Photoequilibration of 1-Naphthylcarbene and 4,5-Benzobicyclo[4.1.0]hepta-2,4,6-triene

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Abstract: Irradiation ($\lambda > 300$ nm) of 1-naphthyldiazomethane (**11**) or 1-naphthyldiazirine (**12**) isolated in an argon matrix at 10 K produces 4,5-benzobicyclo[4.1.0]hepta-2,4,6-triene (**2**) and a small amount of triplet 1-naphthylcarbene (**1**). Cyclopropene **2** is characterized by infrared and UV/visible spectroscopy while triplet 1-naphthylcarbene (**1**) is characterized by infrared, UV/visible, and ESR spectroscopy. Experimental and computed (B3LYP/6-31G*) IR spectra display good agreement. Carbene **1** and cyclopropene **2** are thermally stable in the matrix at 10 K, although they may be interconverted photochemically. Further irradiation of the matrix under a number of conditions ($\lambda > 300$, $\lambda = 342 \pm 10$, $\lambda > 497$, or $\lambda = 544 \pm 10$ nm) causes disappearance of carbene **1** and exclusive growth of cyclopropene **2**. Shorter wavelength photolysis ($\lambda = 290 \pm 10$ nm) triggers reversion of **2** back to **1**. Conversion of either compound to 4,5-benzocyclohepta-1,2,4,6-tetraene (**6**), 2-naphthylcarbene (**8**), or 2,3-benzobicyclo-[4.1.0]hepta-2,4,6-triene (**9**) was not observed under any of our experimental conditions. Matrix isolated cyclobuta[*de*]naphthalene (**4**) disappears slowly upon prolonged UV irradiation ($\lambda > 200$ nm), affording a trace of triplet 1-naphthylcarbene (**1**).

Introduction

Understanding the fundamental principles and mechanisms behind carbene reactivity is a longstanding goal in the study of reactive organic intermediates. Significant attention has focused on intramolecular reactions of carbenes, and, in particular, on the reversible interconversion between divalent carbenes and isomeric, high-energy, tetravalent structures.[1] The fascinating intramolecular rearrangements of phenylcarbene involve cyclized, ring-expanded, and ring-contracted intermediates, depending on the particular reaction conditions.[2,3] Although naphthylcarbenes are simply benzannelated versions of phenylcarbene, the rearrangement chemistry of the two systems contrasts sharply. Naphthylcarbenes **1** and **8** display photochemical cyclization to cyclopropenes **2** and **9**, respectively (Scheme 1),[4] while the corresponding cyclopropene inter-
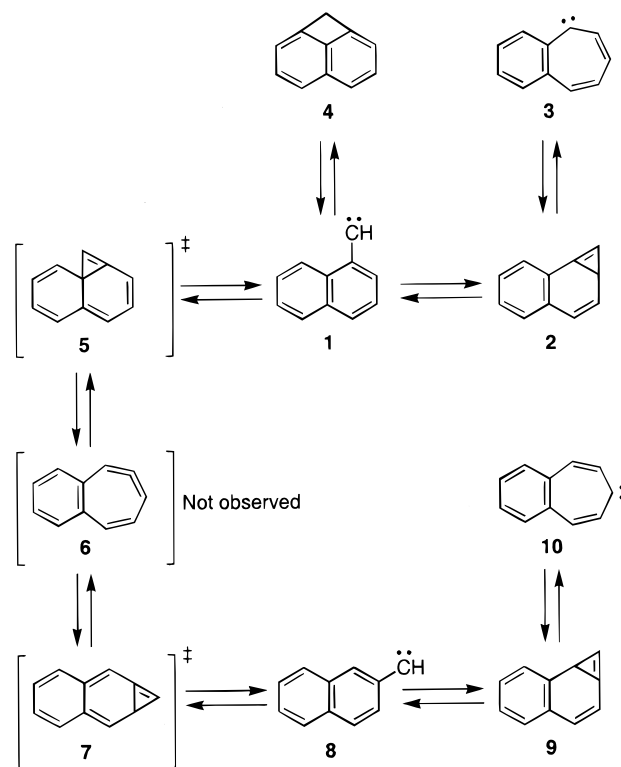
Scheme 1

(1) (a) Jones, W. M.; Brinker, U. H. In *Pericyclic Reactions*; Marchand, A. P., Lehr, R. E., Eds.; Academic Press: New York, 1977; Vol. 1, Chapter 3. (b) Jones, W. M. In *Rearrangements in Ground and Excited States*; deMayo, P., Ed.; Academic Press: New York, 1980; Vol. 1, Chapter 3. (c) Wentrup, C. In *Reactive Intermediates*; Abramovitch, R. A., Ed.; Plenum Press: New York, 1980; Vol. 1, Chapter 4. (d) Gaspar, P. P.; Hsu, J.-P.; Chari, S.; Jones, M. *Tetrahedron* **1985**, *41*, 1479−1507. (e) Platz, M. S.; Maloney, V. M. In *Kinetics and Spectroscopy of Carbenes and Biradicals*; Platz, M. S., Ed.; Plenum Press: New York, 1990; Chapter 8. (f) Wentrup, C. In *Methoden der Organische Chemie* (*Houben-Weyl*); Regitz, M., Ed.; G. Thieme Verlag: Stuttgart, 1989; Vol. E19b, pp 824−976. (g) Platz, M. S. *Acc. Chem. Res.* **1995**, *28*, 487−492.

(2) (a) West, P. R.; Chapman, O. L.; LeRoux, J.-P. *J. Am. Chem. Soc.* **1982**, *104*, 1779−1782. (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*, 2456−2469.

(3) (a) Matzinger, S.; Bally, T.; Patterson, E. V.; McMahon, R. J. *J. Am. Chem. Soc.* **1996**, *118*, 1535−1542. (b) Wong, M. W.; Wentrup, C. *J. Org. Chem.* **1996**, *61*, 7022−7029. (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*, 7030−7039. (d) Patterson, E. V.; McMahon, R. J. *J. Org. Chem.* **1997**, *62*, 4398−4405.

(4) (a) West, P. R.; Mooring, A. M.; McMahon, R. J.; Chapman, O. L. *J. Org. Chem.* **1986**, *51*, 1316−1320. (b) Albrecht, S. W.; McMahon, R. J. *J. Am. Chem. Soc.* **1993**, *115*, 855−859. (c) West, P. R. Ph.D. Dissertation, University of California, Los Angeles, 1981.

mediate in the phenylcarbene system exists in a potential energy well so shallow that it remains experimentally unobserved (Scheme 2).[2,3] Whereas phenylcarbene exhibits a facile ring expansion to the allene, cyclohepta-1,2,4,6-tetraene,[2,5] a ring-expanded intermediate has not been definitively characterized in the naphthylcarbene system. Nonetheless, 4,5-benzocyclohepta-1,2,4,6-tetraene (**6**) is believed to be a key intermediate

Scheme 2

Not observed
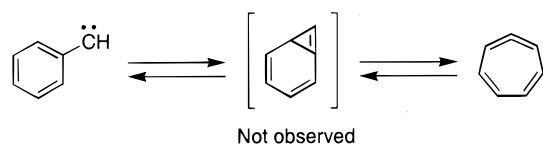
Scheme 3
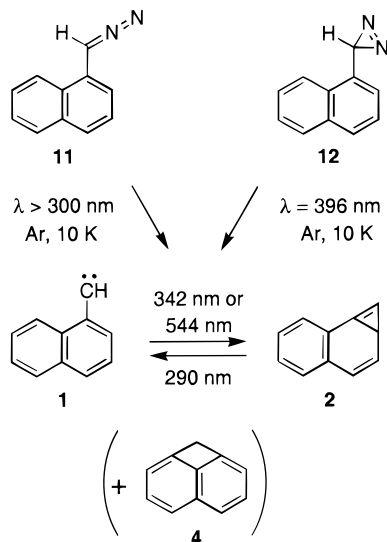
in the thermal interconversion of isomeric 1- and 2-naphthyl-carbenes.[1,4,6] A recent computational investigation afforded several important insights concerning the naphthylcarbene ($C_{11}H_8$) ground-state potential energy surface.[6] One significant result concerns benzobicyclo[4.1.0]heptatrienes **5** and **7**. Long postulated as intermediates in naphthylcarbene chemistry (Scheme 1),[1] both **5** and **7** are computed to be transition states at the B3LYP/6-31G* level of theory.[6] These insights notwithstanding, various important questions concerning structure, spectroscopy, thermal chemistry, and photochemistry of $C_{11}H_8$ intermediates remain unanswered.

