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Triplet 1,3-Diphenylpropynylidene (Ph−C−C−C−Ph)

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Abstract: Photolysis ($\lambda > 571$ nm) of 1,3-diphenyldiazopropyne (**9**) affords triplet 1,3-diphenylpropynylidene (**3**), as characterized by IR, UV/vis, and EPR spectroscopy in low-temperature matrices. Two conformational isomers of triplet **3** are spectroscopically distinguishable. The initially formed, non-relaxed conformer is believed to reflect the geometry of the diazo precursor, as enforced by the rigid matrix. Annealing the matrix permits the structure to relax to the equilibrium D_{2d} geometry. The highly symmetric equilibrium structure of **3** is best envisioned as a 1,3-allenic diradical. Density functional theory calculations suggest that the equilibrium structure does not exhibit a bond-localized structure that would be characteristic of an acetylenic carbene. Chemical trapping with O_2, however, affords products that are familiar as carbene trapping products: carbonyl oxide **10**, ketone **11**, and dioxirane **12**. Irradiation ($\lambda > 261$ nm) of triplet 1,3-diphenylpropynylidene (**3**) results in cyclization to singlet diphenylcyclopropenylidene (**6**), a process that is photochemically reversible at $\lambda = 232$ nm. Diphenyl-1,2-propadienylidene (**7**) was not observed under any irradiation conditions.

1. Introduction

An understanding of the structure, properties, and reactivity of acetylenic carbenes and conjugated carbon chains underpins diverse topics in contemporary chemistry. Propynylidene (**1**), the simplest acetylenic carbene, is an important intermediate in astrochemistry[1,2] and combustion processes,[3,4] while organometallic complexes of alkynyl carbenes are utilized in organic synthesis.[5,6] Fundamental knowledge of electronic delocalization in carbon chains is central to the understanding of conducting polymers and other advanced electronic and optical materials.[7−12]

Key issues associated with acetylenic carbenes involve the nature of the electronic delocalization and the possible involvement of localized, bond-shift isomers. A number of three-carbon and five-carbon derivatives (**1**−**5**) have been investigated experimentally[13−26] and theoretically[27−29] over many years (Chart 1). Calculations predict that the nature of a defect in a carbon chain displays an alternating dependence on chain length: the defect in a chain of formula $HC_{4n+1}H$ (HCH, HC_5H, HC_9H, etc.) is a carbene, while the defect in a chain of formula $HC_{4n+3}H$ (HC_3H, HC_7H, $HC_{11}H$, etc.) is an allenic 1,3-diradical.[30,31] Detailed calculations of triplet HC_3H and HC_5H did not find multiple energy minima that correspond to localized, bond-shift isomers on the potential energy surface.[20,32] Nevertheless, all of these systems appear to exhibit reactivity that is

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Chart 1. Odd-Member Carbon Chains: Delocalized versus Localized

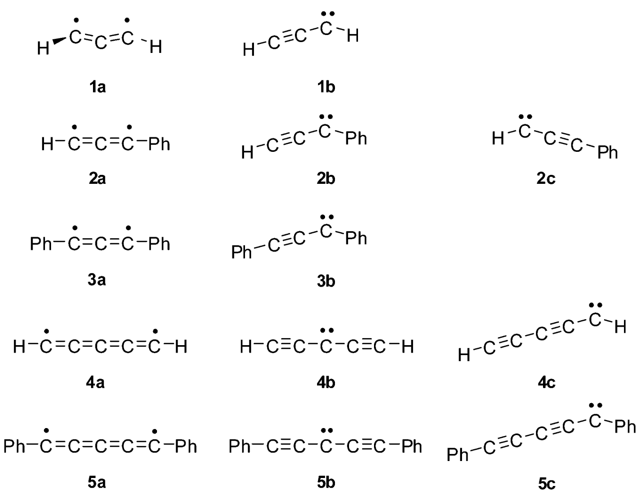

Table 1. Computed (B3LYP/6-31G*) Energies for $C_{15}H_{10}$ Isomers

isomer	energy (hartree)	ZPVE (kcal/mol)	E_{rel}[a] (kcal/mol)	number of imaginary frequencies
^{3}**3a**	−577.4855212	121.37231	2.1	0
^{1}**3a**	−577.4671197	122.42340	14.7	0
^{3}**6**	−577.4205414	121.32226	42.8	0
^{1}**6**	−577.4921476	123.47655	0.0	0
^{3}**7**	−577.412360	121.66524	48.3	0
^{1}**7**	−577.4466075	123.29231	16.2	0
^{3}**8**	−577.3645203	121.90478	78.5	0
^{1}**8**	−577.3858107	121.54504	64.8	1
^{3}**16**	−577.4266455	121.13859	38.8	0
^{1}**16**	−577.4561440	122.43292	21.5	0

[a] Includes ZPVE.

typical of a carbene.[13,25,26,33] Transition metal complexes of these carbenes (as singlets) do exhibit bond-shift isomerism and carbenic reactivity at the remote position,[34,35] which has been exploited in synthetic methodology and in enyne metathesis chemistry.[5,6]

In the current investigation, we describe experimental and computational studies of triplet 1,3-diphenylpropynylidene (**3**).[18] Bond-shift isomers, were they to exist for this Ph−C−C−C−Ph species, would be degenerate by virtue of the symmetrical disubstitution. EPR spectra reveal a type of isomerism that cannot be attributed to bond-shift isomerism. We attribute these isomers to non-relaxed and relaxed conformations of triplet **3**. The structure, spectroscopy, and photochemistry of triplet Ph−C−C−C−Ph (**3**) will be described in detail.

2. Results and Discussion

2.1. Computational Studies. 2.1.1. $C_{15}H_{10}$ Isomers. Optimized structures, harmonic vibrational frequencies, and infrared intensities for singlet and triplet states of $C_{15}H_{10}$ isomers **3, 6, 7**, **8**, and **16** were computed using density functional theory (B3LYP/6-31G*; Table 1, Figure 1).[36] (Few viable alternatives to DFT methods exist for computational studies of molecules of this size.) The computed relative energies for the C_3Ph_2 isomers are in reasonable accord with those of the parent C_3H_2 isomers.[20] Singlet diphenylcyclopropenylidene (**6**) is the lowest energy isomer in the series. Triplet 1,3-diphenylpropynylidene (**3**) lies 2−3 kcal/mol higher, although this energy difference is likely to be underestimated because of the tendency of density functional theory to overemphasize delocalization in carbon chain molecules and other conjugated systems.[32,37,38] The singlet−triplet energy gap (closed-shell singlet state) of 1,3-diphenylpropynylidene (**3**) is approximately 12 kcal/mol, which places the singlet state of **3** (E_{rel} = 14.6 kcal/mol) close in energy to singlet diphenyl-1,2-propadienylidene (**7**) (E_{rel} = 16.2 kcal/mol). Our earlier studies of photoinduced isotope label scrambling in the parent 1,2-propadienylidene led us to consider the possible involvement of singlet cyclopropyne.[20] We therefore computed the cyclopropyne isomer in the diphenyl series. The singlet state of diphenylcyclopropyne (**8**) is significantly higher in energy than the other isomers (E_{rel} = 64.8 kcal/mol) and is computed to be a transition state for the automerization of singlet diphenyl-1,2-propadienylidene (**7**). The triplet state, however, is computed to be a minimum on the potential energy surface. Unlike the parent cyclopropyne, we could not locate a structure for singlet diphenylcyclopropyne in which the tetracoordinate carbon is planar, a result that is not surprising in view of the steric requirements of the phenyl substituents.

