Bond or No Bond?

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When Do Interacting Atoms Form a Chemical Bond? Spectroscopic Measurements and Theoretical Analyses of Dideuteriophenanthrene

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The concept of chemical bonding is fundamental to natural science.[1] Despite its importance, a precise and unambiguous definition of when a chemical bond exists between (usually two) atoms is difficult. For diatomic and small molecules energetic (thermochemical) criteria are sufficient, but for polyatomic systems, the problem prevails although experimental data, for example from vibrational spectroscopy (bond force constants), can be related to bonding. The other approach is based entirely on theory in the context of ab initio schemes derived from wave function and electron density calculations. Although these methods have advanced extraordinarily in recent years,[2] the theoretical definition of bonding is still problematic. The simple reason is that no quantum mechanical "bond operator" exists that would provide the desired answer, for example, as a conventional expectation value. In any case one basic assumption of the present work (that is likely shared by many chemists and physicists) is that the existence of a chemical bond must be related to some observable; in other words, chemical bonding must have an effect on measurable properties of the system. Any definition of bonding that has no real consequences is meaningless in our opinion and must be abandoned.

Of the many theoretical bond concepts that have been proposed in the past, R. Bader's "Theory of Atoms in Molecules" (AIM)[3] is certainly the most fundamental and has also had a strong influence on the thinking of many chemists.[4] In AIM the electron density (which according to the Hohenberg–Kohn theorems of density functional theory (DFT)[5] contains all necessary information) is analyzed topologically. Bonds are defined by a bond path (BP) and a bond critical point (BCP). The BP is a line in space linking the nuclei of bonded atoms where the electron density is a maximum with respect to any neighboring line. It is assumed that a BP is necessary for chemical bonding regardless of its nature (e.g. ionic, covalent, or van der Waals).[6] The BCP represents a stationary point in the electron density and is a minimum along the BP but a maximum in directions perpendicular to the bond path. The values of the density, its Laplacian, or energy-based properties at the BCP can be used to characterize the nature of the interaction.[3,4]

Note that we question neither the foundations of AIM nor its usefulness for the interpretation of electronic structure. However, like every theory AIM has a limited scope which may lead to misinterpretations if it is applied in a too general sense. Herein we describe the rational design of a suitable system and a combination of spectroscopic (infrared and Raman) measurements with a thorough theoretical analysis. To the best of our knowledge, we show for the first time that the results of a rigorous interpretation of AIM regarding the existence of putative bonds are in complete disagreement with our experimental data.

The existence of a BCP and a BP is established as a necessary and sufficient condition for a bond in the basic interpretation of AIM.[3,4] In more recent literature this concept has been extended even further, and BCP and BP are often related to attractive interactions (see, for example, Ref. [7]). The most controversial aspect of this interpretation is the concept of H–H bonding, which was introduced by Matta and co-workers.[6] In many organic molecules (or in molecular crystals) fragments containing C–H bonds are in close proximity in the equilibrium structure, and H···H contacts below the van der Waals distance (2.2–2.4 Å) are found. In such cases a BCP and BP between these formally nonbonded hydrogen atoms is often found. Because in AIM the total energy of the molecule can be partitioned by integration over atomic basins, one can further define a local stabilization energy of the participating atoms that is interpreted as an H–H bonding interaction. For the recently investigated case of 4-methyl[4]helicene the interaction between sterically congested H1 and H12 corresponds to 7–8 kcal mol^{-1}.[8] Similar values (and BCPs) have been found in other polycyclic aromatic hydrocarbons, for example, phenanthrene, tetracene, and planar biphenyl.[6]

According to the accepted view (which interprets this interaction as steric (Pauli) repulsion),[9] such large stabilization energies are counterintuitive because these hydrogen atoms are in a local closed-shell environment, which furthermore has the electrostatically disfavoring polarity $C{-}H^{\delta+}\cdots{}^{\delta+}H{-}C$. Thus, at best only a weak lowering of energy based on van der Waals (London dispersion) interactions can be expected.[10] This contradiction has led to a lively theoretical discussion about the usefulness of AIM for the definition of bonds in these cases. (The rebuttal in Ref. [11] shares the older view of Cioslowski and Mixon.[12]). Although Matta et al. later[8] emphasized that this H–H stabilization energy is merely a local quantity and may be

