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Intramolecular Hydrogen Transfer in (2-Aminophenyl)carbene and 2-Tolylnitrene. Matrix Isolation of 6-Methylene-2,4-cyclohexadien-1-imine[†]

Jens Morawietz, Wolfram Sander,* and Michael Träubel

Lehrstuhl für Organische Chemie II der Ruhr-Universität Bochum, D-44780 Bochum, Germany

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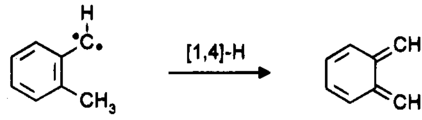
Flash vacuum pyrolysis (FVP) or matrix photolysis of 2-(diazomethyl)phenylamine, 1-azido-2-methylbenzene (2-tolyl azide), *o*-aminobenzyl alcohol, or 2-indolinone provide entries into the C_7H_7N hypersurface. The matrix-isolated (argon, 10 K) products have been characterized by IR and UV-vis spectroscopy in combination with high level (MP2/6-31G(d) and HF/6-31G(d,p)) *ab-initio* calculations. FVP (500−800 °C) of the first three of these precursors produces high yields of *E*/*Z*-mixtures of 6-methylene-2,4-cyclohexadien-1-imine (*o*-iminoquinone methide), while the bicyclic isomer benzoazetine is not formed under these conditions. FVP of 2-tolyl azide at very high temperatures (>900 °C) leads to the formation of benzaldimine and benzonitrile. Photolysis of the matrix-isolated precursors allows one to selectively generate the *E*- and *Z*-isomer of the iminoquinone methide as well as benzoazetine. In addition, 2-tolylnitrene and 1-aza-3-methyl-1,2,4,6-cycloheptatetraene are produced as intermediates in the photolysis of 2-tolyl azide. The nitrene is thermally stable up to 80 K (in xenon matrix), although the hydrogen migration to give (*E*)-*o*-iminoquinone methide is calculated to be exothermic by 42 kcal/mol. Irradiation of 2-(diazomethyl)phenylamine directly yields the quinone methide while (*o*-aminophenyl)carbene, which is the most reasonable intermediate, is not observed.

Introduction

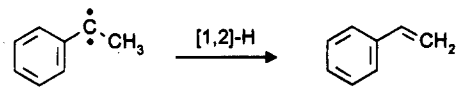
Hydrogen and alkyl shifts are typical reactions for the singlet states of carbenes[1] and nitrenes[2] and determine the lifetimes of these species in many cases, while they are less common for the triplet states. For several singlet carbenes direct spectroscopic observation of the [1,2]-H transfer by means of matrix spectroscopy[3] or time resolved spectroscopy (laser flash spectroscopy, LFP)[4] has been reported in literature.

In solution the formally spin-forbidden rearrangement of triplet carbenes to singlet products is generally slower than other carbene reactions (e.g. dimerization or H-abstraction from the solvent to form radical pairs). In inert-gas matrices at cryogenic temperatures intermolecular reactivity is largely suppressed, and thus rearrangements of triplet carbenes can be observed if the barrier of activation is very low or quantum mechanical tunneling is rate-determining.

The [1,4]-H shift in triplet 2-tolylcarbene (**1**) to give *o*-xylylene (**2**) has been thoroughly studied by McMahon and Chapman.[5] The thermal rearrangement of carbene **1** was followed by IR and UV-vis spectroscopy at temperatures as low as 4.6 K. From the small temperature dependence of the rate and the large kinetic isotope effect observed on deuteration of the methyl group, a tunneling mechanism was proposed. In contrast to this, phenylethylidene (**3**) is stable at 10 K, and thus the [1,2]-H shift in this carbene does not appear to involve tunneling. In Xe at 65 K the rate constant for the disappearance of triplet-**3** was determined to be 2.9×10^{-4} s^{-1} and the upper limit for the activation barrier to be 4.7 kcal/mol.[5] In a recent LFP study Platz et al. determined the activation energy for the rearrangement of singlet-**3** to be 4.3 kcal/mol.[4a]



1 **2**



3 **4**

Platz et al. studied the [1,5]-H shift in 8-methyl-1-naphthylcarbene (**5**) to produce 1,8-naphthoquinodimethane (**6**).[6−8] Irradiation of 1-(diazomethyl)-8-methylnaphthalene in organic glasses at 4 K directly gave **6**, while carbene **5** could not be detected. Both the hydrogen

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[†] This is dedicated to Prof. Wolfgang Kirmse on the occasion of his 65th birthday.

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(1) For reviews see: (a) Kirmse, W. *Carbene Chemistry*; Academic: New York, 1971. (b) *Methoden der Organischen Chemie (Houben-Weyl)*, 4th ed.; Regitz, M., Ed.; Thieme Verlag: Stuttgart, 1989; Vol. E19b. (c) Sander, W.; Bucher, G.; Wierlacher, S. *Chem. Rev.* **1993**, *93*, 1583−1621.

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(3) Wierlacher, S.; Sander, W.; Liu, M. T. H. *J. Am. Chem. Soc.* **1993**, *115*, 8943−8953.

(4) For recent examples see: (a) Sugiyama, M. H.; Celebi, S.; Platz, M. S. *J. Am. Chem. Soc.* **1992**, *114*, 966−973. (b) Liu, M. T. H.; Bonneau, R. *J. Am. Chem. Soc.* **1992**, *114*, 3604−3607.

(5) McMahon, R. J.; Chapman, O. L. *J. Am. Chem. Soc.* **1987**, *109*, 683−692.

(6) (a) Platz, M. S. *J. Am. Chem. Soc.* **1979**, *101*, 3398−3399. (b) Platz, M. S. *J. Am. Chem. Soc.* **1980**, *102*, 1192−1194.

(7) Platz, M. S.; Carrol, G.; Pierrat, F.; Zayas, J.; Auster, S. *Tetrahedron* **1982**, *38*, 777−785.

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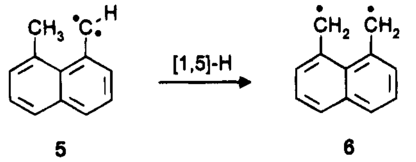
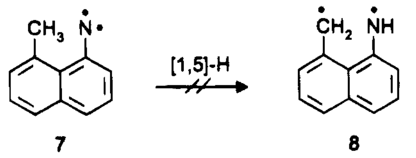
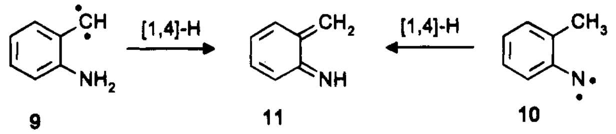
shift in the excited diazo compound and hydrogen tunneling in carbene **5** were proposed as reasonable mechanisms for the formation of **6**. Due to the short distance the hydrogen has to move, a tunneling process seems to be reasonable.[7] In a later publication it was shown that the carbene is a real intermediate and can be trapped by methanol.[8]





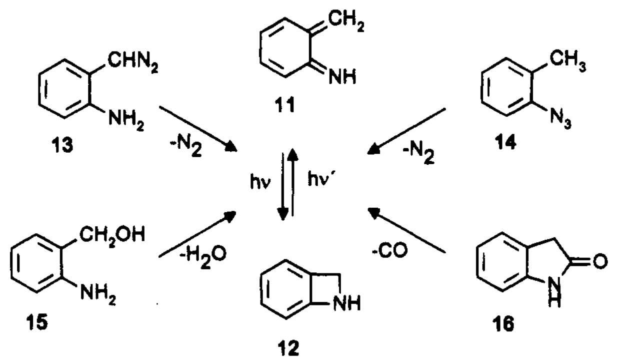
In contrast to carbene **5**, nitrene **7** is completely stable in organic glasses at temperatures up to 77 K.[7] Irradiation of 1-azido-8-methylnaphthalene produced nitrene **7** and diradical **8** simultaneously, and the ratio of **7** and **8** did not change on annealing or on secondary photolysis. Thus, there is a fundamental difference in the stabilities of carbene **5** and nitrene **7**. This difference might be related to the larger singlet-triplet energy gap ΔE_{ST} in nitrenes compared to carbenes. In phenylnitrene both experimental[9] and theoretical[10] investigations predict ΔE_{ST} close to 18 kcal/mol, while for phenylcarbene ΔE_{ST} is estimated to less than 10 kcal/mol.[11,12]

To explore the differing reactivity of carbenes and nitrenes bearing H-atoms in proximity to the reactive center we chose to investigate the thermal and photochemical rearrangements of (2-aminophenyl)carbene (**9**) and 2-tolylnitrene (**10**). Both species are expected to be triplet ground state molecules, and hydrogen migration leads to the same product, 6-methylene-2,4-cyclohexadien-1-imine (**11**).



Several derivatives of quinone methide **11** and the isomeric benzo[*b*]azetine **12** have been described in literature.[13] Smolinsky observed only polymeric material as products of the pyrolysis of 2-azido-1,3-dimethylbenzene.[13a] This was taken as evidence that a labile quinoid compound and no benzoazetine was formed as product. Burgess and McCullagh synthesized the stable *N*-phenylbenzoazetine by irradiation of 3-phenyl-4*H*-benzo-1,2,3-triazine.[13b] Synthesis of the first stable derivative of **11** was described by Iwamura et al.[13c]

Scheme 1



The parent quinone methide **11** has been previously described by Ripoll et al. using tetrahydroquinoline or *o*-aminobenzyl derivatives as thermal precursors[14] and by us in a preliminary report using 2-(diazomethyl)-phenylamine (**13**), *o*-aminobenzyl alcohol (**15**), or 2-indolinone (**16**).[15] Flash vacuum pyrolysis (FVP) of these precursors at temperatures of 850–1050 °C with subsequent trapping of the products at 77 K[14a] or 10 K[15] produced mixtures of C_7H_7N isomers which were assigned to quinone methide **11** and benzoazetine (**12**) based on the observed IR and UV-vis spectra. Ripoll et al. were able to record photoelectron spectra of the FVP products and postulated a thermal equilibrium between **11** and **12**, with **12** being the more stable isomer.[14b] These observations were supported by semiempirical MNDO calculations, which predict **12** to be more stable than **11** by 5.81 kcal/mol,[14b] while according to our AM1 calculations **12** is less stable than **11** by 11.2 kcal/mol.[15] This demonstrates that more precise *ab-initio* calculations are required to estimate the relative stabilities of these isomers.

