

With the method described, a good separation of the first six straight-chain, saturated primary amines as well as of octylamine and decylamine was achieved, the distance travelled increasing with increasing length of the carbon chain. A branched chain causes the compounds to move faster, *e.g.* isopropylamine runs faster than propylamine. The effect caused by increased branching of the carbon chain tends to be more pronounced the closer the branch is situated to the amino group; the great difference between the distances travelled by primary and secondary amines with the same number of carbon atoms is most striking (*cf.* diethylamine and butylamine). Double bonds retard movement, and so also do alicyclic groups; phenyl groups have a very strong retarding effect.

The preparation of derivatives of compounds containing amino groups attached directly to a benzene ring is not possible. Further, it has not been possible to prepare derivatives from diamines or amines containing acidic groups (phenols etc.). Finally it has proved impossible to obtain derivatives from *di-sec.*-butylamine and phentermine, possibly due to some sort of steric hindrance.

It should be noted that alcohols, hydrazine compounds, tertiary amines, and ammonia do not interfere in the procedure outlined above.

*Department of Organic Chemistry,
The Technical University, Bygning 201,
Lyngby (Denmark)*

AAGE JART
ALLAN J. BIGLER

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Charge-transfer complexes of 2,4,6-trinitrophenyl-N-methylnitramine (tetryl) and 2,4-dinitrochlorobenzene with some amines

Thin-layer chromatography has been efficiently employed for the investigation of various charge-transfer complexes. For example studies on complexes of terpenes¹⁻⁴, glycerides⁵, hydrocarbons⁶ with silver and polynitro aromatic compounds with hydrocarbons⁷ have been reported. Recently the π -complexes of a number of aromatic amines with 2,4,6-trinitrotoluene (*s*-TNT) and *m*-dinitrobenzene (*m*-DNB) have been investigated⁸ by this technique.

In the present paper, studies of the π -complexes of 2,4,6-trinitrophenyl-N-methylnitramine (tetryl) and 2,4-dinitrochlorobenzene (DNCB) with some amines are

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reported. By employing a TLC technique it was possible to separate and characterise π -complexes obtained from 2–3 μg of different amino compounds.

Experimental

All the solvents employed for irrigation of chromatoplates were dried and freshly distilled. Kodak photographic glass plates (22 × 22 cm) were used as supports and the ascending irrigation technique was used. The distance travelled by the solvent front in each case was kept constant, *i.e.* 18.0 cm. The temperature of irrigation was $20^\circ \pm 1^\circ$. The colors of the complexes varied from yellow to deep red and could be easily located.

Adsorbents. (1) Kieselgel G (E. Merck)

(2) Kieselgel G + Kieselguhr G (9:1, E. Merck)

(3) Kieselguhr G (E. Merck)

(4) Cellulose benzoate (benzoyl content 54.8 %; 100 mesh, B.S.S.) containing 1 % CaSO_4 .

(5) Cellulose acetate (acetyl content 38.6 %; 100 mesh, B.S.S.) containing 1 % CaSO_4 .

(6) Cellulose powder, ashless (Whatman, 100 mesh, B.S.S.) containing 1 % CaSO_4 .

Preparation, spotting of complexes and irrigation of the plates. The chromatoplates were prepared by taking a homogenous slurry of the adsorbent in a suitable solvent, pouring it on the glass plates and tilting them from side to side; a uniform coating of the adsorbent was thus achieved. The plates were kept at room temperature overnight and activated at 110° for 1 h (cellulose benzoate and acetate plates were activated at 60° for 3 h in a vacuum oven). The plates were impregnated with tetryl/DNCB by irrigating them with a 3 % solution in acetone before spotting. The amounts of various adsorbents, solvents and average coatings are given in Table I.

TABLE I

Serial No.	Coating	Weight of the adsorbent (g)	Solvent	Average coating of adsorbent (mg/cm^2)
1	Kieselgel G	30	Chloroform (60 cc) -methanol (30 cc)	7.9
2	Kieselgel G + Kieselguhr G	30	Methanol (90 cc)	7.2
3	Kieselguhr G	32	Ethanol (70 cc)	6.2
4	Cellulose benzoate- CaSO_4	26.25	Water- (40 cc) ethanol (20 cc)	8.4
5	Cellulose acetate- CaSO_4	26.25	Water-(40 cc) ethanol (20 cc)	8.1
6	Cellulose- CaSO_4	27	Water (80 cc)	6.9

The tetryl/DNCB-amine complexes were prepared directly on the above plates by spotting ethanolic solutions of various amines (15 μl containing 2–4 μg) with a standard microcapillary. This gave instantaneous spots of the colored complexes. The plates were left in a desiccator for half an hour after which they were irrigated with

various solvents. Tables II and III give the R_F values of various π -complexes along with their colors. Two typical chromatoplates showing the resolutions of π -complexes of tetryl and DNCB with amines are given in Figs. 1 and 2, respectively.

