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Thin-Layer Chromatography of the N-Substituted Maleimides on Alumina: Stereochemical Factors*

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Summary

The N-phenyl-; N-benzyl-; *o*, *m*, and *p* N-(methylphenyl)-; *o*, *m*, and *p* N-(chlorophenyl)-; *o* and *p* N-(methoxyphenyl)-; and *o*, *m*, and *p* N-(nitrophenyl)maleimides were prepared. Ultraviolet spectroscopic studies indicated that in all cases the *o* isomers were sterically hindered and nonplaner, whereas the *m and p* isomers were planer accompanied by increased delocalization of the π electrons. Chromatography in four solvent systems on alumina-G showed the *o*-Me and *o*-Cl compounds to be retained more firmly, than the MeO and NO_2 families. It was concluded that charge-transfer interaction of delocalized π electrons with the surface was secondary to specific group interactions, that the projecting imide carbonyl group of the *o*-Me and *o*-Cl isomers was favorable to retention, and that there was concerted action of the carbonyl and substituent groups of the MeO and NO_2 families with the surface, so that the planer *m* and *p* isomers were better adsorbed because of a favorable posture on the surface.

Martin (*1*) proposed that the standard chemical potential for the equilibrium distribution of a substance between two phases,

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$\Delta\mu^0$, is a linear sum of terms, $\Delta\mu_i^0$, each of which represents a structural feature of the molecule, i.e.,

$$\Delta\mu^0 = \Sigma\ \Delta\mu_i^0 \tag{1}$$

As long as structural features are limited to definite combinations of atoms or functional groups, e.g., hydroxyl, carbonyl, etc., and the methylene group of homologous series, determination of these group parameters is a difficult, tedious but definable problem. The careful studies of Green et al. (*2,3*) with reverse-phase, paper-partition (PC), horizontal, "tankless" chromatography showed that careful experimentation coupled with cautious definition of a "chromatographic function group" yielded a surprisingly workable set of values. The principal objection to Martin's equation in its original form, i.e., that it did not provide for the separation of isomers, which is the origin of much of the impact of chromatography as a separation technique, can partially be overcome by more detailed definitions of the structural groups, e.g., primary hydroxyl groups as distinct from secondary groups, and even to the extent of classifying individual hydrogen atoms on the basis of their immediate environment, e.g., olefinic, paraffinic, aromatic, etc. (*2–4*). Green and McHale (*2*) carefully point out that Martin was clear on this point, for in his original work he warned that the linear sum is valid only if the free energy of transport for a given group from one phase to another is independent of the remainder of the molecule. This formulation has found expression not only in liquid-liquid chromatography but in gas-liquid chromatography (GLC) as the retention index (*5*), solid-liquid thin-layer systems (TLC) (*4,6,7*), and gas-solid adsorption chromatography (GSC) (*8,62*). Naturally these group constants depend not only upon the solute chromatographed but upon the immobile phase, solid (*4,6–8*) which may orient the solute in a particular position (*4*) or liquid, the immobile liquid load (*9,10*) in PC and GLC, and the mobile phase and its composition when in equilibrium with the stationary phase (*11,12*). Green and McHale (*2*) suggest that Martin's formulation contains two components, a "ground constant" typical of the chromatographic system only, and increments which reflect each structural feature of the solute molecule.

Snyder (*7*) writes an equation far more comprehensive than Eq. (1) or those in the treatment of Green and McHale. His partition coefficient, K, is given by

$$\log K = \log V_a + \alpha(S^0 - \epsilon^0 A_S) + \Sigma\ \Delta_{\text{eas}} \tag{2}$$

where V_a is the adsorbent surface volume equal to the volume of an adsorbed solvent monolayer per unit weight of adsorbent and α is the adsorbent activity function, which depends upon the adsorbent surface energy. Both these parameters are properties of the adsorbent. The quantity S^0 is the adsorption energy of the solute from pentane onto an adsorbent for which $\alpha = 1$. It is a function only of the solute for a particular adsorbent type and is independent of the solvent. Parameter A_S is the effective molecular area of the solute and is generally the area of the adsorbed solute on the adsorbent; ϵ^0 is the solvent eluant strength equal to the adsorptive energy of the solvent per unit area of adsorbent. The term $\Sigma\ \Delta_{\text{eas}}$ introduces anomalous separation effects; it generally vanishes. The solute parameter, S^0, is, in turn,

$$S^0 = \sum^{i} Q_i^0 + \sum^{j} q_j^0 - f(Q_k^0) \sum^{i \neq k} Q_i^0 \tag{3}$$

The Q_i^0 terms are group adsorption parameters assigned on the assumption of independent adsorption groups with no intramolecular interactions. The summation over all groups is essentially Eq. (1). The q_j^0 terms represent the contribution arising from interaction of groups within the molecule. The last term accounts for "localization." The adsorbent exposes sites of great affinity for various solute groups. A sufficiently strongly adsorbing group will localize over such a site and remaining adsorptive solute groups will not be able to overlap other adjacent sites. Their adsorption energies will be proportionally reduced. The adsorption energies of these nonlocalized groups, given by $\Sigma^{i \neq k} Q_i^0$, will be lowered by the factor $f(Q_k^0)$ which is determined by the adsorption energy of the localized group, Q_k^0, and its position in the solute molecule. Localization is important on alumina whenever a Q_i^0 value exceeds about 1.5; the effect is less important with silica (*6,7*). Zechmeister (*13*) also points out that localization of strongly adsorbing groups on the surface may be detrimental to adsorption of remaining solute groups.

Group constants, Q_i^0, as they represent a molecular dissection of the solute, cannot adequately portray the total electronic attitude of the molecule as determined by the interlocking roles of all the structural features (*6*). Each functional group is not independent of the environment provided by intragroup influence (*14*); hence the q_j^0 term of Eq. (3), and, for that matter, Q_i^0, is not wholly independent of the immobile phase which may selectively enhance the effect of one structural feature over another (*8*), so that a set of general rules applicable to solute structure is an elusive phantom and reality may require that they be recast for each chromatographic system.

One such feature is the delocalization of π electrons in conjugated or aromatic systems. Presumably this effect would be incorporated in Eq. (1) as an additional "group" constant or as a Q_i^0 term in Eq. (3) if the π electrons interacted through a specific π-electron complex bond [charge-transfer forces (*6*)], might also appear in q_j^0 as a reflection of various inductive and orientation influences transmitted by the aromatic character, and can appear in the localization term as it affects the geometric attitude of the solute toward the surface. It is the purpose of this investigation to properly order, as far as possible, this contribution among specific structural group constants and perhaps set guidelines for selection of a retentive phase which exploits this feature.

The Solutes. Zechmeister and Cholnoky (*15*) reported that the degree of adsorption on certain active adsorbents of the diphenyl polyenes decreased with a decrease in the number of conjugated double bonds between the terminal aromatic rings. The adsorbability of polynuclear aromatic rings on alumina (*15,16*) increases with the number of such rings and the extent of conjugation in the molecule; the colored, more conjugated naphthacene is held more tenaciously than its colorless isomer, chrysene. Klemm et al. (*16*) pictured the formation of π complexes of the aromatic systems with active sites on alumina. Retention was favored by extensive conjugation and the degree of planarity. Giles and McKay (*17*) assigned partial positive charges to surface aluminum atoms and nominated them as points of attachment of delocalized π electrons. As early as 1947 Meunier and Vinet (*18*) treated the elution sequence, color, and change of color or adsorption of vitamins and steroids by the "looseness" of the π electrons and their availability to attach to such centers. Gas chromatographers in both GLC and GSC have used the same language (*8,19–21*).

