

Curious or dubious: The story of a hydrocarbon with an exceptionally short C=C bond length

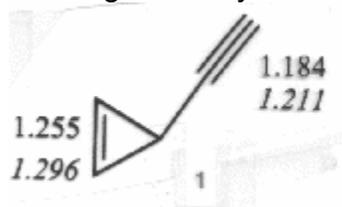
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One of the greatest achievements in molecular sciences this century has been the accurate determination of structures of a large number of chemical systems. While a variety of spectroscopic and diffraction methods have been used successfully for this purpose, X-ray crystallography has led the way. For the vast majority of chemists, single crystal X-ray structure determination represents the ultimate unimpeachable evidence for the proposed structure. The geometric details obtained through crystallography have also served as the basis for our present understanding of structural chemistry. These data represent an important source of parameterization as well as benchmarks for empirical theoretical models. The quality of quantum chemical procedures, which often use drastic approximations while solving the Schrödinger equation, has also been judged through comparisons of structural predictions with X-ray results.

Interestingly, in recent years, the roles seem to have been reversed. The accuracy of quantum chemical calculations is getting better all the time. And X-ray structure determination is not always devoid of problems, a fact well recognized by the best of professional crystallographers¹. It is now being suggested that artifacts in experiment may perhaps be identified through comparisons with computational studies. Not a pleasing prospect to many. A recent as yet unresolved controversy provides an example of arguments we may expect between cutting edge theory and experiment.

One always hopes to find something interesting with small ring systems and the rather innocuous hydrocarbon 3-ethynylcyclopropene (**1**) amply fulfills the expectations. The X-ray structure determined at 120 K by Baldrige *et al.*² revealed an unusual feature. While all the geometrical parameters were typical of the subunits present in the molecule, the double bond length in the ring was found to be exceptionally short. In fact, the value of 1.255 Å represents the shortest formal double bond ever measured crystallographically in a hydrocarbon.

Acceptor groups are known to reduce the remote bond length in cyclopropyl units, with many examples known from different types of experiments³. The elegant analysis of Hoffmann invoking the cyclopropane Walsh orbitals in inducing this structural distortion is textbook material in qualitative MO theory⁴. Even the simplest of theoretical methods reproduce this effect. However, the bond contraction in **1** is of a far greater magnitude. Baldrige *et al.* therefore chose to test what high level *ab initio* theory had to say regarding the C=C length in **1**. Using a variety of theoretical methods ranging from Hartree-Fock to correlated procedures and also density functional methods in conjunction with large basis sets including polarization functions, the calculated bond length was consistently larger, being in the range 1.27 to 1.30 Å. The authors concluded that the 'deviation could come from difficulties in approximating the orbital arrangement in **1**'.



This disturbing conclusion provoked Schleyer and Schaefer to bring to bear considerable computational power to solve the problem⁵. A sophisticated procedure with the acronym CCSD (T)/TZ2P + f was used, i.e. coupled cluster singles and doubles method including a perturbative triples correction in conjunction with a triple zeta basis set embellished with 2 sets of polarization functions and a set of *f* functions. This level has been shown to reproduce gas phase experimental bond lengths to within 0.008 Å, and the fact was again demonstrated with results for acetylene, methylacetylene and cyclopropene. Geometry optimization yielded a bond length of 1.2957 Å for the double bond in **1**. The key discrepancies between the experimental and *calculated* bond lengths are shown in the structure drawing.

Under these circumstances, it is customary to assume that theory is at fault. The best level is perhaps not good enough. However, this is unlikely in the present instance. The second serious charge against theory is that it refers to the gas phase and direct comparison with the solid state structure is strictly not tenable. It is true that significant differences between gas phase and condensed phase structures have been documented experimentally. A dramatic example involves the complex HCN-BF₃, for which the N-B distance differs by

0.84 Å between the gas phase (microwave) and solid state (X-ray)⁶. However, these differences occur in strongly polar systems with weak bonds. Furthermore, the gas phase structure as well as the changes due to the polar reaction field in the condensed phase are both adequately reproduced through calculations⁷. Strong medium effects are not expected in a nonpolar hydrocarbon like **1**.

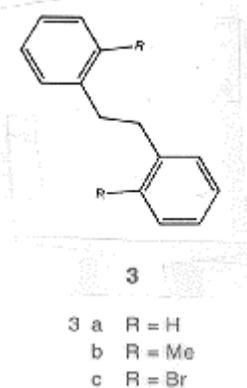
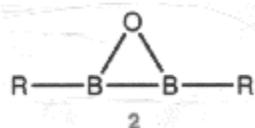
The needle of suspicion should therefore then turn towards experiment. The most common problems associated with X-ray structure determination are errors in space group assignment, errors in atom assignment and the presence of disorder and twinning in crystals. Marsh^{8,9} and Parkin¹⁰ have over the years highlighted many instances of incorrect structure determinations resulting from the above causes. Recently, Parkin has pointed out¹¹ a more subtle phenomenon. The least-squares refinement procedure may converge to a *false minimum*. A dramatic example of two fundamentally different structures which both yield an acceptably low *R* factor and well-behaved displacement parameters is provided in Figure 16 of a recent paper by Murphy *et al.*¹¹. However, this artifact is a consequence of the presence of a heavy atom in a polar space group. It appears unlikely that the crystal structure determination of **1** suffers from any of the problems mentioned here. The experimentalists, being seasoned campaigners, cannot be expected to be unaware of these issues. It is worth noting that many of the protagonists in this controversy have been involved in earlier skirmishes involving problems of structure determination. It is perhaps appropriate to recall a few examples.

