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## Note

### Gas chromatographic analysis of aromatic sulphonylamines. II

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The analysis of dichlorosulphonylamine isomers described here is an extension of our earlier gas chromatographic studies on arylsulphonylamines<sup>1-3</sup>. The electric dipole moments and nuclear magnetic resonance (NMR) spectra of a series of substituted N-sulphonylamines ( $\text{Ar-N}=\text{S}=\text{O}$ ) indicated that these compounds adopt preferentially a *cis*- or *syn*-structure (*Z*-configuration) with respect to the central  $-\text{N}=\text{S}-$  bond<sup>4-6</sup>. Since the earliest studies of their structural properties<sup>7,8</sup>, it has been generally assumed that N-sulphonylamines exist as a rapidly equilibrating mixture of geometrical isomers. Examination by thermal analysis has enabled the stability of arylsulphonylamines to be determined<sup>9,10</sup>, making it possible to apply gas chromatography for their analysis.

A thin-layer chromatographic (TLC) method for the analysis of arylsulphonylamines has been described<sup>11-13</sup>. In this paper, we describe gas-liquid chromatography investigations of the isomeric dichlorosulphonylanilines.

## EXPERIMENTAL

### Equipment and conditions

A Varian Aerograph 2860 gas chromatograph equipped with a flame-ionization detector was used. The column (50 m  $\times$  1 mm I.D.) was made of stainless steel. The packings used were polyphenyl ether OS-138, Silar 10C on Chromosorb G AW DMCS (80-100 mesh), Apiezon N and OV-275 on Gas-Chrom Q (50-100 mesh). The hydrogen flow-rate was 20 ml/min, air flow-rate 200 ml/min, carrier gas (hydrogen) flow-rate 7 ml/min, detector temperature 220°, column temperature 180°, inlet temperature 200° and chart speed 10 mm/min. A 1.0- $\mu\text{l}$  Hamilton syringe was used for the injections.

### Procedure

A 20% solution of the aromatic sulphonylamines in benzene was used for the analysis, the volume injected being 0.03  $\mu\text{l}$  in each instance. The quality of the standards obtained was checked by NMR and mass spectroscopy<sup>14</sup>.

## RESULTS AND CONCLUSION

The best results for the separation were obtained by using column A (50 m  $\times$

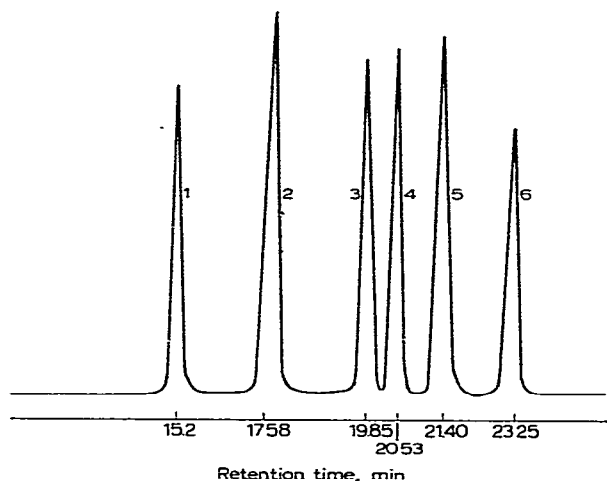


Fig. 1. Chromatographic separation of arylsulphonylamines. Peaks: 1 = 2,6-dichlorosulphonylaniline; 2 = 3,5-dichlorosulphonylaniline; 3 = 2,5-dichlorosulphonylaniline; 4 = 2,4-dichlorosulphonylaniline; 5 = 3,4-dichlorosulphonylaniline; 6 = 2,3-dichlorosulphonylaniline.

1 mm I.D.) packed with polyphenyl ether OS-138 stationary phase at a column temperature of 180°, the complete separation of six dichlorosulphonylaniline isomers being achieved (Fig. 1).

Similar results were obtained with column B (50 m × 1 mm I.D.) packed with Silar 10C on Chromosorb G (80–100 mesh) at 200°. Less satisfactory results were obtained by using column C (50 m × 1 mm I.D.) packed with Apiezon N stationary phase at 180–200° which resulted in the dichlorosulphonylaniline isomers emerging in a different sequence, as shown in Table I.

