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Phenylethynyl: Matrix Isolation Electron Spin Resonance and Molecular Orbital Study

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Electron spin resonance spectra of phenylethynyl radical generated in argon matrices were examined. Spectral analysis showed that the radical is a π radical $\mathrm{Ph\dot{C}{=}C{:}}$ as had been found earlier for the same radical generated in solution. An EHT-MO study of phenylethynyl not only elucidated the crossing of its σ and π radical states but also explained the unusually large anisotropy of its **g** tensor.

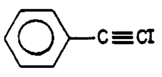
Introduction

When a peripheral σ bond is cleaved homolytically off an aromatic molecule or an olefinic system, a question of interest is whether the resulting radical remains as a σ radical in which the unpaired electron stays in the nonbonding, "broken" σ orbital, or becomes a π radical as a result of an electron transfer from the highest occupied π orbital into the cleaved σ bond. Earlier electron spin resonance (ESR) studies of phenyl and other larger aryl radicals demonstrated that these radicals remain as σ radicals.[1,2] A theoretical study showed that the factor most deterrent for transfer of a π electron into the semifilled σ orbital is a large electron–electron repulsion term expected if the relatively localized σ bond becomes doubly occupied.[2] It has been shown that ethynyl, $\mathrm{HC{\equiv}C\cdot}$,[3-5] and cyanogen, $\mathrm{N{\equiv}C\cdot}$,[6,7] radicals are also σ radicals.

Coleman et al., however, showed that the phenylethynyl radical is a π radical.[8] Their conclusion was based on an isotropic ESR spectrum of the radical observed upon UV irradiation of supercooled phenyliodoacetylene. We report here ESR spectra of phenylethynyl radicals trapped in argon matrices at ~4 K and results of molecular orbital calculations (EHT and INDO) of the radical. The powder pattern spectrum affirmed the π state of the radical but also revealed an unusually large **g** tensor anisotropy. The molecular orbital study not only elucidated the nature of the σ and π level crossing but also offered an explanation for the anisotropy of the **g** tensor.

Experimental Section

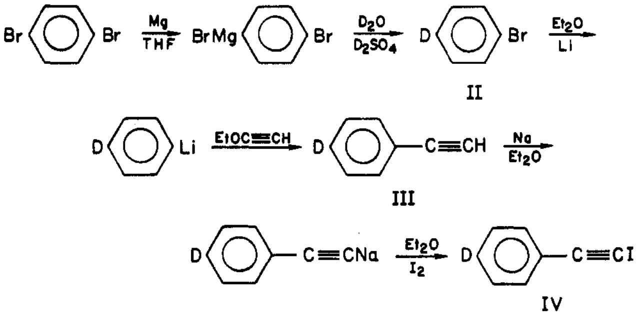
Detailed description of an experimental setup which would permit trapping of vapor-phase species in an argon matrix, photolysis of the trapped species, and observation of the ESR spectrum of the resulting radicals has been reported previously.[9] In the present series of experiments phenylethynyl radicals were produced by photolysis of phenyliodoacetylene (I). A high-pressure Xe–Hg arc lamp (Oriel, 1 kW) equipped with a UV filter (Corning, 7–54) was used for this purpose. All the spectra reported here were obtained while the matrix was maintained at ~4 K. The frequency of the spectrometer locked to the sample cavity was 9.425 GHz.



I

Phenyliodoacetylene (I) was prepared from the phenylacetylene by the procedure of Nef.[10] The product was distilled at reduced pressure and the pure fraction was collected at 55 °C (0.05 mm), literature value 117 °C (15 mm). The colorless oil showed no aliphatic peaks in its ^{1}H NMR spectrum.

