Title

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ABSTRACT

The effect of solvents and temperature on the optical absorption spectrum of a number of substituted aromatic disulfides is reported.

The problems offered by the disulfide link and the exchange reactions between disulfides, and between disulfides and thiols, are receiving increasing attention. Recently the base-catalyzed exchange between various alkyl disulfides and the corresponding thiols was studied by means of a radioactive-tracer technique.[1] Our initial purpose was to extend these investigations to a large number of compounds in a variety of experimental conditions using a spectrophotometric technique that, if applicable, would have been incomparably faster.

To evaluate the possibilities of this approach, it was, in the first place, necessary to determine the absorption spectra of a number of disulfides. Because the literature gives little data on this subject, we undertook the determination of the spectra. Aromatic disulfides were chosen for consideration since they are likely to exhibit upon substitution the largest spectral variations.

The p-dimethylamino derivative was prepared by the reaction of sulfur monochloride with p-dimethyl aniline.[2] Other disulfides were prepared by oxidation of the corresponding thiol. Some were Eastman Kodak products that had been recrystallized.

A Cary Model-14 spectrophotometer was used. Spectra were taken at room temperature and at -150°. For the low-temperature spectra, the absorption cell was placed in a Dewar flask equipped with an optical-

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[1] Fava, Iliceto, and Camera., J. Am. Chem. Soc., in press.

[2] V. Mertz and W. Weith., Ber. 19, 1571 (1886).

quartz window and nitrogen gas was circulated in the flask. Temperatures down to -150° may be reached by regulating the gas flow. The spectra of the aromatic disulfides are given in the following figures.

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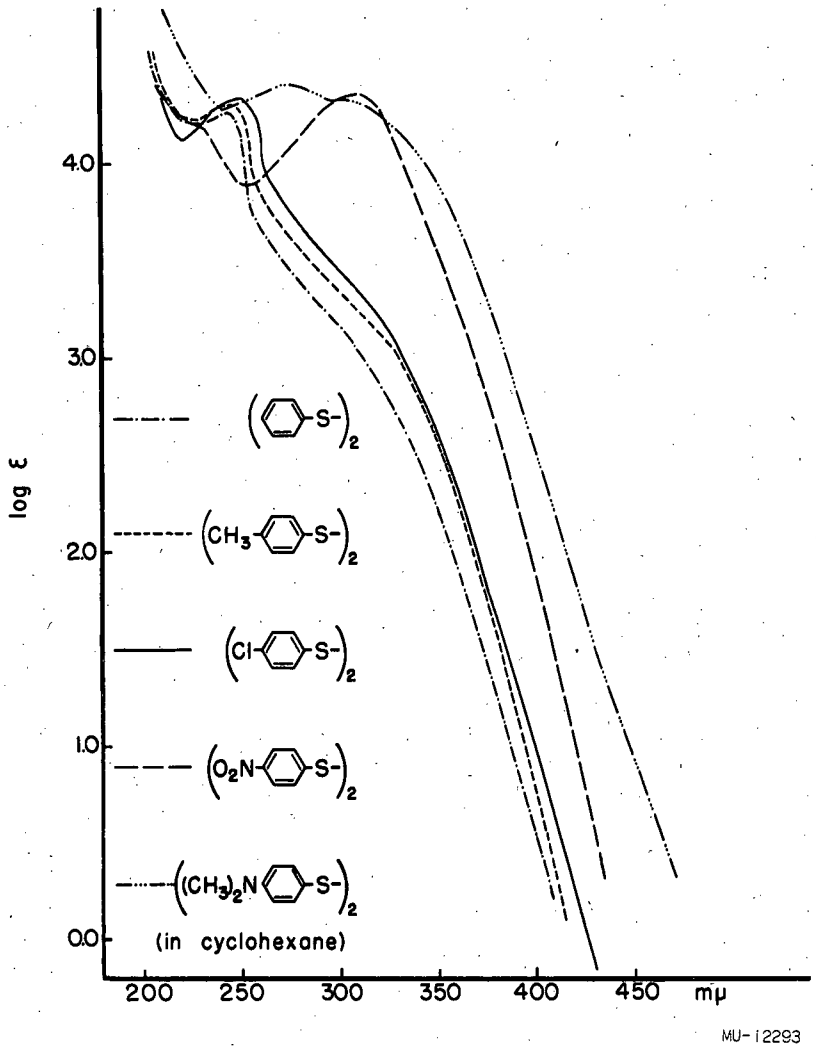

Fig. 1. Effect of nuclear para substitution on absorption spectrum of diphenyl disulfide.

