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Photodissociation of aromatic azides

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Abstract. Quantitative data on the photochemical activity of aromatic azides and on the mechanism and kinetics of azido group photodissociation are analysed and described systematically for the first time. The results of quantum chemical calculations of the azide structure in the ground and lower electronically excited states and the potential energy surfaces along the reaction coordinate of the $N-N_2$ bond dissociation are considered. The bibliography includes 164 references.

I. Introduction

Aromatic azides represent a class of compounds with the general formula ArN_3. Azides are widely applied; therefore, their properties are actively studied. The key reaction of azides is dissociation of the $N-N_2$ bond induced by radiation or heating with evolution of molecular nitrogen to give highly reactive intermediates, nitrenes

$$RN_3 \xrightarrow{h\nu \text{ or } \Delta} RN + N_2 .$$

During the last decade, considerable progress has been achieved in the understanding of the mechanism of azide photodissociation, which is due, first, to development of spectral methods and advancement of laser flash photolysis (LFP) facilities for the study of short-lived intermediates, and, second, development of new quantum chemical methods and appropriate computer software for the calculation of properties of short-lived intermediates in order to interpret experimental data.

The achievements in this field include, first of all, direct spectroscopic detection of singlet and triplet nitrenes and their transformation products. Using LFP techniques with pico- and femtosecond time resolution, the kinetic characteristics of nitrene reactions, *viz*., intramolecular cyclisation to benzazirine followed by ring expansion to dehydroazepine, intersystem crossing processes and other chemical reactions, were measured. Advanced high-level quantum chemical calculations were used to assign bands in the spectra of various intermediates and to determine their relative stabilities. The properties of nitrenes and their transformation products were the subject of a number of reviews [1–5] including more recent ones.[6,7] The results of a study of azide photooxidation are considered in a review.[8]

Meanwhile, the proper photodissociation of organic azides, which triggers the cascade of subsequent intramolecular transformations, remained beyond the attention of researchers. This review fills this gap. We consider the factors that determine the photochemical activities of azides, their relationship with the absorption spectra of azides and analyse the kinetic characteristics of photodissociation obtained in the last decade by LFP and the results of quantum chemical calculations of azide structures in the ground and excited states and potential energy surface (PES) profiles in these states along the reaction coordinate of the $N-N_2$ bond dissociation.

II. Correlation between the spectral and chemical properties of azides

The photochemical activity of an aromatic azide is characterised by two key parameters: the spectral sensitivity, which is determined by the azide absorption spectrum, and the quantum yield of the azido group photodissociation (φ). For nitrenes in the singlet state in the absence of quenchers, this is determined by the following relation:

$$\varphi = \frac{k_r}{k_r + k_{ic} + k_{isc} + k_f}, \qquad (1)$$

where k_r is the rate constant for the $N-N_2$ bond cleavage in the excited state; k_{ic}, k_{isc} and k_f are the rate constants for internal conversion, intersystem crossing and fluorescence (emission). To describe the dissociation of nitrenes in the triplet state, the multiplier φ_T (φ_T is the quantum yield of the triplet state) should be added to the numerator of Eqn (1). The theoretical limit $\varphi = 1$ is attained if $k_r \gg k_{ic} + k_{isc} + k_f$.

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Even in the earliest quantitative studies dealing with the photochemical activity of some aromatic azides, it was found that the quantum yields of photodissociation of these azides are close to the theoretical limit.[9,10] Subsequently, the quantum yields of photodissociation of aromatic azides were measured for derivatives of phenyl azide,[11–19] naphthyl azide,[9,13] hetaryl azides derived from pyridine,[20,21] pyrimidine,[22,23] quinoline,[9,11,24] acridine,[25] triazine,[26–28] benzothiazole[11,28] and other compounds.[29–43] Below we present the formulas of some relatively simple compounds of this group (azides **1**–**11**) (the photodissociation quantum yields of these azides are summarised in Table 1).

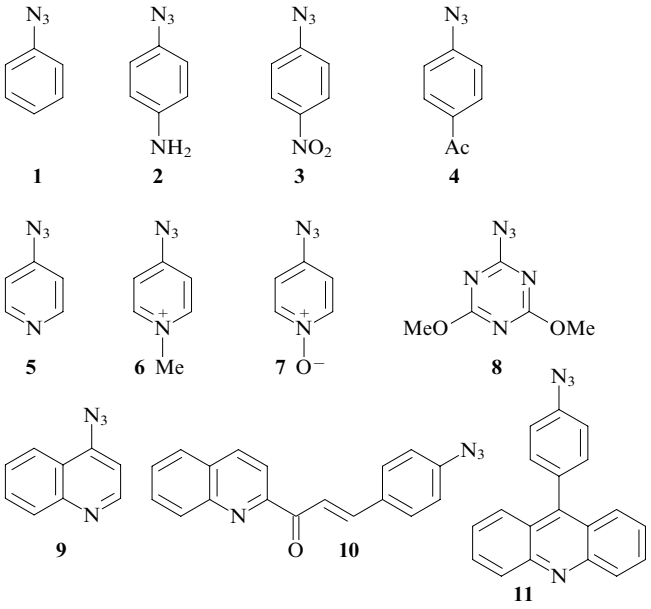


Table 1. Quantum yields of photodissociation of aromatic azides on irradiation at different wavelengths (λ).

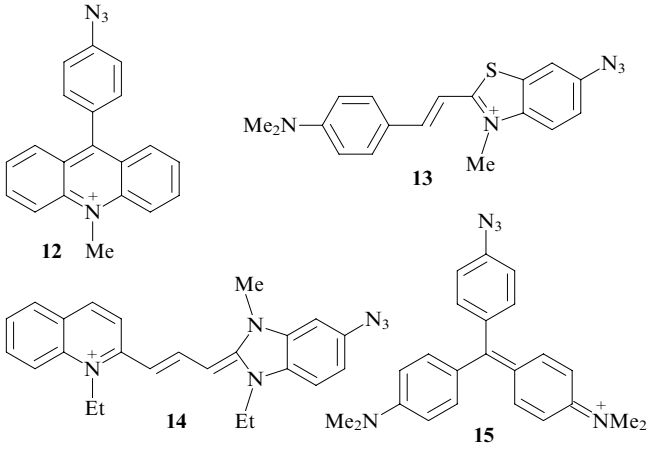
Azide	λ/nm	φ	Ref.
1	254	0.53	9, 13, 17
2	313	0.96	2
3	310	0.70	9, 15
4	280	0.59	9, 11
5	254	0.83	21
6	254	0.27	21
7	313	0.51	43
8	254	0.90	43
9	313	0.49	24
10	365	0.85	18
11	365	0.88	37
12	365	2×10^{-3}	37
13	538	10^{-3}	35
14	563	10^{-5}	35
15	620	10^{-5}	35

Photodissociation of azides is an irreversible reaction with the quantum yield being almost independent of the temperature, the presence of oxygen, the nature of the solvent, or the azide concentration (Refs 9, 12, 17 and 23).†

† Note that in a series of publications, the photodissociation quantum yield was found to sharply increase with an increase in azide concentration (photoinitiated autocatalytic chain decomposition) but these data were not confirmed by other researchers (for details, see Ref. 1).

One of the applications of aromatic azides is photoaffinity modification of biopolymers.[29–31] For this purpose, it is desirable to use 'soft' long-wavelength UV ($\lambda > 300$ nm) or visible light, which penetrates into the cells of living organisms but does not cause photodestruction of the biological material, *i.e.*, proteins and polynucleotides.[32–34] However, most of the known azides absorb in the UV range, which restricts their use.

The spectral sensitivity range of azides can be extended by using sensitisers or by shifting their absorption spectrum to the visible range. To this end, azido dyes, *i.e.*, azido derivatives of dyes of various classes, were synthesised.[30,35–43] These azides include compounds **12**–**15** (shown without counter-ions). It was found that despite the presence of absorption bands in the visible region, most of azido dyes are insensitive to the visible light, *i.e.*, they have very low (about 10^{-5}–10^{-2}) quantum yields of photodissociation (see Table 1).



Analysis of the data presented in Table 1 shows the presence of a qualitative correlation between the φ and λ values: as the azide absorption spectrum shifts to the visible region and the wavelength of the incident light increases, the quantum yield of photodissociation of the azido group sharply drops.

This correlation is illustrated in Fig. 1. It is of interest that the experimental points fill the 'upper left' and 'lower right' areas, whereas the whole visible region with high φ values

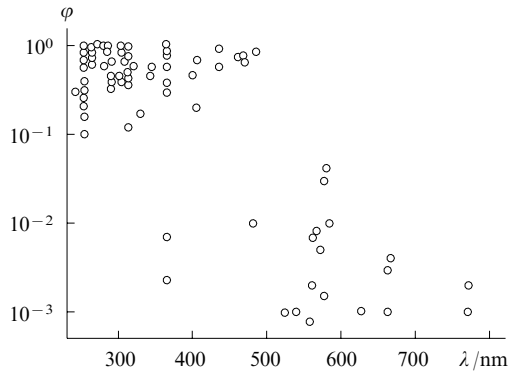


Figure 1. Correlation between the quantum yield of photodissociation of aromatic azides and excitation wavelength.
If several absorption bands are present, data for the long-wavelength band are given. In the UV region, the points arranged vertically one above another correspond to azide photolysis with light from a mercury lamp (254, 313, 365 nm lines). Therefore, some of the points at these wavelengths coincide, in particular, those for φ values of 0.6–0.9.

