(Exptl). Let us distinguish between these values for the parent arene and for some other adsorbate by designating them as R_P and R_A, respectively. Now a reference plate (No. 5 in Table I) was selected and all R_F(Exptl.) values from the other plates were standardized to this reference plate by means of eqn. (1), as previously described[17].

$$\delta R_A = \delta R_P \left[\frac{R_A(1 - R_A)}{R_P(1 - R_P)}\right] \qquad (1)$$

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TABLE I

EXPERIMENTAL AND STANDARDIZED R_F VALUES FOR TLC OF METHYLANTHRACENES[a]

Position(s) of methyl substituent(s)	Plate No. 1		Plate No. 2		Plate No. 3		Plate No. 4		Plate No. 5[b]	Plate No. 6	Plate No. 7		Median standardized R_F[c]
	Exptl.	Stand.	Exptl.	Stand.	Exptl.	Stand.	Exptl.	Stand.	Exptl.	Exptl.	Exptl.	Stand.	
None	0.39	0.40	0.39	0.40	0.43	0.40	0.43	0.40	0.40	0.40	0.42	0.40	0.40
1	0.35	0.36			0.39	0.36			0.36		0.38	0.36	0.36
2	0.33	0.34			0.37	0.34			0.33		0.37	0.35	0.34
9	0.34	0.35			0.38	0.35			0.32		0.36	0.34	0.34
2,3	0.27	0.28	0.26	0.27	0.31	0.28	0.30	0.27	0.27	0.27	0.31	0.29	0.28
2,6	0.28	0.29			0.33	0.30			0.29		0.32	0.30	0.30
2,7	0.29	0.30			0.34	0.31			0.30		0.34	0.32	0.31
9,10	0.30	0.31	0.30	0.31	0.34	0.31	0.33	0.30	0.30	0.29	0.33	0.31	0.30
2,3,9			0.23	0.24			0.26	0.24		0.23			0.24
2,6,9			0.25	0.26			0.28	0.26		0.25			0.26
2,3,6,7			0.15	0.16			0.18	0.16		0.15			0.16
2,3,9,10			0.20	0.21			0.21	0.19		0.19			0.20
2,3,6,7,9,10			0.12	0.12			0.14	0.13		0.11			0.12

[a] See Experimental section on handling of data for the significance and derivation of these data.

[b] Taken as reference plate.

[c] Reported simply as R_F in Table III. R_F values reported in Tables II and V–VIII were derived in the same way.

These standardized data are recorded in Table I as R_F(Stand.). The median standardized R_F value was then recorded and used simply as R_F in further calculations and comparisons (as in Table III). Deviation from the median value was $\leqslant$ 0.02—even when cases with δR_F values as large as 0.16 were included.

Our results for polymethylarenes are given in Tables II and III; for monoalkylarenes, in V–VII; and for a few substituted azulenes, in VIII. Other data reported in the tables were obtained as follows: R_M = log $[(1/R_F) - 1]$, $\Delta R_M = R_M$ for the substituted arene minus R_M for its parent arene, m is the number of carbon atoms in a straight-chain alkyl substituent, n is the number of methyl substituents on the arene nucleus, n' is the number of vicinal methyl arrangements on the arene nucleus, σ^* is TAFT's polar substituent constant[19], $c = +0.49$, E_s is the steric substituent constant[19] for the adsorption process, and ρ^* is the reaction constant for the adsorption process. Further elaboration on some of these items is given in the Discussion and in the Appendix. ρ^* and E_s values for each monoalkylarene system were calculated from eqn. (2) (see Appendix). Thus, E_s is first

$$\Delta R_M = \rho^*(\sigma^* - c) + E_s \tag{2}$$

taken as zero for the methyl substituent in the set and, thence, ρ^* for this set is calculated. Next this value of ρ^* is used to ascertain a value of E_s for every other substituent in the set. Calculation of ρ^* for polymethylarenes is made by means of eqn. (3) (see Discussion).