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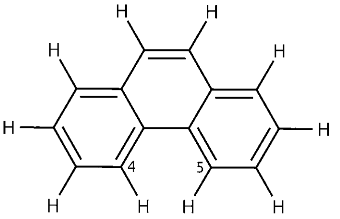
offset by "destabilized atoms" in other parts of the molecule, it is by no means clear what physical meaning (if any) such energy partitioning schemes have (for the related case of helium encapsulated inside adamantane see Ref. [13]). To the best of our knowledge this question has never been addressed experimentally. We here present for the first time decisive experimental evidence supporting the traditional view of steric repulsion. Our study is based on the idea that the local lowering of atomic energy should be measurable by a spectroscopic method that is locally sensitive to changes in bonding (i.e., vibrational spectroscopy). Phenanthrene (**1**),



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which has a BCP calculated between C4–H and H–C5 in the "bay region" of the molecule (see Figure 1) and a local H–H "bond energy" of about 9.4 kcal mol^{-1},[6] is used as example.

Formation of the questionable H–H bond should result in changes of the vibrational frequencies for the adjacent (covalent) C–H bonds. For example, in conventional hydrogen-bonded systems $B^{\delta-}\cdots{}^{\delta+}H{-}A$ with bond energies of the same order of magnitude (e.g. 5 kcal mol^{-1} for the water dimer), the bonding is accompanied by large frequency shifts of the H–A stretching vibrations of about 50–150 cm^{-1}.[14] If the H–H bonding is "real" in our sense, we thus can expect similar shifts for **1**, and their magnitude can be related to the strength of the interaction.[15] Unfortunately it is almost impossible to observe this directly because the presence of many C–H vibrations in the same energy range prevents resolution and interpretation of the spectra for **1** and related systems. As a solution to the problem we propose selective isotopic substitution of the hydrogen atoms H–C4 and H–C5 by deuterium. The C–D and the C–H vibrations are completely separated simply by a change in the vibrating masses, but the electron density and electronic structure remain unchanged (within the usual Born–Oppenheimer approximation).

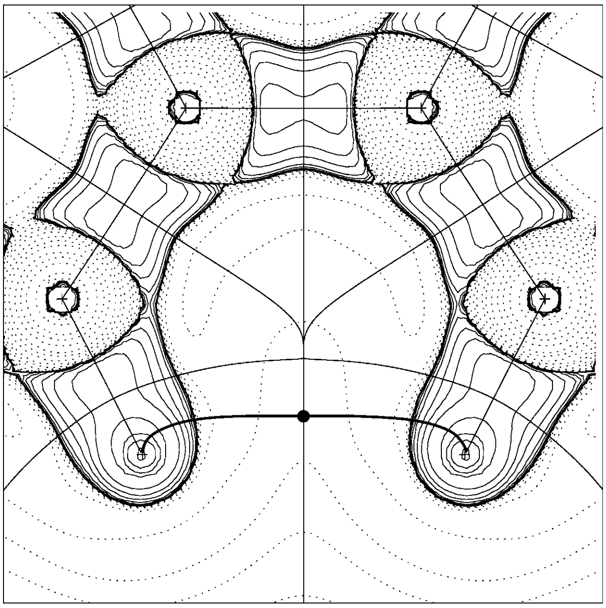

Figure 1. Laplacian of the total electron density in the molecular plane of **1** (bay region between C4–H and H–C5) on the PBE/cc-pVTZ theoretical level (other ab initio methods provide very similar data). Contour lines are 0.001, 0.002, 0.004, 0.008, 0.020, 0.040, 0.080, 0.200, 0.400, 0.800, 2.000, 4.000, 8.000, 20.000, 40.000, 80.000, 200.000, 400.000, 800.000 atomic units, negative values with dashed lines). The bold line and the dot along the C4–H⋯H–C5 "bond" indicate the corresponding BP and BCP, respectively. Electron density and derived properties calculated at the BCP: $\rho = 1.3423\times10^{-2}$ a.u., $\nabla^2(\rho) = 4.9335\times10^{-2}$ a.u., ellipticity $= 8.2\times10^{-1}$.

