

Regularities in Energies and Geometries of Biaryls: An *ab Initio* Electronic Structure Study

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Results of BLYP/6-311G** electronic structure calculations on 29 different conformers/isomers of biaryls possessing the phenyl, naphthyl, and anthryl moieties reveal significant regularities in properties of these species. Stabilities and geometries of unsubstituted biaryls composed of two convex aryl moieties depend mostly on the connectivities of the proximate hydrogen atoms involved in steric repulsions. The computed BLYP/6-311G** energies and lengths of the intermoiety C–C bonds in such biaryls are determined within 0.46 kcal/mol and 0.0040 Å, respectively, by the topologies of these connectivities, whereas the average intermoiety twist angles are less transferable, the corresponding uncertainty amounting to ca. 7°. The observed regularities in properties of biaryls imply insensitivity of the π -electron conjugation between the aryl moieties to the details of electronic structures of the entire molecules. Thanks to these regularities, the Z and E conformers of unsubstituted biaryls consisting of two convex aryl moieties are almost isoenergetic and therefore are expected to be equally populated at ambient temperatures.

Introduction

Biaryls are the key intermediates in the formation of polycyclic aromatic hydrocarbons (PAHs) and soot that occurs during oxygen-poor combustion of many solid fuels such as coal and wood.^{1–4} Aryl radicals, which are the precursors of biaryls, are generated under these conditions from simple PAHs and/or their alkyl derivatives through a thermally induced cleavage of the C–R (where R is either a hydrogen or an alkyl group) bonds. At higher temperatures, biaryls undergo cyclo-dehydrogenation, yielding pericondensed PAHs. Since many of these PAHs are potent carcinogens, research on the formation and properties of biaryls is of great practical interest.

Although the individual kinetics of the formation of aryl radicals may well depend on their stabilities (which, contrary to the common belief, are governed mostly by steric rather than electronic factors⁵), both the experimental data and the results of limited modeling are believed to indicate that the relative yields of biaryls produced in the course of pyrolytic processes are, at least at lower temperatures, thermodynamically controlled.⁴ In other words, fast equilibration takes place among the end products of radical reactions, resulting in the preferential formation of the most stable species. Consequently, reliable theoretical predictions of stabilities of biaryls hold the key to the identification of viable pathways to various combustion-generated substances.

The relative energies and geometries of biaryls are determined by a balance between two phenomena, namely stabilization due to the π -electron conjugation between the aryl moieties, which decreases with increasing intermoiety twist angle, and steric repulsions between proximate hydrogens, which favor an orthogonal arrangement of the aryl moieties. The delicate nature of this balance is revealed by the experimentally determined geometries of the biphenyl molecule, which is found to be twisted by ca. 44° in the gas phase⁶ but planar or almost planar in solid state.⁷ In principle, the magnitude of the π -electron conjugation between the aryl moieties, and thus the intermoiety

twist angle, should be sensitive to the details of electronic structure of the entire biaryl molecule. In addition, the patterns of bond lengths within the aryl moieties should affect all interatomic distances, altering the extent of steric repulsions between the proximate hydrogens. However, the results of recent semiempirical AM1 calculations appear to indicate that the geometries and relative stabilities of several biaryls depend mostly on the topology of the bond chains that connect the proximate hydrogens involved in steric repulsions.⁴

The present study has two main objectives. First of all, it aims at establishing a benchmark for less accurate electronic structure calculations on biaryls. Such a benchmark has been long overdue, considering the virtual nonexistence of reliable *ab initio* predictions for higher biaryls, which is in stark contrast to the abundance of recent high-quality calculations on the biphenyl molecule.⁸ The verification of the regularities observed in the AM1 data⁴ constitutes the second objective of the present work.

Details of Calculations

For large molecules with low symmetries, such as those investigated in the present study, one has to resort to methods of the density functional theory (DFT) in order to include electron correlation effects in electronic structure calculations. Accordingly, geometry optimizations of all the biaryls obtained by combining the phenyl, 1-naphthyl, 2-naphthyl, 1-anthryl, 2-anthryl, and 9-anthryl moieties were carried out at the BLYP/6-311G** level of theory⁹ with the GAUSSIAN 94 suite of programs.¹⁰ In addition, vibrational frequencies were calculated for the biphenyl molecule.

