

Conformational Analysis of Spirocyclopropane- and Spirooxirane-annulated Dibenzobicyclo[4.4.1]undecanes by ^1H NMR Spectroscopy and X-Ray Crystallography

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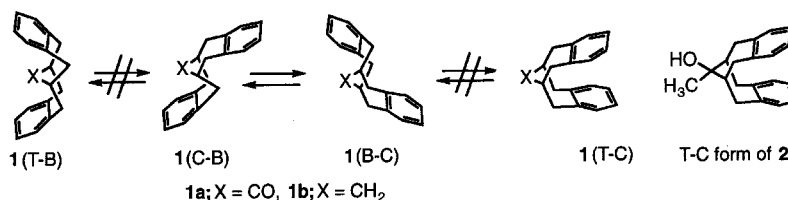
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Conformational behaviour of dibenzo[*c,h*]bicyclo[4.4.1]undecanes having a dichloro- and a dibromo-cyclopropane ring, together with an oxirane ring on the methylene bridge, has been studied by ^1H NMR spectroscopy and X-ray crystallography.

Of the possible conformations of bicyclo[4.4.1]undecane, the twin-boat type usually is the most unstable and the twin-chair the most stable. The twin-chair conformer is unstable in the case of dibenzobicyclo[4.4.1]undecane **1**, owing to electronic repulsion between the π -electrons of the two layered benzo-unit, and thus **1** exists as an equilibrium mixture of the chair-boat and boat-chair conformers.¹ A twin-chair conformation with layered benzo-units is seen in the acetal and the alcohol **2** (Scheme 1),^{4,5} which have substituents on the methylene bridge of a dibenzobicyclo[4.4.1]undecane system.



Scheme 1

The present article reports on the conformational behaviour of dibenzobicyclo[4.4.1]undecanes having a spiro-annulated three-membered ring on the methylene bridge.

The methylene derivative **3** was prepared by dehydration of the alcohol **2** and converted into the spirocyclopropanes **4** and **5** by [2 + 1] cycloaddition with dihalocarbenes.^{6,7} Reductive removal of the halogen substituents of **4** with LiAlH_4 ⁸ gave **6**. In contrast, the dichloro derivative **5** gave a mixture of **6** and the monochloro derivative **7**. The desired **6** was more conveniently prepared by a Simmons–Smith reaction.⁹ Oxirane **8** was obtained by epoxidation¹⁰ with *m*-chloroperoxybenzoic acid (*m*-CPBA) (Scheme 2).

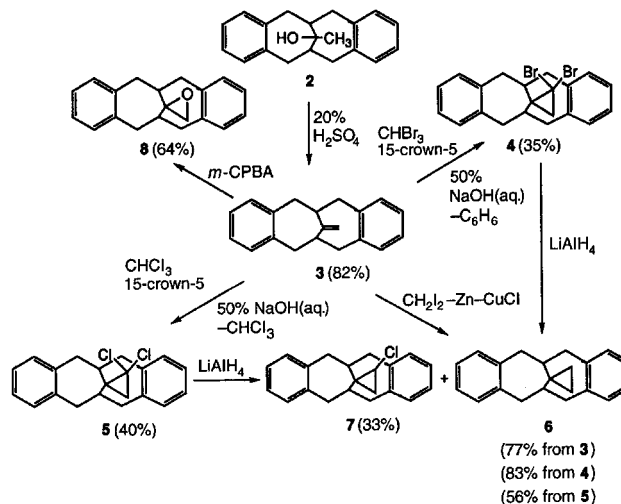
The flexible **6** exists at room temperature as an equilibrium of a mixture of the two indistinguishable chair-boat (C-B) and boat-chair (B-C) conformers. In the ^1H NMR spectrum of **6** at -60°C , one of the two methylene groups of the spirocyclopropane moiety shows an up-field shift, since the methylene protons are shielded by the ring current of the benzene ring of the boat-like benzocycloheptene unit.

Introduction of halogen atoms does not fix the conformation of **4**, **5** or **7**, while oxirane **8** is also flexible (Scheme 3). The conformer ratios for **4**, **5** and **8** are given in Table 1. The ratio of **7** could not be determined because of overlapping of the signals. The parameters ΔH° , ΔS° , and ΔG° for **4**, **5** and **8** were determined from the signals for the methylene protons of the spirocyclopropane rings and the oxirane ring in variable temperature ^1H NMR spectra in CDCl_3 run over a temperature range from -60 to 0°C (Fig. 1 and Table 2).

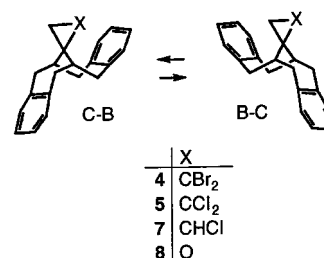
The predominant conformation of **4** and **5** in solution is the C-B type, although it could be expected that the C-B confor-

mation, in which the dihalogenomethylene group is positioned above the boat-like benzocycloheptene ring, might be sterically less preferable. On the other hand, **4** takes the B-C conformation in the solid state, as revealed by X-ray crystallographic analysis (Fig. 2).

