

# Nonclassical, Cyclically Delocalized 4N/3e Radical Cations and 4N/2e Dications: One- and Two-Electron Oxidation of Proximate, *syn*-Periplanar Bisdiazene-Oxides

Kai Exner,<sup>†</sup> Horst Prinzbach,<sup>\*,†</sup> Georg Gescheidt,<sup>\*,‡</sup>  
Birgit Grossmann,<sup>§</sup> and Jürgen Heinze<sup>\*,§</sup>

Institut für Organische Chemie und  
Biochemie der Universität, Albertstrasse 21  
D-79104 Freiburg, Germany  
Institut für Physikalische Chemie der Universität  
Klingelbergstrasse 80, CH-4056 Basel, Schweiz  
Institut für Physikalische Chemie der Universität  
Albertstrasse 21, D-79104 Freiburg, Germany

Received October 28, 1998

By one-/two-electron reduction of specifically constructed, rigidly preorganized bisdiazenes<sup>1,2</sup> unusually effective in-plane ( $\sigma$ ) homoconjugation/homoaromaticity (4N/5e, 4N/6e) was demonstrated. That oxidation of such bisdiazenes after "protection"<sup>3</sup> and activation<sup>4</sup> in the form of their tetra-*N*-oxides leads to novel, O-stabilized 4N/3e radical cations ( $1^{+\bullet}$ ) and (presumably) 4N/2e dications ( $1^{2+}$ ) is the subject of this paper.

As an exemplary case, the tetra-*N*-oxide **1** was prepared together with reference trioxide **2** (1:1 mixture with the 4,5,10-trioxide) from bisdiazene **3**<sup>3</sup> along standard procedure; the latter had been a rewarding testing object in the oxidation as well as in the reduction study.<sup>2,3</sup> While no bathochromic shift due to ON=NO/ON=NO interaction was expressed in the UV spectra of **1** ( $\lambda_{\max}(\text{H}_2\text{O}) = 263 \text{ nm}$ ; cf. **6**  $\lambda_{\max}(\text{H}_2\text{O}) = 261 \text{ nm}$ ), the absorption of **2** ( $\lambda_{\max}(\text{H}_2\text{O}) = 276 \text{ nm}$ ) was quite different from that of **6** and **5** ( $\lambda_{\max}(\text{H}_2\text{O}) = 228 \text{ nm}$ ). The DBO-dioxide **6**, the ON=NO reference for **1** and **2**, has recently been reported (Blackstock et al.<sup>5</sup>) to give a solution stable  $\pi$ -radical with a lifetime of seconds to minutes at room temperature ( $E_{1/2} = 1.65 \text{ V}$ , hfcfs (mT) 0.122 (2N), 0.086 (4H)). For DBO-monoxide **5** no radical cation formation could so far be observed by CV ( $E_{\text{ox}} > 3 \text{ V}$ );  $4^{+\bullet}$  is extensively investigated.<sup>6</sup>

<sup>†</sup> Institute for Organic Chemistry and Biochemistry, University of Freiburg.

<sup>‡</sup> University of Basel.

<sup>§</sup> Institute for Physical Chemistry, University of Freiburg.

(1) Exner, K.; Hunkler, D.; Gescheidt, G.; Prinzbach, H. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 1910.

