1,3-Di-tert-butyl-6H-benzo[b]naphtho[1,2-d]pyran-6-thione, a Severely Helically Distorted Thionolactone-Bridged Biaryl* 

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The title compound 2c, a potentially useful synthetic intermediate in stereoselective biaryl synthesis, has been prepared from the oxolactone 1c, by treatment with Lawesson's reagent. An X-ray structure analysis reveals its strongly helically distorted structure, the overall molecular distortion even slightly exceeding that of the corresponding oxo compound 1c.

Introduction

Lactone-bridged biaryls of type 1 [2] are most remarkable heterocyclic compounds: they possess a biaryl axis, which, in most cases, is configuratively unstable but can be 'twisted' atropisomer-selectively by stereocontrolled ring opening to give essentially one - now configuratively stable - atropisomeric cleavage product. The source of stereochemical information may be the metal activated (since deprotonated) O N -, H -, or other nucleophiles, a chiral Lewis acid that coordinates to the basic exocyclic oxygen, or an additional element of planar chirality resulting from a /-transition metal arene complex [3 - 6]. We have recently extended this useful principle to the atropisomer-selective cleavage of the corresponding, likewise configuratively labile thionolactones 2a and 2b, chirally modified by ruthenium biphosphane complexes [7, 8]. In this paper, we report on the preparation and X-ray structure analysis of the related, but sterically much more hindered tert-butyl-substituted analog 2c.

Experimental

General

The reaction was carried out under argon using standard Schlenck type techniques. The solvent was dried appropriately and distilled under argon prior to use. 1,3-Di-tert-butyl-6H-benzo[b]naphtho[1,2-d]pyran-6-one (1c) was prepared according to a procedure described earlier [2]. 1H and 13C spectra were recorded on a Bruker AC 200 spectrometer, and are referenced to internal CHCl3 (1H, δ 7.26 ppm; 13C, δ 77.00 ppm). The melting point was determined by DTA and is uncorrected. For mass spectrometry (electron ionization 70 eV), a Varian MAT CH 7 instrument was used. The elemental analysis was performed by the microanalytical laboratory of the Institute of Inorganic Chemistry of the University of Würzburg.

Preparation of the thionolactone 2c

To a solution of 1.87 g (5 mmol) of the corresponding oxolactone 1c in toluene (400 ml) 2.02 g (5 mmol) of Lawesson's reagent [2,4-bis(4-methoxyphenyl)-2,4-dithiooxo-1,3,2,4-dithia-diphosphetane] were added [7]. The mixture was refluxed for 10 h, then additional 2.02 g (5 mmol) of Lawesson's reagent were added and the whole was refluxed for further 10 h. It was then allowed to cool, yield 2.02 g (5 mmol). 

Fig. 1. Structures of lactone- and thionolactone-bridged biaryls.
cool to room temperature and the solvent was removed in vacuo. The resulting solid was crystallized from CH₂Cl₂ / petroleum ether, to give 2c as orange-colored crystals, in 75% yield. m.p. 166-169°C. IR (KBr): ν (C=S) 1170 cm⁻¹, 1H NMR (CDCl₃, 200 MHz): δ 1.00 (s, 9 H, C₄H₉₂); 1.41 (s, 9 H, C₄H₉₂); 7.40 (d, J = 2.0 Hz, 1 H, 2-H or 4-H); 7.42 (dd, J₁₉₋₁₁ = 8.3 Hz, J₁₉₋₁₁₋₂ = 8.3 Hz, J₁₉₋₁₁₋₉ = 1.4 Hz, 1 H, 1H); 7.56 (dd, J₁₉₋₁₁₋₁₀ = 6.9 Hz, J₁₀₋₁₀₋₉ = 7.5 Hz, J₁₀₋₁₀₋₁₁ = 1.1 Hz, 1 H, 10H); 7.66 (d, J = 2.0 Hz, 1 H, 4-H or 2-H); 7.72 (d, J₆₋₇ = 8.7 Hz, 1 H, 8-H); 7.79 (d, J₆₋₇ = 7.5 Hz, 1 H, 9-H); 8.15 (d, J₁₂₋₁₁ = 1H, 12-H); 8.54 (d, J₃₋₄ = 8.7 Hz, 1H, 7-H). ¹³C NMR (CDCl₃, 60 MHz): δ = 31.0 (s, CH₃), 32.7 (s, CH₃), 34.9 (s, C(CH₃)₃), 39.3 (s, C(CH₃)₃), 109.7-153.2 (16 signals), 199.3 (C=S). MS: m/z (%) 374(100) [M⁺], 359(21) [M⁺ - C₅H₆], 344(34) [M⁺ - 2 × CH₃], 318(61) [M⁺ - C₄H₈], 303(21) [M⁺ - C₅H₅], 292(21) [M⁺ - C₆H₆].

