Angewandte
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Chemical Bonding

DOI: 10.1002/anie.201302350

A Response to the Critical Comments on "One Molecule, Two Atoms, Three Views, Four Bonds?"

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C_2 · chemical bonding · multiconfigurational systems · quadruple bond

Sason: Frenking and Hermann have criticized our work in Nature Chemistry and the trialogue in Angewandte Chemie on quadruple bonding in C_2,[1,2] and raised some useful points, which I thought I may be able to answer with some hard facts.

In the trialogue,[2] I argued that one can put an experimental value on the bond energy of the 4th bond in C_2, using the difference between the successive bond dissociation energies (BDEs) of the two C–H bonds of acetylene. Using the experimental and theoretical data, Henry and I showed that $\mathrm{BDE(CH\text{-}1)} = 133.5\ \mathrm{kcal\,mol^{-1}}$ and $\mathrm{BDE(CH\text{-}2)} = 116.7\ \mathrm{kcal\,mol^{-1}}$, which leads to $\mathrm{BDE(4th)} = 16.8\ \mathrm{kcal\,mol^{-1}}$ as the experimental bond energy of the 4th bond. Gernot argues reasonably, that this bond energy determination is based on the assumption that the other bonds in C_2 are not affected, and since the C–C distance changes from 1.208 Å in $HCC^{\bullet}$ to 1.243 Å in C_2, Gernot feels that the assumption was wrong, and the BDE difference, $\mathrm{BDE(CH\text{-}1)} - \mathrm{BDE(CH\text{-}2)} = 16.8\ \mathrm{kcal\,mol^{-1}}$, reflects in fact the relaxation of the C_2 molecule rather than the strength of the 4th bond. To test this, David has now calculated the energy change of C_2 from 1.210 Å to 1.245 Å, using CCSD(T)/aug-cc-pV5Z and CCSD(T)/CBS (CBS—complete basis set limit). The values are $1.116\ \mathrm{kcal\,mol^{-1}}$ and $1.115\ \mathrm{kcal\,mol^{-1}}$. Valence bond (VB) calculations led him to a consistent value of $1.22\ \mathrm{kcal\,mol^{-1}}$. These values show that Gernot is mistaken in his concerns, *and that the experimental BDE(4th) value is 15.7–15.8 kcal mol*$^{-1}$*, in perfect agreement with the original VB calculations.*[1]

Gernot later argues that the difference between the two BDE(CH) values reflects the fact that, as C_2 is formed upon second C–H bond dissociation, the reference state of the carbons atoms changes from ^5S to the ^3P ground state, and this is reflected in a BDE lowering. As we show in the following two paragraphs, the electronic configuration of the carbon atoms is 78–81 % $2s^12p^3$. The state is virtually ^5S, and there is no basis for assuming it is ^3P. Thus, showing that the CC bond-length change has negligible effect and refuting the argument about the reference-state change, the only factor that is responsible for the lowering of the second C–H bond dissociation is the 4th bond in C_2.

Gernot criticizes our estimate of the *intrinsic bond energy*, D_{in} (the intrinsic bond energy, going from the bottom of the energy well to the fragments in their reference states as in the molecule) of C_2 versus HCCH.[1] He argues that, while the reference state for the HC fragments is undoubtedly $^4\Sigma_g^+$, the reference state for C in C_2 is the ^3P ground state of the carbon atom (with a $2s^22p^2$ population), while we use in Ref. [1] the ^5S state (with a $2s^12p^3$ population). Gernot bases his argument on the fact that in both molecules the potential energy curves for dissociation correlate to his favored fragment states; $^4\Sigma_g^+$ in the case of $\mathrm{HCCH} \rightarrow 2\,\mathrm{CH}$, and ^3P in the case of $C_2 \rightarrow 2\,C$. However, this argument is not strict, since the $\mathrm{HCCH} \rightarrow 2\,\mathrm{CH}$ dissociation curve can be made to correlate smoothly to the $^2\Pi$ state of the CH fragments along a nonlinear path.[3]

In fact, the reference state of the fragments cannot be determined by the smooth or nonsmooth correlations to the dissociation limit but rather *by the states of the fragments within the molecules*. In this sense, Gernot's argument ignores the fact that the VB calculations[1] show that the dominant state of C in C_2 has primarily $2s^12p^3$ population and *not* $2s^22p^2$. But, let's assume that we do not want to believe the VB calculations. So, David has performed NBO population analyses for the C_2 molecule using MRCI and CASSCF(8,15) in three basis sets, 6-31G*, cc-pVTZ, and aug-cc-pVTZ. The population in the 2s orbital of carbon ranges from 1.193e to 1.223e, which means that the reference state of the C atoms in the C_2 molecule is close (78–81 %) to $2s^12p^3$, namely ^5S. This population still leads to $D_{in}(C2) > D_{in}(HCCH)$.

