Structure of Triplet Propynylidene

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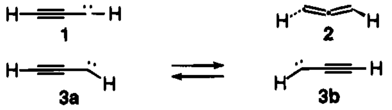
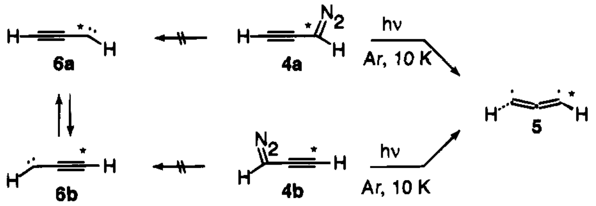
As part of our ongoing effort to understand electronic delocalization in open-shell, conjugated π-electron systems,[1] we describe experimental and theoretical studies of triplet H–C–C–C–H. This species is often referred to as propargylene or propynylidene, in reference to its structural formulation as the parent acetylenic carbene.[2] A 1,3-allenic diradical structure is also possible. Early experimental evidence (ESR) suggested a linear carbenic structure (**1**) for HC_3H.[3] Early theoretical studies at the STO-3G level suggested an allenic diradical structure (**2**, C_2),[4] but later studies incorporating Møller–Plesset treatment of electron correlation favored a bent carbenic structure (**3**, C_s).[5] One important consequence of a bent carbene structure is the possibility that the system could exhibit bond-shift isomerism (e.g., **3a** $\rightleftarrows$ **3b**). Recent claims of bond-shift isomerism in acetylenic carbenes[6] have been brought into question,[1] however. When a more sophisticated treatment of configuration interaction (QCISD/6-31G*) is used, theory accurately reproduces the experimental infrared spectrum of HC_3H in terms of a bent 1,3-allenic diradical structure (**2**, C_2).[7] The discrepancy with the ESR experiment remains, as does the controversial notion of bond-shift isomerism. We now report mechanistic and spectroscopic evidence that resolves earlier discrepancies between various pieces of experimental and theoretical data. In addition, an analysis of the QCISD/6-31G* wave function for HC_3H in terms of natural resonance theory[8] provides insight into the electronic structure of this highly unusual species.



We utilized ^{13}C-labeling studies in conjunction with matrix-isolation spectroscopy to distinguish between localized, equilibrating carbenes (C_s) and a bent 1,3-allenic diradical (C_2). As a prelude to the isotopic labeling experiments, we obtained the IR, UV/vis, and ESR spectra of unlabeled HC_3H upon photolysis (λ > 472 nm) of diazopropyne, matrix-isolated in argon at 10–15 K.[9,10] The IR spectrum shows excellent agreement with the spectrum reported by Maier.[5b] The UV/vis spectrum of triplet HC_3H has not been reported previously.[11] The triplet ESR spectra obtained in Ar, N_2, or CH_4 exhibit much higher resolution than Skell's original spectrum,[3] which was obtained in poly(chlorotrifluoroethylene). Given the higher resolution, we are able to distinguish the triplet in two distinct sites in each matrix (Figure 1a).[12–15] The distinct matrix sites observed in the ESR experiments could not be resolved by IR or UV/vis spectroscopy.

In the key experiments, photolysis (λ > 472 nm) of either [1-^{13}C]diazopropyne (**4a**) or [3-^{13}C]diazopropyne (**4b**),[10] matrix-isolated in argon at 10–15 K, produces identical IR and ESR spectra.[16] This could be taken as evidence that both precursors yield a single species or that each precursor yields an equilibrium mixture of two (or more) species. Two lines of evidence argue in favor of a single species:



(1) The experimental IR spectrum exhibits excellent agreement with the IR spectrum computed for H–^{13}C–C–C–H (**5**, C_2) at the QCISD/6-31G* level and does not exhibit good agreement with the IR spectrum computed for a 1:1 mixture of H–C≡C–^{13}C–H and H–C–C≡^{13}C–H (**6a**, **6b**, C_s) at the MP2/6-31G* level (Table 1). Specifically, the computed spectrum for the mixture of C_s isomers exhibits very poor agreement with the observed C–H stretching vibrations.

