

Note

Some data on the thin-layer and high-performance liquid chromatographic separation of some dithia[3.3]phanes

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Dithia[3.3]phanes are important intermediates in the synthesis of the strained [2.2]phanes. Phanes have been characterized by chromatographic techniques in only a limited number of cases; high-performance liquid chromatographic (HPLC) and gas chromatographic investigations have been carried out on [2.2]naphthalenophane derivatives and [3.3]phanes¹. Some additional HPLC separations on a chiral stationary phase have been performed on several [2.2]phanes with heteroatoms (S, O, N) in the bridge².

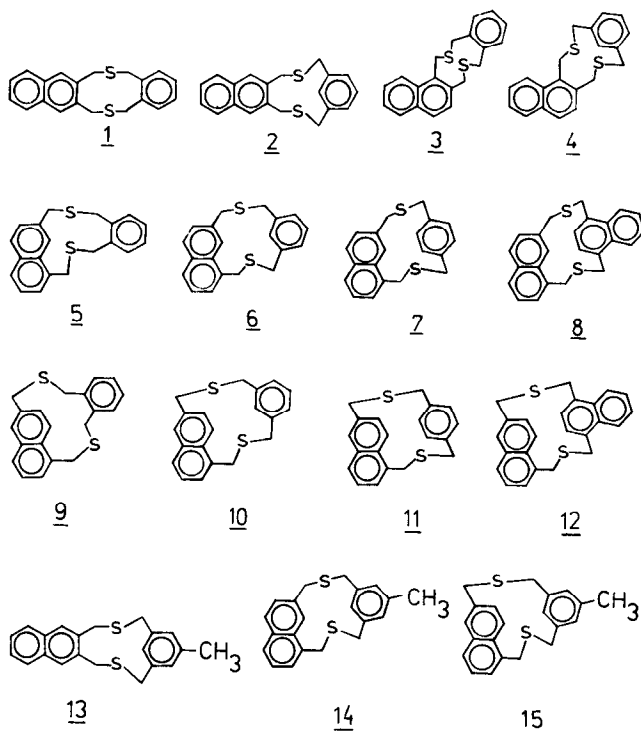
In this work we established conditions for the thin-layer chromatographic (TLC) and HPLC separation of fifteen dithia[3.3]phanes. Earlier analogous conditions had been elaborated for some of these compounds on silica and alumina^{3,4}; here the stationary phase considered was silica with a modified surface (RP₁₈) in both techniques. The influence of Ag⁺ ions in the mobile phase on the separation of the selected dithia[3.3]phanes was studied. We are aware that compounds 1–15 are never encountered as products in the same reaction, but the established analytical conditions can prove helpful when separating some stable isomers of other dithia[3.3]phanes, or when purifying this type of compound by preparative liquid chromatography.

EXPERIMENTAL

Compounds 1–15 were obtained from the respective di(bromomethyl)naphthalenes and di(mercaptomethyl)benzene derivatives (1–4⁵, 5–12⁴ and 13–15⁶) by means of the high-dilution technique, and they were further separated chromatographically.

TLC

The compounds were separated on ready-made chromatographic plates covered with modified-surface silica (RP₁₈F_{254S}; Art.No.15423, Merck, Darmstadt, F.R.G.). The mobile phases were methanol–water (98:2, 95:5 and 90:10, v/v) and acetonitrile–methanol (50:50, v/v). Solutes were spotted in aliquots of 5 μ l as 1% benzene solutions, with UV detection at 254 nm.



