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Citation: *The Journal of Chemical Physics* **77**, 2235 (1982); doi: 10.1063/1.444145

View online: <http://dx.doi.org/10.1063/1.444145>

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Vibronic absorption spectra of phenyl alkyne cations in solid argon at 20 K

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Phenyl alkyne samples at high dilution in argon were subjected to argon resonance radiation during condensation at 20 K. Sharp band origins at 579.0 and 586.0 nm agree with the differences between sharp first and fourth photoelectron bands for phenyl acetylene and 1-phenyl-1-propyne, which identifies the molecular cation absorptions. Vibronic assignments are supported by isotopic substitution and comparison to spectra of phenyl acetylene. Substituent vibrations dominate the red transition, which is predominantly $\pi(\text{ring}) \leftarrow \pi(\text{alkyne})$, whereas ring vibrations dominate the UV transition for 1-phenyl-1-propyne, which is localized on the aromatic ring.

INTRODUCTION

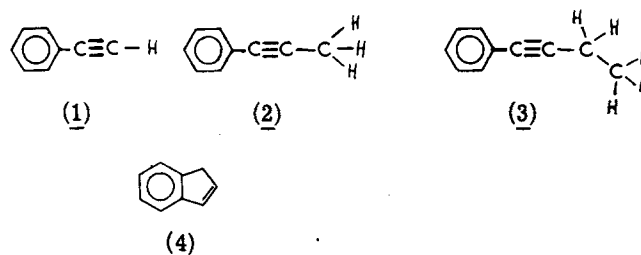
The molecular cations of conjugated aromatic olefins have received extensive study by photoelectron,¹⁻³ ion cyclotron resonance photodissociation,⁴ and mass spectrometry, where molecular ion rearrangement has been of considerable interest.⁵ A recent matrix photoionization study provided further evidence for molecular ion rearrangements on photolysis of the parent ion trapped in solid argon.⁶ The corresponding conjugated aromatic alkyne cations have, however, received less attention. Photoelectron spectra (PES) have been reported for phenyl acetylene (1),^{1,2,7} phenyl propyne (2),⁷ and phenyl butyne (3).^{7(b)} An attempt to observe the emission spectrum for phenyl acetylene cation has failed, presumably owing to lower excited states not giving optically allowed transitions to the ground state.⁸ Along a different line, hydrogen randomization in isotopic phenyl acetylene cations in mass spectrometric studies has suggested expansion to an eight-membered ring intermediate.⁹ Since the electron-impact primary ion mass spectra of the C_9H_8 isomers 1-phenyl-1-propyne (2) and indene (4) are similar, it has been inferred that these C_9H_8^+ molecular ions eliminate hydrogen to give C_9H_7^+ fragment ions with the same noncyclic structure.¹⁰

Matrix absorption spectra (MAS) of phenyl alkyne cations were recorded for comparison with PES band positions and for observation of vibrational structure. Through the use of isotopic precursors, vibrational assignments for the cations can be made and compared to the neutral molecule.

EXPERIMENTAL

The cryogenic vacuum apparatus, argon resonance discharge lamps, experimental procedure, and photolysis methods have been described in earlier reports.^{6,11-13} Phenyl alkyne vapor diluted with argon (mixture ranged from 200/1 to 13 000/1) was condensed at 1–2 mmol/h on a 20 ± 2 K sapphire plate during irradiation by a windowless resonance lamp for 4–6 h; the lamp used argon flowing through a 3 mm i.d. orifice quartz tube at about 150 mTorr pressure excited by a microwave discharge. The product yield and spectral resolution in (1) experiments were particularly sensitive to sample concentration and adjustment of the microwave discharge reso-

nance lamp. Absorption spectra were recorded on a Cary 17 spectrophotometer using expanded scales and reduced scan speeds before and after photolysis by a high-pressure (1000 W) mercury arc with glass short-wavelength cutoff filters. Phenyl acetylene, phenyl propyne, and indene samples were acquired from Aldrich Chemical; phenyl butyne was obtained from ICN-K & K Laboratories. Phenyl- d_1 -acetylene was prepared by exchanging (1) with excess NaOD in D_2O for 3 h at room temperature; an NMR spectrum showed the sample to be free of impurity. Phenyl- d_5 -acetylene was purchased from Merck, Sharp and Dohme; phenyl- d_8 -acetylene was prepared by exchanging the d_5 compound with excess NaOD in D_2O overnight. After several freeze-thaw-pump cycles, the samples were vaporized into the mixing vessel and diluted with argon.



RESULTS

Matrix photoionization experiments performed with phenyl alkynes will be described in turn.