Out of the 21 biaryls in question, 10 possess (at least in principle) two distinct conformers. Throughout this paper, the conformers with the long axes of the aryl moieties positioned at angles smaller than 90° are denoted by the letter Z, whereas the others are called E conformers. One should note that energy minima could not be located for the E conformers of the 1,1'-binaphthyl and 1,1'-bianthryl molecules, making the total number of the species under study equal to 29.

Due to the presence of both soft (the intermoiety twist angle) and hard (bond lengths and angles, and the dihedral angles

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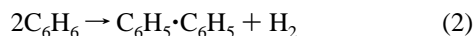
within the aryl moieties) vibrational modes, many of the geometry optimizations required large numbers of gradient calculations. Occasionally, optimization restarts and suitably designed guesses of the Hessian matrices were also necessary. The average intermoiety twist angles in the final structures were calculated as follows: Let C₁–C₂ denote the bond that links the aryl moieties, and C₁–C₃, C₁–C₄, C₂–C₅, and C₂–C₆ stand for the bonds adjacent to it. In general, there are four different dihedral angles describing the twist between the aryl moieties, namely C₃–C₁–C₂–C₅, C₃–C₁–C₂–C₆, C₄–C₁–C₂–C₅, and C₄–C₁–C₂–C₆. For two of these angles, 0° ≤ φ₁, φ₂ ≤ 90°, whereas for the other two, –180° ≤ φ₃, φ₄ ≤ –90°. The average intermoiety twist angle is given by

$$\varphi = (1/4)[\varphi_1 + \varphi_2 + (180 + \varphi_3) + (180 + \varphi_4)] \quad (1)$$

For example, the optimized values of the φ₁, φ₂, φ₃, and φ₄ dihedral angles in the E conformer of 1-(2-anthryl)anthracene are 58.3, 60.6, –123.2, and –117.9°, respectively, yielding φ equal to 59.5°.

Results and Discussion

The overall accuracy of the present calculations can be assessed from the results obtained for the biphenyl molecule. The computed intermoiety twist angle equals 40.3° and the length of the intermoiety C–C bond is 1.493 Å. These figures compare very favorably with the experimental gas-phase values of 44.4 ± 1.2° and 1.507 ± 0.004 Å obtained from electron diffraction measurements,⁶ although the slight underestimation of both the bond length and the twist angle indicates some exaggeration of the π-electron conjugation between the phenyl moieties at the BLYP/6-311G** level of theory. The energy of the reaction



is predicted at 6.3 kcal/mol (at 0 K, ZPEs included), which is reasonably close (taking into account that the reaction 2 is not isodesmic) to the corresponding standard enthalpy of 3.7 kcal/mol calculated from the experimental ΔH°_f values of 19.80 and 43.30 kcal/mol listed for benzene and biphenyl, respectively, in the recent compilation.¹¹

The computed dissociation energies ΔE and lengths R of the intermoiety C–C bonds are listed in Table 1 together with the average intermoiety twist angles φ. In order to be converted to the standard bond enthalpies, the quoted values of ΔE have to be corrected for the neglect of the ZPEs, finite temperature effects, and systematic errors. For example, the bond dissociation energy (BDE) for the biphenyl molecule, which equals 109.0 kcal/mol (Table 1), yields the standard bond enthalpy of 106.1 kcal/mol upon the inclusion of the difference in ZPEs (–4.4 kcal/mol) and the thermal correction of (5/2)RT¹² (+1.5 kcal/mol). The corresponding experimental estimate, obtained by subtracting the ΔH°_f of biphenyl (equal to 43.3 kcal/mol¹¹) from twice the ΔH°_f of the phenyl radical (equal to 81.2 ± 0.2 kcal/mol¹³ or 78.9 ± 0.8 kcal/mol¹⁴), amounts to 119.1 ± 0.4 or 114.5 ± 1.6 kcal/mol. Thus, the computed BDE appears to be 8–13 kcal/mol too low. However, the bulk of this error originates from the systematic overestimation of the stability of aryl radicals by 3–5 kcal/mol at the BLYP/6-311G** level of theory,⁵ giving credence to the relative values of BDEs calculated for the biaryls under study.

