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X-Ray structure of the inherently dissymmetric olefin D,L-*trans*-1,2,3,4,1',2',3',4'-octahydro-4,4'-biphenanthrylidene

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Abstract. X-Ray data for inherently dissymmetric D,L-*trans*-1,2,3,4,1',2',3',4'-octahydro-4,4'-biphenanthrylidene are presented; the molecular symmetry is C_2 . Small double-bond torsion and twist boat cyclohexene conformations have been established.

X-Ray structure of the inherently dissymmetric olefin D,L-*trans*-1,2,3,4,1',2',3',4'-octahydro-4,4'-biphenanthrylidene

Chiroptical studies associated with olefinic chromophores¹ and the role of π -bond torsion in olefinic double bonds^{2,3} are the subject of continuing interest during recent years. Interconversions between folded – and twisted – conformations of bisfluorenylidene, bianthrone and biacridans have been examined by temperature dependent NMR spectroscopy⁴. X-Ray analysis⁵ revealed a double bond torsion of 39° in the 1,1'-bis(isopropoxycarbonyl)-9,9'-bifluorenylidene, although no separation into enantiomers could be achieved of any of these possibly dissymmetric olefins.

Recently we were able to resolve both the *cis* – as well as – the *trans*-form of the inherently dissymmetric 1,2,3,4,1',2',3',4'-octahydro-4,4'-biphenanthrylidene⁶ (**1**). X-Ray data of these olefins could furnish information concerning the amount of torsion in the pivot double bond, as well as the distortions in other parts of the skeleton and the helical shape of this molecule.

We now report the X-Ray crystal structure of D,L-*trans*-1,2,3,4,1',2',3',4'-octahydro-4,4'-biphenanthrylidene (**1**).

Crystal data: $C_{28}H_{24}$, tetragonal, space group $I4$, $a = b = 13.234$ (5) Å, $c = 11.444$ (5) Å, $d(X) = 1.195$ g·cm⁻³, $Z = 4$.

The intensities of 1211 reflections ($\theta \leq 27.5^\circ$) were collected with an ENRAF NONIUS CAD4 diffractometer, using Zr-filtered MoK α -radiation ($\omega/2\theta$ -scan mode). 265 Reflections had intensities $< 2.5 \sigma(I)$. The crystal structure was solved by direct methods (MULTAN77-SYSTEM) and refined by full-matrix least-squares techniques (XRAY76-SYSTEM) with weights based on counting statistics.

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The final $R_F = 0.018$ (including hydrogen atoms) for 946 reflections. The structure of the molecule and the adopted numbering scheme are pictured in figures 1 and 2.

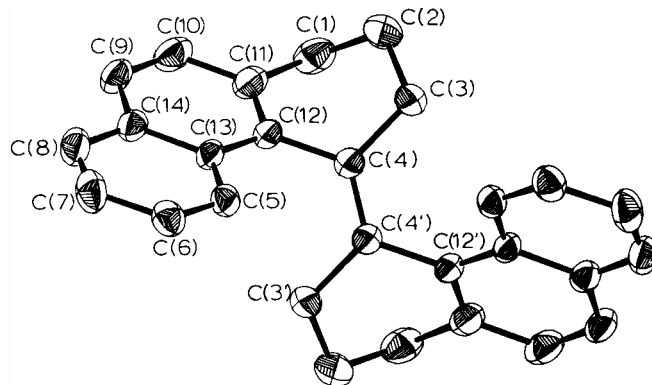


Fig. 1. The molecule of **1** seen along the molecular C_2 -axis (coinciding with the crystallographic 4-axis) with adopted numbering of atoms.

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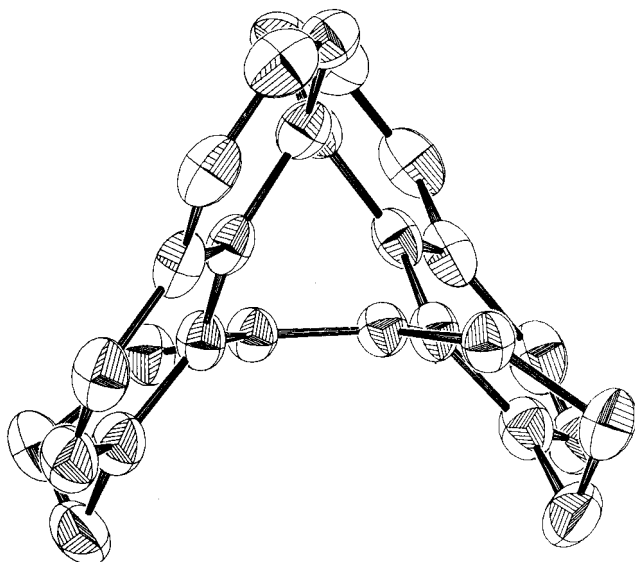


Fig. 2. The molecule of **1** seen along the line through the center of C(4)–C(4'), perpendicular on the C₂-axis and the C(4)–C(4') bond.

