Nitrenes, Diradicals, and Ylides. Ring Expansion and Ring Opening in 2-QuinazolylNitrenes

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Received December 12, 2005

Tetrazolo[1,5-a]quinazoline (9) is converted to 2-azidoquinazoline (10) on sublimation at 200 °C and above, and the azide—tetrazole equilibrium is governed by entropy. 2-Quinazolylnitrenes 11 and 27 and/or their ring expansion products 14 and 29 can undergo type I (ylidic) and type II (diradicaloid) ring opening. Argon matrix photolysis of 9/10 affords 2-quinazolylnitrene (11), which has been characterized by ESR, UV, and IR spectroscopy. A minor amount of a second nitrene, formed by rearrangement or ring opening, is also observed. A diradical (19) is formed rapidly by type II ring opening and characterized by ESR spectroscopy; it decays thermally at 15 K with a half-life of ca. 47 min, in agreement with its calculated facile intersystem crossing (19T → 19OSS) followed by facile cyclization/rearrangement to 1-cyanoindazole (21) (calculated activation barrier 1–2 kcal/mol) and N-cyanoanthranilonitrile (22). 21 and 22 are the isolated end products of photolysis. 21 is also the end product of flash vacuum thermolysis.

An excellent linear correlation between the zero-field splitting parameter D (cm⁻¹) and the spin density F on the nitrene N calculated at the B3LYP/EPRIII level is reported (R² = 0.993 for over 100 nitrenes).

Matrix photolysis of 3-phenyltetrazolo[1,5-a]quinazoline (25) affords the benzotriazacycloheptatetraene 29, which can be photochemically interconverted with the type I ring opening product 2-isocyano-R-diazo-R-phenyltoluene (33) as determined by IR and UV spectroscopy. The corresponding carbene 37, obtained by photolysis of 33, was detected by matrix ESR spectroscopy.

Introduction

The rearrangements of aryl- and heteroarylnitrenes have been the subject of intense interest for several years. Three major types of reaction have been identified: ring expansion to seven-membered ring cumulenes (e.g., 3 or 5), ring opening to ylides, ketenimines, or nitriles such as 2, 7, and 8, and ring contraction to five-membered ring nitriles. A general ring opening reaction, leading to open-chain nitrile ylides 2, was identified in 3-pyridylnitrene, 3-pyridylcarbene, and related molecules 1 (type I ring opening, Scheme 1). In the case of 2-pyridylnitrene (4), 1,3-diazacycloheptatetraene (5) and cyanovalenketenimine (7) are formed on photolysis, whereas 5 together with glutarcononitrile (8) and cyanopyrrole is formed on flash vacuum thermolysis (FVT). Presumably, ring opening to diminediy 6a/dienylnitrene 6b is the source of 7 and 8 (type II ring opening, Scheme 1). A similar ring opening reaction is also seen in 1-isouquinolynitrene and other heterocyclic nitrenes.
The formation of azide 10 from tetrazole 9 on heating can be ascribed to entropy. The calculated energy difference between azide and tetrazole in the gas phase, corrected for zero-point vibrational energy, is 0.16 kcal/mol. The calculated enthalpy difference is 0.86 kcal/mol. The calculated entropy difference is 5.74 (cal/mol)/K. Thus, at 298 K, \( \Delta G(\text{gas phase}) = -0.88 \text{ kcal/mol} \), with the azide as the most stable form. In the crystalline state, the lattice energy is likely to stabilize the solid tetrazole. Since \( \Delta G = \Delta H - T \Delta S \), increased temperature will result in a lower \( \Delta G \); i.e., it will shift the azide–tetrazole equilibrium toward the azide. This phenomenon of azide–tetrazole equilibria being governed by entropy has been established experimentally in the case of tetrazol[1,5-\( \alpha \)]-pyridines/2-azidopyridines.\(^{5}\)

**Nitrene 11 and the \( D-\rho \) Correlation.** The azide 10 was deposited in an Ar matrix at 20 K and photolyzed at either 308 or 254 nm in the cavity of an ESR spectrometer. A triplet nitrene signal developed within a few minutes in the region above 7000 G, and a half-field signal at 1468 G was observed as well (zero-field splitting parameters \( D = 1.1465 \text{ cm}^{-1} \) and \( E = 0.0064 \text{ cm}^{-1} \); see Figure 1a). This signal shows distinct \( X_2 \) and \( Y_2 \) lines and therefore has a relatively large \( E \) value. This is typical of 2-pyrimidynitrenes\(^{6}\) and 2-triazinynitrenes,\(^{7}\) where the same type of splitting is observed. This ESR spectrum is ascribed to 2-quinazolynitrene 11 (Scheme 2).

There is an excellent linear correlation between the zero-field splitting parameter \( D \) and the calculated spin density \( \rho \) in a wide variety of nitrenes and carbones.\(^{8,9}\) The correlation for over 100 nitrenes is shown in Figure 2 (see also Figure S3 in the Supporting Information). The calculated natural spin density \( \rho \) of the nitrene N in 11 is 1.6279, and this data point fits very well on the \( D-\rho \) correlation (see Figure 2).

The formation of 11 was confirmed by UV–vis and IR spectroscopy. The UV–vis spectrum resulting from Ar matrix photolysis of 10 at 308 nm is shown in Figure 3. The vibrational progression above 350 nm is typical of arylnitrenes.\(^{10}\) The spacing of the lines between 465 and 568 nm corresponds to ca. 0.16 eV, with the main band at 529 nm. The spectrum is in good agreement with CASPT2 predictions for the triplet nitrene 11 (Figure 3).

