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MARKED EFFECTS OF RING SIZE ON THE CORRELATED ROTATION OF THE CYCLOALKYL GROUPS OF 1,1-DICYCLOALKYLMETHYLENECYCLOALKANES

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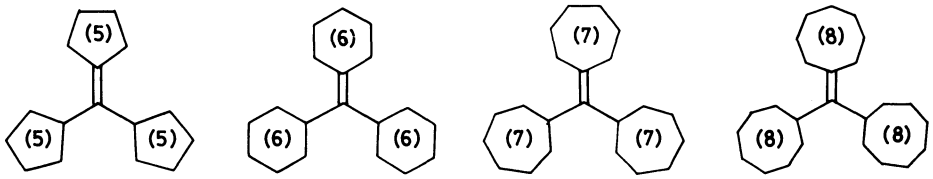
Correlated rotation of the cycloalkyl groups has been observed by ^{13}C NMR for the title compounds containing six-, seven-, or eight-membered rings. The $\Delta H^{\ddagger}$ value increases with the increase in the ring size, attaining 79.5 ± 2.1 kJ mol^{-1} when all the three rings are eight-membered. Molecular mechanics calculations indicated that the magnitude of internal angles is a major contributing factor.

Although many examples of hindered internal rotation have been reported,[1] such rotation of alkyl groups about the sp^2-sp^3 bond in simple olefins is limited to several cases.[2] Above all, the correlated rotation has been reported only for tetraisopropylethylene[2c,2d] and tetraneopentylethylene.[2f] The structural properties of such crowded olefins are of interest in relation to the behavior of an elusive compound, tetra-t-butylethylene.

We now wish to report that the two rotating cycloalkyl groups of 1,1-dicycloalkylmethylenecycloalkanes (6, 7, and 8) take on antisymmetric orientation in the ground state and undergo correlated rotation with the $\Delta H^{\ddagger}$ values which markedly increase with the increasing ring size. In contrast to these olefins, no definitive evidence for the correlated rotation has been obtained with compound 5. The results, combined with molecular mechanics calculations, suggest the importance of taking the internal angles into account, when the steric requirement of a cycloalkyl group is to be considered.



5 6 7 8

All the compounds (5 - 8) were prepared quantitatively by refluxing the corresponding tricycloalkylmethyl p-nitrobenzoates in DMF and by simply passing a hexane solution of the crude olefin through a silica gel column.[3] In Fig. 1 are reproduced the ^{13}C NMR spectra at two temperatures for all the sp^3 carbons of 6, 7, and 8.[4] The signals show marked dependence of line-shape on the temperature, and each signal splits into two lines of equal intensity at lower temperatures.[5] Notably, the sp^3 carbon signals of 8 are already split even at 24 °C. These observations indicate that the two cycloalkyl groups of 6, 7, and 8 assume antisymmetric orientation in the ground state and that these systems exist as an equilibrating mixture of the two antisymmetric

