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1- and 3-Nitreno-2-naphthylcarbenes. A Combined Experimental and Computational Study

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The structures, energies, and thermal stabilities of E and Z isomers of a singlet, a triplet, and a quintet states of naphthalene bearing nitrene and carbene units on adjacent (1,2- and 3,2-) positions were examined by DFT methods. For both 1,2- and 3,2-isomers, singlet quinoidal diradicals were predicted to be the ground state with the corresponding triplet state lying slightly higher in energy. The quintet state of the 1,2-isomer was found to lie approximately 30 kcal mol^{-1} (1 kcal = 4.184 kJ) above the ground state, while that of the 3,2-isomer was predicted to lie only 9 kcal mol^{-1} above the ground state. This difference is discussed in terms of loss of energy due to aromaticity between the two isomers. Thermal stability of the ground state in terms of ring-opening and -closure reactions indicated that both isomers prefer to decay by the latter process forming naphtho[*b*]azetes. Attempts to generate and characterize the ground state quionoidal diradical by matrix IR spectroscopic methods in Ar at low temperature all resulted in the detection of the azete.

A one-centered diradical such as carbene and nitrene has two multiplicities, singlet and triplet states, and hence occupies a unique position in organic chemistry. One important feature of those exotic species is the presence of two nonbonding electrons and two available orbitals.[1] In bent carbenes, for instance, the two orbitals have different energies, often denoted as σ and π. Within this simple picture, four electronic states, one triplet and three singlets, can be envisioned as depicted in Figure 1a. The diversities in structures and reactions of carbenes and nitrenes accompanied by such complicated electronic situations attract the interests of a diverse group of scientists and their properties have been gradually revealed by the multidisciplinary contributions of organic chemists, spectroscopists, kineticists, and theoreticians.[1,2]

Scientists then became attracted by a more challenging issue in this field. One issue is to understand how two diradical units interact when introduced on a π-linker such as a phenyl ring as depicted in Figure 1b.[3] This issue was initially triggered by a motivation to construct a high-spin organic molecule.[4,5] Since a dicarbene having a 1,3-benzoquinodimethane framework (meta topology) was established to have a quintet state,[6] research activities on such poly(diradical) species have focused on systems with *m*-phenylene bridges. In other words, connecting the diradical units in a conjugating manner (ortho or para topology) have been intentionally avoided.

In the last fifteen years, systematic studies have begun to unfold properties and structures of species linked in *p*- and *o*-phenylene systems, which have revealed unexpectedly rich aspects of these species.[3c,3d,7–9] The para and ortho topology tends to favor low-spin state. Based on simple valence bond theory, one can assume that two diradical subunits introduced in para fashion interact with each other in $\sigma^1\pi^1$ configuration to form a diradical state with localized double bonds which is best thought of as a quionoidal σ, σ diradical. It has been shown that parent *p*-phenylenebis(carbene) has a singlet quinoidal σ, σ diradical with the corresponding triplet state lying slightly higher in energies by only 1–2 kcal mol^{-1}.[7a] However, electronic configuration can be switched when the local electronic configuration at the carbene center is changed. Thus, *p*-phenylenebis(fluorocarbene) is shown to have a σ^2, σ^2 dicarbene structure rather than a quinoidal one (Scheme 1).[7c] This switching has been explained in terms of fluorine being a powerful singlet carbene stabilizer.

While the electronic effect of the *o*-phenylene system is very similar to the para, the proximity of the reactive centers allows the species to decay by undergoing either a ring-open-

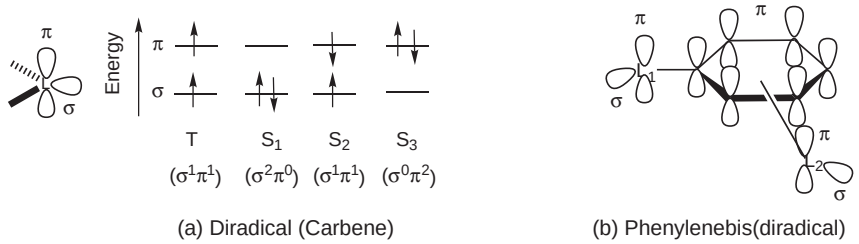

Figure 1. (a) Electronic states of diradical species. (b) Active space for phenylene-linked diradical centers.

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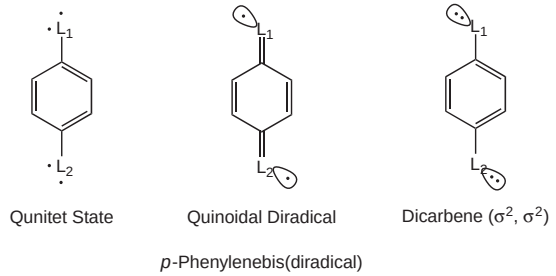
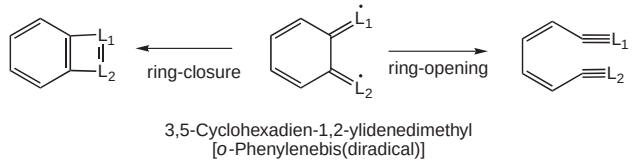
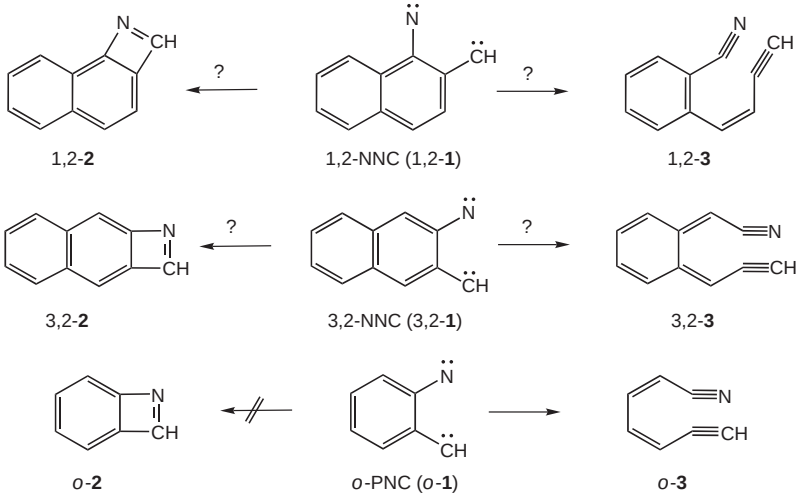


Scheme 1.



Scheme 2.



