

Absorption Spectra and Structure of Sulphinic Acids.

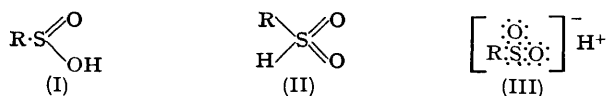
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Of the two possible structures (I) and (II) for sulphinic acids the former is favoured on ground of infrared and ultraviolet spectra. Probable assignments have been made of infrared bands in the spectra of benzene-, toluene-*p*-, naphthalene-2-, and *o*-methoxybenzene-sulphinic acids, and their esters, salts, and chlorides. The dissociation equilibria of benzenesulphinic acid in dry and moist carbon tetrachloride have been studied, and the character of the association discussed.

LITTLE work has been done on the structure of the sulphinic acid group since the publication by Otto and Rössing (*Ber.*, 1892, **25**, 230), in which they showed that ions of aromatic sulphinic acids may react in two different forms. With alkyl halides, the salts yield sulphones, but with ethyl chlorocarbonate they give esters. Connor in Gilman's "Organic Chemistry" (Vol. I., 1948, p. 914) discusses the two possible tautomeric forms (I) and (II) and concludes that sulphinic acids are best formulated as (III). This implies, however, some sort of fast proton oscillation between unequivalent positions, which is rather unlikely.

Guryanova and Syrkin (*Zhur. fiz. Khim.*, 1949, **23**, 105) determined the dipole moments of some aromatic sulphinic acids in benzene and dioxan solutions and compared their experimental values with those calculated for structures (I) and (II), assuming a planar arrangement of the atoms in (I). The measured moments lay between the two calculated



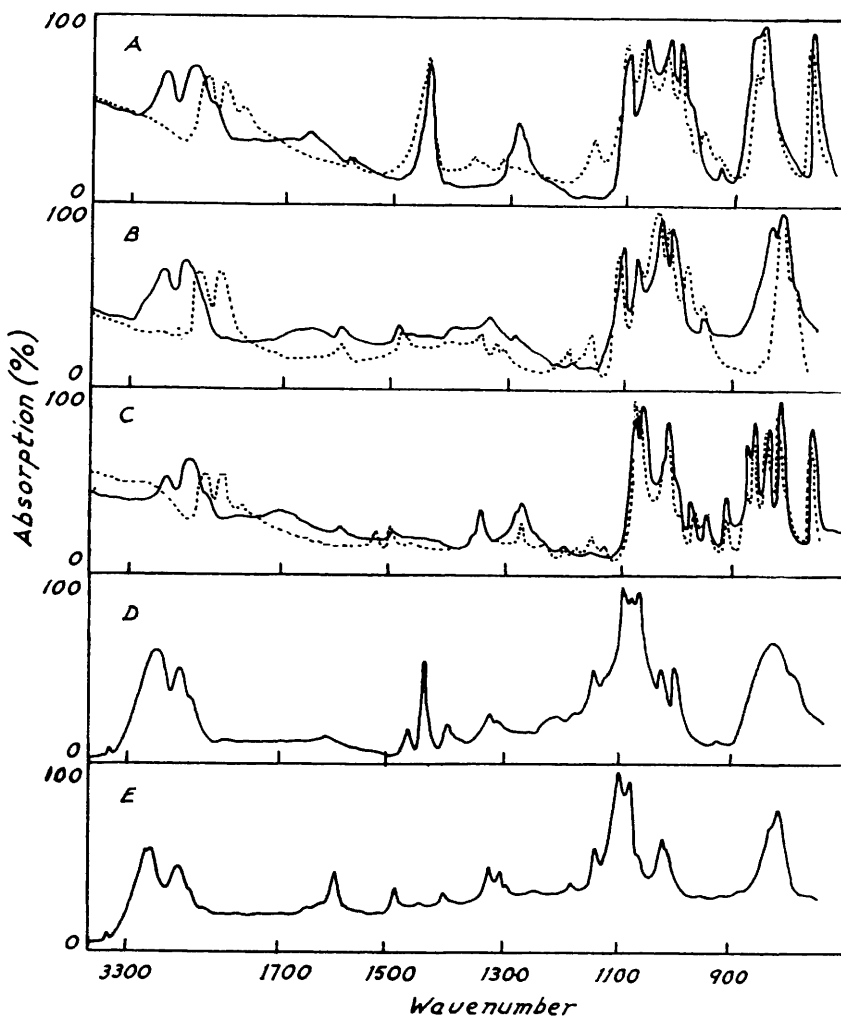
values, and the authors concluded that sulphinic acids in solution were a mixture of both tautomeric forms. The same authors published also infrared spectra of some solid sulphinic acids in the high-frequency region as well as Raman data for solutions in dioxan. Two peaks are apparent, at 2500 and 2560 κ^* respectively, the latter being assigned to a S-H frequency, in agreement with the conclusion derived from dipole-moment determinations.

