A Dynamic ^1H and ^{13}C Nuclear Magnetic Resonance Study of *cis*-1,6-Dimethyl-2,5,7,10-tetraoxabicyclo[4.4.0]decane (4a,8a-Dimethylhexahydro-*p*-dioxino[2,3-*b*]-*p*-dioxin)

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The ^1H and ^{13}C n.m.r. spectra of *cis*-1,6-dimethyl-2,5,7,10-tetraoxabicyclo[4.4.0]decane have been studied over a wide temperature range (204—293 K). Temperature-dependent phenomena observed in both the ^1H and ^{13}C n.m.r. spectra can be attributed to a ring-inversion process between the enantiomeric forms of a double-chair conformation for the title compound. Line-shape analysis has been performed to obtain thermodynamic parameters for the ring-inversion process of these enantiomers. Molecular mechanics calculations have been used to obtain the minimum-energy conformation and to make structural comparisons with previous studies on 2,5,7,10-tetraoxabicyclo[4.4.0]decanes.

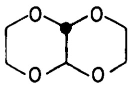
Conformational analysis of compounds containing oxygen atoms has been successfully performed by comparison with the respective hydrocarbon compounds.[1] In the study of heterocyclic systems the conformational analysis of the α-diketone acetalisation products has attracted much attention. This interest stems from their ease of preparation,[2] their use in industrial processes,[3] and their unusual conformational properties.[4,5] In particular the array of C–O and C–C bond dipoles in these compounds results in enhanced anomeric effects,[6] giving rise to 'rabbit ear', or *gauche* dipole–dipole interactions.

In studies of α-diketone acetalisation reactions the occurrence of the *trans*-isomer (1) when preparing 2,5,7,10-tetraoxabicyclo[4.4.0]decanes has been of particular interest.[7] A number of studies have now shown that only the *cis*-isomer (2) and/or the isomeric bis(dioxolan-2-yl) compound (3) are obtained from such acetalisation reactions. To date no trace of the *trans*-isomer (1) has yet been found although a number of different synthetic approaches have been used.[4,5]

In the course of studies on possible protecting groups for α-diketones we had occasion to investigate the products obtained from the reaction of butane-2,3-dione (4) and 2-ethoxy-1,3-dioxolane (5). We now report results from this study in which the room-temperature and variable-temperature ^1H and ^{13}C n.m.r. spectra have been analysed for *cis*-1,6-dimethyl-2,5,7,10-tetraoxabicyclo[4.4.0]decane.† We have also performed molecular mechanics calculations (MM2) on the title compound in order to make structural comparisons with previous MM1 studies on 2,5,7,10-tetraoxabicyclo[4.4.0]decanes.

Results and Discussion

(i) *N.m.r. Studies.*—Under a number of conditions the reaction of (4) with 1.1 equiv. of (5) gave only a single product, in excellent yield, after recrystallisation from hexane. This product, by spectroscopic analysis, was found to be consistent with (6). No evidence of the *trans*-isomer (7), or the isomeric bis(dioxolan-2-yl) species (8), could be detected in the crude reaction mixtures by either t.l.c. or n.m.r. analysis. At room temperature the ^1H n.m.r. spectra of (6) exhibits a single methyl resonance and an AA'BB' multiplet, the chemical shift of which was found to be solvent dependent *e.g.*, CCl_4, $CDCl_3$, CD_2Cl_2; δ 3.6—4.1, C_6D_6, C_7D_8; δ 3.3—3.85. Analysis of the AA'BB' multiplet by a modified LAOCOON III program[8] was facilitated by the solvent effects on $\Delta\nu_{AB}$, which altered line positions and their intensities. The spectral parameters found for CCl_4, $CDCl_3$, CD_2Cl_2, C_6D_6, and C_7D_8 are given in Table 1, with the computer-simulated spectra obtained from these parameters being shown in Figure 1. The actual spectra obtained are shown for comparison; the agreement between experimental and simulated spectra was found to be better than 0.2 Hz, with $\omega_{\frac{1}{2}}$ 1.6 Hz.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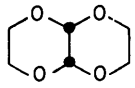
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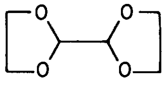
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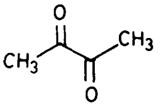

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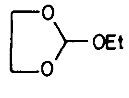

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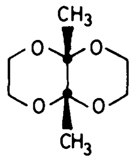

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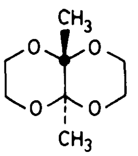

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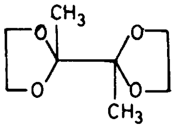

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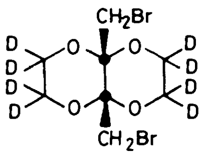

(9)

