Pseudorotation and Ring Inversion in 1-Substituted Cyclooctenes[1]

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The stereodynamics of a series of 1-substituted cyclooctenes have been studied by dynamic NMR spectroscopy and molecular mechanics calculations and compared with previous results. Two separate processes are identified in the NMR spectra, with substituent dependent barriers between 7.6 and 8.2 kcal mol^{-1} for the first process and between 5.3 and 8.2 kcal mol^{-1} for the second process.

A consideration of models and calculations suggests that the ground state conformation is a twist boat–chair, that the former process is a pseudorotation through a chair–chair conformation, and that the latter is a pseudorotation through boat–boat conformations. Both pseudorotations are necessary to achieve ring inversion, *i.e.* the interconversion of enantiomeric conformations, so inevitably ring inversion will always have the higher of the two barriers measured. However, the rate determining pseudorotation may change as the size or rigidity of the 1-substituent increases. A substituent conjugating with the double bond, or which is sterically large, affects the boat–boat pseudorotation more than the chair–chair one.

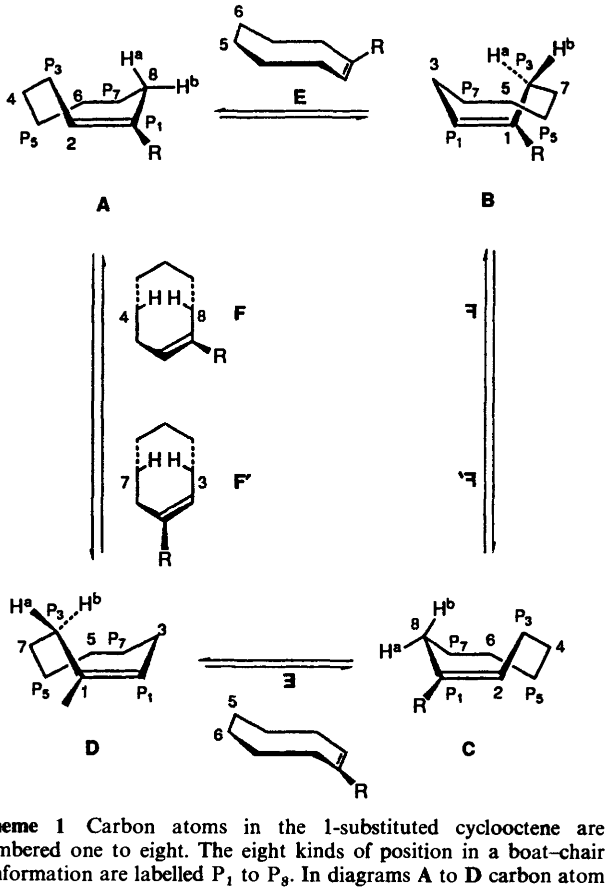
The preferred conformation of cyclooctene **1a** is a slightly twisted boat-chair[2–4] like **A** (R = H in Scheme 1) in which there are eight different kinds of positions P_1 to P_8. Anet has shown[2,3] that two successive sets of changes occur in the NMR spectrum as the temperature is lowered and these correspond to conformational processes with barriers of 8.2 and 5.3 kcal mol^{-1} which were called ring inversion and pseudorotation, respectively. Weigert and Strobach have reported[5] on the pseudorotation in 1-fluorocyclooctene **1b**. In the present work a dynamic NMR study of a series of 1-substituted cyclooctenes, which allowed us to characterize ring inversion and pseudorotation in some detail, is reported.

Different combinations of rotations[4] about the carbon–carbon single bonds allow the interconversion of **A** with equivalent conformations **B**, **C** and **D**, and inspection of models suggests that Scheme 1 represents this complete circuit, although a wide range of less stable kinds of conformations may exist and be visited. **A** interconverts with **B** *via* the chair–chair conformation **E** and with **D** *via* two successive boat–boat conformations F and F′. Enantiomeric versions of F and F′ take a molecule **B** on to conformation **C** which is the enantiomer of **A**. Both the processes in Scheme 1 are necessary to achieve interconversion of the enantiomers.

