was evaporated and the residue was chromatographed on neutral alumina (30 g) and eluted with PE (200 ml), PE–B 17:3, 8:2, 5:5 (150 ml each), and B (500 ml). Evaporation of the fractions gave the results shown in Table I.

**Registry No.**—**1,** 4121-35-1; acetic anhydride, 108-24-7; **2,** 16101-29-4; **3a,** 16101-30-7; **3b,** 16101-31-8; **4a,** 16101-32-9; **4b,** 16101-33-0.

**Acknowledgment.**—We are indebted to the Arts and Sciences Research Committee of the American University of Beirut for financial support. We are grateful to Professor Costas H. Issidorides for his advice and encouragement. We thank Professors E. P. Papadopoulos and W. T. Smith for the nmr spectra, and Dr. Jean Märki of Varian AG, Zürich, for the nmr decoupling experiments.

## Synthesis and Properties of 1H-Naphtho[2,1-*b*]thiete 2,2-Dioxide[1,2]

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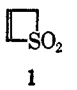
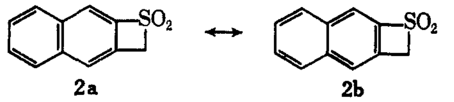
In recent years, the chemistry of thiete 1,1-dioxide (**1**) and its derivatives has been given considerable attention. In earlier papers of this series, we described the preparation of fused aromatic derivatives of **1** in which the double bond of the four-membered sulfur-containing ring was incorporated into the delocalized $\pi$ cloud of naphthalene.[4,5] Our interest in such molecules has been associated with the question of whether the steric strain imposed by the heterocyclic ring would cause measurable double-bond fixation in the naphthalene system. Previous results[4a] have indicated that the fusion of a thiete dioxide to the 2,3 bond of naphthalene as in **2** does not significantly alter the ground or excited state properties of the aromatic moiety.

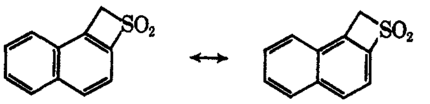


**1**



**2a** **2b**

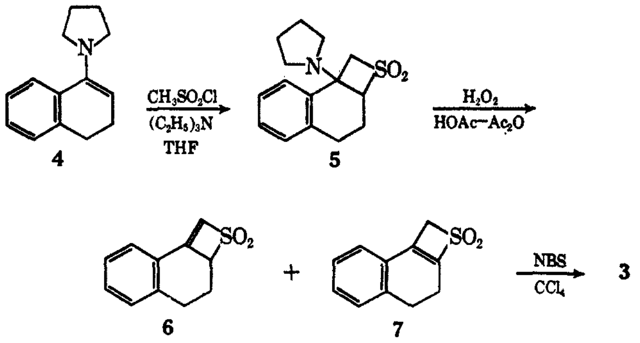
Because the $\alpha,\beta$ bonds of naphthalene are known to possess greater double bond character than the $\beta,\beta$ bonds,[6] the possibility that fusion of a thiete dioxide ring to the 1,2 bond of naphthalene might result in bond fixation was considered. For this reason, it was deemed of interest to prepare **3**; in this paper the synthesis and physical properties of this molecule are described.



**3a** **3b**

The reaction of 1-(3,4-dihydro-1-naphthyl)pyrrolidine (**4**) with methanesulfonyl chloride and triethylamine in dry tetrahydrofuran afforded, in 58% yield, colorless crystals of the thietane dioxide **5**. The structure of **5** follows from its spectral parameters (see Experimental Section) and from the well-precedented course of sulfene–enamine cycloaddition reactions.[7] In the presence of an acetic acid–acetic anhydride solution of hydrogen peroxide, **5** was converted in 91% yield into a mixture consisting of thiete dioxides **6** and **7** (ratio *ca.* 1.5:1, nmr analyses, See Scheme I). Equilibration of this mixture with powdered potassium hydroxide in tetrahydrofuran gave a solid that was enriched in **7** (ratio *ca.* 1:3). Further attempts at equilibration did not alter this ratio. The question of apparent equilibrium composition[8] is interesting. The results indicate the endocyclic isomer to be more stable in agreement with the Brown–Brewster–Shechter rule.[9] Whether this preference can be attributed to eclipsing interactions, or to angle strain effects, or to a combination of these factors,[10] remains an open question.

