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Energy Barriers for the Ring Inversion of 1,2:3,4:5,6-Tris(bicyclo[2.2.2]octeno)- and 1,2,3,4,5,6-Hexamethylcycloheptatrienes

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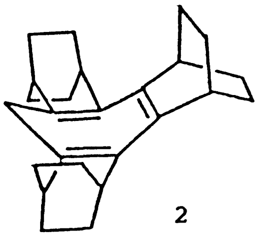
The energy barriers for the cycloheptatriene ring inversion of the titled compounds were determined by dynamic NMR method. It was clarified that annelation with three rigid bicyclooctene units brings about much less steric destabilization to the planar form of the ring as compared with substitution with six methyl groups. This result was supported by molecular mechanics calculations.

Cycloheptatriene (**1**) is known to exist in a non-planar boat form undergoing rapid ring inversion.[1)] The low-temperature NMR studies demonstrated the barrier for inversion to be approximately 6 kcal mol^{-1};[2)] this value was also obtained by theoretical calculations assuming a planar transition state structure.[3)] Although the presence of bulky substituents or fused benzene rings has been reported to increase this barrier,[4)] there seems to be no report on the ring inversion of 1,2,3,4,5,6-hexasubstituted cycloheptatriene except for the tribenzo derivative.[4b)] Here we describe the results of the first dynamic NMR study on such hexaalkylsubstituted cycloheptatrienes, i.e. the titled compounds **2** and **3**. In view of the remarkable stability recently observed for the supposedly planar cation **4**,[5)] it seemed of particular importance to estimate the steric influence of the presence of three annelated bicyclic units upon energy barrier for ring inversion involving the planar transition state.



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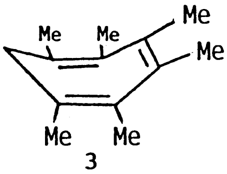

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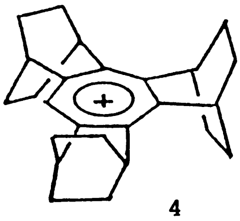

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While the synthesis of **2**[6)] (30% yield) required a large excess (22 equiv.) of CH_2N_2 in CuBr-catalyzed ring expansion of the corresponding benzene derivative[7)] in refluxing dichloroethane,[5)] only 3 equiv. of CH_2N_2 was sufficient to obtain **3**[8)] (26% yield) from hexamethylbenzene (**5**) by the same procedure. In contrast to the formation of **2** as a single product, products formed by further addition of methylene were obtained from **5** in approximately 29% yield. Desired products were successfully separated by the use of column chromatography over SiO_2 impregnated with $AgNO_3$ (7%) (eluent, hexane-ether).

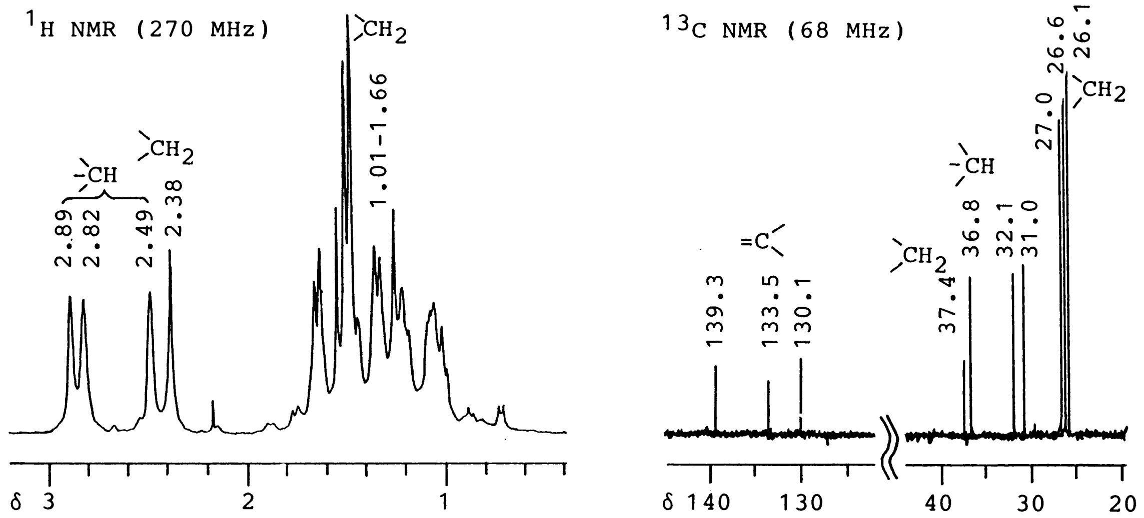
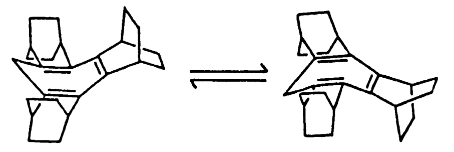


