DOI: 10.1002/chem.200500850

Hydrogen–Hydrogen Bonding in Planar Biphenyl, Predicted by Atoms-In-Molecules Theory, Does Not Exist

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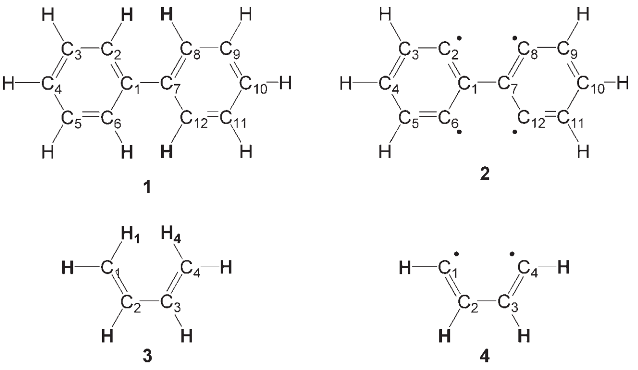
Abstract: Based on an Atoms-in-Molecules (AIM) analysis, Matta et al. (*Chem. Eur. J.* **2003**, *9*, 1940) recently claimed evidence for the existence of hydrogen–hydrogen bonding between *ortho*-hydrogen atoms, pointing towards each other from adjacent phenyl groups in planar biphenyl. This AIM result is opposed to the classical view that nonbonded steric repulsion between the *ortho*-hydrogen atoms is responsible for the higher energy of the planar as compared to the twisted geometry of biphenyl. In the present work, we address the question if hydrogen–hydrogen bonding in biphenyl exists, as suggested by AIM, or not. To this end, we have analyzed the potential energy surface for internal rotation of biphenyl in terms of two interacting phenyl radicals using density functional theory (DFT) at BP86/TZ2P. A detailed analysis of the bonding mechanism and a quantitative bond energy decomposition in the framework of Kohn–Sham DFT show that Pauli (or overlap) repulsion, mainly between C^{ortho}–H^{ortho} phenyl MOs, prevents biphenyl from being planar and forces it to adopt a twisted equilibrium geometry. Furthermore, a derivative of biphenyl in which all four *ortho*-hydrogen atoms have been removed *does* adopt a planar equilibrium geometry. Thus, our results confirm the classical view of steric repulsion between *ortho*-hydrogen atoms in biphenyl and they falsify the hypothesis of hydrogen–hydrogen bonding.

Keywords: atoms-in-molecules (AIM) theory • biphenyl • bond energy decomposition • density functional calculations • hydrogen–hydrogen interaction • steric repulsion

Introduction

It is known from an electron diffraction experiment[1] that biphenyl (**1**) has an equilibrium geometry in which the two phenyl groups are mutually twisted with a dihedral angle ϕ (defined as C_2-C_1-C_7-C_8 in Scheme 1) of 44.4°.[1] The planar ($\phi = 0°$) and perpendicular ($\phi = 90°$) conformations constitute transition states for internal rotation at 1.4 and 1.6 kcal mol^{-1} above the twisted equilibrium structure.[1]

Chemistry literature has attributed these observations to the fact that the perpendicular conformation interrupts π-electron delocalization over the two phenyl rings, whereas the planar conformation experiences nonbonded steric repulsion between *ortho*-hydrogen atoms, pointing towards each other from adjacent phenyl groups in planar biphenyl. Indeed, in planar biphenyl, the distance between these *ortho*-hydrogen atoms (1.94 Å at the BP86/TZ2P level) is



Scheme 1. Model systems of this study.

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Supporting information (Cartesian coordinates of **1a**, **1b**, **1c**, **2**, **3**, and **4**) for this article is available on the WWW under http://www.chemeurj.org/ or from the author.

smaller than the sum of their van der Waals radii (2.4 Å). This classical interpretation has recently been dismissed by Matta, Hernández-Trujillo, Tang, and Bader[2] based on Atoms-in-Molecules (AIM)[3] analyses. In their paper, Matta, Hernández-Trujillo, Tang, and Bader claim to have evidence for stabilizing hydrogen-hydrogen bonding interactions (as opposed to nonbonded steric repulsion) between *ortho*-hydrogen atoms in planar biphenyl, in the form of the existence of a bond path between the two H nuclei and the corresponding bond critical points. In addition, according to the AIM calculations,[2] hydrogen atoms taking place in the supposed H–H bonding are about 5 kcal mol^{-1} stabilized in planar biphenyl with respect to "noninteracting" hydrogen atoms in the twisted conformer. This was interpreted by Matta, Hernández-Trujillo, Tang, and Bader as a stabilization of the overall molecular energy by about 20 kcal mol^{-1} due to a H–H bonding interaction in the planar as compared to the twisted geometry.[2] The fact that the planar structure nevertheless is 1.4 kcal mol^{-1} higher in energy than the twisted one has been attributed by Matta, Hernández-Trujillo, Tang, and Bader[2] to the increase in the atomic energy of atoms C_1 and C_7 (see Scheme 1) that goes with the lengthening of the C_1–C_7 bond as the *ortho*-hydrogen atoms have to be accommodated in the molecular plane in the planar form.

