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CONFORMATIONAL ANALYSIS OF 7-ALKYL-3-OXABICYCLO-[3.3.1]NONANES AND COMPLEXES WITH LANTHANIDE SHIFT REAGENTS

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Abstract—The conformation of 3-oxabicyclo[3.3.1]nonane and of some of its 7α- and 7β-alkyl substituted derivatives has been studied with the use of ^{13}C and ^{1}H NMR spectroscopy. A comparison is made with the carbocyclic analogues; it turns out that the replacement of the 3-methylene group by oxygen has no substantial influence on the conformational preferences. With the aid of $^{3}J_{HH}$ coupling constants it is shown that the geometry of the cyclohexane rings is about the same as in the corresponding carbocyclic compounds. The results of calculations on the lanthanide induced shifts indicate that the tetrahydropyran ring is not flattened but probably somewhat puckered. The calculated location of Eu(III) in complexes of $Eu(dpm)_3$ with the 3-oxabicyclo[3.3.1]nonanes is compared with that in the complexes of the related compounds 2-oxaadamantane and 4-methyltetrahydropyran. The data indicate that the lanthanide ion coordinates "axially" to the latter compound.

Bicyclo[3.3.1]nonane has been shown to exist predominantly in the double-chair (cc) conformation.[1,2] In this conformation a strong repulsion occurs between $H_{3\alpha}$ and $H_{7\alpha}$, which is reflected in a substantial flattening of both wings of the system. An alkyl group at the 3β- or 7β-position enhances the preference of the substituted ring for the chair conformation. Substitution of $H_{3\alpha}$ or $H_{7\alpha}$ by an alkyl group, however, forces the substituted ring into the boat conformation. In the boat-chair (bc) and the chair-boat (cb) conformers both wings are flattened, due to $H_{3\beta}$–H_9 (or $H_{7\beta}$–H_9) and $H_{7\alpha}$–$H_{2\alpha}/H_{4\alpha}$ (or $H_{3\alpha}$–$H_{6\alpha}/H_{8\alpha}$) interactions.

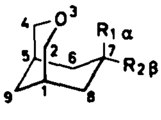
Replacement of the 3-methylene unit in bicyclo[3.3.1]nonane by ether oxygen changes the 3,7 and 3,9 interactions in the cc and bc conformation respectively. It has been suggested that the gauche–gauche 1,5-O–CH_2 interaction is non-repulsive.[3] Therefore, the introduction of oxygen might have implications on the geometry of the wings in the various conformers and also on the relative stabilities of these conformations.

The conformation of 3-oxabicyclo[3.3.1]nonane (1) has been investigated by Stapp and Randall[4] and by Zefirov and Rogozina.[5] These authors demonstrated with the use of ^{1}H NMR spectroscopy that this compound predominantly occurs in the cc conformation. Unfortunately, the separation of the signals in the ^{1}H NMR spectrum was not large enough to allow a determination of vicinal coupling constants. So no conclusions concerning any flattening could be drawn.

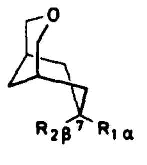
The present investigation deals with a conformational analysis of compound 1 as well as its 7α- and 7β-Me, i-Pr and t-Bu derivatives (2–7).[6] From the results of previous investigations[1] as well as from an inspection of Dreiding models it can be concluded that for compounds 1–4 the contribution of the cb and the bb conformers to the conformational equilibrium can be neglected; for compounds 5–7, the cb, bc and bb conformations should be taken into consideration.