Scheme 3.

ing to give dienediyne derivatives or a ring-closure to form benzocyclobutadiene derivatives (Scheme 2). The selectivity for ring-opening versus closure is found to be highly dependent upon the nature of the local diradical subunits. While this makes the study of ortho isomers more complicated, it can provide valuable insights about the intrinsic chemical reactivity of such species.[9]

Extension of the issue to a polynuclear aromatic ring such as naphthalene and anthracene, although more challenging, is expected to provide information concerning the role of aromaticity in structures, energies, and reactivities of such exotic species. For instance, in an *o*-phenylenedi(carbene) system, the quintet state (Q) is located surprisingly higher in energy by approximately 30 kcal mol^{-1} above the ground singlet quinoidal diradical.[7a] On the basis of resonance structures, one may argue that formally there is one less π bond in the quintet state as compared to the ground state. However, the stabilization energy due to aromaticity (i.e., 36 kcal mol^{-1}) is sacrificed in the quinoidal ground state. The loss of energy due to aromaticity accompanied by conjugation is more diverse in polynuclear aromatic systems than simple phenyl ring and hence structures, energies, and reactivities will change much more diversely.

In spite of those potential interests, it is only recently that the structure and properties of 1,4-naphthalenebis(diradicals) have been examined,[10] and almost nothing is known about the nature of bis(diradical) connected to 1,2- and 2,3-naphthalene linkers.

In this context, we would like to report here a study of a conjugated nitreno-carbene connected on a naphthalene linker in an "ortho" fashion. Thus, naphthalene 1- and 3-nitreno-2-naphthylcarbenes (NNCs) have been investigated in an integrated way by combining experimental and computational techniques. Thus, we characterized structures of 1,2-NCC (1,2-**1**) and 3,2-NCC (3,2-**1**) and estimated their thermal decay pathway in terms of the ring-closure leading to product **2** or ring-opening forming product **3** by DFT methods (Scheme 3). Attempts were also made to generate **1** and to examine their thermal reactivities in order to verify the computational prediction by using matrix isolation spectroscopic means. The results will be compared and discussed with those observed for *o*-phenylenenitrenocarbene (*o*-PNC, *o*-**2**),[9c] which has a singlet quinoidal diradical as the ground state that decays by undergoing ring-opening to 2,4-heptadien-6-ynenitrile (*o*-**3**) (Scheme 3).

Results

1-Nitreno-2-naphthylcarbene (1,2-NNC). Computational Studies: Geometries of three important electronic states were examined in this study. They are E and Z isomers of a singlet state (^{1}A′), a triplet state (^{3}A′), and a quintet (^{5}A′) state, all of which have σ^1p^1, σ^1p^1 electronic configuration. Their approximate valence bond depictions are shown in Figure 2. Geometries were optimized at B3LYP/6-31G(d) level of theory. The stationary points were characterized by vibrational analyses and found to be minima on the corresponding potential energy surface.

Important geometric characteristics obtained for 1-nitreno-2-naphthylcarbene (1,2-NNC) are shown in Figure 3. Not sur-

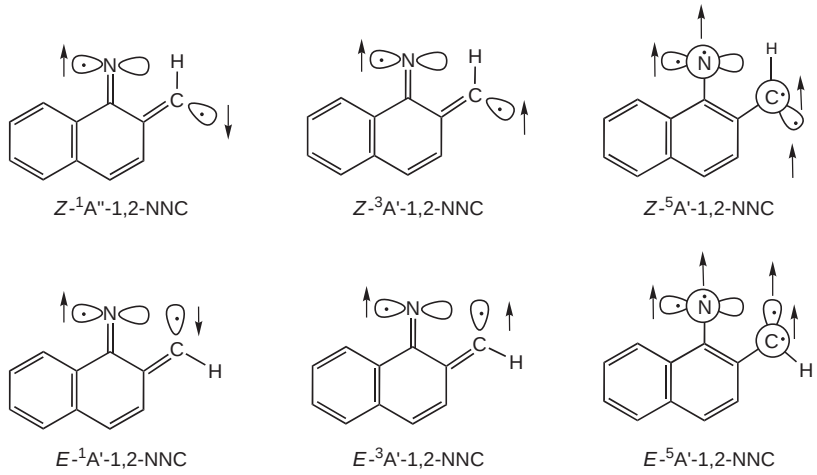


Figure 2. Valence bond descriptions of electronic states arising from the coupling of nitrene and carbene via the 1,2-naphthalene linker.

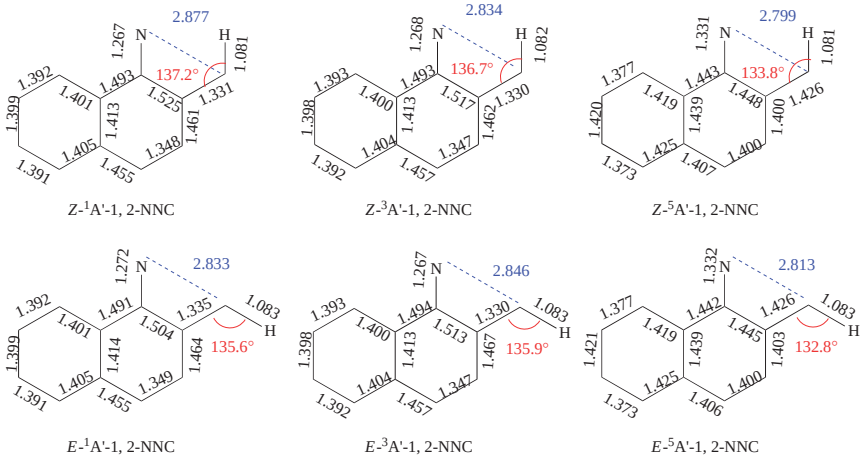


Figure 3. Selected geometric parameters (distances in Å, angle in degrees) for ^{1}A′, ^{3}A′, and ^{5}A′ electronic states of 1-nitreno-2-naphthylcarbene (1,2-NCC) at UB3LYP level of theory. Only important angles are indicated for the sake of clarity. All other angles are normal (121 ± 2°).

prisingly, the geometries of the E and Z isomers are very similar, and this is reflected in their relative energies. The only noteworthy difference is that the bond length between the carbon adjacent to the reactive center (i.e., C_1–C_2 distance) in the Z isomer is slightly longer than that in the E isomer, presumably due to hyperconjugation.[9c]

The geometry of ^{1}A′ and ^{3}A′ states displays significantly more bond alteration in one of the aromatic rings than that of the ^{5}A′ state. In all three A′ states, the angle at the divalent carbon is around 133–137°, close to that expected for a triplet carbene (or a vinyl radical).

Thus, ^{1}A′ and ^{3}A′ states are better thought of as quinomethideimide diradicals, while the ^{5}A′ state has naphthalenoid geometry. ^{5}A′ state can be thought of as being constructed from two local triplet subunits (a carbene and a nitrene) linked via the 1,2-naphthalene unit.

