to D.M.P., the National Science Foundation for its support through Grant CHE-8912070 to R.H., and the National Institutes of Health for support under Grant GM-39932.

Appendix

For the computations we use the extended Hückel method,[35] a semiempirical molecular orbital procedure, with weighted H_{ij}'s.[36] The parameters used in the calculations are reported in Table IV. For the H_{ii} of Mn we carried out a charge-iteration calculation on $[Mn(H_2O)_6]^{2+}$, O_h with Mn–O 2.1 Å. This choice produces reasonable atomic net charges for the tetranuclear models **6** and **7** (see Table II). Charge iteration for Mn in a higher oxidation state should produce a contraction of the atomic orbitals (the exponents ζ of the Slater-type orbitals become bigger) and lower the H_{ii} (valence-orbital ionization potential). The use of a different set of parameters for higher oxidation states of Mn does not qualitatively change our results. The three-dimensional graphics have been carried out by a computer program named CACAO, described elsewhere.[37]

Registry No. O_2, 7782-44-7; Mn, 7439-96-5.

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Topological Properties of Electron Density in Search of Steric Interactions in Molecules: Electronic Structure Calculations on Ortho-Substituted Biphenyls

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Abstract: The bond critical points in the electron density are not necessarily associated with bonding interactions. When the distance between two atoms is smaller than their contact interatomic separation (CIS), an attractor interaction line passing through the corresponding bond critical point appears, indicating a nonbonding repulsive interaction. Sterically crowded molecules are defined as those possessing such interaction lines at their equilibrium geometries. The appearance (or disappearance) of the interaction lines along the reaction paths allows for classification of the barriers to rotation into the categories of those sterically hindered, sterically facilitated, and sterically neutral. The values of contact interatomic separations provide a measure of the steric crowding in molecules that is, due to its mathematical rigor, superior to the concept of the van der Waals radii. The HF/6-31G** electronic structure calculations on biphenyl and its ortho-substituted derivatives illustrate the applications of the aforementioned theoretical concepts.

Introduction

Among many concepts often taken for granted by chemists is that of a chemical bond. For a large fraction of the molecules currently known, chemical intuition aids in assigning the bonding patterns. However, making intuitive decisions about which atoms are linked through chemical bonds becomes a confusing and error-prone task once less common chemical systems are considered. The case of organolithiums[1,2] can serve as a good example of the difficulties encountered in making unequivocal bond assignments without a formal definition of the chemical bond.

In principle, one might derive the bonding patterns from knowledge of bond orders. However, such an approach is of limited value, as an arbitrary cutoff would have to be decided upon to determine what magnitude of the bond order is sufficient to make a pair of atoms linked by a bond. Moreover, most of the currently used bond orders and indices[3,4] are based on a partitioning of the Hilbert space spanned by basis functions used in ab initio calculations, which brings further (unnecessary) lack of rigor. The same is true about some other schemes that find optimal locations of chemical bonds.[5]

The electronic wave function of any chemical system contains all the information about its electronic structure. Therefore, one cannot imagine any formal definition of bonding universally applicable to all molecules not taking the relevant characteristics of the electronic wave function into account. The link associating the electronic wave function and chemical bonds is not as elusive as one might think. In fact, as demonstrated by Bader,[6,7] the knowledge of the electron density, $\rho(\vec{r})$, is sufficient to define the bonding pattern of any molecule. In order to accomplish that, the critical (extremal or stationary) points, at which the gradient of $\rho(\vec{r})$ vanishes

$$\vec{\nabla}\rho(\vec{r}_{\text{crit}}) = 0 \qquad (1)$$

are located first. The extremal points characterized by two negative and one positive eigenvalues of the Hessian matrix **h**

$$h_{pq} = \frac{\partial}{\partial p}\frac{\partial}{\partial q}\rho(\vec{r})|_{\vec{r}=\vec{r}_{\text{crit}}} \qquad p, q = x, y, z \qquad (2)$$

are known as the bond points, whereas those with two positive eigenvalues are called ring points. At each bond point, two gradient paths (the lines of steepest ascent in $\rho(\vec{r})$), known collectively as the attractor interaction lines, originate. The attractor

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interaction lines terminate at the corresponding critical points known as attractors. All the gradient paths that terminate at a given attractor form an attractor basin.

