Different Behavior of Nitrenes and Carbenes on Photolysis and Thermolysis: Formation of Azirine, Ylidic Cumulene, and Cyclic Ketenimine and the Rearrangement of 6-Phenanthridylcarbene to 9-Phenanthrylnitrene

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Flash vacuum thermolysis (FVT) of 9-azidophenanthrene 8, 6-(5-tetrazolyl)phenanthridine 18, and [1,2,3]triazolo[1,5-f]phenanthridine 19 yields 9-cyanofluorene 12 as the principal product and 4-cyanofluorene as a minor product. In all cases, when the product is condensed at or below 77 K, the seven-membered ring ketenimine 24 is detectable by IR spectroscopy (1932 cm\(^{-1}\) up to 200 K. Photolysis of Ar matrix isolated 8 at \(\lambda = 308\) or 313 nm generates at first the azirine 26, rapidly followed by the ylidic cumulene 27. The latter reverts to azirine 26 at \(\lambda > 405\) nm, and the azirine reverts to the ylidic cumulene at 313 nm. Nitrene 9 is observed by ESR spectroscopy following FVT of either azide 8, tetrazole 18, or triazole 19 with Ar matrix isolation of the products. Nitrene 9 and carbene 21 are observed by ESR spectroscopy in the Ar matrix photolyses of azide 8 and triazole 19, respectively.

Introduction

The rearrangements and interconversions of aromatic carbenes and nitrenes, e.g., phenylnitrene 1 and 2-pyridylcarbene (eq 1), have been the subject of intense interest.\(^1\) Recently, DFT calculations\(^2\) revealed that annelated derivatives of the cyclic ketenimine 2 may exist in an ylidic (zwitterionic) form 6 rather than the classical o-quinoid ketenimine form 7. The cost of charge separation in the ylide is compensated by the recovery of the resonance energy of the benzene ring. 4-Quinolynitrene and 1-naphthynitrene 3 can in principle undergo ring expansion in two directions, either via the high energy azirine 4a (which is a transition state) or the lower

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Results and Discussion

FVT. 9-Azidophenanthrene 8 was subjected to flash vacuum thermolysis (FVT) at temperatures between 450 and 600 °C (no significant reaction took place at lower temperatures). The following products were isolated and identified from the FVT reaction at 500 °C: 9-cyanofluorene 12 (73%), phenanthrene (7%), 9,9′-azophenanthrene 11 (10%), and 9-aminoaphenanthrene 10 (10%). Compounds 10 and 11 are the typical triplet aryl nitrene products, and their formation demonstrates that some intermolecular reaction take place under FVT conditions. Compound 12 is the expected product of ring contraction.\(^3\)

Closer inspection of the Ar matrix IR spectra and GC/MS analyses of the crude thermolysis products revealed that minor amounts of 4-cyanofluorene 13 and 1-cyanofluorene 16 were also present (2.5% of each at 500 °C; 6.7% of 13 and 3.7% of 16 at 600 °C by GC).\(^5\) These compounds were identified by direct comparison with synthetic samples. Because it is known that cyano groups can undergo migrations in aromatic systems at high temperatures, and such shifts can be accelerated strongly by chemical activation,\(^6\) it was necessary to check the FVT of 9-cyanofluorene 12. FVT of 12 at 600–800 °C did not result in any isomerization. At 1000 °C a 5% rearrangement to 1-cyanofluorene 16 took place; 4-cyanofluorene was not detectable. A 1% yield of fluorene was also obtained, which indicates the occurrence of a free radical pathway. Therefore, in any FVT reaction where 9-cyanofluorene 12 is formed at elevated temperature, and/or in strongly exothermic reactions, where chemical activation is likely, minor amounts of 1-cyanofluorene 16 may be expected as a byproduct.

Formation of 9-cyanofluorene 12 could proceed via ring opening to diradical 14 (Scheme 1), but calculations reported below indicate that there is a lower energy transition state for the concerted ring contraction, \(9 \rightarrow 12\). CASPT2/CASSCF(8,8) calculations with the cc-PVDZ-Dunning basis set for phenyl nitrene \(1\) OSS (open-shell singlet) give an activation energy of 31 kcal/mol for the concerted ring contraction to 5-cyanocyclopentadiene. This is further discussed in the Calculations section.

