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Nitrene-Carbene-Carbene Rearrangement. Photolysis and Thermolysis of Tetrazolo[5,1-*a*]phthalazine with Formation of 1-Phthalazinylnitrene, *o*-Cyanophenylcarbene, and Phenylcyanocarbene

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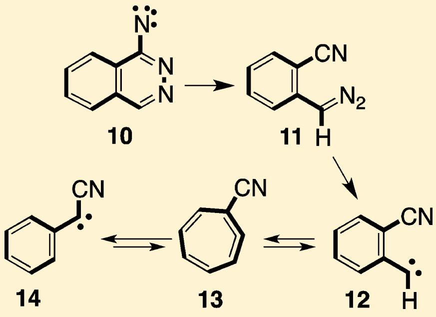
Supporting Information

ABSTRACT: 1-Azidophthalazine **9A** is generated in trace amount by mild FVT of tetrazolo[5,1-*a*]phthalazine **9T** and is observable by its absorption at 2121 cm^{-1} in the Ar matrix IR spectrum. Ar matrix photolysis of **9T**/**9A** at 254 nm causes ring opening to generate two conformers of (*o*-cyanophenyl)diazomethane **11** (2079 and 2075 cm^{-1}), followed by (*o*-cyanophenyl)carbene ^{3}**12**, cyanocycloheptatetraene **13**, and finally cyano(phenyl)carbene ^{3}**14** as evaluated by IR spectroscopy. The two carbenes ^{3}**12** and ^{3}**14** were observed by ESR spectroscopy (D/hc = 0.5078, E/hc = 0.0236 and D/hc = 0.6488, E/hc = 0.0195 cm^{-1}, respectively). The rearrangement of **12** ⇄ **13** ⇄ **14** constitutes a carbene−carbene rearrangement. 1-Phthalazinylnitrene ^{3}**10** is observed by means of its UV−vis spectrum in Ar matrix following FVT of **9** above 550 °C. Rearrangement to cyanophenylcarbenes also takes place on FVT of **9** as evidenced by observation of the products of ring contraction, viz., fulvenallenes and ethynylcyclopentadienes **16**−**18**. Thus the overall rearrangement **10** → **11** → **12** ⇄ **13** ⇄ **14** can be formulated.



■ INTRODUCTION

The matrix photochemistry of several hetarylnitrenes has been described recently.[1] For example, 2-quinazolinylnitrene **1** undergoes ring opening to a diradical **4** and ring expansion to a seven-membered ring carbodiimide **3** (best seen in the phenyl derivative **3b**), and the latter can be photochemically interconverted with the isocyanophenyldiazo compound **5**.[2] Moreover, the formation of a second, minor nitrene was observed by ESR spectroscopy. The D value of this nitrene was in good agreement with the phenylnitrene derivative **6**. 2-Quinazolinylnitrene **1** and 3-phthalazinylnitrene **8** are potentially connected via the intermediates **2** and **3** and the transition state **7** as illustrated in Scheme 1, but no evidence for the existence of **8** has been obtained previously.

During our efforts to generate phthalazinylnitrene **8a** we have discovered a novel type of nitrene-carbene-carbene rearrangement and are pleased to report the results herein.

■ RESULTS AND DISCUSSION

1. Photolysis. Tetrazolo[5,1-*a*]phthalazine exists exclusively in the tetrazole form **9T** in the solid state and in solution. Also sublimation of the tetrazole through a hot tube up to 250 °C with isolation of the material in an Ar matrix at 20 K gives no indication of the formation of the azide valence tautomer **9A** in the IR spectrum (Figure S1, Supporting Information). However mild flash vacuum thermolysis (FVT) at 450 °C, which is just below the temperature where decomposition of the tetrazole starts, causes the appearance of a very weak peak at 2121 cm^{-1} in the Ar matrix IR spectrum, which may be ascribed to the azide **9A**. The vast majority of the sample still exists in the tetrazole form **9T**. This is unsurprising in view of the calculated energy difference, ΔE = 10 kcal/mol and ΔG(298 K) = 8.55 kcal/mol at the B3LYP/6-31+G** level. This would correspond to only ca. 0.3% azide at equilibrium at 450 °C. In the case of the parent compound, tetrazolo[1,5-*a*]pyridazine, the calculated energy difference between azide and tetrazole is ca. 5 kcal/mol, and 1−2% of the azide valence tautomer was observable by IR spectroscopy following FVT at 250−400 °C.[1b,3] 1-Azidophthalazines and 3-azidopyridazines were previously unknown, but in the case of tetrazolo[1,5-*a*]pyrimidine/2-azidopyrimidine it is known that although the tetrazole is the stable form at room temperature, the positive $T\Delta S$ term causes increasing amounts of the azide form at elevated temperatures.[4]

Photolysis of the matrix-isolated tetrazole **9T** at 222 nm causes a decrease in the IR absorptions of the tetrazole, but the expected nitrene **10** is not observed. Instead, new bands assigned to the *s-Z* and *s-E* conformers of diazo compound **11** develop at 2079 and 2075 cm^{-1} within 10 s of photolysis (Scheme 2, Figure 1, and Figures S1−S4, Supporting Information). The calculated absorptions of **11** are at 2122 and 2118 cm^{-1} (654 km/mol) at the B3LYP/6-31G** and the absorption due to the CN group is ca. 20 times weaker (2247 cm^{-1}, 36 km/mol) (Supporting Information). Further photolysis of this matrix for 30 s at 222 nm causes a further