From Table 1 it can be seen that the vicinal coupling constants J_{ea} and $J_{e'a'}$ are equal. This is consistent with (6) possessing the *cis*-configuration, while undergoing a rapid chair–chair interconversion at room temperature as shown in Figure 2. An isomer with a rigid *trans*-configuration such as (7) would not be able to undergo such a chair–chair interconversion. The existence of small quantities of either the twist–boat or boat forms of (6) can be excluded for the following reasons. First, the i.r. spectrum of (6) in solution or in a KBr disc are identical; secondly, the coupling constants J_{ea}, J_{ee}, J_{aa}, and J_{gem} for (6) are in good agreement with cyclic heteroatom systems, which are

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† This compound has previously been referred to as *cis*-9,10-dimethyl-1,4,5,8-tetraoxadecalin.[5]

Table 1. Chemical shifts, coupling constants, and $\Delta\nu_{AB}$ values (in Hz) for iterated spectra shown in Figure 1 for the AA′BB′ multiplet of (**6**) at room temperature

	ν_{AA}		ν_{BB}					
Solvent	Hz	p.p.m.	Hz	p.p.m.	$\Delta\nu_{AB}$	$J_{ee} = J_{aa}$	$J_{ea} = J_{e'a'}$	J_{gem}
CCl_4	355.93	3.95	322.00	3.57	33.93	6.60	3.16	−11.53
$CDCl_3$	365.78	4.06	333.08	3.70	32.70	6.81	3.04	−11.60
CD_2Cl_2	361.23	4.07	329.61	3.66	31.62	6.67	3.16	−11.68
C_6D_6	346.54	3.85	301.83	3.35	44.71	6.62	3.32	−11.73
C_7D_8	344.44	3.83	300.77	3.34	43.67	6.63	3.35	−11.68

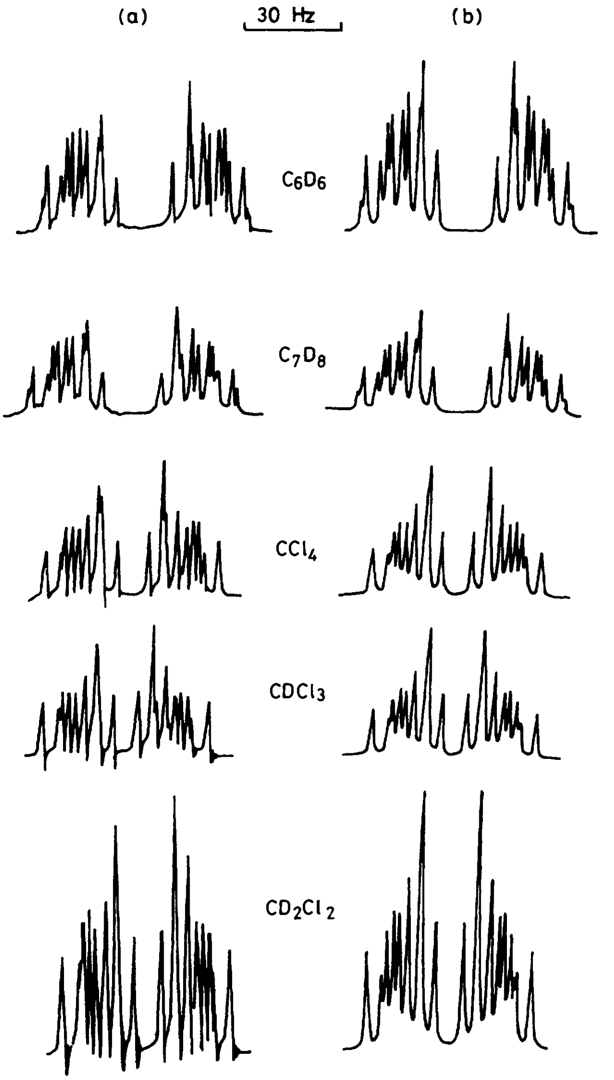


Figure 1. Actual (a) and simulated (b) spectra for the AA′BB′ multiplet obtained in the 90 MHz ^1H n.m.r. spectrum of (**6**) in various solvents at room temperature

Table 2. Coupling constants (in Hz) for saturated heterocyclic ring compounds[9]

Compound	$J_{aa} + J_{ee}$	J_{ea}	J_{gem}
cis-2,3-Dichloro-1,4-dioxane	12.6	3.1	−12.2
cis-2,3-Diphenyl-1,4-dioxane	12.7	3.0	−11.9
cis-Naphthodioxane	12.6	2.9	−11.7
1,4-Dioxane	13.0	2.7	
cis-2,5-Dimethyl-1,4-dioxane	11.4	2.6	−11.8
Morpholine	13.1	3.0	

