

Fig. 1. SN-9972: system of isopropyl ether-*n*-butyl alcohol vs. 2*M* (total) citrate buffer at pH 3.86; concentration of base, 1.0 mg. per ml. of each phase. SN-8233: system of isopropyl ether-*n*-butyl alcohol vs. 2*M* (total) citrate buffer at pH 3.52; concentration of base 0.8 mg. per ml. of each phase. Concentrations determined by absorption at 390 $m\mu$; dashed lines, theoretical; solid lines, experimental

H, 7.14, 7.19; N, 9.99, 10.04; $(\text{COOH})_2$, 21.00; drug base, 79.88.

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Cyclic Sulfides. II. Ring Size and the Ultraviolet Absorption Spectra¹

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The measurement of the ultraviolet absorption of ethylene sulfide¹ has now allowed a discussion of the effect of ring size upon the spectra of cyclic sulfides. The data are presented² in Fig. 1. Perusal shows that the four membered ring sulfide has the weak absorption band at the longest wave length. It is difficult to offer a complete explanation designating the energy levels and the transitions involved. However, an empirical relationship can be discerned between the electron density and basicity

(1) Part I. R. E. Davis, *J. Org. Chem.*, **23**, 216 (1958).

(1a) National Science Foundation predoctoral fellow, 1955-1957.

(2) The experimental methods have been previously reported.¹ The sulfides were prepared by known procedures: 3 membered ring,¹ 4 membered,³ 5 membered,⁴ 6 membered.⁵

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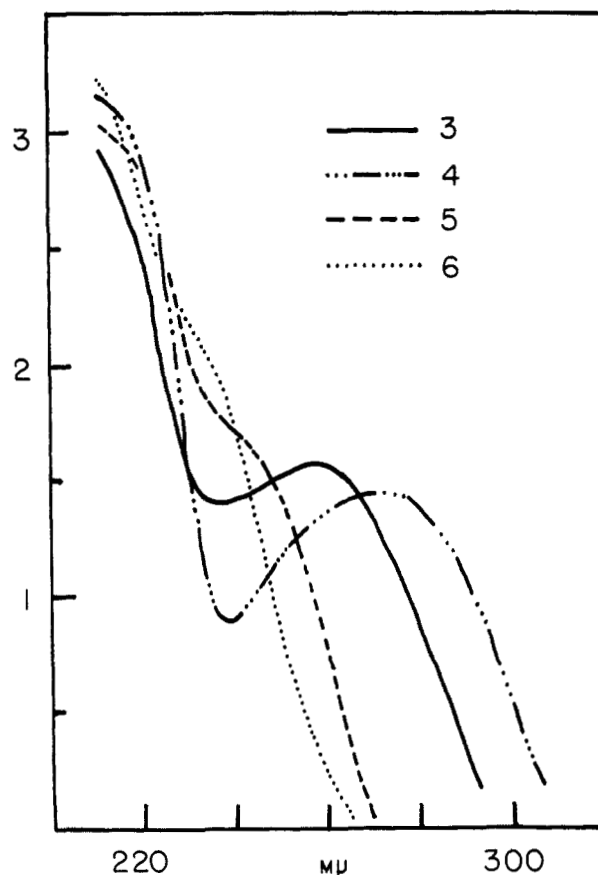


Fig. 1. Spectra of cyclic sulfides in absolute ethanol. Log ϵ vs. λ in $m\mu$. 3 ethylene sulfide, 4 trimethylene sulfide, 5 tetramethylene sulfide, 6 pentamethylene sulfide

of the sulfur atom and the position of the transition in divalent sulfur compounds. The more the electron density on the sulfur, the further the absorption towards longer wave lengths. This can be seen in the following series.

The sulfur atom spectrum⁶ serves as the basis for discussion. Hydrogen sulfide^{7,8} (λ_{max} hexane 190 $m\mu$ log ϵ 3.2) can be compared with sodium sulfide⁹ (λ_{max} 230 $m\mu$ log ϵ 3.8 in aqueous sodium hydroxide). Ethanethiol^{7,8} has a band at 195 $m\mu$ (log ϵ 3.15) and an inflection at 225 $m\mu$ (log ϵ 2.2) in ethanol. The sodium salt of 1-*n*-butanethiol⁹ in aqueous sodium hydroxide has a band at 240 $m\mu$ (log ϵ 3.7). The spectra of dialkyl sulfides⁵ show strong bands in the region 210-215 $m\mu$ with inflections near 230 $m\mu$ (log about 2). Alkyl groups donate electrons to the sulfur. Unbonded pairs of electrons are needed in divalent sulfur compounds on the sulfur atom to have absorption above 200 $m\mu$.

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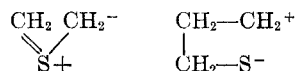
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Dimethyl sulfone and triethyl sulfonium chloride^{10,11} have no absorption above 200 m μ .

