Why Does C₂ Cause so Many Problems?

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This small modest molecule has been the subject of a lot of attention over the past years as to what the bonding situation is between these two atoms, as can be seen from the selection of references given here [1–8]. To put it in very simple terms, there appear two main theories—a quadruple bond and not a quadruple bond (in fact somewhere in between two and three bonds). In the latest issue of *Chemistry—A European Journal*, four groups put forward arguments in favor of one or other of these two theories [9–12].

Dr. Anne Deveson has asked the main authors of these four papers, Professor Dieter Cremer (Southern Methodist University, Dallas, TX, USA), Professor Gernot Frenking (Marburg University, Germany), Professor Mario Piris (Euskal Herriko Unibertsitatea, Donostia, Spain), and Professor Sason Shaik (The Hebrew University, Jerusalem, Israel), to tell us why this is so important.

Please describe your findings in an easy to understand way.

Mario Piris: The carbon atom has four valence electrons and four valence orbitals. Consequently, carbon could unpair these four electrons by putting each one in a different valence orbital, or in each of the resulting four sp³ hybrid atomic orbitals. The pairing of each of the electrons of two adjacent carbon atoms could, in principle, result in a quadruply bonded dimer. However, the quantum mechanics of the molecular electronic structure puts in place other (subtle) effects that might result in a reduced bond order. Indeed, we found that C₂ bears a bond order intermediate between ethylene and acetylene.

Sason Shaik: Chemists think that a triple bond is the highest bond multiplicity for carbon. We show that C_2 has a quadruple bond that reproduces the bond energy, bond length, and force constant of the molecule.

Dieter Cremer: Other researchers claim that C_2 is a molecule with a quadruple bond. We cannot confirm this. It has unusual bonding in so far as its bonding is based on a π -double bond augmented with some weak σ bonding. But neither the bond multiplicity (measured by the bond order) nor the intrinsic bond strength support a bonding model based on a quadruple bond.

Why is it important to know?

Dieter Cremer: C_2 plays an important role in the catalyzed formation of fullerenes and carbon-nanotubes and is a frequent intermediate in combustion processes: The blue glow of hydrocarbon flames of Bunsen burners and gas hops results from C_2 . Apart from this, it has the peculiar property that its first excited state is just 2 kcal/mol above the ground state.

Gernot Frenking: Dimeric molecules of first octal-row atoms are cornerstones of elementary bonding models in chemistry. It is important to understand these models and their relationship to the nature of the interatomic interactions in order to give a reasonable description of molecular structures and reactivities. Among the first octal-row dimers, C₂ is the most interesting species, because the bonding situation cannot straightforwardly be described with a simple Lewis model.

Sason Shaik: The bonding in C_2 has been a longstanding enigmatic issue, with different Lewis structures being proposed, and calculated bond orders ranging from 2.2 to 3.76, depending on the method being used, and hence clearly not God-given. It became therefore necessary to settle the question by using Valence Bond Theory, which is the only method, among exact quantum theories, that directly describes a molecule in terms of Lewis structures.

What initiated your interest in C₂?

Mario Piris: We have been interested for a long time in the developing density matrix functional theory as an alternative to (electron) density functional theory for cases in which the latter fails. Homolytic bond dissociations and electronic structures with a large degree of static correlation are two such notable cases. The carbon dimer represents a system in which both such effects play a role. Consequently, we took it as a test case for assessing the reliability of our ground-state natural orbital functional theory developments.

Sason Shaik: The chemical bond is the heartland of chemistry. The fact that the community could not tell much about the bonding in an elementary molecule like C_2 was mindboggling. As such, our initiation was the need to understand and perhaps cause a paradigm shift ...

In your opinion, why is this topic so controversial?

Mario Piris: Because this is one neat example in which numbers (of various accuracies) yield not so different results, but radically different interpretations. This is embarrassing for theoreticians, and this is why it is so controversial. The fact that when theoreticians are asked "What is the bond order of the carbon dimer?", they find serious difficulties at giving a plain answer, clearly puts forward the need of the theory of providing sound insights ... supported by accurate numbers, a goal that nowadays may be within reach.

Gernot Frenking: Bond strength and bond multiplicity are elementary notions in chemistry. Calculations using molecular orbital (MO) and valence bond (VB) theory correctly reproduce the bond length and bond dissociation energy of C_2 and HCCH, but the interpretations of the results are conflicting. VB calculations suggest that C_2 has a longer and yet stronger C–C bond than acetylene, owing to the occurrence of a fourth bond, while the analysis of the MO calculations comes to the opposite conclusion. Clearly, a bond cannot at the same time be stronger

and weaker than another bond.

Dieter Cremer: Different aspects of chemical bonding are described in three ways:

i) By focusing on the bond multiplicity that is quantitatively assessed by the bond order.

ii) By focusing on the bond dissociation energy that is a reaction parameter and reflects the ease of breaking a specific bond in a molecule and depends on both the strength of a bond and all additional electronic effects increasing the stability of the reaction fragments.

iii) By focusing on the intrinsic strength of a bond, which is reflected by its local stretching force constant.

A) C_2 is discussed controversially because these three quantities (bond multiplicity, bond dissociation energy, and intrinsic bond strength) are often used indiscriminately in the discussion without realizing that different quantities are compared.

B) When carrying out highly accurate descriptions of C_2 , methods are used for which an accurate and generally accepted analysis of bond multiplicity, bond dissociation energy, or intrinsic bond strength are not available. This opens up the possibility of individual interpretations.

We avoided problems A) and B) by clearly distinguishing between the three quantities and by using established highly accurate methods for which a quantity such as the bond order or the local stretching force constant are well-defined. We believe that discussions such as that one on the bonding in C2 help to improve and/or develop generally accepted analysis methods for which this has not been done so far.

Sason Shaik: Four bonds in C2 is a new paradigm. Breaking rules is fun for some, a nightmare for others ...

Thank you very much.

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