* The use of the symbol κ (Kayser) for cm^{-1} is optional in Chemical Society publications (cf. Lecomte, *J. Opt. Soc. Amer.*, 1953, **43**, 410; see *Ann. Reports*, 1954, **51**, 12).

The only other spectroscopic work on sulphinic acids is that by Houlton and Tartar (*J. Amer. Chem. Soc.*, 1938, **60**, 544) on Raman spectra of sulphinic salts in water.

More attention has been paid to the structure of sulphinic esters. Phillips (*J.*, 1925, 2553) resolved several *n*-alkyl toluene-*p*-sulphinates and concluded that the sulphinic ester group was pyramidal with the sulphur atom at the apex. Ziegler and Wenz (*Annalen*,

FIG. 1. Infrared spectra of sulphinic acids (—) and deuterated sulphinic acids (-----).



A, Solid benzenesulphinic acid. B, Solid toluene-*p*-sulphinic acid. C, Solid naphthalene-2-sulphinic acid. D, Benzenesulphinic acid in CHCl_3 , and E, toluene-*p*-sulphinic acid in CHCl_3 (both 0.2 mole/l.; 0.1-mm. cell).

1934, 511, 109) reached the same conclusion for some other sulphinic esters. Parachor determinations by Sugden, Reed, and Wilkins (*J.*, 1925, 1525) indicate that one S:O group in the sulphinic esters has sulphoxide character. The near-ultraviolet absorption spectrum of methyl toluene-*p*-sulphinate (Bredereck, Bäder, and Hörschele, *Chem. Ber.*, 1954, **87**, 784) showed an auxochromic effect of the sulphinic ester group ($\log \epsilon$ 3.5) which was used as evidence for strong conjugation between the aromatic ring and this group.

The present authors were interested primarily in the hydrogen bonding in sulphinic

acids, but more reliable proofs of the structure were required first; the infrared and ultra-violet spectra have been determined for a series of sulphinic acids and their salts, esters, and chlorides.

Infrared Spectra.—In the spectra of the solid sulphinic acids investigated, three groups of strong bands seem to appear consistently in the regions 2790—2340, 1090—990, and 870—810 κ respectively (Fig. 1, *A—C*). Guryanova and Syrkin (*loc. cit.*) do not list exact positions of both high-frequency bands, but in general appearance their curves are similar to ours. There are considerable differences between the spectra of solid acids and their solutions in carbon tetrachloride or chloroform (Fig. 1, *D, E*). Both the high-frequency sets of bands move to higher frequency in solution, their position being now near 2900 and 2500 κ , and their relative intensities also change. In sufficiently dilute solution a new band appears also at 3700 κ in carbon tetrachloride, or at 3600 κ in chloroform. The apparent molal extinction coefficients of this group of bands for benzenesulphinic acid are listed in Table 1 and discussed below. Instead of several bands near 1050 κ in the solid, a doublet appears in solution some 30 κ lower, and the band near 850 κ also shifts to somewhat higher frequencies in solution.

The solution work is rendered difficult by the instability of sulphinic acids, particularly