In this article, we present a series of matrix isolation experiments involving the spectroscopic characterization and photochemistry of 1-naphthylcarbene (**1**), 4,5-benzobicyclo-[4.1.0]hepta-2,4,6-triene (**2**), and cyclobuta[*de*]naphthalene (**4**) (Scheme 3). Despite the long-standing interest in naphthylcarbene chemistry,[1,4,6–17] these studies provide the first description of the reversible photoequilibrium between **1** and **2**, as well as the first detailed characterization of 1-naphthylcarbene by infrared and UV/visible spectroscopy and 4,5-benzobicyclo-[4.1.0]hepta-2,4,6-triene by UV/visible spectroscopy. In a result reminiscent of our earlier study of 2-naphthylcarbene,[4b] we find no evidence for rearrangement of 1-naphthylcarbene (**1**) to 2-naphthylcarbene (**8**) under any of our photolysis conditions. Interestingly, prolonged UV irradiation of cyclobuta[*de*]naphthalene affords a small amount of the ring-opening product, 1-naphthylcarbene (**1**).

Background

The ESR spectrum of triplet 1-naphthylcarbene (**1**) in benzophenone at 77 K was reported by Trozzolo, Wasserman, and Yager.[7] Restricted

rotation about the aryl–carbene bond gives rise to two observable rotational isomers.[7–9] The unfavorable steric interaction between the C–H bonds at the carbene center and the 8-position of the naphthalene ring causes the *s-Z* rotamer (**1b**) to lie ca. 1 kcal/mol higher in energy than the *s-E* rotamer (**1a**).[6] Senthilnathan and Platz estimated the barrier

1a (*s-E*) **1b** (*s-Z*)
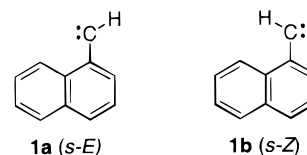
for interconversion of the *s-E* and *s-Z* isomers to be greater than 4.5–6.3 kcal/mol.[8] Carbene **1**, generated from the corresponding diazo or diazirine precursor, has been chemically intercepted in solution with a variety of trapping agents.[10] Griffin and Horn observed the transient electronic absorption spectrum of triplet 1-naphthylcarbene ($\lambda_{max} = 355$ nm) following laser flash photolysis of 1-naphthyldiazomethane (**11**) in 2,2,4-trimethylpentane solution.[10a] Neither the infrared spectrum nor the fluorescence spectrum of triplet 1-naphthylcarbene have been reported, although the corresponding spectra of triplet 2-naphthylcarbene are known.[4b,11]

In terms of chemical reactivity, vinyl carbenes undergo reversible thermal and photochemical ring closure to cyclopropenes.[12,13] Chemical trapping experiments provide evidence for a similar cyclization of naphthylcarbenes to benzobicyclo[4.1.0]hepta-2,4,6-trienes. Coburn and Jones trapped 2,3-benzobicyclo[4.1.0]hepta-2,4,6-triene (**9**), generated via rearrangement of 4,5-benzocycloheptatrienylidene (**10**), as a Diels–Alder adduct.[14] Billups and co-workers demonstrated the existence of bicyclo[4.1.0]heptatriene derivatives as discrete intermediates by chemical trapping studies.[15] Albrecht and McMahon monitored a photoequilibrium between matrix-isolated 2-naphthylcarbene (**8**) and 2,3-benzobicyclo[4.1.0]hepta-2,4,6-triene (**9**) by IR, UV/visible, and ESR spectroscopy.[4b] West et al. recorded the infrared spectrum of 4,5-benzobicyclo[4.1.0]hepta-2,4,6-triene (**2**) upon irradiation of matrix-isolated 1-naphthyldiazomethane (**11**), but the inability to detect 1-naphthylcarbene precluded the conclusion that cyclopropene **2** arose as a direct result of carbene cyclization.[4a,c]

Cyclobuta[*de*]naphthalene (**4**) is the major product obtained in the flash vacuum pyrolysis of both 1-naphthyldiazomethane (**11**) and 2-naphthyldiazomethane (**13**) (Scheme 4).[4a,16] Small amounts of **4** are also formed upon irradiation of 1-naphthyldiazomethane (**11**) or 4,5-benzobicyclo[4.1.0]hepta-2,4,6-triene (**2**) in low-temperature matrices.[4a,c] The stable hydrocarbon **4**, formally the result of C–H bond insertion in 1-naphthylcarbene, has been calculated as the global minimum on this portion of the $C_{11}H_8$ potential energy surface.[6] Becker and Wentrup proposed the interconversion between 1- and 2-naphthylcarbene, via a 4,5-benzocyclohepta-1,2,4,6-tetraene (**6**) intermediate, to rationalize the

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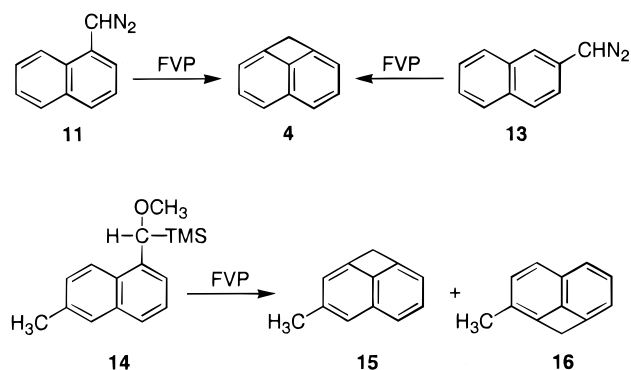
(12) (a) Closs, G. L.; Krantz, K. D. *J. Org. Chem.* **1966**, *31*, 638. (b) Closs, G. L.; Closs, L. E. *J. Am. Chem. Soc.* **1963**, *85*, 99–104. (c) Closs, G. L.; Closs, L. E.; Böll, W. A. *J. Am. Chem. Soc.* **1963**, *85*, 3796.

(13) (a) Misslitz, U.; de Meijere, A. In *Methoden der Organische Chemie* (*Houben-Weyl*); Regitz, M., Ed.; G. Thieme Verlag: Stuttgart, 1989; Vol. E19b, pp 664–755. (b) Gajewski, J. J. *Hydrocarbon Thermal Isomerizations*; Academic: New York, 1981; pp 21–27. (c) Berson, J. A. In *Rearrangements in Ground and Excited States*; deMayo, P., Ed.; Academic: New York, 1980; Vol. 1, pp 315–322. (d) Padwa, A. *Acc. Chem. Res.* **1979**, *12*, 310–317. (e) Reference 1a, pp 123–136.