In most chemical systems, the only attractors are nuclei. The nonnuclear attractors occur only in a limited number of molecules, such as Li_2 and Na_2.[6] On the basis of generalization of empirical observations concerning several small molecules, the existence of a bond point between a pair of attractors has been originally thought to be the necessary and sufficient condition for the existence of a chemical bond between the nuclei.[6,7] For this reason, the attractor interaction lines in chemical systems at equilibrium geometries have become known as bond paths. It has been stated that "the presence of a bond path linking a pair of nuclei implies that the corresponding atoms are bonded to one another".[8]

In many molecules, such an identification is supported by the "strong" bonds, which are characterized by large values of the corresponding $\rho(\vec{r}_{\mathrm{crit}})$. However, in the course of investigating the electronic structures of many less common chemical systems, we have recently uncovered[9] several instances of unexpected bond points which fall into two categories. In charge-transfer complexes, ionic pairs, and other systems with weak interactions, the additional bond points (together with the corresponding ring points) describe delocalized interactions between two weakly coupled moieties. Therefore, the corresponding attractor interaction lines, although occurring between unexpected pairs of atoms, describe attractive interactions that can be interpreted as chemical bonds. On the other hand, the electron densities in many other systems exhibit topological features that cannot be reconciled with the notion of bond points being indicative of bonding interactions.

The cases of the kekulene molecule and the $C(NO_2)_3^-$ ion are fairly typical for such a situation.[9] In the first system, the six inner hydrogen atoms, which are separated by 1.851 Å, are linked by highly curved interaction lines, forming an inner hexagonal ring.[10] In the second system, the steric interactions between the oxygen atoms separated by 2.673 Å give rise to three unexpected pairs of bond and ring points.[11] It is obvious that in both the kekulene molecule and the $C(NO_2)_3^-$ ion the presence of additional bond points indicates significant *nonbonding repulsive* interactions. These bond points have characteristic properties that allow one to distinguish them from their ordinary counterparts:[9] They invariably have low electron densities and small positive values of the electron density Laplacian. They usually have low bond ellipticities with their major axes always lying in the directions perpendicular to the ring surfaces. The corresponding attractor interaction lines are usually significantly curved. In addition, the characteristic ratio[12] given by

$$\kappa = -(\vec{r}_B - \vec{r}_R)(\mathbf{h}_B - \mathbf{h}_R)(\vec{r}_B - \vec{r}_R)/(\rho_B - \rho_R) \qquad (3)$$

where the subscripts B and R stand for the bond point and the corresponding ring point, respectively, is usually very close to 12.

Similar bond and ring points, together with the corresponding attractor interaction lines, are encountered in many other molecules, including benzenoid hydrocarbons such as phenanthrene, chrysene, and benzanthracene.[12] Their existence means that the current interpretation of interaction lines has to be modified in favor of a new one stating that interaction lines delineate major, but not necessarily bonding, interactions present within a given chemical system. The name bond path should be used only in conjunction with the interaction lines describing ordinary "strong" bonds and weak attractive interactions such as those arising from charge transfer.

One should not view the bonding/nonbonding dichotomy as a challenge to the internal consistency of the topological theory of atoms in molecules. To the contrary, as demonstrated in this paper, the bond points describing steric interactions can themselves play an important role in understanding electronic structures of molecules.

Topological Properties of Electron Density in Search of Steric Interactions

According to the commonly used definition, a particular molecule is sterically crowded with respect to a pair of atoms if their internuclear separation is less than the sum of the relevant van der Waals radii. The van der Waals radii[13] are usually obtained from the minimum nonbonding internuclear distances encountered in molecular crystals. The underlying assumption that atoms can be described as impenetrable spherical objects (the hard spheres approximation) is only qualitatively correct. Another way of determining van der Waals radii is based on taking an arbitrary small value of the electron density (usually 0.002 au[14]) as a cutoff for the atomic envelope.[6] Although such an approach offers the possibility of determining the van der Waals radii directly from the electron density in question, it suffers from a lack of rigor. For the aforementioned reasons, the van der Waals radii offer only a semiquantitative assessment of the steric crowding in molecules.

Bader's theory of atoms in molecules provides a rigorous definition of an atom as the union of a nuclear attractor and its basin.[6] The atoms are bordered by atomic surfaces. When two atoms approach each other, their atomic surfaces remain distinct until a bond point appears between them. The appearance of the bond point together with the corresponding interaction line is associated with a fold catastrophe.[6,12,15-17] Physically, the catastrophe signals the occurrence of one of the following two phenomena: For attractive interactions, it is the formation of a chemical bond or the onset of delocalized bonding. For bond points associated with steric interactions, it is two atoms getting close enough to have their atomic surfaces come into direct contact. Depending on which of the above two cases occurs, a further reduction of the internuclear separation either strengthens the chemical bond or causes the atomic surfaces to distort because of the steric interactions, not unlike two soap bubbles pressed against each other.

