JOC Article

A Perimidine-Derived Non-Kekulé Triplet Diradical[†]

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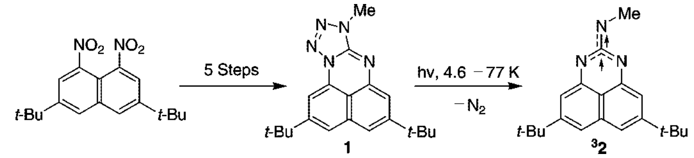

6,9-Di(*tert*-butyl)-1-methyltetrazolo[1,5-*a*]perimidine (**1**) has been synthesized from naphthalene in seven steps. The EPR spectra, recorded after irradiation of **1** in a butyronitrile matrix at 77 K ($\lambda = 351$ nm) and in Ar and Xe matrixes at 4.6 K ($\lambda \geq 345$ nm), showed a six-line, high-field signal ($\Delta m_S = \pm 1$), centered at 3350 G in butyronitrile, along with a half-field signal ($\Delta m_S = \pm 2$), which is characteristic for triplets. Simulation of the observed EPR spectra gave values for the zero-field splitting parameters of $|D/hc|/\mathrm{cm}^{-1} = 0.0105$, $|E/hc|/\mathrm{cm}^{-1} = 0.0014$ in butyronitrile and $|D/hc|/\mathrm{cm}^{-1} = 0.0107$, $|E/hc|/\mathrm{cm}^{-1} = 0.0016$ in Ar. These EPR parameters are consistent with the diradical 5,8-di(*tert*-butyl)-2-(*N*-methylimino)perimidine-1,3-diyl (**³2**) as source of the EPR spectra. Linearity of the Curie−Weiss plot and UB3LYP and (14/14)CASPT2 calculations of the singlet−triplet energy difference ($\Delta E_{ST} \approx 8{-}10$ kcal/mol) indicate that the triplet is the ground state of **2**, as predicted for such a nondisjoint diradical.

Introduction

Since Dowd's observation by EPR spectroscopy of parent trimethylenemethane (TMM),[1] TMMs[2–8] have developed into a very thoroughly studied class of non-Kekulé molecules.[9] Matrix-isolation techniques allowed detection of TMMs by EPR,[1,2] UV−vis absorption[10,11] and emission,[10–12] and IR spectroscopy.[13]

By contrast to TMM *hydrocarbon*s, *aza*TMMs are rare. A diazaTMM (**³11**)[14] and alkyl-substituted triazaTMMs (**³13**)[15] have been observed by EPR spectroscopy. MonoazaTMMs,[16,17] diazaTMMs,[18] and phenyl-substituted triazaTMMs[19] were invoked as intermediates to explain the products of photochemical and thermal denitrogenation reactions. A few computational studies of azaTMMs have been published.[17c,20–22]

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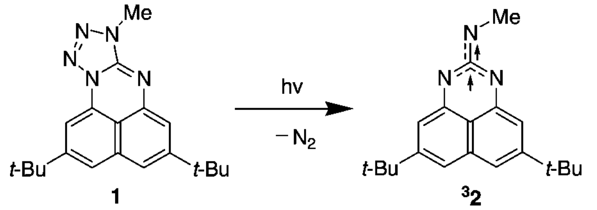
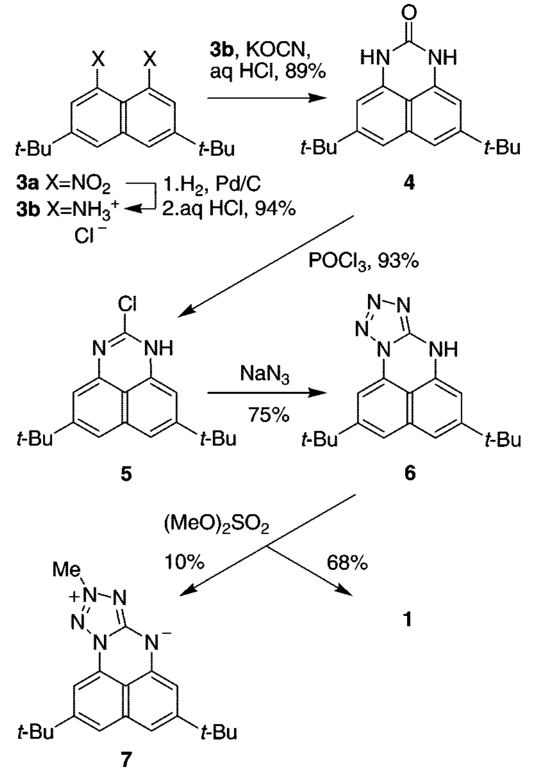
We report here on the novel 1,8-naphthalene-bridged triazaTMM triplet diradical ^{3}**2**, which is a perimidine-derived[23] non-Kekulé molecule. It represents an example of spin coupling of a pair of aminyl radicals by two different ferromagnetic coupling units, viz., the 1,1-connected MeN=C group and the 1,8-connected naphthalene bridge.[6b] Connection of two nitrogens of triazaTMM to the naphthalene bridge at C1 and C8 was expected to retard or prohibit collapse of **2**, yielding a diaziridine ring, just as the ethano bridge increases the persistence of Berson's 2-isopropylidenecyclopentane-1,3-diyl[2c] compared with the parent TMM.[2b] Alternatively, if **2** is viewed as being derived from the diaza analogue of 1,8-naphthoquinodimethane (^{3}**14**),[24] connecting the radical centers to a MeN=C group should inhibit N−N bond formation.



