

Note

Thin-layer separation of some dithia[3.3]phanes. II.

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In part I¹ I reported on the thin-layer chromatographic (TLC) separation of dithia[3.3]phanes constituted of xylene fragments linked with another xylene, 1,2- or 2,3-dimethylenaphthalene group. In this paper I present analogous results dealing with newly synthesized dithia[3.3]phanes, incorporating 1,6- and 1,7-dimethylenaphthalene fragments. The synthetic procedure utilized is described, and the compounds obtained are shown in Fig. 1. The TLC separations were performed with silica and alumina as stationary phases, and employing several mobile phases.

EXPERIMENTAL

The ¹H NMR spectra of the compounds investigated were measured using a

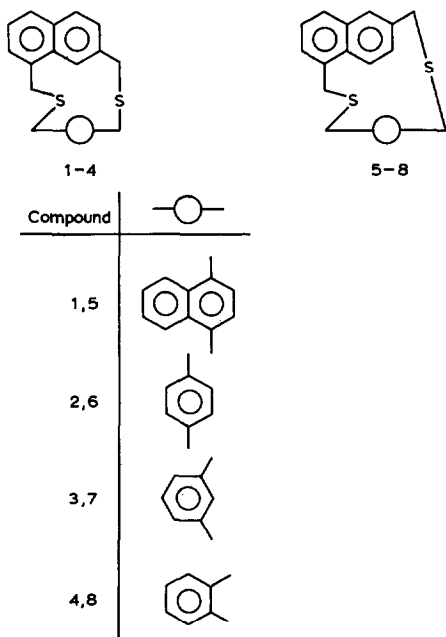


Fig. 1. Chemical structures of the compounds synthesized.

Varian Model FT80A spectrometer, deuteriochloroform or [$^2\text{H}_6$]dimethyl sulphoxide as solvents and tetramethylsilane (TMS) as an internal standard. The mass spectra were recorded with an LKB 2900 spectrometer, the ionization energy being 70 eV. The melting points determined are uncorrected.

1,6-Di(bromomethyl)naphthalene and 1,7-di(bromomethyl)naphthalene² were obtained from the respective hydrocarbons and *N*-bromosuccinimide in carbon tetrachloride. 1,2-Di(mercaptomethyl)benzene, 1,3-di(mercaptomethyl)benzene, 1,4-di(mercaptomethyl)benzene and 1,4-di(mercaptomethyl)naphthalene were synthesized from the respective halogen derivatives through the *S*-alkylisothiourea salts. Dithia[3.3]phanes were obtained according to the method described for compound 1.

2,13-Dithia[3.3](1,4)(1,7)naphthalenophane, 1^{3,4}

To 1.5 dm³ of vigorously stirred boiling ethanol, containing 0.4 g of sodium hydroxide, in a 3-dm³ flask, a mixture of 1,4-di(mercaptomethyl)naphthalene (5 mmol) and 1,7-di(bromomethyl)naphthalene (5 mmol) in benzene-ethanol (4:1, v/v) was added dropwise over *ca.* 20 h. Then the mixture was boiled for 2–3 h. The ethanol was distilled off under reduced pressure, and the dry residue was extracted with chloroform. The extract was evaporated and the residue was separated on a silica gel column (500 × 25 mm I.D.), using carbon tetrachloride as the eluent. Thus 0.5 g (26.9%) of compound 1 were obtained, m.p. 169–171°C. ¹H NMR, δ 3.64–4.44 (m,8H), 6.07 (s,1H), 7.22–7.56 (m,9H). Mass spectrum: 372 (M⁺).

2,13-Dithia[3]paracyclo[3](1,7)naphthalenophane, 2, was obtained from 1,7-di(bromomethyl)naphthalene and 1,4-di(mercaptomethyl)benzene. Yield 35.4%. m.p. 206–208°C. ¹H NMR: δ 3.60 (s,2H), 3.71 (s,2H), 3.88 (s,2H), 3.93 (s,2H), 6.08 (s,1H), 7.07–7.58 (m,9H). Mass spectrum: 322 (M⁺).

2,13-Dithia[3]metacyclo[3](1,7)naphthalenophane, 3, was obtained from 1,7-di(bromomethyl)naphthalene and 1,3-di(mercaptomethyl)benzene. Yield 44.1%. m.p. 166–169°C. ¹H NMR: δ 3.53 (s,4H), 3.65 (s,2H), 3.84 (s,2H), 6.73 (s,2H), 7.22–7.78 (m,8H). Mass spectrum: 322 (M⁺).

2,13-Dithia[3]orthocyclo[3](1,7)naphthalenophane, 4, was obtained from 1,7-di(bromomethyl)naphthalene and 1,2-di(mercaptomethyl)benzene. Yield 37.2%. m.p. 162–164°C. ¹H NMR: δ 3.28 (s,2H), 3.51 (s,4H), 3.84 (s,2H), 6.91 (s,1H), 7.30–7.84 (m,9H). Mass spectrum: 322 (M⁺).

