JOURNAL OF PHYSICAL ORGANIC CHEMISTRY
J. Phys. Org. Chem. 2001; **14:** 197–200

1,4-Naphthoquinonediazide-2-carboxylic acid: a diazo compound with a long-lived triplet excited state

Götz Bucher,* Holger Wandel and Wolfram Sander

Lehrstuhl für Organische Chemie II, Ruhr-Universität Bochum, Universitätsstr. 150, 44801 Bochum, Germany

Received 24 August 2000; revised 13 November 2000; accepted 22 November 2000

ABSTRACT: Laser flash photolysis (308 nm) of 1,4-naphthoquinonediazide-2-carboxylic acid **1** in 2-methyltetrahydrofuran (MTHF) leads to the detection of a long-lived (5.3 μs) triplet excited state, whose triplet energy, obtained by measuring the phosphorescence spectrum of **1** in an Ar- matrix at 10 K, is ca 55 kcal mol^{-1} (1 kcal = 4.184 KJ). The first triplet excited state of **1** is quenched efficiently by 1,3-dienes and molecular oxygen. By calculating the spin density distribution it can be shown that ^{3}**1** is not a typical naphthalene triplet, as it bears significant spin density at the diazo moiety. Copyright © 2001 John Wiley & Sons, Ltd.

KEYWORDS: 1,4-naphthoquinonediazide-2-carboxylic acid; triplet excited state; laser flash photolysis

INTRODUCTION

Carbenes are generally generated by photolysis or thermolysis of diazo compounds or diazirines. As the decomposition mechanism may be of importance for product distribution, the question of whether carbene formation occurs via primary C═N scission and subsequent intersystem crossing (ISC) on the carbene surface, or via an intermediate triplet excited state of the diazo precursor, has been adressed in mechanistic studies.

Carbene and biradical precursors that form reactive intermediates by photodediazotation usually do so fairly efficiently, and their excited states are very short-lived. Exceptions to this rule have only recently been discovered. A class of relatively rigid polycyclic derivatives of 2,3-diazabicyclo[2.2.1]hept-2-ene was found to have triplet lifetimes up to 630 ns, with triplet energies of 62.5 ± 1 kcal mol $^{-1}$ (1 kcal = 4.184 kJ). The triplet quantum yield was determined in one case to be as high as 0.5 ± 0.2.[2] In the case of 2,3-diazabicyclo-[2.2.2]octane, the first excited singlet state is exceedingly long lived; fluorescence lifetimes up to 1 μs have been reported.[3,4] In this case, however, the ISC efficiency is very low, and sensitization experiments have led to an estimated lifetime of ca 7 ns for the first excited triplet state of this compound.[5,6]

Diazo compounds (and diazirines) with alkyl substituents attached to the diazo carbon atom may undergo hydrogen shifts on the excited singlet surface. Examples of such reactions have been presented by Celebi *et al.*[7] and Reed and Modarelli.[8] The degree of rearrangement occuring on the surface of the excited diazo compound depends on the C—H bond enthalpy of the bond being broken during the rearrangement. Thus, cyclopropylphenyldiazomethane (with a relatively strong tertiary C—H bond) yields almost exclusively products derived from carbene reactions, and a high yield of the carbene can be trapped by pyridine, while the pyridine ylide of isopropylphenylcarbene (the tertiary C—H bond being significantly weaker in this system) is formed only in low yield.[7] In the photochemistry of diaryldiazo compounds hydrogen shifts cannot occur, and dediazotation usually is a highly efficient and very rapid process. Dupuy *et al.* have studied the photolysis of diphenyldiazomethane by picosecond time-resolved techniques and found the fluorescence attributed to triplet diphenylcarbene to grow in within 15 ps[9].

To the best of our knowledge, only one instance of a diazo compound with an excited state lifetime comparable to those of the azo compounds mentioned above has been reported. 2-Diazo-1,3-diphenyl-1,3-propadienone has been reported to have a triplet lifetime of 15 μs.[10] In this paper, we report the finding of a second example of such a diazo compound and on the characterization of its first triplet excited state.

