Aromaticity and hydrogenation patterns in highly strained fullerenes

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Abstract

Gradient corrected density functional theory is applied to evaluate the structure and energetics of hydrogenation patterns in the C_{36} molecule and its component fragments. Overall strain and resonance energies for these compounds are determined using homodesmotic reactions that connect C_{36} and its constituent chemical components to simpler non-aromatic, unstrained compounds. Our calculations indicate that the dramatic difference in energetic stability between two similar solid C_{36} structures is due to the number of disrupted aromatic rings rather than to differential strain. © 2002 Elsevier Science B.V. All rights reserved.

The discovery of covalently bound, stable, spherical carbon molecules has brought forth a broad new class of compounds that hold the promise of great practical utility and provide interesting new insights to chemical concepts such as aromaticity and strain energy. These compounds exhibit novel patterns of C—C bonds and carbon hybridization combined with various degrees of ring strain. The most highly studied of these is C_{60} Buckminsterfullerene, first characterized in 1985 [1]. A large number of quantum chemical studies have explored the structure of this compound [2], possible pathways to its formation and degradation and its reduction by hydrogen, halogens and alkyl cations.

In addition to the C_{60} archetype, a wide variety of other fullerenes have been synthesized or theoretically investigated. One of the smallest stable fullerenes is C_{36}, for which an efficient synthesis process has recently been discovered, allowing characterization of this species [3]. Comparison of experimental and theoretical NMR spectra for C_{36} suggests a D_{6h} symmetry singlet ground state [3,4], but energies predicted using gradient corrected density functional theory (DFT) find a D_{6h} triplet state and a D_{3d} singlet state to be slightly lower in energy [5,6]. Despite these predictions, the D_{6h} symmetry structure has been the focus of most subsequent studies and may be the structure most
consistent with measured ionization energies and IR spectra [7]. The D$_{6h}$C$_{36}$ structure consists of a six-membered cyclic polyacene ‘belt’, with two benzene ‘caps’ (see Fig. 1).

An important property of C$_{36}$ is its ability to form a solid involving at least six covalent σ bonds for each C$_{36}$ monomer unit – a stoichiometry that is also consistent with a D$_{6h}$ monomeric unit. Earlier theoretical studies of possible solid phase structures yielded a number of low energy binding conformations for D$_{6h}$C$_{36}$ [8] and found a significant difference in electronic properties between two very similar crystal structures (S1-ABC and S1-AB in [8]). Both structures involve six σ bonds to carbons on the cyclic polyacene belt and differ only in the symmetry of these bonds. The first structure (a D$_{3h}$ monomeric unit) has both a large binding energy and gap, and the second structure (a D$_{3d}$ monomeric unit) has only half the binding energy of the first and is metallic. Previous calculations indicate that the differences in these binding energies correlate with differences in stability of the two hexahydrogenated forms (C$_{36}$H$_6$) in which the D$_{3h}$ form is 3.1 eV more stable than the D$_{3d}$ structure [8]. In order to understand the origin of such a large change in electronic properties from such a small change in structural properties, one must understand, in detail, the interplay between strain and resonance energies in D$_{6h}$C$_{36}$.

Although much of the research on C$_{36}$ is motivated by its possible role as a high-temperature superconductor [9], this molecule is interesting in its own right as a model compound for the combined effects of aromaticity and strain in conjugated rings. The realization that cyclic polyenes have special chemical properties that can be explained in terms of resonance between two or more valence-bond structures was one of the great early successes of applying quantum theory to chemical phenomena. (Note however that Pauling emphasized that the roots of resonance theory pre-date quantum mechanics and that it was developed purely from empirical data, ‘without help from physics’ [10].) Resonance between different Kekulé structures of the carbon–carbon π-bonds has been used to explain many properties of aromatic hydrocarbons, including the patterns of their C–C bond lengths, their special stability to chemical substitution, and their novel magnetic and spectroscopic properties.

Additional data about the stability of conjugated systems can be determined from hydrogenation reactions that open one or more double bonds. By breaking up the cyclic polyene rings, hydrogenation will disrupt the aromaticity and alter (favorably or unfavorably) the ring strain. Hydrogenation energies have a long history of use to evaluate the magnitude of resonance stabilization, including some of the earliest measurements of the benzene resonance energy [11]. The simplest stable hydrogenation product of C$_{60}$, C$_{60}$H$_2$, has been studied both by experiment [12] and theory [13]. These agree that the most stable C$_{60}$H$_2$ isomer involves the H$_2$ addition across a single C–C bond between two of the fused six-membered rings, which disrupts the resonance in only two of these rings. The predicted next lowest energy structure (7.6 kcal/mol) involves the para-addition of the H$_2$ in a single six-membered ring and similarly disrupts the resonance in two rings. The next two
higher energy isomers disrupt the resonance in four six-membered rings and have energies of 20.9 and 24.0 kcal/mol. Thus, qualitative resonance concepts can be used to rationalize the hydrogenation pattern in C\textsubscript{60}.

