Photochemistry of Phenyl Azides Bearing 2-Hydroxy and 2-Amino Groups Studied by Matrix-Isolation Spectroscopy: Generation and Characterization of Reactive *o*-Quinoid Compounds

Hideo Tomioka*a, Takeshi Matsushitaa, Shigeru Murataa, and Shiro Kosekib

Chemistry Department for Materials, Faculty of Engineering, Mie University^a, Mie 514, Japan Telefax: (internat.) +81(0)592/31-9416 E-mail: tomioka@chem.mie-u.ac.jp

Department of Chemistry, Faculty of Education^b, Mie University Tsu, Mie 514, Japan

Received May 20, 1996

Key Words: 1,4-H Migration / Calculations, ab initio / Photochemical interconversion

Broad-band irradiation ($\lambda > 370$ nm) of 2-hydroxyphenyl azide (1) in Ar at 10 K monitored by IR resulted in the formation of at least three major products, all of which were shown to be photointerconvertible under these conditions. The two products showing carbonyl stretching absorption bands were assigned to an *E/Z* mixture of 6-imino-2,4-cyclohexadien-1-one (3), while the product showing sharp absorption bands in the cumulenic double bond region was assigned to 6-imino-1,3,5-hexatrien-1-one (4). These assignments were fully supported by comparison of the experimental IR spectra

The photochemistry of phenyl azides has attracted continuous and ever increasing interest^[1] in view of the usual applications in heterocyclic syntheses^[1], in photoresist technologies^[1,2], and in the biochemical methods of photoaffinity labeling [1,3,4]. The complete picture of the chemical reactions initiated by the elimination of nitrogen is beginning to unfold. Thus, photolysis of phenyl azide generates singlet phenylnitrene which is in equilibrium with the rearranged product, i.e., azacycloheptatetraene. This highly strained intermediate, characterized by IR spectroscopy^[5,6], accounts for solution-trapping results, giving, for example, 2-amino-3H-azepines in the presence of amines. The singlet nitrene undergoes intersystem crossing to the triplet, again characterized by spectroscopic means^[7,8], which either produces azobenzene by dimerization or affords aniline by abstraction of a hydrogen atom from the solvent in fluid solution. The triplet nitrene, on the other hand, was shown to undergo ring expansion upon photoexcitation within the matrix^[5,6].

The chemistry of phenylnitrenes with functional groups at the ortho position has been recognized and employed as a very useful route to nitrogen heterocycles^[1,9], since these nitrenes usually interact with the proximate functional group to produce an important class of azacyclic compounds which are otherwise difficult to obtain. However, spectroscopic studies to detect and characterize the intermediates involved in these intramolecular reactions are relawith the theoretical data calculated at the HF/6-31G** level of theory. Similar irradiation ($\lambda > 350$ nm) of 2-aminophenyl azide (**6**) in Ar at 10 K also afforded three photointerconvertible products, which were assigned to a mixture of (*E*,*E*)-(*E*,*Z*)- and (*Z*,*Z*)-1,2-diimino-3,5-cyclohexadiene (**8**). The assignments were again supported by ab initio calculations. The reactions are discussed in terms of a 1,4 H shift in the photolytically generated phenylnitrenes (**2** and **8**) from the azides (**1** and **7**).

tively scarce. Therefore, it is of great interest to know how the intermediates proposed in the chemistry of "simple" phenylnitrenes are trapped by the proximate functional groups. For instance, by using matrix-isolation techniques, we^[10] and others^[11] have provided spectroscopic evidence that in the photolysis of 2-nitrophenyl azide forming benzofuroxan, 2-bis(nitroso)benzene, which was proposed^[12] to be generated in the photointerconversion of benzofuroxan, is actually produced. More recently, we have revealed that, under matrix conditions, 2-(methoxycarbonyl)phenylnitrene not only undergoes ring expansion to form 3-(methoxycarbonyl)-1,2,4,6-azacycloheptatetraene but also undergoes unusual formal 1,4-methoxy migration to generte carbonyl oximino benzenes, which then undergo cyclization to afford azetinone^[13]. A similar fascinating chemistry was also observed with phenylcarbenes bearing functional groups at the ortho positions^[14-16]. These studies clearly indicate that the chemistry of these species is unexpectedly rich not only in terms of new types of intermediates but also with respect to reaction patterns, which have not been observed so far under ambient conditions.

As an extension of our work on the intramolecular interaction of a divalent center with proximate functional groups thereby generating a new reactive species, we investigated the photochemistry of *o*-amino- and *o*-hydroxyphenyl azides in an argon matrix at 10 K and found that the nitrene center undergoes an interesting hydrogen abstraction from

the ortho substituents to generate a series of *o*-quinoid compounds, which are characterized by a combination of spectroscopy with theoretical calculation.

Results and Discussion

Photolysis of 2-Hydroxyphenyl Azide (1)

Deposition of 2-hydroxyphenyl azide $(1)^{[17]}$ in an argon matrix at 20 K gave the IR spectrum shown in Figure 1a. Broad-band irradiation (370 min, $\lambda > 370$ nm) of the sample cooled to 10 K was monitored by infrared spectroscopy, which revealed a rapid and simultaneous disap-

Figure 1. (a) IR spectrum of 2-hydroxyphenyl azide (1) matrixisolated in Ar at 10 K; (b) IR spectrum obtained by irradiation ($\lambda > 370$ nm) of 1 in Ar at 10 K; bands marked \oplus , \bigcirc and \blacktriangle are due to photoproducts **A**, **B** and **C**





pearance of both absorption bands due to azido (2132 and 2092 cm^{-1}) and hydroxy (3554 cm⁻¹) groups and growth of new absorption bands due to the formation of a cumulenic double bond (2124, 2108 and 2028 cm^{-1}) and carbonyl groups (1680 and 1676 cm⁻¹) (Figure 1b). A careful analysis of these product absorption bands by plotting their intensities as a function of irradiation time and wavelength of light revealed that there were at least three major products designated as A (1676, 1570, 1376, 1218, 1142, 1070 and 722 cm⁻¹), **B** (1680, 1342, 1066, 902 and 706 cm⁻¹), and C (2124, 2108 and 2028 cm^{-1}). Control experiments showed that these products were all interconvertible upon irradiation (Scheme 1). Thus, irradiation of the initial photomixtures, containing all the major photoproducts, with light of $\lambda > 420$ nm resulted in the disappearance of the bands due to **B** and **C** and in the concurrent growth of the bands due to the formation of A. Irradiation of the mixture containing A as major component with light of $\lambda > 390$ nm and 370 nm reproduced the IR bands ascribable to B and C, respectively.