Results and Discussion

Naphtho-annelated iminodihydrotetrazole **1** was synthesized from di(*tert*-butyl)dinitronaphthalene **3a**[25] in five steps (Scheme 1). The first four steps have precedence in the series devoid of *tert*-butyl groups,[26–29] and these reactions are detailed in the Supporting Information. Owing to the ambident character of 1-substituted 5-aminotetrazoles,[30] treatment of **6** with dimethyl sulfate afforded a mixture (87:13) of the yellow, 1,4,5-substituted tetrazole **1** and the deep-red, mesoionic 1,3,5-substituted tetrazole **7**. The difference in polarity between **1** and **7** allowed expeditious separation by flash chromatography. The yellow crystals of **1** are stable at temperatures below 200 °C. Differential thermoanalysis indicated exothermic decomposition at 224 °C. Very slow decomposition of **1** occurred on heating of a solution in benzene-d_6 at 150 °C. Strong fluorescence with maxima at 449, 480, and 510 nm was observed for **1** at 77 K in a matrix made from a mixture of diethyl ether,isopentane, and ethanol (5:5:2).

SCHEME 1. Synthesis of 1



A number of experiments were performed to characterize the product(s) of **1** that resulted from photolysis at room temperature. On irradiation, using various light sources, solutions in acetonitrile or benzene rapidly turned red or red-brown.

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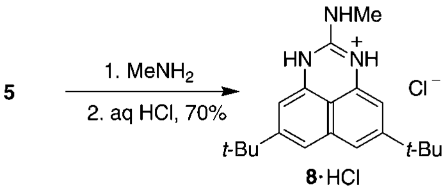
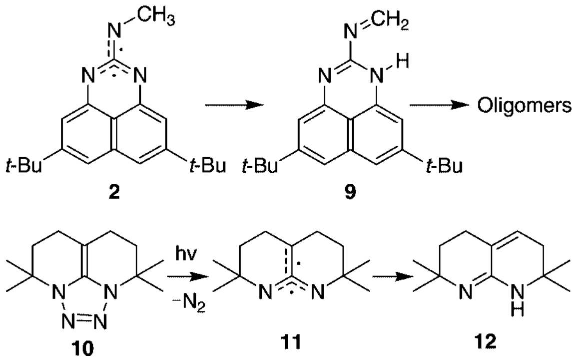
Monitoring this process by UV−vis spectroscopy revealed that the result depended on the initial concentration of **1**. In an 8 × 10^{-5} M acetonitrile solution, the two bands of **1** in the near UV at 375 and 326 nm decayed, but new absorptions appeared only at much shorter wavelengths ($\leq$260 nm), while three isosbestic points at 245, 301, and 435 nm were maintained until high conversion. By contrast, at 30-fold higher concentration, a broadband with barely discernible fine structure emerged in the near-UV. This band persisted on continued irradiation and was evidently superimposed on the tail stretching out from strong bands at shorter wavelengths (see the Supporting Information).