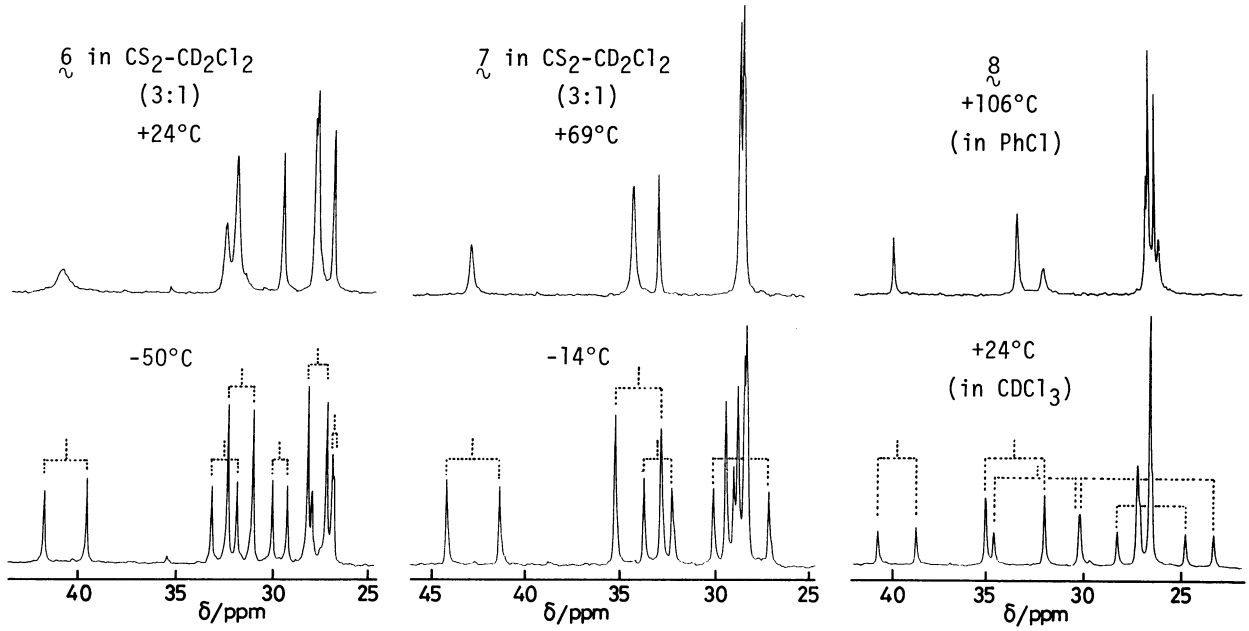


Fig. 1. ^{13}C NMR spectra at 25.00 MHz for all the sp^3 carbons of 6, 7, and 8 at two temperatures.

conformers, for example, 6a and 6a' in the case of 6 (Fig. 2). Molecular mechanics (MM2)[6] calculations showed that the three conformations, 6a, 6b, and 6c, correspond to three energy minima, 6a being the most stable and 6b and 6c being less stable than 6a by 6.5 and 10.6 kJ mol^{-1}, respectively, in enthalpy (Fig. 2).[7] Therefore, fortuitous existence of the two symmetric conformers 6b and 6c in an equal population is unlikely. The same will also be true with compounds 7 and 8.

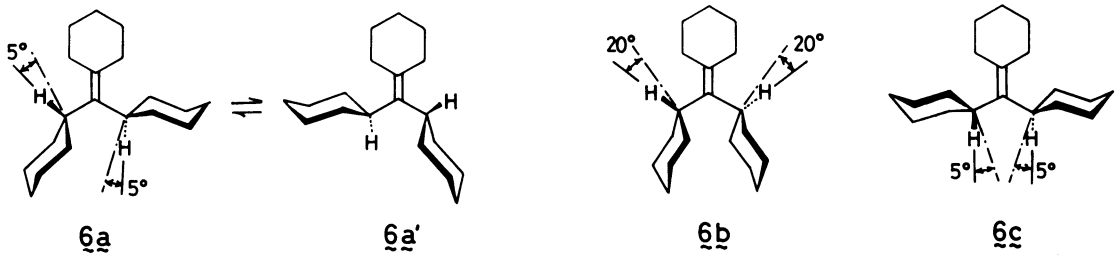


Fig. 2. Three minimum energy conformations of 6. The angles show rotations of the methine hydrogens from the plane composed of sp^2 and methine carbons.

Line-shape analyses[8] for all the sp^3 carbon signals observed for 6, 7, and 8 afforded the activation parameters summarized in Table 1. The rate of interconversion of the two cycloalkyl orientations at 25 °C decreases by a factor of ca. 10, when each of the three rings is expanded by one methylene unit. The $\Delta H^{\ddagger}$ values increase in the order 6 < 7 < 8 by an increment of 12 - 14 kJ mol^{-1}.

