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Strain in Biphenylene and Some of Its Derivatives

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The strain energies in biphenylene and some of its bridged derivatives have been calculated by using a high-level ab initio method (G3MP2//B3LYP-6-31G*) in order to resolve the long-standing discrepancy in the previously reported values. The results show that the strain energy of biphenylene is approximately 222 kJ/mol, which is lower than the previously reported values. The strain energies in 1,8-bridged biphenylene derivatives were also calculated and turned out to be larger than previously suggested. Our results highlight the need to use thermodynamic information in conjunction with structural data when discussing strain energy or molecular deformation.

Introduction

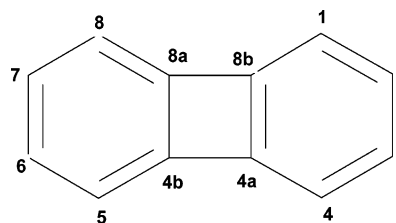
The strain in organic molecules which contain three- or four-membered rings has been studied extensively.¹ Such molecules are often unstable and difficult to synthesize. The biphenylene (1) is a classical example of a molecule where considerable strain pertaining to the four-membered, unsaturated ring is expected.² The biphenylene molecule contains a formal cyclobutadiene ring but is chemically stable. Many reactions do not lead to the opening of the four-membered ring as expected.² The reported estimates of ring strain energy vary considerably and cover the range of 151–419 kJ/mol.² They were obtained by using semiempirical or Hartree–Fock methods whose treatment of electron correlation is inadequate for accurate calculations of total electron energies. Furthermore, the additional strain introduced into the biphenylene molecule when the bridge linking the 1- and 8-positions of biphenylene (Schemes 1 and 2) is inserted was claimed to be small in spite of significant angle deformation and bond length alternations upon bridging.^{3,4}

We therefore used high-level ab initio calculations to investigate the molecular strain and help to check the previously reported claims. The molecular size of biphenylenes makes them less amenable to high-level ab initio calculations and such were not reported to date.

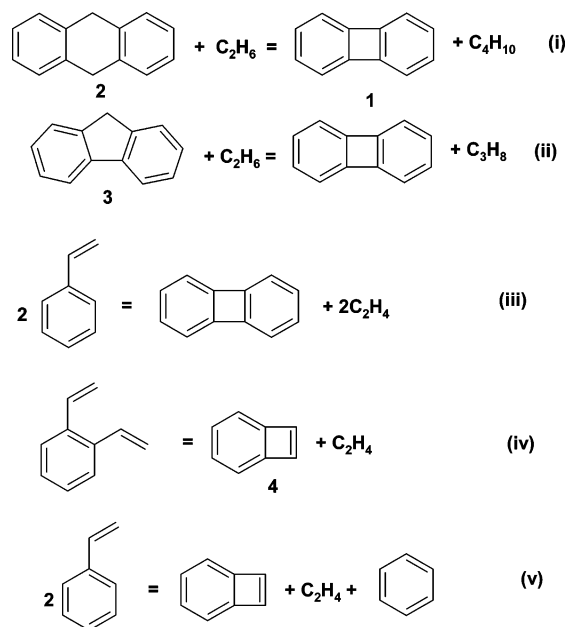
Theoretical Methods

The quantum chemical calculations were performed with the Gaussian 03 program.⁵ The total electronic energy for each molecule was computed using the G3MP2/B3LYP method⁶ which has rms deviation of at least 4 kJ/mol. The method includes full geometry optimization at the B3LYP/6-31G* level followed by single-point QCISD-type calculations. All the optimized structures corresponded to minima on their potential energy surfaces as was inferred from the absence of imaginary vibrational frequencies. In order to estimate the ring strain energy (RSE) in biphenylene and its derivatives we used the enthalpies of isodesmic reactions given in Scheme 2. The calculated and experimentally determined geometries for molecules participating in these reactions are compared in Table 1 and presented as evidence that the selected method adequately

SCHEME 1



SCHEME 2



describes the molecular structures. Nucleus-independent chemical shifts (NICS)⁷ were calculated at the GIAO/6-311G++(d,p)//B3LYP-6-31G* level.