Irradiation of **1** in benzene or saturated hydrocarbons gave a red-brown material, decomposing above 280 °C. Its ^{1}H NMR spectrum displayed only a broad signal of low intensity in the chemical shift range expected for *tert*-butyl groups, suggesting formation of an ill-defined, oligomeric product. This result was supported when the photolysis was monitored by ^{1}H NMR spectroscopy: The sharp signals of **1** disappeared but new signals did not emerge. The same observation was made in the presence of a 10-fold excess of dimethyl fumarate, which was added as diylophilic trapping reagent.[31] Unfortunately, attempts to isolate a pure compound by recrystallization or chromatography met with failure. As we suspected that the product might contain 2-aminoperimidine moieties, we synthesized **8**·HCl from **5** and compared the presumed oligomeric product with the free base **8**.



The IR and UV spectra of **8** resembled those of the isolated product. The UV spectra of **8** and the product showed broad near-UV absorptions that apparently arose from closely related chromophors. In addition, the EI mass spectrum of **8** (m/z of $M^+ = 309$) was almost superimposable on that of the crude photoproduct, except that a small peak with $m/z = 323$ and smaller peaks of even higher m/z indicated sources of larger fragments (see the Supporting Information).

SCHEME 2. Hydrogen Shifts in AzaTMM Diradicals



These results are consistent with formation of an oligomeric product, containing 2-aminoperimidine moieties, when **1** is photolyzed at high concentrations. A rationalization of this hypothesis is possible if diradical **2** is assumed to isomerize by a 1,4-hydrogen shift to afford **9** (Scheme 2). Oligomerization is known to occur for imines that are formed by the reactions of formaldehyde with primary amines that possess primary and secondary alkyl groups.[32] An analogous 1,4-hydrogen shift does occur in diradical **11**, as indicated by the formation of **12** on irradiation of **10** at −60 °C or on heating at 90 °C.[14]

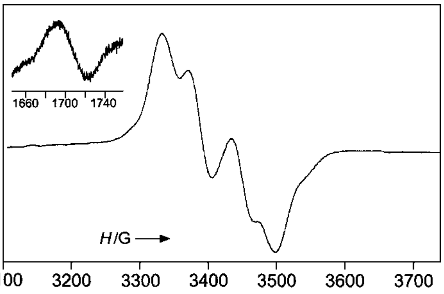
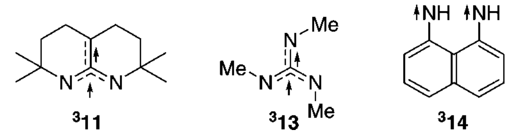


FIGURE 1. First derivative of the $\Delta m_S = \pm 1$ EPR absorption of ^{3}**2** in an Ar matrix at 4.6 K; the inset shows the expanded signal of the half-field transition ($\Delta m_S = 2$).

TABLE 1. Zero-Field Splitting Parameters $|D/hc|$/cm^{-1} and $|E/hc|$/cm^{-1} for Some Non-Kekulé Triplet Diradicals



triplet	$\lvert D/hc\rvert$/cm^{-1}	$\lvert E/hc\rvert$/cm^{-1}
^{3}**2** (Ar)	0.0107	0.0016
^{3}**2** (butyronitrile)	0.0105	0.0014
^{3}**11**[a]	0.031	0.0014
^{3}**13**[b]	0.033 ± 0.001	≈0
^{3}**14**[c]	0.0257	<0.0004

[a] Reference 14. [b] Reference 15. [c] Reference 24.

The EPR-active photoproduct that resulted from irradiation of **1** in an Ar matrix at 4.6 K with $\lambda \geq 345$ nm of a high-pressure mercury lamp (Figure 1) gave a six-line EPR spectrum, as expected for triplet diradicals that are devoid of 3-fold or higher rotational symmetry. The observed EPR spectrum could be simulated with the zero-field splitting (zfs) parameters that are listed in Table 1. Nearly the same EPR spectrum was observed in a butyronitrile matrix at 77 K (see the Supporting Information), but simulation of this spectrum required zfs parameters that differed slightly from those used to simulate the spectrum obtained in the Ar matrix. The intensity of both spectra increased on continued irradiation. In the butyronitrile matrix, the triplet signals persisted for several hours at 77 K but decayed on warming the matrix to 97 K. The central signal, attributed to a doublet radical, was observable at temperatures as high as 150 K. We assign structure ^{3}**2** as the source of the triplet signal in Figure 1 on the basis of (a) the structure of precursor **1**, (b) the product formed from photolysis of **1** at room temperature, and (c) the size of the zfs parameters.

