Matrix isolation and photochemistry of 1- and 2-naphthylchlorocarbene

Pawel Rempala and Robert S. Sheridan *

Department of Chemistry, University of Nevada, Reno, NV 89557, USA

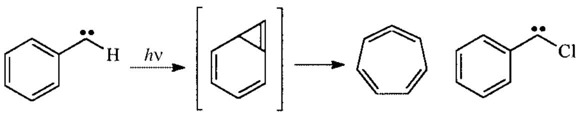
Received (in Cambridge, UK) 23rd June 1999, Accepted 14th September 1999

We have for the first time characterized the 1- and 2-naphthylchlorocarbenes by IR and UV/vis spectroscopy in N_2 matrices at 10 K. Although evidence suggests the presence of predominantly only one geometric isomer in the case of the 1-naphthylchlorocarbene, the IR and UV/vis spectra of the 2-naphthylchlorocarbene indicate two distinct conformations. With selective irradiation, the longer-wavelength absorbing *s-Z*-isomer of 2-naphthylchlorocarbene can be photochemically driven to the alternate *s-E* conformation. Irradiation of the 1- and 2-naphthylchlorocarbenes induces cyclization to 7-chloro-4,5-benzobicyclo[4.1.0]hepta-2,4,6-triene and 7-chloro-2,3-benzobicyclo[4.1.0]hepta-2,4,6-triene, respectively. The cyclization can be reversed by irradiation at shorter wavelengths.

Our results on the *singlet* naphthylchlorocarbenes photochemical ring-closures parallel observations of Chapman, McMahon, and co-workers on the parent *triplet* 1- and 2-naphthylcarbenes (P. R. West, A. M. Mooring, R. J. McMahon and O. L. Chapman, *J. Org. Chem.*, 1986, **51**, 1316; S. W. Albrecht and R. J. McMahon, *J. Am. Chem. Soc.*, 1993, **115**, 855). In particular, under matrix isolation conditions, the naphthylcarbenes appear to photochemically only cyclize to the corresponding cyclopropenes, which in turn only photochemically ring-open back to the carbenes. Ring-expansion in these systems to benzocycloheptatetraenes is not detected.

Introduction

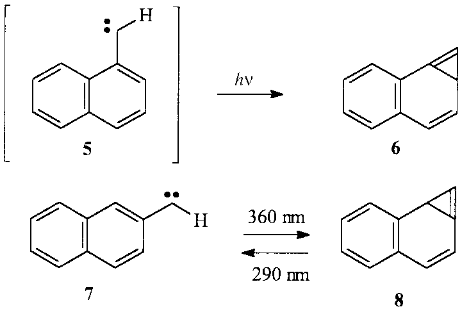
Phenylcarbene (**1**), with its status as the simplest aryl carbene and yet displaying a rich rearrangement chemistry, has been subjected to extensive experimental studies.[1] Similarly, **1** has received considerable attention from computational chemists, as evidenced by recent publications.[2] The triplet ground state of carbene **1** is well-established, and indeed triplet arylmethylene subunits have played a prominent role in attempts to engineer high-spin materials. On the other hand, phenylcarbene rearrangements are believed to all arise from the singlet state, lying *ca.* 4 kcal mol^{-1} higher in energy than the triplet.[2]



1 **2** **3** **4**

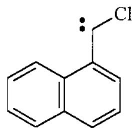
Phenylchlorocarbene (**4**) has long served as a spectroscopic prototype for singlet carbene solution chemistry, and similarly has been examined exhaustively.[3] The best estimate of the singlet–triplet gap in **4** is 7 kcal mol^{-1}, based on recent DFT calculations.[4] The reversal in energetic order of states compared to the parent **1** can be attributed to a combination of Cl lone-pair π-donation and σ-electron withdrawal in the singlet. Interestingly, whereas triplet phenylcarbene (**1**) undergoes photoinduced ring-expansion to give **3** extremely readily under low-temperature matrix isolation conditions, singlet **4** is quite robust when subjected to the same treatment. It has been suggested that ring-expansion of **4** takes place likewise under long-term irradiation.[5]

The triplet naphthylcarbenes present an interesting contrast to **1**. The 1- and 2-isomers, **5** and **7**, respectively, were first detected by EPR in organic matrices in 1965.[6] Both isomers were found to possess triplet ground states, and two sets of signals were found for each suggesting the presence of *s-Z*, *s-E* geometrical isomers.[7] Senthilnathan and Platz[8] explored the EPR of the two conformers of **7** in greater depth, and showed that interconversion did not occur thermally at low temperatures. Matrix isolation and solution experiments which have followed over the years have revealed chemistry which does not quite parallel that of **1** (Scheme 1). Although benzobicycloheptatriene **2** is a logical intermediate between **1** and its rearrangement product **3**, and has received the support of high-level *ab initio* calculations,[2a,b] this species has never been directly observed. However, Chapman and co-workers[9] reported that broad-band irradiation of matrix isolated diazo-precursors to carbenes **5** and **7** produced directly the corresponding benzobicycloheptatrienes **6** and **8**. McMahon and Albrecht[10] later showed that more careful irradiation of 2-diazomethylnaphthalene gave **7** in inert matrices, characterizable by IR, UV/vis, and EPR. The carbene could in turn be converted to **8** by judicious choice of photolysis wavelength, and conversely **8** could be converted back to carbene **7**. In contrast to phenylcarbene (**1**), neither of the naphthyl systems **5** nor **7** was observed to ring expand to benzocycloheptatetraenes. It should finally be noted that the chemistry of naphthylcarbenes has been investigated also by a variety of other methods in solid media[11] and in solution.[12]

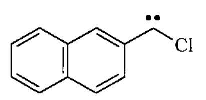


Scheme 1

In this context, we now report exploration for the first time of the *singlet* naphthylcarbenes, 1-naphthylchlorocarbene (**9**) and 2-naphthylchlorocarbene (**10**). We have found these species to



9



10

similarly undergo facile photochemical rearrangements reversibly in nitrogen matrices. Trapping experiments and *ab initio*/DFT calculations have been used to verify the identities of the various intermediates involved.

Experimental

Syntheses of precursors

NMR spectra were obtained on General Electric QE 300 (300 MHz at proton) or Varian Unity plus-500 (500 MHz at proton) instruments and were referenced to residual protio solvent. UV/Vis spectra were obtained on a modified Perkin-Elmer Lambda 4C UV/VIS spectrophotometer. IR spectra were recorded on a Perkin-Elmer System 2000 FT-IR spectrometer with 1 cm^{-1} resolution and are reported here for matrix isolated compounds (See also matrix isolation section).