The mechanism of formation of 4-cyanofluorene 13 is thought to involve ring opening to the carbene 15 (Scheme 1). Calculations reported below show that this carbene can cyclize to 13 in a highly exothermic reaction (~92 kcal/mol). The cyclization of 2-biphenylylcarbene to fluorene takes place via "isofluorene" (9\(\text{aH}\)-fluorene) and has a very small calculated barrier.\(^7\)

When the FVT of 8 was carried out with isolation of the products on a KBr target, either as a neat solid film at 77 K or with Ar at 20 K for IR spectroscopic monitoring, a new species absorbing strongly at 1932 cm\(^{-1}\) was observed together with 9-cyanofluorene, which has characteristic strong bands at 1451, 759, and 742 cm\(^{-1}\) and CN stretching vibrations at 2262 and 2234 cm\(^{-1}\) (Figure 1).

The 1932 cm\(^{-1}\) signal disappeared on warming between 150 and 200 K and is ascribed to the dibenzo[\(d,f\)]=1-azacycloheptaene 24 (Scheme 2). No discrete product was identified as a result of the warming, but dimerization analogous to that of the carbodiimide (dibenzo[\(d,f\)]=1,3-diazacycloheptaene) analog\(^6\) is a possibility. Compound 24 is the first seven-membered ring ketene.

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\(^{5}\) The thermal ring contractions of 9-phenanthridynitrene to a mixture of 9- and 4-cyanoarbazoles, its ring expansion to dibenzo[\(d,f\]=1,3-diazacycloheptaene, and the dimerization of the latter to a stable 2,4-dimino-1,2-diazetidine derivative have been reported: (a) Wentrup, C.; Thetaz, C.; Mayor, C. Helv. Chim. Acta 1972, 55, 2633. (b) Wentrup, C.; Winter, H.-W. J. Am. Chem. Soc. 1980, 102, 6150.


imine to be stable enough to be detected in an FVT experiment without recourse to matrix isolation photochemistry. In other words, this is the first direct proof that arylnitrenes actually undergo ring expansion to azacycloheptatetraenes in the gas phase under thermal conditions. The two benzo rings confer considerable stability to the molecule, just as is the case for the cyclic carbodiimide analogue.\(^5\) Nevertheless, \(24\) is a delicate compound. It was observable only when an “internal” oven was used, consisting of a 10 cm long, 0.7 cm i.d., electrically heated quartz tube suspended in a vacuum chamber directly flanged onto the cryostat cold head so that the FVT products can travel to the cold KBr target without any wall collisions occurring. If an “external” oven was used, consisting of a similar quartz tube but with a 5 cm unheated length connecting it to the cold head, no trace of the 1932 cm\(^{-1}\) absorption was detectable.

The wavenumber of the ketenimine function in \(24\) is in line with expectations; 1895 cm\(^{-1}\) for 2; 1902–1909 for 5 \((X = N)\) and 1913–1926 for 5 \((X = CH)\).\(^5,6,8\) The calculated IR spectrum of \(24\) (Figure 1a) predicts the cumulenic stretching vibration at 1947 cm\(^{-1}\) at the B3LYP/6-31G* level it is at 1934 cm\(^{-1}\). The o-quinoid ketenimine “bond-shift” isomer \(28\) (Scheme 2) is not an energy minimum, and hence its IR spectrum was not calculated. However, judging from our computational experience with the ring expansion products of the quinolyl- and naphthylnitrenes,\(^5,8\) o-quinoid ketenimines of this type, e.g., 7 (eq 2), should absorb strongly around 1800 cm\(^{-1}\), i.e., in between the aromatic ketenimines such as 5 and 24 and ylidic cumulenes such as 6 and 27 (see below).

We have reported the aromatic carbene--nitrene rearrangement (eq 1)\(^8\) and demonstrated that nitrenes are inherently more stable than the isomeric carbenes.\(^14\) Thus, 2-pyridylcarbene rearranges thermally to phenyl nitrene 1. Modern calculations have confirmed this.\(^10\) Arylcarbenes can be generated by FVT of 5-aryltetrazoles by consecutive loss of two nitrogen molecules, a reaction leading to aryl diazomethanes initially.\(^6,11\) The same arylidiazomethanes may be formed by reversible ring opening of triazoloazines.\(^6,11\) Therefore, to generate carbene 21, tetrazole 18 was prepared by addition of \(HN_3\) to phenanthridine-6-carbonitrile 17, and triazole 19 by oxidation of the hydrazine of phenanthridine-6-carboxaldehyde with \(\text{MnO}_2\).