The conformations of the compounds mentioned were investigated with the use of ^{1}H and ^{13}C NMR spectroscopy.[7] Lanthanide shift reagents (LSR) were used to obtain a separation of the signals in the ^{1}H NMR spectrum. From the $^{3}J_{HH}$ coupling constants information about the extent of flattening was obtained. The magnitudes of these coupling constants are compared with those of related carbocyclic derivatives and with the dihedral angles in these compounds obtained from empirical force field calculations.[1]

The $^{3}J_{HH}$ coupling constants, however, do not give information concerning the geometry of the tetrahydropyran ring. Therefore, the agreement between calculated and experimental lanthanide induced shifts of compound 1 as a function of the extent of flattening of this ring was investigated. The results were compared with those of



cc



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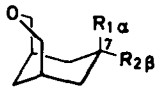
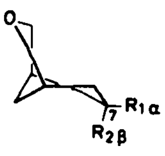


bc



bb

1 $R_1 = R_2 = H$
2 $R_1 = H; R_2 = Me$
3 $R_1 = H; R_2 = i\text{-}Pr$
4 $R_1 = H; R_2 = t\text{-}Bu$

5 $R_1 = Me; R_2 = H$
6 $R_1 = i\text{-}Pr; R_2 = H$
7 $R_1 = t\text{-}Bu; R_2 = H$

compound **6**. For comparison, calculations on the mode of coordination of shift reagents with the somewhat related compounds 4-methyltetrahydropyran (**8**) and 2-oxaadamantane (**9**) were included.

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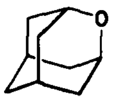

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RESULTS AND DISCUSSION

^{13}C *NMR spectroscopy*

The ^{13}C chemical shift data of the 3-oxabicyclo[3.3.1]nonanes are collected in Table 1. Peak assignments were made with the use of the off-resonance technique, the relative intensities, and intercomparison of the chemical shifts within families of derivatives, taking into account substituent effects.

In order to reveal conformational factors in the ^{13}C chemical shifts of compounds **1**–**7**, it is primarily necessary to correct for substituent influences. Previously, we have shown that the substituent influences in cyclohexane and bicyclo[3.3.1]nonane are about the same and independent of the ring conformation.[7] Therefore, it is assumed that the same substituent effects can be applied for 3-oxabicyclo[3.3.1]nonane too.

After correcting for the 7-substituent (only α, β and γ substituent influences were taken into account), the chemical shifts of corresponding carbon atoms, within a series of analogously substituted compounds turn out to agree closely (standard deviation less than 1 ppm). The average values for the corrected ^{13}C chemical shifts are given in Table 2.

For comparison the average ^{13}C chemical shifts for the various established conformations of the carbocyclic system[7] are included. The ^{13}C chemical shifts clearly demonstrate that 3-oxabicyclo[3.3.1]nonane (**1**) and its 7β-substituted derivatives (**2**–**4**) occur predominantly in the cc conformation, whereas the 7α-substituted derivatives (**5**–**7**) prefer the cb conformation. In particular the ^{13}C chemical shifts of C_6 and C_7 agree very well with those of the parent system. Obviously, the shifts of the other C atoms are subject to the influence of the heteroatom, but the conformational influences on these shifts observed in the carbocyclic compounds can still be recognized here.

Vicinal proton–proton coupling constants

^1H NMR spectra (100 MHz) of compounds **1**–**7** were recorded with increasing amounts of $Eu(dpm)_3$ or

Table 1. ^{13}C chemical shifts of 7-substituted 3-oxabicyclo[3.3.1]nonanes

compound	chemical shifts (ppm)						
	C_1	C_2	C_6	C_7	C_9	alkyl group	
1	30.0	73.4	31.2	22.5	33.3		
2	30.7	73.0	40.4	28.1	33.2	24.2	
3	30.6	73.2	35.4	38.9	33.2	19.9	35.0
4	30.5	73.2	31.9	41.9	32.9	27.0	32.8
5	27.9	74.7	35.0	24.8	26.6	22.0	
6	27.7	75.2	30.1	36.2	26.5	20.4	33.2
7	28.4	74.8	27.5	39.4	26.9	27.6	