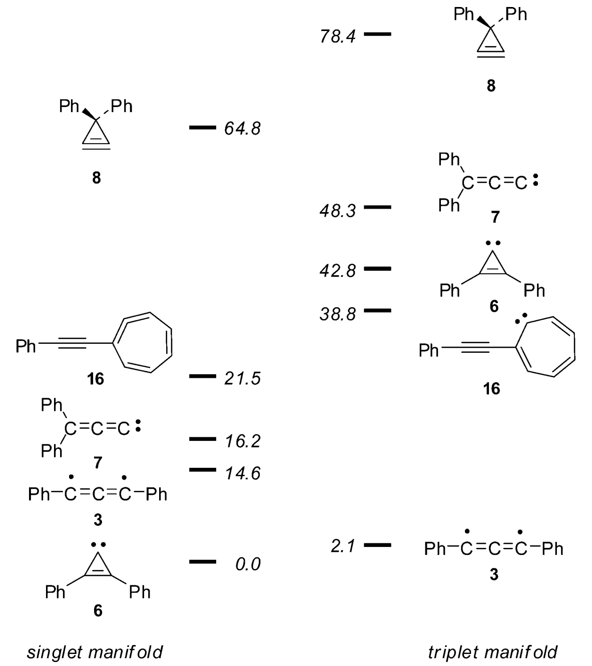

Figure 1. Computed relative energies (kcal/mol; B3LYP/6-31G*, including ZPVE) of $C_{15}H_{10}$ isomers. (Structure ^{1}**8** is a transition state.)

The ring-expanded structures ^{1}**16** and ^{3}**16** are analogous to those observed in the rearrangements of arylcarbenes:[39−43] ^{1}**16**

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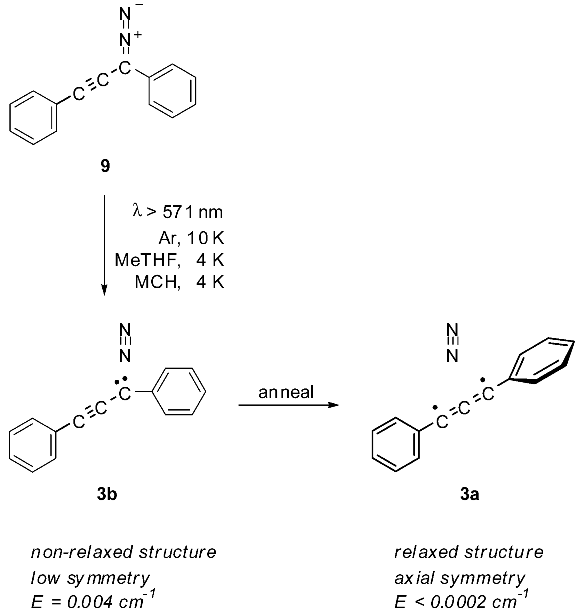
Table 2. Computed (B3LYP/6-31G*) Energies for Conformers of Triplet Ph−C−C−C−Ph (**3**)

isomer	C–C–Ph angle (θ,deg)	dihedral angle (ϕ,deg)[b]	energy (hartree)	ZPVE (kcal/mol)	E_{rel}[a] (kcal/mol)	number of imaginary frequencies
^{3}3b	125	0	−577.472466	122.05664	8.9	0
^{3}3b	135	0	−577.479233	121.95810	4.5	0
^{3}3b	145	2	−577.482621	121.80839	2.3	0
^{3}3b	155	55	−577.484232	121.63951	1.1	0
^{3}3b	165	88	−577.485198	121.57039	0.4	0
^{3}3a	180	90	−577.4855212	121.37231	0.0	0
^{3}3a	180	0	−577.4846747	121.56935	0.7	1

[a] Includes ZPVE. [b] Dihedral angle between the planes defined by the phenyl rings.

is a 1,2,4,6-cycloheptatetraene derivative,[44] while **^{3}16** is a 2,4,6-cycloheptatrienylidene derivative.[45] Although the structures are analogous, the energetics appear to be rather different. In the parent case, 1,2,4,6-cycloheptatetraene is approximately 13 kcal/mol lower in energy than triplet phenyl carbene;[41−43] in the current system, cycloheptatetraene derivative **^{1}16** is approximately 20 kcal/mol higher in energy than triplet **3a**. We surmise that these differences arise from a significantly greater thermodynamic stability of triplet **3a** versus triplet phenyl carbene. The increased delocalization that is inherent in the "propargylene" moiety of triplet **3a**, along with the increased delocalization afforded by the two phenyl substituents, represents a structure that is considerably more delocalized, and greatly stabilized, relative to triplet phenyl carbene. Moreover, the delocalization in triplet **3a** is likely to be overestimated by the computational method employed (see above), which will accentuate the computed energy difference between singlet **16** and triplet **3a**. It seems unlikely that a phenylethynyl substituent imparts a significant perturbation to the relative thermodynamic stabilities of the 1,2,4,6-cycloheptatetraene moiety.

