Application of Force Field Calculations to Organic Chemistry. 9.[1] Possibilities of Correlated Conformational Processes among Mobile Ethano Bridges of Polycyclic Hydrocarbons by Bond Drive Calculations

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Abstract: Possibilities of observing the chirality inversion in various types of polycyclic hydrocarbons by correlated nonbonded repulsive interactions among component rings have been sought by means of molecular mechanics calculations. In perhydro[0.0]paracyclophane (**1**) and *endo,endo*-tetracyclo[6.2.2.2^{3,6}.0^{2,7}]tetradecane (**10**), twisting of any one of the ethano bridges gives rise to induced twisting of all other bridges in the same direction and leads to inversion. In *endo,endo*-9,10-dimethyl-*syn*-dicyclopentane (**8**), inversion appears to be achieved by combination of correlated ethano bridge twisting with Eaton's stereochemical pivot mechanism. For both perhydrotriquinacene (**11**) and perhydrohexaquinacene (**12**), the high-energy C_{3v} intermediates need not be involved to achieve inversion. Instead, successive twisting of three ethano bridges provides energetically the most favorable path for conversion into respective mirror images. A possibility of unique cooperative movements between adjacent ethano bridges is suggested for the latter paths. Calculated barrier heights for the inversion of **1**, **8**, **10**, **11**, and **12** are all less than 5 kcal/mol.

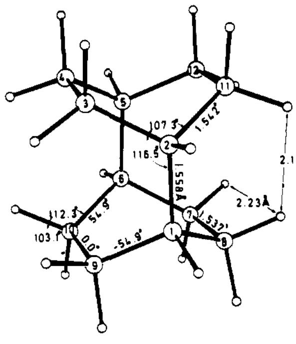
Steric consequences of intramolecular nonbonded interactions, either repulsive[2] or attractive,[3] are recently attracting considerable attention.[4,5] Repulsive interactions in such crowded molecules as triarylmethanes[2a,6] and tri-*tert*-butylsilane[2b] are the origin of a phenomenon called "correlated internal rotation", in which the rotation of one of the bulky groups induces rotation of the other group(s) in the vicinity.[7] Mislow and his group have successfully combined molecular mechanics calculations[8] with dynamic NMR experiments in the studies of this phenomenon.[2a,6]

In the molecules studied by Mislow, the bulky groups simply collide upon each other during the rotation of one of them unless the other groups rotate to avoid collision. The "gear effect" refers to less crowded molecules and has been observed to occur between vicinal isopropyl groups in cyclic systems.[2b,9] The intramolecular correlated movements of groups may occur in still less crowded mobile molecules, if the mobile portions approach well within the repulsive force field between them. The search for such possibilities would provide clues to the general mechanism of "conformational transmission"[10] and the basis for the understanding of molecular dynamics.

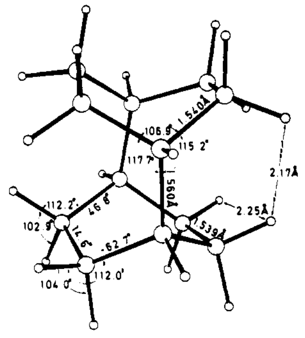
A number of polycyclic molecules are known in which component rings having some mobilities are located closely to each other, either in face-to-face or side-by-side fashion, and the study of interaction among such rings appears to provide a handy starting point. In order to reduce mechanistic complexities, we concentrate in this paper on the consequences of intramolecular interactions among *ethano* bridges. If one ethano bridge undergoes a twisting motion and the distance to other ethano bridge(s) is small enough, the motion will be propagated through nonbonded repulsion and thus induce correlated conformational change in the molecule. Such a change can be conveniently observed if it leads to chirality inversion of the molecule. The possibility of analyzing the change by DNMR technique is also desirable. With these two conditions for future experiments in mind, we examined here various types of known polycyclic hydrocarbons having more than two ethano bridges in the vicinity by molecular mechanics calculations. Artificial twisting of the ethano bridge was effected by the Wiberg–Boyd bond drive technique.[11,12] Regarding the force field, Allinger's latest version (MM2)[13] appeared particularly suitable in view of its modest size and hardness of hydrogen atom and the modified torsional potential function, both being critically important for our present purpose. This force field was used throughout this work.

Results and Discussion

Tricyclo[4.2.2.2^{2,5}]dodecane (1). We start from molecules having some of the component rings in face-to-face disposition. Fusion of two cyclohexane rings at C_1 and C_4 gives **1**, wherein the two pairs of ethano bridges are in the desired disposition. This molecule offers a good starting point. In both "eclipsed" (**1A**, D_{2h}) and "twisted" (**1B**, D_2) conformations, the opposing endo hydrogen atoms are calculated to be only 2.1 Å apart. **1** was recently synthesized in two laboratories.[14,15] These research groups suggest the energetic disadvantage of **1A** relative to **1B** as well as a possibility of the interconversion of chiral **1B** into its mirror image **1B′** through **1A**.