We tested the reliability of calculated isodesmic reaction enthalpies for the reactions (i)–(iii) in Scheme 2 by comparing them with enthalpies for the same reactions obtained using experimental standard enthalpies of formation from the NIST compilation.⁸ The calculated enthalpies for (i)–(iii) are 213.7, 209.5, and 221.7 kJ/mol, respectively, whereas the enthalpies calculated using NIST data for reactants and products in the

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TABLE 1: Key Experimental and Calculated Geometry Parameters of Biphenylenes Obtained by X-ray and Electron Diffraction^{a,b}

molecule	C1–C8b Å	C1–C2 Å	C2–C3 Å	C4a–C8b Å	C4a–C4b Å	C8a–C8b Å
5	1.372 <i>1.373</i>	1.428 <i>1.420</i>	1.370 <i>1.390</i>	1.432 <i>1.424</i>	1.524 <i>1.509</i>	1.524 <i>1.509</i>
5a	1.341 <i>1.359</i>	1.407 <i>1.424</i>	1.395 <i>1.397</i>	1.406 <i>1.413</i>	1.560 <i>1.556</i>	1.453 <i>1.450</i>
5c	1.356 <i>1.362</i>	1.421 <i>1.423</i>	1.384 <i>1.395</i>	1.411 <i>1.414</i>	1.549 <i>1.544</i>	1.459 <i>1.462</i>
5k	<i>1.362</i>	<i>1.423</i>	<i>1.395</i>	<i>1.415</i>	1.546 <i>1.542</i>	1.444 <i>1.464</i>
5h	1.339 <i>1.358</i>	1.413 <i>1.422</i>	1.380 <i>1.397</i>	1.402 <i>1.412</i>	1.564 <i>1.558</i>	1.451 <i>1.450</i>

^a Numbers in italic font correspond to DFT geometry. ^b The experimental geometries are from refs 3, 4, and 9.

TABLE 2: Reaction Enthalpies for (i)–(vi) and Ring Strain Energies (RSE) (kJ/mol) of Benzocyclobutene and Biphenylenes Calculated at the G3(MP2)//B3LYP Level (Schemes 2 and 3)^a

a	b	c	d	e						
213.7	209.5	221.7	241.3	247.4						
4	5									
241.3	220.0									
5a	5b	5c	5d	5e	5f	5g	5h	5i	5j	5k
57.8	75.2	42.5	71.8	29.5	64.8	41.1	70.6	69.0	54.1	55.6

^a The RSE energies were obtained from enthalpies of isodesmic reactions in Schemes 2 and 3.

same reactions amount to 218.3, 220.5, and 230.3 kJ/mol, respectively. Since the calculation method itself (uncertainties in experimental enthalpies notwithstanding) can have the energy uncertainty of up to 8 kJ/mol we consider the agreement between two sets of values good enough to inspire confidence in the conclusions drawn from the results of our calculations. The experimental discrepancy in enthalpy of, e.g., fluorene, obtained by different measurements amounts to 8 kJ/mol.

The RSEs thus obtained are listed in Table 2.

Results and Discussion

The biphenylene molecule (**1**) and its bridged derivatives (**5**) contain a formal cyclobutadiene ring and provide interesting examples on which to study ring strain and inter-ring resonance interactions. The C4a–C4b bond length in **1** (1.524 Å) has the magnitude similar to the typical CC single bond and is much longer than the ring CC bonds.⁹ However, even within the six-membered ring there is significant bond length alternation. For example, C1–C8b and C1–C2 bonds differ by 0.056 Å. Furthermore, the bond length difference between C4a–C8b and C4a–C4b is even larger at 0.092 Å. We have also performed the analysis of aromatic properties of **1** by calculating NICS in the center of molecular planes of the six- and four-membered rings NICS(0) and at the point 1 Å above the molecular planes for the same rings NICS(1).

