

STRUCTURE ANALYSIS OF NEW SPIRO AND DISPIRO SYSTEMS WITH SEVEN-MEMBERED RING USING CLASSICAL AND SYNCHROTRON RADIATION SOURCES

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Spirane is a compound having one atom (usually a quaternary carbon) as the only common member of two rings. The common atom is known as the spiro atom. [1] Spirane is called heterocyclic if the ring is composed, besides carbon atoms, of two or more different kinds of atoms, *e.g.* O, S. Spiranes appearing in naturally originated compounds and those of synthetic origin may appear in the form of monospiranes (with one spiro atom) and polyspiranes (with more than one spiro atom) (Fig. 1).

Interest in spirane systems has grown during recent years because of their potential use for stereochemical studies and theoretical calculations [2]. Furthermore, some of these systems were detected as parts of natural products possessing antibiotic and fungicide activity [3]. Studies carried out in our laboratory were connected with compounds containing 1,5-dioxepine or 1,5-dithiepine systems with various substituents [4].

Tetratosylate of 1,1,2,2-tetrakis(hydroxy-methyl)cyclopentane was employed as a substrate in a reaction scheme leading to constitutionally symmetrical seven-membered dispiranes with oxygen and sulfur heteroatoms. In both cases an alternative product, the eight-membered propellane was not obtained. A propellane consists of three rings fused by two common atoms (Figure 2).

Due to complex geometry, spiranes may appear in several isomeric forms.

Spiranes may appear as:

- optical isomers (axial and helical) [5] - related by a centre of inversion,
- constitutional isomers with different sequence of connected atoms and with different spiro ring size,
- ring reversal isomers related by ring inversion [6] (Fig. 3).

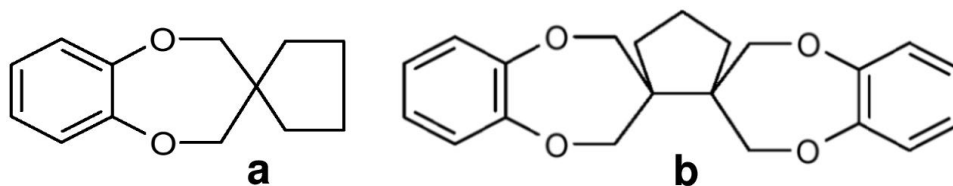


Figure 1. Seven-membered ring - mono (a) and dispirane (b)

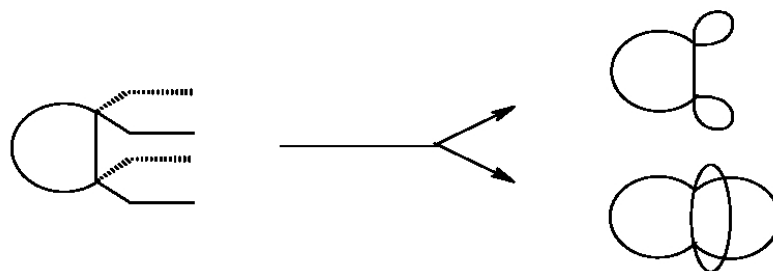


Figure 2. General reaction scheme leading to dispirane (above) and its propellane isomer.

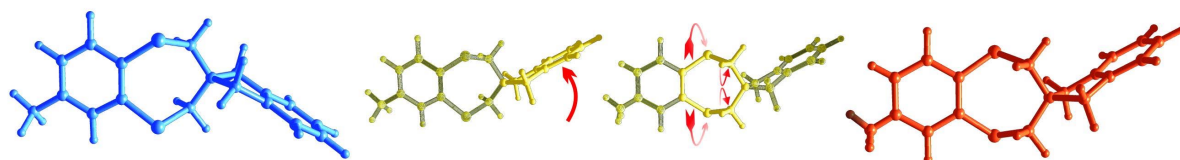


Figure 3. Spiro isomers differentiated by inversion of both seven- and five-membered rings.

Crystal structure analysis of new spiranes synthesized at the Department of Organic Chemistry, Jagiellonian University was carried out to identify connectivity scheme and possible isomeric forms, as well as provide description of the molecular conformations. Since the diffraction pattern was recorded on single-crystal samples selected from bulk material, also phase analysis was carried out to characterise the bulk sample, *i.e.*, to detect the possible presence of polymorphs and other phases.

The refined structural models were compared with previously published molecular structures of dispiranes [7, 8] and used as starting models for energy minimisation calculations, providing structural data bank for seven-membered ring systems.

Two further, poorly crystallising, dispirane homologues $C_{23}H_{26}S_4$ and $C_{23}H_{26}O_4$ did not afford single crystals suitable for single-crystal diffraction experiment, therefore an attempt was undertaken to base the structure elucidation on high-resolution powder diffraction using synchrotron radiation. The experiment was carried out at room temperature on the B2 beamline at DESY-HASYLAB using capillary mount and 0.71003 Å wavelength, with primary beam collimator and scintillation counter with analyzer crystal to enhance resolution (Fig. 4). Structure solution using global optimisation techniques and starting models as

calculated by quantum-mechanical energy minimisation at various levels of the theory is in progress.

Acknowledgments: The measurements were carried out under DESY-HASYLAB Project I-01-041. This work was supported by the IHP Contract HPRI-CT-1999-00040/2001-00140 of the European Commission.

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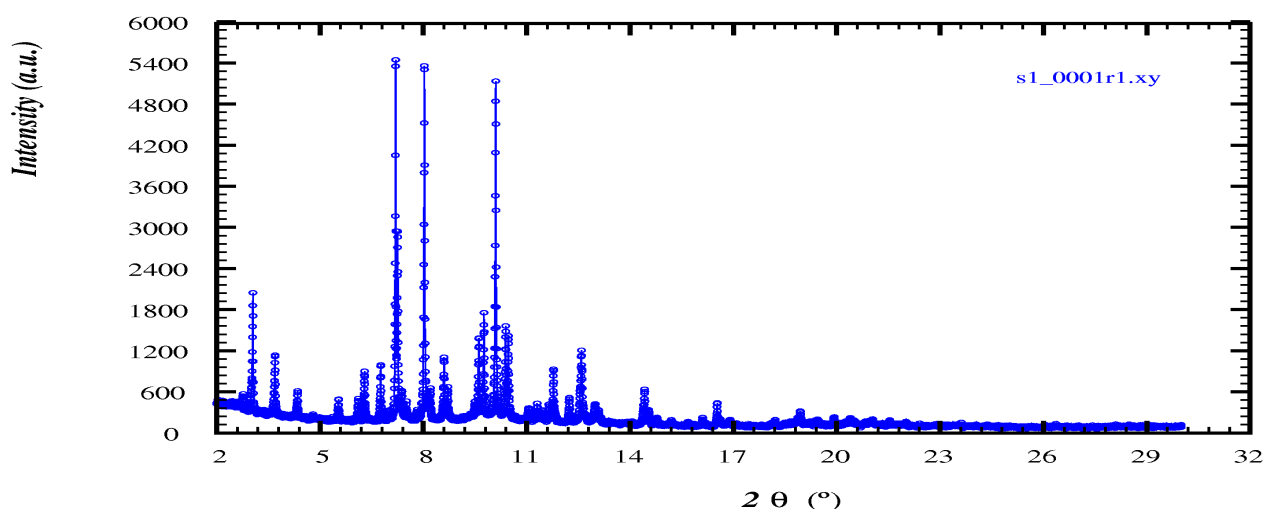


Figure 4. High-resolution powder pattern for $C_{23}H_{26}S_4$ recorded up to sample diffraction limit.