3-Ethynylcyclopropene: a highly suspicious crystal structure

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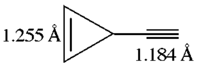
High level *ab initio* structures for 3-ethynylcyclopropene contain a typical cyclopropene C=C double bond of 1.296 Å, in sharp contrast to a recent X-ray structure in which the C=C double bond (1.255(2) Å) is purported to be the shortest yet observed among all hydrocarbons.

Baldridge *et al.* recently reported an X-ray crystal structure for 3-ethynylcyclopropene **1** in which the 'curiously short' 1.255 Å double bond is 'the shortest crystallographically observed C=C double bond known in any hydrocarbon.'[1] Their computed geometry at the spin restricted Hartree–Fock (RHF) level gave a double bond length of 1.27 Å, and inclusion of correlation effects *via* density functional theory† increased their best theoretical estimate to 1.28 Å, 0.03 Å longer than the experimentally inferred value. This discrepancy was not resolved. The authors suggested that the 'deviation could come from difficulties in approximating the orbital arrangement in **1**',[1] *i.e.* that their theoretical levels might not be definitive. Given this disturbing structural difference coupled with reassurances that crystal packing effects and high angle refinement procedures should have only a 'very small effect' in the X-ray structure,[1b] we investigated the structure of **1** using high level coupled cluster techniques.



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We optimized‡ the C_s structure of **1** using the coupled cluster singles and doubles method[8] with a perturbative triples correction [CCSD(T)][9,10] within a TZ2P + f basis set.§ For wavefunction expansions dominated by a single reference determinant, the CCSD(T) approach within a suitable basis set is well known to accurately reproduce structural parameters. At the level chosen, bond lengths between heavy (non-hydrogen) atoms within closed shell molecules are typically in error relative to gas phase experimental values by less than 0.008 Å.[16,17]

Comparison of the TZ2P + f/CCSD(T) and X-ray structures (Fig. 1) reveals a substantial difference in the double bond length and a smaller difference in the triple bond length of the ethynyl group. The *ab initio* double and triple bonds are respectively 0.041 and 0.027 Å longer than those of their X-ray counterparts. Indeed, the only structural parameters in good agreement are the single bond linkage of the ethynyl group and the majority of bond angles. The exceptional similarity of our TZ2P + f/CCSD(T) double and triple bonds to microwave values for the related fragment molecules in Fig. 2 (cyclopropene,[18] propyne,[19] and acetylene[18]) supports the study of substituent effects by Baldridge *et al.* in suggesting that there are no strong adjacent orbital interactions affecting either of these bonds in **1**. Indeed, the X-ray C=C cyclopropene distance in 3-vinylcyclopropene is 1.279 Å (0.024 Å longer than the X-ray distance in **1**).[20]

At every correlated level employed (Table 1) the double bond is more than 0.035 Å longer than experiment. Although the X-ray structure r_α is inherently different from the theoretical equilibrium geometry r_e, differences of this magnitude seem unlikely. Appreciable bond contraction is observed upon increasing the DZP basis to TZ2P with both the MP2 and CCSD(T) methods, and the convergence of these bonds with respect to the basis set was examined further at the MP2 level. However, additional polarization functions [TZ2P + f and TZ2P(f,d)] or even upgrading the basis set on carbon to quadruple-ς quality (cc-pVQZ/TZ) has only a small effect

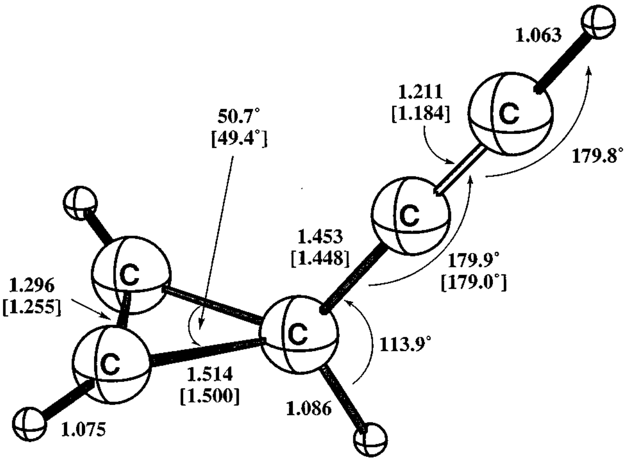
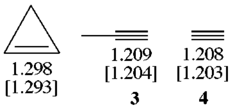


Fig. 1 The structure of 3-ethynylcyclopropene **1** optimized at the TZ2P + f/CCSD(T) level of theory. Bond lengths are in Å and bond angles are in degrees. Experimental bond lengths and angles are given in brackets.



