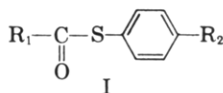Fig. 1. Translucent picture made by superimposing the infrared spectra curves of compound 1 from West Indian mahogany and cycloeucalenol from Eucalyptus. In the few places where there is no perfect congruency of the two curves the lower line is that of compound 1

Ultraviolet Absorption Spectra of Some Ortho-Anisyl Esters and Thiolesters

G. Cilento

In previous papers[1] evidence was presented that in the photoexcited state of the 240 mμ transition shown by p-anisyl thiolesters (I: R_1 = CH$_3$, C$_6$H$_5$, p-CH$_3$O—C$_6$H$_4$, p-NO$_2$—C$_6$H$_4$; R_2 = OCH$_3$) sulfur utilizes a d orbital; that is, there is some migration of negative charge outside the anisyl ring.

$$R_1 - \underset{\underset{O}{\|}}{C} - S - \underset{}{\bigcirc} - R_2$$

I

Bordwell and Boutan[2] have criticized this view on the ground that the bathochromic shift of the first primary band[3] on passing from p-hydroxyphenyl thiolacetate (I: R_1 = —CH$_3$; R_2 = —OH) to the corresponding anion is of the same magnitude as that occurring on passing from phenol itself to the phenolate anion and that therefore sulfur should not be concerned in this transition of para substituted phenyl thiolacetates. In answer to this objection, it should be noted that the expansion effect appears to be weak, the energy for "raising" an electron from the p level to the d level in sulfur being only slightly overbalanced by the increased delocalization of the π-electron system of the ring. Parallel examples are found in such cases where one of the two groups is capable of only a weak resonance effect. Thus on passing

from p-chlorobenzonitrile (λ_{max} = 237.5 mμ)[4] to p-chloronitrobenzene (λ_{max} = 280 mμ)[4] the shift (42.5 mμ) is almost identical to that (44.5 mμ) resulting on passing from benzonitrile (λ_{max} = 224 mμ)[4] to nitrobenzene (λ_{max} = 268.5 mμ).[4,5]

Spectroscopic indication of the enlargement of the M-shell of a sulfur atom flanked by a carbonyl group has now also been presented by Knott.[6a] However, Knott,[6b] in commenting on the ultraviolet absorption spectra of aryl thiolesters, points out that since such molecules are not planar, contributions involving a sulfur decet are hindered or excluded. This objection is answered in a simplified way, schematically represented in Fig. 1 where R is either an alkyl or aryl group.

The expansion effect being weak, it should disappear when the groups are ortho to each other, as

(1) (a) G. Cilento, Experientia, 8, 421 (1952); (b) J. Am. Chem. Soc., 75, 3748 (1953); (c) G. Cilento and W. F. Walter, J. Am. Chem. Soc., 76, 4469 (1954).

(2) F. G. Bordwell and P. J. Boutan, J. Am. Chem. Soc., 78, 854 (1956).

(3) The nomenclature of the bands, used here is that of Doub and Vandenbelt, ref. 4.

(4) L. Doub and J. M. Vandenbelt, J. Am. Chem. Soc., 69, 2714 (1947).

(5) The objections of Bordwell and Boutan based on the comparative spectral study of thiocyanates can be rebutted on the ground that while in an excited state of the transition in phenyl thiocyanate the sulfur atom would be expected to act as a moderate donor incorporating the nonbonding 3 pπ electrons in the aromatic 2 pπ shell, in the excited state of p-hydroxyphenyl thiocyanate another energetically equivalent conjugation is feasible in which the donor properties of the HO-group and the acceptor properties of the sulfur atom are used.

Several arguments can be advanced against their suggestion that the effect of the p-CH$_3$O group in aryl thiolesters is merely to resolve the absorption. The strongest one is to note that on passing from p-CH$_3$O—C$_6$H$_4$—COS—C$_6$H$_5$ to p-CH$_3$O—C$_6$H$_4$—COS—C$_6$H$_4$—OCH$_3$-p the same band obtained on passing from phenyl thiolacetate to p-anisyl thiolacetate arises in a region where formerly there was only a broad, rather shallow minimum[1b] being thus meaningless to speak of resolution in such a case.