In 1992, Cioslowski and Mixon[4,5] already carried out a study based on AIM theory of the planar and twisted biphenyl conformers. For the planar structure the authors also noticed the existence of an attractor interaction line (or bond path)[3] between the *ortho*-hydrogen atoms. However, Cioslowski and Mixon pointed out that: "The existence of an attractor interaction line between a pair of nuclei does not necessarily imply the presence of bonding between those nuclei. Instead the attractor interaction lines should be interpreted as those delineating major (either bonding or nonbonded, attractive or repulsive) interactions in a given molecular system".[4] Results by others[6] support the interpretation of Cioslowski and Mixon (see also the rebuttals in references [7] and [8]), which is opposed to Bader's view according to which the presence of a bond path is a necessary and, importantly, also a sufficient condition for the existence of a bonding interaction.[9] The problem is however that the latter is an unproven premise. The bond path between *ortho*-hydrogen atoms in biphenyl disappears when the H–H bond distance *r*(H,H) is larger than 2.18 Å. This suggests that any H–H interaction, be it nonbonded (according to Cioslowski and Mixon) or bonding (according to Matta, Hernández-Trujillo, Tang, and Bader), vanishes in the twisted equilibrium structure of biphenyl for which *r*(H,H) = 2.34 Å.

Abstract in Catalan: *Recentment Matta i col·laboradors (Chem. Eur. J.* ***2003****, 9, 1940), a partir d'una anàlisi d'àtoms en molècules (AIM), han reivindicat l'existència d'enllaç hidrogen-hidrogen entre els hidrògens orto dels dos fenils en la molècula de bifenil plana. Aquest resultat d'AIM s'oposa a la visió clàssica que la repulsió estèrica no-enllaçant entre els hidrògens en orto és la responsable de la major energia de la conformació plana del bifenil envers la geometria alternada. En aquest estudi, qüestionem l'existència d'aquest enllaç hidrogen-hidrogen proposat per AIM. Així doncs, hem analitzat la superfície d'energia potencial per la rotació interna del bifenil mitjançant la interacció de dos fenils radicals, fent ús de la teoria del funcional de la densitat (DFT) al nivell BP86/TZ2P. Una anàlisi detallada del mecanisme d'enllaç i una descomposició quantitativa de l'energia d'enllaç demostren que la repulsió de Pauli (o de solapament), sobretot entre els orbitals moleculars* C^{ortho}–H^{ortho} *dels fenils, evita que el bifenil presenti una conformació plana i el força a adoptar la geometria d'equilibri alternada. A més, un derivat del bifenil en el qual s'han eliminat els quatre hidrògens orto sí que adopta la geometria d'equilibri plana. Per tant, els nostres resultats confirmen la visió clàssica de la repulsió estèrica entre els hidrògens orto en el bifenil, i invalida la hipòtesi d'un enllaç hidrogen-hidrogen.*

In the present study, we wish to address the question whether the above H–H contacts between *ortho*-hydrogen atoms in biphenyl are really bonding, as proposed by Matta, Hernández-Trujillo, Tang, and Bader[2] on the basis of AIM theory, or if they are nonbonded, as advocated by Cioslowski and Mixon,[4,5] also on the basis of AIM theory, as well as the earlier chemistry literature.[10] To this end, we have explored the potential energy surface (PES) for internal rotation of biphenyl in terms of two interacting phenyl radicals using density functional theory (DFT)[11] at the BP86/TZ2P level of theory.[12,13] Along the PES, we analyze the phenyl–phenyl bonding mechanism in the conceptual framework of the molecular orbital (MO) model that is contained in Kohn–Sham DFT and we carry out a quantitative decomposition of the bond energy into electrostatic attraction, Pauli repulsion (which is responsible for any steric repulsion), and bonding orbital interactions.[14,15] Inspired by the outcome of these analyses, which point to H–H steric repulsion and not H–H bonding, we have designed a numerical experiment in which we study the behavior of a derivative of biphenyl in which all four *ortho*-hydrogen atoms have been removed (see **2** in Scheme 1). If the nature of the H–H interaction is really repulsive as shown by the preceding analysis, this derivative should adopt a planar equilibrium geometry.