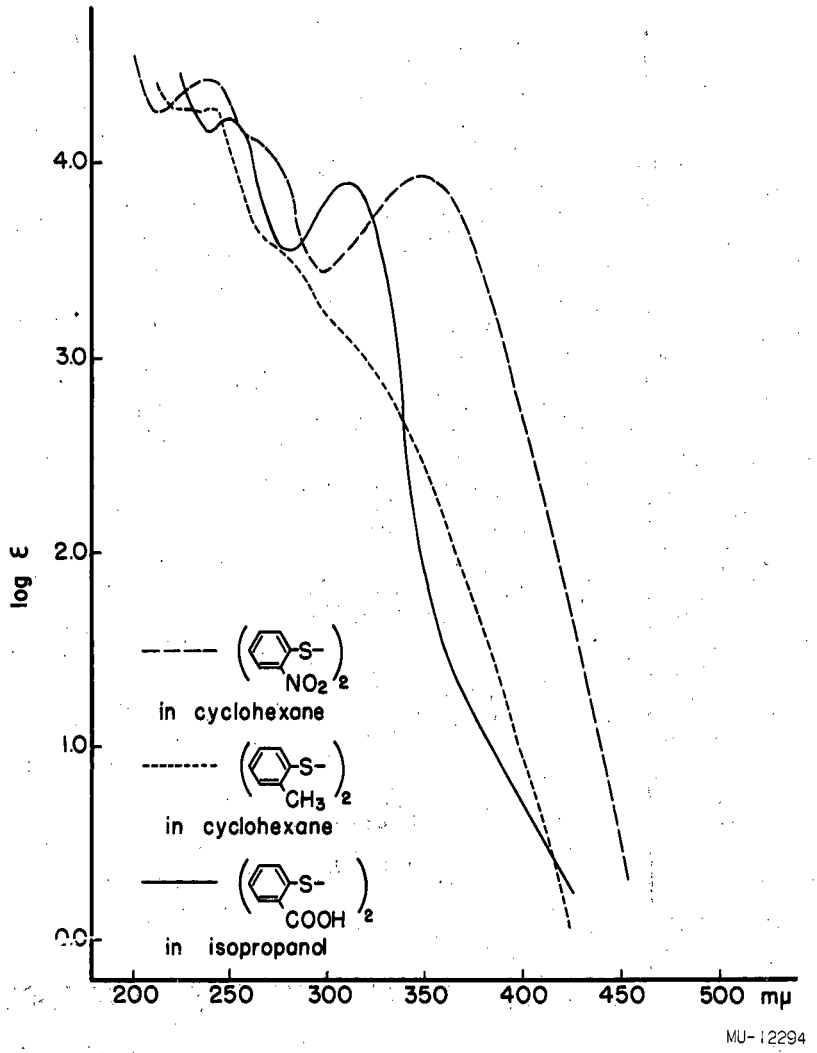

Fig. 2. Effect of nuclear ortho substitution on absorption spectrum of diphenyl disulfide.