The conformer ratio of **5** is dependent on the E_T -30 value of the solvent. With an increase in E_T -30, the proportion of C-B conformer tends to increase. The solvent effect is less clear in **4**. These facts seem to be in agreement with PM3 calculations of the dipole moment: the calculated dipole



Scheme 2



Scheme 3

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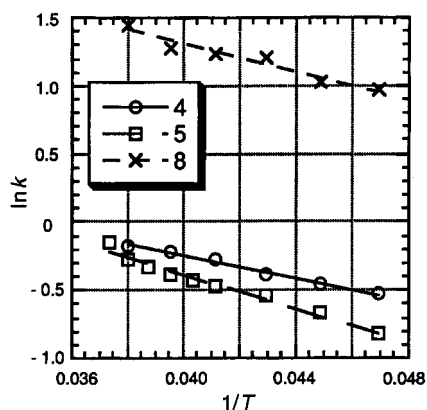


Fig. 1 van't Hoff plot for 4, 5 and 8

moment of the C-B conformer is larger than that of the B-C conformer and the difference between the values is larger in 5 than in 4.

The oxirane 8 prefers the B-C conformation in order to avoid the electronic repulsion between the lone-pair electrons of the oxygen atom and the π -electrons of the benzene ring. The ratio for 8 is more temperature-dependent than

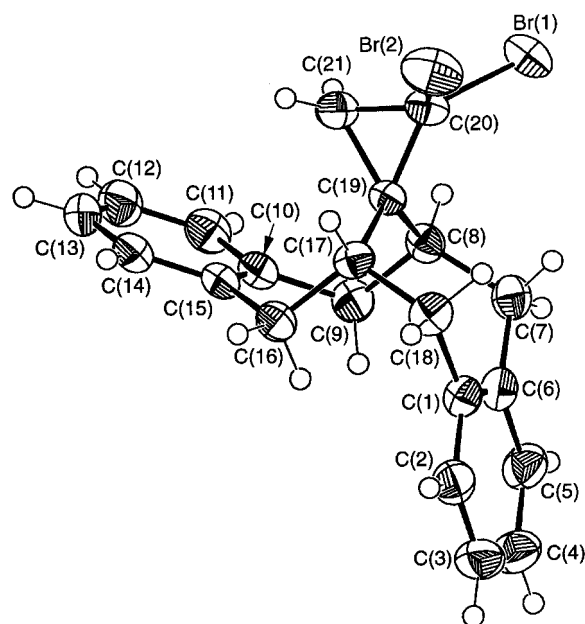


Fig. 2 ORTEP drawing of 4

Table 1 Conformer ratios^a and calculated dipole moments of 4, 5 and 8

Compd.	Dipole moment ^b (B-C/C-B)	Ratio of B-C/C-B conformers in solvent (E_T -30)				
		[² H ₆]Acetone (42.2)	CD ₂ Cl ₂ (41.1)	CDCl ₃ (39.1)	[² H ₈]THF (37.4)	[² H ₈]Toluene (33.9)
4	1.21 D/1.35 D	40/60	37/63	37/63	47/53	43/57
5	1.07 D/1.61 D	28/72	29/71	31/69	40/60	43/57
8	1.38 D/2.06 D	90/10	71/29	68/32	100/0	100/0

^aAt -60 °C. ^bPM 3 calculation.

Table 2 Parameters ΔH° , ΔS° and ΔG° for the B-C and C-B equilibria^{a,b}

Compd.	ΔH° (kJ mol ⁻¹)	ΔS° (J mol ⁻¹ K ⁻¹)	ΔG° (kJ mol ⁻¹) ^c
4	3.49	11.9	-0.06
5	5.15	17.4	-0.04
8	4.91	28.6	-3.61

^aIn CDCl₃. ^b $K = [B-C]/[C-B]$. ^cAt 25 °C.

those for 4 or 5 (Fig. 1); it is estimated that in chloroform at 25 °C, more than 99% of 8 exists as the B-C conformer, having a smaller calculated dipole moment. The large difference in ΔS° for 8 may reflect tight solvation on the oxygen atom in the B-C conformer as compared to the C-B conformer.

Crystal Data for 4.—C₂₁H₂₀Br₂, $M_r = 432.19$, orthorhombic, $a = 24.926(6)$, $b = 17.125(1)$, $c = 8.253(2)$ Å, $V = 3522.9(12)$ Å³, $D_c = 1.630$ g cm⁻³, space group $Pbca$, $Z = 8$, $F(000) = 1728$, $\mu(\text{CuK}\alpha) = 5.791$ cm⁻¹. Data were collected on an Enraf Nonius CAD-4 diffractometer using a graphite monochromator with CuK α radiation ($\lambda = 1.54184$ Å). The structure was solved by direct methods (SIR 92).¹¹ The final R value was 0.033 ($R_w = 0.0886$). The estimated standard deviations for the geometrical parameters involving non-hydrogen atoms lie within the following ranges: bond lengths, 0.004–0.006 Å; bond angles 0.2–0.4°.

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Techniques used: IR, ¹H NMR, mass spectrometry

References: 11

Schemes: 3

Figures: 2

Tables 3–6: Bond lengths and angles, fractional atomic coordinates and equivalent isotropic thermal parameters, and anisotropic thermal parameters for 4

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