However their objection to our statement[1b] that in aryl thiolesters sulfur acts equally well as donor and acceptor is sound. The adjective "well" in that statement is misleading being in contrast with what was clearly stated in a preceding paragraph.

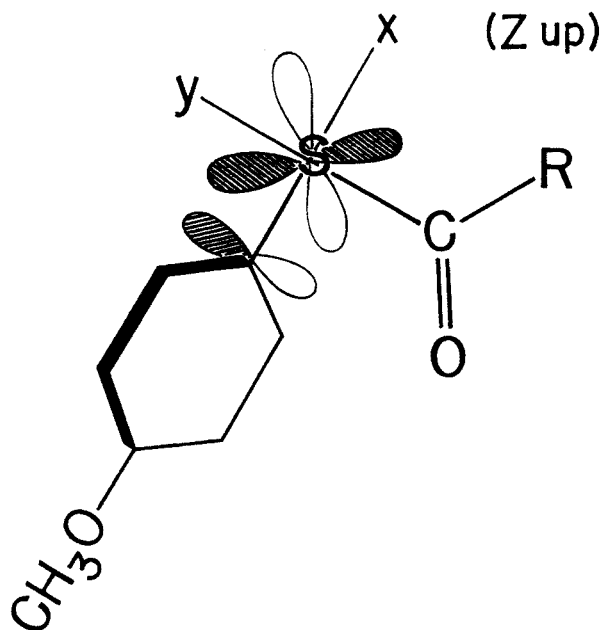(6) (a) E. B. Knott, J. Chem. Soc., 937 (1955); (b) J. Chem. Soc., 949 (1955).

Fig. 1. Schematic representation of the possibility of conjugation between the 2 pπ shell of a twisted anisyl group (xz plane) and the sulfur $d_x + y$ orbital. (Only the p_y orbital on the nearest aromatic carbon atom is shown.)

conjugative effects are usually smaller for ortho than for para substituents.[7,8] This has indeed been confirmed by studying the absorption spectra of o-anisyl esters and thiolesters (II: $R_1 = CH_3—$, $C_6H_5—$; X = O,S).
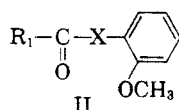
The spectra of o-anisyl acetate and of o-anisyl thiolacetate are represented in Fig. 2, where for comparative purpose the spectra of the corresponding nonsubstituted compounds[1c] have also been included. In the spectrum of the anisyl ester the peak at 217 mμ is certainly the primary aromatic absorption; the system of bands at longer wavelengths is the secondary absorption. In the corresponding thiolester the absorption at shorter wave lengths is presumably due to the overlapping of the thiolester band and of the primary band of the ring. The absorption toward the red is the secondary aromatic band.

The spectra of o-anisyl benzoate, of o-anisyl thiolbenzoate, and for comparative purpose of the unsubstituted parent compounds,[1b] are shown in Fig. 3. The peaks at 224 mμ and 232 mμ in the spectrum of o-anisyl benzoate are to be ascribed to the primary anisyl band and to the primary benzoyl absorption, respectively. The absorption above 260 mμ is the overlap of both secondary bands.

(7) L. Doub and J. M. Vandenbelt, *J. Am. Chem. Soc.,* **71,** 2414 (1949).

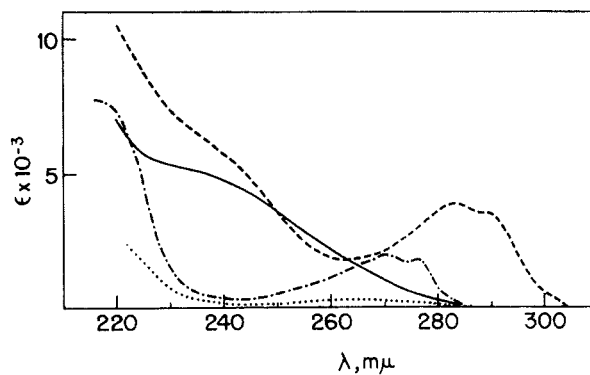(8) *Cf.* C. K. Ingold, *Structure and Mechanism in Organic Chemistry,* G. Bell and Sons Ltd., London 1953, p. 267.