SCHEME I



Bromination of either the equilibrated or nonequilibrated mixture with N-bromosuccinimide in carbon tetrachloride solution led to the evolution of hydrogen bromide and the formation of **3** in 50–60% yield. The nmr spectrum of **3** displayed a singlet at $\delta$ 5.50 due to the $\alpha$-sulfonyl protons and a complex six-proton multiplet in the 7.42–8.18 region (aromatic hydrogens). No abnormal chemical shifts are seen; furthermore, the great degree of similarity in the ultraviolet spectra of **3**, **2**, and methyl 2-naphthyl sulfone (**8**) (see Table I) indicates that the naphthalene ring is not unusually affected by the nature of the ring fusion found in **3**.

The mass spectrum of **3** has a molecular ion at *m/e* 204 and a base peak at *m/e* 139, corresponding to an ion formed by the expulsion of a hydrogen and sulfur

[1] Paper XXXVIII of the series entitled "Unsaturated Heterocyclic Systems;" for previous paper, see L. A. Paquette, *Tetrahedron Lett.*, in press.

[2] The authors are grateful to the National Science Foundation for Grant GP-5977 which contributed to the financial support of this research.

[3] Fellow of the Alfred P. Sloan Foundation, 1965–1967.

[4] (a) L. A. Paquette, *J. Org. Chem.*, **30**, 629 (1965); (b) L. A. Paquette and T. R. Phillips, *ibid.*, **30**, 3883 (1965).

[5] In an independent study, D. C. Dittmer and N. Takashina [*Tetrahedron Lett.*, 3809 (1964)] reported the synthesis of the 3,8-diphenyl derivative of **2**.

[6] L. F. Fieser and M. Fieser, "Advanced Organic Chemistry," Reinhold Publishing Corp., New York, N. Y., 1961, p 880.

[7] For a summary of this rather extensive literature, see (a) L. A. Paquette and M. Rosen, *J. Amer. Chem. Soc.*, **89**, 4102 (1967); (b) G. Opitz, *Angew. Chem. Intern. Ed., Engl.*, **6**, 107 (1967); (c) T. J. Wallace, *Quart. Rev.* (London), **20**, 67 (1966).

[8] Owing to the fact that **7** could not be isolated in pure form, the equilibrium could not be approached from both directions However, the same result was obtained in a duplicate run.

[9] H. C. Brown, J. H. Brewster, and H. Shechter, *J. Amer. Chem. Soc.*, **76**, 467 (1954).

[10] A. Schriesheim, R. J. Muller, and C. A. Rowe, Jr., *ibid.*, **84**, 3164 (1962).

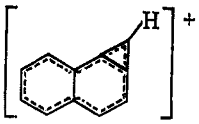
TABLE I

COMPARISON OF THE ULTRAVIOLET SPECTRA OF **2**, **3**, AND METHYL 2-NAPHTHYL SULFONE (**8**)

| **3**<br>$\lambda_{max}^{EtOH}$, mμ (ε) | **2**<br>$\lambda_{max}^{EtOH}$, mμ (ε) | **8**<br>$\lambda_{max}^{EtOH}$, mμ (ε) |
|---|---|---|
| 323 (1,200) | 327 (1,550) | 323 (1,380) |
| 315 (620) | 319 (sh) (1,110) | *a* |
| 308 (800) | 313 (1,640) | 311 (1,000) |
| 290 (2,670) | 294 (4,240) | . . . |
| 279 (3,730) | 289 (4,440) | . . . |
| 272 (3,470) | 284 (4,630) | 277 (4,470) |
| 263 (2,670) | 272.5 (sh) (5,470) | . . . |
| 230 (63,300) | 233 (69,000) | 229 (85,000) |
| | 214 (sh) (30,600) | . . . |