Here we report on the thermal and photochemical interconversion and spectroscopic (IR and UV-vis) characterization of a variety of C_7H_7N isomers, including **11** and **12**, generated by irradiation or FVP of precursors **13–16** (Scheme 1). Geometries, relative stabilities, and IR spectra of several C_7H_7N isomers have been calculated using high-level *ab-initio* theory.

Results and Discussion

2-(Diazomethyl)phenylamine (13). Aryldiazomethane **13** was generated by warming 2-aminobenzaldehyde tosylhydrazone lithium salt in vacuo to 90–100 °C and trapping the volatile product directly in argon at 10 or 30 K. Due to its instability, it was not possible to isolate **13** at room temperature. Characteristic IR vibrations of **13** are intense absorptions at 2070 and 2066 cm^{-1}, assigned to the C=N=N str mode (the splitting might be caused by matrix site effects or Fermi-

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(9) (a) Travers, M. J.; Cowles, D. C.; Clifford, E. P.; Ellison, G. B. *J. Am. Chem. Soc.* **1992**, *114*, 8699–8701. (b) McDonald, R. N.; Davidson, S. J. *J. Am. Chem. Soc.* **1993**, *115*, 10857–10862.

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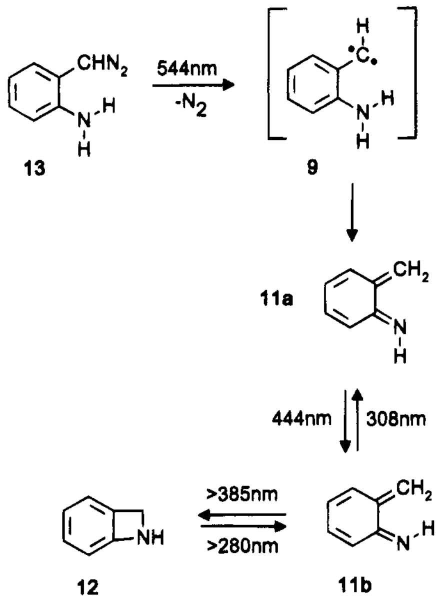
(15) (a) Sander, W.; Morawietz, J. *Tetrahedron Lett.* **1993**, *34*, 1913–1916. (b) [Benzoazetine was also produced by UV irradiation at that time but not identified and described as "third compound X" (ref 15). With **14** as a new precursor of **11**/**12**, we were able to obtain better spectra, and by using a deep-UV lamp we could demonstrate that **11a,b** and **12** are produced in photostationary equilibria, can be interconverted, and are thus isomers.]

Scheme 2



resonance), and the asymmetric and symmetric NH_2 str modes at 3472 and 3381 cm^{-1}, respectively. The characterization of **13** was confirmed by mass spectroscopic analysis of the thermolysis products of the lithium salt. Warming to 60 °C produced an intense M^+ signal at *m*/*z* 133 (56%) assigned to **13** and a fragmentation pattern in accordance with the proposed structure.

Aryldiazomethane **13** is thermally more labile than the other C_7H_7N precursors investigated (vide infra), and under FVP conditions almost completely decomposes at 300 °C. Major product ions are at *m*/*z* 107, 105, and 78. While the ions at *m*/*z* 105 (C_7H_7N) and 78 are also formed from **14** and **15** under FVP conditions (although at higher temperatures), the intense ion peak at *m*/*z* 107 is only observed in the thermolysis of **13**. The most reasonable structure for this ion is 1-amino-2-methylbenzene, produced from carbene **9** via H-abstraction from surface contaminations. FVP (600 °C) of **13** with subsequent trapping in argon at 10 K leads to mixtures of *E*- and *Z*-quinone methide **11a** and **11b** (approximately 1:1) as the major products, while benzoazetine (**12**) is not formed under these conditions (Scheme 2). **11a**, **11b**, and **12** can be photochemically intertconverted and have been characterized by IR and UV-vis spectroscopy.

Irradiation ($\lambda = 544$ nm) of diazomethane **13**, matrix-isolated in argon at 10 K, results in the formation of (*E*)-*o*-quinone methide (**11a**) with intense IR absorptions at 1643, 1537, 1085, and 866 cm^{-1} (Table 1, Figure 1). **11a** is also produced from several other precursors (Scheme 1). Irradiation of **11a** or **13** with $\lambda = 444$ or 432 nm results in high yields of the *Z* isomer **11b** with intense peaks at 1530, 1075, 897 and 772 cm^{-1} (Table 2, Figure 2). Irradiation of **11b** at 308 nm (XeCl Excimer laser) yields **11a** in a photostationary equilibrium (Scheme 2).

Table 1. IR Data of (*E*)-6-Methylene-2,4-cyclohexadien-1-imine (11a), Matrix-Isolated in Argon at 10 K and Calculated at the RMP2-FC/6-31G(d) Level

	experiment[a]		calculated[b]		
vib	ν (cm$^{-1)}$	I^c	ν (cm$^{-1)}$	I^c	assignment[d]
39	–	–	3269	0.01	NH str.
38	3090.0	0.04	3084	0.2	CH_2 asym str.
36	3045.1	0.14	3069	0.34	CH str.
32	1642.7	0.16	1635	0.11	C=C, C=N str.
31	1587.2	0.06	1572	0.01	
30	1543.2	0.22	1553	0.12	
29	1537.1	0.45	1536	0.16	
28	1427.0	0.26[e]	1425	0.01	CH_2 b, C–C str.
27	1406.2	0.27	1406	0.62	NH ip, CH_2 b, C–C str.
26	1360.4	0.16	1343	0.09	CH ip, C–C str.
25	1324.3	0.31	1317	0.24	CH_2 b, NH, CH ip
24	1276.7	0.26	1261	0.47	CH_2 r, C–C str.
	1270.4	0.13			NH ip, CH ip
23	1173.6	0.05	1164	0.09	CH ip
22	–	–	1152	0.01	CH ip
21	1084.5	0.66	1070	0.59	CH_2 r, 6ring ip, NH ip
20			975	0.01	CH_2 r, 6ring ip
19	961.2	0.05	930	0.01	CH_2 r, 6ring ip
	957.8	0.04			
18	926.0	0.32	876	0.82	CH_2 w
	922.7	0.35			
17	–	–	866	0.08	HC=CH torsion
16	866.3	1	850	1	CH_2 w, NH oop, CH oop
	864.2	0.60			
15	–	–	843	0.02	HC=CH torsion
14	824.5	0.06	837	0.01	6ring ip
	821.6	0.04			
13	765.1	0.13	756	0.06	CH_2 t, CH oop
12	–	–	728	0.08	NH oop, CH oop, CH_2 t
11	–	–	700	0.04	6ring ip
10	651.8	0.1	630	0.24	NH oop, CH oop, CH_2 t
9	–	–	555	0.01	6ring ip
8	–	–	532	0.03	6ring oop
7	502.0	0.15	488	0.18	6ring ip
6	446.2	0.08	421	0.01	6ring ip
5	426.3	0.06	405	0.17	6ring oop

[a] **11a**, generated by irradiation ($\lambda = 544$ nm, argon, 10 K) of **13**. [b] RMP2-FC/6-21G(d) calculation, scaled by 0.95. [c] Relative intensity. [d] Approximate description. The assignment of experimental to calculated vibrations is tentative and based on band positions and relative intensities. ip: in plane deformation, oop: out of plane deformation, b: bending, w: wagging, r: rocking, t: twisting. [e] Band is overlapping with **11b**, intensity is not corrected.

The assignments of **11a** and **11b** were confirmed by *ab-initio* calculations of the IR spectra at the RMP2-FC/6-31G(d) level[16,17] (Tables 1, 2, Figures 1, 2) and by comparison with other related ortho quinoid systems. The spectra of **11** exhibit a large number of intense IR absorptions almost uniformly distributed in the range 400–1600 cm^{-1}, which makes the assignment of experimental and calculated absorptions difficult. In our preliminary communication **11b** was erroneously assigned the structure of benzoazetine **12**[15b] on the basis of RHF calculations of the IR spectra of **11a** and **12**.[15a] The higher quality of the MP2-calculated spectra compared to the RHF frequencies and intensities allows for the reassignment of the experimental spectra. The arguments for our new assignment are as follows:

(i) The calculations of the IR spectra are now at a higher level (MP2 vs RHF), the mean deviation of experimental and calculated frequencies is smaller and thus the assignment more confident. In the range 4000–1000 cm^{-1} the agreement of experimental and MP2-calculated IR absorptions is good, while below 1000 cm^{-1} the deviation is larger. Single point calculations at the MP4 level (vide infra) confirm that there is still a considerable error in the MP2 results, presumably because of the partial diradicaloid character of the quinones.