$$\frac{\Delta R_M}{n} = -0.49\,\rho^* \tag{3}$$

DISCUSSION

Observation of Tables II and III shows that, in general, for polymethylnaphthalenes and polymethylanthracenes adsorbability on alumina in TLC increases (*i.e.* R_F decreases) as the number of substituents n increases. Similar, but more limited, results (on alumina) were reported for methylated naphthalenes by KUCHARCZYK et al.[20] in TLC (solvent n-hexane), by KARR et al.[21] in LSC (eluent cyclohexane), and by us[22] in gas–solid adsorption chromatography. The same trend was also observed for the benzene series in LSC by us[1] (eluent petrol) and by SNYDER[3] (eluent n-pentane, see Table IV). In the azulene system, however, insertion of a methyl group at C-1 did not measurably alter the R_F value from that of the parent arene though insertion of three methyl groups decreased R_F considerably (see Table VIII). In the fluorene system the expected effect of increasing adsorbability by means of an in-planar methyl substituent (at C-1, C-2, or C-3) and of decreasing it by means of an out-of-planar projecting methyl group (at C-9) was found by KARR et al.[23] (eluent cyclohexane) in LSC. However, BERGMANN et al.[24] found that fluorene was adsorbed more strongly than any of its monomethyl derivatives (not separated) when a thin layer of mildly activated alumina was used. It seems probable that these latter workers were actually observing partition chromatography, rather than adsorption chromatography, since their R_F values for Silica Gel G and Alumina G with the same solvent n-heptane were closely similar[25].

Some inconsistencies also exist in data obtained in the naphthalene series.

TABLE II

TLC DATA FOR METHYLNAPHTHALENES[a]

Position(s) of methyl substituent(s)	R_F[b]	R_M	n	n'	$\Delta R_M/n$
None	0.53	—0.05	0	0	—[c]
1	0.49	+0.02	1	0	0.07
2	0.49	0.02	1	0	0.07
1,2	0.42	0.14	2	1	0.10
1,3	0.47	0.05	2	0	0.05
1,4	0.46	0.07	2	0	0.06
1,5	0.47	0.05	2	0	0.05
1,6	0.46	0.07	2	0	0.06
1,7	0.46	0.07	2	0	0.06
1,8	0.46	0.07	2	0	0.06
2,3	0.44	0.11	2	1	0.08
2,6	0.47	0.05	2	0	0.05
2,7	0.46	0.07	2	0	0.06
1,2,3	0.32	0.33	3	2	0.13
1,2,4	0.40	0.18	3	1	0.08
1,3,7	0.40	0.18	3	0	0.08
1,4,5	0.38	0.21	3	0	0.09
2,3,5	0.35	0.27	3	1	0.11
1,2,3,4	0.25	0.48	4	3	0.13
1,2,4,7	0.31	0.35	4	1	0.10
1,2,3,4,6	0.21	0.58	5	3	0.13
1,2,3,4,6,7	0.14	0.79	6	4	0.14
				Average	0.08[d]

[a] Temperature 27.8 ± 0.8°; humidity equilibration (with saturated aqueous $ZnCl_2$ solution) ca. 10 %; solvent cyclohexane.
[b] Median standardized R_F value.
[c] Taken as standard of comparison. An uncertainty of 0.01 in R_F will produce an uncertainty ≤ 0.01 in the values of this column (except for the monomethyl derivatives, where the latter uncertainty ≈ 0.02).
[d] Corresponds to $p^* = —0.2$, as per eqn. (3).

Thus, OGNYANOV[26] reported slightly higher R_F values for the monomethylnaphthalenes than for the parent naphthalene itself, but he had difficulty in obtaining reproducible data. SNYDER[3] found that 1-methylnaphthalene was considerably more strongly retained on a column than was the 2-isomer, in contrast to our observation that these isomers had the same R_F values and to the observation of KUCHARCZYK that the order of adsorbability was reversed. For the five dimethylnaphthalenes examined by KUCHARCZYK the range in R_F values (from 0.39 to 0.52) was greater than was that of ours (from 0.44 to 0.47) for the same isomers. It is thus difficult to make a meaningful comparison of the relative orders found.

The R_F values for monoalkylarenes (and a few allied compounds) investigated here (see Tables V–VIII) are, in general, consistent with the results previously reported by us in LSC[1]. Thus, although the methyl substituent in these cases always increases adsorbability (lowers R_F) with respect to the parent arene, a larger alkyl group initiates a reversal in the overall trend. Thus, for the arene nuclei naphthalene, anthracene, and phenanthrene (as well as for the one case studied in the azulenes, cf. results of ATTAWAY et al.[27]) the order of increasing adsorbability as fostered by alkyl substituents is Me > Et ≈ H ≥ n-Pr > i-Pr > t-Bu. One also sees that in the series

of n-alkyl substituents adsorbability decreases with increasing length of the alkyl chain. This latter generalization is opposite to that found by SNYDER[3], as reproduced in Table IX (vide infra).