(14) Coburn, T. T.; Jones, W. M. *J. Am. Chem. Soc.* **1974**, *96*, 5218–5227.

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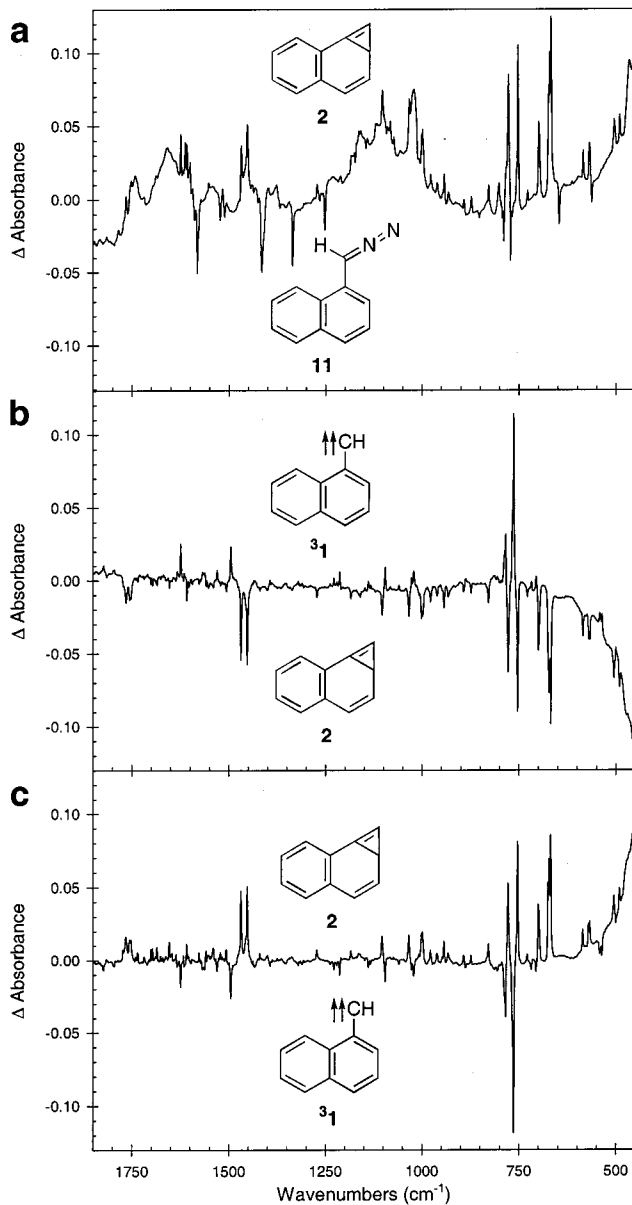
Scheme 4

Figure 1. (a) IR difference spectrum showing spectral changes upon photolysis ($\lambda > 300$ nm, 30 min, 100% conversion) of 1-naphthyldiazomethane (**11**) in argon at 10 K. The spectrum shows disappearance of **11** and appearance of 4,5-benzobicyclo[4.1.0]hepta-2,4,6-triene (**2**). (b) IR difference spectrum showing spectral changes upon photolysis ($\lambda = 290 \pm 10$ nm, 39 h, 100% conversion) of cyclopropene **2** (Ar, 10 K). The spectrum shows disappearance of **2** and growth of carbene **1**. (c) IR difference spectrum showing spectral changes upon photolysis ($\lambda > 497$ nm, 90 min, 100% conversion) of carbene **1**. The spectrum shows disappearance of **1** and reappearance of **2**.

formation of **4**.[16] Engler and Shechter later invoked the same carbene–carbene rearrangement to explain the production of both 3- and 2-methyl-1*H*-cyclobuta[*de*]naphthalene (**15** and **16**) from pyrolysis of 6-methyl-1-naphthylcarbene precursor **14** (Scheme 4).[17] Using flash vacuum pyrolysis followed by matrix isolation trapping, West et al. observed **4**, along with a small amount of a second product, common to the pyrolysis of both 1- and 2-naphthyldiazomethane. Although tentatively identified as allene **6**,[4a] the second species has yet to be characterized unequivocally. Recent calculations by Xie et al. support the assignment of 4,5-benzocyclohepta-1,2,4,6-tetraene (**6**) as an intermediate between the isomeric carbenes **1** and **8**.[6] Nevertheless, the circumstantial nature of the experimental evidence for **6** means that the mechanism for naphthylcarbene isomerization remains enigmatic.

Results and Discussion

Characterization of Photoproducts. Irradiation ($\lambda > 300$ nm, 30 min) of 1-naphthyldiazomethane (**11**) isolated in an argon matrix at 10 K results in complete disappearance of **11** accompanied by appearance of 4,5-benzobicyclo[4.1.0]hepta-2,4,6-triene (**2**), a small amount of 1-naphthylcarbene (**1**), and a trace amount of cyclobuta[*de*]naphthalene (**4**) (Scheme 3; Figures 1 and 2).[18] (The detailed justification for the structural assignments of carbene **1** and cyclopropene **2** is presented below.) IR and UV/visible spectra rule out the formation of 1-naphthyldiazirine (**12**). Cyclopropene **2** and hydrocarbon **4** presumably arise as secondary photoproducts of carbene **1**. Because of the strongly overlapping absorption spectra of **11** and **1** (Figure 2), we have not found conditions that permit selective irradiation of the diazo compound **11** without coincidental absorption by carbene **1**. In an attempt to circumvent the complications caused by these overlapping absorptions, we employed 1-naphthyldiazirine (**12**) as an alternate precursor to **1**. The absorption maximum of 1-naphthyldiazirine is reasonably well separated from the absorption maxima of diazo compound **11** and carbene **1** (Figure 2). Band-pass irradiation ($\lambda = 396 \pm 10$ nm, 4 h) of diazirine **12** results in complete disappearance of **12** and the appearance of diazo compound **11**, carbene **1**, and a trace amount of cyclopropene **2**.[19] This suggests that 1-naphthyldiazirine (**12**) may give 1-naphthylcarbene (**1**) directly,[20] although we cannot preclude the possibility of **1** also being formed by decomposition of a vibrationally excited diazo compound. Independent control experiments demonstrate that

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(17) Engler, T. A.; Shechter, H. *Tetrahedron Lett.* **1982**, *23*, 2715–2718.

(18) In this experiment, cyclobuta[*de*]naphthalene (**4**) is detectable only by UV/visible spectroscopy (Figure 2). The concentration of **4** in the matrix remains constant throughout subsequent photolyses.

(19) Information available as Supporting Information.