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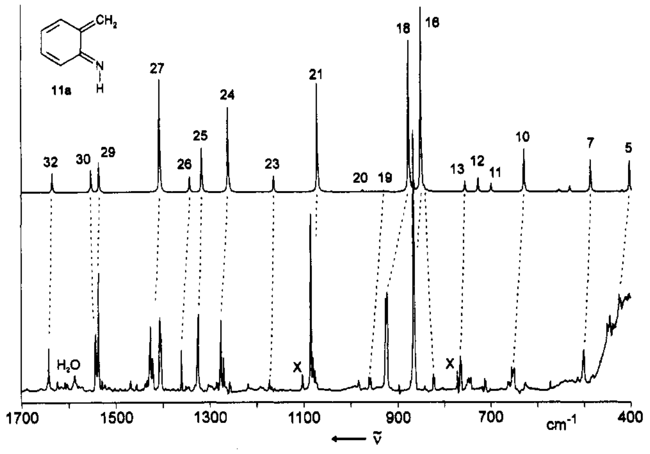


Figure 1. IR spectrum of (*E*)-6-methylene-2,4-cyclohexadien-1-imine (**11a**), matrix-isolated in argon at 10 K. Bottom: Spectrum of **11a** generated by FVP (600 °C) of **14** with subsequent trapping in argon at 10 K. IR absorptions of **11b** were removed by subtraction. Top: Spectrum calculated at the RMP2-FC/6-31G(d) level of theory. The band positions are scaled with 0.95 and a Lorentz line-shape with 2 cm^{-1} at half height is assumed.

Table 2. IR Data of (*Z*)-6-Methylene-2,4-cyclohexadien-1-imine (11b), Matrix-Isolated in Argon at 10 K and Calculated at the RMP2-FC/6-31G(d) Level

	experiment[a]		calculated[b]		
vib	ν (cm^{-1})	I[c]	ν (cm^{-1})	I[c]	assignment[d]
39	3274.2	0.03	3255	0.07	NH str.
37	3099.3	0.07	3092	0.2	CH str.
35	3056.1	0.18	3067	0.3	CH str.
32	1644.8	0.07	1632	0.13	C=N, C=C str.
31	1590.6	0.09	1572	0.03	
30	1548.9	0.17	1539	0.13	
29	1529.6	0.65	1534	0.52	
28	1399.9	0.05	1426	0.42	NH ip, CH_2 b, C−C str.
27	1423.3	0.37	1409	0.01	CH_2 b, C−C str
26	1356.2	0.10	1339	0.23	CH_2 b, NH ip, CH ip
25	1329.0	0.55	1322	0.43	NH ip, CH ip, C−C str.
24	1264.0	0.43	1251	0.5	NH ip, CH ip, C−C str.
23	1168.1	0.38	1154	0.5	NH ip, CH ip
22	–	–	1148	0.02	CH ip
21	1075.4	0.93	1067	1	CH_2 r, 6ring ip, NH ip
20	979.1	0.20	968	0.22	CH_2 r, 6ring ip
19	943.2	0.08	929	0.01	CH_2 r, 6ring ip
18	–	–	898	0.05	HC=CH torsion
17	897.1	0.57	873	1	CH_2 w, NH oop, CH oop
16	–	–	867	0.02	HC=CH torsion
15	859.7	0.30	847	0.99	CH_2 w
14	834.3	0.17	840	0.11	CH_2 r, 6ring ip
13			776	0.2	CH oop
12	771.8	1	747	0.97	CH_2 t, CH oop
11	718.5	0.45	699	0.09	6ring ip
	707.9	0.07			
10	643.5	0.23	637	0.8	6ring oop
9	638.9	0.22	621	0.52	CH_2 t, 6ring oop
8	–	–	554	0.02	6ring ip
7	–	–	502	0.19	6ring oop
6	439.6	0.27	422	0.25	6ring ip

[a] **11b**, generated by irradiation (λ = 444 nm, argon, 10 K) of **11a**. [b] RMP2-FC/6-31G(d) calculation, scaled by 0.95. [c] Relative intensity. [d] Approximate description. The assignment of experimental to calculated vibrations is tentative and based on band positions and relative intensities. ip: in plane deformation, oop: out of plane deformation, b: bending, w: wagging, r: rocking, t: twisting.

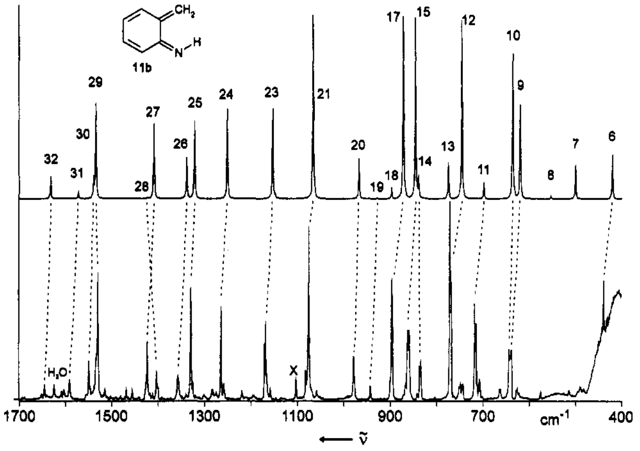
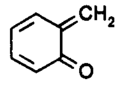


Figure 2. IR spectrum of (*Z*)-6-methylene-2,4-cyclohexadien-1-imine (**11b**), matrix-isolated in argon at 10 K. Bottom: Spectrum of **11b** generated by FVP (600 °C) of **14** with subsequent trapping in argon at 10 K followed by 444 nm irradiation. IR absorptions of remaining **11a** were removed by subtraction. Top: Spectrum calculated at the RMP2-FC/6-31G(d) level of theory. The band positions are scaled with 0.95 and a Lorentz line-shape with 2 cm^{-1} at half height is assumed.

(ii) There are similarities between several strong IR absorptions of **11a** and **11b** (Table 1 and 2), *o*-benzoquinone methide (**17**),[18] and *o*-xylylene (**18**).[1,19–21] All four compounds have in common medium to strong absorptions around 1550 cm^{-1} (**11a**: ν_{29} at 1537 cm^{-1}, **11b**: ν_{29} at 1530 cm^{-1}, **17**: 1560 cm^{-1}, **18**: 1552 cm^{-1}), assigned to combinations of C=CH_2 and C=X stretching modes, and 860 cm^{-1} (**11a**: ν_{16} at 866 cm^{-1}, **11b**: ν_{15} at 860 cm^{-1}, **17**: 859 cm^{-1}, **18**: 870 cm^{-1}), assigned to CH_2 deformation modes (wagging).



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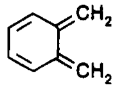

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In contrast, **12** does not exhibit IR absorptions in the range 1500–1600 cm^{-1} and 805–900 cm^{-1} (Table 3). The most prominent differences in the spectra of **11a** and **11b** are the low intensities of ν_{23}, ν_{12}, and ν_{10} in **11a** compared to the medium to strong bands in **11b**.

The formation of **11** from **13** was also monitored by UV-vis spectroscopy. A 544 nm-irradiation results in the decrease of the absorptions of **13** at 315, 274, and 240 nm, and increase of an absorption with a maximum at 368 nm, assigned to **11a**. Irradiation (λ = 444 nm) into the red tailing of the 368 nm absorption results in the formation of **11b** with an absorption maximum at 358 nm. Thus, the UV-vis spectra of **11a** and **11b** (Figure 4) are very similar with strong absorption maxima around 360 nm, while **12** absorbs at much shorter wavelength (λ_{max} = 276 nm) (vide infra).

The long-wavelength UV maxima of **11** are in accordance with the expectation for the extended π-systems in these quinoid compounds. CNDO/S calculations[22] using the *ab-initio* (RMP2-FC/6-31G(d)) optimized structures predict strong absorptions at 338 (3.6) and 282 (3.7)

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(20) Flynn, C. R.; Michl, J. *J. Am. Chem. Soc.* **1974**, *96*, 3280–3288.

(21) Tseng, K. L.; Michl, J. *J. Am. Chem. Soc.* **1977**, *99*, 4840–4842.

(22) Del Bene, J.; Jaffé, H. H. *J. Chem. Phys.* **1968**, *48*, 1807–1813.

Table 3. IR Data of Benzoazetine (12), Matrix-Isolated in Argon at 10 K and Calculated at the RMP2-FC/6-31G(d) Level

	experiment[a]		calculated[b]		
vib	ν (cm^{-1})	I[c]	ν (cm^{-1})	I[c]	assignment[d]
39	3366.1	0.02	3344	0.01	NH str.
37	–	–	3078	0.12	CH str.
34	–	–	3025	0.10	CH_2 asym str.
33	–	–	2960	0.19	CH_2 sym str.
32	–	–	1614	0.01	C=C str.
31	1601.6	0.29	1587	0.12	C=C str.
30	–	–	1470	0.01	CH_2 b
29	1464.2	0.13	1449	0.11	CH ip, C=C str
28	1455.5	0.61	1442	0.15	CH ip, C=C str
27	–	–	1415	0.01	CH ip, C=C str
26	1299.4	0.27	1288	0.13	C–C str., C-N str., CH_2 w, NH def, CH ip
25	–	–	1238	0.03	C–C str., C-N str., CH_2 w, NH def, CH ip
24	–	–	1237	0.01	CH_2 w, NH def, CH ip
23	1193.4	0.27	1204	0.05	CH_2 w, CH ip
22	–	–	1146	0.01	CH ip
21	1126.4	0.05	1118	0.01	6ring ip, 4ring ip
20	1093.4	0.1	1084	0.08	CH_2 t, NH def
19	–	–	1068	0.02	CH_2 t, 6ring ip, 4ring ip
18	990.7	0.2	986	0.05	CH_2 r, NH def
17	–	–	984	0.06	CH_2 r, 6ring ip
16	919.8	0.08	915	0.01	C-N str.
15	908.8	0.08	884	0.06	NH def, 6ring ip, 4ring ip
14	–	–	834	0.01	HCCH torsion
13	–	–	818	0.01	HCCH torsion
12	803.6	0.22	789	0.04	6ring ip, 4ring ip
11			785	0.02	CH oop
10	747.8	1	725	1	CH oop, NH def
9	661.6	0.94	681	0.40	CH oop, NH def
8	626.8	0.84	621	0.05	6ring ip, 4ring ip
7	541.3	0.01	525	0.01	6ring ip
6	513.5	0.43	501	0.05	6ring oop
5			462	0.02	6ring oop
4			413	0.02	6ring ip

[a] **12**, generated by irradiation (λ > 385 nm, argon, 10 K) of **11**. [b] RMP2-FC/6-31G(d) calculation, scaled by 0.95. [c] Relative intensity. [d] Approximate description. The assignment of experimental to calculated vibrations is tentative and based on band positions and relative intensities. ip: in plane deformation, oop: out of plane deformation, b: bending, w: wagging, r: rocking, t: twisting.

