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CONFORMATIONAL ANALYSIS—XCII

THE STRUCTURES AND INVERSION BARRIERS OF CYCLOOCTATETRAENE, TETRAMETHYLCYCLOOCTATETRAENE, AND OCTAMETHYLCYCLOOCTATETRAENE[a,1]

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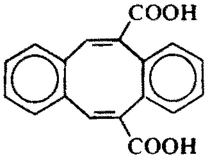
Abstract—The molecular structures of the title compounds have been calculated by the molecular mechanics (SCF-Westheimer) method in fair agreement with experiment. The calculated barriers to mechanical inversion are, respectively, 15·1, 24·3, and 94 kcal/mol. For cyclooctatetraene, the major contribution to the barrier is the bending energy required to force the ring planar. For the methylated derivatives, in addition to this term, the major contributions are primarily a result of unfavorable van der Waals interactions in the planar transition state, and deformations the molecules undergo to relieve those repulsions.

Since its original synthesis by Willstätter, cyclooctatetraene (COT) has been a compound of fundamental importance in the understanding of conjugated π systems.[2] The structure of the molecule now seems to be rather accurately known.[2–4] The molecule is non-planar, having a shape commonly described as a "tub". The ring is capable of inversion, and a number of experiments have been directed toward the understanding of the thermodynamics of such systems. Mislow and Perlmutter[5] estimated the activation energy for the inversion of the dibenzodicarboxy derivative (DCOT) to be about 27 kcal/mol, based on optical activity studies. From an examination of models, they concluded that the cyclooctatetraene ring must pass through a planar form in the ring inversion process.

Assuming this planar form to be the transition state, they concluded that 27 kcal/mol would be an upper limit for COT itself, since in the case of DCOT, not only would the two phenyl rings tend to reduce the π-electron stabilization of a planar form, but the —COOH steric interactions would also destabilize it. Anet[6] examined the ring inversion of COT itself by low temperature NMR studies and found a ΔG‡ of 13·7 kcal/mol. Further studies[7] involving a substituted COT found that two processes were actually taking place: ring inversion and bond shift. Ring inversion (Fig 1) should proceed through a planar-alternate transition state while bond shift (Fig 2) requires a planar form with regular (equal) bond lengths.



DCOT

With $R = \text{—C(CH}_3)_2\text{OH}$, Anet found ΔG‡ = 14·7 kcal/mol for inversion and ΔG‡ = 17·1 kcal/mol for bond shift.

It is a straightforward task for us to calculate the structures and certain relative energies of the COT conformations, using a previously described force field method.[8] We find the tub favored over the planar-alternate form by 15·1 kcal/mol (a ΔH‡ value), in good agreement with Anet's value for the barrier to mechanical inversion. The geometry of the tub agrees moderately well with experiment

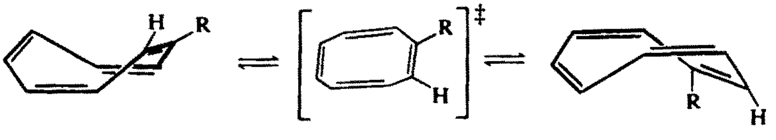


Fig 1. Cyclooctatetraene ring inversion.

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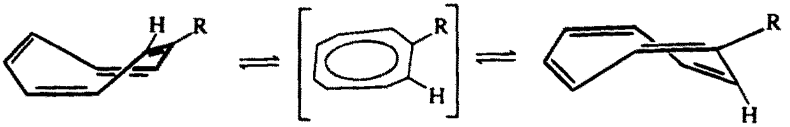


Fig 2. Cyclooctatetraene bond shift.

Table 1*

	COT			TMCOT		OMCOT	
	exp.[3]	exp.[4]	calc.	exp.[4]	calc.	exp.[4]	calc.
C=C	1·340 (3)	1·330 (6)	1·340	1·330 (5)	1·340	1·326 (1)	1·340
C_{sp^2}—C_{sp^2}	1·475 (8)	1·456 (12)	1·491	1·481 (6)	1·493	1·483 (5)	1·501
C_{sp^2}—C_{sp^3}				1·516 (7)	1·506	1·513	1·504
C=C—C_{sp^2}	126·1 (0·5)	126·8 (1·9)	122·7	124·66 (20)	122·7	122·2 (0·5)	118·2
C=C—C_{sp^3}				121·59 (19)	121·06	123·0	112·8
C—C—C_{sp^3}				113·64 (20)	119·22	114·8	118·9
C=C—C=C	43·1 (0·5)	55·7 (3·9)	65·8		68·40	66·6 (4·3)	73·4

*The standard deviations in the last figure are given in parentheses.