The 1-naphthalenecarboxamidine[13] and 2-naphthalenecarboxamidine[14] necessary for 3-chloro-3-(*n*-naphthyl)diazirine syntheses ($n = 1$, 2) were described in the literature previously. Diazirines were prepared *via* modified Graham oxidation[15] of the corresponding amidines in which the DMSO solvent was replaced by methanol.[16]

3-Chloro-3-(1-naphthyl)diazirine (11). 1-Naphthalenecarboxamidine hydrochloride (0.20 g)[13] was dissolved in 12 ml of methanol, and 0.50 g of NaCl was added. Purechlor sanitizer (10 ml, 12.5% NaClO) was mixed with 2 g of NaCl and 0.11 g of NaOH. The resulting hypochlorite saturated with NaCl was filtered, and 6 ml of the solution was used in the Graham oxidation. The hypochlorite solution was added dropwise to the amidine salt solution in methanol (ice-bath cooled or kept at room temperature) over a period of 10 minutes. The mixture was stirred for 40 minutes at room temperature. To the resulting orange–yellow suspension 7 ml of water was added and the water–methanol phase was extracted with 3 × 15 ml of pentane. The pentane extract was dried with $MgSO_4$, then filtered through a ~5 cm layer of silica placed in a disposable Pasteur pipette. After evaporation of pentane *in vacuo*, 120 mg of diazirine as yellow oil was obtained (61% yield). ^{1}H NMR ($CDCl_3$, 500 MHz) δ_H [ppm, $CHCl_3$ 7.27 ppm] 8.77 (dd, 1H, $J = 8.5$ Hz, 1 Hz), 7.94 (dd, 2H, $J = 8.5$ Hz, 0.5 Hz), 7.79–7.74 (m, 2H), 7.65–7.62 (m, 1H), 7.48 (dd, 1H, $J = 8.5$ Hz, 7 Hz); ^{13}C NMR ($CDCl_3$, 300 MHz at proton) δ_C [ppm, $CDCl_3$ 77.23 ppm] 134.31, 131.90, 131.33, 130.31, 129.13, 127.63, 127.01, 125.43, 125.33, 124.31, 45.51 (C_{diaz}); UV/Vis (pentane) λ_{max}/nm 340, 350 (br); IR (N_2 matrix, 10 K) ν_{max}/cm^{-1} 3073 (w), 3063 (w), 2956 (w), 1575 (s), 1515 (m), 1401 (w), 1377 (w), 1350 (w), 1288 (w), 1252 (m), 1219 (w), 1214 (w), 1184 (m), 1174 (w), 1171 (w), 1167 (w), 1147 (w), 1128 (w), 1114 (w), 1058 (w), 1024 (w), 993 (m), 990 (m), 903 (w), 895 (s), 887 (w), 863 (w), 806 (m), 790 (vs), 774 (s), 659 (w), 650 (w), 636 (m), 550 (w), 527 (w), 514 (w).

3-Chloro-3-(2-naphthyl)diazirine (17). 2-Naphthalenecarboxamidine hydrochloride (0.20 g)[14] was subjected to modified Graham oxidation as described above for 1-naphthylcarboxyamidine hydrochloride, giving 110 mg of pale-yellow solid diazirine (56% yield). ^{1}H NMR (500 MHz) δ_H [ppm, $CHCl_3$ 7.27 ppm] 7.88–7.85 (m, 3H), 7.63 (d, 1H, $J = 2$ Hz), 7.57–7.54 (m, 2H), 7.20 (dd, 1H, $J = 2$, 9 Hz); ^{13}C NMR ($CDCl_3$, 300 MHz at proton) δ_C [ppm, $CDCl_3$ 77.23 ppm] 133.43, 133.20, 132.69, 128.66, 128.37, 127.86, 127.39, 127.20, 126.34, 122.72, 47.55 (C_{diaz}); UV/Vis (N_2 matrix, 10 K) λ_{max}/nm 324, 339, 359, 377, 399; IR (N_2 matrix, 10 K) ν_{max}/cm^{-1} 3071 (m), 1571 (vs), 1515 (m), 1372 (m), 1373 (m), 1361 (m), 1354 (m), 1281 (m), 1277 (m), 1223 (w), 1198 (m), 1190 (m), 1175 (w), 1164 (w), 1147 (w), 1133 (m), 1041 (m, br.), 1028 (m), 1117 (vs), 995 (w), 983 (w), 981 (w), 961 (m), 933 (m), 914 (m), 905 (w), 902 (w), 854 (m), 822 (m), 817 (m), 797 (m), 752 (m), 651 (w), 631 (w), 594 (w), 580 (m).

Matrix isolation experiments

General descriptions of the low temperature apparatus and matrix isolation techniques have been published previously.[17,18] Matrix isolation experiments were carried out in nitrogen matrices at 10 K, prepared by codeposition of sample and the carrier gas. Sample temperature during codeposition was +5 °C for 3-chloro-3-(1-naphthyl)diazirine (**11**) and room temperature for 3-chloro-3-(2-naphthyl)diazirine (**17**). Flow of the carrier gas was monitored by pressure decrease in the gas reservoir (3 L, typical pressure drop rate of 1–1.5 torr min^{-1} = 133–200 Pa min^{-1} was maintained, which at room temperature corresponds to gas flow of 0.16–0.24 mmol min^{-1}). In a typical experiment 170 torr of nitrogen was deposited (28 mmol) on a cold finger of a closed-cycle helium cryostat at 21 K (CsI window surface ≈ 4 cm^2). The matrix prepared at 21 K was cooled next to the working temperature (10 K). Although the amount of co-deposited photoprecursor could not be determined in our experimental setup directly, comparison was made with other matrices prepared from mixtures of volatile diazirines (3-chloro-3-(3-furyl)diazirine and phenylchlorodiazirine) and a matrix gas in known proportions (determined by pressure ratio). Integral intensity of the strong characteristic diazirine IR absorptions ~1600 cm^{-1} were measured for those matrices and compared (after adjustment for amount of deposited carrier gas) with the same parameter for chloronaphthyldiazirine matrices. Assuming similiar absolute IR absorption cross-sections, we conclude that chloronaphthyldiazirine matrices used in our study have dilution ratios of about 1 : 800.

A Mercury lamp (100 W) equipped with a grating monochromator (Photon Technology International) was used for most irradiations. A high-pressure xenon lamp (200 W) and appropriate filters were used for broad-band irradiations.

Density functional and *ab initio* calculations

GAUSSIAN94, Revision D.4 running on a Silicon Graphics Power Challenge computer was used for most calculations.[19] Geometry optimizations were followed by frequency calculations for B3LYP and MP2 methods. CIS calculations were performed on B3LYP/6-31G(d,p) optimized geometries, unless stated otherwise.

Results and discussion

Matrix isolation photochemistry of 3-chloro-3-(1-naphthyl)-diazirine

(1) Characterization of 1-naphthylchlorocarbene (9). Irradiation of a N_2 matrix containing isolated 3-chloro-3-(1-naphthyl)diazirine (**11**) at 10 K (366 nm, 70 m) caused the disappearance of starting material IR and UV/vis spectra, and concommitant appearance of new absorptions. The initial photoproduct exhibited most intense IR bands (Table 1) at 1217 and 752 cm^{-1}, and strong, structured absorptions in the UV/vis at 339, 364, 387, 402 and 426 nm (Fig. 1). A very weak and broad visible absorption in the range of 600–850 nm was just detectable. The logical assignment for this initial intermediate is singlet 1-naphthylchlorocarbene **9**. For confirmation, the carbene **9** was generated in a similar fashion in a nitrogen