In the IR spectrum a series of peaks between 500 and 1200 cm\(^{-1}\) can be correlated with the calculated IR spectrum of triplet nitrene 11 (Figure 4). The highest intensities of the IR and the UV–vis spectra assigned to nitrene 11 were obtained within the first minutes of irradiation and by using \( \lambda = 308 \text{ nm} \).

**Diradical 19.** Depending on the time scale of the ESR experiment, another triplet species, having the characteristics of a diradical, appeared as well (Figure 1b). This species had \( D = 0.1187 \text{ cm}^{-1} \) and \( E = 0.0026 \text{ cm}^{-1} \). The diradical formed

\[ \text{Tetrazole–Azide Equilibrium.} \quad \text{Tetrazolo}[1,5-\alpha]\text{quinazoline (9) (eq 1) was prepared from 2-chloroquinazoline and sodium azide. The compound exists exclusively as the tetrazole in the solid state and in chloroform solution at STP as evidenced by the absence of a peak near 2100 cm}^{-1} \text{ in the IR spectrum. However, addition of trifluoroacetic acid to a solution in CDCl}_3 \text{ causes the formation of the azide tautomer 10 (see eq 1) as determined by } ^1\text{H} \text{NMR spectroscopy. Thus, in a solution of CDCl}_3{^-\text{TFA}} (1:1), the ratio of 9 to 10 is 21:79. Gentle sublimation of the solid tetrazole 9 at 106–108 °C and condensation of the vapor with Ar to form a matrix at 20 K results in essentially the tetrazole being isolated, with only a trace of the azide. The resulting IR spectrum of the matrix is in very good agreement with the calculated spectrum of 9 (B3LYP/6-31G**; the spectra are shown in the Supporting Information, Figure S1). In contrast, sublimation of the tetrazole 9 at 200 °C and condensation with Ar afforded a totally different matrix spectrum, being essentially that of azide 10 (main peak at 2154 cm\(^{-1}\)) together with minor amounts of tetrazole 9. Again, the experimental IR spectrum of 10 is in very good agreement with the calculated one (B3LYP/6-31G**; the spectra are shown in the Supporting Information, Figure S2).\(^{4}\)

\[ \text{(1)} \]


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(9) The first correlation between \( D \) values and spin densities in nitrenes was reported by Smolinsky et al.: Smolinsky, G.; Snyder, L. C.; Wasserman, E. Rev. Mod. Phys. 1963, 35, 576.

The concentration and/or the extinction coefficients of the bands of the diradical 19 were too low for its secure identification by IR and UV−vis spectroscopy.

