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Headline Articles

Photochemical Transformations of Quintet *m*-Phenylenedinitrenes

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Photochemical transformations of quintet dinitrenes have been studied for the first time by FTIR spectroscopy during the photolysis of 1,3-diazidobenzene and its 2-methyl- and 2,4,6-trimethyl-substituted derivatives in solid argon at 13 K. The reactions involve two competitive processes. In the first one, the intramolecular insertion of the nitrene unit into the 1,6-aromatic bond induces ring-opening, which leads to the formation of aminoacetylenes. The second process involves the intramolecular addition of the nitrene unit to the 1,2-aromatic bond followed by ring-opening to form 4(2*H*-azirin-2-ylidene)-2-butenenitrile derivatives. Methyl groups in *ortho*-positions to the nitrene units of quintet dinitrenes efficiently protect their aromatic ring from nitrene attacks, substantially increasing the photochemical stability of such species. However, even quintet 2,4,6-trimethylphenylene-1,3-dinitrene decomposes to ring-opened products on extended irradiation. This indicates that quintet dinitrenes are much more photochemically reactive species than triplet nitrenes. Undesirable photochemical rearrangements of the latter at early stages of the photolysis of 1,3-diazidobenzenes are suppressed on introducing the methyl group in position 2 of these azides.

In the last decade, much attention has been focused on explorations of high-spin nitrenes that are promising magnetic materials for electronics.[1] Dozens of quintet dinitrenes[2] and several septet trinitrenes[3] have now been characterized by EPR spectroscopy and some of them have been studied using FTIR[4] and UV–vis spectroscopy.[5] However, nothing is known so far about the photochemical stability and chemical transformations of quintet dinitrenes. Recent FTIR studies of singlet *o*- and *p*-phenylenedinitrenes have shown that such species are photochemically very labile and readily decompose to form various ring-opened products.[6,7] In comparison with singlet *o*- and *p*-phenylenedinitrenes, quintet *m*-phenylenedinitrenes have much larger energy gaps (12–15 kcal/mol)[3a,5] between their quintet-spin ground state and triplet-spin excited states and should therefore be more photochemically stable. On the other hand, these energy gaps for quintet dinitrenes are substantially smaller than singlet–triplet energy gaps for triplet arylnitrenes (18–22 kcal/mol).[4,5] Despite these rather large singlet–triplet energy gaps, many triplet arylnitrenes readily rearrange into ring-expanded products on photolysis in cryogenic matrices.[8] Such rearrangements of triplet arylnitrenes are undesirable reactions during the photochemical generation of quintet dinitrenes from aromatic diazides. An efficient method to avoid the loss of high-spin products during the photochemical synthesis can be the protection of the aromatic rings from nitrene insertion reactions by introducing appropriate substituents in *ortho*-positions to the nitrene units.[4] Previous studies have found that *o*-methyl groups are among the best protecting groups for such purposes.[9] Thus, for instance, triplet 2,6-dimethylphenylnitrene is one of the most photochemically stable triplet arylnitrenes.[10] In this work, we report our FTIR, EPR and UV–vis studies of the photolysis of 1,3-diazidobenzene and its 2-methyl- and 2,4,6-trimethyl-substituted derivatives in cryogenic matrices, providing the first information regarding the photochemical behavior of quintet dinitrenes.

Results and Discussion

New diazides **2b**, **c** were synthesized from commercially available diamines **1b**, **c** in a manner similar to that used for the preparation of diazide **2a**[11] (Scheme 1).

EPR studies of the photolysis of diazides **2a–c** with light at $\lambda > 300$ nm were carried out in degassed 2-methyltetrahydrofuran (2MTHF) solutions frozen at 77 K. Figure 1 shows the X-band EPR spectra obtained from each sample at microwave frequencies of 9.243, 9.212 and 9.231 GHz. All signals remained unchanged at 77 K for at least 2 h, but disappeared at once upon thawing of the matrix.

An EPR spectrum obtained from the photolysis of **2a** for 4 min (Fig. 1a) showed a set of signals at 79, 140, 300 (major), 380, 474, 605, 683, 840 and 982 mT and was almost identical to that earlier reported by Murata and Iwamura.[12] The strong peak at 683 mT is attributable to the x,y-transition of triplet azidonitrene **3a** ($|D/hc| = 1.010\ \mathrm{cm}^{-1}$ and $|E/hc| = 0.000\ \mathrm{cm}^{-1}$), while all other signals can be assigned to quintet dinitrene **4a**,

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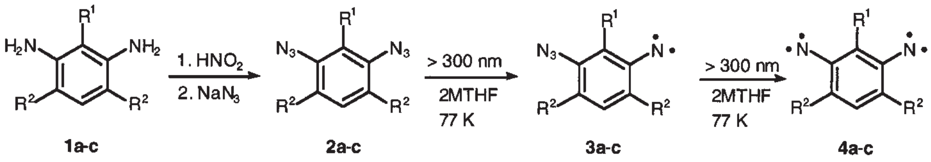


a : R^1 = R^2 = H, **b:** R^1 = Me, R^2 = H, **c:** R^1 = R^2 = Me

Scheme 1.

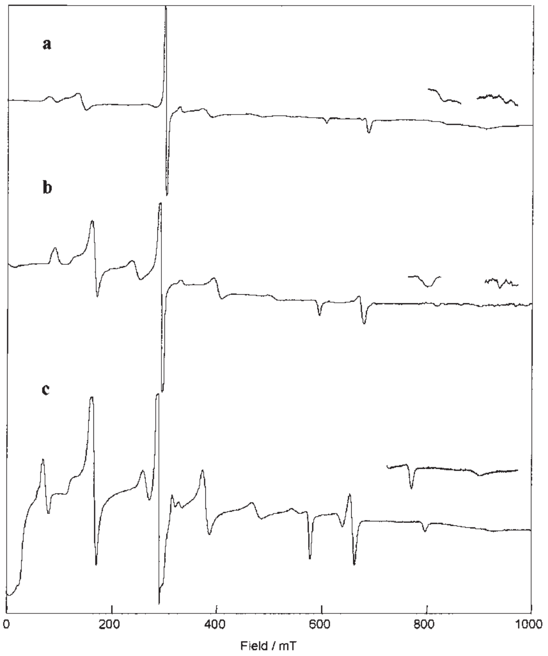


Fig. 1. EPR spectra after irradiation ($\lambda > 300$ nm, 2MTHF, 77 K) of diazide **2a** ($\upsilon_0 = 9.243$ GHz) (a), diazide **2b** ($\upsilon_0 = 9.212$ GHz) (b), and diazide **2c** ($\upsilon_0 = 9.231$ GHz) (c).

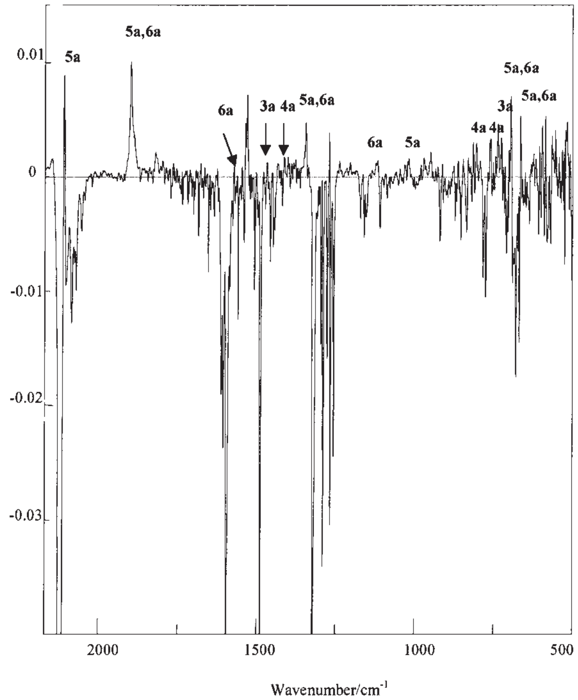


Fig. 2. Difference spectrum before and after irradiation ($\lambda > 300$ nm, 1 min) of diazide **2a** in Ar at 13 K.

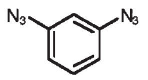
except for a weak signal at 330 mT attributable to a radical impurity from 2MTHF.[12] A new and important observation of this work is the detection of a weak EPR signal of quintet **4a** at 982 mT. All previous calculations[12,13] of the zero-field splitting (zfs) *D*- and *E*-parameters of quintet **4a** were based on the assumption that the weak signal at 840 mT is the highest Z-transition of this quintet, and that its Y-transition overlaps with the x,y-transition of triplet **3a** at 683 mT. This allowed Murata and Iwamura[12] to estimate the zfs *D*- and *E*-parameters of quintet **4a** as $|D/hc| = 0.162$ cm^{-1} and $|E/hc| = 0.025$ cm^{-1}, while similar estimations of Wasserman et al.[13] were $|D/hc| = 0.156$ cm^{-1} and $|E/hc| = 0.029$ cm^{-1}. According to our EPR studies,[14] quintet **4a** displays its highest Z- and Y-transitions at 982 and 840 mT and therefore has the zfs *D*- and *E*-parameters of $|D/hc| = 0.207$ cm^{-1} and $|E/hc| = 0.043$ cm^{-1}. These values are in good agreement with the zfs *D*- and *E*-parameters of quintet **4a** ($|D/hc| = 0.206$ cm^{-1} and $|E/hc| = 0.041$ cm^{-1}) determined by Takui et al.[15] with the aid of the eigenfield simulation method.

The photolysis of diazides **2b**, **c** led to the appearance of EPR spectra of triplet **3b**, **c** and quintet **4b**, **c** that much resembled the EPR spectra of triplet **3a** and quintet **4a**. An EPR spectrum obtained from the photolysis of **2b** for 20 min (Fig. 1b) showed a peak of triplet **3b** at 674 mT ($|D/hc| = 0.978$ cm^{-1} and $|E/hc| = 0.000$ cm^{-1}) and a set of signals for quintet **4b** at 89, 165, 237, 293 (major), 399, 505, 593, 813 and 965 mT ($|D/hc| = 0.202$ cm^{-1} and $|E/hc| = 0.039$ cm^{-1}). An EPR spectrum obtained from the photolysis of **2c** for 10 min (Fig. 1c) showed a peak of triplet **3c** at 658 mT ($|D/hc| = 0.918$ cm^{-1} and $|E/hc| = 0.000$ cm^{-1}) and a set of signals for quintet **4c** at 72, 166, 265, 289 (major), 379, 476, 578, 634, 793 and 920 mT ($|D/hc| = 0.184$ cm^{-1} and $|E/hc| = 0.040$ cm^{-1}). Owing to much higher intensities of all EPR signals of quintet **4c**, its highest Z- and Y-transitions at 920 and 793 mT are well observable already in the main spectrum. An increase in intensities of EPR lines of quintet dinitrenes on going from **4a** to **4c** suggests that progressive methylation of the benzene ring at *ortho*-positions to the nitrene centers considerably increases the yields of quintet products.

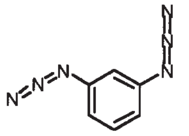
In order to investigate in details the photochemical behavior of quintet **4a–c**, FTIR and UV–vis studies of the photolysis of diazides **2a–c** in Ar matrices at 13 K were carried out.