RESULTS AND DISCUSSION

When 1,4-naphthoquinonediazide-2-carboxylic acid (**1**) in 2-methyltetrahydrofuran (MTHF) was subjected to laser flash photolysis (10 ns/100 mJ pulses from an XeCl

---

**Correspondence to:* G. Bucher, Lehrstuhl für Organische Chemie II, Ruhr-Universität Bochum, Universitätsstr. 150, 44801 Bochum, Germany.
Contract/grant sponsor: Fonds der Chemischen Industrie.
Contract/grant sponsor: Deutsche Forschungsgemeinschaft.

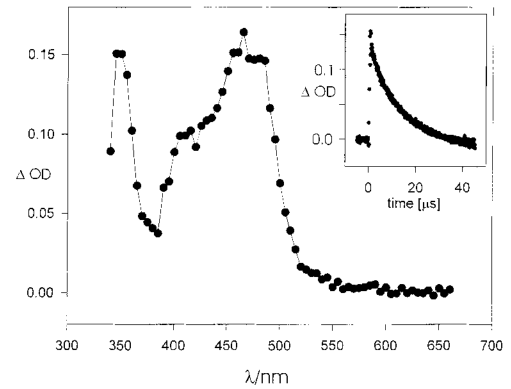


Figure 1. Transient absorption spectrum, measured 4 μs after LFP (308 nm) of **1** in MTHF (1 atm Ar). Inset: typical transient decay trace, monitored at $\lambda = 460$ nm

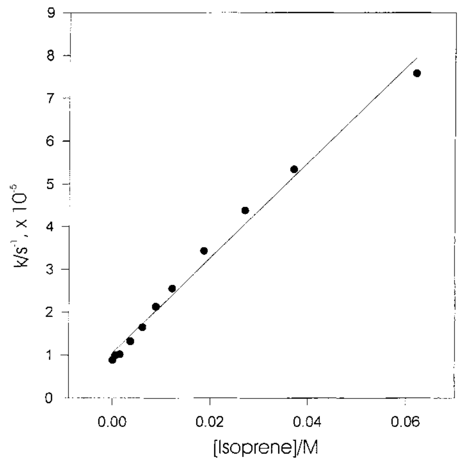
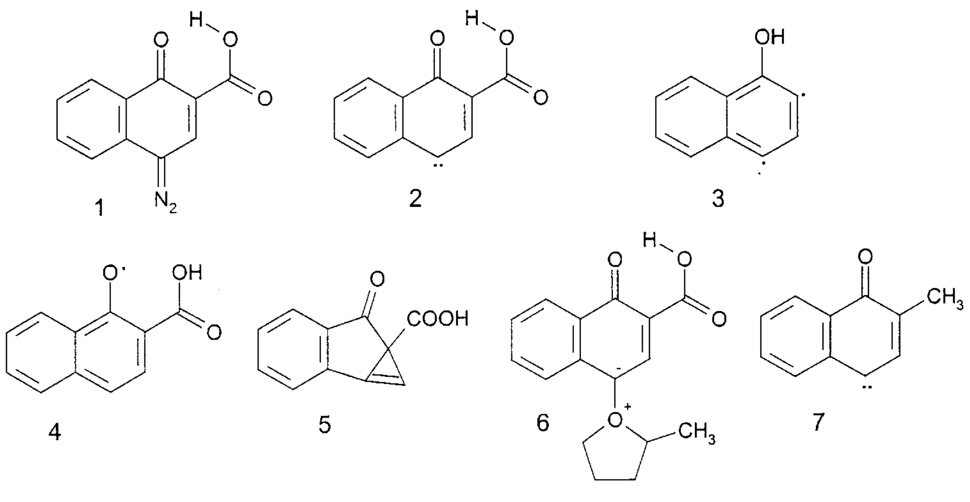


Figure 2. Plot of the decay rate constant of the transient observed upon LFP of **1** in MTHF ($\lambda_{mon} = 460$ nm, 1 atm Ar) versus the concentration of isoprene. Straight line: linear fit

excimer laser, 308 nm) (the LFP and matrix isolation setup used in these experiments has been described before;[11]) a transient signal with a lifetime $\tau \approx 5.3$ μs and $\lambda_{max} = 460$ nm was detected (Fig. 1). The transient was quenched efficiently by molecular oxygen and 1,3-cyclohexadiene, and not at all by 1,4-cyclohexadiene or cyclopentene.

A number of possible reactive intermediates have to be considered, among which the most obvious candidate is the carbene **2**, but 2,4-didehydro-1-naphthol (**3**), which is formed by decarboxylation of **2**, is another intermediate to be taken in account. Further possibilities are the naphthoxy radical **4**, the bicyclic compound **5**, and the MTHF ylide **6** (Scheme 1).