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under these irradiation conditions diazo compound **11** is stable, while carbene **1** slowly equilibrates with cyclopropene **2** (1:1 ratio after 4 h). Broad-band photolysis ($\lambda > 300$ nm, 30 min) of diazirine **12** in an argon matrix at 10 K gives complete disappearance of **12** with concurrent growth of 1-naphthyldiazomethane (**11**), 1-naphthylcarbene (**1**), and 4,5-benzobicyclo-[4.1.0]hepta-2,4,6-triene (**2**) in a ratio of approximately 1.4:1.3:1.[19] Continued irradiation ($\lambda > 300$ nm, additional 20 min) completes the transformation of diazo compound **11** to a mixture of carbene **1** and cyclopropene **2**. In the initial photolysis of diazirine **12** at $\lambda > 300$ nm, it is unclear whether carbene **1** is formed directly from the diazirine or whether it arises entirely as a result of secondary photolysis of diazo compound **11**.
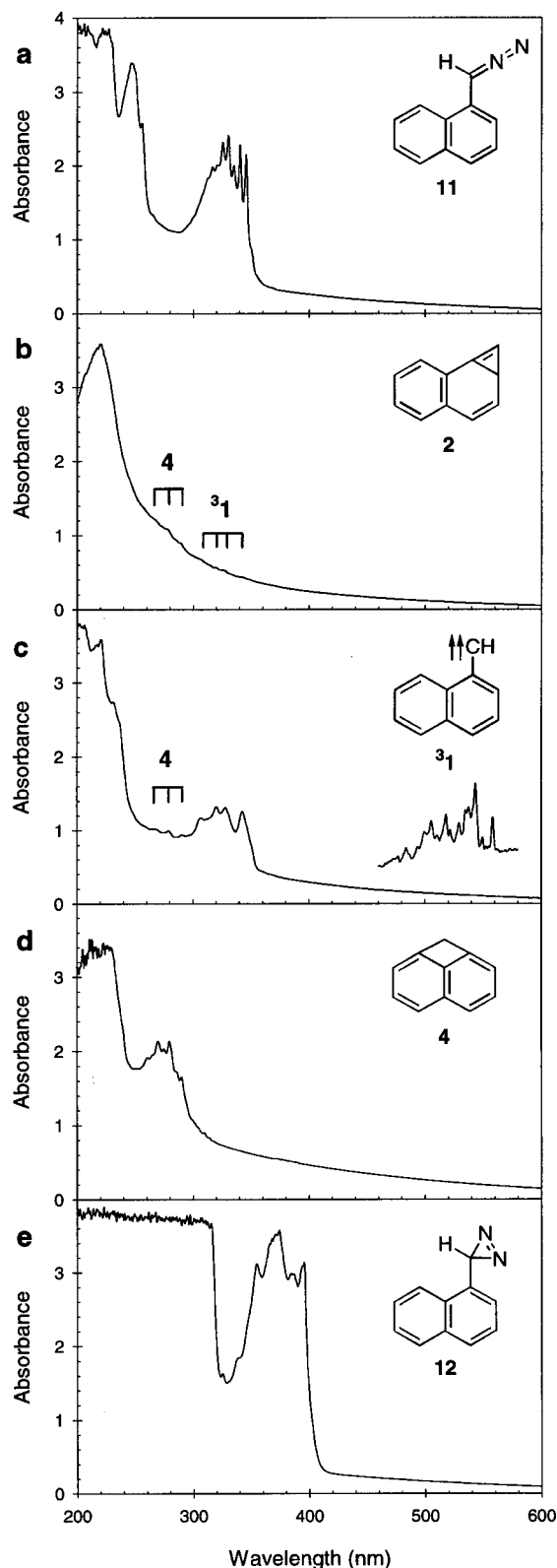
Figure 2. (a) UV/visible spectrum of 1-naphthyldiazomethane (**11**) in argon at 10 K. (b) Spectrum of 4,5-benzobicyclo[4.1.0]hepta-2,4,6-triene (**2**) obtained after photolysis ($\lambda > 300$ nm, 15 min, 100% conversion) of diazo compound **11**. Trace amounts of 1-naphthylcarbene (^{3}**1**) and cyclobuta[*de*]naphthalene (**4**) are also present. (c) Resultant spectrum of 1-naphthylcarbene (^{3}**1**) following photolysis ($\lambda = 290 \pm 10$ nm, 88 h) of tricyclic compound **2**. Inset: The weak absorptions in the visible region were observed in a separate experiment utilizing a thicker matrix. (d) Spectrum of authentic cyclobuta[*de*]naphthalene (**4**) (Ar, 10 K). (e) Spectrum of authentic 1-naphthyldiazirine (**12**) (Ar, 10 K) taken during the IR experiment.
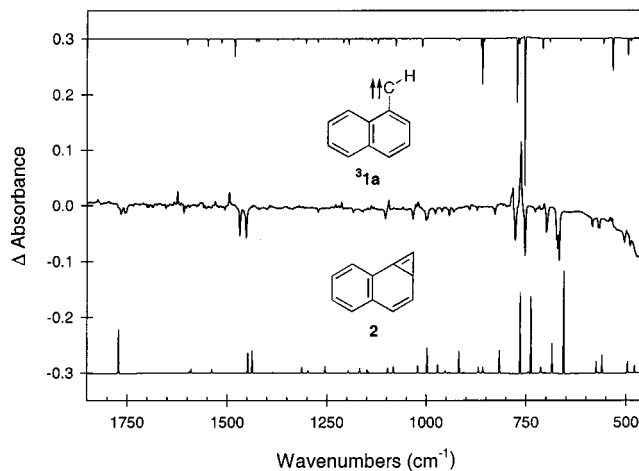
Figure 3. Top: Computed (B3LYP/6-31G*, scaled by 0.9613) IR spectrum of *s-E*-1-naphthylcarbene (**1a**). Center: IR difference spectrum showing appearance of carbene **1** and disappearance of cyclopropene **2** upon irradiation at $\lambda = 290 \pm 10$ nm. Bottom: Computed (B3LYP/6-31G*, scaled by 0.9613) IR spectrum of 4,5-benzobicyclo[4.1.0]hepta-2,4,6-triene (**2**).

Triplet 1-naphthylcarbene (**1**) was characterized by infrared, UV/visible, and ESR spectroscopy: IR (Ar, 10 K) 3069 m, 3059 m, 1897 w, 1823 w, 1495 m, 1228 m, 1213 m, 1095 m, 1021 m, 784 s, 764 s, 718 w, 706 w, 542 w, 536 w cm^{-1}; UV/visible (Ar, 10 K) λ_{max} 558, 550, 544, 538, 535, 530, 522, 518, 511, 506, 500, 484, 343, 328, 320, 307, 231 nm; ESR (Ar, 16 K) *s-Z*-isomer (**1b**) $|D/hc| = 0.4390$ cm^{-1}, $|E/hc| = 0.0223$ cm^{-1}, $Z_1 = 1276$ G, $X_2 = 4788$ G, $Y_2 = 5682$ G, $Z_2 = 8088$ G; *s-E*-isomer (**1a**) $|D/hc| = 0.4610$ cm^{-1}, $|E/hc| = 0.0201$ cm^{-1}, $Z_1 = 1516$ G, $X_2 = 4904$ G, $Y_2 = 5715$ G, $Z_2 = 8322$ G; microwave frequency $= 9.536$ GHz. The zero-field splitting parameters closely match those previously reported for 1-naphthylcarbene.[7] Our experiments allow us to obtain the first detailed UV/visible spectrum of 1-naphthylcarbene.[21] The series of weak, highly structured bands ($\lambda_{max} = 558-484$ nm) arises from vibronic coupling and is characteristic of triplet arylcarbenes[22] and doublet arylmethyl radicals.[23] The absorption spectrum of **1** closely parallels that of 2-naphthylcarbene (**8**), which displays similar weak bands from 561 to 486 nm.[4b] The strong infrared absorptions in the fingerprint region (784 and 764 cm^{-1}) are similar to those in 1-naphthyldiazomethane (**11**) (789 and 772 cm^{-1}). Such vibrations arise from CH out-of-plane deformations and are indicative of a naphthyl ring monosubstituted at the 1 position.[24] The frequency-scaled B3LYP/6-31G* computed infrared spectrum of carbene **1** closely matches that obtained experimentally (Figure 3).

