Ring-Expansion Reaction of Cyano-Substituted Singlet Phenyl Nitrenes: Theoretical Predictions and Kinetic Results from Laser Flash Photolysis and Chemical Trapping Experiments

ARTICLE *in* JOURNAL OF THE AMERICAN CHEMICAL SOCIETY · JANUARY 2001

Impact Factor: 12.11 · DOI: 10.1021/ja002594b

8 AUTHORS, INCLUDING:

Nina Gritsan
Russian Academy of Sciences
168 PUBLICATIONS **2,055** CITATIONS
SEE PROFILE

Matthew S Platz
The Ohio State University
327 PUBLICATIONS **7,139** CITATIONS
SEE PROFILE

Ring-Expansion Reaction of Cyano-Substituted Singlet Phenyl Nitrenes: Theoretical Predictions and Kinetic Results from Laser Flash Photolysis and Chemical Trapping Experiments

Nina P. Gritsan,*,‖ Igor Likhotvorik,† Meng-Lin Tsao,† Nil Çelebi,† Matthew S. Platz,*,† William L. Karney,§ Carl R. Kemnitz,‡ and Weston Thatcher Borden*,‡

Contribution from the Newman and Wolfrom Laboratory of Chemistry, Ohio State University, 100 West 18th Avenue, Columbus, Ohio 43210, the Department of Chemistry, University of San Francisco, 2130 Fulton Street, San Francisco, California 94117-1080, the Department of Chemistry, Box 351700, University of Washington, Seattle, Washington 98195-1700, and Institute of Chemical Kinetics and Combustion and Novosibirsk State University, 630090 Novosibirsk, Russia

Received July 14, 2000. Revised Manuscript Received October 31, 2000

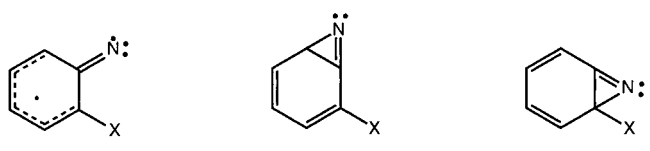
Abstract: On the basis of the open-shell electronic structure of the lowest-singlet state of phenylnitrene, it is predicted that substitution of a radical-stabilizing cyano group at an *ortho* carbon should facilitate cyclization at that carbon, whereas cyano substitution at the *para* carbon should retard the rate of cyclization. These qualitative predictions have been tested computationally by performing (8/8)CASSCF and CASPT2/6-31G* ab initio calculations and experimentally by carrying out laser flash photolysis and chemical trapping studies. The calculations and experiments both find that, unlike the case with *ortho* fluoro and *ortho* methyl substituents, the rate of cyclization at a substituted carbon is not retarded by an *ortho* cyano group. In contrast, a *para* cyano group is found, both computationally and experimentally, to raise the barrier to cyclization of singlet phenylnitrene by >1 kcal/mol.

Starting with the first reports by Huisgen[1a,b] and Doering,[1c] the chemistry of aryl nitrenes has been the subject of numerous investigations.[2] Singlet phenylnitrene (**^{1}1**) undergoes ring expansion to azacycloheptatetraene (**3**) via the intermediacy of azabicyclo[4.1.0]heptatriene (**2**, Scheme 1).[3] With only rare exceptions,[4] the bicyclic intermediates in the ring-expansion reactions of aryl nitrenes cannot be observed or chemically trapped, suggesting that the cyclization step in Scheme 1 is rate-determining (i.e., $k_C \ll k_E$).

This hypothesis is supported by the results of ab initio calculations.[5] In nearly exact agreement with the experimental value for the barrier to the cyclization of **^{1}1** to **2** (5.6 ± 0.3 kcal/mol),[3i,k] the best computational estimate is ∼6 kcal/mol, and the calculations also find that the barrier to the ring opening of **2** to **3** is only about half as large.

Substituent effects on the ring-expansion reactions of phenylnitrene have been studied. Banks and co-workers discovered that bimolecular reactions of singlet pentafluorophenylnitrene compete successfully with ring expansion.[6] Platz and co-workers have shown that it is the fluorines at the two *ortho* carbons which raise the barrier to cyclization of the perfluorinated nitrene.[3e,h,7] Two *ortho* methyl groups also reduce the rate of cyclization.[8]

When, as in **^{1}4a**,[8b] only one *ortho* methyl substituent is present, cyclization is almost as fast as in unsubstituted phenylnitrene, because attack occurs preferentially at the unsubstituted *ortho* carbon to form **5a**, rather than **6a**.[9a] When, as in **^{1}4b**,[10] only one *ortho* fluoro substituent is present, cyclization also occurs preferentially at the unsubstituted *ortho* carbon to form **5b**.[9b] Although, at 298 K cyclization of **^{1}4b** is 8 times slower than in unsubstituted phenylnitrene, cyclization of **^{1}4b** is still 30 times faster than in 2,6-difluorophenylnitrene.



^{1}4 **5** **6**

a, X = CH_3; **b**, X = F; **c**, X = CN

CASSCF and CASPT2/6-31G* calculations have reproduced these experimental findings and, in fact, predicted some of them

† Ohio State University.
§ University of San Francisco.
‡ University of Washington.
‖ Institute of Chemical Kinetics and Combustion.

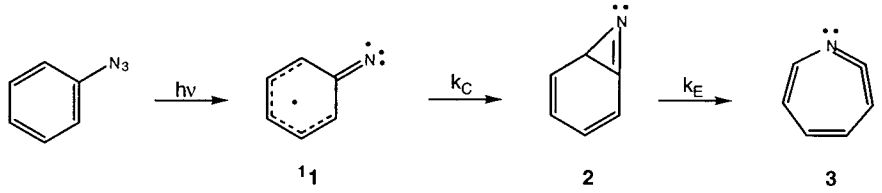
(1) (a) Huisgen, R.; Vossius, D.; Appl, M. *Chem. Ber.* **1958**, *91*, 1. (b) Huisgen, R.; Appl, M. *Chem. Ber.* **1958**, *91*, 12. (c) Doering, W. v. E.; Odum, R. A. *Tetrahedron* **1966**, *22*, 81.

(2) Reviews: (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. (h) Platz, M. S. *Acc. Chem. Res.* **1995**, *28*, 487. (i) Borden, W. T.; Gritsan, N. P.; Hadad, C. M.; Karney, W. L.; Kemnitz, C. R.; Platz, M. S. *Acc. Chem. Res.* **2000**, *33*, 765.

(3) (a) Chapman, O. L.; LeRoux, J.-P. *J. Am. Chem. Soc.* **1978**, *100*, 282. (b) Schrock, A. K.; Schuster, G. B. *J. Am. Chem. Soc.* **1984**, *106*, 5228. (c) 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. (d) Leyva, E.; Platz, M. S. *Tetrahedron Lett.* **1985**, *26*, 2147. (e) Leyva, E.; Platz, M. S.; Persy, G.; Wirz, J. *J. Am. Chem. Soc.* **1986**, *108*, 3783. (f) Shields, C. J.; Chrisope, D. R.; Schuster, G. B.; Dixon, A. J.; Poliakoff, M.; Turner, J. J. *J. Am. Chem. Soc.* **1987**, *109*, 4723. (g) Li, Y.-Z.; Kirby, J. P.; George, M. W.; Poliakoff, M.; Schuster, G. B. *J. Am. Chem. Soc.* **1988**, *110*, 8092. (h) Marcinek, A.; Leyva, E.; Whitt, D.; Platz, M. S. *J. Am. Chem. Soc.* **1993**, *115*, 8609. (i) Gritsan, N. P.; Yuzawa, T.; Platz, M. S. *J. Am. Chem. Soc.* **1997**, *119*, 5059. (j) Born, R.; Burda, C.; Senn, P.; Wirz, J. *J. Am. Chem. Soc.* **1997**, *119*, 5061. (k) Gritsan, N. P.; Zhu, Z.; Hadad, C. M.; Platz, M. S. *J. Am. Chem. Soc.* **1999**, *121*, 1202.

10.1021/ja002594b CCC: $20.00
Published on Web 01/24/2001

Scheme 1



before the experiments were performed.[11] For example, the calculations correctly predicted not only that cyclization of singlet *o*-fluorophenylnitrene (**^{1}4b**) would occur at the unsubstituted *ortho* carbon, forming **5b**,[9b] but also that cyclization at this carbon would encounter a barrier 0.9 kcal/mol higher than that for cyclization of unsubstituted phenylnitrene.[10b] Although the existence of small electronic effects on the barriers to cyclization was acknowledged, the computational results were interpreted as indicating that steric effects play the major role in raising the barriers to cyclization at substituted *ortho* carbons.