Minor Nitrene. A third triplet species giving rise to a weak XY\textsubscript{2} signal near 6900 G was also detected in the ESR spectra following photolysis at 308 nm (Figure 1c; see also Figures S4 and S5). This signal was relatively stronger when 254 nm photolysis was used. This species has \( D = 0.9587 \text{ cm}^{-1} \) and \( E \leq 0.0008 \text{ cm}^{-1} \). The rates of formation and disappearance of slower than nitrene 11, but it was thermally unstable, even at 15 K. The diradical did not appear at all if the scanning time of the spectrometer (200 s per scan) exceeded its lifetime. Thus, it does not appear in Figure 1a (160 scans) but in Figure 1b (6 scans) (see also Figures S4 and S5 in the Supporting Information). This spectrum is assigned to one or more of the conformers of the diradical 19 (Scheme 2), which would form on ring opening of either nitrene 11 or the ring-expanded triazacycloheptatetraene 14 (Scheme 2). All three conformers of the triplet diradical (19a−c) are computational energy minima (see below). Although one of the mesomeric structures of each conformer of 19 is a nitrene, this has little weight because it is an \( o \)-quinoid, and therefore, the ESR spectrum does not look like that of a nitrene (the calculated natural spin densities on the three nitrogen atoms in 19b are 1.027, 0.461 (−NCN), and 0.314 (−NCN), and in 19c 1.074, 0.450, and 0.309. The decay of the ESR signal of 19 is ascribed to intersystem crossing to the open-shell singlet, which has a very low barrier for transformation to the end products 21 and 22 (energy difference between triplet 19T and open-shell singlet 19OSS, 1−2 kcal/mol; activation barrier for 19bOSS → 21, 1.3 kcal/mol at the CAS\textsubscript{SCF}(8,8) level; see the Calculations).
FIGURE 2. Correlation between the zero-field splitting parameter $|D/\hbar|$ (cm$^{-1}$) and natural spin density $\rho$ for triplet nitrenes. NR, calculated at the UB3LYP/EPRIII level. Hereafter the splitting parameter $|D/\hbar|$ is usually referred to as $D$. The correlation fits the equation $D = 1.96673\rho - 2.0577$ cm$^{-1}$ with standard deviation on $D = \pm 0.04$ cm$^{-1}$. $R^2 = 0.993$ for all data. This figure is shown on a larger scale, and the data for $D$ and $\rho$ and the references are listed in the Supporting Information. Key for nitrene substituent R: 1, H; 2, trifluoromethyl; 3, phenyl; 4, 4-azidophenyl; 5, 2-methyl-6-carboxyphenyl; 6, 2,4,6-trimethyl-2-pyridyl; 7, 2-naphthyl; 8, 2-quinolyl; 9, 8-azido-1-naphthalenyl; 10, 2-octyl; 11, n-propyl; 12, 9-azido-9-fluoren-9-yl; 13, o-carboran-1-yl; 14, cyclopentyl; 15, methyl; 16, adamantyl; 17, cyclopropyl; 18, norbornyl; 19, 9-oxo-9-fluoren-2-yl; 20, (o-phenylenedioxy)boranyl; 21, 4-azido-6-dimethylamino-s-triazin-2-yl; 22, 4,6-bis(dimethylamino)-s-triazin-2-yl; 23, 4,6-dimethoxy-s-triazin-2-yl; 24, 4,6-diazido-s-triazin-2-yl; 25, 4,6-dimethylpyrimidin-2-yl; 26, 2-pyrimidyl; 27, 4-pyrimidyl; 28, 4,6-bis(2-pyrimidyl)-2-aryl; 29, 2-quinolyl; 30, 3,5-bis(trifluoromethyl)-2-aryl; 31, 4-phenyl; 32, 3,4-diphenylpyridine; 33, 5-trifluoromethyl-2-pyridyl; 34, 2,3,5,6-tetrafluoro-4-pyridyl; 35, 4-trifluoromethyl-2-pyridyl; 36, 3-trifluoromethyl-2-pyridyl; 37, 6-trifluoromethyl-2-pyridyl; 38, 2-pyridyl; 39, 2-quinolyl; 40, 4,6-dimethylpyridazin-3-yl; 41, 2-pyrazinyl; 42, 3-biphenylyl; 43, 4-fluorophenyl; 44, 4-acetyl-2-fluoro-5-methyl-2-pyridyl; 45, 2-fluoro-5-methyl-2-pyridyl; 46, 2-(trifluoromethyl)phenyl; 47, phenyl; 48, 4-methoxyphenyl; 49, 3-tolyl; 50, 3-amino-2-trifluoromethylphenyl; 51, 4-quinazolyl; 52, 2-biphenyl; 53, 3-dimethylaminophenyl; 54, 3-nitrophenyl; 55, 4-azidobiphenyl-3′-yl; 56, 4-carboxyphenyl; 57, 4-tolyl; 58, 4-nitrophenyl; 59, 4-ethylphenyl; 60, 3-carboxyphenyl; 61, 4-hydroxynaphthalen-1-yl; 62, 3,5-diazido-2,4,6-tricyanobenzene-1-yl; 63, 3-methoxyphenyl; 64, 2-(3-bromo-4-propyl)phenyl; 65, 4-cyanophenyl; 66, 2-quinolyl; 67, 4-acetylamino)phenyl; 68, 3-isouquinolyl; 69, 4-carboxythiophenyl; 70, 4-biphenyl; 71, 7-azido-2-phenanthenyl; 72, 4-azidobenzene; 73, 4-(phenylethynyl)phenyl; 74, 2-naphthyl; 75, 6-phenanthridine; 76, 7-azido-3-dibenzofuran-7-yl; 77, 4-acetylphenyl; 78, 3-azidobiphenyl-4′-yl; 79, 2-fluorenyl; 80, 4-azido[1,1′-bipheny]-4-yl; 81, 2′-cyano-2-biphenyl; 82, 4-quinolyl; 83, 9-oxo-9H-fluoren-2-yl; 84, 7-azido-9H-fluoren-2-yl; 85, 7-azido-9-oxo-9H-fluoren-2-yl; 86, 1-isouquinolyl; 87, 9-phenanthryl; 88, (E)-[4-[4-azidophenyl]vinyl]phenyl; 89, 1-naphthyl; 90, 8-methyl-1-naphthalenyl; 91, 8-nitro-1-naphthalenyl; 92, 8-carboxy-1-naphthalenyl; 93, 2-anthryl; 94, (E)-[4-[4-azidophenyl]vinyl]phenyl; 95, 8-azido-1-naphthalenyl; 96, 8-hydroxy-1-naphthalenyl; 97, (E)-[4-[4-azidophenyl]azo]phenyl; 98, 1-pyrenyl; 99, 1-anthryl; 100, (E,E)-[4-[4-azidophenyl]azo]phenyl; 101, 8-amino-1-naphthalenyl; 102, 9-anthryl; 103, 10-methoxy-9-anthryl; 104, 10-phenyl-9-anthryl; 105, 10-nitro-9-anthryl; 106, 1-cyano-9-anthryl.

The three triplet species are different, but the low intensity of the ESR signal at 6900 G makes the identification of its carrier tentative. Two nitrenes isomeric with 11, viz., 1-phthalazine nitrene (15) or 3-cinnolinyl nitrene (18) (Scheme 2), need to be considered. These are annelated derivatives of 3-pyridazinylnitrene, which we have observed previously (see Figure 2), and they would be expected to give rise to $X\bar{Y}Z_2$ lines in the ESR spectrum. Nitrenes 15 and 18 have calculated natural spin densities on the nitrene $N$, $\rho = 1.5124$ and 1.5395, respectively, and on this basis they would be expected to have $D$ values near 0.91 and 0.97 cm$^{-1}$, respectively. 18 fits well on the $D-\rho$ correlation (Figure 2), so the weak signal observed at 6900 G (Figure 1c) could be due to 18, formed via 13, 16, and/or 17, although 15 cannot be ruled out (the standard deviation on $D$ for all data in Figure 2 is $\pm 0.04$ cm$^{-1}$).

The phenylnitrene derivative 20 has to be considered as another possible source of the weak 6900 G signal. This nitrene could be formed by alternate ring opening of 11 (eq 2), and it can exist in $Z$ and $E$ forms, both of which are calculated energy minima in the triplet state. The calculated natural spin density on the nitrene $N$ in (Z)-20 is 1.5125, and in (E)-20 it is 1.4804. The value for (E)-20 is rather too low for this nitrene to be considered; however, the value for (Z)-20 fits on the $D-\rho$ correlation (predicted $D = 0.92$ cm$^{-1}$). Therefore, 18 and (Z)-20 remain as plausible candidates for the minor nitrene, with 15 as a further possibility. The formation of nitrene 34 in Scheme 3 makes (Z)-20 the strongest contender for the minor nitrene. The formation of nitrene 20 corresponds to a type II ring opening (cf. Scheme 1). If 20 is formed, it could be expected to ring close again to 11, 13, 16, or 17, or it could give rise to a small amount of 2-cyanoindazole. This has a calculated CN stretching vibration 11 cm$^{-1}$ higher than that of 1-cyanoindazole (21). Weak signals at 2271–2277 cm$^{-1}$ in

FIGURE 3. UV–vis spectrum of nitrene 11 formed by photolysis of azide 10 in an Ar matrix at 10 K using $\lambda = 308$ nm. Heavy bars are CASPT2-calculated transitions for triplet nitrene 11.