Quantitatively, we have treated our R_F data for monoalkylarenes in terms of a TAFT relationship, as given in eqn. (2). The use of this relationship (which involves σ^* rather than some analogous substituent constant of the Hammett type) is theoretically justified on the basis that the substituent is attached directly to the reaction site in the molecule[19], i.e. to the π-electronic system of the arene. Experimentally, use of σ^* is justified inasmuch as R_F did not change significantly with change in the position of substitution of a particular alkyl group in a particular arene system. Although this experimental observation is not a crucial point (and might not hold for some of the bulkier groups) it does indicate that resonance effects (hyperconjugation) for the substituent may be ignored. In our calculations we make the assumption that the methyl group shows no steric hindrance to adsorption ($E_s = 0$) and that ρ^* is constant for each set of data, while E_s varies with the substituent. In view of the fact that adsorbability should be fostered by increased availability of electron density on the π-system (if the alumina surface is indeed electron-attracting) one should find that $\rho^* < 0$, as is, in fact, the case. Somewhat surprisingly, however, for all of our sets of data (except the azulenes) and for the data of SNYDER ρ^* remains relatively constant, at -0.1 to -0.2 (see footnotes to the Tables). The major criterion for the successful adaptation of eqn. (2) to our data is that one should find an internally consistent series of E_s values which can be rationalized in terms of our proposed model for preferential flatwise adsorption of the arene ring onto the alumina surface. Observation of calculated E_s data (which should become increasingly more negative as steric

TABLE III

TLC DATA FOR METHYLANTHRACENES[a]

Position(s) of methyl substituent(s)	R_F[b]	R_M	n	n'	$\Delta R_M/n$
None	0.40	0.18	0	0	—[c]
1	0.36	0.25	1	0	0.07
2	0.34	0.29	1	0	0.11
9	0.34	0.29	1	0	0.11
2,3	0.28	0.41	2	1	0.12
2,6	0.30	0.37	2	0	0.10
2,7	0.31	0.35	2	0	0.09
9,10	0.30	0.37	2	0	0.10
2,3,9	0.24	0.50	3	1	0.11
2,6,9	0.26	0.45	3	0	0.09
2,3,6,7	0.16	0.72	4	2	0.14
2,3,9,10	0.20	0.60	4	1	0.11
2,3,6,7,9,10	0.12	0.87	6	2	0.12
				Average	0.10[d]

[a] Temperature 28.5°; humidity equilibration (with saturated aqueous $CaCl_2$ solution) ca 30 %; solvent cyclohexane.
[b] Median standardized R_F value, as given in Table I. R_F range: 0.26 for 20 % humidity; 0.28 for 30 % (used here); 0.14 for 52 %.
[c] See footnote c in Table II.
[d] Corresponds to $\rho^* = -0.2$, as per eqn. (3).

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TABLE IV

LSC DATA FOR POLYALKYLBENZENES[a]

Position(s) of alkyl substituent(s)	$\underline{R}^*$	$Log \underline{R}^{*b}$	n	n'	$Log \underline{R}^*/n$
For methyl substituents					
None	(1.00)[c]	0	0	0	—[c]
1	1.20	0.079	1	0	0.079
1,2	1.75	0.243	2	1	0.122
1,3	1.32	0.121	2	0	0.061
1,4	1.34	0.127	2	0	0.064
1,2,3	2.52	0.401	3	2	0.134
1,2,4	1.84	0.265	3	1	0.088
1,3,5	1.41	0.149	3	0	0.050
1,2,3,5	2.47	0.393	4	2	0.098
1,2,4,5	2.49	0.396	4	2	0.099
1,2,3,4,5	4.25	0.628	5	4	0.126
1,2,3,4,5,6	6.0	0.78	6	6	0.13
		Overall average			0.096
		Average for cases of $n' = 0$			0.064[d]
For ethyl substituents					
None	(1.00)[c]	0	0	0	—[c]
1	1.11	0.045	1	0	0.045
1,2	1.47	0.167	2	1	0.084
1,3	1.20	0.079	2	0	0.040
1,4	1.15	0.061	2	0	0.031
		Average for cases of $n' = 0$			0.039[e]

[a] Data for $\underline{R}^*$, the relative equivalent retention volume, are taken from Table VIII in reference 3 and refer to n-pentane as eluent and 0.5 % H_2O–Al_2O_3 as absorbent.

[b] As indicated in reference 3, $log \underline{R}^* = R_M$ (and equals ΔR_M, since $log \underline{R}^*$ for the parent arene = 0).