(Table 1) with our calculated structure being more puckered than the diffraction structure.

In going from the tub to the planar-alternate form, the C_{sp^2}=C_{sp^2} double bond increases 0·014 Å in length and the single bond shrinks 0·018 Å.

Unfortunately, the bond shift energy barrier cannot be calculated by the present method as it now stands. The problem can best be looked at in the following way. If we consider the orbital energies of the electronic configurations for a planar structure with alternating bond lengths, there are two configurations on which we may focus, V_0 and V_{4455} (Fig 3).

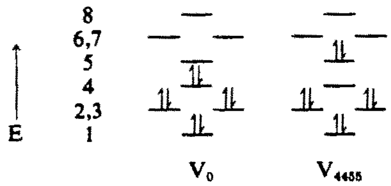


Fig 3. Cyclooctatetraene π-electronic configurations.

In the structure with alternating bond lengths, V_0 is the ground state and V_{4455} corresponds to an excited configuration. V_0 is a satisfactory representation of the ground state, as far as bond order calculations are concerned.

When the bond lengths become equal, the pair of orbitals ψ_4 and ψ_5 (Fig 3) become degenerate. The V_{4455} configuration therefore becomes of the same energy as the V_0 configuration, and the ground state is a combination of the two. If the bond orders are calculated only from V_0, an alternating bond length arrangement is found. The V_{4455} configuration also corresponds to an alternating bond length arrangement, but with the long and short bonds interchanged, so that the sum of the two configurations will correspond to regular bond lengths.

The probable solution to the problem in principle is to carry out a configuration interaction treatment, and to calculate the bond orders after the configuration interaction, rather than before. However, this is a very atypical situation, and at present we are not prepared to deal with it quantitatively, but will simply conclude that our present mechanical model is not an adequate model of the real molecule, and the calculated energy for the planar molecule with equal bond lengths (13 kcal/mol above the planar structure with alternating bond lengths) is going to be too high, relative to the other structures (Fig 4). The calculated value is only an upper limit.

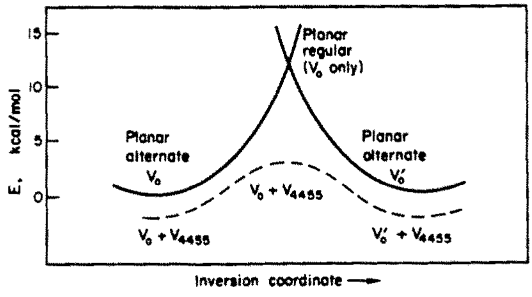


Fig 4. Potential energy diagram for bond shift in the planar COT molecule.

Dewar *et al.*[9] have also examined theoretically the inversion of cyclooctatetraene. Their calculations (MINDO) indicated to them that the calculated energy difference between the non-planar and planar alternating structures was 17 kcal/mol, in good agreement with experimental values. However, they calculated an energy difference between the alternating and symmetrical planar forms of 13·9 (MINDO/2) or 15·4 (π approximation) kcal/mol. This number is much larger than the experimental value, so they concluded that the transition state was not the symmetrical form, but rather that the bond shift took place by a symmetrical non-planar structure, which they felt might indeed correspond to the "crown" structure considered earlier as a possibility for COT itself. No support, experimental or theoretical, has been put forth for such a crown structure as the transition state, and we regard this as improbable. Dewar's calculations also involve only a single determinental wave function, and we feel that this is simply not adequate for the planar-regular structure.

