

SYNTHESIS AND CONFORMATIONAL ANALYSIS OF THE THREE 3,7-DIMETHYLBICYCLO[3.3.1]NONANES

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Abstract—The stereospecific synthesis of the three isomers of 3,7-dimethylbicyclo[3.3.1]nonane is described. The conformations of these compounds were studied with the use of ¹³C and ¹H NMR spectroscopy. The 3β,7β-dimethyl derivative exists predominantly in the *cc* conformation, the 3α,7β-dimethyl derivative predominantly in the *bc* conformation, whereas 3α,7α-dimethylbicyclo[3.3.1]nonane exists as a mixture of the *cb/bc* and the *t-bb* conformations, which rapidly interconvert. The Δ*H* and Δ*S* values for the conformational equilibrium in question, were determined by variable temperature ¹³C NMR. The results of these experiments fit well with those of molecular mechanics. The enthalpies of activation of the interconversion of the various conformers of 3α,7α-dimethylbicyclo[3.3.1]nonane were also calculated and compared with those of the parent system bicyclo[3.3.1]nonane.

The chemistry of bicyclo[3.3.1]nonanes is of interest because of the relation of these compounds with several natural products (e.g. alkaloids) as well as with adamantanoid compounds. In particular, the 3- and 7-substituted bicyclo[3.3.1]nonanes are potential precursors of otherwise difficult accessible 1,2-disubstituted adamantane derivatives.² In addition, the bicyclo[3.3.1]nonane system shows some interesting conformational features.^{3,4} Three groups of conformations must be envisaged: (i) the rigid double chair conformation (*cc*), (ii) the rigid chair-boat conformations (*cb*, *bc*), and (iii) the flexible double boat conformations (*bb*, *t-bb*). For the systems studied up to now, the eclipsed double boat conformation (*bb*) appeared to be a transition state between the two double twist-boat conformations (*t-bb*). Severe interactions between both six-membered rings occur in all bicyclo[3.3.1]nonane conformations, e.g. in the *cc*, H_{2a} and H_{7a} are in close proximity, whereas in the *bc* unfavourable interactions occur between H_{2a}/H_{4a} and H_{7a} and between H_{3β} and one of the H₉ atoms. Consequently, the wings in both the *cc* and the *bc* are strongly flattened.⁴

It is now well-established that in bicyclo[3.3.1]nonane (1) the energy difference between the *cc* and the *bc* is 10.5 kJ mole⁻¹,⁴⁻⁷ whereas the energy difference between the *bc* and the *t-bb* is computed to be 22.6 kJ mole⁻¹.⁴ Substituents at the 3- and 7-positions have a strong influence on the conformational preferences.⁴ A substituent at the 3β- or 7β-position stabilizes the *cc*; on the other hand a 3α/7α-group forces the substituted wing into the boat conformation. When substituents are present on both the 3α- and 7α-positions, the *cc* is strongly disfavoured, whereas the population of the other conformations depends on the size of the substituents. With two bulky groups such as in compound 2 (Scheme 1), the *t-bb* predominates; with one small and one bulky group both the *t-bb* and the *cb* contribute (e.g. compounds 3, 4). When the 3α- and 7α-substituents are small (e.g. compounds 5-8) both the *cb* and the *bc* can contribute. A special situation arises when the 3α- and 7α-positions are substituted with small and identical groups: then the *cb* and the *bc* are isometric and play an important role. The dicarboxylic acid 6 and its di-Me ester 7 have been shown to exist predominantly of the rapidly

interconverting *cb* and *bc*,^{3,8} which is reflected in averaged ¹H and ¹³C signals for the exchanging nuclei in the two wings of the system. The interconversion is fast with respect to the NMR time scale, therefore, until now no activation energy for this interconversion could be determined. Empirical force field calculations seem an attractive approach to obtain an estimate of this barrier. This method has been shown to be a very reliable tool for the determination of the energy barriers between conformations, in particular of hydrocarbons.⁹

From an extrapolation of the conformational data of compounds 3-7 it may be expected that in 3α,7α-dimethylbicyclo[3.3.1]nonane (8) the *t-bb* and the *cb/bc* are populated. Therefore, this compound seems suitable for the determination of conformational energies and energy barriers. The present investigation deals with a conformational analysis of that compound with the use of ¹H and ¹³C NMR spectroscopy and molecular mechanics. For comparison the two epimeric 3,7-dimethylbicyclo[3.3.1]nonanes (9-10) are included in the ¹³C NMR study. Stereoselective syntheses of the three isomers are described.

