Chemical Bonding

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Critical Comments on “One Molecule, Two Atoms, Three Views, Four Bonds?”

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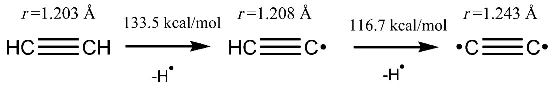
stability of molecules

The scientific part of the above-mentioned lengthy and colloquial paper,[1] henceforth called “trialogue”, focuses on the question about the bonding situation in C_2. At the end of the discussion, which we found more confusing than enlightening, the paper leaves the impression that the carbon–carbon bond in diatomic C_2 is stronger than in acetylene. It is suggested that this is a result of a fourth bond, which provides an additional bonding energy of approximately 15 $\mathrm{kcal\,mol^{-1}}$, which was previously suggested by Shaik et al. who state that “…the intrinsic bonding energy in the quadruply bonded C_2 is larger than that in the triply bonded HCCH”.[2] Prior to the publication of the trialogue, one of us (G.F.) had an intensive discussion by email with the proponents of a quadruple bond in C_2, which convinced him that there is no basis for claiming that C_2 has a stronger C–C bond than acetylene. Here are our arguments:

1. The most compelling argument against stronger bonding in C_2 compared with acetylene comes from the C–C stretching mode in the two molecules. The quadratic force constant (12.18 mdyn Å^{-1}) and the vibrational frequency (1855 $\mathrm{cm^{-1}}$)[3] of C_2 in its $^1\Sigma_g^+$ ground state are significantly smaller than the force constant (15.80 mdyn Å^{-1}) and the frequency (1974 $\mathrm{cm^{-1}}$)[4] for the C–C stretching mode in HC≡CH. This finding is shortly mentioned by Shaik on page 3024 in the trialogue, where he says that this is explained in their previous work.[2] The explanation that is given therein is the statement that the potential energy curve of C_2 near the minimum may become shallow because of an avoided crossing between the $X^1\Sigma_g^+$ ground state and the $B'^1\Sigma_g^+$ excited state, which has one π bond less than the ground state. But the quadratic force constant is a property *at the equilibrium geometry*, where the first derivative of the energy with respect to the atomic coordinates is zero. It is an expression of the intrinsic strength, which acts on the nuclei at the equilibrium distance (r(C–C)) of 1.243 Å,[3] where, according to Shaik et al., the C–C bond in C_2 is stronger than that in HC≡CH, which has an r(C–C) of 1.208 Å. Moreover, accurate calculations show that the avoided crossing takes place rather far from the equilibrium value at a distance of around 1.6 Å.[5] *The force constants and the C–C stretching frequencies provide direct evidence that the C–C bond in C_2 is significantly weaker than in acetylene.*

2. In the trialogue, Shaik and Rzepa claim that there is experimental evidence for the strength of the fourth bond in C_2, which is estimated to be 16.8 $\mathrm{kcal\,mol^{-1}}$. This number comes from the difference between the bond dissociation energies (BDE) of the first and second C–H bond of acetylene, which are experimentally available (Scheme 1).



Scheme 1. Bond dissociation energies for successive hydrogen loss of acetylene and C–C bond lengths of the molecules. Note that the sketch of C_2 is not a representation of the actual bonding situation, but rather a formal expression for the situation when both C–H bonds of acetylene are ruptured.