The first oxadiborairane, **2**, was synthesized and characterized by X-ray crystallography by Boese and coworkers¹². Refinement led to a structure with nearly linear CBB units and B–O bond lengths of 1.545 and 1.510 Å. For the parent system, *ab initio* calculations predict a much shorter distance, ca. 1.40 Å. The calculations appear reasonable since the molecule is a formally 2p aromatic system. Boese did manage to get a structure with B–O lengths of 1.38 Å if allowance was made for disorder of the boron and oxygen atoms. However, the *R* factor was higher. Going by conventional wisdom, results were provided only for the structure with long B–O bonds. Subsequent higher level calculations by Schleyer *et al.*¹³ confirmed that the B–O bonds had to be shorter than what had been ‘observed’. Prompted by the theoretical evidence, Boese went back to the earlier structural model. Although the *R* factor could still not be used to unambiguously distinguish between the two possibilities, he was sufficiently convinced to revise the structure in favour of the one calculated. The paper¹³ concludes with a remarkable admonition: ‘when their results do not agree with high level *ab initio* calculations, experimentalists are encouraged to consider other possible interpretations of their data if this leads to better accord between theory and experiment’.

It is worth mentioning another debate concerning an unusually short bond for the possible resolution of the problem concerning the bond length in **1**. For over half a century, the central C–C bond in 1,2-diarylethanes (**3**) was thought to have an unusually short length, based on X-ray structures.

Jeffrey¹⁴ suggested that the central bond is short in all systems in which two unsaturated groups are separated by three single bonds. However, any orbital interaction involving the flanking p MOs with the central C–C bond can only lead to elongation¹⁵. This led Winter and coworkers¹⁶ to state that the central bond shortening results from ‘a so far unrecognized electronic effect of the p -systems’. The likelihood that the problem may entirely be in the X-ray structure was recognized by Kahr when he redetermined the structure of a derivative **3b** with two innocuous bromine substituents. The central length was 1.54 Å. Clearly, the substituent effect could not be that dramatic as to alter a distal bond length. In a collaborative effort with Siegel *et al.*¹⁷, a convincing case for the presence of an experimental artifact was made through comparison with theory. In contrast to all the crystal structures *ab initio* calculations at the HF/6-31G* level (now considered a modest level) yield a central bond length of 1.54 Å, as normal as can be.

The riddle was solved by Ogawa and coworkers¹⁸ by carrying out the structure determination of **3a** at several temperatures. The central bond length changes from 1.506 Å to the almost normal 1.529 Å as the crystal is cooled from 240 to 100 K. In the related dimethyl derivative **3c**, the distance is nearly normal in the entire temperature range. The results were interpreted in terms of limited intramolecular motion in the crystal. If the molecule is assumed to vibrate in a direction perpendicular to the plane made by the central four carbon



atoms, the average distance between the central carbon atoms will appear to be shorter than the actual value.

The above interpretation is not restricted to 1,2-diarylethanes alone. A similar explanation was invoked to account for the apparently short C=C bond lengths found through X-ray crystallography for stilbenes¹⁹. In general, molecules with fragments of uneven sizes may not pack uniformly tightly. Some parts may have greater room for large-amplitude motion. This in turn may affect geometrical parameters determined as averages. The same phenomenon may occur in **1**. The molecule has a rigid ring connected to a rod-like ethynyl unit. Movement of the latter much in the manner of a stick-shift in a car could tilt the cyclopropene unit back and forth. The average distance between the carbon atoms would appear shorter as a result. Large amplitude motion of the ethynyl fragment has been demonstrated earlier in a different structure²⁰. However, it must be pointed out that the structure analysis of **1** was performed at a fairly low temperature (120 K). Also, Baldrige *et al.* specifically ruled out elongated anisotropic displacement parameters in the direction of the double bond. Nevertheless, a careful examination of the thermal ellipsoids may still be useful.

Before indulging in further speculations on the origins of the failure of theory or experiment, it is perhaps preferable to first identify which one of them is wrong and by how much in the present case. This is best done using alternative experiments, rather than through additional higher level calculations. Neutron diffraction is one possibility. Another approach could be to persuade a synthetic chemist to make derivatives of **1**, preferably with a group which causes the least electronic and steric perturbation and to follow it up with low temperature X-ray structure determination.

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