Scheme 1



2.1.2. Ph−C−C−C−Ph (^{3}3). In the current investigation, a key point of interest centers on structural details of the triplet ground state of 1,3-diphenylpropynylidene (**^{3}3**). We studied conformational isomers that exhibit variation with respect to both the C−C−C$_{ipso}$ angle (θ) of the carbon chain and the dihedral angle (ϕ) between the phenyl rings (Table 2). DFT calculations predict a D_{2d} structure for triplet **3** in which the three-carbon chain is linear and the phenyl rings lie in perpendicular planes (**^{3}3a**, $\phi = 90°$; Figure 1). A structure in which the phenyl rings are coplanar (**^{3}3a**, $\phi = 0°$) lies <1 kcal/mol higher in energy; this structure is a transition state with a low-frequency imaginary vibration (18i cm^{-1}) involving torsional motion of the phenyl rings. Calculation of the coplanar structure (**^{3}3a**, $\phi = 0°$), using a larger basis set, affords a transition state with an imaginary vibration of even lower frequency than the earlier calculation (6i cm^{-1} vs 18i cm^{-1}; B3LYP/6-311G* vs B3LYP/6-31G*). Attempts to identify a stationary point (either a transition state or an energy minimum) with a dihedral angle between the phenyl rings of approximately 45° invariably led to the perpendicular triplet (**^{3}3a**, $\phi = 90°$). The identification of a specific conformer of triplet **3** as an energy minimum or a transition state represents a subtle issue that may be beyond the capabilities of the theoretical methods employed in the current investigation. The potential energy surface for phenyl ring rotation in triplet **3** is very flat. At this level of theory, the coplanar structure (**^{3}3a**, $\phi = 0°$) is a transition state for aryl ring rotation in the perpendicular triplet **^{3}3a** ($\phi = 90°$).

Spurred by the experimental observation of significant annealing effects on the EPR spectra of triplet **3**, we computed a series of structures for triplet **3** in which the C−C−C$_{ipso}$ angle (θ) of the carbon chain was varied from that of the diazo compound precursor ($\theta = 125°$) to that of the fully optimized **^{3}3a** ($\theta = 180°$) (Table 2). It is interesting to note that bending the linear triplet **3** by 35° (from $\theta = 180°$ to $\theta = 145°$), which is accompanied by a significant change in the dihedral angle between the phenyl rings (from $\phi = 90°$ to $\phi = 2°$), costs only 2 kcal/mol in energy. This behavior underscores the flatness of the potential energy surface. Even at $\theta = 125°$, the structure optimizes to a minimum on the potential energy surface with an energy that is only 9 kcal/mol higher than that of the fully optimized triplet **3a**. The closed-shell singlet state of **3** is computed to exhibit a C_{2h} structure that appears to be best depicted as an allenic 1,3-diradical (**^{1}3a**).[36]

2.2. Generation and Characterization of Ph−C−C−C−Ph (3). Photolysis ($\lambda > 571$ nm) of 1,3-diphenyl-diazopropyne (**9**) (Ar, 10 K) produces spectroscopic features readily attributable to triplet 1,3-diphenylpropynylidene (**3**) (Scheme 1), as monitored by EPR (Figure 2), UV/vis (Figure 3), and IR spectroscopy (Figure 4). As described previously, the triplet EPR spectrum obtained following the initial photolysis changes rather

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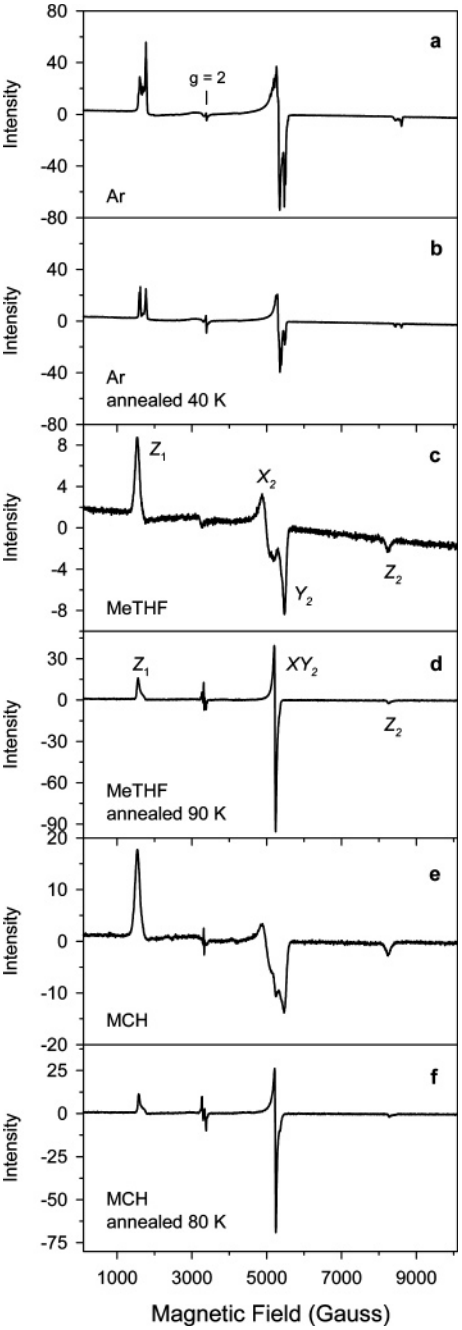

Figure 2. EPR spectra of triplet 1,3-diphenylpropynylidene (**3**) obtained upon irradiation (λ > 571 nm) of 1,3-diphenyldiazopropyne (**9**). (a,c,e) Initially formed triplet prior to annealing. (b,d,f) Relaxed triplet after annealing.

