# *Ab initio* heats of formation of medium-sized hydrocarbons–10. Studies of barrelene and related compounds

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        <u>Abstract</u> – Ab initio calculations of bicyclo[2.2.2]octa-
        2,5,7-triene (barrelene), bicyclo[2.2.2]octa-2,5-diene,
        bicyclo[2.2.2]oct-2-ene, and bicyclo[2.2.2]octane were
        performed at the 6-31G* and 6-31G** SCF levels and the 6-31G*
        RMP2 level.  The results for these and model compounds, such
        as norbornadiene and Dewar benzene, enable comparison with
        the experimental thermochemistry in the barrelene series and
        a reassessment of the extent of destabilization in barrelene.

## INTRODUCTION

Molecular heats of formation are at the foundation of thermochemistry.  Until
recently, these quantities were obtained experimentally using well known
measurements such as heats of combustion, vaporization, and hydrogenation.
It is becoming clear, particularly for organic molecules, that theoretical
methods can provide an important source of heats of formation.  For molecules
which are difficult to prepare or to isolate in pure form, the need for
theoretical methods is obvious.  However, even for relatively common mole-
cules, experimental methods sometimes give conflicting values (albeit to high
precision); this is due in part to complicating effects of solvent, phase
changes, catalysts, sample purity and size, and inaccuracies associated with
small differences of large numbers.  In the future, it is quite likely that
theory and experiment will form a healthy partnership in the exploration of
thermochemistry.

Ab initio calculations can now be implemented in rather large basis sets,
with geometry optimization, even for molecules of moderate size.  Standard-
ization of the basis sets has led to a large data base of ab initio energies
and new strategies permit these energies to be employed in the accurate
calculation of heats of formation.  In the present work we apply these
methods to the thermochemistry of bicyclo[2.2.2]-octa-2,5,7-triene, commonly
known as barrelene.

## BARRELENE AND ITS HYDROGENATION PRODUCTS

The enthalpies of hydrogenation of bicyclo[2.2.2]octa-2,5,7-triene <u>1</u>
(barrelene), bicyclo[2.2.2]octa-2,5-diene <u>2</u>, and bicyclo[2.2.2]oct-2-ene <u>3</u>,
to bicyclo[2.2.2]octane <u>4</u>, measured by Turner and coworkers (ref. 1 & 2),



<u>1</u>

<u>2</u>

<u>3</u>

<u>4</u>
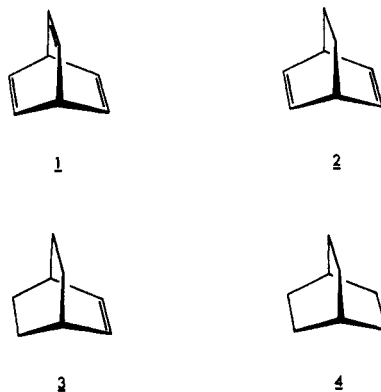
are -93.8 ± 0.31, -56.21 ± 0.10 and -28.25 ± 0.20 kcal/mol. The heats of formation of 3 and 4 have been obtained by Wong and Westrum (ref. 3) and their difference gives an enthalpy of hydrogenation for 3 --> 4 of -28.55 ± 0.42 kcal/mol, in good agreement with Turner's result. The enthalpy change for 3 ---> 4 is similar to that for cyclohexene ---> cyclohexane, -28.42 kcal/mol (ref. 4). On the other hand, the monohydrogenation of barrelene 1 is much more exothermic, -37.57 ± 0.41 kcal/mol. The larger magnitude could arise from destabilization of barrelene (due to strain in its sigma system and repulsions of the pi electrons of its double bonds) and/or homoantiaromatic character, as discussed by Goldstein and Hoffmann (ref. 5).

The nearly identical enthalpies of hydrogenation for 2 --> 3 and 3 --> 4, -27.96 and -28.25 (or -28.55) kcal/mol, respectively, are surprising; one might have expected the strain energies in the series to increase with increasing numbers of double bonds, making the heat of hydrogenation for 2 --> 3 more negative than that of 3 --> 4.

In view of these interesting experimental results, we have undertaken a theoretical study of the barrelene series of molecules. We report here the ab initio energies of 1, 2, 3 and 4 obtained at the 6-31G* SCF level (ref. 6) with full geometry optimization; energies at these geometries were also calculated at the 6-31G** SCF and 6-31G* RMP2 levels.