RESULTS AND DISCUSSION

Syntheses

The three epimeric 3,7-dimethylbicyclo[3.3.1]nonanes (8-10) have been synthesized by Zefirov *et al.* via catalytic hydrogenation of 3,7-dimethylenebicyclo[3.3.1]nonane, but the configurations of these compounds were not established.¹⁰ In the present study, the corresponding methyl 7-methyl-9-oxobicyclo[3.3.1]nonane-3-carboxylates, the configuration and the conformation of which has been established previously,¹¹ were used as starting compounds in the synthesis of compounds 8-10.

A Clemmensen reduction of methyl 7α-methyl-9-oxobicyclo[3.3.1]nonane-3α-carboxylate (11) gave exclusively the corresponding 9-CH₂ compound 12 (Scheme 2). Then, reduction with LAH yielded the 3α-hydroxymethyl derivative 13, which was converted into the desired 3α,7α-dimethylbicyclo[3.3.1]nonane (8) via tosylation and another LAH reduction. Starting from methyl 7β-methyl-9-oxobicyclo[3.3.1]nonane-3α-car-

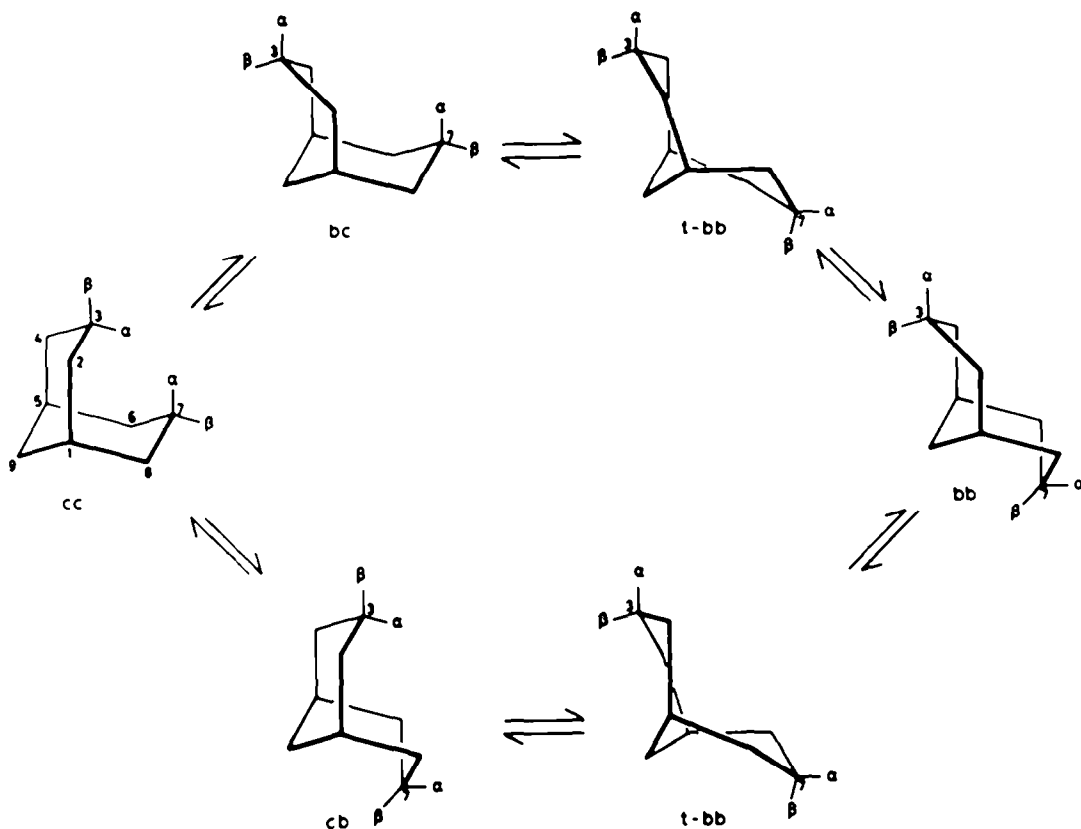
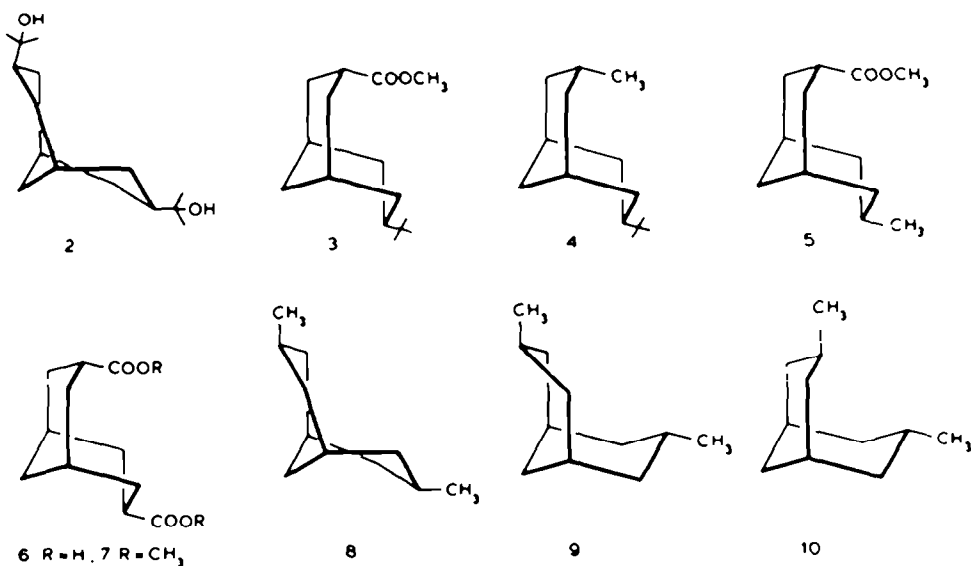