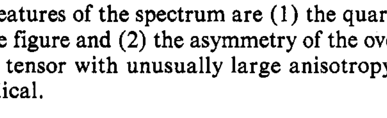
p-Deuteriophenyliodoacetylene (IV) was prepared starting from *p*-dibromobenzene following the scheme



1-Bromo-4-deuteriobenzene (II) was prepared by a procedure adopted from that given by Gilman.[11] The indicated Grignard reagent was hydrolyzed in deuterium oxide acidified with D_2SO_4. *p*-Deuteriophenylacetylene (III) was prepared from *p*-deuteriophenyllithium by reacting with ethoxyacetylene by the method described by Kooyman.[12] It was obtained in 62% yield: bp 142–143 °C, $n_D^{20} = 1.5524$. α-(*p*-Deuteriophenyl)-β-iodoacetylene (IV) was prepared from (III) by the method of Nef[10] as indicated.

Spectra and Assignments

Figure 1a shows the ESR spectrum observed when I was trapped in an argon matrix and photolyzed. The spectrum is assigned to the phenylethynyl radical.



Conspicuous features of the spectrum are (1) the quartet pattern indicated in the figure and (2) the asymmetry of the overall signal indicating a **g** tensor with unusually large anisotropy for a hydrocarbon radical.

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TABLE I: Assessed g and Hyperfine Coupling Tensors of Phenylethynyl[a]

	x	y	z	A_{iso}[b]	$\lvert A_{iso}\rvert$[e]	A_{iso}[c] INDO(π)	A_{iso}[c] INDO(σ)
g	2.0038	2.0080	2.0023				
$A(H_o)$, G	-2.0	-5.0	-3.5	-3.5	2.22	-5.51	+1.44
$A(H_m)$, G	NR[d]	NR	NR		0.81	+3.12	-0.06
$A(H_p)$, G	-2.0	-5.0	-3.5	-3.5	2.16	-5.50	+0.48

[a] Accuracies: ±0.0002 for g and ±0.2 G for A. [b] This work. Determined by $A_{iso} = (A_x + A_y + A_z)/3$. [c] Predicted by INDO calculation (see text). [d] NR = not resolved. [e] Reference 8.

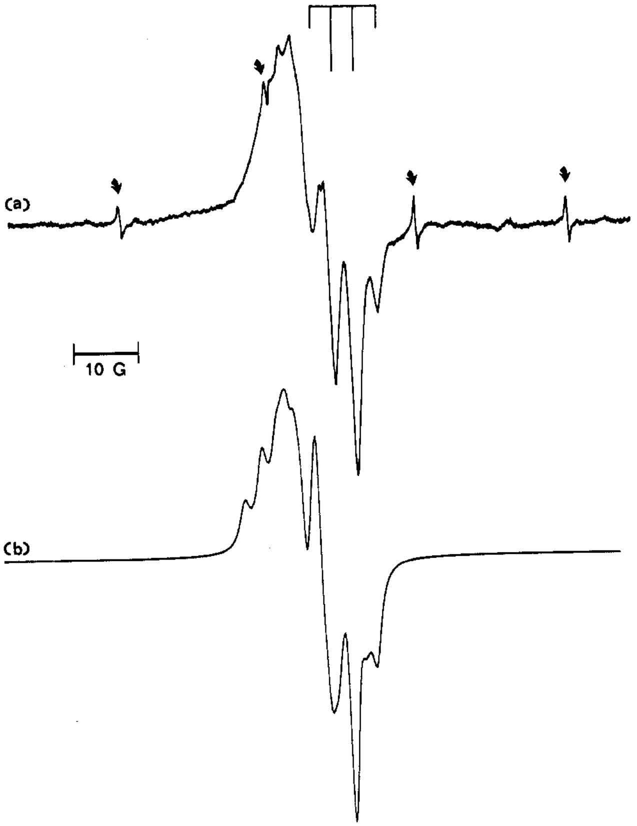
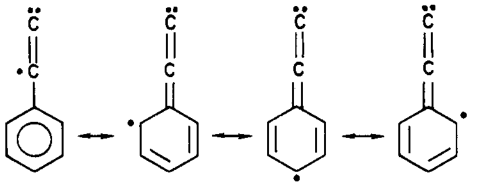


Figure 1. ESR spectra of phenylethynyl radicals generated in an argon matrix: (a) observed and (b) simulated based upon the assignment given in Table I. The magnetic field increases from left to right. The solid arrows in (a) indicate the quartet due to methyl radicals.