Kiselev (8,22,23) divides solutes into four groups. Group a contains molecules which show no specific interactions but are adsorbed only through the universally present dispersion forces. Group b includes molecules with negative charge concentrated on the periphery of individuals linkages, i.e., π-electron bonds of unsaturated and aromatic hydrocarbons, and molecules with functional groups with lone electron pairs (e.g., the oxygen atoms of ethers and ketones, and some nitrogen atoms). The picture is complicated if functional groups with oxygen and nitrogen also contain protonized hydrogen atoms capable of hydrogen bonds. These situations are excluded from group b. Group c contains molecules with locally concentrated positive charges in small radius bonds and a diffusive distribution of the corresponding negative charge over neighboring bonds. Group d contains molecules with small radius neighboring linkages with positive charge concentrated on one of them and electron density concentrated on the periphery of the other, e.g., alcoholic hydroxyl groups.

Snyder (*6*) lists five general features of solute structure which contribute to adsorption through the group-interaction terms q_j^0 [Eq. (3)]:

1. Nonplaner solutes are adsorbed to a lesser extent than planer solutes, possibly because of the planer adsorbent surface. The discussion of alumina to follow indicates that alumina may well be an exception to this rule.

2. A bulky solute group adjacent to an adsorptive group may inhibit adsorption through steric hindrance.

3. Two adjacent groups may interact to reduce the surface bonding of one of them. Intramolecular hydrogen bonding is the outstanding example.

4. Electronic interaction of two groups may affect the group which may be thought to make the major contribution to adsorption when considered out of context with the remainder of the molecule. This is particularly important for aromatic solutes with one very adsorptive group.

5. Two adjacent groups so situated as to permit simultaneous interaction with an adsorption site are generally more strongly adsorbed. On the other hand, a polyfunctional molecule with a highly adsorptive group will also tend to exhibit localization.

A test of the roles of planarity, delocalized π electrons, and specific group interactions was concieved to be the chromatography of isomers consisting of bridged aromatic groups where substitution about the bridge could force the aromatic groups out of a common plane and interfere with conjugation between the two rings to reduce electron delocalization. Principally because of the ease of synthesis but also because of favorable solubility relations, the substituted N-phenylmaleimides and N-benzylmaleimide (**1**) were selected. Substitution of suitably large groups in the 2 or 2 and 6

N-Phenylmaleimide N-Benzylmaleimide

(**1**)

positions (*ortho*) should produce the desired interference, while the same substitutions in the 3, 4, or 5 positions (*meta* and *para*) should allow full electron delocalization across both rings. In such isomers, where functional groups and molecular weight are identical, one would hope that differences in retention are due to specific intermolecular interactions which involve either delocalized π electrons or the positions of the substituents relative to the carbonyl group, i.e., the isomers, one with a substituent in the 2 position and the other with it in the 5 position differ in the distance from the substituent to the carbonyl and the substituent and carbonyl are, respectively, "in" or "not in" the same plane. The transmission of electronic effects across the ring must also be considered. In this sense the study is not strictly of delocalized electrons, which is better represented by the polynuclear aromatics, but compares the influence of electron delocalization with the geometric arrangement of functional groups. This same interaction can occur with the solvent to alter the solubility of the isomeric solutes, or the solvent can compete with the solute for adsorbent active sites.

The important features of the solute molecule are:

1. The carbonyl groups of the imide linkage; the oxygen bears a partial negative charge. Snyder (*6,24*) lists the alumina group adsorption parameter for the carbonyl of (Ar)—CO—R (Ar, aromatic; R, aliphatic) as 3.74, R—CO—R as 5.0, (Ar)—CO—(AR) as 4.36, and an amide (—CO—NH_2) as 6.20. If these are also indicative of the carbonyl of the imide linkage, localization must play a major role with the maleimides.

2. The nitrogen atom of the imide linkage with a positive charge [oxygen is more electronegative than nitrogen (25)].

3. The delocalized π electrons of the conjugated rings.

4. The substituent. The carbonyl group and the aromatic nature of the N-substituted maleimides clearly place them in Kiselev's group b. There is little liklihood that the positive nitrogen predominates over these two influences, for its positive nature is the result of being less electronegative than the oxygen, and not from any inherent electropositive nature, as exhibited by the organometallic compounds which Kiselev had in mind for this groups.

The Retentive Phase. Alumina. The crystalline high-melting solutes restricted chromatography to liquid-liquid or liquid-solid systems. Since adsorption chromatography seems more sensitive to minor differences in molecular architecture, the study was initiated with TLC using alumina. Results with silica are to be reported in a subsequent communication. A discussion of alumina is relevant only when referred to the potential centers of the solute molecules discussed earlier.

"First-type" adsorbents in Kiselev's (*8*) scheme are devoid of functional groups and exchange ions. They are nonspecific adsorbents, e.g., graphitized carbon black. "Second-type" adsorbents interact specifically with molecules with peripheral negative centers, i.e., group b solutes. These are adsorbents with acidic hydroxyl groups (potential hydrogen bonds for proton-accepting solute groups), e.g., hydroxylated acid oxides as silica, and those where positive charge is shifted to the surface and concentrated in a small region, while the negative charge is distributed over a larger volume, e.g., zeolites. A group b solute should be retained by a "second-type" adsorbent. "Third-type" adsorbents have concentrated electron densities at their peripheries, e.g., ether, nitrile, carbonyl, etc. (potential hydrogen bonds for proton-donating groups) and bond c or d solutes. Such complementarity has been emphasized by others, e.g., Giles and McKay (*17*) and Basu (*26*), where one partner is characterized by high electron affinity and the other by a low ionization potential.

Commercial alumina is prepared by low-temperature dehydration of alumina trihydrate and is a mixture of γ-alumina, some alumina monohydrate, and some sodium carbonate. Its activity as an adsorbent depends inversely upon its water content. Giles (*27*) concluded that water attacked active sites to produce deactivation. Ideally each normally inaccessible aluminum atom is surrounded by six oxygen atoms and each oxygen by four aluminums. Damage and distortion of the surface by grinding and abrasion will expose positively charged aluminum atoms. Water may be adsorbed and ionized to give surface hydroxyls; $Al(OH)_3$ in highly damaged areas and basic $(Al(OH)_2^+ + OH^-)$. AlO·OH in other areas are protonic $(AlO{\cdot}O^- + H^+)$. Activation and reverse hydration varies the ratio of these regions, the protonic surface and Al_2O_3 with its positive aluminum atom being the activated surface. Thus alumina has aspects of both "second-" and "third-type" adsorbents. The deactivated surface would seem to be the hydroxylated situation. This should not be confused with the hydroxylated surface of silica. As Kiselev (*23*) emphasizes, acidic hydroxide surfaces can be expected to be vastly different from alkaline surfaces. Our own work with silica supports the contention that they do differ. It is likely that AlO·OH and $SiO{\cdot}(OH)_2$ are more alike, i.e., protonated, than are $Al(OH)_3$ and silica.

Bernal (*28*) does not feel that the dehydroxylation of the surface occurs with the ease implied here. The earlier discussion of the solutes strongly indicates that they are proton acceptors, both by virtue of the carbonyl group and the delocalized π electrons. [Kiselev (*8,23*) concludes that hydrogen bonding exists between the protonated hydroxyl surface of silica and the π electrons of aromatic nuclei; cf. Pimentel and McClellan (*29*) and Josien and Sourisseau (*30*).]