Fig. 1. Schematic representations of the conformations of bicyclo[3.3.1]nonane (1).



Scheme 1.

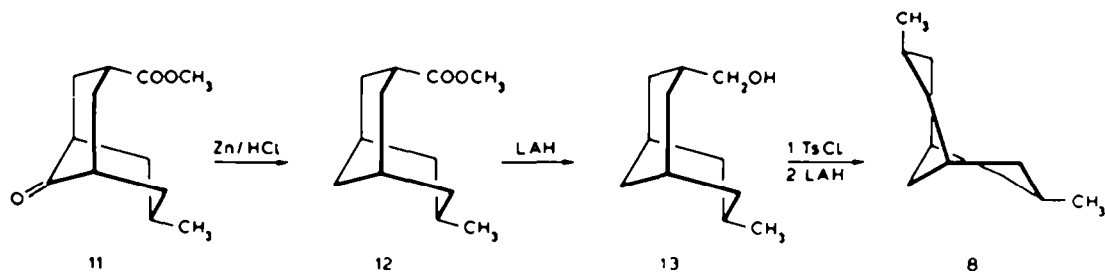
boxylate (14), 3 α ,7 β -dimethylbicyclo[3.3.1]nonane (9) was synthesized in an analogous way.

Compound 14 was also the starting compound in the synthesis of 3 β ,7 β -dimethylbicyclo[3.3.1]nonane (10). During a Huang-Minlon reduction of 14, almost complete epimerization towards the reduced 3 β -carboxylic acid 15 occurred (Scheme 3). The 3 β -position of the COOH group in compound 15 was proved by the splitting patterns of the ^1H NMR signals. Moreover, the Me

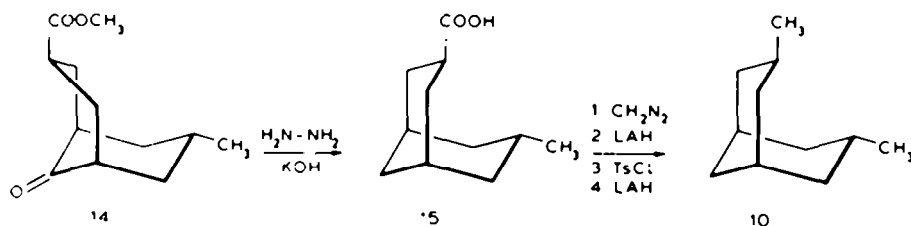
ester of 15 differed from 12 and from the product of the Clemmensen reduction of 14. The COOH group of compound 15 was reduced to Me again via the hydroxymethyl and the tosylate derivative.

