# Bicyclo(6.2.0)decapentaene

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Abstract – Molecular mechanics caluclations (MMP2) on the title compound
and related molecules, cyclobutadiene, cyclodecapentaene and others are
described.   Heats of formation, resonance energies and molecular
structures were obtained, and where experimental comparisons are
possible, the agreement is good.

It has been recognized for a long time that while cyclooctatetraene contains eight pi
electrons and according to Hückel's rule is not aromatic, the title compound,
bicyclo(6.2.0)decapentaene (and certain related compounds) seems to satisfy Hückel's rule
for aromaticity in a formal sense, and there has been some discussion as to whether these
would be aromatic compounds (Ref. 1).   Recently the crystal structure of a derivative of the
title compound was reported (Ref. 2), and it was found that the compound was planar, but had
alternating bond lengths as in structure A.
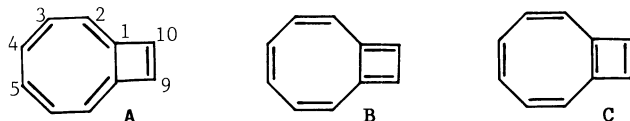
There are several different ways which have been used to define aromaticity.   The definition
can be in terms of the heat of formation of a compound, or in terms of the position of the
proton signals in the NMR spectrum, reflecting the ring current, or it is sometimes taken
that a compound with alternating bond lengths is not aromatic, while one with equal or
similar bond lengths is.   In addition, for rings larger than six-membered, planarity can be
taken as an indication of aromaticity, while nonplanarity indicates its lack.   Also,
inertness to chemical reaction is considered as evidence for aromaticity, while a high
degree of reactivity indicates anti-aromaticity.   Comparing benzene with cyclooctatetraene,
for example, the former is aromatic and the latter is not by each of these criteria.
Unfortunately, many compounds will be aromatic by some definitions and not by others, and
the whole situation now seems quite muddled.   Aromaticity may be defined in terms of
experimental quantities actually measured, or in terms of theoretical quantities which are
calculated.   Since aromaticity is a hypothetical quantity and not directly measurable in any
case, we prefer to make it a purely theoretical (calculated) quantity.   This has the
advantage that compounds that have not been (and perhaps cannot be) isolated for
experimental studies may still be investigated in this way.

While there is no generally accepted and completely agreed upon theoretical definition of
aromaticity, perhaps the one most often used at the present time is that which is due to
Dewar (Ref. 3) and Breslow (Ref. 4), which relates the pi energy of the molecule to an open
chain polyene fragment which contains the same number of double and single bonds as does the
principal Kekulé form.   This definition has in the past has suffered from the limitation
that the methods available for calculation of the energy of the pi system were not
completely general, and it was hard to relate the calculated result to any properties of the
real molecule in most cases.   We now have available a completely defined and exact way for
carrying out the necessary calculations using the molecular mechanics method, which includes
a self-consistent field pi-electron calculation.   The method has limitations that are well-
known to exist for each of these kinds of calculations.   For example, the single determinant
Hartree-Fock calculation contains limitations that can be removed by using a multi-
determinantal wave function (configuration interaction).   But the present method is exactly
defined, and these limitations are well known and do not seem serious.

A theoretical study of the title compound seemed warranted, in view of the conflicting
criteria for aromaticity that it displays by the fact that it is planar on the one hand

(aromatic), but contains alternating bond lengths (non-aromatic) on the other. We must be careful to sort out strain in the sigma system from that in the pi system. Both of these will show up in the heat of formation. But clearly, aromaticity is a property of the pi system, and any contribution to the strain energy from the sigma system must be factored out and removed before the contribution of aromaticity to the heat of formation can be understood.

There now exists a computer program which permits one to carry out calculations of the kind desired for the compound at hand. This program (MMP2, Ref. 5) calculates molecular structures by allowing for both the strain energy in the sigma system and the electronic energy of the pi system. The basic calculational method was described earlier (Ref. 6, and 7). The details of the calculation have been changed slightly, and the parameters have been refined (to the MM2 level from the MM1, Ref. 8,9).