In the biphenyl molecule, the proximate hydrogens engaged in steric repulsions are linked through chains of four carbon atoms. Arrangements involving chains of five or six carbons are also possible in principle,⁴ giving rise to six general classes

TABLE 1: Calculated Properties of the Ar₁·Ar₂ Biaryls

class	Ar ₁	Ar ₂	conformer (symmetry)	ΔE ^a (kcal/mol)	R ^b Å	φ ^c (deg)
1,4/1,4	C ₆ H ₅	C ₆ H ₅	– (D ₂)	108.96	1.4932	40.32
	C ₆ H ₅	2-C ₁₀ H ₇	– (C ₁)	109.04	1.4924	38.61
	C ₆ H ₅	2-C ₁₄ H ₉	– (C ₁)	109.04	1.4919	40.55
	2-C ₁₀ H ₇	2-C ₁₀ H ₇	E (C ₂)	109.39	1.4916	33.81
	2-C ₁₀ H ₇	2-C ₁₀ H ₇	Z (C ₂)	109.39	1.4918	40.85
	2-C ₁₀ H ₇	2-C ₁₄ H ₉	E (C ₁)	109.19	1.4909	35.42
	2-C ₁₀ H ₇	2-C ₁₄ H ₉	Z (C ₁)	109.27	1.4908	38.17
	2-C ₁₄ H ₉	2-C ₁₄ H ₉	E (C ₂)	109.08	1.4892	35.24
	2-C ₁₄ H ₉	2-C ₁₄ H ₉	Z (C ₂)	109.16	1.4900	40.70
	C ₆ H ₅	1-C ₁₀ H ₇	– (C ₁)	106.46	1.4999	59.05
1,4/1,5	C ₆ H ₅	1-C ₁₄ H ₉	– (C ₁)	106.55	1.4998	61.68
	1-C ₁₀ H ₇	2-C ₁₀ H ₇	E (C ₁)	106.69	1.4993	61.80
	1-C ₁₀ H ₇	2-C ₁₀ H ₇	Z (C ₁)	106.61	1.4994	59.37
	1-C ₁₀ H ₇	2-C ₁₄ H ₉	E (C ₁)	106.47	1.4983	58.76
	1-C ₁₀ H ₇	2-C ₁₄ H ₉	Z (C ₁)	106.36	1.4991	59.72
	2-C ₁₀ H ₇	1-C ₁₄ H ₉	E (C ₁)	106.82	1.4982	60.61
	2-C ₁₀ H ₇	1-C ₁₄ H ₉	Z (C ₁)	106.67	1.4984	58.15
	1-C ₁₄ H ₉	2-C ₁₄ H ₉	E (C ₁)	106.67	1.4970	59.47
	1-C ₁₄ H ₉	2-C ₁₄ H ₉	Z (C ₁)	106.59	1.4975	56.55
	C ₆ H ₅	9-C ₁₄ H ₉	– (C ₂)	104.90	1.5054	89.66
1,5/1,5	1-C ₁₀ H ₇	1-C ₁₄ H ₉	E (C ₁)	104.94	1.5058	86.97
	2-C ₁₀ H ₇	9-C ₁₄ H ₉	– (C ₁)	105.17	1.5060	90.00
	2-C ₁₄ H ₉	9-C ₁₄ H ₉	– (C ₁)	105.02	1.5058	90.00
	1-C ₁₀ H ₇	1-C ₁₀ H ₇	Z (C ₂)	104.79	1.5069	87.00
1,4/1,6	1-C ₁₀ H ₇	1-C ₁₄ H ₉	Z (C ₁)	104.90	1.5057	81.89
	1-C ₁₄ H ₉	1-C ₁₄ H ₉	Z (C ₂)	105.25	1.5053	84.48
1,5/1,6	1-C ₁₀ H ₇	9-C ₁₄ H ₉	– (C ₁)	103.79	1.5079	89.59
	1-C ₁₄ H ₉	9-C ₁₄ H ₉	– (C ₁)	103.83	1.5072	88.77
1,6/1,6	9-C ₁₄ H ₉	9-C ₁₄ H ₉	– (D ₂)	103.10	1.5103	90.00

^a Dissociation energy of the intermoiety C–C bond (at 0 K, ZPEs not included). ^b The length of the intermoiety C–C bond. ^c The average intermoiety twist angle, eq 1.

