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# Thin Layer Chromatographic Studies of Anils II. Separation, Identification and Determination

By

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Thin layer chromatographic behaviour of ten anils was studied on silica gel adsorbent mixed with starch binder with ten solvent systems. Simultaneous separation, identification and determination of ternary mixtures of isomers was stressed. The $R_F$ increasing order was found to be dependent on the solvent and independent of the degree of saturation of the chamber. The correlations of $R_F$ with $\lambda_{max}$ and $\nu$ (C=O) of isomers were established and used in their identification. Six anils were separated in methanol—benzene (1 : 1).

A fairly good number of primary aromatic amines[1–3] and carbonyl compounds[4–6] has been studied by thin layer chromatography (*TLC*) and a few anils, the condensation products of α-ketoaldehydes with primary aromatic amines have been studied for the first time by *Upadhyay* et al.[7]. Separation of isomers has also been a long persisting problem and only a few attempts[8, 9] have been successfully made so far. In the continuation of our early investigations the present communication on the separation of many anils has shown that the *TLC* method is successful.

The relationship between the stretching frequencies of the carbonyl group (> C=O) of isomeric anils with their $R_F$ values in different solvents were studied and used in their identification. At $\lambda_{max}$ values, corresponding to > C=O group of the anils, the optical density of the elutes were measured to estimate quantitatively the mixture components.

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## Experimental

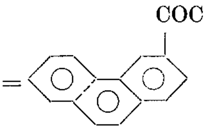
### Synthesis and Characterisation of Anils

p-Diethylaminoanil was prepared in alcoholic medium at room temperature and dried at reduced pressure. The other anils were synthesized[7, 11] by condensing the appropriate weights of the corresponding amine and 3-phenanthryl glyoxal in acetic acid.

Table 1. *Characteristics of Anils* *

| | Anil | Colour | M.P., °C | Yield, % | $\lambda_{max}$ values C=O nm, P | | C=N nm, S | Stretching Frequencies C=O cm$^{-1}$ | C=N cm$^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|
| **1** | $R = NC_6H_4$—$NO_2$ (*o*-) | Yellow | 128–129 | 72 | 293 | 320 | 277 | 1681 | 1618 |
| **2** | $R = NC_6H_4$—$NO_2$ (*m*-)[11] | Buff | 103–104 | 76 | 297 | 321D | 267 | 1688 | 1629 |
| **3** | $R = NC_6H_4$—$NO_2$ (*p*-) | Yellow | 115–116 | 69 | 295 | 319 | 270 | 1684 | 1667 |
| **4** | $R = NC_6H_4$—COOH (*o*-) | Buff | 202 | 70 | 295 | 318 | 278 | 1695 | 1613 |
| **5** | $R = NC_6H_4$—COOH (*m*-) | Orange | Decompose | 70 | 296 | 352 | 260 | 1724 | 1613 |
| **6** | $R = NC_6H_4$ COOH (*p*-) | Orange | 192 | 76 | 298 | | 269 | 1739 | 1667 |
| **7** | $R = NC_6H_4$—N*Et*$_2$ | Dark brown | 95 | 90 | 300 | | 285 | 1667 | 1613 |
| **8** | $R = NC_6H_4$—Cl (*p*-) | Orange | 135 | 68 | 303 | 360 | 303 | 1730 | 1613 |
| **9** | $R = NC_6H_4$—Br (*p*-) | Yellow | 217–218 | 80 | 300 | 350 | 300 | 1695 | 1613 |
| **10** | $R = NC_6H_4$—I (*p*-) | Violet green | 145 | 92 | 300 | 352 | 300 | 1667 | 1600 |

R =



D = diffused, P = Primary, S = Secondary.

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* Formulae checked by N-determination.

The anils were recrystallized from chloroform.

Ultraviolet spectra were recorded on G 2400 DU Spectrophotometer in chloroform and the infrared spectra on a Perkin-Elmer infracord in KBr medium. Characteristics of the anils are noted in Table 1.

### Plate Preparation and Development

Silica gel (N.C.L., Poona, India) having been freed from iron and chloride ions and mixed with starch (E. Merck, Darmstadt, GFR) as binder (19 : 1, *w/w*) was used for coating the glass plates. An aqueous slurry was used to prepare the layers of 0.10 cm thickness, with a home-built apparatus[10]. The coated plates were dried at ≈ 100 °C for 2 hours in an oven. Sample solutions were prepared in acetone and applied with fine capillaries.

The $R_F$ values were determined on 18 × 3 cm glass strips, and the results were checked using 18 × 10 cm glass plates. The $R_F$ values (Table 2) were found to be essentially independent of plate size.

The plates were developed in glass chambers with ground-in-lids by ascending technique. The time of development given in Table 2 is for a distance of 10–11 cm travelled by the solvent front. The developed plates were air dried and spots were clearly discernible in day light and their colours remained stable for over six months.

## Results and Discussion

Benzene—methanol (1 : 1, $v/v$) showed the highest resolving capability in which the separation of six compounds (from m-nitroaniline, m-aminobenzoic acid, p-diethylaminoaniline, p-chloroaniline, p-bromoaniline and p-iodoaniline) was promising. Abnormally high $R_F$ values in mixtures (benzene—alcohol: 1 : 1, $v/v$), greater than that of benzene or alcohol, may be attributed[12] to the interaction of the carbonyl group of the anils with alcohol in presence of benzene (inert solvent) which disrupted the association among alcohol molecules as a consequence of increased protonation or pH led to the formation of hemiacetals or ketals. Azeotropic properties of the mixtures may also account for this abnormality.