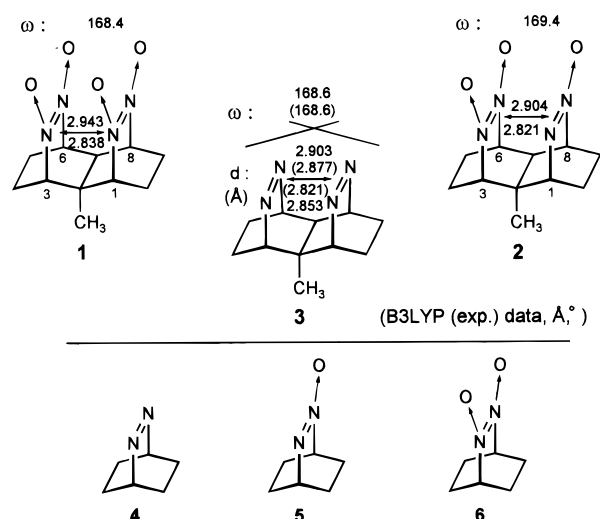
(2) For the one-/two-electron oxidation of preorganized dienes to 4C/3e and 4C/2e ions see: Prinzbach, H.; Gescheidt, G.; Martin, H.-D.; Herges, R.; Heinze, J.; Prakash, G. K. S.; Olah, G. A. *Pure Appl. Chem.* **1995**, *67*, 673; and references therein; Weber, K.; Lutz, G.; Knothe, L.; Mortensen, J.; Heinze, J.; Prinzbach, H. *J. Chem. Soc., Perkin Trans. 1* **1995**, 1991; Martin, H.-D.; Mayer, B.; Weber, K.; Prinzbach, H. *Liebigs Ann.* **1995**, 2019; Trifunac, A. D.; Werst, D. W.; Herges, R.; Neumann, H.; Prinzbach, H.; Etzkorn, M. *J. Am. Chem. Soc.* **1996**, *118*, 9444; Prakash, G. K. S. In *Stable Carbocation Chemistry*; Prakash, G. K. S., Schleyer, P. v. R., Eds.; Wiley: New York, 1997; p 137; Gescheidt, G.; Prinzbach, H.; Davies, A. G.; Herges, R. *Acta Chim. Scand.* **1997**, *51*, 174; Etkorn, M.; Wahl, F.; Keller, M.; Prinzbach, H.; Barbosa, F.; Peron, V.; Gescheidt, G.; Heinze, J.; Herges, R. *J. Org. Chem.* **1998**, *63*, 6080.

(3) Removal of electrons from such bisdiazenes occurred from *n*-orbitals to give  $\sigma$  radical cations: Prinzbach, H.; Fischer, G.; Rihs, G.; Sedelmeier, G.; Heilbronner, E.; Yang Z.-z. *Tetrahedron Lett.* **1982**, 1251; Marterer, W.; Prinzbach, H.; Rihs, G.; Wirz, J.; Lecoultrre, J.; Heilbronner, E. *Helv. Chim. Acta* **1988**, *71*, 1937.

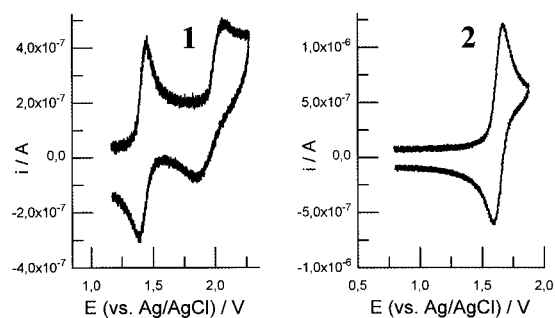
(4) The energy of the  $\pi$  orbitals increases along the series diazene > diazenoxide > diazenedioxide: Gilbert, K. E. *J. Org. Chem.* **1977**, *42*, 609; Bünzli, J. C. G.; Snyder, J. P. *J. Org. Chem.* **1977**, *42*, 614.

(5) Greer, M. L.; Sarker, H.; Mendicino, M. E.; Blackstock, S. C. *J. Am. Chem. Soc.* **1995**, *117*, 10460.