The quartet pattern appears to possess a 1:3:3:1 intensity ratio indicating hfc (hyperfine coupling) constants of equal magnitude to three protons. The symmetry consideration dictates that one of them must be the para proton. If the phenylethynyl radical were a σ radical, where the spin density is localized on the terminal carbon, the hfc constant to the para proton must be much smaller than those of other protons. In the case of phenyl radical, for example, the isotropic hfc constants to the ortho, meta, and para protons are 17.4, 5.9, and 1.9 G, respectively.[1] The phenylethynyl radical trapped in argon matrix must hence be a π radical as concluded by Colemann et al.[8] for the same radical generated in solution.

The principal valence bond structures of phenylethynyl are thus



and the quartet with the successive spacing of 3.5 G is assigned to the ortho and para protons. To substantiate the assignment, the experiment was repeated with *p*-deuteriophenyliodoacetylene. A triplet with the same spacing of 3.5 G was observed in place of the quartet (Figure 2).

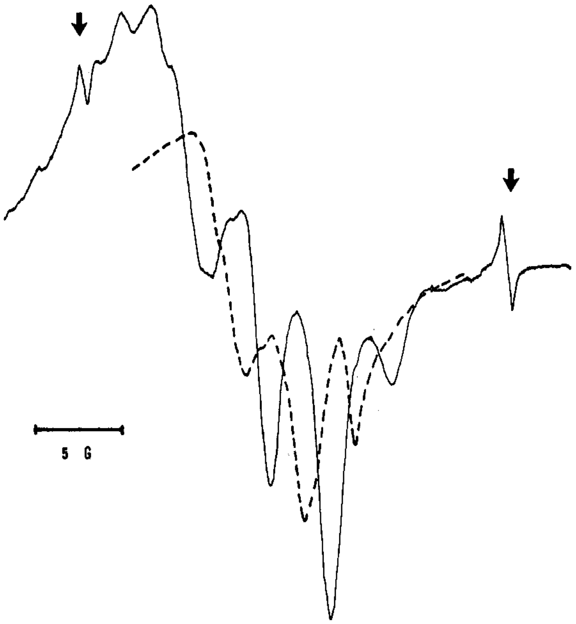


Figure 2. ESR spectra of *p*-deuteriophenylethynyl (dotted line) and the normal species (solid line) compared in an expanded scale. The magnetic field increases from the left to right. The arrows indicate the inner components of the methyl quartet.

It is essential to realize, however, that the directions of the principal axes of the hfc tensors of these protons as well as those of the g tensor are different from each other within the plane of the radical. The observed quartet (or the triplet) is thus expected to occur only in the direction perpendicular to the molecular plane. It has been shown that, for a π radical, the diagonal elements of the principal hfc tensor of a peripheral proton can be approximately given by the following:[13,14]

$$A_{\parallel} = -12.0\rho_c \text{ G}$$

$$A_{\perp,\parallel} = -22.0\rho_c \text{ G}$$

$$A_{\perp,\perp} = -35.0\rho_c \text{ G}$$

Here ρ_c is the spin density at the carbon to which the proton is attached, and $A_{\perp,\parallel}$, for example, is the component perpendicular to the C–H bond but parallel to the p_π orbital of the carbon. The resolved 3.5-G spacing is thus assigned to $A_{\perp,\parallel}$, and the remaining components can be estimated from these expressions. A computer program that would simulate the ESR spectrum of randomly oriented radicals possessing anisotropic g and hfc tensors has been described.[14] The program takes into account the orientation of each principal hfc tensor relative to that of the g tensor. Figure 1b is the computer-simulated spectrum based upon a Lorentzian line shape with the line width of 1.8 G, the hfc elements estimated above, and the g tensor adjusted for the best fit. The elements of the g tensor and the principal hfc tensors of the ortho and para protons thus determined are shown in Table I. Conventions (or assumptions) adopted are (1) the *z* axes of all the tensors are perpendicular to the molecular plane, (2) the *x* axes of the g tensor and the para-proton hfc tensor coincide with the symmetry axis