The interconversion of two conformations by a series of rotations about bonds is called a pseudorotation. By convention the set of pseudorotations which interconverts any conformation with its enantiomer is called ring inversion although this name is commonly reserved for such an interconversion of enantiomeric forms of the most stable conformation. If this ring inversion involves a series of pseudorotations, then the most demanding of these is called the rate-determining step.

Structure **C** is thus the ring-inverted form for **A**, as is **B** for **D**, and, if R is not a hydrogen, twist-boat-chair conformations **B** and **D** are different from **A** and **C** since the substituent occupies a different position P_2 rather than P_1. In a pair of ring-inverted conformations like **A** and **C** any carbon atom occupies the same position P_n, but the dihedral angles along each n to $n + 1$ bond have changed sign but not magnitude and, most importantly for dynamic NMR studies, the hydrogens of each CH_2-group have exchanged pseudo-axial and pseudo-equatorial positions.

On the other hand, whatever the group R, individual carbon atoms in the ring take up a different position in **B** and **D** from that which they have in **A** and **C**. The atom C-8, for instance, is at position P_8 in **A** and at position P_3 in **B** and **D**.



Scheme 1 Carbon atoms in the 1-substituted cyclooctene are numbered one to eight. The eight kinds of position in a boat–chair conformation are labelled P_1 to P_8. In diagrams **A** to **D** carbon atom numbers and conformational position labels are indicated alternately.

Thus if either of the processes of passage through conformation **E** or **F** is slow in the NMR timescale, ring inversion will be slow, because a molecule will not be able to pass from one conformation to its mirror image. The two types of conformations **A**,**C** and **B**,**D** can still be visited by the other

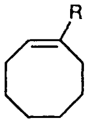
Table 1 Free energies of activation ($\Delta G^{\ddagger}$) for ring reversal and pseudorotation of **1a–f**

	Ring reversal[a]				Pseudorotation[b]					
Compound	$\Delta G^{\ddagger}$/kcal mol^{-1}	Δν/Hz	T/°C[c]	MHz[d]	$\Delta G^{\ddagger}$/kcal mol^{-1}	Δν/Hz	T/°C[c]	MHz[d]	Ratio[e]/%	Signal
1a	8.2				5.3					
1b	—				6.1	630	−129		60/40	F
1c	7.6 ± 0.15	190	−105	400	7.1 ± 0.1	170	−120	50.3	60/40	*C*HMe$_2$
1d	7.55 ± 0.15	225	−105	400	7.1 ± 0.1	55	−129	200	70/30	=CH
1e	7.7 ± 0.15	210	−103	400	7.4 ± 0.1	90	−114	50.3	55/45	C-*ipso* (Ph)
					7.4 ± 0.1	130	−114	50.3	55/45	=*C*–R
					7.5 ± 0.1	60	−120	200	55/45	=CH
1f					8.2 ± 0.15	45	−109	200	83/17	=CH
	7.9 ± 0.15	185	−107	400	8.1 ± 0.15	90	−117	400	82/18	=CH
	8.15 ± 0.15	280	−99	600	8.25 ± 0.15	135	−99	600	75/25	=CH

[a] For ring reversal the chemical shift difference (Δν) corresponds to that of the CH$_2$ hydrogens with the largest separation. [b] For pseudorotation the separation of the signals is reported in the last column. [c] The temperature (T) corresponds to the one where line shape simulation was best achieved. [d] Spectrometer frequency. [e] Ratio is that of the two conformers generated by the restricted pseudorotation.

process, however, so the observation in the NMR spectrum will be that each carbon still gives rise to only one NMR signal but that the two hydrogens of any CH$_2$ group are now different. This can be confirmed by following the fate of H$_a$ and H$_b$ in Scheme 1. When both processes are slow on the NMR timescale, two sets of signals will be seen for all carbons and hydrogens.