4,5-Benzobicyclo[4.1.0]hepta-2,4,6-triene (**2**) was characterized by infrared and UV/visible spectroscopy: IR (Ar, 10 K) 3855 w, 3777 w, 3712 w, 3024 s, 2996 s, 2972 s, 1765 m, 1752 m, 1701 w, 1696 w, 1685 w, 1653 m, 1608 m, 1507 w, 1469 s, 1453 s, 1420 w, 1273 w, 1184 w, 1164 w, 1104 m, 1034 m, 999 m, 978 w, 961 w, 943 m, 933 w, 892 w, 873 w, 829 w, 778 s, 753 s, 700 s, 672 s, 668 s, 586 m, 570 w, 567 w,

(21) Due to the similar electronic absorptions of carbene **1** and its diazo precursor **11**, Griffin and Horn indicated that the true λ_{max} for 1-naphthylcarbene should be at a wavelength slightly shorter than the transient 355 nm peak that they observed.[10a] The absorption maximum that we observe (λ_{max} 343 nm) is consistent with Horn's description.

(22) For leading references, see: (a) McMahon, R. J.; Chapman, O. L.; Hayes, R. A.; Hess, T. C.; Krimmer, H. P. *J. Am. Chem. Soc.* **1985**, *107*, 7597−7606. (b) Reference 1e, p 311.

(23) Porter, G.; Strachan, E. *Trans. Faraday Soc.* **1958**, *54*, 1595−1604.

(24) Socrates, G. *Infrared Characteristic Group Frequencies*, 2nd ed.; Wiley & Sons: New York, 1994; pp 127−129.

505 w, 491 w, 418 w, 411 w cm^{-1}; UV/visible (Ar, 10 K) λ_{max} 220 nm. The UV/visible spectrum of cyclopropene **2** is nearly featureless (one broad absorption at 220 nm), and is quite similar to the spectrum of the closely related 2,3-benzobicyclo[4.1.0]-hepta-2,4,6-triene (**9**) obtained upon photolysis of 2-naphthyl-carbene (**8**).[4b] The weak infrared bands at 1765 and 1762 cm^{-1} are characteristic of substituted cyclopropenes.[12b] Furthermore, the experimental IR spectrum of **2** compares well with the calculated, scaled B3LYP/6-31G* spectrum (Figure 3). Alternate photoproducts such as cyclopropene **5** and allene **6** can be ruled out on the basis of their drastically different computed infrared spectra.[19]

Description of Photoequilibrium. A photoequilibrium between 1-naphthylcarbene (**1**) and 4,5-benzobicyclo[4.1.0]hepta-2,4,6-triene (**2**) can be directly observed by infrared and UV/visible spectroscopy. As described above, a mixture of carbene **1** and cyclopropene **2** can be prepared by broad-band photolysis ($\lambda > 300$ nm) of 1-naphthyldiazomethane (**11**) matrix isolated in argon at 10 K (Scheme 3; Figures 1 and 2). Irradiation of the resultant mixture under conditions where triplet carbene **1** absorbs strongly but cyclopropene **2** does not ($\lambda > 300$, $\lambda = 342 \pm 10$, $\lambda > 497$, $\lambda = 544 \pm 10$ nm) results in the disappearance of the infrared, UV/visible, and ESR spectroscopic bands attributed to **1** and a corresponding growth of the infrared and UV/visible peaks assigned to cyclopropene **2**. The ratio of *s-Z*:*s-E* rotamers of carbene **1** does not change during photolysis.[25–27] Irradiation of the matrix under conditions where cyclopropene **2** absorbs strongly but carbene **1** does not ($\lambda = 290 \pm 10$ nm) induces rearrangement of **2** to **1**. The photo-equilibration of 1-naphthylcarbene and 4,5-benzobicyclo[4.1.0]-hepta-2,4,6-triene appears to be highly reversible through several cycles. Thermal equilibration of carbene **1** and cyclopropene **2** does not occur under our reaction conditions; both species are thermally stable at 10 K.

Photochemistry of Cyclobuta[*de*]naphthalene (4). Control experiments demonstrate that cyclobuta[*de*]naphthalene (**4**) is unreactive in argon at 10 K under the irradiation conditions employed in probing the photoequilibrium between carbene **1** and cyclopropene **2** ($\lambda = 290 \pm 10$, $\lambda > 300$, $\lambda = 342 \pm 10$, or $\lambda > 497$ nm). At shorter wavelengths, the electronic transitions in **4** become accessible (Figure 2) and photochemistry ensues. Prolonged full arc irradiation ($\lambda > 200$ nm, 90 h) results in a slow, steady decrease in the signals for **4** accompanied by the appearance of weak spectroscopic signals: IR[28] (Ar, 10 K) 754 cm^{-1}; UV (Ar, 10 K) λ_{max} 603, 483, 456, 360, 340, 327 nm; ESR (Ar, 14 K) 648, 912, 1456, 1513, 1670, 4895 G; microwave frequency = 9.538 GHz. The ESR signals at 1513 and 4895 G correspond to the most intense transitions (Z_1 and X_2) of triplet *s-E* 1-naphthylcarbene (**1a**) (Figure 4).[29] The infrared band at 754 cm^{-1} matches a strong absorption of
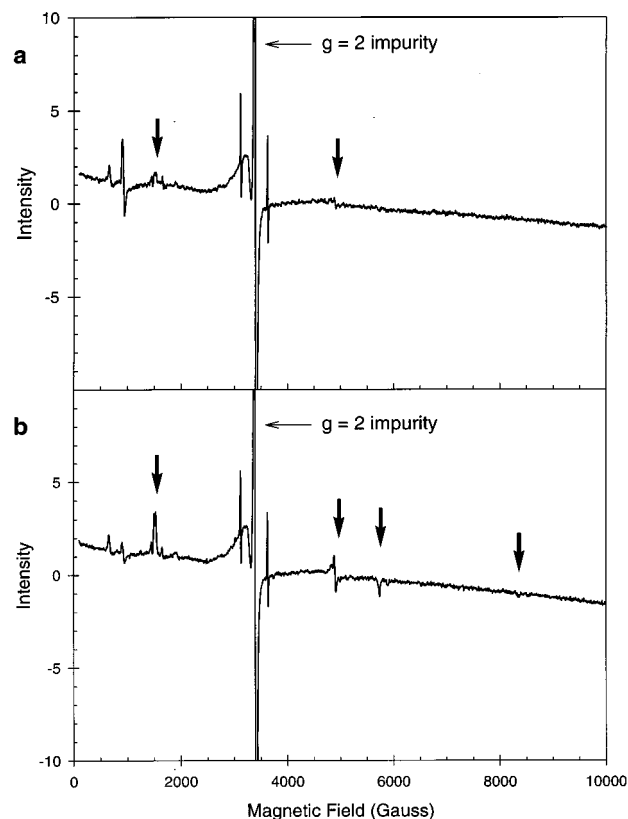
Figure 4. (a) ESR spectrum resulting from irradiation ($\lambda > 200$ nm, 15 h) of cyclobuta[*de*]naphthalene (**4**) isolated in an argon matrix at 15 K. Arrows indicate signals which arise from triplet 1-naphthylcarbene (**1**). (b) Spectrum showing an increased concentration of carbene **1** following irradiation at $\lambda = 290 \pm 10$ nm for 16 h.

cyclopropene **2**. Because the overall conversion of the photolysis is low, and because the most intense IR bands of **2** and **4** overlap significantly, we could not identify other IR peaks to corroborate the assignment of **2**. Subsequent irradiation ($\lambda = 290 \pm 10$ nm), using conditions known to convert cyclopropene **2** to carbene **1**, causes a substantial increase in the intensity of the triplet carbene spectrum (Figure 4). The signal is sufficiently strong to allow detection of one additional ESR band (5732 G) corresponding to the Y_2 transition of carbene **1a**, although the *s-Z* isomer still is not detected.[30] These results are consistent with a mechanism in which full arc irradiation of **4** affords carbene **1**, which itself persists in low, steady-state concentration because of the photoequilibrium with cyclopropene **2**. Indeed, independent experiments establish that under full arc photolysis

(25) The ratio of *s-E*:*s-Z* rotamers remains constant as observed by ESR spectroscopy. Additionally, all infrared bands attributed to **1** appear and disappear at the same rate.