Energy of each state is calculated at the same level of theory (Table 1). The Z isomer is found to be favored over the E isomer by approximately 1 kcal mol^{-1}, independent of the multiplicity. Quinoidal diradical ^{1}A′-1,2-NNC is calculated to be the ground state, with ^{3}A′-1,2-NNC lying slightly higher by 1–2 kcal mol^{-1} in energy. The quintet state (^{5}A′-1,2-NNC) lies approximately 30 kcal mol^{-1} above the ground state.

We next estimate thermal stability of the ground state (^{1}A′-1,2-NNC) in terms of ring-closure forming naphtha[1,2-*b*]azete (1,2-**2**) and ring-opening leading to (2-cyanophenyl)-buta-1-en-3-yne (1,2-**3**). It has been shown in the reaction of the corresponding *o*-phenylene system that the Z isomer undergoes ring-opening while ring-closure takes place in the E isomer.[9b] Thus, energy barriers and enthalpies of the ring-opening reaction from *Z*-^{1}A′-1,2-NNC and that of the ring-closure reaction from *E*-^{1}A′-1,2-NNC were calculated at B3LYP/6-31G(d) level of theory and are reported in Table 2. The data predict that the ring-closure reaction from the E isomer is energetically more favorable than the ring-opening reaction from the Z isomer by 3.6 kcal mol^{-1}. The interconversion of these two geometric isomers can be achieved via linearization of the vinyl group. The barrier of this process is calculated to be ≈3 kcal mol^{-1}.[9b] Thus, it is predicted that both isomers of ^{1}A′-1,2-NNC can be observed if generated under very inert and low energy conditions, such as in a noble gas matrix at very low temperature.

Matrix-Isolation Spectroscopic Studies: In order to confirm the computational prediction, we attempted to generate

Table 1. Total (Hartree) and Relative (kcal mol^{-1}) Energies of 1- (1,2-NNC) and 3-Nitreno-2-naphthylcarbene (3,2-NCC) at the B3LYP/6-31G(d) Level of Theory and Calculated (B3LYP) Spin-Squared Expectation Values ($\langle S^2 \rangle$)[a),b)]

	Energy	$\langle S^2 \rangle$
E-^{5}A′-1,2-NNC	32.0	6.03
Z-^{5}A′-1,2-NNC	30.9	6.03
E-^{3}A′-1,2-NNC	2.24	2.02
Z-^{3}A′-1,2-NNC	1.33	2.02
E-^{1}A′-1,2-NNC	1.23	1.11
Z-^{1}A′-1,2-NNC	0 (−477.830156)	1.09
E-^{5}A′-3,2-NNC	9.61	6.05
Z-^{5}A′-3,2-NNC	8.64	6.05
E-^{3}A′-3,2-NNC	7.05	2.19
Z-^{3}A′-3,2-NNC	6.36	2.19
E-^{1}A′-3,2-NNC	—	—
Z-^{1}A′-3,2-NNC	0 (−477.80688)	1.74
E-^{5}A′-*o*-PNC	23.2	6.03
Z-^{5}A′-*o*-PNC	22.2	6.03
E-^{3}A′-*o*-PNC	3.1	2.02
Z-^{3}A′-*o*-PNC	2.2	2.02
E-^{1}A′-*o*-PNC	1.2	1.20
Z-^{1}A′-*o*-PNC	0 (−324.22239)	1.16

a) With the 6-31 G(d) basis set and including ZPE corrections based on the UB3LYP frequencies scaled by 0.981. The values of $\langle S^2 \rangle$ expected for pure singlet, triplet, and quintet are 0.0, 2.0, and 6.0, respectively. b) The values calculated for *o*-nitrenophenylcarbene (*o*-PNC)[9c] are also included for comparison.

and characterize 1,2-NNC by using matrix isolation spectroscopic technique. 1-Azido-2-naphthyldiazomethane [1,2-**1**-$(N_2)_2$], a potential precursor of 1,2-NNC, was prepared according to the procedures detailed in the Experimental Section and was deposited in an Ar matrix at 20 K. The matrix containing 1,2-**1**-$(N_2)_2$ was cooled down to 10 K and irradiated ($\lambda >$ 350 nm). IR monitoring of the irradiation of 1,2-**1**-$(N_2)_2$ indicated that the peaks due to azide and diazo groups appeared to diminish simultaneously in intensity as new absorption bands were observed. In order to avoid complication due to possible secondary photodecompositions of potentially photolabile products,[11] the irradiation was terminated at a relatively early stage and the absorption bands due to an initial photoproduct were obtained by subtracting the initial spectrum from the irradiated one. A comparison of the experimental spectrum with that calculated for possible products suggested the observed bands did not coincide with that calculated for the ground state of 1-nitreno-2-naphthylcarbene (^{1}A′-1,2-NNC) but they match much better with that calculated for the ring-closure product (1,2-**2**) (Figure 4 and Scheme 4). All attempts to detect bands due to ^{1}A′-1,2-NNC by changing irradiation time and wavelength were unsuccessful.

3-Nitreno-2-naphthylcarbene (3,2-NNC). Computational Studies: Essentially the same calculations were carried out for 3-nitreno-2-naphthylcarbene (3,2-NNC) at B3LYP/6-31G(d) level of theory. Important geometric characteristics obtained for 3,2-NNC are shown in Figure 5.

Table 2. Calculated Barriers of the Ring-Opening ($\Delta H^{\neq}_{ro}$/kcal mol^{-1}) and Ring-Closure Reactions ($\Delta H^{\neq}_{rc}$/kcal mol^{-1}) and Enthalpies of the Ring-Opening (ΔH_{ro}/kcal mol^{-1}) and Ring-Closure Reactions (ΔH_{rc}/kcal mol^{-1}) for 1- (1,2-NNC) and 3-Nitreno-2-naphthylcarbenes (3,2-NCC) at the B3LYP/6-31G(d) Level of Theory[a),b)]

	$\Delta H^{\neq}_{ro}$	ΔH_{ro}	$\Delta H^{\neq}_{rc}$	ΔH_{rc}
E-^{1}A′-1,2-NCN	—	—	4.9	−38.0
Z-^{1}A′-1,2-NCN	8.5	−36.7	—	—
E-^{1}A′-3.2-NCN	—	—	0	−62.8
Z-^{1}A′-3,2-NCN	5.5	−30.7	—	—
E-^{1}A′-*o*-PNC	—	—	6.8	−49.9
Z-^{1}A′-*o*-PNC	4.3	−44.4	—	—

a) Including ZPE corrections based on the B3LYP harmonic vibrational frequencies scaled by 0.981. b) The values calculated for *o*-nitrenophenylcarbene (*o*-PNC)[9c] are also included for comparison.