Table 2. Average ^{13}C chemical shifts for 3-oxabicyclo[3.3.1]nonane and bicyclo[3.3.1]nonane[a]

compound	^{13}C chemical shifts (ppm)					
	C_1	C_2	C_3	C_6	C_7	C_9
3-oxabicyclo[3.3.1]nonanes						
1-4	30.4	73.2	--	31.1	22.0	33.7
5-7	27.9	74.9	--	26.1	19.1	26.7
bicyclo[3.3.1]nonanes						
cc	28.1	31.5	22.3	31.5	22.3	34.4
cb	25.9	33.3	16.4	26.7	19.0	28.6
bb	26.3	31.4	20.7	31.4	20.7	23.7

[a] Substituent effects were deduced from ^{13}C chemical shifts in bicyclo[3.3.1]-nonanes; Me: α 5.6, β 9.2, γ 0.7; i-Pr: α 17.6, β 3.4, γ -0.5; t-Bu: α 20.0, β 1.7, γ 0.0 ppm.

Eu(fod)$_3$ until optimal separation of the various multiplets was achieved. The signals were assigned by the magnitude of the induced shifts, the splitting patterns, and by using double resonance techniques. From the expanded spectra the coupling constants were derived by first-order analysis. A further refinement of the values obtained was achieved by computer simulation of parts of the spectra. Line broadening, due to large amounts of shift reagent added, was sometimes a limiting factor in determining accurate coupling constants. The magnitudes of the coupling constants were independent of the amount of shift reagent added. Moreover, the relative induced shifts were constant over the whole range of measurements. Therefore, it seems safe to assume that the complexation has no important influence on the conformation of the substrates. The coupling constants obtained are listed in Table 3.

In particular $J_{12\beta}$ and $J_{18\beta}$ are diagnostic for the conformation of the bicyclo[3.3.1]nonane derivative. All values of $J_{12\beta}$ measured are small (<4 Hz), showing that in all compounds investigated the tetrahydropyran ring predominantly (>90%) exists in the chair conformation. For 3-oxabicyclo[3.3.1]nonane itself (1) and its 7β-alkyl derivatives (2–4) the value of $J_{18\beta}$ is small (<4 Hz), showing these compounds to prefer the cc conformation. From the value of $J_{18\beta}$ in the compounds with a 7α-substituent (5–7), which is about 11.5 Hz, it may be concluded that these derivatives predominantly occur in the cb conformation. Information about the extent of flattening can be obtained from an inspection of the couplings between H$_6$ and H$_7$. These coupling constants are very close to those in related carbocyclic compounds;[1] from force field calculations it may be concluded that in these compounds the angle between the C$_1$C$_8$C$_6$C$_5$-plane and the C$_6$C$_7$C$_8$-plane is about 145° (the angle between the C$_1$C$_2$C$_4$C$_5$- and C$_1$C$_6$C$_8$C$_5$-planes is about 116°).[2] It may be assumed that in the 3-oxabicyclo[3.3.1]nonanes the extent of flattening is about the same. Going from the unsubstituted compound 1 to the 7β-t-butyl derivative 4, there is a slight decrease of $J_{6\alpha 7\alpha}$. This is in accordance with the results of the force field calculations,[2] which showed that in bicyclo[3.3.1]nonane the strain introduced by a 3β-t-butyl group is relieved by bending H$_{3\alpha}$ into the direction of the center of the ring system, resulting in an increase of the dihedral angle between H$_{3\alpha}$ and H$_{2\alpha}$.

In conclusion: the substitution of the 3-methylene unit in 7-substituted bicyclo[3.3.1]nonanes by ether oxygen has no substantial influence on the conformational preferences and on the geometry of the carbocyclic 6-membered ring in these compounds. Because of the presence of the heteroatom, no information about the flattening of the tetrahydropyran ring could be obtained from the coupling constants.