Scheme 1 shows the BDEs and the bonding situation in HCC and C_2 according to the arguments that are given by Shaik et al. They claim that the coupling of the unpaired electrons in C_2 results in a fourth bond, which provides an additional stabilization that causes the BDE of the second C–H bond to be 16.8 $\mathrm{kcal\,mol^{-1}}$ smaller than the BDE of the first C–H bond. This reasoning rests on the assumption that the other three bonding components (a σ and a degenerate π bond) do not change when one goes from HCC to C_2. The C–C distances show that this assumption is not justified! While the C–C bond length in HCC (1.208 Å)[6] remains nearly the same as in HCCH (1.203 Å), supporting the notation of a triple bond in both molecules, the bond length in C_2 (1.243 Å) is clearly longer after breaking the C–H bond of HCC. Quantum chemical calculations at various levels of theory indicate that the C–C stretching mode of $X^2\Sigma^+$ HCC has a vibrational frequency that is approximately 100 $\mathrm{cm^{-1}}$ larger than in $X^1\Sigma_g^+$ C_2.[7] The C–C bond lengthening and smaller stretching mode is contrary to the proposed bond strengthening in C_2 through formation of the fourth bond. There is no reason to assume that the smaller BDE for breaking the second C–H bond comes from stronger C–C bonding, which can be equally caused by a less strongly bonded, but energetically more favorable electronic structure. It has long been known that the electronic state of a molecule

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with a weaker bond may be lower in energy than that of a molecule that has a stronger bond.[8] In the trialogue, this becomes obvious from Figure 5, which shows that highly excited states of C_2 possess shorter C−C distances than the ground state. Badger's rule, which relates shorter bonds with stronger ones, is not valid if one takes the BDE as a measure for the strength of a bond,[9] but is generally valid if one takes the intrinsic interaction energy between the fragments in the proper electronic reference state. Here lies another serious problem in the arguments that were put forward in support of a stronger bond in C_2 compared with HCCH.

3. Shaik et al. argue that the correct reference state of the carbon atoms in C_2 is the highly excited ^{5}S state, which has four unpaired electrons (Figure 1 a). Taking the excited ^{5}S state of a carbon atom, which is 96.4 kcal mol^{-1} above the ^{3}P ground state,[10] the intrinsic interaction energy D_{in} of C_2 was calculated to be 313.7 kcal mol^{-1} at the MRCI level and 303 kcal mol^{-1} using VB methods.[2] This value was then compared with the interaction energy for the C≡C bond in acetylene, which was calculated at the MRCI level to be $D_{\text{in}} = 252.7$ kcal mol^{-1}. The latter value uses the $^4\Sigma_g^+$ excited state of CH (Figure 1 b) as reference state, which is 16.7 kcal mol^{-1} above the $^2\Pi$ ground state. The conclusion was that C_2 has an intrinsically stronger C−C bond than acetylene because $D_{\text{in}}(C_2) > D_{\text{in}}(\text{HCCH})$.

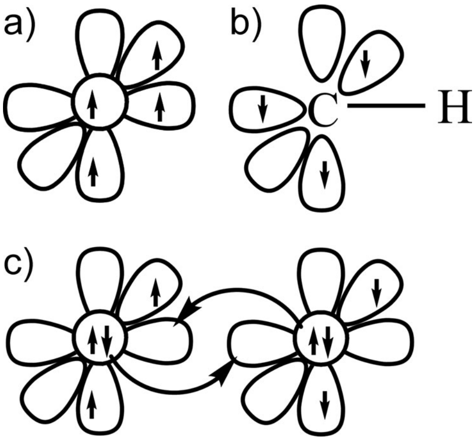

Figure 1. Schematic representation of a) a carbon atom in the excited ^{5}S state and b) a CH group in the excited $^4\Sigma_g^+$ state. c) Schematic representation of the σ bonding between two carbon atoms in the ^{3}P ground state.

