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Carbene and Nitrene Rearrangements: A Theoretical Study of Cyclic Allenes and Carbenes, Carbodiimides, and Azirines

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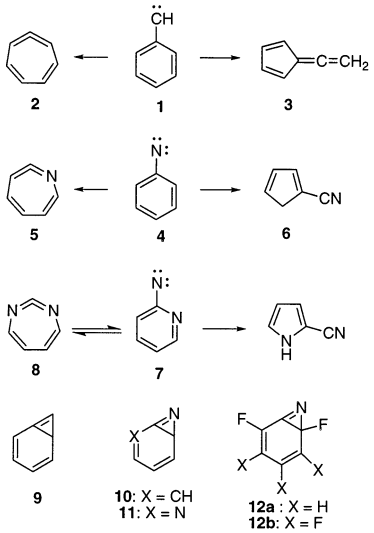
Received April 30, 2002

B3LYP/6-31G(d) calculations of structures, energies, and infrared spectra of several rearrangement products of (hetero)aromatic nitrenes and carbenes are reported. 3-Isoquinolylnitrene **36** ring closes to the azirine **37** prior to ring expansion to the potentially stable but unobserved seven-membered-ring carbodiimide **38** and diazacycloheptatrienylidene C_s-**39S**. A new, stable cycloheptatrienylidene, C_s-**19S**, is located on the naphthylcarbene energy surface. 4-Quinolylnitrene undergoes reaction via the azirine **50** in solution, but ring expansion to the stable seven-membered-ring ketenimine **47** under Ar matrix photolysis conditions. There is excellent agreement between calculated infrared spectra of 1,5-diazacyclohepta-1,2,4,6-tetraene **54** (obtained by photolysis of 4-pyridyl azide), 1-azacyclohepta-1,2,4,6-tetraene **5**, 1-azacyclohepta-1,3,5,6-tetraene **55**, and 1-azacyclohepta-1,3,4,6-tetraene **56** and the available experimental data.

Introduction

The ring expansion and ring contraction of arylcarbenes and arylnitrenes, exemplified by phenylcarbene **1** and phenylnitrene **4** in the diagram below, is a subject of long-standing and continuing interest.[1] The interconversion of 2-pyridylnitrenes **7** via 1,3-diazacyclohepta-1,2,4,6-tetraenes **8** under conditions of flash vacuum thermolysis (FVT) has been established by ^{15}N and substituent labeling.[2] Several seven-membered-ring carbodiimide intermediates of type **8** have been characterized by IR spectroscopy,[3−5] and the dibenzo derivative of **8** was observed to dimerize at −40 °C to afford a diazete derivative, which was characterized by X-ray crystallography.[3] Formation of the triplet nitrenes **4** and **7** under both FVT and photolysis conditions has been ascertained by ESR spectroscopy.[6] The photochemical ring expansion of **7** to **8** is of synthetic value as a means of preparation of diazepine derivatives by solution photolysis.[7] In contrast, the end products of FVT of **7** are cyanopyrroles (2- and 3-cyanopyrroles interconvert thermally via a series of 1,5-shifts of H and CN), together with minor amounts of glutacononitrile and 2-aminopyridine.[2,3,4]



The potential bicyclic intermediates in these reactions, the cyclopropenes such as **9** and azirines **10**−**11**, have never been observed, and calculations indicate that they exist in shallow minima well above the energies of the seven-membered rings, e.g. **2** and **5**.[5,8] For example, azirine **11** is predicted by the B3LYP/6-31G* method to lie ca. 13 kcal/mol above the cyclic carbodiimide **8**, but to have a barrier of only ca. 3 kcal/mol toward ring opening to **8**.[5] The direct matrix-IR spectroscopic obser-

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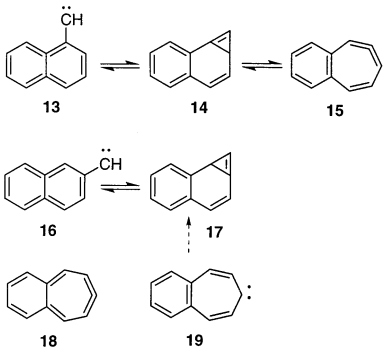
10.1021/jo0258756 CCC: $22.00
Published on Web 11/13/2002

vation of the fluorinated azirines **12** has been reported,[9] but in laser flash photolysis experiments only the thermodynamically stable end products, the azacycloheptatetraenes, were observed.[1e]

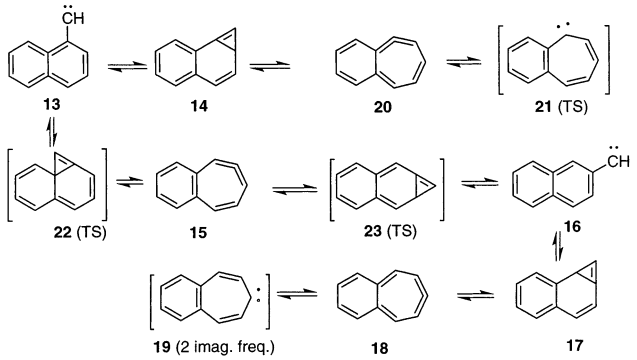
There is more direct evidence for cyclopropene and azirine intermediates in the naphthalene series. Chapman et al. reported the matrix-photochemical interconversion of 1-naphthylcarbene and the tricyclic cyclopropene **14**.[10] The seven-membered ring allene **15** had



