

Synthesis, Structure, and Electrical Properties of Naphthacene, Pentacene, and Hexacene Sulphides

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Pentacene and hexacene both react with sulphur to form stable hexasulphides for which double fused thiathiophthen structures (6) and (8) or (9) are proposed. The electrical conductivity of hexacene hexasulphide is similar to that of the well-known naphthacene tetrasulphide (1) and 10^9 times greater than that of pentacene hexasulphide. Replacement of the sulphur in (1) by selenium gives a tetraselenide (14) of similar conductivity to (1). The new naphthaceno[5,6-*cd*][1,2]dithiole (10) is described.

IN 1939 Marschalk¹ reported attempts to make heptacene by dehydrogenation of hydroheptacenes with sulphur. Instead of heptacene he obtained an unidentified, green, insoluble solid which contained sulphur. Similar products resulted from reaction of sulphur with hydrogenated derivatives of hexacene, pentacene, and naphthacene but not from dihydroanthracene. Surprisingly, no further work has been reported on the intractable products from pentacene, hexacene, and

heptacene, although the more soluble naphthacene compound, naphthacene (tetracene) tetrasulphide, has been well characterised chemically² and its structure (1) confirmed³ by X-ray crystallography.

Matsunaga⁴ reported that naphthacene tetrasulphide had an unusually high electrical conductivity and various aspects of this property such as the dependence on

² C. Marschalk and C. Stumm, *Bull. Soc. chim. France*, 1948, 418; C. Marschalk and L. Woerth, *ibid.*, 1952, 147; Z. S. Ariyan and L. A. Wiles, *J. Chem. Soc.*, 1962, 1725.

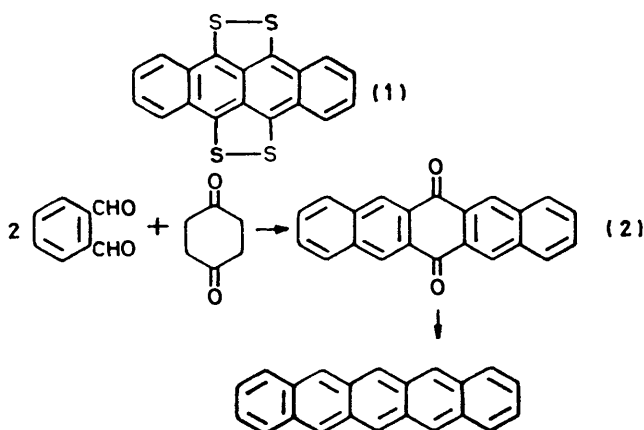
³ J. Toussant and O. Dideberg, *Bull. Soc. roy. Sci. Liège*, 1967, **36**, 666.

⁴ Y. Matsunaga, *J. Chem. Phys.*, 1965, **42**, 2248.

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¹ C. Marschalk, *Bull. Soc. chim. France*, 1939, **6**, 1122.

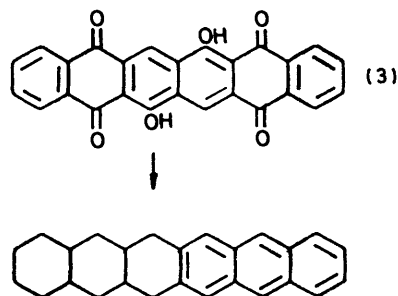
pressure⁵ and temperature⁶ have since been investigated. There is, however, no satisfactory explanation for the high conductivity. This paper describes attempts to explain the high conductivity by measurements of the conductivities of a series of structurally related compounds, including the pentacene and hexacene sulphides first made by Marschalk.¹ The work described here gives little indication of the relationship between structure and conductivity. The nature of this relationship has emerged from more recent work in this laboratory which will be the subject of another publication. The present paper is largely concerned with synthetic and structural aspects of the unusual compounds involved.



Since Marschalk's reaction of hydropentacene with sulphur presumably involved intermediate formation of the fully aromatic hydrocarbon, we began our investigations by reacting sulphur directly with pentacene. Pentacene, prepared by aluminium-cyclohexanol reduction of the quinone (2), reacted rapidly with an excess of sulphur in boiling trichlorobenzene. Precipitation of dark green needles of the product was complete after 3 h. In contrast, the reaction of naphthacene with sulphur is slower, requiring 24 h for completion.

