[CONTRIBUTION FROM THE CHEMISTRY LABORATORY, UNIVERSITY OF CINCINNATI AND THE CANCER RESEARCH LABORATORY, UNIVERSITY OF FLORIDA]

PREPARATION AND ABSORPTION SPECTRA OF 1,2- AND 2,3-DISUBSTITUTED DIBENZOTHIOPHENE DERIVATIVES[1]

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In a continuation of a study of the chemical, physical, and biological properties of carcinogenic amines and allied compounds the preparation and spectral properties of some new dibenzothiophene derivatives were investigated. In previous papers (1, 2) the structures of new dibenzoselenophene derivatives were proven by comparison of their spectra with the spectra of analogous iso-*pi*-electronic dibenzothiophene derivatives. Similarly the structures of new 3,4-disubstituted dibenzothiophene derivatives were proven by spectral comparison with iso-*pi*-electronic carbazole derivatives (3). The proof of structure in these papers and the present paper is based on the principle that analogous derivatives of iso-*pi*-electronic molecules are also iso-*pi*-electronic, and consequently spectrally similar. For example, carbazole and dibenzothiophene are iso-*pi*-electronic and spectrally similar (3). Consequently, the iso-*pi*-electronic 3-nitrocarbazole and 2-nitrodibenzothiophene are also spectrally similar (3).

The nitration of 2-carbethoxyaminodibenzothiophene followed by deacylation, reduction, and reaction with selenium dioxide gave a yellow glistening compound. This derivative formed a dark blue-purple solution in concentrated sulfuric acid; it had a typical high intensity, low energy piaselenole band (4) at λ_{max} 373, Fig. 1. From these facts and the analyses it is evident that the compound is a piaselenole. Reduction of the nitro-2-aminodibenzothiophene in acetic acid gave an imidazole, the spectrum of which is shown in Fig. 2, Curve I. Thus, the nitration of 2-carbethoxyaminodibenzothiophene must have taken place in either the 1- or 3- position. The spectrum of nitro-2-carbethoxyaminodibenzothiophene apparently shows a strong steric effect, Fig. 3. This would seem to indicate that the nitro group is in the hindered 1-position. In Fig. 4 the spectra of nitro-2-aminodibenzothiophene and 3-amino-4-nitro-9-methylcarbazole (5) are compared. The remarkable resemblance between the two spectra is self-evident. This is further evidence that the nitro group is in the 1-position. The two nitroamines show a typical moderate intensity band in the visible spectral region characteristic of *ortho* aromatic nitroamines (4). 1-Nitro-2-aminodibenzothiophene has its nitroamine band at 446 mμ, log ϵ 3.45; 4-nitro-3-amino-9-methylcarbazole has its band at 481 mμ, log ϵ 3.66. The other bands in these compounds are characteristic of a 2-nitrobiphenyl type compound. This is shown in Fig. 5 where the spectrum of 2-amino-1-nitrodibenzothiophene in 2 *N* hydrochloric acid is, as to be expected, similar to the spectrum of 2-nitrobiphenyl (6).

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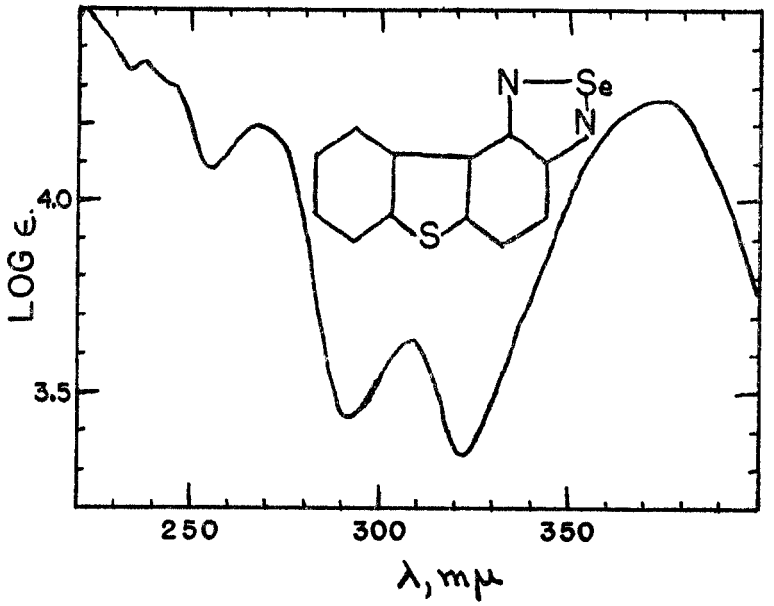