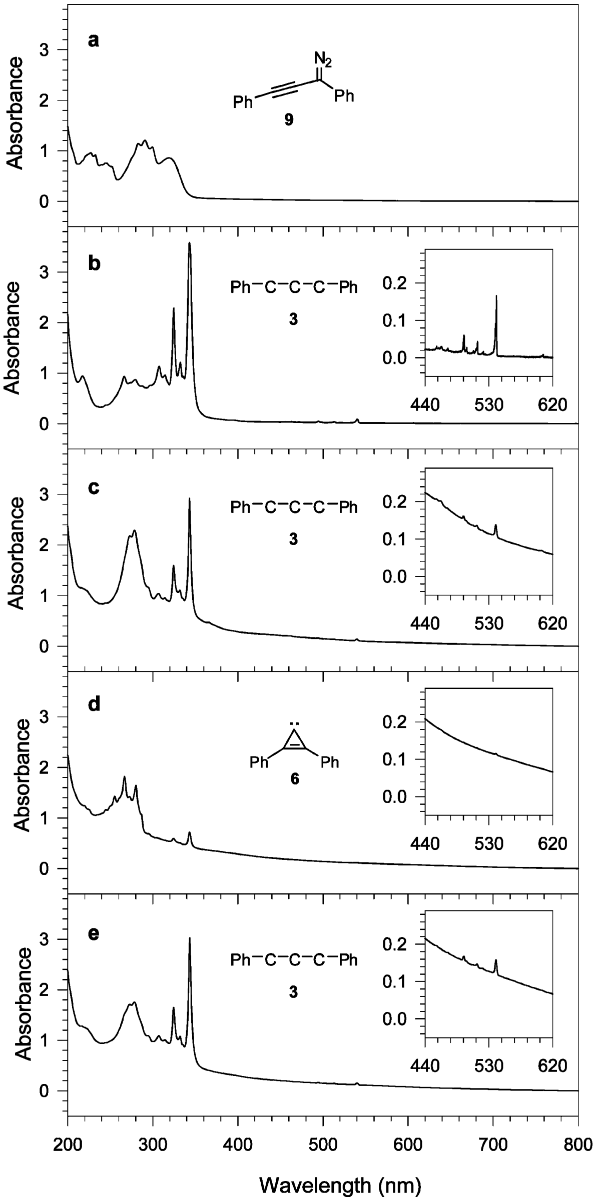

Figure 3. UV/vis spectra: (a) diphenyldiazopropyne (**9**) prior to irradiation (Ar, 10 K); (b) triplet 1,3-diphenylpropynylidene (**3**) obtained upon photolysis (λ > 571 nm) of **9** (Ar, 10 K); (c) spectrum obtained upon warming the matrix to 39 K and recooling to 10 K; (d) diphenylcyclopropenylidene (**6**) obtained upon irradiation of triplet **3** (λ > 261 nm; Ar, 10 K); and (e) triplet 1,3-diphenylpropynylidene (**3**) regenerated upon short-wavelength irradiation of **6** ($\lambda = 232 \pm 10$ nm; Ar, 10 K).

significantly upon annealing the matrix.[18] The effects of annealing on the UV/vis and IR spectra are more subtle.

2.2.1. EPR and UV/Vis Spectroscopy. The changes in the EPR spectra that are observed upon annealing—the collapse of distinct X_2 and Y_2 transitions to give a single XY_2 transition (Figure 2)—reflect a transformation from a structure of lower symmetry to a structure of higher symmetry. The structure of higher symmetry is consistent with that predicted by DFT calculations for triplet 1,3-diphenylpropynylidene (**^{3}3a**). The D_{2d} structure computed for triplet **3** would be expected to display a single XY_2 transition (i.e., a small E value), which is characteristic of an axially symmetric triplet.[46-48] The zero-field splitting parameter, D, reveals increasing delocalization upon phenyl substitution in the series HCCCH (**1a**), 0.628 cm^{-1},[14,15,19] HCCCPh (**2a**), ca. 0.53 cm^{-1},[23,49] and PhCCCPh (**3a**), ca. 0.48 cm^{-1}, which is consistent with the proposed structural assignment. Comparison of D values for the three-carbon and five-carbon chain systems is also instructive. The D values of the non-relaxed triplets PhC$_3$Ph (**3b**) and PhC$_5$Ph (**5c**) are quite similar (0.48 cm^{-1}). Upon annealing, however, the D values change in opposite directions. The D value for the relaxed triplet

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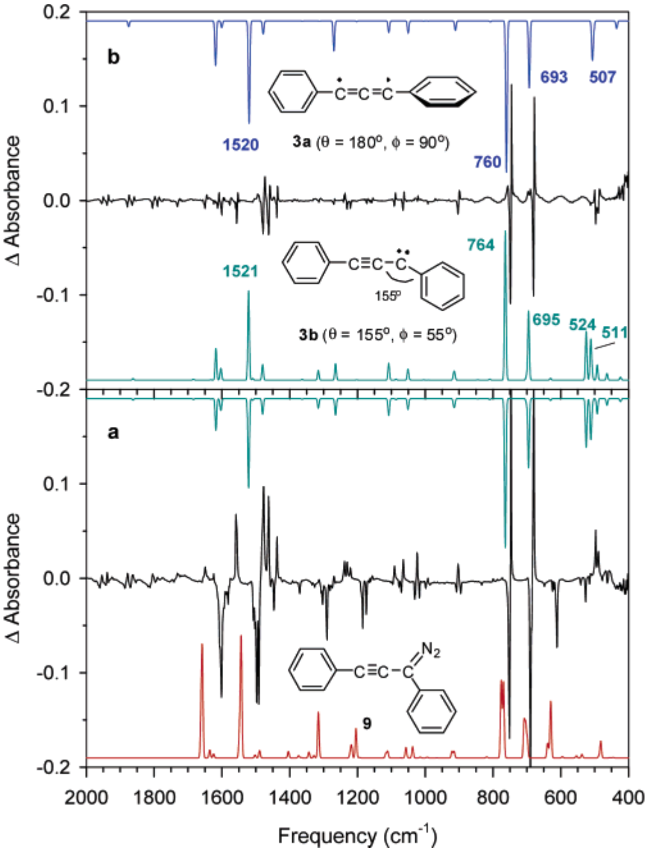

Figure 4. (a) Bottom: Unscaled computed (B3LYP/6-31G*) IR spectrum of diazo compound **9**. Middle: IR subtraction spectrum obtained upon photolysis ($\lambda > 571$ nm) of diphenyldiazopropyne (**9**) showing the growth of 1,3-diphenylpropynylidene (**3**) with the concomitant disappearance of **9** (Ar, 10 K). Top: Computed IR spectrum of triplet **3b** ($\theta = 155°$, $\phi = 55°$). (b) Bottom: Computed IR spectrum of triplet **3b** ($\theta = 155°$, $\phi = 55°$). Middle: IR subtraction spectrum showing the spectral changes associated with annealing the sample (warming to 50 K followed by recooling to 10 K). Top: Computed IR spectrum of triplet **3a** ($\theta = 180°$, $\phi = 90°$).

PhC_3Ph (**3a**) is slightly smaller than that for the non-relaxed **3b** (0.468 vs 0.484 cm^{-1}), while the D value for the relaxed triplet PhC_5Ph (**5a**) is slightly larger than that for the non-relaxed **5c** (0.497 vs 0.482 cm^{-1}).[22] On one hand, it seems counterintuitive that the shorter conjugated system would exhibit greater delocalization (i.e., smaller D value). On the other hand, the annealing behavior appears to be consistent with other experimental and theoretical evidence ascribing predominant 1,3-diradical character for triplet PhC_3Ph (**3a**; $D = 0.468$ cm^{-1}) versus 1,1-diradical (carbenic) character for triplet PhC_5Ph (**5b**; $D = 0.497$ cm^{-1}).[24,30,31]

The initially formed triplet of lower symmetry likely arises from a non-relaxed conformation of triplet **3**. The differing EPR spectra (before and after annealing) are not artifacts of any particular matrix medium, because EPR spectra obtained in different matrixes—argon, 2-methyltetrahydrofuran (MeTHF), and methylcyclohexane (MCH)—all exhibit similar features. Similar annealing effects have been observed on the EPR spectra of hindered triplet diarylcarbenes,[50−53] as well as substituted triplet alkynyl carbenes.[18,22,23,49] The non-relaxed triplet is likely to be constrained with respect to both C−C−C_{ipso} angle (θ) and dihedral angle (ϕ) (structure **3b**; Scheme 1). Calculations reveal that such structures may exist as minima on the potential energy surface and that the energetic penalty for imposing geometric constraints on these structures is modest (Table 2). Such a non-relaxed triplet may be expected to resemble a "localized" aryl carbene structure, in terms of both the EPR spectrum (distinct X_2 and Y_2 transitions) and the UV/vis spectrum (characteristic $\pi-\pi^*$ absorption with extensive vibronic coupling in the region 450−550 nm) (Figure 3).[48] The observed data are in accord with these expectations. Annealing the matrix leads to a significant diminution and broadening of the visible absorption features. Good models for the electronic absorption spectrum of the chromophore in the relaxed, D_{2d} structure of triplet **3a** are not available in the literature.