There is no doubt that the $^4\Sigma_g^+$ state of CH is the proper reference state for the formation of the C≡C triple bond in acetylene. It is also reasonable to consider the $^4\Sigma_g^+$ state of CH and the ^{5}S state of C as reference states for HC≡C. However, the introduction of the ^{5}S state of a carbon atom as reference state of the $^1\Sigma_g^+$ ground state of C_2 is arbitrary and unjustified! The use of the excited ^{5}S state of C is the very source of the numerical misapprehension in the work of Shaik et al. Quantum chemical calculations (see Figure 5 in the trialogue) show that C_2 in the $^1\Sigma_g^+$ ground state smoothly dissociates into carbon atoms in the ^{3}P ground state.[5,11] The bond formation of C_2 can straightforwardly be explained in terms of orbital interactions between two (^{3}P) carbon atoms, as schematically shown in Figure 1 c. The singly occupied p(π) AOs of the carbon atoms result in the degenerate π bond, while the doubly occupied 2s AOs mutually engage in 2s→2p(σ) donor–acceptor interactions. This bonding model is related to the proposals by Trinquier and Malrieu[12a] and by Goddard and Carter,[12b] who suggested that the heavier group-14 homologues of ethylene H_2EEH_2 bind through the $^1A_1$ state of EH_2, resulting in donor–acceptor bonds that lead to nonplanar equilibrium geometries.[12c] A geometrical distortion is not possible for C_2, but the weaker donor–acceptor interactions in C_2 compared with the stronger electron-sharing σ bond in HCCH plausibly explains why the former molecule has a weaker C−C bond than the latter. Ironically, this would also suggest that there is a quadruple bond in C_2, but the bonding components are quite different from what is suggested by Shaik et al.[2] In spite of weaker bonding with respect to HC≡C, the stabilization of C_2 does not come *from the formation of a fourth bond, but from the much lower energy of the carbon atom in the* ^{3}*P ground state as reference state than the* ^{5}*S state (96.4 kcal mol*$^{-1}$*), which compensates for the weaker bond in dicarbon.*[13]

Although the interpretation of the σ bonds with donor–acceptor interactions between two (^{3}P) carbon atoms is in agreement with the rather weak C−C bond and is therefore a useful bonding model,[14] it is not a faithful representation of the chemical bond in C_2. Shaik et al. rightly point out that C_2 requires a multideterminant ansatz for a correct description of the electronic structure. A very suitable approach is a full-valence CASSCF calculation, which considers all possible configurations in the valence space. The calculation of C_2 at the CASSCF(8/8)/cc-pVZT level gives numerical data for all configurations where the eight valence electrons occupy the eight valence orbitals. Figure 2 shows the most important configurations and their weight in the wave function, which is given by the square of the coefficient of the associated Slater determinant.

It becomes obvious that the Hartree–Fock determinant (Figure 2 a), which qualitatively gives a double bond,[15] is not a sufficient representation of the electronic structure of C_2, because it contributes only 71 % to the wave function. The second most important contribution, which is shown in Figure 2 b, comes from the excitation from the antibonding $2\sigma_u$ MO to the bonding $3\sigma_g$ MO. This configuration may be assigned as a quadruple bond. However, the weight of the latter determinant is only 13.6 %, which is clearly not sufficient to declare C_2 a quadruply bonded species. This is further supported by the other configurations shown in Figure 2 c and d, which have smaller weights than that shown in Figure 2 b, but the occupation of the antibonding $1\pi_g$ weakens the C−C bond. The only configuration that may be related to the interaction between carbon atoms in the ^{5}S state is 2b, but the small weight of 13.6 % does not justify the statement that the ^{5}S state should be used as reference state for C_2. The weights of the configurations shown in Figure 2 suggest that the effective bond order of C_2 is between two and three. This means that the C−C bond in C_2 has a lower bond order than in HC≡CH, which is in agreement with the experimentally observed smaller force constant in dicarbon.