The apparent absence of large electronic effects on the cyclization reactions of derivatives of phenylnitrene[12] was attributed to the electronic structure of the lowest-singlet state.[11] Minimization of the Coulombic repulsion between the two electrons of opposite-spin in the nonbonding molecular orbitals (NBMOs) results in this state of phenylnitrene resembling a cyclohexadienyl radical, with an iminyl radical center doubly bonded to the remaining ring carbon.[13] Therefore, cyclization of **^{1}1** and **^{1}4** only requires movement of the imino nitrogen out of the molecular plane, allowing it to form a bond to the 2p-π orbital on one of the two *ortho* carbons, where an electron of opposite spin appears.

One might expect that a radical-stabilizing, *ortho* or *para* substituent, such as a cyano group, would tend to localize the unpaired π electron in the six-membered ring at the carbon to which the substituent is attached. This localization should make attack by the nitrogen at the cyano-substituted *ortho* carbon in **^{1}4c** electronically more favorable than attack at the unsubstituted *ortho* carbon, thus tending to counteract the steric effect due to the larger size of cyano relative to hydrogen. Therefore, attack at a substituted *ortho* carbon is more likely to occur when the substituent is cyano, rather than a less radical-stabilizing substituent, such as fluoro or methyl.

Consistent with this hypothesis, Smalley and co-workers have found that singlet *o*-cyanophenylnitrene (**^{1}4c**) undergoes ring expansion to afford not only **5c**, the product formed by cyclization away from the cyano substituent, but also **6c**, the product formed by cyclization toward the cyano group.[14a] Similar results have been found in the ring expansion of singlet *o*-acetylphenylnitrene.[14b]

Because no unpaired spin appears at the *meta* carbons of **^{1}1**, a cyano substituent at one of these carbons would be anticipated to have only a small effect on the barrier to cyclization at either of the two, nonequivalent *ortho* carbons, especially since *meta* fluoro[10b] substitution does not influence the rate constant for cyclization of phenylnitrene. However, if a *para* cyano substituent tends to localize spin at the carbon to which it is attached, the concomitant decrease in unpaired spin density at the *ortho* carbons would be expected to raise the barrier to cyclization.

To test these qualitative predictions, we have performed ab initio calculations, laser flash photolysis experiments, and chemical trapping studies. In this paper we report the results of these combined theoretical and experimental investigations.

Computational Methodology

Geometry optimizations were performed with the 6-31G* basis set,[15] using complete active space (CAS)SCF calculations.[16] An eight-electron, eight-orbital active space, hereafter designated (8/8), was used for all species. The (8/8) active space for the reactants consisted of seven π MOs, plus the in plane 2p AO on nitrogen. The active space for the transition states and products consisted of six orbitals that were mainly π in character plus a σ/σ^* pair for the incipient azirine C−N bond.

(8/8)CASSCF/6-31G* vibrational frequencies were calculated for all stationary points to verify whether each was an intermediate or a transition state. The unscaled (8/8)CASSCF frequencies were also used to compute the zero-point vibrational corrections to the energies. The CASSCF calculations were performed using the Gaussian 94 suite of programs.[17] The geometries, absolute energies, and vibrational corrections for all of the stationary points are available as Supporting Information.

CASPT2/6-31G* calculations[18] were performed at the (8,8)-CASSCF/6-31G* stationary point geometries. The CASPT2 calculations were carried out with MOLCAS.[19] Because the CASPT2 calculations include dynamic electron correlation,[20] but the CASSCF calculations do not, we deem the CASPT2 results to be the more accurate.

(4) (a) Carroll, S. E.; Nay, B.; Scriven, E. F. V.; Suschitzky, H.; Thomas, D. R. *Tetrahedron Lett.* **1977**, 3175. (b) Dunkin, I. R.; Thomson, P. C. P. *J. Chem. Soc., Chem. Commun.* **1980**, 499. (c) Nielson, P. E.; Buchardt, O. *Photochem. Photobiol.* **1982**, *35*, 317. (d) Younger, C. G.; Bell, R. A. *J. Chem. Soc., Chem. Commun.* **1992**, 359. (e) Morawietz, J.; Sander, W. *J. Org. Chem.* **1996**, *61*, 4351.

(5) Karney, W. L.; Borden, W. T. *J. Am. Chem. Soc.* **1997**, *119*, 1378.

(6) (a) Banks, R. E.; Sparkes, G. R. *J. Chem. Soc., Perkin Trans. 1* **1972**, 2964. (b) Banks, R. E.; Prakash, A. *Tetrahedron Lett.* **1973**, 99. (c) Banks, R. E.; Prakash, A. *J. Chem. Soc., Perkin Trans. 1* **1974**, 1365.

(7) (a) Poe, R.; Grayzar, J.; Young, M. J. T.; Leyva, E.; Schnapp, K.; Platz, M. S. *J. Am. Chem. Soc.* **1991**, *113*, 3209. (b) Poe, R.; Schnapp, K.; Young, M. J. T.; Grayzar, J.; Platz, M. S. *J. Am. Chem. Soc.* **1992**, *114*, 5054. (c) Marcinek, A.; Platz, M. S. *J. Phys. Chem.* **1993**, *97*, 12674. (d) Marcinek, A.; Platz, M. S.; Chan, S. Y.; Floresca, R.; Rajagopalan, K.; Golinski, M.; Watt, D. *J. Phys. Chem.* **1994**, *98*, 412. (e) Gritsan, N. P.; Zhai, H. B.; Yuzawa, T.; Karweik, D.; Brooke, J.; Platz, M. S., *J. Phys. Chem. A* **1997**, *101*, 2833.

(8) (a) Dunkin, I. R.; Donnelly, T.; Lockhart, T. S. *Tetrahedron Lett.* **1985**, *26*, 359. (b) Gritsan, N. P.; Gudmundsdóttir, A. D.; Tigelaar, D.; Platz, M. S. *J. Phys. Chem. A* **1999**, *103*, 3458.

(9) (a) Sundberg, R. J.; Suter, S. R.; Brenner, M. *J. Am. Chem. Soc.* **1972**, *94*, 513. (b) Leyva, E.; Sagredo, R. *Tetrahedron* **1998**, *54*, 7367.

(10) (a) Schnapp, K. A.; Poe, R.; Leyva, E.; Soundararajan, N.; Platz, M. S. *Bioconjugate Chem.* **1993**, *4*, 172. (b) Gritsan, N. P.; Gudmundsdóttir, A. D.; Tigelaar, D.; Zhu, Z.; Karney, W. L.; Hadad, C. M.; Platz, M. S. *J. Am. Chem. Soc.* Manuscript submitted.

(11) Karney, W. L.; Borden, W. T. *J. Am. Chem. Soc.* **1997**, *119*, 3347.

(12) Gritsan, N. P.; Tigelaar, D.; Platz, M. S. *J. Phys. Chem. A* **1999**, *103*, 4465.

(13) (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.; García, V. M.; Bo, C.; Caballol, R. *J. Comput. Chem.* **1996**, *17*, 42.

(14) (a) Lamara, K.; Redhouse, A. D.; Smalley, R. K.; Thompson, J. R. *Tetrahedron* **1994**, *50*, 5515. (b) Berwick, M. A. *J. Am. Chem. Soc.* **1971**, *93*, 5780.

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

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

Table 1. (8/8)CASSCF and CASPT2/6-31G* Energies (kcal/mol),[a] Relative to the Reactants, for the Transition Structures and Products in the Cyclization Reactions of Singlet Phenylnitrene (^{1}**1**) and of the *o*- (^{1}4c), *m*- (^{1}4d), *p*- (^{1}4e), and 2,6-Dicyano (^{1}4f) Derivatives

	cyclization		CASSCF		CASPT2	
nitrene	mode[b]	azirine	TS	product	TS	product
^{1}**1**	−	**2**	8.9	4.7	8.6	1.6
o-cyano (^{1}**4c**)	away from	**5c**	8.3	4.5	8.6	2.2
	toward	**6c**	8.4	2.6	7.5	0.3
m-cyano (^{1}**4d**)	away from	**5d**	8.6	4.4	8.2	1.2
	toward	**6d**	8.1	2.9	7.6	−0.7
para-cyano (^{1}**4e**)	−	**5e** = **6e**	9.4	5.0	9.8	3.3
2,6-dicyano (^{1}**4f**)	−	**5f** = **6f**	8.2	3.1	8.0	1.5

[a] Including zero-point energy (ZPE) corrections which range from −0.3 to 0.1 kcal/mol for transition structures and from 0.9 to 1.4 kcal/mol for products. [b] Mode of cyclization, toward or away from the substituted carbon.