The pentacene sulphide did not melt and was thermally stable during differential thermal analysis up to 480°, compared with 300° for naphthacene tetrasulphide. It was very insoluble, but purification for conductivity measurements, elemental analysis, and mass spectroscopy was possible by recrystallisation from large volumes of nitrobenzene. The elemental analysis corresponded to C₂₂H₈S₆ and the mass spectral molecular weight of 464 confirmed this formula. I.r. and u.v. spectra were similar to those of naphthacene tetrasulphide and the i.r. spectrum showed the presence of *o*-disubstituted benzene rings. X-Ray analysis was complicated by twinning, but did show a unit cell with angles of *ca.* 90° and dimensions 3.93, 14.83, and 9.28 Å. The unit cell distances have some similarities to those pub-

lished³ for naphthacene tetrasulphide: 3.93, 18.15, and 9.85 Å.



Knowing that naphthacene, with four reactive meso-positions, forms a tetrasulphide and pentacene, with six reactive meso-positions, forms a hexasulphide, we examined the reaction of the hexacene system, which has eight reactive meso-positions. Attempts to synthesise hexacene by the route established by Clar⁷ were not successful. The quinone (3), prepared from 1,5-dihydroxynaphthalene and phthalic anhydride, could not be reduced with zinc dust.

From his own results, Clar recommended reduction of the quinone (3) with hydrogen iodide and phosphorus.⁸ We found that this reduction gave a mixture of hydrocarbons ranging from dihydro- to eicosahydro-hexacene. The relative intensity of peaks in the mass spectrum of this mixture is shown in Table I.

TABLE I

Mass spectral analysis of a hydrohexacene mixture							
<i>m/e</i>	330	332	336	338	342	344	348
Relative intensity	5	50	25	80	100	15	20

The hydrohexacene mixture reacted with sulphur more slowly than the fully aromatic pentacene. After 14 h a black insoluble solid was isolated with an empirical formula, C₂₆H₁₀S₆, confirmed by high resolution mass spectroscopy. The stability and spectral characteristics were very similar to those of pentacene hexasulphide. All attempts to form an octasulphide by, *e.g.*, reaction with sulphur at 260° for 48 h, were unsuccessful, showing that the high stability of the six sulphur system is more important than the number of reactive meso-positions in the hydrocarbon. We propose that the high stability of the hexasulphides of both pentacene and hexacene is due to formation of an all aromatic double thiathiophthen system.

Thiathiophthens can be represented by resonance structures such as (4a) and (4b) or by the structure with tetravalent sulphur, (4c). They are members of a series of resonance-stabilised sulphur compounds containing 2–5 sulphur atoms.⁹ Members of this series with an odd number of sulphur atoms, such as (4), are neutral, while those with an even number, such as (5), are cationic.¹⁰

⁵ M. Kochi, H. Inokuchi, and Y. Harahada, *Bull. Chem. Soc. Japan*, 1966, **39**, 386 (*Chem. Abs.*, 1966, **64**, 13,520e).

⁶ Y. Harahada and H. Inokuchi, *Bull. Chem. Soc. Japan*, 1966, **39**, 1443 (*Chem. Abs.*, 1966, **65**, 12,981h).

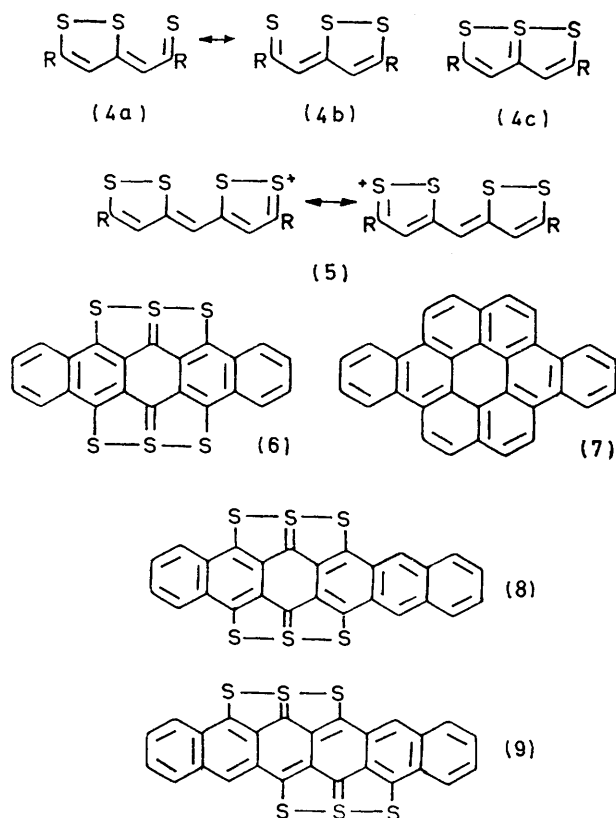
⁷ E. Clar, *Ber.*, 1939, **72**, 1817.