In this Letter, we explore the structure and energetics of the C\textsubscript{36} molecule by studying the hydrogenation patterns in C\textsubscript{36} and its component fragments and discuss how simple resonance concepts can rationalize the observed substitution patterns. We also determine the overall strain and resonance energies by considering homodesmotic reactions connecting C\textsubscript{36} and its constituent chemical components to simpler non-aromatic, unstrained compounds.

All compounds described in this paper were optimized using DFT with the Becke three-parameter hybrid exchange functional [14] and Lee–Yang–Parr gradient corrected electron correlation functional [15] (B3LYP) with the 6-31G* basis set. Natural bond orbital (NBO) analysis was performed at these optimized geometries using the B3LYP/6-31G* wave function. All calculations were done using GAUSSIAN 98 [16].

We make extensive use of homodesmotic stabilization energies (HSEs) as defined by George et al. [17]. The HSE is the energy to dissociate any hydrocarbon (C\textsubscript{a}H\textsubscript{b}) into small, unstrained, non-aromatic compounds in such a way that preserves the number of C–C bond types (e.g. C\textsubscript{sp}^3–C\textsubscript{sp}^3) and number of carbon atoms of each hybridization and hydrogen count. There is some flexibility in the compounds used to balance this reaction, and we have used the reaction as originally defined:

\[
\text{C}_aH_b + \frac{a}{2} \text{C}_2H_4 + 2(a-b)\text{C}_3H_6 \xrightarrow{\text{HSE} = \Delta H^\circ} \left(\frac{2a-b}{2}\right)\text{C}_4H_6 + (a-b)\text{C}_4H_8
\]

where C\textsubscript{2}H\textsubscript{4} is ethylene, C\textsubscript{3}H\textsubscript{6} is propene, C\textsubscript{4}H\textsubscript{6} is transbutadiene, and C\textsubscript{4}H\textsubscript{8} is isobutene. By balancing the carbon–carbon bond types and C–H combinations, the HSE is a good measure of the stabilization or destabilization due to aromaticity or ring strain. We have used the B3LYP/6-31G* method, without zero point energy or thermal corrections to calculate the HSEs. For those hydrocarbons in this study for which experimental \(\Delta H_f\) is available (benzene and naphthalene), our predicted HSEs are within several kcal/mol of experiment.

The results of optimizing the structures linear acyclic and cyclic polyacenes with 6, 8, 10, 12, and 14 fused phenyl rings are listed in Table 1. For each compound, this table lists the homodesmotic stabilization energy for both the linear and cyclic forms. For the cyclic forms, Table 1 also lists the energy to dissociate the compound into \(n\)-distorted benzenes (analogous to those in Fig. 1), and the energy to relax these distorted benzenes from planar benzene. Table 2 lists the relative reaction energies for the addition of hydrogen atoms to C\textsubscript{36} and the related polyacenes in two different hydrogenation patterns. Note that the linear and cyclic polyacenes were optimized within symmetry constraints and may not correspond to true minima. All optimized structures and total energies are available in the supplementary tables or from the authors.

| Table 1 Homodesmotic stabilization energies (kcal/mol) for both the linear and cyclic of polyacenes with 6, 8, 10, 12, and 14 fused phenyl rings |
|-----------------|-----------------|-----------------|-----------------|
| HSE (linear)    | SE (cyclic)     | \(E_{\text{dissociation}}\) | \(E_{\text{strain}}\) |
| Benzene         | 21.7            | ×               | ×               |
| Naphthalene     | 33.1            | ×               | ×               |
| Hexacene        | 56.5            | –186.0          | –24.4           | –340.8          |
| Octacene        | 65.7            | –115.3          | 13.1            | –275.9          |
| Decacene        | 74.6            | –72.1           | 48.7            | –240.6          |
| Dodecacene      | 83.4            | –41.1           | 81.0            | –220.7          |
| Tetradecacene   | 92.1            | –17.4           | 110.9           | –210.7          |