2.2.2. IR Spectroscopy and Chemical Trapping. The infrared spectrum of triplet Ph−C−C−C−Ph (**3**), as generated upon photolysis ($\lambda > 571$ nm) of diazo compound **9** (Ar, 10 K), is shown in Figure 4a. The IR spectrum exhibits subtle, but reproducible, changes upon annealing the matrix (Figure 4b). These changes are consistent with the interpretation in terms of the conformational relaxation of the initially formed triplet **3b** to the D_{2d} structure **3a**. The experimental IR spectra of the two species are very similar. Both exhibit strong deformation modes that are characteristic of a monosubstituted benzene ring (**3b**, 748, 680 cm^{-1}; **3a**, 745, 678 cm^{-1}).[44,54] Calculations establish that the vibrational frequency of these two deformation modes varies with the bond angle at the carbene center (θ); the computed frequency for each mode decreases as θ increases from 125° to 180°.[36] Thus, the shift to lower frequency upon annealing is consistent with an increase in carbene angle. The computed spectra depicted in Figure 4b ($\theta = 155°$ and $\theta = 180°$) represent our best assessment of the limiting cases regarding the variation in bond angle. Structures that are significantly bent ($\theta = 125°−135°$; i.e., θ similar to that in the diazo compound precursor) are inconsistent with the experimental IR spectra, both before and after annealing. For these structures, calculations predict an alkynyl stretching vibration at ca. 1930 cm^{-1}, with moderate intensity, which is not observed in the experimental spectra. The structure with $\theta = 145°$ also appears to be inconsistent with the experimental IR spectra because of the relatively poor agreement between computed and experimental values of a low-frequency deformation (calc. 551 cm^{-1}; expt. ca. 500 cm^{-1}). To the best of our knowledge, this is the first instance in which annealing effects on EPR spectra of triplet carbenes have been corroborated by detailed modeling of the corresponding IR spectra.

The identity of triplet 1,3-diphenylpropynylidene (**3**) is further confirmed through oxygen trapping studies (Scheme 2).[24,36,48] Photolysis ($\lambda > 571$ nm) of 1,3-diphenyldiazopropyne (**9**) in an argon matrix doped with 5% O_2 produces a mixture of triplet **3** and trapping product, 1,3-diphenylpropynone (**11**) (major product), along with small amounts of carbonyl oxide **10**, dioxirane **12**, and esters **13** and **14**. Subsequent warming of the matrix to 35 K and recooling to 10 K results in trapping of residual triplet 1,3-diphenylpropynylidene (**3**) by O_2 to produce

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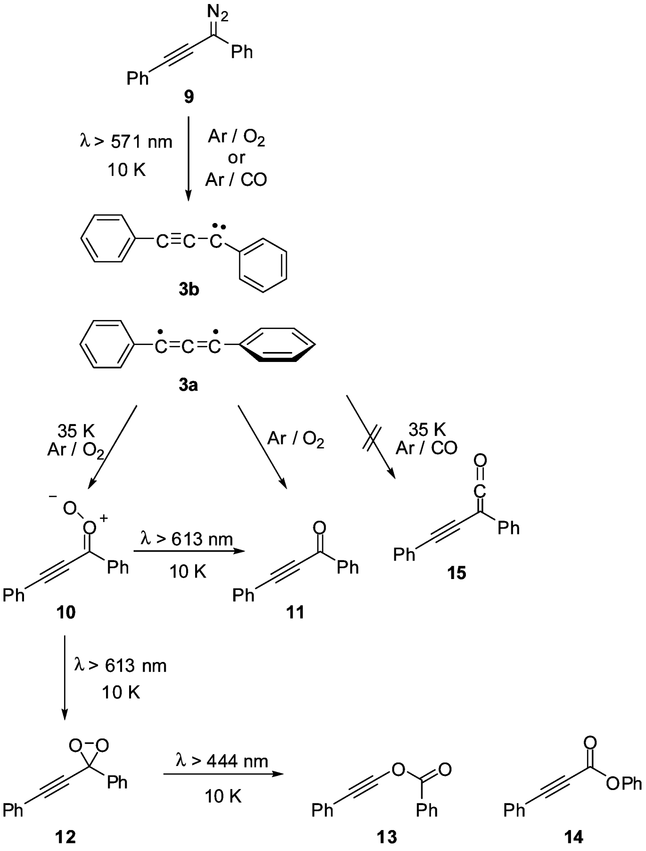
Scheme 2

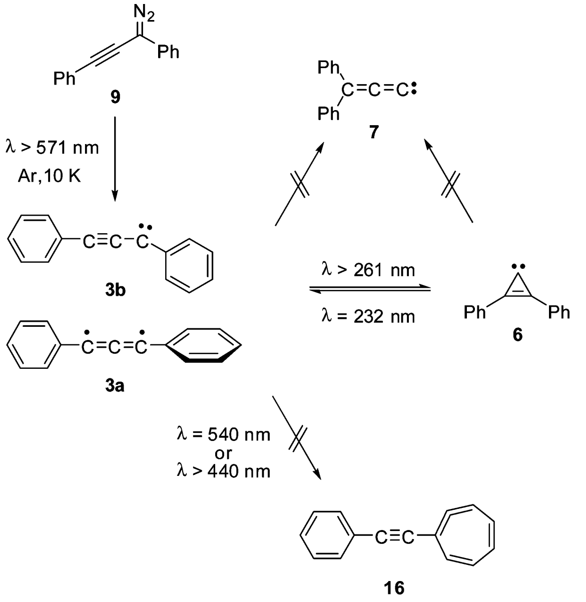


carbonyl oxide (**10**), which exhibits strong IR absorptions characteristic of an O−O stretch at 969 and 929 cm^{-1} and an acetylenic C≡C stretch at 2194 cm^{-1}. Further long-wavelength photolysis ($\lambda > 613$ nm) results in the growth of dioxirane **12** and ketone **11** and the disappearance of carbonyl oxide **10**. Dioxirane **12** undergoes further photochemistry at $\lambda > 444$ nm to lead to the growth of esters **13** and **14**. In these experiments, the identity of ketone **11** was confirmed by comparison of the infrared spectrum with that of an authentic sample (Ar, 10 K). The identities of carbonyl oxide **10**, dioxirane **12**, and esters **13** and **14** were assigned on the basis of their characteristic photochemistry and by comparison to computed infrared spectra.