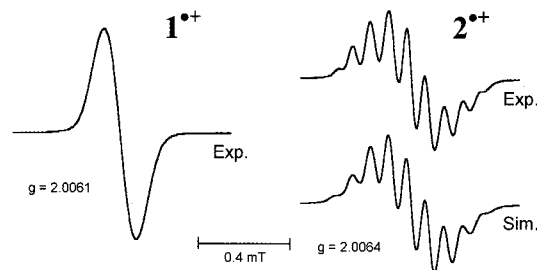
(6) Gerson, F.; Quin, X.-Z. *Helv. Chim. Acta* **1988**, *71*, 1498; Williams, F.; Guo, Q.-X.; Petillo, P. A.; Nelsen, S. F. *J. Am. Chem. Soc.* **1988**, *110*, 7887; cf. Gescheidt, G.; Lamprecht, A.; Rüchardt, C.; Schmittel, M. *Helv. Chim. Acta* **1991**, *74*, 2094.



In the CV experiments with trioxide **2** (Figure 1) the oxidation potential proved practically identical to that of **6** ( $E_{1/2}(\mathbf{2}) = 1.65 \text{ V}$ ). The ESR spectra obtained for **2** through electrooxidation in the cavity of the spectrometer (Figure 2) were satisfactorily simulated with parameters ( $^1\text{H}$  hfcfs (mT) 0.125(1H), 0.080(1H), 0.078(2H);  $^{14}\text{N}$  hfcfs 0.109(1N), 0.094(1N)) closely related to those of  $6^{+\bullet}$ ; again the small  $^{14}\text{N}$  hfcfs are typical for a  $\pi$ -type ON=NO<sup>+</sup> radical cation bearing most of its spin density on the O atoms.<sup>5</sup> This interpretation is supported by the measured *g*-factor of  $g = 2.0064$ . The radical cation of trioxide **2** is obviously best represented with the odd electron mostly localized in the ON=NO part ( $2^{+\bullet}$ ).<sup>7</sup>



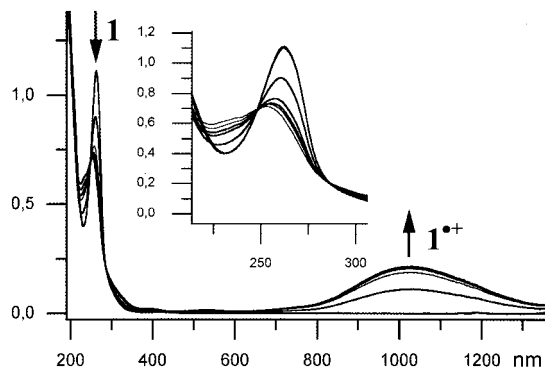
**Figure 1.** CV spectra of **1** and **2** ( $\text{CH}_3\text{CN}$ , Ag/AgCl, 0.1 M TBAPF<sub>6</sub>, 0.5 V s<sup>-1</sup>. **1**: 253 K, **2**: 298 K).



**Figure 2.** Experimental and simulated ESR spectra of **1** and **2** (bulk electrolysis **2**: TFA/ $\text{CH}_2\text{Cl}_2$ , 0.1M TBAClO<sub>4</sub>, 269 K, **1**: TFA, 0.1 M TBAPF<sub>6</sub>, 238 K).

The CV spectrum of the hardly soluble tetroxide **1** (Figure 1) exhibits two oxidation waves at  $E_{1/2}(298 \text{ K}) = 1.37$  and 1.91 V,

(7) At the B3LYP/6-31G\* level radical cation  $2^{+\bullet}$ , differently from  $1^{+\bullet}$ , is best described as a "localized" species with ca. 90% (10%) spin density on the ON=NO (ON=N) chromophore, dication  $6^{2+}$  as a loosely bound R-NO<sup>+</sup> dimer (NIMAG = 0) with a N-N distance of 1.845 Å.