('upper right') contains not a single point! This is even more surprising because, judging by the dissociation energy of a rather labile $N-N_2$ bond equal to 30–35 kcal mol^{-1} (Refs 44–47), the energy of a light quantum with a wavelength of up to 800 nm should suffice for destruction of the azido group (provided that this energy is concentrated on the dissociating bond). However, the experimentally recorded maximum wavelength at which the azide is still photolysed in a noticeable quantum yield ($\varphi > 0.1$) is 485 nm for 4-(4-azidostyryl)-1-methylquinolinium iodide ($\varphi = 0.84$).[42]

In terms of light sensitivity, aromatic azides can be split into two groups: most of azides (currently 81 azides) belong to the group of photoactive compounds; the quantum yields of their dissociation induced by irradiation at the long-wavelength absorption band (LWAB) are $0.1 < \varphi < 1$ (most often > 0.5), while a smaller number (24 azides) are photoinert compounds for which $\varphi \leqslant 0.01$ upon irradiation at the LWAB. The known photoactive azides are sensitive only to UV and short-wavelength visible light.

Note also that the experimental points in Fig. 1 are distributed rather evenly in the region of both photoactive and photoinert azides. Between these regions, there is some 'forbidden gap' containing no experimental points. The dissociation quantum yields of azides change jumpwise on going from the short- to the long-wavelength range bypassing the 'forbidden gap'.

According to quantum chemical calculations, the correlations between the spectral and photochemical properties of aromatic azides are due to the fact that the absorption spectra and the photochemical activities of these compounds depend on the same factors: the structure and energies of frontier molecular orbitals (see Section IV).

It should be emphasised that the observed $\varphi - \lambda$ correlation is typical of irradiation of azides particularly at the LWAB because this is accompanied by population of the lower excited singlet state S_1. The quantum yield of azide photodissociation may sharply increase on going from excitation at the LWAB to excitation at short-wavelength absorption bands. In the latter case, higher electronically excited states S_n and T_n ($n > 1$) are populated.

The dependence of the quantum yield of photodissociation on the exciting light wavelength over the whole spectral range was studied most fully for azido dye **15**, *p*-azido-Malachite Green.[48] The absorption spectrum of this azide and the elucidated dependence of φ on λ are shown in Fig. 2. The plot of φ *vs.* λ is stepwise: at room temperature, $\varphi < 10^{-3}$ in the range of 450–600 nm (excitation to the S_1 state), $\varphi = 10^{-2}$ in the range of 350–450 nm, and $\varphi = 0.1$ for $\lambda < 350$ nm (excitation to S_n states, $n > 1$). As temperature decreased from room temperature to 77 K, the quantum yield increased in all spectral ranges but that for irradiation at the LWAB remained $< 10^{-2}$.

Studies of two dozens of azido and diazido triphenylmethane and carbocyanine dyes have shown[35] that for these compounds the dependence of the quantum yield on the exciting light wavelength is also stepwise. The quantum yields are in the range of 10^{-5}–10^{-2} for irradiation with long-wavelength light (500–600 nm) but they increase to 0.1 (and more) on irradiation with UV light. On the basis of these trends, the following conclusions were drawn: photodissociation of the azido group occurs in the excited singlet state; most likely, the mechanism of this reaction includes predissociation caused by the intersection of the attraction term of the

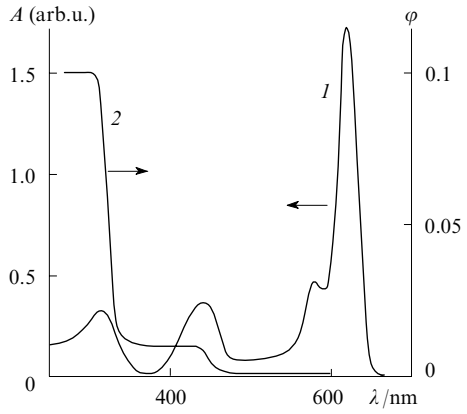
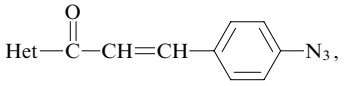


Figure 2. Absorption spectrum of azide **15** (curve *1*) and quantum yield of its photodissociation *vs.* excitation wavelength (curve *2*).[48]
A is absorbance.

electronically excited state corresponding to energy distribution throughout the whole molecule with the repulsion term of the $N-N_2$ bond, which enables energy transition from one term to the other. The increase in the dissociation quantum yield requires that the azido group be conjugated as fully as possible with the fragment responsible for long-wavelength absorption.[49]

The photodissociation mechanism of azides is considered in detail in the next Section. Here we will briefly discuss the assumption about the necessity of conjugation of the azido group with the fragment responsible for the long-wavelength absorption. The involvement of the azido group electrons in the transition responsible for the LWAB is manifested experimentally as the shift of the absorption maximum of azide with respect to that of a similar compound without the azido group. This shift is observed, for example, in the spectra of azidocinnamoylarenes, chalcone derivatives



where Het is a heterocyclic (pyridine, quinoline, quinoxaline or thiophene) residue.[18] Thus the introduction of an azido group into 2-cinnamoylquinoline induces a bathochromic shift of the LWAB from 328 to 350 nm (azide **10**). The long-wavelength absorption bands of the azidocinnamoylarenes show maxima at 350–360 nm and photodissociation quantum yields of 0.6–0.9; high φ values are retained for the whole absorption band including that in the visible region.

Thus, the larger the bathochromic shift of the LWAB upon introduction of the azido group into the molecule the higher the probability that the azide thus formed would be photosensitive upon excitation at this band.

Nevertheless, subsequent studies demonstrated that the lack of bathochromic shift does not suggest the photostability of a compound on exposure to long-wavelength light. The position of the LWAB in 9-(4-azidophenyl)acridine (**11**) does not differ from the position of analogous band in the initial 9-phenylacridine but this azide was efficiently photolysed throughout the whole absorption band including the visible region.[37]

In order to perform targeted synthesis of azides with light sensitivity in a specified spectral range, it is necessary to understand the mechanism of photodissociation of the azido group, know the nature of the reactive state and the structural factors that determine the photoactivity of azides.

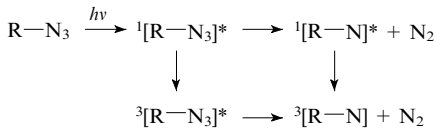
III. Experimental data on the mechanism and kinetics of photodissociation

The mechanism of the photodissociation of aromatic azides has been studied by many researchers. The concepts developed in early studies were discussed in reviews and monographs.[2, 10, 50] However, in the last decade important experimental results concerning the multiplicity of the reactive excited state of the azide and photodissociation kinetics were obtained.

The problem of the multiplet nature of the state of a dissociating excited azide is of particular interest due to the fact that the ground state of the azide is singlet, whereas that of the nitrene is triplet. Therefore, dissociation following direct photoexcitation of the azide may proceed along two pathways:

(i) singlet mechanism: after absorption of a light quantum, the excited singlet azide decomposes to give initially singlet nitrene, which is then converted into triplet one;

(ii) triplet mechanism: the excited singlet azide first undergoes intersystem crossing to the excited triplet state and then decomposes to give nitrene directly in the ground (triplet) state.



Indirect data including the structures of the reaction products, the effect of additives (quenching agents, sensitisers), change in the product ratio upon changes in the photolysis conditions (temperature, solvent) attested that the $N-N_2$ bond cleavage takes place in the excited singlet azide.[51–54] Using special traps, the product of the singlet reaction pathway, *viz*., substituted azepine, was detected and shown to be formed in a step-by-step reaction upon rearrangement of a singlet nitrene rather than in concerted decomposition of the azide and ring expansion reactions.[55] Azides containing special intramolecular traps for singlet and triplet nitrene, *viz*., 2-pyrazolylphenyl azide and its derivatives, were also prepared.[56, 57] After dissociation of the azido group in these compounds, the resulting singlet nitrene attacks the lone pair of nitrogen (electrophilic attack) and the triplet nitrene attacks the methyl group (radical attack).

The singlet mechanism of azide photodissociation was first directly confirmed in 1976 using nanosecond LFP of 1-azidopyrene.[58] The authors recorded the absorption spectrum of a singlet nitrene (a band at 455 nm, lifetime at room temperature in benzene of 22 ns), which was converted into the triplet nitrene (a band at 420 nm) and then (in a second-order reaction) into 1,1′-azopyrene. According to the authors' estimate, the lifetime of the singlet azide did not exceed 7 ns. The nanosecond LFP of this azide was repeated in another study;[59] the band at 455 nm was ascribed to an equilibrium mixture of azirine with singlet 1-pyrenylnitrene. In the same publication, singlet 1-naphthylnitrene was shown to be also in equilibrium with azirine; therefore, the formation time of triplet nitrene was 2.8 μs (in benzene). In the studies of simpler azides, *viz*., phenyl azide and its derivatives,[60] the resolution of nanosecond LFP was insufficient to observe singlet nitrenes. Their rearrangement products, ketene imines, were detected by IR spectroscopy (a typical band at 1890 cm^{-1}); they reacted with azide and diethylamine or were irreversibly converted into triplet nitrene in 4.8 ms. Nanosecond LFP of 4,4′-bisazidobiphenyl demonstrated that the precursor of a triplet nitrene was formed in less than 5 ns and converted into the triplet nitrene within 19 ns.[61]

The spectrum of excited singlet azide with a lifetime of < 6 ps was observed[62] in the picosecond LFP of *p*-dimethylaminophenyl azide; however, the reported assignment of the spectra of intermediates was not quite comprehensive.

The data listed above have long remained the only spectral evidence for the formation of singlet nitrenes. As the resolving power of LFP equipment increased, pico- and femtosecond facilities have started to be used for the photolysis of azides; thus the most short-lived intermediates (excited singlet azides) were detected and the rate constants for their dissociation and for the formation of singlet nitrenes were measured.