FIGURE 4. (Top) calculated (B3LYP/6-31G**) and (bottom) experimental IR spectra of triplet nitrene 11 obtained by photolysis of azide 10 in an Ar matrix at 10 K using $\lambda = 308$ nm.
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Figure 5. (a) Calculated IR spectrum of \textit{anti}-21, (b) calculated IR spectrum of \textit{anti}-22, (c) difference IR spectrum resulting from exhaustive photolysis of azide 10/tetrazole 9 (negative peaks) at 254 nm in an Ar matrix at 10 K (inset: detail showing peaks due to 21 (2260 cm\(^{-1}\)) and 22 (2255 and 2236 cm\(^{-1}\))), and (d) IR spectrum of azide 10/tetrazole 9 deposited in an Ar matrix at 10 K. Calculations are at the B3LYP/6-31G* level.

Many of the IR spectra where 21 is present (2260 cm\(^{-1}\); see below) could therefore possibly be due to traces of 2-cyanotetrazole.

Ring Opening and Ring Contraction to 21 and 22. Photolysis of an Ar matrix of azide 10 at ca. 10 K at 308, 254, or 222 nm with FTIR detection caused conversion of any remaining tetrazole to azide, conversion of the azide to the nitrene (best observed by photolyzing at 308 nm; see above), and finally disappearance of the nitrene 11 with concomitant formation of two new nitriles showing absorptions in the 2230–2260 cm\(^{-1}\) range and NH absorption around 3410 cm\(^{-1}\) in the IR spectrum (Figure 5). The carrier of this spectrum is identified as a mixture of 21 and the \textit{anti} form of N-cyanoanthraniliminitrrile (22) (see Scheme 2). Careful monitoring of the photolyses revealed that 21 is formed more rapidly than 22. Thus, for the first minutes of photolysis at 308 nm, only 21 was detectable. Compound 21 was identified by direct comparison with samples prepared from indazole and BrCN and by FVT of 9/10 (see below and Figure S11 in the Supporting Information). Important wavenumbers of 21 are 2260 (CN), 1507, 1429, 1373, 1027, 908, 748, and 746 cm\(^{-1}\). Compound 22 was identified on the basis of comparison with a previous investigation of this compound\(^1\) as well as the good agreement with the IR spectrum calculated at the B3LYP/6-31G* level (Figure 5). Important experimental wavenumbers of 22 are 3411/3406, 2255 (NHCN), 2236 (CN), 1595, 1511, 1439, 1306, 1256, 1167, and 757 cm\(^{-1}\). The calculated IR spectrum of the corresponding \textit{syn} form of 22 shows a less satisfactory agreement (Figure S7). The \textit{anti} form of 22 is stabilized by a hydrogen bond between NH and the \(\text{o-cyano}\) group. Other compounds that can be excluded on the basis of comparison with the calculated spectra are \(N-(2\)-cyanophenyl)carbodiimide (2-NC–C\(\text{H}_2\)-CH=N=C=NH) and (2-isonocyanophenyl)diazomethane (2-CN–C\(\text{H}_2\)-CH=N=C=NH) (see Figures S8 and S9 in the Supporting Information).

In addition to compounds 21 and 22, a very small peak at 1990 cm\(^{-1}\), shown in Figure S10 in the Supporting Information and not visible in Figure 5, is suggestive of formation of a trace of the ring-expanded carbodiimide 1,3,4-triazabenzo[7,8]heptatetraene (14) (calculated value 1994 cm\(^{-1}\), very strong, Figure S10). The position of this peak is characteristic of seven-membered cyclic carbodiimides of this type.\(^7c,12,13\) The alternative, higher energy \(\text{o-quinoid}\) isomer 16 has a calculated strong absorption at 1938 cm\(^{-1}\) and was not observed (the calculated spectrum is shown in Figure S14 in the Supporting Information). The zwitterionic isomer 17, which can be regarded as a cyclic nitrile imine, \(^8,10,12\) was also not observed. The highest calculated vibrational frequencies of this molecule are in the 1500–1600 cm\(^{-1}\) range (Figure S15 in the Supporting Information). The diazirenes 12 and 13 have calculated \(v_{\text{C=C}}\) at 1745 and 1707 cm\(^{-1}\); respectively, and were not observed (the calculated IR spectra of 12 and 13 are shown in Figures S12 and S13 in the Supporting Information). The formation of 11, 14, and 19 is summarized in Scheme 2 and will be discussed further below. The two facile reaction routes of diradical 19, leading to 21 and 22 (Scheme 2), readily explain the instability of the diradical observed in the matrix by ESR spectroscopy (see the Calculations).

Flash Vacuum Thermolysis to 21. Preparative FVT of tetrazole 9/azide 10 at 500–700 °C afforded 21 as the main product. This compound was isolated from the FVT reaction, purified by chromatography, and characterized by elemental analysis, comparison with a sample prepared from indazole and cyanogen bromide, and the excellent agreement with the calculated IR spectrum (Figure S11).