⁸ B. Boggiano and E. Clar, unpublished results.

⁹ E. Klingsberg, *Quart. Rev.*, 1969, **23**, 537.

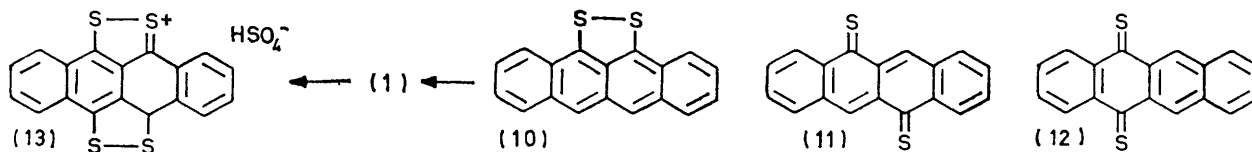
¹⁰ E. Klingsberg, *J. Heterocyclic Chem.*, 1966, **3**, 243.

The structure (6) proposed for pentacene hexasulphide is isoelectronic with that of the stable hydrocarbon dibenzo[*a,j*]coronene (7), m.p. 496–499°, and the u.v.



spectrum of pentacene hexasulphide was found to be similar to that of the coronene (7).¹¹

In the case of hexacene hexasulphide, two structural isomers are possible, both of which are double thia-thiophthen systems. Since the substance is too insoluble for n.m.r. analysis, we were unable to distinguish between the possible structural isomers (8) and (9).



It is likely that the product is a mixture of the two isomers.

As mentioned earlier, reaction of the hexacene system with an excess of sulphur at high temperature gave only the hexasulphide and not the octasulphide. By comparison with the thiathiophthen series, a dicationic hexacene octasulphide analogous to (5) might be expected. Accordingly, attempts were made to react the hexacene system with an excess of sulphur under various oxidative conditions, but again only the hexasulphide was formed.

¹¹ E. Clar, 'Polycyclic Hydrocarbons,' Academic Press, London, 1964, vol. II, p. 90.

The electrical measurements in Table 2 show that hexacene hexasulphide has a conductivity similar to that of naphthalene tetrasulphide. In contrast, the pentacene compound is an insulator with a conductivity less than that of the structurally similar hexacene compound by a factor of 10⁹. The conductivities do not correlate with ease of loss of an electron as measured by the appearance potential of the parent ions in the mass spectrum.

TABLE 2

Conductivity data and appearance potentials of polyacene sulphides			
	Naphthalene tetrasulphide	Pentacene hexasulphide	Hexacene hexasulphide
Appearance potential (eV)	7.2	8.0	9.9
Conductivity, $\sigma_{20}/\Omega^{-1}\text{cm}^{-1}$	5.2×10^{-5}	1.2×10^{-13}	8.3×10^{-5}
Activation energy, E_A/eV	0.21	0.7	0.15

No structure–conductivity relationship was apparent from the results shown in Table 2, and accordingly a series of compounds more strictly analogous to naphthalene tetrasulphide was prepared. Three variations on the naphthalene tetrasulphide structure are described: (i) variation in the number of sulphur atoms; (ii) preparation of other oxidation states; and (iii) replacement of sulphur by selenium.

