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CHARGE TRANSFER THIN-LAYER CHROMATOGRAPHY AND MULTIPLE SITE COMPLEXATION

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SUMMARY

The effect of impregnating silica gel with different types of acceptors on the separation of different aromatic hydrocarbons by thin-layer chromatography has been investigated. Benzoquinone and substituted benzoquinones were studied in detail, and it was found that benzoquinone was most sensitive to moderate differences in the structure of most aromatic hydrocarbons.

Benzoquinone-impregnated silica gel thin-layer chromatographic R_F values were measured for a number of aromatic hydrocarbons, and the "binding constant" of Harvey and Halonen calculated for these hydrocarbons. The question of multiple site complexation between the aromatic hydrocarbon and either the silica gel surface or the benzoquinone was studied extensively. The R_F values for the biphenyl–terphenyl–quaterphenyl series appears to give some evidence for some type of multiple site binding. A novel method of locating spots on impregnated silica gel adsorbent has also been devised. It involves spraying with a dilute naphthacene solution; the yellow fluorescence of naphthacene is quenched everywhere except on the spots.

INTRODUCTION

Electron donor–acceptor complexes, or pi complexes, have been used extensively in various types[1] of chromatography. The complexes are considered to be formed from a pi acceptor, or pi acid, and a pi donor, or pi base. A requirement for a good acceptor in chromatography is that there must be more than one strong electronegative or electron-withdrawing group attached to the carbon atoms of the pi bond. The main requirements of donor molecules for chromatographic use are that steric hindrance and electron-withdrawing groups should be minimal.

Morris[2] and Barrett *et al.*[3] independently introduced the impregnation of the adsorbent into adsorption chromatography with the thought that a chemical could react selectively with a particular constituent or a functional group that might be present in the sample. Morris and Barrett *et al.* impregnated the adsorbent with silver(I) ions to effect the separation of *cis* and *trans* isomers of olefins.

Harvey and Halonen[4] and Berg and Lam[14], formalized the term "charge

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transfer chromatography" in applying the formation of pi complexation to thin-layer chromatographic (TLC) separations. They predicted that the migration of aromatic hydrocarbons over impregnated silica gel adsorbent could be selectively retarded to a degree depending on the strength of the charge transfer (CT) complex formed. They did in fact observe that when a CT complex is formed, migration of the donor is usually retarded on TLC plates. If the donor molecule does not migrate, it is assumed that the CT complex it forms is so stable that the solvent interactions are too weak to facilitate migration. None of these workers made any attempt to interpret or study situations where the R_F values increase. We believe that increasing the number of acceptor molecules on the silica gel plate reduces the total number of available hydroxyl sites per square area. Therefore in the case where the donor molecule will interact more with the hydroxyl sites than with the acceptor, the adsorption will be decreased and the R_F values will be increased.

To evaluate the effect of impregnation of adsorbents, Harvey and Halonen[4] proposed the so-called binding constant B, defined as:

$$B = \frac{R_F - R'_F}{R_F} \times 100$$

where R_F is the value obtained on non-impregnated silica gel and R'_F is the value obtained on impregnated silica gel for the same donor molecule. The binding constant should reflect the strength of the charge transfer complex formed by a donor on a particular adsorbent impregnated with a particular acceptor. A comparison of the binding constants of a series of compounds should reveal relative strengths with which the molecules bond to the surface at one or more sites.

The value of the binding constant can be positive, negative, or zero. A positive value for the binding constant represents the formation of CT complexes. Large positive values signify strong CT complexes, which will be reflected by small R_F values on impregnated plates. A value of zero for a binding constant means that the migration is unaffected by the presence of the impregnator in the plate. Negative values for the binding constant signify that the migration rate is increased for the impregnated plate as compared to non-impregnated plates. Presumably, the acceptor is blocking enough Si–OH sites to reduce the hydrogen bonding of the donor to these sites; the complex formed by the acceptor is too weak to compensate for this binding.

It is thought that the aromatic hydrocarbons are adsorbed to the silica gel surface by orienting their pi electrons to the surface silanol groups. Hydrogen bonds then can form between the silanol groups and the pi electron cloud, thus forming a weak CT complex. Snyder[5] has stated that the amount of adsorption does not depend directly on the energy of the highest filled π orbitals of the donor molecules as would be expected.