In light of the above discussion, it is obvious that the following two definitions have a rigorous theoretical basis and a clear interpretation:

Definition 1: A molecule at its equilibrium geometry is sterically crowded with respect to a pair of atoms if and only if an attractor interaction line characteristic of steric repulsions connects the two atoms in the molecular graph.

Definition 2: For a pair of atoms in a given molecule, the contact interatomic separation (CIS) is equal to the distance between the two nuclei at which a fold catastrophe occurs, leading to the appearance of an attractor interaction line characteristic of steric repulsions and connecting the two nuclei in question.

Since no assumptions concerning shapes of the participating atoms and the charactertistics of the repulsive interactions between them are necessary in the above definitions, they are clearly superior to those involving van der Waals radii. *The steric crowding can be assessed directly from the electron density in question.* The values of CIS should not be regarded as sums of some kind of atomic radii, since the spherical symmetry of atoms was not assumed. To the contrary, such an assumption would be a false one, as it is well-known that the atomic basins do not have spherical shapes.

To illustrate the scope of the new definitions, a few examples are in order. The kekulene molecule (R_{HH} = 1.851 Å) is sterically crowded with respect to the H–H interactions, whereas the icosahedral $C_{60}H_{60}$ molecule[18] (R_{HH} = 2.007 Å) and the planar

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transition state of *cis*-butadiene (R_{HH} = 2.335 Å) are not. The icosahedral $C_{60}F_{60}$ molecule[8] (R_{FF} = 2.152 Å) is crowded with respect to the F–F interactions, and the $C(NO_2)_3^-$ ion (R_{OO} = 2.673 Å) is crowded with respect to the O–O interactions. Taking the above values into account, one may conclude that, in the above chemical systems, the CIS for the H–H pair is smaller than 2.2 Å. On the other hand, the values of CIS for the F–F and O–O pairs must be greater than 2.1 and 2.6 Å, respectively.

Two questions concerning the above definitions remain. The issue of transferability of CISs between different molecules is an important one. Also important is the question of the existence of combination rules relating (at least in an approximate manner) the values of CISs between the pairs A–A, B–B, and A–B. Questions of this kind can only be answered by studying molecules with soft internal degrees of freedom, such as a rotation around a single bond, in which the internuclear separations can be adequately tuned to precipitate steric interactions. For this reason, we report below the results of electronic structure calculations on biphenyl and its ortho-fluoro-substituted derivatives.

Steric Interactions in Ortho-Substituted Biphenyls

The biphenyl molecule has been the subject of many experimental structure determinations and electronic structure calculations. The most recent electron diffraction data indicate a twisted structure with the dihedral angle between two phenyl rings equal to 44.4 ± 1.2°.[19] The same report quotes the barriers to rotation equal to 1.4 ± 0.5 kcal/mol at 0° and 1.6 ± 0.5 kcal/mol at 90°. On the other hand, the torsional angles in 2,2′-difluorobiphenyl and perfluorobiphenyl are believed to be equal to 60 and 70°, respectively, on the basis of older data.[20] For the former molecule, only the cis isomer is reportedly observed in the gas phase.

In order to characterize all the stationary points on the potential energy hypersurface relevant to the rotation around the C–C bond in the biphenyl, 2,6-difluorobiphenyl, 2,2′-difluorobiphenyl, and 2,2′,6,6′-tetrafluorobiphenyl molecules, we performed full geometry optimizations (within a given symmetry point group) at the HF/6-31G** level using the GAUSSIAN 90 suite of programs[21] running on a Cray Y-MP digital computer. The Hartree–Fock energies of the optimized structures, together with the corresponding values of the twist angles, defined as the dihedral angles involving four relevant carbon atoms, are presented in Table I. For the unsubstituted biphenyl molecule, there are two distinct transition states and one minimum. The minimum corresponds to the twist angle of 45.5°. Comparing this value to that previously reported at the HF/6-31G level (45.4°),[22] we conclude that augmenting the basis set with polarization functions hardly changes the position of the minimum. The same is true about the barriers to rotation. As at the HF/6-31G level,[22] the calculated relative energy of the perpendicular transition state compares favorably with the experimental data, whereas the barrier at 0° is much too high. We conclude that either the electron correlation plays an important role in determining the energetics of the planar structure or the experimental value is incorrect.