(2) The ^{13}C-hyperfine coupling observed in the triplet ESR spectrum (Figure 1b) is consistent with a single species (**5**) and is inconsistent with a mixture of two species (**6a, 6b**). Even though the spectrum is quite complex because of both hyperfine coupling and the presence of two matrix sites, we obtain an excellent simulation of the X_2 and Y_2 region of the spectrum by simply applying a *single* hyperfine coupling to the triplet ESR spectrum derived from the unlabeled isomer (Figure 1c).[17,18] A hyperfine coupling constant of 38 G provides the best fit. The simulation thus provides strong evidence that the ESR spectrum arises from a *single* species. Attempts to simulate the spectrum

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[9] Propynylidene (**2**): IR (Ar, 10 K) 3265 (m), 1621 (w), 550 (m), 403 (w), 249 (s), 246 (m) cm^{-1}; UV/vis (Ar, 10 K) 210, 236, 240, 247, 252, 260, ca. 315 (broad absorption exhibiting vibronic fine structure) nm; ESR (Ar, 15 K) (major matrix site) $|D/hc| = 0.640$ cm^{-1}, $|E/hc| = 0.000\,977$ cm^{-1}, $Z_1 = 3445$, $X_2 = 5877$, $Y_2 = 5921$, $Z_2 = 10\,238$ G, microwave frequency, 9.5318 GHz.

[10] Diazo compounds were prepared by pyrolysis of the corresponding tosylhydrazone sodium salts. For details of the matrix-isolation experiment, see: Seburg, R. A.; McMahon, R. J. *J. Am. Chem. Soc.* **1992**, *114*, 7183–7189 and references therein.

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[16] [1-^{13}C]Propynylidene (**5**): IR (Ar, 8 K, from both **4a** and **4b**) 3273 (w), 3257 (m), 1612 (w), 547 (w), 400 (w) cm^{-1}; ESR (Ar, 15 K, from **4a**) $|D/hc| = 0.641$ cm^{-1}, $|E/hc| = 0.001\,30$ cm^{-1}, microwave frequency = 9.5322 GHz.

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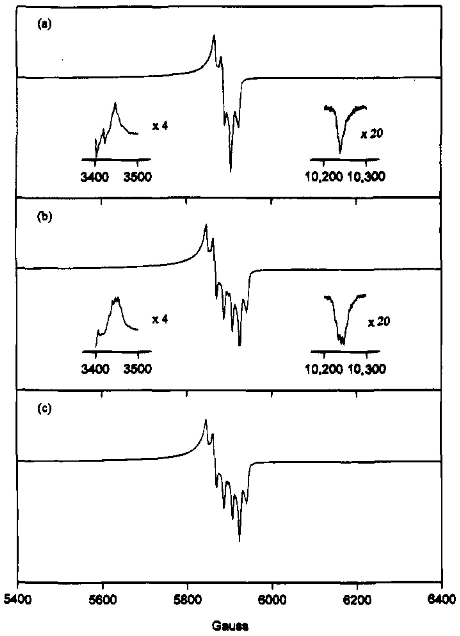


Figure 1. (a) ESR spectrum of propynylidene (**2**) obtained upon photolysis (>472 nm) of diazopropyne, matrix-isolated in argon at 15 K. (b) ESR spectrum of [1-^{13}C]propynylidene (**5**) obtained upon photolysis (>472 nm) of [1-^{13}C]diazopropyne (**4a**), matrix-isolated in argon at 15 K. (c) Simulated ESR spectrum of [1-^{13}C]propynylidene (**5**).

Table 1. Experimental and Computed Infrared Spectra of H−^{13}C−C−C−H[a]

exptl	(**5**) QCISD/6-31G*	(**6a**) MP2/6-31G*	(**6b**) MP2/6-31G*
3273 (1.00)	3424 (1.00)	3538 (3.38)	3524 (3.40)
3257 (5.48)	3410 (1.71)	3421 (0.97)	3433 (0.98)
1612 (0.80)	1618 (1.67)	1663 (3.09)	1637 (3.16)
	1244 (0.01)	1207 (1.16)	1225 (1.06)
547 (2.22)	503 (1.91)	553 (1.31)	557 (1.15)
400 (1.11)	425 (0.43)	529 (3.08)	527 (3.29)
	413 (1.43)	472 (0.96)	473 (0.95)

[a] Positions in cm^{-1}; relative intensities are given in parentheses. Positions for computed spectra are uncorrected. Relative intensities were obtained by dividing computed intensity (in Kubelka−Monk units) by 17.2.

using *two* hyperfine coupling constants (e.g., a larger coupling constant arising from **6a** and a smaller coupling constant arising from **6b**) provide extremely poor fits to the experimental spectrum.