1A



1B

Mislow[16] states that the ground state of **1** has D_2 symmetry based on calculations with the Allinger 1971 force field. Our calculations (Table I) reveals that **1A** is only 1.1 kcal/mol more strained than **1B**, a result hardly surprising if one recalls the small energy difference estimated between boat and twist-boat cyclohexane (ca. 1 kcal/mol).[17] Even though the boat six-membered ring in **1A** is certainly more strained than the free boat cyclohexane,[18] the same is true with **1B**[18] and the extra strain cancels each other by taking the difference. Thus, the chance of observing the inversion **1B** ⇄ **1B′** by dynamic NMR experiments must be scarce.[19,20]

Nevertheless, **1** is profoundly interesting with regard to the correlated phenomenon. First, it may be noted that highly

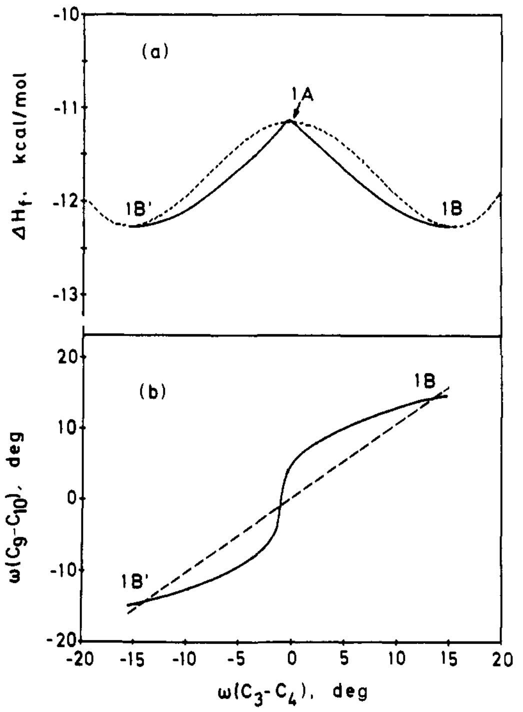


Figure 1. Calculations of inversion in tricyclo[4.2.2.2^{2,5}]dodecane (**1**) by ethano-bridge drive. (a) Enthalpy profile during one-bond drive (solid line) and synchronous four-bond drive (dotted line). (b) Response of dihedral angle at C_9–C_{10} bridge to the forced drive at C_3–C_4 bridge. Dashed line (– –) corresponds to identical response.

Table I. D_{2h} and D_2 Conformations of Tricyclo[4.2.2.2^{2,5}]-dodecane (**1**) and Boat and Twist-Boat Cyclohexane Based on MM2 Force Field Calculations[a]

	1A (D_{2h})	**1B** (D_2)		cyclohexane boat (C_{2v})	cyclohexane twist-boat (D_2)
enthalpy	−11.16	−12.26		−23.06	−24.17
strain energy	42.33	41.23		9.08	7.97
steric energy					
stretch	2.04	2.29		0.44	0.47
bend	10.07	9.50		0.99	0.78
stretch-bend	0.90	0.91		0.16	0.13
nonbonded	16.21	16.20		5.17	4.90
torsion	21.05	20.28		6.26	5.63
total	50.28	49.18		13.02	11.92
	Ring Torsion Angles				
11-2-3-4	55.0	−62.7	6-1-2-3	52.1	−63.4
2-3-4-5	0.0	14.6	1 2-3-4	0.0	30.5
3-4-5-12	−55.0	46.8	2-3-4-5	−52.1	30.5

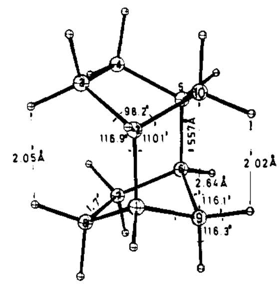
[a] Energies in kcal/mol, angles in deg.

symmetric **1A** does not necessarily need to be the barrier in the inversion. This is because **1A** can be reached only if four ethano bridges of **1B** undergo synchronous twists in the same direction (the energy profile of this process reproduced with a dashed line, Figure 1a). Instead, a slight thermal twist of only one ethano bridge is enough to engender inversion of the whole molecule without passing through **1A**. Suppose we start to drive the bridge C_3–C_4 of **1B**. This move is transmitted most rapidly to the opposite bridge C_9–C_{10} mainly through nonbonded repulsion to bring about a twist in the same direction albeit a few degrees delayed.[21] The other two bridges also start to twist spontaneously with increasingly small angles in the order C_{11}–C_{12} and C_7–C_8.[22]

Figure 1b illustrates the response of the C_9–C_{10} bridge to the drive of the C_3–C_4 bridge in the course of inversion. The delayed response continues until the C_3–C_4 bridge passes through the eclipse stage, after which the response is *suddenly amplified*.[21] Namely, the C_9–C_{10} bridge twists itself more than the C_3–C_4 does. The amplified response occurs at other bridges as well. Thus, as soon as the eclipse at the C_3–C_4 bridge is passed, the other three bridges pass their eclipse stages quickly one after another, and the molecule is on the "downhill" path in the potential hypersurface toward the mirror image **1B′**.