Table I. Properties of the Rotamers of the Ortho-Substituted Biphenyls[a]

rotamer	symm	twist angle φ, deg	HF energy E_{HF}, au	rel energy[b] ΔE, kcal/mol
		Biphenyl		
maximum	D_{2h}	0.0	−460.266 434	3.40
minimum	D_2	45.5[c]	−460.271 845[c]	0.00
maximum	D_{2d}	90.0	−460.269 345	1.57
		2,6-Difluorobiphenyl		
maximum	C_{2v}	0.0	−657.956 684	6.50
minimum	C_2	53.4	−657.967 039	0.00
maximum	C_{2v}	90.0	−657.965 893	0.72
		2,2′-Difluorobiphenyl		
maximum	C_{2v}	0.0	−657.948 134	12.72
minimum	C_2	54.7[d]	−657.968 402	0.00
maximum	C_2	92.2[e]	−657.966 637	1.11
minimum	C_2	128.7[f]	−657.968 019	0.24
maximum	C_{2h}	180.0	−657.958 724	6.07
		2,2′,6,6′-Tetrafluorobiphenyl		
maximum	D_{2h}	0.0	−855.614 375	31.45
minimum	D_2	59.2	−855.664 489	0.00
maximum	D_{2d}	90.0	−855.663 029	0.92

[a] All quantities calculated at the HF/6-31G** level of theory (unless indicated otherwise) with full optimization of geometry within the given symmetry. Only one value of the twist angle listed for each of the rotamers is related by symmetry. [b] Energies, uncorrected for the zero-point contributions, relative to the lowest energy rotamers. [c] Values at the HF/6-311G** level: φ = 46.2°, E_{HF} = −460.349 592 au. [d] The dihedral angle involving the carbon atoms linked with hydrogens. The other relevant dihedral angle is 57.2°. [e] The dihedral angle involving the carbon atoms linked with hydrogens. The other relevant dihedral angle is 93.6°. [f] The dihedral angle involving the carbon atoms linked with hydrogens. The other relevant dihedral angle is 130.2°.

The topological properties of the electron density in biphenyl are representative of the series of molecules under study and therefore can be used to confirm that the observed additional interaction lines describe steric interactions, as they satisfy the conditions spelled out in the Introduction. That this is indeed the case is illustrated by the calculated values for the planar transition state of the biphenyl molecule. The electron density at the bond critical point belonging to the H–H interaction line is 1.302 × 10^{-2} au, which is at least an order of magnitude smaller than the typical value for a "strong" bond. The respective Laplacian of the electron density is positive and equals 5.561 × 10^{-2} au, whereas the ellipticity is 0.370. The eigenvalues of the Hessian matrix correspond to the major axis of ellipticity that is perpendicular to the ring plane. The characteristic ratio, eq 3, is equal to 11.92. One concludes that all the conditions described in the Introduction are satisfied by the features associated with the H–H interaction line in the planar biphenyl molecule. That is also the case for the H–H, H–F, and F–F interaction lines pertinent to the other molecules under study. It should be noted that as the twist angles are increased from the initial values of 0°, the characteristic ratio mentioned above remains almost constant until the bond and ring critical points coalesce (in case of which the definition (3) is understood to involve a left-side limit with respect to the twist angle).

In 2,6-difluorobiphenyl and 2,2′,6,6′-tetrafluorobiphenyl, the molecular symmetry dictates the same pattern of two transition states and one minimum. The presence of fluorine atoms in the ortho positions greatly influences both the position of the minimum and the relative energies of the rotamers. The twist angles of the minima become progressively larger with the increasing number of fluorine atoms. The barriers to rotation involving planar transition states also increase dramatically. For the sake of simplicity, in all cases the planar transition states were assumed to have the ortho substituents lying within the ring planes. However, it is very probable that, in the case of the tetrafluoro derivative and possibly also the molecules with two fluorine atoms, relaxing the above constraint would lower the barriers at 0°. This would result in the potential energy hypersurfaces possessing cusps at the positions of the transition states due to a "flip-flop" effect involving switching between two isoenergetic rotamers related by a plane of symmetry.