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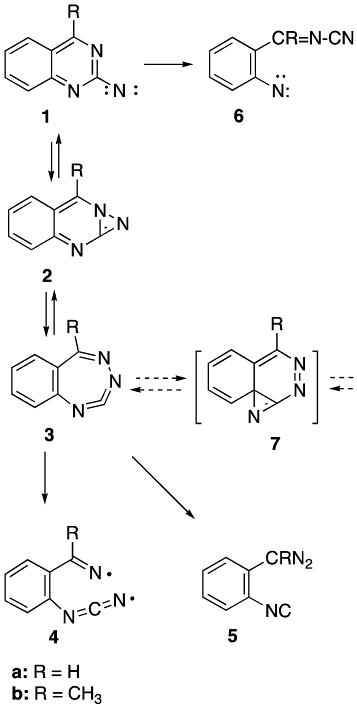
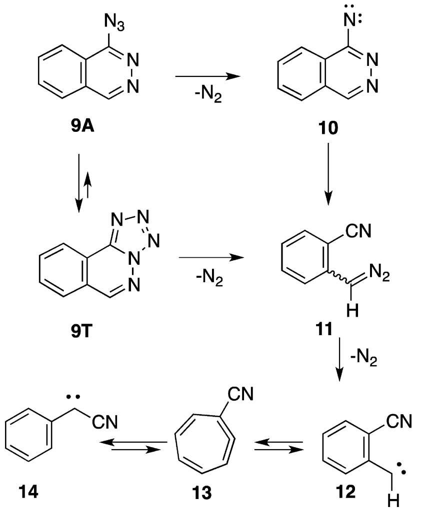
Scheme 1. 2-Quinazolinylnitrene and Its Isomers



Scheme 2. Azidophthalazine-Tetrazolophthalazine-(*o*-Cyanophenyl)diazomethane-Cyanophenylcarbene-Cyanocycloheptatetraene Rearrangement[a]



[a] See text for the description of **14**.

decrease of the bands belonging to tetrazole **9T** and development of a new nitrile band at 2230 cm^{-1} together with a band at 744 cm^{-1}, both ascribed to the carbene **12** (calculated at 2230 cm^{-1} (32 km/mol) and 828 cm^{-1} (970 km/mol)) (Figure 1). Both **11** and **12** have a nitrile band at 2230 cm^{-1}, but it is very weak for the diazo compound and is essentially due to carbene **12** at this stage. Carbene **12** was also obtained on photolysis at λ > 300 nm or by using the broadband irradiation of a high pressure Hg/Xe lamp, but diazo compund **11** was best observed by using the 222 nm irradiation.

The rearranged carbene **14** described below is not predicted to have an observable nitrile group frequency in the IR (see

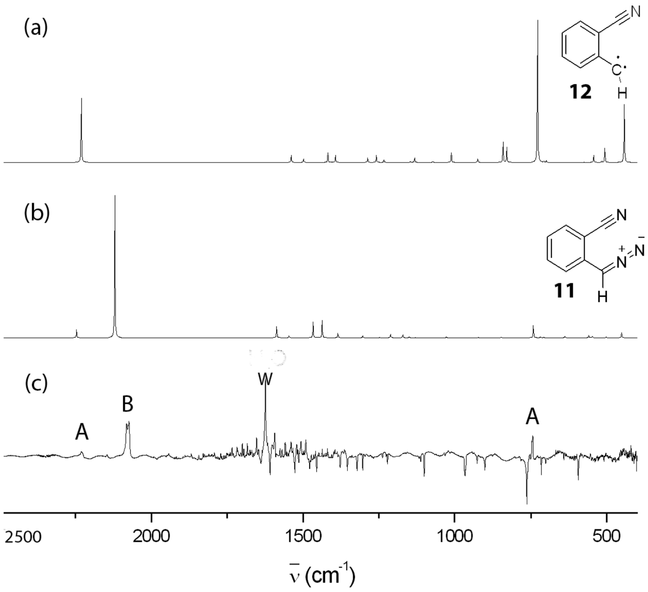


Figure 1. (a) Calculated IR spectrum of triplet carbene **12** (A). (b) Calculated IR spectrum of diazo compound **11** (B) at the B3LYP/6-31+G** level (wavenumbers scaled by 0.9613). (c) IR difference spectrum after 40-s photolysis of matrix isolated **9T** at 222 nm. Positive peaks A (2230, 744 cm^{-1}) and B (2079, 2075 cm^{-1}) are due to the products formed. Negative bands are due to the disappearing **9T**. W = water. Ordinates: absorbance in arbitrary units. A larger version of this spectrum is available in the Supporting Information (Figure S3).

Supporting Information). The intensities of the diazo peaks at 2075–2079 cm^{-1} decrease slightly (on irradiation >300 nm) or increase slightly (on broadband photolysis); therefore, they barely appear in the difference spectra shown in Figure 2. Furthermore, new bands appear more slowly, especially at 788, 747, and 728 cm^{-1} (Figure 2).

