

Ab Initio Study of the Ring Expansion of Phenylnitrene and Comparison with the Ring Expansion of Phenylcarbene

William L. Karney*[†] and Weston Thatcher Borden*

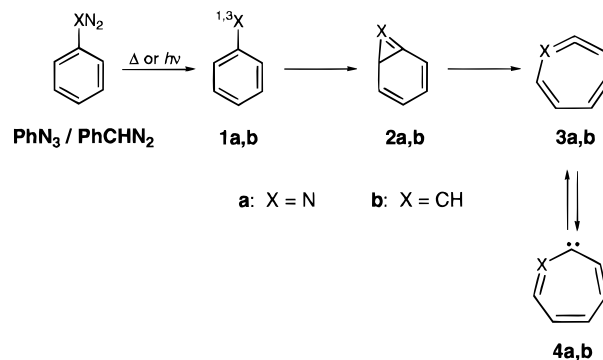
Contribution from the Department of Chemistry, Box 351700, University of Washington, Seattle, Washington 98195-1700

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Abstract: The rearrangement of singlet phenylnitrene (**1a**) to 1-azacyclohepta-1,2,4,6-tetraene (**3a**) has been studied computationally, using the CASSCF and CASPT2N methods in conjunction with the 6-31G*, cc-pVDZ, and 6-311G-(2d,p) basis sets. Ring expansion from the ¹A₂ state of **1a** is predicted to occur in two steps via 7-azabicyclo[4.1.0]-hepta-2,4,6-triene (**2a**) as an intermediate. The rearrangement of **1a** to **2a** is estimated to have a barrier of ca. 6 kcal/mol and to be rate-determining. Azirine **2a** is unlikely to be detected, because of the small calculated barrier (ca. 3 kcal/mol) to its rearrangement to **3a**. At the CASPT2N/6-311G(2d,p)/CASSCF(8,8)/6-31G* + ZPE level of theory, the reaction **1a** → **3a** on the lowest singlet potential energy surface is calculated to be exothermic by 1.6 kcal/mol. This reaction is predicted to be ca. 19 kcal/mol less exothermic, but to have a barrier ca. 9 kcal/mol lower than the analogous ring expansion of ¹A' phenylcarbene (**1b**) to cyclohepta-1,2,4,6-tetraene (**3b**). Factors which contribute to these and other energetic differences between the ring expansion reactions of **1a** and **1b** are discussed. The lowest singlet state of planar 1-azacyclohepta-1,3,5-trien-7-ylidene (**4a**) is an open-shell singlet (¹A'') which is calculated to be ca. 20 kcal/mol above **3a** and to be the transition state for enantiomerization of **3a**. Unlike cycloheptatrienylidene (**4b**), **4a** is predicted to have a triplet ground state and an energy difference between ¹A'' and the lowest triplet (³A'') of ca. 1 kcal/mol. The similar geometries of and small adiabatic energy difference between these two states of **4a** is probably the reason why triplet **4a** has not been detected by EPR.

Thermolysis or photolysis of phenyl azide (PhN₃) in the presence of nucleophiles affords ring-expanded products (Scheme 1).^{1,2} This reaction has been exploited for applications in synthesis, photoaffinity labeling, and photoresist technology,³ but the details of the mechanism have long been debated.² The products of nucleophilic trapping following decomposition of PhN₃ were initially rationalized as arising from 7-azabicyclo[4.1.0]hepta-2,4,6-triene (**2a**).¹ This explanation was generally accepted in subsequent studies⁴ and supported by calculations⁵ until 1978, when Chapman and LeRoux characterized 1-azacyclohepta-1,2,4,6-tetraene (**3a**) using matrix isolation.⁶ The existence of the cyclic ketenimine⁷ **3a** was confirmed by later

Scheme 1



[†] Present address: Department of Chemistry, Streitwieser Group, University of California, Berkeley, California 94720-1460.

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(1) (a) Huisgen, R.; Vossius, D.; Appl. M. *Chem. Ber.* **1958**, *91*, 1. (b) Huisgen, R.; Appl. M. *Chem. Ber.* **1958**, *91*, 12. (c) Doering, W. v. E.; Odum, R. A. *Tetrahedron* **1966**, *22*, 81.

(2) Reviews of aryl nitrene chemistry: (a) Smith, P. A. S. In *Nitrenes*; Lwowski, W., Ed.; Wiley-Interscience: New York, 1970; Chapter 4. (b) Scriven, E. F. V. In *Reactive Intermediates*; Abramovitch, R. A., Ed.; Plenum: New York, 1982; Vol. 2, Chapter 1. (c) Wentrup, C. *Reactive Molecules*; Wiley-Interscience: New York, 1984; Chapter 4. (d) Platz, M. S. In *Azides and Nitrenes: Reactivity and Utility*; Scriven, E. F. V., Ed.; Academic: New York, 1984; Chapter 7. (e) Platz, M. S.; Maloney, V. M. In *Kinetics and Spectroscopy of Carbenes and Biradicals*; Platz, M. S., Ed.; Plenum: New York, 1990; pp 303–320. (f) Platz, M. S.; Leyva, E.; Haider, K. *Org. Photochem.* **1991**, *11*, 367. (g) Schuster, G. B.; Platz, M. S. *Adv. Photochem.* **1992**, *17*, 69.

(3) (a) *Azides and Nitrenes: Reactivity and Utility*; Scriven, E. F. V., Ed.; Academic: New York, 1984. (b) Kotzyba-Hibert, F.; Kapfer, I.; Goeldner, M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1296; *Angew. Chem.* **1995**, *107*, 1391. (c) Iddon, B.; Meth-Cohn, O.; Scriven, E. F. V.; Suschitzky, H.; Gallagher, P. T. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 900; *Angew. Chem.* **1979**, *91*, 965.

(4) (a) Sundberg, R. J.; Brenner, M.; Suter, S. R.; Das, B. P. *Tetrahedron Lett.* **1970**, 2715. (b) Sundberg, R. J.; Suter, S. R.; Brenner, M. *J. Am. Chem. Soc.* **1972**, *94*, 513. (c) DeGraff, B. A.; Gillespie, D. W.; Sundberg, R. J. *J. Am. Chem. Soc.* **1974**, *96*, 7491.

(5) (a) Shillady, D. D.; Trindle, C. *Theor. Chim. Acta* **1976**, *43*, 137. (b) See also: Gleiter, R.; Rettig, W.; Wentrup, C. *Helv. Chim. Acta* **1974**, *57*, 2111.

(6) Chapman, O. L.; LeRoux, J.-P. *J. Am. Chem. Soc.* **1978**, *100*, 282.

matrix⁸ and solution⁹ spectroscopic studies, which also established that **3a** is the species trapped by nucleophiles in solution.⁹

Other aspects of the mechanism have been clarified by various groups. The ring expansion has been shown to be a singlet process,¹⁰ involving initial loss of nitrogen from PhN₃ to form singlet phenylnitrene (¹A₂-**1a**).¹¹ Intersystem crossing of singlet **1a** to the triplet ground state (³A₂-**1a**) competes with thermal isomerization of singlet **1a** to **3a**.¹² Ketenimine **3a** undergoes

(7) For review of cyclic cumulenes see: Johnson, R. P. *Chem. Rev.* **1989**, *89*, 1111.

(8) 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.

(9) (a) Schrock, A. K.; Schuster, G. B. *J. Am. Chem. Soc.* **1984**, *106*, 5228. (b) Shields, C. J.; Chrisope, D. R.; Schuster, G. B.; Dixon, A. J.; Poliakoff, M.; Turner, J. J. *J. Am. Chem. Soc.* **1987**, *109*, 4723. (c) Li, Y.-Z.; Kirby, J. P.; George, M. W.; Poliakoff, M.; Schuster, G. B. *J. Am. Chem. Soc.* **1988**, *110*, 8092.

(10) Splitter, J. S.; Calvin, M. *Tetrahedron Lett.* **1968**, 1445.

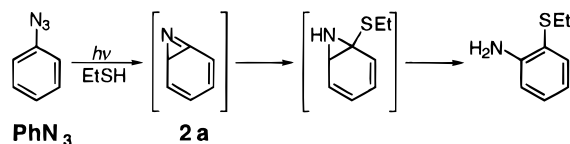
(11) Marcinek, A.; Leyva, E.; Whitt, D.; Platz, M. S. *J. Am. Chem. Soc.* **1993**, *115*, 8609.

(12) (a) Leyva, E.; Platz, M. S. *Tetrahedron Lett.* **1985**, *26*, 2147. (b) Leyva, E.; Platz, M. S.; Persy, G.; Wirz, J. *J. Am. Chem. Soc.* **1986**, *108*, 3783. (c) The experimental barrier height for the ring expansion of **1a** has been revised upward from ca. 3 to ca. 6 kcal/mol, because the rate constant for intersystem crossing (*k*_{isc}) of singlet phenylnitrene is now believed to be 10⁶–10⁷ s⁻¹, rather than 10¹⁰ s⁻¹, as previously assumed.^{12b} Platz, M. S., private communication.

thermal reversion to triplet **1a** over time in solution at ambient temperature.⁹ In addition, triplet **1a** and **3a** can be photochemically interconverted in a cryogenic matrix.¹³

Although singlet **1a** has never been directly observed, the triplet ground state has been characterized by ESR,¹⁴ UV-vis,¹⁵ and IR¹³ spectroscopy. Photoelectron spectroscopy of the anion of **1a** has yielded a value of 18 kcal/mol for the singlet-triplet splitting (ΔE_{ST}) of **1a**.¹⁶

The proposed¹ bicyclic intermediate (**2a**) in the ring expansion of **1a** has never been directly observed. However, the analogous azirines, formed by photolysis of 1- and 2-naphthyl azides, have been characterized by IR,¹⁷ and trapping of substituted derivatives of **2a** has been reported.¹⁸ The strongest evidence to date for the intermediacy of **2a** is the observation that photolysis of **PhN₃** in ethanethiol affords *o*-thioethoxyaniline in 39% yield, presumably from nucleophilic trapping of **2a**.^{18a} Nevertheless, whether **2a** is really an intermediate in the formation of **3a** remains an open question.