(26) Recently, Khasanova and Sheridan observed two rotational isomers of 2-furylchlorocarbene by IR spectroscopy in a low-temperature matrix. The rotamers showed different rates of photochemical reaction upon irradiation at a wavelength 10–20 nm higher or lower than that of the apparent λ_{max} resulting from the overlapping absorption spectra of the two conformers. We attempted the analogous experiment with our system ($\lambda = 356 \pm 10$ nm). In this instance, however, the ratio of *s-E*:*s-Z* isomers of carbene **1** did not change.

(27) Khasanova, T.; Sheridan, R. S. *J. Am. Chem. Soc.* **1998**, *120*, 233–234.

(28) The subtle spectral changes are difficult to observe by infrared spectroscopy. Very few bands can be distinguished from the baseline and only the steady disappearance of **4** can be tracked with certainty.

(29) Because cyclobuta[*de*]naphthalene (**4**) was prepared by flash vacuum pyrolysis of 1-naphthyldiazirine (**12**), we speculated that a trace amount of diazirine contaminant in the matrix could be responsible for the ESR signal observed on photolysis of **4**. However, extended photolysis ($\lambda = 396 \pm 10$ nm) of **4** under conditions where diazirine **12** is known to afford triplet 1-naphthylcarbene (**1**) failed to produce the triplet ESR signal of carbene **1**.

(30) The other species produced by full arc irradiation of cyclobuta[*de*]-naphthalene are unidentified although some photochemical changes are observed spectroscopically. Full arc irradiation of hydrocarbon **4** shows no change by UV/visible spectroscopy, although subsequent photolysis ($\lambda = 290 \pm 10$ nm, 20 h) causes emergence of new UV/visible bands (λ_{max} 484, 416, 327, 316, 298, 284 nm). Further irradiation ($\lambda > 200$, $\lambda = 290 \pm 10$ or $\lambda > 300$ nm) produces no discernible change. The spectroscopic bands do not decay in the dark at 10 K, even over several hours. Full arc irradiation ($\lambda > 200$ nm) of **4** followed by broad-band photolysis ($\lambda > 497$ nm) results in complete disappearance of the 912 G ESR signal as well as the expected disappearance of carbene **1**. The 912 G signal can be partially regenerated by photolyzing at $\lambda = 290 \pm 10$ nm or completely regenerated by full arc irradiation. The intensity of the other ESR signals (648, 1456, 1670 G) does not change under any of the photochemical conditions.
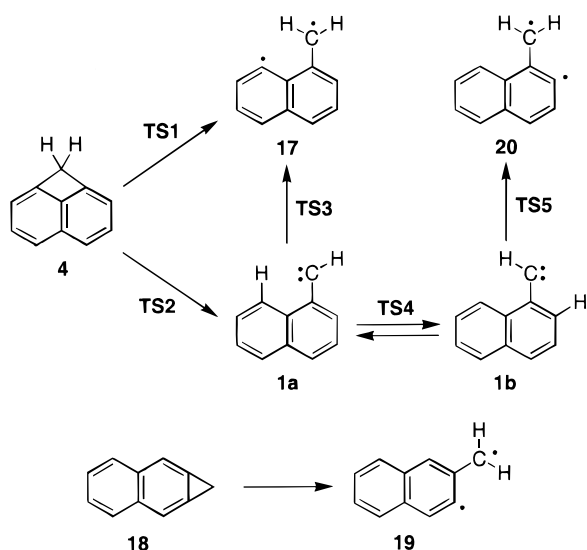
Scheme 5

Table 1. Computed Energies (B3LYP/6-31G*) for $C_{11}H_8$ Isomers

species	energy[a]	ZPVE[b]	rel energy + ZPVE[c]
^{1}**1a**	6.94	0.46	7.4
^{1}**1b**	8.41	0.38	8.8
^{3}**1a**	−423.8760769	0.149210	0.0
^{3}**1b**	0.95	−0.06	0.9
2	−0.40	1.08	0.7
4	−29.16	2.51	−26.7
5 (TS)	31.66	−0.68	31.0
6	−12.60	1.32	−11.3
^{1}**17**	0.33	−0.13	0.2
^{3}**17**	0.99	−0.03	1.0
^{1}**20**	4.59	−0.22	4.4
^{3}**20**	0.68	0.05	0.7
^{1}**TS1**	14.19	−0.36	13.8
^{1}**TS2**	40.25	−2.43	37.8
^{1}**TS3**	34.28	−3.36	30.9
^{1}**TS4**	21.83	−1.25	20.6
^{1}**TS5**	44.25	−2.51	41.7
^{3}**TS3**	30.31	−3.28	27.1
^{3}**TS4**	5.10	−0.97	4.1
^{3}**TS5**	53.08	−3.64	49.4

[a] Absolute energy for ^{3}**1a** in hartrees, energies relative to ^{3}**1a** in kcal/mol. [b] Total zero point vibrational energy for ^{3}**1a** in kcal/mol (unscaled), ZPVE relative to ^{3}**1a** in kcal/mol. [c] In kcal/mol.

($\lambda > 200$ nm), cyclopropene **2** slowly disappears to form small amounts of 1-naphthylcarbene and cyclobuta[*de*]naphthalene.[19]

The transformation of excited state **4** to triplet carbene **1** raises interesting mechanistic questions. One might imagine this process occurring either by C−C bond homolysis to yield diradical **17** followed by hydrogen migration to give **1** or by a carbene extrusion reaction to afford **1** directly (Scheme 5). In the isomeric naphtho[*b*]cyclopropene (**18**), photochemical C−C bond homolysis occurs upon Pyrex-filtered irradiation ($\lambda > 280$ nm) to afford the triplet diradical **19**.[31] Density functional theory calculations for the singlet ground-state potential energy surface predict barriers of 40.5 kcal/mol for C−C bond homolysis in **4** to give singlet **17** and 64.4 kcal/mol in **4** to give singlet 1-naphthylcarbene (**1a**) (Table 1). Although the ground state surface is not directly relevant to the photochemical rearrangement of **4** to **1**, these calculations establish that diradical **17** and carbene **1** are both energetically accessible upon $\lambda > 200$

(31) Pan, W.; Jones, M.; Esat, B.; Lahti, P. M. *Tetrahedron Lett.* **1998**, *39*, 1505−1508.

nm photolysis of cyclobuta[*de*]naphthalene (**4**) (photon energy < 143 kcal/mol). Not only are the singlet ground state of diradical **17** and the triplet ground state of carbene **1** virtually isoenergetic (ca. 26.7 kcal/mol above cyclobuta[*de*]naphthalene (**4**)), but the triplet state of diradical **17** and the (singlet) ground state of cyclopropene **2** lie less than 1 kcal/mol higher in energy (Table 1).[32,33]

As described above, full arc irradiation ($\lambda > 200$ nm) of **4** affords weak, as-yet unassigned signals in the ESR and UV/visible spectra. In this context, we gave further consideration to the spectroscopic and chemical properties expected of diradical **17** and its isomer, **20**. Formally, these diradicals may be considered as arising from 1-naphthylcarbene (**1**) by an intramolecular hydrogen shift (Scheme 5). Relative energies, computed at the level of B3LYP/6-31G*, are represented in Table 1. DFT calculations on these systems cannot be expected to be accurate to within 1 kcal/mol, which means that we cannot exclude the possibility that diradical **17** could give rise to the observed ESR signals, with the triplet as either the ground state or a low-lying, thermally accessible excited state. With greater certainty, the calculations predict a triplet ground state for the isomeric diradical **20**. Thus ^{3}**20**, which could arise from the photochemistry shown in Scheme 5, cannot be ruled out as a carrier of the observed ESR signals. Furthermore, the computed IR spectra for ^{1}**20** and ^{3}**20** display intense absorptions in the vicinity of 754 cm^{-1}, thereby preventing the exclusion of these species as carriers of the experimentally observed IR absorption. Finally, we recommend due caution in considering structural assignments for these weak ESR and UV/visible signals. Additional work, employing different precursors, will be required to clarify these matters.