TABLE I  
CHROMATOGRAPHIC SEPARATION OF DICHLOROSULPHINYLANILINE ISOMERS

<i>Compound</i>	<i>Retention times on column A (180°)</i>	<i>Relative retention times on column A (180°)</i>	<i>Relative retention times calculated in comparison with n-octadecane</i>
Methane	4.45	—	—
2,6-Dichlorosulphonylaniline	15.30	0.658	0.879
3,5-Dichlorosulphonylaniline	17.58	0.756	1.010
2,5-Dichlorosulphonylaniline	19.85	0.854	1.140
2,4-Dichlorosulphonylaniline	20.53	0.909	1.179
3,4-Dichlorosulphonylaniline	21.40	0.945	1.229
2,3-Dichlorosulphonylaniline	23.25	1.000	1.335

Under some conditions the dichlorosulphonylaniline and dichloroaniline isomers were separated on column A which resulted in the dichlorosulphonylaniline isomers and dichloroanilines emerging in a different sequence, as shown in Table II. The relative retention times of the dichlorosulphonylamines and dichloroanilines were calculated

TABLE II  
CHROMATOGRAPHIC SEPARATION OF DICHLOROSULPHINYLANILINE AND DICHLOROANILINE ISOMERS

Compound	Retention times on column A (180°)	Relative retention times (180°)	Relative retention times calculated in comparison with <i>n</i> -hexadecane
Methane	4.45	—	—
2,6-Dichloroaniline	9.36	0.402	1.000
2,4-Dichloroaniline	13.10	0.563	1.402
2,5-Dichloroaniline	13.12	0.563	1.402
2,3-Dichloroaniline	14.40	0.618	1.541
2,6-Dichlorosulphinylaniline	15.30	0.658	1.638
3,5-Dichlorosulphinylaniline	17.58	0.756	1.882
3,5-Dichloroaniline	18.30	0.787	1.956
2,5-Dichlorosulphinylaniline	19.85	0.854	2.125
2,4-Dichlorosulphinylaniline	20.53	0.909	2.191
3,4-Dichlorosulphinylaniline	21.40	0.946	2.286
2,3-Dichlorosulphinylaniline	23.25	1.000	2.488
<i>n</i> -Hexadecane	9.34	—	1.000

in comparison with 2,3-dichlorosulphinylaniline and with *n*-hexadecane and *n*-octadecane, and the values are given in Tables I and II.

The complete separation of six dichlorosulphinyllamine isomers and six dichloroanilines was achieved (Fig. 2).

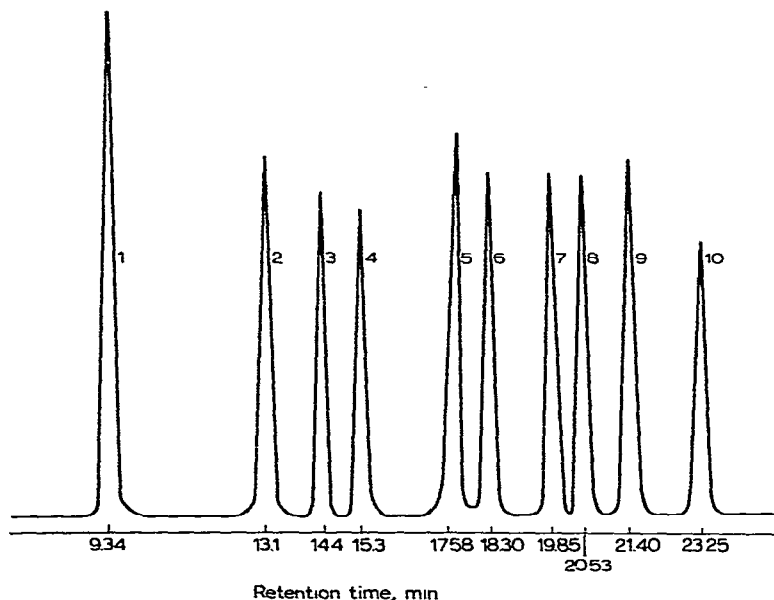


Fig. 2. Chromatographic separation of dichlorosulphinyllamine and dichloroaniline isomers. Peaks: 1 = 2,6-dichloroaniline; 2 = 2,4-dichloroaniline and 2,5-dichloroaniline; 3 = 2,3-dichloroaniline; 4 = 2,6-dichlorosulphinyllamine; 5 = 3,5-dichlorosulphinyllamine; 6 = 3,5-dichloroaniline; 7 = 2,5-dichlorosulphinyllamine; 8 = 2,4-dichlorosulphinyllamine; 9 = 3,4-dichlorosulphinyllamine; 10 = 2,3-dichlorosulphinyllamine.

Many difficulties arise when analysing arylsulphinylamines by use of gas-liquid chromatography owing to the similar boiling points of the isomers and to their pronounced susceptibility to atmospheric moisture, which results in their hydrolysis. Dichlorosulphinylamines can be determined in the presence of dichloroanilines, despite the trans-sulphonylation reaction which occurs.

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