The data indicate the formation of four different species: first, diazo compound **11** (2075–2079 cm^{-1}, Figure 1); second, cyanophenylcarbene **12** (2230 and 744 cm^{-1}, Figure 1 and Supplementary Figure S4); and third, cyanocycloheptatetraene **13** (2236, 788, 747, and 728 cm^{-1}, Figure 2). As in the case of the parent cycloheptatetraene,[5,6] the intensity of the allenic stretching vibration of **13** is low (1802 cm^{-1}, 13 km/mol at the B3LYP/6-31G** level), and a very weak band near 1800 cm^{-1} may be due to this species. Most interestingly, the photolysis at λ >300 nm produces three more peaks at 1383, 672, and 727 cm^{-1} (the latter barely resolved from the peak at 728 cm^{-1} due to **13**) (Figure 2d and Supplementary Figure S5), which are indicative of the fourth product, phenylcyanocarbene **14** (Scheme 1 and Figure 2). This species (**14**) is also formed on photolysis at 222 nm and on broadband photolysis, but the best results are obtained at λ > 300 nm.

The UV–vis spectra of matrices obtained by photolysis of **9T** feature prominent vibrational progressions at 390–450 nm (Figure 3) very similar to the spectrum of phenylcarbene (λ_{max} = 430 nm)[6] but red-shifted by ca. 20 nm in accord with the extra conjugation with the CN group. Cyanocarbene, H–C–CN, features a similar vibrational progression in the range 250–295 nm.[7] The spectrum in Figure 2 may be due to either (*o*-cyanophenyl)carbene **12** (*s-Z* or *s-E*) or phenylcyanocarbene **14**, or a mixture of both. The longest-wavelength transitions calculated for **12** and **14** at the TD-B3LYP/6-31+G** level are 418 and 397 nm, respectively. Thus, the agreement is best for

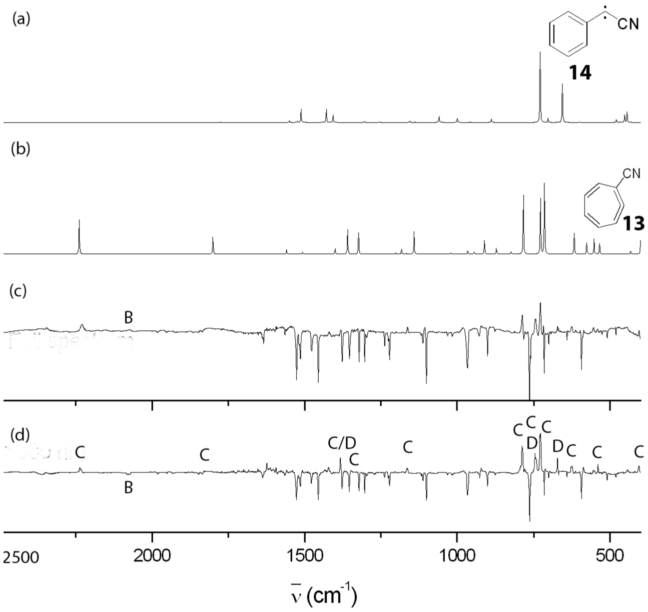


Figure 2. (a) Calculated spectrum of triplet carbene **14** (D). (b) Calculated spectrum of cycloheptatetraene **13** (C) at the B3LYP/6-31+G** level (wavenumbers scaled by 0.9613). (c) IR difference spectrum after broadband photolysis of matrix isolated **9T** for 14 min (high pressure Hg-Xe lamp). (d) IR difference spectrum after photolysis of matrix isolated **9T** for 46 min at λ > 300 nm. Negative peaks are due to **9T** being consumed. Positive bands are ascribed to cyanocycloheptatetraene **13** (bands marked C at 2236, 788, 747, and 728 and perhaps 1800 cm^{-1}) or phenylcyanocarbene **14** (bands marked D at 672, 727, and 1383 cm^{-1}). Note very weak diazo bands at 2075−2079 cm^{-1}, marked B, either slightly negative or slightly positive, i.e., the diazo compound **11** is being produced and consumed at about equal rates in these photolyses. Ordinates: absorbance in arbitrary units. See Supplementary Figures S3−S5 for spectra of **11** and **12** and for a larger scale version of Figure 1d. See text for carbene structures.

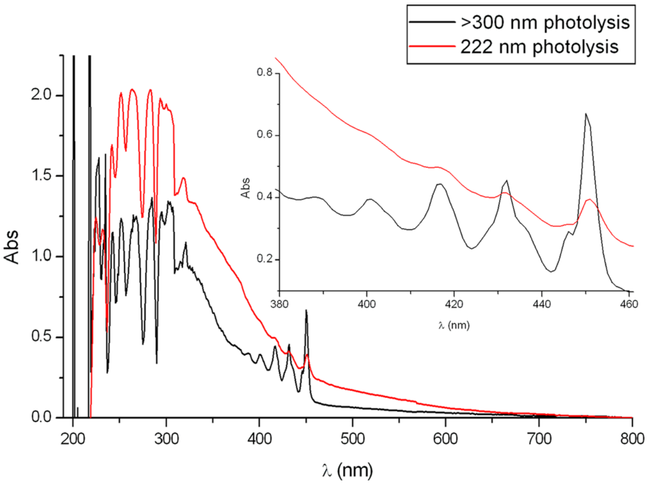


Figure 3. UV−vis spectra (Ar, 20 K) of the products of photolyses of **9T**. The inset shows an expansion of the visible region. The bands in the UV region are due largely to **9T**. For the UV spectrum of **9T** itself see Supplementary Figure S2. Note: IR and UV−vis spectra were obtained for the same matrices, i.e., by using CsI and KBr windows, which absorb strongly between 200 and 250 nm. Thus the spectra are easily saturated in this region, thereby making background subtraction difficult.