Summary

1-Naphthylcarbene (**1**) and 4,5-benzobicyclo[4.1.0]hepta-2,4,6-triene (**2**) exist in a reversible photoequilibrium in argon at 10 K, as characterized by infrared, UV/visible, and ESR spectroscopy. Cyclobuta[*de*]naphthalene (**4**) undergoes, to a small extent, photochemical ring opening to 1-naphthylcarbene (**1**) under high-energy irradiation ($\lambda > 200$ nm). No evidence is obtained for the photochemical isomerization of 1-naphthylcarbene (**1**) to 2-naphthylcarbene (**8**).

Methods

Computational Methods. Calculations were performed with the Gaussian 98 package.[34] Because density functional methods adequately handle the geometries and energies of a variety of carbenes and diradicals,[3,6,35] we used the Becke three-parameter gradient-corrected

(32) Density functional theory often does not adequately handle open-shell singlet species.[33] Multireference or multiconfigurational techniques are better suited to these species. In this instance, the use of an alternate method would preclude a direct comparison of singlet **17** to the manifold of other species on the naphthylcarbene potential energy surface reported by Xie.[6]

(33) (a) Gräfenstein, J.; Kraka, E.; Cremer, D. *Chem. Phys. Lett.* **1998**, *288*, 593−602. (b) Cramer, C. J.; Smith, B. A. *J. Phys. Chem.* **1996**, *100*, 9664−9670 and references therein.

(34) Gaussian 98, Revision A.6, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. Gaussian Inc.: Pittsburgh, PA, 1998.

exchange functional[36] with the correlation functional of Lee, Yang, and Parr[37] (referred to as B3LYP). Closed-shell singlet states were computed using restricted wave functions, while triplet and open-shell singlet states were computed with unrestricted wave functions.[38,39] We utilized the 6-31G* basis set for geometry optimizations as well as single point energy and harmonic vibrational frequency calculations. The frequency calculations give the zero-point vibrational energy correction and verify each structure as a true minimum or transition state on the potential energy surface. Transition states were characterized by tracing atomic motion along the imaginary frequency or by an intrinsic reaction coordinate (IRC) calculation. Computed vibrational frequencies were scaled by a factor of 0.9613, as recommended by Wong.[40]

Matrix Isolation Spectroscopy. Techniques and apparatus for low-temperature matrix isolation spectroscopy are described elsewhere.[22a,41] Generally, the same deposition temperature of the sample and argon flow rate are used regardless of the particular instrumental technique employed.[42] The matrix thickness (i.e. the amount of sample) is the same for ESR and IR experiments, while a UV/visible matrix is thinner. Photolysis times differ depending on the instrumental technique employed. IR spectra were recorded on a Nicolet 740 FT-IR spectrometer equipped with a MCT-B detector. Ultraviolet/visible spectra were acquired with a Hitachi U-3210 spectrophotometer. ESR experiments were conducted on a Bruker ESP 300 spectrometer with a Bruker ER 042 MRH E microwave bridge and an EIP Model 625A microwave frequency counter. Zero-field splitting parameters were assigned by a best fit of the observed spectrum to the spin Hamiltonian[43] (assuming $g_x = g_y = g_z = g_e$).

General Experimental Methods. Dichloromethane was freshly distilled over CaH_2. Tetrahydrofuran was distilled first from CaH_2 followed by Na/benzophenone. Compounds from commercial sources gave acceptable ^1H NMR spectra and were used without further purification. Uncorrected melting points were measured in open capillaries with a Thomas-Hoover Unimelt apparatus. All ^1H NMR spectra were obtained with a 300 MHz Bruker AC 300 spectrometer, with chemical shifts reported in parts per million downfield from Me_4-Si. Mass spectra were obtained from a Kratos MS-80RFA with a DS55/DS90 detector.

1-Naphthaldehyde Tosylhydrazone. Freshly distilled 1-naphthaldehyde (1.0 g, 6.4 mmol; Aldrich) in 3 mL of absolute ethanol is added to a solution of *p*-toluenesulfonhydrazide (1.2 g, 6.4 mmol) in 6 mL of absolute ethanol. The slurry is refluxed for 30 min and half of the solvent removed by rotary evaporation. After standing overnight, the crude solid is collected by vacuum filtration and rinsed with a small portion of cold absolute ethanol. The off-white solid is recrystallized twice from absolute ethanol to obtain 1.5 g (72%) of pure tosylhydrazone: mp 132.0–132.6 °C (lit.[4a,44] mp 132–133 and 144–146 °C); ^1H NMR ($CDCl_3$) δ 2.36 (s, 3H), 7.29 (d, $J = 8.3$ Hz, 2H), 7.40 (t, $J = 7.8$ Hz, 1H), 7.50 (m, 2H), 7.69 (d, $J = 6.6$ Hz, 1H), 7.83 (d, $J = 7.5$ Hz, 2H), 7.95 (d, $J = 8.3$ Hz, 2H), 8.39 (s, 1H), 8.49 (s, 1H), 8.55 (m, 1H); mass spectrum m/z (rel intensity) 324 (M$^+$, 11), 278 (47), 169 (42), 156 (72), 139 (100), 127 (58), 91 (82); HRMS calcd for $C_{18}H_{16}N_2O_2S$ 324.0933, found 324.0944.

1-Naphthaldehyde Tosylhydrazone Lithium Salt. A solution of 1-naphthaldehyde tosylhydrazone (500 mg, 1.5 mmol) in 14 mL of dry THF is cooled to −78 °C and then treated with 0.75 mL (1.7 mmol) of 2.3 M *n*-butyllithium in hexane. The solution is warmed to room

temperature. Removal of the solvent by rotary evaporation and subsequent drying in vacuo gives a light orange solid that has a lifetime of several weeks when stored under nitrogen in a freezer.