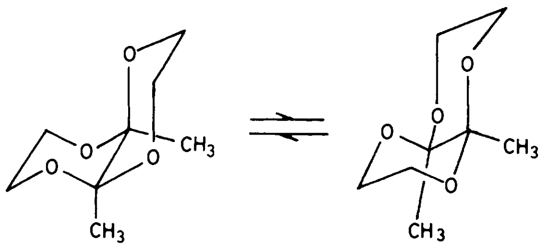


Figure 2. Equilibration of enantiomeric double chair conformations for (**6**)

known to invert between chair conformations, as shown from the parameters given in Table 2.[9] Thirdly, the coupling constants for (**6**) are independent of the solvent used; the presence of other conformational forms *e.g.*, double twist boat, would have caused discrepancies in the values of coupling constants on changing the solvent. Finally the *R* value[10] and the torsional angle $\psi^{10,11}$ are in close agreement with those recently obtained by Fuchs *et al.* in their analysis of *cis*-2,3-disubstituted 1,4-dioxanes,[12] as shown in Table 3. Such *R* and values for (**6**) are consistent with values, *i.e.* $2.0 \leqslant R \leqslant 2.28$, $57.2° \leqslant \psi \leqslant 58.7°$, previously observed for a number of heterocyclic molecules known to possess chair conformations.[10]

On lowering the temperature dramatic changes occurred to the AA′BB′ multiplet in the ^1H n.m.r. of (**6**) in CD_2Cl_2, as shown in Figure 3. At −70 °C two diffuse multiplets were observed at δ 3.3—3.6 and 3.7—4.4, of relative intensities 1:3. No doublet formation was detected for the bridgehead methyl resonance, although a slight broadening was observed and no observations could be made below −70 °C in CD_2Cl_2 since crystallisation occurred. Again this dynamic behaviour was consistent with the *cis*-configuration implied from analysis of the room-temperature spectra. Similar spectral characteristics have been shown for (**2**), at −104 °C, with an apparently unsymmetrical two peak pattern of relative intensity 1 : 3 being obtained.[13] However, the low-temperature spectrum for (**2**), shown in Figure 4, lacks well resolved lines, in contrast to that of (**6**) as shown in Figure 3. For both (**2**) and (**6**) the low-temperature spectra obtained implies a single conformer, in which three of the four protons seen in the room temperature AA′BB′ multiplet possess similar chemical shifts.

A simpler low-temperature spectrum was obtained for (**6**), at −70 °C, using $[^2H_8]$toluene as solvent as shown in Figure 5. Three multiplets, in the ratio of 1:2:1, were obtained in the δ 2.65—4.4 region, their appearance again being indicative of an ABCD spin system. Variable-temperature behaviour in the ^{13}C n.m.r. was also observed for (**6**), in $[^2H_8]$toluene, as shown in Figure 6. On cooling, the peak at δ 61.2 p.p.m., attributable to the methylene carbons in (**6**), gradually broadened before giving a doublet of peaks at δ 58.9 and 63.5 p.p.m. at −60 °C. The

Table 3. Comparison of n.m.r. spectroscopic data of (**6**) with *cis*-2,3-disubstituted dioxanes known to exist in chair forms[12]

Compound	$J_{ee} = J_{aa}$ [a]	$J_{ea} = J_{e'a'}$ [a]	J_{gem} [a]	R [b]	ψ [c] (°)
cis-2,3-Dimethoxy-1,4-dioxane	6.35	2.98	−11.70	2.13	57.7
cis-2,3-Diphenoxy-1,4-dioxane	6.32	3.05	−11.86	2.07	57.3
cis-2,3-Diacetoxy-1,4-dioxane	6.30	3.15	−11.88	2.00	56.7
(**6**)	6.81	3.04	−11.60	2.24	58.5

[a] All coupling constants are in Hz and for $CDCl_3$ as solvent. [b] $R = J\ trans/J\ cis = \frac{1}{2}(J_{aa} + J_{ee})/\frac{1}{2}(J_{ae} + J_{a'e'})$ (see ref. 10). [c] $\cos\psi = [3/(2 + 4R)]^{\frac{1}{2}}$ (see refs. 10 and 11).

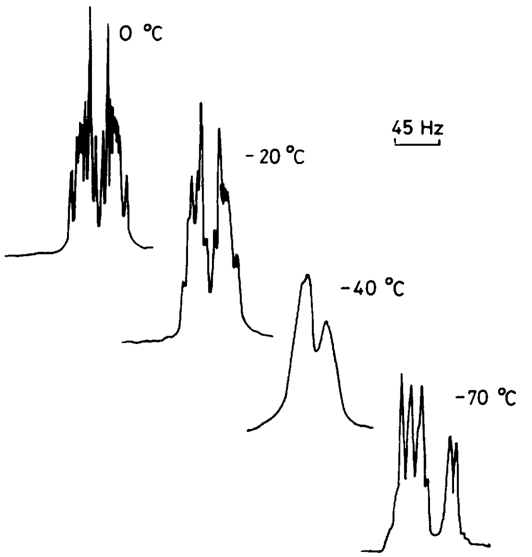


Figure 3. Variable-temperature 90 MHz ^1H n.m.r. spectrum for (**6**), in CD_2Cl_2, showing the collapse of the AA′BB′ multiplet between δ 3.5 and 4.15