In the present investigation a number of 1-substituted cyclooctenes **1c–f** was examined to assess the effect of such substitution on the two barriers (ring inversion and pseudorotation) including the possible effects of conjugation between the substituent R and the double bond. This is an aspect of ring conformational isomerisation that has not previously received attention as far as we know.



1a R = H
1b R = F
1c R = CHMe$_2$
1d R = cyclopentyl
1e R = Ph
1f R = *N*-pyrrolidyl

Such conjugation effects should appear in **1e** and **1f**, particularly in comparison of the latter with **1d**. We also tried (by using the results of molecular mechanics calculations and the trend of the low temperature chemical shifts) to identify the more stable of the two conformers **A** and **B** of Scheme 1, which are seen in the NMR spectra when both processes are slow.

Results

Compounds **1c–e** (R = Pr^i, *Cyclopentyl*, Ph).—The ^{1}H 400 MHz spectrum (in CCl$_2$F$_2$–CD$_2$Cl$_2$) of the methylene region of **1c** displays, at room temperature, six two-proton multiplets: two at 2.16 and 2.08 ppm (CH$_2$ hydrogens α to the double bond) and four overlapping at *ca.* 1.52, 1.52, 1.48 and 1.48 ppm (remaining four sets of CH$_2$ hydrogens). On reducing the temperatures to below −60 °C the signal at 1.52 ppm broadened considerably (much more than the one at 1.48 ppm) and below −105 °C split into a pair of equally intense signals (1.73 and 1.26 ppm). Also the 1.48 ppm signal eventually split symmetrically below −120 °C. The decoalescences are due to a slow ring inversion process that gives separate axial and equatorial signals for each of these CH$_2$ groups. Line shape simulation at the coalescence temperature (Table 1) yields a ΔG^* for the ring inversion of 7.6 kcal mol^{-1}, a value only slightly lower than that reported for cyclooctene itself (8.2 kcal mol^{-1}).[2]

On further reducing the temperature many of the lines in the spectrum of **1c** split into pairs of signals of unequal intensity due to the slowing down of the pseudorotational process. An alternative explanation of these changes, slow rotation about the substituent-to-ring bond, seems unlikely. The proton spectrum thus becomes quite complex so the investigation of the second dynamic process was better carried out at the ^{13}C frequency. In fact the ^{13}C spectrum of **1c** (in CHF$_2$Cl) displays, as expected, ten lines that broaden below −100 °C and eventually split, at −140 °C, into pairs of lines with a 60:40 intensity ratio. For instance, the following lines could be easily identified, the first shift corresponding to that with higher intensity: =*C*–R (149.6 and 147.2 ppm); =*C*–H (121.4 and 123.0 ppm); *C*HMe$_2$ (37.65 and 34.15 ppm). Line shape simulation of the latter pair yields ΔG^* equal to 7.1 kcal mol^{-1} at −120 °C (Table 1). The free energy of activation in **1c** is markedly higher than that reported for the same process in cyclooctene (5.3 kcal mol^{-1}).[2]

The methyl groups of the isopropyl substituent are diastereotopic when ring inversion is slow and should give separate signals. This doubling is obscured at intermediately low temperatures by the broadening due to the low temperature process, but in the ^{13}C spectrum at −135 °C four methyl signals are seen, one 40:60 doublet at 22.1 and 21.2 ppm and another 60:40 doublet at 21.5 and 20.6 ppm.

Similar results were obtained for the analogous derivative **1d** (R = cyclopentyl) where the two processes have the same barriers as in **1c** (Table 1), the conformer ratio being 70:30. In **1e** (R = Ph) the two barriers (7.7 and 7.4 kcal mol^{-1}, respectively) are almost equal within the experimental errors.