We also applied this method to the calculation of the barrier to inversion in tetrabenzocyclooctatetraene, and assuming the transition state is planar, obtained an activation energy of 159 kcal/mol. The energy barrier which had been reported[10] for the process was only 5 kcal/mol, and our conclusion was that the experimental energy barrier was necessarily in error.[11] The same conclusion was also reached by CNDO calculations,[11] and independently by NMR and optical activity studies.[12]

In 1969, Ganis *et al.*[13] published a paper in which they reported the free energy of activation at 120° for the bond shift of the endocyclic bonds of 1,3,5,7-tetramethylcycloocta-*cis*,*cis*,*cis*,*cis*-1,3,5,7-tetraene (TMCOT). The value, 22·5 ± 2 kcal/mol, was a good deal larger than that reported for COT itself, 13·7 kcal/mol.[6]

Ganis and coworkers were not able to offer an explanation for this substantial energy difference, but they did conclude that it was *not* due to the difference in the nonbonded interactions in COT and TMCOT, which they decided was too small to be the main cause of the increase of the energy barrier. However, they conceded that the necessary potential functions for carrying out such a calculation were not really available. The van der Waals functions they actually used in their calculations were taken from early references,[14] and it has been more recently shown[15,16] that those functions are not adequate for many purposes. They happen to work adequately in the specific cases employed by the original authors, but they lack generality.

The molecular structure of cyclooctatetraene (COT) was reported by electron diffraction,[3] and recently also by X-ray crystallography.[4] Those of tetramethylcyclooctatetraene (TMCOT) and octamethylcyclooctatetraene (OMCOT) are known from crystallographic studies.[4] A comparison of the experimental and calculated structures for the ground states of these molecules is given in Table 1.

There are no adjustable parameters in these calculations. All of the necessary parameters were fixed from earlier studies on simple molecules. The ground state geometries are calculated in only fair agreement with experimental structures. We next calculated the barrier to a mechanical inversion, where the molecule becomes planar, but the long bonds stay long and short ones stay short. The barriers calculated for this process for COT and TMCOT were respectively, 15·1 and 24·3 kcal/mol. These are to be compared with the experimental values of 13·7 and 22·5 kcal/mol, where the former is in fact the energy of mechanical inversion, but the latter is the energy of bond shift.

Our conclusion is that our barrier calculations are in reasonable agreement with experiment in general, and in COT in particular, where the experimental values are known. We believe they are equally good for tetramethylcyclooctatetraene, and predict that the energy for bond shift in the tetramethyl compound is mainly involved in getting to the planar conformation, not in the second step (contrary to the suggestions of Ganis and coworkers).

From the results of our calculations, it is interesting to look at the details of the origin of the large barrier which is predicted. In cyclooctatetraene itself, mechanical inversion is disfavored by two effects, an increase in the van der Waals energy of the molecule and an increase in the angular bending energy. There is a decrease in the torsional energy in going to the planar form, but it is small and compensates only for about 40% of the increase from the above two causes (Table 2).

There is a moderate amount of van der Waals repulsion (2·1 kcal) in COT, which increases rather markedly when the molecule becomes planar (to 11·0 kcal). The reason for this is that as the bond angles are expanded from about 124° to about 135°, the two hydrogens on the same double bond are squeeezed together more, and in addition as the molecule becomes planar there is a buttressing effect of all the hydrogens on their neighbors. The bending energy increases markedly (by 18·3 kcal) as a result of the geometrical constraints in the planar form. The stretching energy increases from 0·1 to 0·5 kcal/mol, again in an attempt to relieve the van der Waals repulsion. The torsional energy in the molecule markedly improves by 12·5 kcal. We do not count stretch-bend interactions in bonds of the kind herein, so that term is zero. Thus the total energy increase is calculated to be 15·1 kcal for flattening out the cyclooctatetraene molecule.

To go through the same calculation for the tetramethyl derivative (Table 2), the van der Waals

Table 2. Internal energy partition of COT and TMCOT

	COT			TMCOT			
Partition	Tub	Planar alternate	ΔE	Tub	Planar alternate	ΔE	ΔΔE
van der Waals	2·10	10·99	8·88	0·00	11·20	11·19	2·31
stretching	0·10	0·46	0·36	0·22	1·53	1·31	0·96
bending	0·84	19·10	18·26	1·04	27·00	25·95	7·70
torsion	20·48	8·00	−12·48	22·06	8·00	−14·06	−1·58
stretch-bend	0·0	0·0	0·0	−0·02	−0·17	−0·14	−0·14
TOTAL	23·53	38·55	15·11	23·31	47·56	24·25	9·24