Fig. 2. Absorption spectra in C_2H_5OH of: $H_3C—C—O—$ C_6H_5 ......; $H_3C—C—S—C_6H_5$ ————; $H_3C—C—O—C_6H_4$ $—OCH_3(o)$ -..-..-.; $H_3C—C—S—C_6H_4—OCH_3(o)$ ————
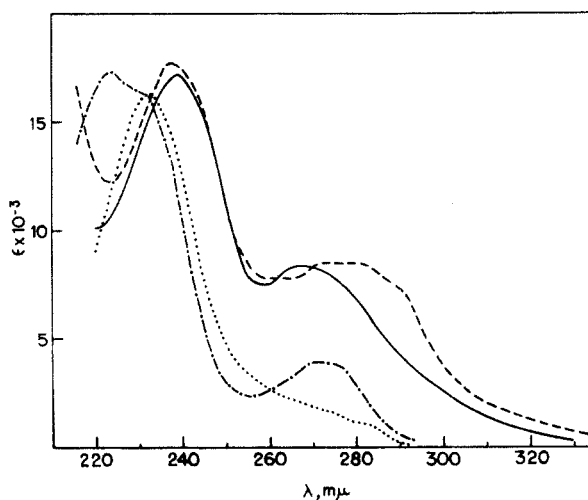
Fig. 3. Absorption spectra in C_2H_5OH of: $C_6H_5—C—O—$ C_6H_5 .....; $C_6H_5—C—S—C_6H_5$ ————; $C_6H_5—C—O—$ $C_6H_4—OCH_3(o)$ -.-.-.-.; $C_6H_5—C—S—C_6H_4—OCH_3(o)$

In the spectrum of the anisyl thiolester the maximum at 238 mμ is certainly the primary benzoyl absorption, whereas the primary anisyl absorption in the region 260–285 mμ is presumably the overlap of the thiolester band and of both secondary ring absorptions.

In conclusion, it is seen that there is no evidence of an absorption band due to conjugation of the anisyl ring with sulfur in the ortho derivatives.

EXPERIMENTAL

Guaiacol acetate was prepared from acetic anhydride and guaiacol.[9]

(9) H. O. Mottern, *J. Am. Chem. Soc.,* **56,** 2107 (1934).

Guaiacol thiolacetate. Thioguaiacol was prepared from the diazonium salt of *o*-anisidine and potassium ethyl xanthogenate according to Mauthner.[10] The mercaptan (7.3 g.) was allowed to react with acetyl chloride (3.8 ml.). A large excess of pyridine (15 ml.) was added and the mixture added to water and ice. Carbonate was added, the oil was collected, washed several times with water, dissolved in ethyl ether, the ethereal solution was dried, and the ether distilled off. The oily residue was twice distilled, b.p. (0.1 mm.) 101°. The compound is a liquid, colorless when pure; it gives a positive reaction of Raschig-Feigl.

Anal. Calcd. for $C_9H_{10}O_2S$: C, 58.21; H, 5.53; S, 17.58. Found: C, 58.40; H, 5.77; S, 17.77.

When the present work was in progress this thiolester was described by Charonnat and Lazelari[11] who report b.p. (15 mm.) 145°. However their sample was reported as being yellowish and, therefore, probably was not very pure.

Guaiacol benzoate was prepared by condensation of benzoyl chloride and guaiacol in the presence of pyridine. The mixture was treated with water, the product collected, and washed with alkali, acid, and water. The ester was twice recrystallized from methanol, m.p. 58–59°. Reported m.p. 57–58°.[12]

Guaiacol thiolbenzoate was prepared in a way similar to that used for guaiacol benzoate. This new compound is a colorless solid, which melts at 105.5–106.5°.