Proton-donating solutes are more strongly adsorbed than proton-accepting solutes (*27*), which would seem to indicate that the protonanted surface properties of alumina are not of primary importance. Giles and McKay argue convincingly that delocalized π electons are fixed by the small proportion of positively charged aluminum atoms exposed on the surface [0.06% of the surface is used in the adsorption of phenanthrene (*17*)]. Water adsorbed to the neighboring oxygen will enhance this positive charge [$AlO{\cdot}(OH)_2$ relative to Al_2O_3); (*31*)]. The same positive atoms could serve as a point of attachment of the solute carbonyl group. Kemm *et al.* (*16*) suggested that planer aromatic hydrocarbons are adsorbed flatwise. Giles (*17,27*) argues for end-on adsorption in associated clusters from the adsorption isotherm shape [cf. Giles (*32*)].

Forming Solvent. For solutes chromatographed simultaneously on the same plate or on plates prepared in the same manner, the adsorbent surface volume, V_a, and the adsorbent activity, α, should be the same. Variations in K must involve differences in the solute parameter S (which is the concern of this communication), eluant strength ϵ°, the effective molecular area of the solute A_S, and the anomolous separation term Δ_{eas} (which has been assumed to be zero). A disucssion of exclusively solute properties must remove any solvent dependence. Snyder (*6*) gives a method of calculating the eluant strength of a binary mixture:

$$\epsilon^\circ = \epsilon_A + \frac{\log\,(X_B 10^{\alpha n_b(\epsilon_B - \epsilon_A)} + 1 - X_B)}{\alpha n_b} \tag{4}$$

where ϵ_A is the eluant strength of the weaker eluant A, ϵ_B the eluant strength of solvent B, n_b the adsorbate size of the solvent molecule B, X_B the mole fraction of B, and α the adsorbent activity. Parameters listed for alumina can be used to calculate eluant strength in order to rank the solvents used.

EXPERIMENTAL

Synthesis. The N-substituted maleimides were in general prepared by mixing, with vigorous stirring, equimolar benzene solutions of maleic acid. The resulting acid with anhydrous sodium acetate and acetic anhydride (*33*) heated on a water bath resulted in ring closure to form the maleimide. Water was added to the mixture or it was poured over ice to recover the product. The solid was washed with 10% aqueous sodium bicarbonate and recrystallized from appropriate solvents. Where the product formed as an oil, repeated extractions with hot water were often necessary to produce crystalline material. The data to follow list, under maleamic acid, product melting point [both that observed (uncorrected) and the literature values]. Under the maleimides are listed the quantities of acid, anhydrous sodium acetate (NaOAc) and acetic anhydride (Ac_2O); the experimental conditions; treatment of the oil where one was obtained; solvents for recrystallization; yield; the melting point observed (uncorrected) and that reported in the literature; and, if literature values were not listed or were much different from the observed value, the elemental analysis (*34*) (accepted accuracy of each elemental determination, 0.2%).

N-Phenylmaleimide

Maleamic acid: Aniline. Product m.p.: 202 to 203°C; literature: 199°C (*35*).

Maleimide: 35 g of the acid, 3.5 g of NaOAc, and 70 ml of Ac_2O; 70 to 80°C for 45 minutes. Recrystallized twice from cyclohexane. 40% yield. Product m.p.: 88 to 89°C; literature: 90°C (*33*).

N-Benzylmaleimide

Maleamic acid: Benzylamine. Product m.p.: 135°C; literature: 138°C (*36*).

Maleimide: 31 g of the acid, 3.1 g of NaOAc, and 150 ml of Ac_2O; 60 to 65°C for 5 hours or 80°C for 90 minutes. The brown oil was repeatedly extracted with hot water and cooled. Recrystallized three times from cyclohexane with decolorizing carbon (Norit) present the first two times. 36% ·yield. Product m.p.: 70 to 71°C; literature: 73°C (*37*).

Analysis:
Calc.: C, 70.60%; H, 4.82%; N, 7.48%
Found (*34*): C, 71.78%; H, 5.30%; N, 6.66%

The poor agreement of the elemental analysis with the calculated values initiated an analysis of the sample analyzed. It was found to contain 7.0 to 7.5% occluded cyclohexane. If it is assumed that the sample contained 7.3% solvent, the calculated values become C, 71.78%; H, 5.5%; N, 6.92%.

N-(*o*-Methylphenyl)maleimide

Maleamic acid: *o*-Toluidine. Product m.p.: 116 to 117°C; literature: 118°C (*38*).

Maleimide: 20.5 g of the acid, 2.1 g of NaOAc, and 30 ml of Ac_2O; 50 to 60°C for 45 minutes. The oil was extracted with cyclohexane and evaporated. Crystals were manually separated from the residual oil and recrystallized from cyclohexane. 8.7% yield. Product m.p.: 72 to 73°C; literature: 70 to 71°C (*33*).

N-(*m*-Methylphenyl)maleimide

Maleamic acid: *m*-Toluidine. Product m.p.: 170 to 170.5°C; literature: 172°C (*39*).

Maleimide: 15 g of the acid, 1.5 g of NaOAc, and 250 ml of Ac_2O; 80°C for 5 hours. Oil crystallized on standing. Recrystallized from *n*-hexane. Product m.p.: 38 to 39°C.

Analysis:
Calc.: C, 70.58%; H, 4.85%; N, 7.48%; O, 17.09%
Found (*34*): C, 70.55%; H, 4.86%; N, 7.45%; O, 17.14%

N-(*p*-Methylphenyl)maleimide

Maleamic acid: *p*-Toluidine. Product m.p.: 199°C; literature: 201°C (*40*).

Maleimide: 20.5 g of the acid, 2.1 g of NaOAc, and 50 ml of Ac$_2$O; 70 to 80°C for 45 minutes. Recrystallized once from absolute ethanol and once from cyclohexane. 67% yield. Product m.p.: 148 to 149°C; literature: 149°C (*33*).

N-(*o*-Chlorophenyl)maleimide

Maleamic acid: *o*-Chloroaniline. Product m.p.: 130 to 131°C; literature: 132°C (*41*).

Maleimide: 22.5 g of the acid, 2.5 g of NaOAc, and 30 ml of Ac$_2$O; 80 to 85°C for 45 minutes. 90% yield. Product m.p.: 73 to 74°C; literature: 59 to 60°C (*42*).

Analysis:
Calc.: C, 57.85%; H, 2.91%; N, 6.75%; Cl, 17.08%
Found (*34*): C, 58.32%; H, 3.24%; N, 7.40%; Cl, 17.49%

N-(*m*-Chlorophenyl)maleimide

Maleamic acid: *m*-Chloroaniline. Product m.p.: 193 to 194°C; literature: 188°C (*41*).

Maleimide: 22.5 g of the acid, 2.5 g of NaOAc, and 50 ml of Ac$_2$O; 70 to 80°C for 30 minutes. Recrystallized twice from absolute ethanol and once from cyclohexane. 72% yield. Product m.p.: 93.5 to 94.5°C.

Analysis:
Calc.: C, 57.85%; H, 2.91%; N, 6.75%; Cl, 17.08%
Found (*34*): C, 58.42%; H, 3.23%; N, 6.98%; Cl, 17.77%

N-(*p*-Chlorophenyl)maleimide

Maleamic acid: *p*-Chloroaniline. Product m.p.: 200°C; literature: 199°C (*41*).

Maleimide: 22.5 g of the acid, 2.5 g of NaOAc, and 35 ml of Ac$_2$O; 75 to 80°C for 35 minutes. Recrystallized once from benzene/cyclohexane mixture and once from cyclohexane. 94% yield. Product m.p.: 116°C; literature, 110°C (*42*).

Analysis:
Calc.: C, 57.85%; H, 2.91%; N, 6.75%; Cl, 17.08%;
O, 15.41%
Found (*34*): (1) C, 58.18%; H, 3.11%; N, 6.81%; Cl, 17.50%
(2) C, 57.84%; H, 2.94%; N, 6.12%; Cl, 16.90%;
6.09%;
O, 15.81%
15.61%

N-(*o*-Nitrophenyl)maleimide

Maleamic acid: *o*-Nitroaniline. Product m.p.: 133.5 to 134°C; literature: 134°C (*35*).