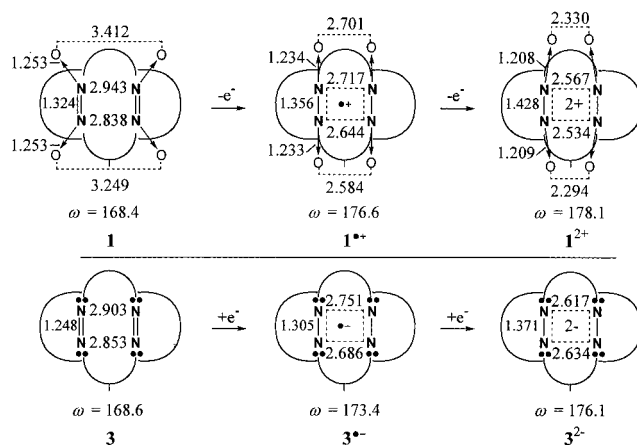


**Figure 3.** UV/IR control of the oxidation **1**  $\rightarrow$  **1<sup>•+</sup>** ( $\text{CH}_3\text{CN}$ , 1.6 V vs Ag/AgCl, 0.1 M TBAPF<sub>6</sub>, 238 K).

with the first, reversible one being shifted relative to **2** (**6**) by ca. 0.3 V to lower anodic potential; dication formation is accompanied by a follow-up process. Spectroelectrochemical measurements (Figure 3) confirmed the formation of a colorless species (**1<sup>•+</sup>**), at room-temperature somewhat more persistent (ca. 30 min) than **6<sup>•+</sup>**,<sup>5</sup> with a NIR absorption at 1020 nm as sole distinctive signal. Isosbestic points at 248 and 285 nm for oxidation and reduction indicate a neat reversible reaction. When chemical oxidation of **1**, as for **2**, had failed ( $\text{Ti}(\text{CF}_3\text{CO}_2)_3$ , DDQ/TFA/ $h\nu$ , (Ph-2,4-Br<sub>2</sub>)<sub>3</sub>N<sup>+</sup>SbCl<sub>6</sub><sup>-</sup>), ESR studies again were performed during *in situ* electrolysis (Figure 2). Independent of solvent and temperature ( $\text{CH}_3\text{CN}$ ;  $\text{CH}_3\text{CN}/\text{CF}_3\text{CO}_2\text{H}$ , 230 K;  $(\text{CF}_3)_2\text{CHOH}$ ;  $(\text{CF}_3)_2\text{CHOH}/\text{CF}_3\text{CO}_2\text{H}$ , 279 K) a single, very intense, and very narrow line was registered which could not be further resolved.

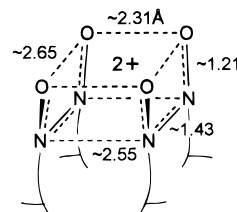
B3LYP/6-31G\* calculations<sup>8</sup> were performed for **1<sup>•+</sup>**, **1<sup>2+</sup>**, **2<sup>•+</sup>**, **4<sup>•+</sup>**, and **6<sup>•+</sup>**. While for **6<sup>•+</sup>** the <sup>1</sup>H and <sup>14</sup>N hfcs differed substantially from the experimental data,<sup>9</sup> the <sup>1</sup>H and <sup>14</sup>N hfcs of **4<sup>•+</sup>** were reproduced within 0.03 mT compared with the experiment. For **1<sup>•+</sup>** and **1<sup>2+</sup>** (Figure 4) the calculations establish their delocalized nature as novel 4N/3e and ( $\sigma$ -bishomoaromatic?) 4N/2e systems.<sup>10</sup> With the spin population in **1<sup>•+</sup>** even more concentrated at the O atoms than in **2<sup>•+</sup>**, with  $\rho(4\text{O}(3\text{O})) = 0.98$  (0.83) and  $\rho(4\text{N}) = 0.02$  (0.17) for **1<sup>•+</sup>**(**2<sup>•+</sup>**), and the nodal plane of the SOMO separating the two ON=NO units, the smaller <sup>1</sup>H and <sup>14</sup>N hfcs (smaller bandwidth) for **1<sup>•+</sup>** are plausible. To be noted, the elongation of the N=N bonds and the shortening of the transannular N,N distances upon oxidation come close to that for the reduction **3**  $\rightarrow$  **3<sup>•-</sup>**(**2<sup>-</sup>**), and the transannular N-N distance in **1<sup>2+</sup>** (average 2.55 Å) close to that of the 4C/2e dications.<sup>2</sup> For **1/1<sup>•+</sup>** the pertinent structural changes (N-O, N=N) amount to roughly half the changes calculated for **6/6<sup>•+</sup>**.<sup>6</sup>