Computational Results

Table 1 summarizes our CASSCF and CASPT2/6-31G* results for the cyclization reactions of *o*-, *m*-, *p*-, and 2,6-dicyanophenylnitrene (^{1}**4c**−**f**). The zero-point corrected energies of the two possible products, **5** and **6**, are given, relative to the reactants. Also shown are the relative energies of the transition structures, **TS** (^{1}**4**→**5**) and **TS** (^{1}**4**→**6**), leading to each of the products. For comparison, the CASSCF and CASPT2 relative energies for the cyclization reactions of unsubstituted phenylnitrene (^{1}**1**)[5] are given, too.

As discussed previously,[5] CASSCF and CASPT2 calculations both overestimate the stability of the open-shell electronic structure of ^{1}**1** by 2−3 kcal/mol. This is shown by comparison of the CASSCF and CASPT2 activation energies for cyclization of ^{1}**1** to **2** with the results of both multireference CISD calculations and the experimental value.[3i,k] However, comparison of the previously calculated CASSCF and CASPT2 barrier heights for methyl and fluoro substituents[11] with the experimental values measured by Gritsan and Platz and co-workers[8b,10b] shows that the calculations do a good job in predicting the differences between the activation energies for cyclization away from and toward an *ortho* substituent.

Inspection of the data in Table 1 reveals that, with one exception, the cyclization reactions of ^{1}**1** and ^{1}**4** are all computed to be slightly endothermic. At the CASPT2 level the endothermicity is computed to range from 0.3 to 3.3 kcal/mol. The single exception is cyclization of ^{1}**4d** to ^{1}**6d**, which is calculated to be exothermic by −0.7 kcal/mol. Presumably, the extended linear conjugation in the product is responsible for the CASPT2 finding that this cyclization reaction is thermodynamically more favorable than any of the others.

In contrast to the cyclization reactions, electrocyclic ring opening of the cyclization products (**2**, **5**, and **6**) is calculated to be exothermic by 1−4 kcal/mol at the CASPT2 level.[5,21] Ring opening is also computed to require passage over a 2−3 kcal/mol lower energy barrier than reversion of the intermediates to the reactants. Therefore, cyclization is the rate determining step in the ring expansion reactions of ^{1}**1** to **3** and of ^{1}**4** to derivatives of **7** and **8** (Scheme 2).

Of particular interest are the results in Table 1 for cyclization of singlet *o*-cyanophenylnitrene (^{1}**4c**). The barrier to cyclization of ^{1}**4c** away from the cyano substituent to give **5c** is calculated to be about the same as that for cyclization of ^{1}**1**, and the barrier to cyclization of ^{1}**4c** toward the cyano substituent to give **6c** is predicted to be either about the same as (CASSCF) or slightly lower than (CASPT2) the barrier to cyclization of ^{1}**4c** away from the cyano group. This prediction is very different from the computational[11] and experimental results for cyclization of *o*-methylphenylnitrene (^{1}**4a**)[8b,9a] and *o*-fluorophenylnitrene (^{1}**4b**),[9b,10b] where cyclization away from the *ortho* substituent to give **5a** or **5b** is strongly preferred over cyclization toward the substituent to give **6a** or **6b**. However, as noted in the Introduction, the predicted formation of **6c**, as well as that of **5c**, in the cyclization of ^{1}**4c** has already been confirmed experimentally.[14a]

This difference between ^{1}**4c** and ^{1}**4a** or ^{1}**4b** can reasonably be attributed to the greater ability of cyano, compared to that of methyl or fluoro, to localize the electron in the π NBMO at the *ortho* carbon to which the substituent is attached. Nevertheless, one might wonder to what extent product stability affects the cyclization barriers. For example, presumably for the same reason that **6b** is computed to be lower in energy than **5b**,[11] cyclization product **6c** is calculated to be 1.9 kcal/mol lower in energy than cyclization product **5c**. This thermodynamic preference for forming **6c**, rather than **5c**, could play a role in the lower kinetic barrier computed for rearrangement of **4c** to **6c** than to **5c**.

However, despite the fact that **6b** is computed to be lower in energy than **5b** by 6.0 kcal/mol,[11]the CASPT2 barrier connecting ^{1}**4b** to **6b** is 2.8 kcal/mol *higher* than the barrier connecting ^{1}**4b** to **5b**. Therefore, the 1.9 kcal/mol lower energy of **6c**, relative to **5c**, is probably not the principal reason the CASPT2 barrier for formation of **6c** is computed to be 1.1 kcal/mol lower than that for formation of **5c**.

Since cyclization at the substituted carbon in ^{1}**4c** is predicted to be slightly faster than cyclization at the unsubstituted carbon, it seems likely that cyclization of singlet 2,6-dicyanophenylnitrene (^{1}**4f**) would also be computed to be slightly faster than that of unsubstituted phenylnitrene (^{1}**1**). However, with cyano groups at both *ortho* carbons, as in ^{1}**4f**, the unpaired π spin density at each of these carbons should be smaller than at the single, cyano-substituted, *ortho* carbon in ^{1}**4c**. Therefore, the barrier to cyclization might be expected to be somewhat higher for ^{1}**4f** than for ^{1}**4c**.

Table 1 shows that these two qualitative predictions about the height of the barrier to cyclization of ^{1}**4f**, relative to the barriers for cyclization of ^{1}**1** and ^{1}**4c**, are confirmed by the results of our calculations. In contrast, calculations[11] and experiments[3e,i,7,10] both find that 2,6-difluorophenylnitrene cyclizes much more slowly than ^{1}**1** and than singlet *o*-fluorophenylnitrene (^{1}**4b**). As already noted, unlike the case with a cyano substituent, cyclization at a fluorinated *ortho* carbon has a considerably higher barrier than cyclization at an unfluorinated *ortho* carbon.

Unlike the case in either ^{1}**4c** or ^{1}**4f**, in the cyclization of *m*-cyanophenylnitrene (^{1}**4d**) steric effects are unlikely to play a significant role in the transition state. In addition, since the cyano group is on a carbon at which the π NBMO in the reactant

(17) 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. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*, Revision B.3; Gaussian, Inc.: Pittsburgh, PA, 1995.

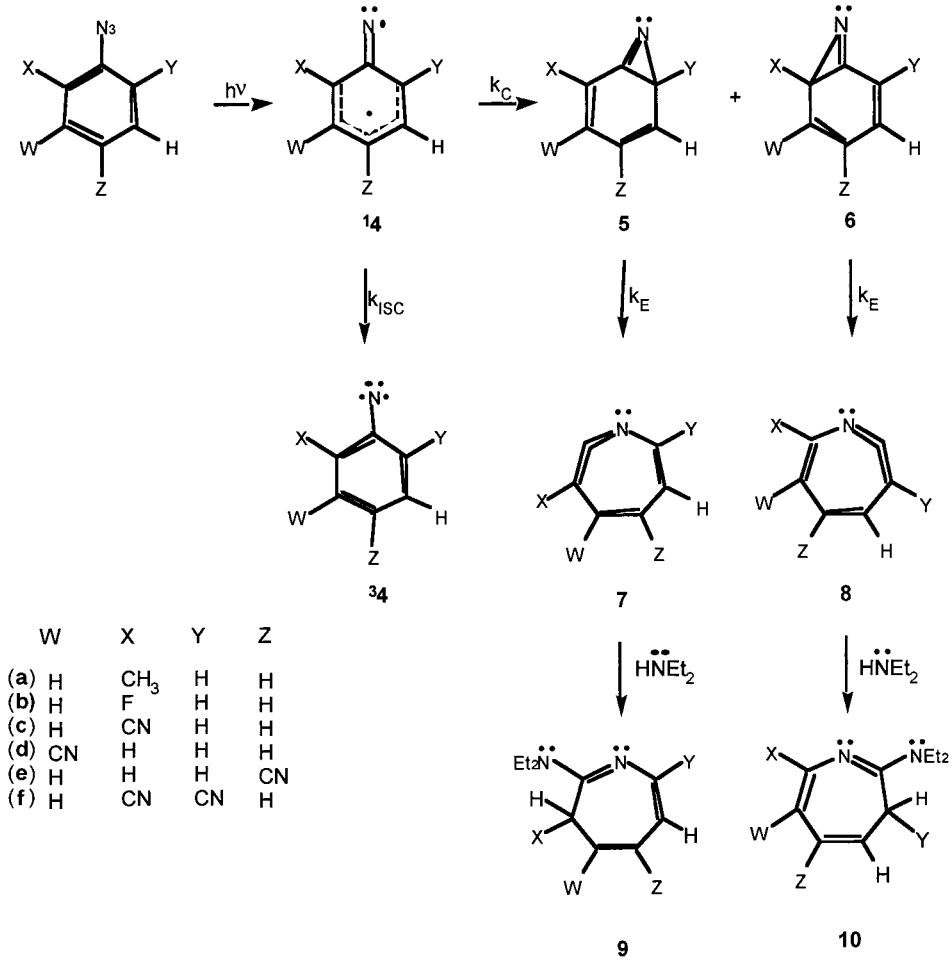
(18) Andersson, K.; Malmqvist, P.-Å.; Roos, B. O. *J. Chem. Phys.* **1992**, *96*, 1218.