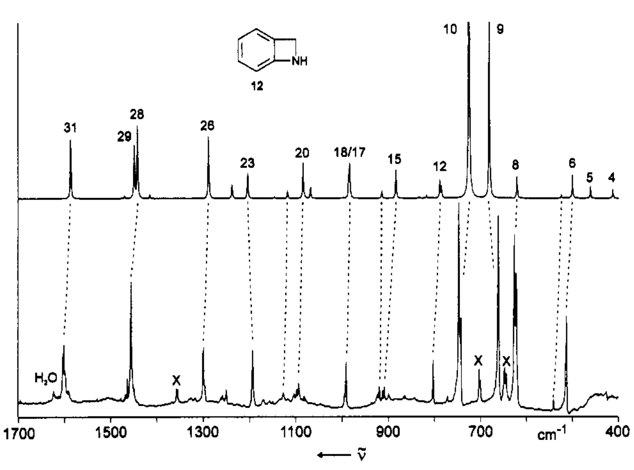

Figure 3. IR spectrum of benzoazetine (**12**), matrix-isolated in argon at 10 K. Bottom: Spectrum of **12** generated by FVP of azide **13** at 600 °C with subsequent trapping in argon at 10 K. Top: Spectrum calculated at the RMP2/6-31G(d) level of theory. The band positions are scaled with 0.95 and a Lorentz line-shape with 2 cm^{-1} at half height is assumed.

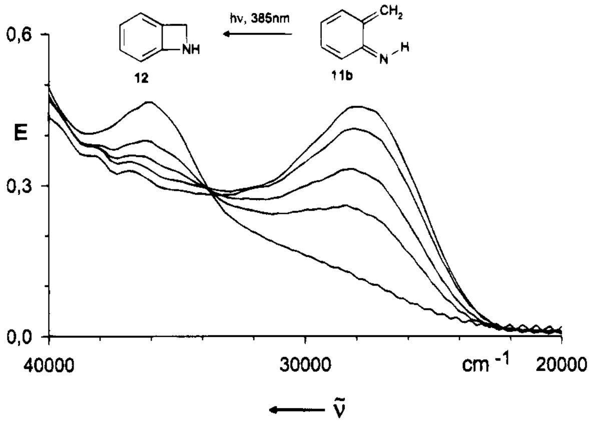

Figure 4. UV-vis spectra showing the photochemical conversion of **11b** to **12**. Irradiation of **11b**, matrix-isolated in argon at 10 K at λ > 385 nm. The maximum at 27900 cm^{-1} (358 nm) assigned to **11b** decreases and the maximum at 36200 cm^{-1} (276 nm) assigned to **12** increases in intensity.

nm (log ϵ) for **11a** and 328 (3.6), 287 (3.6), and 272 (3.4) nm (log ϵ) for **11b**. Thus, both experiment and theory show a blue shift of approximately 10 nm of the longest-wavelength absorption maximum in **11b** compared to **11a**, which results from the nonplanarity, and therefore less efficient overlap, of the π-system in **11b**.

Irradiation of **11** (mixture of E/Z isomers) at shorter wavelength (λ >385 nm) produces benzoazetine **12** almost quantitatively. The experimental IR spectrum is in good agreement with the *ab-initio* (RMP2-FC/6-31G(d)) calculated spectrum (Table 3, Figure 3). In the UV spectrum the longest wavelength absorption maximum is observed at 276 nm (Figure 4), which is a typical region for benzenoid systems and which demonstrates the absence of a quinoid structure. On irradiation into this transition (λ > 280 nm) quinone methide **11** (photostationary equilibrium of E/Z isomers) is formed back, which confirms that **11a**, **11b**, and **12** are isomers.

The question arises whether carbene **9** is formed as a distinct intermediate during the photolysis of **13**. The IR spectra of mixtures of **11a**, **11b**, and **12** produced by 544 or 308 nm irradiation of **13** do not show additional bands which could be assigned to **9**. Irradiation of matrix-isolated **13** in the cavity of an ESR spectrometer does not lead to a signal of a triplet species. A sensitive reaction for the identification of matrix-isolated triplet carbenes is the thermal reaction with molecular oxygen (typical reaction conditions are 0.5–2% O_2 in argon at 30–35 K) to form carbonyl *O*-oxides, which are readily characterized by IR or UV-vis spectroscopy.[23] Annealing of 2% O_2-doped argon matrices containing the products of the photolysis of **13** at 30–35 K does not yield a carbonyl oxide. From these experiments we conclude that the stationary concentration of carbene **9** in the matrix must be small. Whether the carbene is thermally labile at 10 K and rapidly rearranges to **11**, or **11** is formed via excited states of diazomethane **13** and carbene **9** is not involved at all, cannot be deduced from our experiments.

The conclusion from these experiments is that the C_7H_7N isomers **11a**, **11b**, and **12** can be produced in high yields: **11a** by 544 nm irradiation of **13**, **11b** by 444 nm irradiation of **11a**, and **12** by >385 nm irradiation of **11** (Scheme 2). Shorter-wavelength irradiation (>280 nm or 308 nm) results in a photostationary equilibrium of all three C_7H_7N isomers. The direct formation of the

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Table 4. IR Data of 2-Tolylnitrene (10), Matrix-Isolated in Argon at 10 K and Calculated at the UHF/6-31G(d,p) Level

10: experiment[a]		**10**: calculated[b]		phenylnitrene[c]	
ν (cm$^{-1)}$	I^d	ν (cm$^{-1)}$	I^d	ν (cm$^{-1)}$	I^d
1561.6	0.29	1560	0.14	1552	0.68
1516.3	0.06	1547	0.12	1524	0.33
1459.9	0.06	1495	0.01		
1447.8	0.08	1482	0.01	1497	0.09
1433.8	0.13	1466	0.01	1426	0.13
				1408	0.06
1381.0	0.13	1341	0.04		
				1309	0.05
1297.9	0.34	1309	0.14	1299	0.07
				1287	0.47
				1286	0.49
				1250	0.05
1158.6	0.04			1148	0.32
1143.1	0.11	1185	0.05		
1137.7	0.10	1181	0.01		
1110.6	0.12	1126	0.05		
1098.3	0.13	1089	0.01	1079	0.22
1032.0	0.09	1034	0.01	1008	0.17
				964	0.06
				885	0.05
				820	0.12
747.3	0.47			746	1.00
744.9	1.00	737	1.00		
685.1	0.23	670	0.03	654	0.55

[a] **10**, generated by irradiation (λ = 336 nm, argon, 10 K) of **14** or **19**. [b] UHF/6-31G(d) triplet calculation, scaled by 0.95. The assignment of experimental to calculated vibrations is tentative and based on band positions and relative intensities. [c] Reference 24. [d] Relative intensity.

E-isomer **11a** on photolysis of **13** implies that the hydrogen atom closest to the newly formed carbene center, or electronically excited diazo group, migrates, and *E*/*Z* isomerization does not take place under these conditions.

Photolysis of 1-Azido-2-methylbenzene (14). The photochemistry of matrix-isolated azide **14** is similar to that of phenyl azide as described by Hayes and Sheridan.[24] Irradiation at 308 nm leads to a compound tentatively assigned to 1-aza-3-methyl-1,2,4,6-cycloheptatetraene (**19**). The most intense IR absorption of **19** is observed at 1898 cm^{-1} (Table 5), close to the cumulene absorption reported for the parent compound (1893 cm^{-1}) and a series of 4- and 6-substituted azacycloheptatetraenes (strongest absorptions at 1883–1906 cm^{-1}).[25] The calculated (RMP2-FC/6-31G(d)) IR spectrum of **19** is in good agreement with the experimental spectrum (Table 5). However, the differences in the calculated spectra of **19** and its 7-methyl regioisomer are not large enough for the unequivocal discrimination based on the IR spectrum.

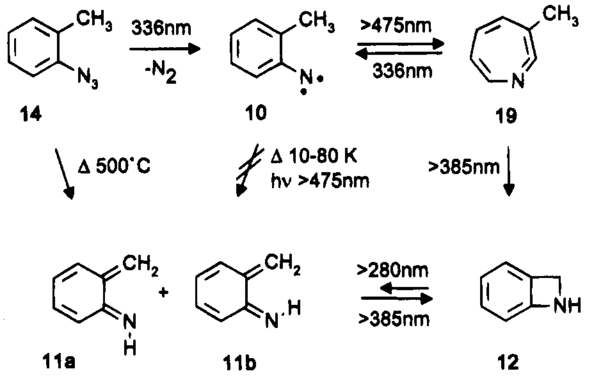
Irradiation (λ = 336 nm) of **14** or **19** yields 2-tolylnitrene (**10**) with strong IR absorptions at 1562, 1298, 745, and 685 cm^{-1} (Table 4). The corresponding absorptions in phenylnitrene are at 1552, 1287, 746, and 654 cm^{-1}, respectively.[24] Irradiation (λ > 475 nm) of **10** results in the rearrangement back to azacycloheptatetraene **19** (Scheme 3), which provides further evidence for the nitrene. The interconversion of **10** and **19** is completely reversible, which reveals that only one regioisomer of **19** is formed. At >385 nm irradiation **19** rearranges to benzoazetine (**12**), presumably via **10** and **11** as intermediates.