Phenyl acetylene

Ten experiments were performed with phenyl acetylene, (1), and the spectrum using a 200/1 sample is shown in Fig. 1(b). A strong absorption system was observed beginning at 578.6 nm ($A=0.10$) after 3 h of sample deposition. Weak, broad bands observed at 608.5 and 593 nm have been observed in previous styrene experiments⁶ and assigned to the styrene radical cation. A sharp, strong band was also observed at 346.8 nm ($A=0.13$) with weaker bands at 340.0, 328 ($A=0.02$), 325.2, 318, and 316 nm; the 316 nm band, observed in styrene experiments, is due to $\phi-\dot{\text{C}}\text{HCH}_3$ radical.⁶ No absorption was observed at 520.5 nm or near 800 nm. Photolysis with 590–1000 nm radiation for 30 min re-

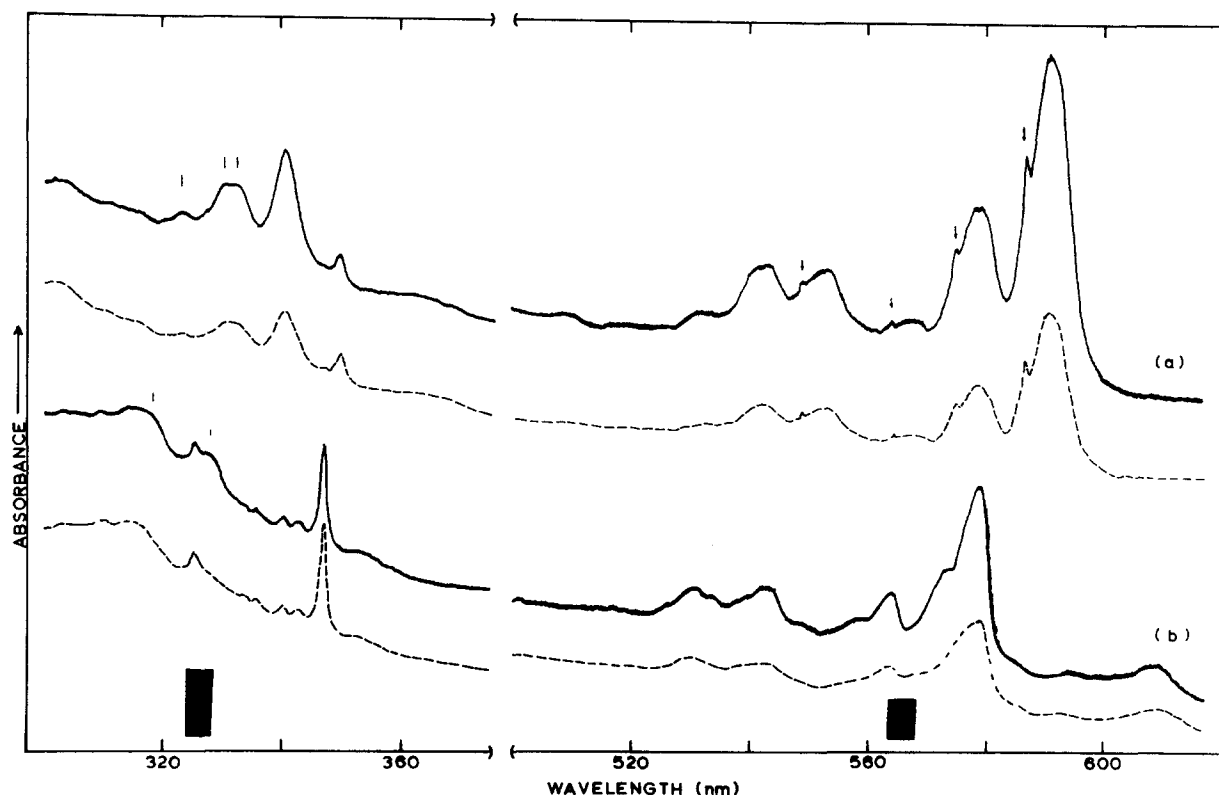


FIG. 1. Absorption spectra of phenyl alkyne samples in argon (200/1) subjected to argon resonance photoionization during condensation at 20 ± 2 K. Dashed traces recorded after 500–1000 nm photolysis for 30 min. (a) $\phi\text{-C}\equiv\text{C-C}_2\text{H}_5$, visible 0.2 Å range; UV 0.5 Å range, (b) $\phi\text{-C}\equiv\text{C-H}$, 0.2 Å range for both regions. Vertical bars denote band positions predicted from PES.

duced the structured red band system by 15%, a similar exposure to 500–1000 nm radiation reduced the red system to 50% of its original absorbance, and a final 380–1000 nm photolysis reduced the red system and the 328 and 318 nm bands to 25% of their original absorbances without affecting the sharp 346.8 and 325.2 nm bands. Figure 2(b) illustrates the spectrum from a 4000/1 experiment with the strong origin ($A=0.26$) at 579.0 nm after 6 h of sample deposition. The vibrational components listed in Table I were reproduced in a 1000/1 experiment within ± 0.1 nm.