For a number of reasons, an assignment of the transient observed to the carbene **2** appears highly unlikely. First, **2** has been characterized by matrix isolation spectroscopy.[12] Its UV–Vis spectrum in an Ar matrix consists of two strong absorption maxima at $\lambda = 342$ and 358 nm, plus a weak and broad band between $\lambda \approx 425$ and 600 nm, which clearly is not consistent with the transient spectrum monitored here. Second, **2** is unlikely to survive in MTHF for more than 10 ns. This can be inferred from the known reactivity of carbene **7**, which reacts with cyclohexane (which is less reactive than MTHF) with a rate constant $k = 8.4 \times 10^6\,\mathrm{l\,mol^{-1}\,s^{-1}}$.[13] Less clear is the situation when biradical **3** is considered, as no derivative of *m*-benzyne has ever been characterized by LFP. But again, its UV–Vis spectrum in an Ar matrix ($\lambda_{max} \approx 350$ nm)[9] is not consistent with the spectrum obtained by LFP in MTHF, which also applies to cyclopropene **5** (cyclopropene **5** is unknown, but the UV–Vis spectrum of unsubstituted benzobicyclo[3.1.0]hexadienone has been measured.[14]). As far as the naphthoxy radical **4** or the ylide **6** is concerned, it appears unlikely that they would be quenched rapidly by 1,3-cyclohexadiene, but not by 1,4 cyclohexadiene. Overall, all reactive intermediates typically encountered after LFP of diazo



Scheme 1

Table 1. Quenching rate constants (T_1) for **1**[a]

Quencher	$k_q \times 10^{-7}$ ($\mathrm{l\,mol^{-1}S^{-1}}$)	$\mathrm{E_T}$ ($\mathrm{kcal\,mol^{-1}}$)[b]
1,3-Cyclohexadiene	75.5	52.4
(*Z*)-Piperylene	1.7	57.4
Isoprene	1.1	60.0

[a] In MTHF, ambient temperature.
[b] Triplet energy of quencher.[16]

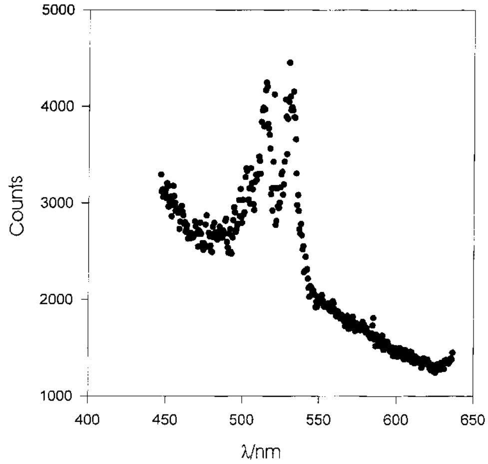


Figure 3. Phosphorescence spectrum of **1**, matrix-isolated in Ar, 10 K. The increase in emission towards shorter wavelengths is due to the fluorescence of **1**

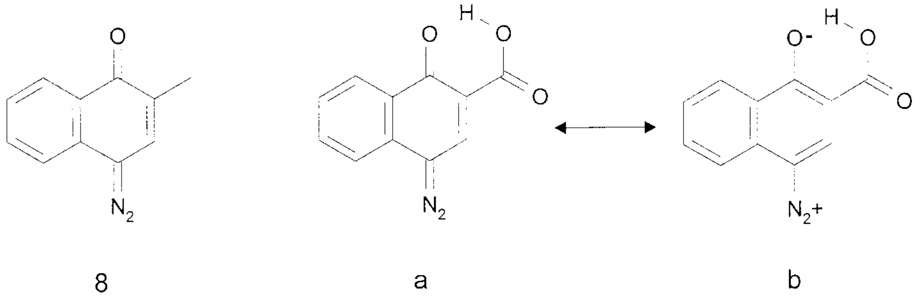
compounds can be ruled out. Instead, the reactivity pattern of the transient monitored resembles that of a naphthalene derivative in its triplet excited state. In order to check for this possibility, we performed two series of experiments.

First, some rate constants for quenching of the transient were measured Fig. 2. Table 1 gives the values obtained for 1,3-cyclohexadiene, (*Z*)-piperylene and isoprene. A correlation between the triplet energy of the quencher used and the rate constant measured is evident.