TABLE II

 R_F VALUES AND COLORS OF π -COMPLEXES OF TETRYL WITH AMINES

Sample No.	Complex-forming amines	Color of the complex	Kieselgel G impregnated with 3% tetryl			
			Mono-chloro-benzene-ethyl acetate (9:1)	Toluene	Xylene-carbon tetrachloride (3:1)	Ethylene dichloride-petroleum ether (4:1)
1	N-Methylaniline	light violet	0.70	0.49	0.39	0.89
2	N,N-Dimethylaniline	light violet	0.80	0.65	0.51	0.93
3	Aniline	yellowish brown	0.48	0.33	0.22	0.73
4	<i>o</i> -Anisidine	brownish violet	0.54	0.27	0.17	0.74
5	<i>p</i> -Anisidine	orange	0.31	0.12	0.09	0.33
6	Diphenylamine	violet	0.87	0.83	0.71	0.97
7	α -Naphthylamine	violet	0.55	0.32	0.21	0.82
8	β -Naphthylamine	brownish red	0.50	0.27	0.18	0.74
9	<i>o</i> -Toluidine	brownish red	0.51	0.23	0.23	0.77
10	<i>m</i> -Toluidine	yellowish brown	0.48	0.27	0.20	0.72
11	<i>p</i> -Toluidine	yellowish brown	0.42	0.22	0.15	0.60
12	Benzidine	brown	0.23	0.04	0.03	0.21
13	<i>m</i> -Chloroaniline	reddish brown	0.59	0.33	0.24	0.86
14	<i>p</i> -Chloroaniline	reddish brown	0.53	0.26	0.18	0.80

TABLE III

 R_F VALUES AND COLORS OF π -COMPLEXES OF DNCB WITH AMINES

Sample No.	Complex-forming amines	Color of the complex	Kieselgel G impregnated with 3% DNCB		Kieselgel G + Kieselguhr G (9:1) impregnated with 3% DNCB	
			Mono-chloro-benzene-ethyl acetate (9:1)	Toluene-ethylene dichloride (3:1)	Xylene-ethyl acetate (4:1)	Carbon tetrachloride-petroleum ether (3:1)
1	N-Methylaniline	light yellow	0.66	0.58	0.76	0.84
2	N,N-Dimethylaniline	reddish brown	0.81	0.68	0.85	0.92
3	Aniline	light orange	0.49	0.36	0.56	0.62
4	<i>o</i> -Anisidine	reddish brown	0.55	0.43	0.57	0.69
5	<i>p</i> -Anisidine	orange	0.28	0.12	0.35	0.26
6	Diphenylamine	reddish brown	0.85	0.87	0.79	1.00
7	α -Naphthylamine	reddish brown	0.57	0.42	0.56	0.59
8	β -Naphthylamine	yellowish brown	0.51	0.35	0.50	0.52
9	<i>o</i> -Toluidine	pale yellow	0.56	0.47	0.55	0.68
10	<i>m</i> -Toluidine	bright yellow	0.52	0.38	0.51	0.66
11	<i>p</i> -Toluidine	bright yellow	0.44	0.27	0.47	0.42
12	Benzidine	dark orange	0.21	0.07	0.29	0.01
13	<i>m</i> -Chloroaniline	light yellow	0.63	0.58	0.62	0.72
14	<i>p</i> -Chloroaniline	light yellow	0.56	0.48	0.55	0.58