Compound **1f** (R = N-*Pyrrolidyl*).—In the case of this derivative a more complex situation is encountered in that, in addition to ring inversion and pseudorotation, torsion about the =C–N bond joining the five- and the eight-membered rings is restricted at low temperature.[6] From the ^{1}H 400 MHz spectrum, not significantly distinct ΔG^* values (Table 1) of 8.1 (at −117 °C) and 7.9 (at −107 °C) kcal mol^{-1}, respectively, were obtained for pseudorotation and ring inversion (the ratio of conformers being *ca.* 80:20). Simulation at a different frequency (200 MHz) confirmed the value for pseudorotation (Table 1). It was of paramount importance to confirm that barriers are equal at the same temperature, but only at 600 MHz is there at least one common temperature (−99 °C) where both the dynamic processes could be simultaneously measured. The free energies of activation were again found to be the same for

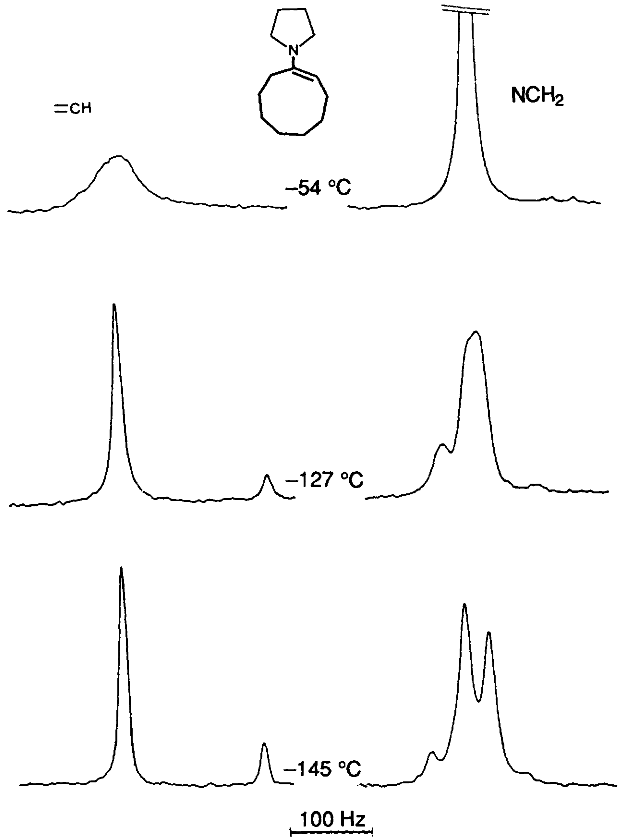


Fig. 1 ^{13}C NMR (75.5 MHz) signals of =CH and NCH_2 carbons of 1-(1-cyclooctenyl)pyrrolidine (**1f**) in CHF_2Cl at various temperatures. Below −40 °C the single lines broaden at different extent (see trace at −54 °C) and at −124 °C both split into a pair of lines with a 4:1 intensity ratio. On further cooling, the two signals of =CH remain unchanged whereas those of the NCH_2 group broaden again (see trace at −127 °C) and eventually each of them further splits into a 1:1 doublet because of the restricted torsion about the N–C bond linking the two rings. (Note that the upfield line of the minor doublet overlaps the downfield line of the major one.)

Table 2 Chemical shifts (with respect to TMS) of the two ethylenic carbons and of the ethylenic hydrogen in compounds **1c–f** at low temperature. The relative amount of the conformers due to restricted pseudorotation is also indicated.

		Chemical shift/ppm				
Compound	Conformer	=C(quat)	=CH	=CH	*T*/°C	Solvent
1c	60%	149.6	121.4	5.15	−135	CCl_2F_2
	40%	147.2	123.5	5.48	−135	
1d	70%	145.7	122.8	5.28	−135	CHF_2Cl–CCl_2F_2
	30%	143.5	124.0	5.54	−135	
1e	55%	143.8	130.3	6.20	−130	$CHFCl_2$–CCl_2F_2
	45%	145.0	129.0	5.90	−130	
1f	80%	145.0	96.9	4.30	−135	CHF_2Cl
	20%	147.6	94.8	4.08	−135	

both ring reversal and pseudorotation (8.2 kcal mol^{-1}), within the uncertainty of the line shape fitting. This is in substantial agreement with the previous measurements at lower frequency and at different temperatures.