FIG. 1. THIANAPHTHENO[3,2-*e*]PIASELENOLE

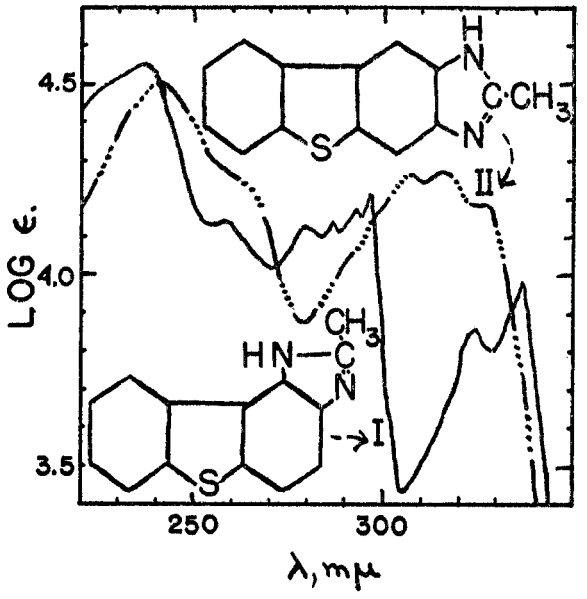

FIG. 2. I, 2-METHYL-1-THIANAPHTHENO[3,2-*e*]BENZIMIDAZOLE; II, 2-METHYL-1-THIANAPHTHENO[2,3-*f*]BENZIMIDAZOLE.

All these facts are strong evidence that the nitration of 2-carbethoxyaminodibenzothiophene takes place in the 1-position.

The nitration of 2-benzenesulfonylaminodibenzothiophene gives a mononitro compound. When this compound was hydrolyzed and then reduced in acetic

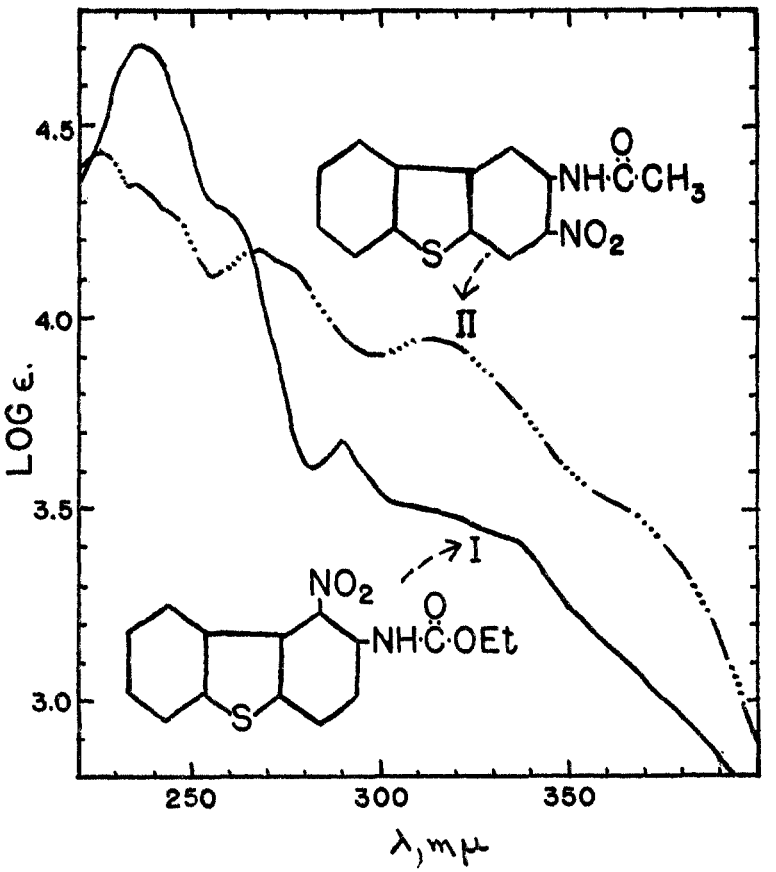

FIG. 3. I, 1-NITRO-2-CARBETHOXYAMINODIBENZOTHIOPHENE; II, 2-ACETYLAMINO-3-NITRODIBENZOTHIOPHENE.