[a] Inflections in the curve were not reported, but are obvious in the published spectrum: V. A. Koptyug and V. A. Plakhov, *Russ. J. Phys. Chem., Engl. Transl.* **35**, 434 (1961).

dioxide. This ion is very likely the derived naphthocyclopropenium cation **9**.[11]



**9**

In conclusion, it should be noted that the spectroscopic methods employed herein are capable of detecting only complete bond fixation[12] and do not provide information concerning the "degree" of bond fixation. In fact, it appears that magnetically induced ring currents and electronic absorption spectra are reasonably nonresponsive to severe geometric distortion. In this regard, comparison of the ultraviolet and nmr spectra of indane, benzocyclobutene,[13] and benzocyclopropene[14] indicates many similarities despite a difference in strain of approximately 50 kcal/mol. Decidedly, therefore, the strain in **3** is not sufficiently great to give rise to the type of restricted bond alternation found in 1,2-diphenylnaphtho[*b*]cyclobutadiene.[15]

### Experimental Section

Melting points were determined with a Thomas-Hoover melting point apparatus and are corrected. Infrared spectra were recorded with a Perkin-Elmer Infracord Model 137 spectrometer fitted with sodium chloride prisms. Ultraviolet spectra were determined with a Cary 14 recording spectrometer. Nuclear magnetic resonance spectra were obtained with a Varian A-60 spectrometer purchased with funds made available through the National Science Foundation. The mass spectrum was measured with an AEI MS-9 mass spectrometer at an ionizing energy of 70 eV. The microanalyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark.

**1-(3,4-Dihydro-1-naphthyl)pyrrolidine (4).**—A solution of 20.0 g (0.137 mol) of α-tetralone, 10.5 g (0.148 mol) of pyrrolidine, and 0.2 g of *p*-toluenesulfonic acid in 250 ml of toluene was refluxed under a Dean–Stark trap in a nitrogen atmosphere for 24 hr. Approximately 2.5 ml of water was collected in the trap and the reaction mixture turned yellow. The solution was cooled and concentrated *in vacuo*. The residue was distilled at reduced pressure to give 15.9 g (58.2%) of **4**: bp 85–90° (0.25 mm) $n^{25}$D 1.5914; $\lambda_{max}^{CCl_4}$ 6.15 μ (–C=C—N<); $\delta_{TMS}^{CCl_4}$ 1.60–4.0 (complex pattern, 12 H, $-CH_2CH_2-$ and pyrrolidino group), 5.0 (triplet, $J$ = 5.0 Hz, 1 H, vinyl proton), and 6.85–7.42 (complex pattern, 4 H, aromatic ring protons).

**1-(3,4-Dihydro-1H-naphtho[2,1-*b*]thiet-8b(2aH)-yl)pyrrolidine S,S-Dioxide (5).**—To a cold (0°) solution of 12.6 g (0.063 mol) of **4** and 6.55 g (0.065 mol) of triethylamine in 50 ml of dry tetrahydrofuran was added dropwise with stirring a solution of 7.32 g (0.063 mol) of methanesulfonyl chloride in 50 ml of the same solvent. After stirring at room temperature for 2 hr, the precipitated triethylamine hydrochloride was filtered and washed well with tetrahydrofuran. Dissolution of the precipitated solid in water indicated that no organic product remained occluded in this material. The filtrate was evaporated under reduced pressure and the resulting oil was triturated with methanol at 0° to give 10.1 g (57.8%) of **5** as a colorless crystalline solid: mp 101–102° (methanol); $\lambda_{max}^{CHCl_3}$ 7.60, 8.09, 8.47, 8.80, and 9.00 μ ($-SO_2-$); $\delta_{TMS}^{CDCl_3}$ 1.51–1.90 (multiplet, 4 H, $-CH_2-$ of pyrrolidino group), 2.19–3.05 (complex pattern, 8 H, $-CH_2-N-$ and $-CH_2-CH_2-$), 4.07–5.05 [broad triplet (4.83, $J$ = 7.0 Hz) superimposed on the low-field portion of an AB quartet, $J$ = 15.0 Hz, 3 H, α-sulfonyl protons], and 7.17–7.42 (complex pattern, 4 H, aromatic ring protons).