In a process that resembles the ring expansion of phenylnitrene, the carbene analogue of **1a**, phenylcarbene (**1b**), yields 1,2,4,6-cycloheptatetraene (**3b**, Scheme 1).^{2c,19-21} Like **1a**, carbene **1b** has a triplet ground state which has been characterized by ESR,²² UV-vis,¹⁹ and IR,¹⁹ but singlet **1b** has not yet been detected spectroscopically. Like **3a**, cyclic allene **3b** has been observed by IR.¹⁹ Cumulene **3b** can be generated photochemically from triplet **1b**, as well as thermally from precursors of **1b**.¹⁹ Bicyclo[4.1.0]hepta-2,4,6-triene (**2b**) has been proposed as an intermediate in the ring expansion of **1b**.^{23,24}

- (13) Hayes, J. C.; Sheridan, R. S. *J. Am. Chem. Soc.* **1990**, *112*, 5879.
 (14) (a) Smolinsky, G.; Wasserman, E.; Yager, W. A. *J. Am. Chem. Soc.* **1962**, *84*, 3220. (b) Moriarty, R. M.; Rahman, M.; King, G. J. *J. Am. Chem. Soc.* **1966**, *88*, 842.
 (15) (a) Reiser, A.; Frazer, V. *Nature (London)* **1965**, *208*, 682. (b) Reiser, A.; Bowses, G.; Horne, R. J. *Trans. Faraday Soc.* **1966**, *62*, 3162.
 (16) (a) Travers, M. J.; Cowles, D. C.; Clifford, E. P.; Ellison, G. B. *J. Am. Chem. Soc.* **1992**, *114*, 8699. (b) McDonald, R. N.; Davidson, S. J. *J. Am. Chem. Soc.* **1993**, *115*, 10857.
 (17) Dunkin, I. R.; Thomson, P. C. P. *J. Chem. Soc., Chem. Commun.* **1980**, 499.
 (18) (a) Carroll, S. E.; Nay, B.; Scriven, E. F. V.; Suschitzky, H.; Thomas, D. R. *Tetrahedron Lett.* **1977**, 3175. (b) Nielsen, P. E.; Buchardt, O. *Photochem. Photobiol.* **1982**, *35*, 317. (c) Younger, C. G.; Bell, R. A. *J. Chem. Soc., Chem. Commun.* **1992**, 1359.
 (19) (a) West, P. R.; Chapman, O. L.; LeRoux, J.-P. *J. Am. Chem. Soc.* **1982**, *104*, 1779. (b) McMahon, R. J.; Abelt, C. J.; Chapman, O. L.; Johnson, J. W.; Kreil, C. L.; LeRoux, J.-P.; Mooring, A. M.; West, P. R. *J. Am. Chem. Soc.* **1987**, *109*, 2456.
 (20) Reviews of arylcarbene chemistry: (a) Wentrup, C. *Top. Curr. Chem.* **1976**, *62*, 173. (b) Jones, W. M.; Brinker, U. H. In *Pericyclic Reactions*; Marchand, A. P., Lehr, R. E., Eds.; Academic: New York, 1977; Vol. 1, Chapter 3. (c) Jones, W. M. In *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic: New York, 1980; Vol. 1, Chapter 3. (d) Wentrup, C. In *Reactive Intermediates*; Abramovitch, R. A., Ed.; Plenum: New York, 1980; Vol. 1, Chapter 4. (e) Gaspar, P. P.; Hsu, J.-P.; Chari, S.; Jones, M. *Tetrahedron* **1985**, *41*, 1479.
 (21) For a recent comparison of phenylnitrene and phenylcarbene, see: Platz, M. S. *Acc. Chem. Res.* **1995**, *28*, 487.
 (22) (a) Trozzolo, A. M.; Murray, R. W.; Wasserman, E. *J. Am. Chem. Soc.* **1962**, *84*, 4990. (b) Wasserman, E.; Trozzolo, A. M.; Yager, W. A.; Murray, R. W. *J. Chem. Phys.* **1964**, *40*, 2408. (c) Barash, L.; Wasserman, E.; Yager, W. A. *J. Am. Chem. Soc.* **1967**, *89*, 3931.
 (23) (a) Vander Stouw, G. G.; Kraska, A. R.; Shechter, H. *J. Am. Chem. Soc.* **1972**, *94*, 1655. (b) For calculations supporting the intermediacy of **2b** see: Dewar, M. J. S.; Landman, D. *J. Am. Chem. Soc.* **1977**, *99*, 6179. Wentrup, C.; Mayor, C.; Becker, J.; Lindner, H. *J. Tetrahedron*, **1985**, *41*, 1601.

but, like **2a**, **2b** has not yet been observed, though benzannelated analogues have been characterized.²⁵

Despite the similarities between the ring expansions of **1a** and **1b**, there are significant differences between these two rearrangements.²¹ For example, the thermal ring expansion of singlet **1b** has been observed only in the gas phase at high temperatures,²⁶ whereas ring expansion of singlet **1a** occurs rapidly in solution at low temperatures.¹² Platz has proposed an explanation for this difference in reactivity, based on a one-step mechanism for ring expansion that proceeds from the π^2 electronic configuration of both singlet species.²¹ Platz argues that this configuration is more accessible to singlet **1a** than to singlet **1b**. However, if the ring expansions occur in two steps, such an explanation would require modification. Another difference between the two ring expansion reactions is the fact that **3a** reverts thermally to triplet **1a** in solution,⁹ while reversion of **3b** to triplet **1b** has not been observed.

Although both **1a** and **1b** have triplet ground states, the singlet-triplet splittings are quite different. ΔE_{ST} for **1a** is 18 kcal/mol,^{16,27} whereas ΔE_{ST} for **1b** is less than 5 kcal/mol.^{24,28,29} This can be understood on the basis of simple molecular orbital considerations.²¹ The difference between the nature of the lowest singlet states—open-shell (1A_2) in **1a** and closed-shell ($^1A'$) in **1b**—also has a simple explanation.^{27b}

The C_6H_5N potential energy surface has received less attention from theoreticians than from experimentalists. *Ab initio* calculations on **1a** have focused on the relative energies of the different spin states²⁷ and give good agreement with the experimental singlet-triplet (1A_2 – 3A_2) splitting of 18 kcal/mol.¹⁶ However, to date, the mechanism of the ring expansion of **1a** has been studied using only semiempirical methods.^{5,9c} MNDO calculations by Schuster and co-workers predicted the intermediacy of **2a**, but placed **3a** below **2a** in energy.^{9c} Schuster's calculations found barriers of 12.4 and 3.6 kcal/mol for respectively the first and second steps of the ring expansion. The lower barrier computed for the ring opening of **2a** to **3a** is consistent with the experimental finding that **3a**, not **2a**, is the species that is trapped in solution.^{9c} Recent RMP2/6-31G* calculations by Morawietz and Sander placed **3a** only 0.2 kcal/mol below **2a** in energy.³⁰

Another species considered by Schuster and co-workers is azacycloheptatrienylidene (**4a**), the planar carbene "isomer" of ketenimine **3a**. This species has on occasion been postulated to be the product of the ring expansion of **1a**,^{20a} but **4a** has never been detected. Based on their MNDO calculations, Schuster and co-workers proposed that the experimentally observed thermal reversion of **3a** to triplet **1a** occurs, not via singlet **1a**, but rather via triplet **4a**.^{9c} Recent calculations on

- (24) Several high-level *ab initio* calculations on the rearrangement of **1b** to **3b** have recently been published: (a) Matzinger, S.; Bally, T.; Patterson, E. V.; McMahon, R. J. *J. Am. Chem. Soc.* **1996**, *118*, 1535. (b) Wong, M. W.; Wentrup, C. *J. Org. Chem.* **1996**, *61*, 7022. (c) Schreiner, P. R.; Karney, W. L.; Schleyer, P. v. R.; Borden, W. T.; Hamilton, T. P.; Schaefer, H. F. *J. Org. Chem.* **1996**, *61*, 7030.
 (25) (a) West, P. R.; Mooring, A. M.; McMahon, R. J.; Chapman, O. L. *J. Org. Chem.* **1986**, *51*, 1316. (b) Albrecht, S. W.; McMahon, R. J. *J. Am. Chem. Soc.* **1993**, *115*, 855.
 (26) (a) Joines, R. C.; Turner, A. B.; Jones, W. M. *J. Am. Chem. Soc.* **1969**, *91*, 7754. (b) Schissel, P.; Kent, M. E.; McAdoo, D. J.; Hedaya, E. *J. Am. Chem. Soc.* **1970**, *92*, 2147. (c) Wentrup, C.; Wilczek, K. *Helv. Chim. Acta* **1970**, *53*, 1459.
 (27) (a) Kim, S.-J.; Hamilton, T. P.; Schaefer, H. F. *J. Am. Chem. Soc.* **1992**, *114*, 5349. (b) Hrovat, D. A.; Waali, E. E.; Borden, W. T. *J. Am. Chem. Soc.* **1992**, *114*, 8698. (c) Castell, O.; Garcia, V. M.; Bo, C.; Caballol, R. *J. Comput. Chem.* **1996**, *17*, 42.
 (28) Savino, T. G.; Kanakarajan, K.; Platz, M. S. *J. Org. Chem.* **1986**, *51*, 1305.
 (29) Cramer, C. J.; Dulles, F. J.; Falvey, D. E. *J. Am. Chem. Soc.* **1994**, *116*, 9787.
 (30) Morawietz, J.; Sander, W. *J. Org. Chem.* **1996**, *61*, 4351.

cycloheptatrienylidene (**4b**), the hydrocarbon counterpart of **4a**, have revealed no fewer than *four* low-lying electronic states, with an open-shell singlet lowest in energy, in violation of Hund's rule.^{24c} Thus, the ground-state multiplicity of **4a** and the role of its low-lying electronic states in the transformations observed on the C₆H₅N energy surface represent intriguing questions.