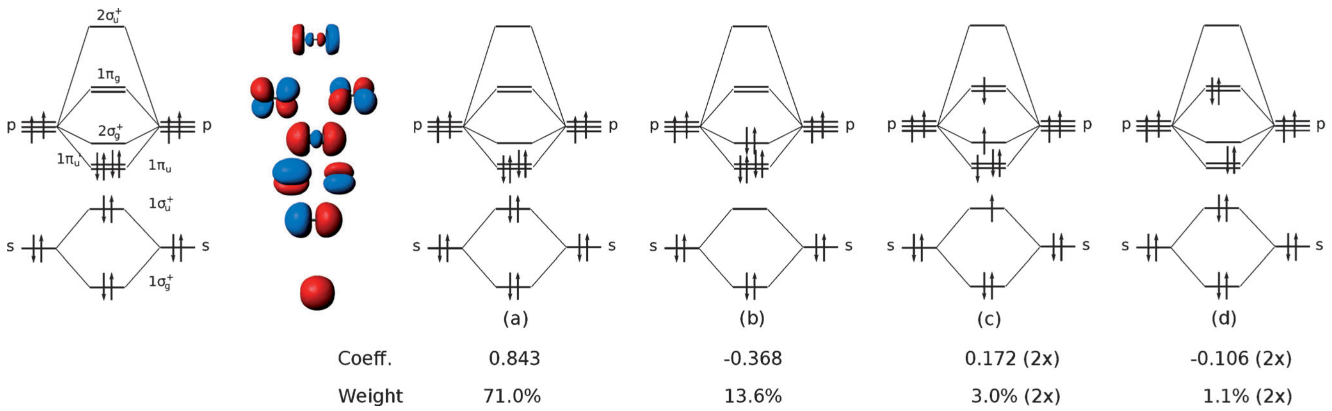

Figure 2. Left: Orbital interactions for C_2. Right: The most important configurations of a full-valence CASSCF(8/8)/cc-PVTZ calculation of C_2, showing the coefficients c and the weights of the configurations.

We think that, in the light of the above arguments, there is no basis for claiming that the C–C bond in C_2 is stronger than in acetylene.

There are further disturbing statements in the trialogue requiring a critical comment. This holds in particular for the remark by Hoffmann on page 3029, where he ridicules theoreticians who calculate the atomization energy of a molecule and take this energy as a measure for its stabilization. He writes: "C_2 illustrates just how silly such claims are. What matters in chemistry, if you are going to coelenterate in the sea or a lab chemical in a bottle is kinetic persistence. And kinetic persistence C_2 does not have." We claim the contrary: Because of its atomization energy, C_2 has a very large kinetic persistence in unimolecular dissociation reactions. It has a nearly infinite lifetime in the universe, where it plays an important role in interstellar and circumstellar chemistry, where carbon compounds are abundant.[16] It was identified already in 1977[17] and its properties have been extensively studied. The reaction of C_2 with helium, the second most abundant element in outer space, was studied theoretically and experimentally in order to address questions about elementary processes in interstellar space.[18] The formation of the universe is closely associated with reactions in the gas phase, involving species that may look exotic for chemists who are in engaged in synthetic chemistry in the condensed phase. Unfortunately, this focus has narrowed the view of many people on chemistry as a discipline that deals only with objects that are accessible to bench chemists. Unlike physics, which considers theoretically as well as experimentally the whole universe in all dimensions, from quantum objects to astrophysical processes, chemistry, as defined by Hoffmann, confines itself to narrow regions of experimental methods, that is, the synthesis, analysis, and investigation of new compounds, where theoreticians are only accepted when they serve the needs of synthetic chemists. But chemistry as the science of transformation and understanding the material world on a molecular scale aims at gaining knowledge about molecular processes and species, irrespective of their persistence under "normal" laboratory conditions. Gas-phase chemistry in interstellar space may not be of interest to synthetic chemists, but this must not lead to the conclusion that objects that cannot be filled into a bottle do not matter in chemistry. Compounds such as He_2^{2+} will probably never become the target of synthetic chemistry, but the finding that covalent interactions between two He^+ ions overcome the inherent Coulombic repulsion is an important scientific knowledge.[19]