On one hand, our undertaking contributes to a better understanding of features on the potential energy surface for internal rotation of this archetypal aromatic molecular rotor, in particular, the barrier associated with the planar conformation and the role therein of H–H contacts between *ortho*-hydrogen atoms. Furthermore, as pointed out by Matta, Hernández-Trujillo, Tang, and Bader,[2] such H–H contacts are not confined to biphenyl. They are ubiquitous in chemistry and may, for example, be important factors that contribute to the cohesion in hydrocarbon molecular crystals and in solid hydrogen. On the other hand, the implications of our findings reach beyond the scope of particular model systems such as biphenyl. They shed light on the status and interpretation of the very concepts of bond paths and bond critical points in AIM theory. Here, we anticipate that our findings support the earlier view as well as the interpretation of Cioslowski and Mixon[4,5] that the H–H interactions between *ortho*-hydrogen atoms in planar biphenyl are nonbonded, that is, repulsive, and that the existence of a bond path with a bond critical point is not a sufficient condition for the presence of bonding interactions.

Theoretical Methods

Computational details: All calculations were performed using the Amsterdam Density Functional (ADF) program.[13] The numerical integration was performed by using the procedure developed by te Velde et al.[13g,h] The MOs were expanded in a large uncontracted set of Slater type orbitals (STOs) containing diffuse functions: TZ2P (no Gaussian functions are involved).[13i] The basis set is of triple-ζ quality for all atoms and has been augmented with two sets of polarization functions, that is, 3d and 4f on C, and 2p and 3d on H. The 1 s core shell of carbon was treated by the frozen-core approximation.[13c] An auxiliary set of s, p, d, f and g STOs was used to fit the molecular density and to represent the Coulomb and exchange potentials accurately in each self-consistent field cycle.[13j]

Equilibrium structures were optimized using analytical gradient techniques.[13k] Geometries and energies were calculated at the BP86 level of the generalized gradient approximation (GGA): exchange is described by Slater's X_α potential[13l] with corrections due to Becke[13m,n] added self-consistently and correlation is treated in the Vosko–Wilk–Nusair (VWN) parameterization[13o] with nonlocal corrections due to Perdew[13p] added, again, self-consistently (BP86).[13q]

Bond analysis: The overall bond energy ΔE associated with forming the biphenyl molecule, Ph–Ph, from two phenyl radicals, $\mathrm{Ph}^{\cdot}(\alpha)$ + $\mathrm{Ph}^{\cdot}(\beta)$ [Eq. (1)],

$$\Delta E = E_{\mathrm{biphenyl}}\text{-}2E_{\mathrm{phenyl}}:\ \mathrm{Ph}^{\cdot}(\alpha)+\mathrm{Ph}^{\cdot}(\beta)\rightarrow \mathrm{Ph{-}Ph} \tag{1}$$

is made up of two major components [Eq. (2)] .

$$\Delta E = \Delta E_{\mathrm{prep}} + \Delta E_{\mathrm{int}} \tag{2}$$

In Equation (2), the preparation energy ΔE_{prep} is the amount of energy required to deform two individual (isolated) phenyl radicals from their equilibrium structure to the geometry that they acquire in the overall molecule. The interaction energy ΔE_{int} corresponds to the actual energy change when these geometrically deformed phenyl radicals are combined to form the biphenyl molecule. It is analyzed in the framework of the Kohn–Sham MO model using a quantitative decomposition of the bond into electrostatic interaction, Pauli repulsion (or exchange repulsion or overlap repulsion), and (attractive) orbital interactions [Eq. (3)].[14–16]

$$\Delta E_{\mathrm{int}} = \Delta V_{\mathrm{elstat}} + \Delta E_{\mathrm{Pauli}} + \Delta E_{\mathrm{oi}} \tag{3}$$