In this paper we describe the results of our computational investigations of the ring expansion of phenylnitrene (**1a**). We address the question of the possible intermediacy of **2a** and compare our results with available experimental data. We also compare our calculations on the ring expansion of **1a** to similar calculations²⁴ on the ring expansion of phenylcarbene (**1b**), in an attempt to understand the differences between these two reactions.²¹ Finally, we report computational results on the low-lying electronic states of azacycloheptatrienylidene (**4a**) and compare these results with those obtained previously on the hydrocarbon (**4b**).

Computational Methods

Geometry optimizations were performed with the 6-31G* basis set,³¹ using complete active space (CAS) SCF calculations.³² An eight-electron, eight-orbital active space, hereafter designated (8,8), was used for all species. The (8,8) active space for **1a** consisted of seven π and π^* MOs, plus the in-plane p AO on nitrogen. For **3a**, the four π and the four π^* MOs of the double bonds were used. The active space for the two transition states (**TS1a** and **TS2a**) consisted of six orbitals that were mainly π in character plus a σ/σ^* pair for the partially formed/broken bond. For **4a**, the seven π and π^* MOs plus the in-plane hybrid orbital on the carbene carbon comprised the active space.

The choice of the orbitals for the active space for **2a** was somewhat problematic. In order to maintain consistency in the size of the active space over the entire singlet potential surface, CASSCF(8,8) calculations were required. Six MOs in **2a**, primarily π in character, were easily chosen. However, which σ/σ^* pair one should choose—the pair corresponding to the C–C bond between the bridgehead carbons or that corresponding to the C–N single bond of the azirine ring—might seem arbitrary, since the pathways that connect **2a** to **1a** and to **3a** each involve breaking a different one of these two bonds.

RHF calculations made it clear that the σ/σ^* pair for the C–N bond was the better choice for two reasons. First, at the RHF/6-31G* optimized geometry of **2a** the C–N single bond of the azirine ring was calculated to be much longer (1.530 Å) than the C–C bond between the bridgehead carbons (1.445 Å). This strongly suggests that the C–N single bond is weaker than the C–C bond between the bridgehead carbons, making the C–N σ/σ^* orbitals a more reasonable choice for inclusion in the active space. Second, due to the nonplanar geometry of **2a**, the orientation of the C–N bond results in its mixing considerably more than the C–C bond with the six π MOs. Therefore, in addition to the six MOs primarily π in character, two orbitals with significant σ/σ^* C–N single bond character were included in the eight-orbital active space for **2a**.

CASSCF(8,8)/6-31G* vibrational frequencies were calculated for all stationary points, in order to verify whether each was an intermediate or a transition state. The unscaled CASSCF(8,8) frequencies were also used to compute the zero-point vibrational corrections to the energies.

CASSCF(8,8) single point energies were recalculated at the CASSCF(8,8)/6-31G* optimized geometries with Dunning's correlation-consistent polarized valence double- ζ basis set (cc-pVDZ)³³ and Pople's 6-311G(2d,p) basis set.³⁴ The latter basis set is valence triple- ζ , and it provides two sets of polarization functions (d orbitals) on carbon and nitrogen and one set (p orbitals) on hydrogen.

The effects of including dynamic electron correlation were determined by CASPT2N calculations.^{35,36,39} CASPT2N single point ener-

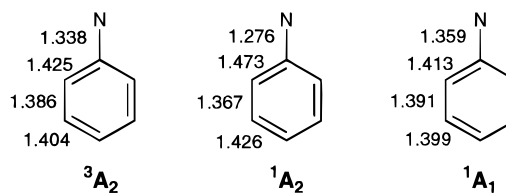


Figure 1. CASSCF(8,8)/6-31G* optimized bond lengths (Å) of three low-lying spin states of phenylnitrene (**1a**).

gies were calculated at the CASSCF(8,8)/6-31G* geometries, using the 6-31G*, cc-pVDZ, and 6-311G(2d,p) basis sets. Unless otherwise noted, the discussions of relative energies of the C₆H₅N stationary points that follow refer to energies calculated at the highest level of theory that was employed in this study, CASPT2N/6-311G(2d,p)//CASSCF(8,8)/6-31G* + ZPE.

The CASSCF calculations were performed using either the *Gaussian 92*⁴² or *Gaussian 94*⁴³ programs. CASPT2N calculations were carried out with the *MOLCAS* program.⁴⁴

Results and Discussion

Ring Expansion of Phenylnitrene. (a) Phenylnitrene (**1a**).

The CASSCF(8,8)/6-31G* optimized bond lengths in the lowest electronic states (³A₂, ¹A₂, and ¹A₁) of **1a** are shown in Figure 1, and their calculated energies are given in Table 1. The calculated singlet–triplet gap (ΔE_{ST}) of 18.5 kcal/mol is in excellent agreement with recent experimental results¹⁶ and

(35) (a) Andersson, K.; Malmqvist, P.-Å.; Roos, B. O.; Sadlej, A. J.; Wolinski, K. *J. Phys. Chem.* **1990**, *94*, 5483. (b) Andersson, K.; Malmqvist, P.-Å.; Roos, B. O. *J. Chem. Phys.* **1992**, *96*, 1218.

(36) Since the “normal” CASPT2 method—usually denoted “CASPT2N”, and sometimes “CASPT2-0”—is known³⁷ to overestimate the stability of some open-shell, relative to closed-shell electronic states, we also performed these calculations with the CASPT2-g1 procedure.^{37,38} We discovered, however, that the latter method is problematic for these systems, since, unlike the case at the CASPT2N level, the weight of the CASSCF reference wave function is very different for each of the open-shell systems at the CASPT2-g1 level, varying from 73.2% for ³A₂-**1a** to 35.0% for ¹A₁-**4a** with the 6-31G* basis set. In contrast, the reference weights remained fairly constant at 78.3 ± 0.4% for both open- and closed-shell species at the CASPT2N level. The CASPT2-g1 and CASPT2N energies differed by up to 4.7 kcal/mol, and in the case of the ¹A₂–³A₂ splitting in **1a**, CASPT2N gave much better agreement with experiment.¹⁶ We therefore consider the CASPT2N relative energies to be the more reliable, and they are given in Table 1.

(37) Andersson, K. *Theor. Chim. Acta* **1995**, *91*, 31.

(38) We thank M. Fülischer for supplying us with the modified version of *MOLCAS*.

(39) Due to the importance of open-shell singlet states in this study, the use of multi-configurational wave functions was essential. We note, however, that the CASPT2N method is not the only choice for including the effects of dynamic electron correlation. Other options include multi-reference configuration interaction (MRCI)⁴⁰ and two-configuration coupled cluster theory with single and double substitutions (TC-CCSD).⁴¹ Since CASPT2N was used in our previous study of the ring expansion of **1b**,^{24c} for the purpose of making meaningful comparisons between those results and the results of calculations on the ring expansion of **1a**, the CASPT2N method was the obvious choice.

(40) Siegbahn, P. E. M. *J. Chem. Phys.* **1980**, *72*, 1647.

(41) Balková, A.; Bartlett, R. J. *Chem. Phys. Lett.* **1992**, *193*, 364.

(42) Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, W. P. M.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. *Gaussian 92, Revision A*; Gaussian, Inc.: Pittsburgh, PA, 1992.

(43) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94, Revision B.3*; Gaussian, Inc.: Pittsburgh, PA, 1995.

(44) Andersson, K.; Blomberg, M. R. A.; Fülischer, M. P.; Karlström, G.; Kellö, V.; Lindh, R.; Malmqvist, P.-Å.; Noga, J.; Olsen, J.; Roos, B. O.; Sadlej, A. J.; Siegbahn, P. E. M.; Urban, M.; Widmark, P.-O. *MOLCAS-3*; University of Lund, Sweden.

(31) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.

(32) (a) Roos, B. O. *Adv. Chem. Phys.* **1987**, *69*, 339. (b) Roos, B. O. *Int. J. Quantum Chem. Symp.* **1980**, *14*, 175.

(33) Dunning, T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007.

(34) Frisch, M. J.; Pople, J. A.; Binkley, J. S. *J. Chem. Phys.* **1984**, *80*, 3265.

Table 1. Calculated Relative Energies (kcal/mol) of C₆H₅N Stationary Points^a

species	CAS(8,8)/ 6-31G*	ΔZPE ^b (NIMAG)	CAS(8,8)/ cc-pVDZ	CAS(8,8)/ 6-311G(2d,p)	CASPT2N/ 6-31G* ^c	CASPT2N/ cc-pVDZ ^d	CASPT2N/ 6-311G(2d,p) ^e
3A₂-1a	-284.59560	59.8 (0)	-284.61686	-284.66355	-285.42619	-285.45224	-285.72007
1A₂-1a	17.5	-0.3 (0)	17.5	17.1	19.1	19.0	18.5
1A₁-1a	42.2	+0.4 (0)	42.5	42.2	37.3	37.8	36.9
TS1a	26.4	-0.3 (1)	26.5	25.6	27.7	28.3	27.7
2a	22.2	+1.1 (0)	22.8	21.7	20.7	22.5	22.6
TS2a	41.7	0.0 (1)	41.2	40.5	25.9	25.7	25.7
3a	21.2	+1.0 (0)	20.7	19.5	17.8	18.0	16.9
1³A''-4a	43.9	-0.5 (0)	43.7	43.3	37.6	36.6	36.2
2³A''-4a	44.8	-0.7 (0)	44.8	44.6	44.1	43.3	43.5
11A''-4a	43.6	-0.5 (1)	43.6	43.3	38.6	37.9	37.6
1A'-4a	63.1	-0.6 (1)	61.8	60.5	64.2	62.9	62.7
1A'-syn-5	39.7 ^f				42.7 ^f		
6	41.8	+0.1 (0)	40.2	38.9	44.0	42.6	42.2

^a Energies were calculated at the CASSCF(8,8)/6-31G* optimized geometries, include corrections for differences in CASSCF(8,8)/6-31G* zero-point vibrational energies, and are given in kcal/mol relative to ³A₂-1a. Values for ³A₂-1a are given in hartrees (1 hartree = 0.6275 kcal/mol).