The presence of three IR bands at $\nu = 1611$, 1605 and 1592 cm^{-1} as well as that of five bands in the region from 1321 to 1255 cm^{-1} in the IR spectrum (Table 1) of starting **2a** indicated that this diazide was present in the matrix as a mixture of three isomers: *E*,*Z*-**2a**, *E*,*E*-**2a** and *Z*,*Z*-**2a**. Brief (0.25–1.5 min) ir-

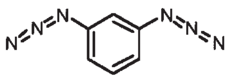
Table 1. IR Spectrum of **2a** in Ar at 13 K and B3LYP/6-31G* Calculated IR Spectra of *E*,*Z*-**2a**, *E*,*E*-**2a** and *Z*,*Z*-**2a**



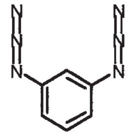
2a



E, *Z*-**2a**
-559.426874 hartrees



E, *E*-**2a**
-559.426809 hartrees



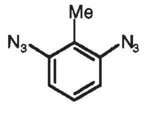
Z, *Z*-**2a**
-559.426589 hartrees

2a/Obs		*E*,*Z*-**2a**/Calcd		*E*,*E*-**2a**/Calcd		*Z*,*Z*-**2a**/Calcd	
ν/cm^{-1}	I[a)]	ν/cm^{-1}	I[a)]	ν/cm^{-1}	I[a)]	ν/cm^{-1}	I[a)]
—		3104	0.00	3091	0.01	3106	0.00
—		3091	0.00	3079	0.00	3101	0.00
—		3086	0.00	3070	0.00	3079	0.01
—		3073	0.00	3047	0.00	3072	0.00
—		—	—	2988	0.01	—	—
—		—	—	2941	0.01	—	—
—		2181	0.27	2182	0.02	2184	1.00[b)]
2117	1.00	2175	1.00[b)]	2176	1.00[b)]	2170	0.30
1611	0.09	1590	0.16	1577	0.01	1583	0.10
1605	0.09	1573	0.05	1576	0.09	1581	0.10
1592	0.10	1475	0.11	1467	0.03	1479	0.11
1488	0.21	1432	0.01	1460	0.00	1426	0.02
1446	0.03	—	—	1455	0.01	—	—
—	—	—	—	1437	0.05	—	—
—	—	—	—	1386	0.00	—	—
1321	0.10	1335	0.05	1331	0.00	1333	0.22
1295	0.09	1316	0.04	1319	0.13	1325	0.00
1288	0.19	1309	0.20	1300	0.12	1297	0.10
1266	0.16	1271	0.01	1217	0.00	1279	0.00
1255	0.13	—	—	1184	0.00	—	—
1170	0.01	1157	0.00	1156	0.00	1149	0.00
1159	0.01	1146	0.00	1139	0.01	1145	0.00
1153	0.01	1092	0.01	1078	0.00	1098	0.03
1108	0.01	1077	0.00	1032	0.00	1068	0.00
—	—	975	0.00	1018	0.04	976	0.00
—	—	938	0.00	923	0.00	943	0.00
919	0.01	903	0.03	867	0.00	923	0.03
871	0.01	856	0.00	842	0.00	866	0.00
853	0.01	850	0.03	790	0.00	832	0.03
782	0.01	764	0.03	766	0.03	770	0.04
773	0.04	761	0.00	753	0.00	748	0.01
709	0.03	668	0.03	691	0.00	666	0.01
686	0.01	665	0.00	685	0.03	665	0.01
678	0.04	644	0.00	576	0.00	637	0.02
—	—	578	0.00	570	0.00	577	0.00
537	0.01	521	0.01	521	0.01	520	0.02
—	—	519	0.00	519	0.00	518	0.00
—	—	—	—	515	0.00	—	—

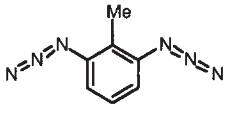
a) Relative intensity. b) Calculated intensities of IR bands of *E*,*Z*-**2a**, *E*,*E*-**2a** and *Z*,*Z*-**2a** at 2175, 2176 and 2184 cm^{-1} are 1177, 1620 and 1000 km/mol, respectively.

radiation of **2a** at $\lambda > 300$ nm resulted in depletion of the IR bands of starting **2a** at $\nu = 2117$, 1611, 1605, 1592, 1488, 1321, 1295, 1288, 1266 and 1255 cm^{-1}. Prominent new IR bands appearing in the difference IR spectra (Fig. 2) at $\nu = 1898$, 1888, 1534 and 1530 cm^{-1} indicated the formation of a mixture of isomeric triplet azidonitrenes *Z*-**3a** and *E*-**3a** (1560–1530 cm^{-1})[8,9] and isomeric didehydroazepines **5a** and **6a** (1900–1880 cm^{-1}).[8] The experimentally observable IR bands of *Z*-**3a**, *E*-**3a**, **5a** and **6a** were in good agreement with B3LYP/6-31G* calculated IR spectra for these compounds (Tables 3 and 4). Our careful examinations of the difference IR spectrum recorded after 1 min of irradiation of **2a** (Fig. 2) revealed also the presence of quintet **4a** as the fifth product. Thus, the three IR bands at $\nu = 1467$ (0.33), 804 (0.67) and 736 (1.00) cm^{-1} of this spectrum match well with the strongest UB3LYP/6-31G* calculated IR bands of quintet **4a** at $\nu =$

Table 2. IR Spectra of **2b**, **c** in Ar at 13 K and B3LYP/6-31G* Calculated IR Spectrum of *E*,*E*-**2b**

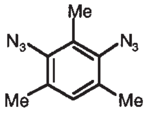


2b



E, *E*-**2b**

-598.7443929 hartrees

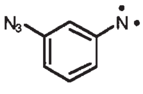


2c

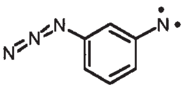
2b/Obs		*E*,*E*-**2b**/Calcd		**2c**/Obs	
ν/cm^{-1}	*I* a)	ν/cm^{-1}	*I* a)	ν/cm^{-1}	*I* a)
—		3111	0	2979	0.05
—		3091	0	2962	0.07
—		3081	0	2934	0.07
—		3070	0	2868	0.04
—		2181	0.01	2129	0.65
2118	1.00	2175	1.00 b)	2118	1.00
—	—	—	—	2109	0.63
1601	0.07	1595	0.17	1624	0.06
1583	0.09	1567	0.02	1611	0.14
1562	0.04	—	—	1600	0.16
1480	0.03	—	—	1593	0.08
1469	0.14	1472	0.09	1481	0.30
1440	0.08	1437	0.00	1468	0.12
1383	0.01	1333	0.00	1452	0.06
1319	0.03	1324	0.06	1442	0.05
1309	0.04	1309	0.16	1426	0.19
1279	0.20	1262	0.03	1405	0.04
1226	0.13	—	—	1379	0.02
1172	0.01	1161	0.00	1330	0.09
1151	0.01	1150	0.01	1300	0.21
1093	0.01	1088	0.00	1288	0.17
1072	0.01	1082	0.00	1276	0.14
1027	0.08	975	0.00	1221	0.02
—	—	931	0.00	1142	0.02
—	—	883	0.01	1024	0.08
—	—	863	0.01	1013	0.03
—	—	844	0.00	948	0.01
—	—	760	0.00	867	0.04
771	0.06	759	0.02	831	0.01
701	0.04	690	0.04	747	0.09
—	—	664	0.00	540	0.03
—	—	644	0.00		
—	—	579	0.00		
536	0.01	521	0.01		
—	—	518	0.00		

a) Relative intensity. b) Calculated intensity of IR band of *E*,*E*-**2b** at 2175 cm^{-1} is 1564 km/mol.

Table 3. IR Bands of Triplet **3a** in Ar at 13 K and UB3LYP/6-31G* Calculated IR Spectra of Triplet *E*-**3a** and *Z*-**3a**

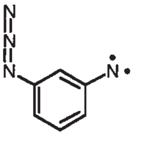


3a



E-**3a**

-449.8951213 hartrees



Z-**3a**

-449.8956097 hartrees

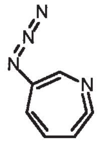
3a/Obs		*E*-**3a**/Calcd		*Z*-**3a**/Calcd	
ν/cm^{-1}	*I* a)	ν/cm^{-1}	*I* a)	ν/cm^{-1}	*I* a)
—		3111	0.00	3106	0.00
—		3105	0.00	3101	0.00
—		3086	0.00	3090	0.00
—		3073	0.00	3077	0.01
2109 b)	0.87	2178	1.00 c)	2180	1.00 c)
1534	1.00	1535	0.08	—	—
1530	0.33	—	—	1529	0.10
—	—	1517	0.06	1518	0.07
—	—	1424	0.05	1428	0.05
—	—	1357	0.03	1361	0.01
—	—	1319	0.21	1314	0.20
1270	0.40	1300	0.02	1296	0.07
—	—	1249	0.00	1250	0.01
1237	0.07	—	—	1230	0.03
—	—	1141	0.00	1135	0.00
—	—	1097	0.01	1102	0.01
—	—	1070	0.01	1062	0.01
—	—	948	0.00	952	0.00
—	—	934	0.00	939	0.00
—	—	904	0.02	921	0.01
—	—	845	0.01	855	0.00
814	0.27	839	0.02	826	0.04
760	0.27	753	0.02	754	0.05
—	—	750	0.05	742	0.00
—	—	649	0.02	641	0.03
—	—	640	0.01	640	0.01
—	—	558	0.00	558	0.00
—	—	517	0.01	522	0.01
—	—	506	0.00	510	0.00

a) Relative intensity. b) Tail which overlaps with IR bands of starting azide, **5a** and **6a**. c) Calculated intensities of IR bands of *E*-**3a** and *Z*-**3a** at 2178 and 2180 cm^{-1} are 731 and 667 km/mol, respectively.

1447 (0.44), 797 (0.71) and 732 (1.00) cm^{-1} (Table 5). It is also important to note that none of *Z*-**3a**, *E*-**3a**, **5a** or **6a** display IR bands at the same wavenumbers as quintet **4a** (Tables 3, 4 and 5, Fig. 2).[16] According to B3LYP/6-31G* calculations, the characteristic IR bands of quintet **4a** at 732 cm^{-1}, triplet *Z*-**3a** at 1528 cm^{-1}, triplet *E*-**3a** at 1535 cm^{-1}, **5a** at 1885 cm^{-1} and **6a** at 1897 cm^{-1} have the oscillator strengths of 34, 65, 61, 165 and 190 km/mol, respectively. Taking into account that precise relative intensities of the respective experimental IR bands of quintet **4a** at 736 cm^{-1}, triplet *Z*-**3a** at 1530 cm^{-1}, triplet *E*-**3a** at 1534 cm^{-1}, **5a** at 1884 cm^{-1} and **6a** at 1898 cm^{-1} are of 0.45, 0.69, 0.43, 0.34 and 1.00, we found that the ratio of these products in the spectrum from Fig. 2 corresponds to 1.0/0.8/0.5/0.2/0.4. These crude estimates suggest that quintet **4a** is the major (34% yield) photoproduct already after 1 min of irradiation of **2a**, and that undesirable ring-expanded products **5a** and **6a** are formed in 21% total yield. Yields of triplet *Z*-**3a** and *E*-**3a** at this stage of the reaction are 28% and 17%, respectively.