(19) Andersson, K.; Blomberg, M. R. A.; Fülscher, M. P.; Karlström, G.; Lindh, R.; Malmqvist, P.-Å.; Neogrády, P.; Olsen, J.; Roos, B. O.; Sadlej, A. J.; Schütz, M.; Seijo, L.; Serrano-Andrés, L.; Siegbahn, P. E. M.; Widmark, P.-O. *MOLCAS-4*; University of Lund: Sweden.

(20) Review: Borden, W. T.; Davidson, E. R. *Acc. Chem. Res.* **1996**, *29*, 67.

(21) Karney, W. L.; Kemnitz, C. R.; Borden, W. T. Unpublished results.

Scheme 2



	W	X	Y	Z
(a)	H	CH_3	H	H
(b)	H	F	H	H
(c)	H	CN	H	H
(d)	CN	H	H	H
(e)	H	H	H	CN
(f)	H	CN	CN	H

has a node, it also seems unlikely that radical stabilization will influence whether **^{1}4d** cyclizes to **5d** or **6d**. In fact, the barrier heights connecting **^{1}4d** to **5d** and **6d** are quite comparable; and the 0.6 kcal/mol kinetic preference that is predicted for cyclization of **^{1}4d** to **6d** could be due, at least in part, to the 1.9 kcal/mol lower energy that is computed for the linearly conjugated product (**6d**) than for the cross-conjugated product (**5d**).

Table 1 shows that the CASPT2 barrier for cyclization of *p*-cyanophenylnitrene (**^{1}4e**) is more than 1 kcal/mol higher than that for cyclization of the *ortho* (**^{1}4c**) or *meta* (**^{1}4d**) isomers. In addition, the energy of the cyclization product, relative to the reactant, is higher for **^{1}4e** → **5e** than for cyclization of either **^{1}4c** or **^{1}4d**. Both facts are attributable to the lower energy of **^{1}4e** compared to that of either **^{1}4c** or **^{1}4d**.

Comparison of the absolute CASPT2 energies of **^{1}4c**−**e** (available in the Supporting Information) reveals that **^{1}4e** is calculated to be 2.8 kcal/mol lower in energy than **^{1}4c**. Presumably, at least part of this energy difference is due to greater destabilizing interactions between the cyano and imino groups when they are *ortho*, rather than *para*, to each other. However, concentration of spin density at the central carbon of a cyclohexadienyl radical probably also makes the *para* cyano group in **^{1}4e** more radical stabilizing than the *ortho* cyano group in **^{1}4c**.

The CASPT2 energy difference of 3.4 kcal/mol between **^{1}4d** and **^{1}4e** is even larger than that between **^{1}4c** and **^{1}4e.** Steric effects are unlikely to play any role in the energy difference between **^{1}4d** and **^{1}4e**, and this energy difference is almost certainly a consequence of the much greater stabilization of the unpaired electron in the π NBMO by the *para* cyano group in **^{1}4e** than by the *meta* cyano group in **^{1}4d**.

In the cyclization products formed from **^{1}4c**−**e**, the energetic advantage of *p*-cyanophenylnitrene (**^{1}4e**) over both the *ortho* (**^{1}4c**) and *meta* (**^{1}4d**) isomers is lost. Consequently, the energy of the cyclization product, relative to the nitrene from which it is formed, is higher for the cyclization product (**5e**) formed from **^{1}4e** than for the cyclization products formed from either **^{1}4c** or **^{1}4d**. In the transition states for the cyclization of these three cyanophenylnitrenes, partial loss of the energetic advantage of **^{1}4e** over both **^{1}4c** and **^{1}4d** is the reason the barrier to cyclization of the *para* isomer is predicted to be larger than those for either *ortho* or *meta*.

Experimental Results

The computational results in Table 1 predict: (a) a larger barrier to cyclization for **^{1}4e** than for **^{1}4c**, **^{1}4d**, **^{1}4f**, or unsubstituted phenylnitrene (**^{1}1**), (b) a slightly larger barrier to formation of **5c** than **6c** in cyclization of **^{1}4c**, and (c) a slightly lower barrier to cyclization for both **^{1}4c** and **^{1}4f** than for **^{1}1**. To test these predictions, we undertook a series of laser flash photolysis and chemical trapping experiments.

Laser flash photolysis (LFP) of *o*-cyanophenyl azide in pentane at 295 K produces a transient spectrum containing a broad absorption between 350 and 400 nm (Figure 1). The carrier of this transient absorption has a lifetime in excess of many microseconds at 295 K. The lifetime (τ) of this intermediate can be reduced significantly in the presence of diethylamine (DEA) and a plot of $1/\tau$ versus [DEA] is linear. This behavior

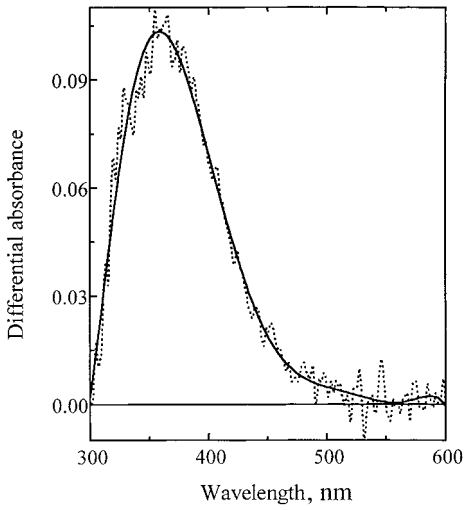


Figure 1. OMA spectrum detected after LFP of 2-cyanophenyl azide in pentane at 295 K, 50 ns after the KrF laser pulse (249 nm) with a 200 ns time window. The solid line is drawn through the averaged experimental points.

is characteristic of didehydroazepines such as **3**.[2g−i] The didehydroazepine transient is formed at 295 K faster than the time resolution of the spectrometer (1−2 ns). The rate constant of its reaction with DEA is very high and equal to $(3.5 \pm 0.3) \times 10^9$ M^{-1} s^{-1} (Table 2). This value is what one would expect for reaction of cyano-substituted didehydroazepine with DEA on the basis of the work of Li, Poliakoff, and Schuster with related didehydroazepines.[3g]

The UV−vis spectra of didehydroazepines **7c** and **8c** (derived from **5c** and **6c**, respectively, Scheme 2), are expected to be very similar; thus, we cannot confidently assign the spectrum to one or the other. Chemical trapping studies, discussed in the next section, indicate that the transient spectrum probably contains contributions from both species (vide infra). Kinetic curves for *3H*-azepine formation in the presence of DEA appeared to be single exponentials. This finding indicates that the rate constants of the reaction of isomeric didehydroazepines with DEA are very similar.

LFP of *o*-cyanophenyl azide in pentane at 185 K produces a transient spectrum which contains a sharp, structured band, with maximum absorbance at 325 nm, and a broader band, with an absorbance between 350 and 400 nm (Figure 2, spectrum 1). The band observed between 350 and 400 nm at 185 K is more structured and decays much more rapidly than the band observed in the same wavelength region at 295 K. Thus, the transient that absorbs between 350 and 400 nm at 185 K cannot be a didehydroazepine, and this absorbance is assigned instead to singlet *o*-cyanophenylnitrene (**^{1}4c**). This absorption cannot be assigned to either benzazirines **5c** or **6c** because matrix-isolated difluorobenzazirine has $\lambda_{max} = 280$ nm.[22] Our CIS/6-311+G* calculations[23] of the spectra of substituted benzazirines demonstrate no significant influence of fluoro- and cyano substituents on the spectra. According to these calculations parent benzazirine has maximum at 269 nm, fluoro-substituted benzazirine, at 273 nm, and **6c**, at 259 nm.