Snyder[5,6] has made several contributions to the understanding of TLC separations on silica gel which are useful for understanding separations on impregnated silica gel. He has proposed[6] that the "reactive" hydroxyl sites are the preferred sites for complexation of the aromatic hydrocarbon, since the approach of the hydrocarbon can break the hydrogen bond between the two hydroxyl groups at each site, allowing for several hydroxyl groups to bond to different orbitals of the same molecule. This would have to involve some multisite bonding. He has also formulated[5] a method for calculating the effective molecular areas by defining benzene as having a base value of six units, which equals 51 Å². The molecular areas for related unsaturated hydrocarbons of the formula C_cH_h is calculated by using the formula:

$$\text{Molecular area } (\text{Å}^2) = 6 + 0.8(h-6) + 0.25(c-h) \qquad (1)$$

Also, the planarity of the aromatic hydrocarbon governs the degree of adsorption. Planar molecules tend to be adsorbed more strongly while non-planar molecules are less adsorbed. This can be rationalized by considering that for adsorption the pi cloud of the donor molecule must achieve a specific orientational distance. Planar molecules can approach bonding sites easier while donors that have some degree of steric hindrance theoretically cannot orientate their entire pi electron cloud to the adsorbent.

EXPERIMENTAL

Reagents

All aromatic hydrocarbons used were purified by sublimation, except for bibenzyl, which was recrystallized. Their melting points were verified by checking against values tabulated in ref. 7. The stock solutions used in spotting the thin-layer plates were made up as 0.02 *M* solutions in benzene except: naphthalene 0.2 *M*; biphenyl, 0.2 *M*, and napthacene 0.002 *M*.

Of the pi acceptors used, *p*-benzoquinone was sublimed; bromanil and chloranil were recrystallized from chloroform, and 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) was recrystallized from ethylene dichloride. The benzene used in the eluent was an ACS-grade solvent; the heptane was solvent grade.

The adsorbent used was either MC and B plain silica gel G (TLC, Stahl) or silica gel treated with an inert fluorescent material that fluoresces green under short-wave UV light (254 nm). A slurry was made with benzene–95% ethanol (92:8) mixed in the ratio of 40 g silica gel to 100 ml solvent. Ethanol was mixed with benzene to improve the solubility of the acceptor when making impregnated plates, and also to increase the binding of the adsorbent on the glass. A slurry made with pure benzene was found to bind very poorly. When impregnated plates were prepared, 5.40×10^{-3} moles of the acceptor were dissolved in 100 ml of the solvent with stirring and added to 40 g of powdered silica gel.

Apparatus and preparation of TLC plates

The glass plates (20 cm × 10 cm) were cleaned by washing with soap and water and then soaking in chromic acid cleaning solution. After a minimum of 4-h soaking, the plates were rinsed with distilled water and dried at 110°. Before the plates were processed, they were wiped with 95% ethanol to remove any grease contaminants.

The Camag applicator (Mutter-Hofstetter design made for 20 cm × 10 cm plates) was used to spread the slurry (Camag, Muttenz, Switzerland). The screw settings on the front exit plate of the applicator were adjusted to 250 μ for uniform adsorbent thickness. This adjustment was checked with a 250-μ spacer before each series of plates were made.

The prepared plates were stored on 20 cm × 20 cm aluminum trays which could be stacked one on top of another. It was found that 14 to 18 plates could be made from the slurry of 100 ml of solvent and 40 g of silica gel G.

The plates were then covered with aluminum foil and stored at room temperature (about 26°) overnight. Any plates that would be used after a 24-h time period were stored in a desiccator. There was no activation of any plates because the *p*-benzoquinone impregnant will decompose at elevated temperatures.

Spot detection was made by: (1) use of an UV view box (Chromato-View; Ultra-violet Products, Inc., San Gabriel, Calif., U.S.A.) capable of producing both long-wave (365 nm) and short-wave (254 nm) mercury lines, or (2) by spraying the plate with a solution of naphthacene (0.05 *M* in benzene) or a 0.002 *M* solution of perylene in benzene. The sprayer used was a Chromatosprayer with Jet-pak made by Scientific Manufacturing Industries, Emeryville, Calif., U.S.A.