The selective synthesis of the isotopologue [4,5-D_2]-**1** (which is described in detail in the Supporting Information) provided 22 mg of material with an isotopic purity of about 92%, sufficient for unambiguous measurements.

Figure 2 shows the result of a quantum chemical calculation (SCS-MP2/QZVP,[16a] for details see the Supporting Information) of the harmonic vibrational normal modes for [4,5-D_2]-**1**. As expected, mainly the C–D fragments "move" in the (mass-weighted) normal modes as indicated by the lengths of the corresponding displacement vectors (Figure 2,

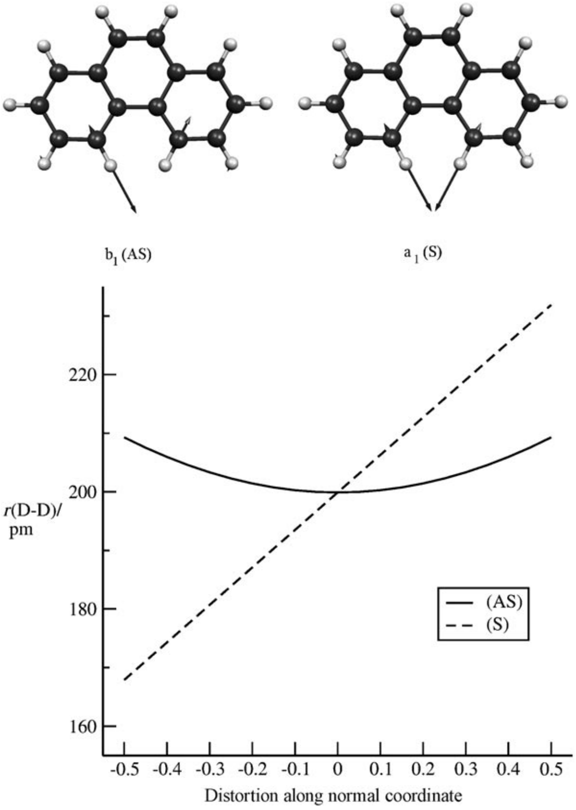

Figure 2. The symmetric (a_1, S) and antisymmetric (b_1, AS) C–D stretching normal vibrations of [4,5-D_2]-**1** at the SCS-MP2/QZVP level of theory and the dependence of both vibrations on the D–D distance.

top). The weak coupling of these vibrations to the rest of the molecule makes the system ideally suited for our analyses of the H–H (D–D) interaction. In a two-state model there are two degenerate, local C–D vibrations that are coupled by the matrix element $k = d^2E/(dr_1dr_2)$; here E is the total molecular energy and r_1 and r_2 are C–D stretching coordinates, respectively. In the antisymmetric (AS) vibration (out-of-phase linear combination of C–D stretching vibrations) the distance between the two D atoms remains almost constant, while it changes linearly with the normal coordinate for the symmetric (S) vibration (see Figure 2). For this reason the splitting between the two states is sensitive to the interaction potential of the deuterium (or hydrogen) atoms. Any large H–H (D–D) interaction potential (irrespective of attractive as predicted by AIM or repulsive as in the conventional view) is expected to strongly influence the energy of the S vibration relative to the AS vibration because of their different dependence on the D–D distance. The magnitude and the sign of the difference S–AS are the central experimental quantities of our investigation.