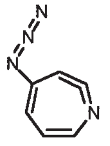
More extended (>1.5 min) irradiation of the matrix led to complete disappearance of characteristic IR bands of **4a**, *Z*/*E*-**3a** and **5a**/**6a** and to the appearance of many new IR bands indicating the formation of a complex mixture of several new photoproducts. Fortunately, some of the new IR bands were very diagnostic. Thus, for instance, the two bands at $\nu =$ 1819 (major) and 1797 (minor) cm^{-1} indicated the formation of compounds having azirine rings.[17] Two very strong IR

Table 4. Experimentally Detected (Ar, 13 K) and B3LYP/6-31G* Calculated IR Bands of **5a** and **6a**



5a

-449.8695429 hartrees



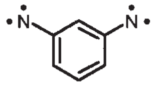
6a

-449.878239 hartrees

5a/**6a**/Obs		**5a**/Calcd		**6a**/Calcd	
ν/cm^{-1}	Ia)	ν/cm^{-1}	Ia)	ν/cm^{-1}	Ia)
—		3108	0.01	3095	0.00
—		3072	0.02	3090	0.02
—		3068	0.02	3065	0.01
—		3035	0.03	3050	0.01
2109b)	1.00	2175	1.00c)	2177	1.00c)
1898	1.00	—	—	1897	0.22
1884	0.33	1885	0.25	—	—
—	—	1574	0.01	1566	0.06
—	—	1506	0.02	1517	0.07
—	—	1387	0.06	1369	0.00
1342	0.47	1315	0.05	1330	0.14
1270	0.40	1307	0.22	1300	0.13
—	—	1287	0.01	1276	0.03
—	—	1173	0.00	1198	0.00
1117	0.13	1141	0.01	1116	0.05
1040	0.10	1057	0.05	1088	0.05
1021	0.13	1019	0.06	1014	0.02
—	—	996	0.00	942	0.02
—	—	927	0.00	926	0.00
—	—	872	0.01	874	0.02
—	—	843	0.01	860	0.01
796	0.13	790	0.06	798	0.03
760	0.27	735	0.01	757	0.03
697	0.30	682	0.10	691	0.02
664	0.47	668	0.01	665	0.03
583	0.40	605	0.00	587	0.02
567	0.27	566	0.02	561	0.01
516	0.33	518	0.01	522	0.01
—	—	—	—	509	0.01

a) Relative intensity. b) Tail which overlaps with IR bands of starting azide and triplet azidonitrenes **3a**. c) Calculated intensities of IR bands of **5a** and **6a** at 2175 and 2177 cm^{-1} are 678 and 858 km/mol, respectively.

Table 5. IR Bands of Quintet **4a** in Ar at 13 K and UB3LYP/6-31G* Calculated IR Spectrum of Quintet **4a**



4a

-340.3689519 hartrees

4a/Obs		**4a**/Calcd	
ν/cm^{-1}	Ia)	ν/cm^{-1}	Ia)
—		3110	0.00
—		3107	0.12
—		3103	0.03
—		3075	0.12
—		1468	0.03
1467	0.33	1447	0.44
—		1392	0.00
—		1296	0.00
—		1292	0.21
—		1261	0.00
—		1252	0.32
—		1209	0.12
—		1116	0.18
—		1058	0.18
—		935	0.00
—		914	0.15
—		912	0.00
—		828	0.00
804	0.67	797	0.71
736	1.00	732	1.00b)
—		728	0.03
—		612	0.32
—		550	0.00
—		514	0.00

a) Relative intensity. b) Calculated intensity of IR band of **4a** at 732 cm^{-1} is 34 km/mol.

bands at $\nu = 3335$ and 3327 cm^{-1} along with a medium intensity band at 3124 cm^{-1} and a weak band at 2117 cm^{-1} evidenced the formation of compounds with the triple carbon–carbon bonds. Two weak IR bands at 2219 and 2210 cm^{-1} also indicated that the new compounds have cyano groups. Our extensive B3LYP/6-31G* calculations of many possible molecules showed that azirine **9a** and acetylene **10a** best match the IR spectrum recorded from the photolysis of **2a** for 3 h (Fig. 3, Table 6).[18] It is interesting to note that very similar photoproducts have previously been detected from the photolysis of 1,4-diazidobenzene in solid argon.[6] Weak IR bands at $\nu = 1797$ and 3335 cm^{-1} suggest that **9a** and **10a** undergo photochemical isomerizations into more stable **11a** and **12a**. However, such isomerizations are rather inefficient in the Ar matrices. Extended irradiation of this matrix with stronger light at $\lambda > 270$ nm destroyed azirines **9a**/**11a** to give 1,4-dicyano-1,3-butadienes **13a** and **13b** (Fig. 3, Table 7).[18] The latter were also the final photoproducts in the photolysis of 1,4-diazidobenzenes[6] (Scheme 2).

Figure 4 shows the UV–vis spectra recorded during the photolysis of diazide **2a** in solid argon at 13 K after 0, 35, 55, 240 and 540 min of irradiation at $\lambda > 300$ nm; the inset of this Figure displays the difference spectrum obtained by subtraction of UV spectrum of **2a** from the UV spectrum recorded after 20 min of irradiation of **2a**. The irradiation of diazide **2a** led to a gradual decrease in intensity of its UV bands with $\lambda_{\max} =$ 244 and 290 nm and to the appearance of new, very weak bands in the region from 290 to 680 nm. The broad structured band in a region from 370 to 440 nm with its maxima at 398, 407 and 428 nm as well as the very broad and weak band extending from 520 to 680 nm with its maximum at 590 nm are typical of triplet arylnitrenes[4,8g,9,19] and can therefore be assigned to triplet **3a**. All these bands completely disappeared after 30 min of irradiation without formation of any new distinct electronic absorption bands that could be assigned to quintet **4a**. Further extended (540 min) irradiation led only to a growth in intensity of the UV band in a region from 250 to 320 nm attributable to **9a**, **10a**, **11a**, **12a** and **13a**, **b**. The UV–vis study

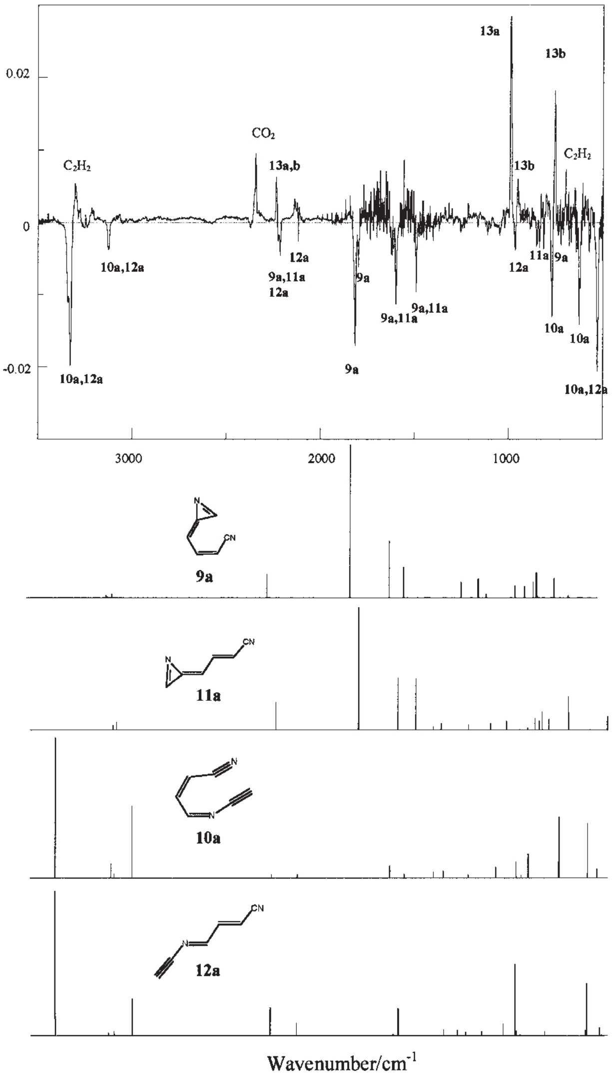


Fig. 3. Difference IR spectrum from photolysis ($\lambda > 270$ nm, 3 h) of **2a** in Ar at 13 K and theoretical (UB3LYP/6-31G*) IR spectra of **9a**, **11a**, **10a**, and **12a**.

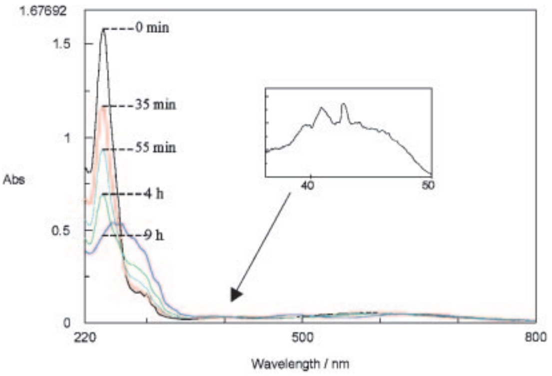
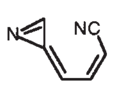
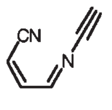


Fig. 4. Photolysis ($\lambda > 300$ nm) of diazide **2a** in solid Ar at 13 K. UV spectra (a) before irradiation; (b) after 35 min of irradiation; (c) after 55 min of irradiation; (d) after 4 h of irradiation; (e) after 9 h of irradiation. In the inset is the difference UV spectrum after 20 min of irradiation.

Table 6. IR Bands of **9a** and **10a** in Ar at 13 K and B3LYP/6-31G* Calculated IR Spectra of **9a** and **10a**



9a
-340.405658 hartrees



10a
-340.4102253 hartrees

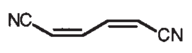
9a/Obs		**9a**/Calcd		**10a**/Obs		**10a**/Calcd	
ν/cm^{-1}	I[a)]	ν/cm^{-1}	I[a)]	ν/cm^{-1}	I[a)]	ν/cm^{-1}	I[a)]
—		—	—	3329	1.00	3369	1.00[b)]
—		3071	0.04	—	—	3081	0.10
—		3052	0.06	—	—	3064	0.04
—		—	—	—	—	2973	0.52
2212	0.24	2226	0.23	2220	0.08	2245	0.02
—		—	—	2110	0.09	2112	0.02
1815	1.00	1797	1.00[b)]	—	0.02	—	—
—	—	—	—	—	1.00[b)]	1630	0.10
1599	0.60	1589	0.42	—	0.01	1555	0.02
1491	0.48	1496	0.42	—	0.09	—	—
1401	0.16	1407	0.03	—	0.03	1404	0.03
—	—	1366	0.05	—	0.00	1353	0.05
—	—	1224	0.04	—	0.01	1222	0.02
—	—	1108	0.05	—	0.05	1081	0.07
—	—	—	—	964	0.24	974	0.12
—	—	—	—	—	0.00	972	0.01
—	—	958	0.00	—	0.13	945	0.02
—	—	916	0.02	—	0.12	912	0.17
—	—	878	0.10	—	0.00	—	—
—	—	856	0.07	—	0.00	—	—
851	0.24	840	0.15	—	0.00	—	—
810	0.14	804	0.08	—	0.01	—	—
721	0.30	705	0.28	—	0.00	752	0.12
691	0.16	700	0.14	770	0.59	749	0.43
—	—	591	0.00	626	0.63	603	0.39
—	—	—	—	—	—	567	0.00
527	0.60	501	0.11	—	—	553	0.06

a) Relative intensity. b) Calculated intensities of IR bands of **9a** and **10a** at 1797 and 3369 cm^{-1} are 189 and 83 km/mol, respectively.