Experimental procedures

The spotting and development for both impregnated and non-impregnated plates was the same. The solutions of aromatic hydrocarbons were applied with micropipets, using a spotting guide. The volume of liquid applied to the spot was determined by the intensity of fluorescence emission of the aromatic hydrocarbon. For very strong emitters the spot was 2 μl, while for very weakly fluorescent aromatics the load was increased to 25 μl. In the case of naphthalene and biphenyl, new stock solutions were made up at 0.2 *M* in benzene and the liquid load was reduced to 5 μl.

Before development, the development tank was lined with filter paper on three sides to ensure tank saturation, and filled with eluent to a depth of about 10 mm. Spotted TLC plates were carefully placed in the tank and allowed to elute until the solvent front had moved exactly 10 cm from the start line.

Spot detection was performed on dried plates in the UV view box. Most aromatic hydrocarbons are fluorescent and can be detected on non-fluorescent silica gel. The relative fluorescence intensities of the hydrocarbons used in this study, using excitation by the 254-nm line of the mercury source, range from zero for azulene, to medium for naphthalene, and to very high for chrysene and anthracene. The corresponding relative intensities using excitation by the 365-nm mercury line range from very low for naphthalene, biphenyl, azulene, triphenylene and *p*-terphenyl, to medium for phenanthrene, pyrene and chrysene, and to high for anthracene and its derivatives. This means that both the exciting wavelength and the detection limit vary with different hydrocarbons. The short-wave mercury line can be used to excite all of the hydrocarbons except azulene, while the long-wave mercury line is only effective for phenanthrene, anthracene, chrysene, and pyrene.

Detection on non-impregnated plates did not present any problems once the liquid load was determined. The plates impregnated with *p*-benzoquinone did present problems. These impregnated plates have a light yellow-brown color which hindered detection of many of the aromatics which fluoresce violet against the background of the non-impregnated silica gel G. Therefore, the problem of detection of the aromatics was two-fold on the impregnated thin-layer plates: first, the problem of the light yellow-brown background, and secondly, the charge transfer interactions.

To overcome these problems, the *p*-benzoquinone-impregnated plate was sprayed with a 0.05 *M* naphthacene solution when the aromatic hydrocarbons did not fluoresce. After spraying with naphthacene (or perylene), the dull yellow background of the plate disappeared after 5 min, and only the spots containing the aromatics fluoresced yellow under UV radiation. (The yellow fluorescence of naphthacene in these spots was not quenched by the benzoquinone because the latter was complexed by the aromatic hydrocarbon in the spot.)

R_F values were measured as usual, but to insure reliable values, each R_F value was measured fifty times on both impregnated and non-impregnated plates. The maximum standard deviation was 1×10^{-2}.

RESULTS AND CONCLUSIONS

Evaluation of acceptors

The state of the acceptor in an impregnated silica gel layer is difficult to describe. It is not in a crystalline state since the acceptor molecules are not close enough together, yet it is not in solution. Since the impregnated silica is a homogeneous mixture, and since it is assumed that the mobile phase does not appreciably disturb the molecular arrangement of the acceptor and silica, it is probably more realistic to consider the acceptor as in a semi-crystalline state.

The acceptor will be bonded weakly to the silica gel since it blocks some "free" hydroxyl sites. It is likely that there will be some hydrogen bonding between the hydroxyl sites and the acceptor carbonyl groups. The extent of this depends on the molecular structure of the acceptor.

It has been shown[8] that *p*-benzoquinone molecules are planar and in crystals are arranged in rows at almost right angles to one another, with the minimum inter-oxygen distance being about 3.6 Å and the minimum intermolecular carbonyl carbon–oxygen distance being about 3.4 Å. There appears to be little intermolecular hydrogen bonding.

Both chloranil and bromanil have been shown[9] to be non-planar in their crystalline form. The carbon atoms are in one plane, but the oxygen and halogen atoms protrude alternately above and below the plane of the ring. This is not the conventional "chair" form, as the carbon atoms are coplanar.