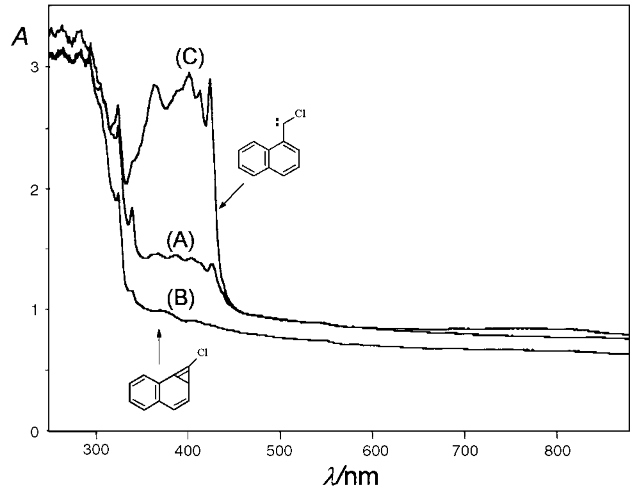


Fig. 1 UV/Vis spectrum of 10 K N_2 matrix containing initially 3-chloro-3-(1-naphthyl)diazirine (A) after 70 minutes of irradiation at 366 nm; (B) after additional 32 h of irradiation at 366 nm; (C) after regeneration of the 340–450 nm absorption band with 0.5 h of $\lambda > 270$ nm irradiation, followed by bleaching with 366 nm irradiation and finally 1 h of irradiation at 297 nm.

matrix doped with 0.3% HCl. Warming the matrix to 30 K caused the disappearance of the IR and UV/vis bands of **9**, and produced 1-(dichloromethyl)naphthalene (**12**) in the IR, as compared with the spectrum of authentic product.

Further support for this product assignment comes from DFT calculations. B3LYP/6-31(d,p) calculations predict two conformational energy minima for carbene **9**. The *s-E*-isomer, **9a**, was found to possess a planar C_s structure (0 imaginary frequencies). Interestingly, the calculated structure showed a small distortion of the carbene *toward* the 8-position, with a C^c–C^1–C^9 angle reduced to 114°, probably from Cl–H^2 repulsion. Phenylchlorocarbene (**4**) exhibits a similar distortion with a C–C–C angle of 112°. The *s-Z*-isomer **9b**, on the other hand, showed rather dramatic influence from steric congestion from the perinaphthyl position. A planar *syn* C_s isomer was found to be a rotational transition state, with one imaginary frequency. The corresponding energy minimum for **9b** was predicted to be twisted out-of-plane, with a C–C–C–Cl dihedral angle of 20°. Here, the C^c–C^1–C^9 angle was also distorted to 134.4°. Despite these deformations, however, the *s-Z*-isomer **9b** was found to be only 4 kcal mol^{-1} higher in energy than the **9a** isomer at this level of theory, vibrationally corrected. As is common in singlet arylcarbenes[4,20] a dominating geometric constraint is the alignment of the carbene p-orbital with the conjugating ring π-system. It was found that the B3LYP calculated IR spectra for the lower energy **9a** isomer fit the experimental spectra quite satisfactorily (Fig. 2, Table 1). The predicted spectrum for the twisted *s-Z*-isomer **9b** gave a significantly less favorable fit. We thus believe that it is the *s-E*-isomer primarily that is observed in our experiments.

For comparison, the *triplet s-E*-chlorocarbene, **9aT**, was also explored with DFT methods. UB3LYP/6-31G(d,p) calculations suggest that this isomer would be *ca.* 4 kcal mol^{-1} higher in energy than the corresponding singlet **9a**. The triplet, as expected, has a larger C^1–C^c–Cl bond angle (131.9°) than the singlet (112.8°), and also has a planar geometry. The IR spectrum predicted for the triplet **9aT** is completely different than experiment (Table 1).

The UV/vis spectrum associated with carbene **9** is more enigmatic. Phenylchlorocarbene (**4**) shows a strong band at 310 nm, and a very broad but weak absorption ranging from 600–850 nm (λ_{max} 750 nm).[21] Similarly, 2-furylchlorocarbene[20] shows corresponding bands at 330 and 600 nm. The long-wavelength absorptions have been assigned, based on CIS calculations, to σ–π* transitions arising from promotion of a lone-pair electron on the carbene center to the LUMO of the π-system. Similar visible excitations, albeit at shorter wavelengths, have been observed in alkylhalocarbenes, *viz.* 570 nm in *tert*-butylchlorocarbene,[22] 540 nm in adamantylchlorocarbene,[16] and 460 nm in cyclopropylchlorocarbene.[23] In the present case of the 1-naphthyl system **9**, the analogous weak visible absorption is at the limits of our detection, but we speculate that the strong UV band system (probably ππ*) is now moved out to the 320–426 nm region. We have found previously that CIS calculations, however, are only marginally successful in modeling the absolute wavelengths of these transitions in phenylchlorocarbene (**4**),[21] with excitations calculated at 531 and 233 nm *vs.* the observed 750 nm and 310 nm. Here CIS/6-31G(d,p) calculations on **9a** predict lowest energy transitions at 540 and 280 nm, so a significant red shift in the second excited state in the naphthyl series has some theoretical support. Verification of these tentative arguments must await higher-level calculations, which are in progress.

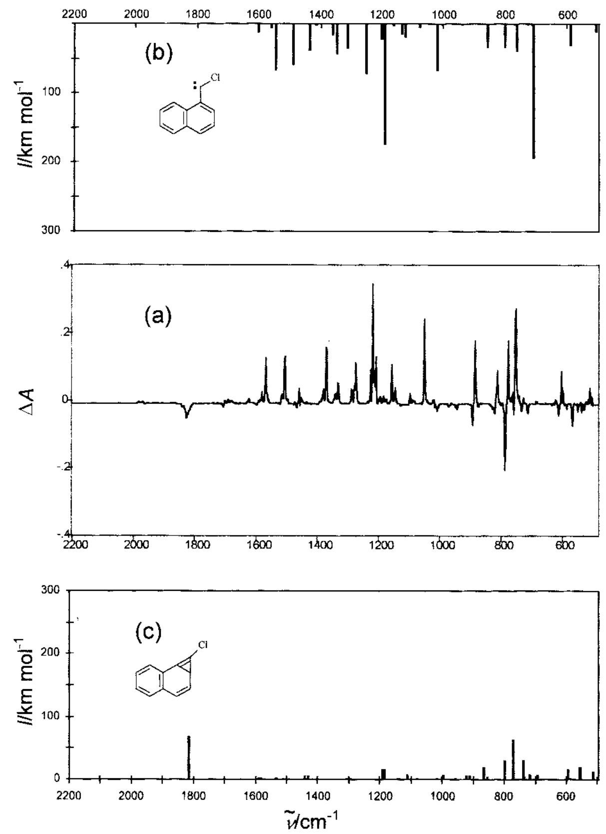


Fig. 2 (a) IR difference spectrum of the matrix described in Fig. 1(c) showing regeneration of 1-naphthylchlorocarbene upon 1 h irradiation at 297 nm (positive peaks) and consumption of cyclopropene **13** (negative peaks); (b) calculated B3LYP/6-31G(d,p) IR spectrum of 1-naphthylchlorocarbene, frequencies scaled by 0.96, absorptions pointing downward to facilitate comparison with Fig. 2(a); (c) IR spectrum calculated for **13** (same method and scaling factor as for 1-naphthylchlorocarbene).