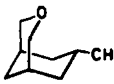
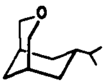
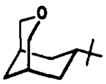
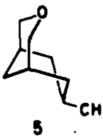
Complexes of 3-*oxabicyclo*[3.3.1]*nonanes and some related compounds with lanthanide shift reagents*

It has been shown that in ^{1}H NMR spectroscopy the chemical shifts induced by lanthanide shift reagents are, in general, of pseudo-contact origin and obey the McConnell–Robertson equation (1), where $\Delta\nu_i$ is the induced shift in the LSR-substrate complex, r_i is the distance between

$$\Delta\nu_i = K(3\cos^2\theta_i - 1)/r_i^3 \qquad (1)$$

the Ln-ion and the nucleus under consideration, θ_i is the angle between the principal magnetic axis of the complex and the vector r_i, and K is a constant.[8] Thus, apart from the position of the Ln-ion, the induced shift is dependent

Table 3. Proton–proton coupling constants of 7-alkyl 3-oxabicyclo[3.3.1]nonanes (Hz)

	 1	 2	 3	 4	 5	 6	 7
$J_{12\alpha}$	≤4	3-4	3-4	3-4	3-4	3-4	≤4
$J_{12\beta}$	≤4	3-4	3-4	3-4	3-4	3-4	≤4
$J_{18\alpha}$	<4	2.9	<4	<4	≤2	≤2	<5
$J_{18\beta}$	3.3	3.8	∼4	<4	11.5	11.5	10-11
$J_{6\alpha 7\alpha}$	5.7	5.3	5-6	5.2	--	--	--
$J_{6\alpha 7\beta}$	≤1.0	--	--	--	12.7	13.2	10-13
$J_{6\beta 7\alpha}$	12.4	12.2	12-13	12.5	--	--	--
$J_{6\beta 7\beta}$	5.7	--	--	--	5.3	5.2	∼5
J_{19syn}	≤4	2.7	<4.5	∼2.5	2.5		
J_{19anti}	≤4		<4.5	∼2.5			
$J_{2\alpha 2\beta}$	-10.8	-10.6	-10.5	-10.6	-10.3	-10.5	-10--11
$J_{6\alpha 6\beta}$	-13.5	-13.5	-13--14	-13.5	-12.5	-13.5	-12--14
$J_{7\alpha 7\beta}$	-13.5	--	--	--	--	--	--
$J_{9syn9anti}$	∼-13	∼-12	-11.8	-12.0	-12.1	-12.2	-12--13

on the geometry of the substrate. Therefore, the lanthanide induced shift data of the 3-oxabicyclo[3.3.1]nonanes (see Table 4) may be useful for obtaining information about the tetrahydropyran ring in these compounds. So computer searches for the location of the Ln-ion in complexes of shift reagents with these compounds were made. The agreement between calculated and observed induced shifts was expressed, as usual, in the crystallographic agreement factor.[8]

An inspection of molecular models showed that only the *exo* lone pair of the O atom in the 3-oxabicyclo[3.3.1]nonanes investigated is available for coordination with Eu(dpm)$_3$. Therefore, the LIS calculations on these compounds were performed with the assumption of a unique position of the Ln-ion.

Since the $^3J_{HH}$ coupling constants demonstrated that the carbocyclic ring in compound **1** has about the same geometry as that in bicyclo[3.3.1]nonane, we started our calculations with a model with both wings flattened to the same extent. Although the agreement factor obtained is satisfactory, the results seem not realistic (Table 5): the angle between Eu–O and the positive X-axis is much too small and the Eu–O distance is outside the range of probable values.[8] Therefore, the C_2OC_4-plane was rotated stepwise around C_2C_4 into the direction of $H_{7\alpha}$ and the calculations were repeated after each step. It appeared that the agreement factor improved slightly: a minimum was reached when the angle between the planes mentioned is 107°. More significantly the calculated position of the Ln-ion for this situation (Table 5) compares well with that in some related complexes. Although the results of these calculations must be interpreted with care, it seems safe to assume that in 3-oxabicyclo[3.3.1]nonane, the tetrahydropyran ring is less flattened than the corresponding ring in the carbocyclic system. The former ring may even be somewhat puckered. Perhaps an attractive interaction between the ether oxygen and $H_{7\alpha}$ is involved.[3] The two syn interactions between $H_{7\alpha}$ and the tetrahydropyran ring may be responsible for the flattening of the cyclohexane part of the 3-oxabicyclo[3.3.1]nonane system.