Fig. 1. NMR spectra of 2 ($CDCl_3$; 25 °C).

Whereas the ^{1}H (270 MHz) and ^{13}C NMR (68 MHz) spectra of 2 (Fig. 1) exhibited sharp signals typical of the cycloheptatriene rapidly inverting its conformation (Eq. 1), they gradually broadened upon lowering the temperature. Especially in ^{13}C NMR, only the signals for methylene carbons of the bicyclooctene frameworks underwent gradual broadening (Fig. 2a) and finally split into three sets of doublets at the temperatures below -90 °C,[9)] where the ring inversion is apparently frozen within the NMR time scale. The temperature-dependent spectral change was simulated by complete line shape analysis[10)] (Fig. 2b). The Arrhenius plot of the kinetic data at the temperature range of -90 to 0 °C gave a good linear correlation (r=0.9982), from which the activation parameters for the ring inversion process of 2 were calculated as follows: E_a=8.5±0.5 kcal mol^{-1}, $\Delta G^{\neq}$(298K)=11.3±0.2 kcal mol^{-1}, and $\Delta S^{\neq}$= -11±3 cal $mol^{-1}K^{-1}$.

In sharp contrast, the ^{1}H NMR spectrum of 3 (Fig. 3) exhibited the signals corresponding to a static boat structure even at room temperature. The signals for the C-7 methylene protons appeared as a pair of doublets (J=11.7 Hz) at δ 2.20 and 1.98, and did not show any appreciable line broadening at the temperature as high as 100 °C[11)] even by use of an instrument of lower frequency (90 MHz). From this result the $\Delta G^{\neq}$ value for the ring inversion



(1)

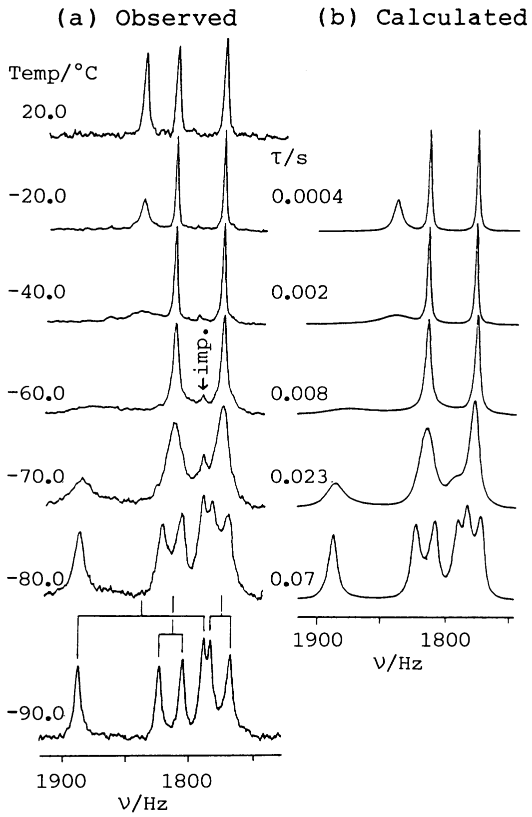

(a) Observed (b) Calculated

Fig. 2. Observed (a) and calculated (b) NMR line shapes for methylene carbons of bicyclooctene frameworks of 2 in CD_2Cl_2:CS_2 = 1:2.