[c] Taken as standard of comparison.

[d] Corresponds to $\rho^* = -0.13$, as per eqn. (3).

[e] Combined with values of E_s and (σ^*-c) for the ethyl group from Table IX one calculates a value of $\rho^* = -0.15$.

hindrance to adsorption increases) in Tables V–VIII shows that this criterion holds, without exception. Thus increasing the length of an n-alkyl chain (which allows the alkyl group to whip around to a greater extent into the region between the alumina surface and the non-adsorbed arene nucleus) makes E_s more negative. Also branching of the side chain at the α-carbon atom to the ring (as for the i-Pr and t-Bu substituents) increases steric hindrance markedly. Moving the branching to the β-carbon atom decreases this effect (cf. i-Bu and s-Bu in Table VI). Of the non-alkyl substituents investigated the allyl, phenyl, and isopropenyl groups are unsaturated. For the allyl substituent (for which the value of σ^* is known only approximately) E_s appears to be positive, consistent with the enhanced adsorption which one finds from the presence of a non-conjugated C=C in the chain. As with the alkyl groups used, R_F for the allyl substituent did not change significantly with the position of substitution on the ring. For the isomeric phenylanthracenes, on the other hand, resonance interaction with the anthracene ring is possible. As the phenyl ring is twisted out of coplanarity with the anthracene moiety, however, resonance interaction (including, as a special part, the effective size of the π-electronic system) will decrease, while steric hindrance to adsorption will increase. By our method of handling the data all of these factors

should show up in the E_s term, in the algebraic order of 9-phenyl < 1-phenyl < 2-phenyl (as is found). The 9-isopropenyl group (probably twisted out of coplanarity with the anthracene ring to a large extent) shows slightly greater adsorbability than does the 9-isopropyl group in the same system.

From Tables V and VI one notes that marked differences in ΔR_F (for the individual compounds) result from changing the chromatographic conditions from cyclohexane and 30% relative humidity to tert.-butylbenzene–cyclohexane and 10% relative humidity. We believe that these differences may be ascribed largely to the change in solvent. Thus, cyclohexane is a poor competitor with all of the alkylarenes for adsorption on alumina, while tert.-butylbenzene can compete more effectively with those compounds which bear bulky substituents than it can with the parent arenes and their derivatives with smaller alkyl substituents. The improved separation of 9-phenyl- and 1-phenylanthracenes in the binary solvent may be another manifestation of this selective competition.

If one tries to apply eqn. (2) and our interpretations to the results of SNYDER[3] for the alkylbenzenes and alkylnaphthalenes (cf. Table IX) one finds inconsistencies. Thus, algebraically E_s for t-Bu $> E_s$ for s-Bu and E_s increases with increasing length of an n-alkyl side chain. The latter of these effects implies that the entire alkyl chain

TABLE V

TLC DATA FOR ALKYL- AND PHENYLANTHRACENES

Substituent[a]	(σ^*-c)	Mobile phase				
		C_6H_{12}-t-BuO $(9:1)$[b]			C_6H_{12}[c]	
		R_F[d]	ΔR_M	E_s	R_F[d]	E_s
2-tert.-Butyl	—0.79	0.52	—0.34	—0.4$_5$	0.49	—0.1$_5$
9-m-Decyl	—0.62[e]	0.47	—0.26	—0.3$_5$	0.49	—0.1$_3$
9-Phenyl	+0.11	0.42	—0.17	—0.1$_5$	0.45	0.0$_0$[f]
9-m-Propyl	—0.61	0.36	—0.06	—0.1$_5$	0.46	—0.0$_8$
2-Ethyl	—0.59	0.35	– 0.04	—0.1$_2$	0.45	—0.0$_6$
None	0[g]	0.33	0.00	0[g]	0.46	0[g]
1-Phenyl	+0.11	0.31	+0.04	+0.0$_6$[h]	0.39	+0.1$_1$[h]
1-Methyl	—0.49	0.30	0.06	0[i]	0.43	0[j]
9-Methyl	—0.49	0.30	0.06	0[i]	0.42	0[j]
2-Methyl	—0.49	0.28	0.10	0[i]	0.42	0[j]
2-Phenyl	+0.11	0.10	0.65	+0.6$_7$[h]	0.22	+0.4$_7$[h]

[a] On anthracene ring system.

[b] Temperature 23 ± 0.5°; humidity equilibration (with saturated aqueous ZnCl$_2$ solution) ca. 10%.