TABLE 1. *Effect of solvent upon the OH absorption in benzenesulphinic acid.*

Concn. (mole/l.)	3700 κ		2900 κ			2500 κ		
	<i>T</i> (%)	ϵ	<i>T</i> (%)	ϵ	$C\epsilon_m^2/\epsilon$	<i>T</i> (%)	ϵ	$C\epsilon_m^2/\epsilon$
	<i>Dry CCl₄ (cell length 50 mm.)</i>							
0.002	71	15	13	89	0.005	20	70	0.006
0.0015	68	22	21	90	0.008	28	74	0.010
0.001	70	31	35	91	0.012	42	75	0.014
0.0008	67	44	42	94	0.016	49	77	0.019
0.0006	70	52	52	95	0.017	58	79	0.020
0.0004	73	68	64	99	0.019	69	82	0.023
	<i>Moist CCl₄ (0.04% of H₂O) (cell length 20 mm.)</i>							
0.003	80	16	29	84	0.009	39	68	0.011
0.0025	79	20	37	86	0.010	45	69	0.012
0.002	82	22	45	87	0.011	52	71	0.013
0.0015	77	38	51	97	0.022	59	76	0.028
0.001	76	60	63	100	0.036	70	77	0.046
0.0008	75	78	68	105	0.046	74	78	0.062

at slightly elevated temperatures. Amongst the products of decomposition are the related sulphonic acids (Pauly and Otto, *Ber.*, 1877, **10**, 2181), the presence of which is shown by the bands near 1200 and 1340 κ (Colthup, *J. Opt. Soc. Amer.*, 1950, **40**, 397), which become strong in *ca.* 10 hr. at room temperature.

The deuterated analogues show a most remarkable change in the high-frequency region. Instead of the bands near 2760 and 2350 κ new ones appear near 2080 and 1850 κ respectively in the solid. In the spectra of deuterated benzene- and naphthalene-sulphinic acids respectively three peaks are visible in this region. Some peaks near 1050 κ are shifted slightly towards higher frequencies, whereas a medium band seem to shift from 1280 to 950 κ . The bands near 840 κ are also slightly affected by deuteration. The differences between the spectra of solids and of solutions are similar to these found with undeuterated acids.

In the spectra of the sulphinic esters the strong band in the middle region of the spectrum appears again, but at somewhat higher frequencies than in the acids (1126—1136 κ). Other characteristic bands seem to be one near 960 κ , and perhaps a broad band near 750 κ .

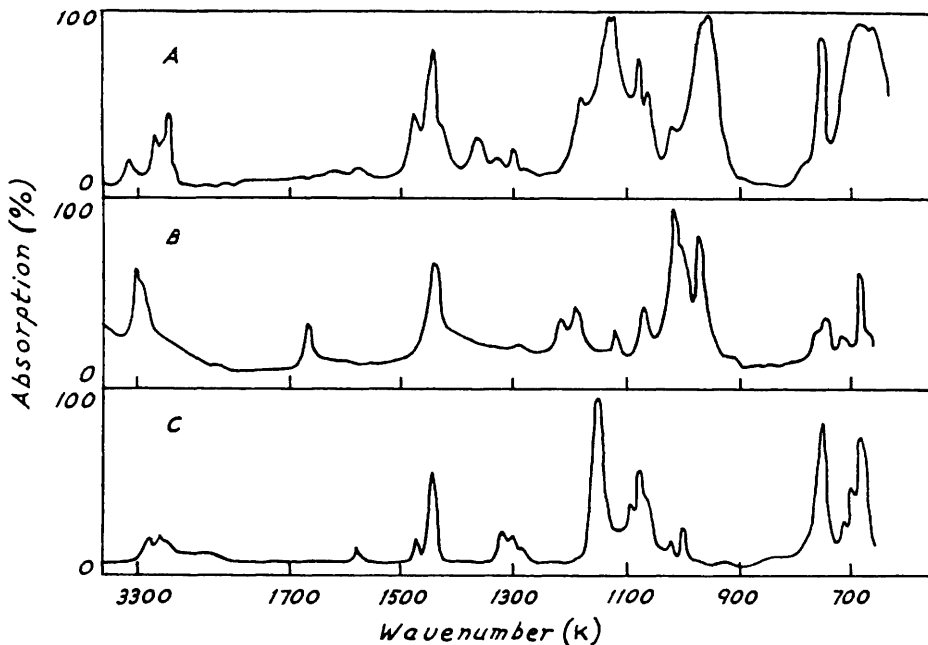
The spectra of acid chlorides contain only one strong band, near 1150 κ , whereas the salts show strong absorption near 1020 and 980 κ , positions which correspond well to those of the Raman bands (Houlton and Tartar, *loc. cit.*). The spectra of derivatives of the benzenesulphinic acid only are reproduced in Fig. 2, the spectra of derivatives of other acids being similar.