*Anal.* Calcd for $C_{15}H_{19}NO_2S$: C, 64.95; H, 6.90; N, 5.05. Found: C, 64.63; H, 7.01; N, 4.65.

**N-Oxide Degradation of 5 and Equilibration of the Resulting Mixture.**—A stirred solution of 6.0 g (0.022 mol) of **5** in 13 ml of glacial acetic acid and 13 ml of acetic anhydride was treated at −10° with 5.0 g (0.044 mol) of 30% hydrogen peroxide solution. The mixture was warmed to room temperature and stirred at that temperature for 12 hr. A colorless solid was seen to crystallize from the yellow solution and on neutralization with a 25% solution of sodium hydroxide more of the same material was precipitated. The solid was filtered and washed with cold methanol and ether to afford 4.1 g (91.1%) of a mixture of thiete dioxides **6** and **7**, mp 135–155°. This material was recrystallized from methanol for analysis as a mixture, mp 142–155° (prior sintering at *ca.* 130°); $\lambda_{max}^{CHCl_3}$ 7.65, 8.42, and 8.80 μ ($-SO_2-$); $\lambda_{max}^{EtOH}$ 267 (ε 12,860); 224 (11,850), 218 (16,290), 212 (14,810), and 207 mμ (13,750); $\delta_{TMS}^{CDCl_3}$ 1.83–3.19 (complex pattern, 4 H, $-CH_2-CH_2-$), 4.40–4.90 [complex pattern (*ca.* 4.54, triplet, $J$ = 3.0 Hz, superimposed on a complex pattern), *ca.* 1.4 H, α-sulfonyl protons (except for the vinylproton)], 6.43 (singlet, *ca.* 0.6 H, vinyl proton), and 6.75–7.45 (complex pattern, 4 H, aromatic ring protons).

*Anal.* Calcd for $C_{11}H_{10}O_2S$: C, 64.05; H, 4.89; S, 15.55. Found: C, 64.08; H, 5.00; S, 15.62.

The above material (5.0 g, 0.024 mol) in 100 ml of dry tetrahydrofuran was added dropwise with stirring under nitrogen to 6.50 g (0.10 mol) of powdered potassium hydroxide. The reaction mixture became yellow in color when stirred for 8 hr at room temperature. Water (*ca.* 200 ml) was added and the mixture was extracted with chloroform. Usual work-up of the chloroform extract afforded 4.2 g (84.0%) of a light yellow solid, mp 159–161°. Recrystallization of this material from methanol gave a different mixture of thiete dioxides (**6** and **7**): mp 168–170° (slight dec); $\delta_{TMS}^{CDCl_3}$ 2.10–3.30 (complex pattern, 4 h, $-CH_2-CH_2-$); 4.52–5.02 [complex pattern (*ca.* 4.60, triplet, $J$ = 3.0 Hz, superimposed on a complex pattern), *ca.* 1.75 H, α-sulfonyl protons (except for the vinyl proton)], 6.55 (singlet, *ca.* 0.25 H, vinyl proton), and 6.85–7.60 (complex pattern, 4 H, aromatic ring protons).

**1H-Naphtho[2,1-*b*]thiete 2,2-Dioxide (3).**—A mixture of 2.0 g (9.7 mmol) of the equilibrated material (**6** and **7**), 1.74 g (9.8 mmol) of N-bromosuccinimide, and a catalytic amount of dibenzoyl peroxide in 100 ml of carbon tetrachloride was refluxed for 3 hr. A reaction was evidenced by the formation of succinimide and by the copious evolution of hydrogen bromide. The mixture was cooled and filtered, and chloroform was added to the filtrate. The solution was transferred to a separatory funnel and washed successively with water, 10% sodium bisulfite solution, and water and dried over magnesium sulfate. Evaporation of the filtrate gave an oily solid residue which afforded, upon trituration with ether, 1.1 g (55.6%) of **3**, mp 174–176°. Pure **3** was obtained from benzene–petroleum ether (60–80°): mp 188°, slight dec; $\lambda_{max}^{CHCl_3}$ 7.60, 8.34, 8.52, 8.66, and 8.90 μ ($-SO_2-$); $\delta_{TMS}^{DMSO\text{-}d_6}$ 5.50 (singlet, 2 H, α-sulfonyl protons) and 7.42–8.18 (complex pattern, 6 H, aromatic ring protons).