For further characterization of 1,3-diphenylpropynylidene (**3**), we sought to trap the carbene with carbon monoxide (Scheme 2). Carbon monoxide reacts with many triplet carbenes to form ketenes.[48] Photolysis ($\lambda > 571$ nm) of 1,3-diphenyldiazopropyne (**9**) in an argon matrix doped with 0.33% carbon monoxide produces triplet 1,3-diphenylpropynylidene (**3**) as the only product. Warming the matrix to 40 K results in the conformational isomerization from the non-relaxed to the relaxed carbene (**3**), but not in ketene formation, as demonstrated by the absence of a strong infrared absorption in the vicinity of 2100 cm^{-1}. Thus, PhC$_3$Ph (**3**) and the parent HC$_3$H (**1**) exhibit similar reactivity patterns, in the sense that both species are trapped by O$_2$, but not by CO, at low temperatures.[20]

2.3. Photochemistry. The electronic absorption spectrum of the non-relaxed triplet **3b** exhibits a weak visible absorption, with vibrational structure, that is characteristic of triplet aryl carbenes (Figure 3b). Because matrix-isolated aryl carbenes often undergo ring expansion, affording 1,2,4,6-cycloheptatetraenes, upon visible irradiation,[44,55,56] we considered the possibility that triplet **3b** might exhibit photochemical ring expansion to yield 1-(phenylethynyl)-1,2,4,6-cycloheptatetraene (**16**) (Scheme 3). Irradiation into the visible absorption of triplet **3b** ($\lambda = 540 \pm 7$ nm or $\lambda > 440$ nm) does not, however, result in observable photochemistry.

Scheme 3



Photolysis ($\lambda > 261$ nm) of triplet 1,3-diphenylpropynylidene (**3**) in an argon matrix at 10 K, either before or after the matrix is annealed at ca. 40 K, results in a decrease in intensity of the IR, UV/vis, and EPR signals of triplet **3** along with the growth of diphenylcyclopropenylidene (**6**) (Figures 3d and 5b). The absence of new EPR signals is consistent with the expectation of a singlet ground electronic state for carbene **6**. The strong C−C stretch at 1332 cm^{-1} is characteristic of a cyclopropenylidene moiety.[20,57] The experimental spectrum matches well with the computed spectrum of singlet diphenylcyclopropenylidene (**6**) (Figure 5b). The photoisomerization of triplet **3** to singlet **6** is reversible. Photolysis ($\lambda = 232 \pm 10$ nm) of diphenylcyclopropenylidene (**6**) leads to the increase of the IR (Figure 3d), UV/vis (Figure 5c), and EPR signals of **3** and the decrease of the IR and UV/vis signals of **6**.

The photochemistry exhibited by the C$_3$Ph$_2$ isomers differs from that of the C$_3$H$_2$ and C$_3$HPh isomers. In the latter cases, 1,2-propadienylidene isomers (H$_2$C=C=C: or H(Ph)C=C=C:) are formed under a variety of irradiation conditions.[20,23,49] In the C$_3$Ph$_2$ system, singlet Ph$_2$C=C=C: (**7**) was not detected under any photolysis conditions, as indicated by the absence of an intense IR band predicted (B3LYP/6-31G*) to lie near 2035 cm^{-1} and the absence of the characteristic 1,2-propadienylidene chromophore in the UV/vis spectrum.

2.4. Bond-Shift Isomerism. Acetylenic carbenes have attracted interest, over many years, because of the possibility that they may exhibit bond-shift isomerism (Chart 1). It is now well-established that triplet ethynyl carbene (**1a**, HC$_3$H; propynylidene, propargylene) and triplet diethynyl carbene (**4b**, HC$_5$H)

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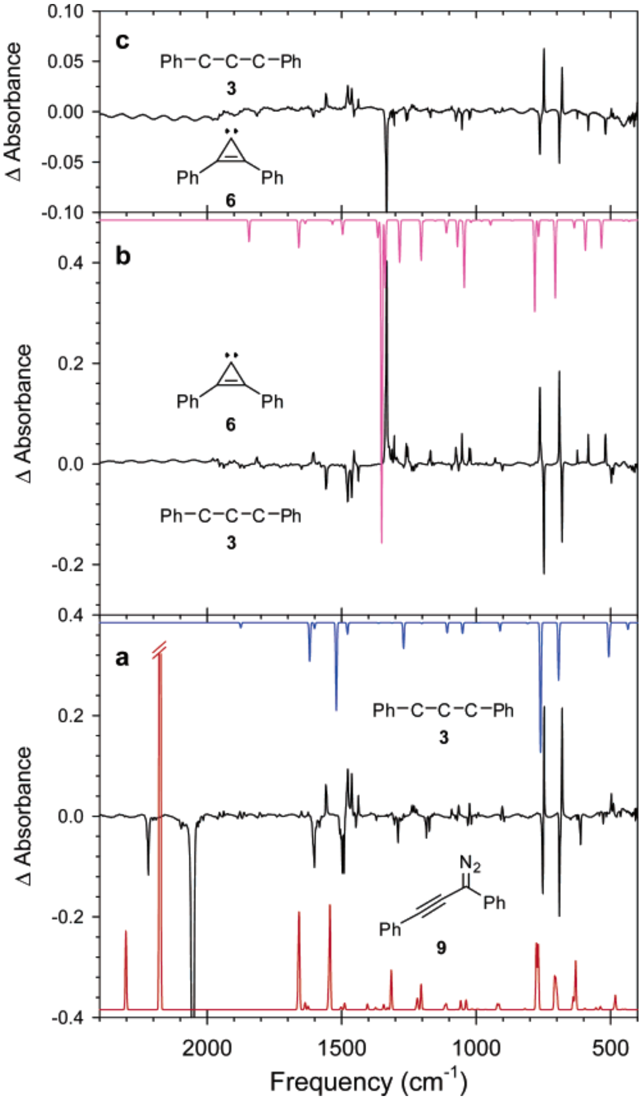