The case of the 2,2′-difluorobiphenyl molecule is slightly more complicated. There are two distinct minima corresponding to cis and trans isomers related by three transition states. The cis isomer lies only 0.24 kcal/mol below the trans one. The barrier separating these two isomers is only 1.11 kcal/mol, which means that a rapid interconversion between the two structures is expected at ambient

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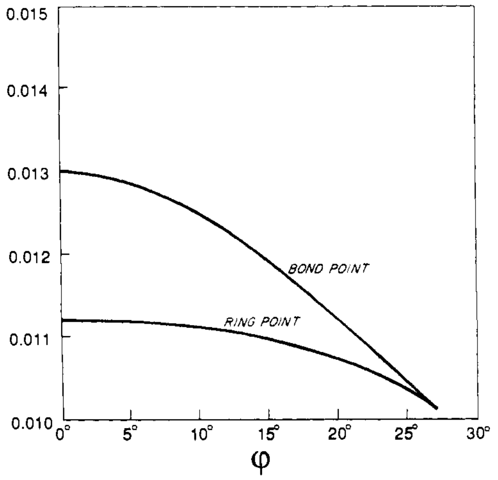

Figure 1. Electron densities of the biphenyl molecule at the bond and ring critical points associated with the H–H interaction lines vs the torsional angle.

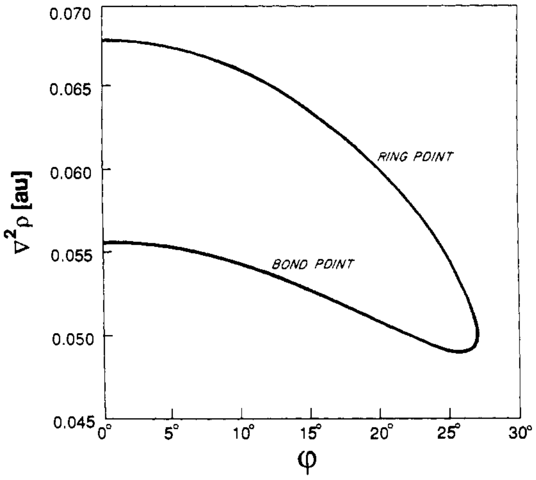

Figure 2. Electron density Laplacians of the biphenyl molecule at the bond and ring critical points associated with the H–H interaction lines vs the torsional angle.

temperatures. This is at variance with the old experimental data,[20] and we believe that more experimental work on this system is definitely warranted. There are two nonequivalent sets of twist angles, one involving dihedral angles with two carbon atoms connected through the formally single bond and two carbon atoms linked with hydrogens and the second involving carbon atoms linked with fluorines. The differences between these angles, which are of the order 1.5–2.5°, indicate small but measurable buckling of the phenyl rings due to the steric repulsions.

In all four molecules, tuning the twist angles while optimizing all the remaining geometrical parameters results in the appearance of attractor interaction lines indicating steric interactions. This phenomenon can be monitored by plotting the electron densities and electron density Laplacians at the relevant critical points against the twist angle. At the critical twist angle, values of both ρ and $\nabla^2\rho$ become identical for the bond and ring points, indicating their coalescence and, once the twist angle is increased further, disappearance of both the critical points and the respective atomic interaction line. This is illustrated in Figures 1 and 2, in which the relevant quantities are plotted for the biphenyl molecule. In this molecule, two symmetry-related pairs of additional bond and ring points are precipitated at the critical twist angle of 27.2° (Table II). The corresponding CIS value for the H–H interaction is 2.179 Å. A very similar value of 2.154 Å is found in the 2,2′-difluorobiphenyl molecule, although in this case the two nonequivalent critical twist angles of 21.4 and 45.2° indicate a very significant distortion of the phenyl rings from planarity. One should note that neither the biphenyl molecule nor the cis isomer of 2,2′-difluorobiphenyl is sterically crowded with respect to the H–H interactions.

Table II. Critical Twist Angles and Contact Interatomic Separations in the Ortho-Substituted Biphenyls

molecule	interacn	φ_0, deg	CIS, Å
biphenyl	H–H	27.2[a]	2.179[a]
2,6-difluorobiphenyl	H–F	45.0	2.495
2,2′-difluorobiphenyl	H–H	21.4[b]	2.154
	F–F	62.2[c]	2.909
	H–F	135.5[d]	2.490
2,2′,6,6′-tetrafluorobiphenyl	F–F	61.6	2.903

[a] The corresponding HF/6-311G** values are 28.2° and 2.192 Å. [b] The dihedral angle involving the carbon atoms linked with hydrogens. The other relevant dihedral angle is 45.2°. [c] The dihedral angle involving the carbon atoms linked with hydrogens. The other relevant dihedral angle is 62.0°. [d] The dihedral angle involving the carbon atoms linked with hydrogens. The other relevant dihedral angle is 134.6°.