(2) Photochemistry of 1-naphthylchlorocarbene (9). Prolonged irradiation (32 h) of matrices containing **9** at 366 nm slowly converted the 1-naphthylcarbene to a new species. The IR of **9** was replaced by a new spectrum distinguished by the presence of a band at 1826 cm^{-1}, together with other absorptions (Fig. 2). At the same time, the UV/vis spectrum assigned to **9** disappeared, leaving only absorption at wavelengths shorter than 340 nm (Fig. 1). This process was reversible. Hence, subsequent irradiation of the matrix with 297 nm light readily returned the IR and UV/vis spectra of carbene **9**. This cycle could be repeated several times.

Based on analogy to previous work on the parent 1- and 2-naphthylcarbenes,[9,10] a logical candidate for the new photoproduct is the chlorobenzobicycloheptatriene **13**. B3LYP/6-

Table 1 Experimental spectrum of the carbene **9** and calculated spectra of **9a** in its singlet and triplet states and **9b** in its singlet state (B3LYP/6-31G(d,p) frequencies scaled by 0.96)

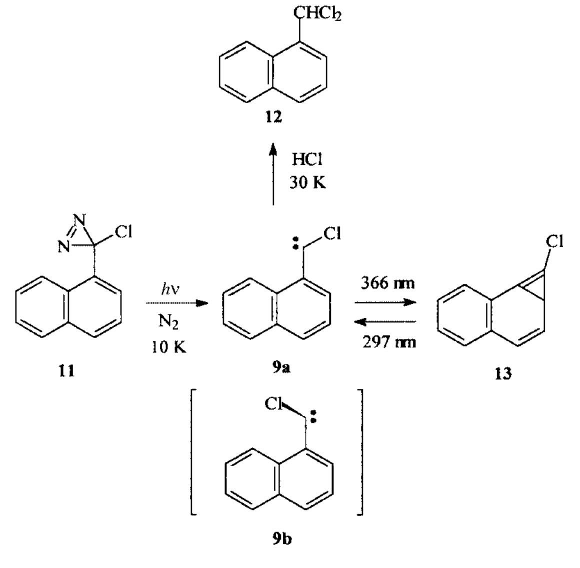
9 experimental		**9a singlet** calculated × 0.96		**9aT triplet** calculated × 0.96		**9b singlet** calculated × 0.96	
ν/cm^{-1}	I/I_{max} (%)	ν/cm^{-1}	I/I_{max} (%)	ν/cm^{-1}	I/I_{max} (%)	ν/cm^{-1}	I/I_{max} (%)
		46	0.7	77	0.1	46	0.5
		129	3.6	120	1.1	116	2.2
		169	2.5	146	3.8	165	2.3
		177	0.1	181	0.1	190	0.4
		214	0.2	252	2.5	262	5.2
		267	5.3	260	0.3	290	1.8
		397	0.0	400	1.1	398	4.4
		409	0.4	410	3.7	404	2.2
		459	0.2	461	0.1	464	1.0
		481	1.6	468	1.1	469	0.3
		507	0.1	508	0.3	508	2.7
510	13.9	508	6.0	527	8.9	523	26.2
598	11.2	590	16.0	595	3.8	566	7.3
603	27.5	615	0.0	610	0.6	616	5.6
621	2.5	711	100.0[a]	697	54.4	659	27.3
727	5.7	715	0.9	708	5.3	715	38.1
752	79.5	728	0.4	751	100.0[b]	730	25.6
775	52.5	764	20.3	766	45.6	760	27.1
812	28.1	770	0.7	770	51.6	771	0.5
885	53.0	802	17.2	774	72.0	796	18.0
		857	17.5	829	0.0	857	0.6
		865	0.0	854	2.3	864	11.3
		931	0.0	887	58.3	926	0.5
		942	0.4	921	1.7	938	0.6
		967	0.2	929	0.7	963	0.5
		983	0.4	953	0.0	967	0.3
		1006	1.1	1010	4.7	1014	1.3
1050	70.6	1024	34.2	1045	17.0	1038	16.0
1096	8.8	1078	2.6	1080	9.5	1068	9.8
1145	13.4	1125	10.0	1120	1.7	1128	2.5
1157	33.0	1136	7.4	1136	1.9	1145	0.9
1183	7.0	1163	2.0	1145	0.8	1156	5.0
1208	39.5	1193	90.3	1191	6.8	1166	100.0[c]
1217	100.0	1204	11.8	1218	43.1	1199	12.4
1226	28.3	1253	37.4	1279	16.7	1256	9.2
1274	34.3	1314	18.5	1299	24.4	1321	3.8
1288	12.5	1348	22.5	1335	11.4	1341	13.1
1331	17.9	1364	8.3	1365	5.5	1364	16.3
1339	8.3	1417	1.0	1415	0.7	1413	4.1
		1435	19.7	1422	2.4	1432	5.2
1370	47.0	1490	30.4	1477	8.4	1494	37.9
1379	12.4	1549	34.8	1514	7.0	1540	14.8
1459	13.3	1562	3.2	1546	5.0	1564	14.1
1505	39.4	1605	7.0	1597	3.4	1601	5.2
1514	8.1						
1566	38.1						
1580	7.5						
1622	4.2						
		3051	0.6	3049	3.8	3052	0.1
C–H stretching bands not resolved		3054	1.3	3054	3.8	3056	2.9
		3063	8.1	3056	0.7	3065	8.5
		3072	7.3	3066	33.2	3079	7.9
		3078	12.5	3069	51.6	3081	12.5
		3088	3.1	3078	46.9	3094	2.2
		3103	2.1	3085	16.5	3134	1.4

Absolute calculated IR intensities for the most intense bands (I/I_{max} = 100%) are: [a] 192.9 for **9a singlet**; [b] 51.9 for **9aT triplet**; [c] 169.0 for **9b singlet**.

31G(d,p) calculations on **13** mimic the experimental IR spectrum reasonably well, although intensities of several bands (particularly that at 1826 cm^{-1}) are not quite as good a match as was observed above for the carbene (Fig. 2). These results are summarized in Scheme 2.

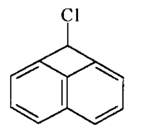
A comparison to the parent 4,5-benzobicyclo[4.1.0]hepta-2,4,6-triene (**6**) is warranted here. Although **6**, produced by Chapman and co-workers[9] directly on irradiation of 1-diazomethylnaphthalene, exhibited a cyclopropene signature in the IR at 1760 cm^{-1}, the chloro-derivative shows a corresponding band at the higher frequency of 1826 cm^{-1}. As these workers pointed out, however, the positions of these cyclopropene bands are highly sensitive to substitution, with the vinylic CH stretch strongly coupled to the double-bond vibration. It is therefore not unusual to observe a shift to higher frequency on substitution of H by a heavier atom in these systems.