In the calculations on the coordination of shift reagents with compound **6**, a model for the substrate, analogous to that of the related carbocyclic compound, afforded an optimal fit between experimental and calculated induced shifts. This shows that the complexation has probably no substantial influence on the geometry of the tetrahydropyran ring. The calculated lanthanide location is in agreement with that in the other compounds investigated. Apparently, the geometry of the **cb** conformation of 3-oxabicyclo[3.3.1]nonanes is analogous to that of the carbocyclic compounds.

Table 4. Relative lanthanide induced shifts

compound	shift reagent	Δv_1[a]
1	Eu(dpm)$_3$	1.00($H_{2\alpha}$)[b,c], 0.84($H_{2\beta}$)[b,c], 0.56($H_{7\alpha}$); 0.37(H_{9syn}); 0.29(H_1,$H_{6\alpha}$,H_{9anti}); 0.22($H_{6\beta}$); 0.18($H_{7\beta}$)
1	Pr(dpm)$_3$	1.00($H_{2\alpha}$)[b,c], 0.80($H_{2\beta}$)[b,c], 0.55($H_{7\alpha}$); 0.38(H_{9syn}); 0.31(H_1,$H_{6\alpha}$,H_{9anti}); 0.24($H_{6\beta}$); 0.20($H_{7\beta}$)
4	Eu(dpm)$_3$	1.00($H_{2\alpha}$)[b,c], 0.83($H_{2\beta}$)[b,c], 0.72($H_{7\alpha}$); 0.37(H_{9syn}); 0.30(H_1,$H_{6\alpha}$,H_{9anti}); 0.25($H_{6\beta}$)
6	Eu(dpm)$_3$	1.00($H_{2\beta}$)[b], 0.81($H_{2\alpha}$)[b]; 0.51($H_{6\alpha}$); 0.39(H_{9syn}); 0.30(H_{9anti},H_1); 0.22($H_{6\beta}$); 0.21($H_{7\beta}$)
8	Eu(dpm)$_3$	1.00(H_{2eq}); 0.82(H_{2ax}); 0.48(H_{3ax}); 0.38(H_{4ax}); 0.31(H_{3eq}); 0.17(Me)[c]
8	Pr(dpm)$_3$	1.00(H_{2eq}); 0.81(H_{2ax}); 0.45(H_{3ax}); 0.36(H_{4ax}); 0.32(H_{3eq}); 0.18(Me)[c]
9	Eu(dpm)$_3$	1.00(H_1); 0.46(H_{4syn}); 0.29(H_{4anti}); 0.27(H_5); 0.24(H_8)
9	Pr(dpm)$_3$	1.00(H_1); 0.47(H_{4syn}); 0.32(H_{4anti}); 0.26(H_5); 0.25(H_8)

[a] The assignments are given in parentheses. Of a set of chemically equivalent atoms only the lowest numbered one is given.

[b] The assignments of $H_{2\alpha}$ and $H_{2\beta}$ may be interchanged.

[c] Not included in the calculations.

Table 5. The coordination of Eu(dpm)$_3$ with cyclic ethers

compound	method of averaging[a]	distance Eu-O (Å)	ϕ[b] (°)	180-θ[c] (°)	population (%)	agreement factor
1[d,e]	1	4.06	90	2.4	100	0.07
1[d,f]	1	3.09	270	43.5	100	0.06
6	1	2.57	270	63.7	100	0.04
8[g]	1	3.20	90	48.0	100	0.03
8[g]	2	3.27	90	54.6	94	0.02
			270	54.6	6	
9	2	3.00	90	39.0	50	0.03
			270	39.0	50	

[a] 1 = unique position, 2 = two-site averaging.

[b] The angle between the XY-plane and the plane formed by Eu-O and the X-axis.

[c] The angle between Eu-O and the positive X-axis.

[d] $H_{2\alpha/4\alpha}$ and $H_{2\beta/4\beta}$ not included in the calculations.