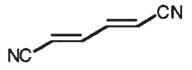
demonstrates that triplet **3a** is formed from diazide **2a** only in low yields and is photochemically very labile to decompose into some other products without strong chromophoric groups in their molecules already after 30 min of the photolysis. These observations are consistent with the results of our FTIR study of the photolysis of **2a**. It is important to note that absolutely the same UV–vis spectra were also recorded from the photolysis of **2a** in degassed frozen 2MTHF solutions at 77 K. The latter proves that the photolysis of **2a** in both solid argon at 13 K and in degassed frozen 2MTHF solutions at 77 K involves the formation of the same reactive intermediates.

The IR spectrum of starting diazide **2b** in solid argon at 13 K showed major bands at $\nu = 2118$, 1601, 1583, 1469, 1279, 1226, 1027, 771 and 701 cm^{-1}. These bands were in good agreement with B3LYP/6-31G* calculated vibrational frequencies of *E*,*E*-**2b** isomer (Scheme 3, Table 2). Contrary to the case of **2a**, no ring-expanded product **5b** or **6b** was formed on irradiation of **2b** with light at $\lambda > 300$ nm. Prominent new IR bands appearing in the first minute of the photolysis were

Table 7. IR Bands of **13a** and **13b** in Ar at 13 K and B3LYP/6-31G* Calculated IR Spectra of **13a** and **13b**



13a
-340.4808097 hartrees

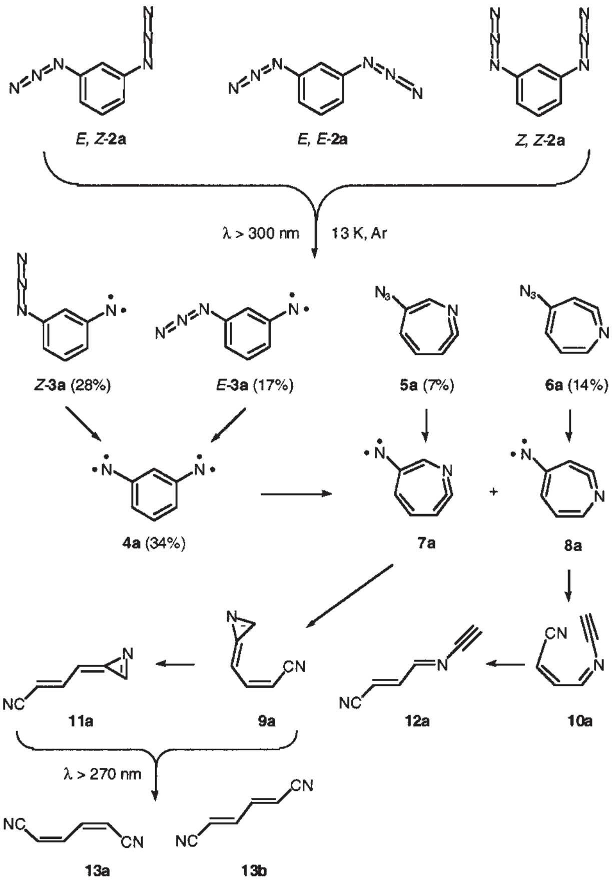


13b
-340.4807857 hartrees

13a/Obs		**13a**/Calcd		**13b**/Obs		**13b**/Calcd	
ν/cm^{-1}	I[a)]	ν/cm^{-1}	I[a)]	ν/cm^{-1}	I[a)]	ν/cm^{-1}	I[a)]
—	—	3089	0.03	—	—	3074	0.15
—	—	3088	0.00	—	—	3067	0.00
—	—	3076	0.08	—	—	3063	0.02
—	—	3069	0.00	—	—	3062	0.00
2230	0.31	2247	0.43	2230	0.20	2250	0.48
—	—	2246	0.00	—	—	2248	0.00
—	—	1616	0.00	—	—	1626	0.14
—	—	1568	0.08	—	—	1592	0.10
—	—	1412	0.00	—	—	1305	0.00
—	—	1340	0.06	—	—	1295	0.06
—	—	1239	0.00	—	—	1280	0.00
—	—	1194	0.03	—	—	1207	0.05
—	—	1084	0.00	—	—	1149	0.00
—	—	987	0.00	—	—	1018	0.00
—	—	955	0.00	991	1.00	993	1.00[b)]
950	0.30	937	0.17	—	—	965	0.03
—	—	869	0.00	—	—	936	0.00
—	—	791	0.00	—	—	858	0.00
757	1.00	756	1.00[b)]	—	—	797	0.15
—	—	732	0.00	—	—	607	0.03
—	—	618	0.00	—	—	527	0.00
—	—	594	0.00	—	—	514	0.00

a) Relative intensity. b) Calculated intensities of IR bands of **13a** and **13b** at 756 and 993 cm^{-1} are 65 and 66 km/mol, respectively.

manifested at ν = 2127, 1531, 1423, 1302, 1045 and 756 cm^{-1}. All these bands were in good agreement with UB3LYP/6-31G* calculated vibrational frequencies of triplet azidonitrene *E*-**3b** isomer (Table 8). Almost the same difference IR spectrum was also obtained on irradiation of **2b** with light at λ = 245 nm for 2 min (Fig. 5). Triplet azidonitrene *E*-**3b** was again a dominant product, and only very weak bands at 2104 and 1897 cm^{-1} (Table 9) indicating the formation of azide-substituted didehydroazepine **6b** in 12% yield were observed. Previous FTIR studies[9a] have shown that the photolysis of *o*-tolyl azide (**14**) in solid argon yields photochemically very stable triplet *o*-tolylnitrene (**15**) (Scheme 3), which rearranges into didehydroazepine **16** only on extended irradiation with light at λ > 475 nm. The irradiation of **16** at λ = 336 nm shifts the equilibrium between **16** and **15** to the side of the latter. In this respect, the absence of **6b** during irradiation of **2b** at λ > 300 nm seems to be quite reasonable. Besides triplet *E*-**3b**, the second major photoproduct from the photolysis of **2b** is quintet **4b**, displaying the IR bands at ν = 1453 (0.08), 1386 (0.28), 1356 (0.25), 1267 (0.24), 1190 (0.20), 1053 (0.15) and 756 (1.00) cm^{-1} (Fig. 5). These bands match well with UB3LYP/6-31G* calculated vibrational frequencies of quintet **4b** at ν = 1441 (0.47), 1383 (0.19), 1349 (0.21), 1294 (0.12), 1144 (0.16), 1036 (0.14) and 738 (1.00) cm^{-1} (Table 8). Relative intensities of the characteristic IR bands of triplet *E*-**3b** at 1531 (0.0127 A, 69 km/mol) cm^{-1} and quintet **4b** at 756 (0.0075 A, 43 km/mol) cm^{-1} suggest that these nitrenes are formed in a ratio of 1:1 after 2 min of irradiation at λ = 245 nm. This



Scheme 2.

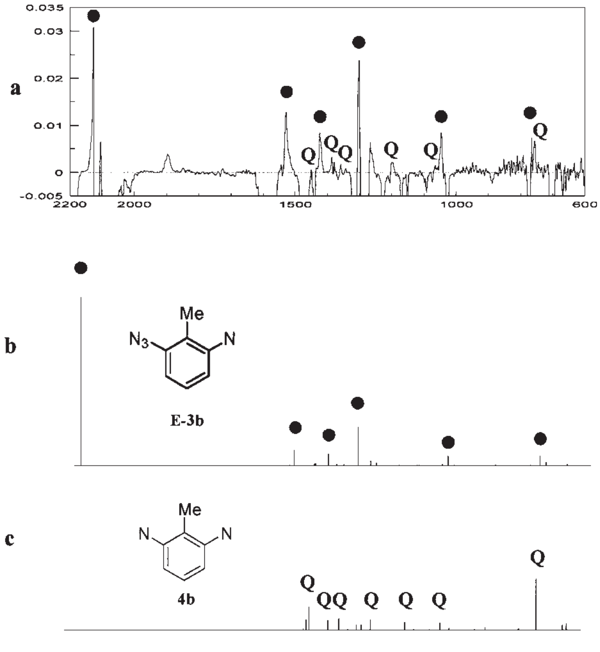
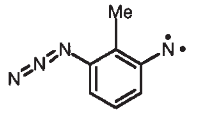
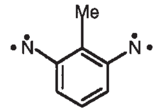


Fig. 5. (a) Difference spectrum before and after irradiation (λ > 245 nm, 2 min) of diazide **2b** in Ar at 13 K. Theoretical (UB3LYP/6-31G*) IR spectra of triplet *E*-**3b** (b), and quintet **4b** (c).

Table 8. IR Bands of Triplet **3b** and Quintet **4b** in Ar at 13 K and B3LYP/6-31G* Calculated IR Spectra of Triplet **3b** and Quintet **4b**



3b
-489.214137 hartrees

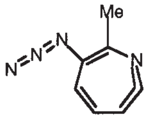


4b
-379.689340 hartrees

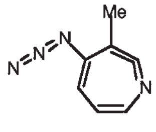
3b/Obs		**3b**/Calcd		**4b**/Obs		**4b**/Calcd	
ν/cm^{-1}	*I*[a)]	ν/cm^{-1}	*I*[a)]	ν/cm^{-1}	*I*[a)]	ν/cm^{-1}	*I*[a)]
—	—	3103	0.01	—	—	3105	0.14
—	—	3085	0.01	—	—	3101	0.05
—	—	3072	0.00	—	—	3074	0.09
—	—	3034	0.01	—	—	3036	0.07
—	—	2985	0.01	—	—	2981	0.16
—	—	2936	0.01	—	—	2932	0.12
2128	1.00	2179	1.00[b)]	—	—	1473	0.00
—	—	1532	0.00	—	—	1459	0.02
1531	0.45	1517	0.09	—	—	1449	0.19
—	—	1455	0.01	1453	0.08	1441	0.47
—	—	1452	0.01	1386	0.28	1383	0.19
1423	0.29	1410	0.07	1356	0.25	1349	0.21
—	—	1385	0.01	—	—	1321	0.02
—	—	1362	0.00	1267	0.24	1294	0.12
1303	0.80	1319	0.22	—	—	1280	0.09
—	—	1280	0.03	—	—	1252	0.21
—	—	1262	0.01	1190	0.20	1144	0.16
—	—	1192	0.00	—	—	1117	0.00
—	—	1136	0.00	—	—	1067	0.02
—	—	1130	0.00	1053	0.15	1036	0.14
—	—	1057	0.01	—	—	1008	0.02
1045	0.29	1039	0.06	—	—	929	0.00
—	—	1021	0.00	—	—	895	0.05
—	—	928	0.00	—	—	827	0.00
—	—	893	0.00	—	—	791	0.02
—	—	840	0.00	756	1.00	738	1.00[b)]
—	—	784	0.00	—	—	655	0.09
766	0.27	754	0.06	—	—	644	0.12
744	0.10	735	0.02	—	—	549	0.00
—	—	670	0.01	—	—	508	0.00
—	—	595	0.01				
—	—	561	0.00				
—	—	518	0.01				
—	—	511	0.00				

a) Relative intensity. b) Calculated intensities of IR bands of **3b** and **4b** at 2179 and 738 cm^{-1} are 763 and 43 km/mol, respectively.