The NICS(0) shifts for six- and four-membered rings are –2.38 and 19.77, respectively. The corresponding NICS(1) values were –4.66 and 9.26. The corresponding HOMA aromaticity indices¹⁰ are 0.915 and 0.14, respectively. These values indicate that although the six-membered ring has aromatic character, the four-membered ring has antiaromatic character. In bridged biphenylenes **5a–5k** the corresponding NICS values decrease making the six-membered ring slightly more “aromatic” and the four-membered ring slightly less “antiaromatic”. For example, in **5a** the NICS(0) in the two rings is –2.16 and

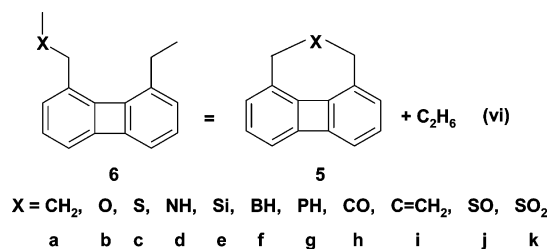
16.87 with NICS(1) values being –5.49 and 8.13, respectively. (The corresponding HOMA indices amount to 0.912 and 0.26, respectively.) The distinct qualitative difference in delocalization properties between the two rings is nonetheless retained.

These observations can be related to the reduced resonance interaction between the two benzene rings and to the reduced aromaticity within the rings themselves.

The important aspect of biphenylenes which has not been investigated to date concerns the expression of the aforementioned structural features through thermodynamic properties. The lack of accurate calculations on biphenylenes could be due to their size which makes high-level calculations computationally demanding. We wish to address two properties related to structure-energetics in biphenylenes. The first property concerns relative magnitude of resonance interaction between aromatic rings and the magnitude of strain in the four-membered ring. The second property concerns additional ring strain which is imposed on the biphenylene when the three-center bridge is inserted into the molecule linking the 1- and 8-positions.

The inspection of isodesmic reactions in Scheme 2 and Table 2 indicates that the enthalpy of reaction (i) can be taken as the representative measure of the combined effects of stabilizing inter-ring resonance and destabilizing four-membered ring strain. Molecule 9,10-dihydroanthracene (**2**) has a folded shape¹¹ with the dihedral angle between benzene ring planes of 144.7°. This shape precludes resonance delocalization/interaction between the two aromatic rings. Furthermore, the presence of methylene groups in a saturated, fused six-membered ring linking two aromatic rings also precludes resonance interactions or ring strain. Therefore, the enthalpy of reaction (i) reflects both the ring strain and resonance effects in **1**. Reaction (ii) comprises fluorene molecule (**3**) which is known to be planar¹² and hence makes stabilizing resonance interaction between aromatic rings possible. At the same time the presence of the fused five-membered ring in fluorene introduces a ring strain which is far less than that in biphenylene. The structure of fluorene can be assumed to comprise half of the total ring–ring resonance interaction in biphenylene because the fused five-membered ring in fluorene contains one methylene spacer group. The difference between the reaction energies of (i) and (ii) is 213.7 – 209.5 = 4.2 kJ/mol. The value of the ring–ring resonance stabilization in **1** can be assumed to be twice this amount, i.e., 8.4 kJ/mol. The small extent of inter-ring resonance which is evident from this value is also consistent with the structural information which describes the C4a–C4b bond as being a single bond.⁹ Adding inter-ring resonance stabilization energy to the enthalpy of reaction (i) gives 213.7 + 2 × 4.2 = 222.1 kJ/mol as the estimate of ring strain in biphenylene. We have not included

SCHEME 3



the 9,10-dihydrophenanthrene molecule in our analysis even though the fused intermediate six-membered ring has even less strain than its five-membered ring counterpart in fluorene. This is because 9,10-dihydrophenanthrene is known to be nonplanar with the dihedral angle between benzene rings¹³ being approximately 21°. The nonplanarity can reduce the extent of resonance between the two benzene rings and thus prevent the separate quantification of variables (ring strain and resonance) we are interested in.

