X-Ray crystal and *ab initio* structure of 3-ethynylcyclopropene: a curiously short carbon–carbon double bond

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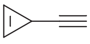
The X-ray crystal structure of 3-ethynylcyclopropene shows that the carbon–carbon double bond of the molecule is unusually short [1.255(2) Å], whereas theoretical calculations suggest a relative insensitivity of the bond length to adjacent orbital interactions.

Recent crystallographic studies of lightly-substituted cyclopropenes have illustrated the uncommon bonding modes in these small-ring hydrocarbons, such as formation of bent, banana-like bonds.[1,2] One of our groups recently reported the preparation of highly unsaturated analogs, such as 3-ethynylcyclopropene **1**,[3]



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and sought to investigate the solid-state structures of these compounds. In keeping with the extraordinary geometrical results, we report herein the X-ray crystal structure of **1** as well as model calculations to explain the experimental atomic distances for **1**.

Molecule **1** was prepared according to the literature method.[3] A single crystal (mp −94 °C) was grown using the low-temperature techniques described previously.[4,5] The structure analysis was performed at 120 K.¶ With intermolecular H··H separations of 2.73 Å or greater, the crystal packing of **1** is assumed not to cause significant distortions. The molecular structure and bond distances and angles are presented in Fig. 1 and Table 1, respectively. As expected, the sp^3 bond angle about C(1)–C(3)–C(2) is highly constrained, being only 49.4°. The most striking feature of the bond lengths found for **1** is the amazingly short C=C bond. At 1.255 Å, this value is midway between the accepted values of a typical double and triple bond.[6] The analogous bond length in structurally related 3-ethenylcyclopropene **2** is somewhat longer at 1.279 Å.[2b] All of the other bond lengths and bond angles of **1** are typical of their respective structural subunits. A systematic error in the measurement of the C(1)–C(2) bond distance is rather unlikely since the ellipsoids of the anisotropic displacement parameters are not elongated in the direction of the double bond.[7] In any case, the C(1)–C(2) bond length in **1** is the shortest crystallographically observed carbon–carbon double bond known in any hydrocarbon.[8]

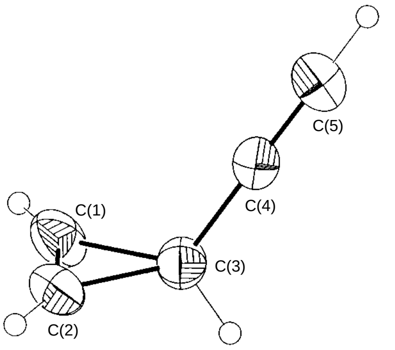
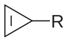


Fig. 1 Molecular structure of **1** with the ellipsoids drawn at the 50% level

Table 1 Interatomic distances and angles for **1**

Atoms	Distance/Å	Atoms	Angle (°)
C(1)–C(2)	1.255(2)	C(1)–C(2)–C(3)	65.2(1)
C(1)–C(3)	1.500(2)	C(2)–C(1)–C(3)	65.4(1)
C(2)–C(3)	1.502(2)	C(1)–C(3)–C(2)	49.4(1)
C(3)–C(4)	1.448(2)	C(1)–C(3)–C(4)	121.4(1)
C(4)–C(5)	1.184(2)	C(2)–C(3)–C(4)	121.4(1)
		C(3)–C(4)–C(5)	179.0(1)



2 R = $CH{=}CH_2$
3 R = NO_2
4 R = CHO
5 R = C≡N
6 R = Me
7 R = H
8 R = F
9 R = NH_2

In order to gain some insight into the nature of the cyclopropene structural fragment, a series of 3-monosubstituted cyclopropenes **2**–**9** was calculated in addition to **1**.[9] We first surveyed the variation in length of the C=C bond with regard to computational method (Table 2). Convergence in RHF methods is around a value of 1.27 Å; the effects of increasing basis set size was minimal. The effects of dynamic correlation were tested using a variety of techniques, including density functional techniques, Moller–Plesset theory of order 2 and the coupled cluster doubles method. The effect of each technique can be identified by focusing on the different dynamic correlation methods using the same basis set [DZ(2df,2p)]. Dynamic correlation of any type tends to increase the predicted bond length from the restricted Hartree–Fock method. Centering on the hybrid method of including dynamical correlation, and further increasing basis set size, one arrives at a convergent value for the double bond length around 1.28 Å, 0.03 Å longer than experiment. We feel it is unlikely that higher level calculations will decrease the bond length any nearer to the experimental value; thus, our best estimate of equilibrium bond length is 1.28 Å.