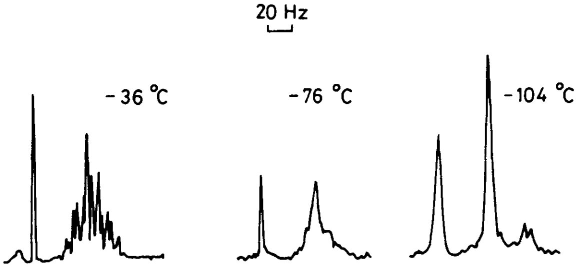


Figure 4. Temperature-dependent ^1H n.m.r. spectrum of the AA′BB′ multiplet of (**2**) in CS_2–CD_2Cl_2 (ref. 13)

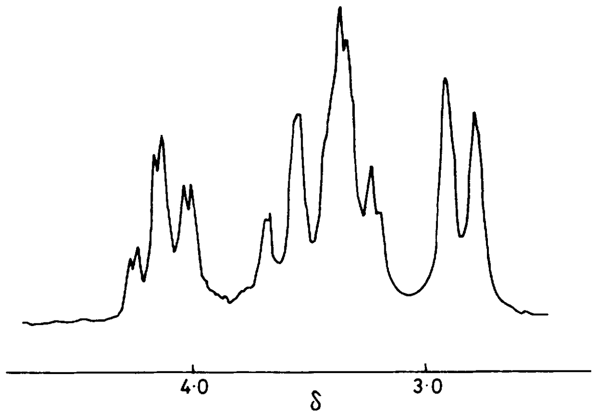


Figure 5. Low-temperature (−70 °C) 90 MHz ^1H n.m.r. spectrum obtained for (**6**) in [$^2H_8$]toluene

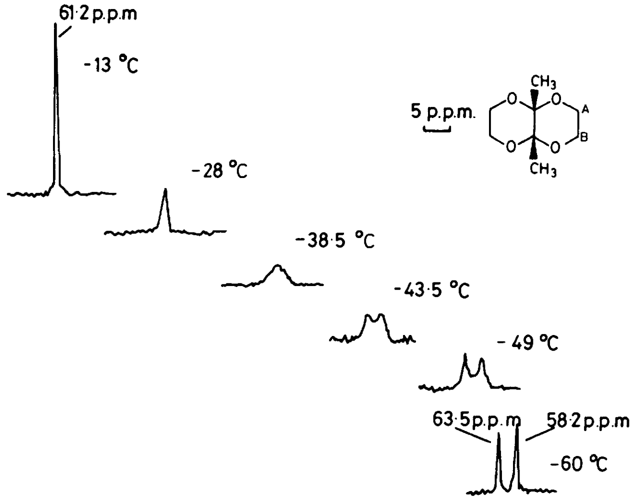


Figure 6. Variable-temperature ^{13}C n.m.r. behaviour for (**6**) for the methylene carbons A,B

methylene carbons appear as a singlet at room temperature due to fast exchange between the enantiomeric forms of (**6**); on lowering the temperature the enantiomeric forms, shown in Figure 2, are frozen out, resulting in enantiotopic methylene carbons, hence the doublet formation. Both the ^1H and ^{13}C n.m.r. variable-temperature spectra, obtained below the coalescence temperature, indicate an ABCD exchange system, which above the coalescence temperature gives an AA′BB′ spin system under rapid exchange ($k \geqslant 100\,000\ s^{-1}$).

Analysis of the low-temperature ^1H n.m.r. spectrum, by LAOCOON III, gave the following parameters: ν_D 2.85, ν_C 3.29, ν_B 3.53, ν_A 4.12 p.p.m., J_{CD} −0.1, J_{BD} 1.1, J_{AD} − 10.7, J_{BC} − 12.9, J_{AC} 3.0, and J_{AB} 11.7 Hz. The large negative values obtained for J_{BC} and J_{AD} indicate that they are the geminal coupling constants. All other couplings are small except for J_{AB}, so this must be the axial–axial coupling. Consequently the resonances of the axial protons appear downfield of the equatorial protons; this is the reverse of that normally observed for *e.g.*, the cyclohexane system.[14] Reversal of axial–equatorial resonances has been observed in other heterocyclic systems containing sulphur atoms, but no explanation has been proferred.[15] The assignments H_A, H_B, H_C, and H_D, shown in Figure 7, are based on precedence that a 1,3-diaxial interaction between a hydrogen and bridgehead methyl is more pronounced than a 1,3-diaxial interaction between a hydrogen and an axial oxygen functionality.[16] Drieding models also indicate that a direct steric effect of the bridgehead methyl with the hydrogens does