The molecular symmetry is C₂ (see fig. 1).

Twisted-boat conformations are present in both cyclohexene moieties. Only small distortions from planarity are present in the naphthalene moieties; deviations from least-squares plane through the naphthalene moiety: C(5) 0.025 Å, C(6) 0.048, C(7) 0.004, C(8) –0.027, C(9) –0.004, C(10) 0.050, C(11) 0.034, C(12) –0.060, C(13) –0.040, C(14) –0.028. Small double bond torsion and deviation from planarity around the double bond carbon atoms (non-ideal sp²-hybridization) is present (figure 3). A normal double bond length was found for the central double bond. [C(4)–C(4') = 1.357 (4) Å].

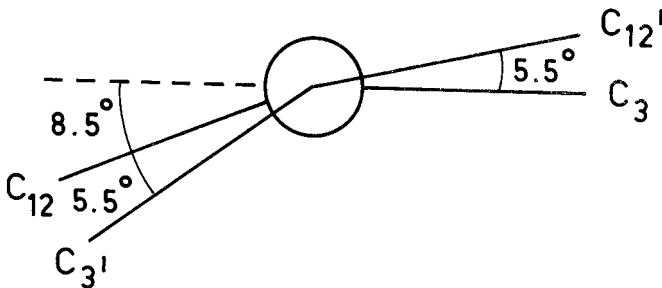


Fig. 3. Projection of the molecule **1** seen along the C(4')–C(4) pivot double bond, with torsion angles.

Recently Mock et al.⁷, on basis of molecular orbital calculations and the analysis of vibrational frequencies, indicated that out-of-plane deformations in ethylene are not

Table Bond distances and angles (standard deviations in parentheses).

C(1)–C(2)	1.528(6) Å	C(11)–C(1)–C(2)	107.9(4)°
C(1)–C(11)	1.494(6)	C(1)–C(2)–C(3)	111.5(3)
C(2)–C(3)	1.561(6)	C(2)–C(3)–C(4)	111.9(3)
C(3)–C(4)	1.522(5)	C(3)–C(4)–C(4')	122.3(3)
C(4)–C(4')	1.357(4)	C(4')–C(4)–C(12)	122.0(3)
C(4)–C(12)	1.496(4)	C(6)–C(5)–C(13)	122.5(3)
C(5)–C(6)	1.360(6)	C(5)–C(6)–C(7)	119.7(4)
C(5)–C(13)	1.414(5)	C(6)–C(7)–C(8)	120.2(4)
C(6)–C(7)	1.406(5)	C(7)–C(8)–C(14)	122.2(3)
C(7)–C(8)	1.329(6)	C(10)–C(9)–C(14)	121.8(4)
C(8)–C(14)	1.417(5)	C(9)–C(10)–C(11)	121.0(4)
C(9)–C(10)	1.354(6)	C(1)–C(11)–C(10)	122.3(4)
C(9)–C(14)	1.405(6)	C(1)–C(11)–C(12)	118.1(3)
C(10)–C(11)	1.410(6)	C(10)–C(11)–C(12)	119.5(3)
C(11)–C(12)	1.388(5)	C(4)–C(12)–C(11)	115.6(3)
C(12)–C(13)	1.428(5)	C(4)–C(12)–C(13)	124.2(3)
C(13)–C(14)	1.433(5)	C(11)–C(12)–C(13)	120.2(3)
		C(5)–C(13)–C(12)	124.5(3)
		C(5)–C(13)–C(14)	116.6(3)
		C(12)–C(13)–C(14)	118.9(3)
		C(8)–C(14)–C(13)	118.8(3)
		C(9)–C(14)–C(13)	118.4(3)
		C(8)–C(14)–C(9)	122.8(3)
		C(3)–C(4)–C(12)	115.3(2)

pure torsions; they are accompanied by significant bending and hence pyramidalization of the bonds at the double bond C atoms. Similar effects are observed in the structure of **1** (figure 3). Furthermore most of the steric interactions in **1** are relieved by adopting the twisted-boat conformations in the cyclohexene moieties making only small double bond torsion necessary. The latter effect may be energetically inexpensive⁷.

Recent calculations on rotational strength indicate torsion of the olefin chromophore as a dominant contribution in determining sign and magnitude of Cotton effects³. It is not clear at the moment to which extent the π -bond torsion explains the large effects observed in the ORD, CD spectra of **1**. The large dihedral angle (56.6°) between the least-squares planes through the naphthalene group and the double bond moiety indicates that conjugation between the naphthalene moieties is strongly reduced. Therefore the bisignate Cotton effects observed at the short wavelength part of the ORD, CD spectra of **1** are probably due to exciton coupling of the naphthalene chromophores.

⁷ W. L. Mock, *Tetrahedron Lett.* 475 (1972); L. Radom, J. A. Pople and W. L. Mock, *Tetrahedron Lett.* 479 (1972).

⁸ N. Harada and K. Nakanishi, *Accounts Chem. Res.* 5, 257 (1972).