However, in the case of the inversion **1B** ⇄ **1B′**, the barriers for the one-bond drive and for going through **1A** are the same (Figure 1a). Hence, the synchronous four-bridge motion, which corresponds to a normal mode of vibration of **1**, will also occur for the thermodynamic reason.[24]

Tricyclo[4.2.1.1^{2,5}]decane (2) and Derivatives (3–8). In order that the correlated conformational process in molecules like **1** be observed by experimental methods, it is desirable to seek structural modifications that increase the height of the barrier for the epimerization between highly optically active antipodes. While derivatives of **1** are not readily accessible,[14,15] the recently reported syn dimer of cyclopentane (**2**)[23,25] and its bridged (**3**,[26] **4**,[27] **5**,[28] and **6**[29]) as well as homologous (**7**[23] and



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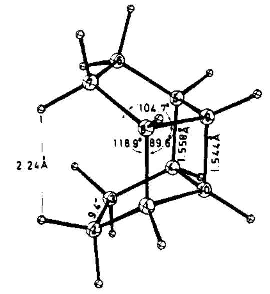

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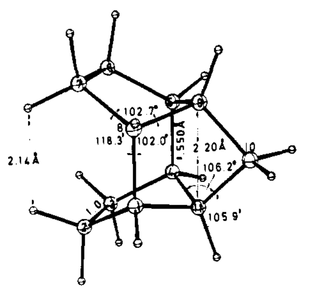

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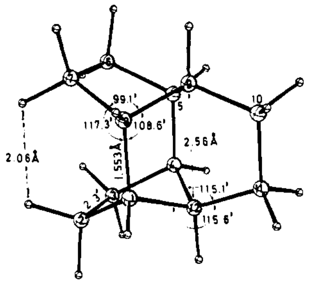

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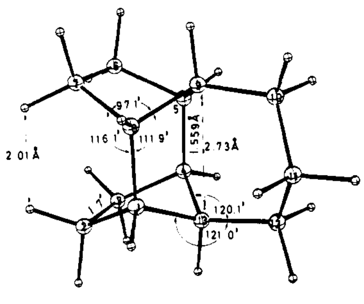

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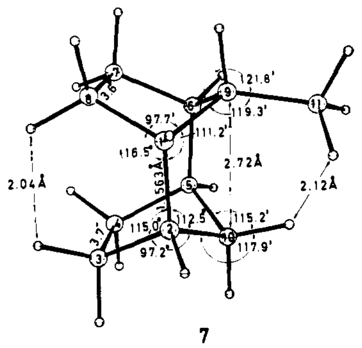

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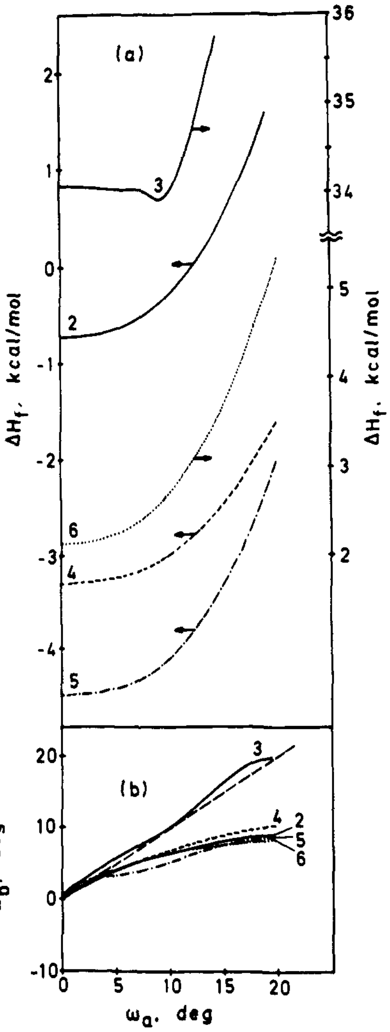
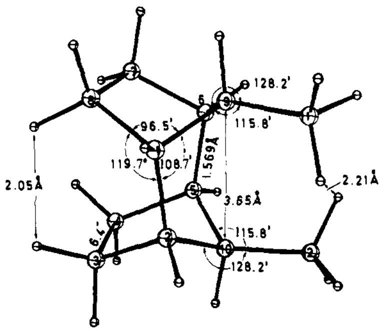


Figure 2. Dihedral angle drive of ethano bridge in tri- and tetracyclic hydrocarbons **2**–**6**. (a) Enthalpy profile during one-bond drive starting from respective minimum-energy conformations. (b) Response of dihedral angle in an ethano bridge (ω_b) to the forced dihedral drive (ω_a) in the opposite ethano bridge. ω_a refers to C_3–C_4 bridge for **2** and C_2–C_3 bridge for **3**–**6**, ω_b refers to C_7–C_8 bridge for **2** and C_6–C_7 bridge for **3**–**6**. Dashed line (– –) corresponds to identical response.