Preparative FVT of tetrazole 18 at 600 °C resulted in partial cycloreversion to nitrile 17 (3–10%), but the main product was 9-cyano fluorenone 12 (isolated in 68% yield), which suggests that a very efficient carbene--nitrene rearrangement \((21 \rightarrow 9)\) is taking place. 6-Methylphenanthridine 22 and small amounts of 4-cyano fluorenone 13, 1-cyano fluorenone 16, and 9-aminophenanthrene 10 were also formed (eq 3). The former product \((22)\) suggests

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FVT conditions. The presence of a small amount of 9-aminophenanthrene is important evidence for the formation of nitrene 9. When this reaction was carried out at 600 °C using the internal oven with product isolation at 20 K for IR spectroscopy, 9-cyanofluorene 12 (2262, 742 cm⁻¹), 4-cyanofluorene (2235 cm⁻¹), and the cyclic ketenimine 24 (1932 cm⁻¹; observable until 200 K on warm up without Ar) were recorded (the IR spectrum is shown as Figure S1 in the Supporting Information). GC/MS of the thermolysate also revealed the formation of substantial amounts of triazolophenanthridine 19, formed by loss of N₂ from the tetrazole 18 and recyclization of the diazo compound 20 so produced.

Similarly, FVT of triazole 19 at 600—750 °C followed by GC/MS analysis afforded 9-cyanofluorene 12, 6-methylphenanthridine, and small amounts of 1- and 4-cyanoanilines and 9-aminophenanthrene. FVT at 550 °C using the internal oven and Ar matrix isolation of the products at 12 K allowed the detection of the cyclic ketenimine 24 (1932 cm⁻¹) and 9-cyanofluorene 12 (2262, 742 cm⁻¹) by IR spectroscopy.

**Photolysis.** The matrix photolysis of azide 8 was quite different. The ketenimine 24 was not observed at all. Instead, brief photolysis of 8 (Ar, 7 K, 313 nm, 30 s) resulted in a new species absorbing at 1742 cm⁻¹. In the course of further photolysis another new species rapidly grew in at 1702 cm⁻¹, and this was the main species after 14 h, i.e., the time required to fully destroy the azide. Photolysis of the 1702 cm⁻¹ species at λ > 405 nm regenerated the 1742 cm⁻¹ species, which could again be converted to the 1702 cm⁻¹ species at 313 nm. It was possible to cycle between these two species several times. Suitable spectral subtraction generated the spectra of the individual compounds, and the good agreement with the DFT-calculated spectra identify them as azirine 26 (ν_{CN} = 1742 cm⁻¹) and ylidic cumulene 27 (1702 cm⁻¹), respectively (Scheme 2 and Figure 2). The corresponding azirine 4b derived from 1-naphthylnitrene 3 (eq 2; X = CH) has ν_{CN} ~ 1730 cm⁻¹, and the ylidic cumulene 6 absorbs at ca. 1700 cm⁻¹. The analogous azirine and ylidic cumulene from 2-naphthylnitrene absorb at ca. 1725—1730 and 1680 cm⁻¹, respectively. The azirine 29 formed by cyclization of 3-isoquinolylnitrene has ν_{CN} = 1725 cm⁻¹ in an Ar matrix.

![Diagram](image)

As explained above, the o-quinoid ketenimine "bond-shift" isomer 28 (Scheme 2) is not a calculated energy minimum, but it would be expected to absorb in the 1800 cm⁻¹ range in the IR spectrum.

Similar matrix photolysis with UV–vis detection revealed a yellow intermediate with an absorption maximum at 450 nm, which is assigned to the ylidic cumulene 27 (Figure 3). This absorption disappeared again on bleaching at λ > 405 nm. The initial UV spectrum shows fine structure in the 325—360 nm region due to azide 8. New, weak, fine structure grows in on photolysis, and by analogy with other arylnitrenes, this may be due to the presence of nitrene 9T. More substantial evidence for the nitrene is given by the ESR spectrum below.

**FIGURE 2.** (a) Calculated IR spectrum of ylidic cumulene 27 (B3LYP/6-31G* with a scaling factor of 0.9613 for wavenumbers). (b) Difference IR spectrum after photolysis at λ = 313 nm (monochromator) showing the formation of cumulene 27 and disappearance of azirine 26. (c) Difference IR spectrum after photolysis at λ > 405 nm showing the formation of azirine 26 and vanishing of ylidic cumulene 27. Spectra b and c are mirror images and show reversible interconversion of 26 and 27. (d) Calculated IR spectrum of azirine 26 (B3LYP/6-31G* level with a scaling factor of 0.9613 for wavenumbers). The abscissa is in wavenumbers.