Maleimide: 6.0 g of the acid, 0.6 g of NaOAc, and 20 ml of Ac_2O; 70 to 80°C for 20 minutes. Recrystallized twice from cyclohexane. 93% yield. Product m.p.: 131 to 132°C; literature: 131°C (*33*).

N-(*m*-Nitrophenyl)maleimide

Maleamic acid: *m*-Nitroaniline. Product m.p.: 197 to 198°C; literature: 197°C (*43*) and 196°C (*44*).

Maleimide: 10 g of the acid, 1 g of NaOAc, and 60 ml of Ac_2O; 70 to 80°C for 1 hour. Recrystallized from cyclohexane. 82% yield. Product m.p.: 131 to 132°C; literature: 134°C (*43*).

N-(*p*-Nitrophenyl)maleimide

Maleamic acid: *p*-Nitroaniline. Product m.p.: 197°C; literature, 198°C (*33*).

Maleimide: 6.0 g of the acid, 0.6 g of NaOAc, and 30 ml of Ac_2O; 80 to 85°C for 45 minutes. Recrystallized from cyclohexane. 93% yield. Product m.p.: 165 to 166°C; literature: 167°C (*33*).

N-(*o*-Methoxyphenyl)maleimide

Maleamic acid: *o*-Methoxyaniline. Product m.p.: 143°C.

Maleimide: 15 g of the acid, 1.5 g of NaOAc, and 50 ml of Ac_2O; 80 to 85°C for 45 minutes. The viscous brown oil was repeatedly extracted with boiling water and cooled. Recrystallized from benzene. 38% yield. Product m.p.: 119 to 120°C; literature: 120°C (*42*).

N-(*p*-Methoxyphenyl)maleimide

Maleamic acid: Sample by the courtesy of D. W. Lamson.

Maleimide: 44.2 g of the acid, 4.4 g of NaOAc, and 100 ml of Ac_2O; 70 to 80°C for 30 minutes. Recrystallized twice from absolute ethanol and once from cyclohexane. 53% yield. Product m.p.: 149 to 150°C; literature: 149 to 150°C (*45*).

Spectra. Ultraviolet spectra (Figs. 1 to 6) of the solutions of the maleimides in Eastman Spectro-Grade Cyclohexane were measured on a Cary Model 11 recording spectrophotometer using 1-cm matched quartz absorption cells.

Adsorbent. The adsorbent used throughout was aluminum oxide-G (No. 8077, Research Specialties, Co., Richmond, Calif.) applied in an aqueous slurry (60 g/100 ml) and reactivated at 120°C for 2 hours or at 400°C for 4 hours.

Thin-Layer Plates. Plates were prepared with a variable-thickness applicator (Kensco Model B, No. 4005, Kensington Scientific Corp., Oakland, Calif.) with a layer thickness of 0.30 mm, which was within the range of 0.15 to 2.0 mm recommended by Bobbitt (*46*) for R_f values which are independent of layer thickness. Plates 20 × 20 cm were used for low-temperature activation, whereas high-temperature reactivation required glass strips 2 × 8 in., because of the restrictive dimensions of the furnace. Coated plates were kept horizontal for 30 minutes to allow the binder to set, activated, cooled to room temperature in a desiccator, and used immediately.

Sample Load. Solute samples in chloroform were applied with a 2-μl micropipet. The sample spots were 1.5-cm apart and 2.0 cm from the base of the plate. Because R_f values depend upon the sample load (*47–49*), a representative of the solutes was tested over a wide range of sample weights to determine the sample load sufficiently large to be detected but small enough that the R_f value was independent of the load. Table 1 shows the result of this study.

TABLE 1

Variation of R_f Value with the Sample Load for N-(*p*-Methylphenyl)maleimide on Aluminum Oxide-G with a Forming Solvent of 1:1 *n*-Hexane/Benzene

Weight, μg	R_f value	Weight, μg	R_f value
1.0	n.d.[a]	75	0.35
2.0	0.31	80	0.35
5.0	0.31	90	0.38
7.5	0.31	100	0.37
10	0.31	120	0.38
15	0.31	134	0.38
20	0.32	150	0.39
40	0.33	200	0.40
50	0.33	300	0.40
60	0.34	400	0.40
67	0.34	600	0.41

[a] n.d., not detectable.

The R_f value increases with increasing sample weight and is accompanied by an increase in spot size and elongation in the direction of solvent flow. The R_f values are essentially constant and the spots remain small and circular with little distortion or tailing in the range 2 to 20 μg. A sample weight of 10 μg was used throughout.

Forming Solvents. Solvents were selected on the basis of preliminary tests described by Bobbitt (*46*), wherein solvents are introduced into the center of solute spots on adsorbent-coated microscope slides. With the exception of hexane, all solvents were redistilled before use. Table 2 shows the solvent compositions.

TABLE 2
Composition of Forming Solvents (v/v)

Solvent designation	Composition
Bnz/CyHx 2:1	Benzene/cyclohexane, 2:1
Bnz/CyHx 1:1	Benzene/cyclohexane, 1:1
CyHx/EtAc	Cyclohexane/ethyl acetate, 4:1
Bnz/Hx	Benzene/hexane, 1:1
Bnz	Benzene

Ascending Chromatography. Chromatograms were formed in a glass chamber 9.25 × 7 in. (base dimensions) and 13 in. high, equipped with a glass rack for two plates and a lid with adjustable glass hooks in Teflon bushings, whereby the rack holding the plates could be suspended from the hooks and lowered into the solvent after equilibration with the solvent atmosphere (Kensco Chamber No. 4007). Freshly activated plates were suspended in the solvent atmosphere 1 hour before chromatography. Upon lowering the plates, the solvent covered the first 1 cm of the plate, placing the solvent line 1 cm from the sample line. A terminal line was drawn 10 cm above the sample line and chromatography was stopped when the solvent reached this limit; this required 20 to 40 minutes, depending upon the solvent. On termination the plates were quickly removed, placed in a horizontal position, and the solvent evaporated off in the atmosphere of the laboratory.

Small variations in temperature during formation of the chromatogram do not appear critical (*46,50*). The data presented here involved temperatures of 24.5 to 27°C.

Visualization of Solute Spots. Several methods were used to reveal the spots on the completed chromatograms: (1) Ultraviolet absorption; (2) chromatograms sprayed with 0.2% ethanolic solution of 2,7-dichlorofluorescein showed enhanced visibility under ultraviolet light (*51*); (3) the hydroxamic test which produces colored complexes with esters and imides (52) as adapted to a spray reagent

(53); and (4) 50% sulfuric acid solution spray followed by baking at 100°C for 15 to 30 minutes (54) charred all organic material and served as a test for homogeniety of the solute preparation.

R_f values were measured from the center of symmetrical spots and from the position of greatest width for the slightly asymmetrical spots.

