

$^{13}\text{C}$ -NMR CHEMICAL SHIFTS AND COUPLING CONSTANTS  $J_{\text{C-H}}$  OF  
SIX-MEMBERED RING SYSTEMS CONTAINING SULFUR-SULFUR LINKAGE

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*Abstract* —  $^{13}\text{C}$ -NMR chemical shifts and coupling constants of methylene groups of several six-membered cyclic compounds having sulfur-sulfur linkage were measured. Some interesting NMR behaviours of a series of cyclic disulfides, thiolsulfinates and thiolsulfonates were observed and structural features of these compounds were investigated.

Despite numerous studies on NMR spectra of various organic compounds, few studies<sup>1,2)</sup> have been carried out on NMR spectra of cyclic compounds bearing sulfur-sulfur linkage. Recently, we reported the unusual chemical shifts in  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra of a series of linear acyclic disulfides, thiolsulfinates and thiolsulfonates.<sup>3)</sup> While no accurate structural analysis of these cyclic compounds have been permitted, chemical reactions of these compounds have been performed quite extensively.

We now have measured  $^{13}\text{C}$ -NMR chemical shifts and  $J_{\text{C-H}}$  of a series of six-membered ring compounds having sulfur-sulfur linkage.<sup>4)</sup> From several interesting NMR behaviours of a series of cyclic disulfides, thiolsulfinates and thiolsulfonates, new structural features on a series of these cyclic compounds were investigated.

Compounds 1a - c,<sup>5)</sup> 2a - c<sup>6)</sup> and 4a - c<sup>5)</sup> were prepared by known methods, while 3a was synthesized from trans-1,2-cyclohexanedicarboxylic acid via several reaction steps, and both 3b and 3c were prepared by the oxidation of 3a with MCPBA in  $\text{CH}_2\text{Cl}_2$ .<sup>2)</sup>

Assignments of  $^{13}\text{C}$ -NMR chemical shifts in completely proton decoupled  $^{13}\text{C}$ -NMR spectra were performed for all the compounds by the technique of off-resonance decoupling of proton,  $^{13}\text{C}$  -  $^1\text{H}$  coupling constants, and relative relaxation times, in comparison with the reported data of various sulfur heterocycles<sup>7)</sup> and of a series of linear compounds in our previous study.<sup>3)</sup>  $^{13}\text{C}$ -NMR chemical shifts thus assigned for all these compounds are shown in Fig. I and Fig. II.