The zfs parameters, measured for ^{3}**2**, ^{3}**11**, ^{3}**13**, and ^{3}**14**, are given in Table 1. The zfs parameter $|D/hc|$ is proportional to the average distance, r, between the unpaired electrons ($|D/hc|$

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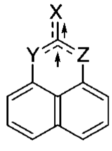
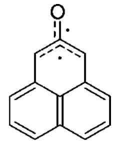
$\sim r^{-3}$ in the dipole approximation).[33] In Table 1, the value of $|D/hc|$ is smallest for ^{3}**2** and largest for azaTMMs ^{3}**11** and ^{3}**13**. Formal exchange of two methyl groups of triazaTMM ^{3}**13** for the 1,8-naphthalene bridge in ^{3}**2** is expected to increase the average distance between the unpaired electrons. Likewise, spanning the nitrogen atoms of ^{3}**14** with a ferromagnetic coupling unit, such as the 1,1-connected MeN=C group in ^{3}**2**, should increase the delocalization of the unpaired electrons and hence the distance between them. In fact, according to its value of $|D/hc|$, ^{3}**2** is the most strongly delocalized TMM type triplet diradical.[2i] The $|E/hc|$ parameter is a measure of the deviation of a triplet diradical from 3-fold or higher rotational symmetry. $|E/hc|$ for ^{3}**2** is about the same size as $|E/hc|$ for diazaTMM ^{3}**11**.

Previous attempts to prepare **16**, at that time considered as potential persistent Favorskii zwitterion, have met with failure.[34] Therefore, ^{3}**2** is the first example of a novel class of non-Kekulé triplet diradicals with the general structure ^{3}**15**.



^{3}**15**



16

Diradical **2** is a nondisjoint diradical, so a triplet ground-state is predicted for it.[35] We have confirmed this qualitative prediction by both experiments and calculations.

Linearity of a Curie–Weiss Law plot (i. e., the intensity I of a triplet EPR signal as a function of the reciprocal absolute temperature) is a necessary but not sufficient condition for concluding that a molecule has a triplet ground-state and that there is a substantial free energy difference between the triplet and the lowest singlet state ($\Delta G_{ST} = G_S - G_T \gg 0$). The Curie–Weiss Law, modified for a Boltzmann distribution between singlet and triplet, eq 1,[36] gives *two* limiting cases where a plot of I versus $1/T$ becomes linear. The most common is $\Delta G_{ST} \gg RT$ (triplet ground-state with a substantial singlet–triplet energy gap). However, if $|\Delta G_{ST}| \ll RT$ (i.e., there is a near degeneracy of the lowest singlet and triplet states), a plot of I versus $1/T$ will also be linear.

$$I = \frac{\text{const}}{T[3 + (\exp\ -\Delta G_{ST}/RT)]}$$

We obtained a linear Curie–Weiss Law plot for ^{3}**2** in the temperature range 4.6–22.9 K (Figure 2). However, the EPR spectra had to be recorded using a low microwave power, whose value (0.20 mW) was chosen to be in a range where the dependence of the signal intensity from the square root of the microwave power was linear. Otherwise, the low-temperature section of the Curie–Weiss Law plot became convex, due to signal saturation associated with slow restoration of the Boltzmann spin distribution.[37] Variation of the intensity with temperature was perfectly reversible between 4.6 and 24 K. However, at 29 K, the intensity slowly decreased, most probably due to the onset of softening of the Ar matrix.