Marschalk² reported that 5-chloronaphthalene reacts with sulphur to give green crystals of naphthalene tetrasulphide in a violet coloured solution. He suspected that the violet colour may be due to an intermediate. We have shown that this is in fact the case by isolating a violet impurity from graded sublimation of crude naphthalene tetrasulphide. This technique gave small quantities (4%) of a more volatile violet impurity, which was itself purified by resublimation. It had m.p. 210°, empirical formula C₁₈H₆S₂, and an n.m.r. spectrum which was consistent with the dithiole structure (10), although it did not rule out the much less likely thio-

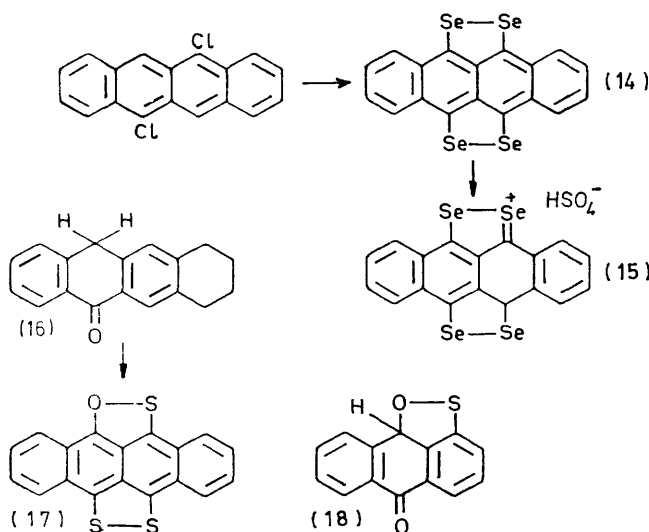
quinone structures (11) or (12). When heated with sulphur, it reacted readily to form the tetrasulphide. The electrical conductivity (σ_{20} $6 \times 10^{-7} \Omega^{-1}\text{cm}^{-1}$) of the disulphide was lower than that of the tetrasulphide.

Naphthalene tetrasulphide can be oxidised to the monocation (13) and dicationic salts.² Our measurements show that the salt (13) has a conductivity (σ $1 \times 10^{-2} \Omega^{-1}\text{cm}^{-1}$) comparable with that reported¹² for charge transfer complexes, where the tetrasulphide (1) is

¹² Y. Matsunaga, U.S.P. 3,403,165 (*Chem. Abs.*, 1969, **70**, 15,357r); Y. Okamoto, S. Shah, and Y. Matsunaga, *J. Chem. Phys.*, 1965, **43**, 1904; E. A. Perez-Albuern, H. Johnson, and D. J. Trevo, *J. Chem. Phys.*, 1971, **55**, 1547.

the donor. The dicationic salts of (1) are less conducting ($\sigma_{20} 3 \times 10^{-8} \Omega^{-1} \text{ cm}^{-1}$). No cationic species were isolated on oxidation of the pentacene and hexacene sulphides (6) and (8) or (9), presumably because this would involve loss of resonance energy.

A further variation of the naphthacene tetrasulphide structure involved replacement of sulphur by selenium. Naphthacene tetraselenide (14) was made by treating ¹³5,11-dichloronaphthacene with selenium. The black, insoluble solid, after sublimation, had a conductivity ($\sigma_{10} 2 \times 10^{-4} \Omega^{-1} \text{ cm}^{-1}$) about twice that of the tetrasulphide (1). Oxidation gave a stable salt (15) with a conductivity ($\sigma_{20} 2 \times 10^{-2} \Omega^{-1} \text{ cm}^{-1}$) about twice that of the sulphur analogue (13).



Replacement of the sulphur in the tetrasulphide (1) by atoms other than selenium is not readily achieved. Attempts were made to prepare mixed oxygen-sulphur products by heating various naphthacenequinones with sulphur and phosphorus pentasulphide. Although these attempts were unsuccessful, a product was obtained by heating compound (16) with sulphur. A blue solid, m.p. 290–300°, was isolated with a mass spectrum corresponding to the empirical formula C₁₈H₈OS₃ and a low conductivity ($\sigma_{20} < 10^{-8} \Omega^{-1} \text{ cm}^{-1}$). Structure (17), involving a 1,2-oxathiole ring, is proposed for this product. A previous example of this system, structure (18), has been proposed for 1-anthraquinone sulphenic acid¹⁴ and since disputed.¹⁵

EXPERIMENTAL

Electrical resistivities were measured by the 4-probe method and for activation energies the temperature was varied from -20 to 50 °C. M.p.s are corrected. N.m.r. spectra were measured with a Varian HR-220 instrument with tetramethylsilane as an internal standard and CDCl₃ as solvent (unless otherwise stated). Mass spectra were

taken with A.E.I. MS 12 and 9 (high resolution) instruments. I.r. spectra were measured with a KBr disc on a Perkin-Elmer 157 spectrometer.

