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2,7-Dithia[8]-, 2,8-Dithia[9]-, and 2,9-Dithia[10](9,10)anthracenophanes. High Reactivity Induced by Aryl-Ring Deformation[1]

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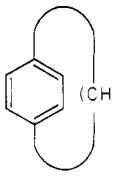
Though all but one member of the [*n*]paracyclophane (**1**) series with *n* = 6–16 have been synthesized,[2] relatively few of the corresponding [*n*](1,4)naphthalenophanes[3] (**2**) and [*n*](9,10)anthracenophanes (**3**) have been reported. In the [*n*](9,10)anthracenophane series, the smallest well-characterized member has a ten-atom bridge,[4,5] although 3,6-dioxo[8](9,10)anthracenophane has been prepared and was found to be susceptible to oxidation by ground-state molecular oxygen.[6] The relatively high reactivity of the central ring of the anthracene moiety makes these compounds especially interesting for probing the effects of aryl ring distortion on reactivity and also suggests their potential as intermediates in the synthesis of [2.2.2.*n*]paddlanes. In this latter regard, Vögtle and Koo Tze Mew[4] have reported the preparation of 2,11-dithia[12]- and 2,15-dithia[16](9,10)anthracenophane and the Diels–Alder addition of dienophiles to these molecules. In this paper we report our efforts to prepare and examine several of the smaller dithia[*n*]anthracenophanes.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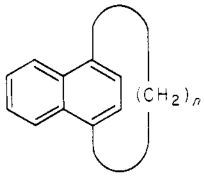
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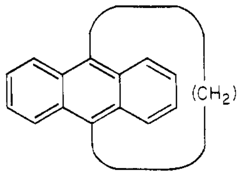

3

Reaction of 9,10-bis(chloromethyl)anthracene[7] with 1,6-hexanedithiol, 1,5-pentanedithiol, or 1,4-butanedithiol in refluxing ethanolic KOH at high dilution afforded 2,9-dithia[10](9,10)anthracenophane (**4**), 2,8-dithia[9](9,10)anthracenophane (**5**), and 2,7-dithia[8](9,10)anthracenophane (**6**), respectively, with yields dropping markedly as the bridge length was decreased.[8] Attempts to prepare 2,6-dithia[7](9,10)anthracenophane (**7**) under these (and higher dilution) conditions were unsuccessful. A previous attempt by others[9] to prepare the corresponding dithia[7]paracyclophane also met with failure.

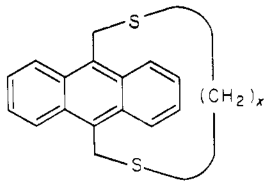
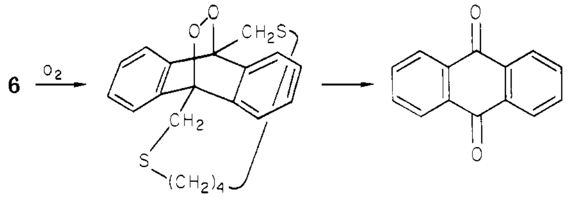

4, $x = 6$
5, $x = 5$
6, $x = 4$

Table I. ^{1}H NMR Spectral Data of **4**–**6** in $CDCl_3$ Solution

compd	aryl protons	benzylic protons	other methylene protons
	chemical shift, δ		
4	7.90 (m, 8 H)	4.82 (s, 4 H)	2.03 (t, 4 H), 1.33 (m, 4 H), 0.23 (br s, 4 H)
5	7.91 (m, 8 H)	4.86 (s, 4 H)	1.78 (m, 4 H), 0.05 (m, 6 H)
6	7.90 (m, 8 H)	4.85 (5, 4 H)	1.50 (m, 4 H), −0.10 (m, 4 H)

Scheme I



6 endoperoxide

Ultraviolet absorption spectra of **4**–**6** show small bathochromic shifts and loss of fine structure with decreasing bridge length [λ_{max}, nm (log ϵ): **4**, 351 (5.5), 368 (5.7), 388 (5.9); **5**, 353 (6.1), 370 (6.3), 390 (6.6); **6**, 371 (6.0), 391 (6.1)]. Analogous, but larger, shifts in the [*n*]paracyclophane series have been reported and have been attributed to aryl ring deformation.[10,11] (Bathochromic shifts have also been reported for [2.2]anthracenophanes and were attributed to transannular π electronic interaction.[12])