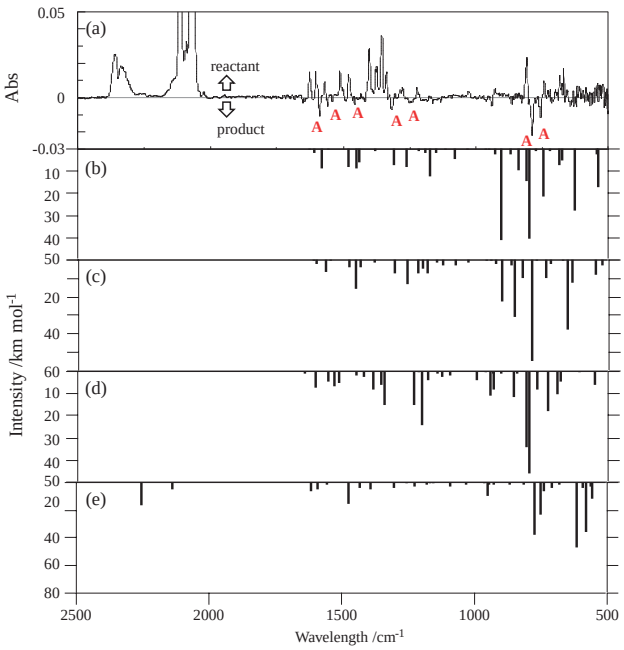
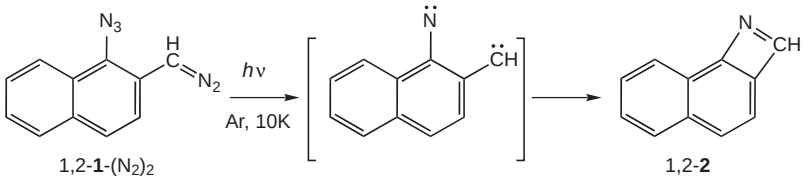


Figure 4. Photolysis of 1-azido-2-naphthyldiazomethane [1,2-**1**-$(N_2)_2$] in an Ar matrix at 10 K. (a) Difference IR spectrum between the photoproduct formed after 1 h of irradiation ($\lambda >$ 350 nm) of 1,2-**1**-$(N_2)_2$ (negative peaks: indicated by A) and 1,2-**1**-$(N_2)_2$ before irradiation (positive peaks). (b, c, d, and e) Calculated (B3LYP/6-31g(d)) spectra of *Z*- (b) and *E*-1-nitreno-2-naphthylcarbene (^{1}A′-1,2-NNC) (c), the ring-closure product (1,2-**2**) (d), and the ring-opened product (1,2-**3**) (e), respectively.

Structural features observed for 3,2-NNC are very similar with those for the 1,2-isomer. ^{1}A′ and ^{3}A′ states are better thought of as quinomethideimide diradical, while the ^{5}A′ state has naphthalenoid geometry and can be thought of as being constructed from two local triplet subunits. A notable difference is that, in ^{1}A′ and ^{3}A′ states of 3,2-NNC, the bond alteration is seen in both rings of naphthalene, while in the 1,2-NNC the bond alteration in ^{1}A′ and ^{3}A′ states is limited to the aromatic ring bearing diradical subunits. Optimization of



Scheme 4.

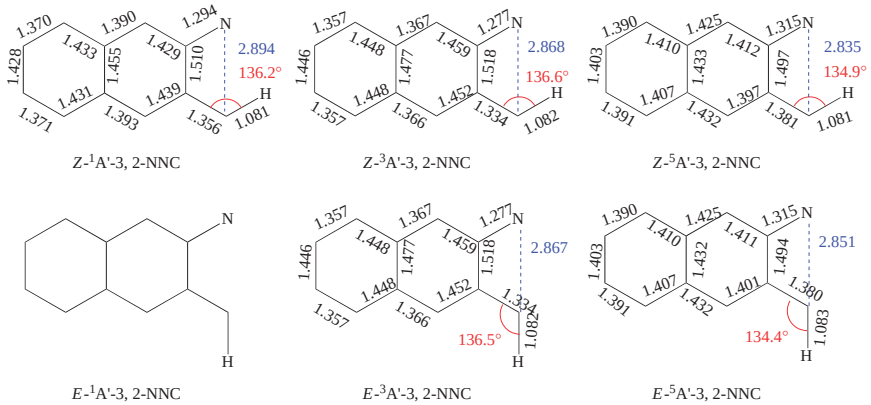


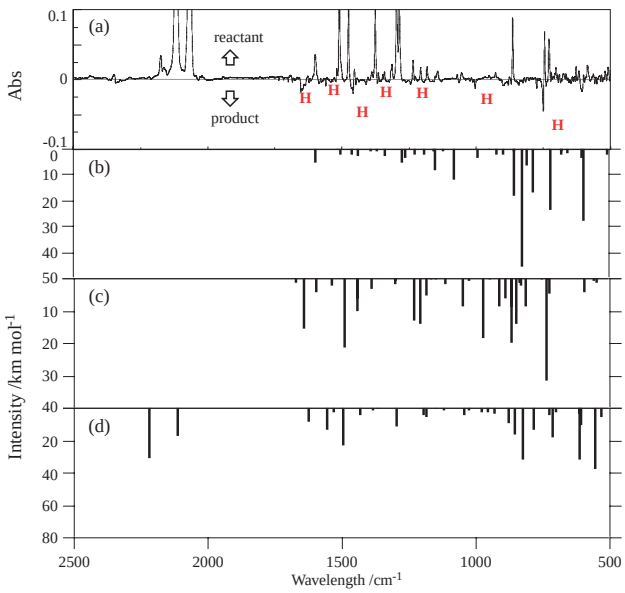
Figure 5. Selected geometric parameters (distances in Å, angle in degrees) for ^{1}A′, ^{3}A′, and ^{5}A′ electronic states of 3-nitreno-2-naphthylcarbene (3,2-NCC) at UB3LYP level of theory. Only important angles are indicated for the sake of clarity. All other angles are normal (121 ± 2°). *E*-^{1}A′-3,2-NNC was not optimized (see text).

the E isomer of ^{1}A′ state resulted in the formation of the ring-closure product (3,2-**2**) and thus was not optimized.

Quinoidal diradical ^{1}A′-3,2-NNC is again predicted to be the ground state, but the next lower lying state ^{3}A′-3,2-NNC is lying higher by 6 kcal mol^{-1} in energy, which is to be compared with the energy difference of only 1–2 kcal mol^{-1} between ^{1}A′-1,2-NCC and ^{3}A′-1,2-NNC. Also, the quintet state (^{5}A′-3,2-NNC) lies only 9 kcal mol^{-1} above the ground state (Table 1). These results indicate that the ground state of 3,2-NNC is significantly less stabilized than that in the 1,2-isomer.