Pentacene.¹⁶—Reaction of aluminium wire (25 g) with dry cyclohexanol (500 ml) containing mercuric chloride (0.5 g) and carbon tetrachloride (2 ml) was initiated by warming, controlled by cooling, and completed by heating under reflux with stirring for 16 h under nitrogen. Pentacene-6,13-quinone (2) (25 g), prepared by condensation of cyclohexane-1,4-dione with *o*-phthalaldehyde, was added and the mixture boiled under reflux for 48 h. After cooling to 50° for 5 h, the solvent was decanted from the dark blue crystalline product, which was then washed with fresh cyclohexanol (3 × 60 ml), and separated by centrifuging at 30°. After washing with hot acetic acid, 25% hydrochloric acid, hot water, and ethanol, the product was dried under vacuum at 80° to give pentacene (12.1 g, 54%), m.p. (decomp.) >300°, i.r. identical with the published¹⁷ spectrum, λ_{max} (ethanol) 296, 323, 345, 502, 536, and 584 nm.

Pentacene Hexasulphide (6).—Pentacene (4 g) was heated under reflux with sulphur (4 g) in 1,2,4-trichlorobenzene (500 ml) and after 0.5 h the solution turned dark green. A green solid began to separate after 1 h and was removed by filtration after 3 h, washed with hot solvent and ethanol before drying at 70° under vacuum. The dark green needles (4.9 g, 73%) were purified by recrystallisation from nitrobenzene and identified as *pentacene hexasulphide* (Found: S, 41.55. C₂₂H₈S₆ requires S, 41.3%), *M* (mass spectrum), 463.8946 (C₂₂H₈³²S₆ requires *M*, 463.8949), decomposition point on differential thermal analysis 485°, ν_{max} 1479, 1412, 1328, 1035, and 760 cm⁻¹, λ_{max} (1,2,4-trichlorobenzene) 391, 420, and 442 nm, λ_{max} (conc. H₂SO₄) 254, 325, 365, 381, 563, and 700 nm.

6,14-Dihydroxyhexacene-5,16;8,13-diquinone (3).⁷—1,5-Dihydroxynaphthalene (32 g, 0.2 mol) and phthalic anhydride (60 g, 0.4 mol) were added in small portions during 15 min to a stirred melt of aluminium chloride (320 g) and sodium chloride (64 g) at 200°, the mixture heated to 210° for 30 min, cooled to 160°, and poured into 10% hydrochloric solution (1.5 l) containing ice. After stirring hot and filtering, the product was washed with dilute hydrochloric acid and water before stirring at 60° in dilute sodium hydroxide (1 l). Standing for 24 h and filtering gave a blue solid, which was again treated with sodium hydroxide and 10% hydrochloric acid, before washing with water and drying under vacuum at 200° to give the crude dark brown product (25.3 g, 30%). A small sample was sublimed under vacuum to give bright red 6,14-dihydroxyhexacene-5,16;8,13-diquinone [*M* (mass spectrum), 420.06339. Calc. for C₂₆H₁₂O₆: *M*, 420.06338], ν_{max} 3400, 1673, 1640, and 1295 cm⁻¹, λ_{max} (dimethyl sulphoxide) 275 and 475 nm.

Mixed Hydrohexacenes.⁸—Dihydroxyhexacenediquinone (4.2 g, 10 mmol) was ground together with alkali-purified red phosphorus (2.5 g, 8.0 mmol) and this mixture, with aqueous hydroiodic acid (44 ml; *d* 1.7), was sealed under vacuum at -196 °C in a Carius tube. After agitating at 210° for 24 h and then cooling, the contents of the tube were filtered and the precipitate was boiled with xylene (100 ml) and filtered to remove phosphorus. The filtrate was chromatographed to remove unchanged quinone on an

¹⁶ V. Bruckner, A. Karzag, K. Kormendy, M. Meszaros, and J. Tomasz, *Acta chim. Acad. Sci. Hung.*, 1960, **22**, 443; V. Bruckner and J. Tomasz, *ibid.*, 1961, **28**, 405 (*Chem. Abs.*, 1964, **61**, 625a).

¹⁷ Sadtler Standard Spectra 15,223.

¹³ C. Marschalk, *Bull. Soc. chim. France*, 1952, 800.