HPLC

The compounds were separated using a liquid chromatograph (Laboratorni pristroje, Prague, Czechoslovakia) composed of an HPP 5001 pump, an LCD 2563 UV-VIS detector equipped with a 254-nm filter, a TZ-4620 recorder and a CI-100

TABLE I

R_F VALUES OF COMPOUNDS 1-15

Compound	Methanol-water (v/v)			Acetonitrile-water (50:50, v/v)
	98:2	95:5	90:10	
1	0.39	0.31	0.18	0.55
2	0.35	0.26	0.17	0.53
3	0.38	0.28	0.20	0.58
4	0.34	0.25	0.17	0.54
5	0.35	0.24	0.18	0.54
6	0.39	0.29	0.23	0.59
7	0.45	0.34	0.24	0.63
8	0.40	0.30	0.19	0.64
9	0.38	0.29	0.18	0.56
10	0.38	0.29	0.18	0.58
11	0.39	0.30	0.18	0.58
12	0.36	0.27	0.16	0.58
13	0.32	0.24	0.13	0.51
14	0.38	0.30	0.17	0.56
15	0.36	0.27	0.14	0.55

TABLE II
HPLC RETENTION TIMES (min) OF COMPOUNDS 1-15

Compound	Methanol-water (v/v)				
	100:0	90:10	85:15	80:20	75:25
1	2.07	5.89	10.57	20.71	33.63
2	2.21	6.28	11.18	20.80	36.54
3	2.03	5.39	9.67	17.28	29.30
4	2.20	6.31	11.27	20.20	36.03
5	2.15	5.96	10.76	18.80	31.32
6	1.99	4.73	7.45	14.02	22.59
7	1.83	3.94	5.74	10.45	18.89
8	1.96	4.63	7.12	14.26	25.70
9	2.08	5.00	7.87	15.51	27.00
10	2.08	4.93	7.56	14.54	24.54
11	2.10	4.98	7.52	14.67	23.82
12	2.12	5.51	9.83	18.83	31.61
13	2.42	7.80	15.35	29.12	52.91
14	2.15	5.60	9.46	20.2	38.00
15	2.24	5.80	9.49	20.0	38.0

integrator. Separations were carried out on a glass column (150 mm × 3.6 mm I.D.) filled with Separon SGX-C18 (octadecylsilica) of particle diameter 5 μm (Laboratorni pristroje) with a mobile phase flow-rate of 0.8 cm³/min. Solutes were applied as 0.1% solutions in tetrahydrofuran. The mobile phases were methanol-water (100:0, 90:10, 85:15, 80:20 and 75:25, v/v); compounds 5-12 were also separated using methanol-water (80:20, v/v) with 2·10⁻² M Ag⁺ ions added.

RESULTS AND DISCUSSION

The *R_F* values obtained by TLC are given in Table I and the HPLC retention times in Table II. Table III gives the results obtained for compounds 5-12 by HPLC with Ag⁺ ions in the mobile phase.

TABLE III
EFFECT OF SILVER IONS ON THE HPLC RETENTION TIMES (min) OF COMPOUNDS 5-12

Compound	Methanol-water (80:20, v/v)	Methanol-water (80:20, v/v) + 2·10 ⁻² M Ag ⁺
5	18.80	3.92
6	14.02	5.13
7	10.45	10.97
8	14.26	8.42
9	15.51	8.55
10	14.54	16.33
11	14.67	7.46
12	18.83	8.94

In TLC the R_F values decrease and in HPLC the retention times increase with increasing concentration of water in the mobile phase. An increase in the proportion of water also results in an enhanced resolving power of the HPLC system.

The data in Table II show that replacement of the hydrogen atom by a methyl group in the smaller aromatic fragment of a given dithia[3.3]phane results in a longer retention. The ^1H NMR spectra established that this replacement induces no conformational changes in the molecules in solution, and for this reason the longer retention can simply be ascribed to an increased effective molecular volume, responsible for the relative retardation.

Complexation of the dithia[3.3]phane molecules with Ag^+ ions in most instances results in shorter retention times and in an enhanced resolution of the chromatographic system.

REFERENCES

- 1 D. Deege, B. Heinecke and G. Schomburg, *Chromatographia*, 15 (1982) 65.
- 2 K. Meurer, A. Aigner and F. Vögtle, *J. Inclusion Phenomena*, 3 (1985) 51.
- 3 P. Kuś, *J. Chromatogr.*, 436 (1988) 338.
- 4 P. Kuś, *J. Chromatogr.*, 442 (1988) 378.
- 5 P. Kuś, *Pol. J. Chem.*, 61 (1987) 95.
- 6 P. Kuś, *Pol. J. Chem.*, in press.