

[CONTRIBUTION FROM KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE UNIVERSITY]

Ultraviolet Absorption Spectra of 3-Arylthianaphthenes^{1,2}ROBERT D. SCHUETZ AND LEON CIPORIN³

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The ultraviolet absorption curves of six 3-arylthianaphthenes have been determined and interpreted according to a theory of steric hindrance to free rotation about the pivot bond of the two aromatic rings.

In a previous communication from this laboratory,⁴ the preparation of a series of 3-arylthianaphthenes was recorded. The purpose of the work described here was to determine the extent to which rotation was restricted about the pivot bond in 3-arylthianaphthenes by an examination of their ultraviolet absorption spectra.

The initial investigation of the effect of restricted rotation in biphenyl compounds on the ultraviolet absorption spectra of such substances was made by Pickett, Walter, and France.⁵ Since then, other investigators⁶ have determined the absorption spectra of biaromatic compounds exhibiting restricted rotation and similar studies have been extended to biaromatic compounds containing heterocyclic nuclei.⁷ These studies have shown that a biaromatic compound exhibits a more intense ultraviolet absorption at longer wave lengths than the uncoupled nucleus because coplanarity gives full extension to the conjugated system. Biaromatic derivatives substituted in the ortho positions with respect to the pivot bond should have difficulty in assuming a coplanar structure and, therefore, show absorption approximately equivalent to the single ring structure.

The 3-arylthianaphthenes for which ultraviolet absorption curves were determined in this investigation are listed in Table I together with the wave length and molar absorptivity of their absorption maxima. The curves of the compounds studied

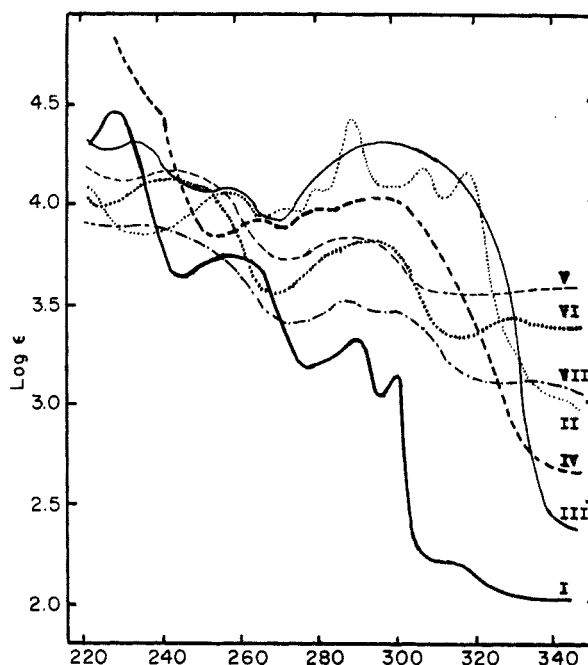


FIG. 1. ULTRAVIOLET ABSORPTION SPECTRA OF 3-ARYLTHIANAPHTHENES. I, Thianaphthene; II, 3,3'-Dithianaphthyl; III, 3-Phenylthianaphthene; IV, 3-(1'-Naphthyl)thianaphthene; V, 5-Chloro-3-(2'-thienyl)-2-thianaphthenecarboxylic Acid; VI, 5-Chloro-3-phenyl-2-thianaphthenecarboxylic Acid; VII, 5-Chloro-3-(*o*-carboxyphenyl)-2-thianaphthenecarboxylic Acid.

have been graphed in Fig. 1. The logarithms of the molar absorptivity has been used to permit inclusion of all the absorption curves on the same scale.

Before proceeding with a discussion of these absorption spectra, it is necessary to assess the effect of the chlorine and carboxyl groups in the 5-chloro-3-aryl-2-thianaphthenecarboxylic acids (V, VI, VII) on the ultraviolet absorption curves of these compounds. This information is needed in order to make an interpretive comparison with the absorption spectra of the 3-arylthianaphthenes containing neither a carboxyl or halogen substituent. With regard to the chlorine substituent, it has been shown^{6b} that chlorine exhibits negligible resonance interaction with the aromatic ring in chlorobenzene. Padhye and Desai⁸ have compared the absorption spectrum of 5-chlorothianaphthene

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(4) R. D. Schuetz and L. Ciporin, *J. Org. Chem.*, **23**, 206 (1958).