Again, energy barriers and enthalpies of the ring-opening reaction from *Z*-^{1}A′-3,2-NNC and that of the ring-closure reaction from *E*-^{1}A′-3,2-NNC were calculated at B3LYP/6-31G(d) level of theory and are reported in Table 2. As mentioned above, *E*-^{1}A′-3,2-NNC undergoes ring-closure reaction with nearly zero energy barrier, while the Z isomer is predicted to undergo the ring-opening reaction with an energy barrier of 5.5 kcal mol^{-1}. The data predict that the E isomer will automatically lead to the ring closure product and hence cannot be detected while the Z isomer may be observable if generated in inert matrix at very low temperature.

Matrix-Isolation Spectroscopic Studies: 3-Azido-2-naphthyldiazomethane [3,2-**1**-$(N_2)_2$], a potential precursor of 3,2-NNC, was deposited in an Ar matrix at 20 K and irradiated ($\lambda > 350$ nm) at 10 K. IR monitoring of the irradiation of 3,2-**1**-$(N_2)_2$ indicated that the peaks due to azide and diazo groups again appeared to diminish simultaneously in intensity as new absorption bands were observed. The IR bands due to the initial photoproduct were obtained again by differential IR spectroscopy and compared with those calculated for possible products. Again the observed bands did not coincide with that calculated for the ground state of 3-nitreno-3-naphthylcarbene (^{1}A′-3,2-NNC) but they match much better with that calculated for the ring-closure product (3,2-**2**) (Figure 6 and Scheme 5). All attempts to detect the bands due to ^{1}A′-3,2-NNC by changing irradiation time and wavelength were unsuccessful.



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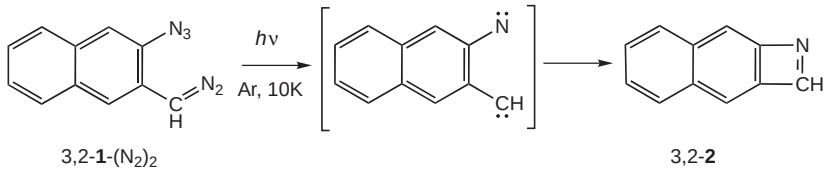

3,2-**1**-$(N_2)_2$ 3,2-**2**

Scheme 5.

Discussion

Geometries and Energies. One of the drawbacks of DFT is its inability to treat multi-configurational problems properly.[12] For instance, singlet diradicals require two Slater determinants for their proper description.[13] Within the UHF formalism, as applied to DFT calculations, one can still obtain "singlet" wave functions by carrying out symmetry-broken calculations. Essentially, this amounts to using only one of the two Slater determinants for the calculation and the resulting wave function is highly spin contaminated with $\langle S^2 \rangle$ value close to unity instead of zero. This suggests that the wave function is approximately a 50:50 mixture of singlet and triplet states and devoid of any physical meaning. However, when the singlet–triplet splitting is very small as in the case of the quinoidal diradicals, this spin-contaminated singlet seems to be a reasonable approximation of the true singlet. Thus, properties like the geometry and IR spectrum for the singlet state can be reasonably approximated by computing the corresponding ones for the triplet. Also it should be noted DFT relative energies come surprisingly close to that calculated by high-level of theory such as CASPT2.[8,9] Thus we use those values calculated by DFT in the following discussion.

Structural features in the geometries optimized for naphthalene systems (1,2- and 3,2-NNC) are essentially similar with those observed for *o*-phenylene system (*o*-PNC). Thus, $^1A'$ and $^3A'$ states are better thought of as quinomethideimide diradical, while $^5A'$ state keeps an aromatic geometry. There is however distinct difference in the structure of quinomethideimide diradical between 1,2- and 3,2-NNC. The geometry of $^1A'$ and $^3A'$ states for the 1,2-isomer displays bond alteration only in one of the aromatic rings, while in $^1A'$ and $^3A'$ states of the 3,2-isomer, the bond alteration is seen in both rings of naphthalene. This means that in $^1A'$ and $^3A'$ states of 1,2-NNC, unpaired electrons are delocalized in only one of the aromatic rings with the remaining ring intact, while in the 3,2-isomer, unpaired electrons are delocalized throughout the molecule. Obviously the loss of the stabilization energy due to aromaticity is much larger in the 3,2-isomer than in the 1,2-isomer. One can calculate stabilization energy due to aromaticity of 61 kcal mol^{-1} for naphthalene.[14] This means that loss of the energy due to aromaticity of one of the naphthalene rings as a result of conjugation in 1,2-naphthalenebis(diradical) is only 25 kcal mol^{-1}.[14,15] This is reflected in the energy difference between quintet and singlet ground state (ΔH_{Q-S}), which is 30.9 kcal mol^{-1} for the 1,2-isomer while the value decreased to 8.6 kcal mol^{-1} in the 3,2-isomer. Similar and much larger change in ΔH_{Q-S} is found between naphthalene 1,4- and 1,5-bis(dinitrenes), where ΔH_{Q-S} for the 1,4- and 1,5-isomers is 39.4 and 8.1 kcal mol^{-1}, respectively.[10]

In this respect, it is interesting to note that ΔH_{Q-S} of *o*-nitrenophenylcarbene (*o*-PNC) is 23.2 kcal mol^{-1},[9b] which is significantly smaller than that of 1,2-NNC. In other words, a singlet quinoidal form in 1,2-naphthalenebis(diradical) is much more stabilized where the loss of energy due to aromaticity is 25 kcal mol^{-1}, as opposed to a quintet state than in the *o*-phenylene system, where the energy loss is 36 kcal mol^{-1}.[14] Not surprisingly, similar energy changes are seen in di(nitrene) connected in 1,4-fashion. Thus, ΔH_{Q-S} is 32.8 kcal mol^{-1} for *p*-phenylenedi(nitrene)[8c] while this value is increased to 39.4 kcal mol^{-1} in 1,4-naphthalenedi(nitrene).[10]

Photolysis Study. Products observed in the irradiation of precursor [**1**-$(N_2)_2$] in argon matrix at 10 K resulted in the formation of naphthoazetes (**2**), regardless of the position of diradical centers. All attempts to detect singlet quinoidal diradicals which are predicted to be the ground state were unsuccessful. Also, a monodiradical (e.g., azidonaphthylcarbene or nitrenonaphthyldiazomethane) expected to be formed by stepwise photoelimination of nitrogen was not detected. This is not surprising since similar attempts to detect *o*-phenylenebis(diradicals) by photolysis of nitrogeneous precursors often resulted in the formation of the final decomposition products, without showing any sign of the intermediate species.[9]

This is partly due to the energy generated by photolysis of nitrogenous precursors. For instance, theory predicts that the S_1 state of diazomethane is 67.5–71.5 kcal mol^{-1} above the ground state and that the S_1 state has sufficient energy to form methylene in an excited (open shell) singlet state.[16]