One experiment performed with an 800/1 sample of $\text{C}_6\text{H}_5\text{C}_2\text{D}$ produced a strong origin at 578.7 ± 0.1 nm ($A=0.18$) after 3 h of sample condensation. The major vibronic peaks were observed at 564.7, 543.0, 533.1, and 530.5 ± 0.1 nm.

Four experiments were done with phenyl- d_5 -acetylene; the bands sharpened with dilution but the yield of the 577.6 nm origin band was about $A=0.06$ per 2 mmol of total sample deposition in the presence of argon resonance radiation regardless of concentration. In addition, a weaker 326 nm shoulder was observed on a stronger 316 nm absorption. Photolysis with 500–1000 nm radiation for 20 min in the 200/1 experiment reduced the 577.6 nm system and the 326 nm band by 25%. In the 800/1 experiment, photolysis with 470–1000 nm light for 15 min reduced the new product bands by 30%

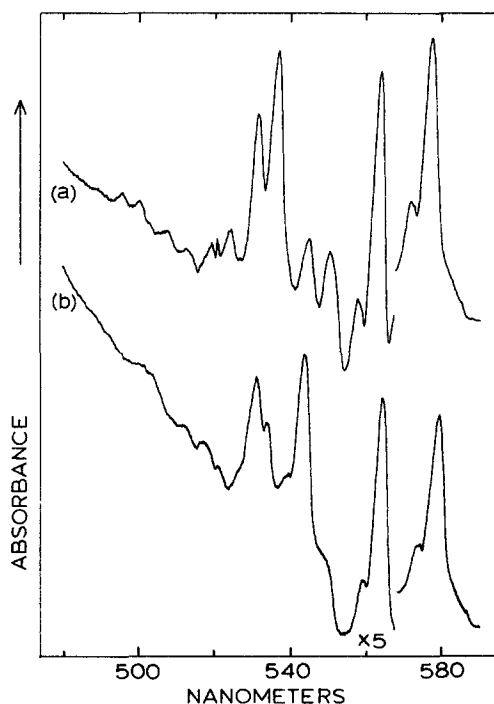


FIG. 2. Absorption spectra of phenyl acetylene samples in argon after argon resonance photoionization during condensation at 20 ± 2 K; origin band recorded on 0.5 Å range, vibronic structure on 0.1 Å range (a) $\text{C}_6\text{D}_5\text{C}_2\text{H}$, 13 000/1; (b) $\text{C}_6\text{H}_5\text{C}_2\text{H}$, 4000/1.

TABLE I. Absorption band positions, spacings, and assignments in matrix photoionization experiments with phenyl acetylene- d_6 .

λ (nm)	ν (cm ⁻¹) ^a	$\Delta\nu$ (cm ⁻¹)	$\Delta\nu$ (cm ⁻¹)	assign. ^b
579.0 ^c	17 271	0		
573.0 ^d	452	181		ν_{24} (162)
564.1	727	456	0	ν_{13} (465)
558.4	908		178	ν_{24}
549.2	18 208	937		ν_{11} (998)
543.5	399	1128	0	ν_8 (1192)
538.2	580		181	ν_{24}
533.8	734	1463		ν_7 (1488)
530.7	843		444	ν_{13}
521.3	19 183		784	ν_{12} (760)
517.4	327		928	ν_{11}
512.0	531	0	1132	ν_8
503.7	853		1454	ν_7
500.5	980	449		ν_{13}
328	30 488	0		
318	31 447	959 \pm 50		ν_{11} (998)

^aRed absorption band positions are accurate to ± 3 cm⁻¹.^bMode number assignment and cm⁻¹ value for neutral molecule (Ref. 17) given for comparison.^cFull width at half-maximum is 137 cm⁻¹.^dFull width at half-maximum is 120 cm⁻¹.

and a like treatment with 290–1000 nm radiation reduced the bands to 15% of their initial absorbances. The structured red absorption recorded in the 13 000/1 experiment is shown in Fig. 2(a) and the bands are listed in Table II. The sharp, weak 520.5 nm absorption is due to the C₂⁻ anion.¹⁴

Three similar experiments were done with phenyl- d_6 -acetylene samples; the spectra exhibited the same band profiles and relative intensities as in d_5 experiments with 0.2–0.5 nm blue shifts in the bands. The sharp origin was observed at 577.1 \pm 0.1 nm ($A = 0.18$); the first major vibronic peak at 562.8 \pm 0.1 nm gave a 440 \pm 6 cm⁻¹ spacing; the second major vibronic peak at 535.8 \pm 0.1 nm gave a 1336 \pm 6 cm⁻¹ spacing.