acid, an imidazole was formed. The spectrum of this imidazole is entirely different from the spectrum of the imidazole derived from 1-nitro-2-aminodibenzothiophene, Fig. 2. The spectrum of the new nitro-2-acetylaminodibenzothiophene is different from the spectrum of 1-nitro-2-carbethoxyaminodibenzothiophene, Fig. 3. On the basis of this evidence one could say that the nitration of 2-benzenesulfonylaminodibenzothiophene takes place in the 3-position. If this is so, then the derived 2-amino-3-nitrodibenzothiophene should have a spectrum similar to the spectrum of iso-*pi*-electronic 3-amino-2-nitrocarbazole (7) and entirely different from the spectra of 2-amino-1-nitrodibenzothiophene and 3-amino-4-nitro-9-methylcarbazole, Fig. 4. This is definitely shown to be so in Fig. 6. In these nitroamines the typical moderate intensity band in the visible region characteristic of *ortho* aromatic nitroamines is very evident. For example, 2-amino-3-nitrodibenzothiophene has its band at 468 mμ, log ε 3.54, while 3-amino-2-nitrocarbazole has its band at 502 mμ, log ε 3.50.

By protonization the *ortho* nitroamine band in 2-amino-3-nitrodibenzothiophene is destroyed and the spectrum of the salt is, as to be expected, similar to

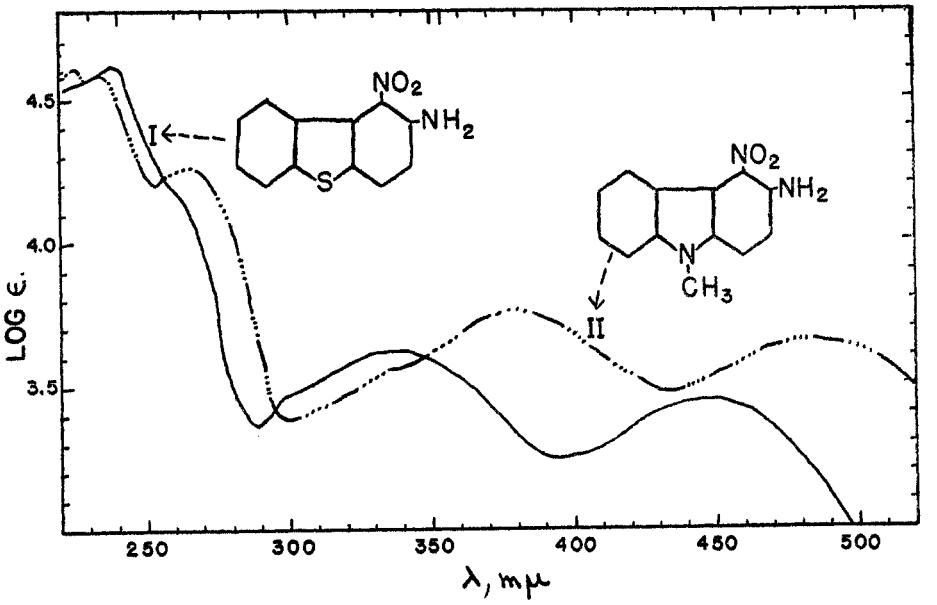

FIG. 4. I, 1-NITRO-2-AMINODIBENZOTHIOPHENE; II, 3-AMINO-4-NITRO-9-METHYLCARBAZOLE.