^b Difference in CASSCF(8,8)/6-31G* zero-point vibrational energy (unscaled), relative to ³A₂-1a. NIMAG = number of imaginary vibrational frequencies. ^c The weight of the CASSCF(8,8)/6-31G* reference wave function ranged from 78.0 to 78.7% for all species. ^d The weight of the CASSCF(8,8)/cc-pVDZ reference wave function ranged from 76.9 to 77.7% for all species. ^e The weight of the CASSCF(8,8)/6-311G(2d,p) reference wave function ranged from 75.4 to 76.3% for all species. ^f Does not include ZPE correction.

previous *ab initio* calculations.²⁷ The closed-shell singlet state (¹A₁) is predicted to lie ca. 37 kcal/mol above the triplet ground state.⁴⁵

Although both nitrene **1a** and the isoelectronic carbene **1b** have triplet ground states, the lowest singlet in **1a** is the open-shell ¹A₂ state, whereas in **1b** the lowest singlet is a closed-shell ¹A' state. This difference between the nitrene and the carbene can be ascribed to the fact that in **1a** the two nonbonding electrons occupy two pure p orbitals. Placing one electron in each allows the electron in the p-π orbital to be delocalized into the benzene ring, thus confining these electrons of opposite spin to different regions of space and, consequently, minimizing their mutual Coulombic repulsion energy in the ¹A₂ state of **1a**.^{27b} In contrast, in **1b** one of the nonbonding orbitals on the carbene carbon is a hybrid with a substantial amount of 2s character. Therefore, the near degeneracy of the nonbonding MOs in **1a** is strongly lifted in **1b**, and both nonbonding electrons occupy preferentially the lower energy σ orbital, rather than the p-π orbital.²¹

This difference between **1a** and **1b** is reflected in the ratios of the occupation numbers of the two nonbonding orbitals in the closed-shell singlet state of the nitrene and carbene. This ratio in the ¹A₁ state of **1a** is 1.56/0.47 = 3.32.⁴⁶ The in-plane p-σ orbital has the greater occupation number, which allows some electron donation from the phenyl group into the p-π orbital on nitrogen. For comparison, the ratio of the occupation numbers in the ¹A' state of **1b** is 1.94/0.11 = 17.6.⁴⁶ Occupancy of the in-plane orbital is favored five times as much in **1b** as in **1a**, due to the 2s character that this σ orbital contains in **1b**.

(b) 1-Azacyclohepta-1,2,4,6-tetraene (3a). The CASSCF(8,8)/6-31G* optimized geometry of **3a** is shown in Figure 2.

(45) CASPT2N overestimates the stability of some open-shell, relative to closed-shell, electronic states.³⁷ For example, for the ¹A' and ³A'' states of phenylcarbene (**1b**), ΔE_{ST} increases from 8.5 kcal/mol at the CASSCF(8,8)/6-311G(2d,p) level to 12.5 kcal/mol at CASPT2N(6-311G(2d,p)), with the CASSCF value being the more accurate.^{24c} In contrast, the ¹A₁-³A₂ energy gap in phenylnitrene (**1a**) actually *decreases* on going from CASSCF to CASPT2N. This difference between **1a** and **1b** may be due to the fact that, as discussed in the text, the in-plane non-bonding orbital is a hybrid in **1b**. Consequently, the ¹A' state of **1b** is described fairly well by a single electronic configuration, in which this orbital is doubly occupied. In contrast, two configurations contribute strongly to the ¹A₁ state of **1a**. This is reflected in the CASSCF(8,8) configuration coefficients. The weights of the two most important configurations for the ¹A' state of **1b** are 85.5% and 1.7%, whereas the weights of these configurations for the ¹A₁ state of **1a** are 68.7% and 19.2%. In both ¹A₁-**1a** and ¹A'-**1b** the most important configuration is the one with the nitrogen/carbon in-plane σ orbital doubly occupied and the p-π orbital vacant.

(46) CASSCF(8,8)/6-31G* values.

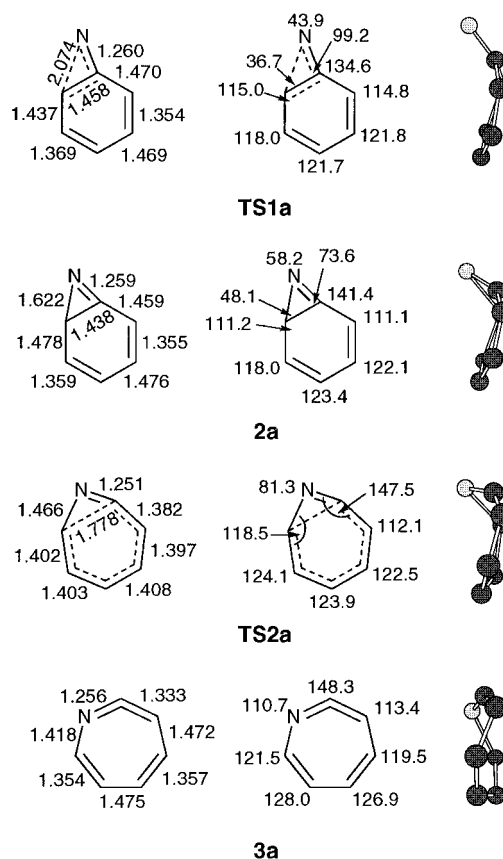
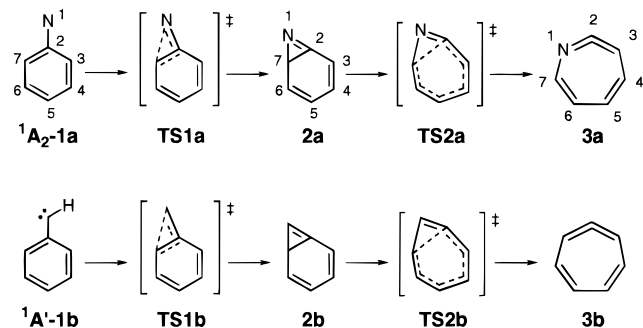


Figure 2. CASSCF(8,8)/6-31G* optimized geometries of **TS1a**, **2a**, **TS2a**, and **3a**. All structures have C₁ symmetry. Distances (left) are in angstroms, and angles (middle) are in degrees. The structures at the right indicate the nonplanar nature of these species.

This species contains a ketenimine moiety which is both bent and twisted.⁷ The N1-C2-C3 angle in **3a** is computed to be 148.3°, compared to a corresponding angle in ketenimine (HN=C=CH₂) of 175.3°, calculated at the CASSCF(4,4)/6-31G* level. The allene unit in **3b** is predicted to be even more highly bent than the ketenimine moiety in **3a**; the C1-C2-C3 angle in **3b** is computed to be 140.8° at the CASSCF(8,8)/6-31G* level.^{24c}

If we define the “twist angle” in **3a** as the difference between 90° and the C7-N1-C3-C4 dihedral angle, then **3a** has a twist angle of 36.0°. For comparison, the twist angle in ketenimine

Scheme 2



is calculated to be only 0.9° at the CASSCF(4,4)/6-31G* level. However, the twist angle of 41.3° in the allene unit of **3b** at the CASSCF(8,8)/6-31G* optimized geometry^{24c} is again larger than that in the ketenimine moiety in **3a**.

(c) **Structures on the Reaction Path Connecting 1a to 3a.** On the reaction path connecting the lowest singlet state of **1a** (1A_2) to singlet **3a** we have located three additional stationary points—an intermediate, 7-azabicyclo[4.1.0]hepta-2,4,6-triene (**2a**), and two transition states, **TS1a** and **TS2a**. The former transition state connects **1a** to **2a**, and the latter links **2a** to **3a**. The CASSCF(8,8)/6-31G* optimized geometries of these three species are shown in Figure 2. The predicted two-step mechanism for ring expansion of **1a** parallels the predicted mechanism of ring expansion of **1b** (Scheme 2).²⁴

The first step of the ring expansion is the insertion of the nitrene nitrogen of **1a** into an adjacent π bond of the ring. Consequently, the geometry of **TS1a** exhibits a pronounced out-of-plane distortion, as well as some bond-length alternation in the six-membered ring. At the end of the first step, the azirine ring in **2a** is approximately 60° out of the plane of the cyclohexadiene ring.

The most striking geometric feature of **2a** is the very long (1.622 Å) C7–N1 bond length. This CASSCF(8,8) bond length is much longer than that (1.530 Å) in the RHF optimized structure, and the 0.092 Å bond lengthening is undoubtedly due to the inclusion in the (8,8) active space of the σ/σ^* pair of orbitals for this C–N bond. In order to check the effect of active space size on the geometry and relative energy of **2a**, we reoptimized the geometry of **2a** with a (6,6) active space, consisting only of the π orbitals. Although the resulting CASSCF(6,6)/6-31G* geometry shows a markedly shorter C7–N1 distance (1.523 Å) than that obtained with the (8,8) active space, the CASPT2N energies for the two geometries differ by less than 0.1 kcal/mol. Thus, although inclusion of the C–N σ/σ^* orbitals in the active space does affect significantly the length of this bond, the CASPT2N energy of **2a** is affected very little.

In **TS2a**, all of the perimeter C–C bond lengths are very similar (1.395 ± 0.013 Å). This is consistent with the fact that conversion of **2a** to **3a** involves a six-electron, disrotatory, electrocyclic ring opening, which is allowed by orbital symmetry⁴⁷ and thus proceeds by a highly delocalized transition state.

(d) **Energetics of the Ring Expansion.** The calculated relative energies of the C_6H_5N stationary points are given in Table 1. The results indicate that the relative energies do not depend strongly on the basis set used. The biggest changes in relative energies on going from 6-31G* to 6-311G(2d,p) amount to only about 1–2 kcal/mol.