RESULTS AND DISCUSSION

Ultraviolet Spectra

N-Benzylmaleimide and N-Phenylmaleimide. Because of the bridging methylene group, N-benzylmaleimide shows less π-electron delocalization or conjugation than N-phenylmaleimide. This is demonstrated by the spectra shown in Fig. 1. Maleimide itself shows four adsorption bands in the near-ultraviolet (55). Its bands at 280 and 230 mμ are assigned to the imide system, —CO—NH—CO—, but must also reflect the whole maleimide ring, because succinimide, which has this same structural feature but lacks a double bond in the five-membered ring, is transparent at wave-

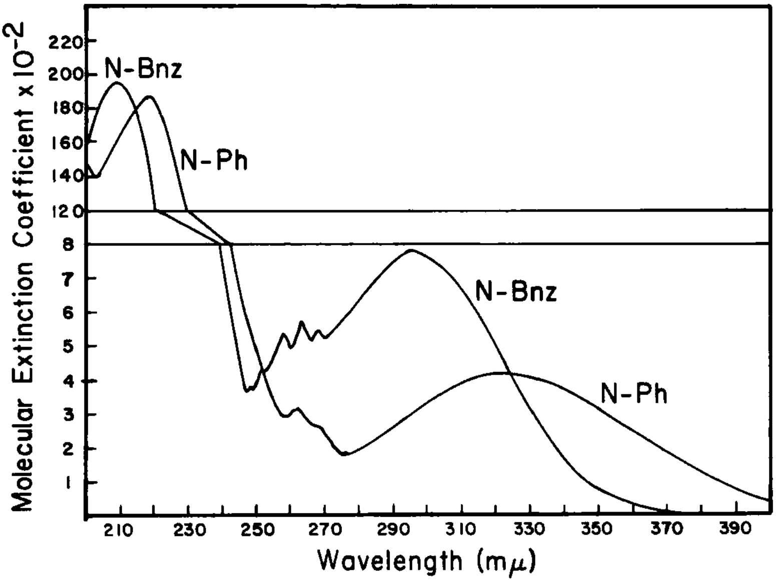


FIG. 1. Ultraviolet spectra of N-phenylmaleimide (N-Ph) and N-benzylmaleimide (N-Bnz).

lengths greater than 260 mμ (55). The α,β-unsaturated carbonyl system, —CO—C═C—CO—, is deemed responsible for the remaining two maxima at 222 and 216 mμ. Benzene shows its characteristic "benzenoid" absorbance with its unique fine structure at 250 mμ. Since N-benzylmaleimide is unconjugated, its spectra should be the simple combination of the spectra of maleimide and methyl benzene. The "structural feature" bonds are compared in Table 3. The peak at 295 mμ for N-benzylmaleimide is presumed to be the 280-mμ "maleimide band" thought to have undergone a bathochromic shift because of the absence of hydrogen bonding in the benzyl derivative compared with its ═NH group. Such an effect has been proposed for the N-alkylmaleimides (55). N-Phenylmaleimide shows a bathochromic shift of the peak at 209 to 219 mμ and a pronounced shift of the peak at 295 to 322 mμ; the benzenoid peaks are less resolved. The large shift of the peak at 295 mμ will be taken here as evidence of conjugative substitution (56). The shifts are completely analogous to those observed for the biphenyls (57).

TABLE 3

Comparison of Ultraviolet Absorption Bands of Maleimide, N-Benzylmaleimide, and N-Phenylmaleimide

	—CO—NH—CO— bands, mμ		—CO—C═C—CO— bands, mμ		Benzenoid bands, mμ
Maleimide	280	230	222	216	250
N-Benzylmaleimide	295		209		247–270
N-Phenylmaleimide	322		219		—

N-(Methylphenyl)maleimides. The effect of twisting single bonds in a conjugated system to force the system out of planarity has three effects (56): (1) Small twists decrease absorption intensities with no change in wavelength of the peaks; (2) decrease in absorption intensity and peak shifts to shorter wavelengths; and (3) the observed spectrum more closely adheres to the additive spectra of the components of the molecule. This is demonstrated in Fig. 2. The N-(*o*-methylphenyl)maleimide, where steric hindrance of planarity is suspected, resembles that of N-benzylmaleimide, where the peak maxima are at lower wavelengths than those for the unhindered N-(*p*-methylphenyl)maleimide, absorption intensities are often enhanced, and the benzenoid peaks are better resolved. The shift

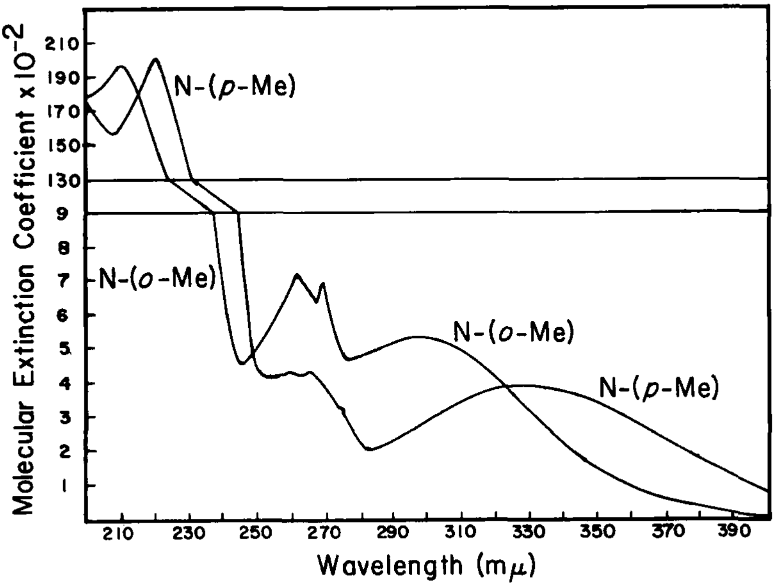


FIG. 2. Ultraviolet spectra of N-(*o*-methylphenyl)maleimide (N-(*o*-Me)) and N-(*p*-methylphenyl)maleimide (N-(*p*-Me)).

of the long-wavelength peak is from 328 to 297 mμ, a change of 31 mμ, on transfer of the Me group from the *p* to the *o* position. The difference between the long-wavelength peak for N-phenylmaleimide (322 mμ) and N-(*p*-methylphenyl)maleimide (328 mμ) likely represents the electron-donating ability of the Me group through hyperconjugation and inductive effects. The short-wavelength band shifts also seen sensitive to steric effects. The benzenoid band for the *o*-Me isomer is that observed for toluene and exemplifies the principle of additivity of spectra in the hindered system, an effect expected from conjugative substitution.

N-(Chlorophenyl)maleimides. Figure 3 shows the same features on passing from the *p* to the *o* isomer, i.e., the long-wavelength peak is shifted from 325 to 282 mμ (43mμ). The shift is likely composed of a greater electron-donating effect of *p*-Cl to π-electron delocalization than the *p*-Me group, but an opposite inductive effect. The nearly identical positions of the peaks for the unhindered *p*-Me (325 mμ) and *p*-Cl (328 mμ) isomers can be explained by assuming that the greater electron-donating effect of Cl is opposed by its inductive effect (58), so the net effect is nearly the same as that of

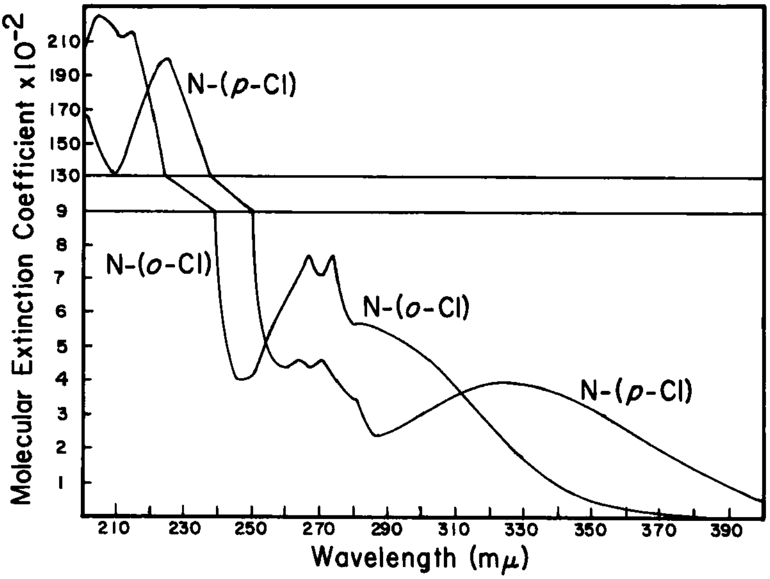


FIG. 3. Ultraviolet spectra of N-(*o*-chlorophenyl)maleimide (N-(*o*-Cl)) and N-(*p*-chlorophenyl)maleimide (N-(*p*-Cl)).