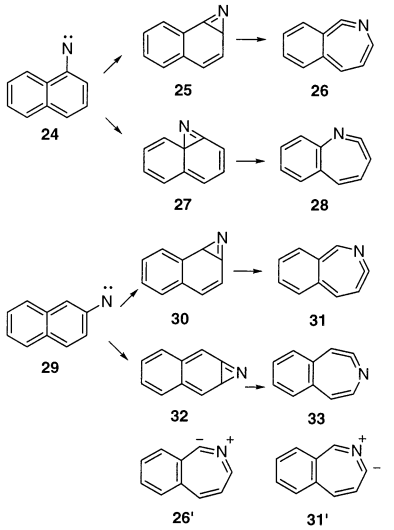
previously been proposed as a link between 1- and 2-naphthylcarbenes, which interconvert on flash vacuum thermolysis (FVT),[11] and it was tentatively identified as a thermal rearrangement product of **13** in the matrix isolation study.[10] Bonvallet and McMahon succeeded in generating **15** photochemically from another precursor and confirming its assignment.[12] 2-Naphthylcarbene **16** likewise interconverts photochemically with the cyclopropene **17** in an Ar matrix, but there was no evidence for the potential ring expansion products, the *o*-quinoid allene **18** or the carbene **19**.[13a] However, **17** has also been generated in solution at −60 °C by photolysis of the sodium salt of the tosylhydrazone of 4,5-benzotropone, a presumed precursor of the elusive carbene **19** or allene **18**.[13b,14]

Xie et al. carried out a detailed theoretical study of the naphthylcarbene rearrangements (Scheme 1).[15] In short, the cyclopropenes **14** and **17**, which retain aromaticity of one ring, were found to be stable structures. The cyclopropenes **22** and **23** are transition states. The allenes **20**, **15**, and **18** are stable structures and, as could be expected, the *o*-quinoid allenes are considerably higher in energy (by ca. 15 kcal/mol) than **15**, which retains one aromatic ring. The cyclic carbenes **21** and **19** were found not to be minima, having one and two imaginary frequencies, respectively. Similar energy ordering of the cyclopropenes had been found previously using combined force field−SCF calculations, and experiments had demonstrated that, despite their high energies, rearrangements through species such as **22** and **23** could occur under FVT conditions.[16]

SCHEME 1



The Ar matrix photolysis of the naphthyl azides was examined by Dunkin and Thomson, who observed medium-weak bands in the 1708−1736-cm^{-1} region ascribed to azirines **25** and/or **27**, and **30** and/or **32**, arising from the 1- and 2-naphthylnitrenes **24** and **29**, respectively.[17] Further photolysis caused the aforementioned bands to be replaced by stronger bands in the 1911−1926-cm^{-1} region, ascribed to the cyclic ketenimines **26** and/or **28**, and **31** and/or **33**. In view of the calculations on the



naphthylcarbenes described above, one would think that azirines **27** and **32** are unlikely intermediates, and as Dunkin and Thomson pointed out, the observed multiple IR bands may have been due to matix effects. Nevertheless, although species such as **27** may not be energy minima, there is ample experimental evidence for nitrene rearrangements formally taking place via transition states of such structures.[16] The *o*-quinoid ketenimines **26** and **31** would seem to be less likely intermediates than **28** and **33** which retain one aromatic ring, but our calculations indicate that zwitterionic (ylidic) structures such as **26′** and **31′** will be of lower energy than the *o*-quinoid ketenimines. This issue will be addressed in a

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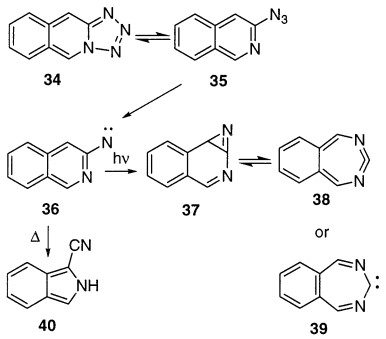
forthcoming publication.[18] An analogous ylide **51′** is described in Scheme 2 in the present paper.

In this paper we start with an examination of the rearrangement products of 3-isoquinolylnitrene **36**. This nitrene is obtained by either photolysis or FVT of the equilibrating tetrazolo- and azidoisoquinolines **34** and **35**, and the triplet **36T** has been observed by ESR spectroscopy in both cases.[6] This system is unique because the "aromatic" azirine **37** is of lower energy than the *o*-quinoid carbodiimide **38.** Hence, **37** is observable in an Ar matrix,[19] but **38** is not, even though there is little doubt that it is reversibly formed: FVT of ^{15}N-labeled **34**/**35** results in complete scrambling of the label among



the two N atoms in the product **40**.[19] Because the carbodiimide **38** is *o*-quinoid, is it possible that the carbene **39** could be a stable and competitive species? If so, what are the consequences for the carbenes described in Scheme 1? These questions will be addressed in the first two sections of the paper. Our experimental work on 4-quinolylnitrene requires a theoretical analysis, which is given in Section 3. For comparison, brief mention of monocyclic ketenimines and allenes is made in Section 4.