The changes in proximity of the methylene bridge to the anthracene ring in **4**–**6** are reflected in the ^{1}H NMR spectra (Table I). The well-known shielding effect of aromatic rings on suitably located protons[2,10] causes the peaks due to the central methylene protons to appear at unusually high field and at highest field in the shortest bridge compound **6**.

Anthracenophanes **4** and **5** are fairly stable in the absence of light and were handled routinely. The smaller bridged **6**, however, underwent oxidation to yield anthraquinone both in solution and in the solid state. A sample of **6** stored for ca. 2 months in the dark had largely decomposed to anthraquinone as evidenced by its ultraviolet spectrum and high-resolution mass spectrum. When oxygen was bubbled through a $CDCl_3$ solution of **6**, complete loss of starting compound was evident (NMR) within 1 week. Evaporation of solvent left a residue that consisted mainly of anthraquinone (TLC, IR) and a small amount (ca. 15%) of a yellow solid, an apparent product of oxidation of **6** [NMR, IR; mass spectrum, m/e 408 (m^+)]. No attempt was made to isolate bridge-derived products which were assumed to be either volatile (and therefore lost in solvent evaporation) or polymeric.

It appears likely that the formation of anthraquinone from **6** results from addition of molecular oxygen (either in its ground state or singlet excited state, formed by sensitization by **6** itself), perhaps forming a transient endoperoxide which undergoes thermal decomposition

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[1] Portions of this work were completed at Wellesley College.

[2] For a review of [*n*]cyclophane chemistry see: Rosenfeld, S. M.; Choe, K. A. In "Cyclophanes"; Keehn, P. M., Rosenfeld, S. M., Eds.; Academic Press: New York, in press.

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[8] All yields were somewhat higher than those for the dithia[*n*](9,10)anthracenophanes with *x* = 8 and 12 (29% and 24%, respectively).[4]

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(Scheme I). Addition of oxygen almost certainly occurs at the unobstructed face of the anthracene ring though, in principle, addition at the other face would give a stereoisomeric endoperoxide. These surmises have not been explicitly tested, but endoperoxide formation by reaction of singlet oxygen with 9,10-disubstituted anthracenes is well documented.[13] The higher reactivity of **6** as compared to **4** and **5** is doubtless due to increased deformation of the anthracene ring in **6**. Thermal cleavage of anthracene endoperoxides generally involves loss of (excited state) molecular oxygen,[13] but thermal O–O bond homolysis to form anthraquinone has been observed.[14] In this regard, endoperoxide **6** is also a dioxa[2.2.2.8]paddlane which, even without the peroxide linkage, may be prone to fragmentation. There appear to be no detailed studies of this sort on 9,10-bridged anthracenes, although anthraquinone formation has been reported in an earlier unsuccessful approach to the smaller (n = 8 or less) [*n*](9,10)-anthracenophanes and presumably involves similar chemistry.[15]

In summary, the title compounds exhibit spectra consistent with anthracene ring deformation, and the most highly strained of these shows enhanced reactivity toward molecular oxygen. These results along with previous reports[6,15] suggest that [*n*](9,10)anthracenophanes with eight or less atoms in the bridging chain will be kinetically unstable in the presence of oxygen, and therefore synthetic approaches to these molecules will require precautions dictated by this enhanced reactivity. We are currently examining the mechanism of oxidation of **6**.

Experimental Section

General Methods. ^{1}H NMR spectra were taken on a Perkin-Elmer R-32 spectrometer at 90 MHz in $CDCl_3$ solution with Me_4Si as an internal reference. IR spectra (thin film) were recorded on a Perkin-Elmer 727B spectrophotometer, and UV spectra were recorded on a GCA-McPherson Series EU-700 spectrophotometer in $CHCl_3$ solution. Chromatographic separations were done by using 2000-μm silica gel thick-layer plates with CH_2Cl_2 as the eluent. All melting points are uncorrected. 9,10-Bis(chloromethyl)anthracene was prepared by the procedure of Miller et al.[7] 1,4-Butanedithiol (Aldrich), 1,5-pentanedithiol (Tridom), and 1,6-hexanedithiol (Aldrich) were used as supplied.

