Mendeleev Commun., 2002, 12(6), 227–229

Zero-field splitting parameters of triplet nitreno-s-triazines: a new insight into the geometry of the nitrene centres of triplet and singlet nitrenes

Sergei V. Chapyshev

Institute of Problems of Chemical Physics, Russian Academy of Sciences, 142432 Chernogolovka, Moscow Region, Russian Federation. Fax: +7 096 515 3588; e-mail: chap@icp.ac.ru

10.1070/MC2002v012n06ABEH001683

The zero-field splitting parameters of triplet nitreno-s-triazines indicate that triplet and singlet nitrenes have sp^3 and sp^2 hybridization of the nitrene centres, respectively.

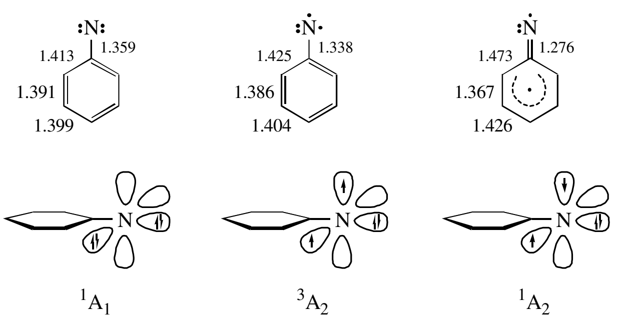


Figure 1 CASSCF(8,8)/6-31G* calculated[3(c)] bond lengths (Å) and molecular models of closed-shell $^1A_1$ singlet, $^3A_2$ triplet and open-shell $^1A_2$ singlet phenylnitrenes.

Nowadays,[1] all physical and chemical properties of nitrenes are explained using models for triplet and singlet nitrene centres, which were introduced by E. Wasserman[2] in 1971. According to these models, the nitrene nitrogen atoms in both closed-shell $^1A_1$ singlet and open-shell $^3A_2$ triplet states are *sp*-hybridized and differ only in the way of filling two orthogonal *p*-orbitals with electrons (Figure 1). In 1992, it has been found that singlet phenylnitrene can also have an electronic configuration of the open-shell $^1A_2$ singlet state with the same orbital occupancy as in the $^3A_2$ state but with the antiparallel orientation of spins.[3] The DZ+d CISD+Q calculations showed that the orbitals of the $^1A_2$ state are very similar to those of the $^1A_1$ state and much differ from the orbitals of the $^3A_2$ state.[3(a)] Despite very different geometries of the $^1A_1$, $^1A_2$ and $^3A_2$ states, no attempt was made to analyse the hybridization of their nitrogen atoms. Here, the results of EPR studies of triplet nitreno-s-triazines, providing strong evidence for different hybridization of the nitrene nitrogen atoms in the $^1A_1$ and $^3A_2$ states, are presented.

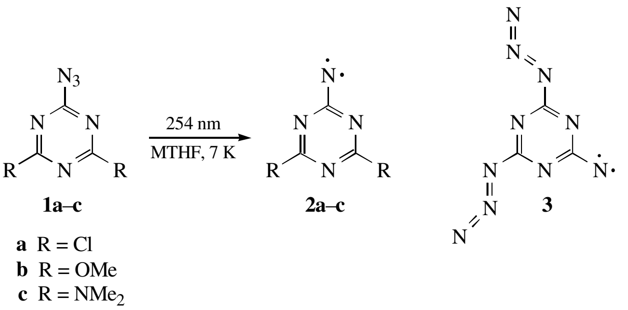
The irradiation of azides **1a**–**c**[†] in a degassed 2-methyltetrahydrofuran (MTHF) solution frozen at 7 K with light at $\lambda = 254$ nm led to the appearance of the EPR spectra of triplet nitrenes **2a**–**c** in the form of two strong and well-resolved X- and Y-transitions at 7800–8200 G (Figure 2). A similar EPR spectrum has been reported recently[4] for triplet diazidonitrene **3**. Standard calculations[5] showed that triplet **2a**–**c** have the zero-field splitting *D*- and *E*-parameters that are close to those of triplet **3** (Table 1).