12, but it cannot be excluded that both are present, or that the long-lived carbene **14** is the major species, especially since the strongest absorptions are obtained on irradiation at >300 nm (Figure 3). This is in agreement with the ESR data reported below. Our calculated longest-wavelength transition for phenylcarbene at the same level is 55 nm too low. A calculated error of −20 nm at the CASPT2 level has also been reported for the longest-wavelength UV absorption of phenylcarbene.[6c]

ESR spectroscopy confirmed the formation of carbenes **12** and **14**. Photolysis of the Ar matrix of **9T**/**9A** at 20 K causes rapid appearance of typical arylcarbene signals assigned to **12** (D/hc = 0.5078, E/hc = 0.0236). This is followed by signals arising from the known phenylcyanocarbene[8] **14** (D/hc = 0.6488, E/hc = 0.0195 cm^{-1}), which becomes the dominant species (Scheme 2 and Figure 4).

The rearrangement of **12** to **14** constitutes a carbene−carbene rearrangement via cyanocycloheptatetraene **13**. It is interesting to note the rather high D value of **14**; phenylcarbenes usually have D values around 0.5, and extra conjugation should lower, not increase the D value if it were

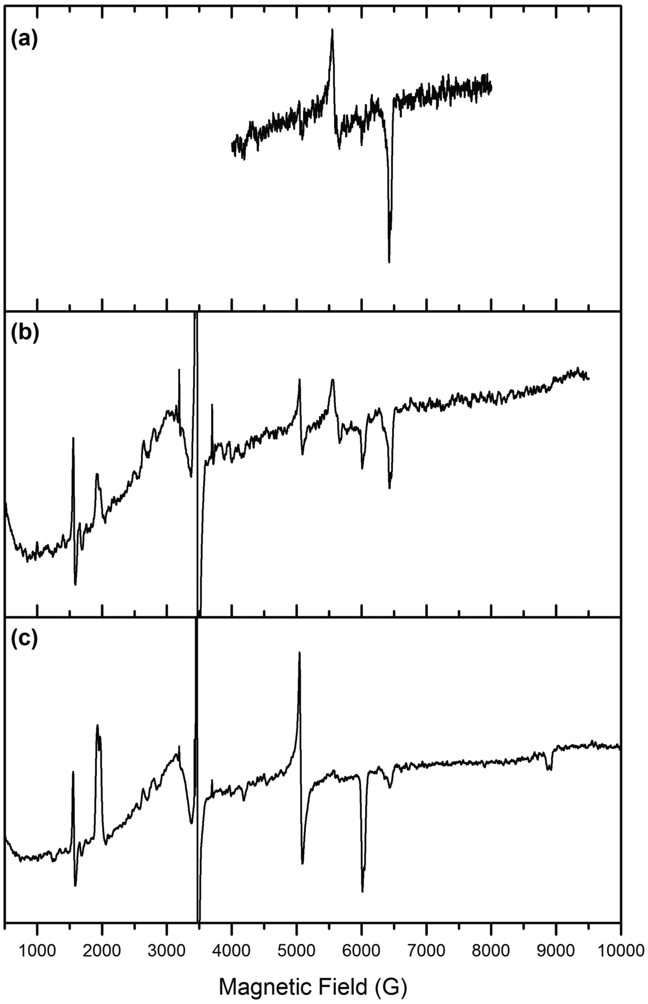
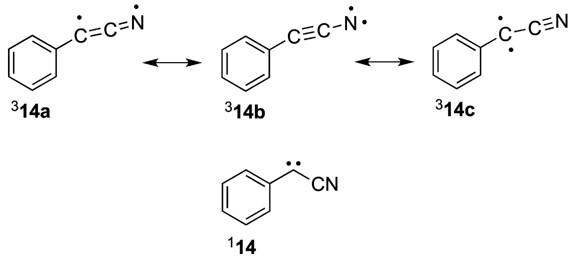


Figure 4. ESR spectra of cyanophenylcarbenes as a function of photolysis time at 222 nm. (a) Initial spectrum ascribed to triplet (*o*-cyanophenyl)carbene, ^{3}**12** (D/hc = 0.5078, E/hc = 0.0236), observed within 10 s of photolysis. (b) Mixture of ^{3}**12** and ^{3}**14**. (c) Phenylcyanocarbene, ^{3}**14** (D/hc = 0.6488, E/hc = 0.0195 cm^{-1}), with a small amount of ^{3}**12** remaining. Ordinates: derivative intensities in arbitrary units.

a true carbene. The high *D* value suggests that triplet **14** may have significant spin density on N as expressed in the canonical structures ^{3}**14a** and ^{3}**14b** in Chart 1.