The restricted N–C torsion did not interfere with these measurements as this process affects only the shifts of the nuclei of the five-membered ring. In fact the NCH_2 ^{13}C signals of the five-membered ring is already split at −127 °C into a pair of lines (intensity ratio 80:20) due to slow pseudorotation, as is the =CH signal (Fig. 1). At −145 °C, however, each of the unequal lines of the former pair is further split into a 1:1 doublet. The ΔG^* values corresponding to this third motion are 7.35 and 7.0 kcal mol^{-1}, respectively,[6] for the torsion in the major and minor conformers.

In Table 2 are reported the ^{13}C chemical shifts observed at low temperature for the ethylenic carbons C-1 and C-2 of **1c–f**, as well as the ^1H shifts of the ethylenic hydrogen 2-H, which can be unambiguously identified in both the conformers of the four compounds. In **1c** and **1d** (where R is a non-conjugating aliphatic group) the more intense C-1 ^{13}C signal is at lower field, whereas the more intense 2-H and the C-2 signals are at higher field. This trend is reversed in **1e** and **1f**, where R is a conjugating group. It is clear from Table 2 that substituents do affect the equilibrium position; the hypothesis that the more stable conformer in **1c** and **1d** becomes the less stable one in **1e** and **1f** plausibly explains the reversal of these three chemical shifts.

That conjugation itself reverses the trend of each of these shifts requires three separate unsupported hypotheses to hold, and Ockham's razor suggests that this is less likely. Moreover, we shall show later that calculations indicate that these three olefinic atoms are identically placed with respect to the phenyl ring in both conformers. At this stage, however, it is not possible to decide which conformer is which (*i.e.* **A** or **B** of Scheme 1) and additional information is obviously required (see Discussion).

Discussion

The free energies of activation for ring inversion in *cis*-cyclooctenes are little dependent upon the nature of the substituent R, the ΔG^* values lying in a quite restricted range (7.6–8.2 kcal mol^{-1}), whatever the substituent (Table 1). On the other hand the substituents substantially affect the pseudorotational barrier: the larger the size of R, the larger is the ΔG^* value (*e.g.* 5.3, 6.1, 7.1 kcal mol^{-1} for R = H, F, Pr^i or cyclopentyl, respectively), yet ring inversion barriers are markedly higher. When the substituent R exhibits a conjugative ability, the lower barriers increase further (7.4 and 8.2 kcal mol^{-1}, respectively, for R = Ph and *N*-pyrrolidyl). This is particularly evident if one compares the two rings having the same size, *viz.* R = cyclopentyl (**1d**) and R = *N*-pyrrolidyl (**1f**). The substantial conjugation of the pyrrolidine group is already known from the restricted N–C torsion.[6]

Before explaining this trend, we assigned the structures of conformer **A** and **B** (see Scheme 1) whose relative stability seems to change when R is a group conjugating with the double bond. Molecular mechanics calculations are often helpful in conformational assignment, and we chose to study the case of **1e** (R = Ph) since other groups R have themselves a wide range of conformational possibilities. In Fig. 2 the corresponding computed[7] structures are displayed. In both conformers the phenyl ring is coplanar with the double bond (the deviation from coplanarity being −2° in **A** and +2° in **B**) in agreement with the presence of conjugative effects. Conformer **A** has an energy 0.7 kcal mol^{-1} higher than that of conformer **B**: the latter should therefore correspond to the more abundant species in **1e**. On the basis of the trend of chemical shifts in Table 2 the same assignment should also apply to **1f**, whereas conformer **A** is the more stable in derivatives **1c**,**1d**.