Following the ideas of Dewar and Breslow, we chose to define "aromaticity" (and "anti-aromaticity") of a molecule relative to the energy of a planar linear conjugated polyene containing the same number of single and double bonds as the principal Kekulé form. A planar compound or structure is aromatic if it has a pi energy less than that of the corresponding polyene, and antiaromatic if the energy is greater (and non-aromatic if the energy is the same). The SCF pi energy plus the sigma energy both calculated for optimized structures with MMP2 specified parameters, is referred to in each case. Our definition is the same as Dewars in spirit, but numerical values differ slightly, because instead of using idealized structures, we use the molecular mechanics (MMP2) structures, which in general are more accurate. Note that resonance energies and aromaticity are only well-defined here for planar systems. If the system is non-planar, we can calculate the energy relative to the planar molecule, and the actual heat of formation, but the sigma and pi systems are no longer orthogonal, and resonance energy is not clearly defined for such cases.

As we consider molecules in which there is a twist about the double bonds, we expect that the "resonance energy" will be reduced, but the strain energy (the torsional conponent) is increased. There is no simple general relationship between these two quantities. We have chosen to define the "non-planar resonance energy" by comparing the calculated pi energy with that for the corresponding planar polyene, and we get a number, usually corresponding to an antiaromatic system. But this number seems not to be very useful in practice. So we are defining a "planar resonance energy for non-planar compounds", which is calculated by dropping out the direction cosine terms in the expressions used to calculate the resonance integrals, which corresponds to "flattening out" the pi system. The total SCF pi energy is recalculated in this way, and again compared with the polyene energy. The "planar resonance energy" is more in accord with our usual ideas about related quantities.

Another shortcoming of the original Dewar method concerns systems with strained sigma bonds, such as azulene or cyclobutadiene. In those cases his definition of resonance energy parallels ours, but Dewar's method does not allow for sigma strain, and hence cannot relate the calculate resonance energy to the experimental heat of formation. In the present method all deformations are explicitly allowed for, and the heat of formation is calculated and may be directly compared with existing experimental data. The geometry of the molecule may be calculated for the planar system (if this corresponds to the structure of minimum energy), or the molecule is allowed to deform from planarity if such deformation leads to a lower energy. In either case the optimized structure is used to calculate the total energy. The actual calculated total energy is compared with the calculated energy of the strain-free elements, and the difference gives the strain energy. If the molecule is non-planar, we are able to calculate the heat of formation, the resonance energy of the planar and non-planar forms, and the total (sigma plus pi) strain for the non-planar form. This gives us as much information on the energy of the molecule, broken into different components, as we can imagine will be useful. The MMP2 program provides this information automatically. This program has been previously described briefly in the literature (Ref. 8), so we will not describe it here, but an outline of applications of the program to problems pertinent as background to the problem at hand will be given. A full description of the program and its operation will be published later.

First, an MMP2 calculation was done on the linear polyenes containing from one to ten conjugated double bonds, and a plot was constructed of the pi energy vs. the number of double bonds. Following Dewar (Ref.3), a straight line was drawn through these, and from the slope and intercept, numerical values were assigned to the double and single bonds so that one may, by summing the appropriate quantities, obtain the heat of formation for any linear polyene (Ref. 10). Then we take as our zero aromatic character point for any desired polyene system, that linear analog containing the same number of each of the single and double bond components as does the principal Kekulé form of the compound under examination.

To illustrate for benzene, the Kekulé form contains three double and three single bonds, and the zero aromatic character value is thus $3 \times (-128.93) + 3 \times (-98.85) = -683.34$ kcal/mol. From the SCF calculation on the pi system of benzene (optimized geometry), the actual pi energy

is -705.47 kcal/mol. Hence the pi system of benzene is 22.13 kcal/mol (705.47 - 683.34) more stable than the Kekulé form, and hence aromatic, with a resonance energy of 22.1 kcal/mol. Our calculated heat of formation for benzene is 20.24 kcal/mol, compared to the experimental value of 19.81 ± 0.13 (Ref. 11). (Dewar assigned a resonance energy of 20.0 kcal/mol, using a slightly different parameterization scheme and an experimental geometry, as well as assumed geometries for the polyenes). Thus for most strainless planar molecules at least, our value for the resonance energy will be quite similar to Dewar's.