What are the photoproducts $(\mathbf{A}-\mathbf{C})$? Analysis of the major IR bands provided some insights into their structures. First, the presence of the bands at 1680 and 1676 cm⁻¹, of **A** and **B** respectively, indicates the presence of carbonyl groups. This, coupled with the simultaneous disappearance of both azido and hydroxy groups, points to 6-imino-2,4-cyclohexadien-1-ones (3) as the most plausible

Figure 2. Relative energies and optimized geometries of 3, 4 and 5, calculated at the HF/6-31G** level of theory





Figure 3. Theoretical (HF/6-31**) and experimental IR spectrum of Z-3 (a) and E-3 (b)

structures for A and B, which must be produced as a result of 1,4-H migration in photolytically generated 2-hydroxyphenylnitrene (2). An analogous intramolecular interaction of the nitrenic center with the functional groups at the ortho positions was reported^[13]. The bands attributed to the cumulenic bond observed in the spectrum of C are obviously too high in frequency as well as in intensity to be assignable to that of hydroxy-1,2,4,6-azacycloheptatetraene which is expected to be formed as a result of ring expansion in the nitrene (2). Thus, most phenylnitrenes undergo ring expansion to generate azacycloheptatetraenes which usually show rather weak bands at $1850-1890 \text{ cm}^{-1}$ in an argon matrix at low temperature^[5,6]. Absence of the hydroxy absorption bands also excluded this possibility. Since C was produced by photolysis of the iminocyclohexadienones (A and **B**), 6-imino-1.3.5-hexatrien-1-one, which must be formed by ring-opening of the dienones (A and B) upon photoexcitation, can be proposed as a plausible structure for C since the analogous photochemical ring-opening reaction for the corresponding bisketene was reported^[18,19].

In order to gain more support for these asssignments, ab initio calculations were carried out for some C_6H_5NO molecules expected to be produced from the nitrene (2) including benzoxazetine (6). The calculations at the HF/6-31G** level of theory revealed that all these molecules have true energy minima on the corresponding potential energy surfaces and that the imino ketone structures (3) are more stable than their ring-opened (4) and ring-closed structures (6) by several tens of kcal/mol (Figure 2). The vibrational frequencies were calculated for those compounds and were compared with the experimental vibrational frequencies observed with **A**, **B**, and **C**. For comparison with the experimental values, the theoretical frequencies were scaled by 0.91, as recommended by Grev et al.^[20]. The calculated fre-

quencies for (Z)-3 and (E)-3 match the experimental data for the photochemically produced compounds A and B, respectively (Tables 1 and 2, Figure 3). The optimized geometries of both isomers of 3 are planar and have an *o*-quinoid structure. The Z isomer was calculated to be more stable than the E isomer by 6.6 kcal/mol. Inspection of the structure suggests that this stabilization is caused by the formation of a hydrogen bond between the imino hydrogen





and the carbonyl oxygen atoms. On the other hand, the IR spectrum of C is in agreement with the calculated frequencies for 4 (Table 3). At least four rotamers are possible for the bisketene monoimine (4). Calculations of the total energy for each of the stationary points indicates that the stability decreases in the order of s-*trans*,s-*trans* > s-*trans*,s-*cis* > s-*cis*,s-*trans* > s-*cis*,s-*cis* with energy differences of less than 5 kcal/mol. Only the most stable s-*trans*,s-*trans* isomer shows a planar structure. Irradiation of α -pyrone in argon at 8 K was shown to give 1-formyl-1,3-butadien-4-one as a

Figure 4. Theoretical (HF/6-31**) and experimental IR spectrum



mixture of four rotamers, since a large number of bands is observed in the ketene region^[21], while ratios are dependent on the irradiation time as well as the matrix temperature. This implies that electronically excited α -pyrone undergoes electrocyclic ring opening, and that in the process of demotion and thermal equilibration a nonthermodynamic mixture of rotamers is formed, and that the required movement occurs even in argon at 8 K. These results suggest that all possible rotamers might be produced in the present electrocyclic opening of 3 upon photoexcitation. However, we were not able to observe the large number of bands in the ketene region. Instead, a single major band appears in most cases and minor bands are observed upon thawing of the matrix from 10 K to 35 K. Calculated frequencies for the rotamers of 4 are very close to each other at this level of calculation. The correspondence of relative intensities is better for s-cis, s-cis-4 among the isomers (Figure 4).

Figure 5. (a) IR spectrum of 2-aminophenyl azide (7) matrix-isolated in Ar at 10 K; (b) IR spectrum obtained by irradiation ($\lambda >$ 350 nm) of 7 in Ar at 10 K; bands marked \oplus , \bigcirc and \blacktriangle are due to photoproducts **D**, **E** and **F**



Finally, for the azetine (6) the calculated frequencies do not appear to match the experimental data calculated at this level of theory. Thus, the predicted relative energies as well as the calculated frequencies of the proposed intermediates in the tautomerization of C_6H_5NO molecules fully support the assignments based on the experimental observations (Scheme 2).

Photolysis of 2-Aminophenyl Azide (7)

Broad-band irradiation (360 min, $\lambda > 350$ nm) of 7^[17], matrix-isolated in argon at 10 K, was monitored by IR spectroscopy, which also revealed a rapid and simultaneous disappearance of both absorption bands arising from the azido (2132, 2114 and 2096 cm⁻¹) and amino (3520 and 3418 cm⁻¹) groups and the growth of new bands (Figure 5). A careful analysis of these product absorption bands by plotting their intensities as a function of irradiation time and wavelength of light suggests that there were at least three major products **D** (1431, 1356, 1341, 1094, 1060, 878 and 706 cm⁻¹), **E** (1278, 1182, 1112 and 714 cm⁻¹), and **F** (1427, 1362, 1054 and 894 cm⁻¹), and that all these products are interconvertible upon irradiation. Thus, irradiation of the initial photomixtures obtained by irradiation ($\lambda >$

Scheme 3



Figure 6. Relative energies and optimized geometries of 9, 10 and 11, calculated at the HF/6-31G** level of theory



Figure 7. Theoretical (HF/6-31**) and experimental IR spectrum of E,Z-9 (a), Z,Z-9 (b) and E,E-9 (c)



350 nm) of 7 with light of $\lambda > 300$ nm tended to increase the bands due to the formation of **E**. Irradiation of this mixture containing **E** with light of $\lambda > 390$ nm gave **F** while longer wavelength irradiation ($\lambda > 420$ nm) resulted in an increase in the bands due to **D** (Scheme 3).