Table 9. Experimentally Detected (Ar, 13 K) and B3LYP/6-31G* Calculated IR Bands of **5b** and **6b**



5b
-489.1929746 hartrees



6b
-489.1958749 hartrees

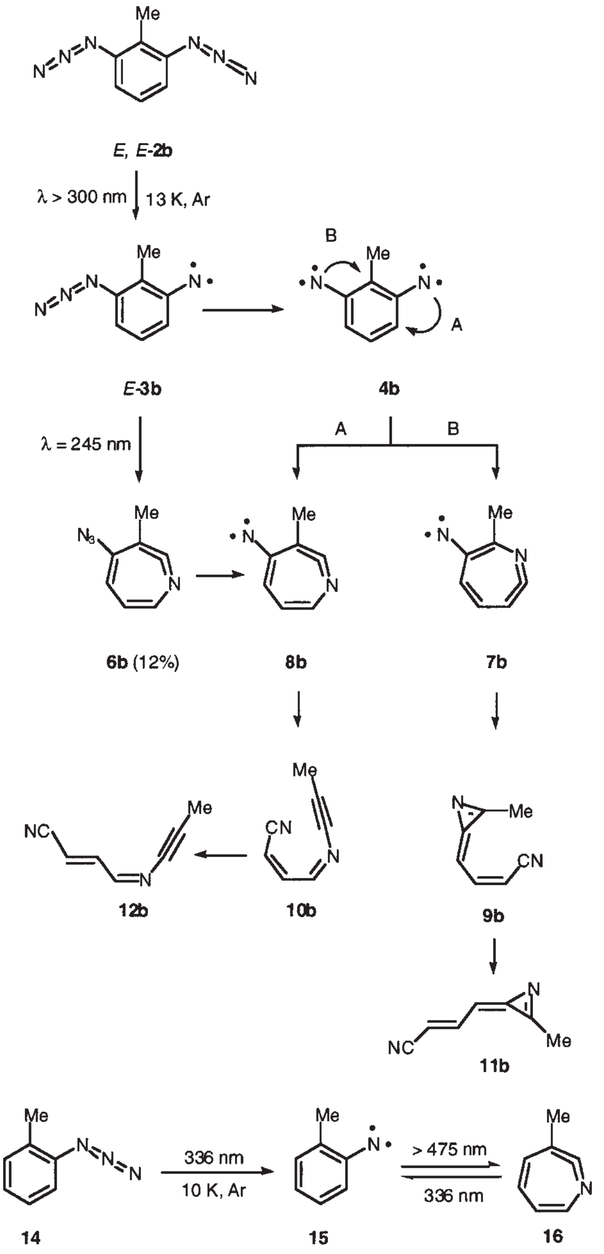
5b/**6b**/Obs		**5b**/Calcd		**6b**/Calcd	
ν/cm^{-1}	*I*[a)]	ν/cm^{-1}	*I*[a)]	ν/cm^{-1}	*I*[a)]
—	—	3113	0.00	3084	0.03
—	—	3048	0.02	3053	0.01
—	—	3047	0.00	3035	0.01
—	—	3029	0.01	3018	0.01
—	—	2978	0.01	2978	0.02
—	—	2927	0.02	2927	0.04
2104[b)]	1.00	2173	1.00[c)]	2172	1.00[c)]
1897	0.55	1894	0.18	1900	0.22
—	—	1572	0.02	1560	0.02
—	—	1529	0.04	1508	0.04
—	—	1451	0.00	1467	0.01
—	—	1439	0.00	1448	0.01
—	—	1386	0.01	1385	0.00
—	—	1374	0.01	1381	0.01
—	—	1318	0.16	1329	0.04
1267	1.00	1299	0.01	1299	0.30
—	—	1209	0.01	1283	0.13
—	—	1198	0.01	1192	0.01
—	—	1098	0.02	1183	0.01
—	—	1090	0.01	1055	0.03
—	—	1046	0.05	1035	0.05
—	—	1025	0.02	1019	0.04
—	—	989	0.00	963	0.00
—	—	924	0.01	930	0.01
—	—	905	0.01	888	0.03
—	—	—	—	861	0.01
—	—	801	0.03	792	0.03
—	—	752	0.02	766	0.02
—	—	723	0.01	735	0.02
—	—	680	0.06	630	0.01
—	—	627	0.01	624	0.03
—	—	599	0.00	549	0.01
—	—	594	0.00	536	0.02
—	—	505	0.01	524	0.01

a) Relative Intensity. b) Tail which overlaps with IR bands of starting azide and triplet azidonitrene **3b**. c) Calculated intensities of IR bands of **5b** and **6b** at 2173 and 2172 cm^{-1} are 801 and 742 km/mol, respectively.

means that the yields of *E*-**3b**, **4b** and **6b** after 2 min of irradiation at $\lambda = 245$ nm are 44, 44 and 12%, respectively. Recall that **6b** was not formed at all on irradiation of **2b** at $\lambda > 300$ nm.

Further irradiation of the matrix at $\lambda > 300$ nm for 3 h led to the disappearance of the characteristic IR bands of *E*-**3b** and **4b** and to the appearance of the characteristic IR bands of azirines **9b**/**11b** and acetylenes **10b**/**12b** (Fig. 6, Table 10). Our crude estimates showed that **9b**/**11b** and **10b**/**12b** are formed in a ratio of 1:10.

The formation of **9b**/**11b** and **10b**/**12b** from quintet **4b** shows that this quintet dinitrene is much more photochemically labile than triplet *E*-**3b**. The main direction of photochemical transformations of quintet **4b** involves the intramolecular insertion of the nitrene into 1,6-aromatic bond presumably to form **8b** (path A). The latter is obviously very unstable and undergoes the ring-opening to give acetylenes **10b**/**12b** in 91% total yield. At the same time, the intramolecular insertion of the nitrene unit into 1,2-aromatic bond (path B) followed by the ring-opening of unstable **7b**, yields azirines **9b**/**11b** as minor (9%)



Scheme 3.

photoproducts. These photochemical reactions start to occur at the stage of generation of quintet **4b** from triplet *E*-**3b**, and **9b**/**11b** and **10b**/**12b** become the major photoproducts already after 5 min of irradiation of **2b** at $\lambda > 300$ nm (Scheme 3).

Figure 7 shows the UV–vis spectra recorded during the photolysis of diazide **2b** in solid argon at 13 K after 0, 1, 3, 5, 7 and 15 min of irradiation at $\lambda > 300$ nm; two insets of this Figure display the difference spectra obtained by subtraction of UV spectrum of **2b** from the UV spectrum recorded after 2 and 11 min of irradiation of **2b**. As in the case of **2a**, the irradiation of diazide **2b** led to a gradual decrease in intensity of its UV bands with $\lambda_{\max} = 242$, 290 and 301 nm and to the appearance of new bands in a region from 300 to 800 nm with their maxima at 309, 324, 401, 408, 418, 422, 434, 590 and 712 nm. The bands at $\lambda_{\max} = 309$, 324, 401, 408, 434 and 590 nm are typical of triplet arylnitrenes[4,8g,9,19] and can therefore be assigned to triplet **3b**. These bands were observed during the first 2 min of the photolysis of **2b** and disappeared on more extended (2–11 min) irradiation which caused the appearance of new bands with maxima at 307, 326, 395, 418, 422 and 712 nm. These new bands can tentatively be assigned to quintet **4b**. The very extended (>30 min) irradiation of the sample destroyed the UV–vis spectrum of quintet **4b** and resulted in the appearance of the UV–vis spectrum identical to that recorded after 540 min of irradiation of **2a**. This final UV–vis spectrum can be assigned to a mixture of ring-opened products **9b**, **10b**, **11b** and **12b**. The results obtained show that the photolysis of **2b** affords triplet **3b** and quintet **4b** as intermediate photoproducts in quantities already sufficient for the UV–vis detection.

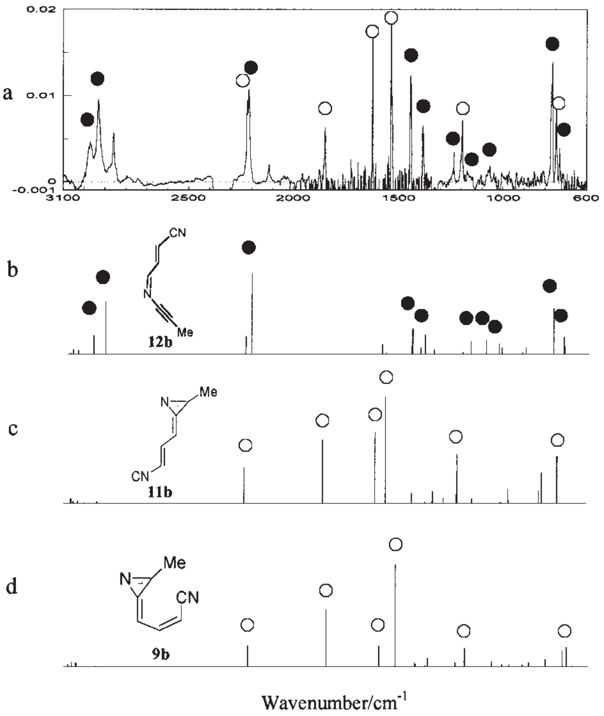
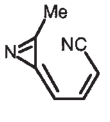


Fig. 6. (a) IR spectrum after irradiation ($\lambda > 300$ nm, 3 h) of diazide **2b** in Ar at 13 K. Theoretical (B3LYP/6-31G*) IR spectra of **12b** (b), **11b** (c), and **9b** (d).

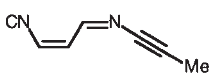
That the photochemical stability of triplet **3b** and quintet **4b** is higher than that of triplet **3a** and quintet **4a** is consistent with results of our FTIR studies of the photolysis of **2a** and **2b**.

The IR spectrum of starting diazide **2c** in solid argon at 13 K showed major bands at $\nu = 2129$, 2118, 2109, 1611, 1600, 1593, 1481, 1468, 1426, 1330, 1300, 1288, 1276, 1024 and 747 cm^{-1} (Table 2). Such a large number of bands in the IR spectrum of **2c** is explained by a large number of rotational isomers for this diazide. Due to the presence of bulky methyl groups in *ortho*-positions to the azido groups, the latter comes out of the plane of the aromatic ring in various directions, forming a great variety of *anti* and *syn* *E*,*E*-, *E*,*Z*- and *Z*,*Z*-isomers. Owing to these geometrical features, diazide **2c** is rather stable toward light at $\lambda > 300$ nm and requires much more irradiation time to be photolyzed. The irradiation of **2c** with light at $\lambda >$ 300 nm for 30 min resulted in very slow depletion of the IR bands of starting diazide and to the appearance of new prominent bands of triplet **3c** and quintet **4c** at $\nu = 1506$, 1447, 1437,

Table 10. IR Bands of **9b** and **10b** in Ar at 13 K and B3LYP/6-31G* Calculated IR Spectra of **9b** and **10b**



9b
-379.7396523 hartrees



10b
-379.7415047 hartrees

9b/Obs		**9b**/Calcd		**10b**/Obs		**10b**/Calcd	
ν/cm^{-1}	I[a]	ν/cm^{-1}	I[a]	ν/cm^{-1}	I[a]	ν/cm^{-1}	I[a]
—	—	3081	0.02	—	—	3086	0.02
—	—	3063	0.05	—	—	3072	0.05
—	—	3047	0.05	—	—	3048	0.05
—	—	3042	0.04	2970	0.33	2976	0.24
—	—	3014	0.00	2932	0.68	2273	0.14
—	—	2951	0.01	2859	0.41	2916	0.66
2215	0.54	2222	0.20	2221	0.67	2246	0.22
1849	0.32	1849	0.56	2215	0.77	2217	1.00[b]
1624	0.92	1596	0.20	—	—	1591	0.12
1534	1.00	1519	1.00[b]	—	—	1572	0.02
—	—	1425	0.04	—	—	1448	0.10
—	—	1421	0.03	1440	0.89	1444	0.32
—	—	1405	0.00	—	—	1405	0.08
—	—	1376	0.01	1383	0.44	1385	0.24
—	—	1363	0.08	—	—	1342	0.07
—	—	1231	0.04	—	—	1205	0.02
1195	0.38	1187	0.18	1235	0.25	1165	0.17
—	—	1058	0.05	—	—	1092	0.17
—	—	1010	0.02	1064	0.13	1031	0.14
—	—	975	0.02	—	—	1017	0.08
—	—	960	0.00	—	—	973	0.08
—	—	911	0.02	—	—	917	0.02
—	—	881	0.04	—	—	901	0.08
—	—	802	0.07	765	1.00	768	0.58
—	—	720	0.15	731	0.30	717	0.24
745	0.46	701	0.19	—	—	711	0.10
—	—	677	0.00	—	—	600	0.00
—	—	596	0.00	—	—	588	0.08
—	—	522	0.00				
—	—	512	0.08				

a) Relative intensity. b) Calculated intensities of IR bands of **9b** and **10b** at 1519 and 2217 cm^{-1} are 266 and 59 km/mol, respectively.

