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# Thin-Layer Chromatography of the Chlorosuccinanils on Alumina: Stereochemical Factors

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# Thin-Layer Chromatography of the Chlorosuccinanils on Alumina: Stereochemical Factors

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## Summary

The ascending thin-layer-chromatographic behavior of *o*-, *m*-, and *p*-N-(chlorophenyl)maleimides and *o*-, *m*-, and *p*-chlorosuccinanils on Alumina-G using benzene/cyclohexane, 2:1 (v/v), and cyclohexane/ethyl acetate, 4:1 (v/v) as developers was compared. The *o*-, *m*-, and *p*-isomeric pairs behaved almost identically. This was taken to mean that $\pi$-electron delocalization, present with *m*- and *p*-N-(chlorophenyl)maleimides, played no role in retention. The *o*-isomers, which are noncoplanar, were more strongly retained. This seems to indicate that solute interaction with the surface is through the carbonyl group, which is sterically more available with the *o*-isomer.

Dichiaro et al. (*1*) chromatographed 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 in thin-layer systems on Alumina-G with forming solvents of benzene/cyclohexane, cyclohexane/ethyl acetate, and benzene/*n*-hexane. Simultaneous studies of the ultraviolet spectra of these solutes showed $\pi$-electron delocalization for the N-phenyl and the *m*- and *p*-isomers. Evidence for this was taken to be the large bathochromic shift of the absorption band of the imide system for these compounds compared to N-benzylmaleimide, where $\pi$-electron delocalization across the two rings is impossible because

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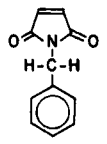
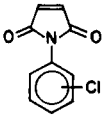
of the intervening methylene group. This shift was not observed with the *o*-isomers and, in addition, the spectra of these compounds were nearly the additive sum of the contributions of the structural groups. The absence of $\pi$-electron delocalization was attributed to noncoplanarity of the two rings because of steric hindrance of the *o*-substituent with the carbonyl groups of the imide group.

If $\pi$-electron delocalization within the solute molecule and interaction of these electrons with the adsorptive surface is responsible for retention, then the hindered compounds, along with N-benzylmaleimide, should show consistently larger $R_f$ values than their respective unhindered isomers. Results were contrary to this expectation. The *o*-Me- and *o*-Cl-hindered compounds were more strongly retained than their unhindered isomers, while the *o*-MeO and *o*-$NO_2$ compounds were less strongly retained in all solvent systems and with Alumina-G reactivated at two widely differing temperatures. The authors suggested that for the Me- and Cl-isomers, retention is primarily due to interaction of the carbonyl group with the surface, the other groups having little tendency to adsorb, and that their interaction is enhanced in the noncoplanar hindered configuration, where the carbonyl groups is made especially available by the "twisted-ring" configuration. Dichiaro et al. (*1*) pictured the interaction of a single carbonyl group with the surface and the molecule oriented with the maleimide ring perpendicular and the phenyl ring parallel to the adsorbent surface. Snyder (*2*) pointed out that the maleimide ring might well be parallel to the solid surface, which would allow simultaneous surface interaction of both carbonyl groups. There is nothing in our data which would distinguish between these two orientations, and the point is well taken. The previous paper presented an argument based on identifiable specific adsorption sites within the alumina surface. Simultaneous interaction of both carbonyls with such sites would depend upon their fortuitous favorable location. Snyder (*3*) feels that such a detailed mapping of the complex surface of alumina is unwarranted, and that a more realistic picture is that of a positive electrical force field of finite thickness, relative to molecular dimensions, extending over the planar surface. Such a viewpoint is more compatible to a maleimide ring parallel to the surface. Delocalized $\pi$ electrons seemed to have little to do with retention. The greater retention of the MeO- and $NO_2$-isomers was attributed to simultaneous adsorption of the carbonyl and other substituent groups, which is favored with the planar compound. If $\pi$-electron

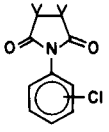
delocalization has any influence, these experiments could not disclose it. A further test of this interaction was conceived to be the removal of conjugative interaction while retaining the geometric configuration of the maleimides. This was accomplished with the chlorosuccinanils:




N-Benzylmaleimide




N-(Chlorophenyl)maleimide




Chlorosuccinanil

where conjugative interaction relative to the maleimides is reduced by the absence of a double bond in the five-membered ring.