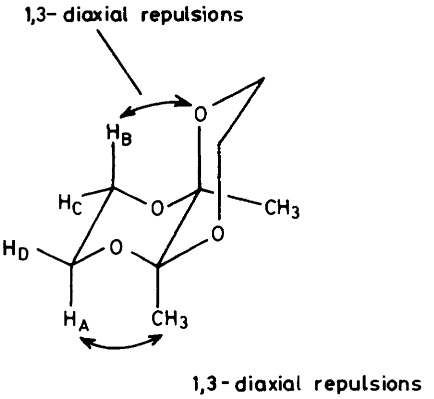


Figure 7. Assignment used in analysis of low-temperature (−70 °C) ^{1}H n.m.r. spectrum of (**6**)

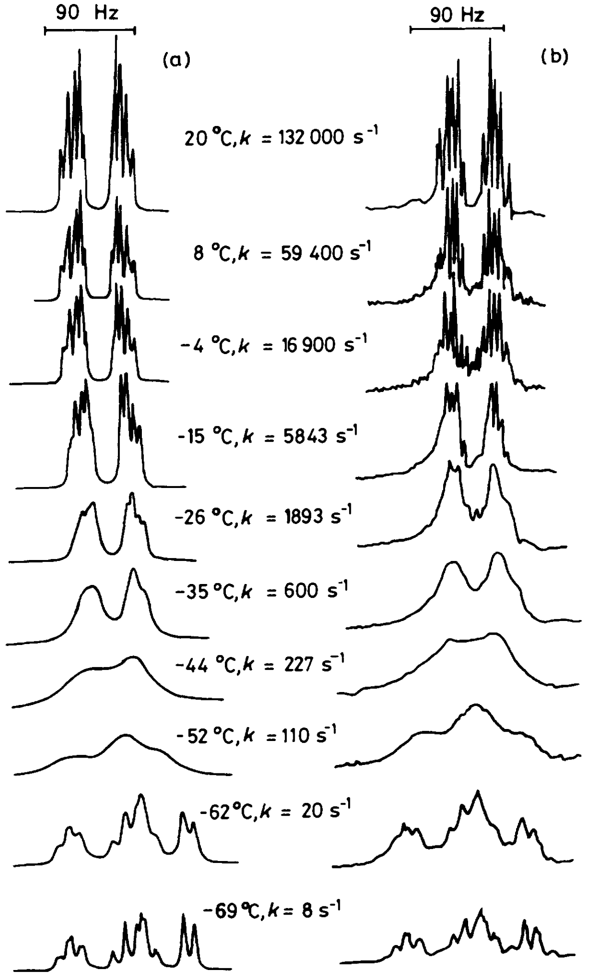


Figure 8. Simulated (a) and actual (b) spectra obtained for the dynamic ^{1}H n.m.r. spectrum of (**6**) in [$^2H_8$]toluene

exist. This is probably a contributing factor for the reversal of the axial and equatorial proton resonances, in conjunction with the dipole–dipole interactions caused by the presence of the axial oxygen functionalities present in (**6**).

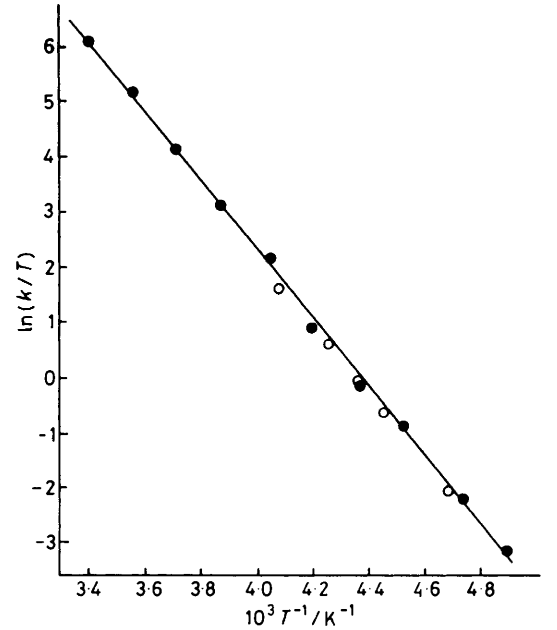


Figure 9. Plot of ln (*k*/*T*) against 1/*T* to evaluate $\Delta H^\ddagger$ for the ring-inversion process for enantiomers of (**6**): ●, ^{1}H data; ○, ^{13}C data

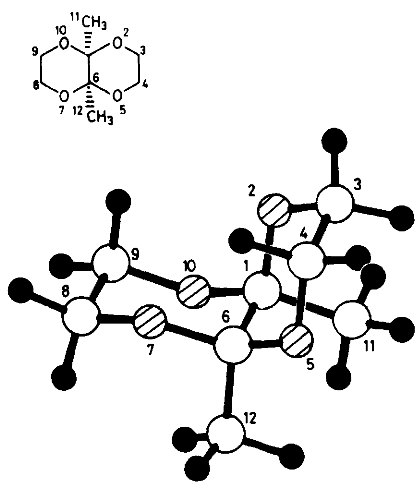


Figure 10. Molecular mechanics (MM2)-determined minimum-energy conformation of *cis*-1,6-dimethyl-2,5,7,10-tetraoxabicyclo[4.4.0]decane (**6**)

