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Note

Gas chromatographic analysis of aromatic sulphinylamines

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Attention has for some time been paid to the arylsulphinylamines owing to their extremely high reactivity. This reactivity is due to the sulphinyl group, which makes these compounds suitable for use in certain chemical processes¹⁻³. Arylsulphinylamines have been used successfully in the synthesis of heterocyclic⁴ and polycyclic compounds⁵, and they also participate in an interesting trans-sulphinylation reaction⁶.

Recently, it has been found that N-sulphinylamine ($C_6H_5-N=S=O$) forms a donor-acceptor system, and the Hammett substituent constant has been determined by means of nuclear magnetic resonance (NMR) spectroscopy.

Examination by thermal analysis has enabled the stability of the arylsulphinylamines to be determined⁷, making it possible to apply gas chromatography for their analysis. Its application to the analysis of dimethylsulphinylamine isomers described here is consequent upon earlier gas chromatographic studies carried out on arylsulphinylamines^{8,9}.

EXPERIMENTAL

Equipment and conditions

A Varian Aerograph 2860 gas chromatograph, equipped with a flame ionization detector, was used. The column (50 m × 1 mm I.D.) was made of stainless steel. The packings used were (A) Apiezon N, (B) Polyphenyl Ether (6 rings) OS-138, (C) Silar 10C on Chromosorb G, AW-DMCS, 80-100 mesh and (D) OV-275 on Gas-Chrom Q, 50-100 mesh. The operating conditions were as follows: hydrogen flow-rate, 20 ml/min; air flow-rate, 200 ml/min; carrier gas (nitrogen) flow-rate, 5 ml/min; detector temperature, 270°; column temperature, 200°; inlet temperature, 200°; chart speed, 10 mm/min.

A 1.0- μ l Hamilton syringe was used for the injections.

Procedure

A 10% solution of the aromatic sulphinylamines in benzene was used for the analysis, the volumes injected being 0.2 μ l in each instance. The quality of the standards obtained was checked by NMR and by mass spectroscopy.

RESULTS AND CONCLUSION

Best results for the separation were obtained by using column A (50 m long, 1 mm I.D.), packed with Apiezon N stationary phase, at a column temperature of 200°, a complete separation of six dimethylsulphinylamine isomers being achieved (Fig. 1).

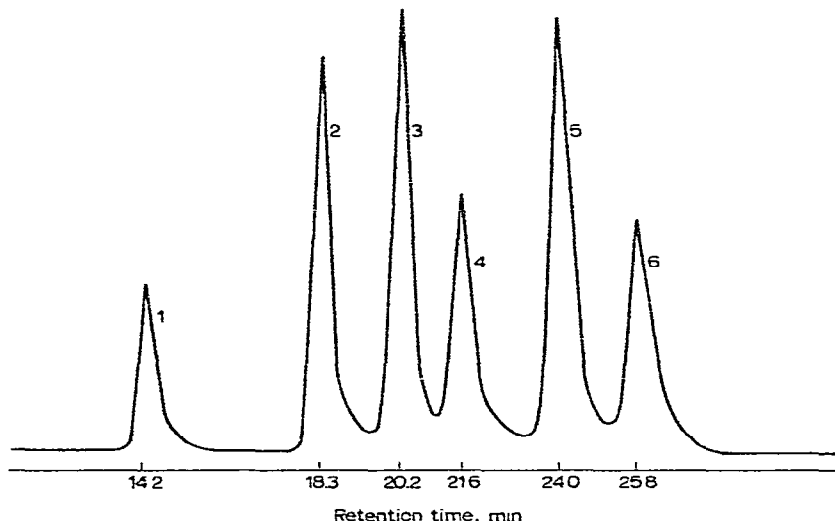


Fig. 1. Chromatographic separation of arylsulphinylamines. Peaks: 1 = 2,6-dimethylsulphinylaniline; 2 = 2,5-dimethylsulphinylaniline; 3 = 3,5-dimethylsulphinylaniline; 4 = 2,4-dimethylsulphinylaniline; 5 = 2,3-dimethylsulphinylaniline; 6 = 3,4-dimethylsulphinylaniline.

Similar results were obtained with column B (50 m long, 1 mm I.D.), packed with Polyphenyl Ether OS-138 stationary phase (6 rings), also at a column temperature of 200°. Less satisfactory results were obtained when a glass column (6 m long, 2.5 mm I.D.), packed with OV-275 on a Gas-Chrom Q support, 50–100 mesh (D), at 200°, was used. Further, use of a column 3 m long, 2.5 mm I.D., packed with Silar 10C on Chromosorb G (AW-DMCS, 80–100 mesh), (C) at 200°, resulted in the dimethylsulphinylamine isomers emerging in a different sequence, as shown in Table I.

TABLE I

CHROMATOGRAPHIC SEPARATION OF DIMETHYLSULPHINYLANILINE ISOMERS

Arylsulphinylamine	Relative retention times			
	Column A ($T = 180^\circ$)	Column A ($T = 200^\circ$)	Column B ($T = 180^\circ$)	Column C ($T = 200^\circ$)
2,6-Dimethylsulphinylaniline	0.532	0.562	0.541	0.750
2,5-Dimethylsulphinylaniline	0.692	0.706	0.683	0.552
3,5-Dimethylsulphinylaniline	0.768	0.786	0.775	0.635
2,4-Dimethylsulphinylaniline	0.824	0.837	0.802	0.697
2,3-Dimethylsulphinylaniline	0.920	0.924	0.931	0.916
3,4-Dimethylsulphinylaniline	1.000	1.000	1.000	1.000
Benzene	0.020	0.027	0.027	—

TABLE II
RELATIVE RETENTION TIMES OF DIMETHYLSULPHINYLAMINES CALCULATED IN
COMPARISON WITH *n*-TETRADECANE

<i>Arylsulphinylamine</i>	<i>Column A</i> (<i>t</i> = 200°)	<i>Column B</i> (<i>t</i> = 200°)
2,6-Dimethylsulphinylaniline	0.668	2.600
2,5-Dimethylsulphinylaniline	0.911	3.325
3,5-Dimethylsulphinylaniline	0.941	3.750
2,4-Dimethylsulphinylaniline	1.000	3.900
2,3-Dimethylsulphinylaniline	1.109	4.550
3,4-Dimethylsulphinylaniline	1.201	4.950
Benzene	0.030	—

The relative retention times of the dimethylsulphinylamines were calculated in comparison with 3,4-dimethylsulphinylaniline and with *n*-tetradecane, and are shown in Tables I and II.

Many difficulties arise when analysing arylsulphinylamines by use of gas-liquid chromatography owing to similarity of boiling temperatures of the isomers and to their pronounced susceptibility to atmospheric moisture, which results in their hydrolysis.

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