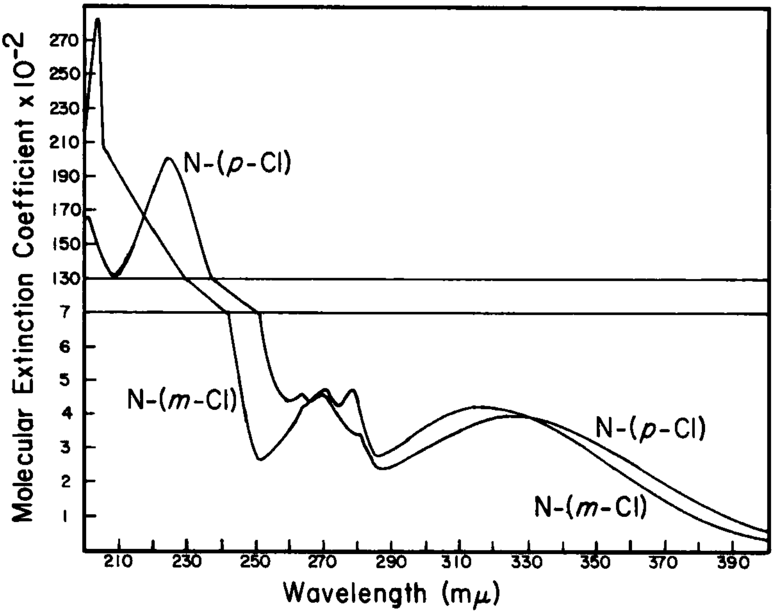


FIG. 4. Ultraviolet spectra of N-(*m*-chlorophenyl)maleimide (N-(*m*-Cl)) and N-(*p*-chlorophenyl)maleimide (N-(*p*-Cl)).

the Me group. For *o* isomers, only the difference in inductive effects of the *o*-Me and *o*-Cl groups can be responsible for the difference in band positions (297 and 282 mμ, respectively), since there is steric hindrance the conjugation. The result of the inductive effect, opposite for the two groups, results in a shift to lower wavelengths on going from *o*-Me to *o*-Cl. The Cl group, because of its greater size, is more effective in hindering coplanarity (59).

Figure 4 shows the spectra of the N-(*p*-chlorophenyl)- and N-(*m*-chlorophenyl)maleimides and demonstrates the sensitivity of the long-wavelength band to both inductive and electron delocalization effects. The chlorine in the *m* position (318 mμ) can exert only its inductive effect, since transmittance of the resonance or delocalization effect is impossible. With the *p* isomer (326 mμ) both effects are operative. The hypsochromic shift of 5 mμ of the *m*-Cl derivative relative to the parent N-phenylmaleimide (322 mμ) must be due exclusively to the inductive effect of this group. The bathochromic shift (3 mμ) for the *p*-Cl derivative relative to the parent involves both inductive and delocalization effects, and it

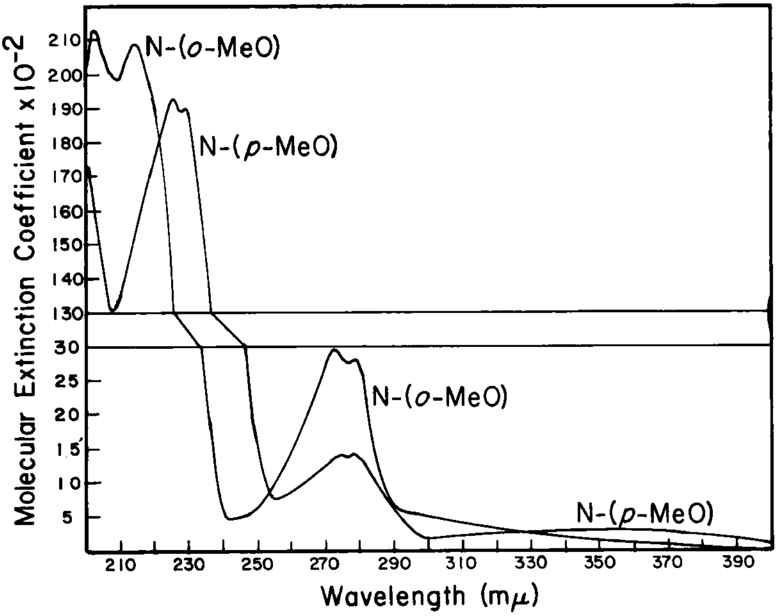


FIG. 5. Ultraviolet spectra of N-(*o*-methoxyphenyl)maleimide (N-(*o*-MeO)) and N-(*p*-methoxyphenyl)maleimide (N-(*p*-MeO)).

seems that substituent electron delocalization effects exert more influence on the position of the long-wavelength peak than do inductive effects for the Cl derivative.

N-(Methoxyphenyl)maleimides. The spectra of the MeO derivative, shown in Fig. 5, is difficult to interpret, possibly because of the complicating strong substituent effect of this group. For the hindered *o*-MeO derivative the long-wavelength band does not even appear, presumably because of the intense peak in the region 260 to 280 mμ. (Note the change of scale for the extinction coefficient in the lower part of Fig. 5, which runs from 0 to 30, whereas it is 0 to 9 for the other compounds.) For the *p*-MeO derivative there is a bathochromic shift (52 mμ) of the long-wavelength band to 347 mμ, relative to the N-benzyl derivative. The MeO group has the smallest hindering radius of any of the groups studied here.

N-(Nitrophenyl)maleimides. Figure 6 is the spectra of the NO_2 derivatives and shows radical differences from the preceding spectra. The unhindered *p*-isomer long-wavelength band (276 mμ) is at a wavelength less than the shoulder we take to be this same

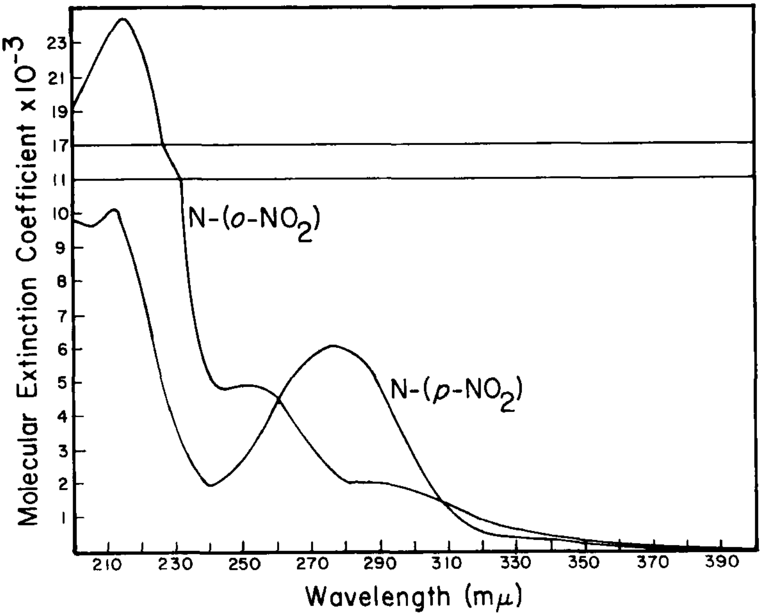


FIG. 6. Ultraviolet spectra of N-(*o*-nitrophenyl)maleimide (N-(*o*-NO_2) and N-(*p*-nitrophenyl)maleimide (N-(*p*-NO_2)

band for the *o* isomer (~290 mμ). The shift is also hypsochromic relative to N-Bnz- (295 mμ) and N-phenylmaleimide (322 mμ). Both the magnitude and direction of the shift is explainable in terms of the strong electron-withdrawing delocalization and inductive effects of the NO_2 group. That the long-wavelength band is nearly the same for the *o*-NO_2 and *o*-Bnz derivatives is taken as evidence of steric hindrance.