The triazole 18 was photochemically inert, and the triazole 19 photolyzed extremely sluggishly. Such behavior has been observed for other triazoloazines. A diazo compound (20) was observed at 2080—2097 cm⁻¹ on photolysis at 222 nm, but the intensities of subsequent photoproducts in the matrix IR spectrum were too weak for a clear-cut demonstration of the rearrangement of carbene 21 to nitrene 9 (via 25, 24, and 23, Scheme 2). However, this rearrangement was revealed by ESR spectroscopy, which is more sensitive than IR.

**ESR Spectroscopy.** Photolysis of triazole 19 in an Ar matrix at 15 K using a 308 nm lamp afforded the carbene 21 (Figure 4a; D = 0.5161 cm⁻¹; E = 0.0257 cm⁻¹). In contrast, FVT of either tetrazole 18 or triazole 19 at 550 °C with Ar matrix isolation at 15 K afforded the ESR spectrum of the nitrene 9 (Figure 4b and Figures S2 and S4 in the Supporting Information; D = 0.8110 cm⁻¹; E ≤ 0.0023 cm⁻¹; averages of several measurements) (the carbene was not detectable under FVT conditions). The thermolysate from the tetrazole was recovered from the cryostat, and examination by GC/MS revealed triazolophenanthridine 19, 9-cyanofluorene 12, 4-cyanofluorene...
Photolysis of azide 8 in an Ar matrix at 15 K at 308 nm also afforded the ESR spectrum of nitrene 9, and thermolysis of this azide in a stream of Ar at 550 °C using the internal oven and condensation of the product to form an Ar matrix at 15 K afforded the ESR spectrum of nitrene 9 (Figure S3 in the Supporting Information).

The zero-field splitting parameters $D$ for both the nitrene 9T and the carbene 21T are in very good agreement with expectations based on correlations with natural (or Mulliken) spin densities calculated with the UB3LYP/EPR-II program within Gaussian 03. Smolinsky et al. were the first to report a correlation between $D$ values and HMO spin densities in arylnitrenes. We have found excellent linear correlations between the measured values of $D$ (cm$^{-1}$) and the calculated natural and Mulliken spin densities on the nitrene nitrogen ($\rho$) in a wide range of aryl- and heteroarylnitrenes, and similarly between $D$ and the spin density on the carbene carbon in aryl- and heteroarylcarbenes.

Calculations. It is now well established that for arylnitrenes (unlike the corresponding carbenes) the open-shell singlet (OSS) states have lower energies than the closed-shell singlets (CSS). It is not possible to calculate the open-shell singlet nitrene 9 OSS using DFT.

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FIGURE 3. UV–vis spectra resulting from the photolysis of 9-azidophenanthrene 8 at $\lambda = 313$ nm showing formation of ylide 27 with an absorption maximum at 450 nm. The heavy bars represent the calculated optical spectrum of ylide 27. The open bar is for azirine 26 (time-dependent B3LYP/6-31G*). The abscissa is in nanometers; the ordinate is in arbitrary intensity units.