Table 5. IR Vibrations of 1-Aza-3-methyl-1,2,4,6-cycloheptatetraene (19), Matrix-Isolated in Argon at 10 K

experiment[a]		calculated[b]		Aza-CHT[c]	
ν (cm$^{-1)}$	I^d	ν (cm$^{-1)}$	I^d	ν (cm$^{-1)}$	I^d
				3025	
1897.6	0.91	1875	1	1895	s
1576.0	0.11	1547	0.03		
1534.0	0.09	1510	0.04		
		1481	0.05		
1443.5	0.13	1464	0.06		
		1401	0.02		
		1393	0.01		
1347.5	0.32	1335	0.19	1348	m
1310.1	0.32	1276	0.2		
		1215	0.01		
		1188	0.03		
		1161	0.01		
				1111	
				1105	
1039.0	0.02	1037	0.05		
1024.8	0.12	1025	0.09		
966.3	0.11	955	0.03	980	
		905	0.01		
942.6	0.16	896	0.08	940	
		885	0.02		
866.4	0.27	835	0.06		
		807	0.02		
763.7	0.47	742	0.19	748	s
734.8	1.00	719	0.44		
				683	m
645.7	0.23	619	0.06	658	m
594.9	0.39	560	0.16	580	
518.4	0.15	495	0.16	510	
		442	0.01		
				370	

[a] **17** generated by irradiation of **16** with λ = 308 nm or **10** with λ > 475 nm. [b] RMP2-FC/6-31G(d) calculation, scaled by 0.95. [c] 1-Aza-1,2,3,4-cycloheptatetraene, ref 25. [d] Relative intensity.

Scheme 3. Matrix Photolysis of Azide 14



The UV-vis spectrum of nitrene **10** in argon at 10 K exhibits a medium intensity band with a distinct fine structure and maxima at 496, 486, and 464 nm and two further absorptions at 382 and 370 nm. These absorptions are red-shifted in Xe to 502, 490, 468, 384, and 374 nm, respectively. Under the conditions of matrix isolation a thermal hydrogen shift is observed neither in argon (annealing at 40 K) nor in xenon (annealing at 80 K), which indicates that there must be a substantial activation barrier for the hydrogen migration in nitrene **10**.

Flash Vacuum Pyrolysis of 1-Azido-2-methylbenzene (14). FVP of azide **14** with detection of the products using a quadrupole mass spectrometer reveals that decomposition of the azide starts at temperatures above 300 °C. At 500 °C the molecular ion (*m*/*z* 133) and the

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(24) Hayes, J. C.; Sheridan, R. S. *J. Am. Chem. Soc.* **1990**, *112*, 5879–5881.

(25) (a) Chapman, O. L.; Le Roux, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 282–285. (b) Donnelly, T.; Dunkin, I. R.; Norwood, D. S. D.; Prentice, A.; Shields, C. J.; Thomson, P. C. P. *J. Chem. Soc., Perkin Trans. 2* **1985** (2), 307–310.

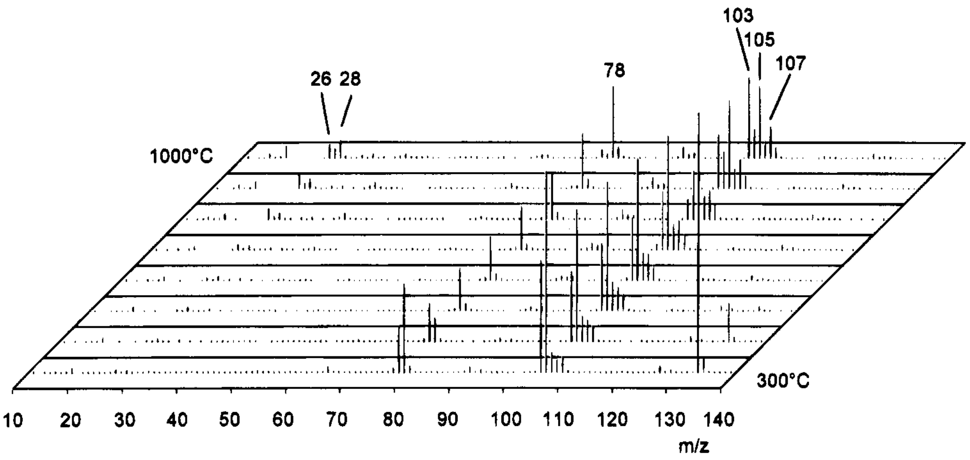

Figure 5. Mass spectra showing the products of pyrolysis (FVP) of azide **14** in the temperature range 300–1000 °C.

fragment ion at *m/z* 79 (C_6H_7 or C_5H_5N) decrease in intensity by more than 95%. Prominent peaks appear at *m/z* 105 (C_7H_7N) and *m/z* 78 (C_6H_6) (Figure 5). This demonstrates the clean fragmentation of **14** to produce C_7H_7N. At temperatures above 900 °C the ion at *m/z* 105 (C_7H_7N) decreases and *m/z* 103 gains in intensity. The most reasonable assignment for the latter ion is benzonitrile (C_7H_5N), produced by loss of hydrogen from C_7H_7N. Further confirmation of these results and the characterization of the C_7H_7N isomers was accomplished by IR investigations of the thermolysis products.

FVP of **14** in the range of 400 to 1000 °C with subsequent trapping of the products in argon at 10 K leads to the formation of quinone methide **11** (mixture of *E/Z* isomers), benzaldimine (**20**), benzonitrile (**21**), and 2-vinylpyridine (**22**) (Scheme 4). Nitrene **10**, azacycloheptatetraene **19**, or benzoazetine (**12**) are not detected under these conditions. Imine **20** was independently synthesized by irradiation ($\lambda > 250$ nm) of benzyl azide (**23**), matrix-isolated in argon at 10 K. The strongest absorption at 1637 cm^{-1} is assigned to the C=N stretching vibration in **20**. 2-Vinylpyridine (**22**) and benzonitrile (**21**) were identified by comparison with authentic matrix isolated samples. At 400–800 °C **11** is almost the sole FVP product while at higher temperatures (>800 °C) the yield of **11** rapidly decreases and **20** becomes the main product. **21** and **22** are only minor constituents at high temperatures.

The formation of benzaldimine **20** can be rationalized by cleavage of the aryl–N bond in **12** to produce diradical **24** which is rapidly stabilized by a 1,3-H shift to give **20**. At very high temperatures (>900 °C) **20** loses two hydrogen atoms and benzonitrile **21** is formed (Scheme 4). The formation of vinylpyridine **22** requires the incorporation of the nitrogen atom into the aromatic system. A possible mechanism involves azacycloheptatetraene **19** which rearranges to pyridylcarbene **25**. Similar nitrene to carbene rearrangements have been reported by Wentrup et al.[2ac,26] Carbene **25** rapidly undergoes [1,2]-H migration to produce **22** in quantitative yield.[26]

Scheme 4. Pyrolysis of Azide 14

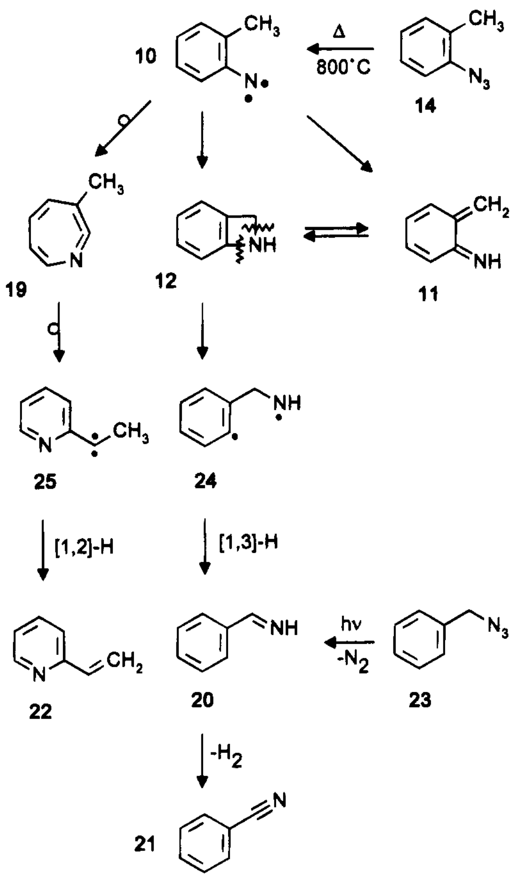

Table 6. Product Ratio after Photolysis of 13 and FVP of 14 and 15 Determined by IR Spectroscopy

precursor	wavelength or temperature	ratio **11a**: **11b**
13	544 nm	only **11a**
13	444 nm	1:9
13	> 420 nm	only **11b**
13	308 nm	1:1
14	400 °C	1.3:1
14	600 °C	1.2:1
14	800 °C	1.3:1
15	850 °C	≈1.6:1[a]

[a] Since there is still unreacted **15** in the pyrolysis mixture, the error in the ratio is large.