[c] Temperature 30 ± 1°; humidity equilibration (with saturated aqueous CaCl$_2$ solution) ca. 30%.

[d] Median standardized R_F value.

[e] Based on the assumption that σ^* for n-decyl equals that for n-butyl.

[f] This value implies that electronic and steric effects of the 9-phenyl group exactly counterbalance one another in this chromatographic process. See also footnote h.

[g] Taken as standard of comparison.

[h] Positive values for E_s imply that electronic (attractive) effects between the substituent and the adsorbent overwhelm steric (repulsive) effects between them.

[i] This assumed value, plus an average value of ΔR_M for the three methylanthracenes of 0.07, leads to $\rho^* = $ —0.1$_2$ (as per eqn. (2)) for results under conditions given in footnote b.

[j] $\rho^* = $ —0.1$_3$ under conditions given in footnote c (cf. footnote i).

TABLE VI

TLC DATA FOR ALKYLPHENANTHRENES

Substituent[a]	(σ* −c)	Mobile phase				
		$C_6H_{12}-t-BuO$ (9:1)[b]			$C_{10}H_{12}$[c]	
		R_F[d]	ΔR_M	E_R	R_F[d]	E_R
9-n-Heptadecyl	−0.62[e]	0.64	−0.48	-0.5_5	0.57	-0.2_0
9-sec.-Butyl	−0.70	0.57	−0.36	-0.4_8	0.57	-0.2_1
9-Isopropyl	−0.68	0.57	−0.36	-0.4_8	0.57	-0.2_0
9-n-Nonyl	−0.62[e]	0.54	−0.30	-0.3_7	0.52	-0.1_1
9-Isobutyl	−0.62	0.51	−0.25	-0.3_2	0.53	-0.1_3
9-Isopropenyl	—	0.51	−0.25	—	0.53	—
9-Cyclopentyl	−0.69	0.46	−0.16	-0.2_1	0.50	-0.0_4
9-n-Butyl	−0.62	0.44	−0.13	-0.2_0	0.50	-0.0_4
2-Ethyl	−0.59	0.40	−0.05	-0.1_2	0.48	-0.0_1
9-Ethyl	−0.59	0.39	−0.04	-0.1_1	0.49	-0.0_5
None	0[f]	0.37	0.00	0[f]	0.50	0[f]
3-Methyl	−0.49	0.35	+0.04	0[g]	0.47	0[h]
1-Methyl	−0.49	0.34	0.06	0[g]	0.47	0[h]
4,5-Methylene	—[i]	0.34	0.06	0[j]	0.48	0[j]
2-Methyl	−0.49	0.33	0.08	0[g]	0.46	0[h]

[a] On phenanthrene ring system.

[b] Temperature 24 ± 0.5°; humidity equilibration (with saturated aqueous $ZnCl_2$ solution) ca. 10%.

[c] Temperature 25 ± 2°; humidity equilibration (with saturated aqueous $CaCl_2$ solution) ca. 30%.

[d] Median standardized R_F value.

[e] Based on the assumption that σ* remains constant for n-alkyl groups of four or more carbons.

[f] Taken as standard of comparison.

[g] This assumed value, plus an average value of ΔR_M for the three methylphenanthrenes of 0.06, leads to $p^* = -0.1_2$ (as per eqn. (2)) for results under conditions given in footnote b.

[h] $p^* = -0.1_2$ under conditions given in footnote c (cf. footnote g).

[i] Calculated value as (per eqn. (2)) is −0.4 ± 0.1.

[j] Assumed value.

per se enhances adsorbability, e.g. through Van der Waals dispersion forces[24] between the chain and the adsorbent surface. Quantitatively, one can check for consistency with this suggestion by plotting log $\underline{R}^*$ versus m, the number of carbon atoms in the normal chain, and examining the plot for linearity. Alternatively, the ratio log $\underline{R}^*$/m should remain positive and nearly constant as m increases beyond a very small number. Examination of the last column in Table IX shows that this is, indeed, the situation for m > 1, i.e. for a chain longer than a methyl group. SNYDER[22] has suggested that with a combination of active alumina and weak solvent (pentane), as used in his experiments, the "methylene group in an alkyl chain competes favorably with solvent molecules for a place on the alumina surface. Consequently, most of the carbon atoms of an alkyl chain are adsorbed and sample adsorption increases with alkyl chain length". On the other hand, our TLC data on alkylarenes (obtained with less active alumina and a more polarizable solvent) fit a model (also proposed by SNYDER[2]) wherein only the first carbon next to the ring lies in the adsorption layer and the remainder of the chain protrudes into the bulk of the mobile phase.