## RESULTS

The ab initio energies of 1 - 4 are given in Table 1. $D_{3h}$ symmetry was assumed for barrelene, $C_{2v}$ for bicyclooctadiene and bicyclooctene. The energy surface for twisting bicyclooctane is extremely flat: a $D_2$ structure having a 4-degree twist angle about the $-CH_2-CH_2-$ bridge has a 6-31G* SCF energy identical to five decimal places (in au) to that of the $D_{3h}$ form; a 19-degree twist increases the energy by only 0.4 kcal/mol. Schmitz et al. (ref. 7) have recently reported an ab initio study of the barrelene series with geometry optimization at the 3-21G SCF level; they found a very small local maximum (4 cal/mol) for the $D_{3h}$ form of 4. We are in essential agreement with their 3-21G results; however, a $D_{3h}$ maximum is not found at the 6-31G* SCF level.

In order to relate the 6-31G* SCF energies to the experimental heats of hydrogenation, while at the same time attempting to cancel computational errors as far as possible, we considered the following hypothetical reaction:
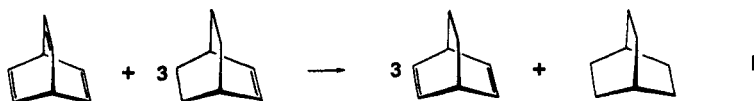


This reaction contains the same number of methines, methylenes and double bonds on each side and in addition contains the same number of intramolecular interactions between double bonds (3), double bonds and dimethylenes (6), and dimethylenes (3). (Zero-point and thermal corrections cf this type are usually quite small.) From the values given in Table 1 we obtain ab initio heats of reaction of -2.89, -3.01, -3.01, and -2.95 kcal/mol at the 3-21G (SCF), 6-31G*(SCF), 6-31G**(SCF) and 6-31G*(RMP2) levels. These values are remarkably consistent, despite very different levels of calculation. The experimental heat of reaction I, calculated from the enthalpy changes for 1 ---> 2 plus 3 ---> 4 minus twice 2 ---> 3, is -9.9 ± 1.1 kcal/mol. The difference between theory and experiment of almost 10 kcal/mol is quite surprising. In light of this, it is useful to consider a second reaction:
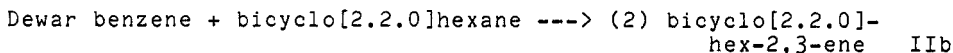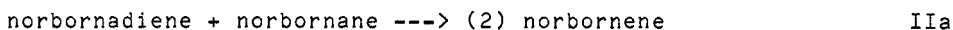
TABLE 1. Ab initio energies in the barrelene series (au)[a]

|                        | 6-31G*SCF | 6-31G**SCF | 6-31G*RMP2 |
|------------------------|-----------|------------|------------|
| barrelene 1            | -307.5093 | -307.5235  | -308.5325  |
| bicyclooctadiene 2     | -308.7159 | -308.7323  | -309.7444  |
| bicyclooctene 3        | -309.9124 | -309.9311  | -310.9481  |
| bicyclooctane 4        | -311.1036 | -311.1247  | -312.1483  |

[a]The 3-21G energies are -305.8105, -307.0128, -308.2053, and -309.3926, for 1 - 4 respectively, which agree with those of ref. 7.

We obtain ab initio heats of reaction of -3.26, -3.33, -3.33 and -2.20 kcal/mol at the 3-21G (SCF), 6-31G*(SCF), 6-31G**(SCF) and 6-31G*(RMP2) levels. The experimental value, based upon the enthalpy change 2 --->3 (-27.96 kcal/mol) minus the enthalpy change 3 ---> 4 (-28.25 kcal/mol), is +0.29 ± 0.5 kcal/mol. There is again a discrepancy between theory and experiment, although less serious than that for reaction I.

Reaction II belongs to a family of hydrogen transfer reactions which include:

norbornadiene + norbornane ---> (2) norbornene                             IIa

Dewar benzene + bicyclo[2.2.0]hexane ---> (2) bicyclo[2.2.0]-
hex-2,3-ene    IIb

Experimental and theoretical enthalpy changes for reactions II, IIa and IIb are given in Table 2. The calculated values are all negative, and the experimental value for IIa is also negative.