Results and Discussion

1. The 3-Isoquinolylnitrene System ($C_9H_6N_2$). The relative energies of the species of interest, calculated at the B3LYP/6-31G* level of theory,[20] are given in Table 1. We have found in other systems that it is important to use basis sets incorporating diffuse functions when calculating molecules that can have some zwitterionic character; this may not have any effect on the geometries or relative energies but can alter the vibrational spectra significantly. In particular, a lowering of the stretching frequency of carbonyl groups in zwitterionic or ylidic compounds by some 30−60 cm^{-1} is not unusual.[21] Therefore, some of the species of interest in this paper were also calculated at the B3LYP/6-31+G* level. In general, this had no effect on the geometries or relative energies, but caused a minor lowering of some vibrational frequencies.

TABLE 1. Calculated Characteristic Wavenumbers and Relative Energies of Some $C_9H_6N_2$ Species[a]

	rel energy/ kcal mol^{-1}	sym	characteristic wavenumbers/cm^{-1} ν_{unscaled} (I)[b]	ν_{scaled}[c]
36T	38.8	C_s	1652 (6)	1588
37	47.1 [47.7]	C_1	1813 (63)	1743 [1737]
			1583 (80)	1521 [1514]
***C*$_s$-39S**	57.1 [56.9]	C_s	1654 (5)	1590 [1581]
			1022 (135)	982 [984]
38	57.1 [58.0]	C_2	2015 (193)	1937 [1929]
40	0 [0]	C_s	3643 (116)	3502 [3497]
			2321 (160)	2231 [2215]

[a] Calculations at the B3LYP/6-31G* level of theory, except values in brackets [ ], which are at the B3LYP/6-31+G* level. See the Supporting Information for complete data. Relative energies are corrected by zero-point vibrational energies. [b] Calculated absolute intensities in km/mol. [c] Scaling factor 0.9613 for all wavenumbers.

TABLE 2. Effect of ^{15}N Labeling of Azirine 37 on the Wavenumbers of the Most Prominent IR Bands (B3LYP/6-31G*, unscaled)

mode no.	assignment	**37** ν/cm^{-1} (I)[a]	**^{15}N-37** azirine-labeled ν/cm^{-1}	$\Delta\nu$[b]	**^{15}N-37** isoquinoline-labeled ν/cm^{-1}	$\Delta\nu$[b]
39	C=N, azirine	1813 (63)	1794	−19	1812	−1
36	C=N, isoquin	1583 (80)	1583	0	1575	−8
29	skeletal vib	1245 (43)	1244	−1	1245	0

[a] Calculated absolute intensities in km/mol. See the Supporting Information for complete data. [b] Difference to unlabeled species in cm^{-1}.

The triplet nitrene **36T** was located as a potential energy minimum. The B3LYP procedure is not well-suited for calculating singlet nitrenes, which may exist as open-shell intermediates, and it exaggerates the singlet−triplet splitting. The energies of the singlet nitrenes are not required in this paper, but as a guide it is useful to recall that the open-shell singlet phenylnitrene lies ca. 18 kcal/mol above the triplet ground state.[1d,e]

Azirine 37. As expected, the azirine ring in **37** is not in the same plane as the isoquinoline system. The annelated benzene ring has bond lengths between 1.389 and 1.407 Å, indicating the aromatic character of this ring. The C=N double bond stretching vibration of the azirine ring is calculated to be at 1743 cm^{-1} (63 km/mol) and the C=N double bond of the isoquinoline ring at 1521 cm^{-1} (80 km/mol, wavenumbers scaled). To facilitate experimental assignments, ^{15}N isotope shifts were also calculated. The two C=N bands exhibit significant red shifts of 19 and 8 cm^{-1}, respectively (Table 2). The use of diffuse functions (B3LYP/6-31+G*) has no effect on the geometry but a small effect on the IR spectrum by lowering the frequencies of the key absorptions by 6−7 cm^{-1} (Table 1).

Carbene 39 and Carbodiimide 38. Optimization of structures with an atom connectivity as in **38** and **39** leads to two stationary points with distinct differences

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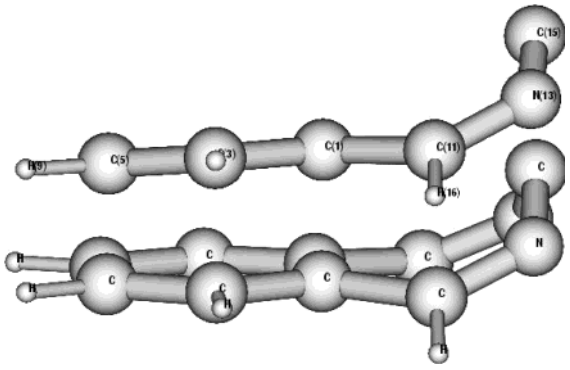


FIGURE 1. Optimized structure for carbene C_s-**39S**, two slightly different views with the carbene center pointing up at the right side and the aromatic ring to the left (B3LYP/6-31G*).

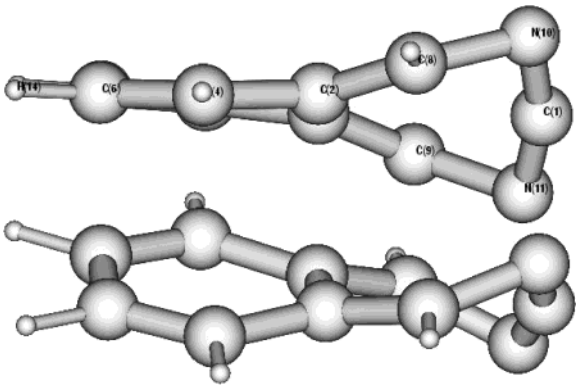


FIGURE 2. Optimized structure for carbodiimide **38**, two slightly different views with the carbodiimide group to the right and the aromatic ring to the left (B3LYP/6-31G*).