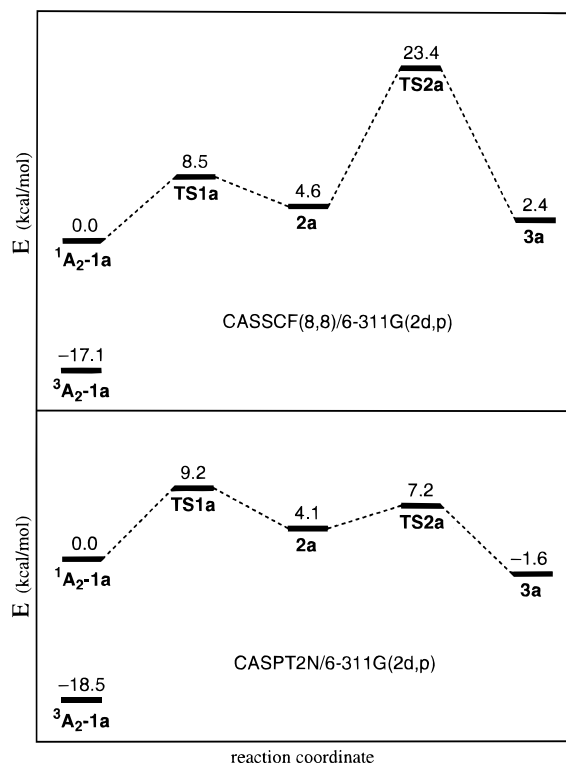


Figure 3. CASSCF(8,8)/6-311G(2d,p) (top) and CASPT2N/6-311G(2d,p) (bottom) relative energies of species involved in the ring expansion of phenylnitrene (**1a**). Energies are for CASSCF(8,8)/6-31G* optimized geometries and include ZPE corrections.

Figure 3 shows graphically the CASSCF(8,8) and CASPT2N relative energies of the species along the reaction path. The most obvious change that occurs on going from the CASSCF to the CASPT2N level of theory is the selective stabilization of **TS2a**. At the CASSCF(8,8)/6-311G(2d,p) level the barrier for the process **2a** \rightarrow **3a** is calculated to be 18.8 kcal/mol, which decreases to 3.1 kcal/mol at the CASPT2N/6-311G(2d,p) level.⁴⁸

The ca. 16 kcal/mol lowering of the relative energy of **TS2a** upon inclusion of dynamic electron correlation is not unusual for a six-electron, pericyclic reaction. For example, both the chair Cope rearrangement and the Diels–Alder reaction of butadiene with ethylene also involve a six-electron delocalized transition state, and a very similar drop (ca. 16 kcal/mol) in the calculated activation barrier is found on going from CASSCF(6,6) to CASPT2N in the former reaction⁵¹ and to RQCISD(T) in the latter.⁵² In both of these examples, the barrier height computed with inclusion of dynamic electron correlation is in much better agreement with experiment than the one calculated

(48) The precipitous drop in the relative energy of **TS2a** on going from CASSCF to CASPT2N suggested that inclusion of dynamic electron correlation might drastically change the location of **TS2a** on the potential surface. Since density functional theory⁴⁹ provides some dynamic correlation, the geometries of **2a** and **TS2a** were also optimized at the B3LYP/6-31G* level of theory.⁵⁰ The B3LYP geometry of **2a** has an N1–C7 distance of 1.567 Å, compared to 1.622 Å in the CASSCF(8,8) optimized geometry. Also, the B3LYP geometry of **TS2a** has a C2–C7 distance of 1.758 Å, compared to 1.778 Å in the CASSCF(8,8) structure. Subsequent CASPT2N/6-31G* energy calculations at the B3LYP geometries yielded absolute energies for **2a** and **TS2a** that were each slightly lower than those obtained with the CASSCF geometries, but the difference in energy between **2a** and **TS2a** remained essentially the same.

(49) Parr, R. G.; Yang, W. *Density Functional Theory of Atoms and Molecules*; Oxford University Press: New York, 1989.

(50) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(51) Hrovat, D. A.; Morokuma, K.; Borden, W. T. *J. Am. Chem. Soc.* **1994**, *116*, 1072.

(52) Li, Y.; Houk, K. N. *J. Am. Chem. Soc.* **1993**, *115*, 7478.

(47) Woodward, R. B.; Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 781; *Angew. Chem.* **1969**, *81*, 797. *The Conservation of Orbital Symmetry*, Verlag Chemie: Weinheim, 1970.

at the CASSCF(6,6) level.⁵³ Thus, it is not surprising that dynamic correlation is important for an accurate description of the energy of **TS2a**.

The most important consequence of the selective stabilization of **TS2a** at the CASPT2N level is that the *first* step of the reaction becomes rate-determining. At the CASPT2N/6-311G-(2d,p) level we calculate the barrier for this step to be 9.2 kcal/mol, which is rather higher than the experimental value of 3 ± 1 kcal/mol published by Platz and Wirz.^{12b}

However, a careful reinterpretation of Platz and Wirz's experimental data has led to a revised estimate of ca. 6 kcal/mol for the barrier height.^{12c} Moreover, multi-reference CISD calculations,⁵⁴ with the Davidson correction for quadruple excitations,⁵⁵ on the ring closure of singlet vinylnitrene show that, as expected,³⁷ CASPT2N spuriously favors the open-shell nitrene reactant over the closed-shell 2*H*-azirine product.⁵⁶ The relative CASPT2N/6-311G(2d,p) energy of the nitrene is in error by 3.4 kcal/mol. If the relative CASPT2N/6-311G(2d,p) energy of singlet **1a** is also too low by a comparable amount, then a better computational estimate of the height of the barrier to the first step of its ring expansion would be ca. 6 kcal/mol. With the upward revision of Platz and Wirz's experimental value for this barrier height and the downward correction of our CASPT2N value, theory and experiment appear to be in good agreement.

The CASPT2N/6-311G(2d,p) barrier for the process **2a** → **3a** is only ca. 3 kcal/mol, and this reaction is calculated to be exothermic by about 6 kcal/mol. These computational results are consistent with the failure of Schuster's time-resolved IR experiments to detect **2a**.^{9b,c} A 3-kcal/mol barrier implies rapid conversion of **2a** to **3a** at room temperature, and a 6-kcal/mol difference in energy between **2a** and **3a** means that at 25 °C the equilibrium would overwhelmingly favor **3a**. In addition, azirine **2a** probably absorbs less strongly than cyclic ketenimine **3a** in the infrared,⁵⁸ rendering detection of the azirine even more difficult.

The CASPT2N energies in Figure 3 indicate that **3a** should also be in equilibrium with singlet **1a** at ambient temperature. Even if the MRCI-derived upward correction of ca. 3 kcal/mol to the energy of ¹A₂-**1a** is included, the energy difference between ¹A₂-**1a** and **3a** is estimated to be only 5 kcal/mol. Therefore, at equilibrium, a small amount of singlet **1a** should be present. Intersystem crossing of singlet **1a** to triplet **1a** should then lead eventually to the irreversible conversion of **3a**

(53) For a review on the importance of including dynamic electron correlation, see: Borden, W. T.; Davidson, E. R. *Acc. Chem. Res.* **1996**, *29*, 67.

(54) The MR-CISD+Q method has been shown to yield very accurate results for energy differences between open- and closed-shell species. For example, see: Matzinger, S.; Fülischer, M. P. *J. Phys. Chem.* **1995**, *99*, 10747.

(55) Langhoff, S. R.; Davidson, E. R. *Int. J. Quantum Chem.* **1974**, *8*, 61.

(56) At the CASSCF(4,4)/6-31G* level singlet vinylnitrene (¹A''-VN) is the transition state for interchange of the enantiotopic pair of hydrogens in 2*H*-azirine (**AZ**).⁵⁷ At the CASSCF optimized geometries the CASSCF, CASPT2N, and MR-CISD (plus Davidson correction) energies (in hartrees) are, respectively, -131.90509, -132.26788, and -132.30504 for **AZ**, and -131.85978, -132.21589, and -132.24971 for ¹A''-VN with the 6-31G* basis set. With 6-311G(2d,p) the CASPT2N and MR-CISD+Q values are -132.40694 and -132.44509 for **AZ**, and -132.35807 and -132.39075 for ¹A''-VN. The CASSCF(4,4)/6-31G* zero-point vibrational energies for **AZ** and ¹A''-VN are 29.8 and 27.0 kcal/mol, respectively.

(57) Previous calculations on the vinylnitrene-azirine interconversion have focused on the closed-shell singlet excited state (¹A') of vinylnitrene, and have found little or no barrier to ring closure for this species. Lohr, L. L., Jr.; Hanamura, M.; Morokuma, K. *J. Am. Chem. Soc.* **1983**, *105*, 5541. Yamabe, T.; Kaminoyama, M.; Minato, T.; Hori, K.; Isomura, K.; Taniguchi, H. *Tetrahedron* **1984**, *40*, 2095.

(58) CASSCF(8,8)/6-31G* calculated IR frequencies (unscaled) and absolute intensities: **2a** (C=N stretch) 1881 cm⁻¹, 15.9 km/mol; **3a** (N=C=C stretch) 1984 cm⁻¹, 85.2 km/mol.

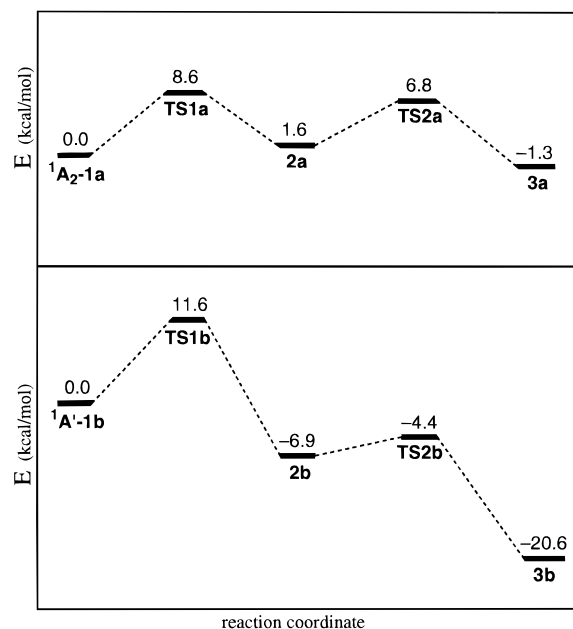


Figure 4. Comparison of CASPT2N/6-31G*/CASSCF(8,8)/6-31G* + ZPE relative energies of species involved in the ring expansions of phenylnitrene (**1a**, top) and phenylcarbene (**1b**, bottom).

to the triplet ground state of **1a**. It has, in fact, been observed that **3a** ultimately reverts to triplet **1a** over time in inert solvents.⁹

Comparison with the Ring Expansion of Phenylcarbene.