Chart 1. Structures of Triplet and Singlet Phenylcyanocarbene 14



The IR spectrum calculated at the B3LYP/6-31G** level does not indicate the presence of a CN group in triplet phenylcyanocarbene, ^{3}**14**, nor is one observed experimentally (Figure 2). A shallow Ph–C–C angle of ca. 160°, and equidistant C=C and C=N bonds in conformity with structure ^{3}**14a** are predicted. In contrast, the singlet, ^{1}**14**, has a distinctly bent carbene-like structure (Chart 1) with a Ph–C–C angle of ca. 118°, C–C single bonds, and a CN triple bond (see Supporting Information). Phenylcyanocarbene has been generated from different precursors in solution and undergoes cyclopropanation of alkenes,[9] but the fact that the reaction is nonstereospecific led to the suggestion that both an initially formed singlet and a ground state triplet might be involved.[9d] Attempts to generate phenylethynylnitrene, Ph–C≡C–N, led instead to chemistry apparently derived from phenylcyanocarbene.[10] The structures (carbene vs nitrene) of cyanocarbene[11] and phenylcyanocarbene[12] have been subjects of much discussion and controversy. The best experimental and theoretical data currently agree that triplet cyanocarbene HCCN is a quasi-linear molecule with a barrier to linearity of the order of 200–300 cm^{-1}, a HCC angle of 146–154°, and a high degree of ketenimine biradical structure, H–C•=C=N•.[11] The ESR spectrum of this species is known, and it has a high *D* value of 0.8629 cm^{-1} ($E \approx 0$).[13] The corresponding all-carbon species triplet propargylene, H–C•=C=C•–H, has been shown to have a symmetric (C_2 or C_{2v}) structure and a zero-field *D* value of 0.64 in Ar, i.e., very similar to that of **14**.[14] Given these results, determination of the ground state, the singlet–triplet splitting, and the structures of the singlet and the triplet phenylcyanocarbene **14**, which has been recently described as a bent singlet arylcarbene,[12] seems worthy of further investigation.

2. Flash Vacuum Thermolysis. The UV–vis spectra of the Ar matrix isolated pyrolyzates from the 550–700 °C FVT reactions also feature overlapping vibrational progressions similar to the one described for the photolysis reaction above (λ_{max} up to 450 nm) but red-shifted with λ_{max} up to 470 nm (Figure 5). The longest wavelength absorption cannot therefore be due to carbene **14** (see calculated transitions above), and our general experience is that arylcarbenes do not survive FVT experiments, but nitrenes do.[1,15] Therefore, the visible spectrum (Figure 4) can also not be due to carbene **12** but can be ascribed to the triplet nitrene ^{3}**10** and is in fact in excellent agreement with the calculated electronic transitions for ^{3}**10** (λ_{max} (calcd) 396, 443, and 483 nm at the TD-B3LYP/6-31+G** level). Vibrational progressions have been observed in the visible spectra of many arylcarbenes and arylnitrenes,[16] and red-shifting of the nitrene spectra relative to the carbenes has been reported.[16d,e] The absorption range in Figure 5 is similar to that of 3-quinolylnitrene.[16a,c] While the singlet nitrene ^{1}**10** may readily undergo ring opening to diazo compound **11** (see Schemes 2 and 4), the triplet ^{3}**10** may not have any easily available rearrangement paths; hence it can survive the FVT experiment. The signal intensities in the visible spectrum decrease with increasing FVT temperature (Figure 5), as the nitrene rearranged, presumably on the singlet energy surface, to yield the final products described next (Scheme 3).

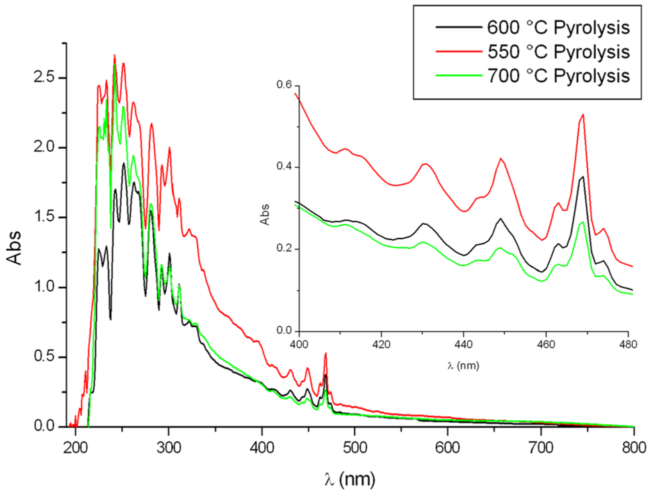
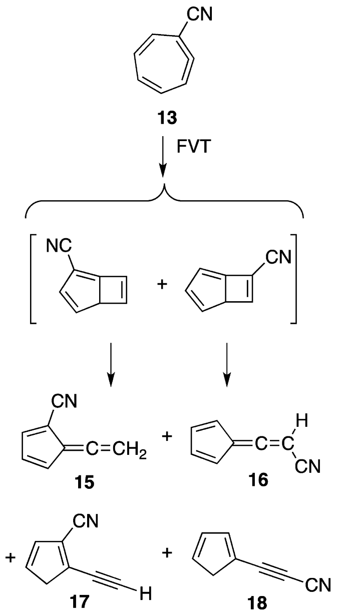


Figure 5. UV–vis spectra (Ar matrix) after FVT of **9T** at 550, 600, and 700 °C. The inset shows an expansion of the visible region. Absorbance in arbitrary units. See caption to Figure 3.

FVT of **9T**/**9A** at 550–700 °C with isolation of the thermolyzate in Ar matrices causes diminution of the peaks due to tetrazole **9T** (and disappearance of the very weak peak due to azide **9A** at 2121 cm^{-1}) and the appearance of new peaks at 3306, 3296 (acetylenic C–H), 2236 (CN), 1966 and 1949 cm^{-1} (allenic C=C=C) (Supplementary Figures S6 and S7).