It does not appear that the crystal structure of DDQ has been determined. However, 2,5-dichloro-*p*-benzoquinone, 2,5-dibromo-*p*-benzoquinone, and 2,5-bromochloro-*p*-benzoquinone have all been shown[10] to be planar, yet 2,3-dichloro-*p*-benzoquinone[10] and chloranil[9] have been shown to be non-planar. This would indicate that the adjacent chlorine atoms are responsible for non-planarity, and it can logically be assumed that DDQ will also be non-planar. The nitrile groups will not sterically interfere with each other or with the carbonyl oxygens, so it can be assumed that they will not contribute to the non-planarity of the molecule.

A number of different benzoquinone-type acceptors were evaluated with regard to their structural effects on TLC separations. Some representative R_F values are listed in Table I. Unsubstituted *p*-benzoquinone itself proved to be of prime importance because it was so sensitive to moderate structural changes. It at first appeared to have no effect on the R_F value of biphenyl, yet it lowered the

TABLE I

EFFECT OF ACCEPTOR STRUCTURE ON R_F VALUES ON IMPREGNATED SILICA GEL

Solvent: benzene–heptane (1:4).

Acceptor	*R_F value*		
	Biphenyl	*Naphthalene*	*Anthracene*
None	0.35	0.40	0.33
Benzoquinone	0.35	0.34	0.27
Choranil	0.37	0.40	0.32
Bromanil	0.36	0.38	0.33
DDQ	0.32	0.36	0.24
Trinitrobenzene *	0.31	0.27	0.24

* Calculated for our conditions using *B* values of Harvey and Halonen[4].

R_F value of naphthalene, which also has two benzene rings. It also lowered the R_F value of anthracene.

Two tetrahalo-substituted benzoquinones were also evaluated, *viz.* 2,3,5,6-tetrachlorobenzoquinone (chloranil) and 2,3,5,6-tetrabromobenzoquinone (bromanil). In both of these, the steric hindrance of the halo substituents was too pronounced to provide much of a difference in R_F values. The minimum possible interplanar distance for chloranil complexes is 3.65 Å and that for bromanil complexes is 3.80 Å. The extent of complexation is small because these distances are less than normally found in pi complexes.

DDQ has two chlorine atoms on one side of the molecule and comparatively small nitrile groups on the other. Since only one side of the molecule might block the approach of a hydrocarbon, one can expect DDQ to be able to complex better with a hydrocarbon than either chloranil or bromanil. As can be seen in Table I, DDQ retards hydrocarbons more than any of the other acceptors. It appears that its high pi acidity relative to benzoquinone is more than enough to overcome its greater steric hindrance (compared to benzoquinone). In spite of this, we decided to investigate benzoquinone in detail because it was more sensitive to moderate structural differences among various aromatic hydrocarbons.

Study of benzoquinone-impregnated TLC plates

Table II shows the donor molecules studied. Each R_F value reported is the mean value of a population of fifty spots. The maximum standard deviation was 1×10^{-2} R_F units. All impregnation R_F values were with the silica gel impregnated with *p*-benzoquinone. Effective molecular areas (Å^2) were calculated according to Snyder's[5] method. Binding constants were calculated according to Harvey and Halonen[4].

In evaluating the R_F values of the non-impregnated silica gel, it must be remembered that these values depend on the degree to which the aromatics are adsorbed on the silica gel. Therefore, it is important to consider the planarity of the donors concerned and their effective molecular areas.

TABLE II

R_F VALUES OF AROMATIC HYDROCARBONS

Solvent: benzene–heptane (1:4).