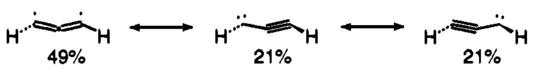
ESR data are frequently used to estimate the bond angle at the "carbene" carbon via two qualitatively different approaches. Equation 1 describes the relationship between the isotropic component of the ^{13}C-hyperfine coupling constant (A_i) and the bond angle (θ) at the carbene carbon.[13,14,19] Equation 2 describes the relationship between the zero-field splitting parameters (D, E) and the bond angle (θ) at the carbene carbon.[13]

$$A_i = {}^1/_2[(1 + \cos\theta)/(1 - \cos\theta)](1191\ \mathrm{G}) \qquad (1)$$

$$(E/D) = [\cos^2(\theta/2)]/[2 - 3\cos^2(\theta/2)] \qquad (2)$$

Our ^{13}C-labeling experiment provides an isotropic hyperfine coupling constant $A_i = 29$ G, which corresponds to a bond angle of 155°.[20] The zero-field splitting parameters $|D/hc| = 0.640$ cm^{-1} and $|E/hc| = 0.000\,977$ cm^{-1} correspond to a bond angle of 174°. The significant discrepancy between these two methods immediately confirms Wasserman's suggestion that the molecule undergoes rotational motion in the matrix.[4] The rotational motion perturbs the zero-field splitting parameters from their true, static values,[4,13−15] thus rendering the analysis via eq 2 inappropriate. The analysis via eq 1 is independent of motional effects.[13,14] Therefore, we take the value of 155° as the properly determined experimental quantity for the C−C−H bond angle in triplet propynylidene (**2** and **5**). This value is subject to the assumptions inherent in the method of analysis[12] but is in good agreement with the value of 153° computed at the QCISD/6-31G* level by Herges and Mebel.[7]

Analysis of the QCISD/6-31G* wave function for HC_3H in terms of natural resonance theory (NRT) provides insight into the electronic structure of this unusual molecule. NRT is a method of analyzing a molecular orbital wave function and determining the important valence bond representations (i.e., resonance structures) for that wave function.[8] The NRT analysis describes the triplet ground state of HC_3H predominantly in terms of one resonance contributor exhibiting 1,3-diradical character and two resonance contributors exhibiting carbene character.[21] Although previous efforts to characterize "propynylidene" attempted to distinguish between diradical and carbene structures, the NRT analysis suggests that the true structure of HC_3H is described not in terms of one or the other but as a nearly equal mixture of the two!



In summary, IR spectroscopy, ESR spectroscopy, and ab initio calculations are all consistent with a C_2 structure for triplet propynylidene (**2**). The zero-field splitting parameters obtained from the triplet ESR spectrum are subject to motional averaging. Wobbling of the molecule about the long axis results in an anomalously small value of E, which led earlier workers to the erroneous conclusion that the molecule is axially symmetric (i.e., linear).[3] The conventional wisdom[2] that "triplet acetylenic carbenes are linear" is thus incorrect in the case of the parent system.

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Supplementary Material Available: Experimental procedures for the synthesis of diazo compounds and tosylhydrazone precursors (17 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(17) Simulation and plotting were carried out using SigmaPlot for Windows. The magnetic field axis of the digitized ESR spectrum of unlabeled propynylidene was offset by $\pm(A/2)$, where A is the hyperfine coupling constant (in gauss). The two data files were then added to provide the simulation of the ^{13}C-labeled isomer. The value of A was varied to obtain the best fit to the experimentally observed spectrum.

(18) Because of the relatively large C−C−H bond angle (*vide infra*), the hyperfine coupling in the Z_1 and Z_2 transitions is small and therefore not resolved; the coupling appears as a broadening of the signal.

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(20) $A_i = {}^1/_3[A_x + A_y + A_z]$.[12,19] A_x (38 G) and A_y (38 G) are obtained from the simulation. We used an upper limit for A_z (10 G), based on the assumption that we could resolve any hyperfine coupling greater than this value. Although the values of A_x, A_y, and A_z may not be diagonalized principal components of the hyperfine interaction tensor, and although the **g**, **D**, and **A** tensors may be noncollinear, the value of the isotropic component, A_i is not affected: Golding, R. M.; Tennant, W. C. *Mol.Phys.* **1973**, *25*, 1163−1171. Also ref 19.

(21) No other single resonance structure contributes more than 1% to the resonance hybrid.