Figure 5. (a) Bottom: Unscaled computed (B3LYP/6-31G*) IR spectrum of diazo compound **9**. Middle: IR subtraction spectrum obtained upon photolysis ($\lambda > 571$ nm, $\lambda > 534$ nm) of 1,3-diphenyldiazopropyne (**9**) showing the growth of 1,3-diphenylpropynylidene (**3**) with the concomitant disappearance of **9** (Ar, 10 K). Top: Computed IR spectrum of triplet **3a**. (b) Bottom: IR subtraction spectrum showing the growth of diphenylcyclopropenylidene (**6**) along with the disappearance of **3** upon photolysis ($\lambda > 261$ nm) of **3** (Ar, 10 K). Top: Computed IR spectrum of singlet **6**. (c) IR subtraction spectrum obtained upon photolysis ($\lambda = 232 \pm 10$ nm) of **6** showing a decrease in the IR bands attributed to **6** with the regrowth of **3** (Ar, 10 K).

both exhibit symmetrical structures (C_2 and $D_{\infty h}$, respectively) and that localized bond-shift isomers are not minima on the respective potential energy surfaces.[20,24,29,32] It is conceivable that substituents might perturb the situation, such that the bond-shift isomers become energy minima. The symmetrical substitution pattern of triplet 1,3-diphenylpropynylidene (**3**), however, would render localized bond-shift isomers to be degenerate. Thus, the experimental observation of conformational isomerism for triplet 1,3-diphenylpropynylidene (**3**) requires an explanation other than traditional bond-shift isomerism. Our current observations are straightforwardly rationalized by the hypothesis that the initially formed triplet carbene is not able to achieve its equilibrium structure because of the influence of the matrix host in enforcing a geometry that resembles that of the precursor diazo compound. Only after annealing the matrix is the equilibrium structure of the triplet carbene achieved. The same hypothesis rationalizes the EPR data observed for triplet phenylpropynylidene (**2b**, **2c**)[21,23] and triplet 1,5-diphenylpentadiynylidene (**5**) systems,[22] without the need to invoke bond-shift isomerism.

In our opinion, the use of the term "bond-shift isomers" in the description of alkynyl carbenes is inappropriate when the initially formed carbene isomer is obtained only through the external influence of the matrix environment. Although our studies do not support the existence of bond-shift isomers for the triplet "alkynyl carbenes" HC_3H (**1a**),[20] PhC_3Ph (**3a**) (this work), and HC_5H (**4b**),[24] the data provide an interesting point of comparison with the organometallic complexes of these species. As ligands in transition-metal complexes, singlet "alkynyl carbenes" exhibit localized carbene structures, bond-shift isomerism, and interesting reactivity patterns that have been exploited in synthetic chemistry.[5,6,34,35] An interesting question that remains unresolved, concerning the "free" alkynyl carbenes, is why the reactivity of these symmetrical, highly conjugated species seems to be so characteristic of a classical, localized carbene.[13,24−26]

3. Summary

Triplet 1,3-diphenylpropynylidene (**3**) has been characterized by IR, UV/vis, and EPR spectroscopy in low-temperature matrices. Two conformational isomers of 1,3-diphenylpropynylidene (**3b** and **3a**) are spectroscopically distinguishable (Scheme 1). The initially formed conformer **3b** reflects the geometry of the diazo precursor, as enforced by the rigid matrix. Annealing the matrix permits the structure to relax to the equilibrium D_{2d} geometry **3a**. The highly symmetric equilibrium structure is best envisioned as a 1,3-allenic diradical. Density functional theory calculations suggest that the equilibrium structure does not exhibit a bond-localized structure that would be characteristic of an acetylenic carbene. Thus, the structure of the delocalized triplet carbene contrasts with that of the localized carbene structure observed in organometallic complexes of (singlet) alkynyl carbenes. Irradiation ($\lambda > 261$ nm) of triplet 1,3-diphenylpropynylidene (**3**) results in cyclization to singlet diphenylcyclopropenylidene (**6**), a process that is photochemically reversible at $\lambda = 232$ nm.

4. Methods

4.1. Computational Methods. DFT computations were performed with the Gaussian 98[58] and Gaussian 03[59] packages using the Becke three-parameter gradient-corrected exchange functional[60] with the correlation functional of Lee, Yang, and Parr[61] (B3LYP). The 6-31G* basis set was used for geometry optimizations, relative energies, and harmonic vibrational frequency computations. Vibrational frequencies were used to determine the nature of the stationary points as an energy minimum, transition state, or saddle point.

4.2. Matrix Isolation Spectroscopy. The apparatus and experimental techniques for low-temperature matrix isolation spectroscopy are described in the Supporting Information. In warming experiments, argon matrixes were capped with xenon to better maintain the integrity of the matrix at elevated temperatures.[62]

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4.3. 1,3-Diphenyldiazopropyne (9). A solution of 1,3-diphenyl-2-propyn-1-one trisylhydrazone (0.15 g, 0.309 mmol) in CH_2Cl_2 (1.7 mL) was added all at once to a suspension of 60% NaH/mineral oil (0.0124 g, 0.309 mmol; Aldrich) in CH_2Cl_2 (5.5 mL) at room temperature in the dark. Within 5 min of stirring at room temperature, the red color of the diazo compound began to appear. After being stirred for 35 min at room temperature, the cloudy red reaction mixture was poured into 22 mL of pentane, and the white precipitate was removed by suction filtration. The solvent was removed from the filtrate in vacuo, allowing the evaporation of solvent to keep the solution cold. Once the solvent was removed, the crude diazo compound was immediately purified by rapid elution (low N_2 pressure) column chromatography (3 cm × 25 cm) in the dark using neutral alumina (activity grade V) and 5:1 pentane/CH_2Cl_2 as the eluent. The diazo compound can be visually observed moving down the column as a red band ($R_f = 0.7$). Once the diazo band was collected, the solvent was removed in vacuo, allowing the evaporation of the solvent to keep the solution cold. The diazo compound was obtained as a deep red oil (0.0460 g, 0.211 mmol, 68% yield). In most instances, the purified diazo compound was used immediately for matrix isolation. However, the diazo compound can be stored at −78 °C under N_2 in the dark for several days without noticeable decomposition. 1,3-Diphenyldiazopropyne (**9**): ^{1}H NMR ($CDCl_3$) δ 7.42 (m, 7H), 7.15 (m, 3H); ^{1}H NMR (CD_2Cl_2) δ 7.32 (m, 10H); IR (CD_2Cl_2, 298 K) 3083 w, 3064 w, 3036 w, 2206 w, 2050 vs, 1596 m, 1491 m, 1452 w, 1444 w, 1366 w, 1288 w, 1275 w, 1182 w, 1172 w, 1071 w, 1027 w, 754 m, 612 w, 527 w cm^{-1}; IR (Ar, 10 K) 3114 w, 3095 w, 3090 w, 3081 w, 3073 w, 3065 w, 3042 w, 3017 w, 2218 m, 2050 vs, 1959 w, 1953 w, 1941 w, 1935 w, 1886 w, 1868 w, 1854 w, 1812 w, 1601 m, 1581 w, 1506 w, 1497 m, 1490 m, 1457 w, 1445 w, 1370 w, 1601 m, 1581 w, 1506 w, 1497 m, 1490 m, 1457 w, 1445 w, 1370 w, 1325 w, 1303 w, 1289 w, 1280 w, 1274 w, 1184 w, 1173 w, 1096 w, 1077 w, 1070 w, 1031 w, 1016 w, 998 w, 907 w, 895 w, 751 s, 690 s, 611 w, 541 w, 526w, 515 w, 463 w cm^{-1}; UV/vis (Ar, 10 K) 227.2, 232.4, 240.0, 244.4, 252.0, 283.2, 290.8, 299.6, 319.2 nm.