The term $\Delta V_{\mathrm{elstat}}$ corresponds to the classical electrostatic interaction between the unperturbed charge distributions $\rho_{\mathrm{Ph}(\alpha)} + \rho_{\mathrm{Ph}(\beta)}$ of the prepared (i.e. deformed) phenyl radicals that adopt their positions in the overall molecule and is usually attractive. The Pauli repulsion $\Delta E_{\mathrm{Pauli}}$ comprises the destabilizing interactions between occupied orbitals and is responsible for any steric repulsion. It arises as the energy change associated with the transition from the superposition of the unperturbed electron densities $\rho_{\mathrm{Ph}(\alpha)} + \rho_{\mathrm{Ph}(\beta)}$ of the geometrically deformed but isolated phenyl radicals to the wavefunction $\Psi^0 = N\ A\ [\Psi_{\mathrm{Ph}(\alpha)}\ \Psi_{\mathrm{Ph}(\beta)}]$, that properly obeys the Pauli principle through explicit antisymmetrization (A operator) and renormalization (N constant) of the product of fragment wavefunctions.[14] The orbital interaction ΔE_{oi} in any MO model, and therefore also in Kohn–Sham theory, accounts for electron-pair bonding,[14] charge transfer (i.e., donor–acceptor interactions between occupied orbitals on one moiety with unoccupied orbitals of the other, including the HOMO–LUMO interactions) and polarization (empty-occupied orbital mixing on one fragment due to the presence of another fragment). Since the Kohn–Sham MO method of DFT in principle yields exact energies and, in practice, with the available density functionals for exchange and correlation, rather accurate energies, we have the special situation that a seemingly one-particle model (a MO method) in principle completely accounts for the bonding energy.[14,17]

The orbital interaction energy can be decomposed into the contributions from each irreducible representation Γ of the interacting system [Eq. (4)] using the extended transition state (ETS) scheme developed by Ziegler and Rauk[18] (note that our approach differs in this respect from the Morokuma scheme,[16] which instead attempts a decomposition of the orbital interactions into polarization and charge transfer).

$$\Delta E_{\mathrm{oi}} = \sum_{\Gamma} \Delta E_{\Gamma} \tag{4}$$

In systems with a clear σ, π separation, this symmetry partitioning proves to be most informative.

Results and Discussion

Biphenyl: The results of our BP86/TZ2P analyses are collected in Table 1 and Figures 1–3 (Cartesian coordinates for all stationary points can be found in the Supporting Information). First, we discuss the results for the internal rotation of biphenyl. The corresponding PES from 0° till (but excluding) 360° along the dihedral angle ϕ defined as C_8-C_7-C_1-C_2 (see **1** in Scheme 1) is characterized by four equivalent equilibrium structures **1a** (at $\phi = 35.5°$, 144.5°, 215.5° and 324.5°), two equivalent planar transition states **1b** (1.6 kcal

Table 1. Phenyl–phenyl bond energy decomposition (in kcal mol^{-1}) and characterization of PES for biphenyl internal rotation: dihedral angle ϕ (in degrees), C_1–C_7 bond length (in Å), relative energy (in kcal mol^{-1}), and number of imaginary frequencies (nimag) for all stationary points.[a]

System[b]	ϕ	$r(C_1\text{-}C_7)$	ΔE_{Pauli}	ΔV_{elstat}	ΔE_{oi}	ΔE_{int}	ΔE_{prep}	ΔE	ΔE_{rel}	nimag
equilibrium structure (**1a**)	35.5	1.484	253.31	−166.84	−204.43	−117.97	6.28	−111.69	0.00	0
planar transition state (**1b**)	0.0	1.491	246.42	−160.80	−203.54	−117.92	7.84	−110.08	1.61	1
perpendicular transition state (**1c**)	90.0	1.494	248.67	−165.40	−197.69	−114.42	5.20	−109.22	2.47	1

[a] Computed at BP86/TZ2P. ϕ is the dihedral angle C_2-C_1-C_7-C_8 (see Scheme 1). For energy decomposition, see the Section on bond analysis. [b] See also Scheme 1 and Figure 1.

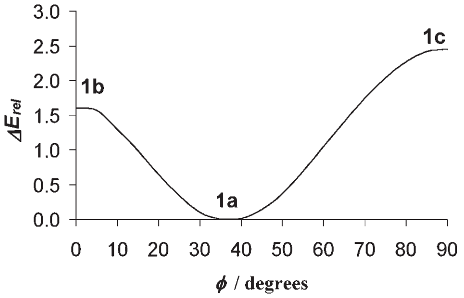


Figure 1. Relative energy ΔE_{rel} (in kcal mol^{-1}) of biphenyl (**1**, see Scheme 1) as a function of the dihedral angle ϕ, computed at BP86/TZ2P.

