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# STRUCTURE DETERMINATIONS OF CYCLOPENTA[b]THIAPYRANS

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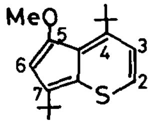
Summary: The detailed molecular structures of substituted cyclopenta[b]thiapyrans were studied by means of $^1$H-NMR spectroscopy and X-ray diffraction method.

In the preceeding paper, we reported acid-catalyzed intramolecular cyclization of 2,6-octadiene-4-ynedial derivatives to substituted cyclopenta[b]thiapyrans (1, 2, and 3).



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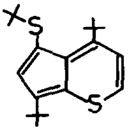

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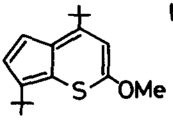

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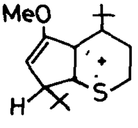

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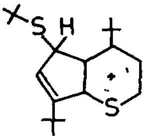

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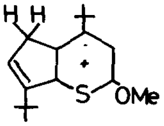

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The $^1$H-NMR parameters of the cyclopenta[b]thiapyrans (1, 2, and 3) are summarized in Table 1. Assignment of the protons ($H_2$) in 1 and 2 was confirmed by deuteration with the treatment of *n*-butyllithium followed by addition of deuterium oxide. The deuterated products showed disappearance of the lowest field doublet in $^1$H-NMR. The fact that the ring protons of the cyclopenta[b]thiapyrans (1, 2, and 3) exhibit signals at low field provides evidence for the existence of a diamagnetic ring current. Because the configuration of 2 shown in Fig. 2 was confirmed by X-ray diffraction method, a moderate upfield shift of the signal of *t*-butylthio group in 2 can be ascribed to a shielding effect of the ring current. Protonation of the cyclopenta[b]thiapyrans occured in 5- or 7- position to give the thiopyrylium ion derivatives (4, 5, and 6). The $^1$H-NMR parameters of the thiopyrylium ions (4, 5, and 6) are summarized in Table 2. The position of the protonation in 1, 2, and 3 was found to be at C-7 in 4 and at C-5 in 5 and 6, respectively.

Table 1. $^1$H-NMR Parameters of 1, 2, and 3 ($CCl_4$-acetone-$d_6$, δ-values, rt)

| 1 | | | 2 | | | 3 | | |
|---|---|---|---|---|---|---|---|---|
| $H_2$ | 7.63 | dd (J=10.0, 0.5) | $H_2$ | 7.80 | d (J=9.5) | $H_5$, $H_6$ | 6.90 | s |
| $H_3$ | 7.17 | d (J=10.0) | $H_3$ | 7.47 | d (J=9.5) | $H_3$ | 6.58 | s |
| $H_6$ | 6.57 | d (J=0.5) | $H_6$ | 7.46 | s | MeO | 4.05 | s |
| MeO | 3.89 | s | $C_4$-*t*-Bu | 1.71 | s | $C_4$-*t*-Bu | 1.56 | s |
| $C_4$-*t*-Bu | 1.52 | s | $C_7$-*t*-Bu | 1.48 | s | $C_7$-*t*-Bu | 1.43 | s |
| $C_7$-*t*-Bu | 1.42 | s | S-*t*-Bu | 1.09 | s | | | |

Table 2. $^{1}$H-NMR Parameters of **4**, **5**, and **6** ($CF_3COOH$-$CD_2Cl_2$, δ-values, -30°C)

| **4** | | | **5** | | | **6** | | |
|---|---|---|---|---|---|---|---|---|
| $H_2$ | 9.44 | d (J=9.0) | $H_2$ | 9.35 | d (J=9 0) | $H_3$ | 7.71 | s |
| $H_3$ | 8.78 | d (J=9.0) | $H_3$ | 8.60 | d (J=9.0) | $H_6$ | 7.29 | t (J=2.0) |
| $H_6$ | 6.24 | d (J=2.5) | $H_6$ | 7.61 | d (J=2.0) | OMe | 4.43 | s |
| OMe | 4.01 | s | $H_5$ | 5 48 | d (J=2.0) | $H_5$ | 4.03 | d (J=2.0, 2H) |
| $H_7$ | 3 87 | d (J=2.5) | $C_4$-*t*-Bu | 1.75 | s | $C_4$-*t*-Bu | 1 59 | s |
| $C_4$-*t*-Bu | 1.64 | s | $C_7$-*t*-Bu | 1.50 | s | $C_7$-*t*-Bu | 1.47 | s |
| $C_7$-*t*-Bu | 1 14 | s | S-*t*-Bu | 1 42 | s | | | |

The molecular structures of **1** and **2** have been determined by means of X-ray diffraction. A Rigaku automated, four-circle diffractometer with graphite monochromatized MoKα radiation was used for the measurement of lattice parameters and intensities. Integrated intensities were measured by the θ-2θ scan method at a scan rate of 4° $min^{-1}$. Backgrounds were counted for 5 s before and after each peak scan. Measurements were carried out at low temperature in order to obtain molecular structures with higher precision. Low temperatures were attained by the gas flow method of liquid nitrogen. Observed intensities were corrected for usual Lp effect but not for absorption.