Both *D*- and *E*-values of triplet **2a**–**c** are of considerable interest. Earlier, EPR studies[2,6] have shown that the derivatives of triplet phenylnitrenes have *D*-values in a range of 0.87–1.05 cm^{-1}, those of triplet pyridylnitrenes,[7] in a range of 1.05–1.11 cm^{-1}, and triplet 2-nitrenopyrimidine[8] has a *D*-value of 1.217 cm^{-1}. On comparison with all these species, triplet **2a**–**c** have the highest values of *D*. This is explained by the effect of heterocyclic nitrogen atoms, which are poor spin-holding centres due to a small size. The more nitrogen atoms in a heterocyclic ring, the higher the *D*-values of triplet heteroarylnitrenes. An increase in the *D*-values of triplet **2a**–**c** is accompanied by an elongation of the C–N bond (Table 1), which significantly exceeds in length the C–N bond of the phenylnitrene $^1A_1$ state (Figure 1). Therefore, it is not surprising that triplet **2a**–**c** display strongly pronounced singlet-type reactivity to form compounds **4** and **5** on photolysis in the presence of the traps of singlet nitrenes.[9] The extraordinarily high *E*-values of triplet **2a**–**c** indicate the nondegeneracy of two magnetic orbitals of these species, owing to which two spins in **2a**–**c** flip at different energies. Almost all previous EPR studies dealt with triplet arylnitrenes, which have very small *E*-values (< 0.002 cm^{-1}).[2,6,7] High values of *E* were found only for some *m*-substituted phenylnitrenes (0.003 cm^{-1}),[2] triplet 2-nitrenopyrimidine (0.005 cm^{-1})[8] and triplet **3** (0.011 cm^{-1}).[4] As usually, high values of *E* for triplet nitrenes were explained by the low symmetry of molecules.[2] The finding that so highly symmetrical molecules as triplet **2a** and **2c** have very high values of *E* for the first time demonstrates that the nondegeneracy of magnetic orbitals in triplet nitrenes not always results from low molecular symmetry. The origin of high values of *E* for triplet **2a**–**c** can be understood from a qualitative analysis of the wavefunctions of triplet nitrenes.

Table 1 X- and Y-transitions, *D*- and *E*-parameters, and UB3LYP/6-31G* calculated spin populations (q_N) on the nitrene centres and the C–N bond lengths of nitrenes **2a**–**c**, **3** and PhN.

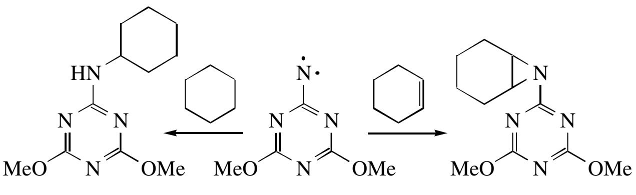
Nitrene	X-line/G	Y-line/G	$\lvert D/hc\rvert$/cm^{-1}	$\lvert E/hc\rvert$/cm^{-1}	q_N	*r*(C–N)/Å
2a	7735[a]	7968[b]	1.377	0.011	1.7549	1.366
2b	7834[a]	8100[b]	1.427	0.013	1.7791	1.371
2c	7938[a]	8165[b]	1.465	0.011	1.7930	1.378
3	—	—	1.402[c]	0.011[c]	1.7728	1.371
PhN	—	—	0.999[d]	0.000[d]	1.6001	1.328

[a]Mid-point. [b]Top-point. [c]From ref. 4. [d]From ref. 6.



1a–**c** **2a**–**c** **3**

a R = Cl
b R = OMe
c R = NMe$_2$



4, 48% **2b** **5**, 52%

All triplet nitrenes can arbitrarily be considered as systems of two unpaired electrons and described by wavefunctions Ψ_T and potential energy curves analogous to those used for describing diatomic systems (Figure 3). Deviations to any side from the optimum distance *r* between two spins should lead to a decrease

---

[†] The synthesis of azides **1a**–**c** was described elsewhere.[12]

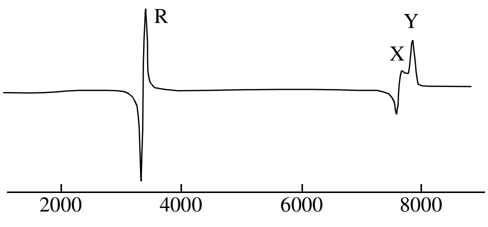


Figure 2 EPR spectrum from the photolysis of azide **1a** ($\nu_0 = 9.520$ GHz, H_0 at 3400 G) with light at $\lambda = 254$ nm for 10 min in MTHF at 7 K. The peaks X, Y and R correspond to X- and Y-transitions of triplet nitrene **2a** and a radical from MTHF, respectively.