GC–MS analysis of the FVT products obtained at 430–600 °C revealed the presence of tetrazole 9 up to 500 °C as well as the formation of 2-aminoquinazoline (23) (11% at 430 °C, 35% at 600 °C), 21 (28% at 430 °C, 65% at 600 °C), and a trace of indazole (24) (0.6–1.8%) (see eq 3). The formation of amines such as 23 is characteristic of triplet (hetero)arylnitrenes, even in low-pressure gas-phase reactions.\(^8\) Substantial amounts of

\(\text{9/10 FVT} \quad \text{21} + \text{23} \rightarrow \text{24} \quad \text{eq 3}\)


2-aminopyrimidines were also seen in the FVT reactions of 2-pyrimidyl nitrenes.14

FVT of 9/10 at 500 °C using the external oven (see the Experimental Section) and Ar matrix isolation of the product afforded the IR spectrum of 21 (Figure S11). The less volatile 2-aminoquinazoline and tetrazole 9 would have condensed in the air-cooled part of the thermolysis tube and not reached the matrix isolation window under these conditions.

4-Phenyl Derivative 25/26. Reversible Ring Expansion to 29 and Ring Opening to Diazoalkane 33. Sublimation of 6-phenyltetrazolo[1,5-a]quinazoline (25) through a hot tube at 200 °C and Ar matrix isolation of the vapor at 10 K afforded the azide valence tautomer 26, characterized by strong bands at 2137, 2131, and 1327 cm⁻¹ (Figure 6a). Preparative FVT of 25/26 at 380 °C afforded 1-cyano-3-phenylindazole (31) in 63% isolated yield. It was identified by elemental analysis, the presence of a strong CN stretching vibration at 2255 cm⁻¹, and hydrolysis to 3-phenylindazole in hot NaOH.

Photolysis of Ar matrix isolated 26 at 308 nm in the ESR cryostat at 15 K caused the appearance of a strong ESR spectrum (Figure 6 in the Supporting Information) very similar to that of 11 shown in Figure 1a. It is therefore ascribed to triplet nitrene 27 (D = 1.147 cm⁻¹, E = 0.0060 cm⁻¹). A diradical like 19 (30) was not observed. However, another weak nitrene signal developed very slowly as well (XY2 at 7039 G, H2 = 3471.1 G, frequency 9.7280 GHz, D = 1.0163 cm⁻¹, E < 0.001 cm⁻¹). This second nitrene is probably due to a ring opening of the quinazoline ring to give the aryl nitrene 34 rather than the phthalazinyl- and cinnolinylnitrenes (35 and 36) (Scheme 3). The azide valence tautomer 26 is likely to be stable enough to be repeated indefinitely because the bleaching of 29 also results in increased intensity of the cyanoindazole 31 (2256 cm⁻¹) (see Figure S18 in the Supporting Information).

Photolysis of azide 26 at 313 or 310–390 nm in the IR cryostat led to the disappearance of the azide absorption at 2131 cm⁻¹ and the formation of three new compounds absorbing at 2006 (A), 2120/2142 (B), and 2256 (C) cm⁻¹. Compound A is assigned as the triazacycloheptatetraene (35 and 36) (Scheme 3). (Z)-34 is analogous to nitrene (Z)-20. The D value near 1.0 cm⁻¹ is characteristic of phenyl nitrenes (cf. Figure 2), and nitrene (Z)-34 fits much better on the D−p correlation than does 35 or 36 (the expected D values for these three nitrenes are 0.98, 0.78, and 0.91 cm⁻¹, respectively).

Photolysis of azide 26 at 313 or 310–390 nm in the IR cryostat led to the disappearance of the azide absorption at 2131 cm⁻¹ and the formation of three new compounds absorbing at 2006 (A), 2120/2142 (B), and 2256 (C) cm⁻¹ (Figures 6b, 6e, and 6f). Compound A is assigned as the triazacycloheptatetraene 29 because of the good agreement with its calculated IR spectrum (the calculated carbodiimide stretch is 1994 cm⁻¹, Figure 6g). Compound C is 31, as verified by separate deposition of this compound (Figure 6c). Compound B is assigned as the (o-isocyanophenyl)diazomethane 33 because of the good agreement with the calculated spectrum (2097 (NC) and 2109 (CN) cm⁻¹, Figure 6d) and the reversible interconversion with 29 (Figure 6e,f). Thus, compound B (33; 2120/2142 cm⁻¹) is bleached at λ > 475 nm, and compound A (29; 2006 cm⁻¹) is formed in its place. Continued photolysis at 310 nm causes the bleaching of the 2006 cm⁻¹ absorption (29) and regeneration of diazo compound 33 at 2120/2142 cm⁻¹. This process cannot be repeated indefinitely because the bleaching of 29 also results in increased intensity of the cyanoindazole 31 (2256 cm⁻¹) (see Figure S18 in the Supporting Information).

Calculations

The energies and IR spectra of the relevant species in Schemes 2 and 3 were calculated at the (U)B3LYP/6-31G* or UB3LYP/6-31G** level using the Gaussian 03 suite of programs. Energies (E) were corrected for zero-point vibrational energies (ZPEs), and all wavenumbers were scaled by a factor of 0.9613. Relative E + ZPE: triplet 2-quinazolylmethylcyclopropane (11T), 0 (absolute E + ZPE = −471.906769 hartrees); 12, 33.2, 13, 21.6, 14, 11.2; triplet nitrene (Z)-2OT, 17.6; (E)-2OT, 20.8; triplet 19aT, 21.4; triplet 21T, 16.1; triplet diradical 19cT, 13.3; triplet nitrene (Z)-2OT, 25.4; triplet nitrene (E)-2OT, 19.7; 21, −26.4; 2-cyanodiazole, −17.6; syn-22, −29.6; anti-22, −36.2; (2-cyanophenyl)carbodiimide, −36.4; (2-isocyanophenyl)diazomethane, 7.72 kcal/mol. Relative E + ZPE: triplet nitrene 27T, 0 (absolute E + ZPE = −702.877843 hartrees); 34T, 21.62; 28, 2.95; 33, 0.13 kcal/mol.