[e] Angle between C_2OC_4- and $C_1C_2C_4C_5$-planes 145°.

[f] Angle between C_2OC_4- and $C_1C_2C_4C_5$-planes 107°.

[g] Methyl group not included in the calculations.

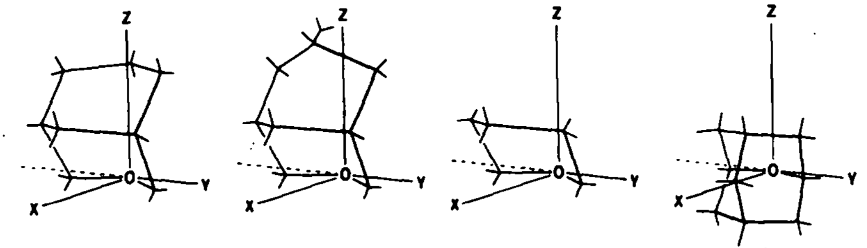


Fig. 1. Positions of the substrates in the coordinate system.

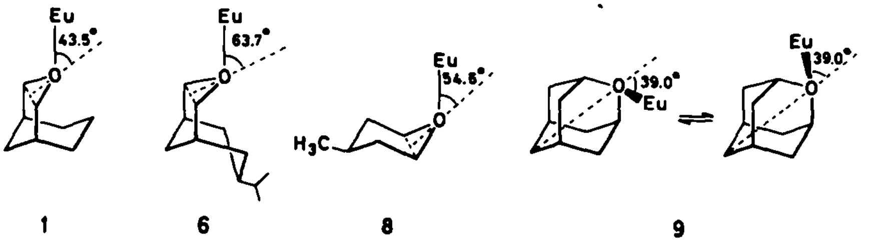


Fig. 2. Calculated Eu(III) locations in Eu(dpm)$_3$ complexes.

For comparison, the LIS calculations were also performed on 4-methyltetrahydropyran (8) and 2-oxaadamantane (9). In these calculations coordination at two sites was considered, situated symmetrically with respect to the plane through the oxygen atom and the two neighbouring C atoms (XY-plane, see Fig. 1). For compound 8 the populations of the Ln-ion at these sites were optimized. The calculated coordination sites resemble those of the 3-oxabicyclo[3.3.1]nonanes.

The complexation of 2-oxaadamantane was studied earlier by Hájek *et al.* with the use of the relaxation reagent Gd(dpm)$_3$.[14] From line broadenings of ^{1}H NMR signals these authors concluded that Gd(III) has a unique coordination site on the X-axis (Fig. 1). The discrepancy between that study and our LIS calculations may be due to the relative inaccuracy of the ^{1}H line broadening data with respect to LIS data.

Surprisingly, the calculated preferred coordination site of 4-methyltetrahydropyran (8) is the axial position in the 6-membered ring. This conclusion is supported by the relative strong broadening of $H_{3ax/5ax}$ and $H_{2eq/6eq}$ with respect to those of $H_{3eq/5eq}$ and $H_{2ax/6ax}$ in the Eu(dpm)$_3$ expanded spectrum after the addition of a small amount of Gd(dpm)$_3$. An inspection of Dreiding models of the "axial" and "equatorial" complexes of 8 with Eu(dpm)$_3$ shows that it is rather unlikely that the preference for the axial position is caused by steric effects. Possibly, the stabilisation of the "axial" complex may be due to a favourable proximity of the $C_3C_4C_5$ part of the substrate to the t-butyl groups of $Eu(dpm)_3$.

Further investigations are in progress with the aim to obtain additional proof for the conformation of 3-oxabicyclo[3.3.1]nonanes and for the unexpected way of coordination of $Eu(dpm)_3$ with 4-methyltetrahydropyran.

EXPERIMENTAL

The 60 MHz ^1H NMR spectra were recorded on a Varian T-60 apparatus. The 100 MHz ^1H NMR spectra were obtained with a Varian XL-100-15 NMR spectrometer system. The 20 MHz ^{13}C NMR spectra were recorded with a Varian CFT-20 apparatus. All spectra were obtained from $CDCl_3$ solns. The spectra were measured at 39°. Chemical shifts of both the ^1H and ^{13}C resonances are given in ppm relative to TMS (δ).