If structure (II) represents the sulphinic acid group, we should expect to find two

strong bands near 1350 and 1150 κ arising from the symmetric and the antisymmetric stretching vibrations respectively of the O:S:O group (cf. the sulphones; Barnard, Fabian, and Koch, *J.*, 1949, 2442; Price and Gills, *J. Amer. Chem. Soc.*, 1953, 75, 4750) and sulphonic acids (Haszeldine and Kidd, *J.*, 1954, 4228). In the latter compounds, the higher-frequency band seems to be the stronger. However, in the spectra of sulphinic acids, the main absorption band in solution is near 1090 κ , reminiscent of the characteristic band of the sulphoxides near 1050 κ (Barnard *et al.*, *loc. cit.*). No strong bands appear between 1300 and 1400 κ .

The assignment of the 1090 κ band to the S:O group in the acids is confirmed by the presence of a similar band in the spectra of the acid chlorides and particularly of the esters, the structure of the latter having been ascertained by the work of Phillips and of Ziegler (*loc. cit.*). The frequency of the S:O band in the esters is higher than in the corresponding

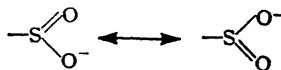
FIG. 2. A, Methyl benzenesulphinate, liquid film. B, Potassium benzenesulphinate, solid. C, Benzene sulphinyl chloride, liquid film.



acids. This recalls a similar relation in the carboxylic series. Barnard *et al.* (*loc. cit.*) also mentioned the influence of negative substituents on the S:O bond, which consisted in a rise of its stretching frequency. The lower frequency of the S:O group in the acids may be due in part also to hydrogen bonding.

Probable assignments may be made for the remaining characteristic bands, the high-frequency ones being discussed in connection with the hydrogen bonding. The band near 860 κ in the spectra of sulphinic acids may be due to the stretching of the S—O bond. The force constants of the sulphur—oxygen bonds are weakened by approximately 40% relatively to analogous carbon—oxygen bonds (Kohlrausch, "Ramanspektren," Akad. Verlagsgesellschaft, Leipzig, 1943, p. 416). Thus, taking the stretching frequency of the C—O bond in carboxylic acid dimers to be near 1300 κ (Hadzi and Sheppard, *Proc. Roy. Soc.*, 1953, 216, 247), we should expect to find the band corresponding to the S—O linkage near 800 κ . This is in a satisfactory agreement with the above assignment. Bands with similar frequencies appear also in the infrared spectra of sulphonic acids, as well as in their Raman spectra; Maschka and Aust (*Monatsh.*, 1954, 85, 891) assigned these also to the S—O stretching mode. In the spectra of the sulphinic salts the bands due to the S:O

group seem to be shifted to lower frequencies, whereas the corresponding S—O band appears at higher frequencies (960 κ). This is similar to the behaviour of the C:O and C—O bands in carboxylic acids on ionisation, and may be explained accordingly by the resonance



The shift of the band near 1280 κ in the spectra of sulphinic acids to lower frequency on deuteration, the ratio of the frequencies being near 1.4, suggests that this band is due to a motion of the OH group, probably a deformation mode. This frequency compares well with the in-plane deformation frequency of the OH group in carboxylic acid dimers (Hadži and Sheppard, *loc cit.*) and peroxy-acids (Giguère and Olmos, *Canad. J. Chem.*, 1952, **30**, 821). The intensity of this band, if compared to that due to S:O stretching, seems to be much smaller than that of the analogous band in the carboxylic acids. Dr. N. Sheppard suggested that in carboxylic acids the $\delta(\text{OH})$ may be abnormally strong because of interaction with the nearby CO frequency.

Hydrogen bonding in sulphinic acids. In agreement with the above assignments, which leave little doubt as to the correctness of structure (I), the band near 2900 and 2500 κ must belong to the stretching vibrations of bonded OH groups, and the sharp band at 3700 κ which appears in dilute solution is doubtless due to the OH stretching of the monomeric acid. The band near 2900 κ appears at a frequency not unusually low for strongly bonded OH groups, and the shift to 2180 κ on deuteration is in agreement with this assignment. A number of cases is known in which strongly shifted OH bands are observed, having positions near to 2500 κ (Lord and Merrifield, *J. Chem. Phys.*, 1953, **21**, 166; Angel and Werner, *Austral. J. Chem.*, 1953, **6**, 294) similar to that of the second band in sulphinic acids. This band might be mistaken for a S—H band because of its low frequency, as assumed by Guryanova and Syrkin (*loc. cit.*). However, their finding that the Raman line at 2550—2560 κ is weak, is in agreement with our assignment, since SH groups give rise to strong Raman lines, whereas OH groups are weak in scattering and strong in infra-red absorption.

