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STRUCTURAL DEPENDENCE OF THE ROTATIONAL BARRIER IN CALICENES

A MOLECULAR ORBITAL APPROACH

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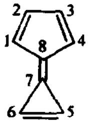
Abstract—Semi-empirical SCF MO calculations have been carried out for calicene and a variety of its derivatives. The pi binding energies of these species were obtained for both a planar structure and a structure where rotation about the intercyclic bond has occurred so that the two rings have assumed a perpendicular arrangement. While the absolute values of pi energy loss calculated by this approach are far too large, the relative values of the rotational barriers for various calicene derivatives follow expectations. It was shown that the incorporation of proper substituents into the molecule could lower the barrier to rotation either by inductive or conjugative effects. These effects would tend to stabilize structures with transfer of charge. Strain energy calculations, to assess the role of steric effects within the calicene system, are also discussed as are considerations of higher energy triplet states in the rotation phenomenon.

The eight pi electron system calicene, 1, has been the subject of much theoretical interest. HMO calculations carried out by Roberts *et al.* predicted that calicene should be a species with appreciable aromatic character.[2] A delocalization energy of $2\cdot94\beta$ (compared with $2\cdot00\beta$ for benzene) was determined. It was felt that a sizable contribution to the true structure of the molecule would be made by canonical representation 2 in which each of the rings has assumed a magic number $(4n+2)$ of electrons. Later calculations using the PPP variation of the SCF approach, yielded conclusions far different from the above.[3] The parent system was determined to be essentially poly-olefinic in character. A modest delocalization energy of only 1·5 kcal/mol was calculated to be present.



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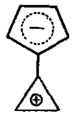

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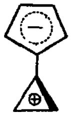

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The parent hydrocarbon itself has yet to be prepared. Various benzologous and/or substituted calicenes have, however, been synthesized.[4] Their properties do not suggest extensive aromatic character or, in many cases, a large contribution of canonical structure 2 to the ground state. X-ray determinations of the structures of 1,2,3,4-tetrachloro-5,6-di-*n*-propylcalicene[5] and 1,2,3,4-tetrachloro-5,6-diphenylcalicene[6] show bond lengths for the 7-8 bond of 1·370 Å and 1·359 Å respectively. These values indicate little single bond character here and little contribution of structure 2. They are in excellent agreement with the value of 1·370 Å for this bond calculated from the PPP-SCF technique.[3] Despite this, however, experiments indicate that rotation about the 7-8 bond may be a facile process.[7,8] Such a phenomenon requires a transition state in which the two monocyclic portions of the molecule assume the relatively perpendicular arrangement 3. The exocyclic bond must, in this geometry, have no pi component. In order to investigate the energetic feasibility of such an occurrence, PPP-SCF calculations have been applied to various calicene systems. It was planned that two related approaches would be utilized. In the first, all pi binding energies were to be determined based on C–C constant bond lengths of 1·40 Å which would be held at this value throughout the iterative procedure. The second utilized the same initial geometries, however, bond lengths would be recalculated from bond orders after each iteration. This variable bond length approach allows for systematic change in two center electron repulsion integral and resonance integral terms. Details of both methods have previously appeared in print.[9] In discussing transition states of type 3 it was assumed that the 7-8 bond would attain an approximate value of 1·515 Å, that of a pure single bond between two sp^2 hybridized C atoms.

Some justification of this approach is warranted. We are undoubtedly oversimplifying the stated problem in assuming that the change in pi binding energies is the sole factor operative. The possibility that some hyperconjugative interaction may stabilize the perpendicular structure is but one example of an effect which cannot be easily included in the present calculations. It must be confessed that the approach utilized greatly overemphasized the absolute magnitude of pi energy loss in the perpendicular configuration. Thus, an energy barrier in the range of 55 to 63 kcal/mol is calculated for calicene. As a corresponding barrier of only 65 kcal/mol is associated with ethylene,[10] that for calicene has certainly been exaggerated. Other related non-alternant systems can show even more unrealistic values for calculated energy barriers. Thus fulvalene, 4, is predicted to show a barrier to rotation twice that of ethylene by the pi electron calculations employed!

Recently an all-electron calculation on the energy barrier in calicene was carried out by Dewar and Kohn.[11] A value of only 26·8 kcal/mol was determined. A zwitterionic perpendicular structure with appreciable hyperconjugative interaction was implied from orbital occupancies and calculated bond lengths.