FIGURE 4. (a) ESR spectrum of carbene 21 obtained after a 45 min photolysis of 19 at 308 nm. (b) ESR spectrum of nitrene 9 obtained by FVT of 19 at 550 °C.
methods. An approximation described by Cramer was used to estimate the energy of OSS at the B3LYP/6-31G* level in Figure 5. This places OSS 19.2 kcal/mol below CSS and 12.5 kcal/mol above T (Figure 5). A CASPT2/CASSCF(8,8) calculation with the ANO basis set places OSS 20.1 kcal/mol below CSS and 15.8 kcal/mol above T (Figure 5). We have used the latter value for the singlet–triplet (S–T) gap in 9. To calculate the transition states connecting OSS with the interesting products 12, 24, and 26, CASSCF calculations would be required, but this would be beyond our current computing resources. DFT calculations of the transition states TS1 (27 kcal/mol) and TS4 (32 kcal/mol on the energy scale of Figure 5) connecting 12 and 24 with the closed-shell singlet, OSS, have been performed, but these energy values can be expected to be too high. In the case of the open-shell naphthylnitrenes, it was found that UB3LYP calculations gave transition state energies for the cyclization to azirines which were in good agreement with CASPT2 calculations. The CASPT2//CASSCF(12,12)/6-31G* calculations on the open-shell 1- and 2-naphthylnitrenes gave barriers of 3–7 kcal/mol for cyclization to azirines analogous to 26, e.g., 4b (eq 2). A UB3LYP/6-31G* calculation of TS5 connecting OSS and 26 gives a value of 2.5 kcal/mol (Figure 5) with a spin contamination factor <S^2> of 0.26. Thus, estimates based on the naphthylnitrenes seem justified. For comparison, activation barriers of 6–9 kcal/mol were found for cyclizations of 2-biphenylnitrene to azirines at CASPT2/CASSCF and CASPT2/DFT levels of theory and 4–8 kcal/mol for cyclization of 2,6-dialkylphenylnitrenes and the parent phenylnitrene at the DFT/CASPT2 level. Cyclization to nonaromatic azirines such as 4a (eq 2) and 23 (Scheme 2) have much higher activation energies due to the loss of the resonance energy of a second benzene ring. On the basis of the comparison with the naphthylnitrenes, TS connecting OSS and ketenimine 24 is estimated as ca. 20 kcal/mol (Figure 5). This nonaromatic transition state TS1 has the structure of azirine 23 in Scheme 2, and this azirine is not found to be a minimum at the DFT level. Since CASPT2 calculations may overestimate the stability of open-shell singlet nitrenes relative to azirines, the true energies of TS1 and TS5 may be a few kcal/mol lower. This would make the cyclization of OSS to azirine 26 virtually barrierless.

A proper description of the ring contraction of nitrene OSS to 9- to 9-cyanoazulene 12 via TS4 again requires CASSCF calculations. We have investigated the analogous ring contraction in phenylnitrene 1 OSS using CASPT2//CASSCF(8,8) calculations and found a transition state for the concerted ring contraction to 5-cyanocyclopenta-
diene 30 with a barrier of 30.9 kcal/mol (eq 4). Assuming a similar barrier for phenylnitrene OSS, this places TS4 at ca. 31 kcal/mol (Figure 5). Ring contraction to 5-cyanocyclopentadiene can also take place from the seven-membered ring ketenimine 2, albeit with a drastically higher calculated activation energy (68 kcal/mol; eq

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4). Thus, starting from the carbene side, 21, it is possible that ketenimine 24 may undergo some direct ring contraction to 9-cyanofluorene 12. The diradical 14 could form by ring opening of either 9 or 24, and it would also be able to ring close to 12. The triplet state 14T is calculated to be 44.2 kcal/mol above 9T (28.4 kcal/mol above 9 OSS), and 14 CSS is 55.9 kcal/mol above 9 OSS (Figure 5). The energy of 14 OSS cannot be calculated directly using DFT methods, but its energy is estimated as ca. 45 kcal/mol using Cramer’s method,13 whereby it is necessary to constrain the molecule to planarity.

The formation of 4-cyanofluorene 13 can take place via ring opening to the singlet 2-(2-cyanophenyl)phenylcarbene 15S, which in its s-trans conformation (43 degrees twist between phenyl rings) is a minimum at ca. 37.3 kcal/mol above 9 OSS (the s-cis conformation is not a minimum; it ring closes to 13). TS4 lies significantly below 15S in agreement with the observation that 12 is the major thermal product even though 13 has a lower absolute energy.

TS2 (37.3 kcal/mol) connects the closed-shell singlet phenanthridycarbene 21S with cyclic ketenimine 24 and has a structure corresponding to the nonaromatic and nonobserved cyclopentene 25 (Scheme 2). The ketenimine 24 is calculated to be the global minimum among the isomeric singlet species in Scheme 2 prior to ring contraction to cyanofluorenes. This molecule (24) preserves two aromatic rings and has no charge separation.

TS3 (26.9 kcal/mol) connects azirine 26 and the ylidic cumulene 27. The azirine 26 is calculated to be 11.4 kcal/mol lower in energy than the ylide 27 (Figure 5). The o-quinoid ketenimine 28 (Scheme 2) was not observed in any of the experiments (it would be expected to absorb in the 1800 cm⁻¹ range in the IR spectrum; see above). It is not an energy minimum at the DFT computational level, but at the Hartree–Fock level it is ca. 10 kcal/mol less stable than 27 and thus not energetically competitive with the observed cumulenes 24 and 27.