A major factor responsible for the marked dependence of the $\Delta H^{\ddagger}$ values on the ring size appears to be the magnitude of the internal angles, θ and ϕ, of the cycloalkylidene moiety and the rotating cycloalkyl group, respectively, the both angles being those at the substituted carbons. Increases in these angles are expected to make the distance between the α-H and 2-H smaller at the transition state (Fig. 3). Molecular mechanics (MM2) calculations of θ and ϕ for the most stable conformations of methyl- and methylene-cycloalkanes as models indicate that these angles increase

Table 1. Activation Parameters and First-order Rate Constants for the Interconversion of the Two Cycloalkyl Orientations at 25 °C.[a)]

	6	7	8
Solvent	CS_2-CD_2Cl_2[b)]	CS_2-CD_2Cl_2[b)]	$CDCl_3$
Temp. range/°C	-17 ∿ 24	15 ∿ 49	44 ∿ 73
$\Delta H^{\ddagger}$/kJ mol^{-1}	47.3±4.6	63.2±5.0	79.5±2.1
$\Delta S^{\ddagger}$/JK^{-1}mol^{-1}	-35±17	0±16	34±7
k/s^{-1}	470[c)]	47[d)]	4.3[c)]

a) Standard errors are at the 90% confidence level. b) 3:1 by vol.
c) Extrapolated. d) Interpolated.

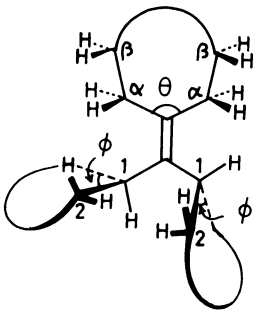


Fig. 3. A formula showing the definitions of θ, φ, and notations of sites.

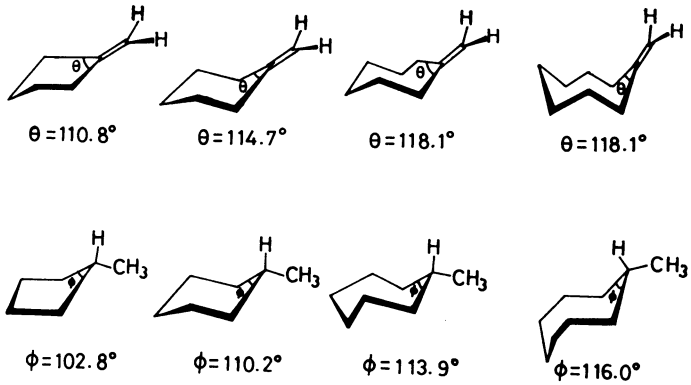


Fig. 4. Internal angles, θ and φ, of methylenecycloalkanes and methylcycloalkanes as models calculated by molecular mechanics (MM2).

with the increase in the ring size (Fig. 4).[9)]

Four possibilities are considered in regard to the interconversion pathway as examplified by 6; i.e., (i) the two-step rotation 6a⇌6c⇌6a', (ii) the two-step rotation 6a⇌6b⇌6a', (iii) the synchronous disrotation, and (iv) the synchronous conrotation. Molecular mechanics (MM2) calculations for the pathways (i) and (ii) afforded the enthalpies of activation of 52 and 67 kJ mol^{-1}, respectively. The former value (52 kJ mol^{-1}) agrees satisfactorily with the experimental determination (47.3 ± 4.6 kJ mol^{-1}), suggesting that the two-step rotation, 6a⇌6c⇌6a', is the most probable. This conclusion is in harmony with that reached by Lunazzi et al. concerning the rotation pathway of diisopropylnitrosoamine (i-Pr_2N-NO).[10)] The conformations of the transition states for the pathways (i) and (ii) are shown in Fig. 5 in the Newman convention.[11)] Investi-