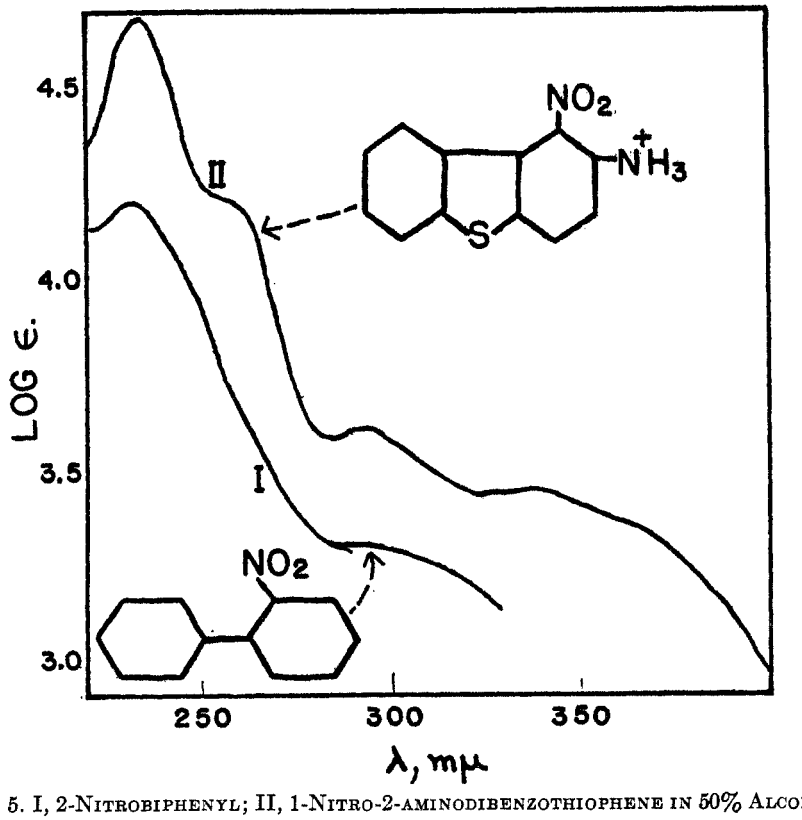

FIG. 5. I, 2-NITROBIPHENYL; II, 1-NITRO-2-AMINODIBENZOTHIOPHENE IN 50% ALCOHOLIC 2 *N* HYDROCHLORIC ACID.