2,9-Dithia[10](9,10)anthracenophane (4). The procedure of Vögtle and Koo Tze Mew[4] was used with precautions to exclude light and oxygen (N_2 atmosphere) during the high-dilution reaction of 9,10-bis(chloromethyl)anthracene and 1,6-hexanedithiol in KOH–ethanol–benzene solution. After a ca. 15-h reflux, the solvents were removed at reduced pressure, and the residue was extracted continuously with $CHCl_3$. Evaporation of $CHCl_3$ left a yellow solid that was chromatographed, affording **4** in 79% yield. A small sample was recrystallized from acetone–H_2O: mp 182–184 °C; IR 3080, 2925, 1675, 1620, 1420 cm^{-1}; high-resolution mass spectrum, calcd for $C_{22}H_{24}S_2$ *m/e* 352.13195, found 352.13139 (M^+); the base peak for **4**–**6** corresponds to expected benzylic cleavage.

2,8-Dithia[9](9,10)anthracenophane (5). Compound **5** was isolated in 57% yield as above: mp 193–196 °C; IR 3080, 2940, 2850, 1665, 1620, 1420 cm^{-1}; high-resolution mass spectrum, calcd for $C_{21}H_{22}S_2$ *m/e* 338.11629, found 338.11665 (M^+).

2,7-Dithia[8](9,10)anthracenophane (6). Compound **6** was isolated in 40% yield as above: mp 157–162 °C; IR 3060, 2925, 1685, 1615, 1429 cm^{-1}; high-resolution mass spectrum, calcd for $C_{20}H_{20}S_2$ *m/e* 324.09727, found 324.09917 (M^+).

Oxidation of 6. A 30-mg sample of **6** was dissolved in 0.5 mL of $CDCl_3$, and oxygen was bubbled through the solution for 30 min. ^{1}H NMR spectra, run at intervals, showed complete loss of starting compound in 1 week. Partial evaporation of solvent and vacuum filtration afforded 5 mg of a yellow solid: mp 173–175 °C dec; IR 3430, 3080, 2940, 1660, 1440 cm^{-1}; partial ^{1}H NMR δ 2.35 (s), 2.95 (m), 3.80 (m), 8.35–9.55 (m); mass spectrum, *m/e* 408 (M^+), 206, 120 (base peak). Evaporation of the remaining solvent from the filtrate left an oily orange residue which was mainly anthraquinone (estimated 80%) by TLC and IR analyses.

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Registry No. 4, 84050-69-1; **5**, 84050-70-4; **6**, 84050-71-5; 1,4-butanedithiol, 1191-08-8; 1,5-pentanedithiol, 928-98-3; 1,6-hexanedithiol, 1191-43-1; 9,10-bis(chloromethyl)anthracene, 10387-13-0; anthraquinone, 84-65-1.

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High-Yield Synthesis of Tetramethyltetraselenafulvalene[1] Avoiding the Use of Gaseous H_2Se

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Cation radical salts of tetramethyltetraselenafulvalene (TMTSF) exhibit metallic[3,4] and even superconducting properties[4-8] at low temperature. The preparative procedures reported so far use expensive (CSe_2, H_2Se) and highly toxic starting materials. We report a procedure starting from elemental selenium and with the further advantage that the risk of handling gaseous H_2Se is avoided.

TMTSF was first prepared from CS_2.[9-12] This procedure with some improvements[13] still gives the highest overall yield. Later TMTSF was obtained via consecutive H_2Se reactions starting from selenoureas[14] or *N*,*N*-dimethylphosgenimminium chloride.[15,17]

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[1] IUPAC name: 4,4′,5,5′-tetramethyl-$\Delta^{2,2'}$-bi-1,3-diselenolylidene.

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