The photochemical *E/Z* interconversion of **11** (444 nm irradiation) allows one to determine the relative intensities of the IR absorptions in **11a** and **11b** and thus the *E/Z* ratio in the FVP products as a function of temperature (Table 6). The estimated equilibrium constants *K* correspond to $\Delta G_{E-Z} \cong 1-1.5$ kcal/mol, which is the same order of magnitude as the ab-initio (UMP4SDQ/6-31G-

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(26) Crow, W. D.; Wentrup, C. *Tetrahedron Lett.* **1968**, *59*, 6149–6152.

Table 7. Structural Parameters of (*E*)- and (*Z*)-6-Methylene-2,4-cyclohexadien-1-imine (11a,b), Benzoazetine (12), Triplet (*o*-Methylphenyl)nitrene (10), Triplet (*o*-Aminophenyl)methylene (9), and 1-Aza-3-methyl-1,2,4,6-cycloheptatetraene (19)

parameter[a]	**11a**[b]	**11b**[b]	**12**[b]	**10**[c]	**9**[c]	**19**[b]	**TS**[b,d]
C(1)–C(2)	149.5	149.5	139.5	142.2	142.0	133.1	141.8
C(1)–C(6)	145.6	145.7	138.3	136.8	140.1	146.5	140.4
C(1)–C(7)	135.4	135.4	151.7	150.3	141.0	149.8	142.2
C(2)–C(3)	146.4	146.1	138.7	141.2	138.1	–	140.9
C(2)–N(8)	129.9	130.0	143.4	133.9	136.3	126.6	136.9
C(3)–C(4)	135.6	135.6	140.6	136.6	137.7	136.8	139.0
C(4)–C(5)	145.1	145.2	140.4	138.7	138.4	145.1	141.8
C(5)–C(6)	135.5	135.5	140.6	139.0	136.6	136.9	139.0
C(7)–N(8)	281.6	299.9	151.6	284.3	280.5	380.0	213.8
C(1)–C(2)–N(8)	119.0	126.1	95.4	120.4	119.4	155.9	104.7
C(2)–C(1)–C(7)	120.6	121.4	89.1	119.5	120.5	128.7	101.8
C(1)–C(2)–C(3)	116.6	116.5	123.4	120.0	119.1	–	120.8
C(2)–C(1)–C(6)	118.3	117.5	122.5	118.0	118.1	106.8	121.0
C(7)–C(1)–C(2)–N(8)	−5.03	22.34	6.09	−0.001	0.032	154.2	24.59
C(2)–C(1)–C(7)–H(10)	−0.42	3.5	109.05	59.4	–	−0.61	56.24
C(1)–C(2)–N(8)–H(11)	179.23	3.9	−122.84	–	−179.78	–	−146.36
Δ*E* HF[e]	−1.4	−0.4	0	−25.4	10.9	36.8	48.5
Δ*E* MP2[f]	5.8	6.4	0	47.8	70.8	33.2	36.8
$<S^2>$ UMP2	–	–	–	2.62	2.54		
SCF + MP2 (au)	−324.5819110	−324.5809818	−324.5911423	−324.5149954	−324.4777332	−324.5381967	−324.532482
Δ*E* MP4[g]	−0.6	0.3	0	–	–	–	–
SCF + MP4 (au)	−324.6706440	−324.6692799	−324.6696716				

[a] Distances in pm and bond angles and dihedral angles in degrees from RMP2-FC/6-31G(d) calculations for singlet ground state and UMP2-FC/6-31G(d) calculations for triplet ground state molecules. [b] Singlet ground state. [c] Triplet ground state. [d] Transition state of the thermal ring opening of **12** to give **11a**. [e] HF/6-31G(d)//HF/6-31G(d) energies relative to **12** (kcal/mol), RHF for singlet and UHF for triplet ground state molecules. [f] MP2-FC/6-31G(d)//MP2-FC/6-31G(d) energies relative to **12** (kcal/mol), RMP2 for singlet and UMP2 for triplet ground state molecules. [g] UMP4SDQ/6-31G(d)//RMP2-FC/6-31G(d) energies relative to **12** (kcal/mol).

(d)//RMP2-FC/6-31G(d) + ZPE) calculated values (Table 8, ΔE_{E-Z} = 1.3 kcal/mol, ΔG_{E-Z} = 3.2 kcal/mol at 400 °C and 4.4 kcal/mol at 800 °C).

In conclusion, there are large differences in the product distribution between matrix-photolysis (Scheme 3) and FVP of **14** (Scheme 4). These differences result from the large thermal barrier of the [1,4]-H migration in nitrene **10** compared to the very low barrier in carbene **9**. While at high temperatures in the gas phase the hydrogen shift (or insertion into the NH bond) is the predominant process, in the matrix no thermal hydrogen migration is observed.

Generation of 11 from other Precursors. FVP in combination with mass spectroscopic detection reveals that the decomposition of *o*-aminobenzyl alcohol (**15**, *m/z* 123) starts at 500 °C. Temperatures of 800–1000 °C are required for a substantial conversion to C_7H_7N (*m/z* 105). As expected, **15** is thermally more stable than the other C_7H_7N precursors **13** and **14**. FVP of **15** at 850 °C with subsequent trapping in argon at 10 K leads to quinone methide **11** as the major product detected by IR spectroscopy. This is in accordance with the results of Ripoll et al.,[14a] however, in contrast to their later report using photoelectron spectroscopy to characterize the FVP products.[14b] In our hands FVP of **15**, or any of the other precursors, did not yield detectable amounts of benzoazetine (**12**).

Irradiation of 2-indolinone **16** with $\lambda > 250$ nm results in the slow decrease of the UV-vis absorptions at 280, 242, 208 nm and in the formation of peaks at 350, 278, 228 nm, indicating the formation of **11**. Due to the strong absorption of **16** in the range required for its photolysis, the photolysis has to be performed at very low concentrations of **16**. At these low concentrations the IR spectra only show the decrease of **16** and the slow increase of CO (2138 cm^{-1}), but no other product peaks.

Ab-Initio Calculations. The structures (Table 7) and vibrational spectra (Tables 1–3, 5) of several C_7H_7N isomers discussed above have been calculated using *ab-initio* theory at the RMP2 level for the closed shell, and UMP2 level for the open shell molecules. At this level, closed shell molecules are expected to be described fairly well, while for open shell molecules, such as carbenes and nitrenes, the error in energy, vibrational frequencies, and particularly intensities might be large. The direct comparison of experimental and calculated spectra allows not only identification of matrix-isolated species, but also estimation of the quality of the calculations. A good agreement of theory and experiment implies that the force field, and thus also the geometry, is calculated reasonably well.

The MP2-FC/6-31G(d) calculated and the experimental IR spectra of **11a**, **11b**, **12**, and **19** are in good agreement in the spectral region between 4000 and 1000 cm^{-1} (Tables 1–3, 5). The larger deviation in the low frequency region (<1000 cm^{-1}) may be attributed to the pronounced anharmonicity of the low energy vibrations. At the RHF level the reproduction of the experimental IR spectra is poor, especially in the region of the double bond stretching modes. This indicates that the inclusion of electron correlation is important to describe the electronic structures of the quinoid systems **11**, the four-membered ring system **12**, and the cumulene **19**.

At the RHF/6-31G(d) level the relative energies of **11a**, **11b**, and **12** are calculated to 0, 1, and 1.4 kcal/mol, respectively, (RHF/6-31G(d,p): **11a** 0, **11b** 1.5, **12** 1.5 kcal/mol), and thus **11a** is predicted to be the most stable of these three isomers. AM1 produces the same relative order of stabilities,[15] while MNDO predicts the reversed relative order.[14]

According to the MP2 calculations **11a** and **11b** are less stable than **12** by 5.8 and 6.4 kcal/mol, respectively (Table 7, Scheme 5). Thus, the order of relative stability ist reversed compared to the RHF calculations. If the zero point vibrational energy (ZPE/MP2/6-31G(d)) is taken into account, the entropy term shifts the equilibrium toward **11a** at temperatures above 400 °C, and **11b** comes also close to **12** (Table 8).

Table 8. Thermochemical Data of 11a and 11b from *Ab-Initio* Calculations (Frequencies Scaled by 0.95, P = 0.01 Pa) Relative to 12.

		11a (kcal/mol)			**11b** (kcal/mol)		
T, K		RHF[a]	MP2[b]	MP4[c]	RHF[a]	MP2[b]	MP4[c]
10	Δ*U*	−2.4	4.1	−2.3	−0.9	5.0	−1.0
	Δ*G*	−2.4	4.1	−2.3	−0.9	5.0	−1.3
298[d]	Δ*U*	−1.8	4.6	−1.8	−0.3	5.4	−0.7
	Δ*G*	−3.2	2.7	−3.7	−1.7	4.4	−1.7
673	Δ*U*	−1.4	5.3	−1.1	0.1	6.0	−0.1
	Δ*G*	−5.1	0	−6.4	−3.6	2.9	−3.2
873	Δ*U*	−1.3	5.4	−1.0	0.2	6.1	0.0
	Δ*G*	−6.2	−1.6	−8.0	−4.7	1.8	−4.2
1073	Δ*U*	−1.3	5.5	−0.9	0.2	6.2	+0.1
	Δ*G*	−7.4	−3.2	−8.9	−5.9	0.9	−4.5

[a] RHF/6-31G(d,p)//RHF/6-31G(d,p). [b] RMP2-FC/6-31G(d)//RMP2-FC/6-31G(d). [c] UMP4SDQ/6-31G(d)//RMP2-FC/6-31G(d). [d] 101325 Pa.