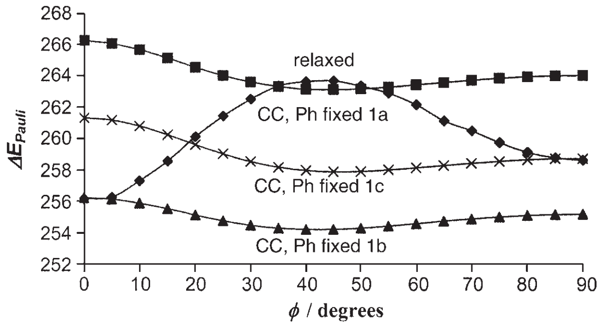


Figure 2. Pauli repulsion ΔE_{Pauli} (in kcal mol^{-1}) between phenyl fragments in biphenyl (**1**, see Scheme 1) as a function of the dihedral angle ϕ, computed at BP86/TZ2P.

mol^{-1} above **1a**, at $\phi = 0°$ and 180°) and two equivalent transition states **1c** with the phenyl groups mutually perpendicular (2.5 kcal mol^{-1} above **1a**, at $\phi = 90°$ and 270°). We will focus on the unique 0°–90° interval along which we find successively TS **1b**, equilibrium structure **1a**, and TS **1c** at 1.6 (exptl 1.4 ± 0.5),[1] 0.0 and 2.5 (exptl 1.6 ± 0.5)[1] kcal mol^{-1} with respect to **1a** (see Table 1 and Figure 1). Note that the C_1–C_7 bond expands by about 0.01 Å if one goes from the equilibrium structure **1a** (1.484 Å) to either the planar TS **1b** (1.491 Å) or the "perpendicular" TS **1c** (1.494 Å, see Table 1). The angle ϕ is the dihedral angle between the two planes defined by the two phenyl groups. Our BP86/TZ2P values agree well with those found in previous theoretical[2,19] and experimental[1] studies.

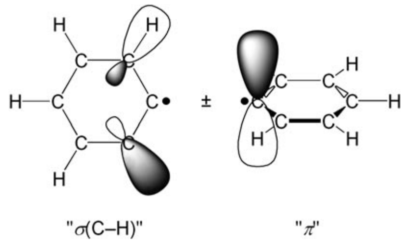
The results of our phenyl–phenyl bond energy decomposition for **1** are collected in Table 1 and graphically represented in Figure 2. At first sight, our results seem to support the model of Matta, Hernández-Trujillo, Tang, and Bader: going from the equilibrium structure **1a** to TS **1b**, the Pauli repulsion *decreases*, from 253.3 to 246.4 kcal mol^{-1}, whereas the orbital interactions are weakened only slightly, from −204.4 to −203.5 kcal mol^{-1} (Table 1). The net bond energy ΔE would not be destabilized (i.e., the energy would not go up) without the contribution to the trend from the electrostatic attraction which is substantially weakened, from −166.8 to −160.8 kcal mol^{-1}. In particular the substantial decrease (by 7 kcal mol^{-1}) in steric repulsion (ΔE_{Pauli}) seems to be in contradiction with the classical view that the higher energy of the planar TS **1b** (as compared to the twisted equilibrium structure **1a**) is caused by nonbonded steric H–H repulsion between the *ortho*-hydrogen atoms. Might a closer look eventually even reveal H–H bonding as proposed by Matta, Hernández-Trujillo, Tang, and Bader?[2] After all, the bonding orbital interactions do not decrease so much.

The answer to this question is *no*. Our analyses do in fact reveal increased H–H steric repulsion if we go to the planar TS **1b** and thus confirm the classical model and falsify the H–H bonding hypothesis of Matta, Hernández-Trujillo, Tang, and Bader. It is of crucial importance to realize that the PES for internal rotation (shown in Figure 1) and the stationary points **1a–c** (analyzed in Table 1) corresponds to a "reaction coordinate" for internal rotation in which for any given dihedral angle ϕ all other geometry parameters are fully relaxed, that is, optimized under the constraint of the given ϕ. For this reaction coordinate, as can be seen in Figure 2 (see ΔE_{Pauli} curve labeled "relaxed"), a minimum in Pauli repulsion is achieved for the planar TS **1b** (and also for the perpendicular TS **1c**). However, it is not justified to infer that steric repulsion is absent or that it favors the planar conformation. The behavior of ΔE_{Pauli} along a single path through the molecular configuration space does not reflect the pure changes in this term as a function of the dihedral angle. It also accounts for *changes in other geometry parameters* that occur in reaction to the primary variations in ΔE_{Pauli}, ΔV_{elstat} and ΔE_{oi}. In particular, as we go from **1a** to **1b**, the C_1–C_7 bond distance increases by about 0.01 Å (see Table 1).