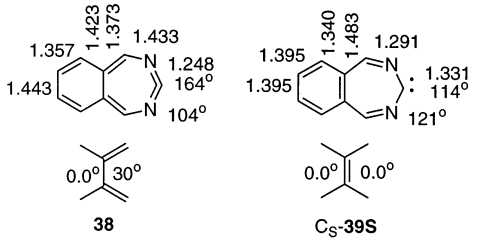
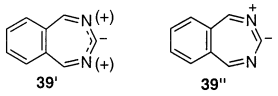


FIGURE 3. Selected calculated parameter for C_s-**39S** and **38**. Bond lengths in Å. Dihedral angles between the two rings are shown below each structure. The data are based on B3LYP/6-31G* calculations.

in geometry and electronic nature, both of which are minima. There is hardly any energy difference between the two structures at the B3LYP/6-31G* level, but the carbene becomes slightly more stable than the allene at the B3LYP/6-31+G* level. The minimum structure obtained for the singlet species **39** (Figure 1) has C_s symmetry, the mirror plane being perpendicular to the benzene ring, and the carbene-type carbon atom is the only atom in the mirror plane. The planar benzene ring has bond lengths between 1.395 and 1.400 Å. The seven-membered ring has the NCN moiety bending away from the plane of the benzene ring, with the carbene-type carbon bending away even further, probably because of Coulombic repulsion between the lone pairs.

The C═N bonds in **39** are short (1.291 Å), but the carbene-type carbon−nitrogen bonds have lengths between single and double bonds (1.331 Å), indicating a degree of delocalization in the direction of the ylide **39′**,



but not as pronounced as for the analogous ylides arising from the naphthylnitrenes[18] and 4-quinolylnitrene (see **51′**, Scheme 2), which are true calculated minima. UB3LYP/6-31G* and 6-31+G* calculations did not result in any change in the energy of **39**, thus indicating that diradical states are unimportant. The squared spin expectation value $\langle S^2 \rangle$ was zero, i.e., there was no spin contamination. It was not possible to optimize a structure with localized bonds as in **39″**. We shall refer to the molecule **39** as a carbene C_s-**39S** with some ylidic character as expressed by formula **39′**. In the all-carbon analogue **19S** discussed in Section 2, the absence of the nitrogen atoms makes the ylidic structure unfavorable, and the molecule becomes a true carbene. The stabilization of C_s-**39S** as expressed in formula **39′** can be gauged by comparing the relatively low energy of this species (Figure 5) with the relatively high energy of **19S** (Figure 6). In C_s-**39S** the angle at the nitrogens is 121°, and the angle at the carbenic center is 114° (Figure 3). The calculated IR spectrum shows weak C═N vibrations and aromatic skeletal vibrations in the 1600-cm^{-1} region (Table 1 and Supporting Information), but as expected, no cumulene-type band. Use of extended basis sets (B3LYP/6-31+G* and B3LYP/6-311++G**) has no effect on the geometry but causes a small lowering of the frequencies near 1600 cm^{-1} (Table 1 and Supporting Information).

The carbodiimide structure **38** (Figures 2 and 3) on the other hand has alternating bond lengths (1.357−1.453 Å) indicating an *o*-quinoid system. The six-membered ring is not planar but slightly warped. The structure has long C−N bonds (1.434 Å) and short C═N bonds (1.248 Å) in the N═C═N group. The cyclic nature of this carbodiimide requires the carbodiimide moiety to be bent, resulting in an NCN angle of 164° (compare 114° in carbene C_s-**39S**).

The necessary twist along the N═C═N group leads to a 1,2-trans type distortion of the substituents at the *o*-positions of the six-membered ring: one −C═N substituent is projecting above the plane, the other below, with the carbodiimide carbon being in that plane. Consequently, the molecule is chiral. The *o*-quinoid system has a dihedral angle of 30°. This geometry results in a C_2 symmetry (compare C_s for the carbene). The rotational axis is defined by the carbodiimide carbon atom and the midpoint between the two *o*-quinoid C═C bonds. The twisted structure of **38** will confer a degree of Möbius aromaticity on this 12π electron system.[22] The calculated IR spectrum has the cumulene band at 2015 cm^{-1} (194 km/mol). Here too, the extended basis set has no effect on the geometry but causes a minor lowering of the

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TABLE 3. Effect of ^{15}N Labelling of Carbodiimide 38 on the Wavenumbers of the Most Prominent IR Bands (B3LYP/6-31G*, unscaled)

Mode #	Assignment	ν/cm^{-1} (*I*)[a]	ν/cm^{-1}	Δν[b]
39	N=C=N	2015 (194)	2006	-9
31	C-H def	1322 (26)	1322	0
25	sym N=C	1059 (48)	1053	-6
24	asym N=C	1049 (2)	1042	-7
23	skeletal	1012 (16)	1011	-1
20	ring def	918 (14)	918	0
18	skeletal	866 (33)	866	0
15	C-H def	749 (33)	749	0
12	C-H def	628 (3)	625	-3
8	ring def	452 (21)	450	-2

[a] Calculated absolute intensities in km/mol. [b] Difference to unlabeled species in cm^{-1}.

FIGURE 4. The two imaginary vibrational modes of carbene C_{2v}-**39S**.

vibrational frequency (Table 1). Introduction of one ^{15}N label results in a red shift of 9 cm^{-1} (Table 3).