The assessment of ring strain in **1** can also be made via an alternative, independent path which utilizes reaction (iii). Isodesmic reaction (iii) predicts the value of 221.7 kJ/mol which is in very good agreement with the value obtained from (i) and (ii). It is interesting to determine the ring strain in related benzocyclobutene (**4**), which like **1** also contains the formal cyclobutadiene moiety. The isodesmic reactions (iv) and (v) give the values of 241.3 and 247.4 kJ/mol for the ring strain in **4**. Bearing in mind that the typical energy uncertainty of G3MP2/B3LYP method is around 4 kJ/mol, the values from the two isodesmic schemes appear to be consistent with each other. Why is the ring strain higher in **4** than in **1**? The reason may be due to the absence of stabilizing inter-ring resonance and more extensive π -delocalization which is present in **1** but absent in **4**. It is known that considerable strain in benzocyclobutene is relieved by the deformation of intra-annular angles (within aromatic ring) and ipso angles at the bridgehead carbon.¹⁴

To put the RSE in **1** in context, we recall that the best current estimate of strain energies in cyclobutadiene, cyclobutene, and cyclobutane are 149, 125, and 112 kJ/mol.¹⁵ The strain in **1** is about 73 kJ/mol higher than in cyclobutadiene. The rationalization for this effect can be proposed as follows. In the antiaromatic systems like cyclobutadiene, the π -electron density favors bond localization and can countermand the tendency of σ -density which favors the opposite effect.¹⁶ This tendency is so strong as to interfere with the aromatic stabilization of the neighboring, fused benzene rings, leading to overall thermodynamic destabilization of **1** versus cyclobutadiene.

The question of changes to the molecular structure of biphenylene when the bridge is inserted between the 1- and 8-positions in **1** has been discussed previously on the basis of X-ray diffraction analysis of crystal structures of **5a**, **5c**, **5h**, and **5k**. Vögtle and coworkers^{3,4} have observed very significant distortion of the four-membered ring from the rectangular to trapezoidal shape. For example, the distortion is evident in the difference between C4a–C4b and C8a–C8b bond lengths which amounts to as much as 0.1 Å. Vögtle and coworkers^{3,4} have commented that slight additional strain introduced into the biphenylene molecule by bridging leads to surprisingly large geometry distortions. We suggest that the bridging introduces additional strain (over and above the one present in parent biphenylene) which can amount up to 33% of the biphenylene strain (Table 2) and thus cannot be considered negligible. This additional strain in **5** derivatives is of course dependent on the type of the bridging group X (Scheme 3). A silicon bridge gives

the smallest additional strain, and therefore the derivative **5e** can be expected to be readily amenable to synthesis. On the other hand the oxygen bridge as in **5b** leads to more strain, and the compound possibly presents a more difficult synthetic challenge. The derivative **5b** has not been synthesized to date. In any case it turns out that molecules can tolerate a large extent of angular or even bond deformation without significant effect on their thermodynamic properties.

Summary

We discussed the molecular structure and strain energy in biphenylenes on the basis of available experimental molecular geometries and high-level ab initio calculations. We have determined the strain and resonance energy in biphenylene and demonstrated that the additional strain imposed by 1,8-bridging strongly depends on the functional group at the apex of the bridge. Such additional strain can reach up to 33% of the strain in parent biphenylene and can thus not be considered negligible.

Furthermore, we have demonstrated that the deformation of geometry is only a qualitative indicator of strain and should be substantiated by calculation of thermodynamic properties using high-level ab initio methods. Such calculations provide a much better, more quantitative description of the strain in molecules than do molecular structure data. Therefore, thermodynamic information should be used in conjunction with the structural information whenever possible in any discussions of strain and geometry deformation.

Supporting Information Available: G3(MP2)//B3LYP energies and calculated geometries for biphenylenes. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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