Similar calculations show, for example, that fulvene has a very slight amount of aromatic character (1.45 kcal/mol), which is exceeded by its strain energy (4.45 kcal/mol).

Before we discuss the title compound, we want to consider some simple related compounds, cyclooctatetraene, cyclobutadiene, and then some 10-pi electron systems related to the problem at hand, namely: naphthalene, azulene, cyclodecapentaene, and a bridged cyclodecapentaene (1,6-methano-10-annulene).

Planar cyclooctatetraene with D_{4h} symmetry is calculated to be slightly anti-aromatic (RE = -2.79 kcal/mol). When the molecule is allowed to become non-planar, it puckers into a tub shape (D_{2d}) and the total energy goes down, and we obtain a geometry (Ref. 12) and heat of formation (calculated 70.41, experimental 71.13 ± 0.33 kcal/mol, Ref. 11) in accord with those of the actual molecule.

1.520

1.346

1.481
(1.476)

1.344
(1.340)

124.6
(126.1)
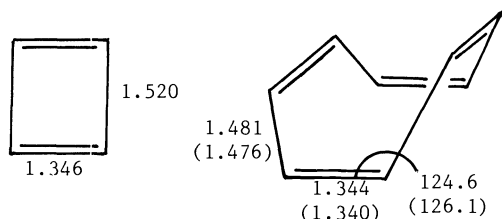
The MMP2 structures of cyclobutadiene and cyclooctatetraene. Experimental values are given in parentheses.

The difference in energy between the planar and non-planar forms is 13.67 kcal/mol, in good accord with the experimental barrier (Ref. 13) to planarity ($\Delta G^{\ddagger} = 13.7$ kcal/mol). This example is particularly informative for the following reason. One sees in the literature comments such as "cyclooctatetraene puckers because it is anti-aromatic", but as pointed out previously (Ref. 14), this is completely erroneous. Although anti-aromatic, puckering cyclooctatetraene serves only to raise its pi energy still further. (The calculated formal resonance energy becomes more unfavorable upon puckering, from -2.79 kcal in the planar molecule to -21.38 in the puckered form.) Although the meaning of formal resonance energy is not very clear for a non-planar system, it is clear the ring does not pucker to relieve the anti-aromaticity. It puckers to relax the strain in the sigma system, even though so doing raises the energy of the pi system. (The total strain energy is 12.18 kcal/mole in the tub form, as opposed to 25.50 kcal/mole in the planar form.) The only way it can relieve the anti-aromatic character would be to change its bonding (e.g. to break a bond and form an open chain).

Next we may consider cyclobutadiene. The SCF treatment in MMP2 assures us that a rectangular structure will be the ground (singlet) state, as is known to be correct (Ref. 15). The compound is calculated to be anti-aromatic by 20.06 kcal/mol, in agreement with Dewar (Ref. 3). The heat of formation is calculated to be 88.97 kcal/mol. MINDO/3 calculations (Ref. 16) give the value as 94.4 kcal/mol, and since the energies of four-membered rings are underestimated by this method, this seems to indicate an expected H_f of 100-105 kcal/mol. The discrepency here is surprisingly large. Because of the overall accuracy of the MMP2 calculations, it seems unlikely that the MMP2 value here is in error by more than about 2 kcal/mole. Interestingly, a very indirect experimental determination has given the value 90 kcal/mole (see discussion in Ref. 17).

Next we may examine azulene. Here we have a molecule which is planar and aromatic, but which has a strained sigma framework. The resonance energy is calculated to be 6.7 kcal/mol, much less than that calculated for either benzene (22.1) or naphthalene (33.7). The heat of formation is correctly calculated (74.28 calcd, 73.5 ± 0.9 exprimental) and the strain energy is 9.67 kcal/mol. (The geometries of these molecules are all well calculated.)