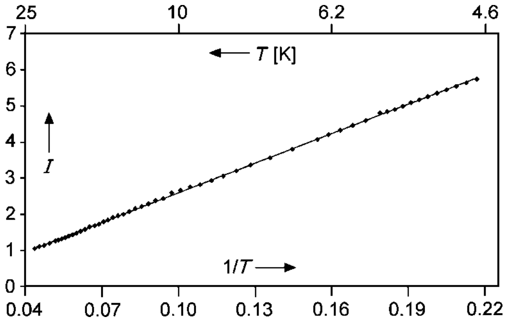
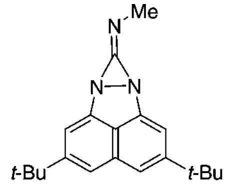


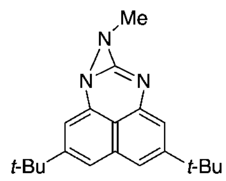
FIGURE 2. Curie–Weiss Law plot; intensity (I, arbitrary units) of the $\Delta m_S = \pm 1$ signal in the EPR spectrum of ^{3}**2** in an Ar matrix as a function of the reciprocal absolute temperature between 4.6 and 22.9.

We calculated the singlet–triplet energy difference $\Delta E_{ST} = E(^{1}\mathbf{2}) - E(^{3}\mathbf{2})$ at both the UB3LYP[38] and (14/14)CASPT2[39] levels of theory, using the 6-31G* basis set.[40] UB3LYP gave a value of $\Delta E_{ST} = 10.4$ kcal/mol, after correcting the "singlet" UB3LYP energy for spin-contamination.[41] (14/14)CASPT2 yielded $\Delta E_{ST} = 8.4$ kcal/mol at the UB3LYP/6-31G* optimized "singlet" and triplet geometries. Reoptimization the geometries at the (14/14)CASSCF/6-31G* level gave $\Delta E_{ST} = 8.5$ kcal/mol. The UB3LYP/6-31G* zero-point energy correction is only −0.27 kcal/mol. Thus, our calculations find ^{3}**2** to be the ground-state by 8–10 kcal/mol.

To probe the presence of conceivable EPR-silent photoproducts, i.e., **9** and the highly strained iminodiaziridines **17** and **18**, we recorded IR and UV–vis spectra (Figure 3) of the photolysate formed from irradiation of **1** in Ar and Xe matrixes. The IR spectra were nearly identical in both matrixes, except for some broadening of the peaks in the latter—a feature common to Xe matrixes—and different relative intensities of certain bands (see the Supporting Information). Only a single new IR band between 1500 and 1655 cm^{-1} appeared on photolysis. Its wavenumber was lower (1573.6 cm^{-1}) than those of the four bands between 1600 and 1655 cm^{-1} observed for **1**. This band was missing when the Ar matrix contained 3% oxygen; hence, it may tentatively be ascribed to ^{3}**2**. Slow warming of the Xe matrix began to cause noticeable changes above 70 K. Annealing of the matrix for 30 min at 75 K resulted in a decrease of all absorptions, indicating softening of the matrix. However, certain uncharacteristic low-frequency bands decreased faster than the average. Most importantly, the absence of bands between 1655 and 2000 cm^{-1} proved that neither **9** nor **17** or **18** appeared, for which C=N absorptions with wavenumbers around 1670[42] and 1800 cm^{-1},[43] respectively, are expected.



17



18

On irradiation of **1** in an Ar matrix, a new band was observed in the near UV. This band showed vibrational structure, with the 0→0 transition at 344 nm as the most intense maximum. The UV–vis spectrum of an irradiated Xe matrix appeared similar; but the vibrational structure was less well resolved, and

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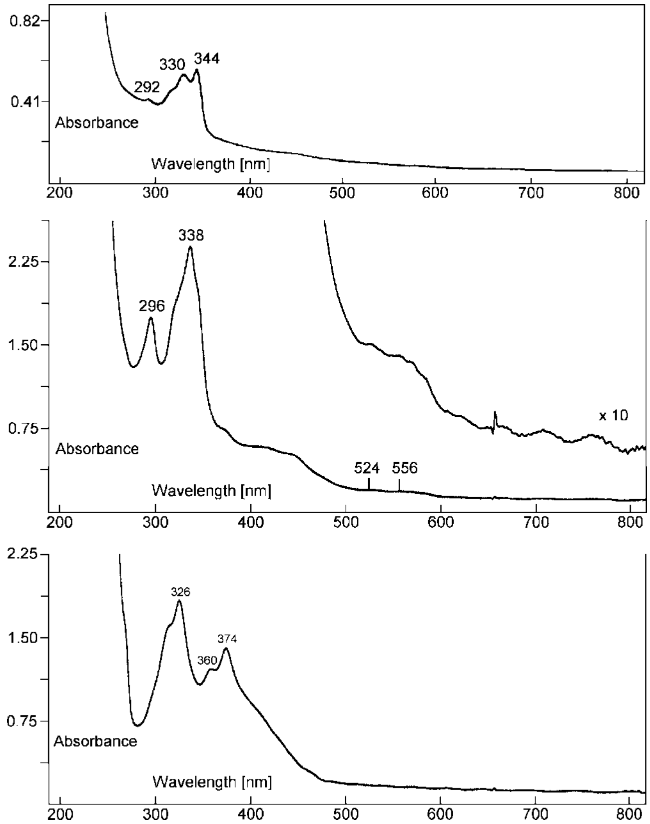