8

8[30]) derivatives appeared to provide an interesting series. Various substitutions on methylene bridges of **2** should affect the distance between two ethano bridges (see calculated distances given in structure drawings) by way of the "pivot" action of bridgehead carbon atoms[23] and hence change the ease of response between the bridges.

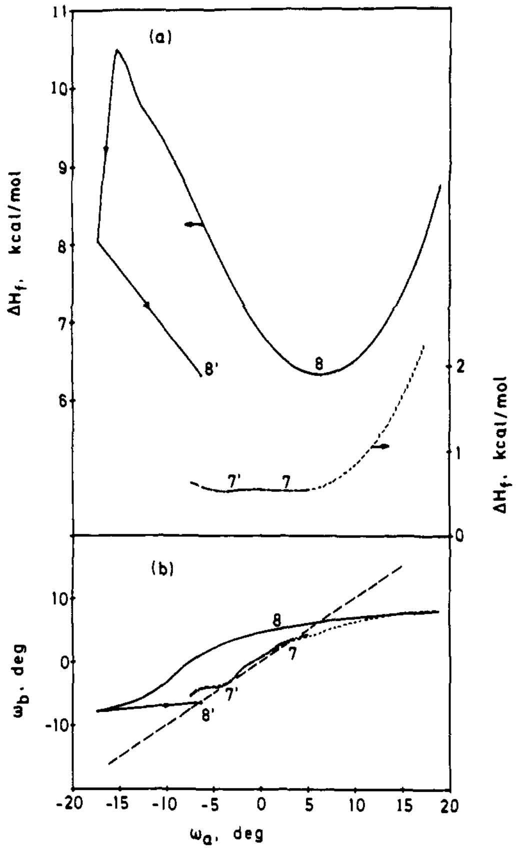


Figure 3. Dihedral angle drive of ethano bridge in *endo*-9-methyl- and *endo,endo*-9,10-dimethyltricyclo[4.2.1.$1^{2,5}$]decane (**7** and **8**). (a) Enthalpy profile of inversion as the function of dihedral angle of an ethano bridge ω_a (**7**: C_3–C_4 ·····, C_7–C_8 –·–). (b) Response of dihedral angle of opposite ethano bridge ω_b (**7**: C_7–C_8 ·····, C_3–C_4 –·–) to the forced drive of ω_a. Dashed line (– –) corresponds to identical response. **7**/**7′** and **8**/**8′** are enantiomeric pairs.

Unfortunately, however, the calculated global energy minimum conformations of these molecules are either eclipsed or nearly so with the twist angles of ethano bridges less than 10° (Figures 2a and 3a). Therefore, they are not likely to show correlated bridge movements and our calculations support this view (Figures 2b and 3b).

Nevertheless, **8** merits some attention. In its energy minimum, **8** is twisted (C_2) to avoid the head-on bumping of two methyl groups and the ethano bridges are staggered by 6.4°. The calculated barrier of inversion of **8** to **8′** is sizable (4.2 kcal/mol) (Figure 3a), most of which arises from the passing of two methyl groups against each other. Actually, the ethano bridge undergoing the forced twist (C_3–C_4) had to be "overtwisted" to −17.2° to achieve the passing.[21] We suggest that the derivative of **2** carrying substituents of appropriate size (larger than methyl) at C_9 and C_{10} will give a high chance of observing the inversion by experiments.

***endo,endo*-Tetracyclo[6.2.1.$1^{3,6}$.$0^{2,7}$]dodecane (9) and *endo,endo*-Tetracyclo[6.2.2.$2^{3,6}$.$0^{2,7}$]tetradecane (10).** We have so far discussed molecules wherein ethano bridges are connected by way of one or two carbon atoms in face-to-face disposition. However, the molecule known to include two ethano bridges at the closest distance (**9**)[32-34] involves three carbon atoms between the bridges and hence is expected to give higher flexibility than the previously discussed structures. X-ray crystal analysis of this molecule[32] revealed C_2 symmetry with a slight twist at both ethano bridges. Unfortunately, the twist is too small, and the low barrier of inversion (Figure 4a, 0.12 kcal/mol) precludes any meaningful discussion on correlated movements.

