1,4-Dibromonaphthalene-2,3-diyl-bis(1'-bromo-2'-naphthoate) • CHCl₃, a Potential Precursor to Lactone-Bridged Teraryls*

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Crystal Structure, Biaryl Coupling, Teraryls

The title compound was prepared from 1,4-di-bromo-2,3-dihydroxynaphthalene by two-fold esterification with 1-bromo-2-naphthoic acid. It crystallizes from chloroform in the triclinic system, space group \( P1 \); \( a = 1226.6(3) \), \( b = 1246.9(3) \), \( c = 1218.8(3) \) pm, \( \alpha = 107.50^\circ \), \( \beta = 90.94^\circ \), \( \gamma = 113.56^\circ \). The asymmetric unit is described with a statistically disordered CHCl₃.

Introduction and Synthesis

The directed regio- and stereoselective construction of chiral biaryl systems constitutes an important goal to be attained for the directed total synthesis of natural and unnatural biaryl systems [2]. Recently, a conceptionally novel and highly efficient approach to stereochemically homogenous, even highly hindered biaryl systems was elaborated, by atropisomer-selective ring cleavage of axially prostereogenic, i.e. configuratively labile lactone-bridged biaryls of type 1 [3–6]. In an attempt to extend this efficient method to the preparation of target molecules with even two or more stereogenic axes, e.g. to the synthesis of teraryls, a promising substrate for respective double ring opening reactions would be the bis-lactone 2. A potential precursor to 2 should be the new diester 3, which we have prepared from the known [7] 1,4-dibromo-2,3-dihydroxy-naphthalene, by double esterification with the likewise synthetically available [8] 1-bromo-2-naphthoic acid. In order to learn more about the probability for a double ring closure of this compound, detailed information about this conformation was desirable, which was expected from an X-ray structure analysis. For this purpose, suited crystals were grown from chloroform, showing a melting point of 416–417 K.

X-Ray Investigation

For the crystal structure analysis a crystal of the size \( 0.3 \times 0.4 \times 0.15 \) mm was chosen. The determination of the cell parameters from 22 reflections (9.8°<0<13.0°) and the measurement of 5148 observed (\( F > 3 o (F) \)) unique reflection intensities (1.75°<0<27.5°; \( h_{\text{min}} = -15 \), \( h_{\text{max}} = 15 \), \( k_{\text{min}} = -16 \), \( k_{\text{max}} = 15 \), \( l_{\text{max}} = 15 \)) were carried out on a Siemens R3m/V four-circle diffractometer (MoKα, 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 \( R = 0.076 \), \( R_w = 0.070 \); reflection data to parameter ratio = 12.93. The electron density of the largest difference peak was found to be 1.56, while that of the largest difference hole was 1.28 eÅ⁻³.

* “Novel concepts in directed biaryl synthesis”, part 46; for part 45, see Lit. [1].

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Results and Discussion

\( \text{C}_2\text{H}_6\text{Br}_4\text{O}_4\cdot\text{CHCl}_3 \), 903.47 g mol\(^{-1}\), crystallizes in the triclinic system, space group \( \text{P}\overline{1} \), with \( a = 1226.6(3) \text{ pm} \), \( b = 1246.9(3) \text{ pm} \), \( c = 1218.8(3) \text{ pm} \), \( \alpha = 107.50(2)° \), \( \beta = 90.94(2)° \), \( \gamma = 113.56(2)° \), \( V = 1609.5(7) \text{ pm}^3 \cdot 10^6 \) and \( Z = 2 \). The density was calculated to be 1.864 g cm\(^{-3}\). Atomic parameters are listed in Table I according to the atom labels of Fig. 1.* The X-ray structure analysis indeed con-

Table I. Positional parameters (\( \times 10^4 \)) and equivalent isotropic displacement parameters (pm\(^2\)\( \times 10^{-1} \)) of 3.

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* Further crystal structure data may be obtained from the Fachinformationszentrum Karlsruhe, GmbH, D-76344 Eggenstein-Leopoldshafen, by quoting the Registry No. CSD 401125.

Fig. 1. Perspective drawing of 3 with the labelling of the atoms corresponding to Table I.

firms the constitution of diester 3, as anticipated from its synthesis and its spectroscopic properties, as well as the presence of one molecule chloro­form per molecule diester as also evident from a combustion analysis. In the crystal the CHCl\(_3\) molecule is statistically disordered with the carbon atom on both sides of the Cl\(_3\) plane. The position of this atom was refined within that plane because of unsuccessful splitting attempts. The corresponding hydrogen atom was omitted from the list of parameters.

With respect to the structure of the diester 3, the three aromatic bicyclic systems are, as expected, practically planar. Of interest is the stereochemical array of the ester bridges, showing the transoid conformation for a sequence C(10)-O(23)-C(24)-C(25), which is nearly identical to the sequence C(1)-O(11)-C(12)-C(13) concerning the respective bond length and angles. Possibly due to the bulky bromo substituents at C(14) and C(26), the ester functionalities do not adopt a co-planar conformation with respect to the aromatic rings of the naphthoic acid parts, thus lacking the possi-
bility of profiting of an energetically favorable conjugation with the aromatic system. Moreover, in order to minimize steric interactions between the two naphthoic acid parts, the two O-naphthoate substituents at C(1) and C(10) adopt anti-conformations with respect to the dioxynaphthalene plane, thus giving rise to a C2-related conformation of the molecule. Important with respect to the synthetic problem to be solved, is the fact that the two scheduled coupling sites C(2) and C(9) on the central naphthalene part are very far away from their expected counterparts C(14) and C(26) on the naphthoate moieties, due to the mentioned steric constraints and the resulting transoid ester conformations. This conformational behavior, although not necessarily relevant for the behaviour in solution, may be a first explanation why, in preliminary coupling experiments, 3 could not be coupled to the desired octacyclic dilactone system 2, thus requiring to develop alternative strategies for the synthesis of this important intermediate.

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