An additional experiment was done with a 100/1 sample of (1) using a 2% H₂ mixture in argon as the discharge gas to provide hydrogen atoms as reaction partners for diagnostic purposes. The styrene radical cation absorption at 608.5 nm ($A = 0.05$),⁶ a broad 361 nm band ($A = 0.06$), and the sharp 346.8 nm band ($A = 0.25$) were increased markedly relative to the 578.6 nm product absorption. Photolysis with 500–1000 nm radiation for 30 min into both red absorption systems decreased the 578.6 nm band absorbance by 35% and the 608.5 and 361 nm band absorbances by 15% without affecting the 346.8, 340.0, and 325.2 nm bands.

Phenyl propyne

A total of seven experiments was done with phenyl propyne (2), and the spectra from a 100/1 experiment after 3.5 h of sample preparation and a series of photolysis studies are shown in Fig. 3. Two strong structured absorptions were observed beginning at 586.0 (A

= 0.28) and 336.0 nm ($A = 0.27$) and a sharp new band was found at 348.5 nm ($A = 0.09$). After 4.5 h of sample preparation in the 5000/1 experiment, the 586.0 and 336.0 nm bands were $A = 0.40$, and C₂⁻ was observed at 520.5 nm ($A = 0.005$); the vibronic bands are given in Table III for each system. A 2% H₂ mixture in argon was used as the discharge gas in a final (2) experiment. The relative yield of the 586 and 336 nm band systems was reduced, and the sharp 348.5 nm band was increased. No change in bandwidth was noted and no β -methyl styrene cation⁶ was detected at 591 nm.

One goal of this work was to compare the absorption spectra of (1) and (2) cations with PES. Photoelectron spectra of (1) have been reported by three groups,^{1,2,7} and the PES of (2) was given by one of these.⁷ The PES of (2), recorded on expanded scale for us by Kovac and Maier, is similar to that for (1) in Fig. 6 of Ref. 1. The ionization energies and vibrational structure from the PES of (2) are given in Table IV.

Phenyl butyne

Six experiments were done with (3) using approximate dilutions in the range of 200/1 to 1600/1. Strong band systems beginning at 590.4 ($A = 0.18$) and 340.2 nm ($A = 0.16$) and a new 349.6 nm band observed in the 200/1 experiment are shown in Fig. 1(a). Additional sharp peaks at 586.3, 574.4, 563.1, and 548.8 nm are indicated by arrows in the figure. A 1 h photolysis with the 585–1000 nm filter decreased both band systems by 10%, and a 20 min exposure to 500–1000 nm light halved both band systems, including the sharp peaks, without affecting the 349.6 nm band, as shown in the dashed trace in Fig. 1(a). A final 290–1000 nm photolysis destroyed both band systems and the 349.6 nm feature. A comparable yield of the two band systems was observed in

TABLE II. Absorption band positions, spacings, and assignments in matrix photoionization experiments with phenyl acetylene- d_5 .

λ (nm)	ν (cm ⁻¹) ^a	$\Delta\nu$ (cm ⁻¹)	$\Delta\nu$ (cm ⁻¹)	assign. ^b
577.6 ^c	17 313	0		
571.5 ^c	498	185		ν_{24} (161)
563.1	759	446	0	ν_{13} (454)
557.2	947		188	ν_{24}
549.8	18 188	875		ν_{11} (956)
544.3	372	1059		ν_8 (1136)
536.0	657	1344	0	ν_7 (1379)
530.9	836	1523		ν_6 (1572)
523.7	19 095		438	ν_{13}
519.1	264		607	
512.4	516		859	ν_{11}
507.3	712		1055	ν_8
500.3	988		1331	ν_7
495.6	20 178		1521	ν_6
326	30 675			

^aRed absorption band positions are accurate to ± 3 cm⁻¹.^bMode number assignment and cm⁻¹ value for neutral molecule (Ref. 17).^cFull width at half-maximum is 110 cm⁻¹.