Second, the luminescence spectrum of **1**, matrix-isolated in Ar at 10 K, was measured.[11] Upon excitation, the compound emitted a blue fluorescence plus a weak green phosphorescence. The luminescence spectrum shows a broad fluorescence maximum with $\lambda_{max} \approx 430$ nm and two phosphorescence bands with $\lambda_{max} = 515.1$ and 530.1 nm (Fig. 3). The occurence of a double phosphorescence band can be explained in terms of a vibrational fine structure with a spacing of 549 $\mathrm{cm^{-1}}$; the position of the lower wavelength band indicates a triplet energy of **1** of ca 55 $\mathrm{kcal\,mol^{-1}}$, typical of naphthalene derivatives.[15,16]

Why would diazo compound **1** have a relatively long-lived first triplet excited state, whereas for example, a very similar molecule such as **8**, the diazo precursor to carbene **7**, does not show such a property?[13] The answer has to be sought in differences between the electronic structures of the two molecules. Hints towards what may be the reason for the differences can be found in the infrared spectra of the two molecules. Here, a comparison of the C=O and N≡N stretching frequencies (Ar matrix, 10 K) is particularly useful: Whereas **8** shows a $\nu_{\mathrm{N{\equiv}N}}$ at 2062.0 $\mathrm{cm^{-1}}$ and $\nu_{\mathrm{C{=}O}} = 1635.8\ \mathrm{cm^{-1}}$,[17] which is typical for quinone diazides, these values are shifted to $\nu_{\mathrm{N{\equiv}N}} = 2105.1$ and 2086.5 $\mathrm{cm^{-1}}$ (band split due to matrix site effects) and $\nu_{\mathrm{C{=}O}} = 1585.9\ \mathrm{cm^{-1}}$ in the case of **1**. The electronic structure of quinone diazides can be described in terms of a diazocyclohexadienone and an internal diazonium–phenolate mesomeric structure (Scheme 2).

Owing to the strong intramolecular hydrogen bridge present in **1**,[12] the zwitterionic structure **b** gains additional weight, which is revealed by the changed IR frequencies, which indicate a higher bond order of the N≡N bond and a lower bond order of the C=O bond in **1** as compared with **8**. Thus, the properties of **1** shift more towards that of a naphthalenediazonium chromophore. It should be noted that some arenediazonium cations do indeed show phosphorescence when irradiated at 77 K; in the case of the parent benzenediazonium cation (as tetrafluoroborate), the phosphorescence maximum was determined to be $\lambda_{max} = 410$ nm.[18] In this study, the quantum yield of phosphorescence was dependent on the irradiation wavelength. Phosphorescence (as well as fluorescence) was only detected upon irradiation with $\lambda = 295$ nm, whereas shorter wavelength irradiation



Scheme 2

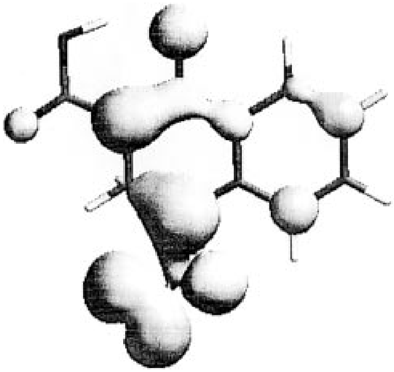


Figure 4. Spin isodensity surface for the first triplet excited state of **1**, projected on to the molecular framework (geometry optimized on the UB3LYP/6–31G* level of theory)

($\lambda = 259$ nm) gave no luminescence, but resulted in efficient dediazotation instead. Diazo compound **1** may thus bear sufficient diazonium character to display characteristics typical of this chromophore.

In order to gain further insight in to the properties of the first triplet excited state of **1**, its geometry was optimized at the UB3LYP/6–31G* level of theory. According to the calculation, the CNN moiety is no longer linear in the triplet excited state, but bent with an angle of 124.6°. Figure 4 shows a spin density isosurface projected on to the molecular framework. It reveals that the spin density is localized mostly on the diazo functionality and in the cyclohexenone subunit, while the annelated benzene ring and the carboxy functionality only receive little spin density. Thus, the triplet excited state of **1** is not a typical naphthalene triplet.