Anal. Calcd. for $C_{14}H_{12}O_2S$: C, 68.82; H, 4.95; S, 13.12. Found: C, 68.71; H, 4.99; S, 12.70.

Absorption measurements were carried out as in an earlier paper.[1c]

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(10) F. H. Mauthner, *Ber.*, **39**, 1347 (1906).
(11) R. Charonnat and I. Lazelari, *Compt. rend.*, **238**, 119 (1954).
(12) Lange's Handbook of Chemistry, 5th ed., Handbook Publishers, Inc., Sandusky, Ohio, 1944.

On Darling's Cyclopropene Derivative and Its Rearrangement[1]

RONALD BRESLOW, RUDOLPH WINTER, AND MERLE BATTISTE

Received July 28, 1958

Few authentic cyclopropene derivatives are known, and the erroneous attribution of cyclopropene structures to some substances, such as Feist's acid,[2] seems to have led to a general distrust of all cyclopropene assignments in the earlier literature. We wish to report that the 1,2-diphenylcyclopropene-3,3-dicarboxylic acid structure (I)

assigned by Darling[3] to a compound obtained by him from vigorous alkaline treatment of a nitrocyclopropane compound is indeed correct, and that the substance is a member of a group of rather stable derivatives of the strained cyclopropene molecule.

We have prepared Darling's compound by an alternate route, utilizing the reaction of diphenylacetylene with diazomalonic ester. After hydrolysis, an acid was obtained which melted at 205° (dec.) [Darling reports[3] "about 190° (dec.)"]. As confirmation of the identity of the two substances we have prepared the dimethyl ester, m.p. 143–143.5° (reported[3] 140–142°), and its dibromide, m.p. 197–198° (reported[3] 194–195°). In addition, we find that the lactone from thermal decomposition of the acid has m.p. 149–151° (reported[3] 149–151°).
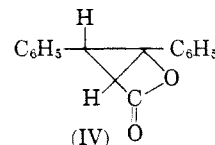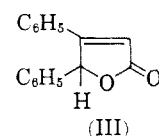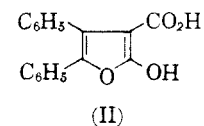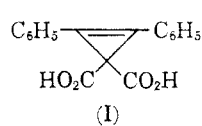
One of the key bits of evidence offered by Darling for the cyclopropene structure was the formation of dibenzoylmethane on oxidation, which we have confirmed. Although this would seem to leave no room for doubt, more or less reasonable arguments, which will not be detailed here, can be made for the possibility of structure II. This, apparently the only alternative to Darling's structure, is however in poor agreement with some of the experimental facts and is completely ruled out by our finding that the corresponding Δ^1-1,2-diphenylcyclopropene monocarboxylic acid, m.p. 209.5–211.5° (dec.), prepared from reaction of diazoacetic ester and diphenylacetylene, followed by alkaline hydrolysis, has an ultraviolet spectrum which is virtually identical with that of the dicarboxylic acid; the two compounds thus have similar structures. On the alternative basis its structure would have to be that of III or a tautomer, which is of course a neutral lactone.

We have prepared[4] III and find that it is in fact identical with the neutral lactone, m.p. 149–151°, which results from pyrolysis of the cyclopropene diacid. Darling had rejected this structure in favor of IV on the basis that the hydrolysis product was not an olefin, but it is known[5] that in base III is hydrolyzed to desylacetic acid.

The diphenylcrotonolactone III is also formed on pyrolysis of the cyclopropene monocarboxylic acid; these rearrangements are readily formulated

(3) S. F. Darling and E. W. Spanagel, *J. Am. Chem. Soc.*, **53**, 1117 (1931).
(4) J. Thiele and F. Straus, *Ann.*, **319**, 155 (1901).
(5) J. Thiele, *Ann.*, **306**, 194 (1899).