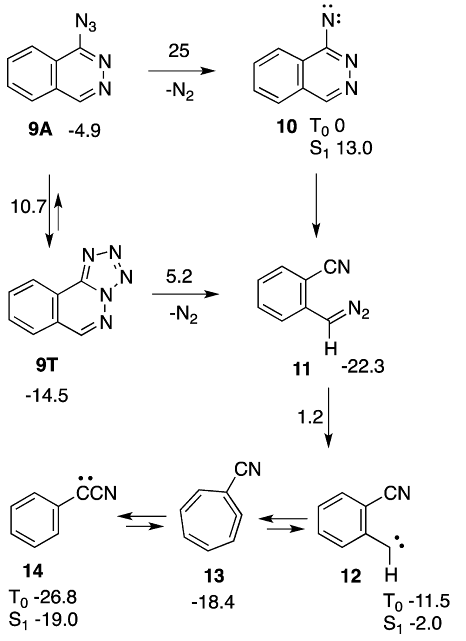
Scheme 3. Ring Contraction Products Resulting from FVT of Tetrazolo[5,1-*a*]phthalazine 9T



These characteristics are indicative of rearrangement to the two principal cyanofulvenallenes **15** and **16** and the two corresponding ethynylcyclopentadienes **17** and **18** in analogy with the rearrangement and ring contraction of phenylcarbene itself (Scheme 3).[17,18] The fulvenallenes have substantially lower calculated energies than the ethynylcyclopentadienes (by ca. 8 kcal/mol; see Supporting Information). It is not excluded that other isomers may be present, as they may interconvert via a series of sigmatropic 1,5-shifts of H and CN in the ethynylcyclopentadienes, and the latter may be formed in wall-induced tautomerizations of the fulvenallenes under high temperature FVT conditions.

3. Mechanism. DFT calculations of the energies of ground states and key transition state structures were calculated at the B3LYP/6-31+G** level of theory. The energies of the open-shell singlet nitrene ($^1A''$) was estimated using the Cramer–Ziegler method.[19] The data are presented in Scheme 4. The tetrazole **9T** lies ca. 10 kcal/mol below the azide, thus explaining why it is not possible to generate appreciable quantities of **9A**. Temperatures above 400 °C are required to generate 0.3% azide at equilibrium, but azides start to decompose at this temperature. The activation barriers for denitrogenation of aryl and pyridyl azides are ca. 30 kcal/mol.[20] A corresponding process generates the nitrene **10** from azide **9A**. In addition, a direct path from the tetrazole to the diazo compound **11** with a transition state energy only 20 kcal/mol above **9T** was found computationally. This value is lower than the energy of the open-shell singlet nitrene, ^{1}**10** (S_1), but not below the triplet, ^{3}**10** (T_o). Nonetheless, as described above, a detectable amount of azide is formed on mild FVT (2121 cm^{-1}). Thermal loss of N_2 from this azide then generates enough nitrene to be detected in the UV–vis spectrum (Figure 5). Carbenes **12** and **14** will be formed at the same time, but since they do not survive FVT experiments, they remain unseen under these conditions.

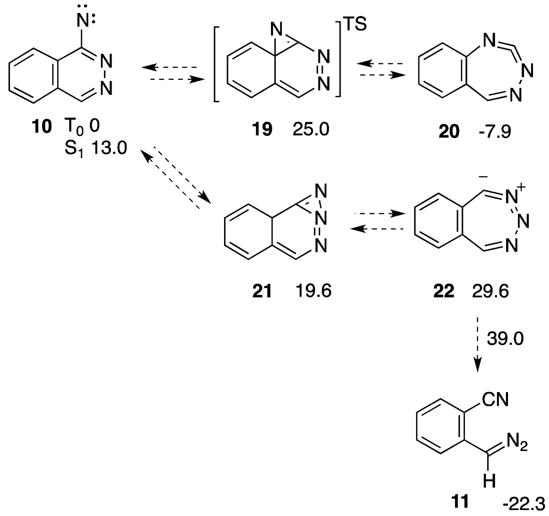
Scheme 4. Reaction Scheme with Energy Values at the B3LYP/6-31+G Level (Numbers in Normal Font) in kcal/mol**



As for the diazo compund **11**, once formed, it readily loses N_2 to generate carbene **12**, which is observed in the photolysis experiments. The carbene–carbene rearrangement **12** → **13** → **14** is completely analogous to the phenylcarbene rearrangement.[21] The more highly conjugated phenylcyanocarbene **14** is calculated to have the lowest energy of these three species on both singlet and triplet surfaces (Scheme 4). Thus, singlet **14** lies17 kcal/mol below **12**, but just 1 kcal/mol below **13**. Triplet **14** lies 15 kcal/mol below triplet **12** and 8 kcal/mol below singlet **13** (Scheme 4). The rearrangement to fulvenallenes and ethynylcyclopentadienes (Scheme 4) is assumed to take place in the same way as the ring contraction of phenylcarbene.[18] The calculated activation barrier is high (50–55 kcal/mol for phenylcarbene), and the reaction only takes place on high-temperature FVT. The reaction is not complete, and there are still appreciable amounts of unchanged tetrazole present in the matrix IR spectra of the pyrolyzates (Supplementary Figures S5 and S6).

