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LETTERS

Cage-delocalised *syn*-periplanar bishydrazine radical cations and dications—en route to σ-bishomoaromatic $4N^{2+}$ systems?[†]

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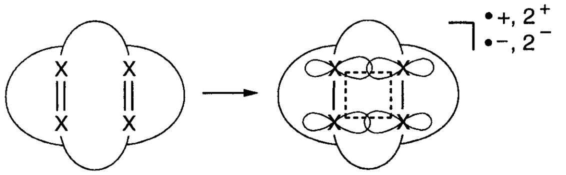
Abstract

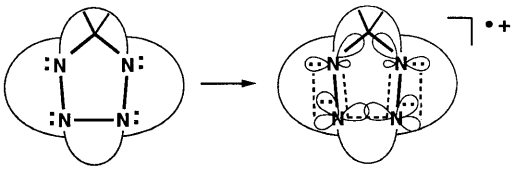
One- and two-electron oxidation of a caged, proximate, *syn*-periplanar bishydrazine leads to highly persistent, 4N/(7)6e (radical) cations—with dominant electron delocalisation along the cage bonds (CV, EPR, B3LYP). A NICS value of −20.6 is evidence for strong electron delocalisation in the caged dication.

Keywords: bishydrazines; *syn*-periplanarity; σ-bishomoconjugation; cage-delocalisation.

The construction of highly proximate, *syn*-periplanar bisdiazenes **A** (X = N) with effective σ-bishomoconjugation between the two chromophores[1] was the prerequisite for the discovery of the non-classical σ-bishomoaromatic 4N/6e dianions **B** (X = N)[2] and 4N(4O)/2e(10e) dications **B** (X = NO).[3] As with the σ-bishomoaromatic 4C/2e dications of the pagodane family **B** (X = C),[4] these ions represent borderline cases of chemical bonding.[5]



A **B**



C **D**

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[†] Dedicated to Harry H. Wasserman on the occasion of his 80th birthday—with fond memories (H.P.) of two years at Yale University (1957–59).

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In an extension of the 4N/6e project, σ-homoconjugation in the 4N radical cation generated by ^{60}Co γ-irradiation of tetrazolidine **2** in a Freon-matrix at 77 K could be demonstrated (one electron oxidation **C**→**D**; N···N bond length of 2.315 Å).[6,7] The surprisingly persistent, electronically non-stabilised **2**, together with tetra-*N*-alkyl hexahydrotetrazine (bishydrazine) **3**, had become available from the most proximate bisdiazene **1** (Fig. 1).[1a]

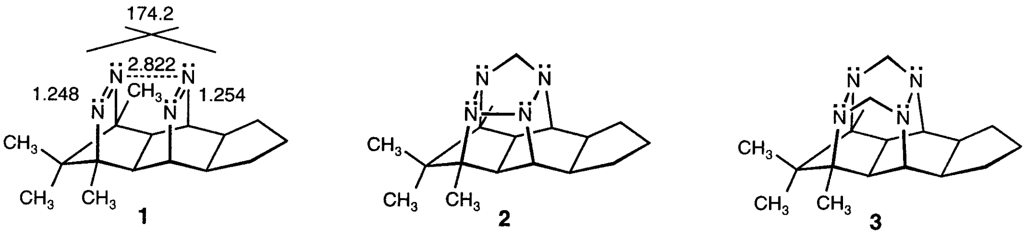
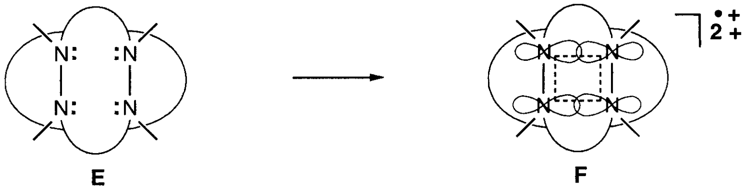


Figure 1. Substrates **1**–**3** (exp. bond lengths, distances, Å; interorbital angle ω, °)

A related and still missing, intriguing bonding motif is the σ-bishomoconjugation in 4N/(7)6e cations of type **F** expected from the oxidation of appropriately caged bishydrazines **E**.[8] For the radical cations of not constrained bishydrazines such as tetraisopropyl sym-tetrahydropyridazine ($E°=0.13$ V versus SCE; 0.135 versus $Ag^+/AgCl$) it is long known (Nelsen et al.[9]) that the charge is localised on one of the hydrazine units, that intramolecular electron transfer is slow on the EPR time scale, and that the second oxidation potential is normally higher by 0.1–0.2 V.[10]



E **F**

Subjects of this letter are the diverging course of the oxidation of **2** in solution, the one-/two-electron oxidation of hexahydrotetrazine **3**, with its rigid boat conformation a first approach towards cages **E**, the electronic structure and magnetic properties of the respective radical cation (CV, EPR, UV, DFT) and dication (CV, DFT).