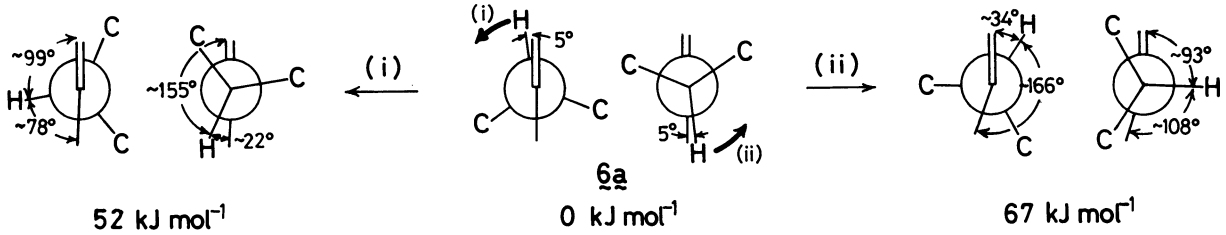


Fig. 5. The Newman projections with respect to the two sp^2-sp^3 bond axes for the transition states based on molecular mechanics (MM2) calculations on the interconversion pathways (i) and (ii). The cyclohexane rings are not indicated for simplicity.

gations of molecular models suggest that the two synchronous pathways [(iii) and (iv)] would energetically be highly unfavorable.[12)]

The $\Delta S^{\ddagger}$ value also increases with the ring size, ultimately going up to 34 ± 7 $JK^{-1}mol^{-1}$ with 8. This suggests that any conformational changes accompanied by reduced symmetry of the rotating rings and cycloalkylidene moiety might occur at the transition state with 7 and 8.

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2) a) P. D. Bartlett and T. T. Tidwell, J. Am. Chem. Soc., 90, 4421 (1968); b) A. F. Casy and R. R. Ison, Tetrahedron, 25, 641 (1969); c) R. F. Langler and T. T. Tidwell, Tetrahedron Lett., 1975, 777; d) D. S. Bomse and T. H. Morton, ibid., 1975, 781; e) J. E. Anderson, C. Doecke, and D. I. Rawson, ibid., 1975, 3531; f) G. A. Olah and G. K. Surya Prakash, J. Org. Chem., 42, 580 (1977); g) H. M. R. Hoffmann, R. J. Giguere, D. Pauluth, and E. Hofer, ibid., 48, 1155 (1983).

3) All the olefins showed satisfactory elemental analyses. 5; viscous liquid: 6; mp 46.0 - 47.5 °C: 7; viscous liquid: 8; mp 65.0 - 67.0 °C.

4) In the case of 5 the signals at δ 26.7, 27.0, 31.0, 31.3, and 42.9 ppm (at 24 °C with an intensity ratio 4:2:4:2:2) show mere line-broadening even at -142 °C in CS_2-CD_2Cl_2 (3:1 by vol.).

5) With all the olefins the sp^2 carbon signals showed no line-broadening down to -130 °C. In the cases of 6 and 8 the signal assigned to the γ-carbon of 6 and that assigned to the δ-carbon of 8 remained singlet. For the notation of the carbon sites see Fig. 3.

6) N. L. Allinger and Y. H. Yuh, QCPE, 11, 395 (1980).

7) Molecular mechanics (MM2) calculations showed that 6a, 6b, and 6c are most stable when the two cyclohexyl rings are in the slightly rotated positions as illustrated in Fig. 2. When the angles in each of the structures become 0°, 6a, 6b, and 6c become less stable by 0.3, 22, and 0.04 kJ mol^{-1}, respectively.

8) H. S. Gutowsky and C. H. Holm, J. Chem. Phys., 25, 1228 (1956).

9) For the calculations on unsubstituted cycloalkanes, see; J. B. Hendrickson, J. Am. Chem. Soc., 83, 4537 (1961); 85, 4059 (1963); 86, 4854 (1964).

10) L. Lunazzi, M. Guerra, D. Macciantelli, and G. Cerioni, J. Chem. Soc., Perkin Trans. 2, 1982, 1527.

11) Molecular mechanics (MM2) calculations showed that the barrier to rotation in the pathway (i) is slightly affected by the ring inversion of the cyclohexylidene moiety.

12) Construction of potential energy surface by means of MM2 calculations is in progress and will be reported in a full paper.

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