Planar Singlet C_{2v} Carbene, C_{2v}-39S. A planar (C_{2v}) structure with a singlet state was found to have bond lengths being consistent with a carbene. It is, however, not a minimum structure but a higher order saddle point (branching point) with *two* imaginary vibrational modes, one at 777.2i cm^{-1} with B_1 symmetry, the other at 376.9i cm^{-1} with A_2 symmetry.

Any structure with C_{2v} symmetry has a C_2 rotational axis and two mirror planes vertical to the rotational axis. The vibrational descriptors A and B indicate symmetric or antisymmetric behavior of the vibration with respect to the rotational axis. The subscripts 1 and 2 indicate symmetric or antisymmetric behavior toward the mirror plane σ_v.

The above-mentioned descriptor B_1 therefore means that in the vibration there is a breach of the rotational C_2 symmetry (B) but the mirror plane is maintained, i.e., during the vibration the symmetry changes from C_{2v} to C_s. The main displacement of atoms in the 777i-cm^{-1} vibration is shown in Figure 4. The vibration points toward the C_s structure of carbene **39S** (see Figures 4 and 5).

A_2 on the other hand indicates that the C_2 axis is maintained, while there is a breach in the mirror plane, changing the symmetry in the vibration from C_{2v} to C_2. The 377i-cm^{-1} vibration points toward the C_2 structure of the carbodiimide **38S**. Thus, the planar C_{2v} structure appears to be a branching point with energy gradients toward the two minimum structures (Figures 4 and 5).

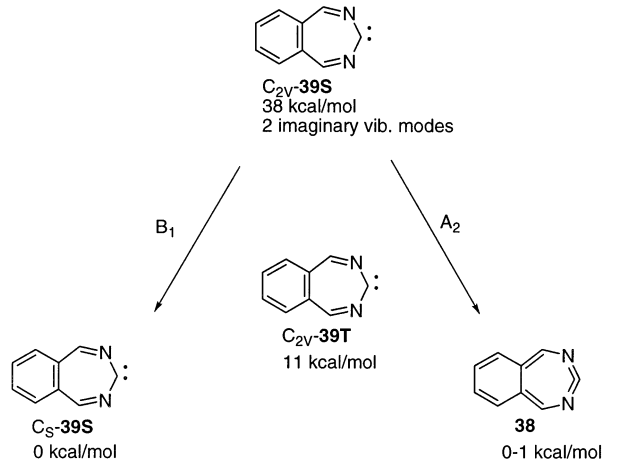


FIGURE 5. Calculated relative energies of three forms of carbene **39** and carbodiimide **38**.

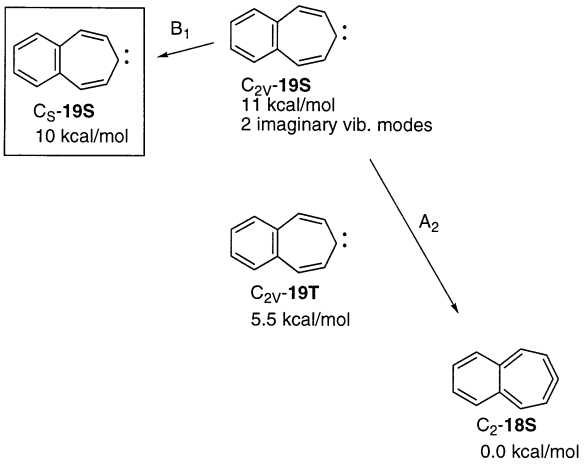


FIGURE 6. Calculated relative energies of three forms of carbene **19** and allene **18**.

Triplet Carbene, C_{2v}-39T. The C_{2v} structure (C_{2v}-**39T**) is a minimum on the triplet surface, being some 11 kcal/mol above the singlet C_s structure (Figure 5). The triplet carbene requires a larger angle at the carbene atom (138°) than the singlet, and this is possible in the planar seven-membered ring. As could be expected for a heteroatom-substituted carbene, the ground state appears to be the singlet. The five-membered-ring analogue, 2,5-diazacyclopentadienylidene, is also a singlet ground state, whereas the 2,4-diazacyclopentadienylidene is a triplet.[23] Attempts to optimize a triplet C_s carbene resulted in conversion to C_{2v}-**39T** (UB3LYP/6-31G*).

2. The Naphthylcarbene Potential Energy Surface ($C_{11}H_8$). The finding that both carbene **39** and carbodiimide **38** are energy minima appears at first sight surprising when the system is compared to some points on the 2-naphthylcarbene (**16**) potential energy surface (PES) described by Xie et al.[15] This system is similar to the 3-isoquinolylnitrene PES in that similar structures can be expected, i.e., **18** and **19**, but different in that the ground state of the cyclic carbene **19** is a triplet (see Scheme 1 and Figure 6).

Xie et al. describe the carbene as having a triplet ground state (C_{2v}-**19T**) and a singlet state 5.5 kcal/mol

(23) Maier, G.; Endres, J. *Chem. Eur. J.* **1999**, *5*, 1590.