Singlet *o*-cyanophenylnitrene has an absorption maximum (∼370 nm) at longer wavelength than unsubstituted singlet phenylnitrene (337, 352 nm).[3k] Decay of the transient assigned to **^{1}4c** results in a spectrum (Figure 2, spectrum 2) which is very similar to the spectrum of triplet *o*-cyanophenylnitrene **^{3}4c**, (although **^{1}4c** may also have some absorption between 300 and 350 nm). The same intermediate is formed as a persistent species upon brief (10 s) photolysis (254 nm) of *o*-cyanophenyl azide in glassy methylcyclohexane at 77 K (Figure 2, spectrum 3). This intermediate is confidently assigned as **^{3}4c** by comparison of its spectrum to that of unsubstituted triplet phenylnitrene (308 nm)[3e,k]

LFP of 2,6-dicyanophenyl azide gave results similar to those found in the LFP study of *o*-cyanophenyl azide. LFP of the dicyano azide at 295 K produces a broad transient absorption with maximum at 360 nm (similar to those of Figure 1) which could be assigned to didehydroazepine **7f**. Azepine **7f** reacts with DEA even more rapidly than a monocyanodidehydroazepine and, as expected,[3g] with a rate constant close to the diffusion limit (Table 2).

The transient spectra obtained at 185 K are shown in Figure 3. The short-lived, structured band with maxima at 362, 384, and 405 nm (Figure 3, spectrum 1) is assigned to singlet 2,6-dicyanophenylnitrene (**^{1}4f**). The long-lived band at 340 nm (Figure 3, Spectrum 2), which is persistent in a glass at 77 K (Figure 3, Spectrum 3), is attributed to **^{3}4f**. The absorption spectra of the cyano-substituted singlet phenylnitrenes are very similar to that of unsubstituted singlet phenylnitrene which has $\lambda_{max} = 337$, 352 nm.

It is interesting to note that cyano substitution leads to a red shift of the UV spectra of both the singlet and triplet phenyl nitrenes. This is readily understood by noting that both singlet and triplet substituted phenylnitrenes have similar open-shell electronic configurations. According to CASSCF/CASPT2 calculations,[3k] all of the calculated bands of singlet phenylnitrene have the same assignment as the corresponding bands of triplet phenylnitrene, but their positions are shifted to the red by about 0.8 eV.

At subambient temperatures, formation of didehydroazepines (**7c**, **8c**, **7f**) and triplet nitrenes (**^{3}4c** and **^{3}4f**) was no longer instantaneous (Figure 4). The decays of the singlet nitrenes **^{1}4c** and **^{1}4f** were monitored at 380 and 405 nm, (Figure 4, curve 1), respectively. The formation of the reaction products (Figure 4, curve 2) were exponential and were analyzed to yield observed rate constants k_{OBS} of singlet nitrene disappearance. The temperature dependence of k_{OBS} for the decay of **4c** and **4f** is shown in Figure 5.

In the LFP of *p*-cyanophenyl azide at ambient and subambient temperature, it was not possible to detect the decay of the transient absorption of **^{1}4e**. However, it was possible to resolve the growth of didehydroazepine **7e** and **^{3}4e** absorption, even at ambient temperature (Figure 6). The absorption growth was fit to an exponential function and analyzed to give an observed rate constant of $k_{OBS} = (1.3 \pm 0.6) \times 10^8$ s^{-1} at ambient temperature, which corresponds to a lifetime of 8 ± 4 ns for singlet nitrene **^{1}4e**. The spectrum of Figure 6 is similar to the spectra of other didehydroazepines and was assigned to **7e**. The rate constant of reaction of **7e** with DEA is $(1.6 \pm 0.2) \times 10^9$ M^{-1} s^{-1}, and it fits well to the same correlation with the Hammett σ value as the rate constants for other 5-substituted 1,2-didehydroazepines.[3g]

Because we measured the absorption growth of the products for reaction of **^{1}4e**, rather than decay of the transient absorption due to **^{1}4e**, the data for the *p*-cyanonitrene are less precise than those for the *o*-cyano- (**^{1}4c**) and the 2,6-dicyanophenylnitrene (**^{1}4f**) systems. It is very clear, however, that singlet *p*-cyanophenylnitrene has the longest lifetime of all of the singlet phenylnitrenes studied in this work. The temperature dependence

(22) Morawietz, J.; Sander, W. *J. Org. Chem.* **1996**, *61*, 4351.
(23) Foresman, J. B.; Head-Gordon, M.; Pople, J. A.; Frish, M. J. *J. Phys. Chem.* **1992**, *96*, 135.

Table 2. Summary of Kinetic Results for Singlet Cyano-Substituted Phenylnitrenes and Didehydroazepines

nitrene	λ_{max}, nm	τ(295), ns	$k_{ISC} \times 10^{-6}$, s^{-1}	log A, s^{-1}	E_a, cal/mol	$k_{DEA} \times 10^{-9}$, $M^{-1}s^{-1}$	solvent
o-cyano (**^{1}4c**)	380	$\sim 2^a$	2.8 ± 0.3	12.8 ± 0.3	5500 ± 300	3.5 ± 0.3	C_5H_{12}
p-cyano (**^{1}4e**)	-	8 ± 4	6 ± 2	13.5 ± 0.6	7200 ± 800	1.6 ± 0.2	C_5H_{12}
2,6-dicyano (**^{1}4f**)	405	$\sim 2.5^a$	4.5 ± 0.5	13.3 ± 0.2	6400 ± 300		CH_2Cl_2
2,6-dicyano (**^{1}4f**)	405	$\sim 2.3^a$	6.2 ± 0.8	13.5 ± 0.2	6500 ± 400	8.3 ± 0.8	C_5H_{12}
2,6-dicyano (**^{1}4f**)	405	$\sim 2.3^a$	5.9 ± 1.5	13.1 ± 1.0	6000 ± 1100		THF

[a] Lifetime estimated by extrapolation of the data to 295 K.

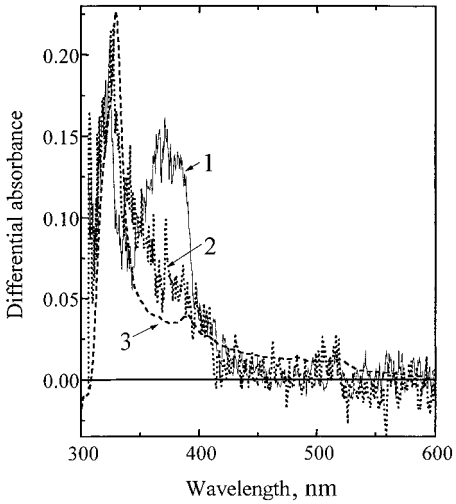


Figure 2. OMA spectra detected after LFP of 2-cyanophenyl azide in pentane at 185 K (1) just after the laser pulse (249 nm) with a 100 ns time window and (2) 300 ns after the laser pulse with 100 ns window. (3) The differential absorption spectrum of triplet nitrene detected after brief (10 s) stationary photolysis (254 nm) of 2-cyanophenyl azide in methylcyclohexane at 77 K.

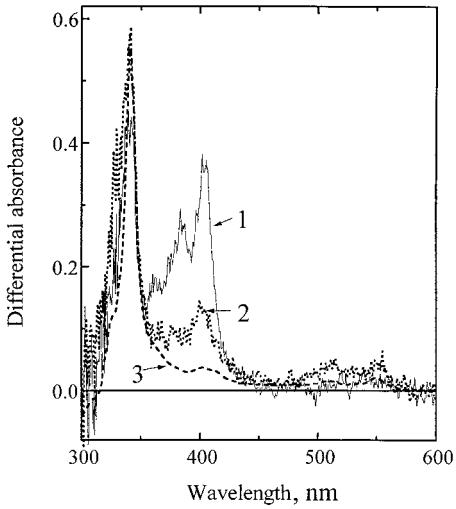


Figure 3. OMA spectra detected after LFP (249 nm) of 2,6-dicyanophenyl azide in CH_2Cl_2 at 185 K (1) just after the laser pulse with 100 ns time window and (2) 500 ns after the laser pulse with 100 ns window. (3) The differential absorption spectrum of triplet nitrene detected after brief (20 s) stationary photolysis (254 nm) of 2,6-dicyanophenyl azide in methylcyclohexane at 77 K.

of k_{OBS} for *p*-cyanophenylnitrene **4e** is also depicted in Figure 5. At all temperatures, singlet nitrene lifetimes increase in the order *o*-cyanophenyl < 2,6-dicyanophenyl < *p*-cyanophenylnitrene.

