

Benzo[*i*]naphtho[*c,d*]bicyclo[5.4.1]-
dodecan-12-oneShin-ichiro Isobe,^a Kanji Kubo,^b Thies Thiemann,^b
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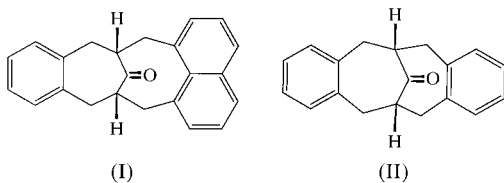
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In the title compound, pentacyclo[11.8.1.1^{3,11}.0^{7,23}.0^{15,20}]-tricoso-3,5,7,9,11(23),15,17,19-octaen-22-one, C₂₃H₂₀O, the bicyclo[5.4.1]dodecan-12-one moiety takes a rigid conformation in which the seven- and eight-membered rings take chair and boat–boat forms, respectively. The molecule has a non-crystallographic mirror symmetry perpendicular to the benzene and naphthalene planes.

Comment

Dibenzobicyclo[4.4.1]undeca-3,8-dien-11-one, (II), which has two seven-membered rings in the molecular structure, exists in a stereodynamic equilibrium between two equivalent chair–boat conformers in solution and in a chair–boat conformation in the solid state, as clarified by X-ray crystal structural analysis (Mataka *et al.*, 1987, 1989; Taniguchi *et al.*, 1998). Molecule (II) is an important precursor of layered compounds, which are interesting study objects for the π – π interaction of facing closely stacked π systems (Mataka *et al.*, 2000). Moreover, it is a starting material for the generation of non-classical cations (Isobe *et al.*, 1999).



The title compound, (I), was found by ¹H and ¹³C NMR in solution to be a rigid composite system of a seven-membered ring in a chair conformation and an eight-membered ring in a boat–boat form. The ¹³C chemical shift values for the methylene C1 and C16 atoms of the seven-membered ring of (I) show a down-field shift of about 4 p.p.m., compared with

the values found for the chair-conformed seven-membered ring of (II).

Due to these results and in order to assess whether (I) can also be a suitable precursor of structures with layered π -systems, we carried out its X-ray crystal structural analysis to gain a better understanding of the rigid composite system of a seven- and eight-membered ring.

As seen in Fig. 1, the molecule has a chemical mirror plane (local C_s symmetry) perpendicular to the benzo and naphtho planes. The seven- and eight-membered rings adopt chair and boat–boat forms, respectively [for nomenclature of cyclo-

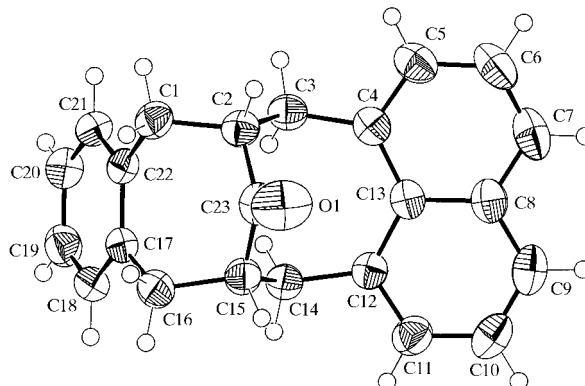


Figure 1

The molecular structure of (I) showing 50% probability displacement ellipsoids.

octane conformers, see Pakes *et al.* (1981)]. The boat–boat conformation in the saturated cyclooctane, which is of D_{2d} symmetry and which corresponds to the C_s symmetry in mono-substituted cyclooctane derivatives, is usually energetically disfavored, where the energy of the conformer is strongly dependent on the repulsion of the apically situated 1,5-H atoms and thus on their distance. For that reason, boat–boat-conformed cyclooctanes often take a twisted boat–boat conformation of lesser symmetry, *i.e.* C₂-symmetry for non-substituted cyclooctane. As the apical C13 and C23 atoms in (I) are sp² hybridized, this absence of protons means the cyclooctane moiety can adopt a rigid non-twisted boat–boat conformation of higher symmetry due to the annelation of the naphtho group (Table 1).

Within the seven-membered ring of (I), the angle between the planes defined by C1/C2/C15/C16 and C1/C16/C17/C22 is 55.3 (1)°, which is larger than the corresponding angle in (II) of 52.2 (1)°. This result indicates that the strain in the seven-membered ring of (I) is bigger than in that of (II), which coincides with the chemical shift by 4 p.p.m. down-field in the ¹³C NMR of the benzylic C1 and C16 atoms in (I), compared with those in (II).

The difference in the conformations of (I) and (II) is also reflected in their chemical reactivity. Thus, conformationally more flexible compound (II) is easily transformed to rigid layered [3.3]orthocyclophane carbinols by the Grignard reaction (Mataka *et al.*, 1987). The same transformation is extremely difficult to achieve in (I) due to the conformationally rigid eight-membered ring.