Given the (substantial) shortening of the N-O ( $\Delta d$  ca. 0.02 Å for **1<sup>•+</sup>**, 0.02, 0.04 Å for **1<sup>2+</sup>**) and transannular O-O distances bringing O4-O10 (O5-O9) in **1<sup>•+</sup>** ( $\Delta d$  ca. 0.7 Å) and **1<sup>2+</sup>** ( $\Delta d$



**Figure 4.** B3LYP/6-31G\* structural details (Å, deg) of parents **1** and **3**, cations **1<sup>•+</sup>**/**1<sup>2+</sup>** and anions **3<sup>•-</sup>**/**3<sup>2-</sup>**.

ca. 0.3, ca. 1.0 Å) close and even below the transannular N-N and the van der Waals O-O distances, the alternative 4O4N/11e and 4O4N/10e representations with a three-dimensional cubic electron delocalization (aromaticity<sup>11</sup>) make up for intriguing speculations.



Work is in progress to explore the structural limitations for cyclic electron delocalization in cofacial bisdiazene-tetroxide ions of modified structure,<sup>12</sup> to obtain additional information through PE analyses, <sup>15</sup>N and <sup>17</sup>O NMR measurements, and, particularly for dications, through oxidations in superacid media.<sup>2</sup>

**Acknowledgment.** This work has been supported by the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie and the BASF AG.

**Supporting Information Available:** Experimental procedures and spectral data of **1** and **2** (IR, <sup>1</sup>H, <sup>13</sup>C NMR, MS) and SOMO **1<sup>•+</sup>**, HOMO **1<sup>2+</sup>** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

JA9837607

(8) Gaussian 94 (Revision E.2), Frisch, M. J. et al. Gaussian, Inc., Pittsburgh, PA, 1995. B3LYP cf. Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648; Lee, C.; Yang, W.; Parr, R. G. *Phys. Chem. B* **1998**, *37*, 785.

(9) Extensive calculations reveal that B3LYP/6-31G\* reliably describes the structure and spin density distribution of **6<sup>•+</sup>**. But B3LYP, irrespective of the basis set, fails to properly evaluate the Fermi contact interaction in ON=NO radical cations.

(10) According to model calculations on the MP2 level the delocalization in these ions is not an artifact of the hybrid functional.

(11) For the problem of three-dimensional aromaticity see: *Aromaticity and Antiaromaticity*; Minkin, V. I.; Glukhovtsev, M. N.; Simkin, B. Y., Eds.; Wiley: 1994; chapter 9, p 279. For "aromaticity" in inorganic rings see: Schleyer, P. v. R.; Jiao, H.; van Eikema Hommes, N. J. R.; Malkin, V. G.; Malkina, O. L. *J. Am. Chem. Soc.* **1997**, *119*, 12669, and references therein.

(12) Beckmann, E.; Bahr, N.; Prinzbach, H.; Rihs, G. *Tetrahedron Lett.* **1990**, *31*, 1125; Bahr, N.; Beckmann, E.; Mathauer, K.; Hunkler, D.; Keller, M.; Prinzbach, H.; Vahrenkamp, H. *Chem. Ber.* **1993**, *126*, 429; Exner, K.; Hochstrate, D.; Keller, M.; Klärner, F.-G.; Prinzbach, H. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2256; Cullmann, O.; Vögtle, M.; Stelzer, F.; Prinzbach, H. *Tetrahedron Lett.* **1998**, *38*, 2303; Exner, K.; Prinzbach, H. *J. Chem. Soc., Chem. Commun.* **1998**, 749.