(a) Overall Energetics of the Ring Expansions (1 → 3). As depicted in Scheme 2, recent calculations of the reaction path for ring expansion of phenylcarbene (**1b**) have found this reaction, like the ring expansion of phenylnitrene (**1a**), to involve the formation of a bicyclic intermediate (**2b**).²⁴ The relative CASPT2N/6-31G* energies of the reactants, products, intermediates, and transition states in these two reactions are compared in Figure 4.⁵⁹

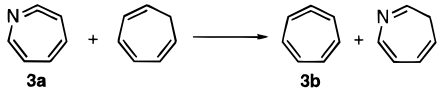
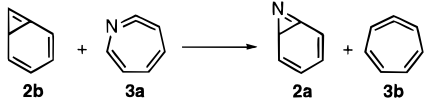

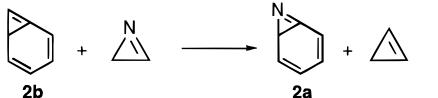
This figure shows that the ring expansion of **1a** to **3a** is calculated to be 19.3 kcal/mol less exothermic than that of **1b** to **3b** and that the rearrangement of **2a** to **3a** is computed to be 10.8 kcal/mol less exothermic than that of **2b** to **3b**. In addition to these differences in the relative energies of the minima on the potential surfaces for the ring expansion reactions of **1a** and **1b**, there are also differences in the relative energies of the transition states that connect them.

In order to understand the reason for the 19.3-kcal/mol difference between the exothermicities of the two ring expansions, we first investigated whether **3a** is much more strained than **3b**. To establish whether the energetic cost of bending and twisting a ketenimine to the geometry in **3a** is greater than that of bending and twisting an allene to the geometry of **3b**, we computed ΔE for isodesmic reaction 1 in Table 2. This reaction compares the energetic effect of removing a cumulene C=C bond from **3a** and **3b**. At the CASPT2N/6-31G* level,⁶⁰ ΔE for this reaction is only -1.2 kcal/mol, suggesting that the two cyclic cumulenes have similar amounts of strain.

(59) The comparison between these two systems is made using results obtained with the 6-31G* basis set for two reasons. First, while the highest level of theory reported here employed the 6-311G(2d,p) basis set, such calculations for the C₇H₆ stationary points with only C₁ symmetry proved too large for us to perform. Second, for the purpose of performing numerous model calculations, in order to discover the reasons for the energetic differences between the ring expansion reactions of **1a** and **1b**, it was more efficient to use the smaller basis set.

(60) Using an (8,8) active space for **3a** and **3b**, and a (6,6) active space for the trienes. All energies are for CASSCF/6-31G* optimized geometries. CASSCF(6,6)/6-31G* energies (hartrees): cycloheptatriene, -269.76401; azacycloheptatriene, -285.76390. CASPT2N/6-31G* energies: cycloheptatriene, -270.60807; azacycloheptatriene, -286.63539.

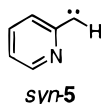
Table 2. Isodesmic Reactions Relevant to the Ring Expansions of Phenylnitrene and Phenylcarbene^a

no.	reaction	ΔE (kcal/mol)
1		-1.2
2		-10.7
3		-14.2
4		+3.0

^a All energies are calculated at the CASPT2N/6-31G* level, pertain to CASSCF(*n,n*)/6-31G* optimized geometries, and are uncorrected for ZPE differences. An (8,8) active space was used for **2a** and **3a** as described in the text. Analogous (8,8) active spaces were used for **2b** and **3b**, respectively.^{24c} An active space consisting of all π electrons and all π/π^* orbitals was used for all other species.

Next we calculated the energies of ketenimine (HN=C=CH₂) and allene (H₂C=C=CH₂) at their fully optimized geometries, and at the bent and twisted geometries of the corresponding cyclic cumulenes. At the CASSCF(4,4)/6-31G* level, ketenimine at the geometry of **3a** is 16.1 kcal/mol higher in energy than fully optimized ketenimine, and allene at the geometry of **3b** is 16.1 kcal/mol higher than fully optimized allene.⁶¹ Thus, the energetic costs associated with distorting ketenimine and allene to the geometries of the corresponding portions of **3a** and **3b** are the same, implying again that **3a** and **3b** have very similar amounts of strain.

Since the large difference between ΔE for the two ring expansions is not attributable to a difference in the strain energies of the final products, it appears that this difference must reside in the reactants. Because it is impossible to compare directly the calculated energies of **1a** and **1b**, we performed calculations on 2-pyridylcarbene (**5**), which is both an isomer of nitrene **1a** and a relatively unperturbed heterocyclic analogue of carbene **1b**. At the CASSCF(8,8)/ and CASPT2N/6-31G* levels, the ¹A' state of *syn*-**5**⁶² is less stable than the ¹A₂ state of **1a** by 21.9 and 23.3 kcal/mol, respectively (Table 1). The much lower energy of the nitrene, relative to the carbene, is sufficient to explain the large difference in ΔE values for the ring expansions of **1a** to **3a** and **1b** to **3b**.



The relative energies of **1a** and *syn*-**5** that we calculate are also consistent with the pyrolysis results of Wentrup and co-workers.^{20a,63} They found that all of the isomeric pyridylcar-

(61) Calculated energies (hartrees): optimized ketenimine, -131.92198; ketenimine at **3a** geometry, -131.89628; optimized allene, -115.91474; allene at **3b** geometry, -115.88900.

(62) Here *syn* refers to the relationship between the carbenic hydrogen and the nitrogen. In the case of the ¹A' state, this conformation was found to be more stable than the *anti* conformation by 3.4 and 3.6 kcal/mol at the CASSCF(8,8)/ and CASPT2N/6-31G* levels, respectively (using CASSCF(8,8)/6-31G* optimized geometries).

benes lead ultimately to **1a**, demonstrating that phenylnitrene is more thermodynamically stable than any of its carbene isomers.

(b) Thermodynamics of the Ring-Opening Steps (2 → 3).

The difference between the exothermicities of the ring-opening reactions of **2a** and **2b** is given by reaction 2 of Table 2. At the CASPT2N/6-31G* level, this reaction is calculated to be exothermic by 10.7 kcal/mol. Since, as we have already discussed, reaction 1 in Table 2 shows that **3a** and **3b** have similar amounts of strain, **2a** must be considerably more strained than **2b**.

In order to establish why this is the case, we investigated whether there is a significant difference in strain energies between having a doubly bonded nitrogen and a doubly bonded carbon in a three-membered ring. The calculated energy change of -14.2 kcal/mol⁶⁴ for isodesmic reaction 3 in Table 2 indicates that it is significantly easier to incorporate a doubly bonded nitrogen than a doubly bonded carbon into a three-membered ring. This is consistent with the geometries of methanimine (HN=CH₂) and ethylene, which we optimized at the CASSCF(2,2)/6-31G* level of theory. These calculations find an optimized H-N-C angle of 111.0° for the former, which is 10.8° smaller than the H-C-C angle of 121.8° for the latter.

The value of ΔE calculated for isodesmic reaction 4 in Table 2 shows that there is a second, opposing, effect that reduces the difference in stability between **2a** and **2b**. Cyclopropene is more easily annelated by a butadiene than is azirine. This effect is calculated to decrease by about 3 kcal/mol the 14 kcal/mol preference for the azirine ring in **2a** over the cyclopropene ring in **2b**.

Taken together, reactions 1, 3, and 4 of Table 2 indicate that reaction 2 should be exothermic by 12.4 kcal/mol, which is 1.7 kcal/mol greater than the exothermicity actually calculated for this reaction. If 2-butene and its 2-aza analogue in reaction 3 are replaced by cycloheptatriene and its 2-aza analogue, the CASPT2N energy of reaction 3 changes by only 1.7 kcal/mol; and, upon summing reactions 1, 3, and 4, reaction 2 is now obtained. Therefore, the exothermicity of reaction 2, which gives the difference between the energies of the ring-opening reactions of **2a** and **2b**, can be rigorously attributed to the exothermicity of reaction 3 and, thus, to the lower strain energy associated with having a doubly bonded nitrogen, compared to a doubly bonded carbon, in a three-membered ring.

(c) Activation Barriers for the Ring-Expansion Reactions.

In the ring expansions of both **1a** and **1b**, the first step is predicted to be rate-determining. Despite the fact that **1b** → **2b** is predicted to be substantially exothermic,²⁴ whereas **1a** → **2a** is predicted to be slightly endothermic, the CASPT2N/6-31G* barrier for this step is some 3 kcal/mol higher for the carbene than for the nitrene (Figure 4). In fact, as discussed above, CASPT2N/6-31G* overestimates the stability of open-shell singlet **1a** and, therefore, overestimates the height of the barrier to its reaction to form **2a**. In addition, CASPT2N/6-31G*

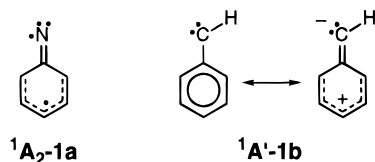
(63) (a) Crow, W. D.; Wentrup, C. *Tetrahedron Lett.* **1968**, 6149. (b) Wentrup, C. *J. Chem. Soc., Chem. Commun.* **1969**, 1386. (c) Reference 2b, pp 212-220. (d) Kuzaj, M.; Lüerssen, H.; Wentrup, C. *Angew. Chem., Int. Ed. Engl.* **1986**, 25, 480; *Angew. Chem.* **1986**, 98, 476. (e) Photochemical interconversion of phenylnitrene and the pyridylcarbenes has also been reported: Chapman, O. L.; Sheridan, R. S.; LeRoux, J.-P. *J. Am. Chem. Soc.* **1978**, 100, 6245. Chapman, O. L.; Sheridan, R. S.; LeRoux, J.-P. *Recl. Trav. Chim. Pays-Bas* **1979**, 98, 334.