FIGURE 3. UV−vis spectrum of **1** in a Xe matrix at 12 K, recorded before (bottom spectrum) and after (middle spectrum) irradiation of **1** with a high-pressure mercury lamp. The UV−vis spectrum, recorded after irradiation ($\lambda \geq 345$ nm) of **1** in an Ar matrix at 10 K, is shown in the top spectrum.

the 0→0 transition appeared to be no longer the most intense band (Figure 3). In addition, the absorption at ca. 450 nm was more pronounced than in the spectrum of the irradiated Ar matrix, and a very weak shoulder around 550 nm showed up at 10-fold gain. The spectrum of the Xe matrix remained unchanged when the temperature was slowly raised to 50 K. At higher temperatures, the optical quality of the matrix deteriorated, thus precluding obtaining additional UV−vis spectra.

We attribute the UV−vis spectra to ^{3}**2**, because it is the ground state; and, according to the IR spectra, other photoproducts such as **9**, **17**, and **18** are missing. The assignment is supported by the resemblance between the UV−vis spectrum that we attribute to ^{3}**2** and the spectra of the triplet diradicals 2-(diphenylmethylene)cyclopentane-1,3-diyl,[10,11] 2,2-dimethyl-1,3-perinaphthadiyl,[37e] and 1,4-perinaphthadiyl.[37a,44]

Conclusion

Irradiation of the 1,8-naphthalene-bridged iminodihydrotetrazole **1** at 4.6−77 K affords strong triplet EPR signals that are ascribed to the novel, perimidine-derived, non-Kekulé, triplet diradical ^{3}**2**. UV−vis spectra, recorded after irradiation of Ar and Xe matrixes containing **1**, are attributed to ^{3}**2**. Matrix IR spectra are not consistent with the presence of hydrogen-shift isomer **9** or of iminodiaziridines **17** and **18**. The observed linearity of the Curie−Weiss plot and the (14/14)CASPT2/6-31G* value of $\Delta E_{ST} = 8.5$ kcal/mol leave no room for doubts that the triplet state of **2** is the ground state, as expected for a nondisjoint diradical.

Diradical ^{3}**2** is the first example of the general, non-Kekulé, type of diradical **15**. Diradicals of this type are promising targets for further syntheses and studies. Precursors of these diradicals may become available through Feldman's intramolecular [3 + 2] cycloaddition strategy.[17]

Experimental Section

Light sources: (a) focused 500 W high-pressure mercury lamp (Osram HBO 500 W/2) equipped with 10 cm water filter and 345 or 375 nm cutoff filter (Schott, Mainz, Germany); (b) focused 500 W high-pressure mercury lamp (Oriel) equipped with 10 cm water filter, 345 nm cutoff filter, and heat absorbing KG1 filter (Schott, Mainz, Germany); (c) 351 nm line of an Ar ion laser (Coherent Innova 100). EPR spectra at 77 K were recorded on a Bruker ESP 300 X-band spectrometer, EPR spectra at 4.6−22.9 K on a Bruker X-band Elexsys E500 ESR spectrometer.