Ring expansions of 1-phthalazinylnitrene **10** to the triazabenzocycloheptatetraenes **20** and **22** (Scheme 5) is unlikely. These are predicted to be relatively high energy processes, and there is no evidence for their involvement. Compound **20** would have provided a route to 2-quinazolinylnitrene, but no products of this nitrene were recorded (cf. Scheme 1). The high energy 2,3,4-triazacycloheptatetraene would have to exist as the ylidic structure **22** in order to retain an aromatic benzene ring.[1,16d] It would be possible for this species to ring-open to diazo compound **11** with a transition state energy of 39 kcal/mol. In view of the much lower energies required for the formation of diazo compund **11** from azide **9A**, tetrazole **9T**, or nitrene **11** (Scheme 4), the involvement of **22** is unlikely.

Scheme 5. Potential but Unobserved Intermediates and Reactions (Energy Values at the B3LYP/6-31+G Level (Numbers in Normal Font) in kcal/mol)**



It should be noted that the classical nitrene-carbene rearrangement is usually strongly in favor of the nitrene because nitrenes are thermodynamically lower in energy than isomeric carbenes.[22] In the present case we are not dealing with isomeric carbenes and nitrenes, and once the system **12** $\rightleftarrows$ **13** $\rightleftarrows$ **14** has been formed, the reaction becomes effectively irreversible.

CONCLUSION

Tetrazolo[5,1-*a*]phthalazine **9T** exists exclusively in the tetrazole form in the solid state and in solution. A small amount of the azide form **9A** is obtained by mild flash vacuum thermolysis of **9T** at 450 °C and is observed by IR spectroscopy (2121 cm^{-1}). Irradiation of **9T** in Ar matrix at 20 K initially produces (*o*-cyanophenyl)diazomethane **11** (2079 and 2075 cm^{-1}), which further eliminates nitrogen to give (*o*-cyanophenyl)carbene ^{3}**12**, as observed by IR and ESR spectroscopy (D/hc = 0.5078, $E|hc$ = 0.0236 cm^{-1}). Further photolysis leads to cyanocycloheptatetraene **13**, which is observed by IR spectroscopy. Finally, phenylcyanocarbene **14** forms, especially on irradiation at $\lambda > 300$ nm. ^{3}**14** is characterized by IR and ESR spectroscopy ($D|hc$ = 0.6488 cm^{-1}, $E|hc$ = 0.0195 cm^{-1}). The ESR spectrum as well as the B3LYP calculated structure indicate that triplet **14** has significant spin density on N and is not well described as a carbene. Both singlet and triplet **14** are of lower calculated energy than **12** and **13**.

FVT of **9** with Ar matrix isolation of the product affords a highly structured UV–vis spectrum with absorptions up to 475 nm, which is ascribed to triplet 1-phthalazinylnitrene, ^{3}**10**, as the only reactive intermediate expected to survive the FVT conditions. FVT of **9** causes ring contraction, presumably of cyanocycloheptatetraene **13**, to yield cyanofulvenallenes and cyano(ethynyl)cyclopentadienes **15**–**18**. Taken together, the results indicate the occurrence of a nitrene-carbene-carbene rearrangement, **10** → **11** → **12** ⇄ **13** ⇄ **14**.

COMPUTATIONAL METHOD

Energies, vibrational frequencies, and electronic transitions were calculated at the (TD)-B3LYP/6-31+G** level of theory using the Gaussian 03 suite of programs.[23] Reported energies include zero-point vibrational energy corrections. The vibrational frequencies were scaled by a factor 0.9613.[24] For the compounds that have lost one or two molecules of nitrogen, the calculated absolute energy (including ZPVE) of the N_2 molecule was added once or twice as appropriate. Transition states were verified by intrinsic reaction coordinate calculations. Energies of open shell species were calculated by the sum method.[19] Geometries, energies, and imaginary frequencies are listed in the Supporting Information.

EXPERIMENTAL SECTION

Matrix isolation experiments employed an apparatus consisting of an FVT oven containing a 10 cm long, 0.7 cm i.d. electrically heated quartz tube suspended in a vacuum chamber directly flanged to the cold head of a closed cycle liquid He cryostat with a wall-free flight path of ca. 3 cm between the exit of the quartz tube and the cold target. The cold target was KBr or CsI for IR and UV spectroscopy and a Cu rod for ESR spectroscopy. The system vacuum was ca. 10^{-5} mbar. The precursor **9** (typically 5–10 mg) was sublimed at 120–140 °C in a stream of Ar, typically 10 hPa/min, passing the vapor through the FVT oven before depositing the material on the cold target for IR, UV–vis, or ESR spectroscopy, usually at 20 K, to form a matrix. Drawings and photographs of the apparatus have been published.[25] Afterward, the KBr, CSI, or Cu target was cooled to 10 K, and IR spectra were recorded with 1 cm^{-1} resolution. Photolysis was carried out using a 1000 W high pressure Hg/Xe lamp equipped with a water filter to absorb IR radiation, monochromator, and appropriate cutoff filters, a 75 W low pressure Hg lamp (254 nm), or an excimer lamp operating at 222 nm (25 $\mathrm{mW/cm}^2$). In FVT experiments, the tetrazole/azide was pyrolyzed at 550–700 °C, and the products were isolated in Ar matrix at 20 K for IR or UV spectroscopy.[25]

Commercially available tetrazolo[5,1-*a*]phthalazine **9** was purified by sublimation at 140 °C in high vacuum and had mp = 215–216 °C (lit.[26] 214–216 °C).