A bishomologous tetracyclotetradecane **10**[35] is also calculated to have C_2 symmetry with a twist of 7° at the four ethano bridges in its global energy minimum conformation. This molecule is more intriguing than **9** as far as the correlated phenomenon is concerned. A forced drive at C_4–C_5 is effec-

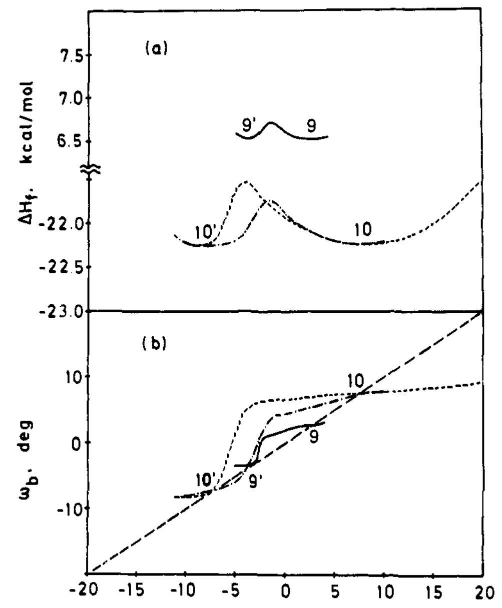
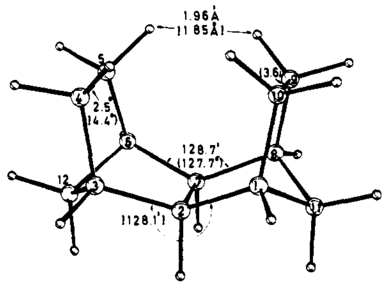


Figure 4. Dihedral angle drive of ethano bridge in *endo,endo*-tetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodecane (**9**) and *endo,endo*-tetracyclo-[6.2.2.2^{3,6}.0^{2,7}]tetradecane (**10**). (a) Enthalpy profile of inversion as the function of dihedral angle of an ethano bridge ω_a (**10**; C_4–C_5 –·–, C_{11}–C_{12} ·····). (b) Response of dihedral angle ω_b of other ethano bridge (**10**; C_9–C_{10} –·–, C_{13}–C_{14} ·····) to the forced drive of ω_a. Dashed line (– –) corresponds to identical response. **9/9′** and **10/10′** are enantiomeric pairs.



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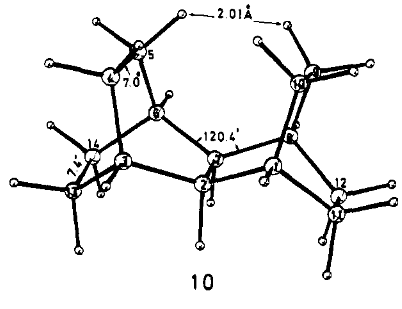
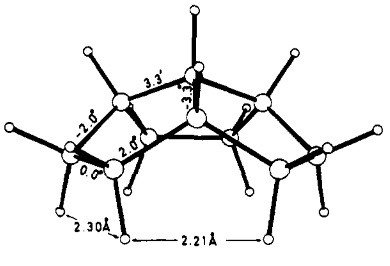


10

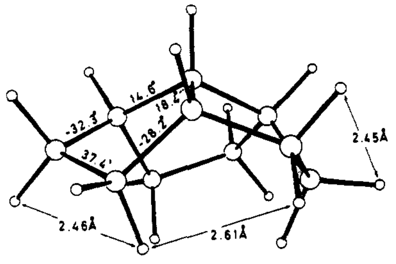
tively transmitted not only to the opposite bridge (C_9–C_{10}) but also to the two other bridges (C_{11}–C_{12} and C_{13}–C_{14}). Figure 4b illustrates the response of the C_9–C_{10} bridge only (–·–). Note that the response becomes oversensitive, as in **1**, after the delayed passing of the barrier.[21] Furthermore, a forced drive at C_{11}–C_{12} is also transmitted to three other bridges with increasing delay as the distance is increased, apparently through successive response. Note that the delay in the appearance of the barrier with regard to ω_a at the C_{11}–C_{12} bridge is more pronounced and the barrier higher than those of the C_4–C_5 bridge drive (Figure 4a). The response between the two farthest bridges is shown in Figure 4b. Namely, all four ethano bridges of **10** are "correlated" and in this regard **10** resembles **1**. This behavior of **10** is undoubtedly related to the flexible nature of the parent bicyclo[2.2.2]octane skeleton.[12b,36] The calculated barriers of inversion in **10** are again too low to observe.