TABLE VII

TLC DATA FOR ALKYL- AND ALLYLNAPHTHALENES

Substituent[a]	$(\sigma^* -c)$	Mobile phase		
		C_6H_{12}[b]		$C_6H_{12}\text{-}t\text{-}Bu\emptyset$ $(II.5:I)$[c]
		R_F[d]	E_8	R_F[c]
1-tert.-Butyl	—0.79	0.57	—0.1$_7$	0.67
2-tert.-Butyl	—0.79	0.57	—0.1$_7$	0.67
1-Isopropyl	—0.68	0.56	—0.1$_5$	0.63
2-Isopropyl	—0.68	0.56	—0.1$_5$	0.62
2-n-Propyl	—0.61	0.54	—0.1$_0$	0.61
1-n-Propyl	—0.61	0.54	—0.1$_0$	0.60
None	0[f]	0.53	0[f]	0.56
2-Ethyl	—0.59	0.52	—0.0$_7$	0.56
1-Ethyl	—0.59	0.51	—0.0$_5$	0.56
1-Methyl	—0.49	0.49	0[g]	0.54
2-Methyl	—0.49	0.49	0[g]	0.53
1-Allyl	—0.31[h]	0.47	+0.0$_6$[i]	0.49
2-Allyl	—0.31[h]	0.46	+0.0$_8$[i]	0.49

[a] On naphthalene ring system.

[b] Temperature 27.5 ± 0.5°; humidity equilibration (with saturated aqueous $ZnCl_2$ solution) ca. 10 %.

[c] Temperature 24 ± 1°; without humidity equilibration (i.e with anhydrous $CaSO_4$ in dry box).

[d] Median standardized R_F value.

[e] Under the conditions used R_F values are not reproducible (in contrast to runs with humidity equilibrated plates) but again the general order of adsorbabilities is maintained. The range and scale of the data presented were taken from a plate in which the separation of methyl and tert.-butyl derivatives was a maximum. A composite interpolation was then made for each compound. With few exceptions, inversions in order occurred only for compounds differing by 0.02 R_F units or less.

[f] Taken as standard of comparison.

[g] Assumed value, from which one obtains $\rho^* = -0.1_4$ (as per eqn. (2)).

[h] See reference 5 for an estimated value of σ^* for this substituent.

[i] See footnote h in Table V.

TABLE VIII

TLC DATA FOR ALKYLAZULENES[a]

Substituent(s)[b]	R_F[c]	ΔR_M
1,4-Dimethyl-7-isopropyl[d]	0.50	—0.05
None	0.47	0[e]
1-Methyl	0.47	0.00
4,6,8-Trimethyl	0.33	+0.36

[a] Temperature 24.5°; humidity equilibration (with saturated aqueous KOAc solution) ca. 20 %.

[b] On azulene ring system.

[c] Median standardized R_F value.

[d] Common name, guaiazulene.

[e] Taken as standard of comparison.

TABLE IX

LSC DATA FOR ALKYLBENZENES AND ALKYLNAPHTHALENES[a]

Substituent	$\underline{R}^*$	$log\ \underline{R}^{*}$ [b]	$(\sigma^* - c)$	E_s	$log\ \underline{R}^*/m$
For benzene system					
None	(1.00)[c]	0	0[c]	0[c]	
Methyl	1.20	0.079	—0.49	0[d]	0.079
Ethyl	1.11	0.045	—0.59	—0.05	0.023
n-Propyl	1.18	0.072	—0.61	—0.03	0.024
Isopropyl	0.96	—0.018	—0.68	—0.13	
n-Butyl	1.24	0.093	—0.62	—0.01	0.023
Isobutyl	1.13	0.053	—0.62	—0.05	
sec.-Butyl	0.93	—0.032	—0.70	—0.14	
tert.-Butyl	1.01	0.004	—0.79	—0.12	
n-Octyl	1.46	0.164	—0.62[e]	+0.07	0.021
n-Decyl	1.52	0.182	—0.62[e]	0.08	0.018
n-Dodecyl	1.69	0.228	—0.62[e]	0.13	0.019
n-Eicosyl	1.90	0.279	—0.62[e]	0.18	0.014
Cyclohexyl	1.67	0.223	—0.64	0.12	
Benzyl	1.52	0.182	—0.28	0.14	
For naphthalene system					
None	(1.00)[c]	0	0[c]	0[c]	
1-Methyl	1.41	0.149	—0.49	+0.06	0.149
2-Methyl	1.22	0.086	—0.49	0[f]	0.086
1-*n*-Butyl	1.69	0.228	—0.62	+0.15	0.057
1-*n*-Hexyl	1.82	0.260	—0.62[e]	+0.18	0.045
1,8-Dimethylene[g]	2.18	0.338	(—2.6)[h]	0[i]	