EXPERIMENTAL

Diazo compound **1** was prepared as described before.[12] The equipment used for laser flash photolysis and for matrix isolation spectroscopy has been described before.[11] In experiments involving matrix isolation spectroscopy, **1** was sublimed at 155 °C/10^{-6} mbar. For laser flash photolysis, a 0.1 mmol solution of **1** in MTHF was employed. In order to avoid depletion of the precursor and product build-up, a flow cell was used. The MTHF used was freshly distilled prior to use. Calculations were performed using the Gaussian *98* suite of programs,[19] employing the hybrid B3LYP method.[20]

Acknowledgements

This work was financially supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

REFERENCES

1. Adam W, Fragale G, Klapstein D, Nau WM, Wirz J. *J. Am. Chem. Soc.* 1995; **117**: 12578–12592.
2. Adam W, Nau WM, Sendelbach J, Wirz J. *J. Am. Chem. Soc.* 1993; **115**: 12571–12572.
3. Solomon BS, Thomas TF, Steel C. *J. Am. Chem. Soc.* 1968; **90**: 2249–2258.
4. Nau WM, Greiner G, Rau H, Wall J, Olivucci M, Scaiano JC. *J. Phys. Chem A* 1999; **103**: 1579–1584.
5. Engel PS, Horsey DW, Scholz JN, Karatsu T, Kitamura A. *J. Phys. Chem.* 1992; **96**: 7524–7535.
6. Caldwell RA, Helms AM, Engel PS, Wu A. *J. Phys. Chem.* 1996; **100**: 17716–17717.
7. Celebi S, Leyva S, Modarelli DA, Platz MS. *J. Am. Chem. Soc.* 1993; **115**: 8613–8620.
8. Reed SC, Modarelli DA. *Tetrahedron Lett.* 1996; **37**: 7209–7212.
9. Dupuy C, Korenowski GM, McAuliffe M, Hetherington WMI, Eisenthal KB. *Chem. Phys. Lett.* 1981; **77**: 272–274.
10. Ortica C, Pohlers G, Scaiano JC, Cameron JF, Zampini A, *Org. Lett.* 2000; **2**: 1357–1360.
11. Bucher G. *Liebigs Ann. Chem.* 1997; 1415–1423.
12. Sander W, Bucher G, Wandel H, Kraka E, Cremer D. *J. Am. Chem. Soc.* 1997; **119**: 10660–10672.
13. Arnold BR, Scaiano JC, Bucher GF, Sander WW. *J. Org. Chem.* 1992; **57**: 6469–6474.
14. Bucher G, Sander W. *J. Org. Chem.* 1992; **57**: 1346–1351.
15. Lissi EA, Encinas MV. In *CRC Handbook of Photochemistry*. Scaiano JC (ed), CRC Press: Boca Raton, FL. 1989; 111–176.
16. Murov SL, Carmichael I, Hug GL. In *Handbook of Photochemistry*. Marcel Dekker: New York, 1993.
17. Sander W, Bucher G, Komnick P, Morawietz J, Bubenitschek P, Jones PG, Chrapkowski A. *Chem. Ber.* 1993; **126**: 2101–2109.
18. Sukigara M, Kikuchi SI. *Bull. Chem. Soc. Jpn.* 1967; **40**: 461–466.
19. Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Zakrzewski VG, Montgomery MA, Stratmann RE, Burant JC, Dapprich S, Millam JM, Daniels AD, Kudin KN, Strain MC, Farkas O, Tomasi J, Barone V, Cossi M, Cammi R, Menucci B, Pomelli C, Adamo C, Clifford S, Ochterski J, Petersson GA, Ayala PY, Cui Q, Morokuma K, Malick DK, Rabuck AD, Raghavachari K, Foresman JB, Ciolowski J, Ortiz JV, Stefanov BB, Liu G, Liashenko A, Piskorz P, Komaroni I, Gomperts R, Martin RL, Fox DJ, Keith T, Al-Laham MA, Peng CY, Nanayakkara A, Gonzalez C, Challacombe M, Gill PMW, Johnson B, Chen W, Wong MW, Andres JL, Gonzalez C, Head-Gordon M, Replogle ES, Pople JA. Gaussian 98, Revision A.6. Gaussian: Pittsburgh, PA, 1998.
20. Becke AD. *J. Chem. Phys.* 1993; **98**: 5648–5652.