The transition structures for the following reactions were also calculated at the (U)B3LYP/6-31G* level. Energies of transition structures are relative to that of 11T (0): 11T → 19aT (TS3, Scheme 2), 28.8; 11T → (Z)-2OT, 34.2; 12 → 14, 37.4; 14 → (α-isocyanophenyl)diazomethane, 57.0 kcal/mol. The following transition structures are relative to that of 27T (0): 27T → 34T (TS7), 34.6; 29 → 33 (TS3), 53.4 kcal/mol.

The energies of the ground states 19a−E, open-shell singlets 19a−cOSS, and corresponding closed shells 19a−cCSS were calculated at the CASSCF(8,8)/6-31G* level (active space consisting of one σ and seven π orbitals). Relative energies are presented in Table 1. Full details are given in the Supporting Information. The energies of the OSSs were only 1−2 kcal/mol above those of the triplets. Therefore, intersystem crossing will be very facile, even at 15 K, where the triplets were found to decay. The energies of the closed-shell singlet diradicals 19a−cCSS were calculated at the CASSCF(8,8)/6-31G* level and were found to be 69.2, 63.7, and 71.9 kcal/mol above those of the OSSs, respectively, at the CASSCF level, 66.8, 57.9, and 69.1 kcal/mol above those of 19a−cCSS, respectively, at the CASPT2 level, and 26−28 kcal/mol above those of the OSSs according to the UB3LYP estimates using the Ziegler–Cramer sum method18 for calculating OSS energies (Table 1). Thus, clearly, the chemically interesting

### Table 1. Calculations on Nitrene 11, Diradicals 19a−c, and Relevant Intermediates and Transition States

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<td>21.6</td>
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<tr>
<td>12−14 (TS4)</td>
<td>34.7</td>
<td>21.6</td>
<td>37.4</td>
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<tr>
<td>14</td>
<td>26.1</td>
<td>14.3</td>
<td>11.2</td>
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<tr>
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<td>35.4</td>
<td>31.3</td>
<td>24.2</td>
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<td>104.6</td>
<td>98.1</td>
<td>50.8</td>
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<td>34.0</td>
<td>29.3</td>
<td>21.4</td>
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<tr>
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<td>45.0</td>
<td>35.4</td>
<td>-</td>
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<tr>
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<td>26.7</td>
<td>24.7</td>
<td>18.9</td>
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<td>45.9</td>
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<td>22.3</td>
<td>16.1</td>
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<tr>
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<td>-</td>
<td>-</td>
</tr>
<tr>
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<td>15.9</td>
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<tr>
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<td>19cT</td>
<td>21.0</td>
<td>19.0</td>
<td>13.3</td>
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*Energies relative to that of triplet 11T in kilocalories per mole. T = triplet, OSS = open-shell singlet, and CSS = closed-shell singlet.*

Figure 6f). Compounds 29 and 33 have similar calculated energies, 2.95 and −0.13 kcal/mol, respectively, with respect to that of the triplet nitrene 27T (without the phenyl substituents they are 11.2 and 7.7 kcal/mol, respectively, with respect to that of nitrene 11T). The calculated transition structure between 29 and 33 (TS8, Scheme 3) lies 53.4 kcal/mol above 33.

Phenylidiazomethanes are usually red. The Ar matrices containing 33 are visibly red. They are formed by photolysis of azide 26 at 313 nm and feature a broad maximum at 510 nm in the UV−vis spectrum. The calculated transition structure energies are relative to that of nitrene 27T, 0.95 and 2.95 kcal/mol above those of the OSSs according to the UB3LYP estimates using the Ziegler−Cramer sum method18 for calculating OSS energies (Table 1). Thus, clearly, the chemically interesting...
diradicals are the triplets and the open-shell singlets. Attempts to optimize the geometries of 19α–cCSS invariably resulted in rearrangement to 21 or 22, which suggests that the activation barriers for these processes are not high. The transition structure for the ring closure of diradical 19bOSS to 21 (TS1, Scheme 2) was obtained at the CASCF(8,8)/6-31G* level and lies a mere 1.3 kcal/mol above 19bOSS (imaginary frequency 237 cm⁻¹). A transition structure for the hydrogen shift 19c → 22 (TS2, Scheme 2) could not be located, but this energy surface is quite flat at the CASSCF(8,8) level, and the activation barrier is therefore expected to be very low. Thus, the low calculated singlet–triplet splittings (19OSS–19T), the low barrier for the cyclization 19bOSS → 21 (TS1), and the suggested low barrier for 19c → 22 (TS2) are in good agreement with the transient nature of 19α–cT, which are disappear in the Ar matrix with a half-life of ca. 47 min (Figure S6).

The transition structure for the ring opening of the closed-shell singlet cyclic carbodiimide 14 to the open-shell singlet diradical 19aOSS (TS5, Scheme 2) was also calculated at the CASSCF-(8,8)/6-31G* and CASPT2 levels (Table 1, 18.9 and 21.1 kcal/mol, respectively, relative to the energy of 14).

The UV–vis spectrum of triplet nitrene 11 was predicted by using CASPT2 calculations (wavelengths, oscillator strengths): 517 nm, 0.008554; 345 nm, 0.002519; 346 nm, 0.01684; 299 nm, 0.011422; 336 nm, 0.023188; 285 nm, 0.009309. The UV–vis spectra of 29 and 33 were calculated by using density functional theory based on time-dependent (TD) response theory.

Natural and Mulliken spin densities in nitrenes and diradicals were calculated using UB3LYP/EPRIII within Gaussian 03. Zero-field splitting parameters D and E (cm⁻¹) were calculated from experimental ESR spectra using Wasserman’s equations.