What are these products (D-F), then? First, it should be noted that no bands appeared in the cumulenic double bond region. This indicates that neither amino-1,2,4,6-azacycloheptatetraenes (12), expected to be formed as a result of ring expansion of the photolytically generated nitrene (8), nor bisketene imines (10), which were observed in the photolysis of 1, were formed. Disappearance of the amino bands and rather significant changes in the aromatic deformation region suggest that aminophenylnitrene (8) is not observed in the product IR bands. Thus, 1,2-diimino-3,5cyclohexadienes (9), expected to be formed as a result of 1,4-H migration in 8, can be considered as the most plausible structure. A priori, three isomers are possible for 9. However, it is very difficult to assign explicitly the observed bands to each of these isomers simply on the basis of experimental observations.

Thus, ab initio calculations were carried out not only for the diiminodienes (9) but also for other $C_6H_6N_2$ molecules (10 and 11) expected to be produced from the nitrene (8).

Scheme 4



The calculations at the HF/6-31G** level of theory showed that all of these molecules have a true energy minimum on the corresponding potential energy surfaces and that the diiminediene structures (9) are far more stable than those of 10 and 11 (Figure 6). The vibrational frequencies for three isomers of 9 were calculated and compared with the experimental values, which clearly showed that the calculated frequencies for (E,Z)-, (Z,Z)- and (E,E)-9 are in fair agreement with the experimental data for the photoproducts **D**, E, and F, respectively (Tables 4-6, Figure 7). The optimized geometries of these isomers are shown in Figure 6. Both the E,E- and the E,Z-isomer are planar, whereas a nonplanar structure is optimized for the Z, Z isomer. The E, Z-isomer was calculated to be the most stable isomer, whereas the *E,E*-isomer is the most unstable one, lying 7-8 kcal/mol higher in energy than the E,Z-isomer. It is probable then that the planar E,Z isomer is stabilized by hydrogen bonding, whereas the destabilization of the E,E-isomer is caused by the repulsive interactions of the lone pairs at the nitrogen atoms. The ring-opened isomers (10) which were not observed experimentally were calculated to be more than 40 kcal/mol less stable than the diiminedienes (9). The stability of the three possible rotamers decreases in the order s*trans*,s-*trans* > s-*trans*,s-*cis* > s-*cis*,s-*cis* with energy differences of less than 7 kcal/mol, and again only the most stable s-trans, s-trans isomer has a planar structure. On the other hand, for the ring-closed isomers (11) which were not observed either, two isomers were calculated, with the C_2 symmetrical E-isomer more stable than the $C_{\rm s}$ symmetrical Zisomer by 6.3 kcal/mol (Scheme 4).

Summarizing Discussion

The present observations have demonstrated that phenylnitrenes and phenylcarbenes bearing proximate functional groups can serve, as a result of intramolecular interaction between the divalent center and the functional group, as very attractive and clean precursors for the generation of new reactive species that are otherwise difficult to prepare. Moreover, these species are relatively easily characterized by spectroscopic means coupled with theoretical calculations because the reactions are usually clean and efficient even in the matrix at very low temperature. The observations also suggest that even the hydrogen atom of hydroxy and amino groups can serve as a reactive center towards the divalent center. Intramolecular H migration involving divalent species within the matrix to generate quinoid compounds is not unprecendented^[15]. For instance, similar 1,4-H migration reactions were also observed with 2-tolylcarbene and 2-aminophenylcarbene^[16].

Photolysis of phenyl azides within a matrix usually results in the formation of azacycloheptatetraenes and triplet nitrenes which are in photoequilibrium upon irradiation^[5h]. It is hence rather unusual that neither nitrenes nor azacycloheptatetraenes are observed in the photolysis of **1** and **7**. The observations suggest that the H migration is very efficient for **2** and **8** even under these conditions. It is interesting to compare the present result with the analogous reaction of 2-tolylnitrene^[16] within a matrix, where hydrogen migration is not observed. In order to explain the difference in reactivities between the present nitrenes and 2-tolylnitrene, several factors such as bond energy, the intermediates undergoing H migration, singlet-triplet splitting and the overall mechanism should be considered.

The bond energies of $PhCH_2-H$ (85 kcal/mol)^[22] and PhO-H (85 kcal/mol)^[22] are almost the same, suggesting that this cannot be a crucial factor. In a stricter sense, however, one should take the transition state (TS) structure into account since the H transfer should require a five-membered cyclic structure (vide intra) where little benzylic stabilization is available. Exact TS structures are dependent on the multiplicities undergoing hydrogen migration.

The reactions in the singlet state are usually believed to proceed in a concerted fashion. This causes steric constraints especially in the transition state of intramolecular reactions. Thus, in the case of a carbene, we expect that the σ^2 configuration is the lowest singlet configuration while the σp configuration is the most probable one of the triplet state. In the case of phenylcarbene, the most stable planar conformer must be the one with the vacant p orbital perpendicular to the plane of the benzene ring where interaction of the vacant p orbital with the aromatic π bond is achieved. Since this type of π bonding is much less significant in the perpendicular conformer, the rotational barrier of the singlet about the bond connecting the divalent center to the benzene ring is significant. In the case of triplet phenylcarbene, both in the planar and perpendicular conformers, interactions occur between the ring π electrons and the half-filled obital. Therefore, the rotational barrier is low.

The calculated (3-21 G) rotational barriers for the singlet and triplet are 11.2 and 5.7 kcal/mol, respectively^[23]. It was shown that, while most intermolecular C-H insertion reactions of phenylcarbene proceed by a concerted singlet mechanism, intramolecular C-H insertion reactions follow a triplet abstraction-recombination mechanism, especially when the TS requires a small-membered ring^[24]. For example, in the intramoleculer C-H insertion of (2-alkoxyphenyl)carbene affording 2,3-dihydrobenzofurans, the concerted insertion of the singlet involving both the p and σ orbital which interact with δ -C-H bonds, requires the rotation. This results in loss of benzylic stabilization and deformation of bond angles. In contrast, the transfer of δ hydrogen to the half-filled, in-plane σ orbital of the triplet carbene can proceed via a favorable six-membered transition state in which the benzylic resonance is not disturbed. If one applies similar TS structure considerations to the 1,4 H migration, the abstraction from the triplet state is energetically more favorable than the concerted migration in the singlet carbene^[24]. Actually, the 1,4-H shift in 2-tolylcarbene was demonstrated to occur in the triplet state^[15].