Conformational analysis

The ^{13}C chemical shift data of the three 3,7-dimethylbicyclo[3.3.1]nonanes (8-10) are collected in Table 1. Peak assignments were made with the use of the off-



Scheme 2.

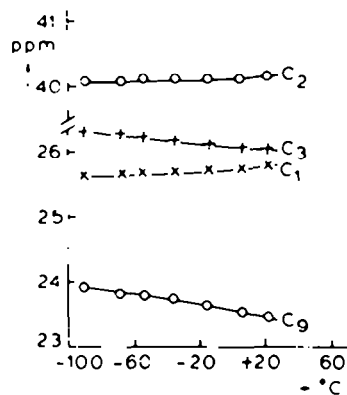


Scheme 3.

Table 1. Experimental ^{13}C chemical shifts (ppm) of the three 3,7-dimethylbicyclo[3.3.1]nonanes (8-10) at 30° in CDCl_3 solution (1.1 M); comparison with calculated chemical shifts (in parentheses)

Compound (conformation)	C_1	C_2	C_3	C_6	C_7	C_9	Me
8	25.7	40.0	25.4	40.0	25.4	23.4	25.0
(t-bb)	(27.7)	(40.6)	(26.3)	(40.6)	(26.3)	(23.7)	
9	26.4	42.9	21.9	35.9	24.7	28.8	22.2; 22.9
(cb)	(27.3)	(42.5)	(22.0)	(35.9)	(24.6)	(28.6)	
10	29.7	41.1	28.4	41.1	28.4	35.3	24.8
(cb)	(29.5)	(40.7)	(27.9)	(40.7)	(27.9)	(34.4)	

resonance technique, the relative intensities and the magnitudes of the longitudinal relaxation times. Previously, we have shown that for the various conformations of bicyclo[3.3.1]nonanes with (pseudo)-equatorial groups at the 3- and 7-positions, the ^{13}C chemical shifts can be calculated by addition of substituent effects to the ^{13}C chemical shifts of the conformation in question of the parent system.^{12,11} Unfortunately, this procedure is not yet applicable to conformations with axial or pseudo-axial 3/7 groups (e.g. the *cb*/*bc* of compound 8), since for these forms no reliable substituent effects are available. In Table 1 a comparison of experimental and calculated ^{13}C chemical shifts is made. The data support the configurational and conformational assignments of compounds 9-10. The differences between the experimental ^{13}C chemical shifts of compound 8 and those calculated for a *t-bb* conformation are somewhat larger. Moreover, the ^{13}C chemical shifts of that compound show non-linear temperature dependencies. Usually, for conformationally homogeneous bicyclo[3.3.1]nonanes, temperature effects are linear, downfield and small (0.004 ppm/°).⁴ After correction for these non-conformational effects, the ^{13}C chemical shifts of C_1 and C_9 appeared to be upfield and rather large (Fig. 2).

Fig. 2. Temperature dependencies of the ^{13}C chemical shifts of compound 8 (corrected for non-conformational influences).

For C_9 the substituent effects of the 3- and 7-Me groups will be rather small. Therefore, the ^{13}C chemical shifts of C_9 in the *cb* and *t-bb* of bicyclo[3.3.1]nonane, which amount to 28.6 and 23.7 ppm, respectively,¹¹ will provide good estimates for the corresponding chemical shifts in compound 8. So the temperature dependence of the C_9 chemical shift in compound 8 indicates an in-

crease of the amount of *t-bb* in the conformational mixture with increasing temperature. Since only 5 ^{13}C signals are observed at -100° , the interconversion between the conformations of compound **8** must be fast with respect to the NMR time scale.

The temperature dependence of the ^{13}C chemical shift of C_9 was used to estimate ΔH and ΔS between the *t-bb* and the *cb/bc* conformations of **8**. The thermodynamic parameters given in Table 2 were calculated using eqn (1)¹¹ and assuming that the non-conformational influence on the ^{13}C chemical shifts is $0.004 \pm 0.001 \text{ ppm}^\circ$, and that the chemical shifts of C_9 in the *t-bb* and the *cb* are in the ranges 22.7–23.3 and 27.6–28.6 ppm, respectively. As

$$-\ln \frac{\delta_T - \delta_{cb}}{\delta_{t-bb} - \delta_T} = \frac{\Delta\text{H}}{RT} - \frac{\Delta\text{S}}{R} \quad (1)$$

a result of the rather large ΔS -value, the *t-bb* is the major conformation at room temperature.