Gernot raises the issue of the force constants (FC) and the frequencies of C_2 and HCCH, and argues that since C_2 has a smaller FC than HCCH (12 vs. 17 $\mathrm{N\,cm^{-1}}$), it follows that the bonding in C_2 must be weaker than in HCCH. This is a valid criticism that has been raised before by Grunenberg,[4] as well as by my fellow trialogue participant, Roald.[1] This criticism is based on the Badger rule, which works very well in many well-behaved series, such as the C–C, C=C, and C≡C bonds. But it is doubtful that it is a universal rule, as may be witnessed for

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example by reading the study of Kaupp et al., who showed the breakdown of the rule for a variety of molecules.[5]

In order to extract some insight on the behavior of the FC in C_2 and HCCH, David calculated these molecules using various wave-function levels with 6-31G*, and determined their FCs and BDEs. Thus, at the Hartree–Fock (HF) level, C_2 has a $FC = 13.33\,N\,cm^{-1}$. Adding the configuration that involves excitation from the weakly antibonding orbital $2\sigma_u$ to the vacant bonding orbital, $3\sigma_g$, in CASSCF(2,2) calculations raises the FC dramatically to $17.35\,N\,cm^{-1}$. This is the configuration that Gernot seems to dismiss as being of minor importance, based on his consideration of the configuration weights in his own CASSCF calculations. We then looked at the effect of π correlation on the FC. Starting from the HF wave function and adding the excitations from the π to the π^* orbitals lowers the FC dramatically to $9.31\,N\,cm^{-1}$. Thus, even though the BDE of the π-CASSCF wave function is much higher than that in the σ-CASSCF wave function, the FC still drops to almost half the value of the σ-CASSCF. The final FC is an average between the σ and π correlation effects, and it no longer reflects the bond energies. The behavior of the HCCH molecule is much less jumpy, and it keeps a relatively high FC at all the levels we tried. Thus, what makes the FC of C_2 lower than that of HCCH is the π correlation that is unique to the former.

Clearly, our calculations of the relaxation energy for C_2 between the distances of 1.210 and 1.245 Å show that the potential energy surface near the minimum is flat, hence causing the low FC. Why is it so? In the original paper,[1] we offered a plausible explanation that this flatness occurs as a result of the avoided crossing of the ground state of C_2 with a $B'^1\Sigma_g^+$ state that has one less π bond than the ground state, and is the state that correlates to the ^3P state of the 2C fragments. If this avoided crossing is strong, it may well flatten the potential-energy curve along the stretching coordinate, as we indeed observe. Clearly, it is about time to investigate the physical makeup of FCs in multiconfigurational cases rather than assuming that the Badger rule is followed flawlessly.

Ironically, in his Figure 1c Gernot uses a quadruple bond in C_2; two strong bonds, and two donor–acceptor bonds, between a filled 2s orbital on one carbon and a vacant 2p orbital on the other, which he considers to be weak. This model is very similar to the ν bonding suggested by Weinhold and Clark;[6] only they consider these to be regular bonds with a shared electron pair, as any other bond in the molecule. In fact, there is little basis to assume that these "donor–acceptor bonds" are weak, since the CC distance is short, and the 2s–2p overlap is substantial. In our original paper,[1] we showed that we can converge on the bond multiplicity in C_2 using two high-level methods, VB and FCI. *In both methods, the molecule was found to have four bond pairs*. The VB method further shows that these bond pairs are composed of three strong bonds, and a weaker 4th bond, which *can be gauged from theory and experiment* to have a bond energy of approximately 16 kcal mol^{-1}. The 4th bond in C_2 and its isoelectronic molecules won't go away…

Henry: With such unique characteristics and energy, it might be fair to say this 4th bond is in a class of its own. But one might also now ask if other interesting examples (and new chemistry) might be identified, perhaps between metal atoms?

Roald: Gernot is correct to criticize me for overemphasizing what he calls "synthetic" chemistry. By which I think he means the chemistry of molecules that in milligram to gram amounts persist for days or longer at room temperature and 1 atm, an a solid, or in a typical organic solvent. I am also internally inconsistent in our trialogue, in that I make the extreme statement he quotes, yet write with glee of how one can account from simplest one-electron theory for bond-length trends in excited states of C_2. Such excited states and the ground state do not meet my own criteria of the persistent molecules mentioned above. Yet they clearly give important insight into electronic structure.

What propelled me to such exaggeration is that I was reacting against a literature getting full of calculations of metastable molecules that are quite incapable of kinetic persistence under ambient conditions in a container. In those calculations—you've all seen them—there are explicit or implicit claims that such molecules will be made not only in a He matrix at 4 K, but in a bottle. Aromaticity is one code word of such a reach (if π is not enough, σ is better). High atomization energies are another criterion invoked. And the pressing of many software buttons serves as a substitute for what could oh so simply be done—the calculation of activation energies for reactions with the small molecules in any likely environment, or dimerization.