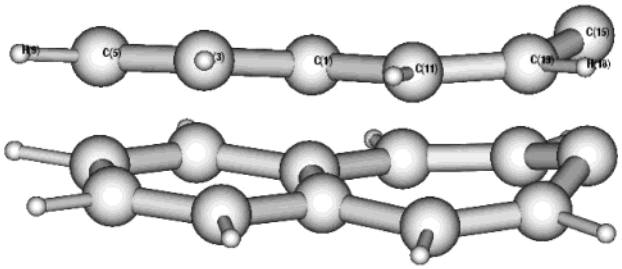


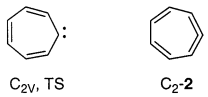
FIGURE 7. Optimized structure for carbene C_s-**19S**, two slightly different views with the carbene center pointing up at the right side and the aromatic ring to the left (B3LYP/6-31G*).

above the ground state. From the Supporting Information to their paper it is obvious that both structures are planar, with C_{2v} symmetry. Xie et al. also report that the vibrational frequency analysis of the singlet carbene shows two imaginary modes, B_1 297.8i cm^{-1} and A_2 234.3i cm^{-1}, with the A_2 mode pointing toward the allene.

As this seemed to be analogous to the diazacarbene/carbodiimide case (**39**/**38**) described above, we recalculated the C_{2v} carbene C_{2v}-**19S**. It was found that the imaginary A_2 mode, indeed, points toward the allene, but also that the B_1 mode, which was not further considered by Xie et al., points toward a C_s structure, just as in the diazacarbene case. Moreover, we have now located a *bent* carbene structure with C_s symmetry, C_s-**19S**, starting with a geometry similar to that of **39** (Figures 6 and 7).[24]

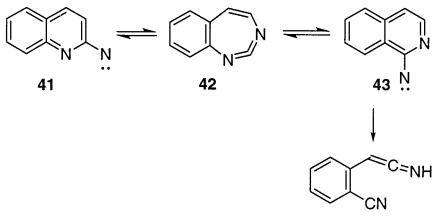
C_s-**19S** was found to be a minimum, lying ca. 10 kcal/mol above allene **18** and bent like **39**, but much less markedly so. The calculated carbene CCC angle in C_s-**19S** is 119°, compared to 118.5 in C_{2v}-**19S** and 142° in allene **18**. This means that, while the benzocycloheptatrienylidene C_s-**19S** is probably difficult to observe experimentally, it may yet be involved in rearrangements.

Note, in contrast, that planar C_{2v}-cycloheptatrienylidene is a transition state (with only one imaginary mode) between the two enantiomeric C_2-cycloheptatetraenes **2** and (at the B3LYP/6-31G* level of theory) no minimum exists for a bent C_s-cycloheptatrienylidene.[8a−c]

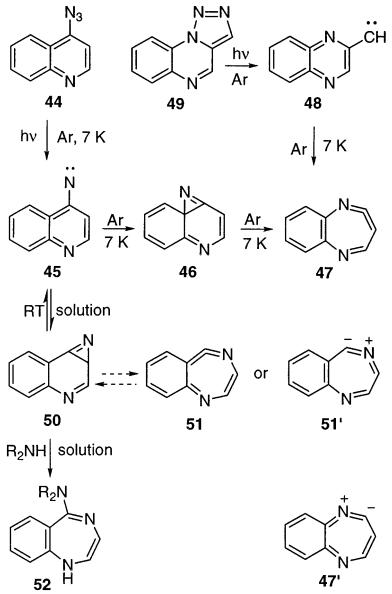


The triplet C_{2v}-**19T** is the ground state in the carbene system of Figure 6. Attempts to optimize a carbene C_s-**19T** led to its collapse to C_{2v}-**19T** (UB3LYP/6-31G*).

3. The Quinolylnitrenes ($C_9H_6N_2$). There are several other isomers of the $C_9H_6N_2$ system described in Section 1. Both 2-quinolylnitrene **41** and 1-isoquinolylnitrene **43** rearrange to the 1,3-diazabenzocycloheptatetraene **42**, on FVT as well as on matrix photolysis (**42**: IR 2007 cm^{-1}



SCHEME 2



(neat, 77 K); 2020 cm^{-1} in Ar matrix, 10 K).[3,6] In adition, 1-isoquinolylnitrene **43** undergoes ring opening to *o*-cyano-*C*-phenylketenimine. Since all three species (**41**−**43**) can interchange, a small amount of *o*-cyano-*C*-phenylketenimine is also formed from **41**.[25] 3-Quinolylnitrene undergoes photochemical ring opening to *o*-isocyano-*C*-phenylketenimine, and both 3-quinolylnitrenes and 4-quinazolylcarbenes undergo thermal ring contraction to 3-cyanoindoles; these systems will be the subject of a forthcoming publication.[26]

Photolysis of 4-azidoquinoline **44** can, in principle, lead to two different azirines, **46** and **50**, by addition to the *ipso* carbon or to the C3−C4 double bond (Scheme 2). Ring expansion of the azirines can lead to either aromatic or *o*-quinoid ketenimines **47** or **51**. Experimentally, we have found that ketenimine **47** is formed in the Ar matrix, where it gives rise to a doublet at 1902, 1904 cm^{-1}.[27] The same species is also formed from the isomeric carbene **48** by photolysis of triazole **49**. (The nitrene **45** also undergoes ring opening to *o*-cyano-*N*-phenylketenimine.[25]) However, in photochemical trapping experiments in solution, the diazepine derivatives **52** are obtained, not products derived from **47**.[27,28] To understand these differences, it is necessary to know the energies of the intermediates and/or transition structures. Calculated data are summarized in Table 4. The use of the extended basis set (B3LYP/6-31+G*) has virtually no effect on the geometries but causes a lowering of key vibrational frequencies by 4−12 cm^{-1}.