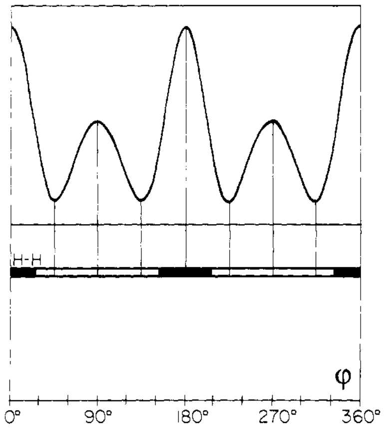

Figure 3. Schematic diagram showing the potential energy curve for rotation in the biphenyl molecule in relation to the presence of the H–H interaction lines.

The 2,6-difluorobiphenyl molecule also escapes steric crowding by twisting around the C–C bond. The H–F interaction line disappears at φ_0 = 45.0° (Table II), whereas the equilibrium geometry has a twist angle of 53.4° (Table I). The CIS for the H–F interactions is equal to 2.495 Å in this case. This is in good agreement with the value of 2.490 Å calculated for the H–F CIS in the 2,2′-difluorobiphenyl molecule. Again, the trans isomer of this molecule is found to be free of crowding. This is, however, not the case with the F–F interactions in the cis isomer. In this molecule, the F–F interaction line is present at the equilibrium geometry and disappears only when the twist angle reaches the value of 62.2°. At this point, the F–F distance is 2.909 Å, which is of course also the value of the F–F CIS in this system. A similar value of 2.903 Å is calculated for the 2,2′,6,6′-tetrafluoro derivative of biphenyl—another sterically crowded molecule.

Discussion

The topological properties of the molecules under study follow a general trend. None of the molecules is crowded with respect to either the H–H or the H–F interactions, but the presence of F–F interaction results in a steric crowding. The relative positions of the stationary points on the potential energy hypersurfaces and the critical twist angles are neatly illustrated by Figures 3–6 in which the potential energy curves plotted schematically against the twist angles are juxtaposed with black bars indicating the presence of a particular type of attractor interaction line. The figures also aid in understanding the following:

Definition 3: The rotation from a rotamer A to a rotamer B is called *sterically hindered* with respect to a particular interaction if the relevant attractor interaction line absent in A appears along the reaction path linking A and B. Conversely, the rotation is *sterically facilitated* if the interaction line present in A disappears along the reaction path. If neither of the above occurs, the rotation is called *sterically neutral.*

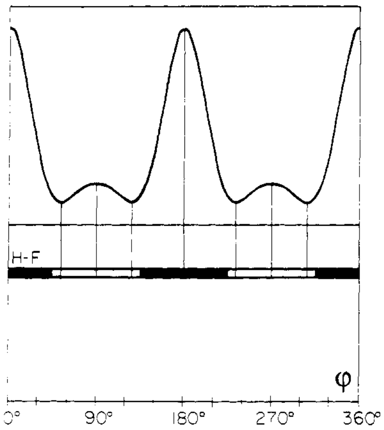

Figure 4. Schematic diagram showing the potential energy curve for rotation in the 2,6-difluorobiphenyl molecule in relation to the presence of the H–F interaction lines.

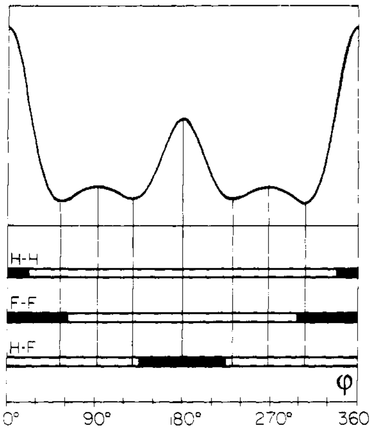

Figure 5. Schematic diagram showing the potential energy curve for rotation in the 2,2′-difluorobiphenyl molecule in relation to the presence of the H–H, H–F, and F–F interaction lines.