*Anal.* Calcd for $C_{11}H_8O_2S$: C, 64.68; H, 3.95; S, 15.70. Found: C, 64.68; H, 3.98; S, 15.39.

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(11) For comparison, see D. C. Dittmer and F. A. Davis, *J. Org. Chem.*, **32**, 3872 (1967).

(12) This point has been raised by a referee.

(13) M. P. Cava and D. R. Napier, *J. Amer. Chem. Soc.*, **80**, 2255 (1958).

(14) E. Vogel, W. Grimme, and S. Korte, *Tetrahedron Lett.*, 3625 (1965).

(15) M. P. Cava, B. Hwang, and J. P. Van Meter, *J. Amer. Chem. Soc.*, **85**, 4032 (1963).

**Registry No.**—**3**, 16205-74-6; **4**, 7007-34-3; **5**, 16205-76-8; **6**, 16205-77-9; **7**, 16205-78-0.

**Acknowledgment.**—We are indebted to Mr. James Carson for technical assistance.

## Synthesis and Proof of Structure of 2,6-Diaminobenzo[1,2-*d*:4,5-*d'*]bisthiazole

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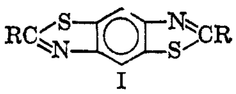
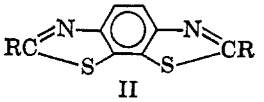
*Received December 14, 1967*

The first reported synthesis of benzo[1,2-*d*:4,5-*d'*]bisthiazoles (I) was that of Green and Perkin[1] in 1903. Since that time, several other workers[2-12] have discussed the synthesis or reactions of these compounds. In each of these cases, either no proof of structure was given, or reference was made to Green and Perkin, who base their structure on the presumed 1,2,4,5 configuration of the intermediate diaminobenzenedithiosulfonic acid. However, the latter workers made no attempt to prove the structure of this compound. Nowhere in the literature is the synthesis of any benzo[1,2-d:4,3-*d'*]bisthiazoles (II) claimed. However, we have recently found that the previously reported benzobisthiazoles are actually II rather than I. We have also found that 2,6-diaminobenzo[1,2-*d*:4,5-*d'*]bisthiazole (Ia, R = $NH_2$) may be prepared by a modified Hugershoff[13] reaction.



I



II

Compound Ia is prepared by the ring closure of *p*-phenylenebisthiourea using bromine in chloroform according to the procedure of Barnikow, *et al.*,[14] for the *meta* isomer. This is the first confirmed synthesis of a "linear" benzobisthiazole from *p*-phenylenediamine.

2,7-Diaminobenzo[1,2-*d*:4,3-*d'*]bisthiazole (IIa, R = $NH_2$), the "angular" compound, was prepared from 1,4-diaminobenzene-2,3-dithiosulfonic acid by the method of Stephens and Wibberly[6] and also by the reaction of *p*-phenylenediamine, ammonium thiocyanate, and bromine in acetic acid according to the procedure of Sureau and Alicot.[10] The products (mp > 350°) from both methods are identical. This unequivocally establishes the structure of the diaminobenzenedithiosulfonic acid prepared by Green and Perkin[1] as 1,4-diaminobenzene-2,3-dithiosulfonic acid instead of the reported 1,4-diaminobenzene-2,5-dithiosulfonic acid.