The first direct proof of the singlet mechanism of photodissociation of the simplest aromatic azide, phenyl azide, was obtained in 1997 when several research groups reported independently recording of the absorption spectra of singlet nitrenes upon the LFP of phenyl azide and its derivatives.[63–65] Here it is appropriate to mention the experimental difficulties in the studies of unsubstituted phenyl azide associated with formation of a resin, which is deposited on the cell walls even in a flow system and hampers the spectral measurements. Therefore, compounds that either dissolve this resin (dichloromethane) or prevent its formation (formic acid, an acetonitrile–diethylamine mixture) are used in the studies of phenyl azide photodissociation. The lower estimate of the lifetime of the excited azide with the use of dichloromethane is 100 ps,[64] that with acetonitrile is 1 ps, and that with formic acid is 300 fs.[66]

For picosecond LFP of 2,4,6-tribromophenyl azide,[64] the measured rate constant for the formation of the singlet nitrene from the excited azide was 6×10^{10} s^{-1}. The rearrangement of *ortho*-bromo-substituted phenylnitrene to ketene imine is retarded but the intersystem crossing to triplet nitrene is accelerated; therefore, the latter was the final intermediate detected by spectroscopy.

Recording of absorption spectra of singlet nitrenes immediately after the laser pulse was achieved in studies of photodissociation of various methyl-substituted phenyl azides,[67] *para*-substituted phenyl azides,[68, 69] cyano-substituted phenyl azides[70] and fluorinated phenyl azide derivatives.[65, 71–73]

A detailed investigation of singlet phenylnitrene has shown[74] that it is responsible for a narrow absorption band at 350 nm and is involved in two competing processes: ring expansion (rearrangement into ketene imine) with an activation energy of 5.6 kcal mol^{-1} and intersystem crossing to triplet nitrene with a temperature-independent rate constant of 3.2×10^6 s^{-1}. In acidic medium, protonation to give the nitrenium cation takes place in addition to these processes.[66, 75] For some *para*-substituted singlet phenylnitrenes, it was found that the activation energy of ring expansion depends little on the nature of the *para*-substituent, whereas intersystem crossing is accelerated in the case of electron-releasing substituents.[68]

In the nanosecond LFP of *o*-biphenylyl azide,[76] the spectrum of singlet nitrene was immediately observed. When a femtosecond LFP unit was used,[77, 78] the spectrum of the excited singlet azide was also recorded (as a broad band at

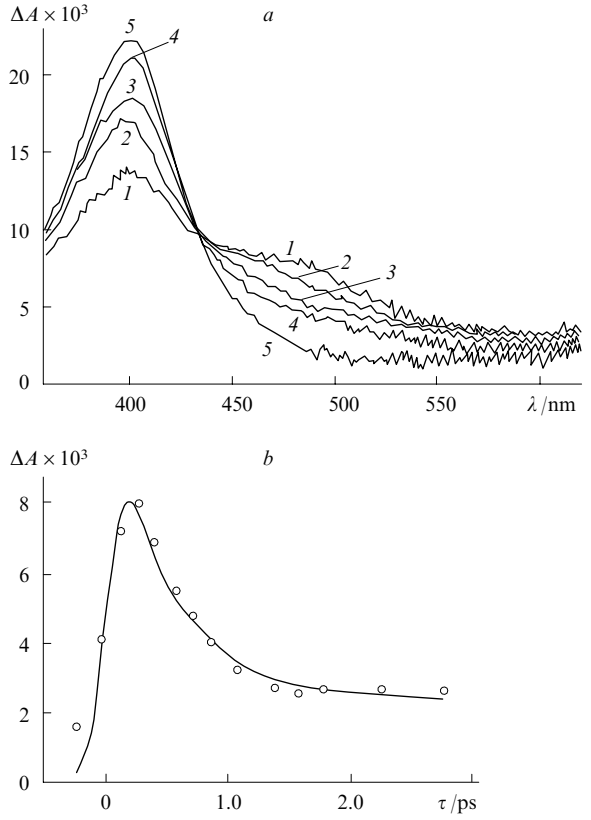
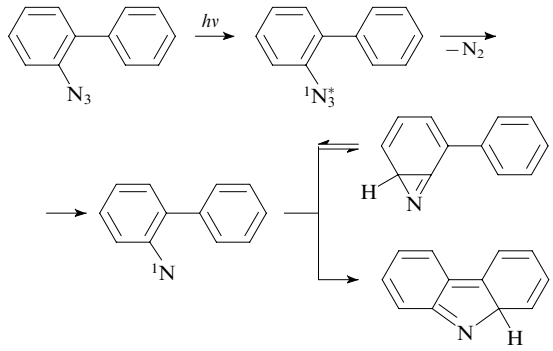


Figure 3. Absorption spectra of *o*-biphenylyl azide in acetonitrile recorded 0.3 – 1.3 ps after the laser pulse (*a*) and kinetics of variation of the absorbance at 480 nm (*b*).[78]
ΔA is absorbance change, τ is time.
(*1*) 0.3 ps, (*2*) 0.4 ps, (*3*) 0.5 ps, (*4*) 0.7 ps, (*5*) 1.3 ps.

450 – 530 nm). The latter species was converted within 450 fs into the singlet nitrene (Fig. 3), which isomerised (16 ps) into benzazirine and isocarbazole.



The absorption band of excited singlet *p*-biphenylyl azide was in the same spectral region as that of the *ortho*-isomer but the transformation time of *p*-biphenylyl azide into the singlet nitrene was 100 fs. The subsequent spectral changes observed during 11 ps were attributed to vibrational relaxation of the excited singlet nitrene.

Apart from the LFP technique, femtosecond IR spectroscopy has also been used to study biphenylyl azides.[79] In the IR spectra, the disappearance of the vibration bands at 2138 cm^{-1} for the azido group was followed by the appearance of ketene imine bands at 1880 cm^{-1} (the intermediate singlet nitrene has no characteristic IR bands). During photolysis of isomeric biphenylyl azides in 88% formic acid, decomposition of azides occurred in less than 1 ps and the resulting singlet nitrenes were then protonated to nitrenium cations.[80]

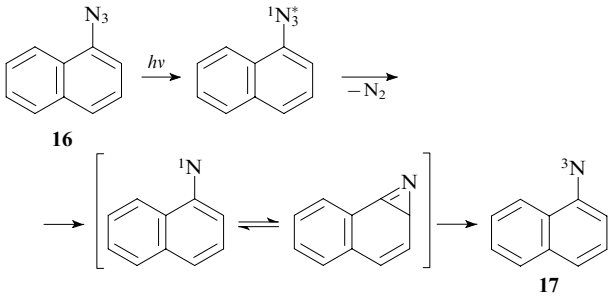
During photolysis of 2-azido-3,5-dichlorobiphenyl, the spectrum of the singlet nitrene was observed 40 ps after the laser pulse.[81] Two chlorine atoms in the molecule of this azide prevent the rearrangement of the arising singlet nitrene into azirine. At room temperature, singlet nitrene was rearranged into isocarbazole (rate constant 3.8×10^9 s^{-1}) and at 77 K, singlet nitrene was converted into triplet nitrene through intersystem crossing (rate constant 1.4×10^7 s^{-1}).

In an LFP study of 2-azidonitrobenzene,[82] the spectrum of the excited azide (a broad band at 400 – 450 nm) and the spectrum of the singlet nitrene were observed successively. Thus, it was shown experimentally that photocyclisation of this azide to benzofuroxan does not take place synchronously with $N-N_2$ bond cleavage but these steps occur consecutively; hence, the singlet nitrene is also a cyclisation intermediate.

The results of studies of substituted phenyl azides prompt the following conclusion: if the benzene ring of the azide bears an *ortho*-substituent (*e.g.*, a nitro or phenyl group) able to interact with the singlet nitrene, the latter undergoes fast intramolecular reactions (in the picosecond time scale); therefore, bimolecular traps for a singlet nitrene are inefficient in these cases.[77,82] An exception is protonation of *o*-biphenylylnitrene in formic acid resulting in the nitrenium cation, which competes with the rearrangement.[80]

The formation of singlet nitrenes was observed in a nanosecond LFP study of heteroaromatic azides, namely, 2-azidopyrimidine,[83] 8-azidoadenosine,[84] 4-azidopyridine *N*-oxide.[85] Photolysis of azidocryptand[86] yields a long-lived singlet nitrene with a lifetime of 1.4 μs. In the presence of sodium and potassium ions, the lifetime of this nitrene decreased to 200 and 160 ns.

It was noted above that the nanosecond LFP of 1-naphthyl azide (**16**) furnishes triplet nitrene **17**; an equilibrium mixture of the singlet nitrene with azirine is formed as the precursor of this product (at room temperature).[59]



At 77 K, a singlet nitrene (formed over a period of < 10 ns) is the only precursor of triplet 1-naphthylnitrene, as at low temperature intersystem crossing prevails over the rearrangement.[87] However, it should be borne in mind that azirine can form photochemically from triplet nitrene.[88]

In the femtosecond LFP of 1-naphthyl azide,[78] the formation of an intermediate absorbing at 460 nm was observed within the spectrometer resolution time (300 fs) (excitation was accomplished by short-wavelength light at 266 nm). On the basis of quantum chemical calculations (see below) this absorption was ascribed to excited S_2 azide. As a result of internal conversion to the S_1 state and $N-N_2$ bond cleavage, the excited azide transformed into singlet nitrene within 730 fs.

A similar sequence of processes was observed in the femtosecond LFP of 2-azidonaphthalene and 2-azido-1-chloronaphthalene.[89] Exposure to light at 266 nm also induced excitation to the S_2 state with the lifetime < 300 fs, *i.e.*, shorter than that of 1-azidonaphthalene. The spectrum of singlet nitrene was observed upon decay of the excited azide. The lifetime of singlet nitrene increased on going from unsubstituted to chloro-substituted naphthylnitrene (the chlorine atom prevents isomerisation).