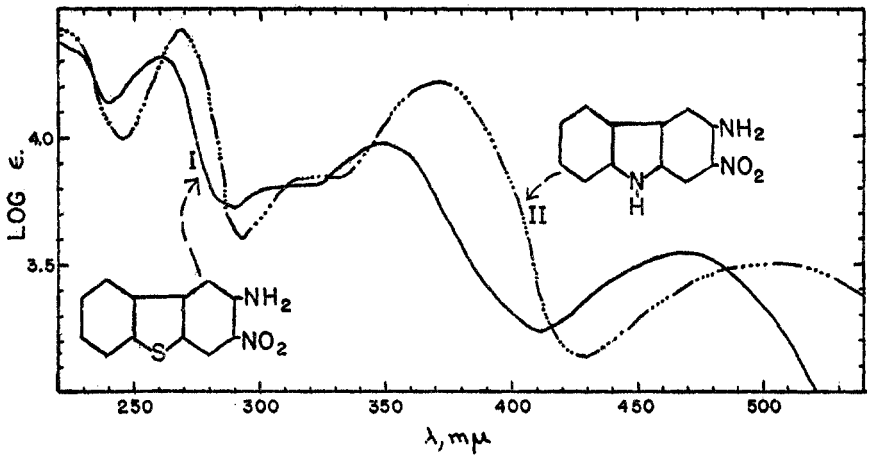

FIG. 6. I, 2-AMINO-3-NITRODIBENZOTHIOPHENE; II, 2-NITRO-3-AMINOCARBAZOLE

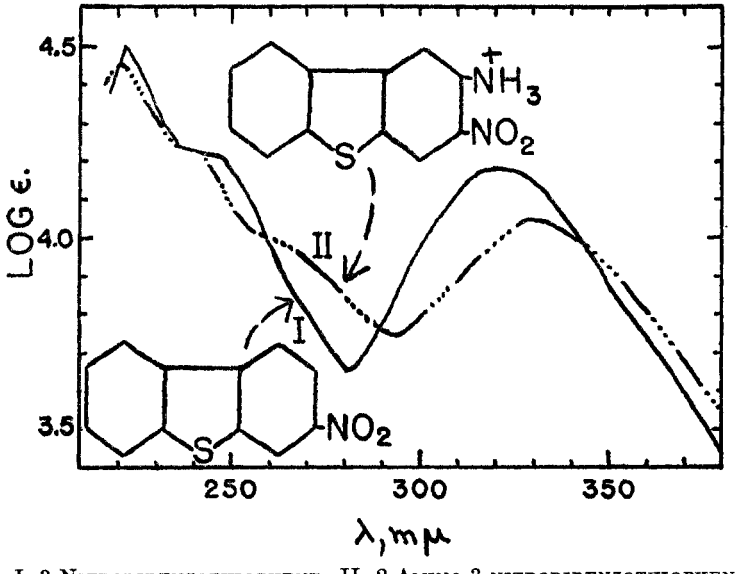

FIG. 7. I, 3-NITRODIBENZOTHIOPHENE; II, 2-AMINO-3-NITRODIBENZOTHIOPHENE IN 50% ALCOHOLIC 8 *N* SULFURIC ACID.

the spectrum of 3-nitrodibenzothiophene, Fig. 7, and dissimilar from the spectrum of 2-amino-1-nitrodibenzothiophene hydrochloride, Fig. 5.

From all this evidence it can be concluded that the nitration of 2-carbethoxyaminodibenzothiophene takes place in the 1-position while the nitration of 2-benzenesulfonylaminodibenzothiophene takes place in the 3-position.

EXPERIMENTAL[3]

1-Nitro-2-carbethoxyaminodibenzothiophene. To a stirred suspension of 19.9 g. of N-2-dibenzothienyl urethan (1) in 400 ml. of acetic acid at room temperature was added 15 ml.

[3] All melting points are uncorrected.

of fuming nitric acid (*d.* 1.5). After a few ml. of the acid had been added, the suspension dissolved. Further addition of nitric acid caused the heavy precipitation of yellow crystals. The filtered dry product melted at 185–189°. Crystallization from heptane or aqueous acetic acid gave 13–14 g. (56–60%) of long yellow needles, m.p. 189–190°.

Anal. Calc'd for $C_{15}H_{12}N_2O_4S$: C, 56.96; H, 3.80; N, 8.86.
Found: C, 57.04; H, 3.70; N, 8.74.

1-Nitro-2-aminodibenzothiophene. Fifty ml. of 15% aqueous sodium hydroxide was added to a hot solution of 5 g. of 1-nitro-2-carbethoxyaminodibenzothiophene in 100 ml. of Methyl Cellosolve.[4] The mixture was refluxed for 1–2 hours and then poured into excess water. The bright orange precipitate was crystallized from chlorobenzene to give 0.35 g. (90%) of bright red plates, m.p. 165–166°.

Anal. Calc'd for $C_{12}H_8N_2O_2S$: N, 11.5. Found: N, 11.4.

1,2-Diaminodibenzothiophene. Hydrogen chloride gas was passed through a hot suspension of 0.4 g. of 1-nitro-2-aminodibenzothiophene and 2.0 g. of hydrated stannous chloride in 8 ml. of Methyl Cellosolve until the red crystals had disappeared and were replaced by yellowish microcrystals. The cool mixture was filtered with the aid of a filter stick. The residue was stirred with 10 ml. of 10% aqueous sodium hydroxide and filtered again. Crystallization of the residue from aqueous methanol and then heptane gave 0.29 g. (80%) of colorless crystals, m.p. 99–100° dec.

Anal. Calc'd for $C_{12}H_{10}N_2S$: N, 13.1. Found: N, 13.0.

2-Methyl-1-thianaphtheno[3,2-e]benzimidazole. Hydrated stannous chloride (6 g.) in 15 ml. of concentrated hydrochloric acid was added to a hot solution of 1.2 g. of 1-nitro-2-aminodibenzothiophene in 30 ml. of acetic acid. The mixture was refluxed for half an hour, cooled, and filtered. The yellowish precipitate suspended in water was made alkaline, filtered, and dissolved in the minimum volume of alcohol. Hydrogen chloride was passed into this solution. The imidazole hydrochloride was precipitated out in microcrystals. The hydrochloride was suspended in water and the mixture was made alkaline. The precipitate was crystallized out of aqueous Methyl Cellosolve to give 0.95 g. (82%) of colorless crystals, m.p. 263–264°.