Discussion

Schemes 2 and 3 summarize the observations and provide a general explanation for the results. Ring expansion could in principle take place in two ways, via 12 to 14 or via 13 to 16. If the ring expansions were fully reversible, nitrenes 15 and 18 could also be formed. As described above, the measured zero-field splitting parameter D is in agreement with 11 as the main triplet species observed by matrix ESR spectroscopy.

Furthermore, a triplet diradical was formed within the first few minutes of photolysis, and it was assigned the structure 19T on the basis of its ESR spectrum. The three conformers 19α–c are all calculated energy minima, but the Z-conformer 19α has a slightly nonplanar arrangement of the two ortho substituents for steric reasons. 19c has the lowest energy, followed by 19b and 19a. The initial optimization of 19a led to ring closure to the triazacyclotriazatrienylidene benzene[1,2,4-triazepin-3-ylidene (44.8 kcal/mol above triplet 11b), but reoptimization led to the nonplanar 19a (21.5 kcal/mol above triplet 11). Three mesomeric structures are shown for each of 19α–c in Scheme 2, whereby the structures with an (H)C=O double bond have the highest weight and the structures with an (H)C–N single bond (nitrene) have the lowest. The calculated structures of 19α–c all have delocalized CNCN moieties.

(21) NBO Version 3.1: Glendenning, E. D.; Reed, A. E.; Carpenter, J. E.; Weinhold, F. Gaussian 03, revision C.01.
excited-state energy surfaces. Thus, there are two likely routes to 19: type II ring opening of either nitrene 11 or triazacycloheptatetraene 14 via TS3 and TS5 (Scheme 2). Moreover, 14 may revert to 11. The open-shell singlet nitrene 11OSS lies only 7 kcal/mol above 14 by CASPT2, and the triplet 11T lies 11–14 kcal/mol below. In the case of the phenyl analogue (Scheme 3), the triazacycloheptatetraene 29 is easily observable by IR spectroscopy, and reversion to the nitrene 27 on photolysis of the interconverting 29/33 mixture was observed by ESR spectroscopy.

The diradical 19 is of crucial importance, as it explains the formation of the products 21 and 22. The formation of 21 as the first product (derived from the diradical 19b) in the low-temperature matrix may be due to the fact that more motion is required for the formation of conformer 19c, which has the correct orientation for the 1,4-H shift that leads to anti-22. The latter compound is stabilized in this conformation by a H-bond between NH and CN (2.7 Å long); thus, the energy of anti-22 is calculated to be 6.5 kcal/mol below that of syn-22. The fact that the isomeric 3-cyanophenylcarbodiimide (29-NC-C=2H,--N==C==NH) was not detected indicates that syn-22 is formed directly in this form and thus lends support to its genesis from diradical 19c. The carbodiimide has almost the same calculated energy as syn-22 (36.4 kcal/mol). We do observe monosubstituted carbodiimides in other matrix reactions, when they are formed directly by different 1,7-H shifts, e.g., in the ylides (Scheme 3). The triazacycloheptatetraene 29, which can be photochemically interconverted with the type I ring opening product 2-isocyanano-α-diazo-α-phenyltoluene (33). Both 29 and 33 are characterized by Ar matrix IR spectroscopy. 4-Phenyl-2-quinazolinyl nitrene (27) is observable by Ar matrix ESR spectroscopy. A second, minor, nitrene signal also observed in the ESR spectrum is likely to be due to ring opening to aryl nitrene 34. FVT of 9/10 and 25/26 affords the ring contraction products 21 and 31, respectively, as the main products.

Experimental Section

The apparatus and procedures for preparative FVT25 and for Ar matrix isolation 26 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 (KBr or CsI for IR spectroscopy, quartz for UV spectroscopy, and a Cu rod (7 cm long, 1.5 mm i.d.) 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. FVT products were isolated in liquid nitrogen (77 K) in the preparative thermolyses, at 7–22 K with Ar for matrix isolation IR and UV experiments and at 15 K with Ar for ESR experiments. Photolysis experiments used a 10 000 W high-pressure Xe/Hg lamp equipped with a monochromator and appropriate filters, a 75 W low-pressure Hg lamp (254 nm), and excimer lamps operating at 222 nm (25 mW/cm2) and 308 nm (50 mW/cm2). IR spectra were recorded with a resolution of 1 cm−1. ESR spectra were recorded on an X-band spectrometer. GC for GC–MS analysis was performed on a 30 m capillary column, injector port temperature 200 °C, temperature program 100 °C for 2 min and then 16 °C/min till 270 °C. Melting points are uncorrected.

N-Cyananthranilonitrile22,116 6-phenyl tetrazolo[1,5-a]quinazoline (25),27 and 3-phenylindazol28 were prepared according to literature methods.

Tetrazolo[1,5-a]quinazoline (9). 2-Chloroquinazoline (1.50 g; 9.1 mmol) and sodium azide (1.17 g; 18 mmol) were dissolved in 7.5 mL of 0.5 M HCl containing 10% EtOH. The mixture was refluxed for 2 h, cooled to room temperature, and filtered, and the resulting crystalline product was purified by column chromatography on silica gel, eluting with CHCl3–MeOH (99:1) to yield 866 mg (55%) of 9 as a white solid: mp 224–226 °C. 1H NMR (CDCl3)


δ 9.38 (s, 1 H), 8.65 (d, J = 8 Hz, 1 H), 8.21 (d, J = 8 Hz, 1 H), 8.15 (t, J = 8 Hz, 1 H), 7.87 (t, J = 8 Hz, 1 H); 1H NMR (CDCl3- CF3COOH (1:1)) (minor isomer 10) δ 9.77 (s, 1 H), 8.80 (d, 1 H), 8.50 (d, 1 H), 8.40 (t, 1 H), 8.10 (t, 1 H); (major isomer 9) δ 9.73 (s, 1 H), 8.35 (d, 1 H), 8.30, (t, 1 H), 8.05 (d, 1 H, 7.95 (t, 1 H); ratio 10:9 = 21:79; 13C NMR (CDCl3) δ 160.8 (CH), 151.6 (C quart), 136.2 (CH), 130.9 (C quart), 129.3 (CH), 128.9 (CH), 117.8 (C quart), 114.1 (CH ppm); the assignments are supported by a DEPT-135 spectrum. The Ar matrix IR spectrum is shown in Figure S1. Anal. Calcd for C9H5N5: C, 56.14; H, 2.94; N, 40.92. Found: C, 55.99; H, 2.79; N, 40.86.