Thus, the formation of singlet nitrenes in the photolysis of aromatic azides has now been proven by both chemical and spectroscopic methods and the fact that photodissociation follows a singlet mechanism is beyond doubt. The photodissociation of triplet azides to give directly triplet nitrenes is possible only under conditions of sensitised photolysis.

Most often, singlet nitrenes are short-lived intermediates with lifetimes of several nano- or picoseconds. The shortest experimentally detected lifetime (1.8 ps) is that of 2-naphthylnitrene.[89] According to quantum chemical calculations, 4-nitrenoacetophenone[73] and 8-nitrenoadenosine[84] have shorter lifetimes, *viz.*, 1.1 ps and 400 fs, respectively. Intramolecular interactions, if present, stabilise the singlet states of nitrenes and their lifetimes considerably increase, for example, the lifetime of nitrenocryptand is ~ 1.4 μs.[86] The properties of singlet nitrenes are considered in detail in reviews.[6,7] Most often, the spectra of singlet nitrenes are recorded immediately after laser pulse; in some cases, it is possible to measure the nitrene formation rate (from the increase in the absorbance) and only in rare cases, it is possible to detect excited singlet azides as precursors of singlet nitrenes and to study the kinetics of dissociation of the azido group. This is due to the exceptionally short lifetime of excited azides (high rate constant for $N-N_2$ bond cleavage).

The absorption spectra of excited singlet azides and the rate constants for their dissociation are summarised in Table 2. The range of azides studied is still limited to several derivatives of phenyl and naphthyl azides. For some azides, the k_r values were estimated from Eqn (1) and by comparison with the rate constants of competing processes. For example, the value $k_r > 3 \times 10^{10}$ s^{-1} was proposed for the rate constant for dissociation of 4-azidoacetophenone in the S_1 state on the basis of comparison with the rate constant for intersystem crossing of aromatic ketones [k_{isc} in Eqn (1)] and with the assumption that, like ketones, this azide has an $n\pi^*$ type lower excited singlet state.[68]

For most azides, the excited singlet states show absorption bands in the visible region and the k_r values vary in the range of $10^{12}-10^{13}$ s^{-1} (see Table 2). Only one publication[64] does present two orders of magnitude lower k_r values; these might be the lower estimates for the dissociation constant obtained due to the too low resolution of the LFP unit.

The rate constants for the decay of singlet nitrenes measured from the decrease in the absorbance vary over a wider range (about three orders of magnitude) than k_r (see Table 2) and for different azides they refer to different routes of transformation of singlet nitrenes: intersystem crossing, intramolecular rearrangement, bimolecular reactions. Thus, the presented k_d values characterise the 'gross' stability of nitrenes with respect to the fastest reaction possible under the particular experimental conditions.

The available limited range of k_r values does not allow one to identify what structural parameters of the azide influence the rate of its dissociation in the excited state. The absence of a correlation between k_r and k_d implies that the formation and decay of singlet nitrenes are controlled by different parameters.

Taking the pre-exponential factor in the equation for the rate constant for the spin-allowed process to be $\sim 10^{13}$ s^{-1}, we get an estimate for the activation energy of dissociation of the azido group in the excited singlet state (photoactive azides): $E_a < 4$ kcal mol^{-1} (at 293 K). Since the quantum yield of photodissociation remains high at low temperature, the upper limit of the activation energy decreases to $E_a < 1$ kcal mol^{-1} (at 77 K).

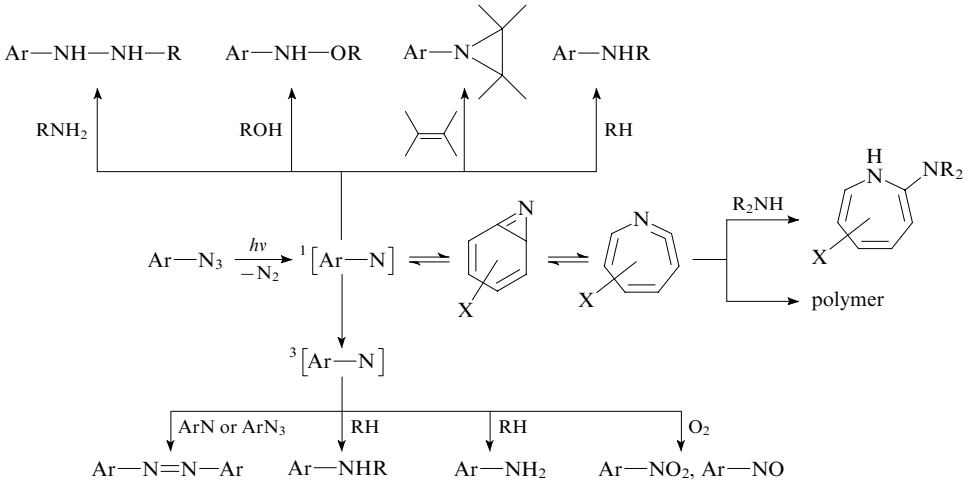
Ab initio quantum chemical calculations give the following E_a values for azide dissociation in the S_1 state: 0.2 kcal mol^{-1} for HN_3 [CASSCF(8,7)/cc-pVDZ method with inclusion of zero-point vibration energy],[90] 7–9 kcal mol^{-1} (upper limit) for 2- and 4-biphenylyl azides, 2 and 5 kcal mol^{-1} for 1- and 2-naphthyl azides, respectively (RI-CC2/TZVP method).[78,89]

When the azide molecule contains other photoactive groups in addition to the azido group, the $N-N_2$ bond cleavage is the predominant process due to the high rate constant for the azido group photodissociation. Indeed, photodissociation of the $N-N_2$ bond prevails over double bond photoisomerisation in azidostyrylquinolines[41] and over photocyclisation of diphenylamine derivatives to carbazole.[43] In azidoiodobenzenes, photodissociation of the labile C–I bond competes with photodissociation of the azido group;[91] however, for perfluorinated derivatives, $N-N_2$ bond cleavage is the primary reaction.[92]

Table 2. Absorption spectra of excited singlet azides, rate constants for dissociation (k_r) of phenyl azide and naphthyl azide derivatives in the excited singlet state and rate constants for the decay (k_d) of singlet nitrenes measured by LFP.

Azide	Solvent	λ/nm	$k_r/10^{10}$ s^{-1}	$k_d/10^9$ s^{-1}	Ref.
PhN_3	CH_2Cl_2	~400	1 ± 0.3	~1.7	64
	88% HCO_2H	~500	> 330	80	66
	MeCN – Et_2NH	–	~100	–	66
4-$Me_2NC_6H_4N_3$	toluene	–	> 17	8	62
2,4,6-$Br_3C_6H_2N_3$	CH_2Cl_2	–	6 ± 0.2	0.94 ± 0.03	64
2-$PhC_6H_4N_3$	MeCN	480	220–360	60	77, 78
	88% HCO_2H	–	> 100	130	80
2,4-Cl_2-6-$PhC_6H_2N_3$	cyclohexane	–	⩾500	3.8 ± 0.8	81
4-$PhC_6H_4N_3$	MeCN	480	~1000	90	77, 78
	88% HCO_2H	–	> 100	87	80
2-$NO_2C_6H_4N_3$	MeCN	–	200 ± 70	120	82
1-Naphthyl azide	MeCN	460	140	80	78
2-Naphthyl azide	MeCN, MeOH	350	> 330	560	89

Scheme 1



Ar = XC_6H_4.

Almost no data on the lifetimes of the excited states of photoinert azides or their deactivation processes are available from the literature. It was been reported that azido dye **15** luminesces at 77 K with a quantum yield of 0.3; its luminescence spectrum is identical to the spectrum of the dye devoid of the azido group and the fluorescence time is 5 ns.[48]

Assuming that the rate constants for photophysical processes (internal conversion and intersystem crossing, fluorescence) for photoinert azides vary within limits normal for aromatic compounds (10^8 to 10^{12} s^{-1}), one can conclude that the sharp decrease in the quantum yields of photodissociation of the azido group on going from photoactive to photoinert azides is related to a sharp decrease in the constant k_r in Eqn (1), *i.e.*, to a sharp increase in the activation barrier to the reaction. For example, the k_r value for azido dye **15** was estimated as 2×10^7 s^{-1} (Ref. 48), which is 5 to 6 orders of magnitude lower than those for photoactive azides. According to quantum chemical calculations, the S_1 states populated upon the excitation of photoactive and photoinert azides at LWAB have different natures. This may account for the inefficiency of photodissociation of the latter compounds (see below).

Thus, photodissociation of aromatic azides upon direct (non-sensitised) excitation occurs from the excited singlet state. The main transformation routes of aromatic nitrenes can be represented as Scheme 1, which also shows the final products of these transformations.[1,2,6,10,93]

The predominance of one or another reaction route depends on the azide structure and experimental conditions: temperature, solvent and the presence of other reagents.

IV. Quantum chemical calculations for the structure of azides and dissociation pathways

Unlike numerous quantum chemical calculations for the energy and the geometric and electronic structures of nitrene molecules, their rearrangement products and transition states that were carried out at a high level,[5,6] caculations for the proper azides were mainly carried out by semiempirical methods. Only for a few simple azides, were *ab initio* and density functional theory (DFT) calculations performed. This is caused by the complexity of optimisation of the excited singlet state; meanwhile, as is clear from the foregoing, it is this state that is responsible for dissociation of the azido group in the direct photolysis of azides.