For the cyclic forms, the energy to dissociate the compound into \(n\)-distorted benzenes (\(E_{\text{dissociation}}\)), and the energy to relax these distorted benzenes to planar benzene (\(E_{\text{strain}}\)) are also listed.
The most commonly cited criterion for aromaticity is energetic stabilization of a compound arising from cyclic conjugation. Typically, this stabilization is determined from hypothetical thermodynamic cycles to form similar product compounds that lack such cyclic conjugation. Such an approach to the aromaticity of linear polyacenes (column 2, Table 1) reveals that the calculated HSEs increase exactly linearly in the number of fused phenyl rings \( R^2 = 0.99 \). In the case of highly strained compounds, it is difficult to uniquely separate strain energy from the stabilizing effects of aromaticity. For the cyclic polyacenes, the HSEs are negative (Table 1, column 3) resulting from the large strains induced in bending the component fused phenyl rings. As expected, the HSEs increase rapidly for the larger cyclic polyacenes with less strain. Some estimate of the energy involved in the aromatic conjugation and bond strain can be derived by the hypothetical reaction to dissociate the cyclic \( n \)-polyacene into \( n \) distorted benzene rings. (Note that this reaction is stoichiometrically balanced using the unconjugated molecules in HSE Eq. (1).) This dissociation energy is listed in column 4 of Table 1, and provides an estimate of the favorable aromatic conjugation arising from fusing the phenyl rings. The additional stabilization arising from ‘macrocyclic conjugation’ in cyclic polyacenes has been studied by Aihara [18]. The strain in the cyclic polyacene can be estimated by the total energy to relax the \( n \) distorted benzenes, which is listed in column 5.

The presence of aromatic stabilization can be inferred from the predicted bond lengths and orbital hybridizations in \( C_{36} \). The C—C bond lengths and carbon hybridizations (calculated using NBO analysis) are shown in Fig. 2. The four distinct C—C bond lengths fall in the range of 1.41–1.49 \( \text{Å} \), compared with 1.40 \( \text{Å} \) in benzene and 1.54 \( \text{Å} \) in cyclohexane (B3LYP/6-31G* optimized values). Based on these bond lengths, the ‘cap’ benzenes retain the most benzene-like C—C bonds (1.41 \( \text{Å} \), as do the C—C bonds within the six ‘belt’ benzenes (1.43–1.44 \( \text{Å} \)). In contrast, the C—C bonds linking the belt to the caps, are essentially non-aromatic single bonds (1.49 \( \text{Å} \)). This structural analysis is

Table 2
Hydrogenated forms of \( C_{36} \) and its components

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Relative hydrogenation energies</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_{36} )</td>
<td>71.0</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>28.5</td>
</tr>
<tr>
<td>Hexacene</td>
<td>79.2</td>
</tr>
<tr>
<td>Octacene</td>
<td>99.5</td>
</tr>
<tr>
<td>Decacene</td>
<td>123.0</td>
</tr>
<tr>
<td>Cyclohexacene</td>
<td>87.8</td>
</tr>
<tr>
<td>Cyclooctacene</td>
<td>154.8</td>
</tr>
<tr>
<td>Cyclodecacene</td>
<td>150.1</td>
</tr>
</tbody>
</table>

Energies are in kcal/mol and given relative to the relevant lower-energy hydrogenated structure. All results are based on B3LYP/6-31G* energies of the B3LYP/6-31G* optimized geometry.

In order to separate the strain and resonance energy components we can use the predicted reaction energies of hypothetical reactions. For example, one estimate of the strain energy in \( C_{36} \) can be determined, as for the cyclic polyacenes described above, from the hypothetical decomposition of \( C_{36} \) to form eight benzene rings that have been distorted to align the C—H bonds along the connecting C—C bond vectors in \( C_{36} \) (Fig. 1). The homodesmotically balanced reaction energy for this dissociation is +106.0 kcal/mol, indicating that the dissociation is unfavorable by 13 kcal/mol per benzene ring. In contrast the subsequent relaxation of the strained benzene rings releases 734.4 kcal/mol (117.7 kcal/mol for the two ‘cap’ benzenes and 83.2 kcal/mol for the six ‘belt’ benzenes). These results indicate that the highly unfavorable heat of formation is due to the distortion of its component benzene rings, while the fusing of the rings yields some stabilization. Whether the origin of this stabilization is due to aromaticity in the polyacene belt cannot be directly determined from this result, but can be further analyzed for the isolated cyclic polyacenes (see below).