Line-shape analysis[17] of the coalescence between the AA′BB′ and ABCD spin systems in the ^{1}H n.m.r. spectra was carried out after inspection of the ^{13}C n.m.r. spectra. By simulation of a two-site exchange solution,[17] rate constants were obtained from the ^{13}C n.m.r. spectra. Using a regression analysis on these data, approximate rate constants for the ^{1}H n.m.r. were then obtained. Comparison of the experimental and best fit simulated spectra[17] with their corresponding exchange rate constants are shown in Figure 8. Again the agreement between these spectra was found to be better than 0.5 Hz. In particular at high exchange an AA′BB′ multiplet was obtained from the proposed ABCD $\rightleftharpoons$ CDAB exchange, confirming the initial hypothesis above. Furthermore a simulated spectrum produced with k 130 000 s^{-1} was found to be totally superimposable on a room-temperature spectrum of (**6**) in [$^2H_8$]toluene, although a

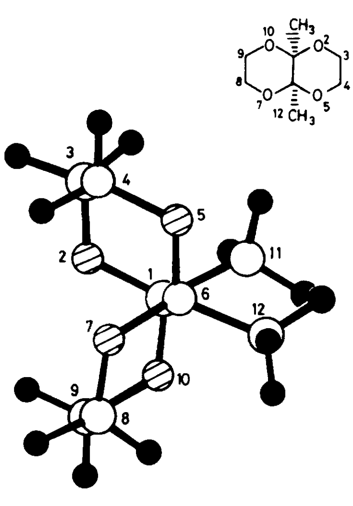


Figure 11. Molecular mechanics (MM2)-determined minimum-energy conformation of *cis*-1,6-dimethyl-2,5,7,10-tetraoxabicyclo[4.4.0]decane (**6**) viewed along the C(1)–C(6) bond

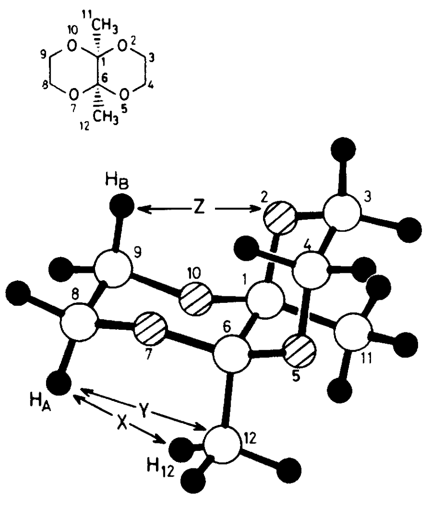


Figure 12. Dipole–dipole interactions of H_A and H_B in the molecular mechanics (MM2)-determined minimum-energy conformation of *cis*-1,6-dimethyl-2,5,7,10-tetraoxabicyclo[4.4.0]decane (**6**)

slight drift was observed in the absolute positions of the AA′BB′ multiplet, *i.e.* 15 Hz, for the high-temperature simulations. The $\Delta\nu_{AB}$ value was, however, found to be exactly that observed in [$^2H_8$]toluene, as shown in Table 1. Such a drift in ν_A and ν_B in the spectra may be accounted for by a temperature-induced chemical shift.

Using the rate constants obtained for the exchange process, from both ^1H and ^{13}C n.m.r. spectra, thermodynamic data for the ring-inversion process were obtained using the Eyring equation.[18] Plotting ln (k/T) against $1/T$ gave a good linear regression (correlation coefficient 0.999), as shown in Figure 9. From the slope the value of $\Delta H^{\ddagger}_{229}$ was found to be 51.5 kJ mol^{-1}, while at the coalescence temperature of 229 K (see Figure 6) $\Delta G^{\ddagger}_{229}$ was found to be 44.5 kJ mol^{-1}.

The value of $\Delta G^{\ddagger}_c$ for (**6**) is very close to that observed previously for (**9**),[5] a deuteriated 9,10-substituted derivative of (**6**), *i.e.* $\Delta G^{\ddagger}_{229}$ for (**9**) was found to be 46.1 kJ mol^{-1}. The $\Delta G^{\ddagger}_c$ value for (**6**) is also similar to the value of 40 kJ mol^{-1} observed for 1,4-dioxane.[9] The $\Delta G^{\ddagger}$ value for (**6**) is, however, much lower than those obtained for decalin and its substituted derivatives, *e.g.* *cis*-9,10-bis(bromomethyl)decalin,[5] $\Delta G^{\ddagger}_c$ 60.6 kJ mol^{-1}. Lowering of the $\Delta G^{\ddagger}_c$ values for heterocycles, compared with their carbocyclic analogues, has previously been attributed to a lowering of the torsional barriers experienced on substituting a heteroatom for a methylene group.[5] This principle, previously applied to monocyclic systems, appears to be equally applicable to the bicyclic systems studied here.