It would be pertinent to consider briefly the quantum chemical data for the structure of the simplest azide, hydrazoic acid HN_3. Owing to the relatively simple structure, this azide has been studied by diverse experimental methods [94–101] and quantum chemical methods at different levels.[90,98,100,102–105]

According to microwave spectroscopy,[106] the HN_3 molecule in the ground ($X\ ^1A'$) state has C_s symmetry, the $HN-N_2$ bond length is 1.243 Å and the NNN bond angle is 171.3°. The electronic configuration of the ground state is $\ldots(8a')^2(9a')^2(2a'')^2$, two highest occupied MO corresponding to the π-non-bonding electron pair localised on the azido group.[105]

Excitation to the S_1 state ($\tilde{A}\ ^1A''$) is related to transition of an electron from π-MO $2a''$ localised outside the molecular plane to the π-antibonding MO $10a'$ localised in the molecular plane. According to CASSCF(8,7)/cc-pVDZ calculations,[90] this is accompanied by a considerable change in the molecular geometry: the $HN-N_2$ bond is elongated to 1.465 Å and the NNN angle decreases to 118.3°.

The barrier to dissociation of the $N-N_2$ bond in the S_1 state calculated by the same method was 1.1 kcal mol^{-1}; with inclusion of the zero-point vibration energy this barrier decreased to 0.2 kcal mol^{-1}, which is consistent with experimental data about the absence of marked energy obstacles to the $N-N_2$ bond cleavage.[96] According to a publication,[97] excitation of the HN_3 molecule at LWAB results in its direct dissociation.

The first quantum chemical calculations of aromatic azides carried out in the π-electron Hückel approximation showed a decrease in the $N-N_2$ bond order [9] and a decrease in the bond energy [107] in the excited state.

The PES along the reaction coordinate of $N-N_2$ bond dissociation in the lower excited singlet (S_1) and excited triplet (T_1) states were calculated by the AM1 method for phenyl azide; the potential barrier to the reaction was 42.2 kcal mol^{-1} in the former case and 13.7 kcal mol^{-1} in the latter case.[108] This provided the conclusion that the azide excitation into the S_1 state is followed first by intersystem crossing to the T_1 state and only then by azido group dissociation. However, this conclusion contradicts the available experimental data (see above).

Fuller semiempirical calculations of the PES of phenyl azide with allowance for not only the distance between the nitrogen atoms, but also the dihedral angles have shown [109] that out-of-plane bending of the azido group considerably

(by 23 kcal mol^{-1}) decreases the energy of the T_1 state whereas the ground state energy increases only slightly (by 3.5 kcal mol^{-1}). In the authors' opinion,[109] the deviation of the terminal nitrogen atom from the molecular plane results in mixing of the lower excited states $^1n\pi^*$ and $^1\pi\pi^*$, which is the motive force of the dissociation process. The aromatic nucleus acts as an antenna, *i.e.*, absorbs light and then the excitation energy is concentrated on the azido group.

The 'antenna' effect as such is observed in alkyl azides containing an aromatic substituent not involved in π-conjugation with the azido group.[110–112] In this case, light is absorbed only by the aromatic nucleus (intramolecular spectral sensitiser) and then the resonance energy transfer to the azido group takes place followed by azido group dissociation.

Budyka *et al.*[113–116] carried out systematic quantum chemical calculations of a series of both photoactive and photoinert azides of various classes in the ground (S_0) and lower excited (S_1, T_1) states and the azide radical anions (D_1^-, D_2^-) in doublet states. The radical anions formed upon electrochemical reduction of azides[117–119] or upon electron phototransfer[120–126] are unstable and dissociate to give nitrene radical anions.

The PES calculations along the reaction coordinate of the N—N_2 bond dissociation showed that in lower electronically excited states of azides and doublet states of radical anions, the potential barrier to this reaction decreases (Fig. 4).[114,115] The structural parameters of the radical anion D_1^- are correlated with the structural parameters of azides in the excited states S_1 and T_1. In all these states, the activation energy for the azido group dissociation is lower than in the S_0 state.[115] An analogy in the behaviour of azides upon photoexcitation and electron transfer is that in both cases the same vacant MO is populated either due to the electron transfer from lower-lying occupied MO or due to accepting of an external electron.

The attempted TD-B3LYP calculations of the structures of a number of simple aryl azides in the excited state failed due to poor convergence of the results of structure optimisation.[77]

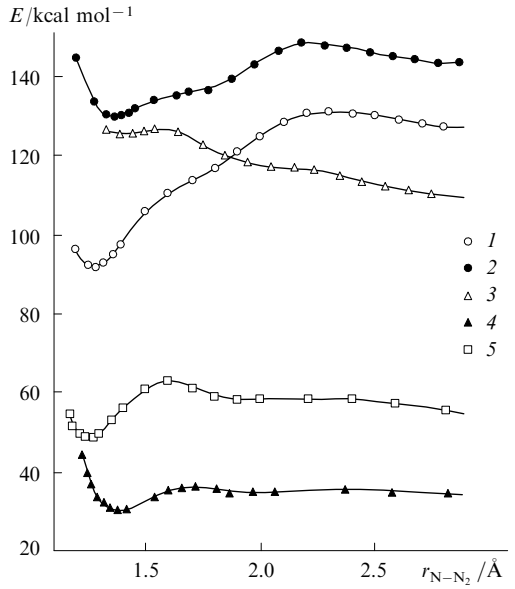


Figure 4. Minimum energy pathways to N—N_2 bond dissociation for 4-nitrophenyl azide **3** in the states S_0 (*1*), S_1 (*2*), T_1 (*3*) and for the radical anion of azide **3** in the states D_1^- (*4*) and D_2^- (*5*).[114,115]
PM3 calculations.

However, *ab initio* RI-CC2/TZVP calculations were successfully carried out.[78,89] The relaxed PES along the dissociation reaction coordinate was also calculated (Fig. 5). The results of these and semiempirical calculations were in qualitative agreement: on passing from the S_0 to S_1 state, the potential barrier to N—N_2 bond dissociation substantially decreases. This prompted the conclusion about the dissociative nature of the S_1 term. The S_2 state, unlike S_1, is stable with respect to dissociation; the structural parameters of azides in this state differ little from those for the ground state.

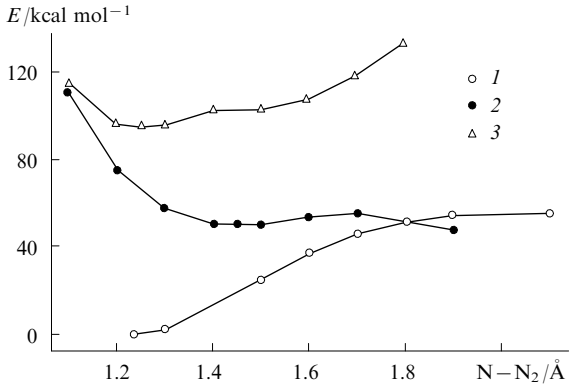


Figure 5. Minimum energy pathways to N—N_2 bond dissociation for 2-naphthyl azide in the states S_0 (*1*), S_1 (*2*) and S_2 (*3*).[89]
RI-CC2/TZVP calculations.

The geometric and electronic parameters of different azides in S_0 and S_1 states are summarised in Table 3. By comparing the calculation results with experimental data on the azide photoactivity, the parameters that determine the quantum yield of photodissociation of the azido group were identified. In the ground state, the azido groups in all aryl azides have similar structures (X-ray diffraction data), namely,[127–129] quasilinear geometry (the NNN bond angle is ~170°), the N—N_2 bond length (1.26–1.30 Å) close to the length of the double bond and a relatively large positive charge on two terminal nitrogen atoms (see Table 3). The azido group is arranged in the plane of the molecule, the rotation barrier around the C—N bond, for example, in azido pyridines being in the range of 3–7 kcal mol^{-1} (MP2/6-31G** calculations).[130]

However, in the S_1 state, the structures of photoactive and photoinert aryl azides are substantially dissimilar (see Table 3). According to PM3 calculations, in photoactive azides **1**–**11**, the N—N_2 bonds are 0.05–0.1 Å longer, the NNN bond angles (130–140°) are smaller, and the charge on the terminal N_2 group (which is abstracted upon dissociation as a neutral nitrogen molecule) is also smaller in the excited state S_1 than in the ground state S_0. The RI-CC2/TZVP calculation[78,89] predicts a somewhat greater difference between the N—N_2 bond lengths (~0.2 Å) and NNN angles (123° in S_1) in the S_1 and S_0 states. Meanwhile, the parameters of photoinert azides **12**–**15** are almost the same in the excited and ground states (PM3 calculations).[116]

The similarity in the structures of different azides in the ground state and the difference in the S_1 state are due to the fact that both photoactive and photoinert azides have the same type of frontier MO in the S_0 state but different types in the S_1 state. For all the studied azides, the frontier MO, *viz.*, the highest occupied (HOMO) and lowest unoccupied (LUMO),

Table 3. Some structural parameters of azides **1**–**15** in the states S_0 and S_1 calculated by PM3 and correlation of photoactivity with filling of σ^*_{NN}-MO in the S_1 state.[113–115]

Azide	r/Å		∠NNN/deg		Z_{N_2}/e		Photoactivity	Filling of σ^*_{NN}-MO
	S_0	S_1	S_0	S_1	S_0	S_1		
1	1.26	1.34	169.6	137.0	0.38	−0.05	photoactive	filled
2	1.26	1.33	169.6	140.2	0.37	−0.07	"	"
3	1.27	1.35	169.2	133.5	0.42	−0.03	"	"
4	1.27	1.34	169.3	135.0	0.40	−0.04	"	"
5	1.27	1.35	169.5	133.4	0.40	−0.03	"	"
6	1.30	1.40	168.4	129.3	0.54	0.08	"	"
7	1.27	1.32	169.7	139.2	0.39	−0.06	"	"
8	1.28	1.38	168.9	127.8	0.47	0.02	"	"
9	1.27	1.35	169.3	137.9	0.41	−0.05	"	"
10	1.27	1.33	169.6	133.3	0.39	−0.05	"	"
11	1.27	1.35	169.5	135.2	0.41	−0.05	"	"
12	1.28	1.36	169.7	168.6	0.45	0.56	photoinert	vacant
13	1.27	1.26	163.3	162.7	0.27	0.22	"	"
14	1.28	1.27	170.2	170.2	0.44	0.47	"	"
15	1.28	1.28	169.4	169.9	0.47	0.43	"	"

Note. The following designations are used: r is the $N-N_2$ bond length, ∠NNN is the bond angle, Z_{N_2} is the Mulliken effective charge on the terminal N_2 group. The calculations were performed for cations without counter-ions.

in the S_0 state are π-type orbitals localised mainly on the aromatic nuclei with minor participation of the atomic p-orbitals of the azido group. This is illustrated in Fig. 6 using 4-azidoacetophenone (**4**) as an example. The orbital localised on the azido group is one of the higher-lying vacant MO. This orbital consists of nitrogen s- and p-orbitals, resides in the molecular plane and is antibonding along the $N-N_2$ bond. In conformity with these features, this orbital should be designated by σ^*_{NN}-MO.[113,114] In azide **4**, the σ^*_{NN} MO is the LUMO + 1 (see Fig. 6). In other studies,[78,89] this MO was identified as the 'in-plane π* azide orbital'.