Under FVT conditions, all the (singlet) species can be expected to be in thermal equilibrium, including 24, 26, and 27 (and perhaps even 28), but the thermodynamically preferred and observable intermediate 24 will dominate prior to ring contraction to the cyanofluorenes 12 and 13. The latter are thermodynamic sinks, and under preparative FVT conditions they become the exclusive rearrangement products.

Conclusion

Both 9-phenanthrynitrene 9 and 6-phenanthrydycar- bene 21 undergo ring expansion in the gas phase under thermal conditions to give dibenzoazacycloheptatetraene 4 (νmax 1932 cm⁻¹). In sharp contrast, under matrix photochemical conditions, the nitrene cyclizes to the azirine 26 (νC=O 1742 cm⁻¹), which can be photochemically interconverted with the novel ylidic cumulene 27 (νmax 1702 cm⁻¹, λmax 450 nm). DFT calculations indicate that 24 is the product of thermodynamic control. Under

FVT conditions it is likely that all the intermediates, 24, 26, and 27 can form, but thermochemistry will favor the former. Although the barrier for ring contraction of 9-phenanthrynitrene 9 to 9-cyanofluorene 12 is higher than that for ring expansion to ketenimine 24, 12 is the thermodynamic sink, and it cannot be avoided that it is formed under FVT conditions.

6-Phenanthrydycarbene 21 is observed by ESR spectroscopy when photochemically generated (D = 0.5161 cm⁻¹, E = 0.0257 cm⁻¹), and it rearranges thermally to 9-phenanthrynitrene 9, which is also observed by ESR spectroscopy (D = 0.8110 cm⁻¹; E ≤ 0.0023 cm⁻¹); thermal rearrangement to ketenimine 24 is observed by IR spectroscopy, and 9-cyanofluorene 12 is a major product of preparative FVT.

Computational Methods

The energies of the relevant species isomeric with phenanthrynitrene were calculated at the B3LYP/6-31G* level of theory using the Gaussian 98 suite of programs.10 The energies, together with those of the triplet nitrene (9T), the closed-shell singlet nitrene (9 CSS), and the open-shell singlet nitrene (9 OSS) are depicted in Figure 5. The energy of the open-shell singlet nitrene was estimated using the method of Cramer.15 The energies of the open-shell singlet and triplet nitrenes were also calculated at the CASPT2 level using the MOLCAS20 suite of programs. According to CASPT2/CASSCF(8,8) with the ANO basis set, the triplet is 15.8 kcal/mol more stable than the open-shell singlet. The active space for CASSCF and CASPT2 calculations was constructed from 8 orbitals, 3 π⁺(A′); 1 π⁻(A′), A on N, and 4 π⁺(A′), with 8 electrons. All reference weights were above 0.6, which is assumed as enough reference weight for the CASSCF wave function in CASPT2 for this size of molecule.

The geometry was optimized with CASSCF(8,8)/ANO, and the single-point CASPT2 energy was obtained for this geometry (the description of states is included in the Supporting Information).

The UV–vis spectra were predicted using density functional theory based on time-dependent (TD) response theory.21 We used the TD-DFT implementation in Gaussian 98 as described recently by Stratmann et al.22 Mulliken and natural spin densities in nitrenes and carbenes were calculated using UB3LYP/EPR-II within Gaussian 03, revision C.01. Zero-field splitting parameters of nitrenes and carbenes were calculated using Wasserman’s equations.23

(18) Bednarek, P.; George, L.; Wentrup, C. To be published. The calculated activation barriers for the 1,5-H shift converting 5-cyano- cyclopentadiene to 1-cyclopenptadiene is 22.6 kcal/mol and that for conversion of 1-cyclopropenadiene to 2-cyclopenptadiene is 17.8 kcal/mol. The calculated energies of 5-, 1-, and 2-cyclopentadienenes are −40.5, −49.6, and −47.7 kcal/mol, respectively, relative to 1 OSS (B3LYP/6-31G*).