This prediction has been confirmed by spectroscopic study. Thus, a fluorescence spectroscopic study of photolysis of diphenyldiazomethane demonstrated the presence of an electronically excited triplet diphenylcarbene which was assumed to be produced by relaxation of the singlet excited state of diphenylcarbene.[17] More recent femto-second time-resolved study of photolysis of diazofluorene allowed the observation of not only electronically excited of diazofluorene but also two singlet states (closed shell and open shell) of fluorenylidene.[18]

Based on those previous observations, we assume that a nascent mono(diradical) generated by photo-elimination of one of two azo groups has sufficient energy to lose the remaining nitrogen and also to allow the resulting bis(diradical) to undergo subsequent thermal reaction. The exothermicity accompanied by the loss of the second nitrogen may also accelerate the subsequent thermal reaction of bis(diradical). It should be also noted that in the condensed phase, the excess energy is rapidly dissipated through collision. In matrix, especially that of monoatomic host such as a noble gas, on the other hand, the energy dissipation is not efficient and hence the heat of the reaction may be channeled into secondary intramolecular reaction.[19]

The computational data predict that although the ring-closure reaction from the E isomer of 1,2-NNC is energetically more favorable than the ring-opening reaction from the Z iso-

mer by 3.6 kcal mol^{-1}, the barrier of the interconversion of these two geometrical isomers is estimated to be ≈3 kcal mol^{-1} [9b] and hence both isomers of ^{1}A′-1,2-NNC are observable if generated in matrix at very low temperature. Exclusive formation of the ring-closure product in the photolysis of 1,2-**1**-$(N_2)_2$ then may mean that the heat of the reaction channeled to the nascent quinoidal diradical is sufficiently large (>3 kcal mol^{-1}) to allow the interconversion of the two geometrical isomers.

The same argument can be applied to explain almost exclusive formation of naphtha[2,3-*b*]azete (3,2-**2**) in the photolysis of 3-azido-2-naphthyldiazomethane [3,2-**1**-$(N_2)_2$]. In this case, the tendency is much more so since *E*-^{1}A′-3,2-NNC is predicted to undergo ring-opening reaction with nearly zero energy barrier, while the Z isomer is predicted to undergo the ring-opening reaction with energy barrier of 5.5 kcal mol^{-1}.

In the case of *o*-phenylene system (*o*-PNC), the ring-opening reaction is predicted to be energetically favored over the ring-closure reaction by 2.5 kcal mol^{-1}.[9b] Experimental work has demonstrated that ground state singlet bis(diradical) undergos thermal ring-opening reaction leading to 2,4-heptadien-6-ynenitrile almost exclusively. Thus, thermal decay pathways are switched from ring-opening to -closure as a π-linker of diradical ceters is changed from phenylene to naphthalene systems.

Conclusion

The present study revealed that the structures and energies of nitrenocarbene introduced in "ortho" conjugative manner on a naphthalene linker are interestingly dictated by the aromatic stabilization energy of the system. Thus, the structural and energetic features of 1,2-NNC are similar with those of *o*-PNC, while 3,2-NNC exhibits completely different features. The ring-closure thermal decay pathway is favored for NNC systems regardless of the position while the ring-opening decay is observed for PNC. The present observations revealed that energy splitting between electronic states is also greatly tuned by the substitution pattern of naphthalene. A higher spin state may become a ground state even in a conjugatively connected bis(diradical) system if a diradical center and an aromatic ring are properly selected.

Experimental

General Methods. ^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL JM-AL300FT/NMR spectrometer in $CDCl_3$ with Me_4Si as an internal reference. IR spectra were measured on a JASCO FT/IR-410 spectrometer, and UV–vis spectra were recorded on a JASCO CT-560 spectrophotometer. The mass spectra were recorded on a JEOL JMS-600H mass spectrometer and AB Voyager-DE PRE MALDI-TOF mass spectrometer. Gel permeation chromatography (GPC) was carried out on a JASCO model HLC-01 instrument. The GPC column was a Shodex H-2001. Thin-layer chromatography was carried out on Merck Kieselgel 60 PF254. Column chromatography was performed on silica-gel (Kanto Chemical) for column chromatography or ICN alumina (ICN Biomedicals) for dry column chromatography.

Preparation of 1-Azido-2-naphthyldiazomethane [1,2-1-$(N_2)_2$]. To a solution of 1-azidonaphthalene-2-carbaldehyde[20] (0.18 g, 0.89 mmol) in dry THF (3 mL) was added *p*-toluenesulfonohydrazine ($TosNHNH_2$) and the mixture was stirred at room temperature for 16 h. THF was removed under reduced pressure to obtain 1-azidonaphthalene-2-carbaldehyde tosylhydrazone as yellow solid in 99% yield (0.26 g); ^{1}H NMR ($CDCl_3$): δ 8.33 (s, 1H), 8.13 (d, J = 9.61 Hz, 1H), 7.92 (d, J = 8.64 Hz, 1H), 7.89 (d, J = 7.90 Hz, 2H), 7.85–7.78 (m, 2H), 7.65 (d, J = 8.64 Hz, 1H), 7.46–7.42 (m, 2H), 7.32 (d, J = 8.08 Hz, 2H), 2.41 (s, 3H). To a solution of 1-azidonaphthalene-2-carbaldehyde tosylhydrazone (0.20 g, 0.59 mmol) in dry THF (10 mL) was added sodium hydride (45.0 mg, 1.00 mmol, 1.7 equiv) and the mixture was stirred at room temperature for 30 min. The resulting precipitate was filtered, washed with dry THF under N_2 to give 1-azidonaphthalene-2-carbaldehyde tosylhydrazone sodium salt in 45% yield (0.1 g), which was used in the next step. 1-Azidonaphthalene-2-carbaldehyde tosylhydrazone sodium salt (100 mg, 25.8 mmol) was placed into a glass tube for sublimation and heated at 120 °C under reduced pressure (1.0×10^{-2} Torr). 1-Azido-2-naphthyldiazomethane [1,2-**1**-$(N_2)_2$] was sublimed onto a cooling portion of the apparatus as red solid in 7% yield (3.7 mg). ^{1}H NMR ($CDCl_3$): δ 8.00 (d, J = 8.45 Hz, 1H), 7.78 (d, J = 7.71 Hz, 1H), 7.68 (d, J = 8.26 Hz, 1H), 7.57–7.41 (m, 2H), 7.08 (d, J = 8.64 Hz, 1H) 5.47 (s, 1H); IR (NaCl plate): 2109 (s), 2058 (s) cm^{-1}. IR (Ar, 10 K): ν 2116 (vs), 2086 (vs), 1628 (w), 1603 (w), 1570 (w), 1512 (w), 1480 (w), 1401 (m), 1375 (m), 1356 (m), 1336 (w), 809 (m), 741 (w), 683 (w), 668 (w) cm^{-1}; UV–vis (Ar, 10 K): λ_{max} 273, 308 nm.