(3) Other potential photoproducts in 1-naphthyl system. Chapman and co-workers[9] suggested that prolonged broad-band irradiation (>226 nm) of parent bicyclo compound **6** produced small amounts of the product formed (formally at least) from insertion of 1-naphthylcarbene into the 8-position CH bond, *viz.* 1*H*-cyclobuta[*de*]naphthalene. Flash vacuum pyrolysis of either the 1- or 2-diazomethylnaphthalenes gave

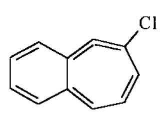


Scheme 2

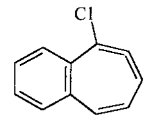
this isomer as a major product. Xie *et al.*,[24] have also found that the cyclobutanaphthalene lies *ca.* 28 kcal mol^{-1} below the benzobicycloheptatriene **6** at the B3LYP/6-311+G* level, and that this isomer represents the global minimum on the $C_{11}H_8$ energy surface. We therefore carried out calculations on the Cl-derivative, **14**. B3LYP/6-31G(d,p) calculations similarly place



14



15



16

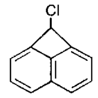
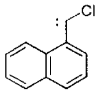
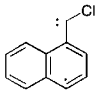
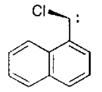
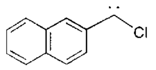
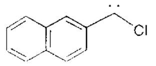
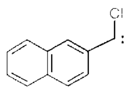
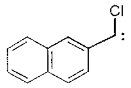
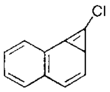
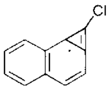
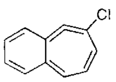
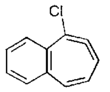
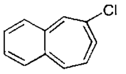
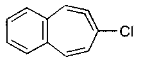
14 26 kcal mol^{-1} lower in energy than **13** in our system. Based on the calculated IR spectrum, however, we do not see appreciable amounts of this product in irradiations of carbene **9** or bicycloheptatriene **13**.

Although phenylcarbene (**1**) on irradiation very readily ring-expands to cycloheptatetraene **3**, examinations by others of the photochemistry of 1- and 2-naphthylcarbenes (**5** and **7**) revealed no similar allenic products.[9,10] We too observe no evidence for potential ring-expanded products such as **15** or **16** in our irradiations in the 1-naphthylchloro systems. Benzocycloheptatetraene **15**, which might be formable from electrocyclic ring-opening of cyclopropene **13**, would be expected to exhibit an *o*-quinodimethane chromophore in the UV/vis spectrum which is not evident. We calculate (B3LYP/6-31G(d,p)) that the alternate ring-expanded product **16** would in fact be 5.3 kcal mol^{-1} below **9a** (**16** is calculated to be 12 kcal mol^{-1} more stable than **15**). Nevertheless, based on comparisons between the experimental and calculated IR spectra we also do not detect major amounts of **16** in our experiments. Calculated energies for various $C_{11}H_7Cl$ intermediates are summarized in Table 2.

Matrix isolation photochemistry of 3-chloro-3-(2-naphthyl)-diazirine (17)

(1) Characterization of 2-naphthylchlorocarbene (10) *s*-*Z* and *s*-*E* conformations. Irradiation of 3-chloro-3-(2-naphthyl)-diazirine **17** matrix isolated in N_2 at 10 K (366 nm, 15 min) gave rise to a new species in the IR with major bands at 1635, 1175, 1126 and 785 cm^{-1} (Table 3) growing at the expense of diazirine bands. At the same time, the UV/Vis spectrum of starting material was replaced by strong, structured absorptions in the 300–450 cm^{-1} region (370, 386, 406, 427 and 436 nm, Fig. 3), together with a very weak and broad absorption spanning 600–850 nm (λ_{max} 750 nm). By analogy to the case of the 1-naphthyl system above, and with the support of DFT calculations (*vide infra*), we assign this species as 2-naphthylchlorocarbene (**10**).

Table 2 Computational results for chloronaphthylcarbenes and their isomers

Structure	B3LYP 6-31(d,p)[a]	ZPE[b]	E_{rel}[c]
 **14**	−883.52796	0.1437	0.0
 **9a singlet**	−883.49633	0.1419	18.7
 **9a triplet**	−883.49146	0.1412	21.4
 **9b singlet**	−883.49045	0.1418	22.4
 **10b singlet**	−883.49898	0.1418	17.1
 **10b triplet**	−883.49030	0.1412	22.1
 **10a singlet**	−883.49641	0.1416	18.5
 **10a triplet**	−883.49067	0.1413	22.0
 **13**	−883.48509	0.1422	26.0
 **18**	−883.48405	0.1421	26.6
 **15**	−883.48520	0.1413	25.4
 **16**	−883.50483	0.1420	13.5
 **20**	−883.48249	0.1411	27.0
 **19**	−883.50502	0.1420	13.3

[a] B3LYP/6-31G(d,p) energy for optimized structures in hartree. [b] Zero-point vibrational energy from B3LYP/6-31G(d,p) frequency calculations in hartree. [c] Total energy (ZPE corrected, ZPE scaled by 0.96) relative to 1-chloro-1-*H*-cyclobuta[*de*]naphthalene **14** in kcal mol^{-1}.

Careful irradiation with select wavelengths showed that the IR and UV spectra of **10** were, in fact, comprised of two differently reactive species. Irradiation of the carbene-containing matrix at 436 nm caused one set of IR bands to decrease and a closely allied set to increase correspondingly (Fig. 4). Simultaneously, the 427 and 436 nm peaks in the visible spectrum bleached while the other UV/vis bands of **10** grew (Fig. 3). DFT calculations confirmed that these two intermediates were *s*-*Z* (**10a**) and *s*-*E* (**10b**) geometric isomers of the 2-napthylchlorocarbene. The B3LYP/6-31G(d,p) method predicted both **10a** and **10b** to be energy minima at planar C_s geometries. Repulsion between the in-plane Cl and the adjacent H was again

Table 3 Experimental IR spectra of the carbenes **10a** and **10b** and their calculated spectra (singlets, B3LYP/6-31G(d,p), frequencies scaled by 0.96)

10a experimental		**10a singlet** calculated × 0.96		**10b singlet** calculated × 0.96		**10b** experimental	
ν/cm^{-1}	I/I_{max} (%)	ν/cm^{-1}	I/I_{max} (%)	ν/cm^{-1}	I/I_{max} (%)	ν/cm^{-1}	I/I_{max} (%)
		48	0.3	46	0.1		
		112	1.6	138	1.5		
		139	0.2	153	0.2		
		185	0.5	178	0.5		
		250	2.8	266	2.6		
		288	1.4	288	3.0		
		393	0.1	372	1.0		
		400	4.7	387	0.0		
		466	4.4	472	6.0	515	7.4
		476	12.3	496	1.3	534	30.8
		482	0.1	501	6.6	598	7.4
502	25.5	500	0.2	517	26.3	618	13.6
514	19.0	608	0.9	607	5.6	676	4.0
550	17.7	618	0.0	620	0.0	722	26.3
704	18.2	676	34.3	690	98.0	749	100.0
764	74.7	733	60.3	715	47.1	770	20.3
785	100.0	736	9.8	738	14.5	820	14.7
863	14.2	751	0.0	751	5.6	874	3.6
869	8.6	752	9.3	751	0.4		
914	11.8	812	11.6	808	19.1		
967	4.4	855	7.4	857	7.7		
		886	4.2	877	26.6	906	53.5
		908	2.6	915	3.3	928	4.6
		938	2.3	938	4.8	962	5.1
		944	1.4	939	4.6	1054	5.9
		960	0.0	958	0.0	1128	34.4
		967	0.0	967	0.0	1157	25.1
1013	3.8	1005	0.6	1008	1.1		
1126	52.6	1105	27.9	1106	32.7		
		1125	0.1	1135	36.5		
		1140	2.4	1138	2.0		
1174	100.0	1153	100.0[a]	1152	82.1		
1213	36.1	1201	20.8	1204	25.3		
1256	38.1	1228	20.3	1239	12.5		
1349	23.0	1245	9.3	1245	100.0[b]	1177	82.2
1367	8.8	1326	12.6	1319	8.1	1221	26.0
1390	21.5	1357	10.6	1350	6.8	1264	24.4
1564	6.2	1366	13.7	1372	14.6	1271	58.3
1590	41.1	1414	0.7	1417	2.2	1276	42.8
1626	20.9	1436	23.0	1436	38.6	1344	15.8
		1482	2.7	1484	1.3	1396	24.0
		1540	10.8	1543	10.6	1452	12.8
		1575	36.1	1578	30.9	1470	8.3
		1607	32.0	1606	52.1	1570	5.3
						1595	14.2
						1628	13.8
		3055	0.2	3053	3.3		
		3059	1.9	3056	2.9		
C–H stretching bands not resolved		3061	1.1	3061	0.1	C–H stretching bands not resolved	
		3071	8.5	3071	12.1		
		3073	1.1	3073	1.6		
		3082	9.4	3083	14.1		
		3087	2.5	3092	2.6		