[a] See footnote a, Table IV.
[b] See footnote b, Table IV.
[c] Taken as standard of comparison.
[d] Use of this assumed value in eqn. (2) gives $\rho^* = $ —0.16 for the benzene system.
[e] See footnote e in Table VI.
[f] Use of this assumed value in eqn. (2) gives $\rho^* = $ —0.13 for the naphthalene system.
[g] Common name, acenaphthene.
[h] Calculated by means of eqn. (2).
[i] Assumed value.

For our polymethylarenes we have treated the R_F data by means of eqn (4) (see Appendix).

$$\frac{\Delta R_M}{n} = -0.49\ \rho^* + \frac{1}{n}\ \Sigma E_{\text{interact}} \tag{4}$$

Observation of Table II shows that values of $\Delta R_M/n$ lie within the range of 0.07 ± 0.02 (*i.e.* essentially within experimental error) for 14 out of 21 methylated naphthalenes studied. Similarly, in Table III the range of 0.09 ± 0.02 encompasses such values for 9 of the 12 methylated anthracenes. Thus, for most of these compounds the second term on the right-hand side of eqn. (4) would appear to be either relatively small or essentially constant. In general, deviations from these values occur for cases where *n* is large and particularly where *n'* (the number of vicinal arrangements) is large.

SNYDER[3] noted the presence of a vicinal effect in the polymethylbenzenes and attributed this to a rotational restriction which is already placed on the methyl groups of the molecule in the non-adsorbed phase because of the necessity for intermeshing of these groups. Since the adsorbed molecule should also show restriction to free rotation

of the methyl groups, the free energy of adsorption for an *ortho* arrangement ought to be less than for a non-*ortho* arrangement (wherein no such restriction would occur in the non-adsorbed molecule). He noted that the same effect should be observed in comparing the adsorbability of a 1-alkylnaphthalene (wherein the hydrogen atom at C-8 would restrict free rotation of the alkyl group in the non-adsorbed molecule) with its 2-isomer. Indeed, his limited data were consistent with this rationalization. Extending this point of view even further, one should expect particularly large effects of enhanced adsorbability in di-α-substituted naphthalenes (*e.g.* 1,4- and 1,5-dimethyl derivatives) and the largest effects in those with *peri* substituents (*e.g.* the 1,8-dimethyl derivative), as compared to non-vicinal di-β-substituted isomers (*i.e.* 2,6- and 2,7-dimethyl derivatives). Other cases of enhanced absorbability might be expected for 9-methyl and 9,10-dimethylanthracenes. Examination of our data (Tables II and III), however, shows that such expectations are not fulfilled. Thus, all of the isomeric dimethylnaphthalenes except 1,2- and possibly 2,3- (*i.e.* those with *bona fide ortho* arrangements) show experimentally indistinguishable R_F values (0.46–0.47). 1,4,5-Trimethylnaphthalene may show some (though no definite) enhanced adsorbability with respect to its isomers studied. Also R_F values for 2- and 9-methylanthracenes, as well as for 2,6-, 2,7-, and 9,10-dimethylanthracenes, are experimentally identical, while that of 2,3,9,10-tetramethylanthracene > that of its 2,3,6,7-isomer. The identity of R_F values for our monomethylnaphthalenes (*cf.* other monoalkylnaphthalenes) has been noted earlier. Thus, although this *peri*-type enhancement of adsorbability may be important in SNYDER's LSC system it seems clear that it is of no pertinence in our TLC system. Further clarification of the vicinal effect in TLC must await the accumulation and study of many more polymethylarenes. We are, however, attracted to the possibility that *ortho*-hyperconjugative structures of the type proposed by WOOLFENDEN AND GRANT[30] for durene may be involved here. Thus, an *ortho* pair of methyl substituents could interact with a single site on the adsorbent (*cf.* the proposal of SNYDER[31] for enhanced adsorbability of *o*-quinones). Then rotation of the molecule in the surface layer of the adsorbent should bring other *ortho* pairs of a vicinal set of three or more methyl groups into proximity with this site (*cf.* our suggestion[17] for enhanced adsorption of *ortho*-azarenes). Moreover, such *o*-hyperconjugative structures are not possible for *peri*-dimethyl substituents.