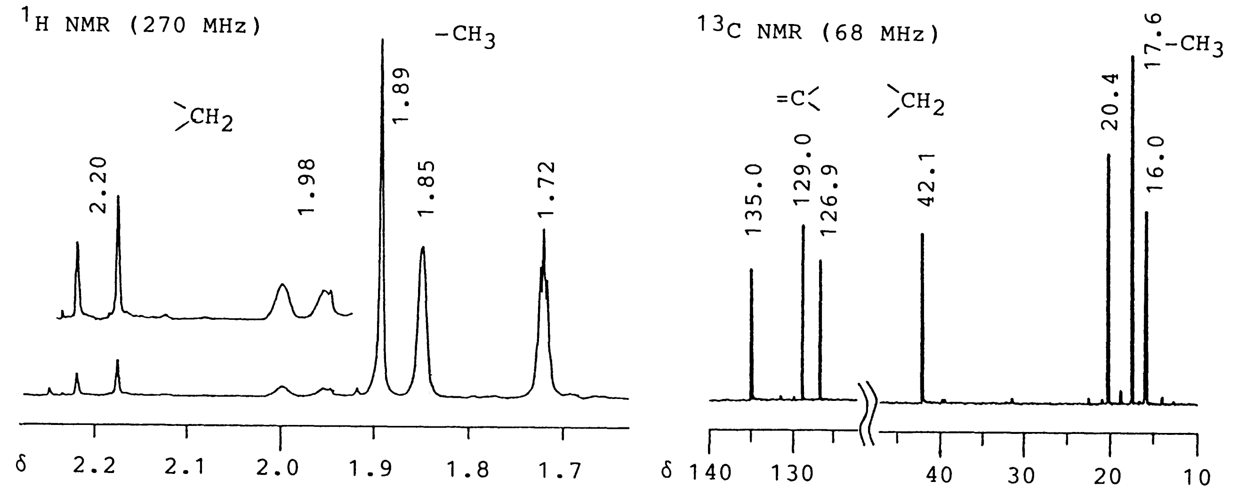


Fig. 3. NMR spectra of 3 ($CDCl_3$; 25 °C).

process was estimated to be greater than 20 kcal mol^{-1}.$^{12)}$

Thus, the energy barrier for the ring inversion of **2** is now found to be only 2.5 kcal mol^{-1} higher than that of unsubstituted cycloheptatriene **1** and more than 12 kcal mol^{-1} lower than that of the hexamethyl derivative **3**.

In order to gain an insight into the cause of these results, molecular mechanics calculations (MMP2(82))$^{3e,13)}$ were carried out for both the boat and planar forms of the cycloheptatrienes **1**, **2**, and **3**. As shown in Table 1, when we take the difference in ΔH^f between the boat and planar forms as the activation energy for inversion, the calculated results show rather qualitative agreement with the experimental results.$^{14)}$ Detailed examination of the calculated results indicated that non-bonded interactions and angle strains are major factors determining the inversion barrier. The increase in total non-bonded interaction energy upon going from boat to planar form is about 3 kcal mol^{-1} greater in **3** than in **2**. In addition, the increase in total angle strain is also 3.5 kcal mol^{-1} greater in **3** than in **2**. These increases in energy are ascribed to the severe constraint of the six methyl substituents in **3** at planar transition state. Such change in strain is greatly reduced for **2**, since alkyl substituents are already bundled in three bicyclic units at the ground state.

In conclusion, it was clarified that annelation with three rigid bicyclooctene units brings about much less steric destabilization to the planar form of the cycloheptatriene ring as compared with substitution with six methyl groups. This is in agreement with high thermodynamic stability of the cation **4** (pK_R+ 13.0 in 50% aq. MeCN),$^{5)}$ and lower stability of hexamethyltropylium ion (pK_R+ 6.6),$^{15)}$ though σ-π conjugation is supposed as one of the major stabilizing factors in the cation **4**.