The changes in the energy terms that are caused purely by internal rotation along ϕ can be revealed by keeping all other geometry parameters fixed. We have explored the corresponding PESs (and their energy components) as a function of ϕ for three different C_1–C_7 bond distances, the one in **1a**, **1b** and **1c**, that is, 1.484, 1.491, and 1.494 Å, using for the phenyl moieties the geometry they adopt in the corresponding stationary point. The resulting ΔE_{Pauli} versus ϕ curves are labeled "CC, Ph fixed **1a**", "CC, Ph fixed **1b**" and "CC, Ph fixed **1c**" in Figure 2. Now it becomes clear that at each of the three C_1–C_7 distances the Pauli repulsion achieves a maximum for the planar **1b**, but also for the perpendicular **1c**, whereas a minimum occurs in between, close to but not exactly at $\phi = 35.5°$ of the equilibrium structure **1a**. In fact, this holds at any given C_1–C_7 distance (full data not shown here): the Pauli repulsion always achieves a maximum for the planar ($\phi = 0°$) and perpendicular conformation ($\phi = 90°$). An analysis of the Kohn–Sham molecular orbital (MO) electronic structure shows that the maximum in Pauli repulsion at $\phi = 0°$ originates from increased overlap between phenyl MOs with sizeable $\sigma(C^{ortho}$–$H^{ortho})$ character on one phenyl fragment with the corresponding ones on the other phenyl fragment of the biphenyl system. For example, going from **1a** to a planar conformation with all other geometry parameters fixed (this corresponds to "CC, Ph fixed **1a**" in Figure 2) leads to increase in the overlap integrals between the two 5*a* and the two 6*b* MOs [both having much $\sigma(C^{ortho}$–$H^{ortho})$ character] on the two phenyl fragments from 0.027 to 0.042 and from 0.024 to 0.044, respectively (not shown in Table 1).

The electrostatic attraction ΔV_{elstat} shows the same trend as ΔE_{Pauli}: going from **1a** to a planar conformation with all other geometry parameters fixed, the electrostatic attraction weakens, from −166.8 to −165.8 kcal mol^{-1} (not shown in Table 1). It is in fact generally true that stronger overlap of the charge distributions of the fragments leads not only to higher steric repulsion but also to more attractive electrostatic interaction. The attractive nature of the electrostatic term is discussed in references [14,20]. In short, the electron–electron repulsion and the nucleus–nucleus repulsion between the two phenyl fragments are both large and positive, but the negative electron–nucleus attraction is stronger. It is a general phenomenon (for neutral fragments)[20] that when we let two fragment charge distributions interpenetrate, the total electrostatic interaction is attractive since the electron–nucleus attraction outweighs the repulsive terms. Here we witness that the electrostatic attraction, in **1a**, between H^{ortho} atoms and the π density of the other phenyl is, in the planar conformation, reduced and not entirely compensated by the electrostatic attraction between the opposing H^{ortho} atoms (see also discussion of ΔE_{Pauli} in next paragraph). The bonding orbital interactions ΔE_{oi} also show a slight increase as we go from **1a** to the planar conformation (with all other geometry parameters fixed), namely, from −204.4 to −206.4 kcal mol^{-1} (not shown in Table 1). This strengthening can be ascribed to the fact that the planar conformation is optimal for π conjugation across the central C_1–C_7 bond. The C_1–C_7 electron-pair bond as such is not much affected by internal rotation.

Interestingly, the increase in energy (or the loss in phenyl–phenyl bond energy ΔE) in the perpendicular conformation ($\phi = 90°$) originates from both, an increase in Pauli repulsion and a weakening of the orbital interaction. The latter can be ascribed again to the π-conjugation between the π-electron systems of the two phenyl fragments; in the perpendicular conformation it is completely interrupted. The increase in Pauli repulsion may be surprising at first sight. We have traced it to the overlap that arises in this conformation between $\sigma(C^{ortho}$–$H^{ortho})$ MOs of b_1 symmetry on one phenyl fragment with π MOs on the other fragment; the essentials of this interaction are illustrated in Scheme 2 in a simplified manner.



Scheme 2.

Finally, the increased steric or Pauli repulsion ΔE_{Pauli} in the planar and perpendicular conformations also causes an increase in the gradient or slope of this repulsive energy term as a function of the C–C distance and also as a function of the geometry of the phenyl groups. Thus, in these and all other points along the PES in which the Pauli repulsion increases as we rotate the system away from **1a** (i.e., $\phi = 35.5°$), a new balance between the steeper ΔE_{Pauli} curve and the attractive ΔV_{elstat} and ΔE_{oi} terms occurs at larger C–C distances and with phenyl groups that are slightly deformed. In **1b**, for example, the C_1–C^{ortho} bonds and C^{ortho}–H^{ortho} bonds bend away from the opposing C^{ortho}–H^{ortho} bonds on the other phenyl group. Thus, as the dihedral angle ϕ decreases from 35.5 (**1a**) to 0° (**1b**), the C^{ortho}-C_1-C_7 angle increases from 121.0 to 121.6°, and the C_1-C^{ortho}-H^{ortho} angle increases from 119.3 to 120.2°. This behavior further emphasizes the repulsive character of the H–H interaction. Note this geometric relaxation relieves the Pauli repulsion to an extent that it may even become smaller than in the sterically less crowded situation (e.g., in the twisted equilibrium geometry **1a**). This is a quite general phenomenon that has been extensively discussed in our recent study on the origin of the ethane rotational barrier.[21] The present result highlights that bond analyses of single points (e.g., only stationary points) along (multidimensional) PESes must be handled with great precaution because they may provide insufficient information for judging the importance and role of the various terms in the bonding mechanism.