The same explanation cannot be applied to the reaction of phenylnitrene unless one takes into account the change in electronic configuration. If one considers singlet phenylnitrene as a planar and approximately sp-hybridized species with the nitrogen lone pair in a $\sigma\pi$ orbital and two nearly degenerate π orbitals, σ and π , $\sigma\pi$ is thought to be the lowest singlet configuration of singlet phenylnitrene since the two p orbitals are nearly degenerate. This difference in the electronic configuration can explain the difference in reactivity between phenylcarbene and phenylnitrene (both in the singlet state). Thus, while singlet phenylcarbene undergoes a concerted insertion reaction with a C-H bond, analogous reactions of singlet phenylnitrenes are rare. Assuming that concerted insertion reactions of singlet carbenes involve the coordination of the empty p orbital with a pair of electrons in a σ bond, this type of coordination is not possible for the singlet nitrene^[25].

Another important factor which influences the reactivity difference between phenylcarbene and phenylnitrene is the singlet-triplet energy gap ($\Delta G_{\rm ST}$). Kinetic studies and chemical trapping studies of phenylcarbene suggest that $\Delta G_{\rm ST}$ is small, probably less than 2 kcal/mol^[26]. However, spectroscopy^[27a] and theory^[27b] agree that $\Delta G_{\rm ST}$ of phenylnitrene is large, approximately 17–18 kcal/mol. Thus, triplet carbene can often serve as a reservoir for an easily accessible, highly reactive singlet since $\Delta G_{\rm ST}$ is small and hence intersystem crossing rates are high. This is not true for phenylnitrene; triplet phenylnitrene will not reform the more reactive singlet states because $\Delta G_{\rm ST}$ is much too large.

On the other hand, triplet phenylnitrene abstracts hydrogen atoms from alkanes rather slowly relative to triplet phenylcarbene. This effect has a thermodynamic origin; the reaction of triplet methylene with methane is exothermic $(\Delta H = -5.6 \text{ kcal/mol})^{[28]}$, whereas the corresponding reactions of triplet nitrene with methane is endothermic ($\Delta H =$ +7.7 kcal/mol)^[29].

Thus, the reactions observed with 2-tosylnitrene agree well with those expected for typical arylnitrenes, while those with 2-hydroxy- (2) and 2-aminophenylnitrenes (8) are unusual in that they undergo H migration very efficiently and resemble those of phenylcarbene. Taking into account the strong π -donating ability of hydroxy and amino groups, electronic effects must play an important role in this case. It is well known in carbene chemistry that electron-donating groups stabilize the electrophilic singlet more than they do the radical-like triplet^[30]. Presumably, π -donating groups stabilize singlet nitrene as well by stabilizing the σ^2 configuration. It was proposed that ring expansion of singlet phenylnitrene to form azacycloheptatetraene occurs in the p^2 configuration which is usually not so high in energy compared to the σ^2 and $\sigma\pi$ configurations^[25]. Thus, the stabilization of the σ^2 configuration relative to the p² configuration should result in an increase in the ring expansion barrier. On the other hand, an increase of the contribution of the σ^2 configuration should result in an increase in the reactivity of singlet nitrene towards an X-H bond. As mentioned before, the concerted reaction in the singlet state must be energetically less favorable than the stepwise reaction in the triplet state for the present 1,4 H migration due to the steric constraints in the TS, if the same mechanism is applied to the H migration of 2 and 8. However, in the case of 2 and 8, proton transfer from polarized X-H bonds to the singlet nitrenic center is more likely and this does not require more severe steric constraints than the concerted migration of hydrogen involving both the p and the σ orbital, respectively. A change in the electronic configuration and a decrease in $\Delta G_{\rm ST}$ should also favor the reaction pathway proceeding from the triplet states. Thus, if the hydrogen migration takes place on the triplet surface, the process must involve surface crossing, i.e., there is a timing of spin inversion and of chemical events. Thus, triplet to singlet intersystem crossing occurs prior to H migration to the singlet or surface crossing occurs after the triplet has begun to abstract a hydrogen atom^[31]. In either case, a decrease in $\Delta G_{\rm ST}$ results in an increase in hydrogen transfer efficiency relative to that of unperturbed phenylnitrene (e.g., 2-tolylnitrene). It should be noted here that 2-aminophenylcarbene was also shown to undergo very efficient H migration to generate o-iminoquinone methide under the same conditions^[16].

One should also take into account the contribution of tunneling in the present H migration, because a tunneling mechanism was proposed to be involved in a similar 1,4-H shift in triplet 2-tolylcarbene with a matrix at low temperatures^[15,32]. It was shown that tunneling is very sensitive to the width and the height of the barrier^[33]. Thus, the observed difference in reactivities between 2-tolylnitrene and **2** and **8** may be ascribed to the difference in tunneling distance.

Finally, photochemical reactivities of *o*-quinoid compounds are also sensitive to the heteroatoms. Thus, *o*-iminoquinone methide undergoes cyclization to form benzoazetitine upon photoexcitation, while a similar photochemical cyclization is not observed with the quinoid compounds

generated from 2 or 8. This can be understood at least qualitatively in terms of the energy difference between the quinoid compound and the bicyclic isomer. Thus benzoazetine was calculated to be slightly more stable than iminoquinone methide, whereas the cyclic isomers of the imino quinoid compounds 3 and 9 were calculated to be less stable than the quinone by 56 and 30-36 kcal/mol, respectively. The difference in the photochemical reactivities cannot be explained simply by the energy differences of the groundstate molecules. Thus, although the energy differences between the quinones and the ring-opened isomers are small, the photochemical ring-opening reaction is observed only with the quinone 3, not with quinone 9. Obviously, the nature of electronically excited states must play a more important role in this case.

The work was supported by a Grant-in-Aid on Priority Areas Research on "Photoreaction Dynamics" from the *Ministry of Education, Science and Culture*, Japan.

Experimental

Calculations: The ab initio calculations were carried out by the program packages Gaussian $92^{[34]}$ or Spartan^[35] on SGI or Sun workstation computers. The geometry of all compounds was optimized at the HF/6-31G** level of theory. Vibrational frequencies and intensities were calculated at the same level of theory.