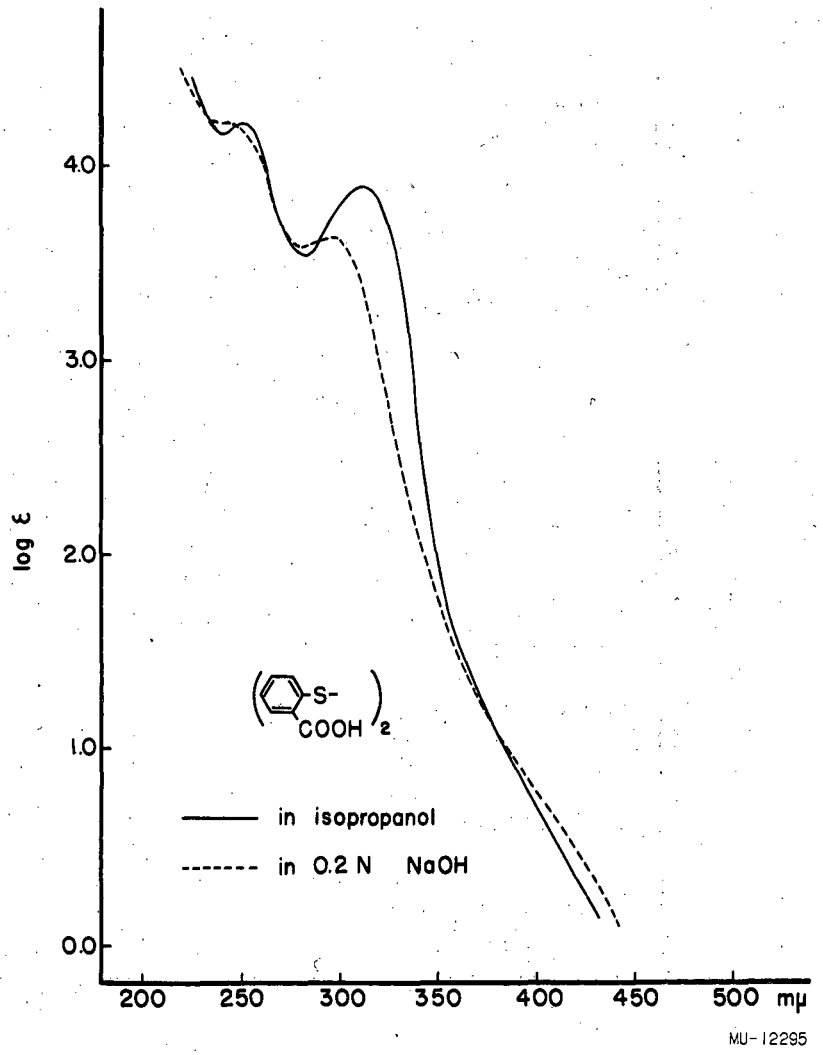

Fig. 3. Effect of base on absorption spectrum of ortho-carboxydiphenyl disulfide.

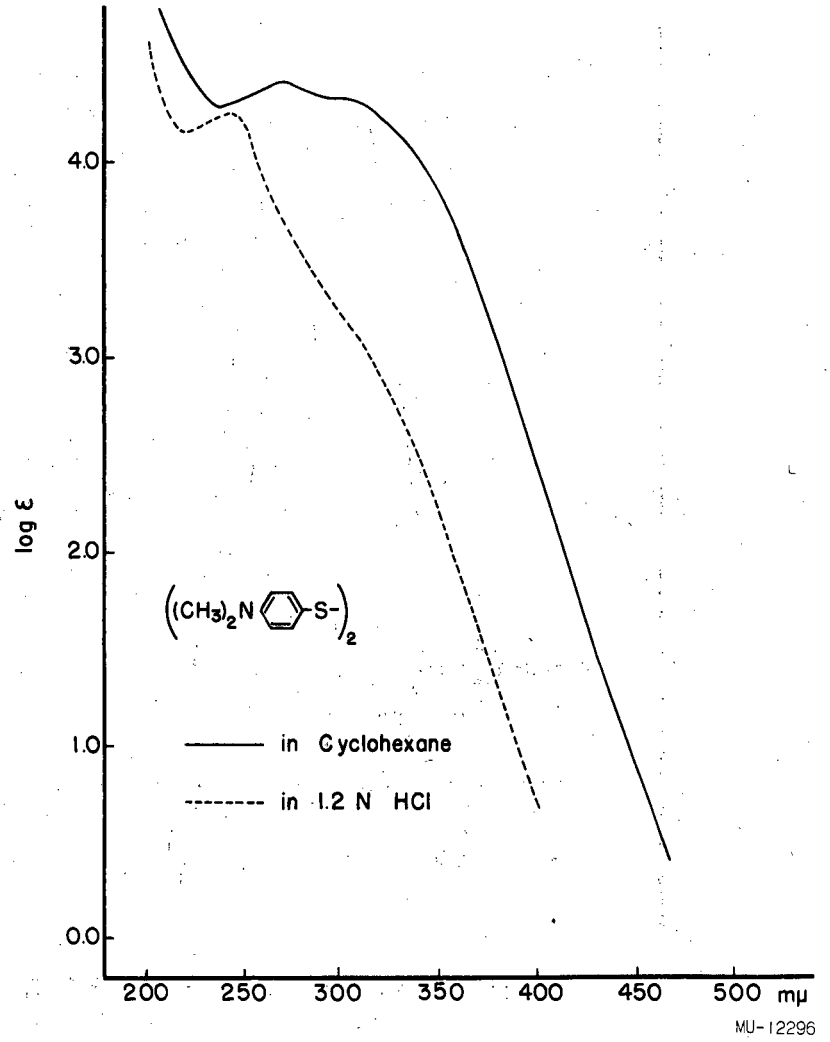

Fig. 4. Effect of acid on absorption spectrum of para-dimethylaminodiphenyl disulfide.