Inspite of the dominant role played by the solvent the chromatographic studies of the ternary isomeric mixtures of the anils gave interesting results, each mixture giving a particular order of the $R_F$ values.

### *Anils from o-, m- and p-Nitroanilines*

The mixture was best resolved in chloroform. The resolving capability of chloroform mixed with various proportions of benzene was tested. Even 20% of chloroform in benzene was found sufficient to give good separations. However, small proportions of chloroform were effective only for the separation of binary mixtures. Toluene was also used to resolve the mixture although it was less effective. For oxygen containing solvents, hydrocarbons and chloroform, different $R_F$ increasing orders, meta-, ortho-, para-; para-, meta-, ortho- and ortho-, para-, meta- were obtained respectively. Alcohol—benzene (1 : 1, $v/v$) azeotropic mixtures behaved like chloroform in establishing the $R_F$ orders whereas butanol—acetic acid (3 : 2, $v/v$) azeotropic mixture showed the similar behaviour as hydrocarbons in establishing the $R_F$ order.

### *Anils from o-, m- and p-Aminobenzoic Acids*

Maximum separation was achieved in butanol—acetic acid (3 : 2, $v/v$). For oxygen containing solvents the $R_F$ values increased in the

*Table 2*

| | Spot Colour | $Et_2O$ | $Me$OH | n-$Bu$OH | $C_6H_6$ | $C_7H_8$ |
|---|---|---|---|---|---|---|
| **1** | Canary yellow | 0.81 | 0.73 | 0.93 | 0.40 | 0.39 |
| **2** | Yellow | 0.80 | 0.65 | 0.83 | 0.40 | 0.34 |
| **3** | Yellow | 0.90 | 0.74 | 0.94 | 0.29 | 0.10 |
| **4** | Yellow | 0.97 | 0.85 | 0.74 | 0.04 | 0.03 |
| **5** | Yellow | 0.99 | 0.88 | 0.98 | 0.00 | 0.00 |
| **6** | Light brown | 0.99 | 0.75 | 0.99 | 0.00 | 0.00 |
| **7** | Light orange | 0.97 | 0.97 | 0.99 | 0.40 | 0.00 |
| **8** | Orangish yellow | 0.99 | 0.75 | 0.99 | 0.56 | 0.44 |
| **9** | Yellow | 0.99 | 0.80 | 0.96 | 0.59 | 0.44 |
| **10** | Yellow | 0.96 | 0.81 | 0.99 | 0.00 | 0.00 |
| Development time | | ¾ h | 1 h | 2½ h | ½ h | ½ h |

order ortho-, meta-, para- which reversed for the chloroform, hydrocarbons and their mixtures. In the resolving solvent the order of $R_F$ was $p < o < m$.

### *Identification of Isomeric Anils*

An interesting feature of the studies was the correlation of the $R_F$ with infrared and ultraviolet results. The stretching frequencies ($\nu$) and $\lambda_{\max}$ values corresponding to the characteristic carbonyl group ($> C{=}O$) of the anils which is highly sensitive to the nature and position of the substituent, were correlated with the $R_F$ values in different solvents. Both, the $\nu\,(C{=}O)$ and $\lambda_{\max}$ of the isomeric anils derived from nitroanilines and aminobenzoic acids fell in the orders $o < p < m$ and $o < m < p$ respectively. The correlations of $\nu\,(C{=}O)$ and $\lambda_{\max}$ with $R_F$ values in the solvents giving best resolution of the isomers, were found very useful in their identification.

### *Quantitative Estimation*

The correlation of $\lambda_{\max}$ with $R_F$ in the resolving solvent was found significant in the determination of isomeric anils. Mixtures were resolved and eluted and optical density measurements were made at the $\lambda_{\max}$ of the components to deduce their concentrations from standard calibration curves.

### Acknowledgements

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| $CHCl_3$ | *Me*OH—$C_6H_6$ (1 : 1) | n-*Bu*OH—$C_6H_6$ (1 : 1) | n-*Bu*OH—*Ac*OH (3 : 2) | $CHCl_3$—$C_6H_6$ (1 : 4) |
|---|---|---|---|---|
| 0.55 | 0.92 | 0.96 | 0.95 | 0.36 |
| 0.78 | 0.95 | 0.99 | 0.91 | 0.30 |
| 0.70 | 0.94 | 0.99 | 0.91 | 0.15 |
| 0.00 | 0.93 | 0.99 | 0.89 | 0.03 |
| 0.00 | 0.84 | 0.99 | 0.99 | 0.00 |
| 0.00 | 0.82 | 0.34 | 0.81 | 0.00 |
| 0.00 | 0.66 | 0.99 | 0.99 | 0.00 |
| 0.76 | 0.23 | 0.98 | 0.99 | 0.61 |
| 0.97 | 0.74 | 0.99 | 0.99 | 0.00 |
| 0.51 | 0.47 | 0.98 | 0.99 | 0.00 |
| 1 h | 1½ h | 1¾ h | 3 h | 1 h |

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