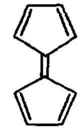
Although even advanced pi electron calculations must be deemed insufficient to evaluate absolute values of rotational barriers, it was felt that they might prove useful in correlating the possible effect of structural modification on the energies of these barriers. A series of substituted calicenes were studied. Present calculations agreed with those of Dewar and Kohn in predicting a zwitterionic structure. A serious difference concerned the intercyclic bond which Dewar and Kohn found to be very short. As this is a direct consequence of hyperconjugation the difference is not surprising. Table 1 shows the calculated pi energies of planar and perpendicular structures obtained from both approaches. While energy differences are presented, it is felt that too much significance must *not* be attached to these terms. Of greater importance should be the relative barriers to rotation which are also presented in Table 1. It is felt that these last terms can provide a valuable insight into the effect of structural modification.

A consideration of the benzologs of calicene shows that, as a general rule, the rotational barrier has not been affected. Annelation of benzene rings to the charge separated structure should tend to delocalize and hence stabilize the charges. It appears, however, that the planar ground state is stabilized to an equal or greater extent. The differences in pi binding energies for 1,2-benzcalicene, 5, and 5,6-benzcalicene, 7, are close to that for calicene itself. In contrast is the behavior of 2,3-benzcalicene, 6. The energy difference here is only four-fifths that of its isomers. The most probable explanation is that the presence of the benzene ring in the planar structure is no longer stabilizing. In this system the benzene ring must be localized in a quinoid structure by the non-aromatic calicene moiety. In the perpendicular structure this ring can re-assume some normal benzenoid character. This system, however, represents an exception. Indeed,

Table 1. Calculated pi binding energies[a] of calicene compounds

	Constant Bond Length				Variable Bond Length			
System	Planar	Perpendicular	Δ	Δ_{rel}	Planar	Perpendicular	Δ	Δ_{rel}
Calicene (1)	−9·753	−7·311	2·442	1·000	−10·115	−7·410	2·705	1·000
1,2-Benzcalicene (5)	−15·765	−13·371	2·394	0·980	−15·909	−13·129	2·780	1·028
2,3-Benzcalicene (6)	−15·106	−13·143	1·963	0·804	−15·264	−12·952	2·312	0·855
5,6-Benzcalicene (7)	−15·838	−13·388	2·450	0·985	−15·911	−13·113	2·798	1·034
Tribenzcalicene (8)	−27·970	−25·188	2·782	1·139	−27·445	−24·531	2·914	1·077
1-Alkylcalicene	−9·790	−7·224	2·566	1·051	−10·187	−7·242	2·945	1·089
2-Aklylcalicene	−9·817	−7·271	2·546	1·043	−10·171	−7·263	2·908	1·075
5-Alkylcalicene	−10·030	−7·718	2·312	0·947	−10·284	−7·722	2·562	0·947
1-Chlorocalicene	−9·986	−7·638	2·348	0·962	−10·229	−7·632	2·597	0·960
2-Chlorocalicene	−9·940	−7·587	2·353	0·964	−10·242	−7·598	2·644	0·977
5-Chlorocalicene	−9·711	−7·095	2·616	1·071	−10·126	−7·104	3·022	1·117
5,6-Dialkyl-1,2,3,4-tetrachlorocalicene	−10·613	−8·894	1·719	0·704	−10·550	−8·899	1·651	0·610
5,6-Dialkyl-1,2-benzcalicene	−16·136	−14·077	2·059	0·843	−16·101	−13·849	2·252	0·833
1-Phenylcalicene	−18·194	−15·963	2·231	0·913	−18·341	−15·776	2·575	0·952
2-Phenylcalicene	−18·144	−15·814	2·330	0·954	−18·347	−15·673	2·674	0·989
5-Phenylcalicene	−18·178	−15·922	2·256	0·924	−18·353	−15·742	2·611	0·965
Triplet calicene	−9·211	−8·396	0·815	0·334	−9·140	−8·524	0·616	0·228
Triplet 1,2-benzcalicene	−14·864	−14·619	0·245	0·100	−14·574	−14·250	0·324	0·120
Triplet 5,6-dialkyl-1,2,3,4-Tetrachlorocalicene	−9·550	−9·034	0·516	0·211	−9·205	−8·533	0·672	0·248

[a] Energies in electron volts.



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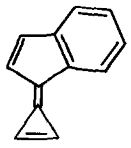

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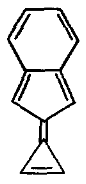

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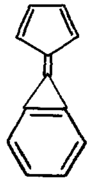

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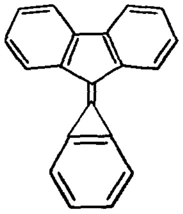

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tribenzcalicene, 8, is calculated to have the largest barrier to rotation of the benzologs here considered.