These results clearly show that higher level calculations are required for a reliable prediction of the relative stabilities. Therefore single point UMP4SDQ/6-31-G(d)//RMP2-FC/6-31G(d) + ZPE/RMP2-FC/6-31G(d) calculations have been performed (Table 8). Now both **11a** and **11b** are predicted to be more stable than **12**, and at 600 °C the equilibrium is far on the side of the quinones **11**, in agreement with the results from the FVP experiments.

The MP2-calculated structures of **11a** and **11b** exhibit the expected alternation of single and double bonds, similar to the experimental[27] and ab-initio (RHF)-calculated[28] structure of *o*-benzoquinone. At the RHF level the bond-alternation is exaggerated which results in the large errors in the calculated IR spectrum mentioned above.

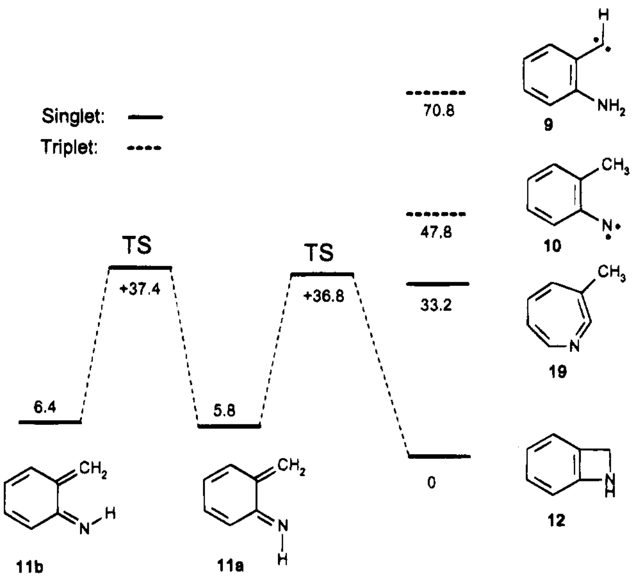
The *E*-isomer **11a** is almost completely planar, while in the *Z*-isomer **11b** the steric interaction of the inwards pointing hydrogen atoms H(10) and H(11), with a distance of only 212.1 pm, leads to a twisting of the NH and CH_2 groups of 22°. The C(7)−N(8) distance of 281.6 pm in **11a** is expanded to 299.8 pm in **11b**. From that results the destabilization of 1.3 kcal/mol (Table 8, UMP4SDQ/6-31G(d)//RMP2-FC/6-31G(d) + ZPE) and, because of the less effective overlap of the π-system, the blue shift of the longest-wavelength absorption maximum of 10 nm in **11b** compared to **11a**. The transition state for the **11b** → **11a** isomerization via inversion at the nitrogen atom is 31 kcal/mol above **11b** (Scheme 5, RMP2-FC/6-31G-(d)).

Benzoazetine (**12**) has a benzenoid structure with the four-membered ring only slightly twisted. The bond angles in the four-membered ring are close to 90 °, and the C(7)−N(8) distance is calculated to 151.6 pm. The MP2-calculated IR spectrum is in good agreement with the experiment (Figure 3, Table 3).

The ring opening of **12** to **11a** requires the rotation of both the CH_2 and the NH group. The transition state is observed at 36.8 kcal/mol (MP2) above **12** with a C(7)−N(8) distance of 213.8 pm. Thus, **12** is calculated to be kinetically stable at room temperature with respect to ring-opening.

The geometries and energies of the triplet molecules carbene **9** and nitrene **10** have been calculated using UMP2-FC/6-31G(d) theory. There is a significant spin contamination with spin-states of higher multiplicity, and thus the calculated properties should only taken as approximate values. The thermal rearrangements of **9** and **10** to produce **11a** are exothermic by 42 and 65 kcal/mol (Table 7), respectively, and thus release a large amount of excess energy. Both carbene **9** and nitrene **10** are almost completely planar with C(7)−N(8) distances of 280.5 and 284.3 pm, respectively. In **9** the distance of the hydrogen atom closest to the carbene center, H(10), is 245.3 pm, while in **10** the distance of H(10) or H(11) to the nitrene center is 282.5 pm. In the latter molecule the larger distance from the reactive center results both from the larger C(7)−N(8) distance and from the staggered minimum conformation of the methyl group. The IR spectrum of **10** has been calculated with a UHF/6-31G(d,p) basis set, and Table 4 reveals the reasonable agreement of theory and experiment.

Scheme 5



Conclusion

All four precursors **13**−**16** provide entries to the C_7H_7N hypersurface and allow the spectroscopic characterization of a variety of novel species. The photolysis of indolinone **16** requires prolonged irradiation with short-wavelength UV light and is of low efficiency. Matrix photolysis or gas phase pyrolysis (FVP) with subsequent trapping in solid argon of **13** or **15** yields *E*/*Z* mixtures of **11** as the primary products. Benzoazetine **12** is only formed on secondary photolysis of **11**, but not thermally by FVP of any of the precursors.

Although the FVP conditions used in our experiments are nonequilibrium conditions, an estimate of the relative stabilities of the C_7H_7N isomers should be helpful for the interpretation of the FVP product distribution. Particularly, the complete absence of **12** in the FVP product mixture needs a comment. The calculated relative stabilities of **11a**, **11b**, and **12** depends highly on the theoretical method used. The semiempirical AM1 and MNDO methods predict reversed relative stabilities and are thus not considered in the further discussion. The *ab-initio* calculations clearly reveal that electron correlation has to be included to obtain reliable results. On the other hand, the size of the C_7H_7N molecules allowed for geometry optimization and calculation of the vibrational frequencies and intensities at the MP2 level, but only single point calculations at the MP4 level were possible.

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At all levels of theory (*E*)-iminoquinone **11a** is predicted to be approximately 1 kcal/mol more stable than the *Z*-isomer **11b**. However, **11a** is calculated at the RHF level 1.4 kcal/mol below **12**, at the MP2 level 5.8 kcal/mol above **12**, and at the MP4 level again 0.6 kcal/mol below **12**. The latter value is the most reliable, but the error might be a few kcal/mol and thus it is not possible to determine the relative stability from these calculations. If ZPE is considered, the energy difference is shifted in favor of **11a** and **11b** by ca. 1 kcal/mol, and the entropy term shifts the equilibrium in the same direction at higher temperatures. From that we conclude with some confidence that at the temperatures used in our FVP experiments (T > 700 K) the entropy term becomes predominant and the equilibrium is on the side of **11a** and **11b**. **12** should be a minor constituent under equilibrium conditions, at least at higher temperatures. This is in accordance with the experimental observation.

The barrier for the ring-closure of **11a** is calculated at the MP2 level to be 31 kcal/mol and for the ring-opening of **12** to be 36.8 kcal/mol, which is high enough to prevent the **11** ↔ **12** equilibration at room temperature, whereas at 500–1000 °C the equilibration should be rapid. Ring cleavage of **12** at high temperatures leads to the irreversible formation of **20** and **21** via diradical **24** (Scheme 4).

Photolysis of azide **14** leads to two high-energy C_7H_7N isomers not accessible from the other precursors: nitrene **10** and azacycloheptatetraene **19**, which are located energetically (UMP2) 47.8 and 33.2 kcal/mol, respectively, above **12** (Scheme 5). Despite the high exothermicity of 42 kcal/mol for the hydrogen shift, nitrene **10** is completely stable in the matrix (in xenon up to 80 K), while carbene **9**, under the assumption that it is formed at all, is too reactive to be observed.

Several explanations for this observation have to be considered:

(i) If the hydrogen migration proceeds on the singlet surface, the magnitude of the singlet-triplet splitting ΔG_{ST} is crucial for the rearrangement of the triplet ground state molecules. A singlet-triplet splitting of >5 kcal/mol will, under the assumption of a rapid ISC, result in a negligible thermal population of the excited singlet states and thus in no thermal reactivity. However, the hydrogen migration could also proceed on the triplet surface and lead to triplet-**11**, or, according to the model proposed by Griller, Nazran, and Scaiano,[29] the intersystem crossing could occur somewhere along the reaction coordinate. Because we were not able to observe carbene **9** directly and measure the activation parameters, our experiments cannot provide a definitive answer to this question. However, the large estimated singlet–triplet splitting in **10** could explain the lack of reactivity of this molecule.

(ii) If tunneling is of importance, the distance of the hydrogen atom closest to the reactive center corresponds to the tunneling distance. Tunneling is very sensitive to the width and the height of the barrier, and a larger tunneling distance in **10** compared to **9** might in part cause the lack of thermal reactivity. On the other hand, the barrier for the rotation of the methyl group in **10** should be very low even in a rigid environment, and thus H(10) can move easily in a position closer to the nitrene center. To differentiate between these hypotheses, tailored model compounds with well defined distances of the reacting center and the closest hydrogen atom have to be investigated.

Experimental Section

Calculations. The *ab-initio* calculations were carried out using the program packages Gaussian 92[30] or TURBOMOLE[16] on SGI, IBM, and HP workstation computers, and standard basis sets. The geometry of **9** and **10** has been optimized at the UMP2-FC/6-31G(d) level of theory, and **11a**, **11b**, **12**, **19** and the transition state of the **11b** → **12** isomerization at the RMP2-FC/6-31G(d) level. The frozen core approximation was necessary to reduce computational time. Vibrational frequencies and intensities have been calculated at the same level of theory. Single point calculations using UMP4SDQ/6-31G(d)//RMP2-FC/6-31G(d) theory have been performed for **11a**, **11b**, and **12**. Because of the size of the molecules triple substitution had to be omitted.

