An Extraordinary Geminal AB Spin System and Restricted Conformational Inversion in 6-Methyl-14*H*-dinaphtho[1,8-*bc*:1′,8′-*fg*]thiocin

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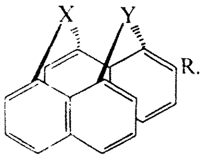
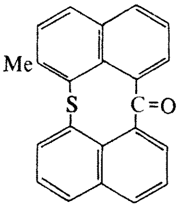
Summary The synthesis and unusual properties of the title compound and derivatives are reported.

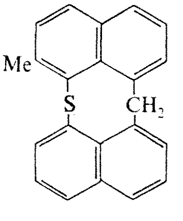
THE examination of molecular models of 7*H*, 14*H*-dinaphtho[1,8-*bc* : 1′,8′-*fg*]cyclo-octatetraene (**1a**) and derivatives suggests that these systems should bring into focus both the unique transannular effects observed in medium rings and the unusual chemistry associated with *peri*-naphthalenes. Examples of such systems have been reported, but they have been limited to cases where both bridging groups were either carbon or the same hetero-atom.[1] The novelty of the system and the intriguing n.m.r. spectral data resulting prompt this discussion of 6-methyl-14*H*-dinaphtho-[1,8-*bc*:1′,8′-*fg*]thiocin (**2**) and derivatives.



(**1a**) X=Y=CH_2, R=H
(**1b**) X=Y=CO, R=H
(**1c**) X=CO Y=CH_2, R=Me
(**1d**) X=Y=CH_2, R=Me
(**1e**) X=Y=SO_2, R=H



(**2**)

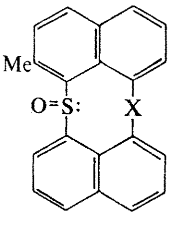


(**3**)

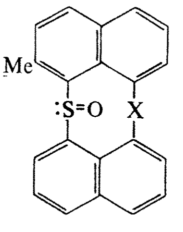
The precursor to (**2**) was obtained by coupling of 2-methylnaphthalenethiol with ethyl 8-bromonaphthoate using copper(I) oxide[2] in dimethylformamide; ring closure was effected with polyphosphoric acid.

All attempts to achieve nucleophilic addition products at the carbonyl group of (**2**) were totally unsuccessful. The sulphide (**3**) was obtained, however, by the Clemmensen reduction of (**2**) in absolute ethanol. A series of oxidative transformations at the sulphur atom in (**2**) and (**3**) was achieved with *m*-chloroperbenzoic acid. Keto-sulphide (**2**) was oxidized to the sulphoxide (**4a**). (The corresponding keto-sulphoxide (**5a**) and keto-sulphone (**6a**) could not be obtained under any conditions tried.) Oxidation of (**3**) could be controlled to yield either a mixture of sulphoxides (**4b**) and (**5b**) or sulphone (**6b**).

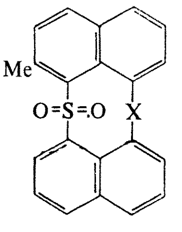
The i.r. and u.v. spectra of these compounds were essentially those expected.† The n.m.r. spectrum of (**3**) consisted of a complex multiplet at δ 7·5, a doublet at δ 4·1 and a singlet at δ 2·8. The relative intensities of these peaks were 12 : 1 : 3. Because this was not in agreement with the predicted ratios of 11 : 2 : 3 even though the analysis and mass spectrum of the sulphide were in agreement with structure (**3**), it was assumed that one of the methylene hydrogens (the *syn*-hydrogen) was superimposed on the aromatic hydrogen resonance. Subsequent double resonance and spin-tickling experiments verified this. The chemical-shift difference between the two geminal methylene hydrogen was 4·08 p.p.m. in perdeuteriobenzene. To our knowledge this is the largest chemical-shift difference observed for geminal hydrogens in a neutral molecule. A summary of the n.m.r. spectra of the bridging methylene protons is given in the Table.



(**4a**) X=CO
(**4b**) X=CH_2



(**5a**) X=CO
(**5b**) X=CH_2



(**6a**) X=CO
(**6b**) X=CH_2

TABLE

Chemical shifts (δ) *of bridging methylene hydrogen in deuteriochloroform solution*

Compound	*syn*-Hydrogen	*anti*-Hydrogen
(**3**)	7·90	4·08
(**4b**)	5·95	4·22
(**5b**)	obscured	4·48
(**6b**)	6·76	4·16

Agosta[3] prepared an optically active 3-nitro-derivative of (**1b**) and found that racemization, presumably by conformational inversion of the eight-membered ring, occurred readily. In our compound (**3**) and in (**1a**) prepared by Lansbury, there appear to be much higher barriers to inversion; the AB spin systems exhibit no signs of impending coalescence up to 160° in the case of (**3**) and up to 200° in the cases of (**1a**)[1b] and (**1d**).[1b]

It was observed that the kinetic product of the oxidation of (**3**) was *syn*-sulphoxide (**5b**) but that (**5b**) was rapidly converted into (**4b**) at room temperature in solution. This isomerization was followed by n.m.r. at 75° by comparing the ratio of the intensities of the methyl resonance of the two isomers. From these data we obtained the rate constant $k_1 = 1{\cdot}06 \pm 0{\cdot}0938 \times 10^{-3}$ sec.$^{-1}$ by least-squares fit for reversible first-order isomerization ($\Delta G^* = 25{\cdot}2$ kcal./mole). The equilibrium constant, K_e, is 9·8. We tentatively suggest that this isomerization occurs *via*

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† The u.v. spectrum of (**3**) was very similar to that recorded by Agosta for (**1b**). The sulphoxide–ketone (**2**) exhibited a maximum at somewhat higher wavelength, λ_{max} 340 nm. (in EtOH). The carbonyl band of (**1c**) appeared at 1655 cm.$^{-1}$ (Nujol) while in (**2**) it appeared at 1645 (KBr or $CHCl_3$). The dipole moment of (**2**) was determined by the heterodyne beat method and was found to be 4·36 ± 0·01D (benzene, 25°).

pyramidal inversion at sulphur rather than ring inversion. The severe steric crowding between the sulphoxide oxygen and the *syn*-hydrogen might be sufficient to cause such ready pyramidal inversion.[4]

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[1] (a) Compound (**1b**) was first synthesized by R. L. Letsinger and J. A. Gilpin, *J. Org. Chem.*, **1964**, **29**, 243. Subsequent studies of (**1b**) have been made by W. C. Agosta, *Tetrahedron Letters*, 1966, 3635; *J. Amer. Chem. Soc.*, **1967**, **89**, 3505; (b) Compounds (**1c**) and (**1d**) have been studied by P. T. Lansbury and M. Klien, *Tetrahedron Letters*, 1968, 1981; (c) Compound (**1e**) has been reported by R. W. Hoffman and W. Sieber, *Angew. Chem. Internat. Edn.*, 1965, **4**, 786.

[2] G. R. Bacon and H. A. O. Hill, *J. Chem. Soc.*, 1964, 1097.

[3] W. C. Agosta, *J. Amer. Chem. Soc.*, **1967**, **89**, 3926.

[4] Bulky groups attached to sulphur are known to accelerate the rate of pyramidal inversions of sulphoxides (D. R. Rayner, A. J. Gordon, and K. Mislow, *J. Amer. Chem. Soc.*, 1968, **90**, 4854).