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Weak Bonds in the Topological Theory of Atoms in Molecules

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Abstract: Ab initio calculations of the electron density in the benzene–tetracyanoethylene (TCNE) complex (three conformations), the guanidinium cyanoformide ionic pair, the kekulene molecule, the trinitromethanide anion, and the C_{60}–Ne complex reveal the existence of unusual weak bonds as defined within the framework of Bader's theory of atoms in molecules. These bonds challenge the traditional ideas about bonding in organic molecules. The features that allow for distinguishing between two classes of weak bonds are discussed.

Introduction

The concept of bonds in molecules and molecular ions is of a paramount importance to chemistry, yet (like aromaticity) it eludes precise numerical definition. In an attempt to quantify the concept of chemical bonding, Bader has proposed a topological theory of atoms in molecules.[1–4] In this approach, a rigorous definition of chemical bonds is based on the properties of the electron density. In particular, one defines atomic interaction lines that terminate at nuclei and pass through a critical point of the (3,−1) type, called a bond point.[1] For a system in its equilibrium geometry, the atomic interaction lines are called bond paths.[5] According to Bader, "existence of a bond path is both a necessary and sufficient condition for the existence of a bond".[5] Such a definition not only yields results that fully agree with chemical intuition in the cases where the bonds are expected but also aids in elucidation of the bonding situation in "unusual" molecules such as, for instance, organolithiums.[6]

What one might regard as a handicap of this approach is that it does not support the notion of free molecules. This can be demonstrated easily taking the Hopf–Poincaré theorem into account.[1] When two molecules are treated as one system, they are linked by at least one atomic interaction line even if their interaction is negligibly small, as, for example, in the He_2 molecule at its van der Waals minimum. The topological approach does not provide a fundamental distinction between the "normal" strong bonds and bonds resulting from weak interactions such as the van der Waals ones. Taking this observation into account, we decided to examine the topological definition in the cases of charge-transfer complexes and ionic pairs, since their electron densities are expected to possess topologies that can afford unusual bonds, rings, and cages. Although there are several reports on the existence of unexpected nonnuclear attractors in molecules,[7,8] instances of the existence of chemically unexpected bonds are less documented in chemical literature.[9,10] In this paper, we describe three instances of weak bonds associated with delocalized interactions. In addition, we describe two cases in which weak bonds arise from steric interactions within molecules.

Weak Bonds in Charge-Transfer Complexes and Ionic Pairs

The first example involves the benzene–tetracyanoethylene (TCNE) complex with the molecular geometry constructed from the HF/6-31G*-optimized geometries of the isolated benzene and TCNE molecules separated by 3.0 Å. Although the geometry of the complex itself was not optimized, we believe that it is close enough to the equilibrium geometry to ensure that the topological features of the electron density should not be altered. Three conformations were studied, with the twist angles between the long molecular axes set at 0°, 15°, and 30°. The second conformation, although being most likely a transition state rather than a true minimum, allows one to follow the evolution of the electron density with the changing twist angle. In all three cases, a cage point (denoted by a star in Figure 1a–1c) was found on the C_2 molecular axis. Interestingly, the cage is bordered by only three rings. One of the ring points (denoted by diamonds) defines the benzene ring, whereas the two remaining ring points are associated with the rings formed by the carbon–carbon bonds of the benzene and TCNE molecules and *two weak* carbon–carbon bonds. The electron density at the bond points (denoted by heavy dots) belonging to these weak bonds is ca. 20 times smaller than at the bond points of the single carbon–carbon bonds (Table I). In the $\varphi = 0°$ and $\varphi = 15°$ conformers (Figure 1a,b), the weak bonds connect the ethylenic carbons of the TCNE molecule with the 1,4-carbons of the benzene molecule. In the $\varphi = 30°$ conformer (Figure 1c), the bond paths terminate at the bond points of the benzene ring. This is a conflict structure,[1] as an infinitesimally small change in φ results in switching the bonds' termini from one pair of the 1,4-oriented carbon atoms to another. The twisting is accompanied by a substantial increase in the bond ellipticity (Table I). In all three cases, the major axes of the bond ellipticities are (almost) parallel to the respective ring surfaces. This, together with the small difference in the magnitudes of the electron density at the intermolecular ring points and at the bond points (Table I), is very similar to the features of the electron density in boranes, nonclassical carbonium ions, and other electron-deficient systems. Such characteristics usually indicate strong delocalization of the electron density responsible for the binding over the surface of the rings. The existence of the weak bonds is in line with the well-known 1,4-reactivity of the benzenoid hydrocarbons toward TCNE.[11] The positive value of $\nabla^2\rho$ at the weak critical points is associated with the closed-shell interactions.[12]