Table 1. IR spectroscopic data of (Z)-6-imino-2,4-cyclohexadien-1one (Z-3), matrix isolated in Ar at 10 K and calculated at the HF/ 6-31G** level of theory

Experiment ^[a]		Calcula	ted[b]	Assignment ^[c]	
Vib.	v[cm ⁻¹]	int.	v[cm ⁻¹]	int.	
28	1676	s	1792	236.3	C=0 str.
27	1647	VW	1717	39.1	C=O,C=N,C=C str.
26	1622	vw	1663	10.6	C=O,C=N,C=C str.
25	1570	w	1616	19.5	C=C str.
24	1390	vw	1419	13.3	C-C str., CH,NH ip
23	1376	vw	1377	29.1	C-C str., CH,NH ip
22			1342	6.0	C-C str., CH,NH ip
21	1218	S	1212	122.5	C-C str., CH,NH ip
	1210	w			
20	1162	vw	1154	6.1	CH,NH ip
19	1142	w	1131	32.3	CH,NH ip
18	1070	VW	1058	29.8	6-ring, NH ip
17			1027	0.6	HC=CH torsion
16			1018	4.0	HC=CH torsion, NH oop
15	942	VW	987	31.4	CH,NH oop
14			917	4.0	6-ring ip
13			869	8.6	СНоор
12			859	2.5	6-ring ip
11			764	4.4	CHoop
10	722	vs	740	145.3	CH,NH oop
9	665	vw	681	12.1	6-ring ip
8			545	0.4	6-ring ip
7	544	vw	532	12.9	CCO,CCN ip

^[a] Measured in Ar at 10 K; vs = very strong; s = strong; m = medium; w = weak; vw = very weak. - ^[b] Theoretical frequencies have been multiplied by 0.91. - ^[c] ip = in plane; op = out of plane.

General Methods: IR: JASCO IR-700 spectrophotometer. - ¹H NMR: JEOL JNM-EX 270 spectrometer, CDCl₃, internal reference TMS. – Column chromatography: silica gel (ICN for dry column chromatography).

Matrix-Isolation Spectroscopy: Matrix experiments were performed by means of standard techniques^[36,37] using an Iwatani

	Experiment[a]		Calcula	ted[b]	Assignment[c]
Vib.	v[cm ⁻¹]	int.	v[cm ⁻¹]	int.	
28	1680	s	1813	212.4	C=0 str.
27	1652	vw	1718	27.1	C=0,C=N,C=C str.
26	1628	vw	1667	8.6	C=O,C=N,C=C str.
25	1604	vw	1626	3.9	C=C str.
24			1411	41.1	C-C str., CH,NH ip
23			1361	0.9	C-C str., CH,NH ip
22	1342	S	1345	147.2	C-C str., CH,NH ip
21			1197	0.4	C-C str., CH,NH ip
20	1170	vw	1163	9.6	CH,NH ip
19	1111	vw	1126	10.2	CH,NH ip
18	1066	m	1048	66.7	6-ring,NH ip
17			1026	0.3	HC=CH torsion
16			1011	7.1	HC=CH torsion, NH oop
15	902	vs	948	128.1	CH,NH oop
14			923	0.6	6-ring ip
13	852	vw	870	2.9	CH oop
12	848	vw	855	1.5	6-ring ip
11			766	0.2	CHoop
10	706	w	720	31.1	CH,NH 00p
9	-		673	1.4	6-ring ip
8			544	0.8	6-ring ip
7	536	vw	526	28.7	CCO,CCN ip

[a-c] See footnotes a-c in Table 1.

Cryo Mini 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 parts of a vacuum shroud surrounding the cold head were fitted with KBr windows for spectroscopic viewing, and the remaining parts were fitted with a quartz plate for UV irradiation and a deposition plate for admitting the sample and matrix gas. For the UV experiments, a sapphire cold window and quartz outer window were used. The temperature of the matrix was controlled by an Iwatani TCU-1 controller (gold vs chromel thermocouple).

Table 3. IR spectroscopic data of 6-imino-1,3,5-hexatrien-1-one (4), matrix isolated in Ar at 10 K and calculated at the HF/6-31G** level of theory

Experiment[a]			a] Calcul	ated[b]	Assignment[c]	
Vib.	v[cm ⁻¹]	int	v[cm ⁻¹]	int.		
			s-cis,s-cis-4			
28 27			2121 2037	1130.6 507.0	C=C=0 str. C=C=N str.	
28 27	2124 2108	VS S	s-cis,s-trans-4 2058 2037	913.7 1464.6	C==C==0 str. C==C=N str.	
28 27	2028	s	<i>s-trans,s-cis-</i> 4 2119 2033	1043.2 1058.0	C==C==0 str. C==C==N str.	
28 27			s-trans,s-trans- 2123 2032	4 1612.1 1589.3	C=C=0 str. C=C=N str.	

[a-c] See footnotes a-c in Table 1.

Organic compounds were sublimed on the cold window and simultaneously a large excess of argon (Seitetsu Chemicals, 99.999%) was deposited. Irradiations were carried out with a Wacom 500-W xenon highpressure arc lamp or an Ushio 500-W mercury high-pressure arc lamp. For broad-band irradiation, Thoshiba cut-off filters were used (50% transmittance at the wavelengths specified).

Table 4. IR spectroscopic data of (E,Z)-1,6-diimino-2,4-cyclohexadiene (E,Z-9), matrix isolated in Ar at 10 K and calculated at the HF/6-31G** level of theory

Experiment[a]		Calcula	ted[b]	Assignment[c]	
Vib.	v[cm ⁻¹]	int.	v[cm ⁻¹]	int.	
30	1555	vw	1738	24.7	C=C,C=N str.
29	1539	w	1691	67.9	C=C,C=N str.
28			1662	13.2	C=C,C=N str.
27			1620	11.0	C=C,C=N str.
26	1431	vw	1422	19.8	C-C str., CH,NH ip
25	1385	vw	1379	29.9	C-C str., CH,NH ip
24	1352	vw	1354	59.8	C-C str., CH,NH ip
23	1314	VS	1313	120.3	CH,NH ip
22			1164	7.1	CH,NH ip
21	1168	vw	1160	13.3	CH,NH ip
20	1094	w	1082	36.2	6-ring,CH,NH ip
19	1060	s	1042	52.8	6-ring,CH,NH ip
18			1021	1.7	HC=CH torsion
17			1013	0.1	HC=CH torsion,NH oop
16	928	w	980	60.8	CH,NH oop
15			924	2.0	6-ring ip
14	878	VS	918	129.6	CH,NH oop
13			858	5.7	6-ring ip
12			852	2.3	CH oop
11	739	vw	750	4.8	6-ring oop
10	706	m	719	50.9	CH,NH oop
9	668	vw	683	3.8	6-ring ip
8			569	0.5	6-ring ip
7	528	vw	515	23.2	CCN ip