The electron donor abilities of the sulfur atom of cyclic sulfides have been observed to be in the order: 4>5>6>acyclic>3 by the complexing with boron trifluoride.¹² The order of NMR δ -values¹³ was found to be 4>3>5>6 for the hydrogens on the carbon adjacent to the sulfur atom. The order of position of the weak band of cyclic sulfides (Fig. 1) is 4>3>5>6.

The explanation of these facts is based on the inherent electronic nature of the ring compounds rather than on steric considerations. The data favor formulas:



as the extreme forms. Each can be obtained as the excited state by consideration of the probable ground state and the geometric properties by molecular orbital treatment. Delocalization of *p*-electrons has also been used to explain other properties of small ring compounds.^{14,15}

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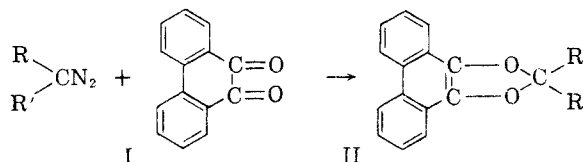
Further Reactions of Phenanthraquinone with Diaryldiazomethanes

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Schönberg and Mustafa¹ found that the action of diphenyldiazomethane on phenanthraquinone yields a methylenedioxy derivative of type II (R, R' = C₆H₅) which gives phenanthraquinone when treated with sulfuric acid.

This reaction has now been extended using *p,p'*-dichlorodiphenyldiazomethane (Ia), *o*-chlorophenylphenyldiazomethane (Ib), *p*-nitrophenylphenyldiazomethane (Ic), and *p*-xenylphenyldiazomethane (Id).² The reactions led to the formation of the methylenedioxy derivatives IIa,b,c,d. The hydrolysis of IIa with concentrated sulfuric acid yielded phenanthraquinone.



I. and II.:

a, R = R' = C₆H₄Cl-*p*

b, R = C₆H₅; R' = C₆H₄Cl-*o*

c, R = C₆H₅; R' = C₆H₄NO₂-*p*

d, R = C₆H₅; R' = C₆H₄-C₆H₅-*p*

EXPERIMENTAL

9,10-(p,p'-Dichlorodiphenylmethylenedioxy)phenanthrene (IIa). To a suspension of phenanthraquinone (0.5 g.) in benzene (20 ml.) was added a benzene solution of *p,p'*-dichlorodiphenyldiazomethane (prepared from 0.8 g. of *p,p'*-dichlorobenzophenone hydrazone in 20 ml. of dry benzene). A mild evolution of nitrogen occurred and continued for 10 min. The quinone dissolved and the solution was kept at room temperature overnight. The red oily residue, obtained after evaporation of the benzene, solidified on washing with cold methyl alcohol and was crystallized from ethyl alcohol as yellow crystals, m.p. 185°. It gives, on treatment with concentrated sulfuric acid, a brown color which changes after some time to a green color; yield 0.7 g.

Anal. Calcd. for C₂₇H₁₆Cl₂O₂: C, 73.1; H, 3.6; Cl, 16.0. Found: C, 73.7; H, 3.7; Cl, 15.7.

9,10-(o-Chlorophenylphenylmethylenedioxy)phenanthrene (IIb) was obtained from phenanthraquinone (0.5 g.) and *o*-chlorophenylphenyldiazomethane (prepared from 0.7 g. of *o*-chlorobenzophenone hydrazone in 20 ml. of dry benzene). It was crystallized from petroleum ether (b.p. 60–80°) as almost colorless crystals, m.p. 207°; yield 0.6 g. It gives a brown then a green color with concentrated sulfuric acid.

Anal. Calcd. for C₂₇H₁₇ClO₂: C, 79.3; H, 4.1; Cl, 8.7. Found: C, 79.4; H, 4.2; Cl, 8.4.

9,10(p-Nitrophenylphenylmethylenedioxy)phenanthrene (IIc) was obtained by treating phenanthraquinone (0.5 g.) with *p*-nitrophenylphenyldiazomethane (prepared from 0.8 g. of *p*-nitrobenzophenone hydrazone in 20 ml. of dry benzene). It was crystallized from petroleum ether (b.p. 80–100°) as orange crystals, m.p. 225; yield 0.7 g. It gives a brownish purple color with concentrated sulfuric acid.

Anal. Calcd. for C₂₇H₁₇NO₄: C, 77.3; H, 4.0; N, 3.3. Found: C, 77.4; H, 4.0; N, 3.5.

9,10-(p-Xenylphenylmethylenedioxy)phenanthrene (IId) was obtained as above, in 60% yield. It was crystallized from petroleum ether (b.p. 80–100°) as yellow crystals, m.p. 170°. It gives an orange color with concentrated sulfuric acid.

Anal. Calcd. for C₃₃H₂₂O₂: C, 88.0; H, 5.0. Found: C, 88.0; H, 5.5.

Hydrolysis of IIa. Half a gram of IIa was mixed with concentrated sulfuric acid (3 ml.) and left overnight, whereby a green solution was formed. The solution was poured onto ice,

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