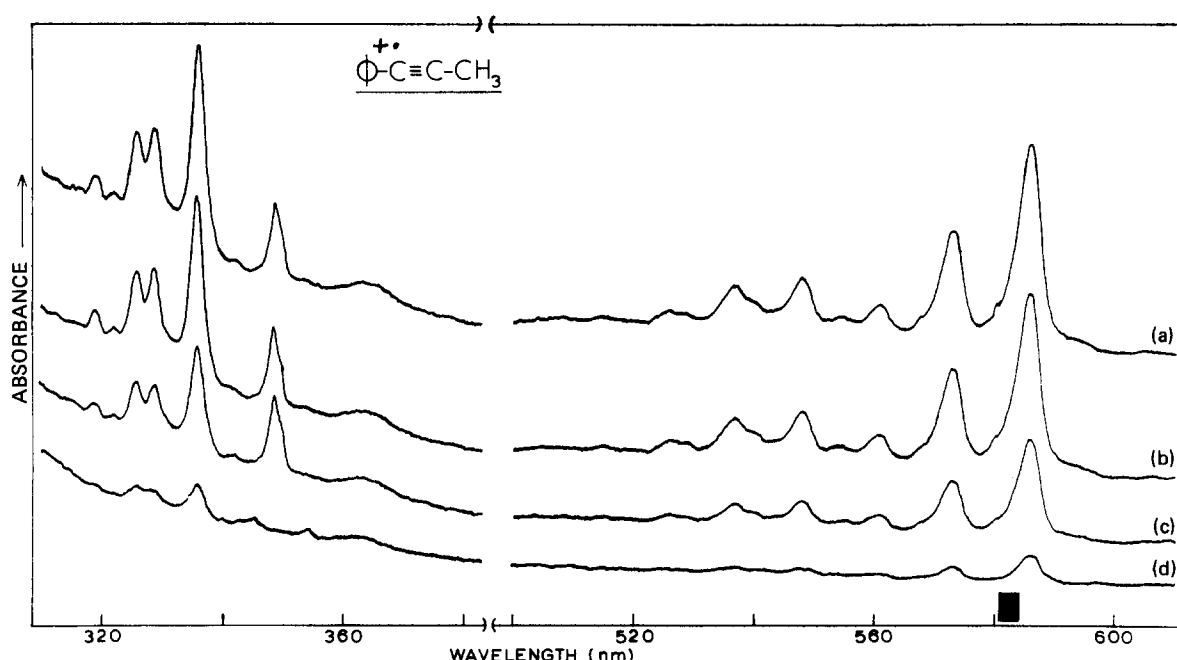


FIG. 3. Absorption spectrum of phenyl propyne in argon (100/1) codeposited with argon resonance radiation from open discharge lamp, trace (a), both regions recorded on 0.5 Å range. Spectrum (b) recorded after 30 m of 580–1000 nm photolysis, trace (c) following 30 m of 500–1000 nm irradiation, and spectrum (d) after 30 m of 290–1000 nm photolysis. Vertical bar denotes red band position determined from PES.

the 1600/1 experiment without the 349.6 nm absorption; band positions are given in Table V. This more dilute experiment revealed a band profile showing three matrix sites; the origin band consisted of a shoulder at 592.0 nm, the peak at 590.4 nm, and a sharp absorption resolved at 586.3 nm.

Indene

Several experiments were done with indene (4) for comparison with the phenyl propyne (2) structural isomer. The spectra were substantially different although band systems were observed in the red and UV regions for each precursor. In two 1500/1 indene experiments, the very sharp red origin was observed at 587.7 nm ($\Delta = 0.10$, FWHM = 50 cm^{-1}) with a very sharp vibronic component at 570.1 nm, and another strong band was observed at 578.9 nm with a vibronic component at 561.9 nm. The UV region revealed a product absorption system beginning at 361.0 nm with vibronic components at 348.3, 343.2, 336.5, and 327.0 nm.

DISCUSSION

The new product absorptions will be identified and compared to photoelectron spectra, and assignments of vibronic structure will be given.

Identification

The sharp red band systems with origins at 579.0, 586.0, and 590.4 nm, respectively, are related by similar vibrational intervals and reduction by visible photolysis. The PES reported by three groups^{1,2,7} for (1) predict a red transition for (1) cation at 2.17 ± 0.04 , 2.21 , and 2.22 ± 0.02 eV; an average value of 2.20 ± 0.02

TABLE III. Absorption band positions and spacings in matrix photoionization experiments with 1-phenyl-1-propyne.

λ (nm)	ν (cm^{-1}) ^a	$\Delta\nu$ (cm^{-1})	$\Delta\nu$ (cm^{-1})
586.0 ^b	17 065	0	
579.5 ^c	256		
573.2	446	381	0
564.2	724	659	
561.0	825		379
554.6	18 031	966	
547.9	252	1187	0
543.6 ^c	396		
539.7	529	1464	
536.8	629	0	377
529.0	904		652
526.2	19 004	375	
514.7	429	0	1177
507.4	708		1456
504.3	829		1577
497.8	20 088	659	
495.2	186	757 (2 × 378)	
491.2 ^d	358	929	
485.3	606	1177	0
478.3	907	1478	
464.9	21 510		904
348.5 ^e			
336.0 ^f	29 762	0	
328.8	30 414	652	
325.9	684	922	
322.0	31 056	1294 (2 × 647)	
319.0	348	1586	
316.5 ^d	596	1834 (2 × 917)	
312.7	980	2218 (2 × 648 + 922)	
309.5	32 310	2548 (4 × 637)	

^aRed and UV bands accurate to ± 5 and ± 10 cm^{-1} , respectively.