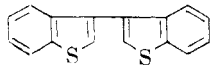
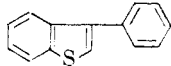
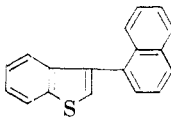
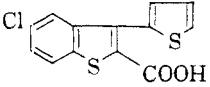
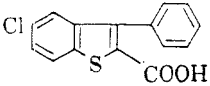
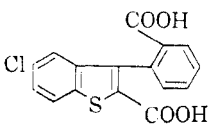
(5) L. W. Pickett, G. F. Walter, and H. France, *J. Am. Chem. Soc.*, **58**, 2296 (1936).

(6) (a) M. Calvin, *J. Org. Chem.*, **4**, 256 (1939). (b) M. T. O'Shaughnessy and W. H. Rodebush, *J. Am. Chem. Soc.*, **62**, 2906 (1940). (c) B. Williamson and W. H. Rodebush, *J. Am. Chem. Soc.*, **63**, 3018 (1941). (d) D. W. Sherwood and M. Calvin, *J. Am. Chem. Soc.*, **64**, 1350 (1942). (e) L. W. Pickett, M. Groth, S. Duckworth, and J. Cunliffe, *J. Am. Chem. Soc.*, **72**, 44 (1950).

(7) (a) A. Crawford and I. F. B. Smyth, *J. Chem. Soc.*, 4133 (1952). (b) G. N. Jean and F. F. Nord, *J. Org. Chem.*, **20**, 1370 (1955).

(8) M. R. Padhye and S. R. Desai, *Trans. Faraday Soc.*, **49**, 1386 (1953).

TABLE I

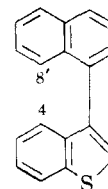
COMPOUND	λ_{\max} M μ	$\epsilon \times 10^{-3}$	Max, M μ	$\epsilon \times 10^{-3}$
I 	227	28.4		
II 	256	12.5	288	27.8
III 	233	21.2	297	22.4
IV 	225	76.5	295	10.9
V 	239	14.6	288	7.1
VI 	236	13.1	294	7.0
VII 	236	7.7	286	3.3

with that of thianaphthene (I). Their results show that the absorption spectra of these compounds are quite similar and that, therefore, chlorine must interact with the thianaphthene (I) nucleus only to a minor degree.

On the other hand, the carboxyl function, due to the double bond character in its structure, can interact with the aromatic ring and extend the resonance of the aromatic structure. The ortho or para carboxyl function shifts the characteristic absorption maximum of biphenyl to longer wave lengths and enhances its absorption intensity.^{6b} The same effect should be operative in a 2-thianaphthenecarboxylic acid. The absorption spectra of several 2-thianaphthyl ketones have been shown to have enhanced absorption intensities.⁹ It is reasonable to assume that the carbonyl group of the ketone and carboxylic acid will affect absorption spectra in a similar manner.

The absorption curve (curve I) for thianaphthene (I) has the fine structure which is characteristic of an unsubstituted aromatic compound. When the conjugated system is extended by substitution of a phenyl group in the 3-position of the thianaphthene nucleus, there is an increase in absorption intensity and a smoothing out of the fine structure (curve III). The same phenomenon is observed in the spectrum of biphenyl as compared to benzene.⁵ However, 3-(1'-naphthyl)-

thianaphthene (IV) (curve IV) has a considerably lower absorption intensity than 3-phenylthianaphthene (III) (curve III). If steric hindrance were not operative, and thus were not preventing coplanarity of the naphthyl and thianaphthyl parts of the molecule, the naphthyl group would be expected to extend the total resonating system by a larger factor than a phenyl group and, as a result, enhance the absorption intensity to a greater degree. The reduction in absorption intensity can be attributed to the hindrance to free rotation about the pivot bond imposed by the hydrogen atoms in the 4- and 8'-positions, thus inhibiting coplanarity of the naphthyl and thianaphthyl groups with a resulting loss in resonance.