Tricyclo[5.2.1.0^{4,10}]decane (11). In the following, we consider



11A

molecules having ethano bridges in close side-by-side dispositions. Perhydrotriquinacene (**11**)[37,38] was once considered to have a "nearly inflexible", cup-shaped structure (**11A**, C_{3v}),[39] but later predicted to be "twisted" (**11B**, C_3) in its



11B

lowest energy conformation based on preliminary force-field calculations.[40] Our extensive search of its potential hypersurface (Figure 5) identified several additional energy minima. In the global minimum (**11B**), the cyclopentane ring is in a conformation intermediate between C_2 and C_s (envelope) with the ethano bridge having a dihedral angle of 37.4°. The shortest nonbonded H–H distance between adjacent ethano bridges is 2.61 Å, which is certainly short compared to the sum of van der Waals radii (3.0 Å).[13] Hence we expected some correlated movements to occur among the ethano bridges of this molecule.[41,12]

We first concentrate on the mechanism of inversion of chiral **11B** into its mirror image **11B′**. The synchronous three-bond drive mechanism involving **11A** as the barrier (13 kcal/mol, Figure 5, dashed line) is a normal mode of vibration. However, we suggest that successive twisting of three ethano bridges into a negative direction is much more favorable on energetic ground (Figure 5, solid lines). This feature may be contrasted with **1**, where the normal vibration mode and the one-bond drive have the same barrier. The highest barrier along the one-bond drive path is only 4.6 kcal/mol above **11B** and appears when the drive of the first bridge passes through the eclipse conformation before falling into a new energy minimum, **11C** (no symmetry element). This barrier seems to be an energy maximum on a "sharp edge", since every attempt to relax the structure inevitably led to either **11B** or **11C**.

In contrast to the first barrier, the second barriers (**11D**[43] and **11E**, both C_s point group), which generate when the two remaining, nonequivalent (+) bridges of **11C** are rotated separately, are saddle points and can be fully relaxed.[44] Continued drive of **11D** and **11E** by the same bridges leads to a common energy minimum, **11C′** (the mirror image of **11C**). However, energetically more likely processes are available for

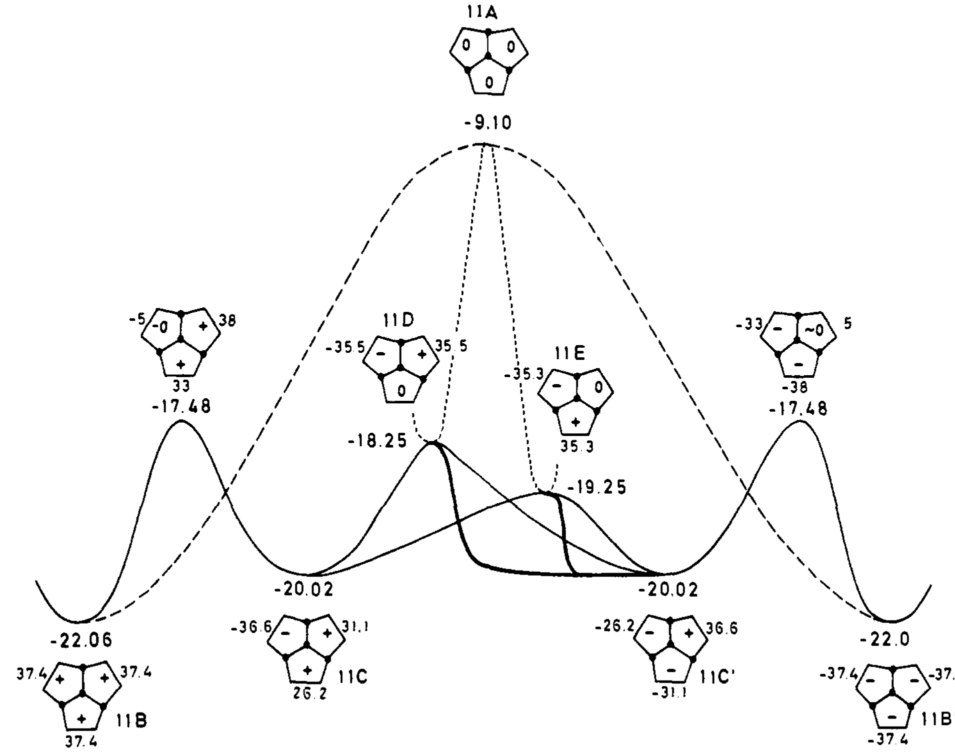
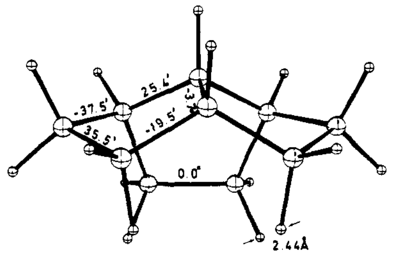
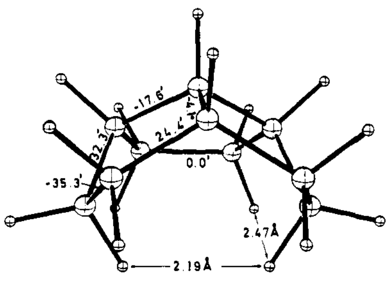