The second case involves an ionic pair of triaminocarbenium (guanidinium) tricyanomethanide (cyanoformide).[13] Topological analysis of the electron density in the HF/6-31G*-optimized structure (Figure 2) uncovers three unusual highly curved bonds between the nitrogen atoms of the cyano and amino groups. As in the previous example, these bond paths pass through bond points

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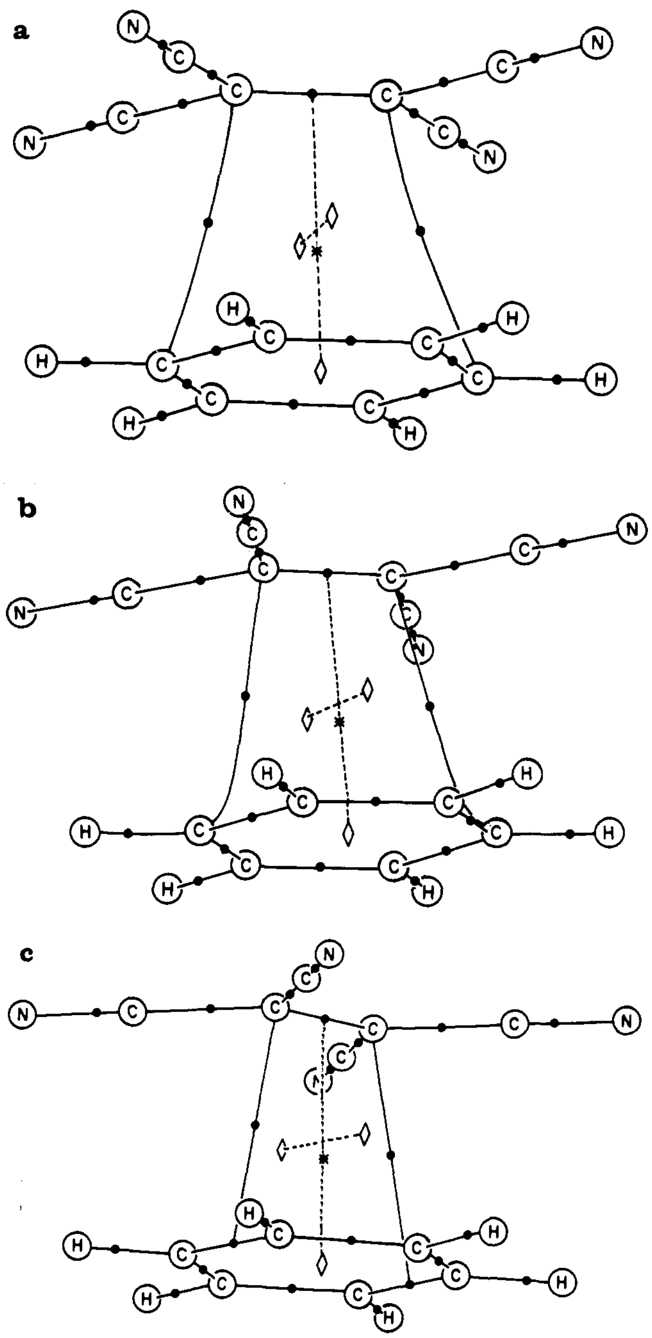

Figure 1. Molecular graph of the benzene–TCNE complex: (a) $\varphi = 0°$, (b) $\varphi = 15°$, (c) $\varphi = 30°$.