As almost all of the known calicene derivatives possess functional groups on both rings, it was decided to investigate such systems by means of an inductive model. In this approach the effect of substituents was taken into account by a suitable modification of the ionization potential of the C atom to which the group is attached. Alkylated conjugated systems have been treated by this approach and found to give results in reasonable accord with polarographic[12] and kinetic experiments.[13] The presence of electron donating and electron withdrawing groups in the 3- and 5-membered rings, respectively, should certainly favor any charge separated structure such as would be found in a perpendicular transition state. Experimentally, systems such as 1,2,3,4-tetrachloro-5,6-dialkyl or diarylcalicenes do show large dipole moments.[14] The results of these calculations are also given in Table 1. They are in complete agreement with expectation. An electron donating group in either position 1 or 2 increases the rotational barrier. The same group in position 5 lowers it. Opposite results are found for electron withdrawing groups. This effect appears to be cumulative. The rotational barrier in 1,2,3,4-tetrachloro-5,6-dialkylcalicene is approximately only 65% that of the parent compound. If the value of 26·8 kcal/mol obtained by Dewar and Kohn is used for the rotational barrier in calicene, a corresponding value for 1,2,3,4-tetrachloro-5,6-dialkylcalicene of 16·4–18·9 kcal/mol can be estimated from the present calculations. This is comparable to the value of 18·0–19·4 kcal/mol estimated for 1-formyl-5,6-di-*n*-propylcalicene.[7] These inductive effects also appear operative in appropriately substituted benzcalicenes.*

A special class of substituted calicenes would be those having phenyl substituents. Any stabilizing effects here would arise principally *via* delocalization rather than inductive interactions. Experiments suggest that these may be substantial. The compound 1,2,3,4,5,6-hexaphenylcalicene has a reported dipole moment of 6·3 D.[15] This is a phenominally high value for a hydrocarbon. Unfortunately this system is too large to be considered with our presently available computer facilities. However, calculations on the three monophenylcalicenes may give partial insight into this situation.

As can be seen from the data in Table 1, a phenyl group will lower the rotational barrier irrespective of point of attachment to the calicene unit. The order of effectiveness appears to be position 1 > 5 > 2. If a simple additivity were assumed for the effects of the phenyl group, a rotational barrier approximately sixty to seventy per cent that of calicene would be predicted for 1,2,3,4,5,6-hexaphenylcalicene. This may overestimate the barrier. Steric interactions will tend to prevent all phenyl groups in the 5-membered ring from occupying a common plane. It should, however, be possible for these groups to achieve a greater degree of coplanarity in the perpendicular structure, hence lowering the barrier to rotation.

In dealing with any substituted calicene, the possibility exists that steric factors, at least in part, may favor a perpendicular structure. Prior work utilizing strain energy calculations within the MO framework for hydrocarbon systems was somewhat encouraging in answering questions of this type.[16] Calculations were carried out using the geometries employed in the constant bond length approach. This is tantamount to a consideration of changes only in non-bonded interactions. Results are found in Table 2.

Interestingly, non-bonded interactions in all but one of the molecules considered favors the planar

Table 2. Non-bonded interactions in some calicenes[a,b]

Molecule	Planar	Perpendicular	Δ
Calicene	−1·599	−1·568	+0·031
1,2-Benzcalicene	−1·236	−1·129	+0·107
1-Methylcalicene	−2·443	−2·297	+0·146
5,6-Dimethyl-1,2-benzcalicene	−2·787	−2·420	+0·367
1-*t*-Butylcalicene	+2·604	−0·685	−3·289

[a] In kcal/mol.

[b] Based on carbon–carbon bond lengths given in text. C_{sp^3}—H; 1·108 Å, C_{sp^2}—H; 1·075 Å, angle strain at minimum value.

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*In treating chloro substituents *via* an inductive model it was assumed that the group had an opposite but equivalent effect of a methyl function. This may underestimate its stabilizing ability.