A related issue concerns the pejorative declaration of Hoffmann about the Quantum Theory of Atoms and Molecules (QTAIM),[20] where he says "…in the hundreds of QTAIM papers that crowd the literature, I have yet to see one that makes a chemical prediction, or suggests an experiment". This statement completely ignores the deep insight into the electronic structure of molecules and solids provided by the QTAIM. For many chemists, a chemical bond is still just a line between two atoms and identified as an electron pair as suggested by Lewis in 1916.[21] Although we know that the electronic structure in a molecule and the nature of the chemical bond is much more complex than it was thought of nearly 100 years ago, most chemists still restrain their description of chemical bonding on sketching Lewis structures. It was Roald Hoffmann himself who contributed in the 1970s to a more deeper understanding of the chemical bond when he and Bob Woodward introduced orbital symmetry as pivotal model for understanding chemical reactions.[22] It was one step forward toward building a bridge between heuristic bonding models and the physical mechanism of a chemical bond. But progress in the theory of chemical bonding did not stop with the development of MO models for understanding the chemical bond. Interatomic interactions involve not only the mixing of the orbitals. There is Pauli repulsion between electrons that have the same spin, which, rather than orbital overlap, determines the bond lengths of most covalent bonds.[23] And there is strong electrostatic attraction, even in molecules such as N_2,[24] which are discussed in most textbooks only in terms of a triple bond. All these components have to be considered when the electronic structure of molecules or solids is thoroughly analyzed. QTAIM is probably the most rigorous theory for electronic structure analysis that has been developed so far. It provides deep insight into the bonding situation and interatomic interactions in molecules and solids and is therefore widely used in diverse areas of chemical research.[25] Together with other modern methods of charge and energy decomposition analysis, it provides a comprehensive picture of chemical bonding that goes beyond writing Lewis structures, which are useful but often not sufficient for describing a chemical bond. C_2 is a striking example.

We wish to thank the authors of the trialogue for the efforts they put into their arguments about the nature of the bonding in C_2. Without their work, we would have never thought so deeply about the chemical bonding in this seemingly simple diatomic molecule. Although we disagree with their conclusions about the bond strength in C_2 and with some statements about stability of molecules and the virtue of chemical research beyond synthetic chemistry, we appreciate the opportunity to examine our understanding of chemical bonding and to sharpen our mind. Now it is up to the readers to do the same.

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[8] A pertinent example is Be_2, which is only weakly bonded in the $X^1\Sigma_g^+$ ground state because the bonding and antibonding contributions of the occupied $2\sigma_g$ and $2\sigma_u$ orbitals essentially cancel each other. Electronic excitation from the antibonding $2\sigma_u$ orbital to higher lying bonding orbitals leads to a multitude of significantly stronger electronic states of Be_2, which are higher in energy, because the gain in the bonding interactions does not compensate for the excitation energy: M. Pecul, M. Jaszunski, H. Larsen, P. Jørgensen, *J. Chem. Phys.* **2000**, *112*, 3671.

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[13] The stabilization of free C_2 compared with the C_2 fragment in HCC, which is caused by the relaxation of the electronic reference state of C, is an instantaneous effect that does not depend on the bond length in C_2. The small energy change of C_2 from 1.210 Å to 1.245 Å, which is mentioned in the response to our comment, is irrelevant for the arguments that are put forward by us.

[14] A bonding model is not right or wrong, but it is more or less useful. The bonding model of quadruple electron-sharing bonds for C_2 is not useful, because it does not agree with the properties of the molecule, while the donor–acceptor model does agree with them.

[15] The bonding and antibonding contributions of the occupied $2\sigma_g$ and $2\sigma_u$ orbitals do not completely cancel each other, because they can mix with the p(σ) AOs. The sp(σ) hybridization enhances the bonding character of the $2\sigma_g$ MO and reduces the antibonding character of the $2\sigma_u$ MO, which means that the effective formal bond order of the Hartree – Fock configuration (Figure 2a) is higher than two. A detailed discussion of the orbital interactions in diatomic molecules is given in: T. A. Albright, J. K. Burdett, M. H. Whangbo, *Orbital Interactions in Chemistry*, Wiley, New York, **1985**.

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