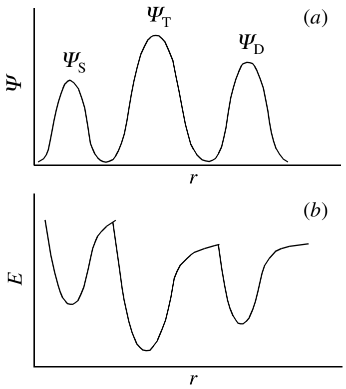


Figure 3 (*a*) Wavefunctions and (*b*) potential energy curves for closed-shell singlet (Ψ_S), triplet (Ψ_T) and open-shell singlet (Ψ_D) arylnitrenes.

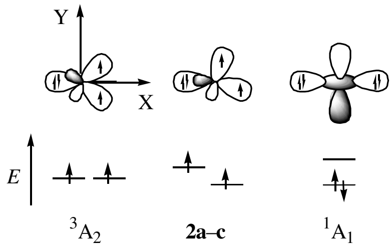


Figure 4 Orbitals and energy levels in the $^3A_2$ and $^1A_1$ states and triplet nitrenes **2a**–**c**.

in the size of Ψ_T and to an increase in the potential energy. At very small *r*, Ψ_T approaches the point with $\Psi_T = 0$, beyond which the wavefunction of closed-shell singlet nitrenes Ψ_S starts to develop (*r* becomes the distance between two electrons in the same orbital). On the other side of Ψ_T, there is another point with $\Psi_T = 0$ and another wavefunction. This new wavefunction Ψ_D describes diradicals with two unpaired electrons on two different radical centres (*r* becomes very large). Since the discovery of such diradicals in 1992, they were called as open-shell $^1A_2$ singlet nitrenes despite the fact that the nitrogen atom in these species is divalent (Figure 1).[‡] The strongly pronounced singlet-type reactivity of triplet **2a**–**c** and very high spin populations on their nitrene centres (small *r*)[2] suggest that the Ψ_T of these species are close to the Ψ_S of closed-shell $^1A_1$ singlet nitrenes. According to the Hund rule, two spins occupy two orbitals and have parallel orientation only if such orbitals are degenerate. Deviations to any side from the optimum *r* between two spins should lift this orbital degeneracy. Namely, this finally leads to a situation when two spins either prefer to occupy the same low-lying orbital (the $^1A_1$ states) or adopt the opposite spin orientation (the $^1A_2$ states). High values of *E* for triplet **2a**–**c** reflect changes in the spatial orientation of magnetic orbitals, which take place on the way from $^3A_2$ to $^1A_1$ nitrenes. Another example of this series is highly symmetrical triplet 2-nitrenopyrimidine ($|D/hc| = 1.217$ cm^{-1}, $|E/hc| = 0.005$ cm^{-1}).[8] These changes in the spatial orientation of magnetic orbitals of triplet nitrenes can be associated only with different hybridization of nitrene nitrogen atoms in the $^3A_2$ and $^1A_1$ states. As is known, five valent electrons of nitrogen with zero valence are described by two wavefunctions, $\Psi(2s)$ and $\Psi(2p)$. Since the nitrene nitrogen atom is univalent, its six valent electrons are described by Ψ_S and Ψ_T, which are not pure *s* or *p*. However, in any case, Ψ_S and Ψ_T should have maximum *s* and *p* components, respectively. Ψ_S has a maximum *s* component (33.3%) in two cases. In one case, two electron pairs occupy two *sp*-orbitals, and one pair of electrons occupies one of two degenerate *p*-orbitals (the Wasserman model).[2] However, the Hund rule says that two electrons cannot occupy only one of two degenerate orbitals. According to this rule, the Wasserman model for the singlet nitrene centre is wrong. In the other case, all three electron pairs occupy three sp^2-hybrid orbitals leaving the high-energy *p*-orbital as vacant in full accord with the Hund rule. Only this type of orbital occupancy in singlet nitrenes meets all requirements of quantum chemistry. Similar considerations show that Ψ_T has a maximum *p* component (75%) when six valent electrons occupy four sp^3-orbitals. The fact that the magnetic orbitals of triplet nitrenes are hybrid was experimentally proved by observations of the hyperfine splitting on the nitrene nitrogen atoms ($a_N = 17$–20 G)[4,6] in the EPR spectra of triplet nitrenes. Moreover, this orbital occupancy does not contradict to the basic principle of wave mechanics,[10] according to which two unpaired electrons can interact with each other only if their wavefunctions are not orthogonal. Thus, both a theory and EPR spectra suggest that typical triplet nitrenes have two nearly degenerate sp^3-hybrid magnetic orbitals and small values of *E* owing to $S_x^2 \approx S_y^2$ in the third term of the triplet state spin Hamiltonian.[11]

$$\hat{H} = g\beta HS + DS_z^2 + E(S_x^2 - S_y^2). \tag{1}$$

On approaching Ψ_T of the $^3A_2$ states to Ψ_S of the $^1A_1$ states, one magnetic orbital gains more *s* component, while another one, more *p* component. As a result, two orbitals adopt different spatial orientations (Figure 4) and different energies despite the high symmetry of molecules. The EPR spectra of triplet **2a**–**c** are the best illustration of such changes.