^bFull-width at half-maximum is 125 cm^{-1} .

^cWeak bands observed only in the most dilute experiment.

^dAdditional bands observed by mercury arc photolysis of 2000/1 precursor sample with 250/1 CH_2Cl_2 present as electron trap.

^eUnaffected by long wavelength photolysis.

^fFull-width at half-maximum is 220 cm^{-1} .

TABLE IV. Ionization energies and vibrational structure in photoelectron spectrum of 1-phenyl-1-propyne.

I. E.	Vertical energy (eV)	Vibrational structure (cm ⁻¹) ^a
1st	8.45	0 <u>400 ± 40</u> 800 ± 40 1560 ± 40 <u>2140 ± 40</u> 2550 ± 40
2nd	9.77	
3rd	9.68	0 <u>2000 ± 40</u> 4000 ± 40
4th	10.59	0 770 ± 40 <u>1130 ± 40</u> 1670 ± 40 2260 ± 40
5th	11.78 broad	
6th	12.39 broad	
7th	14.1 broad	
8th	14.9 broad	

^aThe strongest vibronic peaks are underlined.

eV (17745 ± 160 cm⁻¹) is in sufficient agreement with the 579.0 nm origin (17271 cm⁻¹) to substantiate assignment of the matrix absorption spectrum (MAS) to (1) cation. Even better agreement is found in the (2) case; PES band differences of 2.13 and 2.14 ± 0.02 eV have been measured^{7,15} (17220 ± 160 cm⁻¹ average), which is in excellent agreement with the 586.0 ± 0.1 nm (17065 ± 3 cm⁻¹) origin band and confirms assignment of the MAS to (2) cation. The small red shifts are due to the guest ion-argon matrix interaction. In the (2) cation case, this interaction is less than 1% of the transition energy. The similar MAS in (1), (2), and (3) matrix photoionization experiments demonstrates that the 590.4 nm band system is due to (3) cation, which is consistent with PES for the three precursors.^{7(b)} The PES for indene¹⁶ predicts a red transition at 574 nm, in sufficient agreement with the MAS to identify the 587.7 and 578.9 nm band systems as due to (4) cation (probably in two different matrix sites).

Previous experiments with substituted styrenes revealed a near UV band for these cations.⁶ Band systems at 328, 336, and 340 nm in (1), (2), and (3) experiments, respectively, decreased on photolysis in concert with the red systems identified above as the parent cations. Again, the PES⁷ predicts an allowed transition for (1) cation near 325 nm, in very good agreement with the 328 nm matrix band. Likewise, the PES¹⁵ of (2) predicts a transition in this region for (2) cation, but without the adiabatic ionization energy, an accurate determination of the sharp absorption origin cannot be made.

The molecular cations are produced in these experiments by photoionization with argon resonance light

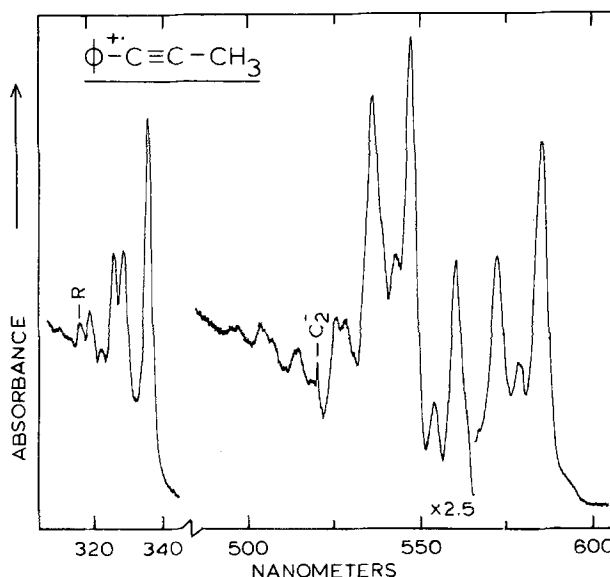


FIG. 4. Absorption spectrum of phenyl propyne in argon (5000/1) subjected to argon discharge radiation during condensation at 20 ± 2 K. Absorbance range 0.5A except 0.2A where indicated $\times 2.5$.

from the discharge lamp (11.6, 11.8 eV)¹² during the condensation process, which entraps the cation in solid argon for spectroscopic and photochemical study. The (1), (2), and (3) cations photolyzed with visible light to a greater degree than the analogous styrene cations,^{4,6} although no photolysis products were observed in the spectra of either system, presumably owing to lower absorption cross sections for the photolysis products. It is interesting to note that the yield of parent cations in these experiments was relatively independent of precursor concentration over a 200/1 to 13 000/1 range. This implies that there is a limit to the concentration of positive and negatively charged species that can be isolated and trapped in the matrix volume. A possible counter anion C_2^- was only detected in the most dilute of the present experiments.