## EXPERIMENTAL

### Synthesis

Equimolar amounts of solutions of succinic anhydride in benzene and of the appropriate chloroaniline in benzene were heated together to yield the chlorosuccinanilic acid. Ring closure was accomplished with acetyl chloride.

***o*-Chlorosuccinanil.** Succinanilic acid: 100 g of succinic anhydride in 400 ml of boiling benzene added to 12.8 g of *o*-chloroaniline in 30 ml of benzene; boiled 15 min and cooled. 94% yield. Product m.p. 143–144°C.

Succinanil: 11.4 g of succinanilic acid refluxed with 50 ml of acetyl chloride for 15 min. Solid product washed with 10% aqueous sodium bicarbonate, water, and dried. Recrystallized from ethanol. 50% yield. Product m.p. 110–111°C; literature 109–110°C (*4*).

***m*-Chlorosuccinanil.** Succinanilic acid: 12.8 g of *m*-chloroaniline added to 10.0 g of succinic anhydride in 400 ml of boiling benzene; a white solid appeared after 5 min of heating. Cooled and filtered. 92% yield. Product m.p. 149–150°C.

Succinanil: Same procedure as with the *o*-isomer. 68% yield. Product m.p. 117–118°C; literature 118–119°C (*4*).

***p*-Chlorosuccinanil.** Succinanilic acid: Same procedure as with the *o*-isomer. 97% yield. Product m.p. 169–170°C.

Succinanil: Same procedure as with the *o*-isomer. 74% yield. Product m.p. 165–166°C; literature 163–164°C (*4*).

### Spectra

Ultraviolet spectra of the solutions of the succinanils in Eastman spectro-grade cyclohexane were measured on a Cary Model 11 recording spectrophotometer using 1-cm matched quart absorption cells.

### Chromatography

The adsorbent, preparation of the thin-layer plates, sample load, forming solvents, ascending chromatography, and spot visualization were identical with those described in the earlier publication (*1*). only two solvent systems were used, benzene/cyclohexane, 2:1 (v/v), eluant strength, $\epsilon^\circ = 0.29$, and cyclohexane/ethyl acetate, 4:1 (v/v), $\epsilon^\circ = 0.41$ (*1*). The chlorosuccinanils and N-(chlorophenyl)-maleimides were chromatographed all together on plates reactivated at 120° for 2 hr.



## RESULTS AND DISCUSSION

### Ultraviolet Spectra

The dramatic shift of the long-wavelength peak from 318 m$\mu$ for N-(*m*-chlorophenyl)maleimide (curve 1b, Fig. 1) to 282 m$\mu$ for N-(*o*-chlorophenyl)maleimide (curve 1a, Fig. 1) is taken as evidence of steric hindrance of a $\pi$-electron delocalized by the chlorine in the ortho position, which forces the rings to be noncoplanar. The spectra of *m*-chlorosuccinanil (curve 2b, Fig. 1) is virtually identical with that of *o*-chlorosuccinanil (curve 2a, Fig. 1) with no change in passing from the potentially planar configuration to the noncoplanar. The absence of the double bond in the five-membered ring is responsible for the lack of extensive $\pi$-electron delocalization. The spatial configuration of the chlorosuccinanils and N-(chlorophenyl)maleimides are identical.

### Chromatography

The $R_f$ values, both absolute and relative to the consistently slower N-(*o*-chlorophenyl)maleimide, are shown in Table 1.