The lanthanide shift reagents were obtained from Merck. They were sublimed at 180°/0.1 mm and after that handled in a glove box, flushed with dry nitrogen. The solvent used in LIS experiments was dried over molecular sieve 3A.

For the simulation of the ^1H NMR spectra the program LAOCOON-8 was used.

In the LIS calculations relative values of $\Delta\nu_i$ were used (Table 4). These were obtained from plots of ν_i vs ν_j at various amounts of shift reagent. As shown by Kelsey the slopes of these lines give $\Delta\nu_i/\Delta\nu_j$.[11,12] For compounds 1 and 9 the ^1H NMR LIS experiments were performed with both $Eu(dpm)_3$ and $Pr(dpm)_3$. The relative $\Delta\nu_i$ values appear to be almost independent of the shift reagent used, indicating that the contributions of contact and complex formation shift may be neglected.[13] In the ^{13}C NMR experiments the values of $\Delta\nu_i$ were dependent on the shift reagent used. These data were therefore not included in the calculations. The cartesian coordinates of the substrates, required for the LIS calculations, were estimated from those of the corresponding carbocyclic compounds as obtained from empirical force field calculations.[2]

The LIS calculations were performed with computer programs, based on those of Armitage *et al.*[9] and Wing *et al.*[10] In the latter program the coordinate transformation was revised.

Dreiding models of $Eu(dmp)_3$ complexes were constructed using structural parameters of some other complexes, obtained by X-ray spectroscopy.[10]

The syntheses of 3-oxabicyclo[3.3.1]nonanes (1–7) have been described previously.[6] 4-Methyltetrahydropyran (8)[14] and 2-oxaadamantane (9)[15] were synthesized according to procedures described in the literature.

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REFERENCES

[1] J. A. Peters, J. M. van der Toorn and H. van Bekkum, *Tetrahedron* 31, 2273 (1975); and refs therein.
[2] J. A. Peters, J. M. A. Baas, B. van de Graaf, J. M. van der Toorn and H. van Bekkum, *Tetrahedron submitted.*
[3] J. Dale, *Tetrahedron* 30, 1683 (1974).
[4] P. R. Stapp and J. C. Randall, *J. Org. Chem.* 35, 2948 (1970).
[5] N. S. Zefirov and S. V. Rogozina, *Tetrahedron* 30, 2345 (1974).
[6] J. A. Peters, B. van de Graaf, P. J. W. Schuyl, Th. M. Wortel and H. van Bekkum, *Ibid.* 32, 2735 (1976).
[7] J. A. Peters, J. M. van der Toorn and H. van Bekkum, *Ibid.* 33, 349 (1977).
[8] For a review see: O. Hofer, *Topics in Stereochemistry* 9, 111 (1976).
[9] I. M. Armitage, L. D. Hall, A. G. Marshall and L. G. Werbelow, *J. Am. Chem. Soc.* 95, 1437 (1973).
[10] R. M. Wing. J. J. Uebel and K. K. Anderson, *Ibid.* 95, 6046 (1973).
[11] D. R. Kelsey, *Ibid.* 94, 1764 (1972).
[12] J. W. ApSimon, H. Beierbeck and A. Fruchier, *Org. Magn. Res.* 8, 483 (1976).
[13] D. J. Chadwick and D. H. Williams, *J. Chem. Soc.* Perkin 2 1974, 1202.
[14] M. Hájek, I. Mohyla, Z. Ksandr and L. Vodička, *Coll. Czech. Chem. Commun.* 41, 3591 (1976).
[15] R. M. Black, G. B. Gill and D. Hands, *Chem. Commun.* 311 (1972).
[16] A. Kirrmann and L. Wartski, *Bull. Soc. Chim. Fr.* 3077 (1965).