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THE CONFORMATIONS OF 1,3,5- AND 1,3,6-CYCLOOCTATRIENE

F A L Anet* and Issa Yavari
Department of Chemistry, University of California, Los Angeles
Los Angeles, California 90024

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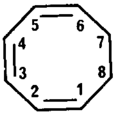
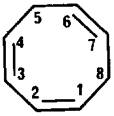
The conformation of 1,3,5-cyclooctatriene (I) has generally been assumed to be a symmetrical boat (I-B, see Figure 1) [1] The presence of eclipsing strains in the C^6-C^7-C^8-C^1 moeity of this conformation is unfavorable, however, and molecular models show that a distortion to give a twist-boat (I-TB) should relieve these eclipsing strains and should also improve the conjugation between the double bonds We now report that this presumption is supported by both ^{13}C NMR data and iterative strain-energy calculations



I



II

The 63 1 MHz ^{13}C NMR spectrum of I in $CHFCl_2$-CHF_2Cl (1 3) shows a dynamic NMR effect in the vicinity of -175° At -150°, the methylene carbons give a single line at δ 28 2, while the olefinic carbons resonances occur at δ 126 8, 127 1, and 137 2 All these lines, except the δ 126 8 resonance, split into 1 1 doublets (δ 26 6, 30 5, 124 6, 129 6, 133 3, 138 1) below -175° Figure 2 shows the splitting that is observed in the high-field region of the spectrum The dynamic NMR behavior of I is consistent with a process that interconverts I-TB(1) which is unsymmetrical and chiral, with its mirror image, I-TB(2), presumably via the plane-symmetrical (achiral) boat form (I-B) The free energy barrier for this process is calculated to be 4 3 kcal/mol at -175°

We have carried out iterative strain-energy calculations on I using Boyd's program.[2] The

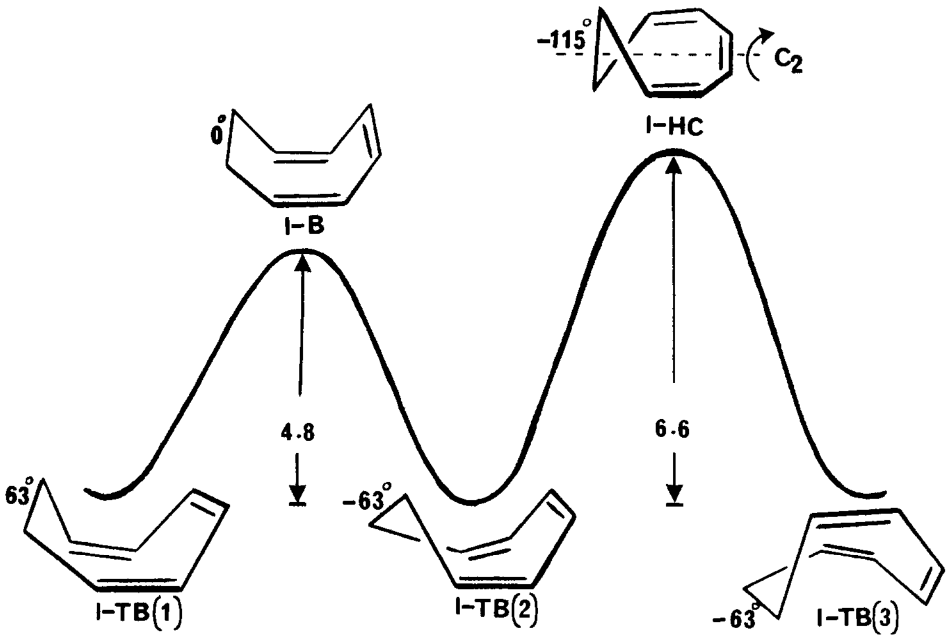


Figure 1 Results of strain-energy calculations on I

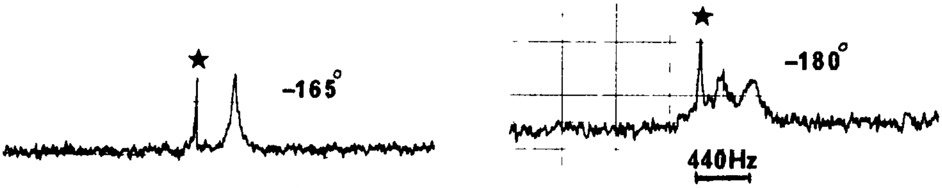


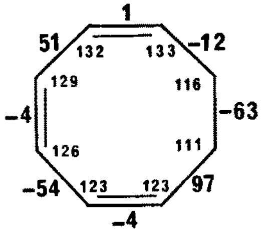
Figure 2 63 1 MHz ^{13}C NMR spectra of the methylene region of I at -165° and -180° The peak marked with an asterisk belongs to the 1,3,6 isomer

parameters for torsion and out-of-plane bending about the double bonds were those of Ermer and Lifson[3] A two-fold torsional potential of 4 25 kcal/mol was used for the single bonds between sp^{2} hybridized carbons With these values the data shown in Figure **1** were obtained