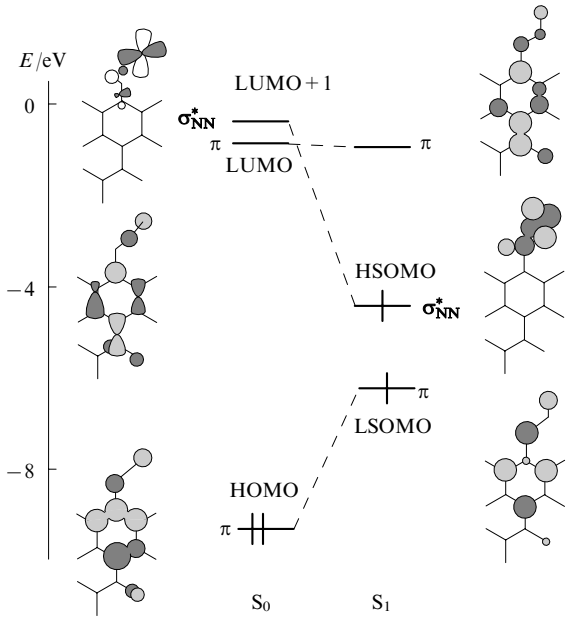


Figure 6. Molecular orbital diagram of 4-azidoacetophenone (PM3 data) in the ground (S_0) and excited (S_1) states.[114]
LSOMO is the lowest singly occupied MO, HSOMO is the highest singly occupied MO.

In photoactive azides, the structure of the frontier MO changes upon excitation to the S_1 state: as a result of relaxation, σ^*_{NN}-MO is occupied instead of the LUMO (see Fig. 6). The decrease in the population of the HOMO, which becomes the lowest singly occupied molecular orbital (LSOMO) in the S_1 state, and filling of the σ^*_{NN} MO, which becomes the highest singly occupied molecular orbital (HSOMO), induce the observed changes in the structural parameters in photoactive azides: electron density transfer from the aromatic nucleus to the azido group, bending of the azido group and elongation of the $N-N_2$ bond. In photoinert azides, the aromatic π-MO is filled in the S_1 state, while σ^*_{NN}-MO remains vacant.[116]

Within the framework of the valence bond method, it can be considered that the atomic orbitals of the central nitrogen atom of the azido group in photoinert azides retain the sp hybridisation (bond angle of ∼180°) upon transition from the S_0 to S_1 state, while in the photoactive azides, the excitation is accompanied by rehybridisation of the atomic orbitals of the central N atom to sp^2 (bond angle of ∼120°).

The data on the ability of aromatic azides to decompose upon irradiation at LWAB with photodissociation quantum yields of $\varphi > 0.1$ and on the population of σ^*_{NN}-MO in the S_1 state are summarised in the two last columns of Table 3. It can be seen that these parameters are directly correlated, *i.e.*, the photoactivity of an azide is related to the population of the σ^*_{NN}-orbital in the excited state. This calculated parameter can be used as a criterion of photoactivity of an aromatic azide: in photoactive azides for which $\varphi > 0.1$, the σ^*_{NN}-MO localised on the azido group, which is antibonding along the $N-N_2$ bond, is occupied in the S_1 state; in photoinert azides with $\varphi < 0.01$, this orbital remains vacant.[115]

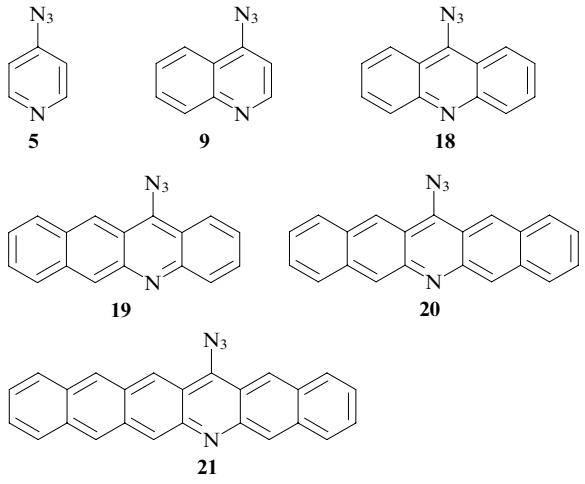
Being guided by this criterion, one can perform a search for a molecular structure of aromatic azide that would ensure specified spectral properties and filling of the σ^*_{NN}-MO in the excited state.

Here it should be emphasised that the considered results refer to the S_1 state. This state is occupied upon excitation of

the molecule with light at LWAB and characterises the long-wavelength light sensitivity of an aromatic azide. On exposure to a shorter-wavelength light, the quantum yield of photodissociation can considerably change [48] because this is accompanied by population of higher excited states (S_n), which differ in structure and properties from S_1 (see, for example, the plot for φ *vs.* λ for azide **15** shown in Fig. 2).

Since a substantial positive charge is concentrated on two terminal nitrogen atoms of the azido group in the ground states of all azides, while dissociation gives rise to a neutral nitrogen molecule, the electron density transfer from the aromatic nucleus to the leaving N_2 molecule should be a necessary stage of the $N-N_2$ bond dissociation. This is actually observed in photoactive azides but not in photoinert ones (see Table 3). Since all photoinert azides are cations, it was suggested that the positive charge of the aromatic nucleus serves as a charge barrier to electron density transfer and thus prevents dissociation.[21] Indeed, on going from neutral compound **11** to positively charged azide **12** with a similar structure, the quantum yield decreases by more than two orders of magnitude. However, azides **5** and **6** also differ only by the nucleus charge but on going from compound **5** to **6**, the quantum yield decreases insignificantly and azide **6** remains photoactive (see Table 1).

It is obvious that the charge effect depends on the dimensions of the aromatic fragment: azides **5** and **11** belong to the same class of azaheteroaromatic azides and differ only in the size of the aromatic nucleus. For detailed investigation of this phenomenon and for elucidating the mutual effect of the size and the charge of the aromatic nucleus on the photochemical activity of the azide, quantum chemical calculations were carried out for catacondensed azaheteroaromatic compounds ranging from pyridine to azahexacene.[131, 132]



The calculations showed that in the ground state, azides **5**, **9**, **18**–**21** have similar structures in neutral and protonated (cationic) forms, namely, quasilinear geometry and a considerable positive charge on the two terminal nitrogen atoms. For azides **5**, **9** and **18**–**20** and protonated azides **5**, **9**, **18** and **19**, parameter changes typical of photoactive azides were observed in the S_1 state, namely, elongation of the $N-N_2$ bond and simultaneous decrease in the order of this bond, bending of the azido group and a decrease in the charge on the terminal N_2 group. The parameters of the azido group in neutral azide **21** and protonated azides **20** and **21** in the S_1 state changed little as compared to the parameters of these azides in the ground state, which is typical of photoinert azides.[132]

Transition from photoactive azides to photoinert ones following an increase in the sizes of the aromatic systems was clearly manifested in the analysis of the structure of orbitals filled in the S_1 state. In neutral azides **5**, **9**, **18**–**20** (azides **5** and **20** in Fig. 7) and protonated azides **5**, **9**, **18**, **19**, the σ^*_{NN}-MO is the highest singly occupied MO. On going to neutral azide **21** (see Fig. 7) and protonated azides **20** and **21**, the type of HSOMO sharply changes; it becomes a π-type orbital localised on aromatic nucleus.