Scheme 2 shows the two decay pathways for singlet cyanophenylnitrenes. As defined in Scheme 2, k_C is the rate constant for cyclization to form the bicyclic azirine intermediates (**5** and **6**), and k_{ISC} is the rate constant for intersystem crossing

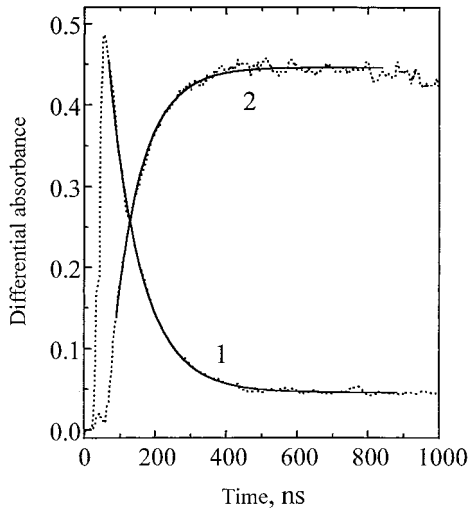


Figure 4. Changes in transient absorption at 405 nm (1) and 340 nm (2) after LFP of 2,6-di-cyanophenyl azide (**1c**) in CH_2Cl_2 at 213 K.

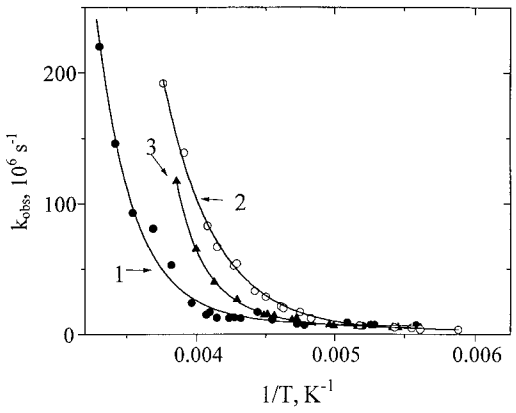


Figure 5. Plots of k_{OBS} versus $1/T$ for (1) *para*-cyanophenylnitrene and (2) *o*-cyanophenylnitrene in pentane and for (3) 2,6-dicyanophenylnitrene in CH_2Cl_2.

of the singlet to the triplet. For each nitrene k_{OBS} is equal to the sum of elementary rate constants k_C and k_{ISC} ($k_{OBS} = k_C + k_{ISC}$).

The bicyclic azirine intermediates pictured in Scheme 2 were not detected in the LFP of **^{1}4c** and **^{1}4f.** The observed rate constant for cyclization of each of these singlet nitrenes is the same as the observed rate constant for the appearance of the didehydroazepine. As with parent singlet phenylnitrene $k_C \ll k_E$. We could not detect the decay of the singlet *p*-cyanophenylnitrene **^{1}4e**, but we assume that $k_C \ll k_E$ in this case, too.

The temperature dependence of k_{OBS} for *p*-cyanophenylnitrene **^{1}4e** is also depicted in Figure 5. The temperature-independent region of Figure 5 is associated with k_{ISC}, and all the temperature dependence is attributed to k_C. Plots of $\ln(k_{OBS} - k_{ISC})$ versus $1/T$ for **^{1}4c**, **^{1}4e**, and **^{1}4f** are linear (Figure 7), which indicates that k_{ISC} is constant over the entire temperature range. From these plots Arrhenius parameters for cyclization of **^{1}4c**, **^{1}4e**, and **^{1}4f** can be extracted. These activation parameters are given in Table 2.

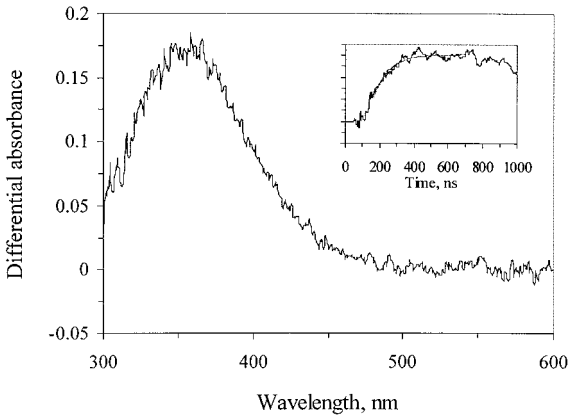


Figure 6. Transient spectrum produced by LFP (249 nm) of *para*-cyanophenyl azide in pentane at 246 K taken over a 100 ns window immediately after the laser pulse. Insert: Change in transient absorption at 355 nm following LFP (249 nm) of *para*-cyanophenyl azide in pentane at 223 K.

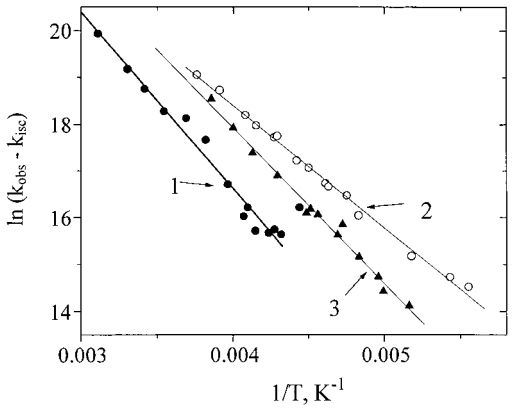


Figure 7. Arrhenius treatment of k_R ($= k_{OBS} - k_{ISC}$) data for (1) *para*-cyanophenylnitrene and (2) *o*-cyanophenylnitrene (2) in pentane and for (3) 2,6-dicyanophenylnitrene in CH_2Cl_2.

The activation parameters for cyclization of *o*-cyano- (**^{1}4c**) and 2,6-dicyanophenylnitrene (**^{1}4f**) are similar. The fact that both the log(A) and E_a for **^{1}4c** are less than those for **^{1}4f** suggests that the data may be influenced by systematic error. If log(A) for **^{1}4f** is set equal to 12.8, the same value as for **^{1}4c**, the calculated E_a value for **^{1}4f** is reduced from 6.4 to 5.9 kcal/mol.

Although this activation energy for cyclization of **^{1}4f** is still larger than that for cyclization of **^{1}4c** by 0.4 kcal/mol, within experimental error the barriers to cyclization of these two singlet nitrenes are the same as each other and as the barrier of 5.6 ± 0.2 kcal/mol for cyclization of unsubstituted singlet phenylnitrene (**^{1}1**).[3i,k] These results confirm that, as predicted computationally, the effects of cyano and fluoro substituents on phenylnitrene cyclizations are very different. Whereas the pair of *ortho* fluoro substituents in singlet 2,6-difluorophenylnitrene retard the rate of cyclization, the pair of *ortho* cyano substituents in **^{1}4f** have little or no effect on the barrier to cyclization.

However, the barrier to cyclization of singlet *p*-cyanophenylnitrene (**^{1}4e**) is 1−2 kcal/mol greater than those measured for **^{1}1**, **^{1}4c**, and **^{1}4f**. There is no doubt that, as predicted both qualitatively and by the CASPT2 calculations, a *para* cyano group does indeed retard the rate of singlet phenylnitrene cyclization.

Variation of solvent has only a small effect on the kinetics. Values of k_{OBS} obtained upon LFP of 2,6-dicyanophenyl azide in pentane, methylene chloride, and tetrahydrofuran are shown in Figure 8. Values of k_{OBS} are largest in THF and are about the same in pentane and methylene chloride. The activation barrier to cyclization of 2,6-dicyanophenylnitrene is 6.0 ± 1.1 kcal/mol in THF, and is 6.5 ± 0.4 kcal/mol in pentane and methylene chloride (Table 2). The barrier to cyclization of parent singlet phenylnitrene is 5.6 ± 0.3 kcal/mol in pentane. Fluorescence increases the error in the data obtained in THF for 2,6-dicyanophenylnitrene.

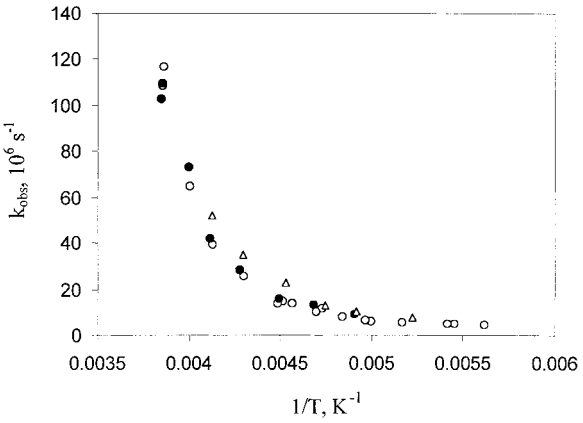
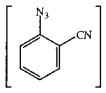
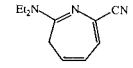


Figure 8. Plots of k_{OBS} versus $1/T$ for 2,6-dicyanophenylnitrene in different solvents: pentane (open circles), CH_2Cl_2 (solid circles), and THF (triangles).