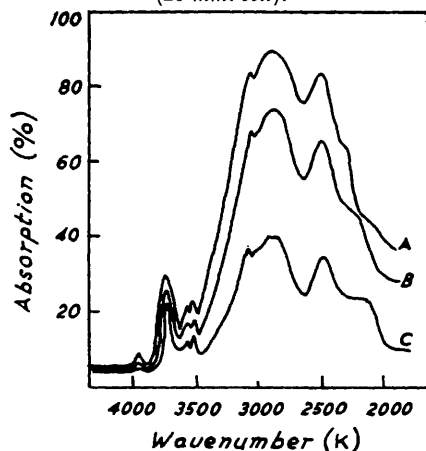
More information about the association of the sulphinic acids through hydrogen bonds may be gathered from the trends of the extinction coefficients of the OH bands at various concentrations. Measurements with benzenesulphinic acid in carbon tetrachloride are collected in Table 1. Wright (*J.*, 1949, 683) has shown that the degree of association of sulphinic acids depends considerably on small quantities of water present in the solvent. Therefore one series of measurements was carried out in carefully dried carbon tetrachloride and, in a second, water was added. Cells with an optical path of 50 mm. were used in the first series of the measurements, since the absorption of the monomer was very small at shorter path lengths. The absorption of water in the moist solvent (water content 0.04%) interfered too strongly with the monomer band in 50-mm. cells, therefore the second series had to be done with a 20-mm. path length, the absorption of the monomer in moist solvent being sufficiently strong. The peak absorptions were used in subsequent calculations, although it would be more correct to use integrated absorptions. However, the latter method was not applicable, because the low-frequency side of the band, culminating near 2500 κ , merges with the absorption of the solvent and therefore the energy transmitted here was too low for quantitative work. The ratio $C\varepsilon_m^2/\varepsilon$ (where C is the concentration of the acid in mole/l., ε the extinction coefficient of the associated band, and ε_m the extinction coefficient of the monomer), varies by as much as 35% in dry solvent, and 50% in moist solvent over the range investigated. This indicates that benzenesulphinic acid forms polymers of an order higher than two. A similar result has been obtained recently by Klemperer, Cronyn, Maki, and Pimentel (*J. Amer. Chem. Soc.*, 1954, **76**, 5846) for secondary amides.

Attempts have been made to determine the fraction α of unassociated molecules by extrapolating the plots of $\log I_0/C \log I$ versus C to zero concentration, and calculating therefrom the dissociation constant K_c (Kempter and Mecke, *Z. phys. Chem.*, 1941, **46**, B, 229). However, for small concentrations the data obtainable with the cell length

which could be used were insufficiently accurate. Apparently, there is less dissociation to monomers in solvent containing water, in agreement with Wright's result. The dissociation constants, $K_c = \alpha C / (1 - \sqrt{\alpha})$, were of the order of 10^{-4} in dry solvent, and 10^{-3} in moist solvent.

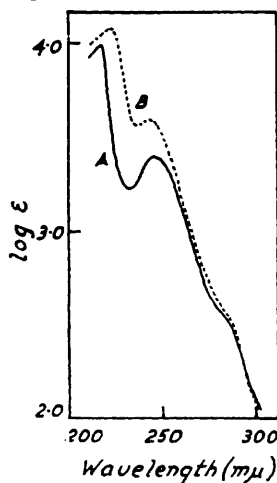
The hydrogen bond in the solid seems to be stronger, since both bands due to bonded hydroxyl are shifted to lower frequencies; also the sulphoxide band is considerably lowered in frequency. The splitting of the latter band, which is particularly well pronounced in the spectra of the solids, may be due to the coupling of similar groups in a chain. This is also the probable cause of the appearance of several bands due to OH groups. Although in the solid and in concentrated solution two bands only are recorded, that near 2900 κ

FIG. 3. *Benzenesulphinic acid in CCl₄*
(20-mm. cell).