Experiment ^[a]		Calculated ^[b]		Assignment[C]	
Vib.	v[cm ⁻¹]	int.	v[cm ⁻¹]	int.	
30	1649	1/14/	1734	17.6	C=C,C=N str.
28	1045	•••	1664	12.7	C=C,C=N str.
26	1427	m	1626	6.2 42.3	C=C,C=N str. C-C str., CH,NH ip
25 24	1362	S	1371 1364	162.5 0.3	C-C str., CH,NH ip C-C str., CH.NH ip
23	1302	vw	1298	37.7	CH,NH ip CH NH ip
21	1174	w	1166	26.4	CH,NH ip
20 19	1104 1054	w m	1091	41.7 62.5	6-ring,CH,NH ip 6-ring,CH,NH ip
18 17			1017 1008	0.0	HC=CH torsion HC=CH torsion,NH oop
16 15	894	VS	938 933	197.5 0.1	CH,NH oop 6-ring,CH ip
14 13			919 854	$0.1 \\ 0.1$	CH,NH oop 6-ring ip
12 11			847 752	0.0 0.0	CH oop 6-ring oop
10	668	vw	707	6.7	CH,NH oop
7 8 7			554 512	0.6	6-ring ip
1			514	20.5	CONT

[a-c] See footnotes a-c in Table 1.

2-Azidophenol^[17] (1): To a stirred solution of 2-aminophenol (50 mg, 0.46 mmol) in 6 \times HCl (2 ml) at 0 °C was added an aqueous solution of sodium nitrite (38 mg, 0.55 mmol). After stirring for 2 h, a solution of sodium azide (60 mg, 0.92 mmol) in water (2 ml) was added dropwise to the stirred mixture. After an additional hour at room temp., the reaction mixture was extracted with CH₂Cl₂, and the extract was washed with water, dried (Na₂SO₄) and concen-

trated. The residue was separated by preparative TLC with 50% CH₂Cl₂/*n*-hexane to give 1 as a red oil; 34%; $-^{1}$ H NMR (CDCl₃): $\delta = 5.40$ (s, 1 H), 6.89–6.97 (m, 2 H), 7.02–7.10 (m, 2 H); IR (Ar, 10 K), $\tilde{\nu} = 3554$ cm⁻¹ (m), 2132 (vs), 2092 (m), 1601 (m), 1588 (vw), 1512 (vw), 1495 (vs), 1353 (m), 1306 (s), 1294 (vs), 1251 (vs), 1207 (vs), 1143 (w), 1089 (vw), 1030 (vw), 795 (vw), 745 (s), 649 (vw), 524 (vw).

Table 5. IR spectroscopic data of (Z,Z)-1,6-diimino-2,4-cyclohexadiene (Z,Z-9), matrix isolated in Ar at 10 K and calculated at the HF/6-31G** level of theory

Experiment[a]			Calculated[b]		Assignment ^[c]
Vib.	v[cm-1]	int.	v[cm ⁻¹]	int.	
30 29	1533	vw	1731 1686	24.1 82.3	C=C,C=N str. C=C,C=N str.
28 27 26	1525	vw	1663 1625 1419	14.1 2.7 3 1	C=C,C=N str. C=C,C=N str.
26 25 24	1360 1312	w vw	1369 1349	16.0 14.9	C-C str., CH,NH ip C-C str., CH,NH ip C-C str., CH,NH ip
23 22	1278 1182	m m	1270 1171	61.6 66.4	CH,NH ip CH,NH ip
21 20 19	1162 1112	w s	1156 1095 1021	19.1 120.8 0.4	CH,NH 1p 6-ring,CH,NH ip HC=CH torsion
18 17	1024	vw	1014 1010	0.2 11.5	HC=CH torsion, NH oop 6-ring,NH ip
16 15	960	vw	924 917	5.8 6.7	6-ring,CH ip NH oop
14 13	896	w	915 857	66.5 0.8	CH,NH oop CH,NH oop
12 11 10	714	vs	632 739 731	9.9 0.3 186.1	6-ring oop CH,NH oop
9 8 7			681 555 517	11.6 0.3 1.7	6-ring ip 6-ring ip CCN ip

 $^{[a-c]}$ See footnotes a-c in Table 1.

Table 6. IR spectroscopic data of (Z)-1,6-diimino-2,4-cyclohexadiene (E,E-9), matrix isolated in Ar at 10 K and calculated at the HF/6-31G** level of theory

Experiment[a]		Calculated[b]		Assignment ^[c]	
Vib.	v[cm ⁻¹]	int.	v[cm ⁻¹]	int.	
30 29 28 27 26 25	1649 1427 1362	vw m s	1734 1693 1664 1626 1418 1371	17.6 42.2 12.7 6.2 42.3 162.5	C=C,C=N str. C=C,C=N str. C=C,C=N str. C=C,C=N str. C-C str., CH,NH ip C-C str., CH,NH ip
24 23 22 21	1302 1174	vw	1364 1298 1169 1166	0.3 37.7 0.9 26.4	C-C str., CH,NH ip CH,NH ip CH,NH ip CH,NH ip
20 19 18	1104 1054	vw m	1091 1031 1017	41.7 62.5 0.0	6-ring,CH,NH ip 6-ring,CH,NH ip HC=CH torsion
17 16 15	894	vs	1008 938 933	11.1 197.5 0.1	HC=CH torsion,NH oop CH,NH oop 6-ring,CH ip
14 13 12 11 10 9 8 7	668	vw	854 847 752 707 680 554 512	0.1 0.0 0.0 6.7 0.1 0.6 28.5	Cring ip CH cop 6-ring cop CH,NH cop 6-ring ip 6-ring ip CCN ip

[a-c] See footnotes a-c in Table 1.

2-Azidoaniline^[17] (5): To a stirred solution of 4 (5.9 g, 22.5 mmol) and MeOH (14 ml) was added 80% hydrazine hydrate (1.41 ml, 24.8 mmol) all at once. After a few minutes the reaction become very viscous. An additional MeOH (7 ml) was added and stirring was continued. After 30 min, 3 N NaOH aqueous solution (9 ml) and water (90 ml) were added to the reaction mixture, which was subsequently extracted with Et₂O. The organic layer was washed with water and dried (Na₂SO₄). Evaporation of the solvent produced 5 as a white solid: 79%; m.p. 60.0-63.0°C. - ¹H NMR $(CDCl_3)$: $\delta = 6.70$ (d, 1 H), 6.79 (dd, 1 H), 6.94 (dd, 1 H), 7.03 (d, 1 H); 1R (Ar, 10 K) $\tilde{v} = 3520 \text{ cm}^{-1}$ (w), 3418 (w), 2132 (vs), 2114 (vs), 2096 (m), 2084 (m), 1616 (s), 1593 (vw), 1510 (m), 1497 (m), 1306 (s), 1270 (m), 1151 (w), 1126 (w), 794 (vw), 756 (vw), 738 (m), 652 (w).