Naphtho[1,2-*b*]azete (1,2-2): IR (Ar, 10 K): ν 1588 (m), 1560 (m), 1539 (w), 1456 (w), 1316 (m), 1165 (w), 1132 (w), 939 (m), 864 (m), 787 (m), 757 (m) cm^{-1}; UV–vis (Ar, 10 K): λ_{max} 295 nm.

Preparation of 3-Azido-2-naphthyldiazomethane [3,2-1-$(N_2)_2$]. To a solution of 3-azido-2-naphthylmethanol[21] (1.0 g, 5.02 mmol) in dry CH_2Cl_2 was added pyridinium chlorochromate (1.6 g, 7.42 mmol) and the mixture was stirred for 3 h at room temperature. The mixture was washed with water and the organic layer was dried. The crude product obtained after evaporation of the solvent was chromatographed to give 3-azidonaphthalene-2-carbaldehyde as a yellowish solid in 79% yield (0.68 g). ^{1}H NMR ($CDCl_3$): δ 10.44 (s, 1H), 8.42 (s, 1H), 7.94 (d, J = 8.25 Hz, 1H), 7.80 (d, J = 8.25 Hz, 1H), 7.62 (dd, J = 8.25, 8.25 Hz, 1H), 7.61 (s, 1H), 7.50 (dd, J = 8.25, 7.92 Hz, 1H); IR (NaCl plate): 2118 (s), 1694 (s) cm^{-1}. 3-Azidonaphthalene-2-carbaldehyde (0.68 g, 3.45 mmol) was converted to the corresponding tosylhydrazone as described above in 99% yield (1.45 g). ^{1}H NMR ($CDCl_3$): δ 8.35 (s, 1H), 8.12 (s, 1H), 7.91 (d, J = 8.25 Hz, 2H), 7.83 (d, J = 7.9 Hz, 1H), 7.71 (d, J = 7.9 Hz, 1H), 7.52–7.40 (m, 2H), 7.46 (s, 1H), 7.31 (d, J = 7.9 Hz, 2H), 2.39 (s, 3H). The sodium salt of 3-azidonaphthalene-2-carbaldehyde tosylhydrazone (50 mg) obtained as described above was heated in a sublimation tube at 120 °C under reduced pressure (1.0×10^{-2} Torr) to obtain 3-azido-2-naphthyldiazomethane [3,2-**1**-$(N_2)_2$] as a red solid in 97% yield (30 mg). ^{1}H NMR ($CDCl_3$): δ 7.69–7.63 (m, 2H), 7.46 (s, 1H), 7.39–7.35 (m, 2H), 7.25 (s, 1H), 5.29 (s, 1H); IR (NaCl plate): 2108 (s), 2060 (s) cm^{-1}. IR (Ar, 10 K): ν 2118 (vs), 2065 (vs), 1599 (w), 1509 (m), 1502 (w), 1477 (m), 1453 (w), 1374 (m), 1363 (w), 1315 (w), 1297 (m), 1286 (m), 1233 (w), 1206 (w), 863 (m), 745 (m), 727 (m) cm^{-1}; UV–vis (Ar, 10 K): λ_{max} 370, 355, 322, 310, 281, 274 nm.

Naphtho[2,3-*b*]azete (3,2-2): IR (Ar, 10 K): ν 1649 (m), 1559 (w), 1460 (m), 1224 (w), 1064 (w), 1002 (w), 774 (w), 750 (m), 604 (w) cm^{-1}; UV–vis (Ar, 10 K): λ_{max} 254 nm.

Matrix-Isolation Spectroscopy. Matrix experiments were performed by means of standard techniques[22,23] using a closed-cycle helium cryostat. For IR experiments, a CsI window was attached to the copper holder at the bottom of the cold head. Two opposing ports of a vacuum shroud surrounding the cold head were fitted with KBr with a quartz plate for UV irradiation and a deposition plate for admitting the sample and matrix gas. For UV experiments, a sapphire cold window and a quartz outer window were used. The temperature of the matrix was maintained by a controller (gold vs. chromel thermocouple).

Irradiations were carried out with a 500-W xenon high-pressure arc lamp. For broad-band irradiation, cutoff filters were used (50% transmittance at the specified wavelength). For monochromatic light irradiation, a monochrometer was used.

Computational Procedures. DFT calculations were carried out using the Gaussian 94,[24] programs. Optimized geometries were obtained at the B3LYP/6-31G(d)[25] levels of theory. Vibrational frequencies obtained at the B3LYP level of theory were scaled by 0.961 and zero-point energies (ZPE) by 0.981.[26] Transition states were located using Gaussain program (Rational Function Optimization-pseudo-Newton-Raphsonthe method).[27] The nature of each stationary point was confirmed with harmonic frequency calculations, i.e., minima have exactly one imaginary frequency related to the expected movement.

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References

1 a) W. Kirmse, *Carbene Chemistry*, 2nd ed., Academic Press, New York, **1971**. b) C. Wentrup, *Reactive Molecules: The Neutral Reactive Intermediates in Organic Chemistry*, John Wiley & Sons, New York, **1984**. c) *Carbene (Carbenoid)*, *Methoden der Organischen Chemie (Houben-Weyl)*, ed. by M. Regitz, Thieme, Stuttgart, **1989**, Vol. E19b. d) *Carbenes*, ed. by M. Jones, R. A. Moss, Wiley Interscience, New York, **1973**, Vol. 1. e) *Carbenes*, ed. by R. A. Moss, M. Jones, Wiley Interscience, New York, **1975**, Vol. 2.

2 a) *Kinetics and Spectroscopy of Carbenes and Diradicals*, ed. by M. S. Platz, Plenum Press, New York and London, **1990**. b) *Advances in Carbene Chemistry*, ed. by U. H. Brinker, JAI Press, Greenwich, CT, **1994**, Vol. 1. c) *Advances in Carbene Chemistry*, ed. U. H. Brinker, JAI Press, Stamford, CT, **1998**, Vol. 2. d) *Advances in Carbene Chemistry*, ed. by U. H. Brinker, Elsevier, Amsterdam, **2001**, Vol. 3.

3 For reviews, see: a) *Diradicals*, ed. by W. T. Borden, Wiley, New York, **1982**. b) D. A. Dougherty, *Acc. Chem. Res.* **1991**, *24*, 88. c) P. S. Zuev, R. S. Sheridan, *Tetrahedron* **1995**, *51*, 11337. d) A. Nicolaides, H. Tomioka, in *Photochemistry of Organic Molecules in Isotropic and Anisotropic Media*, ed. by V. Ramamurthy, K. S. Schanze, Marcell Dekker, New York, **2003**, Vols. 9 and 10 p. 133. e) A. Nicolaides, H. Tomioka, *J. Photosci.* **2003**, *10*, 165.