2,13-Dithia[3.3](1,4)(1,6)naphthalenophane, 5, was obtained from 1,6-di(bromomethyl)naphthalene and 1,4-di(mercaptomethyl)naphthalene. Yield 21.4%. m.p. 132–134°C. ¹H NMR: δ 3.25–4.43 (m,8H), 4.65, 4.74, 5.74, 5.83 (AB q,2H, *J* = 7.1 Hz), 6.53–7.97 (m,8H). Mass spectrum: 372 (M⁺).

2,13-Dithia[3]paracyclo[3](1,6)naphthalenophane, 6, was obtained from 1,6-di(bromomethyl)naphthalene and 1,4-di(mercaptomethyl)benzene. Yield 23%. m.p. 163–166°C. ¹H NMR: δ 3.07–4.30 (m,8H), 4.94, 5.04, 5.64, 5.74 (AB q,2H, *J* = 8 Hz), 6.86–7.62 (m,8H). Mass spectrum: 322 (M⁺).

2,13-Dithia[3]metacyclo[3](1,6)naphthalenophane, 7, was obtained from 1,6-di(bromomethyl)naphthalene and 1,3-di(mercaptomethyl)benzene. Yield 44.8%. m.p. 113–116°C. ¹H NMR: δ 2.40–4.56 (m,8H), 5.21 (s,1H), 6.68–7.59 (m,9H). Mass spectrum: 322 (M⁺).

2,13-Dithia[3]orthocyclo[3](1,6)naphthalenophane, 8, was obtained from 1,6-di(bromomethyl)naphthalene and 1,2-di(mercaptomethyl)benzene. Yield 21.7%.

TABLE I

 R_F VALUES OF THE DITHIA[3.3]PHANES 1-8

Solvents: a = carbon tetrachloride; b = hexane-1,2-dimethoxyethane (20:1); c = carbon tetrachloride-benzene (5:1); d = carbon tetrachloride-*m*-xylene (10:3); e = hexane-xylene(mixed) (1:1); f = carbon tetrachloride-cyclohexane (1:1); g = hexane-cyclohexane-benzene (2:2:1); h = carbon tetrachloride-hexane-cyclohexane (3:1:1).

Compound	Silica					Alumina				
	a	b	c	d	e	a	b	f	g	h
1	0.12	0.32	0.31	0.30	0.21	0.52	0.35	0.20	0.22	0.28
2	0.16	0.39	0.34	0.33	0.24	0.53	0.45	0.22	0.25	0.31
3	0.25	0.42	0.47	0.46	0.34	0.66	0.52	0.33	0.35	0.41
4	0.31	0.44	0.57	0.56	0.47	0.72	0.56	0.37	0.42	0.49
5	0.16	0.35	0.36	0.35	0.24	0.50	0.38	0.18	0.21	0.27
6	0.21	0.42	0.43	0.41	0.32	0.62	0.51	0.30	0.33	0.40
7	0.20	0.42	0.41	0.39	0.31	0.62	0.52	0.31	0.33	0.40
8	0.23	0.43	0.49	0.47	0.37	0.67	0.53	0.32	0.36	0.44

m.p. 151-153°C. $^1\text{H NMR}$: δ 1.76-4.69 (m,8H), 6.47-7.55 (m,10H). Mass spectrum: 322 (M^+).

Thin-layer chromatography

Separation of the investigated dithia[3.3]phanes was performed using commercial ready-made glass plates covered with silica (Art. No. 5634), and plastic plates with alumina (Art. No. 5581) (E. Merck, Darmstadt, F.R.G.). A 2- μl volume (10 $\mu\text{g}/\mu\text{l}$) of the dithia[3.3]phane solution in chloroform was applied to the plates. Five mobile phases were chosen for silica, and another five for alumina. Detection was carried out in UV light (254 nm).

RESULTS AND DISCUSSION

The R_F values of the compounds chromatographed using different eluents are shown in Table I. They seem to depend on the structures of the molecular fragments: 1,4-dimethylenenaphthalene < *p*-xylylene < *m*-xylylene < *o*-xylylene group. Comparing the 1,6- and 1,7-dimethylenenaphthalene derivatives, it was observed that 1,4-dimethylenenaphthalene and *p*-xylylene fragments coupled with the 1,7-dimethylenenaphthalene group are more readily adsorbed, *i.e.*, give lower R_F values, than the respective isomers containing the 1,6-dimethylenenaphthalene fragment; also that *m*- and *o*-xylylene derivatives of 1,7-dimethylenenaphthalene are adsorbed less readily than their counterparts having the 1,6-dimethylenenaphthalene structure. These regularities are characteristic of most of the chromatographic systems applied.

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