In Table 2, the experimental ΔH and ΔS values are compared with those obtained by molecular mechanics. The ΔH values calculated with the Engler and with the Allinger MM2 force field agree well with the experimental values. The ΔS values, however, differ significantly: the large entropy difference between the *t-bb* and the *cb/bc* is not predicted by the force field calculations.

The calculated geometries of the various conformers of compound **8** are analogous to those of the 3(,7)-substituted bicyclo[3.3.1]nonanes, described previously:⁴ the boat wings in the *cb/bc* are not twisted and the rings in all conformers are distinctly flattened. From the dihedral angles obtained, the vicinal proton–proton coupling constants in the *t-bb*, *bc*, and *cb* conformers were estimated with the use of the semi-empirical relationship of Altona *et al.* (Table 3).^{14,15} A best fit between experimental and calculated coupling constants exists for a conformational mixture containing 87% *t-bb* and 13% *cb/bc*, which agrees well with the ΔG value obtained from the ^{13}C NMR chemical shifts (Table 2).

In order to get an impression about the energy barriers between the various conformers of **8**, dynamic force field calculations⁶ with the use of the Engler force field were performed (Fig. 3). For comparison, the analogous data on the parent system bicyclo[3.3.1]nonane are also included (Fig. 4). A striking difference in the conformational energy profiles obtained is that in 3 α ,7 α -dimethylbicyclo[3.3.1]nonane (**8**), a twisted *cc* is the transition state between the *bc* and the *cb*, whereas in bicyclo[3.3.1]nonane (1), the *cc* is the lowest energy minimum. As should be expected, in compound **8** the interconversion between the *bc* and the *cb*, predominantly occurs via the *t-bb* conformers, whereas in **1** a route via the *cc* is favourable. All energy barriers calculated for compound **8** are rather low.

Table 2. ΔG , ΔH , and ΔS values for the *cb/bc* \rightleftharpoons *t-bb* equilibrium in 3 α ,7 α -dimethylbicyclo[3.3.1]nonane (**8**) at 25° ; a comparison between experimental and calculated values

Method ^a	ΔH	ΔS	ΔG (20°)
	kJ mol^{-1}	$\text{J mol}^{-1} \text{ K}^{-1}$	kJ mol^{-1}
^{13}C chemical shifts	2.7 – 5.4	20–66	-4.2 – -8.4
^1H coupling constants			-4.6
MM Engler force field	3.8	3	2.8
MM Allinger MM2 force field	0.8	3	0.1

^a MM = Molecular Mechanics.

Table 3. Experimental and calculated vicinal proton–proton coupling constants

H-atoms	Experimental ^a ± 0.2 (Hz)	Calculated (Hz) ^b		Calculated for 13% <i>cb/bc</i> 87% <i>t-bb</i>
		<i>cb/bc</i>	<i>t-bb</i>	
12 α	2.9	2.4	3.6	3.5
12 β	8.5 ^c	7.5	8.9	8.7
2 α 3 β	12.3	6.0	10.6	10.0
2 β 3 α	6.2 ^c	6.2	5.6	5.7
19	3.2	3.3	3.4	3.4

^a Obtained from first order analysis of a 300 MHz spectrum of a solution in CCl_3 at 20° ; ^b With the use of the semi-empirical relationship of Altona *et al.*^{14,15}; ^c ± 0.5 .