With this background, the calculation of the structure of the title compound is straightforward. There are three Kekulé forms that one can draw for the compound (A-C), and structures approximating each of these were used as starting points, and then the energy was minimized by optimizing each structure. The molecules were constrained to be planar. Two of these structures (A and B) reached different energy minima, while the third structure (C) proved not be a minimum, but went over to structure B. The implications here are most

unusual. The calculations indicate that there are two non-equivalent valence bond tautomers (A and B), and in valence bond language, resonance forms A-C each contribute to the structure of each of the two tautomers A and B, but in different proportions. Previously established examples of non-equivalent valence tautomers of this kind (involving only the pi system) where there are two separate energy minima, are rare, but cyclobutadiene is one example (Ref. 17).

It is well known that pi system calculations contain certain defects. The scheme used herein is based upon a standard SCF calculation,[3] and variants of it have been well discussed previously. The only defects anticipated in terms of structure would be those which result from the lack of inclusion of long range resonance integrals (they are included only between bonded atoms, ordinarily), and of electron correlation (single determinantal wave function). There is no reason to suppose that these omissions would cause any more difficulty here than they do in other studies on planar aromatic systems.

The activation barrier which separates structures A and B would be of interest, but we were not able to calculate it. We have tried compressing the 4,5 bond beginning with structure A to try to force the molecule to go over to structure B, but this does not happen. Apparently one would have to simultaneously compress and expand several bonds to get this to happen, and it is not obvious how that could be done calculationally in a way that would mimic the actual molecular behavior.

The nature of the cyclooctatetraene tub is such that the twisting is about the formally single bonds, not about the double bonds. And it is known that cyclobutene is planar. The result of these two facts is that structure A tends to remain planar, since non-planarity would require either a cyclooctatetraene with twisted double bonds or a non-planar cyclobutene. When the calculational model was twisted, it returned to the planar conformation. However, the twisting potential here is rather small. When the eight-membered ring was deformed into a tub, and the ring carbons were constrained to being $\pm$ 0.03 $\overset{\circ}{A}$ above and below the mean plane, and the energy of the molecule was then minimized with respect to all degrees of freedom except for the out-of-plane tub deformation, the total energy of the molecule increased by only 0.15 kcal/mol. Thus we attribute the fact that the molecule is experimentally found to have a shallow tub conformation to the action of crystal packing forces in response to the presence of the (non-coplanar) phenyl substituents in the molecule actually examined in the crystallographic study.

On the other hand, structures B and C can twist away from planarity without any problem, since the cyclooctatetraene tub can have the twisting confined to the single bonds, and the cyclobutene can be planar. Structure B, when constrained to planarity, was calculated to be stable in the sense that it did not go back to A, but it had an energy 11 kcals above the latter. Most of this energy difference comes from the pi system (anti-aromaticity), with the sigma systems being comparably strained in the two cases. However, when B was allowed to pucker, its energy went down considerably. The energy minimum was reached at a dihedral angle (2-3-4-5) of 65.9°, at which point the energy was only 3.65 kcal/mol above that of A.

These numbers are of interest, because they definitely say that there are two conformations in equilibrium. While the energy difference is sufficient that it will probably not be possible to directly detect B in the parent compound, it would seem likely that by positioning suitable groups in the molecule in such a way as to destabilize conformation A, it should be possible to obtain molecules which preferentially have conformation B. Indeed, the 2,7-dimethyl derivative has a markedly different ultraviolet absorption spectrum from other members of the series, which suggests the possibility of a different conformation (Ref 1).

These two structures, which correspond to the only energy minima we have found, both put a formal single bond in the intraannuler position. Thus the molecule is not so much related to the naphathalene type of bicyclic system, but is rather a perturbed cyclodecapentaene, more like azulene. The geometries of the molecules are summarized in Table I. Note that in structure A that there is essentially no "cyclobutadiene character" present, because only one bond in the four-membered ring (9,10) is "double" (short), and even this one has a pi bond order of only 0.90. In structure B, there are two double bonds in the four-membered ring, and definite "cyclobutadiene character". Note that in B the single bonds in the four-membered ring are much longer than the butadiene-type single bond (or the other formally single bonds in the structure). This is expected, as cyclobutadiene has a pi bond order of zero for its single bonds, while for butadiene types, the bond orders are about 0.25. The bond order of the 1,8 bond is 0.15 in A and -0.01 in B.