The chemical shift of carbon-1 moves toward down field as the oxidation state

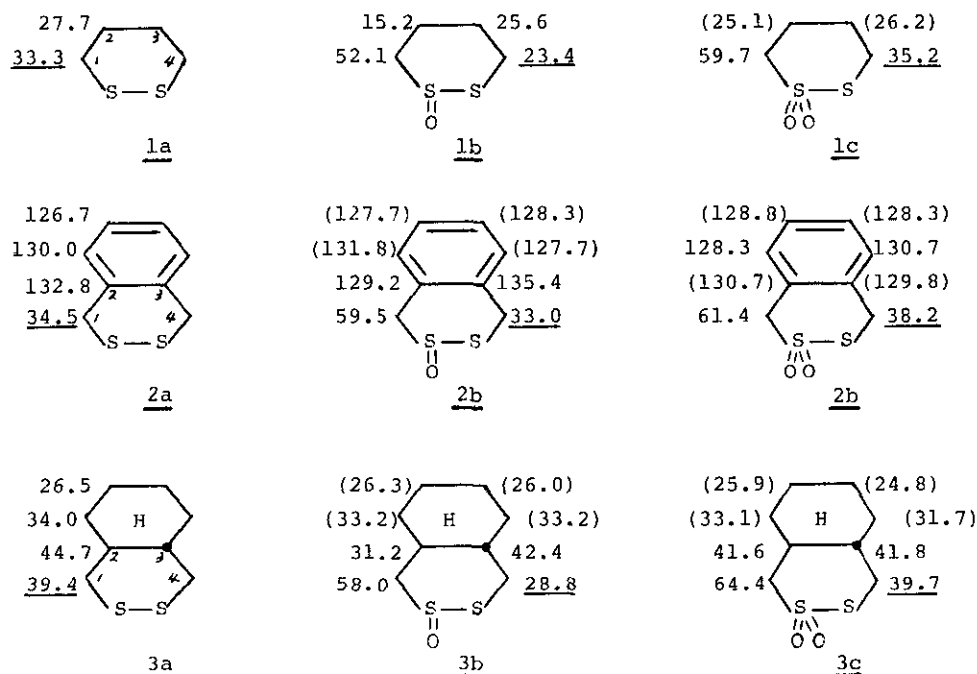


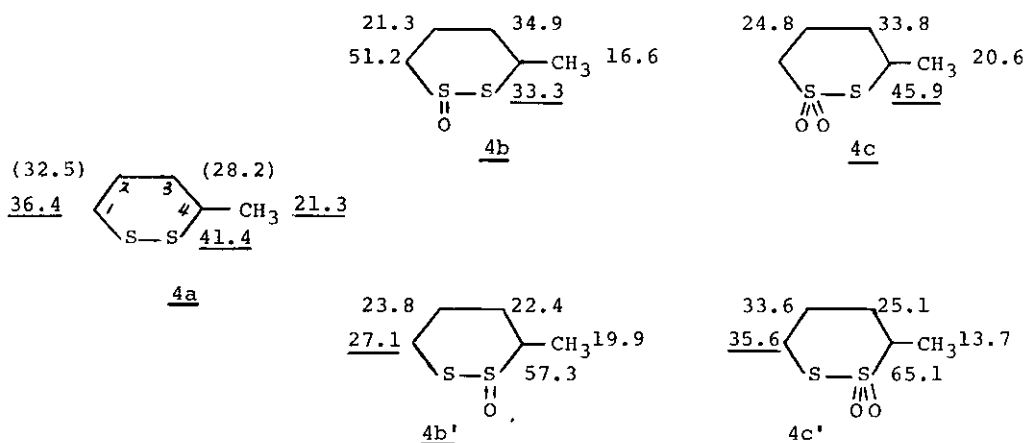
Fig. 1  $^{13}\text{C}$ -NMR Chemical Shifts ( ppm )

\* Chemical shifts parenthesized cannot be assigned correctly.