**1** (5-methoxy derivative): A deep blue crystal with dimensions of 0.28×0.23×0.25 mm was used. Crystal data are listed in Table 3. Among the 2371 reflections measured ($2\theta \leq 60°$) 1457 were classed observed ($|F_0| > 3\sigma(F_0)$). The structure was solved by the direct method (MULTAN 78)[1]; some difficulties being arisen in peak interpretation. As the $Z$ value (=2) suggests the molecule locating on the center of symmetry. However, without considering a disordered structure, any packing of molecule is impossible because the molecule itself is not centrosymmetric.

Table 3. Crystal data of cyclopenta[b]thiapyranes

| **1** | | **2** | |
|---|---|---|---|
| $C_{17}H_{24}OS$ | $F.W.$ = 276.4 | $C_{20}H_{30}S_2$ | $F.W.$ = 334.6 |
| Monoclinic | $P2_1/c$ | Monoclinic | $P2_1/n$ |
| [-160°C] | $V$ = 806.5(3) Å$^3$ | [-153°C] | $V$ = 3945(3) Å$^3$ |
| $a$ = 11 664(2) Å | $Z$ = 2 | $a$ = 24 189(8) Å | $Z$ = 8 |
| $b$ = 6 356(1) | $D_x$ = 1.14 g $cm^{-3}$(-160°C) | $b$ = 7.316(4) | $D_x$ = 1 13 g $cm^{-3}$(-153°C) |
| $c$ = 11 593(2) | $D_m$ = 1.10 ( 27°C) | $c$ = 24 190(7) | $D_m$ = 1 10 ( 27°C) |
| β = 110.24(2)° | μ(MoKα) = 1 9 $cm^{-1}$ | β = 112.86(2)° | μ(MoKα) = 2.6 $cm^{-1}$ |

As shown in Fig. 1, two molecules with ½ occupancy locate on the same center of symmetry causing overlaps of the C(3) onto C(7'), S onto O, and all the four carbon atoms of *t*-butyl group connecting to C(3) onto those connecting to C(7'). In the refinement an artificial atom with average atomic scattering factor of ($\frac{1}{2}f_O + \frac{1}{2}f_S$) was assumed for the overlapped, half S and half O atoms. The refinement was done by the block-diagonal least-squares method (HBLS V)[2] using isotropic temperature factors for non-hydrogen atoms. The refinement converged quickly at rather high $R$ value of 0.22.

Expectedly, the molecule showed unusually deformed structure because of the overlapping of two molecules. Further refinement was tried under constraint conditions (ORXFLS4)[3] assuming that the cyclopenta[b]thiapyran ring of the present molecule **1** has the same structure as that of **2**, the structure of which will be described later. No trial has been made to separate the carbon atoms between two *t*-butyl groups.
The structure parameters of cyclopenta[b]thiapyran ring converged smoothly to the constrained values, however, peak separation between the S and O atoms was unsuccessful in contrast to that between the C(3) and C(7') atoms. In spite of the interesting packing structure of this compound the detailed discussion on its structure will be limitted.

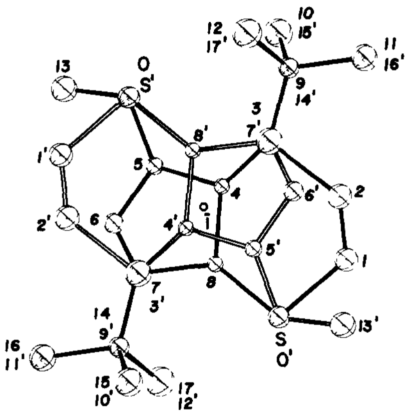


Fig. 1. Disordered Structure of **1**. Atomic numberings are different from those shown in the $^1$H-NMR part.