¹⁴ P. N. Rylander, *J. Org. Chem.*, 1956, **21**, 1296.

¹⁵ J. A. Barltrop and K. J. Morgan, *J. Chem. Soc.*, 1956, 4245.

alumina column (30 × 1.5 cm), eluting with xylene (600 ml). The xylene solution was evaporated to 10 ml and acetone (250 ml) was added giving a yellow solid, which was separated, dried, and shown to be a mixture of hydrohexacene isomers (1.0 g, 29%) (Found: C, 91.45; H, 7.85. Calc. for C₂₆H₂₈: C, 91.75; H, 8.25%), R_F 0.9 on silica gel (CHCl₃), τ 2.3—3.3 (5H, m, ArH) and 7.0—9.3 (17H, m, CH₂), ν_{max.} 2880, 1600, 1580, 1492, and 750 cm⁻¹, λ_{max.} (CHCl₃) 450 and 370 nm, m/e (mass spectrum), 330, 332, 336, 338, 342, 344, and 348.

Hexacene Hexasulphide (8) or (9).—The mixed hydrohexacenes (0.5 g, 1.2 mmol) and sulphur (2.0 g, 6.2 mmol) were heated under reflux under nitrogen in 1,2,4-trichlorobenzene (150 ml) for 24 h and the hot solution was filtered. The black solid product was washed with hot solvent (200 ml), dried under vacuum at 200° for 24 h, and the low-molecular-weight impurities were removed by sublimation at 350° and 0.01 mmHg leaving black *hexacene hexasulphide* (0.5 g) (Found: S, 37.3. C₂₆H₁₀S₆ requires S, 37.75%), M (mass spectrum), 513-910 (¹²C₂₆¹H₁₀³²S₆ requires M, 513-911), ν_{max.} 1485, 1408, 975, 900, and 755 cm⁻¹, λ_{max.} (1,2,4-trichlorobenzene) 722 (ε 13,800), 655 (2800), 462 (1000), 404 (6100), 384 (1000), and 317 (40,000) nm.

Naphthacene Tetrasulphide (*Naphthaceno*[5,6-cd:11,12-c'd']*bis*[1,2]*dithiole*) (1).²—Naphthacene (2.0 g, 9 mmol) and sulphur (4.0 g, 125 mmol) were stirred under reflux for 24 h in 1,2,4-trichlorobenzene (50 ml), filtered hot, and the filtrate was cooled. Crude naphthacene tetrasulphide (2.0 g, 61%) was removed by filtration and Soxhlet extracted with toluene for 2 h, leaving a residue of naphthacene tetrasulphide (1.25 g), which was further purified by sublimation at 300° and 0.01 mmHg (Found: C, 61.55; H, 2.3. Calc. for C₁₈H₈S₄: C, 61.35; H, 2.3%), M (mass spectrum), 351-9579 (Calc. for ¹²C₁₈¹H₈³²S₄: M, 351-9578), λ_{max.} (1,2,4-trichlorobenzene) 316 (ε 42,000), 462 (10,000), 596 (469), and 649 (2800) nm.

Tetracene 5,6-Disulphide (*Naphthaceno*[5,6-cd][1,2]*dithiole*) (10).—The purification of crude naphthacene tetrasulphide from several preparations by sublimation as described before gave a 4% yield of a more volatile violet impurity *naphthacene-5,6-disulphide*, m.p. 210° (Found: S, 21.55. C₁₈H₁₀S₂ requires S, 22.05%), M (mass spectrum), 290-0219 (¹²C₁₈¹H₁₀³²S₂ requires 290-0224), τ (CCl₄) 2.20 (2H, s, 11- and 12-H₂), 2.35 (2H, d, J 1 Hz, 4- and 7-H₂), 2.55 (2H, d, J 1 Hz, 1- and 10-H₂), and 2.85 (4H, m, 2-, 3-, 8-, and 9-H₄) λ_{max.} (methanol) 236, 297, 402, 425, and 560 nm, ν_{max.} 1620, 1601, 1495, 1300, 947, 873, 782, and 740 cm⁻¹.