Table I shows that the comparison between the MMP2 values for the bond lengths with experiment is good, but certainly not perfect. The bond lengths in the eight-membered ring generally agree except that the 4,5 bond seems to be calculated to short. But the agreement is much less good in the four-membered ring, where all of the bond lengths are calculated to be too short. The reason for this discrepency is not known. Since MMP2 gives excellent

geometries for dozens of structures (Ref. 19), it is important to locate disagreements such as this, as they will permit future improvements in the force field. It may be that the Hartree-Fock approximation is insufficiently good in cyclobutadiene-like structures for obtaining accurate bond lengths, and this possiblity will be examined.

TABLE I

Calculated Geometric Quantities

	STRUCTURE A		STRUCTURE B
Bond	Length/Bond Order (Exper. [a])		
1,2	1.342/.91	(1.336)	1.462/.25
2,3	1.455/.29	(1.432)	1.348/.95
3,4	1.354/.92	(1.374)	1.479/.18
4,5	1.462/.28	(1.415)	1.347/.97
1,8	1.475/.15	(1.535)	1.520/-.01
1,10	1.471/.28	(1.446)	1.356/.97
9,10	1.365/.90	(1.403)	1.518/.05

a) E.S.D. .009 – .012Å, probable errors about $\pm$ 0.02 Å

This molecule (structure A) may be contrasted with azulene, which is also essentially a perturbed cyclodecapentaene. In azulene, however, by the same type of calculation there is only a single energy minimum, and all of the bonds except the intraannular one are nearly equal in length. (The latter bond is again extremely long.) Structure B has bonds alternating in length partly because of the demands of non-planarity, but structure A has alternating bond lengths only because of the perturbation resulting from the 1,8-bond. We will return to this point below.

The resonance energies of the compounds discussed above are summarized in Table II.

TABLE II

Heats of Formation (H_f^O, Gas, 25°C), Resonance Energies (RE) and Strain Energies (SE) (kcal/mol)

Compound	H_f^O	RE^a	SE
Cyclobutadiene	88.97	-20.06	59.90
Cyclooctatetrene D_{2d}	70.41	-21.38 (-2.48)	12.18
Cyclooctatetraene D_{4h}	84.03	-2.79	25.50
ccccc-10-Annulene D_{5h}	157.20	1.17	89.29
ccccc-10-Annulene-C_s	104.02	-30.61 (3.88)	38.89
cctct-10-Annulene-C_2	88.29	-17.29 (8.64)	28.34
1,6-Methano-10-Annulene C_{2v}	82.95	-7.55 (12.83)	28.02
Naphthalene	35.65	33.70	-2.00
Azulene	74.28	6.74	9.67
A	130.35	-4.02	54.97
B	134.00	-39.84 (-16.42)	46.23

[a] The first number given is the non-planar resonance energy. The number in parentheses is the "planar" resonance energy. See text.

Also included there are some 10-annulene (cyclodecapentaene) structures. The all-cis isomer of the latter in a planar comformation and in a more stable non-planar conformation were studied. Interestingly, the planar all-cis isomer (constrained to D_{10h} symmetry) has quite a low resonance energy (1.17 kcal). The C-C bonds are 1.396 Å in length. The

cis,cis,trans,cis,trans-isomer was examined in several ways. The hydrogens in the interior prevent the molecule from becoming planar, but the "planar resonance energy" is much larger (4.81 kcal/mol) than for the all-cis form, but it is still pretty small. These calculations do not include 1,6 overlap. For the cctct isomer, this overlap is significant, and when included, it increases the (planar) resonance energy to 8.64 kcal/mol. There are also interesting geometric consequences from this 1,6 overlap. Without it, the molecule would seem to have a choice of two kinds of geometry. The C-C bond lengths could be all essentially equal (like azulene), or they could be alternately long and short, a polyene. Calculations show the latter geometry to be of lower energy. Because of the non planarity of the molecule, there is twisting about some of the C-C bonds. With a polyene structure the twisting can be mainly about the single bonds, and this is energetically preferable to equal bond lengths, where the twisting would be about bonds of intermediate bond order.