- ^[1] [^{1a]} E. F. V. Scriven, Azides and Nitrenes, Reactivity and Utility, Academic Press, New York, **1984**. [^{1b]} W. Lwowski, Nitrenes, Interscience, New York, **1970**. [^{1c]} B. Iddon, O. Meth-Cohn, Int. Ed. Engl. 1979, 18, 900. – ^[1d] E. F. V. Scriven in Reactive *Intermediates* (Ed.: R. Abramovitch), Plenum, New York, **1981**, Vol. 2, Chapter 1. – ^[1e] W. Lwowski in *Reactive Intermediates* (Eds.: M. Jones, R. A. Moss), Wiley, New York, 1981, Chap-
- ter 8.
 ^[2] ^[2a] E. W. Meijer, S. Nijhus, F. C. B. M. van Vroonhoven, J. Am. Chem. Soc. **1988**, 110, 7209. ^[2b] M. Yan, S. X. Cai, M. N. Chem. Soc. **1988**, 110, 7209. ^[2b] M. Yan, S. X. Cai, M. N.
- Wybourne, J. F. W. Keana, J. Am. Chem. Soc. **1993**, 115, 814. ^[3] ^[3a] K. Kanakarajan, R. Goodrich, M. J. T. Young, S. Soundararajan, M. S. Platz, J. Am. Chem. Soc. 1988, 110, 6536. - [3b] N. W. Shaffer, M. S. Platz, *Tetrahedron Lett.* **1989**, *30*, 6465. – ^{13e]} N. Soundararajan, M. S. Platz, J. Org. Chem. **1990**, *55*, 2034. 55, 3640.
- ^[4] V. Chowdhry, F. H. Westheimer, Ann. Rev. Biochem. 1979, 48,
- ^[5] ^[5a] O. L. Chapman, J. P. LeRoux, J. Am. Chem. Soc. 1978, 100, ¹⁵⁴ O. L. Chapman, J. P. LeROUX, J. Am. Chem. Soc. 1916, 100, 282. – ^[5b] O. L. Chapman, R. S. Sheridan, J. Am. Chem. Soc. 1979, 101, 3690. – ^[5c] I. R. Dunkin, P. C. P. Tompson, J. Chem. Soc., Chem. Commun. 1980, 499. – ^[5d] I. R. Dunkin, P. C. P. Tompson, J. Chem. Soc., Chem. Commun. 1982, 1192. – ^[5e] I. R. Dunkin, P. C. P. Tompson, J. Chem. Soc., Chem. Commun. 1982, 1192. – ^[5e] I. R. Dunkin, P. C. P. Tompson, J. Chem. Soc., Chem. Commun. 1980, 499. – ^[5e] I. R. Dunkin, P. C. P. Tompson, J. Chem. Soc., Chem. Commun. 1982, 1192. – ^[5e] I. R. Dunkin, P. C. P. Tompson, J. Chem. Soc., Chem. Commun. 1982, 1192. – ^[5e] I. R. Dunkin, P. C. P. Tompson, J. Chem. Soc., Chem. Commun. 1982, 1192. – ^[5e] I. R. Dunkin, P. C. P. Tompson, J. Chem. Soc., Chem. Commun. 1982, 1192. – ^[5e] I. R. Dunkin, P. C. P. Tompson, J. Chem. Soc., Chem. Commun. 1982, 1192. – ^[5e] I. R. Dunkin, P. C. P. Tompson, J. Chem. Soc., Chem. Commun. 1982, 1192. – ^[5e] I. R. Dunkin, P. C. P. Tompson, J. Chem. Soc., Chem. Commun. 1982, 1192. – ^[5e] I. R. Dunkin, P. C. P. Tompson, J. Chem. Soc., Chem. Commun. 1982, 1192. – ^[5e] I. R. Dunkin, P. C. P. Tompson, J. Chem. Soc., Chem. Commun. 1982, 1192. – ^[5e] I. R. Dunkin, P. C. P. Tompson, J. Chem. Soc., Chem. Chem. Chem. Soc., Chem. Chem. Chem. Soc., Chem. Chem. Soc., Chem. Chem. Soc., Chem. C R. Dunkin, J. Donelly, T. S. Lockhart, *Tetrahedron Lett.* 1985, 26, 359. – ^[51] C. Wentrup, H. W. Winter, J. Am. Chem. Soc. **1980**, *102*, 6159. – ¹⁵⁸ C. Wentrup, C. Thétaz, E. Tagliaferri, H. J. Linder, B. Kitsche, H. W. Winter, H. P. Reisenauer, *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 566. – ^{15h} J. C. Hayes, R. S.
- Sheridan, J. Am. Chem. Soc. 1990, 112, 5879.
 ^[6] ^[6a] R. S. Sheridan, Organic Photochemistry (Ed.: A. Aadwa), Marcel Dekker Inc., New York, 1987, Vol. 8, pp. 159-248. ^[6b] I. R. Dunkin, Chem. Soc. Rev. 1980, 9, 1.
- [7] [7a] R. J. Sundberg, R. W. Heintzelman, J. Org. Chem. 1974, 39, 2546. - [^{7b]} B. A. Degraff, D. W. Gillespie, R. J. Sundberg, J. Am. Chem. Soc. **1974**, 96, 7491. - [^{7c]} M. Sumitani, S. Naga-kura, K. Yoshihara, Bull. Chem. Soc. Jpn. **1976**, 49, 2995. -^[7d] P. E. Nielsen, O. Buchard, *Photochem. Photobiol.* **1982**, *35*, 317. – ^[7e] C. J. Shields, D. R. Chrisope, G. B. Schuster, A. J. Dixon, M. Poliakoff, J. J. Turner, J. Am. Chem. Soc. **1987**, 109, 4723. -^[71] Y. Z. Li, J. P. Kirby, M. W. George, M. Poliakoff, G. B. Schuster, J. Am. Chem. Soc. **1988**, 110, 8092. -^[7g] A. K. Schuster, C. B. Schuster, J. Am. Chem. Soc. **1988**, 110, 8092. -^[7g] A. K. Schrock, G. B. Schuster, J. Am. Chem. Soc. **1984**, 106, 5234, 5229, -1^{7h]} T.-Y. Liang, G. B. Schuster, J. Am. Chem. Soc. **1987**, 109, 7803, -1^{7i]} A. Albini, G. Bettinetti, G. Minoli, J. Am. Chem. Soc. 1991, 113, 6928.
- [8] M. S. Platz, V. M. Maloney in Kinetics and Spectroscopy of Carbenes and Biradicals (Ed.: M. S. Platz), Plenum Press, New York, 1990, pp. 303-320.
- ^[9] C. Wentrup, Adv. Heterocycl. Chem. 1981, 28, 279.