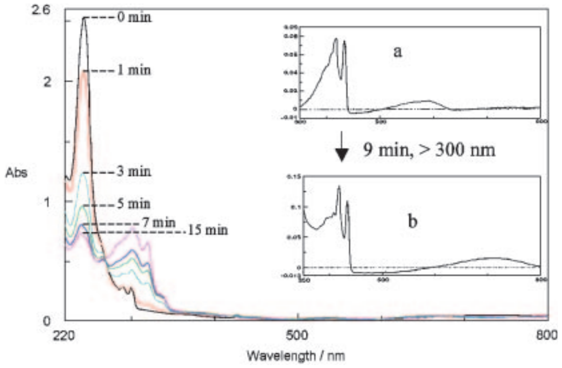


Fig. 7. Photolysis (λ > 300 nm) of diazide **2b** in solid Ar at 13 K. UV spectra (a) before irradiation; (b) after 1 min of irradiation; (c) after 3 min of irradiation; (d) after 5 min of irradiation; (e) after 7 min of irradiation; (f) after 15 min of irradiation. In inset is the difference UV spectra after (a) 2 and (b) 11 min of irradiation.

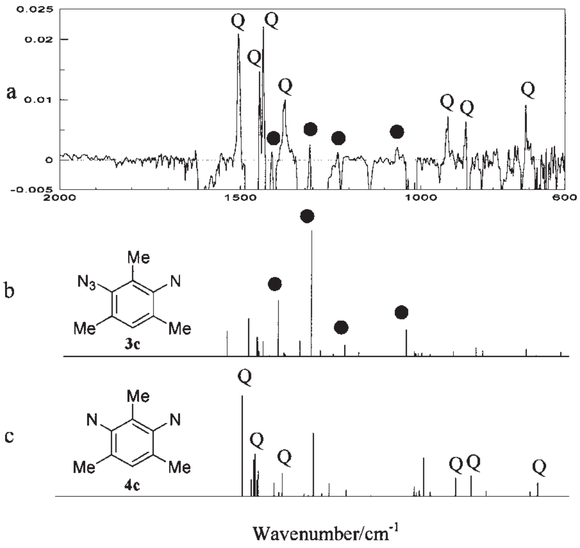
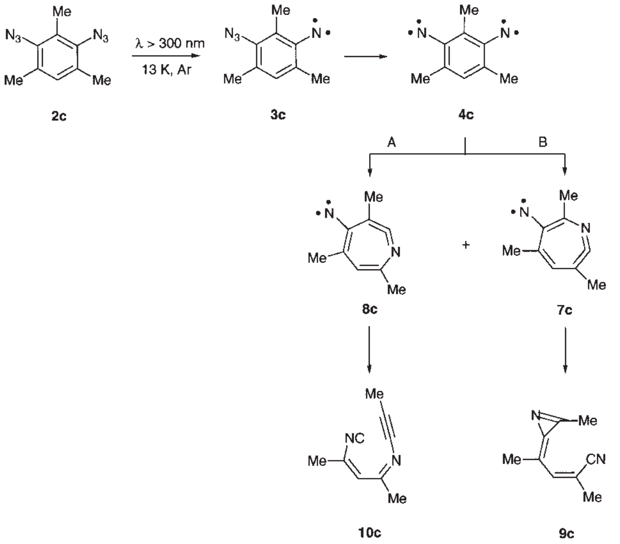


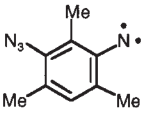
Fig. 8. (a) Difference spectrum before and after irradiation (λ > 300 nm, 30 min) of diazide **2c** in Ar at 13 K. Theoretical (UB3LYP/6-31G*) IR spectra of triplet **3c** (b), and quintet **4c** (c).



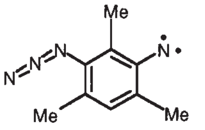
Scheme 4.

1380, 1377, 1308, 1064, 928, 926, 875 and 708 cm^{-1} (Fig. 8, Scheme 4). During all this time, no characteristic IR bands of ring-expanded products at around 1900 cm^{-1} were observed. The observable new bands matched well with UB3LYP/6-31G* calculated vibrational frequencies of triplet **3c** and quintet **4c** (Tables 11 and 12).[20] Relative intensities of IR bands of triplet **3c** at 1065 (0.002 A, 32 km/mol) cm^{-1} and of quintet **4c** at 925 (0.007 A, 6 km/mol) cm^{-1} suggest that the yields of **3c** and **4c** at this stage of the photolysis are 5 and 95%, respectively. It is interesting to note that the yield of triplet **3c** never exceeded 5% even at the initial (1–3 min) stages of the photolysis of **2c**. As UB3LYP/6-31G* calculations show, the energy of triplet azidonitrene **3c** is higher by about 13 kJ/mol than the energy of quintet **4c** + N_2.

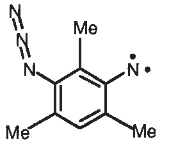
Table 11. IR Bands of Triplet **3c** in Ar at 13 K and B3LYP/6-31G* Calculated IR Spectra of Triplet *E*-**3c** and *Z*-**3c**



3c



E-3c
-567.8478047 hartrees

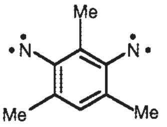


Z-3c
-567.8484322 hartrees

3c/Obs		*E*-**3c**/Calcd		*Z*-**3c**/Calcd	
ν/cm^{-1}	I[a]	ν/cm^{-1}	I[a]	ν/cm^{-1}	I[a]
—	—	3055	0.02	3058	0.03
—	—	3034	0.01	3028	0.00
—	—	3013	0.02	3014	0.03
—	—	3011	0.02	3011	0.02
—	—	2988	0.02	2984	0.02
—	—	2981	0.02	2981	0.02
—	—	2978	0.02	2980	0.02
—	—	2934	0.02	2931	0.02
—	—	2931	0.03	2930	0.02
—	—	2928	0.02	2929	0.04
—[b]	—	2178	1.00[c]	2179	1.00[c]
—	—	1550	0.01	1547	0.04
—	—	1487	0.04	1487	0.06
—	—	1462	0.01	1464	0.03
—	—	1461	0.03	1462	0.02
—	—	1457	0.02	1459	0.00
—	—	1453	0.02	1448	0.02
—	—	1448	0.01	1447	0.00
—	—	1427	0.01	1430	0.00
1380[b]	0.30[b]	1405	0.10	1405	0.08
—	—	1391	0.01	1390	0.00
—	—	1389	0.00	1388	0.00
—	—	1384	0.00	1385	0.00
—	—	1345	0.00	1346	0.02
1308[b]	1.00[b]	1319	0.18	1314	0.19
—	—	1287	0.01	1288	0.01
—	—	1253	0.02	1252	0.00
1230	0.30	1221	0.00	1220	0.02
—	—	1186	0.00	1182	0.00
1064	0.60	1046	0.05	1051	0.04
—	—	1030	0.01	1028	0.01
—	—	1028	0.00	1027	0.00
—	—	1023	0.00	1024	0.00
—	—	1019	0.00	1018	0.00
—	—	1005	0.00	1006	0.00
—	—	988	0.00	984	0.00
—	—	920	0.00	921	0.01
—	—	856	0.01	858	0.02
—	—	819	0.00	838	0.01
—	—	743	0.02	719	0.01
—	—	695	0.00	691	0.00
—	—	622	0.01	623	0.00
—	—	590	0.00	590	0.00
—	—	553	0.00	560	0.00
—	—	542	0.00	544	0.00
—	—	521	0.02	521	0.02
—	—	501	0.00	519	0.00

a) Relative intensity. b) Overlaps with IR bands of starting azide **2c**. c) Calculated intensities of IR bands of *E*-**3c** and *Z*-**3c** at 2178 and 2179 cm^{-1} are 698 and 668 km/mol, respectively.

Table 12. IR Bands of Quintet **4c** in Ar at 13 K and UB3LYP/6-31G* Calculated IR Spectrum of Quintet **4c**



4c
-458.3284077 hartrees

4c/Obs		**4c**/Calcd	
ν/cm^{-1}	I[a]	ν/cm^{-1}	I[a]
—[b]	—	3044	0.37
—[b]	—	3037	0.11
—[b]	—	3031	0.09
3010	0.40	3013	0.43
—[b]	—	2979	0.26
—[b]	—	2976	0.29
—[b]	—	2972	0.40
—[b]	—	2933	0.14
2928	0.40	2928	0.40
2925	0.49	2925	0.49
1506[b]	0.94[b]	1490	1.00[c]
—[b]	—	1485	0.12
—[b]	—	1459	0.37
—[b]	—	1457	0.20
1447[b]	0.65[b]	1455	0.43
1437	1.00	1446	0.26
—[b]	—	1403	0.14
—	—	1390	0.03
—	—	1382	0.03
1377	0.41	1381	0.23
—	—	1322	0.03
—	—	1310	0.00
—[b]	—	1297	0.63
—	—	1274	0.03
—[b]	—	1254	0.11
—	—	1206	0.06
—	—	1140	0.00
—	—	1023	0.03
—[b]	—	1021	0.09
—	—	1015	0.03
—	—	1007	0.06
—[b]	—	995	0.37
—	—	978	0.06
925	0.35	908	0.17
875	0.30	866	0.20
—	—	824	0.06
—	—	705	0.06
708	0.40	684	0.14
—	—	604	0.00
—	—	551	0.03
—	—	532	0.00

a) Relative intensity. b) Overlaps with negative IR bands of starting azide **2c**. c) Calculated intensity of IR band of **4a** at 1490 cm^{-1} is 35 km/mol.