Azirines. As would have been expected because of the strained tricyclic geometry and the loss of aromaticity

(24) This behavior has been independently discovered by: Bonvallet, P. A.; Todd, E. M.; Kim, Y. S.; McMahon, R. J. *J. Org. Chem.* **2002**, *67*, 9031.

(25) Reisinger, A.; Addicott, C.; Wentrup, C. Unpublished results. Addicott, C. Ph.D. Thesis, The University of Queensland, Brisbane, Australia, 2002.

(26) Mitschke, U.; Finnerty, J.; Addicott, C.; Lukosch, A.; Lan, N. M.; Wentrup, C. Manuscript in preparation.

(27) Addicott, C.; Reisinger, A.; Wentrup, C. Unpublished results. Addicott, C. B.Sc. Honours Thesis, The University of Queensland, Brisbane, Australia 1998.

(28) Kaname, M.; Tsuchiya, T.; Sashida, H. *Heterocycles* **1999**, *51*, 2407.

TABLE 4. Calculated Characteristic Wavenumbers and Relative Energies of Some $C_9H_6N_2$ Species[a]

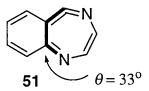
	rel energy/ kcal mol^{-1}	sym	characteristic wavenumbers/cm^{-1} $\nu_{unscaled}$ (I)[b]	ν_{scaled}[c]
46			ring opens to **47**	
50	6.4 [6.5]	C_1	1824 (32)	1753 [1749]
47	0.0 [0]	C_1	1985 (145)	1908 [1896]
47′			converts to **47**	
51′	18.4 [17.3]	C_1	1739 (158)	1672 [1664]
51	18.9 [18.7]	C_1	1887 (363)	1814 [1807]

[a] Calculations at the B3LYP/6-31G(d) level of theory, except values in brackets [ ], which are at the B3LYP/6-31+G* level. Relative energies are corrected by zero-point vibrational energies. [b] Calculated absolute intensities in km/mol. [c] Scaling factor 0.9613 for all frequencies.

in both six-membered rings, the bridgehead azirine **46** is not a minimum, and during the optimization it ring-opens to the ketenimine **47**. Azirine **50**, however, is a minimum and only 6 kcal/mol above the cyclic ketenimine **47**, and 12.5 kcal/mol below **51**. The bond lengths in the aromatic ring vary between 1.393 and 1.404 Å. The calculated C=N vibration of the azirine ring is at 1824 cm^{-1}, compared to 1813 cm^{-1} for the isomeric azirine **37**.

Diazabenzocycloheptatetraenes. Ring-opening of the azirines can in principle lead to four benzannelated seven-membered rings, two of which would be aromatic, the other two *o*-quinoid in character. No minimum was found for the ylidic *o*-quinoid structure **47′** (Scheme 2); attempts to optimize this structure led instead to the stable ketenimine **47**. The *o*-quinoid ketenimines **51** can in principle avoid the *o*-quinoid character by becoming ylidic (**51′**); however, there is very little energy difference between **51** and **51′** (Table 4). They would be easily distinguished by their IR spectra, but experimentally neither is observed.[26] UB3LYP/6-31G* and 6-31+G* calculations did not change the energy of **51′**, indicating that diradical states may be unimportant. The squared spin expectation value $\langle S^2 \rangle$ for this molecule is zero as required for a singlet species.

Ketenimine **47** is the most stable structure in this series, 18−19 kcal/mol more stable than **51**/**51′** and also 12.5 kcal/mol more stable than the cyclic carbodiimide **38**, which is discussed in Section 1. The aromatic compounds **47** and **51′** have planar aromatic rings while the seven-membered rings are bent. The *o*-quinoid ketenimine **51** has alternating bond lengths in the *o*-quinoid part (1.364−1.442 Å) and a dihedral angle θ of 33°, resulting in a warped seven-membered ring. The cumulenic vibrations of these four structures vary over a 250-cm^{-1} range (see Table 4).



51

Ylidic structures such as **51′** would be easily distinguished from the cumulenes and azirines by the low wavenumbers (1672 [1664] cm^{-1}) of their strongest band. The seven-membered ring in **51′** has the following calculated bond lengths: C−C($^-$) 1.480 Å, C=N 1.253 Å, N=CH 1.293 Å, CH−CH 1.467 Å, CH=N 1.289 Å, and N−C 1.418 Å.

TABLE 5. Calculated Characteristic Wavenumbers and Relative Energies of Some Monocyclic Cumulenes[a]

molecule	rel energy/ kcal/mol	sym	characteristic wavenumbers/cm^{-1} $\nu_{unscaled}$ (I)[b]	ν_{scaled}[c]	exptl
54		C_1	1942 (165)	1867	1872
			1317 (13)	1325	1333
			849 (36)	815	824
			666 (53)	640	649
5	0.0	C_1	1967 (164)	1891	1895
			1389 (17)	1335	1348
			1015 (22)	975	980
			774 (52)	743	748
			703 (38)	675	683
			675 (14)	648	658
55	7.8	C_1	1891 (2)	1818	
			1568 (33)	1508	
			829 (40)	797	
			746 (45)	716	
			729 (38)	701	
56	3.5	C_1	1884 (12)	1811	1810
			1411 (21)	1356	1363
			1300 (17)	1249	1256
			910 (30)	874	900
			856 (19)	833	850
			834 (23)	801	810
			717 (36)	689	700
			608 (39)	584	603

[a] B3LYP/6-31G*. Only major IR bands other than the cumulenic bands are given; see Supporting Information for complete data. Relative energies are corrected by zero-point vibrational energies. [b] Calculated absolute intensities in km/mol. [c] Scaling factor 0.9613.