TABLE V. Absorption band positions and spacings in matrix photoionization experiments with 1-phenyl-1-butyne.

λ (nm)	ν (cm ⁻¹) ^a	$\Delta\nu$ (cm ⁻¹)	$\Delta\nu$ (cm ⁻¹)
590.4 ^b	16 938	0	
577.9	17 304	366	
566.0	17 668	2×364	
551.7	18 126	1188	0
542.6	18 430	1492	
540.5	18 501		375
530.5	18 850		2×362
340.2	29 394	0	
332.3	30 093	699	
329.9	30 312	918	
322.7	30 989	1595	

^aRed bands are accurate to ± 10 cm⁻¹ and the UV bands are accurate to ± 20 cm⁻¹.

^bFull width at half-maximum is 230 cm⁻¹.

The sharp band systems at 346.8, 348.6, and 349.6 nm in (1), (2), and (3) experiments exhibited a different photolysis behavior; these systems were not affected by visible light but were destroyed by 340–1000 nm photolysis. The marked increase in yield of these bands with H_2 added to the discharge suggests a hydrogen addition product. The 346.8 nm band system will be examined in detail in a later publication.

Assignments

The electronic assignments for (1) cation follow from the PES. The ground state (1^2B_1) ion is formed by removal of the outermost ring π electron. Transitions are expected to the 2^2B_1 states involving ionization of the out-of-plane alkyne π orbital (2^2B_1) in the red region and ionization of the strongly bonding aromatic π orbital (3^2B_1 , a_{2u} for benzene) in the UV region. Molecular orbital calculations for (1) show that ionization in the 1^2B_1 state arises from an orbital localized 72% on the ring and 28% on the alkyne, the 2^2B_1 state hole is localized 39% on the ring and 61% on the alkyne, and the 3^2B_1 state hole is 88% from the ring.¹ Hence, the red transition exhibits some charge-transfer character and the UV transition is largely confined to the aromatic ring. A transition to the 2^2B_2 state involving ionization of the localized in-plane alkyne π orbital, predicted near 800 nm, is not allowed. Observation of strong, allowed transitions near 580 nm for the phenyl alkyne cations without absorption near 800 nm confirms the band assignments in the PES. The red band origin for phenyl acetylene cation shifts 9 cm^{-1} to higher energy for d_1 substitution, 42 cm^{-1} higher upon d_5 substitution, and a total of 57 cm^{-1} higher for d_6 substitution, which is the expected effect.

Before considering vibrational assignments for each cation, note that vibrational intervals of 1130–1180 and 450–360 cm^{-1} dominate each red absorption system and that vibrations in the 600, 900, and 1500 cm^{-1} regions are observed in the UV systems. These vibrations reflect the molecular subunits most affected by the transitions, which heavily involves the alkyne substituent in the red transition and the aromatic ring in the UV transition.

Vibrational assignment of the vibronic bands of $C_6H_5C_2H$ cation is relatively straightforward with the precursor molecules and $C_6D_5C_2H$ cation spectra available for support. Normally, only symmetric modes are expected to be vibronically active; all of the intervals given in Table I correlate well with neutral molecule a_1 modes except the smallest 180 ± 10 cm^{-1} interval for three of the weakest bands. The 180 ± 10 cm^{-1} spacing is slightly larger than the 162 cm^{-1} value for the out-of-plane bending mode $\nu_{24}(b_1)$ of (1).¹⁷ The weak 180 ± 10 cm^{-1} spaced bands are assigned to this vibronically allowed out-of-plane bending mode. The increase over the neutral molecular value is attributed to π delocalization between the ring and alkyne carbons in this 2^2B_1 excited state.

The 450 ± 6 cm^{-1} values assigned to ν_{13} for (1) cation show a displacement to 378 ± 3 cm^{-1} for (2) cation, and 364 ± 5 cm^{-1} for (3) cation, which is a substantial sub-

stituent effect. This pronounced effect suggests involvement of the substituent in a bending mode. Antisymmetric b_1 and b_2 bending modes for (1) have been identified at 349 and 513 cm^{-1} ¹⁷; neither of these possibilities fits the 450 ± 6 cm^{-1} intervals as well as the 465 cm^{-1} mode $\nu_{13}(a_1)$, which involves the ring carbon skeleton and the substituent.