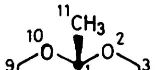
(ii) *Molecular Mechanics Calculations and Molecular Structures*.—In the absence of an *X*-ray crystallographic structure determination we have performed MM2 calculations on (**6**) in order to determine the minimum-energy conformation, which is shown in Figure 10. The conformation depicted in Figure 10 clearly shows the double chair conformation in (**6**), as indicated from the ^1H n.m.r. analysis in this work. On first inspection the conformation of (**6**) as shown in Figure 10 appears to have little distortion from an idealised *cis*-decalin. The lack of distortion, by either flattening or puckering, is more clearly shown in Figure 11, where a view looking along the C(1)–C(6) bond is shown. Again the chair conformation is evident in both rings, as well as the dihedral angle of 54° present between the bridgehead methyl groups.

Structural data for the MM2-determined conformation of (**6**), depicted in Figures 10 and 11, are given in Table 4 along with data from previous investigations. Overall, the MM1 data obtained by Jorgensen *et al.*[19] for (**1**) and (**2**) are in good agreement with the MM2 data obtained by us for (**6**) except where the methyl groups exert a direct effect, *e.g.* lengthening of the bond C(1)–C(6) bond in (**6**) compared with (**1**) or (**2**). However, discrepancies between MM1 and *X*-ray data for (**1**), *e.g.*, experimental and calculated bond lengths, does highlight the need for caution in making comparison between such data for conformations of heterocycles.[12] For (**6**) there does appear to be slightly better agreement between the calculated bond angles of (**6**) and the *X*-ray bond angles of (**1**), although the bond lengths still exhibit poor correlation. However, a direct comparison between (**1**) and (**6**) on these points is suspect in the absence of any *X*-ray data for (**6**).

Further inspection of the minimum-energy conformation of (**6**), using the CHEMGRAF package,[20] provided a possible explanation for the unusual chemical shift observed for the axial protons, designated H_A and H_B, in Figure 7, and subsequently used in the analysis of the ABCD multiplet of (**6**). The rationale for the downfield chemical shift seen is based on the distances *X*,*Y*,*Z* shown in Figure 12. The closest approach of any of the bridgehead methyl hydrogens to the ring proton H_A (distance *X*) is 185 nm, when a dihedral angle of 30° for C(7)–C(6)–C(12)–H(12) is present. In contrast, distance *Y* between the methyl carbon and H_A was found to be 263 nm, with the same dihedral angle. In the case of H_B the shortest distance *Z* between H_B and the axial oxygen is 239 nm, with a dihedral angle of 62° for H_B–C(9)–C(10)–C(1) and 60° for C(9)–C(10)–C(1)–C(2). Thus, H_A appears to experience a much higher through-space dipole–dipole interaction with the three methyl hydrogens (185 nm) than H_B with the axial oxygen lone pairs (239 nm). The dipole interaction of H_A and the methyl carbon can be effectively disregarded because the distance *Y* is 263 nm. This structural analysis is also consistent with the initial hypothesis used to designate H_{A-D} *i.e.* a 1,3-diaxial interaction between a hydrogen and a bridgehead methyl is more pronounced than a 1,3-diaxial interaction between a hydrogen and an axial oxygen functionality.[16]

(iii) *Relative Stabilities of* 2,5,7,10-*Tetraoxabicyclo*-[4.4.0]*decane Isomers*.—Recently Jorgensen *et al.*[19] have shown, by MM1 and molecular orbital calculations, that *cis*-2,5,7,10-tetraoxabicyclo[4.4.0] decane (**1**) is 12—15 kJ mol^{-1} more stable than the corresponding *trans*-isomer (**2**), and 16—

Table 4. Molecular mechanics (MM1 and MM2)-calculated and *X*-ray-determined structural data for *cis*-1,6-dimethyl-2,5,7,10-tetraoxabicyclo[4.4.0]decane (**6**) and *cis*- and *trans*-2,5,7,10-tetraoxabicyclo-[4.4.0]decane (**2**) and (**1**).



(**6**)

(**2**)

(**1**)

	(**6**)	(**2**)		(**1**)
Bond length (nm)	MM2	MM1[a]	*X*-ray[a,b]	MM1[a]
1-2	140.9	140.4	143.0, 142.8	140.5
2-3	140.2	153.1	144.5, 143.6	141.1
3-4	153.1	140.9	151.0, 151.7	153.3
4-5	140.7	140.7	145.0, 144.2	141.1
5-6	140.9	152.0	140.0, 141.6	140.5
1-11	155.1		152.9	153.2
6-12	153.0			
	153.0			
Torsion angles (°)				
8-7-6-5	174.1			178.6
7-6-7-4	59.4			179.0
11-1-6-12	54.1			
2-3-4-5	54.8			
Bond angles (°)				
1-2-3	113.8		109.3, 110.5	109.5
2-3-4	110.6		110.1, 110.4	111.0
3-4-5	109.8		109.8, 110.0	111.0
4-5-6	111.6		113.4, 113.2	109.5
5-6-7	108.9		108.3, 107.1	107.4
11-1-2	109.8			
10-1-11	108.4			
11-1-6	111.2			

[a] Taken from ref. 19. [b] Two values are given due to non-exact C_2 symmetry.