(64) Calculated energies (hartrees) for CASSCF(2,2)/6-31G* optimized geometries: For *trans*-N-methylethanamine: CASSCF(2,2)/6-31G*, -172.13701; CASPT2N/6-31G*, -172.67231. For *trans*-2-butene: CASSCF(2,2)/6-31G*, -156.13773; CASPT2N/6-31G*, -156.64769. For cyclopropene: CASSCF(2,2)/6-31G*, -115.85030; CASPT2N/6-31G*, -116.22023. For 2H-azirine: CASSCF(2,2)/6-31G*, -131.87235; CASPT2N/6-31G*, -132.26715.

underestimates by about the same amount of energy the barrier to rearrangement of **1b** to **2b**.²⁴ Thus, calculations at higher levels than CASPT2N/6-31G* find that phenylcarbene (**1b**) has a barrier to intramolecular reaction that is ca. 9 kcal/mol higher than that in phenylnitrene (**1a**).

As emphasized by Platz, the very different rates of ring expansion of phenylnitrene and phenylcarbene, which result from the large difference in barrier heights, causes the chemistries of **1a** and **1b** to be quite different.²¹ Platz has formulated the fundamental question concerning the difference between the chemistries of **1a** and **1b** very simply: "Why is ring expansion of singlet phenylnitrene so much faster than that of singlet phenylcarbene?"²¹

We believe that the answer to this question is that **1a** reacts from an open-shell singlet state (1A_2), whereas the singlet state from which **1b** reacts is closed-shell ($^1A'$). The geometry of 1A_2 -**1a** (Figure 1) shows that it is best depicted as a cyclohexadienyliminyl diradical.²⁷ Consequently, upon movement of the nitrogen atom out of the molecular plane, formation of the three-membered ring requires only closure of an N-C-C bond angle. In contrast, since **1b** reacts from the $^1A'$ electronic state, closure of the three-membered ring by a comparable pathway requires that the contribution of the higher energy ionic resonance structure for $^1A'$ -**1b** increases along the reaction coordinate.



Azacycloheptatrienyliidene (4a)—Effects of the Nitrogen Lone Pair. Enforcing planarity on azacycloheptatetraene (**3a**) gives azacycloheptatrienyliidene (**4a**). We have considered four spin states of the planar (C_s symmetric) carbene **4a**: the closed-shell singlet ($^1A'$), an open-shell singlet ($^1A''$),⁶⁵ and two triplets ($^3A''$ and $^2^3A''$) that differ in which of the two nearly degenerate π^* MOs is occupied. The π^* MO that is singly occupied in each A'' state is depicted in Figure 5a, and the π bonding in each state is indicated in Figure 5b.

Figure 5b also presents the CASSCF/6-31G* optimized geometries of the $^1A'$, $^1A''$, $^3A''$, and $^2^3A''$ states of **4a**. In addition to the large difference between the bond angle at the carbene carbon in the open-shell (135–138°) vs closed-shell (120.3°) states, there are substantial differences between the C-C bond lengths in the four states. The latter can be understood on the basis of the π^* MO that is occupied in each state and the π bonding that results.

(65) A second open-shell singlet state ($2^1A''$), in which the same π^* MO is singly occupied as in $2^3A''$, has σ and π electrons of opposite spin appearing on the carbene carbon. As is the case in cycloheptatrienyliidene (**4b**),^{24c} the large Coulombic repulsion between these electrons of opposite spin makes the $2^1A''$ open-shell singlet state much higher in energy than $1^1A''$, since in the latter the σ and π electrons of opposite spin are confined to different sets of atoms.⁶⁶

(66) Borden, W. T.; Davidson, E. R. *J. Am. Chem. Soc.* **1977**, *99*, 4587. Borden, W. T. In *Diradicals*; Borden, W. T., Ed.; Wiley-Interscience: New York, 1982; p 1. Borden, W. T. *Mol. Cryst. Liq. Cryst.* **1993**, *232*, 195.

(67) When **6** was optimized to a potential minimum at the CASSCF-(8,8)/6-31G* level by following the imaginary mode for the planar species $^1A'$ -**4a**, the geometry for **6**, shown in Figure 6, was obtained, with an energy of -284.52149 hartrees. An energy calculation at this geometry, using a slightly modified (8,8) active space, yielded an energy of -284.52915 hartrees, which is the energy we report in Table 1. Unfortunately, attempts to reoptimize the geometry using the modified active space were unsuccessful. Because the nitrogen lone pair overlaps the π system in this nonplanar species, a better MCSCF calculation would employ a ten-electron, nine-orbital (10,9) active space that includes the nitrogen lone pair. However, the energy thus obtained could not be compared to any of our other results, all of which were obtained with an (8,8) active space.

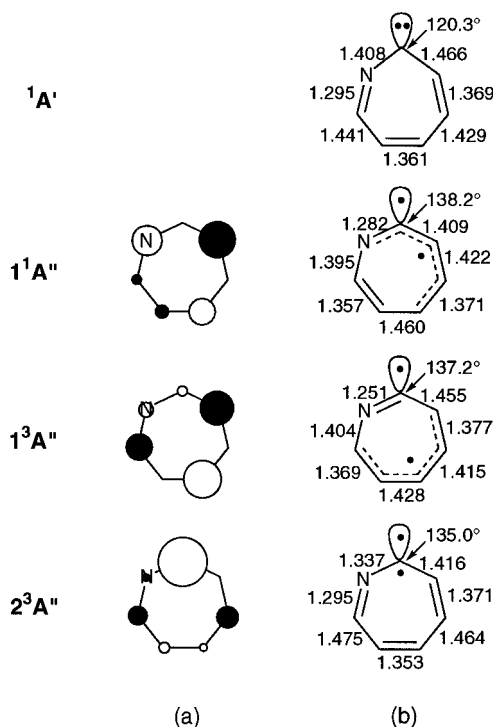


Figure 5. (a) Schematic drawings of the singly occupied π^* molecular orbital in the three A'' states of planar (C_s symmetric) azacycloheptatrienyliidene (**4a**). The size of each p- π AO reflects the relative size of its coefficient in the π^* MO. (b) CASSCF(8,8)/6-31G* optimized geometries of the four spin states of **4a**, showing approximate π bonding patterns and the degree of delocalization of the unpaired π electron.

The closed-shell singlet ($^1A'$) has no electrons in the π^* orbitals. As in the analogous state of cycloheptatrienyliidene (**4b**),²⁴ the bond lengths in the $^1A'$ state of **4a** indicate only a small amount of delocalization of the six π electrons into the empty p- π orbital at the carbene carbon. Although $^1A'$ -**4a** has an aromatic π system, delocalization of the π electrons is not extensive, since, unlike the case in tropylium cation, π delocalization in $^1A'$ -**4a** requires transfer of π electrons to a neutral carbon.

In both $^1A''$ and $^3A''$, the π^* singly occupied molecular orbital (SOMO) has the nodal pattern expected for a pentadienyl NBMO mixed in an out-of-phase fashion with the bonding π MO of a double bond (Figure 5a). However, the high Coulombic repulsion engendered in the $^1A''$ state if the electron in the π^* SOMO appears at the carbene carbon (where the unpaired electron of opposite spin is localized in a σ orbital)^{24c} causes the positions of the nodes in the π^* SOMO to be somewhat different in $^1A''$ and $^3A''$. Consequently, the bond-length pattern is slightly different in these two electronic states.

The π^* SOMO in $^2^3A''$ is similar in form to that in $^1A''$ and $^3A''$ but is largely localized on the carbene carbon. Consequently, the pattern of bond-length alternation in $^2^3A''$ resembles that in the closed-shell $^1A'$ state. The shorter bonds to the carbene carbon in $^2^3A''$ can largely be ascribed to the difference between the hybridization of the carbene carbon in these two states.

The calculated energies for the four spin states of planar **4a** are shown in Table 1. At the CASSCF level, $^1A''$ and $^3A''$ are computed to be extremely close in energy, and both are predicted to be only slightly lower in energy (ca. 1 kcal/mol) than $^2^3A''$. At the CASPT2N level, however, both $^1A''$ and $^3A''$ are stabilized relative to $^2^3A''$. This selective stabilization is understandable, since, as depicted in Figure 5b, both $^1A''$

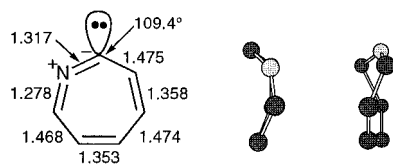


Figure 6. CASSCF(8,8)/6-31G* optimized structure (C_1 symmetry) of closed-shell singlet azacycloheptatrienyliene (**6**), showing bond lengths (Å) and the bond angle at the carbene carbon (degrees). The structures at center and right show the nonplanar geometry of this species.

and $1^3A''$ are more delocalized than $2^3A''$ and should therefore be more stabilized by inclusion of dynamic electron correlation.⁵³

At the CASPT2N level $1^3A''$ falls below $1^1A''$ by 1.4 kcal/mol in **4a**. This is the opposite ordering of the two analogous spin states (3A_2 and 1A_2) in **4b**, for which the ground state is predicted to be the open-shell singlet (1A_2).^{24c} This difference between these two carbenes can be attributed to the presence of the lone pair of electrons on nitrogen in **4a**. Two-center, three-electron bonding in the molecular plane of **4a**, involving the lone pair, produces some unpaired σ spin density on nitrogen. Coulombic repulsion between the σ and π electrons of opposite spin on nitrogen in $1^1A''$ causes it to lie slightly above $1^3A''$ in energy.