TABLE 2: Average Properties of Biaryl Classes

class	Δ(ΔE) ^a (kcal/mol)		φ (deg)	
	BLYP/6-311G** ^b	AM1 ^c	BLYP/6-311G** ^b	AM1 ^c
1,4/1,4	0.0	0.0	38.4 ± 2.4	41 ± 2
1,4/1,5	2.6 ± 0.2	2.0 ± 0.3	59.5 ± 1.6	60 ± 2
1,5/1,5	4.2 ± 0.1	3.6 ± 0.3	89.2 ± 1.5	69 ± 2
1,4/1,6	4.2 ± 0.2	7.1	84.5 ± 2.6	66
1,5/1,6	5.4 ± 0.1	5.2 ± 0.1	89.2 ± 0.6	89 ± 1
1,6/1,6	6.1	6.9	90.0	90

^a ΔE relative to the average ΔE for the 1,4/1,4 class. ^b Present calculations. ^c Reference 4.

of biaryls denoted by 1,4/1,4, 1,4/1,5, 1,5/1,5, 1,4/1,6, 1,5/1,6, and 1,6/1,6 in Table 1. There is surprisingly little variation in the values of ΔE and R within each class, whereas the average intermoiety twist angles vary somewhat more, especially for the species of the 1,4/1,4 type. The trends uncovered by comparing different classes of biaryls agree with the expectations based upon “chemical intuition”: as the steric congestion increases, the intermoiety C–C bonds become weaker and longer, and the molecules become more twisted. Qualitatively, these regularities are similar to those found in the results of the previously published AM1 calculations (Table 2). However, the typical values of φ in the species belonging to the 1,5/1,5 class (the “cove,cove” class⁴) are much higher (88.5° vs 69°) at the BLYP/6-311G** level of theory, putting the reliability of the AM1 geometry predictions for such molecules in doubt.

Interesting trends are observed in the computed properties of the Z/E pairs of conformers that are members of the 1,4/1,4 class. For a given biaryl molecule, the two conformers possess virtually identical values of ΔE and R, but the Z species is always significantly more twisted. These differences in the values of φ can be readily explained by the patterns of the C–C bond lengths in the aryl moieties. These patterns can be easily

deduced from the Kekulé structures of the biaryls, which are the same as those of the respective uncoupled arenes. In all cases, the two carbon chains that link the proximate hydrogens possess the shorter-intermoiety-longer/longer-intermoiety-shorter patterns of C—C bonds in the E conformers, whereas the shorter-intermoiety-shorter/longer-intermoiety-longer patterns are found in their Z counterparts. Consequently, for a given value of φ , two of the proximate hydrogens are closer and the other two are more distant in the Z conformers comparing with the analogous pairs of atoms in the E species. Because of the steep increase in steric repulsions at shorter H···H distances, the former arrangement is somewhat less favorable, giving rise to greater twist angles at the equilibrium geometries of the Z species.

Due to the involvement of four C—C bonds for one pair of the proximate hydrogens, analogous arguments are much less clearcut for the members of the 1,4/1,5 class, which exhibit diminished differences between the average intermoiety twist angles in the Z/E conformer pairs. In contrast, the Z conformer of the 1-(1-naphthyl)anthracene molecule, which belongs to the 1,4/1,6 class, is much less twisted than its 1,5/1,5-type E counterpart, although both species possess almost identical values of ΔE and R (Table 1).

Conclusions

Stabilities and geometries of unsubstituted biaryls composed of two convex aryl moieties depend mostly on the connectivities of the proximate hydrogen atoms involved in steric repulsions. Results of the present calculations demonstrate that the energies and lengths of the intermoiety C—C bonds in such biaryls are determined within 0.46 kcal/mol and 0.0040 Å, respectively, by the topologies of these connectivities. On the other hand, the average intermoiety twist angles are less transferable, the corresponding uncertainty amounting to as much as 7° and diminishing with increasing steric repulsions.

The observed regularities in properties of biaryls imply insensitivity of the π -electron conjugation between the aryl moieties to the details of electronic structures of the entire molecules. The variability present in the intermoiety twist angles of the biaryls belonging to the 1,4/1,4 class is accounted for by steric rather than electronic effects. Thanks to the regularities in the total energies, the Z and E conformers of unsubstituted biaryls composed of two convex aryl moieties are almost isoenergetic and therefore are expected to be equally populated at ambient temperatures.

The present investigation provides benchmarks for less accurate electronic structure calculations on biaryls. The previously published results of semiempirical calculations⁴ are in qualitative agreement with the new data, although the intermoiety twist angles in some of the molecules under study are found to be poorly reproduced by the AM1 method. The

existence of regularities in the total energies of biaryls makes the estimation of their standard enthalpies of formation and relative stabilities a trivial task, whereas the transferability of twist angles provides a means for quick checks of experimental geometries.

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