Aromatic hydrocarbon (Area in Å²)	*R_F value*		*B*
	Plain silica gel	*Impregnated silica gel*	
C_6H_5-R-C_6H_5 series			
Biphenyl (83)	0.39	0.44	−13
Diphenylmethane (94*)	0.36	0.36	0
Bibenzyl (100**)	0.40	0.42	−5
Long ring series			
9-Methylanthracene (94)	0.47	0.32	32
9,10-Dimethylanthracene (100)	0.44	0.32	27
Naphthalene (69)	0.45	0.42	7
Anthracene (87)	0.36	0.32	11
Naphthacene (105)	0.00	0.00	0
Phenyl substitution series			
Triphenylmethane (159)	0.27	0.25	7
trans-1,2-Diphenylethene (114)	0.34	0.32	6
Triphenylethene (167)	0.29	0.28	3
Tetraphenylethene (218)	0.20	0.23	−15
1,4-Diphenyl-1,3-butadiene (122)	0.30	0.34	−13
1,6-Diphenylhexatriene (132)	0.26	0.26	0

* Diphenylmethane is not planar and models indicate its area is less than that of two benzene rings; this area is an estimate using eqn. (1).

** Bibenzyl is almost planar and models indicate its area is almost the same as two benzene rings laid end to end.

In considering the planarity of the donor molecules, it is reasonable to assume that the more planar the molecule, the more easily it will be adsorbed on the surface of the silica gel at the "free" hydroxyl sites. As stated earlier, the "free" hydroxyl sites are slightly mobile, which will make them more available to bond to slightly planar donors and to at least a small extent to non-planar donors. In the case of non-planar molecules, the hydroxyl sites may not always be able to extend themselves to the degree needed for adsorption, which will result in high R_F values and very little adsorption.

The effective molecular area of the donor molecule will indicate an approximate maximum number of "free" hydroxyl sites available for adsorption. Utilizing Snyder's[5] calculated value of four to five hydroxyl sites per 100 Å² and the effective molecular area of the donor, a general evaluation of the R_F value can be made. The larger the effective molecular area representing the donor molecule, the greater the possibility for adsorption to take place.

In the first series of biphenyl, diphenylmethane, and bibenzyl in Table II, there seems to be no effect in increasing the carbon linkage. Actually, the increase in the effective molecular area is not large enough to increase the maximum number of "free" hydroxyl sites available to the donor molecule. Complicating the situation is the fact that neither biphenyl nor diphenylmethane are completely planar. The two rings of biphenyl are twisted[11] about 23° and models indicate that the two rings of diphenylmethane are not coplanar either. It is possible that at any given time one hydroxyl site can bond strongly to the benzene ring that is oriented completely parallel to the silica gel surface, and that a second hydroxyl site then bonds weakly to the other, non-planar benzene ring. (In any given 100 Å^2 covered by one of these molecules, there are four to five hydroxyl sites available for such bonding.)

When silica gel is impregnated by the amount of benzoquinone used in our experiments, about half of the surface is covered by benzoquinone. The negative B values in Table II therefore reflect an interaction with benzoquinone that is weaker than that with the silica gel hydroxyl sites. There is no increase in aromaticity in this case because the carbon linkage which has been added is a saturated linkage. The strength of the pi complex formed does not increase because there is no increase in the conjugation of this series.

In the remaining two series (Table II), there is a definite increase in the degree of adsorption. This additional increase can be attributed to both the increase in the number of available sites and the increase in aromaticity. The increase in aromaticity is the more important factor. With the expansion of the pi electron cloud, there are additional site(s) at which a pi complex may form. Therefore, with the additional pi complexation, and with the increase in the number of available hydroxyl sites, it is reasonable to assume that the degree of adsorption should increase.

In the large ring series of naphthalene–anthracene–naphthacene, the R_F values for impregnated silica gel decrease while the binding constants do show some increase. There is a slight increase in adsorption of the unsubstituted aromatics on impregnated silica gel. (In the case of naphthacene there is no migration on either the non-impregnated plate or the impregnated plate under the solvent conditions stated in the experimental section.) In contrast, there is a large increase in the adsorption of 9-methyl- and 9,10-dimethylanthracene on impregnated silica gel (large B values). Since it can be calculated that there are two to three hydroxyl sites and one benzoquinone per 100 Å^2, it is obvious that the methyl-substituted anthracenes are complexing with benzoquinone far more strongly than anthracene itself.

Our R_F values are in general much lower than those reported by Harvey and Halonen[4] for naphthalene, anthracene, and 9-methylanthracene on silica gel alone. We believe this reflects the difference in the activation used: they activated their plates by heating at 60° or 100° whereas our plates were allowed to air dry at room temperature. Our B values for benzoquinone are also much lower than their[4] B values for trinitrobenzene. This reflects the fact that trinitrobenzene forms stronger pi complexes than benzoquinone.

