7,15,17,19-Tetra-alkoxy-2,3,4,5,10,11,12,13-octathiatricyclo[12,2,2,$2^{6,9}$]eicosa-6,8,14,16,17,19-hexaene

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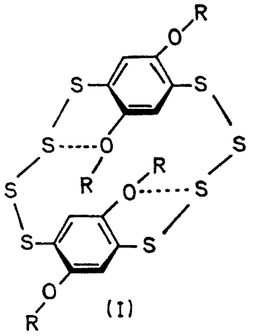
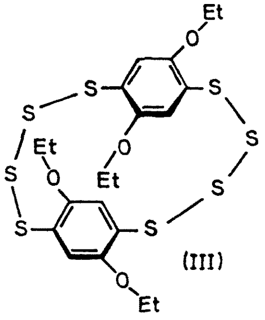
Summary The catalysed reaction of sulphur monochloride and 1,4-diethoxybenzene gives the unexpected novel macrocyclic polysulphur compound mentioned in the title.

WE report novel macrocyclic polysulphur compounds of type (I) isolated in an attempted synthesis in the thianthrene series. The uncatalysed reactions of dialkoxybenzenes with sulphur monochloride (S_2Cl_2) in inert solvents yield linear sulphides,[1] the same reactants in the presence of anhydrous aluminium chloride or a mineral acid–clay catalyst† in carbon disulphide or chloroform yield vastly different sulphur heterocycles. Under catalytic conditions both *ortho*-dimethoxy- and -diethoxy-benzenes gave 2,3 : 7,8-tetrasubstituted thianthrenes (II; R = Me, m.p. 175—176°;[2] R = Et, m.p. 129—130°). An analysis of the n.m.r. spectrum of (II; R = Et) shows a single aromatic peak at 7·0 p.p.m. and an integrated intensity ratio of aliphatic to aromatic hydrogens of 4·8. These data are consistent with the suggested thianthrene structure and inconsistent with the corresponding disulphide.

In the case of the *para*-diethoxybenzene under similar catalytic conditions, unexpected novel large-ring crystalline polysulphides were obtained with relatively high sulphur content. A closer study of one of them [I; R = Et, m.p. 185° (vitrification); mol. wt. and analysis for $C_{20}H_{24}O_4S_8$] by spectroscopic methods has confirmed the structure. Single orange crystals of (I; R = Et) ($CHCl_3$) are monoclinic, space group $P2_1/c$, $Z = 4$ (M 584), $a = 10{\cdot}15$, $b = 9{\cdot}23$, $c = 29{\cdot}6$ Å, $\beta = 115°\ 39'$, D_c 1·49 g. cm.$^{-3}$; 60 Mc./sec. n.m.r. spectrum ($CDCl_3$; Me_4Si as internal standard) δ 7·23 (s, ArH), 4·03 (m, –CH_2–) and 1·47 p.p.m. (t, CH_3). Both Dreiding and Fischer–Hirschfelder molecular models indicate that the planes of the rings are parallel. We have not, however, overlooked the possibility of structure (III). The relative positions of the ethoxy-groups on the two rings have not been established; but molecular models suggest these shown in (I), for which the orientation of the rings about the tetrasulphide linkages would suffer minimal constraint. The u.v. absorption maximum ($CHCl_3$) occurs at λ_{max} 371 nm.‡ (ϵ 10,242). The large bathochromic shift observed in (I) compared to known tetrasulphides (290—330 nm.)[3] allows speculation on internal steric strain (*cf.* cyclic disulphides[4]). We suggest a non-bonding attractive interaction between sulphur and oxygen as represented in (I). Recent *X*-ray crystallographic studies have shown several parallels in the literature for such S · · · O intramolecular interaction.[5] Models of (I) show that the five-membered hetero-ring thus formed with the S — S · · · O interaction, lies in the same plane as the benzene ring.


(I)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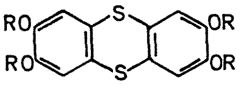
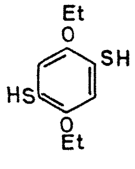

(II)


(IV)

Reduction of (I) gave a crystalline dithiol [(IV; m.p. 119°; SH stretching band at 2560 cm.$^{-1}$; n.m.r. ($CDCl_3$) δ 6·73 (s, ArH), 3·84 (s, SH), and 3·96 (m,CH_2), and 1·41 (m, CH_3)]. The assigned structure (IV) for the dithiol was confirmed by an independent unambiguous synthesis for its 2,5-di(ethylthio)-derivative m.p. 78—78·5°. Starting from *p*-benzoquinone and ethanethiol and subsequent reaction with diethyl sulphate gave a product identical (m.p. 78°, m.m.p., and i.r.) with the above mentioned derivative of (IV); thus furnishing further evidence for structure (I). Further examples of compounds of type (I) and related structures have been prepared. Elemental analysis for compounds reported are satisfactory.

A set of crystallographic data is being collected on an automatic diffractometer in the Chemistry Department at Brookhaven National Laboratory by Dr. I. Bernal.

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† "Montmorillonite catalysts, K-series" Chemical Products Division of Chemetron Corporation, Louisville 1, Kentucky.

‡ The absorption spectra of polysulphides shift towards longer wavelengths as the number of sulphur atoms increase in the molecule (C. C. Price and S. Oae, "Sulphur Bonding," Ronald Press Company, New York 1962, p. 38). Further u.v. studies are under way.

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