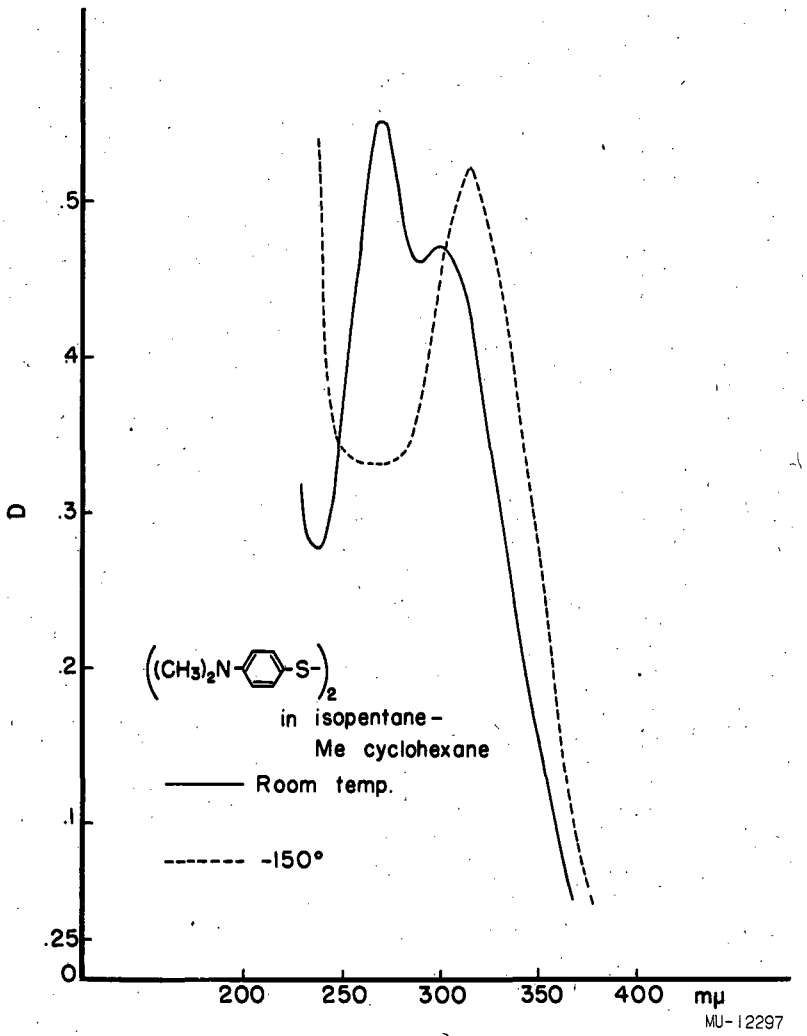

Fig. 5. Effect of temperature on absorption spectrum of para-dimethylaminodiphenyl disulfide.

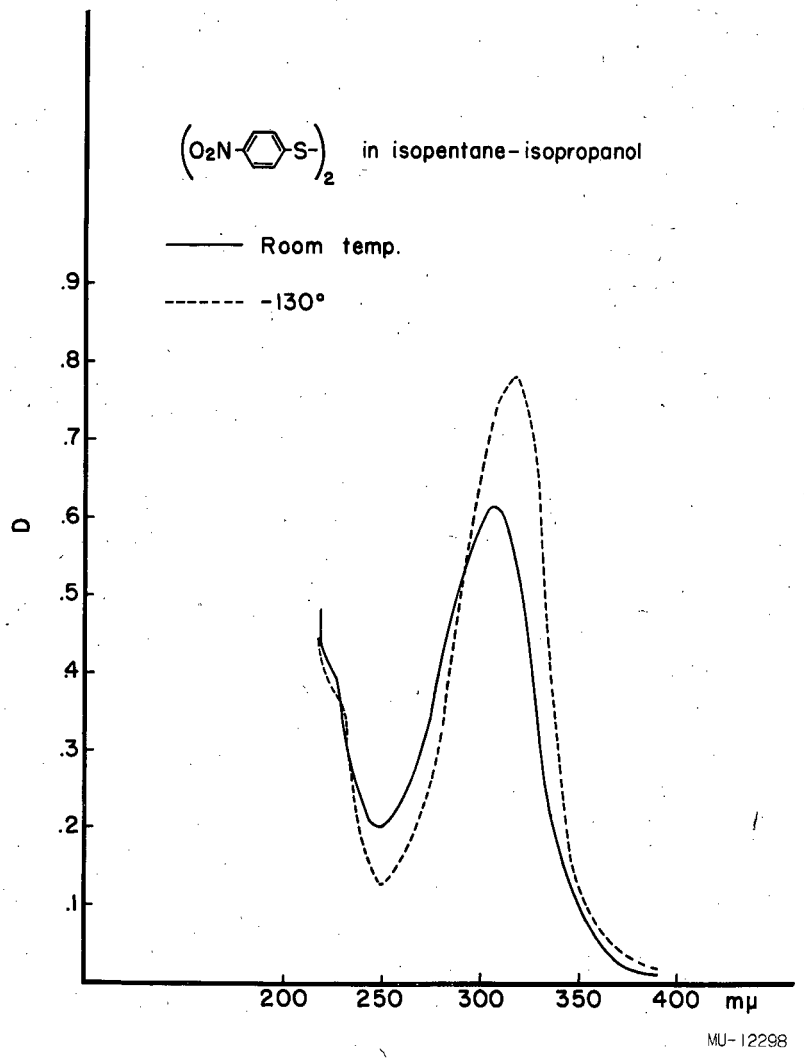

Fig. 6. Effect of temperature on absorption spectrum of para-nitrodiphenyl disulfide.