We would now like to consider the way of passing between the four conformations **A–D** of Scheme 1, as suggested by models and molecular mechanics calculations. There are two different pathways which seems more obvious than others.[3,4]

Pathway 1 involves a transition from a twist boat–chair **A** to a chair–chair conformation **E**, which is symmetrical except for the substituent. Reversal of this process returns the molecule to **A**, or the mirror image of the reversal can be carried out to give a different twist-boat–chair **B**. Such a process involves movements

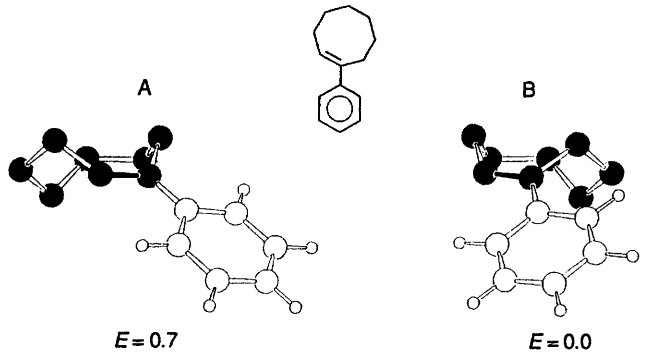
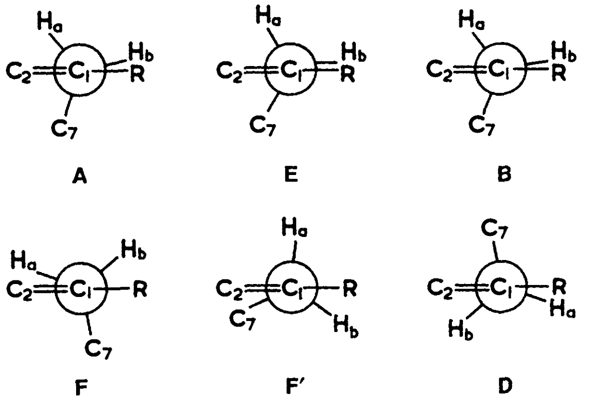


Fig. 2 Representation of the structures of the two conformers **A** and **B** (see also Scheme 1) of **1e**, as obtained from MM-2 calculations. The hydrogens of the cyclooctene ring (where the carbons are represented by full circles) have been omitted for a clearer presentation. In derivative **1e** the energy computed for conformer **B** is 0.7 kcal mol^{-1} lower than that of conformer **A**.



Scheme 2

largely at the 4,5,6,7-positions and little change at any point in the eclipsing interactions of R with CH_2–C(7) along the 1–8 bond (see **A**–**E**–**B** in Scheme 2).

The second pathway involves a transition from **A** to a boat–boat conformation **F** which can move on to a second boat–boat conformation **F′** in which the substituent has a different location. Reversal of the original step from **F** returns to **A**, but from **F′** goes on to **D**. The **A** to **D** interconversion involves movements about most carbon–carbon bonds, but particularly successive eclipsing of R with H_b, H_a and eclipsing of C-7 with the double bond along the C(1)–C(8) bond (see Scheme 2).

At ambient temperature both pseudorotation processes are fast on the NMR timescale and so geminal protons are equivalent and the eight different ring carbons have only one signal each. If either process becomes slow, geminal protons become non equivalent, because the other process does not exchange a proton between all four possible locations shown in **A** to **D**. The carbons, however, still only have one signal, in that each carbon can visit its two available positions by whichever pseudorotation process is still fast. It is only when both pseudorotations are slow that the carbons become non-equivalent.

The above consideration of dihedral angle changes along the C(1)–C(8) bond during the two pseudorotation pathways (Scheme 2) suggests that only the boat–boat barrier should rise markedly with the increasing size or inflexibility of R, so the high and low temperature processes can be identified as pseudorotations through chair–chair **E** and through boat–boat **F** and **F′**, respectively.