The above considerations on 10-annulene provide interesting insights, but what does the molecule really do? In reality there is appreciable 1,6 overlap (previously studied by force field calculations, Ref. 6,18), and this both increases the resonance energy (by 3.41 kcal/mol in the present work) and it lowers the heat of formation more than the increase in resonance energy would suggest (from 94.66 to 88.29 kcal/mol). The geometry is still that of a polyene, as shown. However, the effect of the 1,6 overlap (5,10 in the figure shown) is clearly evident, as the molecule is deformed somewhat toward a naphthalene. The latter has the 1,2 bond shorter than the 2,3 or the 1,10 (where the naphthalene numbering system is used). The pentaene has an unsymmetrical polyene structure which is deformed by a few thousanths of an Angstrom in that direction from the regular polyene.
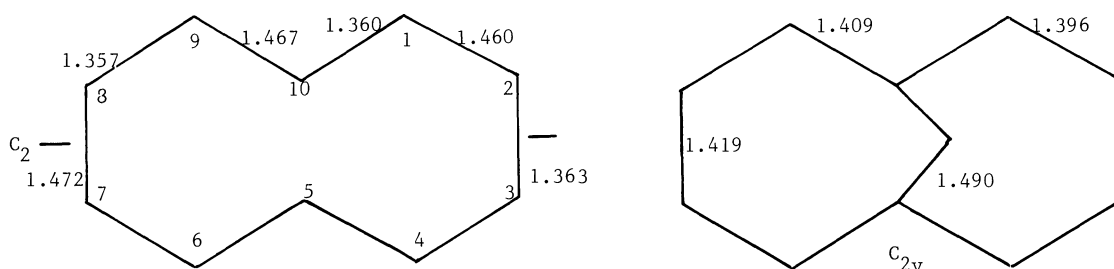
Interestingly, when the bridged pentaene (1,6-methano-10-annulene) is considered, it adopts a rather different structure, both by calculation and by experiment, which does not have a polyene character at all, but is very naphthalene-like. This is a consequence of moving the 1,6 carbons out-of-plane in the same direction in the latter compound, but in opposite directions in the parent 10-annulene.

Finally we might consider the series summarized in Table III.

TABLE III

Resonance Energies (kcal/mol)

Compound	RE ("Planar")
cctct-10 Annulene-C_2	
without 1,5 - overlap	4.8
with 1,5 - overlap	8.6
Naphthalene	33.7
Azulene	6.7
Bicyclo(6.2.0)decapentaene (A)	-4.0

The cctct isomer of 10-annulene when 1,6 overlap is not included has a "planar" resonance energy of 4.8 kcal/mole, and we can take this as a reference point. When 1,6 overlap is included, the RE almost doubles to 8.6 kcal. But if this overlap is allowed to become very large, by bonding the two atoms together to give naphthalene, the RE increases greatly to 33.7 kcal/mole. The conclusion is that the 1,6 overlap increases very much the RE, the greater the overlap, the greater the RE.

When the overlap is 1,5 instead of 1,6, the increase in the RE is quite small (compare azulene and naphthalene, Table III). This perturbation leads to an almost negligible change in the RE (compare cctct without overlap and azulene).

And finally, the RE shows A to be significantly antiaromatic. This kind of interaction 1,4 reduces the RE of cctct from 4.8 to -4.0, a change of -8.8, compared to 33.7 - 4.8 = 28.9 kcal/mole for addition of the 1,6-bond in naphthalene. Thus, the antiaromaticity introduced by this perturbation is about 30% as great as that introduced by the intraanular bond in naphthalene.

<u>Conclusions</u>   The MMP2 calculations yield a planar structure with alternating bond lengths and antiaromatic character as the ground state for the title compound, in agreement with experimental data.   They also indicate the existence of a second, less stable non-planar conformation.   The Dewar-Breslow definition of aromaticity in terms of the energy relative to a reference polyene is useful for the understanding bonding in this molecule and related systems, and is adapted to the molecular mechanics calculations.   Planarity and alternating bond lengths are poor criteria for judging aromaticity, as the examples shown have little correlation between these properties and the (thermodynamic) definition.

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