The closed-shell singlet state ($^1A'$) of **4a** is predicted to be considerably higher in energy than the open-shell $1^1A''$ state, by 17 kcal/mol at the CASSCF level, and by 25 kcal/mol at the CASPT2N level. In contrast, in **4b** the energy difference between these two states (1A_1 and 1A_2) is only a few kcal/mol.^{24c}

The dramatic destabilization of the $^1A'$ state of **4a** is due to the four-electron interaction between the carbenic lone pair and the nonbonding lone pair on the adjacent nitrogen. The resulting overlap repulsion is probably responsible for the finding that the planar closed-shell singlet state of **4a** is not a transition state for enantiomerization of **3a**. This contrasts with the hydrocarbon case, for which the closed-shell 1A_1 state of **4b**, as well as the open-shell 1A_2 state, is found to be a transition state for enantiomerization of allene **3b**.²⁴

The $^1A'$ state of **4a** is a transition state, but for interconversion of the enantiomers of another non-planar species (**6**), whose geometry is given in Figure 6.⁶⁷ 2-Azacyclohepta-1,2,4,6-tetraene (**6**) is an isomer of **3a** in which the roles of the lone pairs on nitrogen and carbon are reversed. The nitrogen is the central atom of a 2-azaallene unit, formed by overlap of the nitrogen lone pair with the empty p orbital on the carbene carbon. This zwitterionic structure was proposed as a resonance structure for **3a** by Chapman and LeRoux,⁶ but our computational results clearly show that **3a** and **6** have very different geometries.

The out-of-plane distortion of the $^1A'$ state of **4a** to **6** provides dramatic energy lowering. At the CASPT2N level, **6** lies only 5–6 kcal/mol higher in energy than the open-shell $1^3A''$ and $1^1A''$ states of **4a**, and **6** lies ca. 1 kcal/mol lower in energy than the second triplet state ($2^3A''$). This precipitous drop in energy undoubtedly results from replacing the unfavorable overlap between the nitrogen and carbon lone pairs in **4a** by the favorable overlap of the nitrogen lone pair with the empty orbital at the carbenic carbon in **6**. Nevertheless, it should be noted that the zwitterionic character of **6** results in its being calculated to be ca. 25 kcal/mol higher in energy than the isomeric 1-azacyclohepta-1,2,4,6-tetraene (**3a**).

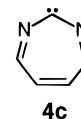
CASSCF(8,8)/6-31G* vibrational analysis predicts one imaginary frequency for not only the closed-shell $^1A'$ state of **4a** but also for the open-shell $1^1A''$ state. The imaginary vibrational mode for the latter state also corresponds to an out-of-plane

distortion of the ring. When the $1^1A''$ state was distorted very slightly along this imaginary mode and then reoptimized, the optimization led to **3a**. Thus, at this level of theory $1^1A''$ -**4a** appears to be a transition state for enantiomerization of **3a**.

In cycloheptatrienyliene (**4b**), the hydrocarbon analogue of **4a**, the open-shell singlet state (1A_2) is predicted to be the lowest energy transition state for enantiomerization of cyclohepta-1,2,4,6-tetraene (**3b**).²⁴ An open-shell singlet (1A_2) transition state has also been found for internal rotation in allene.⁶⁸ We calculate $1^1A''$ -**4a** to be ca. 21 kcal/mol higher in energy than **3a** at the CASPT2N/6-311G(2d,p) level. This predicted value for the barrier to enantiomerization of **3a** is essentially the same as that calculated for the racemization of **3b**,^{24c} and it is approximately half of the experimental value of ca. 42 kcal/mol for internal rotation in allene.⁶⁹

Although triplet **4b** has been detected by ESR,^{63d} and a derivative of triplet **4a** has been implicated in solution trapping experiments,⁷⁰ there have been no reports of the direct observation of **4a**. Intersystem crossing from the triplet ground state ($1^3A''$) to the open-shell singlet state ($1^1A''$) may occur readily, since the adiabatic energy difference between the two states is predicted to be only ca. 1 kcal/mol, and the geometry of the singlet is not drastically different from that of the triplet. Following intersystem crossing, the $1^1A''$ state of **4a** would be expected to relax rapidly to one of the enantiomers of **3a**, for whose interconversion it is the transition state. Thus, direct detection of triplet **4a** may prove to be extremely difficult.⁷¹

As discussed above, incorporation of a nitrogen adjacent to the carbenic center in **4b** stabilizes the $1^3A''$ state of **4a**, relative to the $1^1A''$ state, and results in the triplet being the predicted ground state by ca. 1 kcal/mol. If nitrogen atoms were incorporated on *both* sides of the carbenic center, as in 1,6-diazacyclohepta-1,3,5-trien-7-ylidene (**4c**), one might expect the triplet to fall substantially below the singlet, perhaps making spectroscopic detection of the triplet possible. CASPT2N/6-31G* calculations on **4c** do, indeed, find that the 3A_2 state of **4c** lies 2.6 kcal/mol below the open-shell 1A_2 state,⁷² and Wentrup and co-workers have, in fact, observed the ESR spectrum of triplet **4c**.^{63d}



Conclusions

Our calculations find that ring expansion of 1A_2 phenylnitrene (**1a**) to 1-azacyclohepta-1,2,4,6-tetraene (**3a**) occurs via an

(68) (a) Dykstra, C. E. *J. Am. Chem. Soc.* **1977**, *99*, 2060. (b) Seeger, R.; Krishnan, R.; Pople, J. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1977**, *99*, 7103. (c) Staemmler, V. *Theor. Chim. Acta* **1977**, *45*, 89. (d) Lam, B.; Johnson, R. P. *J. Am. Chem. Soc.* **1983**, *105*, 7479. (e) Staemmler, V.; Jaquet, R. In *Energy Storage and Redistribution in Molecules*; Hinze, J., Ed.; Plenum: New York, 1983; pp 261–273. (f) Rauk, A.; Bouma, W. J.; Radom, L. *J. Am. Chem. Soc.* **1985**, *107*, 3780. (g) Pedash, Y. F.; Ivanov, V. V.; Luzanov, A. V. *Theor. Exp. Chem.* **1992**, *28*, 114; *Teor. Eksp. Khim.* **1992**, *28*, 130.

(69) (a) Roth, W. R.; Ruf, G.; Ford, P. W. *Chem. Ber.* **1974**, *107*, 48. (b) Brudzynski, R. J.; Hudson, B. S. *J. Am. Chem. Soc.* **1990**, *112*, 4963.

(70) (a) Murata, S.; Sugawara, T.; Iwamura, H. *J. Chem. Soc., Chem. Commun.* **1984**, 1198. (b) Murata, S.; Sugawara, T.; Iwamura, H. *J. Am. Chem. Soc.* **1985**, *107*, 6317.

(71) We have postulated that detection of triplet **4b** is possible, because the triplet state detected is not 3A_2 , which is comparable to $1^3A''$ in **4a**, but 3B_1 , which is comparable to $2^3A''$ in **4a**.^{24c} In **4b**, 3B_1 lies close to, if not below, 3A_2 , so that the former triplet state should certainly be populated. In contrast, as discussed in the text, our CASPT2N calculations on **4a** place $2^3A''$ well above $1^3A''$, so that the former triplet state is unlikely to be appreciably populated in **4a**.

(72) CASPT2N/6-31G*/CASSCF(8,8)/6-31G* energies (hartrees) of C_{2v} -symmetric **4c**: 3A_2 state, -301.38689; 1A_2 state, -301.38270; 3B_1 state, -301.37040; 1A_1 state, -301.33007.

intermediate, 7-azabicyclo[4.1.0]hepta-2,4,6-triene (**2a**). The first step of the rearrangement is predicted to have a barrier of ca. 6 kcal/mol and to be the rate-determining step. Because of the small (3 kcal/mol) calculated barrier to the symmetry-allowed, electrocyclic ring opening of **2a** to **3a**, azirine **2a** is unlikely to be detected.

Comparison of our computational results on the rearrangement of **1a** to **3a** with similar calculations²⁴ on the analogous ring expansion of **1b** to **3b** indicates that both steps in the ring expansion are substantially less exothermic for the nitrene (**1a**) than for the carbene (**1b**). We attribute the smaller exothermicity for the ring expansion of **1a** to **3a** to the greater thermodynamic stability of nitrene **1a**, relative to carbene **1b**. The smaller exothermicity for **2a** → **3a**, compared to **2b** → **3b**, is due to the fact that the doubly bonded nitrogen in **2a** causes less strain than the doubly bonded carbon in the three-membered ring of **2b**.

The first step of the ring expansion is also less exothermic in phenylnitrene (**1a**) than in phenylcarbene (**1b**). However, in agreement with experiment, the barrier to the rearrangement of **1a** to **2a** is computed to be much lower than that for rearrangement of **1b** to **2b**. We attribute this difference to the difference between the electronic structures of the lowest singlet states of **1a** and **1b**. The open-shell ¹A₂ state of **1a** is a diradical, and this allows closure to **2a** to occur with minimal electronic

reorganization. In contrast, significant electronic reorganization is necessary in order for the closed-shell ¹A' state of **1b** to undergo ring closure to **2b**.

Planar 1-azacyclohepta-1,3,5-trien-7-ylidene (**4a**) is predicted to have a triplet ground state (³A''), which is computed to lie only 1.4 kcal/mol below the lowest energy, open-shell singlet (¹A'') and 7.3 kcal/mol below a second triplet (²A''). The ¹A'' state of **4a** is found to be the transition state for racemization of **3a**, with a calculated barrier of ca. 21 kcal/mol. The closed-shell singlet state (¹A') of **4a** is the transition state for racemization of zwitterion **6**, which is computed to be ca. 25 kcal/mol higher in energy than the equilibrium geometry of **3a**.

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Supporting Information Available: Cartesian coordinates for CASSCF(8,8)/6-31G* optimized geometries of **1a–4a**, **TS1a**, **TS2a**, ¹A'-*syn*-**5**, and **6**, plus a table of absolute energies for these species (5 pages). See any current masthead page for ordering and Internet access instructions.

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