The above results fully corroborate the classical view that nonbonded steric H–H repulsion between *ortho*-hydrogen atoms forces biphenyl to avoid a planar conformation, which would be favorable from the point of view of maximal π conjugation, and to adopt instead a twisted equilibrium geometry. Our results also falsify the conclusion of Matta, Hernández-Trujillo, Tang, and Bader[2] that there is a bonding H–H interaction in the planar conformation. This conclusion probably holds for most, if not all analogous systems. For example, we find exactly the same behavior in 1,3-butadiene (**3**) which may be viewed as a (nonaromatic) substructure of biphenyl (**1**) corresponding to the C_2-C_1-C_7-C_8 fragment of the latter (see Scheme 1). The global minimum for internal rotation around the C_2–C_3 bond of **3** is *trans*-1,3-butadiene in which there is no direct contact between the "*ortho*-hydrogen atoms" H_1 and H_4. *cis*-1,3-Butadiene, on the other hand, is a local minimum with a twisted structure with a dihedral angle of 29.3° and 3.7 $kcal\,mol^{-1}$ above the *trans* conformation. The higher energy of the *cis* isomer as well as its twisted conformation can be traced to H–H steric repulsion between the "*ortho*-hydrogen atoms" H_1 and H_4 which are now in close proximity. This steric repulsion is also responsible for the small barrier of 0.3 $kcal\,mol^{-1}$ associated with approaching the fully planar *cis* conformation ($\phi = 0°$), which is the TS for internal rotation.

Biphenyl without *ortho*-hydrogen atoms: a numerical experiment: Inspired by the above result, we have carried out a numerical experiment that complements the analyses. If steric H–H repulsion between *ortho*-hydrogen atoms causes biphenyl to avoid a planar conformation and to adopt instead a twisted equilibrium geometry, the planar conformation may be stabilized and possibly turn from a TS for internal rotation into an equilibrium structure, simply by removing the four *ortho*-hydrogen atoms. Doing this leaves us with the tetraradical **2** which has a quintet ground state (see Scheme 1). And indeed, not unexpectedly (after the above discussion) and yet nicely, we find that **2** has a planar equilibrium structure with a C_1–C_7 bond length of 1.483 Å (not shown in a Table), that is, slightly shorter than that in biphenyl (**1a**) which amounts to 1.484 Å (see Table 1).

Internal rotation leads to the perpendicular conformation which is a TS for internal rotation at 4.1 $kcal\,mol^{-1}$ above the planar equilibrium structure (Figure 3). Note that the twisted structure has disappeared as a stationary point. This further consolidates the conclusion that there is nonbonded steric H–H repulsion between *ortho*-hydrogen atoms in planar biphenyl and *no* H–H bonding that was suggested by Matta, Hernández-Trujillo, Tang, and Bader.[2] And likewise, if we go from butadiene (**3**) to species **4** (see Scheme 1), by removing hydrogen atoms H_1 and H_4, the *cis* isomer becomes a completely planar structure.

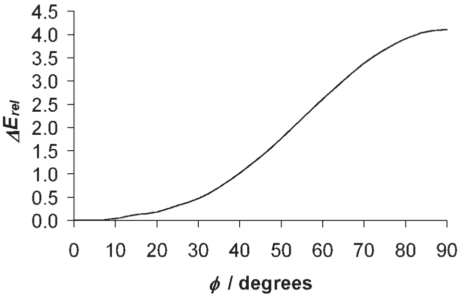


Figure 3. Relative energy ΔE_{rel} (in kcal mol^{-1}) of the biphenyl derivative **2** missing all *ortho* hydrogens (see Scheme 1) as a function of the dihedral angle ϕ, computed at BP86/TZ2P.