1-Naphthyldiazomethane (11). The lithium salt of 1-naphthaldehyde tosylhydrazone (100 mg, 0.3 mmol) is placed in the bottom vial of a sublimation apparatus. The system is purged with dry nitrogen and evacuated to 0.02 mmHg, and the coldfinger is cooled to −78 °C. Red diazo compound accumulates on the coldfinger as the sublimation vial is slowly heated to 90 °C. The system is removed from the heat and vented to dry nitrogen as the coldfinger warms to room temperature. The red solid is rinsed into a deposition tube with dry CH_2Cl_2 and the solvent is removed under vacuum at −41 °C. The diazo compound (40 mg) is suitable for matrix isolation without further purification. The compound can be stored under nitrogen in a freezer for several weeks: mp 46.0–47.0 °C dec (lit.[10c] mp 41 °C); ^1H NMR ($CDCl_3$) δ 5.57 (s, 1H), 7.08 (dd, $J = 7.8$, 1.8 Hz, 1H), 7.40–7.59 (m, 4H), 7.68 (m, 1H), 7.82 (m, 1H); mass spectrum m/z (rel intensity) 168 (M$^+$, 33), 155 (15), 140 (100), 127 (13), 113 (7); HRMS calcd for $C_{11}H_8N_2$ 168.0687, found 168.0692. The sample is sublimed (room temperature, $\leq 10^{-6}$ mmHg) and co-deposited with argon to form a matrix: IR (Ar, 10 K) 3143 w, 3075 m, 3060 w, 2069 vs, 1594 m, 1582 s, 1522 w, 1512 w, 1469 s, 1452 s, 1415 s, 1336 s, 1266 w, 1252 m, 1173 w, 1146 w, 1093 w, 1012 w, 853 w, 789 s, 772 s, 647 m, 563 m cm^{-1}; UV/visible (CH_3CN, 298 K) λ_{max} (ϵ, M^{-1} cm^{-1}) 483 (50), 331 (12 600), 250 (19 300), 225 (29 700) nm; UV/visible (Ar, 10 K) λ_{max} 346, 341, 336, 331, 326, 321, 317, 313, 256, 247 nm.

1-Naphthyldiazirine (12). A 21 mL portion of 10 M dry methanolic ammonia is cooled to −41 °C in a three-neck round-bottom flask equipped with an addition funnel, dry ice condenser, and septum. Dropwise addition of a mixture of *tert*-butyl hypochlorite[45] (2.1 mL, 17.7 mmol) and *tert*-butyl alcohol (2.1 mL) via addition funnel is followed by warming of the system to −20 °C. Rapid addition of freshly distilled 1-naphthaldehyde (4.4 mL, 32.4 mmol; Aldrich) results in a pale yellow solution that is stirred at −20 °C for 1 h. The condenser is warmed and the solution stirs for an additional 10 h as the ammonia evaporates. A sticky yellow solid is isolated by vacuum filtration and then washed with 50 mL of ether to afford 1.36 g of 1,3,5-tris(1-naphthyl)-2,4,6-triazabicyclo[3.1.0]hexane[46] as a powdery white solid.[47] A portion of the white solid (1.0 g) is suspended in 9 mL of dry methanol at 0 °C under argon. Dropwise addition of *tert*-butyl hypochlorite (0.42 mL, 3.5 mmol) in the dark gives a pale yellow solution that is stirred in the dark for 1.5 h at 0 °C. The reaction mixture is poured into a solution of 8.3 g of $Na_2S_2O_5$ in 67 mL of water and stirred for 30 min. The resultant mixture is extracted with 3×10 mL of CH_2Cl_2 and the organic extracts combined, dried over Na_2SO_4, filtered, and concentrated to a yellow oil. The diazirine (**12**) is isolated by column chromatography (silica gel, CH_2Cl_2, highest R_f band): ^1H NMR ($CDCl_3$) δ 2.68 (s, 1H), 6.54 (dd, $J = 7.2$, 1.1 Hz, 1H), 7.36 (t, $J = 7.7$ Hz, 1H), 7.55 (td, $J = 8.1$, 1.5 Hz, 1H), 7.62 (td, $J = 8.4$, 1.5 Hz, 1H), 7.79 (d, $J = 8.3$ Hz, 1H), 7.90 (d, $J = 8.1$ Hz, 1H), 8.32 (d, $J = 8.5$ Hz, 1H); mass spectrum m/z (rel intensity) 168 (M$^+$, 3), 156 (23), 140 (100), 128 (27), 113 (8); HRMS calcd for $C_{11}H_8N_2$ 168.0687, found 168.0721. A matrix is formed by subliming a sample of diazirine (room temperature, $\leq 10^{-6}$ mmHg) and co-depositing with argon: IR (Ar, 10 K) 3108 w, 3077 m, 3065 m, 3026 w, 1626 s, 1621 s, 1609 m, 1602 m, 1590 m, 1574 m, 1516 m, 1448 w, 1404 s, 1333 m, 1269 m, 1248 m, 1180 w, 1171 w, 1146 w, 1098 m, 1057 m, 1055 m, 1029 m, 972 m, 857 w, 790 s, 773 s, 746 m, 730 w, 622 m, 570 m, 441 m, 425 w cm^{-1}; UV/visible (Ar, 10 K) 346, 341, 335, 331, 326, 321, 317, 313, 256, 247 nm.

Cyclobuta[*de*]naphthalene (4). A round-bottom flask containing 1-naphthyldiazirine (**12**) is fixed with an unpacked quartz tube followed by a cold trap (−78 °C). The system is evacuated to $\leq 10^{-2}$ mmHg and the quartz tube maintained at a temperature of 550–600 °C with a tube furnace. Gentle heating (40 °C) of the diazirine allows collection

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(37) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(38) Treatment of open-shell singlet species with hybrid DFT methods such as B3LYP often gives spin-contaminated results.[33,39] Structures ^{1}**17** and ^{1}**20** had spin-operator expectation values ($\langle S^2 \rangle$) of 1.07 and 1.03, respectively. Ideally, a singlet species should have $\langle S^2 \rangle = 0$.

(39) Marquardt, R.; Balster, A.; Sander, W.; Kraka, E.; Cremer, D.; Radziszewski, J. G. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 955–958 and references therein.

(40) Wong, M. W. *Chem. Phys. Lett.* **1996**, *256*, 391–399.

(41) Seburg, R. A.; McMahon, R. J. *J. Am. Chem. Soc.* **1992**, *114*, 7183–7189.

(42) The ratio of matrix to sample is always approximately 500:1.

(43) Wasserman, E.; Snyder, L. C.; Yager, W. A. *J. Chem. Phys.* **1964**, *41*, 1763–1772.

(44) Munshi, A. A.; Shah, N. M.; Trivedi, J. P. *Ind. J. Chem.* **1963**, *1*, 311–313.

(45) Teeter, H. M.; Bell, E. W. *Org. Synth.* **1952**, *32*, 20–22.

(46) Wright, B. Ph.D. Dissertation, Ohio State University, 1983.

(47) NMR and mass spectral characterization are complicated by the compound's insolubility in a wide variety of solvents.

of a dark gray solid in the cold trap. Column chromatography (silica gel, hexane, highest R_f band) affords cyclobuta[*de*]naphthalene (**4**) as a low-melting solid: ^{1}H NMR (CDCl$_3$) δ 4.80 (s, 2H), 7.11 (d, $J =$ 6.3 Hz, 2H), 7.46 (dd, $J = 8.5$, 6.2 Hz, 2H), 7.57 (d, $J = 8.5$ Hz, 2H). Sublimation of the material (-9 °C, $\leq 10^{-6}$ mmHg) and co-deposition with argon gives matrix-isolated cyclobuta[*de*]naphthalene: IR (Ar, 10 K) 2974 m, 2949 m, 2945 m, 1722 m, 1600 w, 1513 w, 1362 m, 1217 m, 1010 m, 791 s, 761 m, 529 m, 476 w cm^{-1}; UV/visible (Ar, 10 K) 314, 310, 291, 280, 275, 270, 265, 261, 251 nm.

Supporting Information Available: Spectral data for photochemical experiments on **11**, **12**, and **4**, Cartesian coordinates, and calculated IR spectra for selected structures in Table 1, and a scheme of relative energies of **1**, **17**, and **20** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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