Naphthacene Tetrasulphide Hydrogen Sulphate (13).¹⁷—Naphthacene tetrasulphide (7.5 g, 21.3 mmol) and lead dioxide (2.6 g, 11 mmol) were shaken for 4 h in 45% sulphuric acid (200 ml; AnalaR) and the mixture poured into water (1.4 l). Filtration gave a red solid, which was purified by recrystallisation from hot water, to give red needles of naphthacene tetrasulphide hydrogen sulphate (1 g, 11%), λ_{max.} (water) 235 (ε 2590), 293 (449), 322 (798), 457 (599), and 539 (1047) nm.

Naphthacene Tetrasulphide Bis(hydrogen sulphate).¹⁸—

¹⁸ C. Marschalk and J. P. Niederhauser, *Bull. Soc. chim. France*, 1950, 452.

Powdered naphthacene tetrasulphide (1 g, 3 mmol) was added slowly to conc. sulphuric acid (20 ml; AnalaR) and the yellow solution was stirred for 3 h at 20°, cooled to 0°, and poured into iced water (80 ml) giving a dark brown solid, naphthacene tetrasulphide bis(hydrogen sulphate) (1.2 g, 77%), m.p. >300° (Found: C, 39.85; H, 1.9; S, 35.5. Calc. for C₁₈H₁₀S₈O₈: C, 39.55; H, 1.85; S, 35.2%), λ_{max.} 235, 258, 269, 306, and 412 nm.

5,11-Dichloronaphthacene.¹³—Naphthacene (6.8 g, 27 mmol) and sulphur monochloride (10.8 g, 80 mmol), freshly distilled from charcoal and sulphur, were heated under reflux in chlorobenzene (60 ml) for 1 h. Cooling and filtration gave a red solid, which was purified by recrystallisation to give 5,11-dichloronaphthacene (2.1 g, 25%), m.p. 220° (lit.,¹³ 220°).

Naphthacene Tetraselenide (14).¹³—5,11-Dichloronaphthacene (2.0 g, 8 mmol) and selenium (1.0 g, 13 mmol) were heated under reflux with stirring in Dowtherm A [diphenyl ether (73.5%)—biphenyl (26.5%)] (200 ml) for 6 h under nitrogen. Filtering gave a dark green product (1.0 g), which was purified by subliming twice at 222—230° and 0.01 mmHg and recrystallising from 1,2,4-trichlorobenzene to give naphthacene tetraselenide (0.37 g), λ_{max.} (1,2,4-trichlorobenzene) 321 (ε 13,500), 465 (1971), 598 (54), and 656 (567) nm.

Naphthacene Tetraselenide Hydrogen Sulphate (15).¹³—Naphthacene tetraselenide (0.30 g) suspended in formic acid (6 ml) was treated dropwise with 4% hydrogen peroxide (0.2 ml) until the colour turned from green to blue. Towards the end of the addition a slight orange colouration ensued, due to dication formation, but the blue was restored by addition of sodium sulphite solution. Saturated potassium hydrogen sulphate (20 ml) was added, the mixture was filtered, the precipitate was washed with water and dried *in vacuo* to give naphthacene tetraselenide hydrogen sulphate, λ_{max.} (water), 245, 322, 440, and 620 nm.

Reaction of 5,7,8,9,10,12-Hexahydronaphthacene-5-one and Sulphur.—The ketone (16) (2.2 g), prepared from 7,8,9,10-tetrahydronaphthacene-5,12-quinone,¹⁹ and sulphur (1.4 g) were heated under reflux with stirring in 1,2,4-trichlorobenzene (100 ml) under nitrogen. After 4 h, more sulphur (1.7 g) was added and after 12 h the mixture was cooled and filtered to give a black insoluble polymeric precipitate (Found: C, 69.8; H, 2.55; S, 19.5%). The blue filtrate was evaporated and the residue was sublimed twice at 300° and 0.01 mmHg giving 1,2-dithiolo[3',4',5':11,12]-*naphthaceno*[5,6-cd]*oxathiole* (17), m.p. 290—300°, M (mass spectrum), 336, 320 (M - 16), 307, 292, 264, 168, and 132. A peak at 338 due to ¹²C₁₈¹H₈¹⁶O³⁴S³²S₂ had 14% of the intensity of the 336 peak due to ¹²C₁₈¹H₈¹⁶O³²S₃ (calculated intensity 13%).

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¹⁹ B. M. Mikhailov and A. D. Chinaeva, *Zhur. obshchei Khim.*, 1952, 22, 162 (*Chem. Abs.*, 1952, 46, 11,170h).