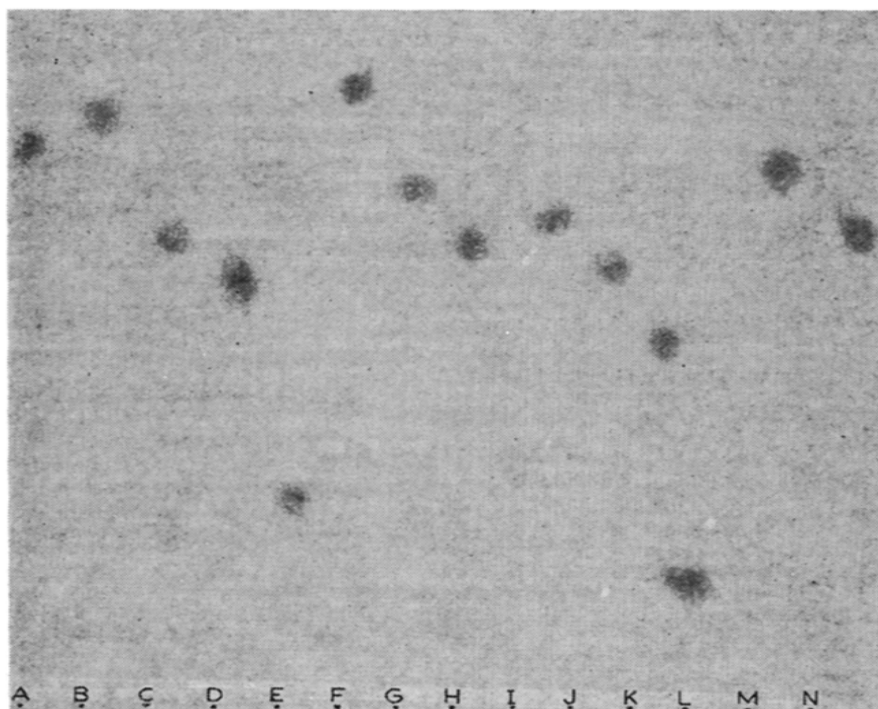


Fig. 1. Chromatoplate showing the resolutions of the charge-transfer complexes of tetryl with the following amines: A = N-Methylaniline; B = N,N-dimethylaniline; C = aniline; D = *o*-anisidine; E = *p*-anisidine; F = diphenylamine; G = α -naphthylamine; H = β -naphthylamine; I = *o*-toluidine; J = *m*-toluidine; K = *p*-toluidine; L = benzidine; M = *m*-chloroaniline and N = *p*-chloroaniline. Adsorbent: Kieselgel G impregnated with 3% tetryl; solvent: ethylene dichloride-petroleum ether (4:1, with 3% tetryl); system: ascending.

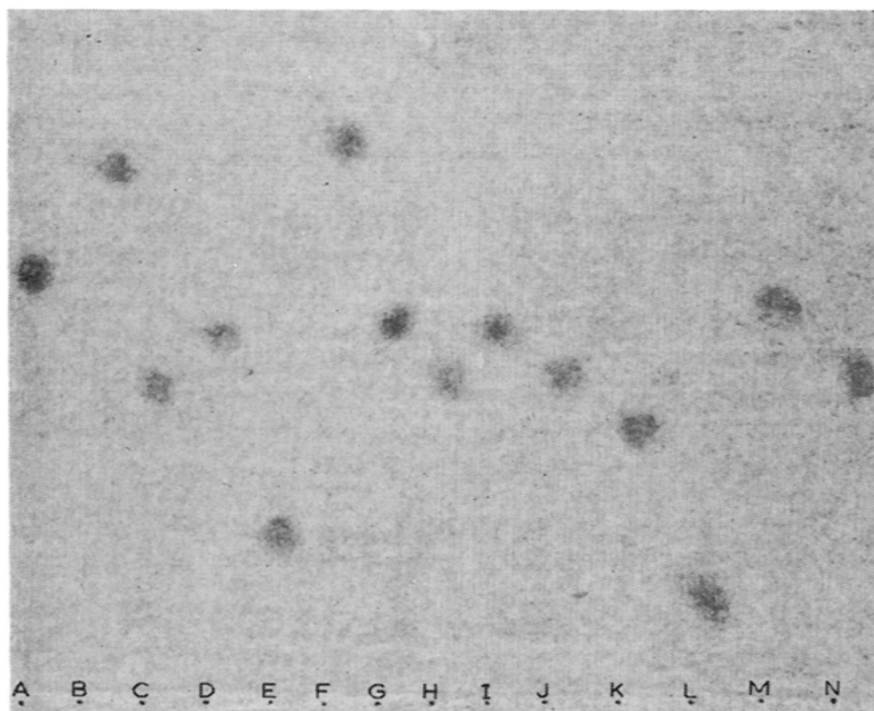


Fig. 2. Chromatoplate showing the separations of the complexes of 2,4-dinitrochlorobenzene with amines (A-N). Adsorbent: Kieselgel G containing 3% DNCB; solvent: ethyl acetate-mono-chlorobenzene (1:9, with 3% DNCB); system: ascending.

Discussion and results

The charge-transfer complexes of aromatic amines with tetryl and 2,4-dinitrochlorobenzene were found to be highly unstable, particularly when polar solvents were used for crystallization or irrigation on reversed phase systems. All the complexes broke down into tetryl or DNCB and the individual amines when spotted and run on different adsorbents (untreated with the nitro aromatic compounds) employing all possible irrigating solvent systems. Thus the adsorption forces were found to be even stronger than solvent forces. Since cellulose powder, due to its hydrophilic nature, had a strong rupturing effect on the weak physical linkages in the π -complexes, it was esterified. Even when highly acetylated and benzoylated cellulose samples were used as adsorbents no useful results were obtained.

In the case of Kieselguhr G the compounds travelled with the solvent front. Kieselgel G containing 3% tetryl/DNCB proved to be the best adsorption medium for the study of these complexes. In order to prevent further break-down of the complexes, 3% of the acceptor molecule was added to the irrigating non-polar solvent.

The distance of migration of the tetryl/DNCB-amine complexes was found to be parallel to the relative basicities of the individual amines. Complexes of more basic amines had lower R_F values than those which were less basic, e.g. aniline < N-methylaniline < N,N-dimethylaniline. It was found that the complexes of *para*-substituted anilines had the least mobilities compared with those which were *meta*- and *ortho*-substituted. Complexes of *p*-anisidine had lower R_F values than those of *o*-anisidine; those of *p*-chloroaniline had lower R_F values than those of *m*-chloroaniline; and of *p*-toluidine < *m*-toluidine < *o*-toluidine. Diphenylamine being a weak base, its complexes had high R_F values.

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Defence Science Laboratory,
Metcalfe House, Delhi-6 (India)

D. B. PARIHAR
S. P. SHARMA
K. K. VERMA

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