- [10] S. Murata, H. Tomioka, *Chem. Lett.* 1992, 57.
 [11] [11a] I. R. Dunkin, M. A. Lynch, A. J. Boulton, N. Henderson, *J. Chem. Soc., Chem. Commun.* 1991, 1178. ^[11b] N. P. Hacker, *Commun.* 1991, 1178. J. Org. Chem. 1991, 56, 5217. ^[12] G. Galzaterri, R. Gleiter, K.-H. Knauer, H.-D. Martin, E.
- Schmidt, Angew. Chem., Int. Ed. Engl. 1974, 13, 86.
- ^[13] H. Tomioka, N. Ichikawa, K. Komatsu, J. Am. Chem. Soc. 1993, 115, 8621.
- ^[14] H. Tomioka, N. Ichikawa, K. Komatsu, J. Am. Chem. Soc. 1992, 114, 8045.
- ^[15] R. J. McMahon, O. L. Chapman, J. Am. Chem. Soc. 1987, 109, 683.
- ^[16] ^[16a] W. Sander, J. Morawietz, *Tetrahedron Lett.* **1992**, *33*, 5753. - [16b] J. Morawietz, W. Sander, M. Träubel, J. Org. Chem. 1995, 60 6368
- ^[17] J. H. Hall, E. Patterson, J. Am. Chem. Soc. 1967, 89, 5856.
- ^[18] H. Tomioka, H. Fukao, Y. Izawa, Bull. Chem. Soc. Jpn. 1978, 51. 540.
- ^[19] G. Maier, L. H. Franzl, H.-G. Harton, K. Lanz, H. P. Reisenauer, Chem. Ber. 1985, 118, 3196.
- ^[20] R. S. Grev, C. L. Janssen, H. F. Schaefer, J. Chem. Phys. 1991, 95. 5128.
- ^[21] O. L. Chapman, C. L. McIntosh, J. Pacansky, J. Am. Chem. Soc. 1973, 95, 244
- [22] A. J. Gordon, R. A. Ford, The Chemist's Companion, Wiley, New York, 1972
- [23] [23a] W. Kirmse, K. Kund, E. Ritzer, A. E. Dorigo, K. N. Houk,
 J. Am. Chem. Soc. 1986, 108, 6045. [23b] G. Hömberger, A. E. Dorigo, W. Kirmse, K. N. Houk, J. Am. Chem. Soc. 1989, 111.475
- [24] [24a] W. Kirmse, G. Hömberger, J. Am. Chem. Soc. 1991, 113, 3925. [24b] W. Kirmse, I. S. Özkir, J. Am. Chem. Soc. 1992, 114, 7590. [24c] W. Kirmse, I. S. Özkir, D. Schnitzler, J. Am. Chem. Soc. 1993, 115, 792. [24d] W. Kirmse, D. Schnitzler, Tetrahedron Lett. 1994, 35, 1699.
 [25] M. S. Plotz, Acc. Chem. Pag. 1005, 28, 487
- ^[25] M. S. Platz, Acc. Chem. Res. 1995, 28, 487.
- ^[26] K. W. Haider, M. S. Platz, A. Despres, E. Migirdicyan, Chem. Phys. Lett. 1989, 164, 443.
- [27] [27a] M. J. Travers, D. C. Cowles, E. P. Clifford, G. B. Ellison, J. Am. Chem. Soc. 1992, 114, 8699. ^[27b] S. J. Kim, T. P. Hamilton, H. F. Schaefer III, J. Am. Chem. Soc. 1992, 114, 5349.
- ^[28] S. G. Lias, J. E. Bartmess, J. F. Liebman, J. L. Holmes, R. D. Levin, W. G. Mallard, J. Phys. Chem. Ref. Data 1988, 17.
- ^[29] J. Berkowitz, Acc. Chem. Res. 1989, 22, 413.
- ^[30] See for instance, G. B. Schuster, Adv. Phys. Org. Chem. 1986, 22.311.
- ^[31] The surface crossing mechanism has been proposed by Griller et al., to explain kinetic parameters for the reaction of triplet arylcarbenes with the O-H bond of alcohol; D. Griller, A. S. Nazran, J. C. Scaiano, J. Am. Chem. Soc. 1984, 106, 198; D. Griller, A. S. Nazran, J. C. Scaiano, Tetrahedron 1985, 41, 1525. The mechanism was discussed in detail by M. S. Platz in ref. (8), pp. 325-344.
- ^[32] Tunneling was also proposed in the 1,5 H shift in 8-methyl-1naphthylcarbene; M. S. Platz, J. Am. Chem. Soc. **1979**, 101, 3398, **1980**, 102, 1192; M. S. Platz, G. Carrol, F. Pierrat, J. Zayas, S. Auster, *Tetrahedron* **1982**, 38, 777; M. C. Biewer, M. S. Platz, M. Roth, J. Wirz, J. Am. Chem. Soc. 1991, 113, 8069.
- ^[33] R. P. Bell, The Tunnel Effect in Chemistry, Chapman and Hall, New York, 1980.
- ^[34] GAUSSIAN 92: M. J. Frisch, G. W. Trucks, M. Head-Gordon, P. M. W. Gill, M. W. Wong, J. B. Foresman, B. G. Johnson, H. B. Schlegel, M. A. Robb, E. S. Replogle, R. Gomperts, J. L. Andres, K. Raghavachari, J. S. Binkley, G. Gonzales, R. L. Martin, D. J. Fox, D. J. DeFrees, J. Baker, J. J. P. Stewart, J. A.
- Pople, Gaussian, Inc., Pittsburgh, PA, **1992**. Version 4.0, Wavefunction Inc., 18401 Von Karman Ave., Suite 370, Irvine, CA 92715, USA.
- ^[36] H. Tomioka, N. Ichikawa, K. Komatsu, J. Am. Chem. Soc. 1992, 114, 8045.
- ^[37] R. J. McMahon, O. L. Chapman, R. A. Hayes, T. C. Hess, H. P. Krimmer, J. Am. Chem. Soc. 1985, 107, 7597.

[96133]