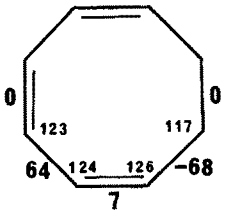
As expected, the twist-boat is the ground state of I, and the boat is the transition state for enantiomerization of the chiral twist-boat conformations The calculated barrier for this process (4 8 kcal/mol) is in very good agreement with the NMR finding Figure 1 also shows the best path for ring inversion in I, a process that has a transition state with C_2 symmetry and a calculated barrier of 6 6 kcal/mol The free-energy barrier for this process has been found to be 6 2 ± 0 5[1a] and 6 7 ± 0 2[4] kcal/mol by ^{1}H NMR studies The strain-energy calculation is again in excellent agreement with the NMR data

The twist-boat conformation of I explains why cis and trans-7,8-dichlorocycloocta-1,3,5-trienes have almost equal energies,[1b] as the chlorine atoms in the twist-boat form of the cis isomer are staggered Very recently, it has been found that η^6-1,3,5-cyclooctatriene-chromium tricarbonyl also has a twisted conformation and that the chiral barrier is 8.3 kcal/mol, about 4 kcal/mol higher than in the free ligand [5]

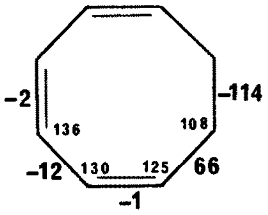
Torsional and internal angles for the conformations depicted in Figure 1 are given below



I-TB
(Twist-Boat)



I-B
(Boat)



I-HC
(Half-Chair)

The 7,8 bond is almost perfectly staggered in I-TB The sp^2-sp^3 bonds have torsional angles that are not very far from the energy-minimum positions for these bonds (0° and 120°) The sp^2-sp^2 single bonds are fairly twisted from their energy minima at 0° and 180°, but less so than in the symmetrical boat Some of the internal angles in I-TB are opened up, but the strain energy that results is more than compensated by the lower torsional strains

We have also investigated the low-temperature ^1H and ^{13}C NMR spectra of 1,3,6-cyclooctatriene (II), but no dynamic NMR effect was observed down to -180°. The only conclusion that can be drawn is that one or more of the following features are present in II (1) conformational sym-

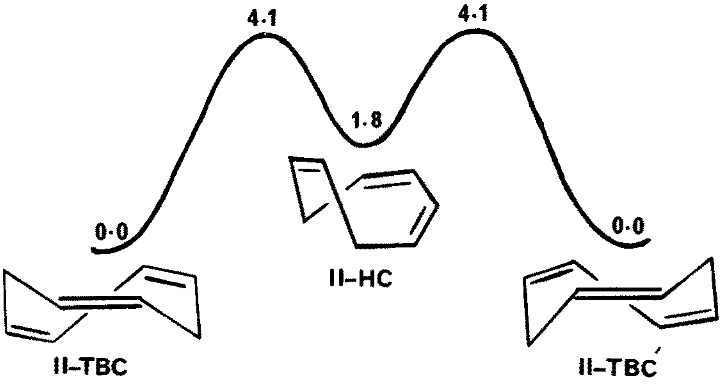
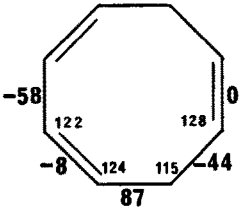


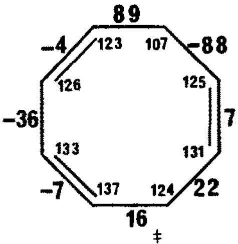
Figure 3 Results of strain-energy calculations on II

metry, (2) low (*ca* 4 kcal/mol) conformational energy barriers, and (3) chemical shift coincidences Experiments on partially deuterated II are planned

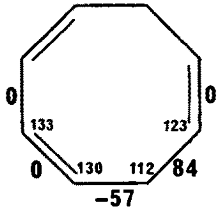
Strain energy calculations on II gave the data shown in Figure 3 The ground state conformation (a twist-boat-chair, TBC) has C_2 point-group symmetry and is chiral The transition state for enantiomerization of II-TBC has C_1 symmetry and is only 4 1 kcal/mol above the ground state. The half-chair conformation (II-HC) is an intermediate in this process The lack of any dynamic NMR effect in II is consistent with the symmetry and low barrier in II-TBC. The internal and torsional angles in II-TBC, etc., are shown below



II-TBC
(Twist-boat-chair)



$II^{\ddagger}$
(Transition State)



II-HC
(Half-chair)

The enthalpy difference, $H°$(II) - $H°$(I), in acetic acid at 25° has been found to be 3 5 kcal/mol [6] Equilibration of I with II in *t*-BuOH-*t*BuOK at 100° converts II essentially completely into I,[7] and thus $\Delta G° \geqslant$ *ca* 3 kcal/mol Our calculations show that I-TB has a strain-energy that is 3 9 kcal/mol lower than that of II-TBC. Differences in zero point energies, vibrational enthalpies, and entropies of these two conformations are calculated to be virtually zero, and thus the calculated $\Delta H°$ and $\Delta G°$ for I $\rightleftharpoons$ II is also 3 9 kcal/mol Finally, the calculated twist angles for the diene systems in I-TB and II-TBC agree with those obtained by PE spectroscopy [8]

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