The 1130 ± 6 cm^{-1} interval assigned to the ϕ -C stretching mode $\nu_8(a_1)$ for (1) cation is lower than ν_8 for the (1) precursor (1192 cm^{-1})¹⁷ and the ϕ -C stretching mode (1183 ± 6 cm^{-1}) for (2) and (3) cations. This assignment is supported by the $C_6D_5C_2H$ species, where ν_8 shifts to 1136 cm^{-1} for the molecule and 1057 ± 6 cm^{-1} for the cation; however, the matrix ν_8 assignment of 1130 ± 6 cm^{-1} for (1) cation is in disagreement with assignment¹ of a 1050 ± 20 cm^{-1} interval in the fourth PE band to this mode. The intervals of 1458 ± 6 and 932 ± 5 cm^{-1} are the ring C-C stretching modes ν_7 and ν_{11} for (1) cation, which are about 30 and 66 cm^{-1} higher for the neutral molecule. The removal of a π electron delocalized over the alkyne and aromatic π systems¹ should reduce the carbon skeletal vibrational modes. The d_5 counterparts for these modes at 1338 ± 8 and 867 ± 8 cm^{-1} for the ion are compatible with neutral molecule values at 1379 and 956 cm^{-1} .

The vibronic fine structure for the red (2) cation absorption is similar to that described above for (1) cation, as might be expected; unfortunately, no detailed vibrational assignment is available for the molecule. The dominant vibronic bands exhibit 378 and 1182 ± 6 cm^{-1} intervals. The increase in the ϕ -C stretching mode from 1130 ± 6 cm^{-1} for (1) cation to 1182 ± 6 cm^{-1} for (2) cation may be rationalized by more electron density on the alkyne substituent in the 2^2B_1 state for (2) owing to the greater stabilizing effect of the methyl group.

The ultraviolet absorption for 1-phenyl-1-propyne cation is assigned to the $3^2B_1 - 1^2B_1$ [$\pi(\text{ring}) - \pi(\text{ring})$] transition involving the aromatic ring analogous to the $2^2A_u - 2^2E_g$ transition of benzene cation. It is immediately recognized that the 652 ± 6 cm^{-1} vibrational interval is near the Jahn-Teller active¹⁸ $\nu_{18}(e_{2g})$ mode of benzene, 606 cm^{-1} , and a PES measurement of 670 cm^{-1} for this mode of benzene cation.¹⁹ The 922 ± 6 cm^{-1} interval is slightly lower than the 966 ± 6 cm^{-1} value ascribed to the aromatic ring-breathing mode for the upper state in the $\pi(\text{ring}) - \pi(\text{alkyne})$ transition; it is reasonable for the ring breathing mode to be lower in a state with a hole more localized in the strongly bonding ring π orbital than in a state with the hole more localized in the acetylenic π orbital. The 1586 ± 6 cm^{-1} interval is near the 1601 cm^{-1} value for the ν_6 ring C-C stretching mode for (1). Similar vibronic intervals appropriate for aromatic ring vibrations were found in the UV band system for (3) cation.

Several further comments about the PES of (2) can be made. The 2140 ± 40 cm^{-1} interval in the first and the 2000 ± 40 cm^{-1} interval in the third PES band of (2) are assigned to the C \equiv C stretching mode. Since the ground state ion depletes the alkyne orbital only slightly, the C \equiv C stretching mode should be near the neutral molecule value [2120 cm^{-1} for (1)]¹⁷; however, the third ion-

ization involves the in-plane localized alkyne orbital and a greater reduction in the C≡C stretching mode is expected. The 400 ± 40 and 1560 ± 40 cm^{-1} intervals in the first PES band are probably due to the same modes as the 378 ± 6 and 1580 ± 6 cm^{-1} intervals in the MAS. The major intervals in the fourth PES band at 1130 ± 40 cm^{-1} probably correspond to the 1183 ± 6 cm^{-1} MAS interval assigned to the ϕ -C stretching mode.

Spectra of structural isomers

The spectra for the (2) and (4) cation isomers are clearly different in band position and vibrational spacings in the red absorptions, and the UV system origins are 336.0 nm for (2) cation and 361.0 nm for (4) cation. Although the red band systems fall in the same region, the major repeat interval is 378 ± 6 cm^{-1} for (2) cation and 525 ± 6 cm^{-1} for (4) cation showing a pronounced substituent effect. The matrix photoionization technique produces and traps the molecular cation maintaining structural integrity. However, the 70 eV electron impact primary ion mass spectra of (2) and (4) are similar, which provided the natural straightforward conclusion that these C_9H_7^+ molecular ions eliminate hydrogen to give C_9H_7^+ fragment ions with a common presumably non-cyclic structure.¹⁰ The common fragment ion structure for these different structural isomers should, we believe, be attributed to the very high electron energy used to produce the primary ions and not the ions themselves. Low energy ionization should maintain the structural integrity of the molecular ion, as has been demonstrated here with the matrix photoionization technique.

ACKNOWLEDGMENTS

The authors gratefully acknowledge financial support from the National Science Foundation under Grant CHE

79-10966, and thank B. Kovac and J. P. Maier for providing the expanded scale PES of 1-phenyl-1-propyne.

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