MOPAC (version 6)[31] was used for the semiempirical AM1[32] calculations. The CNDO/S[22] method developed by Del Bene and Jaffe and the RMP2-FC/6-31G(d) optimized structures have been used for the calculation of the UV-vis spectra of **11a** and **11b**. The seven highest occupied and the seven lowest unoccupied molecular orbitals have been considered when constructing singly and doubly excited configurations. The energy of the CI states was restricted to 15 eV.

Matrix Spectroscopy. Matrix isolation experiments were performed by standard techniques with an APD CSW-202 Displex closed cycle helium cryostat. Matrices were produced by deposition of argon (Linde, 99.9999%) or mixtures of argon and oxygen (Messer Griesheim, 99.998%) on top of a CsI (IR) or sapphire (UV-vis) window with a rate of approximately 0.15 mmol/min. Infrared spectra were recorded by using a Bruker IFS66 FTIR spectrometer with a standard resolution of 1 cm^{-1} in the range 400–4000 cm^{-1}. UV-vis spectra were recorded on a Hewlett-Packard 8452A diode array spectrophotometer with a resolution of 2 nm. ESR spectra were recorded on a Bruker ER-420 spectrometer. Irradiations were carried out with use of Osram HBO 500 W/2 or Ushio USH-508SA mercury high-pressure arc lamps in Oriel housings equipped with quartz optics. IR irradiation from the lamps was absorbed by a 10-cm path of water. For broad-band irradiation Schott cut-off filters were used (50% transmission at the wavelength specified). For narrow-band irradiation, interference filters in combination with dichroic mirrors ("cold mirrors") and cut-off filters were used. A Lambda Physik EMG 100 Excimer laser was used for irradiation with 308 nm (XeCl).

Materials and General Methods. ^1H- and ^{13}C-NMR spectra were taken on a Bruker AM 400. Mass spectra (EI, 70 eV) were taken on a Varian MAT CH7 or MAT 8222. A VG SXP 600 (70 and 24 eV) quadrupole mass spectrometer was directly coupled to a pyrolysis oven for the on-line optimization of FVP experiments. Pyrolysis reactor parameters are as follows: IR: A (aperture area)/mm^2 = 50, Z_w (collision number) = 55, k_e (escape rate constant)/s^{-1} = 333 $(T/M)^{0.5}$, w (collision frequency)/s^{-1} = 2 × 10^4 $(T/M)^{0.5}$. MS: A (aperture area)/mm^2 = 9, Z_w (collision number) = 200, k_e (escape rate constant)/s^{-1} = 97 $(T/M)^{0.5}$, w (collision frequency)/s^{-1} = 1.9 × 10^4 $(T/M)^{0.5}$.

All reactions involving moisture sensitive reactants were performed under an atmosphere of dry nitrogen or argon.

Aminobenzaldehyde Tosylhydrazone. 2-Aminobenzaldehyde was prepared from 2-nitrobenzaldehyde according to a literature procedure.[33] Tosylhydrazide (1.55 g, 8.3 mmol)

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was added to a solution of freshly prepared 2-aminobenzaldehyde (1 g, 8.3 mmol) in 30 mL of dry THF. The solution was stirred under N_2 for 12 h at room temperature. Removal of the solvent at reduced pressure followed by washing the obtained product with ether and drying in vacuo gave 1.89 g (78 %) of the tosyl hydrazone as a colorless solid: mp 160 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 2.35 (s, 3H), 6.52 (m, 3H), 6.65 (d, 1H, ^3J = 3.9 Hz), 7.05 (m, 2H), 7.40 (d, 2H, ^3J = 4.1 Hz), 7.73 (d, 2H, ^3J = 4.1 Hz), 7.97 (s, 1H), 11.16 (s, 1H);^{13}C NMR (100 MHz, DMSO-d_6) δ 21.16, 114.42, 115.19, 115.27, 127.32, 129.85, 130.61, 132.32, 143.68, 147.57, 151.54; IR (KBr) 3436 (0.3), 3390 (0.42), 3178 (0.40), 1618 (0.39), 1596 (0.39), 1493 (0.37), 1363 (0.43), 1334 (0.61), 1167 (1), 954(0.43), 773 (0.39), 561 (0.43), 543 (0.46) cm^{-1}; MS m/z 289 (M$^+$), 106. Anal. Calcd for $C_{14}H_{15}N_3O_2S$: C, 58.11; H, 5.22; N, 14.52; S, 11.08. Found: C, 58.20; H, 5.27; N, 14.74; S, 11.15.

2-Aminobenzaldehyde Tosylhydrazone Lithium Salt.[34] Methyllithium (0.44 mL, 1.6 M, 0.69 mmol) was added at −70 °C under N_2 to a solution of aminobenzaldehyde tosylhydrazone (200 mg, 0.69 mmol) in dry THF. After stirring for 30 min and warming to room temperature the solvent was removed under reduced pressure. The remaining solid was dried in vacuo and was used without further purification.

2-(Diazomethyl)phenylamine (13) was prepared by vacuum thermolysis of **14** at 90°−100 °C and directly codeposited with a large excess of argon on top of a cold window (30 K): IR (Ar, 10 K): 3472.2 (0.02), 3381.1 (0.02), 2070.2 (1), 2065.9 (1), 1624.7 (0.06), 1585.2 (0.01), 1505.7 (0.06), 1501.8 (0.06), 1460.8 (0.03), 1384.6 (0.04), 1323.9 (0.02), 1299.8 (0.02), 1271.8 (0.03), 1157.1 (0.02), 1081.4 (0.01), 1075.1 (0.01), 744.9 (0.09), 631.1 (0.03), 544.8 (0.01), 433.4 (0.02) cm^{-1} (rel intensity).

1-Azido-2-methylbenzene (14) was prepared according to a literature procedure[35] : ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.21 (s, 3H), 7.11 (m, 4H); MS m/z 133 (M$^+$), 105; IR (Ar, 10 K) 2154.0 (0.23), 2141.1 (0.28), 2133.5 (1), 2131.4 (0.94), 2119.1 (0.52), 2117.9 (0.46), 2114.1 (0.56), 2100.6 (0.27), 2092.9 (0.17), 2078.4 (0.18), 1592.4 (0.08), 1501.8 (0.3), 1492.2 (0.34), 1320.0 (0.24), 1310.4 (0.14), 1298.3 (0.48), 1295.9 (0.39), 1285.8 (0.29), 1102.6 (0.16), 751.1 (0.21), 749.2 (0.26), 653.3 (0.18) cm^{-1} (rel intensity).

(Azidomethyl)benzene (23) was prepared according to a literature procedure:[36] IR (Ar, 10 K) 2142.0 (0.4), 2111.6 (0.48), 2098.4 (1), 2073.7 (0.43), 2071.6 (0.42), 1498.5 (0.15), 1461.3 (0.19), 1445.5 (0.16), 1384.9 (0.17), 1374.8 (0.12), 1352.0 (0.21), 1253.4 (0.58), 1239.5 (0.23), 1199.1 (0.16), 1159.9 (0.25), 1131.6 (0.53), 1080.4 (0.11), 887.1 (0.19), 849.5 (0.11), 751.1 (0.21), 697.8 (0.59), 569.4 (0.15) cm^{-1} (rel intensity).

Benzaldimine (20) was generated by irradiation (λ > 250 nm) of azide **23**, matrix-isolated in argon at 10 K. IR (Ar, 10 K) 1637.3 (1.0), 1583.2 (0.63), 1496.5 (0.21), 1454.0 (0.58), 1389.9 (0.3), 1317.0 (0.23), 1213.5 (0.46), 1179.7 (0.46), 1163.8 (0.18), 1149.1 (0.44), 1090.9 (0.57), 1071.0 (0.14), 926.9 (0.24), 825.3 (0.91), 800.4 (0.3), 725.0 (0.89), 683.9 (0.61), 621.8 (0.37), 615.6 (0.47) cm^{-1} (rel intensity).

***o*-Aminobenzyl alcohol (15)** was purchased from Janssen: IR (Ar, 10 K) 3640.0 (0.28), 3484.8 (0.5), 3390.0 (0.59), 1592.9 (0.55), 1504.9 (0.64), 1468.9 (0.55), 1382.9 (0.5), 1322.0 (0.18), 1305.4 (0.28), 1276.2 (0.14), 1209.6 (0.14), 1157.5 (0.14), 1003.8 (0.68), 957.5 (0.41), 929.3 (0.18), 753.0 (1), 729.0 (0.32), 615.6 (0.5), 534.2 (0.36) cm^{-1} (rel intensity).

2-Vinylpyridine (22) was purchased from Aldrich: IR (Ar, 10 K) 1587.1 (0.79), 1570.0 (0.42), 1474.5 (0.8), 1436.9 (0.37), 1399.3 (0.17), 1311.8 (0.11), 1301.2 (0.13), 1247.2 (0.06), 1151.5 (0.16), 1020.7 (0.09), 1000.3 (0.16), 990.2 (0.29), 933.4 (0.43), 913.6 (0.26), 804.2 (1), 741.0 (0.43), 583.8 (0.11), 558.8 (0.06) cm^{-1} (rel intensity).

Benzonitrile (21) was purchased from Janssen. IR (Ar, 10 K) 2236.2 (0.59), 1602.0 (0.09), 1585.0 (0.08), 1494.4 (0.72), 1449.6 (0.53), 1288.2 (0.1), 1178.9 (0.08), 1071.6 (0.09), 1028.4 (0.2), 921.8 (0.08), 758.1 (1), 689.4 (0.88), 548.7 (0.41) cm^{-1} (rel intensity).

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Supporting Information Available: Structures of several C_7H_7N isomers, IR spectrum obtained by FVP of **9**, and IR spectrum obtained by irradiation of the FVP products (4 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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