It might be noted that, in general, our results are consistent with the observations of KARR *et al.*[21] for the naphthalene system. They found that the parameter which caused the largest change in adsorbability in their LSC studies was the degree of alkyl (especially methyl) substitution on the ring. Effects of position(s) of substitution and size of alkyl group (generally presumed to be methyl or *n*-alkyl in the hydrocarbon oils studied) were of secondary importance in this regard.

APPENDIX

Derivation of eqns. (2) *and* (4)

Let us treat the energetics of the adsorption process of adsorbate A in terms of the chemical potential relationship given in eqn. (5)[17], which

$$\frac{\Delta\mu_A}{RT} = -k \ln\left(\frac{1}{R_A} - 1\right) \tag{5}$$

can be put in form (6) by means of substitution and simplification. Here k' is a constant

$$\frac{\Delta\mu_A}{k'} = R_M \tag{6}$$

which is presumed to be characteristic of each set of experimental data. We than derive the relationship for ΔR_M as per eqn. (7), where P refers to the

$$\Delta R_M = \frac{1}{k'}(\Delta\mu_A - \Delta\mu_P) \tag{7}$$

standard of comparison, i.e. to the parent arene. Although this relationship strictly refers to true R_F values it has been noted that observed R_F values (which are normally 10–20 % less than the true values)[29] may be employed in practice for the calculation of ΔR_M because of an approximate cancellation of errors.

If we now consider the entire π-electronic system of the parent arene as the reaction center we can separate ΔR_M into polar and steric effects of each substituent i (i.e. first-order effects) plus (in the case of more than one substituent) interaction effects, $E_{\text{Interact.}}$, of the substituents with one another (i.e. higher order effects). This relationship may be expressed in the general form of an extended TAFT equation[10], as shown in eqn. (8).

$$\Delta R_M = \rho^* \sum_i (\sigma_i^* - c) + \sum_i E_{s_i} + \sum E_{\text{Interact}} \tag{8}$$

In eqn. (8) ρ^* is the reaction constant for the adsorption process; σ_i^* is the polar substituent constant of group i as obtained from available tables of data[10]; c is +0.49 (the reported σ^* value for H) and serves to transform the standard of comparison from the methyl group (as used by TAFT) to the H atom (as used here); E_{s_i} is the steric substituent constant of group i for the adsorption process; and the last term on the right-hand side includes special polar and steric factors which result from the geometric arrangement of the various substituents on the arene nucleus. For the special case of monoalkylarenes eqn. (8) simplifies to eqn. (2). In the case of polymethylarenes (for which the second term on the righthand side is taken as zero) one has the simplified eqn. (9)

$$\Delta R_M = -0.49 \, n\rho^* + \sum E_{\text{Interact}} \tag{9}$$

where n is the number of methyl substituents. Dividing through by n gives eqn. (4).

Calculation of error in values for $\Delta R_M/n$

Using subscripts A for the adsorbate and P for the parent arene (see Experimental) one can write eqn. (10).

$$\Delta R_M = \log\left(\frac{1}{R_A} - 1\right) - \log\left(\frac{1}{R_P} - 1\right) \tag{10}$$

Differentiating and assuming R_P is a constant one obtains eqn. (11).

$$\delta\Delta R_M = \frac{-0.434 \, \delta R_A}{R_A(1 - R_A)} \tag{11}$$

Taking $\delta R_A = 0.01$ and dividing by n gives eqn. (12) for calculation of the error.

$$\delta \left(\frac{\Delta R_M}{n} \right) = - \frac{0.0434}{n R_A (1 - R_A)} \tag{12}$$

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SUMMARY

Thin-layer chromatography of monoalkylarenes in the naphthalene, anthracene, and phenanthrene series, of polymethylarenes in the first two series, and of a few alkyl-substituted azulenes was conducted on alumina in a environment of constant humidity. Results are found to be consistent with a TAFT linear free-energy relationship involving the total π-electronic system of the parent arene as the flatwise adsorbing group, which senses both polar effects (that serve to increase adsorbability) and steric effects (that serve to decrease adsorbability due to hindrance between the substituent and the alumina surface) of the substituent(s). In the polymethylarenes it is found that isomers with vicinal arrangements of substituents generally have the largest adsorbabilities. Discussion of these results and comparison with reported data from other studies are presented.

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