Given the result of the basis set analysis on **1**, we opted for a highly polarized basis set available in CADPAC, and performed computations on **1**–**9** using RHF/8s6p3d and B3PW91/8s6p3d methods (Table 3). The range of computed double bond lengths is only 0.02 Å, indicating a weak sensitivity of C(1)–C(2) length with regard to the C(3) substituent. The addition of dynamic electron correlation increases the predicted bond lengths uniformly by *ca.* 0.015 Å across the series, and makes no change in the trend. The experimentally measured value for **2** (1.279 Å) is well-bracketed by the computational predictions, but the values predicted for **1** are 0.01–0.02 Å longer than that

Table 2 The double bond length in **1** as a function of computational method

Method	Bond length/Å
RHF/6-31G(d,p)	1.2722
RHF/6-31GE	1.2749
RHF/DZ(2df,p)	1.2749
RHF/DZ(2df,2p)	1.2740
RHF/DZ(3df,3pd)	1.2704
RHF/8s6p3d	1.2710
BPW91/6-31GE	1.3022
BPW91/DZ(2df,2p)	1.3036
B3PW91/6-31G	1.3015
B3PW91/DZP	1.3003
B3PW91/6-31GE	1.2923
B3PW91/DZ(2df,2p)	1.2930
B3PW91/8s6p3d	1.2838
B3LYP/8s6p3d	1.2833
MP2/6-31G(2d,p)	1.3029
MP2/DZ(2df,2p)	1.3016
CCD/DZ(2df,2p)	1.2951
Experiment	1.2550

Table 3 C(1)–C(2) distance calculated for **1**–**9**

Compound	R	Distance/Å	
		RHF/8s6p3d	B3PW91/8s6p3d
3	NO_2	1.279	1.295
4	CHO[a]	1.265	1.279
	CHO[b]	1.263	1.278
5	C≡N	1.267	1.283
1	C≡CH	1.268	1.284
2	$CHCH_2$[a]	1.270	1.285
	$CHCH_2$[b]	1.270	1.286
6	Me	1.273	1.289
7	H	1.271	1.287
8	F	1.283	1.300
9	NH_2[c]	1.273	1.289
	NH_2[d]	1.274	1.290
average		1.271	1.287
standard deviation		0.006	0.006
range		0.020	0.022

[a] *anti* conformer (C_s symmetry). [b] *gauche* conformer (C_1 symmetry). [c] Lone pair *syn* (C_s symmetry). [d] Lone pair *anti* (C_s symmetry).

observed experimentally. This deviation could come from difficulties in approximating the orbital arrangement in **1**, even by the extreme basis sets we are using.

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Notes and References

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¶ *Crystal data* for **1**: C_5H_4, M = 64.0876, cylindric single crystal of 0.3 mm diameter, a = 8.731(3), b = 6.169(3), c = 7.981(3) Å, β = 110.13(3)°, V = 403.6(3) Å^3 (from 30 refined reflections in the range of $20 < 2\theta < 25°$), 120 K, monoclinic, space group $P2_1/c$, Z = 4, ρ_{calc} = 1.055 g cm^{-3}, Mo-Kα radiation, μ = 0.06 mm^{-1}, 1164 data collected ($2\theta_{max}$ = 60°), 952 unique reflections (R_{merg} = 0.011), 718 observed [$F_o \geqslant 4\sigma(F)$], correction for a cylindrical crystal, structure refinement (C atoms anisotropic, H atoms isotropic without constraints, no extinction correction) with Siemens SHELXTL-PLUS (Ver. 4.2), 63 parameters, R = 0.0399, R_w = 0.0412, $w^{-1} = \sigma^2(F_o) + 0.0003F_o^2$, maximum residual electron density of 0.17 e Å^{-3}. CCDC 182/864.

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7 With high bond orders, *e.g.* triple bonds, X-ray methods tend to determine bond distances too short because in the refinement procedure the atom positions are shifted towards the bonding electrons. In such cases the ellipsoids are streched in the bonding direction; however, this is not the case with **1** (Fig. 1). This effect can be reduced by high angle refinements or applying a weighted scheme which increases the weights for high angle data. In our case this had only a very small effect.

8 A search of the Cambridge crystallographic data base revealed the previous record holder of shortest C=C bond in a hydrocarbon to be 3-ethenylcyclopropene **2** [ref. 2(*b*)].

9 Reported here are Restricted Hartree–Fock (RHF), density functional (DFT), hybrid density functional (HDFT), Moller–Plesset perturbation theory (MP2) (ref. 10) and coupled cluster doubles (CCD) (ref. 11) theories. These calculations were performed using CADPAC (ref. 12) and GAUSSIAN94 (ref. 13) programs. Basis sets are reported including 6-31G(ndqf,mp) (ref. 14), 6-31GE, DZ(nd,mp), (ref. 15) and the 8s6p3d basis set, where the number of f functions (q = 0–1), d functions (n = 0–3) and p functions (m = 0–3). The 6-31GE and 8s6p3d basis sets are special to CADPAC. The former basis is obtained from the 6-31G basis by (i) adding diffuse s and p functions with exponents 1/3 that of the lowest exponent in the parent basis, and (ii) using two sets of polarization functions, which are slightly on the diffuse side. The result is a basis set between DZP and TZ + 2P type basis sets in quality which is biased towards property calculations. The latter basis is one of the largest polarized double-z sets used in this study. The DFT method employed was Beck's 1988 functional (ref. 16) along with Perdew and Wang's 1991 gradient-corrected correlation functional (ref. 17), denoted BPW91. The HDFT method includes a mixture of Hartree–Fock exchange with DFT exchange-correlation, denoted B3PW91. This is Becke's 3 parameter functional (ref. 18) where the nonlocal correction is provided by the Perdew 91 expression (ref. 17). A B3LYP [correlation functional including both local and nonlocal terms provided by Lee, Yang and Parr (refs. 18, 19)] calculation is done for comparison purposes. The nature of each stationary point was uniquely characterized by analytically calculating and diagonalizing the matrix of energy second derivatives (Hessian) to determine the number of imaginary frequencies.

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