At a quick glance, the phenyl substitution series does not seem to exhibit any consistent trend. It is true that one of the main differences in the compounds of this series is the length of carbon linkage between the phenyl rings. But, with a closer examination of the series, it will be recognized that this series is composed of two different types of compounds. The first type is compounds in which only one phenyl ring can be parallel to the surface of the silica gel. Both triphenylmethane and tetraphenylethene fall into this category. Diphenylmethane could be considered to fall into this class as well. All of these compounds are sterically oriented so that only one phenyl ring is able to be completely parallel to the silica surface. It would be expected that these compounds would complex very weakly with benzoquinone on the surface of the silica gel. However, they can complex moderately well with the hydroxyl sites on the silica gel because this type of interaction probably does not require a completely parallel orientation. Thus these compounds have low R_F values but small or negative B values.

In contrast to these compounds, triphenylethene, diphenylbutadiene, and diphenylhexatriene can orient themselves so that at least two phenyl rings are parallel to the silica gel surface. Triphenylethene ought to complex more with benzoquinone than tetraphenylethene and indeed its B value is larger. Diphenylbutadiene and diphenylhexatriene also ought to complex with benzoquinone strongly, but for some reason their B values are not positive. It may be that both compounds strongly prefer to complex with the hydroxyl sites for some electronic reason.

The possibility of multiple site complexation

Although they studied rather large ring systems, Harvey and Halonen[4] did not consider the possibility that aromatic hydrocarbons might interact at more than one bonding site on either plain silica gel or impregnated silica gel. Snyder[12] does picture adsorption of bibenzyl on two SiOH sites on plain silica gel; he also implies that naphthalene (two fused rings) is not large enough to overlap two SiOH sites. It occurred to us that the polyphenyl series might provide a useful test of whether multiple site complexation was occurring (Table III).

In referring to the molecular models of this series, it will become apparent that this series consists of molecules which are not quite planar. The two benzene rings of biphenyl, the first member of the series, are not quite coplanar. One ring is twisted an approximate angle[11] of 23 ° to the other phenyl ring, and this spatial orientation will decrease the effective molecular area of the molecule. (Snyder's

TABLE III

BEHAVIOR OF POLYPHENYL HYDROCARBONS

Solvent: benzene–heptane (1:4); impregnation with benzoquinone.

Polyphenyl (Area in Å²) *	*No. of SiOH sites per area* **	*R_F Value* ***		*B*
		Plain silica gel	*Impregnated silica gel*	
Fluorene (85) ("rigid biphenyl")	3+ to 4	0.34	0.30	12
Biphenyl (83)	3+ to 4	0.39	0.44	−13
p-Terphenyl (114)	4+ to 6	0.28	0.27	4
p-Quaterphenyl (155)	6 to 8	0.25	0.17	32

* This area is relative to a base value of 51 Å² for benzene.

** This is based on an estimate of four to five sites per 100 Å².

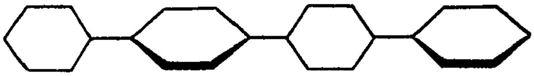
*** Each R_F value is the mean of fifty measurements, with a maximum standard deviation of ±0.01 R_F units.

effective molecular area calculation does not take into consideration the spatial geometry of the molecule but only the empirical formula.) This may reduce the interaction of biphenyl with the hydroxyl sites because of the lower probability of a given hydroxyl site interacting with the non-planar phenyl ring. Similar problems are involved with the interaction of *p*-terphenyl and *p*-quaterphenyl with the SiOH sites; these will be discussed later.

Plain silica gel. The first question is whether there are multiple site interactions between any of the polyphenyls and plain silica gel. One notes that the R_F value of biphenyl is lower than that of naphthalene (Table II), which cannot undergo multiple site bonding[12] and which is a stronger pi donor in general. Fluorene, whose structure approaches that of "rigid biphenyl", has an R_F value about 10% lower than that of biphenyl (Table III). In contrast, it is 4.5 times stronger a donor towards tetracyanoethylene[13], which complexes only one ring in solution (equivalent to a one-site interaction on a TLC plate). It is thus possible that one ring of biphenyl is interacting strongly with a hydroxyl site, and the other (twisted) ring is interacting weakly with a second hydroxyl site. It can be postulated that the reason fluorene does not interact more strongly with the silica gel than it does relative to biphenyl is that it is only interacting more strongly than biphenyl with the second hydroxyl site.