6,9-Di(*tert*-butyl)-1-methyltetrazolo[1,5-*a*]perimidine (1) and 6,9-Di(*tert*-butyl)-2-methyltetrazolo[1,5-*a*]perimidine (7). A stirred mixture of **6** (1.61 g, 5.0 mmol) and dimethyl sulfate (4.06 g, 32 mmol) was heated at 80 °C for 5 h followed by distillation of the excess of dimethyl sulfate at 0.1 Torr. The brown, solid residue was dissolved in CH_2Cl_2 and separated by flash chromatography with CH_2Cl_2 on a 60 × 4.5-cm column packed with Al_2O_3 (activity II−III, 50−200 μm, 1.7 bar N_2). The first, yellow, fraction afforded a yellow powder (**1**, 1.14 g, 68%, melting range 210−230 °C, dec). Recrystallization from butanol gave bright yellow needles (0.5 g, mp 224 °C, dec, differential thermoanalysis). MS (EI, 70 eV): m/z (rel intens) = 335 (100) [M^+], 320 (3), 307 (89) [$(M - N_2)^+$], 292 (52), 277 (5), 265 (17), 251 (18), 236 (34). IR (KBr): 1650 cm^{-1} (m), 1627 (w), 1604 (s); (Xe matrix, 12 K) (rel intens) 1653.2 cm^{-1} (69), 1632.4 (35), 1606.9 (100). UV (acetonitrile): λ_{max} [nm] (log ϵ) 240 (4.345), 326 (3.852), 375 (3.754). ^{1}H NMR (250 MHz, C_6D_6): δ 1.30 (s, 9 H), 1.37 (s, 9 H), 2.88 (s, 3 H), 7.22 (d, J = 1.6 Hz, 1 H), 7.29 (d, J = 1.6 Hz, 1 H), 7.34 (d, J = 1.6 Hz, 1 H), 7.37 (d, J = 1.6 Hz, 1 H). ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.35 (s, 9 H), 1.38 (s, 9 H), 3.84 (s, 3 H), 6.96 (d, J = 1.6 Hz, 1 H), 7.12 (d, J = 1.6 Hz, 1 H), 7.21 (d, J = 1.6 Hz, 1 H), 7.33 (d, J = 1.6 Hz, 1 H). ^{13}C NMR (63 MHz, $CDCl_3$): δ 31.05 (3 CH_3), 31.19 (3 CH_3), 32.1 (CH_3), 35.03 (quat C), 35.12 (quat C), 100.9, 112.6, 114.2, 119.1 (CH), 115.5, 131.2, 135.6, 143.5, 144.8, 150.2, 153.0 (quat C). Anal. Calcd for $C_{20}H_{25}N_5$: C, 71.61; H, 7.51; N, 20.88. Found: C, 71.40; H, 7.55; N, 20.76.

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The second fraction yielded a red powder (**7**) (0.17 g, 10%, mp 225−230 °C). Recrystallization from acetonitrile afforded deep red needles (0.10 g, mp 231 °C). MS (EI, 70 eV): *m*/*z* (rel intens) = 336 (24) [(M + 1)$^+$], 335 (100) [M$^+$], 320 (18), 310 (5), 305 (6), 304 (6), 296 (10), 293 (25), 279 (9), 263 (8). IR (KBr): 1632 cm^{-1} (m), 1590 (s). UV (acetonitrile): λ_{max} [nm] (log ϵ) 234 (4.557), 277 (3.918), 340 (3.914), 364 (3.815), 382 (3.841), 484 (3.125). ^{1}H NMR (250 MHz, CDCl$_3$): δ 1.34 (s, 9 H), 1.35 (s, 9 H), 4.29 (s, 3 H), 6.92 (d, *J* = 1.6 Hz, 1 H), 6.94 (d, *J* = 1.6 Hz, 1 H), 7.06 (d, *J* = 1.6 Hz, 1 H), 7.32 (d, *J* = 1.6 Hz, 1 H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 31.0 (3 CH$_3$), 31.3 (3 CH$_3$), 35.0 (2 quat C), 42.5 (CH$_3$), 100.6, 112.08, 112.24, 120.0 (CH), 116.5, 130.8, 135.8, 145.0, 149.8, 153.4, 157.1 (quat C). Anal. Calcd for $C_{20}H_{25}N_5$: C, 71.61; H, 7.51; N, 20.88. Found: C, 71.87; H, 7.81; N, 20.72.