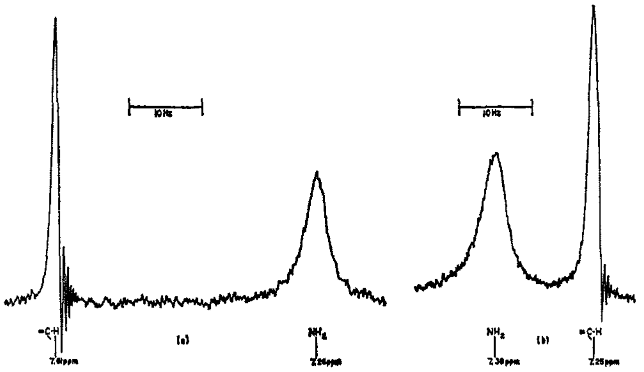


Figure 1.—(a) Normal 100-MHz nmr spectrum of compound Ia; (b) normal 100-MHz nmr spectrum of compound IIa. Sweep rate is 1 Hz/sec.

The structural assignments were made on the basis of nmr spectra. Because of the symmetry of the proposed molecular structures, both compounds Ia and IIa have a normal spectrum consisting of two absorptions only (Figure 1): a narrow line representing the aromatic protons and a relatively broad line corresponding to the amine hydrogens; the integrated intensities are in the ratio 1:2, respectively. In compound Ia, the aromatic absorption appears downfield of the amine band at 7.61 ppm ($\delta$ scale); while in IIa, the aromatic protons are shifted to 7.25 ppm and occur on the high-field side of the $NH_2$ peak. Because of the various factors contributing to electronic shielding in these closely related molecules, any assignment of structure on the sole basis of chemical shifts would be tenuous at best.

The symmetrical structures may be distinguished unambiguously, however, from the $C^{13}$ satellite spectra. When one aromatic hydrogen is bonded to a $C^{13}$ atom, the magnetic equivalence of the two protons in the ring is destroyed. (Under conditions of natural abundance, the probability that both protons are attached to $C^{13}$ is negligible.) The resulting satellite spectrum[15,16] corresponds to the AB portion of an ABX spin system, which now manifests the proton–proton coupling constant, $J_{AB}$. The latter enables us to discern whether the protons are *ortho* or *para* to one another.

The four innermost lines of the satellite spectrum lie close to the predominant $C^{12}$–H resonance, and are obscured by it. Since $J_{C^{13}-H} \approx 160$ Hz for an aromatic system, however, we may still investigate the pairs of lines which appear about 80 Hz on either side of the normal aromatic signal.

The limited solubility of the compounds and the low natural abundance of carbon-13 (1.1%) necessitate the use of signal enhancement techniques. Figure 2 depicts the time-averaged spectra—after 400 successive

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(1) A. G. Green and A. G. Perkin, *J. Chem. Soc.*, **83**, 1201 (1903).

(2) S. R. H. Edge, *ibid.*, **121**, 772 (1922); **123**, 2330 (1923).

(3) M. T. Bogert and E. M. Abrahamson, *J. Amer. Chem. Soc.*, **44**, 826 (1922).

(4) M. T. Bogert and W. S. Taylor, *Collect. Czech. Chem. Commun.*, **3**, 480 (1931).

(5) N. Steiger, U. S. Patent 2,454,260 (November 16, 1948).

(6) F. F. Stephens and D. G. Wibberly, *J. Chem. Soc.*, 3336 (1950).

(7) W. Reid and R. Bender, *Ber.*, **89**, 1893 (1956); **91**, 2798 (1958).

(8) A. I. Kiprianov, A. V. Stetsenko, and E. D. Sych, *Ukr. Khim. Zh.*, **22**, 760 (1956).

(9) K. V. Martin, *J. Amer. Chem. Soc.*, **80**, 233 (1958).

(10) R. F. M. Sureau and M. J. Alicot, *French Patent* 1,224,183 (June 22, 1960).

(11) R. Neeff, *German Patent* 1,164,003 (February 27, 1964).

(12) A. Fravolini, G. Grandolini, and G. Monzali, *Ann. Chem.* (Rome), **54**, 80 (1964).

(13) A. Hugershoff, *Ber.*, **34**, 3130 (1901); **36**, 3121 (1903).

(14) G. Barnikow, H. Kunzek, and M. Hofmann, *J. Prakt. Chem.*, [4] **27**, 271 (1965).

(15) A. D. Cohen, N. Sheppard, and J. J. Turner, *Proc. Chem. Soc.*, 118 (1958).

(16) Varian NMR at Work Series, No. 97.