Specific Experimental Conditions and IR Peak Listings. Matrix Isolation of Tetrazolo[5,1-*a*]phthalazine 9T. Sublimation: 120–130 °C. FVT: 170 °C. Carrier gas Ar, 400 hPa. Temperature: 20–21 K. Wavenumbers (relative intensity) assigned to **9T**: 3455 (0.03), 3075 (0.03), 1982 (0.02), 1952 (0.02), 1848 (0.03), 1835 (0.03), 1724 (0.04), 1590 (0.22), 1565 (0.07), 1527 (0.55), 1515 (0.27), 1478 (0.22), 1455 (0.52), 1377 (0.33), 1353 (0.39), 1321 (0.37), 1303 (0.39), 1238 (0.11), 1221 (0.27), 1112 (0.14), 1100 (0.51), 965 (0.42), 925 (0.18), 900 (0.28), 783 (0.08), 763 (1.00), 716 (0.50), 593 (0.58), 509 (0.15), 480 (0.07) cm^{-1}.

Photolysis of Matrix Isolated 9T at 222 nm. Continued from previous matrix isolation. Photolysis for 10 and 30 s at 222 nm. Wavenumbers from difference spectra (relative intensity) assigned to diazo compound **11**: 2079 (0.93), 2075 (1.00). Assigned to carbene **12**: 2230(0.12), 744 (0.59) cm^{-1}.

Further Photolysis of Matrix Isolated 9T at 222 nm. Continued from previous photolysis experiment. Photolysis for 2, 5, and 15 min at 222 nm. Wavenumbers (relative intensity) from difference spectra assigned to diazo compound **11**: 2080 (0.29), 2075 (0.28). Assigned to carbene **12**: 2230 (0.20), 744 (0.87), 554 (0.24). Assigned to cyanocycloheptatetraene **13**: 787 (0.22), 747 (1.00), 728 (0.26). Assigned to carbene **14**: 672 (0.18) cm^{-1}.

Photolysis of Matrix Isolated 9T > 300 nm. Continued from photolysis at 222 nm. Photolysis for 30 s and 5, 10, and 30 min. Compound **11** has disappeared. Wavenumbers (relative intensity) cm^{-1} assigned to **12**: 744 (0.36), 554 (0.07). Assigned to cyanocycloheptatetraene **13**: 2236 (0.12), 1624 (0.23), 1422 (0.13), 1383 (0.37), 1164 (0.11), 921 (0.11), 788 (0.65), 747 (0.47), 742 (0.34), 728 (part of 1.00), 624 (0.17), 587 (0.13), 539 (0.21), 405 (0.17). Assigned to **14**: 1383, 728 (part of 1.00), 672 (0.35) cm^{-1}.

Broadband Photolysis of Matrix Isolated 9T. Sublimation: 120–130 °C. FVT: 200 °C. Carrier gas Ar, 120 hPa. Photolysis for 30 s, 1, 2, 5, and another 5 min. Compound **11** not identified. Wavenumbers (relative intensity) assigned to **12**: 744 (0.49), 554 (0.21). Assigned to **13**: 2236 (0.31), 1624 (0.20), 1420 (0.08), 1380 (0.15), 1162 (0.23), 1106 (0.23), 921 (0.27), 788 (0.60), 746 (0.46), 728 (1.00), 718 (0.29), 672 (0.24), 624 (0.24), 540 (0.17), 405 (0.13). Assigned to **14**: 672 (0.24) cm^{-1}.

FVT of 9T at 550 °C and Matrix Isolation. Sublimation: 120–140 °C. FVT: 550 °C. Carrier gas Ar, 240 hPa. IR wavenumbers (relative intensity) assigned to **15**: 2236 (0.11), 1966 (0.32), 1949 (0.29), 1082 (0.10), 876 (0.42), 777 (0.28), 600 (0.27). Assigned to **16**: 3306 (0.24), 1590 (0.11), 1494 (0.14), 1454 (0.10), 1446 (0.09), 1342 (0.18), 763 (0.32), 737 (0.25), 721 (0.59), 675 (0.14), 695 (0.11), 564 (0.10). **9T**: 756 (1.00) cm^{-1}.

FVT of 9T at 600 °C and Matrix Isolation. Sublimation: 120–140 °C. FVT: 600 °C. Carrier gas Ar, 100 hPa. IR wave numbers (relative intensity) assigned to **15**: 2236 (0.11), 1966 (0.33), 1948 (0.30), 1082 (0.11), 876 (0.45), 777 (0.22), 600 (0.31). Assigned to **16**: 3306 (0.23), 3296 (0.08), 1590 (0.21), 1494 (0.15), 1457 (0.07), 1342 (0.16), 763 (0.28), 737 (0.12), 721 (0.53), 675 (0.15). **9T**: 756 (1.00) cm^{-1}.

FVT of 9T at 700 °C and Matrix Isolation. For this experiment a tube insert filled with quartz wool was placed in the back of the oven to prevent the compound from subliming backward. The sublimation oven temperature was 250 °C. FVT: 700 °C. Carrier gas Ar, 180 hPa. IR wavenumbers (relative intensity) assigned to **15**: 2236 (0.13), 1966 (0.39), 1948 (0.35), 1082 (0.11), 876 (0.43), 777 (0.22), 600 (0.24). Assigned to **16**: 3306 (0.15), 3296 (0.04), 1590 (0.20), 1494 (0.13), 1342 (0.15), 763 (0.21), 721 (0.40), 675 (0.09). **9T**: 756 (1.00) cm^{-1}.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Ar matrix UV and IR spectra. Cartesian coordinates, calculated energies and vibrational frequencies, and where relevant electronic transitions of intermediates and transition states.

This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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