Confirmation of this hypothesis comes from molecular mechanics calculations carried out on cyclooctene **1a** (R = H). The energies of the boat–boat conformer **F** and the chair–chair conformer **E** are computed to be 3.52 and 5.95 kcal mol^{-1}, respectively, relative to the ground state **A**. The pseudorotation transition states are not precisely **F** and **E**, but should nonetheless reflect these relative energies. Accordingly, the easier pseudorotation in **1a** is that involving the boat–boat conformation and as Scheme 2 predicts it is more sensitive to substitution to the point that the lower barrier reaches the size of the higher barrier in **1f**. In the latter case, where the two barrier sizes cannot be distinguished experimentally, they need not be identical but they cannot be assigned to one process or the other. The increasing trend of the boat–boat interconversion barriers (accompanied by the little varying values for the chair–chair interconversion barrier) might suggest that for a substituent with an even greater steric or electronic interaction, two experimentally distinguishable barriers might once again be obtained. The higher barrier (still called ring inversion) would represent passage through the boat–boat conformation which has become the rate determining step in ring inversion.

A conjugating substituent as in **1f** has a greater effect on pseudorotation than one of a similar size as in **1d**. It is not possible to gauge whether a change in hybridization produces this effect. On the other hand, the partial double bond character of the exocyclic bond in conjugated compounds **1e** and **1f** should certainly reduce the flexibility of the substituent and thus can reasonably be expected to accentuate its steric effect.

Conclusion

The effects of substituents in the 1-position of cyclooctene on the barriers to conformational rearrangements lead to a plausible rationalisation of the stereodynamics of such rings. Because of the 1-substituent, there are two different kinds of twist boat–chair conformation **A** and **B** of different energy, each of which has a ring inverted enantiomer **C** and **D**, respectively. The enantiomeric pair **A** and **C** are thus different from the enantiomeric pair **B** and **D**.

Dynamic NMR spectroscopy shows two different pseudorotation processes, and substituent effects and molecular mechanics calculations suggest that these two pseudorotations convert any one conformation into different enantiomers of the other conformation. Thus, if two different pseudorotations occur successively, any conformation is converted to its enantiomer, *i.e.* ring inversion is achieved, and the barrier to ring inversion is whichever is the higher of the two pseudorotation barriers.

The different effect of substituents on the two pseudorotation processes along with models and calculations suggest that the high barrier substituent-insensitive process is passage through the chair–chair conformation, whereas the low barrier substituent-sensitive pseudorotation process is passage through a pair of boat–boat conformations.

With a sterically demanding substituent, therefore, or with one which conjugates with the double bond, the two barriers are apparently similar, and spectral changes do not allow a determination of which is which.

Appendix

A brief description of how to reach chair–chair (**E**) and boat-boat (**F**) conformations[4] using models now follows.

Boat–Boat (**F**).—Construct a model like **A**, and holding C-8 firmly in the right hand, take C-4 and move it upwards and inwards toward C-8. Structure **F** will result. Thereafter moving C-3 towards C-7 underneath the plane of the molecule, then turning the molecule over, will produce **F′**. Reversing the original motion takes **F** to **A** or **F′** on to **D**.

Chair–Chair (**E**).—From **A**, as before, holding C-8 in the right hand, take C-5 in the left hand and move it away and upwards from C-8 to arrive at the chair–chair (**E**). Reversing this process returns to **A**, but moving C-6 downwards and inwards towards C-3 results in structure **B**.

Experimental

Materials.—Derivatives **1c** and **1d** were prepared by the same method, a description of which is given for the latter case.

1-*Cyclopentylcyclooctene* (**1d**). 1-Cyclopentylcyclooctanol (4 g, 20 mmol) was added to a solution of phosphoric acid (10 g, 100 mmol) in water (40 cm^3). The mixture was refluxed for 1.5 h, extracted with ether, washed, dried and concentrated. The raw product was distilled at reduced pressure, b.p. (10 mmHg) 130–134 °C and subsequently purified by column chromatography on silica.