Once obtained, the diazo compound was dissolved in a minimal amount of CH_2Cl_2, and transferred to a small glass tube (1 cm × 7 cm) used for subliming the compound onto the matrix isolation window. The solvent was removed in vacuo at −41 °C, and the tube was vented to N_2. After the sample tube was transferred to the matrix isolation apparatus, the sample was subjected to three freeze−pump−thaw cycles at 77 K, and the sample tube was evacuated to 2×10^{-6} Torr at room temperature. Once the pressure in the matrix isolation vacuum system had fallen below to 2×10^{-6} Torr, the sample tube was cooled to −78 °C with powdered dry ice, and the cold window was cooled to 30 K. The diazo compound was sublimed from the sample tube at room temperature and co-deposited with argon onto a cold window (CsI for IR spectroscopy; sapphire for UV/vis spectroscopy) maintained at 30 K. The small glass sample tube (1 cm × 7 cm), which places the diazo compound ca. 7−9 cm away from the cold window, was essential for efficient sublimation of the diazo compound at room temperature. For EPR experiments in argon, the diazo compound was co-deposited with argon on a copper rod maintained at 10 K.

For EPR experiments involving frozen organic glasses, a solution of 1,3-diphenyldiazopropyne (**9**) was prepared by rapidly weighing the purified diazo compound and dissolving in the appropriate amount of solvent (2-methyltetrahydrofuran, MeTHF, or methylcyclohexane, MCH, spectroscopic grade) to give a solution of concentration ca. 5 mM. A small volume of this solution (ca. 0.4−0.5 mL) was placed in a 3 mm quartz EPR tube (Wilmad Glass Co., Inc.; model 727-SQ-250M) with a Pyrex 14/20 ground glass joint attached to the top. The sample was subjected to five freeze−pump−thaw cycles at 77 K in the dark, and the tube was sealed under vacuum with an O_2/gas torch. In most instances, the sample was used immediately. However, the solution can be stored at −78 °C in the dark for several days without noticeable decomposition. To prevent crystallization and ensure that a glass was formed for the liquid helium experiments, the sample was first frozen to a glass by immersing in liquid nitrogen and rapidly transferring (ca. 1−2 s) the tube from the liquid nitrogen dewar to the pre-cooled liquid helium cryostat at 4 K.

4.4. Non-relaxed Triplet 1,3-Diphenylpropynylidene (3b). IR (Ar, 10 K) 3119 w, 3085 w, 3076 w, 3065 w, 3057 w, 3024 w, 3007 w, 1954 w, 1939 w, 1924 w, 1878 w, 1864 w, 1804 w, 1790 w, 1649 w, 1576 w, 1556 m, 1510 w, 1478 m, 1461 m, 1438 m, 1270 w, 1241 w, 1231 w, 1221 w, 1173 w, 1163 w, 1158 w, 1092 w, 1065 w, 1023 w, 903 w, 748 s, 680 s, 497 w, 489 w, 461 w cm^{-1} (Figures 4a and 5a); UV/vis (Ar, 10 K) λ_{max} 217.2, 266.4, 279.2, 287.2, 297.2, 307.6, 314.4, 324.8, 332.4, 335.6, 343.2, 456.4, 459.6, 463.3, 472.3, 494.9, 498.1, 498.7, 507.6, 508.5, 510.9, 511.8, 512.8, 513.9, 520.8, 522.1, 539.5, 540.8 nm (Figure 3); EPR (Ar, 10 K) $|D/hc| = 0.484$, $|E/hc| = 0.00423$ cm^{-1}; Z_1 1778, X_2 5316, Y_2 5490, Z_2 8571 G; microwave frequency 9.5304 GHz (Figure 2).

4.5. Relaxed Triplet 1,3-Diphenylpropynylidene (3a). IR (Ar, 10 K) 3114 w, 3108 w, 3090 w, 3081 w, 3071 w, 3060 w, 3044 w, 1950 w, 1934 w, 1920 w, 1873 w, 1859 w, 1797 w, 1785 w, 1645 w, 1572 w, 1553 m, 1503 w, 1494 w, 472 m, 1458 m, 1435 m, 1267 w, 1236 w, 1170 w, 1154 w, 1088 w, 1062 w, 1021 w, 898 w, 756 w, 745 s, 695 w, 690 w, 678 s, 499 w, 485 w, 461 w cm^{-1} (Figure 4b); UV/vis (Ar, 10 K) 273.2, 278.4, 294.4 nm (Figure 3); EPR (Ar, 10 K) $|D/hc| = 0.468$, $|E/hc| < 0.0002$ cm^{-1}; Z_1 1612, XY_2 5306, Z_2 8404 G; microwave frequency 9.5313 GHz (Figure 1).[18,49]

4.6. Diphenylcyclopropenylidene (6). IR (AR, 10 K) 3110 w, 3093 w, 3086 w, 3074 w, 3061 w, 3042 w, 3034 w, 3008 w, 1978 w, 1959 w, 1916 w, 1899 w, 1814 w, 1805 w, 1606 w, 1603 w, 1454 w, 1332 s, 1313 w, 1304 w, 1259 w, 1254 w, 1170 w, 1075 w, 1051 m, 1024 w, 1021 w, 962 w, 929 w, 762 s, 690 s, 623 w, 583 m, 518 m cm^{-1} (Figure 5); UV/vis (Ar, 10 K) λ_{max} 220.0, 225.2, 244.8, 255.2, 266.8, 272.8, 280.0, 286.4, 295.6 nm (Figure 3).

Acknowledgment. We gratefully acknowledge the National Science Foundation for financial support of this project, as well as support for the Departmental EPR spectrometer and computing facilities.

Supporting Information Available: Synthetic procedures, experimental IR spectra from oxygen trapping studies, plots of computed IR spectra for conformers of triplet 1,3-diphenylpropynylidene (**3**), Cartesian coordinates for computed (B3LYP/6-31G*) structures, harmonic vibrational frequencies and IR intensities, and complete literature citations for refs 58 and 59. This material is available free of charge via the Internet at http://pubs.acs.org.

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