# Chemical shifts underlined are notable unusual chemical shifts.<sup>3)</sup>

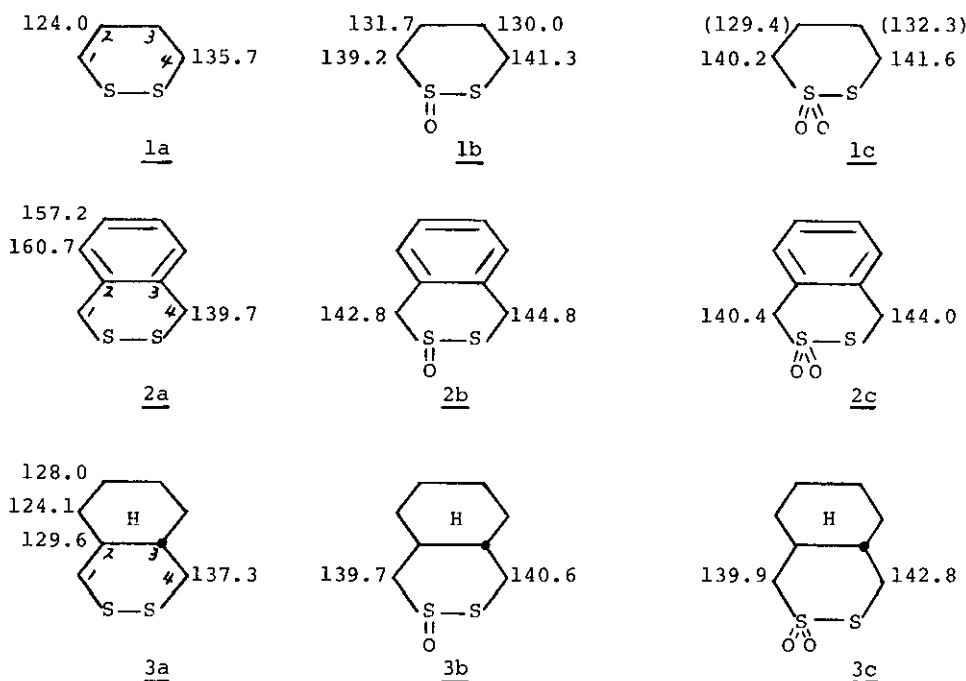
of the adjacent sulfur atom increases from a, b to c as expected, while the chemical shift at carbon-4 does not show any correlation with the expected electronegativities, and the highest chemical shift is observed in b. This phenomenon was also seen in the series of linear compounds.<sup>3)</sup> The unusual high field shift of carbon-4 of b is considered to be due to the well known  $\gamma$ -effect.<sup>7)</sup> The  $\gamma$ -effect can be seen also at carbon-2 in all b. The  $\gamma$ -effect has been known to be observed only in axial sulfoxide<sup>7)</sup> or analogous sulfilimine<sup>7,8)</sup> of conformationally locked ring compounds but not in equatorial derivatives.<sup>2,7)</sup> Therefore, the fact that a sufficiently large  $\gamma$ -effect can be observed clearly in all these thiol-sulfonates, suggests the axial orientation of the oxygen atom of b, in keeping with the data in the recent report,<sup>2)</sup> since an axial isomer is known to be thermodynamically more stable than an equatorial one in the cyclic sulfoxides bearing rigid ring system.<sup>9)</sup> No formation of the equatorial isomer of b is rationalized in terms of a fast equilibration between both isomers via incipient cleavage and formation of sulfur-sulfur bond.<sup>10)</sup>

Meanwhile, by the results above mentioned and the  $^{13}\text{C}$ -NMR data ( Fig. II ),

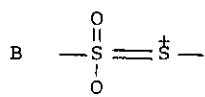
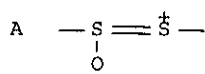

 Fig. II  $^{13}\text{C}$ -NMR Chemical Shifts ( ppm )

was justified our postulation that two isomers<sup>11)</sup> of monoxides of 4a are not stereoisomers but regioisomers. This was also supported by the fact that selective oxidations of the two isomers( 4b and 4b' ) with  $\text{NaIO}_4$ <sup>12)</sup> gave the corresponding thiol-sulfonates 4c and 4c', respectively.

Values of  $J_{\text{C-H}}$  were measured for the series of a - c of 1 - 3 using NOE.


 Fig. III  $J_{\text{C-H}}$  Value ( Hz )

The unusually large coupling constants of carbon-4 of b and c ( Fig. III ) are considered to be due to the contributions of the resonance structures of b and c as shown by A and B.<sup>13)</sup> This may also be in good agreement



with the result of UV study of linear diaryl system of b and c in which the red shift was observed when solvent was changed from nonpolar to polar solvent.<sup>14,15)</sup>

Thus, from <sup>13</sup>C-NMR chemical shifts and J<sub>C-H</sub>'s of the series of these compounds the following conclusions were

obtained: (1) both unusual chemical shifts at carbon-1 and 4 and γ-effect were observed in cyclic systems as well as in acyclic system, (2) stereoisomerism around the sulfur atom of the thiolsulfinate was not found to exist while oxygen of the thiolsulfinate was oriented toward axial, (3) two isomers of monoxides of 4a were not stereo- but regio-isomers, (4) coupling constants of carbon-hydrogen of b and c at carbon-4 indicated large contribution of the structures A and B.

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