The multiple site hypothesis also accommodates the R_F values of *p*-terphenyl and *p*-quaterphenyl on plain silica gel, if the most favorable orientations of the twisted rings are assumed to predominate. In the most favorable orientation of terphenyl, it can orient its two outer rings in a plane parallel to the silica gel surface, while the center, twisted, ring will be at an approximate angle of at least 23° to the surface:

(This orientation allows for greater interaction with the silica gel surface than the situation where only one ring can have a parallel orientation.) In this orientation, it is possible for *p*-terphenyl to interact strongly with two hydroxyl sites and weakly with one hydroxyl site. If this occurs, it would rationalize the R_F of *p*-terphenyl being lower than either that of fluorene or biphenyl. This again contrasts with the fact that fluorene is 1.5 times a stronger donor towards tetracyanoethylene than is *p*-terphenyl[13]. Tetracyanoethylene complexes over one ring of any of these three donors, and this implies that more than one ring per donor must be interacting with the silica gel. In either of the most favorable orientations of *p*-quaterphenyl, there will always be two rings oriented in a plane parallel to the silica gel surface and two twisted rings. One of these is:



In this orientation, it is possible for *p*-quaterphenyl to interact strongly with two hydroxyl sites and weakly with two hydroxyl sites. Its R_F value is thus not much lower than that of *p*-terphenyl because it is interacting via only one more twisted ring.

Although the multiple site concept is only a hypothesis at this point, it does appear to accommodate the R_F measurements on plain silica gel. The hypothesis will now be tested with the data on silica gel impregnated with *p*-benzoquinone.

Impregnated silica gel. It should be recalled that about half of the surface of the impregnated silica gel is covered by *p*-benzoquinone molecules; this also probably blocks half of the available hydroxyl sites listed in Table III. If fluorene and biphenyl are again compared, it appears that fluorene is interacting more strongly with benzoquinone than with the hydroxyl sites, whereas biphenyl is not. It is likely that only one benzoquinone complexes with fluorene; it is possible that a hydroxyl site can complex with fluorene at the same time, but it is not necessary since fluorene complexes so strongly with acceptors like benzoquinone. In the case of biphenyl, the negative B value indicates that there is little if any interaction between the *p*-benzoquinone and this aromatic hydrocarbon. It appears that this molecule interacts more strongly with two hydroxyl sites than with one molecule of impregnant. Therefore, because of the decrease in the number of "free" hydroxyl sites per 100 Å^2, the R_F value shows an increase as compared to that on a non-impregnated plate.

The results (Table III) for *p*-terphenyl and *p*-quaterphenyl at first glance do not appear to conform to the multiple site hypothesis. However, there is only one benzoquinone molecule per 100 Å^2. This limits *p*-terphenyl to interacting with one benzoquinone at a time whereas *p*-quaterphenyl may interact with two benzoquinones at a time. Thus *p*-terphenyl may interact simultaneously with one benzoquinone and one hydroxyl site whereas *p*-quaterphenyl may simultaneously interact with two benzoquinones. It would be difficult to rationalize the dramatic 30% decrease from 0.25 to 0.17 R_F units for *p*-quaterphenyl without involving some sort of multiple site hypothesis. The small decrease in the R_F value for *p*-terphenyl may be rationalized by recalling that it does not bond strongly in solution to "one-ring" acceptors like tetracyanoethylene[13]. It is only about 2.5 times as strong a donor towards tetracyanoethylene as is biphenyl so that a small decrease in R_F value on impregnated silica gel is not unreasonable.

At this point in time, the multiple site hypothesis appears to be reasonable in that it rationalizes R_F trends in the biphenyl–terphenyl–quaterphenyl series. The hypothesis needs further testing but would appear to be useful in predicting TLC separations.

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