Absolute calculated IR intensities for the most intense bands (I/I_{max} = 100%) in km mol^{-1} are: [a] 230.9 for **10a singlet**; [b] 156.4 for **10b singlet**.

evident in the slight distortions in each structure analogous to that observed in the *s*-*E*-isomer of the 1-carbene. As shown in Fig. 4, the calculated IR spectrum for *Z*-isomer **10a** fits the experimental bands that disappear on 436 nm irradiation. Similarly, the excellent match between theoretical and observed IR spectra allows us to assign the *E*-geometry **10b** to the intermediate that grows on 436 nm photolysis. As in the case of the 1-isomer, calculated spectra for the corresponding *triplet* states of **10a** and **10b** did not resemble the experimental IR spectra.

Although again less satisfactory in absolute wavelengths, CIS/6-31G(d,p) calculations parallel the *E*/*Z* distinctions observed in the UV/vis spectra of the carbene. The first two transitions for *s*-*Z*-isomer **10a** ($\sigma\pi^*$ and $\pi\pi^*$) are predicted to occur at 543 and 281 nm, respectively, similar to those calculated for the 1-carbene **9**. On the other hand, the same transitions for *s*-*E*-isomer **10b** are predicted to lie at the somewhat shorter wavelengths 509 and 268 nm. Whereas the longest wavelength band for **10** is too weak for us to confirm the presence of two differently reactive conformations, the calculations support the notion that **10a** is selectively excited at 436 nm irradiation driving it to the alternate conformer, **10b**.

(2) Photochemistry of 2-naphthylchlorocarbene (10). More prolonged irradiations (15 h) of the matrix containing **10** (*E*, *Z*, or both) at 366 or 403 nm caused the disappearance of the IR spectrum of the carbene and the simultaneous growth of a new species with a distinctive band at 1811 cm^{-1}. The UV/vis spectra of the carbenes likewise vanished, with the resulting spectrum showing absorption only below 350 nm (Fig. 3). This process

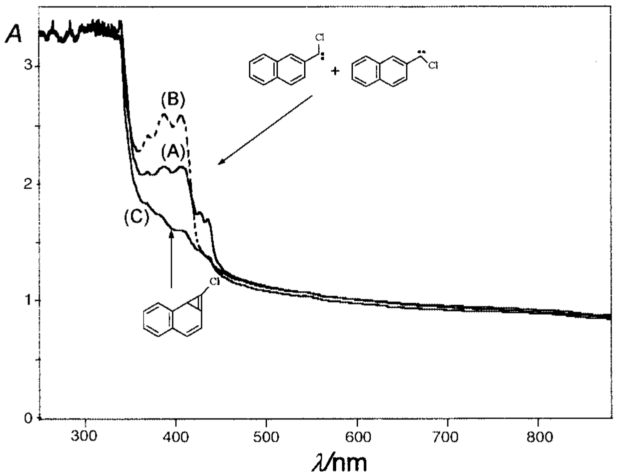


Fig. 3 UV/Vis spectrum of nitrogen matrix containing initially 3-chloro-3-(2-naphthyl)diazirine (A) after 31 h of irradiation at 366 nm; (B) after additional 10 h of irradiation at 436 nm; (C) after additional 15 h of irradiation at 406 nm.

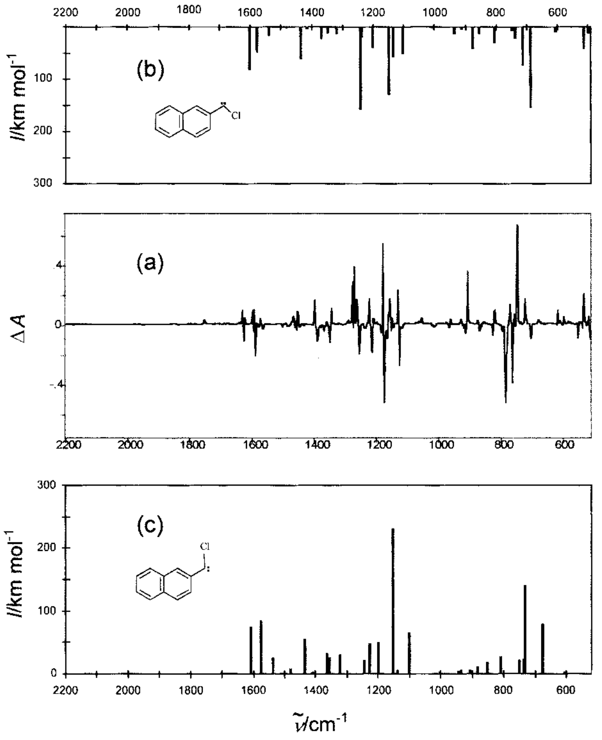


Fig. 4 (a) IR difference spectrum of the matrix described in Fig. 3 (after additional carbene regeneration and bleaching of the red edge of the 340–450 nm absorption band) showing increase of IR signals of the species with absorption shifted toward blue (positive peaks) and decrease in IR intensities of the species with longer wavelength absorptions (negative peaks) upon irradiation at 436 nm; (b) calculated B3LYP/6-31G(d,p) IR spectrum of **10b**, frequencies scaled by 0.96, absorptions pointing downward to facilitate comparison with Fig. 4(a); (c) IR spectrum calculated for **10a** (same method and scaling factor as for **10b**).

was reversible. Subsequent irradiation at 327 nm restored the original mixture of **10a** and **10b** in the IR, together with the strong carbene UV/vis spectra (Figs. 3, 5).

By analogy to the 1-naphthyl system **9**, we would expect that the new photoproduct of carbene **10** is the isomeric benzobicycloheptatriene, **18**. Albrecht and McMahon[10] similarly showed that the parent 2-naphthylcarbene could be photochemically toggled back and forth with the corresponding benzobicycloheptatriene **8**. Indeed, B3LYP/6-31G(d,p) calculations on **18** do a satisfactory job matching the experimental IR spectra, although once again the predicted 1890 cm^{-1} (unscaled) band is somewhat too intense compared to the observed 1811 cm^{-1} absorption (Fig. 5). This C=C stretch, however, is near that described above in **13**. Moreover, the shift in this band from that of the parent **8**, reported to lie at 1750 cm^{-1}, is similar to the correspondance between **13** and **7** in the 1-system. These results are summarized in Scheme 3.