structure! There are no repulsive interactions in calicene itself. The potentially most severe interactions, which could be relieved by rotation about the 7-8 bond, are between some group attached to position 1 and position 6. When this group is hydrogen, the distance between these entities is 3·43 Å. The interaction between H and C atoms at this distance is attractive. Use of "harder" potential terms, other than those of Bartell's which are employed here, might modify these results.[17]. A range of such potential functions exist. Recently Schleyer *et al.* have used "harder" C–C interaction terms in treating polycyclic systems arguing that the older values were derived from properties where H–H interactions predominated.[18] A related effect may be operative here in that most of the attractive interactions are not occurring through space, but, through the molecule. A *t*-Bu group in position 1 is large enough, however, to introduce repulsive interactions. In this case rotation will relieve over three kcal/mol of strain. While in general, therefore, steric factors must be considered as playing little or no part in the rotation phenomenon, the *t*-Bu group will be exceptional. Prinzbach *et al.* point out that the NMR spectrum of 1,3-di-*t*-butyl-5,6-dimethylcalicene is temperature dependent. The protons of the Me groups, while showing non-equivalence at lower temperature will coalesce at temperatures as low as 62°.[8] Our approach shows that the relief of non-bonded interaction here in going to the perpendicular structure is approximately 28 kcal/mol. The steric acceleration must be exaggerated. The planar structure is calculated to possess severe non-bonded interactions by virtue of being held in a geometry with minimal angle strain. While a large portion of this strain could be eliminated at the expense of bond and/or angle strain, there is probably at least 15 kcal/mol of strain relieved in going to some perpendicular transition state.

A final consideration in the question of possible rotation about the double bond concerns higher energy structures. Calculations for the lowest triplet state of planar calicene shows it to be only slightly less stable than the singlet ground state. The calculations predict a length of 1·434 Å for the 7-8 bond. The increase in single bond character here is also manifest in the lessened energy loss in going to the perpendicular structure. The corresponding energy loss in going from the singlet planar molecule to the perpendicular triplet structure is less than 60% of that found for the corresponding transition through the zwitterion. It has been proposed that rotation about the double bond of ethylene can proceed either through a high energy perpendicular singlet or through a lower energy triplet state in the presence of some species which can favor singlet–triplet interconversion.[10,19] The possibility of increasing the facility of rotation by singlet–triplet interconversion in calicenes could be of experimental interest, although, such interconversion might best be photochemically induced. A subtle dependence upon structure can be seen. Data in Table 1 indicate that the appropriate annelation of benzene rings will tend to stabilize the perpendicular diradical structures. The addition of inductive substituents appears, however, to not markedly affect triplet stabilities. In a comparison of calicene and 1,2,3,4-tetrachloro-5,6-dialkylcalicene, the latter can much more readily rotate from a planar singlet state to a perpendicular singlet state. In going to a perpendicular triplet state, however, the rotational barriers are greater for the substituted compound.

Many of the substituted calicenes treated above were predicted to show lower barriers to rotation than the parent compound. Those molecules possessing groups with favorable inductive effects could most effectively stabilize the charge separated perpendicular structure. While it would be possible to refer to such systems as showing lessened pi character about the intercyclic bond, this is slightly misleading. The calculations would indicate a decreased tendency toward bond alternation in these appropriately substituted derivatives. Table 3 shows the calculated bond lengths for calicene and 1,2,3,4-tetrachloro-5,6-dialkylcalicene as derived from a bond order-bond length relationship.[9] As can be seen from the data, the substituted calicene has an average bond length of 1·407 Å with an average deviation of only 0·025 Å. The average deviation for the corresponding term of the parent system is twice this value. The bond lengths for the substituted calicene are all within the "aromatic" range. A nearly identical variation of bond lengths has been experimentally determined for anthracene.[21] The limited experimental data available, however, tend to indicate that even the most favorably substituted calicene should show severe alternation of bond length.[5,6]

While the above experimental structural results cast doubt on the validity of the inductive model utilized in much of this work, partial *a posteriori* justification of this approach is provided by an examination of calculated dipole moments. The dipole moment of calicene itself is calculated by the constant and variable bond length approaches respectively to be 5·73 D and 4·14 D. The former

Table 3. Calculated bond lengths for some calicenes (in Angströms)

Bond	Calicene	1,2,3,4-Tetrachloro-5,6-dialkylcalicene
1, 2	1·349	1·376
2, 3	1·446	1·437
1, 7	1·451	1·424
5, 6	1·349	1·370
5, 8	1·469	1·437
7, 8	1·370	1·397

result is very close to those obtained by other workers and reported by Prinzbach *et al.*[8] The corresponding values for 1,2,3,4-tetrachloro-5,6-dialkylcalicene are calculated to be 8·85 D and 7·38 D. These are both in reasonable agreement with the experimental value of 7·56 D found for 1,2,3,4-tetrachloro-5,6-dipropylcalicene.[22]

Although the results obtained from application of the inductive model do not agree with the structures obtained from X-ray data, we feel that this approach does have merit in describing the dependence of rotation about the intercyclic bond on structure. Calicene must still be considered as a polyolefinic species with a bond between the two cyclic moieties which is essentially double and showing a relatively high barrier to rotation. Introduction of proper substituents, however, particularly those able to induce and stabilize charge separation, will decrease the pi component of this bond and make rotation a more facile process.

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