Origin of H–H stabilization in AIM theory: So why after all does AIM theory yield 20 $kcal\,mol^{-1}$ of stabilization due to H–H bonding? To find the answer to this question, we first recall that this H–H stabilization is an interpretation by Matta, Hernández-Trujillo, Tang, and Bader of the atomic energies, as defined in AIM theory, of the four *ortho*-hydrogen atoms in planar biphenyl. In AIM theory,[3] the energy E of a molecule in an equilibrium geometry is equal to the sum of atomic energies E_A over all constituting atoms A [Eq. (5)].

$$E = \sum_A E_A \tag{5}$$

Furthermore, an atom A in AIM theory is defined by the atomic basin $\Omega(A)$, the region of space around the corresponding nucleus that is bounded by zero-flux surfaces, that is, the surfaces at which the gradient in the electron density vanishes (and which are perpendicular to the vector field of the density gradient). For an atom accordingly defined in an equilibrium geometry, the virial theorem holds and the atomic energy E_A is equal to minus the kinetic energy T_A of the atom which in turn is obtained as the integral over the atomic basin of the kinetic energy density $K(\boldsymbol{r})$ [Eq. (6)].

$$E_A = -T_A = -\int_{\Omega(A)} K(\boldsymbol{r}) d\boldsymbol{r} \tag{6}$$

While mathematically well defined, the physical status of this quantity E_A is not so clear. While it is quite plausible that E_A differs in magnitude as the geometry of the molecule varies, the precise cause for particular variations may not be so clear. In the present case, for example, one finds 5 $kcal\,mol^{-1}$ of stabilization of the atomic energy of each of the four *ortho*-hydrogen atoms as biphenyl goes from the twisted equilibrium geometry to the planar conformation.[2] Since there is not significant charge transfer from/to the *ortho*-hydrogen atoms to/from the rest of the molecule when going from the twisted to the planar geometry,[2] the reason for the atomic stabilization during this conformational change is likely the reduction of the hydrogen atomic basin volume (due to steric congestion between *ortho*-H atoms) that increases the kinetic energy $T_{H^{ortho}}$ associated with the basin of the *ortho*-hydrogen atom and, as a consequence of the virial theorem, reduces its total atomic energy. The effect observed here is similar to that reported by Haaland et al.[6] for the inclusion complex of He in adamantane. Thus, apparently any situation of steric congestion (steric repulsion) without significant charge transfer from the congested atoms to rest of the molecule would, according to the above AIM definitions leads to a stabilization of the atomic energies and thus to the qualification of the interaction between the atoms involved as “bonding”. We feel that such a qualification is questionable if not unphysical.

Conclusions

The barriers to internal rotation of biphenyl originate from steric or Pauli repulsion as follows from our phenyl–phenyl bond analysis and quantitative bond energy decomposition in the framework of Kohn–Sham density functional theory. The planar conformation of biphenyl (dihedral angle $\phi = 0°$) experiences H—H steric repulsion between *ortho*-hydrogen atoms, which causes this conformation to be a transition state and forces the molecule to adopt a twisted equilibrium geometry with a dihedral angle ϕ of 35.5° (at BP86/TZ2P). Interestingly, this result of our analysis is confirmed by a numerical experiment which, independent of any electronic structure model, proves that removing the four *ortho*-hydrogen atoms that were causing steric repulsion indeed stabilizes the planar conformation, making it in fact an equilibrium structure.

Thus, our results confirm the classical view[10] of steric repulsion between *ortho*-hydrogen atoms in biphenyl and they falsify the hypothesis by Matta, Hernández-Trujillo, Tang, and Bader based on AIM analysis that there is H—H bonding. Our findings also agree with and support the interpretation of Cioslowski and Mixon[4,5] that the existence of a bond path with a bond critical point is not a sufficient condition for the presence of bonding interactions. This conclusion is also reached in a very recent investigation of Haaland and co-workers[6] who furthermore demonstrate that the stabilization of AIM atomic energies in the molecule does not necessarily imply the presence of a bonding interaction. They showed that, despite the strongly antibonding He···^{t}C interactions, AIM yields a stabilization of the helium atomic energy relative to free helium of more than 300 kcal mol^{-1}. All together, there is an increasing body of evidence that the physical interpretation of AIM concepts, such as bond paths and atomic stabilization energies, is unclear.

Acknowledgements

We thank the Departament d'Universitats, Recerca i Societat de la Informació (DURSI) of the Generalitat de Catalunya and the Netherlands organization for Scientific research (NWO-CW), the Spanish MEC (project no. CTQ2005-08797-C02-01/BQM), and the European Union (TMR program) for financial support. Excellent service by the Stichting Academisch Rekencentrum Amsterdam (SARA) and the Centre de Supercomputació de Catalunya (CESCA) is gratefully acknowledged.

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Received: July 20, 2005