More extended (9 h) irradiation of the matrix with light at $\lambda > 300$ nm led to the disappearance of IR bands of quintet **4c** and to the appearance of IR bands of azirine **9c** and acetylene **10c** (Fig. 9, Table 13). These photochemical transformations

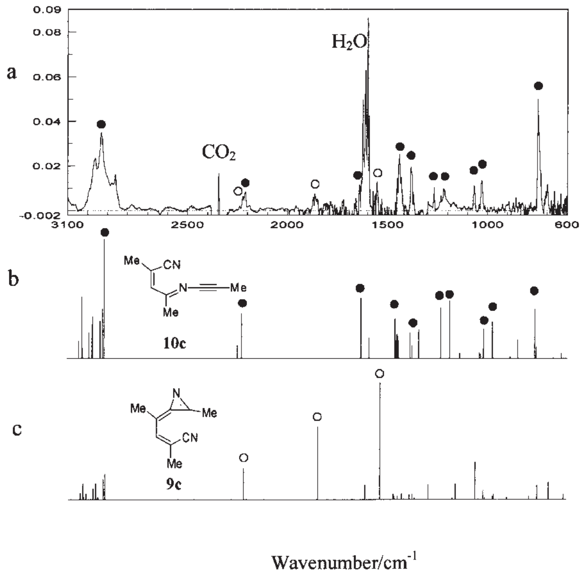


Fig. 9. (a) IR spectrum after irradiation (λ > 300 nm, 9 h) of diazide **2c** in Ar at 13 K. Theoretical (B3LYP/6-31G*) IR spectra of **10c** (b) and **9c** (c).

show that quintet **4c** is photochemically a rather reactive compound despite the protection of its aromatic ring by methyl groups in *ortho*-positions to the nitrene units.

Contrary to the UV spectra of diazides **2a**, **b**, the UV spectrum of diazide **2c** shows only one absorption band with $\lambda_{\max} = 245$ nm (Fig. 10a). Such UV spectra are typical of alkyl azides. This suggests that both azido groups of **2c** lie out of the plane of the benzene ring due to steric hindrance from *ortho*-methyl groups. As a result, diazide **2c** was rather stable toward light at $\lambda > 300$ nm and required long irradiation time. Figure 10a shows the UV–vis spectra recorded during the photolysis of diazide **2c** in a degassed frozen 2MTHF solution at 77 K after 0, 8, 15, 30 and 45 min of irradiation at $\lambda > 300$ nm; the inset of this Figure displays the difference spectrum obtained by subtraction of the UV spectrum of **2a** from that recorded after 8 min of irradiation of **2a**. Brief irradiation (5–10 min) of diazide **2a** led to a slow decrease in intensity of its UV bands with $\lambda_{\max} = 245$ nm and to the appearance of new bands in the region from 260 to 600 nm, with maxima at 284, 311, 326, 411, 425, 434 and 550 nm typical of triplet arylnitrenes.[4,8g,9,19] All these bands can be assigned to triplet **3c**. In comparison with FTIR, the UV–vis spectroscopy is a much more sensitive spectroscopic method and allows the detection of triplet **3c** despite its relatively low yield. More extended (>45 min) irradiation led to the disappearance of bands of triplet **3c** and to the appearance of new bands at 257, 298, 309, 328, 398, 420 and 600 nm attributable to quintet **4c**. These spectral changes are shown in Fig. 10b; the inset of this Figure displays the difference spectrum obtained by subtraction of the UV spectrum recorded after 30 min of irradiation of **2c** from the UV spectrum recorded after 105 min of irradiation of **2c**. Rather strong UV–vis spectrum of quintet **4c** indicates rather high photochemical stability of this species. This is in good agreement with results of our FTIR study of the photolysis of **2c** in solid argon.

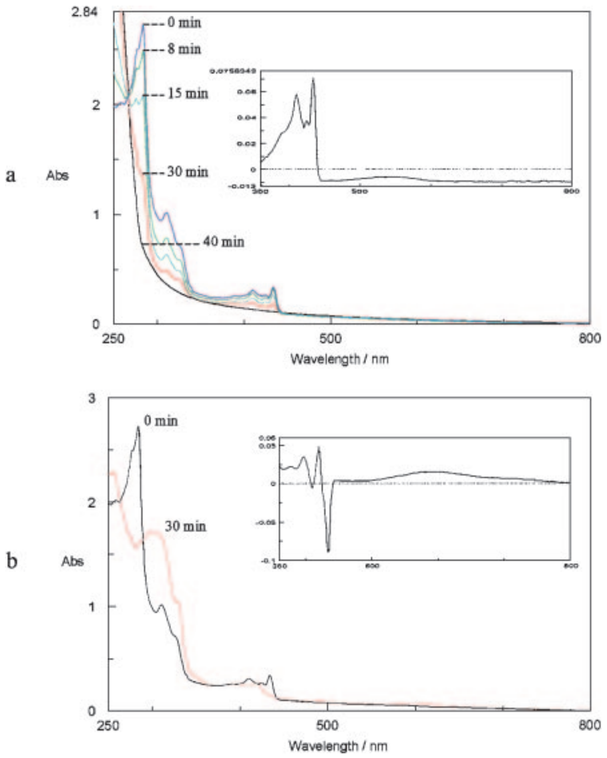


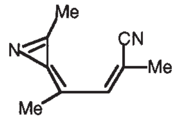
Fig. 10. Photolysis (λ > 300 nm) of diazide **2c** in a 2MTHF glass at 77 K. (a) UV spectra after 0, 8, 15, 30 and 45 min of irradiation. In inset is the difference spectrum after 8 min of irradiation. (b) UV spectra after 0 and 300 min of irradiation. In inset is the difference spectrum after 105 and 300 min of irradiation.

Experimental

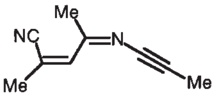
Materials and General Methods. IR spectra were measured on a JASCO A-100 recording spectrometer. ^{1}H NMR spectra were determined with a JEOL JNM-EX 270 spectrometer. UV–vis spectra were recorded with a Hitachi 200-S spectrometer. EPR spectra were determined with a JEOL JES-TE200D spectrometer. Column chromatography was carried out on Fuji Davidson Silica gel BW-127ZH. Thin-layer chromatography was done on Merck Kieselgel 60 PF254. Starting diamines **1a**–**c** were purchased from Tokyo Kasei Kogyo Co. Ltd.

1,3-Diazidobenzene (**2a**) was prepared following the literature procedure.[11] A mixture of *m*-phenylenediamine (1 g, 9.3 mmol) and 50% sulfuric acid (20 mL) was stirred at 0–2 °C. The diamine dihydrosulfate was deazotized by adding sodium nitrite (1.3 g, 18.8 mmol) in small portions. To the stirred solution was slowly added sodium azide (1.3 g, 20 mmol) in small portions at 0–5 °C. After the reaction mixture was stirred for an additional hour, the resulting solution was extracted with CH_2Cl_2. The organic phase was washed (H_2O), dried (Na_2SO_4), filtered, and evaporated under reduced pressure. The residue was chromatographed on a short silica gel column using *n*-hexane as an eluent. Removal of the solvent under reduced pressure gave *m*-phenylenediazide (960 mg, 60%) as a pale yellow oil. ^{1}H NMR ($CDCl_3$) δ 6.65 (t, $J = 2.1$ Hz, 1H), 6.81 (dd, $J = 8.1$ and 2.1 Hz, 2H), 7.32 (t, $J = 8.1$ Hz, 1H); IR (KBr disk, thin film) ν 2968 (w), 2928 (w), 2854 (w), 2112 (vs), 1611 (s), 1586 (s), 1484 (s), 1320 (m), 1285 (s), 1262 (s), 1170 (w), 1159 (w), 1108 (w), 919 (w), 872 (w), 854 (w), 783 (w), 774 (w), 709 (w), 686 (w), 679 (w), 537 (w) cm^{-1}.

Table 13. IR Bands of **9c** and **10c** in Ar at 13 K and B3LYP/6-31G* Calculated IR Spectra of **9c** and **10c**



9c
-458.3719127 hartrees



10c
-458.370508 hartrees

9c/Obs		**10c**/Calcd		**9c**/Obs		**10c**/Calcd	
ν/cm^{-1}	Ia)	ν/cm^{-1}	Ia)	ν/cm^{-1}	Ia)	ν/cm^{-1}	Ia)
—	—	3040	0.05	—	—	3041	0.14
—	—	3028	0.13	2963	0.60	3027	0.51
—	—	3023	0.02	—	—	3021	0.09
—	—	3016	0.00	—	—	2990	0.21
—	—	3011	0.05	—	—	2275	0.28
—	—	2976	0.09	2931	0.82	2970	0.35
—	—	2963	0.13	—	—	2969	0.30
—	—	2951	0.02	—	—	2935	0.30
—	—	2925	0.17	—	—	2922	0.42
—	—	2918	0.21	2862	0.47	2914	1.00c)
2212	0.50	2220	0.27	2224	0.18	2247	0.12
1864	0.61	1848	0.62	2212	0.20	2227	0.37
—	—	1611	0.12	1635	0.23	1630	0.51
1552	1.00	1535	1.00c)	1580	0.19	1589	0.16
—	—	1470	0.03	1460	0.30	1460	0.33
—	—	1467	0.05	—	—	1452	0.14
—	—	1447	0.03	1451	0.47	1450	0.21
—	—	1424	0.05	—	—	1445	0.16
—	—	1414	0.00	1438	0.65	1444	0.19
—	—	1389	0.04	1432	0.43	1442	0.16
—	—	1386	0.00	1383	0.43	1386	0.21
—	—	1372	0.05	1380	0.42	1384	0.21
—	—	1361	0.01	—	—	1375	0.09
—	—	1291	0.13	1371	0.23	1340	0.23
—	—	1173	0.01	1266	0.28	1232	0.42
—	—	1156	0.13	1218	0.25	1188	0.49
1065	—b)	1057	0.32	—	—	1135	0.05
—	—	1041	0.01	—	—	1037	0.05
—	—	1033	0.00	—	—	1031	0.02
—	—	1017	0.08	—	—	1021	0.07
—	—	1008	0.02	—	—	1020	0.07
—	—	968	0.02	1065	0.23	1016	0.26
—	—	963	0.05	1028	0.27	972	0.30
—	—	896	0.01	—	—	884	0.00
—	—	784	0.02	—	—	844	0.16
747	—b)	746	0.12	747	1.00	762	0.42
700	0.38	687	0.15	—	—	753	0.09
—	—	614	0.04	—	—	627	0.05
—	—	591	0.00	—	—	598	0.07
558	0.30	551	0.09	—	—	540	0.05
—	—	543	0.00	—	—	517	0.02

a) Relative intensity. b) Overlaps with IR bands of **10c**. c) Calculated intensities of IR bands of **9c** and **10c** at 1535 and 2227 cm^{-1} are 210 and 43 km/mol, respectively.

2,6-Diazidotoluene (**2b**) was prepared in a manner similar to that used for diazide **2a**. A mixture of 2,6-diaminotoluene (1.2 g, 9.8 mmol), water (5 mL) and concentrated hydrochloric acid (2 mL) was stirred at 0–2 °C. The diamine dihydrochloride was deazotized by adding sodium nitrite (1.4 g, 20 mmol) in small portions. To the stirred solution was slowly added sodium azide (1.4 g, 20 mmol) in small portions at 0–5 °C. After the reaction mixture was stirred for an additional hour, the resulting solution was extracted with CH_2Cl_2. The organic phase was washed (H_2O), dried (Na_2SO_4), filtered, and evaporated under reduced pressure. The residue was chromatographed on a short silica gel column using *n*-hexane as an eluent. Removal of the solvent under reduced pressure gave 2,6-diazidotoluene (600 mg, 34%) as a light yellow solid: mp 76–77 °C. ^{1}H NMR (CDCl$_3$) δ 2.07 (s, 3H), 6.91 (d, $J = 7.9$ Hz, 2H), 7.24 (t, $J = 7.9$ Hz, 1H); IR (KBr disk, thin film) ν 2954 (w), 2926 (w), 2854 (w), 2118 (vs), 1602 (m), 1578 (s), 1559 (m), 1458 (s), 1311 (m), 1277 (s), 1255 (m), 1164 (w), 1145 (w), 1020 (w), 959 (w), 868 (w), 771 (vs), 698 (s), 537 (w) cm^{-1}.