A, 0.005, B, 0.003, and C, 0.001 mole/l.

FIG. 4. *Ultraviolet spectra of (A) benzenesulphinic and (B) toluene-*p*-sulphinic acid.*



shows distinctly a composite character at lower concentrations (Fig. 3), and in the spectrum of deuterated benzenesulphinic acids three bands were clearly resolved. This region of the spectrum of sulphinic acids may be compared with that for solid formic acid, the latter showing peaks at 3226, 2890, 2703, and 2538 κ (Bratož, Hadži, and Sheppard, unpublished work). Solid formic acid forms polymer chains by association (Holtzberg, Post, and Fankuchen, *Acta Cryst.*, 1953, **6**, 127). With reference to the strong shift of the OH band, the authors hope to obtain more information about the strength of the hydrogen bonds in sulphinic acids.

Ultraviolet Spectra.—The sulphinic group causes a bathochromic shift of the ultraviolet absorption of the benzene nucleus, its group *p* band moving to 218 (benzenesulphinic acid) or 223 $m\mu$ (toluenesulphinic acid), with an increase in intensity (Fig. 4). The vibrational

TABLE 2.

	λ_{\max} ($m\mu$)	$\log \epsilon$
Benzenesulphinic acid	218	3.99
	245	3.40
Toluene- <i>p</i> -sulphinic acid	223	4.09
	242	3.59
Methyl benzenesulphinic acid	223.5	3.94
	241.5	3.59
Methyl phenyl sulphoxide *	250	3.6
Methyl phenyl sulphone *	266	2.9
	273	2.8
Methyl <i>p</i> -ethoxycarbonylbenzenesulphinic acid *	272	4.0
„ <i>p</i> -ethoxycarbonylbenzenesulphonate *	279	3.2
„ <i>m</i> -ethoxycarbonylbenzenesulphinic acid *	250	3.6
„ <i>m</i> -ethoxycarbonylbenzenesulphonate *	374	2.85

* Price and Hydock, *J. Amer. Chem. Soc.*, 1952, **74**, 1943.

structure of the group α band is slightly indicated in the esters only. The position of this band is little changed with respect to benzene; the intensity is, however, increased. It appears from the published data on the absorption of aromatic sulphones and sulphoxides that the S:O group intensifies the absorption of the aromatic nucleus more than does the sulphone group (Table 2). The extinction coefficient of the group α band in benzene-sulphinic ester compares well with that of methyl phenyl sulphoxide and it is well above that of methyl phenyl sulphone. This fact, taken together with the similarity in the absorption of the respective acids, is an additional proof of the correctness of structure (I).

EXPERIMENTAL

Preparation of Substances.—Benzene-, toluene-*p*-, and naphthalene-2-sulphinic acid were prepared by reduction of the sulphonyl chlorides (Smiles and Bere, *Org. Synth.*, Coll. Vol. I, 1932, p. 7). *o*-Methoxybenzenesulphinic acid was prepared by Gattermann's method (*Ber.*, 1899, 32, 1142). The acids were recrystallised several times from water and kept over silica gel for drying. Carefully purified samples could be kept in an ice-chest unchanged for several months. Esters were prepared by Phillips's method (*J.*, 1925, 2553), and distilled in a high vacuum. Sulphinyl chlorides were prepared by Hilditch and Smiles's method (*Ber.*, 1908, 41, 4113). Deuterated sulphinic acids were prepared by hydrolysis of the corresponding chlorides with deuterium oxide.

The spectra were recorded with a Perkin-Elmer infrared spectrometer Model 21, equipped with sodium chloride and lithium fluoride prisms. The solids were examined as mulls in Nujol and hexachlorobutadiene. Carbon tetrachloride was dried by refluxing over phosphoric oxide, and chloroform over potassium carbonate. Solutions were made by weighing for each dilution, and were shaken mechanically for 2 hr. No decomposition of sulphinic acids was observed during this time. Solutions in moist carbon tetrachloride were prepared by adding the necessary amount of water to dry solvent. All operations were executed in a constant-temperature room ($22^\circ \pm 1^\circ$). Quantitative absorption determinations were carried out in two separate series of dilutions.

Ultraviolet spectra were measured with a Beckman DU Spectrophotometer, the readings being taken each 0.5 or 1 μ . Ethyl alcohol was used as solvent.

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