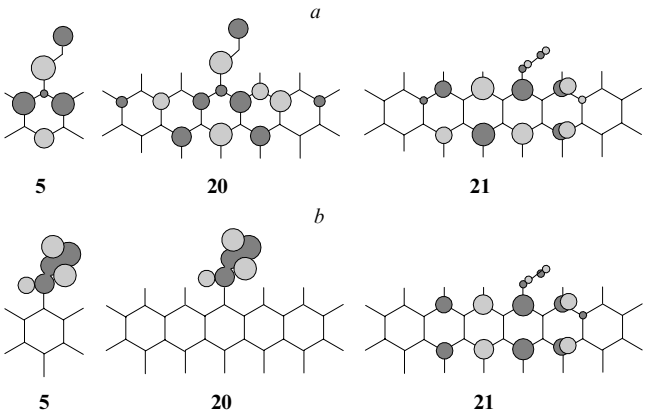


Figure 7. Structures of the lowest (*a*) and highest (*b*) singly occupied MO for azides **5**, **20** and **21** in the S_1 state.[132]

Interesting trends in the variation of the relative positions of HOMO, LUMO and σ^*_{NN}-MO in the ground state are illustrated by Fig. 8 for neutral azides **5**, **9** and **18**–**21**. Both frontier MO are π-type orbitals localised mainly on aromatic nuclei. As the number of annelated benzene rings increases, the HOMO level gradually rises and the LUMO level drops; as a consequence, the HOMO–LUMO energy gap substantially narrows: from 8.98 eV in azide **5** to 5.55 eV in azide **21** (PM3 calculations).[132]

The energy of vacant σ^*_{NN}-MO changes insignificantly, *i.e.*, increases somewhat on going from **9** to **18**. The increase in the level of this MO on going to azide **18** is the result of deviation of the azido group from the plane of the aromatic ring caused by steric crowding created by the *peri*-hydrogen atoms [for

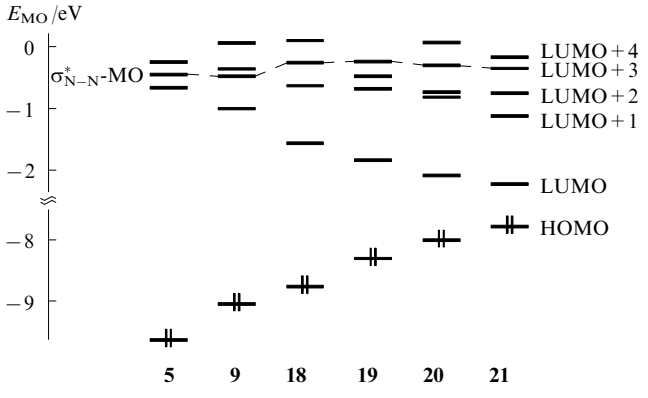


Figure 8. Molecular orbital diagram for neutral azides **5**, **9**, **18**–**21** in the S_0 state.[132]
The position is marked for the σ^*_{NN}-MO, which is the LUMO + 1 in azide **5** and the LUMO + 3 in compound **21**. PM3 data.

9-azidoacridine (**18**), this was shown by X-ray diffraction [133]]. This eliminates conjugation of the azido group with the aromatic system and destabilises σ^*_{NN}-MO.

Since the σ^*_{NN}-MO level is retained and the LUMO level is lowered with an increase in the size of the aromatic system, the energy gap between the σ^*_{NN}-MO and LUMO considerably increases on going from azide **5** to **21** (from 0.21 to 1.87 eV) and the space between these MO is filled by the π-orbitals localised on the aromatic nucleus.

Due to the change in the energy gaps between the MO of neutral and protonated azides **5**, **9**, **18**–**21** in the ground state, σ^*_{NN}-MO is filled in the S_1 state for compounds situated in the beginning of the series (large HOMO–LUMO energy gap, small LUMO–σ^*_{NN}-MO gap) but is no longer filled for compounds situated at the end of the series (small HOMO–LUMO energy gap and large LUMO–σ^*_{NN}-MO gap). The boundary that separates the photoactive (in which the σ^*_{NN}-MO is filled in the S_1 state) and photoinert azides (in which the σ^*_{NN}-MO remains vacant in the S_1 state) is located between compounds **20** and **21** for neutral azides and between **19** and **20** for protonated azides.

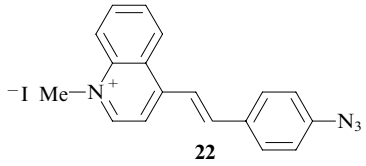
Thus, there is a 'size boundary' for the photoactivity of aromatic azides. The threshold size of the aromatic system above which the σ^*_{NN}-MO is no longer filled in the S_1 state and azide becomes photoinert is 22 and 18 π electrons for neutral (**20**) and protonated (**19**) azides, respectively. A positive charge shifts the threshold size towards a decrease in the number of π electrons.

In the photoinert azides **12**–**15** considered above (see Table 1), the size of the π system is more than 18e, *i.e.*, above the threshold value. Azides **11** and **12** with π system size of 20e represent an interesting example. This is below the threshold value for neutral azides but higher than that for protonated azides. Indeed, neutral azide **11** is photoactive and cation **12** is photoinert (see Table 1). The 'switching off' of the photoactivity on going from neutral to positively charged compound can be attained by protonation; since the degree of protonation depends on the acid concentration, this effect was used to control the azide photoactivity by changing the medium acidity.[38, 39]

Detailed experimental investigation of the dependence of the quantum yield of photodissociation on the charge of the aromatic nuclei of 4-azidopyridine (**5**),[21] 4-azidoquinoline (**9**) [24] and 9-azidoacridine (**18**) (Ref. 25) has shown that these azides retain the photochemical activity on going from the neutral to the protonated form; however, the photodissociation quantum yield for compounds **5** and **9** decreases, remaining however higher than 0.1.

This effect can be attributed to an increase in the activation energy for azide dissociation in the S_1 state on passing from neutral azide **5** to the hydrochloride **5**·HCl (Ref. 21). The increase in the Coulomb barrier results in a decrease in the constant k_r [see Eqn (1)] and, hence, a decrease in φ. On passing from azidoacridine **18** with larger aromatic system to salt **18**·HCl, the quantum yield remains the same as the electron cloud of the aromatic nucleus (14e) shields the positive charge (see Table 1).

The theoretical conclusion stating that for an azide to exhibit a photoactive behaviour in both the neutral and cationic forms the azide π system should not exceed 18e was confirmed experimentally in relation to the azido derivatives of isomeric styrylquinolines.[41, 134, 135] The azidostyrylquinoline π system includes exactly 18 electrons. The absorption bands of these compounds in the neutral form occur in the range of 300–400 nm, while for the protonated form they shift to 400–480 nm. The quantum yield of azido group photodissociation in both forms is 0.7–0.9. A 4-styrylquinoline derivative, azidohemicyanine dye **22**, has the longest-wavelength light sensitivity among all known aromatic azides: on irradiation at 485 nm, the quantum yield of its photodissociation is 0.85.[42]



22

With allowance for correlation between the azide photoactivity and the type of molecular orbital populated in the excited state, it is possible to theoretically substantiate the experimentally observed relationship between the spectral and photochemical properties ‡ of aromatic azides.

Both spectral and photochemical properties of aryl azides are determined by the relative positions of the same frontier MO. The position of the long-wavelength absorption band depends first of all on the HOMO–LUMO energy gap, while the population of σ^*_{NN}-MO depends on the ratio of HOMO–LUMO and LUMO–σ^*_{NN}-MO energy gaps. For a bathochromic shift of LWAB, it is necessary to decrease the HOMO–LUMO gap by increasing the size of the aromatic π system or converting the compound into a positively charged form. However, as a result, the σ^*_{NN}-orbital will inevitably stop to be populated in the S_1 state and the azide will be photoinert.

Hence, it follows that the requirement of long-wavelength light sensitivity of azides is contradictory. On the one hand, to exhibit bands in the visible region, an azide should be a dye, and most of dyes have an extended system of conjugated π bonds and are cations.[136] On the other hand, upon an increase in the size of the π system and positive charging, the azide loses photoactivity and the quantum yield of photodissociation of the azido group sharply decreases to < 0.01.

Note that apart from the size boundary for the photoactivity of aromatic azides related to population of the σ^*_{NN}-MO in the excited state, there is an energetic boundary for photosensitivity. This aspect has been partly addressed above. The energetic boundary is determined by the activation energy of the $N-N_2$ bond dissociation, which is $\sim$35 kcal mol^{-1} for aromatic azides.[137] The energy of light at $>$800 nm is insufficient for the azido group dissociation.

By correlating the photoactivities of azides **5**, **9**, **18**–**21** with their absorption spectra, the long-wavelength limit for light sensitivity of aromatic azides was estimated.[138] The spectra were simulated by PM3-CI and TD-B3LYP methods. Initial compounds of this series in neutral and protonated forms were found to obey an almost linear dependence of the azide LWAB maximum on the number of π electrons in the aromatic system; this was close to the dependence observed experimentally (Fig. 9). Quantum chemical calculations and regression analysis of experimental data have shown that it is possible to obtain photoactive azides (decomposing with quantum yields of $>$0.1) with LWAB being shifted to 580–670 nm, *i.e.*, by 100–200 nm to longer wavelengths with respect to the LWAB

‡ The spectral sensitivity region for most photoactive azides is limited to the UV- and short-wavelength visible ranges; therefore, most of azido dyes exhibiting absorption bands in the visible region are photoinert (see Fig. 1).

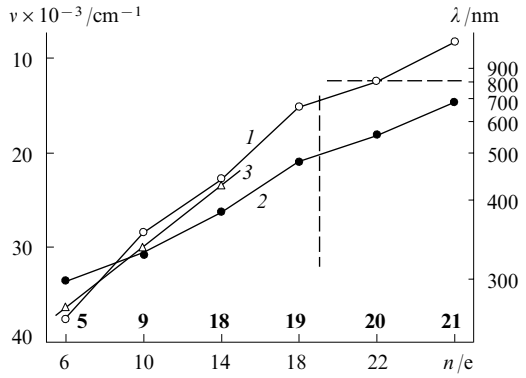


Figure 9. Frequency ν (wavelength λ) of the LWAB maximum of azide *vs.* the number of aromatic π electrons (n) for protonated azides **5**, **9**, **18**–**21**.[138]
(*1*) TD B3LYP/6-31G*//PM3 calculations, (*2*) PM3-CI calculations, (*3*) experimental data (points) and regression line; the vertical dashed line shows the 'size boundary of photoactivity' (azides with smaller π systems are photoactive, those with larger π systems are photoinert); the horizontal dashed line marks the energy boundary of photoactivity (the light energy at higher wavelength does not suffice to cleave the $N-N_2$ bond).

of known azides. As predicted by calculations, azides with longer-wavelength absorption are photoinert ($\varphi < 0.01$).[138]

Thus, studies of the regularities of azide photodissociation have shown that the key factors determining the photochemical activity of aromatic azides include the size and the charge of the conjugated π system. The existence of size and charge effects in the photodissociation of aromatic azides, *i.e.,* dependence of the quantum yield of photodissociation of the azido group on the size and charge of the π system, was substantiated and proved. There exist four regions of photoactivity ratios of the neutral and charged azides (Table 4).