5,8-Di(*tert*-butyl)-2-(*N*-methylamino)perimidine Hydrochloride (8·HCl). Dry methylamine (ca. 20 mL, 0.9 mol) was condensed on **5** (4.60 g, 13 mmol) contained in a thick-walled 40 × 2 cm glass tube equipped with a magnetic stirring bar. The glass tube was cooled with liquid N$_2$, evacuated to 0.1 Torr, and sealed with a torch. The green mixture was stirred at 60 °C for 6 d, when it turned yellow. The excess of methylamine was allowed to evaporate. Addition of aq HCl (2 M, 10 mL) to the residue gave a white precipitate. It was taken up in aq HCl (2 M, 50 mL) and CH$_2$Cl$_2$ (50 mL). The mixture was extracted with aq HCl (2 M) and water and dried with Mg$_2$SO$_4$. Distillation of the solvent under vacuum yielded colorless crystals (3.1 g, 70%, dec range 280−293 °C). Recrystallization from acetone afforded a colorless powder (2.67 g, mp 295−297 °C, dec). MS (EI, 70 eV): *m*/*z* (rel intens) = 309 (100) [M$^+$ of **8**], 308 (10), 294 (20), 279 (3), 278 (4), 267 (12), 253 (8). IR (KBr): 1676 cm^{-1} (s), 1653 (m). ^{1}H NMR (250 MHz, DMSO-*d*$_6$): δ 1.29 (s, 18 H), 3.01 (s, 3 H), 6.92 (br, 2H), 7.25 (d, *J* = 1.2 Hz, 2 H), 8.3 (br, 1 H), 11.3 (br, 2 H). ^{13}C NMR (63 MHz, DMSO-*d*$_6$): δ 28.3 (CH$_3$), 30.8 (3 CH$_3$), 34.7 (quat C), 104.5, 115.2 (CH), 112.4, 133.8, 134.1, 150.1, 150.8 (quat C). Anal. Calcd for $C_{20}H_{28}ClN_3$: C, 69.44; H, 8.16; N, 12.15. Found: C, 69.35; H, 8.13; N, 11.97.

5,8-Di(*tert*-butyl)-2-(*N*-methylamino)perimidine (8). A solution of **8**·HCl (1.04 g, 3.0 mmol) in CH$_2$Cl$_2$ was extracted with aq NaOH (2 M) followed by distillation of the solvent under vacuum to afford pale yellow crystals (0.71 g, 76%, mp 215 °C). The pale yellow solution of **8** in C$_6$D$_6$ turned rapidly red at the surface and decomposed during 1 d. MS (EI, 70 eV): *m*/*z* (rel intens) = 309 (87) [M$^+$], 308 (14), 294 (20), 279 (4), 278 (3), 267 (16), 253 (7), 238 (10), 59 (100). IR (KBr): 1642 cm^{-1} (m), 1608 (s). UV (acetonitrile): λ_{max} [nm] (log ϵ) 214 (4.69), 240 (4.57), 317 (3.97), 334 (3.96). ^{1}H NMR (200 MHz, C$_6$D$_6$): δ 1.33 (s, 18 H), 2.65 (s, 3 H), 6.63 (br, 2 H), 7.19 (d, *J* = 1.5 Hz, 2 H).

Irradiation of 1 (a). A degassed 0.1 M solution of **1** in benzene was irradiated in a 1 cm cell with a 500-W high-pressure lamp (345 nm cutoff filter). Distillation of the solvent under vacuum afforded a red-brown solid decomposing above 280 °C. MS (EI, 70 eV): *m*/*z* (rel intens) = 323 (7), 309 (100), 308 18, 294 (23), 279 (6), 267 (19), 253 (10), 238 (14). UV (acetonitrile): λ_{max} [nm] 345 (broad), 243, 218. ^{1}H NMR (200 MHz, acetonitrile-*d*$_3$): no sharp signals observable. (b) The same product precipitated when a 0.026 M solution of **1** in 2,2-dimethylbutane−pentane (8:3) was irradiated for 10 min as described in (a).

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Supporting Information Available: General experimental and details of irradiation and EPR experiments; experimental procedures for the synthesis of **6** from naphthalene; ^{1}H and ^{13}C NMR spectra; UV−vis absorption and emission spectra; EPR, IR, and EI mass spectra; computational details and results of calculations on ^{1}**2** and ^{3}**2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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