20 kJ mol^{-1} more stable than the bis(dioxolan-2-yl) isomer (**3**). The stability of (**1**) arises from the geometry adopted by the acetal fragments, *i.e.* C–O–C–O, in (**1**) and (**2**). The preference for such acetal fragments is to avoid an *anti,anti*-array, which results in a 'rabbit ear' effect between parallel lone pairs.[4,16,19] In (**2**) an *anti,anti*-array of both C–O–C–O fragments is present and as a consequence (**2**) is destabilised compared with (**1**), which has an *anti,gauche*-array. These types of array, *i.e.* *anti,anti* and *anti,gauche*, are also present in (**6**) and (**7**) respectively and indicate why a preference for (**6**) is obtained. Indeed, the energy differences between (**6**) and (**7**) may well be similar to those seen for (**1**) and (**2**). The preference for *gauche*-arrays in molecules containing acetal fragments is referred to as the 'anomeric effect'.[6] This stereoelectronic phenomenon, long observed in carbohydrates, has been used to explain why certain functionalities, *e.g.* alkoxyl, adopt axial rather than equatorial positions, particularly when that functionality is α to a heteroatom.

The absence of (**7**) in the preparation of (**6**) is entirely due to its method of synthesis; all previous syntheses of various 2,5,7,10-tetraoxabicyclo[4.4.0]decanes have used conditions which can lead to isomerisation.[4,5,19] Consequently any synthetic approach to *trans*-2,5,7,10-tetraoxabicyclo[4.4.0]decanes must not include the potential for isomerisation, *i.e.* a kinetic rather than thermodynamically biased method.

In conclusion we have shown that only the *cis*-isomer of the 1,6-dimethyl-2,5,7,10-tetraoxabicyclo[4.4.0]decane (**6**) is obtained under thermodynamic conditions from (**4**) and (**5**). Analysis of n.m.r. spectral data and the MM2 minimum energy conformation obtained for (**6**) clearly indicates that a double chair form is present. The apparent lack of the *trans*-isomer (**7**) in our studies is in accordance with previous investigations into various 2,5,7,10-tetraoxabicyclo[4.4.0]decanes.[5,12,19]

Experimental

N.m.r. spectra were obtained on a Perkin-Elmer R32 (90 MHz; ^1H n.m.r.) and a Bruker WH90 (22.63 MHz; ^{13}C n.m.r.) instrument at 20 °C. Chemical shifts are for tetramethylsilane as internal standard. Variable-temperature ^1H and ^{13}C n.m.r. studies were recorded after calibration of the respective spectrometers by either a thermocouple or by the induced chemical shift of methanol.[21] I.r. spectra were recorded using a Perkin-Elmer 257 i.r. spectrophotometer. Mass spectra were determined on a V.G. micromass spectrometer by the direct-insertion technique. M.p.s were determined on a Kofler Block.

cis-1,6-*Dimethyl*-2,5,7,10-*tetraoxabicyclo*[4.4.0]*decane*.—To a stirred solution of 2-ethoxy-1,3-dioxolane (6.5 g, 55 mmol), butane-2,3-dione (4.3 g, 50 mmol), and ethanol (50 ml), held at room temperature, was added concentrated sulphuric acid (2 drops). The solution was stirred for 20 min before addition of further 2-ethoxy-1,3-dioxolane (6.5 g, 55 mmol) dropwise over 5 min. On complete addition the solution was stirred overnight before adding solid, anhydrous sodium carbonate (0.25 g), filtration, and removal of the solvent *in vacuo*. The resulting pale yellow crystalline material was recrystallised from hexane to give *cis*-1,6-dimethyl-2,5,7,10-tetraoxabicyclo[4.4.0]decane (**6**) (6.5 g, 92% yield based on dione consumed), as lustrous platelets, m.p. 91 °C (lit.,[22] 90—92 °C), δ_H ($CDCl_3$) 1.41 (6 H, s, CH_3) and 3.54—4.2 (8 H, AA'BB'm), δ_C (C_7D_8) 20.2 (CH_3), 61.2 (C-3, -4), and 95.9 (C-1) p.p.m.; $\nu_{max.}$ ($CHCl_3$) 3 010, 2 980, 2 960, 1 455, 1 380, 1 300, 1 285, 1 200, 1 150—1 100, 930, 920, 870, and 840 cm^{-1}; *m/z* 174 (M^+, 2%), 87 (42), and 43 (100).

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