Matrix Photolysis of Tetrazolo[1,5-a]quinazoline 9. The matrix photolysis of tetrazole 9/azide 10. 9 (ca. 10 mg) was sublimed at 105 °C through an external quartz oven (200–230 °C for photolysis experiments, 430–600 °C for FVT) under vacuum (2.0 × 10−6 mbar) and codeposited with Ar (5 mbar/min from a 2 L reservoir filled with 1 atm of Ar). The Ar matrix IR spectrum is shown in Figure S2.

Matrix Photolysis of Tetrazolo[1,5-a]quinazoline 9/azide 10 yielded 1-cyanoindazole (21) and N-cyanoanthranilonitrile (22). A brief photolysis of 10 (Ar, 10 K, 308 nm, 30 s) afforded species 21 absorbing at 2260 cm−1. In the course of further photolysis another new species rapidly grew in at 2255 cm−1, and this was the main species after long photolysis times (25 h). Bands due to 21 are at 3411, 3406 w, 2255 w (NHCN), 2236 vw (CN), 1595 m, 1429 m, 1373 w, 1265 m, 1233 m, 1149 m, 1140 m, 1027 w, 908 w, 748 m, and 746 m cm−1.

Figure S2.

1-Cyanoindazole (21). Sodium hydride (90 mg, 3.73 mmol) was added to a solution of 413 mg (3.5 mmol) of indazole in 30 mL of dichloromethane (2 mL) and the products were analyzed by GC–MS to give the following composition: tetrazole 9 (60% at 430 °C, 0% at 600 °C, Rf = 9.43 min, m/z = 171), 2-aminoquinazoline (23) (11% at 430 °C, 35% at 600 °C, Rf = 7.36 min, m/z = 145), 21 (28% at 430 °C, 65% at 600 °C, Rf = 5.96 min, m/z = 143), and indazole (24) (0.6% at 430 °C, 1.8% at 600 °C, Rf = 5.66 min, m/z = 118), all identified by comparison with the authentic materials.

1-Cyano-3-phenylindazole (31). Tetrazole 25/azide 26 (mp 202–203 °C; 0.45 g, 1.82 mmol) was subjected to preparative FVT at 380 °C in the course of 4 h. The resulting product was sublimed at 65–75 °C/10−2 mbar to afford 0.25 g (63%) of white, slightly lachrymatory crystals of 31; mp 95–96 °C; very soluble in ether; MS m/z 219; IR (KBr) 2255, 1640 cm−1; IR (Ar, 10 K) 2256 vs, 1617 w, 1495 v, 1365 s, 1357 m, 1150 w, 1111 w, 1064 m, 783 m, 769 w, 745 m, 697 m, 579 w cm−1. Anal. Calcd for C14H9N3: C, 76.70; H, 4.11; N, 19.18. Found: C, 76.64; H, 4.22; N, 19.22. A 0.02 g portion of 31 was hydrolyzed with 5 mL of 0.2 N NaOH at 125 °C for 3 h. After the solution was cooled to room temperature, the precipitate was filtered off, and the solution was neutralized and extracted with EtOAc. The extract was evaporated to dryness, and the resulting solid was recrystallized from petroleum ether or sublimed at 100 °C/10−2 mbar to afford 3-phenylindazole: mp 114–116 °C (lit.26 mp 115–116 °C).

Matrix Photolysis of Tetrazolo[1,5-a]quinazoline 9/azide 10 was sublimed at 150 °C, and the vapor was passed through the FVT tube at 200 °C and then deposited with Ar at 22 K. IR (Ar, 10 K) 2174 w, 2137 s, 2131 s, 2109 w, 1620 m, 1569 m–s, 1552 s, 1543 s, 1327 vs, 1265 m, 1233 m, 777 w, 699 m, 636 w cm−1.

Acknowledgment. This work was supported by the Australian Research Council, the APAC national supercomputing facility (merit allocation scheme), and the Centre for Computational Molecular Science at The University of Queensland. We thank Dr. Michael Kiselewski for preliminary experiments and calculations, Mr. Riko Burgard for assistance with some experiments, and Dr. Tri Le and Mr. George Spatny for uniting help keeping the ESR spectrometer running.

Supporting Information Available: Experimental and calculated IR spectra, D–ρ correlation for over 100 nitrenes, ESR spectra of nitrenes, diradicals, and carbene 37, kinetics of decay of triplet diradical at 15 K, UV–vis spectrum of 33, Cartesian coordinates, absolute energies, and frequencies or electronic transitions of compounds calculated at the B3LYP/6-31G** and CASSCF(8,8)/6-31G* or CASPT2 levels, and structures and spin densities of triplet nitrenes and diradicals 19a–e (UB3LYP/EPRIII). This material is available free of charge via the Internet at http://pubs.acs.org.

Semipreparative FVT of Azide 9. Experimental conditions for the FVT of 9 and matrix isolation of the products were as described above. After the ESR experiments, the copper rod was rinsed with dichloromethane (2 mL) and the products were analyzed by GC–MS.