Table 3. Product Ratios of *3H*-Azepines[a] Formed upon Photolysis of *o*-Cyanophenyl Azides at Ambient Temperature in the Presence of 0.1 M Diethylamine





	Solvent	**9c** (%)	**10c** (%)
0.025M	Pentane	37	63
0.05 M	Pentane	48	52
0.05 M	CH_2Cl_2	67	33
0.05 M	THF	64	36

[a] A species with the same fragmentation pattern as **10c** was also detected by GC−MS, but attempts to isolate this compound failed. It is attributed to the *1H*-azepine analogue of **10c** which is formed initially and isomerizes to **10c**. The data in the table is the sum of the *1H* and *3H*-azepine yields. *1H*-Azepines related to **9c** were not observed by GC−MS.

Chemical Trapping Studies

As mentioned earlier, Smalley and co-workers[14a] have already confirmed the computational prediction, that cyclization of **^{1}4c** toward the *ortho* cyano group should be competitive with cyclization away from it. Smalley and co-workers analyzed the products formed upon photolysis of *o*-cyanophenyl azide in mixtures of water and tetrahydrofuran. They found that the products were generated by trapping of didehydroazepine intermediates **7c** and **8c**, formed by cyclization of **^{1}4c** both toward and away from the cyano group.

In our hands photolysis of *o*-cyanophenyl azide in the presence of diethylamine gives 3H-azepine trapping products, **9c** and **10c** (Scheme 2). Variation of the solvent leads to subtle variation in the product distribution. The solvent effect on the relative rates of cyclization toward and away from the cyano group is small, but finite. The compositions of the mixtures formed under different reaction conditions are shown in Table 3.

Younger and Bell have presented chemical evidence that the cyclization of 3-acetamido-4-trifluoroacetamido phenylnitrene

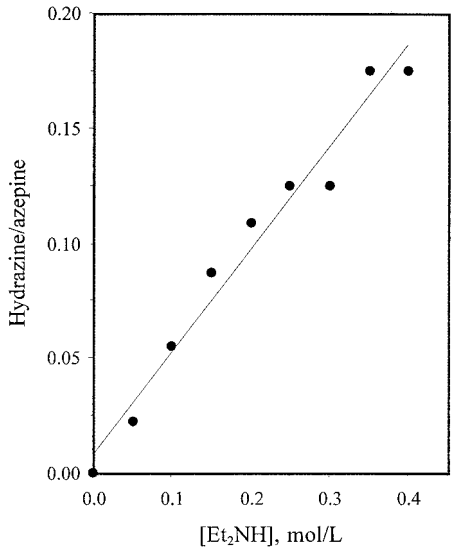
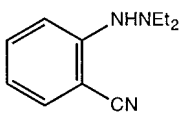


Figure 9. A plot of **11c**/(**9c** + **10c**) versus the concentration of diethylamine.

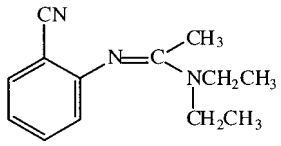
to two isomeric azirines is reversible.[4d] Our laboratory has presented kinetic evidence that cyclization of *o*-fluorophenylnitrene (**^{1}4b** → **5b**) is also reversible.[10b] However, there is no evidence from our LFP studies for reversibility in the cyclization of *o*-cyanophenylnitrene (**^{1}4c**). In addition, the ratio of azepines **9c** and **10c**, formed in pentane, does not change over a diethylamine (DEA) concentration range of 0.05−0.40 M. Thus, our chemical trapping studies also indicate that cyclization of **^{1}4c** is irreversible under the reaction conditions used in the chemical trapping experiments.

At high DEA concentrations hydrazine product **11c** is formed. Phenylnitrene is known to insert into the N−H bond of diethylamine in low yield.[24] Moderate yields of hydrazines are also realized with perfluorophenylnitrene,[7a,26] *p*-nitro- and *p*-cyanophenylnitrene.[25] In the latter case, there has been speculation that the interconversion of the singlet nitrene (**^{1}4c**) and benzazirine **5c** might be reversible.[2a,25,26] A plot of **11c**/(**9c** + **10c**) versus the concentration of diethylamine is linear (Figure 9) with a slope of $0.038 = k_H/k_C$, where k_C is the sum of the rate constants for cyclization of **^{1}4c** to **5c** and **6c**, and k_H is the rate constant for reaction of **^{1}4c** with DEA to form hydrazine **11c**. If we assume that $k_H = 10^7 - 10^8$ M^{-1} s^{-1}, as it is in the reaction of fluorinated aryl nitrenes with pyridine,[7c−e] we deduce that $k_C = 2.6 \times (10^8-10^9)$ s^{-1}. Thus, the deduced lifetime of singlet *o*-cyanophenylnitrene (**^{1}4c**) is between 0.4 and 4 ns at ambient temperature, a value that is in reasonable agreement with the lifetime derived from the LFP experiments.



11c

Also formed, but only in trace amounts, were *o*-diaminobenzene products, derived from trapping **5c** and **6c**, rather than didehydroazepines **7c** and **8c** upon photolysis of *o*-cyanophenyl azide in the presence of diethylamine. One other product, **12c**, was isolated upon photolysis of *o*-cyanophenyl azide in the presence of diethylamine.



12c

This type of minor product has been observed previously in the reactions of electron-deficient arylnitrenes with diethylamine. It has been attributed to electron-transfer reactions of the triplet nitrene.[7a,b,27]

Conclusions

The results of our LFP experiments confirm the predictions, based on both qualitative theory and our quantitative CASPT2 calculations, regarding the effects of cyano substituents on the rate of phenylnitrene cyclization. We find that cyclization at a substituted *ortho* carbon is much faster when the substituent is cyano, rather than methyl[8b] or fluoro.[10b] Our kinetic result, that cyclization at an *ortho* carbon occurs about as fast in singlet 2,6-dicyanophenylnitrene (**^{1}4f**) as in singlet phenylnitrene (**^{1}1**),[3i−k] is consistent with the results of our chemical trapping experiments. Like Smalley and co-workers,[14a] we find that in singlet *o*-cyanophenylnitrene (**^{1}4c**) cyclization at the substituted and unsubstituted *ortho* carbons are competitive.

In contrast to the effect of *ortho* cyano substitution, cyano substitution at the *para* carbon of phenylnitrene (**^{1}1**) makes the rate of cyclization of singlet *p*-cyanophenylnitrene (**^{1}4e**) measurably slower than that of **^{1}1**. The origin of the opposite effects of *ortho* and *para* cyano groups is the same. A cyano substituent is radical-stabilizing and thus tends to localize an unpaired π electron at the carbon to which the cyano group is attached. In the case of an *ortho* cyano group, this facilitates cyclization at the substituted carbon. However, a *para* cyano group diminishes the unpaired π spin density at both *ortho* carbons and thus retards the rate of nitrene cyclization.

Experimental Section

Laser Flash Photolysis. A Nd:YAG laser (Continuum PY62C-10, 35 ps, 10 mJ, 266 nm), KrF (Lumonix, 12 ns, 50 mJ, 249 nm) and XeCl eximer lasers (Lambda Physik, 20 ns, 50 mJ, 308 nm) were used as the excitation light sources. The laser apparatus system at The Ohio State University has been previously described in detail.[7c]

Typically, the solution was contained in a quartz cuvette which was placed in a quartz cryostat. Temperature was varied in the range of 150−300 K and kept to within ±1 K by passing a thermostabilized nitrogen stream over the cuvette. The sample solutions were changed after every laser shot, to avoid effects due to the accumulation of photoproducts. The absorption spectra of long-lived (τ > 300 ns) intermediates were measured using an eximer KrF or XeCl lasers in conjunction with an optical multichannel analyzer (EG & G Princeton Applied Research model 1460).

Low-Temperature Photolysis. Low-temperature (77 K) photolysis was performed in a liquid nitrogen-filled cryostat with plane-parallel quartz windows. Thin-walled 2 mm quartz sample cuvettes were employed. Methylcyclohexane was used as a solvent. Rayonet 254 nm lamps were used to photolyze the samples, and UV−vis spectra were recorded with a Lambda 6 UV−vis spectrophotometer.

Materials. Alkane solvents were used as received, but methylene chloride was purified by passage through a column of alumina. 2-Cyanophenyl azide[14] and 4-cyanophenyl azide[25] were prepared by

(24) (a) Odum, R. A.; Brenner, M. *J. Am. Chem. Soc.* **1966**, *88*, 2074. (b) Sundberg, R. J.; Smith, R. H., Jr. *J. Org. Chem.* **1971**, *36*, 295.