Table 4. Size and charge effects in the photochemistry of aromatic azides.[43]

n	Charge effect	Quantum yield		
		φ_0	φ_+	relation of φ_0 and φ_+
6	weak	> 0.1	> 0.1	$\varphi_0 > \varphi_+$
14	none	> 0.1	> 0.1	$\varphi_0 \approx \varphi_+$
20	strong	> 0.1	< 0.01	$\varphi_0 \gg \varphi_+$
⩾26	none	< 0.01	< 0.01	$\varphi_0 \approx \varphi_+$

Note. n is the number of π electrons in the aromatic system, φ_0 and φ_+ are the quantum yields of azide photodissociation in the neutral and cationic forms, respectively.

1. Azides with small π system size (6e) are photoactive ($\varphi > 0.1$) in both neutral and charged forms; however, the quantum yield of the charged form is somewhat lower. This is a region of a weak charge effect.

2. Azides with medium π system size (~14e) are also photoactive in both forms but the quantum yield of azido group photodissociation does not change in the charged form. This is a region where the charge effect is absent; azides show high quantum yields in both forms ($\varphi > 0.1$).

3. Azides with large π system size (~20e) are photoactive in the neutral form ($\varphi > 0.1$) but lose activity when pass to the charged form ($\varphi < 0.01$). This is a region of pronounced charge effect.

4. Azides with π system size of ⩾26e are photoinert in both neutral and charged forms. This is a region where the charge effect is absent but, unlike the second region, azides show here low quantum yields in both forms ($\varphi < 0.01$).

The results of theoretical and experimental studies of aromatic azides of different structure and photoactivity can be generalised using the views of the orbital nature of electronically excited states. The orbital nature is determined by the type of MO that participate in electron transitions.[139–141] For example, in consideration of styrene *cis*–*trans*-photoisomerisation [142, 143] depending on localisation of the MO populated by the unpaired electron, 'olefinic' and 'aromatic' locally excited states are distinguished, the photoisomerisation quantum yield being dependent on the relative positions of the terms.

The pattern of terms of the ground and locally excited states for photoactive and photoinert azides *vs.* the $N-N_2$ bond length is represented in Fig. 10. In azides, one can distinguish an 'aromatic' locally excited state in which the aromatic π-MO is populated (this corresponds to the $S_{\pi\pi^*}$ term) and an 'azidic' locally excited state in which σ^*_{NN}-MO is populated (this corresponds to the $S_{\pi\sigma^*}$ term). The results of studies suggest the presence of a small (< 1 kcal mol^{-1}) potential barrier (not shown in Fig. 10) for the term $S_{\pi\sigma^*}$ at a 1.6–1.7 Å distance between the nitrogen atoms.

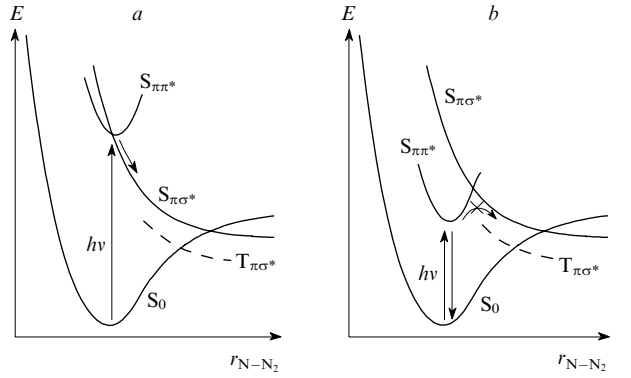


Figure 10. Pattern of terms of the ground (S_0) and locally excited ($S_{\pi\pi^*}$ and $S_{\pi\sigma^*}$) states of photoactive (*a*) and photoinert (*b*) azides *vs.* $N-N_2$ bond length.

To make the picture more comprehensive, Fig. 10 shows also the position of the $T_{\pi\sigma^*}$ term, which is populated in the sensitised photolysis of azides. The ground state of an azide, like that of most molecules, is a singlet state with a closed electron shell. The ground state of nitrene is triplet, and the lower singlet state of nitrene has an open electronic configuration; therefore, these terms intersect. The relative energies of different states of nitrene determine the positions of asymptotes in Fig. 10. For the simplest nitrene HN, the lower singlet state ($a^1\Delta$) and the excited singlet state ($b^1\Sigma^+$) are higher in energy than the ground triplet state ($X^3\Sigma^-$) by 36.0 and 60.7 kcal mol^{-1}, respectively.[7] According to CASSCF(8,7)/cc-pVDZ results,[90] the calculated intersection point of the T_1 and S_0 terms is 40.6 kcal mol^{-1} higher in energy than the ground state minimum of HN_3, which corresponds to the experimental activation energy for thermal

dissociation. According to a publication [144] dealing with the kinetics of thermal dissociation of HN_3, the probability of spin-forbidden singlet–triplet transition is $10^{-3}-10^{-2}$.

In aromatic nitrenes, the energy gaps are considerably narrowed. In PhN, the singlet–triplet splitting between the ground triplet state ($^3A_2$) and the lower singlet state ($^1A_2$) is ~ 18 kcal mol^{-1}, while the excited singlet state ($^1A_1$) is ~ 12 kcal mol^{-1} higher in energy.[6] The RI-CC2/TZVP calculations of the surface potential energy of 1-azidonaphthalene and biphenylyl azides have shown [78] that the terms S_0 and S_1 intersect when the dissociation reaction coordinate (the distance between the nitrogen atoms) is at ~ 1.7 Å. The authors [78] suggest that the intersection of these terms may be a pathway to deactivation of azides from the excited to the ground state.

The position of the $\pi\sigma^*$ terms is determined by the azido group (or nitrene in the asymptote), which has similar structure in all azides depending slightly on the azide structure as a whole. Conversely, the position of the term $S_{\pi\pi^*}$ is dictated by the aromatic π system of the azide. The relative arrangement of the terms S_0, $S_{\pi\pi^*}$ and $S_{\pi\sigma^*}$ determines the spectral and photochemical properties of azides.

The pattern of terms of photoactive azides with small π system size is presented in Fig. 10 *a*. The lower excited singlet (S_1) state has the $S_{\pi\sigma^*}$ nature. Upon irradiation at LWAB, the Franck–Condon transition corresponds mainly to $\pi\pi^*$ excitation;[25, 78, 89, 132] however, the system relaxes rapidly (within hundreds of femtoseconds) to the $S_{\pi\sigma^*}$ state, which is followed by $N-N_2$ bond dissociation at a rate constant of $\sim 10^{12}-10^{13}$ s^{-1}. The quantum yield of the azido group photodissociation is high (0.1–1.0).

As the size of the aromatic π system increases or a positive charge is introduced, the $S_{\pi\pi^*}$ term markedly decreases, and the S_1 state acquires the $\pi\pi^*$ character (this is reflected in Fig. 10 *b*); the azide becomes photoinert. In photoinert azides, excitation at LWAB brings the system to the potential well of the $S_{\pi\pi^*}$ state, which is deactivated through radiative and nonradiative processes. The rate constant for the $N-N_2$ bond dissociation decreases by 5–6 orders of magnitude; as a result, the quantum yield of the azido group photodissociation also sharply decreases (to $\varphi < 0.01$).

Taking into account the pattern of locally excited terms, the above-stated principle of controlling the photoactivity of aromatic azide may be modified: to achieve the specified spectral and photochemical properties, it is necessary to change the position of the $S_{\pi\pi^*}$ term relative to the $S_{\pi\sigma^*}$ term by varying the size and charge of the azide π system.

V. Conclusion

During the last decade, a considerable progress has been attained in the studies of regular features of photodissociation of the azido group in aromatic azides. It was shown that in terms of their photochemical activity, the azides are classified into two groups: photoactive and photoinert azides; the key factors determining the photodissociation quantum yield include the size and charge of the conjugated π system. The existence of relationship between the spectral and photochemical properties of aromatic azides was substantiated, in particular, these properties are determined by the structure and energy characteristics of the frontier molecular orbitals. Experimental data on photodissociation kinetics were obtained and it was shown that the $N-N_2$ bond cleavage in photoactive azides occurs in the subpicosecond time range in the lower excited singlet state.

Data on the dissipation channels of the excitation energy in photoinert azides are almost missing. For these compounds, two-quantum processes of the azido group dissociation are likely to exist, for example, in higher electronically excited singlet or triplet states; this could be used in 3D data recording devices.

A number of unsolved problems in the photochemistry of aromatic azides are noteworthy. Photolysis of simple azides XN_3 (X = H, Cl, Me) occurs along two reaction channels: molecular elimination of N_2 and radical cleavage of the X–N bond,[145–147] the ratio of these channels depending on the irradiating wavelength . For example, in 2-azido-1,3-diphenylpropan-1-one, the quantum yield of the formation of C–N bond cleavage product upon irradiation at 313 nm was 0.05.[148] In the photolysis of HN_3, the quantum yield of H–N bond cleavage increases from 0.04 to 0.2 as the irradiating wavelength decreases from 266 to 248 nm.[149] For aromatic azides, there are only a few mentions of competing C–N bond cleavage.[135, 150]

The problem of relative reactivity of different azide groups in polyazides has not been adequately studied either. Only scarce data on the selective photolysis of polyazidopyridines are available.[151, 152] However, note a progress in the use of polyazide photolysis for production of polynitrenes,[153–164] high-spin model systems for investigation of molecular magnetism and development of organic magnetic materials promising for applications in molecular electronics. Due to the vigorous growth of the number of experimental and theoretical data on this subject, this requires separate consideration.

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