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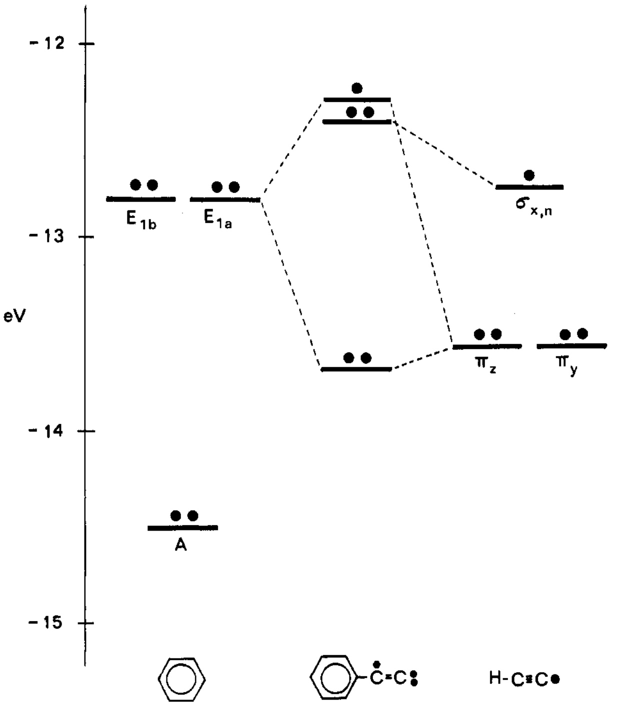
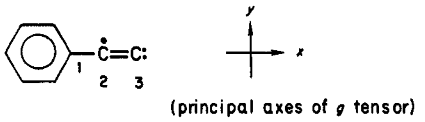


Figure 3. Energy levels of occupied π orbitals of benzene, the occupied π and semifilled σ orbitals of ethynyl, and their correlations to orbitals in phenylethynyl.

of the radical (see below), and (3) the x axes of the ortho-proton hfc tensor make an angle of ±60° with the symmetry axis.



Discussions

Molecular orbitals of phenylethynyl may be thought to comprise those of the benzene system and those of the ethynyl moiety. It should be illustrative to examine the energy levels of the occupied π orbitals of benzene, the occupied π and semifilled σ orbitals of ethynyl, and their correlations to orbitals of phenylethynyl. This was done by the EHT (extended Hückel theory) molecular orbital method.[15] (see Figure 3). Symmetry consideration and the proximity of the energy levels suggest that, when phenylethynyl is formed, the largest amount of mixing among these orbitals would occur between the π_z orbital of ethynyl and the E_{1a} π orbital of the phenyl system. The antisymmetric combination of these orbitals may lead to formation of the highest occupied, hence semifilled, orbital in the combined system. As indicated in the figure examination of the eigenvalues and the eigenfunctions revealed this is indeed the case. The structural parameters used for the calculation are $r(C_1–C_2) = 1.35$ Å and $r(C_2–C_3) = 1.30$ Å. For the phenyl part all the C–C bonds are assumed to be 1.40 Å and all the C–H bonds 1.10 Å.

Most significantly, when the interaction between the π_z orbital of ethynyl and the E_{1a} π orbital of benzene was reduced by assuming the normal single bond distance (1.45 Å between sp^2- and sp-hybridized carbon atoms) and triple bond distance (1.20 Å) for $r(C_1–C_2)$ and $r(C_2–C_3)$, respectively, the EHT calculation predicted the σ radical state for phenylethynyl.