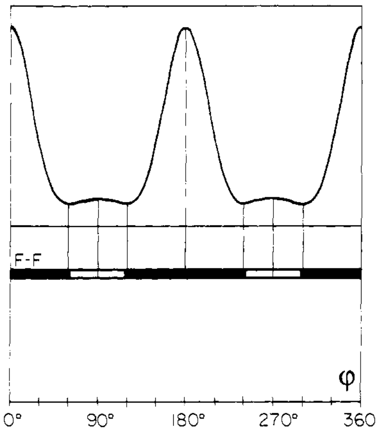

Figure 6. Schematic diagram showing the potential energy curve for rotation in the 2,2′,6,6′-tetrafluorobiphenyl molecule in relation to the presence of the F–F interaction lines.

The above definition is of a topological nature, and therefore it does not imply any particular energetic effects. This is so, because any stationary point on the potential energy hypersurface involves a balance between the attractive and repulsive interactions that results in the vanishing forces on atoms. The partitioning of the total energy into the attractive and repulsive components pertinent to each pair of atoms is not well-defined, although analysis of the changes in the strengths of the total repulsive interactions (the sum of the nucleus–nucleus and the electron–electron repulsions) and the total attractive ones (the nucleus–electron attraction) has been found helpful in understanding the reaction barriers.[23] The classification of barriers to rotation proposed above is not concerned with the *magnitude* of steric repulsive interactions, but rather with their *presence or absence* (as spelled out in definition 1).

Resuming the discussion of the information displayed in Figures 3–6, we observe that, in the biphenyl molecule, the rotation through the barrier involving a planar transition state is sterically hindered, whereas that involving the perpendicular conformation is sterically neutral, since the equilibrium conformation of the biphenyl molecule is already free of steric crowding (Figure 3). The same is true about 2,6-difluorobiphenyl (Figure 4). On the other hand, the latter rotation in the 2,2′,6,6′-tetrafluorobiphenyl molecule is sterically facilitated, as increasing the twist angle relieves the F–F steric crowding present in the minimum-energy conformation (Figure 6). One should also note that, in this tetrafluoro derivative, the rotation through the planar conformation is sterically neutral despite a very large barrier that undoubtedly comes from the steric repulsion involving the fluorine atoms. However, this can be regarded as merely an amplification of the steric crowding already present in the equilibrium structure. Finally, to conclude this part of the discussion, we note that the conversion of the cis structure of the 2,2′-difluorobiphenyl to the trans one involves rotation that is sterically neutral with respect to the H–H and H–F interactions and at the same time sterically facilitated with respect to the F–F interactions (Figure 5).

One may inquire how the calculated values of CIS would change with the improving quality of basis sets. To address this problem we repeated the calculations for the biphenyl molecule, replacing the 6-31G** basis set by the 6-311G** one. We found (see footnotes to Tables I and II) that the twist angle corresponding to the equilibrium structure increased by 0.7°, whereas the critical twist angle at which the fold catastrophe occurs increased by 1.0°. The change in H–H CIS was equal to 0.013 Å. On the basis of this observation, we believe that it is safe to assume that the accuracy of the computed values of CIS is comparable to that of bond lengths.

Finally, we address here the important issues of the transferability of CISs and the combination rules involving them. From the data presented in Table II, it is clear that in the substituted biphenyls the values of CIS are almost constant for a given pair of atoms. From other limited data,[12] we conclude that the values of CIS are transferable between molecules with similar arrangements of atoms involved in bonding to the pair of atoms in question. Therefore, the H–H CIS value of ca. 2.2 Å is relevant to all molecules in which two hydrogens are bonded to the terminal members of a chain involving four carbon atoms. The exact characteristics of bonding between these carbon atoms (such as the bond orders) appear to be of a lesser importance, as the above value of CIS correctly predicts the presence of steric crowding in the equilibrium structures of phenanthrene, chrysene, benzanthracene, and kekulene and its absence in biphenyl and *cis*-butadiene. However, as mentioned in the second section of this paper, steric crowding is not present in the $C_{60}H_{60}$ molecule despite the H–H distance of only ca. 2.0 Å. In contrast to the previous instances, the hydrogens in this molecule are bonded to 1,2-carbon atoms; thus the lack of transferability between chemical systems involving unlike bonding patterns is evident.

At the present time, the data concerning the CISs are too limited to allow us to consider the validity of the combination rules in a serious manner. However, the fact that the arithmetic mean (2.537 Å) of the averaged values of CIS for the H–H (2.167 Å) and the F–F (2.906 Å) interactions is not far from the average CIS for the H–F interactions (2.493 Å) should not be overlooked.

