NOTIZEN

1,3-Dimethoxy-6H-benzo[b]naphtho[1,2-d]pyran-6-thione, a Thionolactone-Bridged Axially Prostereogenic Biaryl*

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The title compound was prepared from the corresponding "ordinary" oxolactone bridged biaryl using Lawesson's reagent. It crystallizes from dichloromethane / petroleum ether in the monoclinic system, space group $P2_1/a$; $a = 1115.7(2)$, $b = 1383.9(2)$, $c = 1042.0(1)$ pm and $\beta = 106.67(1)^\circ$.

Introduction and Synthesis

Lactone-bridged biaryl systems like **1** and **2** constitute most useful synthetic intermediates in the regio- and stereocontrolled synthesis of natural and unnatural biaryl systems: they are easily built up by Pd^{II}-catalyzed intramolecular biaryl coupling, allowing high chemical yields and reliable regioselectivities [2]. Depending on the sizes of the *ortho*-substituents next to the axis, such biaryl lactones do not dispose of a fixed geometry at the axis, but rather isomerize more or less rapidly. Out of this equilibrating enantiomeric mixture, they can be ring opened in high atropisomer-selectivities to give non-bridged configuratively stable biaryl target molecules of high stereochemical purity [3, 4]. We have recently embarked on the extension of this preparatively valuable and theoretically unprecedented procedure to the use of thio-

nolactone-bridged biaryls [5]. In the course of that work, such first biaryl thionolactones **3** and **4** were prepared, structurally investigated, and ring opened after complexation to a ruthenium fragment, giving most promising results. The title compound **4** was prepared from the corresponding known [2] oxolactone **2**, by reaction with Lawesson's reagent. For a structural comparison of this new compound with related oxo- and thionolactones, an X-ray structure analysis was highly desirable. From dichloromethane / petroleum ether, suited crystals of melting point 492 K were obtained.

X-Ray Investigation

For the crystal structure analysis a crystal of the size 0.5 x 0.6 x 0.4 mm was chosen. The determination of the cell parameters from 22 reflections ($10.0^\circ < \theta < 15.4^\circ$) and the measurement of 3072 observed ($F > 3\sigma(F)$) unique reflection intensities ($1.75^\circ < \theta < 27.5^\circ$; $h_{\max} = 14$, $k_{\max} = 17$, $l_{\min} = -13$, $l_{\max} = 12$) were carried out on a Siemens R3m/V four-circle diffractometer (Mo $K\alpha$, Wyckoff-scan, empirical absorption correction). The structure was solved by direct phase determination (Siemens SHELXTL-PLUS). The parameters of the complete structure could be refined by full-matrix anisotropic least-squares to $R = 0.043$, $R_w = 0.042$; reflection data to parameter ratio = 14.70. The electron density of the largest difference peak was found to be 0.22, while that of the largest difference hole was 0.30 eÅ⁻³.

Results and Discussion

C₁₉H₁₄O₃S, 322.38 g mol⁻¹, crystallizes in the monoclinic system, space group $P2_1/a$, with $a = 1115.7(2)$, $b = 1383.9(2)$, $c = 1042.0(1)$ pm, $\beta =$

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Table I. Positional parameters ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{pm}^2 \times 10^{-1}$).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
S	768(1)	3908(1)	7429(1)	54(1)
O(1)	3084(1)	3559(1)	8440(1)	45(1)
C(2)	2006(2)	3767(1)	8733(2)	41(1)
C(3)	2042(2)	3786(1)	10128(2)	40(1)
C(4)	899(2)	3912(1)	10464(2)	48(1)
C(5)	883(2)	3873(2)	11754(2)	50(1)
C(6)	1967(2)	3607(1)	12789(2)	45(1)
C(7)	1929(2)	3469(2)	14120(2)	56(1)
C(8)	2919(2)	3094(2)	15064(2)	64(1)
C(9)	3987(2)	2820(2)	14720(2)	61(1)
C(10)	4083(2)	2986(2)	13458(2)	50(1)
C(11)	3101(2)	3428(1)	12469(2)	42(1)
C(12)	3172(2)	3642(1)	11135(2)	38(1)
C(13)	4326(2)	3701(1)	10748(2)	38(1)
C(14)	5550(2)	3942(1)	11574(2)	43(1)
C(15)	6567(2)	3914(1)	11077(2)	47(1)
C(16)	6416(2)	3724(1)	9726(2)	46(1)
C(17)	5235(2)	3595(1)	8853(2)	44(1)
C(18)	4237(2)	3610(1)	9394(2)	40(1)
O(19)	5611(1)	4267(1)	12820(1)	55(1)
C(20)	6804(2)	4420(2)	13759(2)	67(1)
O(21)	7484(1)	3728(1)	9340(2)	60(1)
C(22)	7348(2)	3765(2)	7934(2)	63(1)

106.67(1)° $V = 1541.1(4) \text{ pm}^3 \cdot 10^6$ and $Z = 4$. The density was calculated to be 1.414 g cm^{-3} . Atomic parameters are listed in Table I according to the atom labels of Fig.1.* The X-ray structure analysis indeed confirms the incorporation of a sulfur atom into the molecule to give **4**. Due to the steric interaction between the methoxy group at C(14) and the hydrogen at C(10), the molecule, despite its high content of aromatic rings, is not at all flat, but helicene-like distorted and thus chiral. In the crystal, the compound is racemic, *M* and *P*-helimeric molecules co-occurring in a 1:1 ratio. Of great

* Further crystal structure data may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftliche Information mbH, D-76344 Eggenstein-Leopoldshafen, by quoting the Registry No. CSD-401158, the names of the authors and the journal citation.

Fig. 1. Perspective drawing of **4** with the labelling of the atoms corresponding to Table I.

interest is also the degree of molecular distortion as a function of the steric hindrance at the biaryl axis and of the carbonyl or heterocarbonyl functionality. Thus, the overall distortion of the inner spiral loop, *i.e.* the sum of the dihedral angles within the series C(10)-C(11)-C(12)-C(13)-C(14)-O(19), [54.2°] is smaller than the one measured for the sterically more hindered methyl analog **3** [63.6°] [5]. For the influence of the sulfur versus the normal oxygen atom for the exocyclic C=X double bond, two contrary effects may be expected: thus, the less distinct tendency of sulfur to form C=X double bonds, compared with oxygen, should lead to a greater weight of the mesomeric structure **4a**, thus predicting a longer C-X bond and a stronger planarization of the system. By contrast, the opposite effect should be expected from the smaller electronegativity of sulfur compared with oxygen. The X-ray structure analysis shows that in this case the first effect seems to be predominant. The thionolactone **4** is slightly less-severely distorted than the corresponding oxolactone **2** [55.5°]. Ring opening reactions of transition metal complexes of **4** using various chiral and achiral nucleophiles, are under investigation.

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