The problem of isolating the strain and aromaticity is particularly acute for \( C_{36} \), which is very highly strained and thermodynamically unstable with respect to decomposition into unstrained, non-aromatic hydrocarbons. Using the B3LYP/6-31G* energy and experimental \( \Delta H_f \)'s for the reaction products, we can estimate a \( \Delta H_f \) for the \( D_{6h} C_{36} \) isomer of 659 kcal/mol – quite similar to the value of 635 kcal/mol determined for \( C_{60} \) [19].
corroborated by the carbon orbital hybridizations predicted using NBO analysis. For comparison, the NBO predicted orbital hybridizations in benzene are $sp^{1.8}$ for the $C-C$ $\sigma$ bond (plus a pure $p$-orbital $\pi$ bond, $p_n$) and $sp^{2.4}$ for the $C-H$ $\sigma$ bonds. For $C_{36}$ the predicted hybridizations are $sp^{1.8}$ and

Fig. 2. Symmetry unique bonds of $C_{36}$ showing bond lengths and hybridizations.

Fig. 3. Three of the linear acyclic and cyclic polyacenes studied: (a) hexacene, (b) octacene, and (c) decacene. (d)-(e) correspond to the cyclic forms of these linear molecules. In (a) two possible ways to hydrogenate the molecule are illustrated: one which disrupts alternate aromatic rings ($C_{2v}$), and one which disrupts all aromatic rings ($C_2$).
In the C—C bonds in the cap benzenes and nearly the same in the C—C bonds in the polycene belt. In contrast, the C—C links connecting the belt to the cap benzenes are sp^2–sp^3 s bonds, with no p_n components.

Table 2 lists our calculated energies for hydrogen substitution patterns in C_{36} and related model compounds that disrupt all aromatic benzene rings relative to the corresponding substitution patterns that disrupt only alternate rings. From resonance considerations, the most stable hydrogenation pattern should be that which disrupts a minimum number of aromatic rings. Indeed, it is 28 kcal/mol less favorable to add hydrogens to both rings of naphthalene than to add to just one ring. A more pronounced difference between the two hydrogen substitution patterns in seen for the hexahydrogenated compounds. For both C_{36} and cyclohexacene, we investigated two hexahydrogenated forms of D_{3d} and D_{3h} symmetry (Fig. 4). The D_{3d} symmetry form disrupts all six aromatic rings in the belt of six fused benzenes and the D_{3h} form disrupts only alternate benzene rings. Our calculations favor the D_{3h}C_{36}H_6 structure by 71 kcal/mol compared to the D_{3d} structure, in good agreement with previous calculations [8]. For the analogous hexa-substituted cyclohexacenes (Fig. 4b) the results are quite similar, the D_{3h} structure is favored by 88 kcal/mol. By comparison, in linear hexacene (see Fig. 3) the energy difference between these two hydrogenation patterns is 79 kcal/mol.
For linear polyacenes, the difference in energy between the two hydrogenation patterns is perfectly linear in the number of fused phenyl rings ($R^2 = 1.00$). For the cyclic polyacenes, the relation of this energy difference to size of system is more complex. In all cases, the substitution favors the pattern that minimizes the number of aromatic rings disrupted. However, for the fullerene and cyclohexacene, the extreme degree of strain in the structure raises the possibility that differential relief of strain in the hydrogenated product may be the cause of the hydrogenation pattern observed.

We may now attempt to answer the question regarding the origin of the large difference in electronic properties for two similar hydrogenation patterns in C$_{36}$ (and the two related crystal structures). First, we have dissociated both D$_{3d}$ and D$_{3h}$ hydrogenated C$_{36}$ (Fig. 5a) into their component bent naphthalenes and benzenes (Fig. 5b), analogous to the dissection of the unhydrogenated compounds described above. Second, the bent structures are compared with their unstrained equivalents (Fig. 5c). Note that the resulting unstrained benzenes are identical between the D$_{3d}$ and D$_{3h}$ structures and are therefore not included. Thus, in moving from left to right across Fig. 5, we see that the energies released due to strain are large in both cases, although the D$_{3d}$ structure is around 40 kcal/mole more strained than the D$_{3h}$ structure. On the other hand, moving from top to bottom of Fig. 5 illustrates that the energy due to aromaticity between the hydrogenated naphthalenes is very similar to the energy difference between the two hydrogenated C$_{36}$ molecules. This result indicates that more of the difference between these two structures is due to the number of disrupted aromatic rings rather than to differential strain.

In conclusion, we employed DFT calculations to explore the interplay between resonance and strain in covalently bonded C$_{36}$ solids. Using a combination of homodesmotically balanced reactions of pure and hydrogenated molecular C$_{36}$ and its component fragments, we show that a disruption of aromatic rings plays a more important role than differential strain in determining the structural stability. These results demonstrate the fine balance between the combined effects of aromaticity and strain in conjugated rings typical of fullerene systems.

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**References**