We conclude that conjugation between the two rings can be almost completely prevented by *o* substituents on the benzene ring. This hindrance as reflected by the spectra appears as effective as the insertion of an insulating methylene group between the rings. Shifts in the long-wavelength band reflect both electron delocalization and inductive effects, both of which are active with the *p* isomer while only the latter is observed for the *o* isomer.

Chromatography

The R_f values, both absolute and relative to N-phenylmaleimide, are listed in Table 4. Two plates were run simultaneously in the chamber. One held the Me and Cl derivatives along with the N-Ph and N-Bnz compounds are controls [designated (1)] and the other the MeO- and NO_2-derivatives with these same controls [designated (2)]. The average difference in R_f values for the N-Ph compound on different plates but run simultaneously in the same chamber and for the N-Bnz compound was 0.01 R_f unit with a maximum of 0.02 unit. Snyder (*7*) suggests that at best reproducibility is about 0.02 R_f unit. The data of Lisboa (*60*) show a standard deviation of ± 0.03 unit. The reproducibility of the controls is well within these limits.

An examination of the relative R_f values shows that the order of decreasing adsorption affinity as determined by the substituent on the benzene ring without regard to ring position is roughly

$$NO_2\text{-Ph} > \text{MeO-Ph} > \text{Me-Ph} > \text{Ph} > \text{Cl-Ph} > \text{Bnz}$$

This is true for all the solvent systems and is the one case of high-temperature reactivation.

The N-phenylmaleimide is more strongly retained than the N-benzylmaleimide, which is to be expected if π-electron delocalization and planarity favor adsorption. Problems arise on the application of this concept to the other compounds. The *o*-Me and

TABLE 4

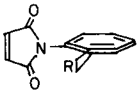
R_f Values and Relative R_f Values of the N-Substituted Maleimides on Alumina-G

		R_f values^a												
		Me			Cl			MeO		NO$_2$				
Activ. temp., °C	Solvent	*o*	*m*	*p*	*o*	*m*	*p*	*o*	*p*	*o*	*m*	*p*	Ph-	Bnz-
120	Bnz/CyHx 2:1	0.38 ($\overline{0.83}$)	0.44 (0.96)	0.40 (0.87)	0.41 ($\overline{0.89}$)	0.51 (1.11)	0.48 (1.04)	0.33 (0.72)	0.28 ($\overline{0.61}$)	0.25 (0.54)	0.19 ($\overline{0.41}$)	0.17 ($\overline{0.37}$)	(1)0.46 (1.00) (2)0.46 (1.00)	(1)0.52 (1.13) (2)0.53 (1.15)
120	Bnz/CyHx 1:1	0.25 ($\overline{0.72}$)	0.33 (0.96)	0.30 (0.87)	0.27 ($\overline{0.78}$)	0.37 (1.07)	0.35 (1.01)	0.16 (0.46)	0.13 ($\overline{0.38}$)	0.10 (0.29)	0.05 ($\overline{0.14}$)	0.03 ($\overline{0.09}$)	(1)0.35 (1.01) (2)0.34 (0.98)	(1)0.40 (1.16) (2)0.41 (1.19)
120	CyHx/EtAc	0.60 ($\overline{0.88}$)	0.68 (0.99)	0.63 (0.92)	0.62 ($\overline{0.91}$)	0.73 (1.06)	0.71 (1.04)	0.52 (0.76)	0.45 ($\overline{0.66}$)	0.37 (0.54)	0.31 ($\overline{0.45}$)	0.27 ($\overline{0.39}$)	(1)0.69 (1.01) (2)0.68 (0.99)	(1)0.74 (1.08) (2)0.73 (1.06)
120	Bnz/Hx	0.26 ($\overline{0.71}$)	0.35 (0.96)	0.32 (0.88)	0.29 ($\overline{0.79}$)	0.40 (1.10)	0.38 (1.04)	0.20 (0.55)	0.16 ($\overline{0.44}$)	0.14 (0.38)	0.08 ($\overline{0.22}$)	0.03 ($\overline{0.08}$)	(1)0.36 (0.99) (2)0.37 (1.01)	(1)0.42 (1.15) (2)0.44 (1.21)
400	Bnz	0.46 ($\overline{0.84}$)	0.53 (0.97)	0.50 (0.92)	0.49 ($\overline{0.90}$)	0.58 (1.06)	0.56 (1.03)	0.40 (0.73)	0.34 ($\overline{0.62}$)	0.31 (0.57)	0.26 ($\overline{0.48}$)	0.23 ($\overline{0.42}$)	(1)0.55 (1.01) (2)0.54 (0.99)	(1)0.62 (1.14) (2)0.62 (1.14)

[a] R_f values relative to the mean value of N-phenylmaleimide are shown in parentheses under the R_f's.

o-Cl isomers are slower than their *m* and *p* isomers by 0.04 to 0.10 R_f units (the mean R_f value was used for the *m* and *p* isomers) for all solvent systems, and the higher activation temperature, i.e., the hindered compound, was the more retained. The *o*-MeO and *o*-NO_2 isomers preceded the *m* and *p* isomers by 0.03 to 0.09 R_f unit (mean value of the *m* and *p*-NO_2 isomers used) and were less retained. These R_f differences exceed the reproducibility of the controls and the limit set by Snyder.

For *o*-Me- and *o*-Cl-isomers, the non-planer configuration (**2**) must present a preferred orientation of the molecule to the surface.



(2)

Since the Cl and Me groups have little adsorptive interaction of their own, the likely candidate for interaction with the surface is the carbonyl oxygen of the imide. In the hindered position the electrons on the nitrogen atom cannot delocalize the benzene ring because its $2p_z$ orbital is orthogonal to the π orbitals of the benzene. The ultraviolet spectra verified this. Delocalization of the nitrogen's electrons toward the carbonyl can still occur, however, to increase the electron density on the oxygen. This alone is not sufficient, since it must also occur with the N-Bnz derivative and is less retained than the N-Ph derivative. Hence the orientation of the group must also be included. For the *m* and *p* isomer the conjugation favors coplanarity, and now there is interference of approach of the carbonyl to the surface by the benzene ring. The free pair of electrons of the nitrogen can delocalize to the benzene ring and reduce the negative charge on the oxygen. There is very little difference in the relative R_f values of the *o*-Me and *o*-Cl isomers; any profound conclusions based on such a small difference would be suspect. The differences between the relative R_f values of the *m* and *p*-Me and *m*- and *p*-Cl isomers are sufficiently different and consistent to invite interpretation. The role of the carbonyl is suppressed and π-electron delocalization now appears with these isomers. Charge-transfer interaction of the delocalized electrons with the surface is encouraged. The electron-withdrawing inductive effect will somewhat reduce the delocalized π-electron density to reduce the interaction of these electrons with the surface. The *p*-Cl isomer is slightly retained over the *m* isomer. The inductive electron-withdrawing power of Cl is enhanced when it is in the *m* position, which would reduce delocalization within the benzene ring. This has been remarked upon in the interpretation of the spectra where a hypsochromic shift of the *m* isomer was attributed to this induction. On the other hand, *p*-Cl substitution exerts a positive resonance effect which returns some electron density to the benzene carbon attached to the nitrogen and to the imide group with its carbonyl. A bathochromic shift was observed. The greater retention of the *p*-Cl can be explained by either greater electron delocalization or a slightly more negative carbonyl oxygen.