(25) (a) Odum, R. A.; Wolf, G. *J. Chem. Soc., Chem. Commun.* **1973**, 360. (b) Odum, R. A.; Aaronson, A. M. *J. Am. Chem. Soc.* **1969**, *91*, 5680. (c)Liang, T.-Y.; Schuster, G. B. *J. Am. Chem. Soc.* **1986**, *108*, 546; **1987**, *109*, 7803.

(26) Abramovitch, R. A.; Challand, S. R.; Scriven, E. F. V. *J. Am. Chem. Soc.* **1972**, *94*, 1374.

known procedures from the corresponding commercially available anilines. The azides were characterized with IR, ^{1}H NMR, ^{13}C NMR spectroscopy, and the spectra were compared with those reported previously in the literature. 2,6-Dicyanoaniline was prepared by the method of Griffiths et al.[28]

2,6-Dicyanophenyl Azide. To a stirred suspension of 2,6-dicyanoaniline[28] (0.3 g) in HCl (37%, 3.06 mL) was added dropwise at 0 °C, a solution of sodium nitrite (126.5 mg in 2.25 mL of water). The solution was stirred a further 10 min and then filtered. To the stirred filtrate was added a solution of sodium azide (450 mg in 3.36 mL of water). The mixture was stirred for 2 more hours and filtered. The water-insoluble filter cake was dissolved in chloroform and filtered, and the filtrate was rotary-evaporated. The solid obtained was recrystallized from benzene:petroleum ether (1:1), and 84.8 mg of crystals were obtained. (27% yield, melting point: 113 °C). The IR spectrum gave an azide absorption at 2149 cm^{-1} and cyano absorption at 2237 cm^{-1}. The ^{1}H NMR spectrum ($CDCl_3$) showed peaks at δ 7.83 (2H, d), 7.35 (1H, t) but no peak at δ 6.80, belonging to amine hydrogens of starting material. ^{13}C NMR gave peaks at δ 143.8, 138.3, 125.5, 113.8, 107.0. HRMS calcd for $C_8H_3N_5$ 169.0388, found 169.0392.

Isolation of 3-Cyano-2-diethylamino-3H-azepine (9c). An argon-purged solution of 2-cyanophenyl azide (0.144 g, 1 mmol) and diethylamine (0.41 mL, 4 mmol) in dry pentane (40 mL, Aldrich) was irradiated with Pyrex-filtered 350 nm light in the Rayonet reactor at 10−12 °C. After 17 h the reaction flask surface almost lost transparency due to the build-up of the dark brown film. The solution was placed in another dry flask, purged with argon, and irradiated for an additional 16 h. The flask was replaced one more time, followed by irradiation of the sample for another 17 h. The mixture was concentrated on the rotary evaporator and separated by preparative TLC (SiO_2, 20 × 20 cm, 63% benzene−33% cyclohexane−4% triethylamine). The yield of **9c** was 31 mg (16%), as a colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.15 (t, J = 7.1, 6H), 3.37 (m, 4H), 5.05 (t, J = 8.5, 1H), 5.16 (br, 1H), 5.92 (dd, J = 7.5, J = 6.4, 1H), 6.51 (dd, J = 8.4, J = 6.4, 1H), 7.29 (d, J = 8.1, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.34, 31.82, 44.07, 106.03, 109.68, 113.69, 131.37, 137.18, 141.25; EIMS *m*/*z* (rel intens) 189 (M^+, 68), 174 (25), 160 (71), 149 (90), 146 (24), 135 (31), 132 (100), 118 (69), 105 (75), 90 (29); HRMS calcd for $C_{11}H_{15}N_3$ 189.1267, found 189.1262.

Isolation of 7-Cyano-2-diethylamino-3H-azepine (10c). A solution of 2-cyanophenyl azide (0.3 g, 2.08 mmol) and diethylamine (0.22 mL, 2.12 mmol) in dry THF (20 mL), freshly distilled from benzophenone ketyl, was degassed by the freeze−thaw method in a flame-dried Pyrex tube, which was then filled with argon. The mixture was photolyzed with 350 nm light in the Rayonet reactor for 20 h at 10−12 °C. After the solvent was removed under reduced pressure, the residue was chromatographed on a 1 in. × 8 in. column of silica gel (eluent: 80% pentane−20% ether). Fractions enriched with 7-cyano-2-diethylamino-3H-azepine (determined by GC) were combined, concentrated, and purified by preparative TLC (SiO_2, 20 × 20 cm, 80% cyclohexane−20% ethyl acetate). The yield of **10c** was 0.04 g (10%), as a colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.01 (br, 3H), 1.15 (br, 3H), 2.65 (br, 2H), 3.27 (br, 2H), 3.36 (br, 2H), 5.32 (dd, J = 15.6, J = 7.6, 1H), 6.28 (m, 2H);^{13}C NMR (125 MHz, $CDCl_3$) δ 12.86, 14.51, 32.00, 43.80, 44.47, 118.15, 119.61, 120.66, 126.20, 128.39, 147.28; EIMS *m*/*z* (rel intens) 189 (M^+, 46), 174 (9), 160 (33), 146 (12), 132 (24), 118 (100), 105 (36), 90 (15), 72 (38); HRMS calcd for $C_{11}H_{15}N_3$ 189.1267, found 189.1270.

Photolysis of 2-Cyanophenyl Azide in Neat Diethylamine. A solution of 2-cyanophenyl azide (0.144 g, 1 mmol) in diethylamine (20 mL), freshly distilled from $LiAlH_4$, was purged with argon and photolyzed in a Pyrex vial at 350 nm for 22 h at 10−12 °C using a Rayonet reactor. The solvent was removed on the rotary evaporator, and the mixture was separated by preparative TLC (SiO_2, 20 × 20 cm, 90% cyclohexane−10% ethyl acetate). The first major TLC band yielded (2-cyanophenyl) 2,2-diethylhydrazine **(11c)** (16 mg, 8.5%) as a white solid: mp 33−35 °C;^{1}H NMR (500 MHz, $CDCl_3$) δ 1.03 (t, J = 7.1, 6H), 2,71 (br, 4H), 5.00 (s, exchanged with D_2O, 1H), 6.63 (m, 1H), 7.22 (m, 1H), 7.32 (m, 2H);^{13}C NMR (125 MHz, $CDCl_3$) δ 12.10, 52.80, 92.53, 113.30, 117.27, 117.63, 132.10, 134.01, 152.21; EIMS *m*/*z* (rel intens) 189 (M^+, 100), 174 (71), 160 (39), 146 (27), 131 (12), 117 (85), 102 (12), 90 (34); HRMS calcd for $C_{11}H_{15}N_3$ 189.1267, found. 189.1268. The second major TLC band yielded *N*,*N*-diethyl-*N*′-(2-cyanophenyl) acetamidine (21.5 mg, 10%) as colorless oil: ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.23 (t, J = 7.1, 6H), 1.91 (s, 3H), 3.44 (q, J = 7.1, 4H), 6.78 (m, 1H), 6.93 (m, 1H), 7.39 (m, 1H), 7.45 (m, 1H);^{13}C NMR (125 MHz, $CDCl_3$) δ 13.76, 15.51, 43.08, 106.33, 119.14, 121.45, 123.81, 133.09, 133.56, 156.40; EIMS *m*/*z* (rel intens) 215 (M^+, 30) 186 (16), 143 (100), 102 (35), 86 (8) 85 (8), 72 (20) HRMS calcd for $C_{13}H_{17}N_3$ 215.1418, found 215.1424. The third major TLC band gave 2-aminobenzonitrile (27 mg, 23%).

Acknowledgment. Support of this work in Columbus and Seattle by the National Science Foundation is gratefully acknowledged. W.L.K. is grateful to the University of San Francisco Faculty Development Fund and The Lily Drake Cancer Research Fund for generous financial support. N.P.G. gratefully acknowledges the support of the National Research Council, and Russian Foundation for Basic Research.

Supporting Information Available: CASSCF-optimized Cartesian coordinates for singlet nitrenes, bicyclic azirines, and transition states discussed in the text, and a table of CASSCF and CASPT2 absolute energies, a table with the wavelengths and oscillator strengths calculated by CIS method for substituted benzazirines, and the plot of observed rate constants versus DEA concentrations for the reaction of cyano-substituted didehydroazepines are available (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA002594B

(27) Polanc, S.; Stanounik, B.; Tisler, M. *J. Org. Chem.* **1976**, *41*, 3152.
(28) Griffiths, J.; Lockwood, M.; Roozpeiker, B. *J. Chem. Soc., Perkin Trans 2* **1977**, 1608.