Table 3. Internal energy partition of OMCOT

	Tub	Planar alternate	ΔE
van der Waals	−3·9803	29·5205	33·5008
stretching	0·3561	5·9590	5·6029
bending	1·9063	74·9732	73·0669
torsion	20·2070	2·5601	−17·6469
stretch-bend	−0·0352	−0·8486	−0·8134
TOTAL	18·4539	112·1641	93·7102

repulsions are much greater in the planar form. In the tub form, there are sizable repulsions, but they are balanced by a number of small attractions, so that the total van der Waals energy begins at zero. As the molecule becomes planar, the Me groups are caught in between the adjacent hydrogens, and severe van der Waals interactions result. These extra van der Waals repulsions contribute 2·3 kcal to the increase in the barrier of TMCOT over that of COT. In an effort to relieve these repulsions, the TMCOT carbon–carbon bonds stretch somewhat, adding an additional 1·0 kcal of stretching energy compared to that in COT. The biggest difference in the energies in the tetramethyl form, compared to the parent, is in bending; the ΔΔE is 7·7 kcal/mol. Some of this comes about because the C—C—C bending constants are bigger than the C—C—H constants, but mainly it is a result of bending by and around the methyl groups in an effort to minimize the van der Waals repulsions which they are undergoing in the planar form. The torsional energy is actually a little more favorable with the methylated compound.

We conclude, therefore, that primarily because of the extra van der Waals repulsions between the Me groups and the neighboring hydrogens of TMCOT in the planar form, and the resulting deformations the molecule undergoes to relieve these repulsions, the barrier to mechanical inversion is about 9 kcal larger than that for cyclooctatetraene itself. This is in agreement with the experimental evidence, although a more direct measurement of the barrier to mechanical inversion would be desirable. Our conclusions are quite the opposite of those of Ganis *et al.*[13] We believe the latter authors erred in using van der Waals functions for hydrogen which are inadequate.

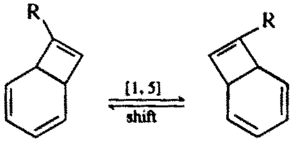
We have also studied octamethylcyclooctatetraene, and find results that are more or less predictable from a consideration of the tetramethyl derivative (Table 3).

In this case, while the methyls can find comfortable positions in the tub form, in the planar form there is tremendous repulsion between them, resulting in a huge increase in van der Waals energy. As with TMCOT, in an effort to relieve this energy the molecule undergoes an appreciable amount of stretching, and a very large amount of bending. The barrier calculated is 93·7 kcal/mol, large enough that inversion is certainly not going to occur under ordinary circumstances. Unsymmetrically substituted compounds of this kind, and probably also the hexamethyl and heptamethyl types as well, should therefore be resolvable into stable enantiomers.

In view of the very high activation energy to inversion, it is likely that strong heating of OMCOT will not lead to inversion, but rather will cause a Woodward-Hoffmann forbidden cycloreversion[17] to hexamethylbenzene and dimethylacetylene, similar in nature to that observed for 6,7-diphenyldibenzo [e,g] [1,4]diazocine.[18]

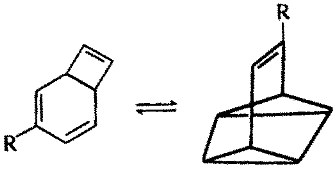
Another possibility is that a suitably symmetric resolved molecule might racemize by another route which would be of lower energy that inversion. Two such routes come to mind. Both require the molecule to form a bicyclo[4.2.0]octatriene; however, they require different bicyclo compounds. The example is shown with mono-substituted COT, but the argument is identical for hepta-substituted COT. The first route requires **1** to undergo an allowed [1,5] suprafacial migration.[19] The product of the migration **1m** is the mirror image of **1**. The molecule is thereby racemized. [1,5] Hydrogen shifts have been observed with activation energies as low as 35 kcal/mol.

The second possible route involves an internal



1 1m

Diels-Alder reaction similar to that postulated by Paquette, Meisinger, and Wingard[20] for conversion of 1,2-dimethylcyclooctatetraene into 1,4-dimethylcyclooctatetraene. In this case **2** would convert into **3**. Since **3** has a plane of symmetry, the molecule will have racemized.



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