Anal. Calc'd for $C_{14}H_{10}N_2S$: C, 70.6; H, 4.20; N, 11.8.
Found: C, 70.8; H, 4.01; N, 12.1.

Thianaphtheno[3,2-e]piaselenole. To a hot solution of 0.21 g. of 1,2-diaminodibenzothiophene in 10 ml. of ethanol was added 0.12 g. of powdered selenium dioxide. A yellow precipitate was immediately formed. Excess water was added to the mixture. The crude product was crystallized from Methyl Cellosolve to give 0.26 g. (92%) of yellow glistening crystals, m.p. 176–177°.

Anal. Calc'd for $C_{12}H_6N_2SSe$: N, 9.69. Found: N, 9.54.

2-Benzenesulfonylamino-3-nitrodibenzothiophene. Fuming nitric acid (*d.* 1.5) (1.5 ml.) was added dropwise to a suspension of 2 g. of 2-benzenesulfonylaminodibenzothiophene (8) in 55 ml. of acetic acid at room temperature. The temperature was kept between 23–33°. The mixture was allowed to stand at room temperature for 3 hours. The crystalline precipitate was crystallized from chlorobenzene to give 1.7 g. (75%) of yellow crystals, m.p. 212°.

Anal. Calc'd for $C_{18}H_{12}N_2O_4S_2$: N, 7.29; S, 16.7.
Found: N, 7.17; S, 16.6.

2-Amino-3-nitrodibenzothiophene. 2-Benzenesulfonylamino-3-nitrodibenzothiophene (20 g.) was dissolved in 80 ml. of concentrated sulfuric acid and was allowed to stand 4–5 hours at room temperature. The solution was poured into about 800 g. of cracked ice. The red-orange precipitate was collected on a Buchner funnel, washed with dilute sodium hydroxide solution, and then with water. There was obtained 16.5 g. of crude product melting at 183–190°. The crude product was suspended in several hundred ml. of pyridine, boiled with charcoal, and filtered. (A large amount of the product was insoluble in pyridine. This was probably sulfonated product.) Excess water was added to the hot filtrate and the

[4] 2-Methoxyethanol.

mixture was allowed to cool. Approximately 2.4 g. (19%) of red microcrystals were obtained, m.p. 246–247°. No attempt was made to improve on the yield.

Anal. Calc'd for $C_{12}H_8N_2O_2S$: N, 11.5. Found: N, 11.6.

2-Methyl-1-thianaphtheno[2,3-f]benzimidazole. A solution of 3 g. of hydrated stannous chloride in 10 ml. of concentrated hydrochloric acid was added to a suspension of 0.6 g. of 2-amino-3-nitrodibenzothiophene in 15 ml. of hot acetic acid. The mixture was refluxed for half an hour. The precipitate was suspended in water and made alkaline with dilute sodium hydroxide solution. Crystallization from aqueous alcohol gave 0.41 g. (70%) of colorless crystals, m.p. 277–278° dec.

Anal. Calc'd for $C_{14}H_{10}N_2S$: C, 70.6; H, 4.20; N, 11.8.
Found: C, 70.8; H, 4.08; N, 11.4.

2-Acetylamino-3-nitrodibenzothiophene. A drop of concentrated sulfuric acid was added to a fine suspension of 0.2 g. of 2-amino-3-nitrodibenzothiophene in 5 ml. of acetic anhydride at room temperature. After standing for 3 hours at room temperature, the red crystals had changed into a yellow powder. Crystallization from acetic acid gave an 85–90% yield of yellow crystals, m.p. 267–268°.

Anal. Calc'd for $C_{14}H_{10}N_2O_3S$: N, 9.79. Found: N, 9.50.

Ultraviolet and visible absorption spectra. All spectra were determined on a Beckman Model DU Spectrophotometer in 95% ethanol unless otherwise stated.

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SUMMARY

The synthesis and ultraviolet absorption spectra of several 1,2- and 2,3-disubstituted dibenzothiophene derivatives has been described. The proof of structure of the new derivatives was based on their spectral similarity to iso-*pi*-electronic carbazole and dibenzothiophene derivatives.

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