Table 1. Heat of Formation and Ring Inversion Barrier Calculated by MMP2

Compd	ΔH^f_{boat} a) kcal mol^{-1}	ΔH^f_{planar} b) kcal mol^{-1}	$\Delta(\Delta H^f)$ c) kcal mol^{-1}	E_a(exptl) kcal mol^{-1}
1	45.5	49.8	4.3	5.7,$^{d)}$ 6.3$^{e)}$
2	16.1	27.6	11.4	8.5
3	2.5	21.3	18.8	>20$^{f)}$

a) 1,6-Nonbonded overlap was included. b) 1,6-Nonbonded overlap was not included (see Ref. 3e). C-1–C-7 were fixed on a plane. c) $\Delta(\Delta H^f) = \Delta H^f_{planar} - \Delta H^f_{boat}$. d) Ref. 2b. e) Ref. 2a. f) See Text.

References

1) For leading references, see; W. E. Heyd and C. A. Cupas, J. Am. Chem. Soc., 93, 6086 (1971); K. Takeuchi, T. Kitagawa, Y. Senzaki, and K. Okamoto, Chem. Lett., 1983, 73.

2) a) F. A. L. Anet, J. Am. Chem. Soc., 86, 458 (1964); b) F. R. Jensen and L. A. Smith, ibid., 86, 956 (1964).

3) a) J. Kao, J. Am. Chem. Soc., 109, 3817 (1987); b) J. M. Shulman, R. L. Disch, and M. L. Sabio, ibid., 104, 3787 (1982); c) S. Saebø and J. E. Boggs, J. Mol. Struc., 87, 365 (1987); d) H. J. Lindner, Tetrahedron, 37, 535 (1981); e) J. T. Sprague, J. C. Tai, Y. Yuh, and N. L. Allinger, J. Comput. Chem., 8, 581 (1987).

4) a) F. A. L. Anet and R. Anet, "Dynamic Nuclear Magnetic Resonance Spectroscopy," ed by L. M. Jackman and F. A. Cotton, Academic Press, New York (1975), Chap. 14; b) M. Nógrádi, W. D. Ollis, and I. O. Sutherland, Chem. Commun., 1970, 158.

5) K. Komatsu, H. Akamatsu, Y. Jinbu, and K. Okamoto, J. Am. Chem. Soc., 110, 633 (1988).

6) White crystals; mp 175.8-177.0 °C; for NMR data see Fig. 1; IR (KBr) ν 2935, 2855, 1600, 1450, 1318, 1248, 1178, 1144, 1126, 1020, 862, 812 cm^{-1}; UV (EtOH) λ_{max} 276 nm (log ε 3.75); MS m/z 332 (M, 100%), 333 (M+1, 23%), 334 (M+2, 3%), 331 (M-1, 70%). The previously reported yield (15%; Ref. 5) was improved by more effective generation of CH_2N_2.

7) K. Komatsu, Y. Jinbu, G. R. Gillette, and R. West, Chem. Lett., 1988, 2029.

8) Colorless oil; for NMR data see Fig. 3; IR (CCl_4) ν 2980, 2920, 2860, 1626, 1434, 1376, 1302, 1276, 1128, 1074, 1048 cm^{-1}. The structure was confirmed by transformation by trityl cation to the known hexamethyltropylium ion in 60% yield: K. Takeuchi, Y. Yokomichi, T. Kurosaki, Y. Kimura, and K. Okamoto, Tetrahedron, 35, 949 (1979).

9) In the ^{1}H NMR spectrum the signal for the C-7 methylene protons became broadened at -20 °C and flattened at lower temperatures. However, due to severe overlapping with other signals, a well assignable spectrum could not be observed by further lowering down to -100 °C.

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

11) At higher temperatures the occurrence of 1,5-sigmatropic hydrogen shift became apparent interfering the observation of ring inversion process.

12) R. J. Kurland, M. B. Rubin, and W. B. Wise, J. Chem. Phys., 40, 2426 (1964).

13) Obtained from QCPE.

14) The overestimation in calculation of the inversion barrier for 2 may be attributed to our assumption that the transition state structure is planar. When only C-1, C-2, C-5, C-6, and C-7 were fixed on a plane, the optimized structure was calculated to be the one with C-3 and C-4 slightly twisted out of the plane and the $\Delta(\Delta H^f)$ was found to be 1 kcal mol^{-1} lower.

15) K. Okamoto, K. Takeuchi, K. Komatsu, Y. Kubota, R. Ohara, M. Arima, K. Takahashi, Y. Waki, and S. Shirai, Tetrahedron, 39, 4011 (1983).

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