The conclusion from this section is that the most stable species in the series, the ketenimine **47**, is observed in the Ar matrix at 7 K. If all the species involved are in photochemical equilibrium, then one can expect to observe the thermodynamically most stable one. The formation of diazepines **52** in solution, on the other hand, is due to kinetic control. Azirine **50** will be formed faster than the higher lying transition state **46**, and it is rapidly trapped in the presence of nucleophiles. The *o*-quinoid ketenimine **51** would give the same products, but it is hardly formed, because it lies 6 kcal/mol above azirine **50**. The alternate ylidic structure **51′** is of the same or slightly lower energy than **51**, and it would not be expected to give the observed products **52**. Thus, this investigation emphasizes that the intermediates seen in matrix isolation experiments are not necessarily the same as those involved in solution chemistry.

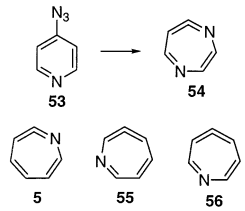
4. Monocyclic Systems. This part summarizes the vibrational data for monocyclic ketenimines **5**[29] and **54**[27,30] and allenes **55**−**56**[31] (Table 5). B3LYP/6-31G* calculations of the energies and IR spectra of the rearrangement products of 2-pyridylnitrenes, viz. carbodiimides of type **8** and azirine **11**, have been reported previously.[5]

There is excellent agreement between theoretical and experimental IR spectra for **8**,[5] **5**, **54**, and **56**. Allene **55**

(29) Chapman, O. L.; LeRoux, J.-P. *J. Am. Chem. Soc.* **1978**, *100*, 282. Hayes, J. C.; Sheridan, R. S. *J. Am. Chem. Soc.* **1990**, *112*, 5879. Donnelly, T.; Dunkin, I. R.; Norwood, D. S. D.; Prentice, A.; Shields, C. J.; Thomson, P. C. P. *J. Chem. Soc., Perkin Trans. 2* **1985**, 307.

(30) Chapyshev, S. V.; Kuhn, A.; Wong, M. W.; Wentrup, C. *J. Am. Chem. Soc.* **2000**, *122*, 1572.

(31) Chapman, O. L.; Sheridan, R. S. *J. Am. Chem. Soc.* **1979**, *101*, 3690. Chapman, O. L.; Sheridan, R. S.; LeRoux, J.-P. *Recl. Trav. Chim. Pays-Bas* **1979**, *98*, 335



is experimentally unknown; it has higher energy than **56**, but it is possible that it has been produced and remained undetected in the original experiments[31] because of the very low calculated intensity of its allenic vibration, and the close proximity of other strong bands to those of other products formed. The very low intensities of the allenic vibrations of **55** and **56** are in agreement with experimental observations on similar compounds.[12,32]

There is a marked blue shift in the characteristic wavenumbers of the cumulenic vibrations in the monocyclic compounds compared to the benzo-annelated structures such as **47** (Table 4) and **28**.[18]

Conclusion

3-Isoquinolylnitrene **36** forms a stable azirine **37**. The bent seven-membered-ring carbene C_s-**39S** has some ylide character as expressed in formula **39′** and is very close in energy to the carbodiimide **38**. Both **38** and **39** are calculated energy minima (Figures 1−5). A new nonplanar singlet cycloheptatrienylidene C_s-**19S** is located on the $C_{11}H_8$ potential energy surface (Figures 6 and 7). Rearrangement of 4-quinolylnitrene **44** leads to the seven-membered-ring ketenimine **47** in Ar matrix (thermodynamic control), but reaction in solution is governed by kinetic control and takes place via the azirine **50** (Scheme 2). There is excellent agreement between calculated and experimental infrared spectra of the monocyclic aza- and diazacycloheptatetraenes **5**, **54**, and **56**.

Computational Method

The calculations discussed here were carried out at the B3LYP/6-31G* and B3LYP/6-31+G* levels of theory, using the Gaussian94 suite of programs.[3] UB3LYP/6-31G* and UB3LYP/6-31+G* were used for singlet and triplet carbenes. Compound C_s-**39S** was also evaluated at the B3LYP/6-311++G** level. The accuracy of these DFT computational methods for structures of the types considered in the present paper was established previously.[5,8,12,15,24,30] Relative energies were corrected by zero-point vibrational energies. Vibrational frequencies were scaled by a factor[33] of 0.9613 throughout.

Acknowledgment. We thank Professor R. J. McMahon, University of Wisconsin, Madison, for fruitful discussions and for sharing his results in advance of publication. This work was supported by the Australian Research Council.

Supporting Information Available: Cartesian coordinates, absolute energies, and vibrational frequencies of all calculated structures. This material is available free of charge via the Internet at http://pubs.acs.org.

JO0258756

(32) West, P. R.; Chapman, O. L.; LeRoux, J.-P. *J. Am. Chem. Soc.* **1982**, *104*, 1779.

(33) Wong, M. W. *Chem. Phys. Lett.* **1996**, *256*, 391. Scott, A. P.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16502.