I used the lack of persistence of C_2 on earth to hint at the emptiness of such claims. But I was wrong, and this is Gernot's point: Molecules are molecules, and there is much to be learned from even the least stable of them. Elsewhere I have written at some length on the reasons we (theoreticians) in fact love to design new molecules, even if they are fleeting.[7]

Sason: Remember Roald, in the trialogue you and I had the same exchange, as you are now having with Gernot. In the end, you agreed that molecules are molecules, are molecules… Yet, I agree with you that bottle-able molecules have special status in chemistry. So, it is normal for a chemist to hold these two viewpoints.

Roald: I do repeat myself.

The near infinite lifetime Gernot refers to for C_2 is in interstellar space, with its unearthly conditions of few collisions, yet much light. Indeed, there is a very important set of chemistries out there, with hints to us of the earth's and our provenance. We can actually recreate those conditions in a laboratory, but it is not what one finds normally on earth.

I don't think I've narrowed the purview of chemistry—my work, from C_2 to ternary borides, from thinking about how one could stabilize square-planar carbon to what happens to an acetylene on a metal surface, engages with the beautiful complexity of both the persistent and fleeting world of matter, across the periodic table.

My statement about QTAIM stands. Hundreds of papers, "deep insight", and no chemistry. But… not only Gernot disagrees with me; even in our small trio there was no unanimity at all on this.

Henry: QTAIM and associated ways of analyzing the first and second derivatives of the electron density can provide merely a skeleton onto which chemistry can be layered, and as such it can be beneficially thought-provoking. Perhaps a specific example might help clarification; understanding the conformation of *cis*-butene. Here, both methyl groups have one C−H bond *cis*-eclipsed with the C=C bond, resulting in a measured H−H contact that is significantly shorter than the sum of the van der Waals radii (≈2.1 A).[8] The topology of the electron density in this H−H region has a critical point with the correct QTAIM properties for a weak "bond", but is it really such? The debate raging on this point has certainly generated heat, but as Roald asks, has it generated new chemistry? In my opinion (one of many), in this specific instance new chemistry is more likely to emerge by refocusing instead on how the other four (staggered) C−H bonds interact with the central π system. In doing so, one is forced to refine one's chemical interpretation of QTAIM for this molecule, itself no bad thing of course.

QTAIM has its place, but only as part of a bigger picture. For example, many of the colleagues I encounter on a daily basis are practical chemists concerned with stereospecific synthesis. They wish to have tools that allow them to rationalize their experiments. In many cases, stereospecific phenomena may derive from regions of low values of the density, and these can be both attractive and repulsive.[9] I do wonder if the language of MO and VB is best suited in this region, or should we move to the dialect of the density?[10] I was thinking of how finely balanced the stereocontrol in the polymerization of, *for example*, lactide is, and how the (attractive or repulsive) interactions between the methyl groups of the lactide and the close-by aromatic groups of the catalyst can mediate the often exquisite selectivities that are revealed experimentally.[9] Another example[11] involves the use of optically active noncoordinating anionic ligands to achieve enantioselective stereocontrol of cationic silver-catalyzed additions of O-H and N-H groups to allenes. Here the reduced density gradients do seem to unmask some important effects. We are trying to rise to your challenge to show you predictions, Roald!

Roald: The balance of small attractive and repulsive forces is indeed essential to explaining biochemical action. And difficult for simple orbital theories to capture. QTAIM is neat in its analytical scheme, and it is descriptive. Despite your examples, Henry (keep on creating them!), I still believe QTAIM is not predictive, nor productive of new chemistry. It does not give the least clue as to the geometry change to be expected on ionization or in the excited state of a molecule. It does not give an experimentalist any guidepost to where an electrophilic or nucleophilic reagent might attack. I do like the picture QTAIM provides of the electronic density and its gradient; that density is an observable, for sure. Yet the method's identification of bond paths and bond critical points with chemical bonds fails to connect in a number of cases with chemical intuition that has stood the test of time. Looking at the Laplacian of the density or kinetic energy densities does help to identify bonds.

Sason: This is what we do in discussing the difference between covalent and charge-shift bonds (e.g., H_2 vs. F_2). In this case, we found QTAIM to be conceptually useful.

Roald: Gernot's comment finally shades into an affirmation of concepts he likes and finds useful—Pauli repulsion and electrostatic attraction in the framework of an EDA analysis. They do add to our understanding, I agree. Gernot goes on to bemoan that practicing synthetic chemists instead still use Lewis structures and simple mixing of orbitals. Indeed they do. And that's what they teach in their courses. For good reasons, I would say; try teaching a course in inorganic chemistry using QTAIM and EDA, while saying that orbital interaction diagrams are just… allegorical. Could it be that "this most rigorous theory," the one that affords "deep insight," in fact has failed (so far) to provide pragmatic chemists with a way of thinking about real chemistry—whether it is that of "synthetic" or of short-lived molecules—that is as useful as are Lewis structures, arrow-pushing, and molecular orbitals?

Received: March 20, 2013

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