Experimental Section

The apparatus and procedures for preparative FVT, 24 for isolation at 77 K, 24 and for Ar matrix isolation 25 were as previously described. The internal oven employed a 10 cm long, 0.7 cm i.d., electrically heated quartz tube suspended in a vacuum chamber directly flanged to the cryostat cold head, with a wall-free flight path of ca. 3 cm between the exit of the quartz tube and the cold target (KBa or CsI for IR spectroscopy, quartz for UV spectroscopy, and Cu for ESR spectroscopy). The external oven consisted of a 20 cm (0.7 cm i.d.) quartz tube ending in a quartz flange directly flanged to the cryostat cold head; this tube was heated on a 10 cm length and had a ca. 5 cm unheated length connecting it to the cold head. For matrix isolation and FVT/matrix isolation, ca. 10 mg of the compounds were sublimed in a stream or Ar at 60–100 °C (azide 8), 70–250 °C (tetrazole 18), 90–110 °C (triazole 19), and 120 °C (9-cyanofluorene 12). FVT products were isolated in liquid nitrogen (77 K) in the preparative thermolyses, by GC/MS methods; mp 90 °C (literature value, 27 92 °C); -m/z 191.

9-Aminophenanthrene 22 were commercial samples. 9,9′-Fluorene-4-carboxylic acid (10 mg, 22%); mp 77 °C (literature value, 31 79); -m/z 191.

Fluorene-1-carboxylic acid with chlorosulfonyl isocyanate to yield 121 mg (63%); mp 92 °C (literature value, 31 94–94.5 °C); GC/MS Rt 10.97 min; m/z 191.

Fluorene-1-carboxylic acid 16. This was prepared analogously to 13 from 210 mg (1 mmol) of fluorene-1-carboxylic acid with chlorosulfonyl isocyanate to yield 121 mg (63%); mp 92 °C (literature value, 31 94–94.5 °C); GC/MS Rt 10.97 min; m/z 191.

9-Azidophenanthrene 8. This was initially prepared by photolysis of 9-bromophenanthrene in hexane at reflux followed by addition to tosyl azide in ether at 0 °C by adaptation of literature procedures. 22 However, this procedure affords as a byproduct a butylated azidophenanthrene which, if not removed completely, gives rise to some butylated cyanofluorene on FVT (detected by GC/MS and IR but not examined further).

Pure 9-azidophenanthrene was prepared as follows: 9-aminophenanthrene (0.525 g, 2.7 mmol) was dissolved in a warm (60 °C) solution of concentrated sulfuric acid (3 mL) in water (18 mL) and diazotized with sodium nitrite (0.225 g, 3.3 mmol) in water (12 mL) at 0 °C. After stirring for 30 min, active charcoal (0.3 g) was added, and the mixture was stirred for another 10 min at 0 °C. The cold yellow solution of diazonium salt was filtered on Celite by suction. Sodium azide (0.30 g, 4.6 mmol) in water (10 mL) was added dropwise to the filtrate at 0 °C. After 3 h, the precipitated azide was collected and recrystallized from methanol/water (20:1) to yield 9-azidophenanthrene as white shiny needles (0.356 g, 60%); mp 112–113 °C (literature value, 33 112–113 °C); literature value, 33b 115–116 °C); sublimes at 80–100 °C (10–3 mbar). The substance is extremely light sensitive and should be kept in the dark. H NMR (CDCl 3) δ 6.65 (dd, J = 9.3 and 1.1 Hz, 1H), 6.82–6.80 (m, 1H), 8.18 (dd, J = 9.2 and 1.2 Hz, 1H), 7.82–7.80 (m, 1H), 7.70 (dd, J = 15.3, 8.4 and 1.4 Hz, 1H), 7.64–7.57 (m, 3H), 7.46 (s, 1H); 13C NMR (CDCl 3) δ 135.1, 131.6, 131.1, 128.2, 127.5, 127.3, 127.1, 126.7, 126.5, 126.1, 126.0, 123.1, 122.6, 113.4 ppm; IR (KBr) 2217(w), 2157(w), 2114, 1761, 1695, 1681, 1476, 1460, 1375, 1326 cm −1; UV (CH 3CN) λ max 318 (sh), 310, 262, 256 (sh), 246 nm (cf. ref 33b). Anal. Calcd for C 14 H 12 N 4: C, 76.70; H, 4.14; N, 19.16. Found: C, 76.71; H, 4.05; N, 19.18.