**2** (5-*t*-butylthio derivative): The crystal used had dimensions of 0.28×0.28×0.18 mm. Crystal data are listed in Table 1. The $Z$ value (=8) shows two crystallographically independent molecules are contained in a unit cell. Even though the crystal belongs to the monoclinic system an unusual *mm* Laue symmetry was observed for the *h0l* reflections instead of *2*. The high Laue symmetry can be interpreted by the structure determined. Out of the 6909 measured reflections ($2\theta \leq 50°$) 4282 were classed observed. The structure was solved by the direct method by choosing a good set of starting reflections manually. The refinement was proceeded in the same manner as in **1** assuming anisotropic temperature factors for non-hydrogen atoms and isotropic ones for hydrogens. The final $R$ index is 0.097. The crystal structure revealed very interesting correlations between all of the $x$ and $z$ atomic coordinates of two crystallographically independent molecules, 1 and 2. Those are; $x_{1i} + z_{2i} = 1.000(2)$, and $z_{1i} + x_{2i} = 0.500(2)$, where figures in parentheses refer to the estimated standard deviations. From these relations the following equations can be easily obtained; $|F(h0l)|=|F(l0h)|=|F(\bar{h}0\bar{l})|=|F(\bar{l}0\bar{h})|$. As the $a$ and $c$ axes have no difference in length the following transformations make new axes almost orthogonal to each other; $\vec{a}' = -\vec{a} + \vec{c}$, $\vec{b}' = \vec{b}$, and $\vec{c}' = -\vec{a} - \vec{c}$. Based on the new axes the relations between the structure factors become; $|F(h'0l')|=|F(\bar{h}'0l')|=|F(h'0\bar{l}')|=|F(\bar{h}'0\bar{l}')|$, which can explain the *mm* Laue symmetry of these reflections.

An ORTEP drawing of **2** molecule is shown in Fig. 2. The selected bond distances and angles are summarized in Table 4. The characteristic features of the structure are: 1) a bond alternation in the cyclopenta[b]thiapyran ring is clearly observed, 2) except $b$ and $j$, all the C-C bonds in the ring have lengths between C(sp$^2$)-C(sp$^2$) single bond [1.48 Å] and C=C double bond [1.34 Å], 3) two C-S bonds, $a$ and $i$, are shorter than the C-S single bond [1.81 Å] and similar to the partial double bond in thiophene [1.73 Å], 4) $j$ is equal to that of C(sp$^2$)-C(sp$^2$) single bond which is also observed in the corresponding bond of azulene molecule.[4] The observation 1) indicates predominant contribution of localized structure I shown below. However, some contribution

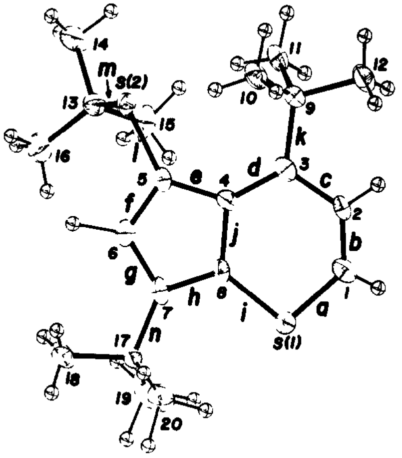
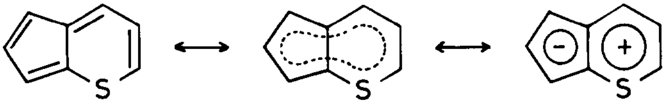


Fig. 2. Molecular Structure of 2.

Table 4. Selected bond distances (Å) and angles (°) of 2.
(1 and 2 refer to the two independent molecules)

| | 1 | 2 | | 1 | 2 | | 1 | 2 |
|---|---|---|---|---|---|---|---|---|
| *a* | 1.673 | 1.696 | ∠*ab* | 129.2 | 124.5 | ∠*gn* | 125.4 | 125.4 |
| *b* | 1.300 | 1.358 | ∠*ai* | 100.2 | 102.2 | ∠*hn* | 130.4 | 129.5 |
| *c* | 1.453 | 1.411 | ∠*bc* | 125.9 | 127.5 | ∠*hi* | 124.0 | 124.3 |
| *d* | 1.399 | 1.415 | ∠*cd* | 118.5 | 120.1 | ∠*hj* | 112.3 | 111.3 |
| *e* | 1.460 | 1.453 | ∠*ck* | 116.3 | 116.1 | ∠*ij* | 123.8 | 124.4 |
| *f* | 1.379 | 1.391 | ∠*dk* | 125.2 | 123.8 | ∠*lm* | 104.3 | 105.1 |
| *g* | 1.429 | 1.410 | ∠*de* | 135.2 | 134.8 | | | |
| *h* | 1.381 | 1.381 | ∠*dj* | 122.0 | 120.8 | | | |
| *i* | 1.733 | 1.725 | ∠*ej* | 102.5 | 103.9 | | | |
| *j* | 1.490 | 1.479 | ∠*ef* | 108.1 | 106.8 | | | |
| *k* | 1.548 | 1.564 | ∠*el* | 132.8 | 133.6 | | | |
| *l* | 1.781 | 1.778 | ∠*fl* | 118.9 | 119.3 | | | |
| *m* | 1.868 | 1.858 | ∠*fg* | 112.6 | 112.9 | | | |
| *n* | 1.528 | 1.543 | ∠*gh* | 104.3 | 105.0 | | | |

of delocalized structures, II and/or III, can not be excluded in view of the observations 2) and 3). A larger contribution of II rather than III seems to be suggested by the observation 4). The result of the dipole moment measurement also supports this conclusion.$^{5)}$



I II III

## References and Notes

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