I am grateful to Professor M. S. Platz for provided laboratory facilities and helpful discussions.

References

1 (*a*) N. P. Gritsan, I. Likhotvorik, M.-L. Tsao, N. Clelbi, M. S. Platz, W. L. Karney, C. R. Kemnitz and W. T. Borden, *J. Am. Chem. Soc.*, 2001, **123**, 1425; (*b*) N. P. Gritsan, A. D. Gudmundsdottier, D. Tigelaar, Z. Zhu, W. L. Karney, C. M. Hadad and M. S. Platz, *J. Am. Chem. Soc.*, 2001, **123**, 1951; (*c*) W. T. G. Johnson, M. B. Sullivan and C. J. Cramer, *Int. J. Quant. Chem.*, 2001, **85**, 492; (*d*) W. T. Borden, N. P. Gritsan, C. M. Hadad, W. L. Karney, C. R. Kemnitz and M. S. Platz, *Acc. Chem. Res.*, 2000, **33**, 765 and references therein.

2 E. Wasserman, *Prog. Phys. Org. Chem.*, 1971, **8**, 319.

3 (*a*) S.-J. Kim, T. P. Hamilton and H. F. Schaefer III, *J. Am. Chem. Soc.*, 1992, **114**, 5349; (*b*) D. A. Hrovat, E. E. Waali and W. T. Borden, *J. Am. Chem. Soc.*, 1992, **114**, 8698; (*c*) W. L. Karney and W. T. Borden, *J. Am. Chem. Soc.*, 1997, **119**, 1378.

4 T. Nakai, K. Sato, D. Shiomi, T. Takui, K. Itoh, M. Kozaki and K. Okuda, *Mol. Cryst. Liq. Cryst.*, 1999, **334**, 157.

5 S. Murata and H. Iwamura, *J. Am. Chem. Soc.*, 1991, **113**, 5547.

6 J. H. Hall, J. M. Fargher and M. R. Gisler, *J. Am. Chem. Soc.*, 1978, **100**, 2029.

7 (*a*) R. A. Evans, M. Wong and C. Wentrup, *J. Am. Chem. Soc.*, 1996, **118**, 4009; (*b*) S. V. Chapyshev, A. Kuhn, M. Wong and C. Wentrup, *J. Am. Chem. Soc.*, 2000, **122**, 1572; (*c*) S. V. Chapyshev, R. Walton, J. A. Sanborn and P. M. Lahti, *J. Am. Chem. Soc.*, 2000, **122**, 1580; (*d*) S. V. Chapyshev, R. Walton and P. M. Lahti, *Mendeleev Commun.*, 2000, 7.

8 M. Kuzaj, H. Luerssen and C. Wentrup, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 480.

[‡] By definition, nitrenes are compounds of univalent nitrogen with six valent electrons.[13] Because the open-shell $^1A_2$ singlet states have divalent nitrogen with seven valent electrons, these species represent a class of divalent nitrogen compounds. Such compounds can also have singlet and triplet spin states,[14] which, similarly to singlet and triplet nitrenes, are described by two different wavefunctions.

9 (*a*) R. Kayama, H. Shizuka, S. Sekiguchi and K. Matsui, *Bull. Chem. Soc. Jpn*., 1975, **48**, 3309; (*b*) H. Yamada, H. Shizuka and K. Matsui, *J. Org. Chem*., 1975, **40**, 1351.

10 *Quantum Chemistry*, ed. K. S. Pitzer, Printice-Hall, Englewood Cliffs, New Jersey, 1963.

11 A. M. Trozzolo and E. Wasserman, in *Carbenes*, eds. M. Jones, Jr. and R. A. Moss, Wiley, New York, 1975, vol. 2, p. 190.

12 R. Kayama, S. Hasunuma, S. Sekiguchi and K. Matsui, *Bull. Chem. Soc. Jpn*., 1974, **47**, 2825.

13 *Azides and Nitrenes, Reactivity and Utility*, ed. E. F. V. Scriven, Academic Press, New York, 1984, ch. 1.

14 P. M. Lahti, A. S. Ichimura and J. A. Sanborn, *J. Phys. Chem. A*, 2001, **105**, 251 and references therein.

Received: 6th November 2002; Com. 02/2010