Derivatives **1c** and **1d** were identified as follows: **1c**: $^1H(CDCl_3)$ 1.05 (6 H, d, Me, Pr^i), 1.5 (8 H, br s, CH_2 ring), 2.15 (4 H, mult., CH_2 ring), 2.23 (1 H, mult., CH, Pr^i) and 5.35 (1 H, t, CH ring); $^{13}C(CDCl_3)$ 21.85 (q), 25.9 (t), 26.25 (t), 26.4 (t), 27.35 (t), 29.6 (t), 29.8 (t), 35.45 (d), 121.55 (d) and 146.7 (s) (Found: *m/z* 125.1562. Calc. for $C_{11}H_{20}$: M, 125.15650).

1d: $^1H(CDCl_3)$ 1.3–1.8 (16 H, br mult., CH_2), 2.10 (4 H, mult., CH_2), 2.35 (1 H, mult., CH), 5.38 (1 H, t, CH ring); $^{13}C(CDCl_3)$ 24.9 (t, 2C), 26.1 (t), 26.4 (t), 26.55 (t), 28.2 (t), 29.7 (t), 29.85 (t), 31.5 (t, 2C), 48.0 (d), 122.0 (d) and 143.6 (s) (Found: *m/z* 178.1728. Calc. for $C_{13}H_{22}$: M, 178.17215).

Cyclopentylcyclooctanol. To a cooled (0 °C) solution of cyclopentyllithium, obtained[8] by reacting a lithium suspension (25%) in mineral oil (14.4 g) with cyclopentylbromide (27 cm^3, 250 mmol) in pentane (100 cm^3), cyclooctanone (14.4 g, 11.7 mmol) was added, dropwise, keeping the temperature below +5 °C in a helium atmosphere. The reaction mixture was stirred overnight at room temperature and a saturated NH_4Cl solution was carefully added dropwise. The organic layer was separated, washed, dried, concentrated and distilled at reduced pressure, b.p. (4 mmHg) 135–140 °C, yielding 11.5 g of product.

Phenylcyclooctene (**1e**)[9] *and* 1-(1-*cycloocten*-1-*yl*)*pyrrolidine* (**1f**)[6] were prepared according to the literature.

NMR Measurements.—Variable temperature spectra were recorded with Varian Gemini 200 MHz, Bruker CXP 300 MHz, Varian VXR 400 MHz and Bruker AMX 600 MHz spectrometers. The samples were prepared by condensing the gaseous solvents (CCl_2F_2, CHF_2Cl, $CHFCl_2$) into NMR tubes (connected to a vacuum line) containing the compound dissolved in CD_2Cl_2 or C_6D_6 for locking purposes. The tubes, kept at the temperature of liquid nitrogen, were then sealed *in vacuo* and allowed to reach room temperature before being introduced in the pre-cooled probes of the spectrometers. The temperatures were calibrated using the temperature dependent signals of pure methanol: for temperatures lower than −100 °C either the ^1H signals of methanol dissolved[10] in CD_3OD–CHF_2Cl or the ^{13}C signals of 2-chlorobutane[11] were employed. The rate constants were obtained by visually comparing the computer simulated spectra with the experimental traces.

Barriers to ring inversion and pseudorotation were calculated from the experimentally determined frequency of conformational interconversion on the basis that passage through the transition state inevitably leads to completion of the process, *i.e.* a transmission coefficient of 1. The discussion of the mechanisms of the processes suggests that the transmission coefficient is probably less than 1, to an extent which is difficult to determine and which varies with the substituent, so that true barrier heights may be somewhat less than those reported.

Molecular Mechanics Calculations.—These were carried out using Allinger's MM2 program.[7] The recently available MM3 program[12] treates hydrogen–hydrogen repulsions better, but is unlikely to affect the present results.

Acknowledgements

D. C. and L. L. thank MURST and CNR, Rome for financial support. The international collaboration was made possible by a NATO grant (RG 86/0200). Thanks are also due to the Interuniversity NMR Service Laboratory (University of Florence) for the use of the 600 MHz spectrometer and to Mr. F. Piantini for assistance.

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Paper 1/00885D
Received 25*th February* 1991
Accepted 1*st May* 1991