The AS (b_1) and S (a_1) vibrational transitions are clearly identified in all spectra by their different intensities (experimental ratio of about 1:8 in the Raman spectra). The higher intensity vibration can be unambiguously attributed to the a_1 transition because the changes of the C–D bond dipole moments (or the polarizabilities for Raman) in the vibrations are added while they almost cancel (at least along the direction of the C_2 axis) for the b_1 transition. In agreement with the calculations (see below) the experimental spectra (Figure 3) reveal a higher transition energy for the a_1 vibration, which indicates a positive sign of the coupling force constant ($k > 0$). The positive sign of k means (for details see the Supporting Information) that the short H···H distance of about 2.0 Å in **1** corresponds to the repulsive part of the H–H interaction potential,[17] which already contradicts the conclusions from AIM.

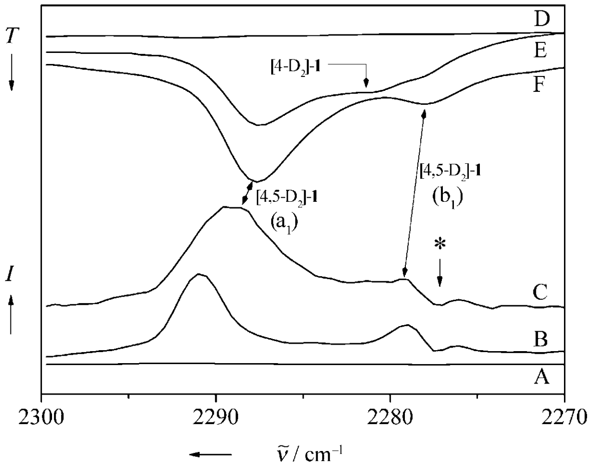

Figure 3. Part of the Raman (A, B, C) and IR (D, E, F) spectra of solid isotopologues of **1** in the region of the C–D stretching vibrations. The spectra were measured at room temperature, except B, which was recorded at about −150°C. A, D: **1**; B, C, F: [4,5-D_2]-**1**; E: mixture of **1**, [4-D]-**1**, and [4,5-D_2]-**1** (≈1:2:1). An absorption due to a water vapor line in the Raman spectra is marked by an asterisk.

The experimental and theoretical vibrational frequencies and corresponding AS–S splittings are compared in Table 1. The experimental value of 9–12 cm^{-1} is very small. As outlined above this is incompatible with the AIM interpretation of strongly interacting D(H) atoms but is in accord with the conventional picture of a weak van der Waals type interaction. The observed splitting is accurately reproduced by DFT- and wave-function-based calculations. The computed values (9.0–11.2 cm^{-1}) are in perfect agreement with those measured. Importantly also the MM3 force field gives a reasonable value although it includes only conventional potential terms. Although these findings already rule out a strong D–D interaction potential, our analysis remains (necessarily) indirect.

Table 1: Experimental and theoretical (harmonic) vibrational frequencies for symmetric (a_1) and antisymmetric (b_1) C–D transitions in [4,5-D_2]-**1**.

Method[a]	$\tilde{\nu}$ (b_1) [cm^{-1}]	$\tilde{\nu}$ (a_1) [cm^{-1}]	Splitting [cm^{-1}][b]	Intensity ratio (a_1/b_1)
IR (exp., 25°C)	2278	2288	10	
Raman (exp., 25°C)	2280	2289	9	
Raman (exp., −150°C)	2279	2291	12	8[d]
SCS-MP2/QZVP	2381.8	2393.0	11.2	26.8[c]
TPSS-D/TZVPP	2322.5	2331.5	9.0	18.0[c]
B3LYP/6-311+G(d,p)	2354.8	2363.4	8.6	17.5[c]/11.2[d]
MM3	2287.0	2296.1	9.1	–

[a] For details regarding quantum chemical calculations and measurement conditions see Ref. [16] and the Supporting Information. [b] $\tilde{\nu}(a_1) - \tilde{\nu}(b_1)$. [c] Ratio of IR intensities. [d] Ratio of Raman intensities.