We make the following observations: (1) The elution order of the succinanils is identical with that of the maleimides in both solvent systems of different elution strength; $\pi$-electron delocalization plays no role in retention. (2) The $R_f$ values are nearly identical,

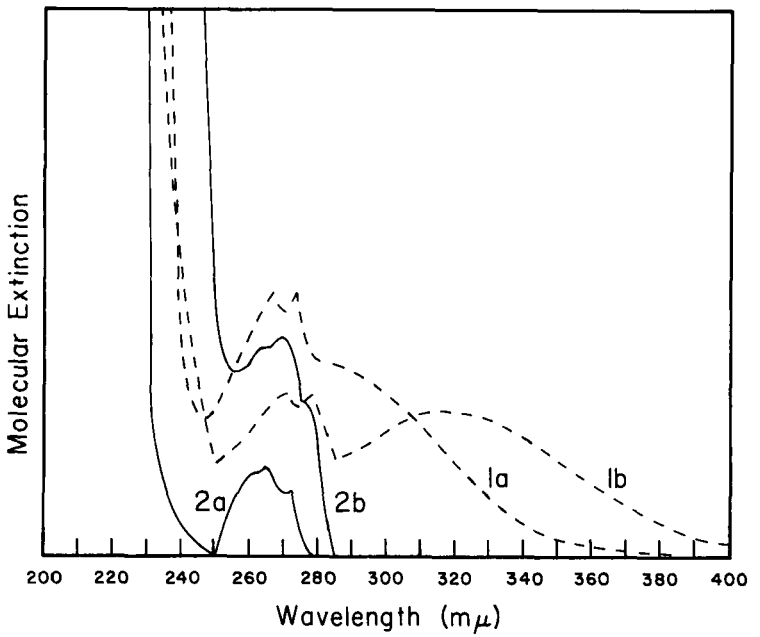



**FIG. 1.** Ultraviolet spectra: 1a, N-(*o*-chlorophenyl)maleimide; 1b, N-(*m*-chlorophenyl)maleimide; 2a, *o*-chlorosuccinanil; 2b, *m*-chlorosuccinanil.

**TABLE 1**

$R_f$ Values of the Chlorosuccinanils and the N-(Chlorophenyl)maleimides on Alumina-G Reactivated at 120°C

| Compound | $R_f$ values[a] | |
|---|---|---|
| | Bnz/CyHx, 2:1 | CyHx/EtAc, 4:1 |
| *o*-Chlorosuccinanil | *0.42* (3) (1.05) | *0.67* (3) (1.06) |
| *m*-Chlorosuccinanil | 0.53 (1) (1.32) | 0.78 (1) (1.24) |
| *p*-Chlorosuccinanil | 0.49 (2) (1.22) | 0.73 (2) (1.16) |
| N-(*o*-Chlorophenyl)maleimide | *0.40* (3) (1.00) | *0.63* (3) (1.00) |
| N-(*m*-Chlorophenyl)maleimide | 0.49 (1) (1.22) | 0.73 (1) (1.16) |
| N-(*p*-Chlorophenyl)maleimide | 0.47 (2) (1.18) | 0.70 (2) (1.11) |

[a] $R_f$ values relative to N-(*o*-chlorophenyl)maleimide are shown in parentheses under the $R_f$'s. The order, least retained (1) to strongest retained (3), is given alongside the absolute $R_f$ values.

**TABLE 2**

Difference of $R_f$ Values between Identically Substituted Chlorosuccinanils and N-(Chlorophenyl)maleimides

| Isomer pair | Difference in $R_f$ values | |
|---|---|---|
| | Bnz/CyHx, 2:1 | CyHx/EtAc, 4:1 |
| ortho | 0.02 | 0.04 |
| meta | 0.04 | 0.05 |
| para | 0.02 | 0.03 |

as shown in Table 2. The previous paper set a difference of 0.02 $R_f$ unit as the lower limit of reproducibility. Two pairs are within the experimental error of what can be expected of the performance of a single compound. We feel that these results support our earlier contention that retention is governed by interaction of one or both carbonyl groups with the adsorbent surface and that chromatographic behavior is best explained by consideration of this group and the electronic effects other substituents may have upon it.



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