Conclusions

The bond critical points are not necessarily indicative of attractive bonding interactions. In molecules with atoms arranged in proximity to each other, attractor interaction lines describing nonbonding steric interactions are a common occurrence. The presence/absence of such interaction lines can serve as the basis

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(23) Reference 3, section 6.4.4, and references cited therein.

for a rigorous definition of sterically crowded molecules. Such a definition does not involve any empirical quantities. In addition, the concept of the van der Waals radii can be replaced by that of contact interatomic separations (CISs). In this manner, not only the bonding patterns but also the pairs of sterically interacting atoms can be pinpointed solely from the knowledge of the electron density. To paraphrase the well-known statement of Levy,[24] one deals with "electron densities in search of steric interactions in molecules".

The computed values of CIS are only weakly dependent on the quality of basis sets used in computation of the electron density. In addition, they appear to be transferable between similar (meaning with analogous atomic connectivities) molecules.

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Registry No. Biphenyl, 92-52-4; 2,6-difluorobiphenyl, 2285-29-2; 2,2-difluorobiphenyl, 388-82-9; 2,2′,6,6′-tetrafluorobiphenyl, 781-16-8.

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An ab Initio Study of a Retro-Wolff Rearrangement: From Diazafulvenone to Cyanovinyl Isocyanate without a Singlet α-Oxocarbene Intermediate

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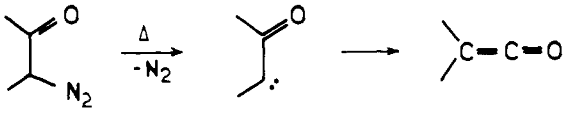
Abstract: Ab initio molecular orbital calculations have been used to study the unimolecular rearrangement of diazafulvenone leading to cyanovinyl isocyanate. The geometries of stationary points were optimized at HF/6-31G** while relative energies were obtained from multireference configuration interaction (MRCISDQ) calculations with the 6-31G** basis set. A singlet oxocarbene structure was not found to be a local minimum but rather a transition structure connecting diazafulvenone to isocyanovinyl isocyanate, the latter molecule being a distinct intermediate during the rearrangement to cyanovinyl isocyanate. Diazafulvenone is calculated to lie 14 and 32 kcal/mol, respectively, above isocyano- and cyanovinyl isocyanate (*Z* conformers) and to be separated from the isocyanide form by an energy barrier of 44 kcal/mol. The diazafulvenone → isocyanovinyl isocyanate interconversion, which can be regarded as a retro-Wolff rearrangement, is thus a concerted reaction without a discrete singlet oxocarbene intermediate. It also constitutes the rate-determining step of the entire rearrangement process, in agreement with experimental observation. As shown by an analysis of localized orbitals, the diazafulvenone → isocyanovinyl isocyanate interconversion involves six electron pairs that circulate following a cyclic motion.

In organic synthesis, the Wolff rearrangement is conveniently employed to convert α-diazo ketones **1** and related compounds to ketenes **3** (eq 1).[1] Although singlet α-oxocarbenes **2** are commonly assumed to be transient intermediates, there is until now neither kinetic nor spectroscopic evidence for their existence.[2] According to the principle of microscopic reversibility, such evidence could also be found by investigating the reverse transformation, namely, the rearrangement of ketenes. MO calculations[3] showed however, that α-oxocarbene lies much higher in energy than ketene, thus rendering the **3** → **2** reaction extremely difficult. In fact, a retro-Wolff rearrangement is rare. Burton and Groh[4] studied the decomposition of hydridosilylketenes and claimed to have the first example of a retro-Wolff rearrangement. However, the evidence is not unequivocal; the formation of the reaction products can be interpreted by involving other reaction mechanisms. Hochstrasser and Wirz[5] reported the reversible formation of ethynol ($HC\equiv C{-}OH$) by photolysis of ketene ($H_2C{=}C{=}O$) in an argon matrix. They suggested that the reaction occurs via decarbonylation of ketene followed by insertion of CO into a C-H bond of methylene and hydrogen transfer to oxygen. More importantly, no evidence for the formation of formylmethylene has been found by these authors.[5] Recently, Bender, Meutermans, and Wentrup[6] investigated the rearrangement of different heterocyclic ketenes using the flash vacuum pyrolysis (FVP) technique and have found that the outcome of the reactions can be formally rationalized in terms of a retro-Wolff rearrangement.



1 2 3

(1)

The diazofulvenone **4**, generated in situ following thermal decomposition of methyl imidazole-2-carboxylate, was found[6] to

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