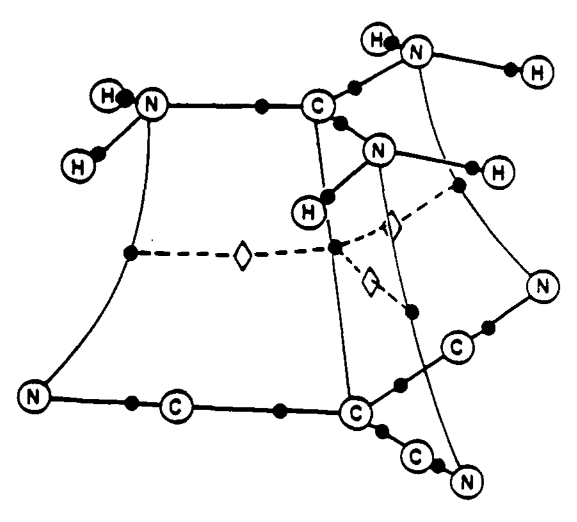

Figure 2. Molecular graph of the $C(NH_2)_3C(CN)_3$ ionic pair.

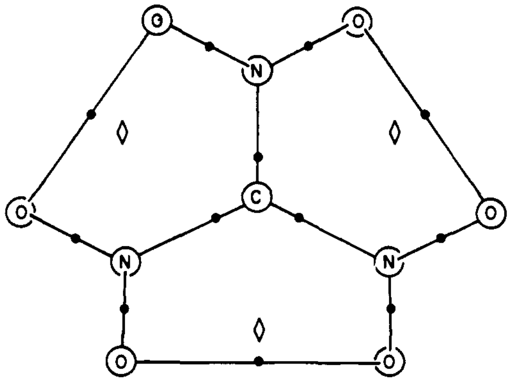

Figure 3. Molecular graph of the $C(NO_2)_3^-$ anion.

of a very low electron density (Table I). These bonds have high ellipticities, although smaller than in the benzene–TCNE complex. Again, the similar magnitudes of the electron densities at the bond and ring critical points and the fact that the major axis of the ellipticity "lies in" the ring surface demonstrate the presence of delocalization of the electron density. One may speculate that the weak bonds describe delocalized ionic interactions between the $C(NH_2)_3^+$ and $C(CN)_3^-$ moieties.

The third example concerns the complex between the C_{60} cluster ("buckminsterfullerene" or "footballene")[14] and the neon atom. Calculations that employ the DZP (Ne) and 4-31G (C) basis sets indicate that the structure with the neon atom positioned at the center of the C_{60} cage corresponds to a minimum on the potential energy hypersurface.[15] The C_{60} cluster itself possesses 60 single and 30 double carbon–carbon bonds. The neon atom is connected to the bond points of the double bonds through 30 bond paths. The bonds have a record high ellipticity of ca. 75 (Table I). As in the previous examples, the major axes of ellipticity are almost parallel to the ring surfaces. The electron densities at the bond points and the corresponding ring points are almost identical.

Weak Bonds Due to Steric Interactions

Our first example involves the trinitromethanide anion, $C(NO_2)_3^-$ (Figure 3), at its equilibrium geometry (as reflected by the nonnegative eigenvalues of the Hessian matrix). In this case, one would not anticipate any bonds in addition to those expected from the structural formula. However, at both the HF/6-31G* and HF/6-31+G* *levels* (at the HF/6-31G*-optimized geometry), the electron density exhibits three ring points as well as three additional bond points. These bond points correspond to low-ellipticity bonds connecting the oxygen atoms of the adjacent nitro groups. The bond ellipticities have their major axes perpendicular to the ring surfaces.

The kekulene (15,23:16,22-dimethenobenzo[1,2-*a*:4,5-*a*′]dipenthaphene)[16,17] molecule constitutes the final example. This coronoid hydrocarbon possesses 24 hydrogen atoms, 18 of which occupy the molecular perimeter (Figure 4). The six remaining hydrogens are located within the molecular cavity demarcated by a superring of benzenoid rings. The distance between these hydrogen atoms is ca. 1.85 Å. The electron density computed at the HF/6-31G** level (at the optimized D_{6h} geometry)[18] reveals the presence of an unexpected six-membered ring defined by six *bonds between the inner hydrogen atoms*. These bonds, which