Experimental

The title compound was prepared from dimethylnaphtho[3,4,5-*de*]-benzo[9,10]bicyclo[5.4.1]dodeca-3,9-dien-12-one-1,6-dicarboxylate (Mataka *et al.*, 1986) *via* hydrolysis of the diester and subsequent pyrolysis of the obtained dicarboxylic acid. The crystal used for the X-ray structure analysis was obtained by recrystallization of (I) from benzene.

Crystal data

$C_{23}H_{20}O$	$D_x = 1.263 \text{ Mg m}^{-3}$
$M_r = 312.39$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/a$	Cell parameters from 24 reflections
$a = 12.455 (5) \text{ \AA}$	$\theta = 9.5\text{--}18.1^\circ$
$b = 12.401 (5) \text{ \AA}$	$\mu = 0.075 \text{ mm}^{-1}$
$c = 11.140 (5) \text{ \AA}$	$T = 296 (2) \text{ K}$
$\beta = 107.259 (5)^\circ$	Prism, colorless
$V = 1643.1 (12) \text{ \AA}^3$	$0.33 \times 0.30 \times 0.13 \text{ mm}$
$Z = 4$	

Data collection

Enraf–Nonius FR590 diffractometer	$R_{\text{int}} = 0.027$
ω – 2θ scans	$\theta_{\text{max}} = 27.98^\circ$
Absorption correction: ψ scan (North <i>et al.</i> , 1968)	$h = -16 \rightarrow 0$
$T_{\text{min}} = 0.962$, $T_{\text{max}} = 0.999$	$k = 0 \rightarrow 16$
4131 measured reflections	$l = -14 \rightarrow 14$
3953 independent reflections	3 standard reflections
1964 reflections with $I > 2\sigma(I)$	frequency: 120 min
	intensity decay: 4.3%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0602P)^2 + 0.0421P]$
$R[F^2 > 2\sigma(F^2)] = 0.051$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.141$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 0.991$	$\Delta\rho_{\text{max}} = 0.18 \text{ e \AA}^{-3}$
3953 reflections	$\Delta\rho_{\text{min}} = -0.22 \text{ e \AA}^{-3}$
217 parameters	
H-atom parameters constrained	

The positional parameters of the H atoms were calculated geometrically and refined using a riding model. Their U_{iso} values were fixed to 1.2 or 1.5 (H_2O) times U_{eq} of the bonded non-H atoms.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *MolEN* (Fair, 1990);

Table 1

Selected torsion angles ($^\circ$).

C23–C2–C3–C4	–47.8 (2)	C13–C12–C14–C15	–75.5 (2)
C2–C3–C4–C13	81.4 (2)	C12–C14–C15–C23	54.9 (2)
C14–C12–C13–C4	–2.0 (3)	C14–C15–C23–C2	57.8 (3)
C3–C4–C13–C12	–4.0 (3)	C3–C2–C23–C15	–63.9 (3)

program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *Xtal_GX* (Hall & du Boulay, 1995); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB1037). Services for accessing these data are described at the back of the journal.

References

- Altomare, A., Burla, M. C., Camalli, M., Cascarano, G. L., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.
- Enraf–Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
- Fair, C. K. (1990). *MolEN*. Enraf–Nonius, Delft, The Netherlands.
- Hall, S. R. & du Boulay, D. (1995). *Xtal_GX*. University of Western Australia, Australia.
- Isobe, S., Taniguchi, M., Sawada, T., Thiemann, T., Yonemitsu, T. & Mataka, S. (1999). *J. Chem. Soc. Perkin Trans. 1*, pp. 2101–2107.
- Mataka, S., Mimura, T., Lee, S. T., Kobayashi, H., Takahashi, K. & Tashiro, M. (1989). *J. Org. Chem.* **54**, 5237–5241.
- Mataka, S., Takahashi, K., Hirota, T., Takuma, K., Kobayashi, H. & Tashiro, M. (1986). *J. Org. Chem.* **51**, 4618–4622.
- Mataka, S., Takahashi, K., Mimura, T., Hirota, T., Takuma, K., Kobayashi, H. & Tashiro, M. (1987). *J. Org. Chem.* **52**, 2653–2656.
- Mataka, S., Thiemann, T., Sawada, T. & Taniguchi, M. (2000). *Synlett*, pp. 1211–1227.
- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- Pakes, P. W., Rounds, T. C. & Strauss, H. L. (1981). *J. Phys. Chem.* **85**, 2469–2475.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
- Taniguchi, M., Mataka, S., Thiemann, T., Sawada, T., Mimura, K. & Mitoma, Y. (1998). *Bull. Chem. Soc. Jpn.* **71**, 2661–2668.