1,3-Diazido-2,4,6-trimethylbenzene (**2c**) was prepared in a manner similar to that used for diazide **2b**. A mixture of 1,3-diamino-2,4,6-trimethylbenzene (1.5 g, 10 mmol), water (10 mL) and concentrated hydrochloric acid (4 mL) was stirred at 0–2 °C. The diamine dihydrochloride was deazotized by adding sodium nitrite (2.08 g, 30 mmol) in small portions. To the stirred solution was slowly added sodium azide (2 g, 30.8 mmol) in small portions at 0–5 °C. After the reaction mixture was stirred for an additional hour, the resulting solution was extracted with CH$_2$Cl$_2$. The organic phase was washed (H$_2$O), dried (Na$_2$SO$_4$), filtered, and evaporated under reduced pressure. The residue was chromatographed on a short silica gel column using *n*-hexane as an eluent. Removal of the solvent under reduced pressure gave 1,3-diazido-2,4,6-trimethylbenzene (600 mg, 30%) as a colorless oil: ^{1}H NMR (CDCl$_3$) δ 2.32 (s, 6H), 2.35 (s, 3H), 6.84 (s, 1H); IR (KBr disk, thin film) ν 2954 (w), 2925 (m), 2848 (w), 2112 (vs), 1604 (w), 1474 (s), 1424 (m), 1405 (w), 1379 (w), 1326 (m), 1283 (s), 1221 (w), 1137 (w), 1021 (m), 868 (w) cm^{-1}.

Computational Chemistry. Density functional theory[21] calculations were carried out using the GAUSSIAN 94 program.[22] The geometry optimizations for all molecules under consideration were implemented at the B3LYP/6-31G(d) level of theory.

Matrix-Isolation Spectroscopy. Matrix experiments were performed by means of standard techniques[23,24] using an Iwatani 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 ports of a vacuum shroud surrounding the cold head were fit with KBr windows for spectroscopic viewing, and the remaining ports were fitted with quartz plate for UV irradiation and a deposition plate for admitting the sample and matrix gas. For 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).

Irradiations were carried out with a Wacom 500-W high-pressure arc lamp or an Ushio 500-W mercury high-pressure arc lamp. For broad-band irradiation, Toshiba cutoff filters were used (50% transmittance at the wavelength specified). In order to follow the progress of reaction in detail, the intensity of the light was tuned by changing the distance between the lamp and the window.

For typical EPR spectral experiments, an appropriate sample of diazide was dissolved in 2-methyltetrahydrofuran (2MTHF) in a 4 mm o.d. quartz sample tube (diazide concentration of ca. 10^{-4} M), subjected to a 5-fold freeze-pump-thaw degassing procedure and sealed under vacuum, frozen at 77 K. The tube was transferred to a Suprasil Ⅱ vacuum-jacketed finger dewar, and photolyzed for 1–9 min with a Ushio 500-W mercury high-pressure arc lamp at >300 nm (Pyrex-filter) at a distance of about 5 cm. After each irradiation, the sample was placed into the cavity of a JEOL JES-TE200D spectrometer. Most spectra were obtained over a 50–9950 G (G) region at a modulation frequence of 100.0 kHz and a microwave power setting of 20 dB. Microwave frequencies were determined using a JASCO Advantest R5372 frequency counter. The zfs *D*- and *E*-parameters of triplet and quintet nitrenes were calculated by standard methods.[8d]

References

1 a) "Magnetic Properties of Organic Materials," ed by P. M. Lahti, Marcel Dekker, New York (1999). b) "Molecular Magnetism: New Magnetic Materials," ed by K. Itoh and M. Kinoshita, Kodansha-Godon and Breach, Tokyo (2000).

2 a) S. Nimura and A. Yabe, "Magnetic Properties of Organic Materials," ed by P. M. Lahti, Marcel Dekker, New York (1999), ch. 7. b) H. Oka, Y. Miura, and Y. Teki, *Mol. Cryst. Liq. Cryst.*, **334**, 41 (1999). c) T. Nakai, K. Sato, D. Shiomi, T. Takui, K. Itoh, M. Kozaki, and K. Okuda, *Mol. Cryst. Liq. Cryst.*, **334**, 157 (1999). d) T. Nakai, K. Sato, D. Shiomi, T. Takui, K. Itoh, M. Kozaki, and K. Okuda, *Synth. Met.*, **103**, 2265 (1999). e) S. V. Chapyshev, R. Walton, and P. M. Lahti, *Mendeleev Commun.*, **2000**, 114. f) S. V. Chapyshev, R. Walton, and P. M. Lahti, *Mendeleev Commun.*, **2000**, 138. g) S. V. Chapyshev, R. Walton, and P. M. Lahti, *Mendeleev Commun.*, **2000**, 187. h) S. V. Chapyshev and P. R. Serwinski, *Mendeleev Commun.*, **2001**, 92. i) Y. Miura, H. Oka, and Y. Teki, *Bull. Chem. Soc. Jpn.*, **74**, 385 (2001).

3 a) S. V. Chapyshev, R. Walton, J. A. Sanborn, and P. M. Lahti, *J. Am. Chem. Soc.*, **122**, 1580 (2000). b) N. Oda, T. Nakai, K. Sato, D. Shiomi, M. Kozaki, K. Okada, and T. Takui, *Synth. Met.*, **121**, 1840 (2001).

4 S. V. Chapyshev, A. Kuhn, M. Wong, and C. Wentrup, *J. Am. Chem. Soc.*, **122**, 1572 (2000).

5 S. V. Chapyshev, *Mendeleev Commun.*, **2002**, 168.

6 A. Nicolaides, H. Tomioka, and S. Murata, *J. Am. Chem. Soc.*, **120**, 11530 (1998).

7 A. Nicolaides, T. Nakayama, K. Yamazaki, H. Tomioka, S. Kozeki, L. L. Stracener, and R. J. McMahon, *J. Am. Chem. Soc.*, **121**, 10563 (1999).

8 a) O. L. Chapman and J. P. LeRoux, *J. Am. Chem. Soc.*, **100**, 282 (1978). b) T. Donnelly, I. R. Dunkin, D. S. D. Norwood, A. Prentice, C. J. Shields, and P. C. P. Thomson, *J. Chem. Soc., Perkin Trans. 2*, **1985**, 307. c) J. C. Hayes and R. S. Sheridan, *J. Am. Chem. Soc.*, **112**, 5879 (1990). d) S. Murata, R. Yoshidome, Y. Satoh, N. Kato, and H. Tomioka, *J. Org. Chem.*, **60**, 1428 (1995). e) S. Murata, R. Nakatsuji, and H. Tomioka, *J. Chem. Soc., Perkin Trans. 2*, **1995**, 793. f) S. Murata, M. Miwa, and H. Tomioka, *J. Chem. Soc., Chem. Commun.*, **1995**, 1255. g) I. R. Dunkin, M. A. Lynch, F. McAlpine, and D. Sweeney, *J. Photochem. Photobiol., A*, **102**, 207 (1997). h) I. R. Dunkin and C. J. Shields, *Spectrochim. Acta, Part A*, **53**, 129 (1997). i) I. R. Dunkin and C. J. Shields, *Spectrochim. Acta, Part A*, **53**, 141 (1997).

9 a) J. Morawietz, W. Sander, and M. Traubel, *J. Org. Chem.*, **60**, 6368 (1995). b) G. Bucher, *Eur. J. Org. Chem.*, **2001**, 2447.

10 a) I. R. Dunkin, T. Donnelly, and T. S. Lockhart, *Tetrahedron Lett.*, **26**, 359 (1985). b) S. Murata, S. Abe, and H. Tomioka, *J. Org. Chem.*, **62**, 3055 (1997).

11 O. M. Forster and H. E. Hierz, *J. Chem. Soc.*, **91**, 1953 (1907).

12 S. Murata and H. Iwamura, *J. Am. Chem. Soc.*, **113**, 5547 (1991).

13 E. Wasserman, R. W. Murray, W. A. Yager, A. M. Trozzolo, and G. Smolinsky, *J. Am. Chem. Soc.*, **89**, 5076 (1967).

14 S. V. Chapyshev, T. Enyo, and H. Tomioka, "Proceedings of International Symposium on Reactive Intermediates and Unusual Molecules (ISRIUM-2001)," Nara (2001), p. 74.

15 N. Oda, K. Sato, D. Shiomi, M. Kozaki, K. Okada, and T. Takui, "Proceedings of International Symposium on Reactive Intermediates and Unusual Molecules (ISRIUM-2001)," Nara (2001), p. 117.

16 For **5a** and **6a**, the data for only one isomer was shown in Table for simplicity. Although other isomers might be formed, at this stage of the reaction, the spectra are consisting of a mixture of many products and hence it is practically impossible to assign all the absorptions.

17 J. Backes, "Methoden der Organischen Chemie, Houben-Weyl," ed by D. Klopmann, Georg Thieme Verlag, Stuttgart (1992), Bd. E16C, S. 366–369.

18 For products formed as a result of ring opening reaction, e.g., **9** to **13**, all possible isomers were calculated, but only isomers whose theoretical IR bands match best the experimental IR bands are recorded in Table.

19 For **2c**, due to the presence of two methyl groups at *ortho*-position with respect to azide groups, the azide groups are forced to come out of the plane of phenyl ring. Therefore, there are too many conformers to calculate. Similarly, **3c** has many possible conformers but here in order to roughly estimate the ratio of **3c** to **4c** upon irradiation of **2c**, two isomers, *E*- and *Z*-**3c** where methyl groups are fixed are calculated and reported in Table.

20 a) A. Reiser and U. Frazer, *Nature (London)*, **208**, 682 (1965). b) A. Reiser, G. Bowes, and R. J. Horne, *Trans. Faraday Soc.*, **62**, 3162 (1966). c) V. A. Smirnov and S. B. Brichkin, *Chem. Phys. Lett.*, **87**, 548 (1982). d) E. Leyva, M. S. Platz, G. Persy, and J. Wirz, *J. Am. Chem. Soc.*, **108**, 3783 (1986). e) A. Albini, G. Bettinetti, and G. Minoli, *J. Am. Chem. Soc.*, **119**, 7308 (1997). f) A. Albini, G. Bettinetti, and G. Minoli, *J. Am. Chem. Soc.*, **121**, 3104 (1999). g) M. Cerro-Lopez, N. P. Gritsan, Z. Zhu, and M. S. Platz, *J. Phys. Chem. A*, **104**, 9681 (2000).

21 K. Kohn, A. D. Becke, and R. G. Parr, *J. Phys. Chem.*, **100**, 12974 (1996).

22 M. J. Frish, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, and J. A. Pople, "Gaussian 94; Revision D.4," Gaussian Inc., Pittsburgh (1995).

23 H. Tomioka, N. Ichikawa, and K. Komatsu, *J. Am. Chem. Soc.*, **114**, 6045 (1992).

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