2 **3** **4**

Fig. 2 Theoretical TZ2P + f/CCSD(T) and gas phase experimental [in brackets] bond lengths (Å) in cyclopropene (**2**), propyne (**3**), and acetylene (**4**).

Table 1 The double and triple bond lengths in **1** as a function of level of theory

Method	$d_{C=C}$/Å	$d_{C\equiv C}$/Å
DZP/RHF	1.2841	1.1973
TZ2P + f/RHF	1.2691	1.1840
DZP/BHLYP	1.2904	1.2066
DZP/B3PW91	1.3047	1.2200
DZP/B3LYP	1.3058	1.2207
DZP/MP2	1.3216	1.2387
DZP/CCSD	1.3168	1.2288
DZP/CCSD(T)	1.3233	1.2353
TZ2P/MP2	1.2957	1.2151
TZ2P/CCSD(T)	1.2981	1.2122
TZ2P + f/MP2	1.2939	1.2146
TZ2P(f,d)/MP2	1.2942	1.2145
(cc-pVQZ/TZ)/MP2	1.2899	1.2112
TZ2P + f/CCSD(T)	**1.2957**	**1.2112**
Experiment	**1.255(2)**	**1.184(2)**

(<0.006 Å) on these bonds, and a similar conclusion for CCSD(T) structures is expected.

Clearly, a high level theoretical equilibrium structure has been obtained which has no extraordinary features and differs dramatically from the X-ray geometry. What is the reason for this disagreement? Our computational reexamination at higher levels than employed earlier[1] increase, rather than decrease, the discrepancies with experiment. Hence, it seems unlikely that the theoretical predictions are incorrect. Solid state effects were considered by the experimentalists, but discounted.[1] Are inaccuracies in the X-ray structure possible? A referee (an expert crystallographer) reexamined the X-ray data in detail, but could find 'neither reasonable nor unreasonable problems with the original work.' Hence, no plausible explanation for the differences exist at present. Further insights will largely hinge on the availability of experimental gas phase data and future solutions of X-ray and neutron diffraction structures for related 3-substituted cyclopropenes.

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Notes and references

† Estimate based on results using the B3PW91 hybrid functional within DZ(2df,2p) and 8s6p3d basis sets. See ref.1.

‡ Methods used in this work include spin restricted Hartree–Fock (RHF), second order Møller–Plesset perturbation theory (MP2), density funnctional theory (DFT), CCSD and CCSD(T). No orbitals are frozen or deleted in the coupled cluster and MP2 procedures. The DFT functionals used are B3LYP, BHLYP and B3PW91 composed of permutations of the correlation functionals of Lee *et al.* (LYP)[2] and Perdew and Wang (PW91)[3] with the exchange functionals of Becke: (B3)[4] and (BH).[5] Stationary point structures are completely optimized within the C_s symmetry constraints using analytic gradient techniques until residual Cartesian coordinate gradients are less than 10^{-6} au. SCF quadratic force constants were determined *via* analytic second derivatives to establish stationary structures as minima. All computations were carried out using the ACESII[6] and Gaussian94[7] program packages.

§ Five basis sets are employed throughout this study. The smallest is a double-ς plus polarization (DZP) basis consisting of the standard Huzinaga–Dunning[11,12] set of contracted Gaussian functions with sets of five d-type and three p-type polarization functions from Dunning's correlation-consistent double-ς (cc-pVDZ) basis sets[13] added to the carbon and hydrogen atoms, respectively. A TZ2P basis set was formed from the Huzinaga–Dunning[11,14] sp sets augmented with two sets of polarization functions from Dunning's cc-pVTZ sets[13,15] (two sets of five d-type functions on C and two sets of p functions on H), and the TZ2P + f and TZ2P (f,d) basis sets include further sets of seven f-type functions ($\alpha = 0.761$) on C plus a set of five d-type functions ($\alpha = 1.057$) on H. The cc-pVQZ/TZ set contains Dunning's[13] cc-pVQZ and cc-pVTZ functions centered on the carbon and hydrogen atoms, respectively. The DZP, TZ2P, TZ2P + f, TZ2P (f,d), and cc-pVQZ/TZ basis sets contain 95, 156, 191, 211 and 331 contracted Gaussian functions, respectively.

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