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Table I. Topological Properties of Weak Bonds in Some Organic Systems[a]

system (method)	ρ_{crit}[b]	$\nabla^2\rho_{crit}$	λ_{crit}[c]			ϵ_{crit}
C_6H_6–$C_2(CN)_4$, $\varphi = 0°$ (HF/6-31G*)	0.0107 (0.0077)	0.0305	−6.38	−2.07	38.96	2.083
C_6H_6–$C_2(CN)_4$, $\varphi = 15°$ (HF/6-31G*)	0.0106 (0.0077)	0.0304	−6.37	−1.66	38.48	2.831
C_6H_6–$C_2(CN)_4$, $\varphi = 30°$ (HF/6-31G*)	0.0106 (0.0077)	0.0302	−6.51	−0.58	37.25	10.184
$C(NH_2)_3C(CN)_3$ (HF/6-31G*)	0.0080 (0.0066)	0.0254	−4.96	−2.76	33.14	0.796
C_{60}–Ne (HF/4-31G and DZP)	0.0024 (0.0023)	0.0145	−1.09	−0.01	15.63	75.413
$C(NO_2)_3^-$ (HF/6-31+G*)	0.0167 (0.0158)	0.0682	−12.86	−11.57	92.59	0.112
$C_{48}H_{24}$, kekulene (HF/6-31G**)	0.0016 (0.0006)	0.0661	−19.36	−15.28	100.69	0.267

[a] All values in atomic units. [b] The electron density at the corresponding ring point is given in parentheses. [c] Eigenvalues of the Hessian at the critical point (×1000).

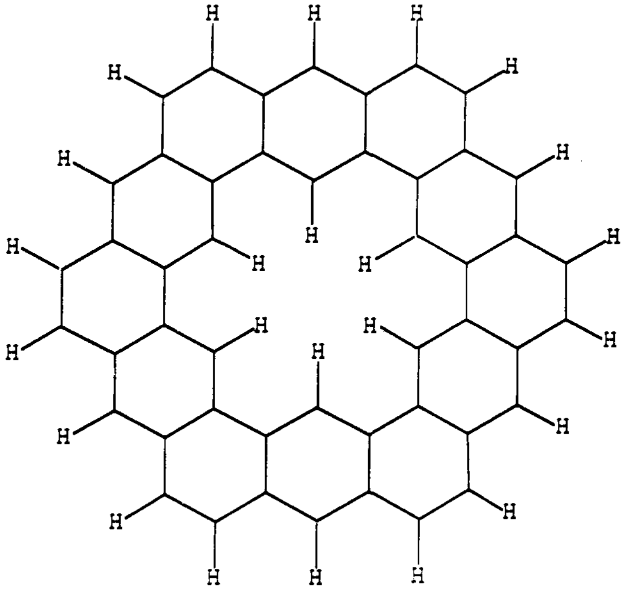

Figure 4. Molecular skeleton of the kekulene molecule.

are highly curved outward the ring, possess a moderate ellipticity (Table I), with the major axis perpendicular to the ring plane.

Discussion and Conclusion

The weak bonds described in this paper fall into two categories. The bonds that stem from delocalized electron interactions present in charge-transfer complexes and some organic ionic pairs have usually high ellipticities. The major axes of bond ellipticities are parallel or almost parallel to the corresponding ring surfaces. On the other hand, the weak bonds that result from steric interactions have low ellipticities with the major axes perpendicular to the ring surfaces. Bonds belonging to both categories can be either straight or curved, and they always have the positive values of the electron density Laplacian at the critical point.

One should comment on the possible dependence of the observed topology of the electron density on the quality of the basis sets used. In addition to the reported calculations, we performed calculations using less extensive basis sets. For example, the benzene–TCNE complex was investigated at the 4-31G level, the $C(NO_2)_3^-$ at the 6-31G* level, the kekulene molecule at the STO-3G level, and the C_{60}–Ne complex at the STO-3G/DZP level. In all instances, we found the same topological features of the electron density as at the higher level. This means that the calculated number of the critical point would not be expected to change even if better basis sets were used.

We refrain here from concluding whether these examples demonstrate limitations of the definition of bonds proposed by Bader or deceptiveness of "chemical intuition". However, we hope that the present paper will stimulate more research directed at investigating properties of the weak bonds in organic systems.

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