C₂₅H₂₆OS (374.54)
Calcd. C 80.17 H 7.00 S 8.56%.
Found C 79.80 H 7.29 S 8.60%.

X-ray investigation

For the crystal structure analysis, a crystal of the size 0.2 x 0.25 x 0.1 mm was chosen. The determination of the cell parameters from 99 reflections (7.3° < θ < 27.5°), and the measurement of 3498 observed (F > 3σ(F)) unique reflection intensities (1.75° < θ < 27.5°; hmax = 17, kmax = 13, lmin = -19, lmax = 19) were carried out on a Siemens P4 diffractometer (MoKα, ω-scan, empirical absorption correction). The structure was solved by direct phase determination (Siemens SHELXTL-PLUS). The parameters of the complete structure were refined by full-matrix anisotropic least-squares to R = 0.067, Rw = 0.065; reflection data to parameter ratio = 14.28. The electron density of the largest difference peak was found to be 0.30, while that of the largest difference hole was 0.21 eÅ⁻³.

Results and Discussion

The synthesis of the thionolactone-biaryl 2c proceeded without problems, following a protocol previously elaborated for the syntheses of 2a and 2b [7]. By crystallization from dichloromethane / petroleum ether, crystals suitable for an X-ray structure analysis were obtained. C₂₅H₂₆OS, 374.54 g mol⁻¹, crystallizes in the monoclinic system, space group P2₁/n, with a = 1353.5(1), b = 1058.9(1), c = 1488.5(1) pm, β = 100.85(1)°, V = 2095.1(3) pm³ x 10⁶ and Z = 4. The density was calculated to be 1.187 g cm⁻³. Atomic parameters are listed in Table I according to the atom labels of Fig. 2. 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-405931, the names of the authors, and the journal citation.

The X-ray diffraction analysis shows 2c to possess the expected dramatically distorted, helicenelike structure (see Fig. 2), in which the naphthalene and the phenyl ring systems (which are, by themselves, distorted) are near-orthogonal to each other.

![Fig. 2. Structure of 2c in the crystal, with the labelling of the atoms corresponding to Table I; hydrogen atoms omitted for reasons of clarity; only the P-enantiomer is shown.](image-url)

As a measure for this molecular distortion, we have previously introduced the dihedral angles α (abcd), β (bcde), and γ (cd ef) (see Fig. 1), and their sum Σ, the overall distortion of the 'inner spiral loop' [2]. These dihedral angles (α = 37.9°, β = 34.4°, γ = 8.7°, Σ = 81.0°) are much larger than those for the sterically less hindered thionolactones 2a and 2b (Σ = 54.2° [7] and Σ = 63.6° [9], resp.). Compared with the corresponding tert-butyl-substituted oxolactone 1c [10], the central dihedral angle β, representing the molecular twisting at the biaryl axis, is slightly smaller for the thionolactone (β = 34.4° for 2c, β = 36.1° for 1c) [8]. A similar effect, i.e. a slight tendency of a less distinct distortion of the thiono-compared with the oxolactones, had previously been found for 2a vs. 1a and 2b compared with 1b [7, 9]. For 2c (X = S), the mesomorphic VB structure B (see Fig. 3), which should lead to a stronger planarization, is apparently of increased importance over the structure A as compared to the corresponding oxo...
compound 1c (X = O), the reason obviously being the tendency of the sulphur to avoid a C=S double bond (as in A), despite its smaller electronegativity as compared to oxygen.

Fig. 3. Mesomeric structures for the central lactone (X = O), resp. thionolactone (X = S) part of 1 and 2.

This more significant planarization of the central part, however, is overcompensated by the other dihedral angles \( \alpha \) and \( \gamma \), which are larger for 2c (\( \alpha = 37.9^\circ, \gamma = 8.7^\circ \)) than for 1c (\( \alpha = 33.7^\circ, \gamma = 8.5^\circ \)) [10], so that, with respect to the overall molecular distortion, 2c (\( \Sigma = 81.0^\circ \)) even exceeds 1c (\( \Sigma = 78.2^\circ \)) and thus constitutes the as yet most severely distorted molecule of this type, which is best visualized by a matched plot as shown in Fig. 4.

Fig. 4. Joint plot of the structures of 1c (—) and 2c (----) in the crystal, matched with respect to the 'first' (i.e. the bis-tert-butyl substituted) ring; hydrogen atoms omitted for reasons of clarity.

As expected from experience with the corresponding oxolactone 1c [10], the racemic thionolactone 2c likewise crystallizes as a racemate, with two \( M^- \) and two \( P^- \)-enantiomers per crystallographic unit. Only very few related 6- or 7-membered related biaryl lactones crystallize in an enantiomerically pure form, starting from the corresponding racemates [11, 12]. The stereoselective ring cleavage of 2c and its transition metal complexes is under investigation.

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