We therefore conducted a detailed study of the various contributions (H–H electrostatic interactions, H–H van der Waals bonding, C–C through-bond coupling) to the coupling force constant k at the force field level. This provides a convenient way for separating the potential into chemically meaningful parts. Based on the MM3 force field (for details see the Supporting Information) we conclude that the major contribution to the coupling comes from a typical van der Waals interaction between the hydrogen atoms. Other terms like "through-bond" coupling due to C-C-C stretching/bending deformations account only for about 3 cm^{-1} of the splitting. And very importantly: as expected, an artificial change of the H–H potential in the direction of attraction in the equilibrium structure of **1** leads to a calculated inverted AS–S splitting, which is in disagreement with experimental observation.

In conclusion, the presented results indicate that there is no need to rewrite chemical textbooks. The existence of a BCP is neither a necessary nor a sufficient condition for a sensible definition of a chemical bond. BCPs might arise just for topological reasons by addition of atomic electron densities as already pointed out by Cioslowski and Mixon.[12] The resulting energy changes are well-defined in AIM but represent only local quantities that must need not be interpreted in a conventional sense as bond energies. Our results are in complete agreement with the traditional view of this H–H interaction as steric (Pauli) repulsion. This has been emphasized in similar situations with purely theoretical reasoning by Bickelhaupt et al. [11] and more recently by Strenalyuk and Haaland.[13a] As long as no conclusive experimental evidence for their "reality" is presented, we suggest to abandon the use of the term "hydrogen–hydrogen bonding" in cases where molecules or their fragments approach closely and are subjected to conventional van der Waals interactions. Intramolecular closed-shell interactions in organic and many main-group-element molecules should be interpreted in a more conventional way, and all theoretical energy partitioning schemes should be applied with great care.

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[10] The local AIM stabilization energies are actually interpreted as stabilizing contributions to the total internal energy as pointed out clearly in Ref. [6], from which we cite: "The stabilization of a hydrogen atom bonded to an aromatic ring that is involved in H–H bonding is calculated to be approximately 5 kcal mol^{-1} in phenanthrene, chrysene, and dibenz[*a,j*]anthracene. Thus the presence of hydrogen atoms with a separation of less than 4 a.u. in these molecules does not result in a repulsive steric interaction, but rather in the formation of a bond path and a stabilizing contribution to the energy, as anticipated for a bonded interaction." The higher thermodynamic stability of phenanthrene compared to its "linear" isomer anthracene as also stated in Ref. [6] has nothing to do with "H–H bonding" but is mainly due to a lower energy of the π system as already predicted by simple (topological) Hückel theory.

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[17] This is also in agreement with considerations of data for simple intermolecular models with short H···H contacts. For example, the intermolecular H···H distance in an in-plane-oriented benzene dimer with D_{2h} symmetry is computed (TPSS-D/TZVPP) to be 2.26 Å, which is about 0.25 Å longer than the C4H···HC5 distance in the equilibrium structure of **1**. As suggested by a referee, we have considered the H–H interaction energy in the electronic triplet state of the H_2 molecules at a distance of 2 Å as a model for the interaction. In qualitative agreement with our view, it also is repulsive (6.5 kcal mol^{-1}). If one considers the higher effective charge of hydrogen in the local CH environment in **1** (about 1.2), which leads to charge concentration (less Pauli repulsion), this value diminishes to 3.8 kcal mol^{-1}, which is in semiquantitative agreement with the results of the force field analysis given in the Supporting Information. Structurally, the steric congestion is also revealed by slightly shorter C4–H/C5–H bond lengths compared to the other C–H bonds (with TPSS-D/TZVPP about 0.001 Å). A corresponding reduction of the bending angle H-C4-C3 is difficult to establish because all H-C-C angles in **1** agree to within 1–2°degree so that a necessary "unstrained" reference angle is not well defined. The structure of a possible reference compound ("extended" phenanthrene) is discussed in the Supporting Information.