4 See for reviews: a) H. Iwamura, *Adv. Phys. Org. Chem.* **1991**, *26*, 179. b) N. Koga, H. Iwamura, in *Carbene Chemistry: From Fleeting Intermediates to Powerful Reagents*, ed. by G. Bertrand, Fontis Media, Lausanne, **2002**, p. 271. c) K. Matsuda, N. Nakamura, K. Takahashi, K. Inoue, N. Koga, H. Iwamura, *ACS Symp. Ser.* **1996**, *644*, 142. d) H. Iwamura, *Proc. Jpn. Acad., Ser. B* **2005**, *81*, 233. e) N. Koga, S. Karasawa, *Bull. Chem. Soc. Jpn.* **2005**, *78*, 1384.

5 T. Itoh, K. Hirai, H. Tomioka, *Bull. Chem. Soc. Jpn.* **2007**, *80*, 138.

6 a) K. Itoh, *Chem. Phys. Lett.* **1967**, *1*, 235. b) E. Wasserman, R. W. Murray, W. A. Yager, A. M. Trozzolo, G. Smolinsky, *J. Am. Chem. Soc.* **1967**, *89*, 5076.

7 a) W. Subhan, P. Rempala, R. S. Sheridan, *J. Am. Chem. Soc.* **1998**, *120*, 11528. b) P. Zuev, R. S. Sheridan, *J. Am. Chem. Soc.* **1993**, *115*, 3788. c) P. S. Zuev, R. S. Sheridan, *J. Am. Chem. Soc.* **1994**, *116*, 9381.

8 a) H. Tomioka, K. Komatsu, T. Nakayama, M. Shimizu, *Chem. Lett.* **1993**, 1291. b) S. Koseki, H. Tomioka, A. Toyota, *J. Phys. Chem.* **1994**, *98*, 13203. c) A. Nicolaides, H. Tomioka, S. Murata, *J. Am. Chem. Soc.* **1998**, *120*, 11530. d) A. Nicolaides, T. Enyo, D. Miura, H. Tomioka, *J. Am. Chem. Soc.* **2001**, *123*, 2628. e) T. Enyo, A. Nicolaides, H. Tomioka, *J. Org. Chem.* **2002**, *67*, 5578. f) S. V. Chapyshev, H. Tomioka, *Bull. Chem. Soc. Jpn.* **2003**, *76*, 2075.

9 a) S. Koseki, H. Tomioka, K. Yamazaki, A. Toyota, *J. Phys. Chem. A* **1997**, *101*, 3377. b) A. Nicolaides, T. Nakayama, K. Yamazaki, H. Tomioka, S. Koseki, L. L. Stracener, R. J. McMahon, *J. Am. Chem. Soc.* **1999**, *121*, 10563. c) H. Tomioka, S. Sawai, *Org. Biomol. Chem.* **2003**, *1*, 4441. d) T. Enyo, N. Arai, N. Nakane, A. Nicolaides, H. Tomioka, *J. Org. Chem.* **2005**, *70*, 7744.

10 P. R. Serwinski, R. Walton, J. A. Sanborn, P. M. Lahti, T. Enyo, D. Miura, H. Tomioka, A. Nicolaides, *Org. Lett.* **2001**, *3*, 357.

11 It has been shown that some of those species were extremely photo-labile and decomposed even in a noble-gas matrix at low temperature. See, for instance, Refs. 8c, 8g, and 10.

12 I. Shavitt, in *Methods of Electronic Structure Theory*, ed. by H. F. Schaefer, III, Plenum Press, New York, **1977**, p. 189.

13 W. T. Borden, in *Diradicals*, ed. by W. T. Borden, Wiley, New York, **1982**, p. 1.

14 A. J. Gordon, R. A. Ford, *The Chemist's Companion*, Wiley, New York, **1972**, p. 131.

15 See also a more modern definition of NICS: a) P. v. R. Schleyer, H. Jiao, N. J. R. v. Eikema Hommes, V. G. Malkin, O. L. Malkina, *J. Am. Chem. Soc.* **1997**, *119*, 12669. b) H. Jiao, P. v. R. Schleyer, R. Warmuth, K. N. Houk, B. R. Beno, *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2761. c) T. K. Zywietz, H. Jiao, P. v. R. Schleyer, A. de Meijere, *J. Org. Chem.* **1998**, *63*, 3417.

16 a) B. Bigot, R. Ponec, A. Sevin, A. Devaquet, *J. Am. Chem. Soc.* **1978**, *100*, 6575. b) N. Yamamoto, F. Bernardi, A. Bottoni, M. Olivucci, M. A. Robb, S. Wilsey, *J. Am. Chem. Soc.* **1994**, *116*, 2064. c) F. Bernardi, M. Olivucci, M. A. Robb, T. Vreven, J. Soto, *J. Org. Chem.* **2000**, *65*, 7847. d) J. F. Arenas, I. López-Tocón, J. C. Otero, J. Soto, *J. Am. Chem. Soc.* **2002**, *124*, 1728.

17 Y. Wang, E. V. Sitzmann, F. Novak, C. Dupuy, K. B. Eisenthal, *J. Am. Chem. Soc.* **1982**, *104*, 3238.

18 J. Wang, J. Kubicki, E. F. Hilinsky, S. L. Mecklenburg, T. L. Gustafson, M. S. Platz, *J. Am. Chem. Soc.* **2007**, *129*, 13683.

19 B. F. LeBlanc, R. S. Sheridan, *J. Am. Chem. Soc.* **1988**, *110*, 7250.

20 G. E. Boswell, J. F. Licause, *J. Org. Chem.* **1995**, *60*, 6592.

21 M. Alajarín, A. Vidal, M.-M. Ortín, *Org. Biomol. Chem.* **2003**, *1*, 4282.

22 H. Tomioka, N. Ichikawa, K. Komatsu, *J. Am. Chem. Soc.* **1992**, *114*, 8045.

23 R. J. McMahon, O. L. Chapman, R. A. Hayes, T. C. Hess, H. P. Krimmer, *J. Am. Chem. Soc.* **1985**, *107*, 7597.

24 M. J. Frish, 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, Jr., 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, J. A. Pople, *Gaussian 94 (Revision D.4)*, Gaussian Inc., Pittsburgh, **1995**.

25 a) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785. b) B. Miehlich, A. Savin, H. Stoll, H. Preuss, *Chem. Phys. Lett.* **1989**, *157*, 200. c) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648.

26 A. P. Scott, L. Radom, *J. Phys. Chem.* **1996**, *100*, 16502.

27 J. Simons, P. Jørgensen, H. Taylor, J. Ozment, *J. Phys. Chem.* **1983**, *87*, 2745.