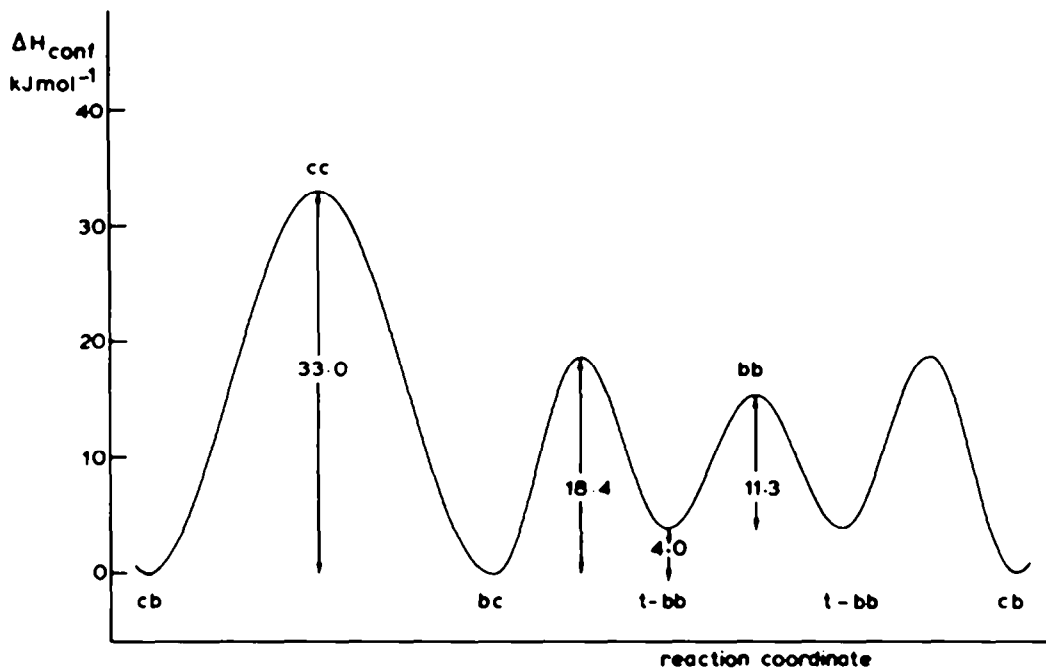


Fig. 3. Conformational energy profile 3a,7a-dimethylbicyclo[3.3.1]nonane as obtained by molecular mechanics with the use of the Engler force field.

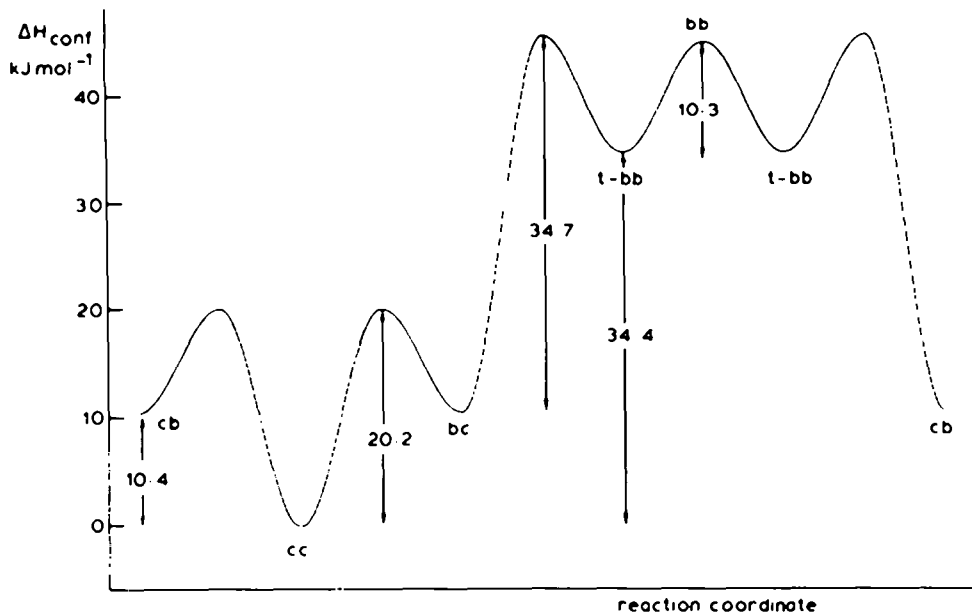


Fig. 4. Conformational energy profile of bicyclo[3.3.1]nonane as obtained by molecular mechanics with the use of the Engler force field.

which is in agreement with the fact that the slow exchange region in ^1H and ^{13}C NMR experiments on this compound could not be reached.