Inspection of the absorption spectra of 5-chloro-3-(2'-thienyl)-2-thianaphthenecarboxylic acid (V) (curve V) and 5-chloro-3-phenyl-2-thianaphthenecarboxylic acid (VI) (curve VI) reveal a very close similarity. The isoelectronic relationship between benzene and thiophene would predict such a similarity in the spectra of these compounds. Both absorption curves show a re-

(9) P. Ramart-Lucas and M. Martynoff, *Compt. rend.*, 2247 (1953).

duced intensity compared to those compounds which are not substituted in the 2-position with respect to the pivot bond. This undoubtedly is a result of the steric inhibition to free rotation supplied by the carboxyl group which prevents coplanarity of the thienyl or phenyl group with the thianaphthyl group thereby reducing the resonance of the systems. As previously noted, the carboxyl group tends to enhance absorption due to its interaction with the aromatic ring. That the opposite occurs is a further indication that the carboxyl group is sterically inhibiting full resonance in these structures.

When a second carboxyl group is placed adjacent to the pivot bond, as in 5-chloro-3-(*o*-carboxyphenyl)-2-thianaphthenecarboxylic acid VII (curve VII), the absorption maximum almost disappears. Thus, resonance through the pivot bond appears to be virtually nonexistent due to the lack of coplanarity of the thianaphthyl and phenyl groups; such coplanarity being prevented by steric hindrance of the two carboxyl groups.

The absorption spectrum of 3,3'-dithianaphthyl (II) (curve II) is somewhat more difficult to fully explain in that while there is an increase in the absorption intensity as compared to that of thianaphthene (I) (curve I) the fine structure of the thianaphthene (I) (curve I) has been retained. However, the many-fold increase of intensity in the 290 $m\mu$ region of the dimer compound II (curve II) strongly suggests that a very considerable resonance exists between the two halves of 3,3'-dithianaphthyl (II) (curve II). Except for the fine structure of 3,3'-dithianaphthyl (II) (curve II) it is closely comparable to that of the naphthalene (IV) (curve IV) and the phenyl (III) (curve III) analogs. In fact, the main envelope of

the absorption curve for 3,3'-dithianaphthyl (II) (curve II) corresponds more closely to the phenyl analog (III) (curve III) than to the naphthalene analog (IV) (curve IV) which indicates that the two thianaphthyl rings interfere less with each other in being coplanar than do the two naphthalene rings in 1,1'-binaphthyl.

In conclusion, it can be stated, with a reasonable degree of certainty, that 5-chloro-3-(*o*-carboxyphenyl)-2-thianaphthenecarboxylic acid (VII) and very probably 3,3'-dithianaphthyl (II) exist in a noncoplanar structure and should therefore be capable of optical resolution. However, it is not to be inferred that evidence for noncoplanarity is sufficient by itself for predicting the possibility of resolution in compounds where optical activity is due to restricted rotation.

EXPERIMENTAL

The ultraviolet absorption spectra were determined employing a Beckman Model DU Spectrophotometer equipped with equally matched, one-centimeter, fused quartz cells. The solvent used in every case was Eastman Kodak c.p. grade cyclohexane which was further purified by passage through a column of silica gel. The matching of the quartz cells was frequently checked by comparing readings taken with cyclohexane alone in the cells.

The solutions were prepared by the volume dilution method and were all of the order of $10^{-5}M$. The procedure used in preparing the solutions was as follows. A sample of 2×10^{-5} mole was accurately weighed out on an analytical balance and dissolved in 100 ml. of cyclohexane measured in a calibrated volumetric flask. A 5-ml. aliquot of this solution was then diluted to 100 ml. in a calibrated volumetric flask. An aliquot of the latter solution was transferred to a quartz cell.

Absorbance readings were taken over a range of wave lengths from 220 to 340 $m\mu$. The values for the absorbance readings were converted to molar absorptivity by means of the equation,

$$\epsilon = \frac{A}{bc}$$

where ϵ is the molar absorptivity, A is the absorbance, c is the concentration of the light absorbing species in moles per liter, and b is the length in centimeters of the light path in the absorbing solution. Values for the logarithms of the molar absorptivity were then tabulated.

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