TABLE 2. Heats of reactions II, IIa and IIb (kcal/mol)

| Reaction | 6-31G*(SCF) | 6-31*(RMP2) | expt.              |
|----------|-------------|-------------|--------------------|
| II       | -3.3        | -2.2        | 0.29[a]            |
| IIa      | -6.2        | -5.4        | -1.85[a], -2.2[b]  |
| IIb      | -3.3        | -2.6        |                    |

[a]Ref. 1.
[b]Ref. 8.

It thus seems possible that the experimental enthalpy change for bicycloocta-diene ---> bicyclooctene is in error. A theoretical estimate of this hydrogenation energy can be obtained by converting the 6-31G* SCF energies of the barrelene series to heats of formation by means of the group equivalent scheme of Wiberg (ref. 9), and subtracting them to obtain heats of hydrogenation. (The Wiberg parameters were obtained using the ab initio energy of a planar form of 1,4-pentadiene, whereas its $C_2$ form is more stable by 3.8 kcal/mol; the experimental value of trans-2-butene used by Wiberg was also corrected from -4.82 to -2.99 kcal/mol. Refitting yielded the following revised group equivalents (in au): $CH_2$, -39.02681; CH, -38.45268; CH=, -38.45385.) The results obtained with these new parameters are given in Table 3.

The calculated heats of formation of bicyclooctene and bicyclooctane, 4.96 and -23.46 kcal/mol, are in good agreement with the experimental values of Wong and Westrum (ref. 3), 4.88 ± 0.19 and -23.67 ± 0.23 kcal/mol. It thus appears that the enthalpy of hydrogenation for 2 ---> 3 should be ca. -31.69 rather than -27.96 kcal/mol. The enthalpy change of reaction II would then be -3.44 kcal/mol and that of reaction I, -2.44 kcal/mol. Both are in much better agreement with the theoretical values of I and II, ca. -3 kcal/mol. It might be pointed out that heats of hydrogenation measured in acetic acid,

as in the method of Turner and coworkers, can be algebraically too large by
as much as 1 kcal/mol. Hydrogenation energies calculated by differencing
heats of formation calculated using the group equivalent method tend to have
similar errors. However, both of these systematic errors should largely
cancel for reactions such as I and II, which contain the same number of
double bonds in reactants and products.

TABLE 3. Calculated heats of formation and hydrogenation[a]

| Compound | Heat of Formation (kcal/mol) | Reaction | Heat of Hydrogenation (kcal/mol) |
|---|---|---|---|
| 1 | 74.77 | 1 ---> 2 | -38.12 (-37.57) |
| 2 | 36.65 | 2 ---> 3 | -31.69 (-27.96) |
| 3 | 4.96 (4.88) | 3 ---> 4 | -28.42 (-28.25,-28.55) |
| 4 | -23.46 (-23.67) | | |

[a]Experimental values of refs. 1-3 are given in parentheses.

One further theoretical result supports the preceding argument: the 6-31G*
SCF length of the CC bond between the bridgehead carbon and the olefinic
carbon is equal to 1.538, 1.520 and 1.513 Å, for 1, 2, and 3, respectively.
This length in 1 is unusually large for a bond between $sp^2$ and $sp^3$
carbons and is probably related to non-bonded repulsions between double bonds
(but not necessarily homoantiaromatic character). In any event, the
progression of these bond lengths in 1, 2, and 3 parallels their calculated
heats of hydrogenation, -38.12, -31.69, and -28.42 kcal/mol. The corres-
ponding bonds in norbornadiene and norbornene are 1.539 and 1.521 Å;
norbornadiene has both the larger bond length and larger exothermicity of
monohydrogenation.

## CONCLUSION

If the theoretical thermochemistry of the barrelene series is correct, then
the extra instability of barrelene, attributable to some combination of
strain energy and homoantiaromatic character, is much less than had been
thought previously. Thus a re-investigation of the heat of hydrogenation for
2 ---> 3 or a direct determination of the heat of formation of 2 would be
quite useful. A similar conclusion has been reached by Schmitz, Allinger,
and Flurchick using atom and group equivalents in their recent ab initio
study (ref 7). The limited homoantiaromatic character found here for
barrelene is consistent with the absence of homoaromatic character recently
found for triquinacene (ref. 10) using theoretical methods.

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