6-(5-Tetrazolyl)phenanthridine 18. A mixture of 1 g (5 mmol) of 6-cyanophenanthridine, 3.25 g (50 mmol) of NaN 3, and 2.65 g (50 mmol) of NH 4 Cl was suspended in 50 mL of DMP and refluxed for 6 h. The solvent was removed in vacuo, and the residue was taken up in 50 mL of H 2 O and brought to pH 2 with concentrated HCl. The product thus precipitated was filtered and recrystallized from EtOH to give 0.7 g (63%); mp 203–206 °C. H NMR (DMSO-d 6 ) δ 154.8, 144.2, 142.3, 132.8, 131.7, 129.8, 129.4, 128.8, 128.4, 127.5, 124.0, 123.3, 122.8, 122.6 ppm. Anal. Calcd for C 14 H 12 N 4: C, 68.01; H, 3.67; N, 28.32. Found: C, 67.60; H, 3.53; N, 28.36.

[1.2.3]Triazolol[1,5-f]phenanthridine 19. Phenanthridine-6-carboxaldehyde 34 (3.0 g; 14.2 mmol) was dissolved in 250 mL of warm ethanol (60 °C). Concentrated sulfuric acid (6 mL) and hydrazine hydrate (36 mL) were added with stirring. The mixture was allowed to stir at 60 °C for 3 h, cooled to room temperature, and evaporated in vacuo. Water (50 mL) was added, and the solution was extracted with 400 mL of CHCl 3 . Drying over MgSO 4 , filtering, and removal of the solvent in vacuo afforded 250 mg of CHCl 3 and adding 20 g of activated MnO 2 in small portions while stirring. After stirring for 3 h, the mixture was filtered over Celite, and the filtrate was concentrated in vacuo to yield


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ESR Spectra. These were recorded on an X-band spectrometer. Zero-field splitting parameters $D$ and $E$ were evaluated using Wasserman’s method. For the observation of thermally produced nitrenes, 10 mg of the precursor was subjected to FVT in the internal oven described above, in a vacuum of ca. $10^{-6}$ mbar, and the products were codeposited with Ar on a Cu rod (7 cm long, 1.5 mm i.d.) at 15 K.

9-Azidophenanthrene 8 was sublimed at 60 °C, codeposited with Ar, and photolyzed at 308 nm for 2 min at 15 K using the excimer lamp. The ESR spectrum of the nitrene 9 was recorded at a microwave frequency of 9.728299 GHz ($H_0 = 3471.3$ G). $X_3 = 6461.0$ G, $Y_3 = 6515.1$ G, $D = 0.8108$ cm$^{-1}$; $E \leq 0.0020$ cm$^{-1}$.

Tetrazolophenanthridine 18 was sublimed over the temperature interval 70–250 °C and thermolyzed at 550 °C. The ESR spectrum of the nitrene 9 was recorded at a microwave frequency of 9.727944 GHz ($H_0 = 3471.2$ G). $X_3 = 6434.1$ G, $Y_3 = 6541.1$ G, $D = 0.8093$ cm$^{-1}$; $E \leq 0.0024$ cm$^{-1}$.

Triazolophenanthridine 19 was sublimed through the internal oven at 110 °C, codeposited with Ar, and photolyzed at 308 nm using the excimer lamp. The ESR spectrum of carbene 21 was recorded at a microwave frequency of 9.728155 GHz ($H_0 = 3471.2$ G). Resonance fields: $Z_1 = 2035$ G, $X_2 = 5043$ G, $Y_2 = 6100$ G, $Z_2 = 8986$ G, $D = 0.5161$ cm$^{-1}$; $E = 0.0257$ cm$^{-1}$ (Figure 4a).

Triazolophenanthridine 19 was sublimed at 110 °C and thermolyzed at 550 °C. The ESR spectrum of the nitrene 9 was recorded at a microwave frequency of 9.728211 GHz ($H_0 = 3471.3$ G). $X_3 = 6434.4$ G, $Y_3 = 6538.9$ G, $D = 0.8090$ cm$^{-1}$; $E \leq 0.0023$ cm$^{-1}$ (Figure 4b).

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Supporting Information Available: IR spectra of the FVT products from 18; ESR spectra of nitrene 9T formed from 8, 18, and 19; Cartesian coordinates, absolute energies, frequencies, and structures of compounds and transition states calculated at the (U)B3LYP/6-31G* level of theory (for nitrene 9, also at the CASPT2/CASSCF(8,8) level); time-dependent B3LYP/6-31G* calculations of UV–vis spectra; UB3LYP/EPRII optimized geometries and spin densities for nitrene 9T and carbene 21T. This material is available free of charge via the Internet at http://pubs.acs.org.