It has been shown that, for a radical with a nondegenerate ground state $|0\rangle$, deviation of the g tensor from the spin only value g_e (= 2.0023) is given by eq 1.[16] Here i (= x, y, z) represents

$$\Delta g_i = -2\lambda \sum_{n\neq 0} \frac{\langle 0|L_i|n\rangle\langle n|L_i|0\rangle}{E_n - E_0} \tag{1}$$

an axis of the principal **g** tensor, λ the spin–orbit coupling constant, and L_i the orbital angular momentum operator. $E_n - E_0$ is the energy separation between the ground state $|0\rangle$ and an excited state $|n\rangle$ into which the unpaired electron may be promoted via the spin–orbit coupling interaction. In the EHT description, the ground state $|0\rangle$ of phenylethynyl is given by a linear combination of the p_z orbitals of carbon atoms. Equation 1 then immediately states that $\Delta g_z = 0.0$. The largest deviation is expected in the y direction since the smallest energy separation exists between the semifilled π orbital and the nonbonding lone-pair σ orbital. The latter orbital consists mainly of the p_x orbital of the terminal carbon. The assessed **g** tensor (Table I) is in perfect accord with these conjectures.

For a hydrocarbon radical where only the 1s orbital of hydrogen atoms and 2s and 2p orbitals of carbon atoms need to be considered in its molecular orbitals, evaluation of eq 1 in terms of the eigenfunctions and eigenvalues obtained by the EHT method is straightforward. When all the two-center integrals are neglected, it reduces to the following:

$$\Delta g_i = -2\lambda \sum_{n\neq 0}^{\text{MO's}} \frac{[\sum_{\alpha}(C^0_{\alpha k}C^n_{\alpha j} - C^0_{\alpha j}C^n_{\alpha k})]^2}{E_n - E_0} \tag{2}$$

The subscripts i, j, and k stand for the three principal axes, and $C^n_{\alpha k}$, for example, is the coefficient of the 2p$_k$ orbital of the αth carbon in the nth molecular orbital. A subroutine was written for the EHT program that would evaluate eq 2 from the output of the main program. For phenylethynyl with $r(C_1–C_2) = 1.35$ Å and $r(C_2–C_3) = 1.30$ Å, the following result was obtained (the energy terms being measured in eV):

$$\begin{aligned} \Delta g_x &= +0.58\lambda_c \\ \Delta g_y &= +2.32\lambda_c \\ \Delta g_z &= 0.00 \end{aligned} \tag{3}$$

The spin–orbit coupling constant of carbon atom may be assessed from its atomic energy levels; thus $\lambda_c = 0.0036$ eV.[17] Substitution of this value into eq 3 gives $g_x = 2.0044$, $g_y = 2.0107$, and $g_z = 2.0023$ in close agreement with the assessed values. Analysis of the calculation showed that the dominant contribution to the positive g shift in the y direction indeed comes from the nonbonding σ orbital with the lone pair.

As stated earlier the EHT method predicted the σ radical state for phenylethynyl with normal single bond and triple bond distances for $r(C_1–C_2)$ and $r(C_2–C_3)$. The g tensor predicted for this structure was almost isotropic ($g_x = g_y = 2.0023$, and $g_z = 2.0026$). We also examined the phenylethynyl radical with INDO, a semiempirical SCF MO theory.[18] The INDO calculation also predicted the π radical state for the former structure and the σ radical state for the latter. The INDO method directly yields the spin density at each proton 1s orbital, hence its A_{iso} (isotropic hfc constant). The proton A_{iso}'s predicted by INDO for the two structures are included in Table I. The proton A_{iso}'s determined experimentally are certainly in better agreement with those calculated by INDO for the π radical structure.

The present experimental results thus affirmed the π radical state of phenylethynyl. The molecular orbital consideration showed that the π radical state results from mixing of the π_z orbital of the ethynyl group and the E_{1a} π orbital of the phenyl sector; the antisymmetric combination of the two orbitals forms a π orbital lying above the nonbonding σ orbital.

Registry No. Phenylethynyl, 25640-27-1.

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