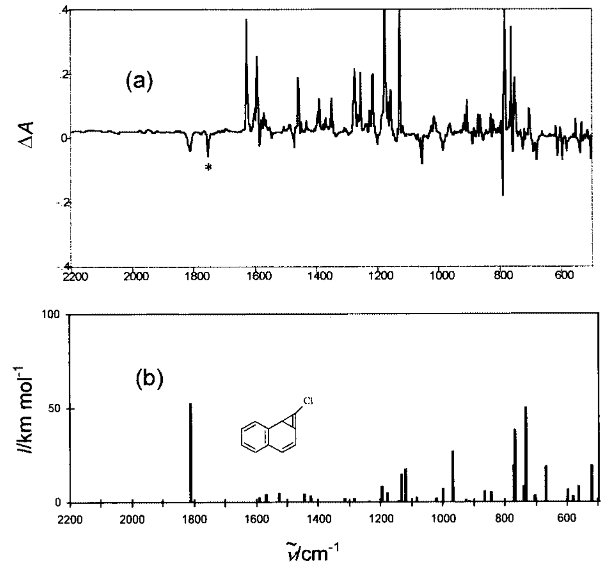
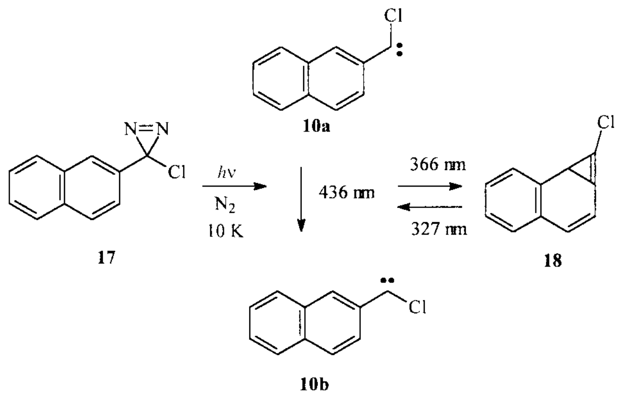


Fig. 5 (a) IR difference spectrum of the matrix described in Fig. 3 showing regeneration of 2-naphthylchlorocarbenes **10a** and **10b** upon 7 h irradiation at 297 nm (positive peaks) and consumption of cyclopropene **18** (negative peaks); (b) calculated B3LYP/6-31G(d,p) IR spectrum of cyclopropene **18**, frequencies scaled by 0.96. Peak marked with an asterisk in the experimental difference spectrum (1750 cm^{-1}) corresponds most likely to 2-naphthoyl chloride resulting from oxidation of the carbene.

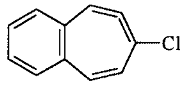


Scheme 3

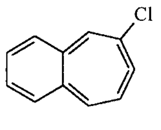
(3) Alternative products in the 2-naphthyl series. As we found with the 1-isomer **9**, calculated IR spectra for alternative structures, such as **14**, **15** and **16**, do not fit experiment. Although **19** is calculated to lie 13.2 kcal mol^{-1} below cyclopropene **18** by B3LYP calculations, the calculated IR spectrum for this benzocycloheptatetraene does not fit the major product observed. Finally, we do not observe a distinct *o*-quinonoid UV spectrum in the photoproduct which would accompany ring-expansion of **18** to the benzocycloheptatetraene **20**. It should be noted, however, that the IR spectra are more complex in the 2-naphthyl series, and thus we cannot exclude the presence of minor amounts of any of these isomeric compounds in our experiments.

Conclusions

We have for the first time characterized the 1- and 2-naphthyl-



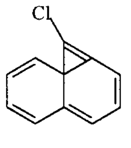
19



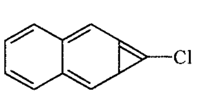
20

chlorocarbenes by IR and UV/vis spectroscopy. Although evidence suggests the presence of predominantly only one geometric isomer in the case of the 1-carbene **9**, the IR and UV/vis spectra of the 2-isomer **10** indicate two distinct conformations. With selective irradiation, the longer-wavelength absorbing *s*-*Z*-isomer **10a** can be photochemically driven to the alternate conformation **10b**. Irradiation of both carbenes **9** and **10** induces cyclization to the corresponding benzobicycloheptatrienes **13** and **18**, respectively. The cyclization can be reversed by irradiation at shorter wavelengths.

Our results on the *singlet* naphthylchlorocarbene photochemical ring-closures parallel observations of Chapman,[9] McMahon,[10] and co-workers on the parent *triplet* 1- and 2-naphthylcarbenes. In particular, under matrix isolation conditions, the naphthylcarbenes appear to photochemically only cyclize to the corresponding cyclopropenes, which in turn only photochemically ring-open back to the carbenes. Ring-expansion in these systems to cycloheptatetraenes, such as **15**, **16**, **19** or **20**, is not detected. Thus, the naphthyl systems behave quite differently than phenylcarbene **1**, which readily ring-expands to cycloheptatetraene **3** on light absorption. It is tempting to speculate on the origin of this dichotomy, following the lead of Wentrup *et al.*[25] and Xie *et al.*,[24] on the parent naphthylcarbene potential energy surface. Simple-mindedly, although electrocyclic ring-opening of the parent bicycloheptatriene **2** to the cycloheptatraene **3** is energetically very favorable, rearrangements of the cyclopropenes **13** and **18** to the corresponding allenes **15** and **20** are predicted to be endothermic. Although it is possible that the ring-expansions might be driven photochemically, it is likely that the quinonoidal systems in **15** and **20** would absorb light strongly, making them less favored in photochemical equilibria. Finally, benzocycloheptatetraenes **16** and **19** are predicted to lie significantly lower in energy than carbenes **9** and **10**, as well as cyclized products **13** and **18**. Nevertheless, to reach these energetically favored products would require the intermediacy of the high-energy cyclopropenes **21** and **22**, processes which must not be able to compete with the alternate, observed cyclizations.

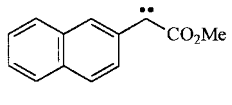


21

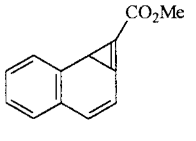


22

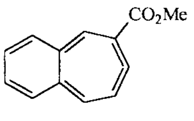
In closing, we note the very recent work by several groups on the related 2-naphthyl(carbomethoxy)carbene (**23**).[26] Interestingly, in that system both a surprisingly long-lived singlet excited state and a triplet ground state of the carbene could be observed both under matrix isolation conditions[26a] and at room temperature in laser time-resolved IR experiments.[26b] The low-temperature photochemistry of carbene **23** is dominated by triplet–singlet interconversion and Wolff rearrangement, and neither cyclization to cyclopropenes such as **24** nor ring-expansion to cycloheptatetraenes such as **25** is observed.



23



24



25

Acknowledgements

We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation (CHE-9622194) for generous support. We also thank Mr Lew Cary for assistance in acquisition of 500 MHz NMR spectra.

References

1 For reviews, see for example: (*a*) M. S. Platz, *Acc. Chem. Res.*, 1995, **28**, 487; (*b*) C. Wentrup, *Reactive Molecules: Neutral Reactive Intermediates in Organic Chemistry*, Wiley, New York, 1984.