Figure 5. Possible pathways of inversion of chiral perhydrotriquinacene (**11B**) into its mirror image (**11B′**). Abscissa is in arbitrary scale. Ordinate is approximately scaled to calculated steric energy. Large figures are the calculated heats of formation in kcal/mol. Plus and minus signs in the structure drawings are those of dihedral angles of ethano bridges. Dihedral angles are given on the bridge in small figures. Solid line: threefold, one-bond drive pathway. Thick line: correlated transformations. Dashed line: three-bond drive pathway. Dotted line: twisting of **11A** keeping C_s point group symmetry (see text and footnote 44).



11D



11E

the transformations from the saddle-point conformers to **11C′**. The saddle-point conformers can be rightly considered to be stable enough to allow thermal agitation to occur in the bridges other than the (0) bridge being driven. We noticed that an artificial increase in the dihedral angle of the (+) bridge of these conformers by a few degrees led spontaneously and rapidly to **11C′** (Figure 5, thick solid lines).[45] These processes appear more favorable than the continued drive of the (0) bridge and provide the most remarkable cases of correlated conformational transmission encountered in this study. They are induced by nonbonded repulsive interactions between endo hydrogen atoms at (+) and (0) bridges.

The rest of the inversion process, **11C′** to **11B′**, is simply the reverse of the route from **11B** to **11C**. As a whole, the inversion of **11B** must be too fast to observe by any known experimental technique, at least for the unsubstituted hydrocarbon, and these computational results are consistent with the fact that no change in the ^{1}H and noise-decoupled ^{13}C NMR spectra could be observed upon lowering the temperature to −100 °C. The spectra are consistent with a rapidly flipping molecule generating the time-averaged spectrum of a C_{3v} symmetrical species.[46]

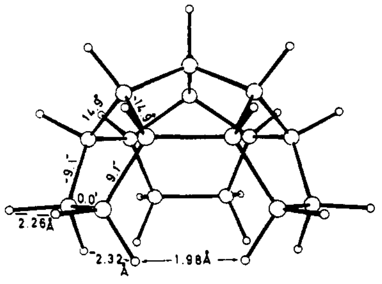
Hexacyclo[11.2.1.0^{2,6}.0^{5,9}.0^{7,14}.0^{8,12}]hexadecane (12). The hydrocarbon (C_{16}-hexaquinane) was recently synthesized and the structure determined by X-ray analysis.[47] In the crystalline state, it exists in a C_3-like conformation wherein the three ethano bridges are twisted.[47] Our calculations satisfactorily reproduced the X-ray structure and predicted that the C_3 conformation (**12B**) is 16.6 kcal/mol more stable than the "eclipsed" C_{3v} conformation (**12A**) as **11B** is to **11A**. As shown, the closest nonbonded 1,6 H–H distance between nonvicinal methylene groups in the concavity of **12B** (2.36 Å) is shorter than the corresponding nonbonded 1,5 H–H distance of **11B** (2.61 Å). Consequently, we expected closer correlations among the ethano bridges of **12** compared to **11**.

Computational scrutiny of the dynamic behavior of **12** gave, however, essentially the same pattern as **11** (Table II). Namely, energetically the most economical pathway of the inversion of **12B** into its mirror image **12B′** consists of three separate "one-bond drive" steps with barrier heights of 4.3, 3.5 (by way of **12D**) or 5.4 (by way of **12E**), and 4.3 kcal/mol relative to **12B**. Correlated, spontaneous twisting may occur at **12D** and **12E**, the saddle-point conformations. Thus, as far as the inversion of the most stable "twist" conformation is concerned, we predict that there is no essential difference between **11** and **12**.

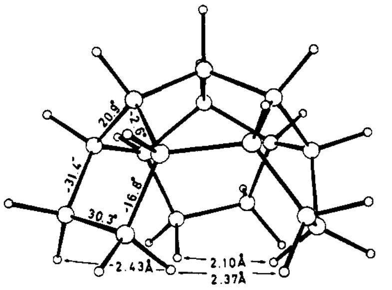
Table II. Conformers of Perhydrohexaquinacene (**12**) Appearing along the Course of Inversion Based on MM2 Force Field Calculations

conformer[a]	dihedral angles of three ethano bridges, deg	$\Delta H_f°$, kcal/mol
12A (C_{3v})	0.0, 0.0, 0.0	11.53
12B (C_3)	30.3, 30.3, 30.3	−5.10
the first barrier	0.1, 25.1, 40.7	−0.80
12C	−34.3, 19.3, 26.5	−2.59
12D (C_s)	−30.9, 0.0, 30.9	−1.60
12E (C_s)	−31.2, 31.2, 0.0	0.26

[a] See Figure 5 for corresponding conformers of **11**.