A similar situation exists for *m*-Me and *p*-Me isomers, where the *p* isomer is slightly but consistently retained over the *m* isomer. The electron-donating properties of the *p*-alkyl group enhance electron delocalization and the charge on the carbonyl group.

The MeO and NO_2 isomers present special problems. Both sets are more strongly retained than the Me or Cl. With regard to inductive effect the strength as electron attractors (*58*) is

$$NO_2 > Cl > RO > Me$$

where, in fact, Me is electron-donating. If the only effect was the inductive influence on the carbonyl, the *o*-NO_2 isomer should behave in nearly the same fashion. This is not the case. An even more dramatic disagreement occurs with the unhindered planer compounds, where the substituent contributes to electron delocalization. The MeO group is electron-donating (bathochromic shift in the ultraviolet spectra), whereas the NO_2 group is strongly electron withdrawing (*58*) (hypsochromic effect). We find it difficult to rationalize the chromatographic behavior of these compounds with delocalization effects and hence with the ultraviolet spectra in the manner employed so far.

The MeO and NO_2 groups differ from the Me and Cl in that the former pair are themselves capable of interacting with the surface, whereas the latter pair are nonadsorptive. In fact, the results are in agreement with the eulotropic order of functional groups established long ago by Brockmann and Volpers (*61*). Snyder (*6,24*) reports a group adsorption parameter on alumina of 1.77 for Ar-O-R and 2.75 for Ar-NO_2 (none are given for Me and Cl). Although not as large as those given for the carbonyl group, they are sufficient to merit consideration and both exceed the value set for the appearance of localization effects. We suggest that a concerted approach of retentive groups to the surface occurs. We do this in spite of the fact Snyder's interpretation would have the localization of the carbonyl reduce the adsorption energy of the MeO and NO_2 groups. However, reduction of participation does not necessarily imply nonparticipation. Snyder admits concerted adsorption by simultaneous interaction of two groups with a *single* adsorbent site but restricts it to adjacent substituent groups (chelate formation) (*6,7*). We here strain the concept to nonadjacent groups and defer any discussion of what may be meant by "adjacent" in terms of intergroup separation distances. We are also unprepared to treat interaction of the molecule with separate adsorbent sites as either the same or different. For the *o* compound these groups are out of plane, and optimum bonding of the carbonyl and either MeO or NO_2 is prevented. When coplaner, cooperative attachment to the surface may be possible. A *p*-NO_2 offers conjugative interaction with the imide group which may explain its greater retention over the *m* isomer.

Equation (4) requires several molecular parameters. Table 5 shows the calculation of the adsorbate areas. The area for benzene was determined from BET data for carbon (*62*) and is somewhat less than the result calculated from covalent radii, presumably because of inefficient packing of the adsorbent surface. The results for alumina were obtained from gas-solid chromatography and were given relative to benzene. We combined these with the area of benzene

TABLE 5

Adsorbate Areas of Solvent Components

		n_b 2.7% H_2O-Al_2O_3 (83°C)
Component	Molecular area A_S (*62*), Å^2	1/6 A_S Bnz
Benzene	48.3[a]	6 (*64*)
	51.1[b]	
Cyclohexane	—	6 (*64*)
Ethyl acetate	—	5.5 (*64*)
Hexane	—	6.0 (*64*)

[a] Determined for carbon adsorbent.

[b] Calculated from covalent radii.

on carbon. Snyder (63) lists $\alpha = 0.69$ for 3% H_2O-Al_2O_3. We elected this value for use because it corresponds to the molecular areas of Table 5. Mole fractions were calculated from the volume composition and liquid densities at 20°C. Elution strengths are shown in Table 6. The eluant strengths of the solvent mixtures containing benzene are essentially the same as benzene itself. Some difference between empirical and theoretical values is to be expected from failure of the theoretical formula to include all the vagaries that arise in chromatography and from poor selection of the numerical values used in the calculation. The results, however, serve to warn off any interpretation based on an assumption that the solvents are very different. Only the CyHx/EtAc solvent is sufficiently different to indicate that the relative R_f values for isomers of the same substituents are dependent upon the solute and not the solvent elution strength for the combinations studied.

TABLE 6

Eluant Strength of Forming Solvents

Solvent	ϵ°	Density, g/cc
n-Hexane	0.00 (*64*)	0.660
Cyclohexane	0.04 (*64*)	0.779
Benzene	0.32 (*64*)	0.879
Ethyl acetate	0.58 (*64*)	0.901
Bnz/CyHx 2:1	0.29	
Bnz/CyHx 1:1	0.26	
CyHx/EtAc	0.41	
Bnz/Hx	0.25	

From the earlier discussion it seems that the electron-rich positions of the solute molecule could attach to either exposed positive aluminum atoms or hydrogen bond to surface hydroxyl groups. We favor the positive aluminum because our work, reported elsewhere (65) with these same compounds on silica gel, which is accepted as a hydrogen-bonding surface, does not distinguish between isomeric compounds. It is difficult to rationalize this dramatic difference in behavior with similar adsorption sites. We also note that the alumina, activated at 400°C, which presumably reduces the number of hydrogen-bonding hydroxyl groups, with an eluant (Bnz) of the same strength as the Bnz/CyHx and Bnz/Hx enhanced retention without changing the solute order. The proposal that the carbonyl of the carbonyl in combination with the MeO or NO_2 groups are responsible for retention rather than charge-transfer interaction with the delocalized π electrons is further supported by the observation that the behavior of the chlorosuccinanils is identical with that of the N-substituted maleimides on both alumina and silica gel (*66*). This set of isomers lacks a double bond in the five-membered ring, which reduces electron delocalization.

The "end-on" adsorption on alumina proposed by Giles (*17,27*) has its counterpart in retention of the projecting carbonyl group of the hindered compounds. If there is a different orientation for the planer isomers, then our assumption of the same solute molecular areas for all isomers is in error. Concerted approach of the groups to the surface may also change this parameter. The "weak localization" term, Δ_{eas}, has also been ignored.

In conclusion, we feel that for the N-substituted maleimides, charge-transfer interaction of the delocalized π electrons with the surface is a secondary factor of little influence in retention and that the functional groups and their spatial position is far more significant.

N-(Chlorophenyl)- and N-(Methylphenyl)maleimides: Nonadsorptive Substituents. Retention is due to the carbonyl of the imide groups and is favored by steric situations where this group projects out of the plane of the rings. Shielding of this group by a planer configuration reduces retention. Retention correlates with the ultraviolet spectra but in a fashion opposits to that expected; i.e., electron delocalization does not imply greater retention; instead, steric hindrance indicates a favorable approach to the surface.

N-(Methoxyphenyl)- and N-(Nitrophenyl)maleimide: Adsorptive Substituents. Retention is due to concerted adsorption of the carbonyl and the substituents groups or the carbonyl, π-electron system, and the substituent groups. Coplanarity favors retention either because of favorable approach to the surface or because both carbonyls and the substituent may interact with the surface. Retention correlates with the ultraviolet spectra in that the latter is an indication of coplanarity of the rings but is faulty in that greater retention occurs with both a bathochromic and hypsochromic shift of the peaks.

Acknowledgments

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The following comments were made by L. R. Snyder subsequent to submission of the manuscript. The surface of alumina defies detailed mapping in terms of specific adsorption sites and is best considered as generating a positive adsorptive force field of finite but molecular dimensions. The maleimide ring could equally well be parallel to the adsorbent surface with both carbonyl groups interacting with this field.

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