Several 3a,7a-disubstituted bicyclo[3.3.1]nonanes can be converted smoothly into 1,2-disubstituted adamantanes. The energy difference between the transition state (cc) and the minima of the $\text{cb} \rightleftharpoons \text{bc}$ equilibrium for compound 8, gives an impression of the magnitude of the conformational energy barriers, involved in ring closures of e.g. bicyclo[3.3.1]nonane-3a,7a-dicarboxylic acid (6) and its derivatives.⁴ Often, the ring closures occur via a carbanion transition state with a planar configuration

around C_3 or C_7 . It should be expected that for this type of reactions the conformational energy barrier is even lower. It may be concluded that the strain in the cc transition state is hardly an obstacle in ring closure reactions of this class of compounds.

EXPERIMENTAL

NMR spectroscopy. ^{13}C NMR spectra were recorded on a Nicolet NT-200 WB spectrometer (50.3 MHz) and on a Varian CFT-20 apparatus (20 MHz). ^1H NMR spectra were obtained with a spectrometer built at the Department of Applied Physics (300 MHz)¹⁶ and with a Varian T-60 spectrometer (60 MHz).

During the variable temp measurements, the probe temp was measured with the use of the chemical shift of the ^{59}Co resonance of a sample of $\text{Co}(\text{acac})_3$ in CH_2Cl_2 . ^{13}C NMR relaxation times (T_1) were measured on the Varian CFT-20 spectrometer with the use of the inversion recovery method ($180^\circ\text{-}\tau\text{-}90^\circ$ pulse sequence). From the samples used for these measurements, oxygen was removed by bubbling N_2 into the solution for 1 min, followed by capping and taping the sample tube.

Mass spectra were recorded by Dr. P. J. W. Schuyf and Mrs. A. H. Knot-Kalkman on a Varian-MAT 311A mass spectrometer.

Calculations. The empirical force field calculations were carried out on a IBM 370/158 computer with our Delft computer program using fully analytical Newton-Raphson minimization procedures. All conformers were characterized by six zero eigenvalues of the final force constants matrix.¹⁸ Complete Tables of thermodynamic and geometric parameters are available from the authors on request.

Methyl 7 α -methylbicyclo[3.3.1]nonane-3 α -carboxylate (12).¹⁹ HCl-Gas was bubbled through a refluxing mixture of 3.2 g of I^{11} (15 mmol), 67 g freshly prepared Zn-amalgam, 85 ml 37% HCl and 85 ml diethyl ether. After 4 hr the conversion was complete. The mixture was added slowly with stirring to 500 ml H_2O (0°). The aqueous layer was extracted with diethyl ether (5×75 ml). The combined organic layers were washed with sat NaCl aq (2×75 ml) and dried over MgSO_4 . After evaporation of the solvents 2.2 g of almost pure 12 (11 mole, 74%) was obtained. This product was used in the next reaction step without further purification: ^1H NMR (60 MHz, CCl_4): δ 0.73 (3H, d, $J = 6$ Hz), 0.9–3.0 (12H), 3.63 (3H, s).

3 α -Hydroxymethyl-7 α -methylbicyclo[3.3.1]nonane (13). A soln of 2.2 g of 12 (11.2 mmole) was added to a suspension of 1.0 g LAH (27 mmole) in 30 ml diethyl ether and the mixture was boiled for 2 hr. After cooling 20 ml H_2O and subsequently 40 ml 4 N H_2SO_4 were added dropwise. The aqueous layer was extracted with diethyl ether (3×20 ml). The combined ether solns were washed with sat NaCl aq (2×20 ml) and dried over MgSO_4 . After evaporation of the solvents 1.5 g of almost pure 13 (8.9 mmole, 80%) was obtained, which was used in the following step without further purification; ^1H NMR (60 MHz, $\text{CCl}_4 + \text{CF}_3\text{COOH}$): δ 0.6–2.4 (15H), 3.63 (2H, d, $J = 6$ Hz).

Tosylate of 3 α -hydroxymethyl-7 α -methylbicyclo[3.3.1]nonane. Tosyl chloride (2.4 g, 13.7 mmole) was added to a soln of 1.5 g of the product of the preceding step in 25 ml pyridine. The soln obtained was stored at 0° over-night. Then the mixture was poured onto 150 ml 1 N HCl (0°). The dispersion obtained was extracted with EtOAc (6×30 ml). The EtOAc soln was washed with 2 N HCl (2×30 ml) and with sat NaCl aq (2×30 ml) and then dried over MgSO_4 . After evaporation of the solvent 2.4 g of the tosylate of 13 (7.8 mmole, 89%) was obtained. This product was used in the following reaction step without further purification; ^1H NMR (60 MHz, CCl_4): δ 0.6–2.2 (17H), 2.43 (3H, s), 3.93 (2H, d, $J = 6$ Hz), 7.27–7.69 (4H, AA'BB' system).