12A



12B

Conclusions

An extensive search has been made among various types of polycyclic hydrocarbons for the possibilities of observing inversion of chirality assisted by correlated nonbonded interactions. Perhydro[0,0]paracyclophane (**1**), a dimethyl syn dimer of cyclopentane (**8**), a tetracyclotetradecane (**10**), perhydrotriquinacene (**11**), and C_{16}-hexaquinane (**12**) are predicted to display unique correlated phenomena. Calculated barriers of inversion for these molecules are, however, less than 5 kcal/mol and hence it is difficult to detect the inversion by conventional experimental techniques. The most promising is tricyclo[4.2.1.1^{2,5}]decane (**2**), with appropriately sized endo substituents at C_9 and C_{10}.

It is pertinent to state here that the correlated propagation of ethano bridge twist movements within molecules as described here has never been described because they occur too rapidly to observe. Only the computational technique as employed here enables us to single out the phenomenon. The proposal mentioned at the beginning of the paper proved correct at least for the intramolecular responses between closely disposed ethano bridges as long as the simple force-field model employed here is tenable. Further applications of the force-field concept to the general mechanism of conformational transmission and other aspects of molecular dynamics will be reported in subsequent papers of this series.

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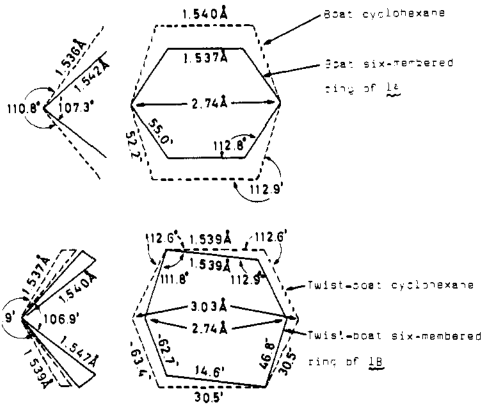

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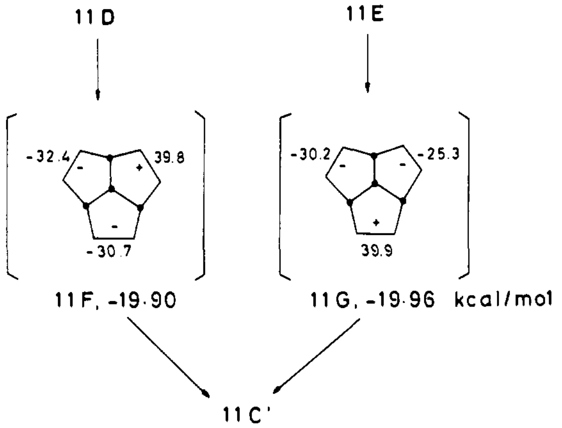

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The Inductive Effect in Molecules and Ions

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Abstract: The description of charge distribution in a molecule in terms of the electron density within defined spheres derived from molecular wave functions is used in the quantitative investigation of the inductive effect.

I. Introduction

One of the simplest concepts in the electronic theory of organic chemistry is the inductive effect. We present for the first time a rigorous method for examining the empirical concepts proposed by Ingold and others. This is achieved using the precise computation of the charge surrounding an atom in a molecule or ion defined by Dean and Richards.[1]

Following Ingold[2] "a group X may be said to be electropositive, or electron repelling, in a compound $X-CR_3$ if the electron content in the residue CR_3 is greater than in the compound $H-CR_3$. It is not a serious difficulty that there is no physically indicated point along the bond X-C or H-C at which X or H ends and C begins: it is known that the single bond radius of the carbon atom is a nearly constant quantity (0.77 Å) which it would be fair to accept as providing a conventional atomic boundary for the purposes of comparison". Ingold distinguishes two different cases when the inductive effect of the methyl group is considered. From a study of absorption spectra and dipole moments, methyl groups are seen to be very weakly electronegative in saturated alkanes. In most other systems, however, where electronegative groups are encountered, methyl groups are electropositive, i.e., electron donating. In this connection, the important property of a methyl group is that it is more polarizable than hydrogen.

II. Methods

There have been many ways suggested for partitioning the charge in molecules.[3] The simplest method is that due to Mulliken and is described as a population analysis.[4] In this method all the electronic charge in a molecule is assigned to the constituent atoms. The charge "belonging" to an atom A is that arising entirely from the atomic orbitals of A, and half of that arising from the overlap of atomic orbitals centered on A with those of all the other atoms in the molecule. In assigning all the one-center charge to the central atom and in partitioning overlap equally, this method is particularly unsuitable for an investigation into the inductive effect where slight electronegativity changes are critical.[5]

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