2 (*a*) W. L. Karney and W. T. Borden, *J. Am. Chem. Soc.*, 1997, **119**, 1378; (*b*) S. Matzinger, T. Bally, E. V. Patterson and R. J. McMahon, *J. Am. Chem. Soc.*, 1996, **118**, 1535; (*c*) P. R. Schreiner, W. L. Karney, P. v R. Schleyer, W. T. Borden, T. P. Hamilton and H. F. Schaefer III, *J. Org. Chem.*, 1996, **61**, 7030; (*d*) M. W. Wong and C. Wentrup, *J. Org. Chem.*, 1996, **61**, 7022.

3 See, for example: (*a*) R. A. Moss, J. R. Whittle and P. Freidenreich, *J. Org. Chem*, 1969, **34**, 2220; (*b*) N. J. Turro, G. F. Lehr, J. A. Butcher, Jr., R. A. Moss and W. Guo, *J. Am. Chem. Soc.*, 1982, **104**, 1754; (*c*) D. Griller, M. T. H. Liu and J. C. Scaiano, *J. Am. Chem. Soc.*, 1982, **104**, 5549; (*d*) I. R. Gould, N. J. Turro, J. Butcher, Jr., C. Doubleday, Jr., N. P. Hacker, G. F. Lehr, R. A. Moss, D. P. Cox and W. Guo, *Tetrahedron*, 1985, **41**, 1587; (*e*) G. A. Ganzer, R. A. Sheridan and M. T. H. Liu, *J. Am. Chem. Soc.*, 1986, **108**, 1517; (*f*) J. E. Jackson, N. Soundararajan, M. S. Platz and M. T. H. Liu, *J. Am. Chem. Soc.*, 1988, **110**, 5595; (*g*) M. B. Jones, J. E. Jackson, N. Soundararajan and M. S. Platz, *J. Am. Chem. Soc.*, 1988, **110**, 5597; (*h*) M. B. Jones and M. S. Platz, *J. Org. Chem.*, 1991, **56**, 1694; (*i*) S. Wierlacher, W. Sander and M. T. H. Liu, *J. Org. Chem.*, 1992, **57**, 1051; (*j*) M. B. Jones, V. M. Maloney and M. S. Platz, *J. Am. Chem. Soc.*, 1992, **114**, 2163; (*k*) J. P. Pezacki, P. D. Wood, T. A. Gadosy, J. Lusztyk and J. Warkentin, *J. Am. Chem. Soc.*, 1998, **120**, 8681.

4 C. Trindle, S. N. Datta and B. Mallik, *J. Am. Chem. Soc.*, 1997, **119**, 12947.

5 (*a*) R. J. McMahon, C. J. Abelt, O. L. Chapman, J. W. Johnson, C. L. Kreil, J. P. LeRoux, A. M. Mooring and P. R. West, *J. Am. Chem. Soc.*, 1987, **109**, 2456; (*b*) W. W. Sander, *Spectrochim. Acta*, *Part A*, 1987, **43**, 637; (*c*) G. A. Ganzer, PhD Thesis, 1987, University of Wisconsin-Madison.

6 A. M. Trozzolo, E. Wasserman and W. A. Yager, *J. Am. Chem. Soc.*, 1965, **87**, 129.

7 Although the authors of this paper originally proposed *cis*/*trans* designation of the geometrical isomers of naphthylcarbenes, as pointed out by Roth and Platz such designation (as well as *syn*/*anti* nomenclature) leaves some field for ambiguity when unequivocal relation of structure and name is desired. In this paper we have implemented the *Z*/*E* nomenclature proposed by Roth and Platz. See: H. D. Roth and M. S. Platz, *J. Phys. Org. Chem.*, 1996, **9**, 252.

8 V. P. Senthilnathan and M. S. Platz, *J. Am. Chem. Soc.*, 1981, **103**, 5503.

9 P. R. West, A. M. Mooring, R. J. McMahon and O. L. Chapman, *J. Org. Chem.*, 1986, **51**, 1316.

10 S. W. Albrecht and R. J. McMahon, *J. Am. Chem. Soc.*, 1993, **115**, 855.

11 (*a*) K. B. Clark, K. Bhattacharyya, P. K. Das, J. C. Scaiano and A. P Schaap, *J. Org. Chem.*, 1992, **57**, 3706; (*b*) K. W. Haider, M. S. Platz, A. Despres and E. Migirdicyan, *Chem. Phys. Lett.*, 1989, **164**, 443.

12 (*a*) G. W. Griffin and K. A. Horn, *J. Am. Chem. Soc.*, 1987, **109**, 4919; (*b*) K. A. Horn and J. E. Chateauneuf, *Tetrahedron*, 1985, **41**, 1465; (*c*) L. M. Hadel, M. S. Platz and J. C. Scaiano, *Chem. Phys. Lett.*, 1983, **97**, 446; (*d*) T. T. Coburn and W. M. Jones, *J. Am. Chem. Soc.*, 1974, **96**, 5218; (*e*) K. E. Krajca, T. Mitsuhashi and W. M. Jones, *J. Am. Chem. Soc.*, 1972, **94**, 3661.

13 L. Weintraub, S. R. Oles and N. Kalish, *J. Org. Chem.*, 1968, **33**, 1679.

14 A. Pinner and Fr. Klein, *Ber. Dtsch. Chem. Gess.*, 1883, **11**, 1475.

15 W. H. Graham, *J. Am. Chem. Soc.*, 1965, **87**, 4396.

16 (*a*) G. Yao, MS Thesis, 1997, University of Nevada, Reno; (*b*) G. Yao, P. Rempala, C. Bashore and R. S. Sheridan, *Tetrahedron Lett.*, 1999, **40**, 17.

17 M. A. Kesselmayer and R. S. Sheridan, *J. Am. Chem. Soc.*, 1986, **108**, 99.

18 J. C. Hayes and R. S. Sheridan, *J. Am. Chem. Soc.*, 1990, **112**, 5879.

19 GAUSSIAN94, Revision D.4, M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R.

Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez and J. A. Pople, Gaussian, Inc., Pittsburgh, PA, 1995.

20 T. Khasanova and R. S. Sheridan, *J. Am. Chem. Soc.*, 1998, **120**, 233.

21 P. S. Zuev and R. S. Sheridan, *J. Org. Chem.*, 1994, **59**, 2267.

22 P. Zuev and R. S. Sheridan, *J. Am. Chem. Soc.*, 1994, **116**, 4123.

23 G. J. Ho, K. Krogh-Jespersen, R. A. Moss, S. Shen, R. S. Sheridan and R. Subramanian, *J. Am. Chem. Soc.*, 1989, **111**, 6875.

24 Y. Xie, P. R. Schreiner, P. v R. Schleyer and H. F. Schaefer III, *J. Am. Chem. Soc.*, 1997, **119**, 1370.

25 C. Wentrup, C. Mayor, J. Becker and H. J. Lindner, *Tetrahedron*, 1985, **41**, 1601.

26 (*a*) Z. Zhu, T. Bally, L. L. Stracener and R. J. McMahon, *J. Am. Chem. Soc.*, 1999, **121**, 2863; (*b*) Y. Wang, T. Yuzawa, H. Hamaguchi and J. P. Toscano, *J. Am. Chem. Soc.*, 1999, **121**, 2875; (*c*) J.-L. Wang, I. Likhotvorik and M. S. Platz, *J. Am. Chem. Soc.*, 1999, **121**, 2883.

Paper 9/05042F