3 α ,7 α -Dimethylbicyclo[3.3.1]nonane (8). A soln of 2.4 g of the product of the preceding step (7.8 mmole) in 30 ml diethyl ether was added dropwise to a suspension of 1.0 g LAH (27 mmole) in 30 ml diethyl ether. The mixture was stirred for 2 hr at room temp and for 2 hr at the b.p. After cooling 10 ml H_2O and 40 ml 2 N H_2SO_4 were added dropwise. The aqueous layer was extracted with diethyl ether (3×30 ml). The combined organic layers were washed with H_2O (3×30 ml) and dried over MgSO_4 . Then the ether was distilled off and the residue was purified by chromatography over alumina (elution with light petroleum). From the eluate the solvents were distilled off and the residue was distilled under reduced pressure to yield 0.4 g 8 (2.6 mmole, 34%); b.p. 65–67/10 mm; mass spectrum (70 eV): important peaks at m/z : 152 (M^+), 137, 123, 109, 95, and 81; ^{13}C relaxation times (T_1) (1.1 M soln in CDCl_3 , 30°): C_1 9.8, C_2 5.9, C_3 10.6, C_4 4.2, C_5 4.6 s.

3 α ,7 β -Dimethylbicyclo[3.3.1]nonane (9). This compound was synthesized by a procedure analogously to that for 8 starting from 14; b.p. 68/10 mm; mass spectrum (70 eV) important peaks

at m/z 152 (M^+), 137, 123, 109, 95, 81; ^{13}C relaxation times (T_1) (2.1 M soln in CDCl_3 , 30°): C_1 8.7, C_2 4.0, C_3 7.4, C_4 4.4, C_5 7.0, C_6 3.9, Me 4.0 s.

7 β -Methylbicyclo[3.3.1]nonane-3 β -carboxylic acid (15). A mixture of 15.5 g of methyl 7 β -methyl-9-oxobicyclo[3.3.1]nonane-3 α -carboxylic acid (85 mmole), 12.6 ml hydrazine hydrate (100%), 24.8 g KOH and 160 ml triethylene glycol was boiled for 1.5 hr. Then the mixture was distilled until a bottom temp of 200° was reached. After that the residue was boiled for another 4 hr. After cooling the mixture was diluted with 950 ml H_2O and then acidified with 570 ml 6 N HCl. The dispersion obtained was extracted with diethyl ether (5×300 ml). The combined diethyl ether soln was washed with H_2O (2×300 ml) and then dried over MgSO_4 . The solvents were evaporated off and the residue was recrystallized once from light petroleum-EtOAc to yield 5.8 g 15 (30.2 mmole, 36%); ^1H NMR (60 MHz, $\text{CCl}_4\text{-d}_2$): δ 0.80 (3H, d, $J = 6$ Hz), 1.01–2.13 (12H).

Methyl 7 β -methylbicyclo[3.3.1]nonane-3 β -carboxylate. The product of the preceding reaction step was esterified with CH_3N ; in diethyl ether. After evaporation of the excess of CH_3N ; and the solvents 5.9 g of the Me ester of 15 was obtained, which was used in the following step without further purification; ^1H NMR (60 MHz, CCl_4): δ 0.83 (3H, d, $J = 6$ Hz), 1.06–2.36 (13H), 2.58–3.33 (1H, m), 3.57 (3H, s).

3 β ,7 β -Dimethylbicyclo[3.3.1]nonane (10). This compound was synthesized starting from the Me ester of 15 following a procedure analogous to that used for the conversion of 12 into 8; b.p. 59–61/8 mm; mass spectrum (70 eV): important peaks at m/z : 152 (M^+), 137, 123, 109, 95, 81; ^{13}C relaxation times (T_1) (2.1 M soln in CDCl_3 , 30°): C_1 8.4, C_2 4.2, C_3 6.7, C_4 3.5, Me 3.3 s.

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