While ^{60}Co γ-ionisation of **2** in matrix had led to the purple radical cation of type **D** ($\lambda_{max}=560$ nm), chemical as well as electrochemical oxidation in solution ended in a moss-green radical cation (Fig. 2, $\lambda_{max}=751$ nm) persistent for days at room temperature (CH_2Cl_2; 203–298 K; $AgBF_4$, $Tl(CF_3CO_2)_3$, or tris(3-bromophenyl) ammoniumyl hexachloroantimonate. CH_2Cl_2, $(CF_3)_2CHOH$, with or without TFA as co-solvent; 0.1 M $TBAPF_6$; 193–278 K; partial to complete consumption of **2**). The CW-EPR spectra of this green radical cation were surprisingly simple and temperature invariant (213–298 K): only splittings due to the presence of four equivalent nitrogen atoms were recorded ($a_{14N}=0.98$ mT, Fig. 2). CW-ENDOR experiments at 220 K revealed small ^{1}H hfcs of 0.13, 0.07 and 0.03 mT, too small to be resolved in the CW-EPR spectra. At 280 K ENDOR signals due to $a_{14N}=0.98$ mT emerged. The temperature dependence of the ENDOR spectra and the perfect match of the ENDOR and the CW-EPR data support the assignments. The identification of the green species as delocalised 4N/7e ion **4** found much support when the oxidation of hexahydrotetrazine **3** produced the same radical cation.[11]

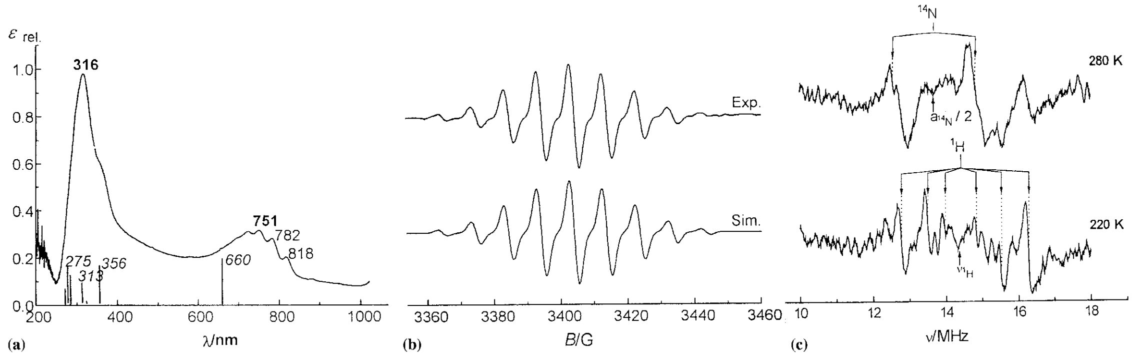


Figure 2. UV–vis spectrum (CH_2Cl_2, 213 K, SbF_6^- counter ion) (a) and EPR spectra of radical cation **4** (CW: CH_2Cl_2, 213 K, modulation 0.05 mT (b); ENDOR: CH_2Cl_2, 220/280 K (c)). The results of TD-B3LYP/6-31G* calculations are shown as vertical lines

The cyclovoltammogram of **3** (Fig. 3) reveals two reversible oxidation steps with $E_{1/2} = 0.05$ and 0.80 V; reversibility is retained at higher temperatures (273 K/0.2 V s^{-1}; 300 K/5 V s^{-1}). While the first oxidation potential lies in a range typical for monohydrazines,[8–10,12] the second one is notably high given the above cited 0.1–0.2 V range for 'independent' bishydrazines. Obviously, the two hydrazine units in **3** interact strongly.

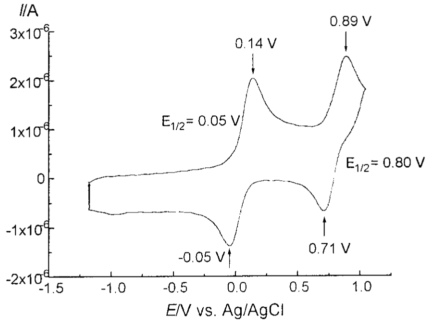


Figure 3. Cyclovoltammogram of **3**: CH_2Cl_2, 0.1 M $TBAPF_6$, 0.5 V s^{-1}, 281 K

B3LYP/6-31G* calculations[13] had been found reliable for the distinction of tight and extended radical cations derived from tetrazolidine **2**.[7,14] For radical cation **4** these calculations predict ^{14}N hyperfine coupling constants (hfcs) 1.00 and 0.95 mT (close to the not further resolved experimental 0.98 mT). The calculated ^1H hfcs of −0.16, −0.10, −0.06 and 0.04 mT reproduce the ENDOR results with sufficient accuracy. The highest occupied molecular orbitals show strong through-bond-coupling of the hydrazine units via both the methano and propano bridges (Fig. 4). An AIM analysis[15] gives no bond critical point between the nitrogens of different hydrazine units. If at all, the in-plane through-space delocalisation (σ, **F**) makes a small contribution, the interaction occurs mainly through-bond. The N–N bonds and N···N distances are comparably shortened (Fig. 5).

What about the bonding situation in the dication of **3**? Optimisation of the structure on the B3LYP/6-31G* level (Fig. 5)[14] confirms retention of symmetry and further shortening of the N–N bonds and N···N distances on the way to **5**. Again, no evidence for significant in-plane bishomoconjugation (**F**) was found from AIM population analyses.

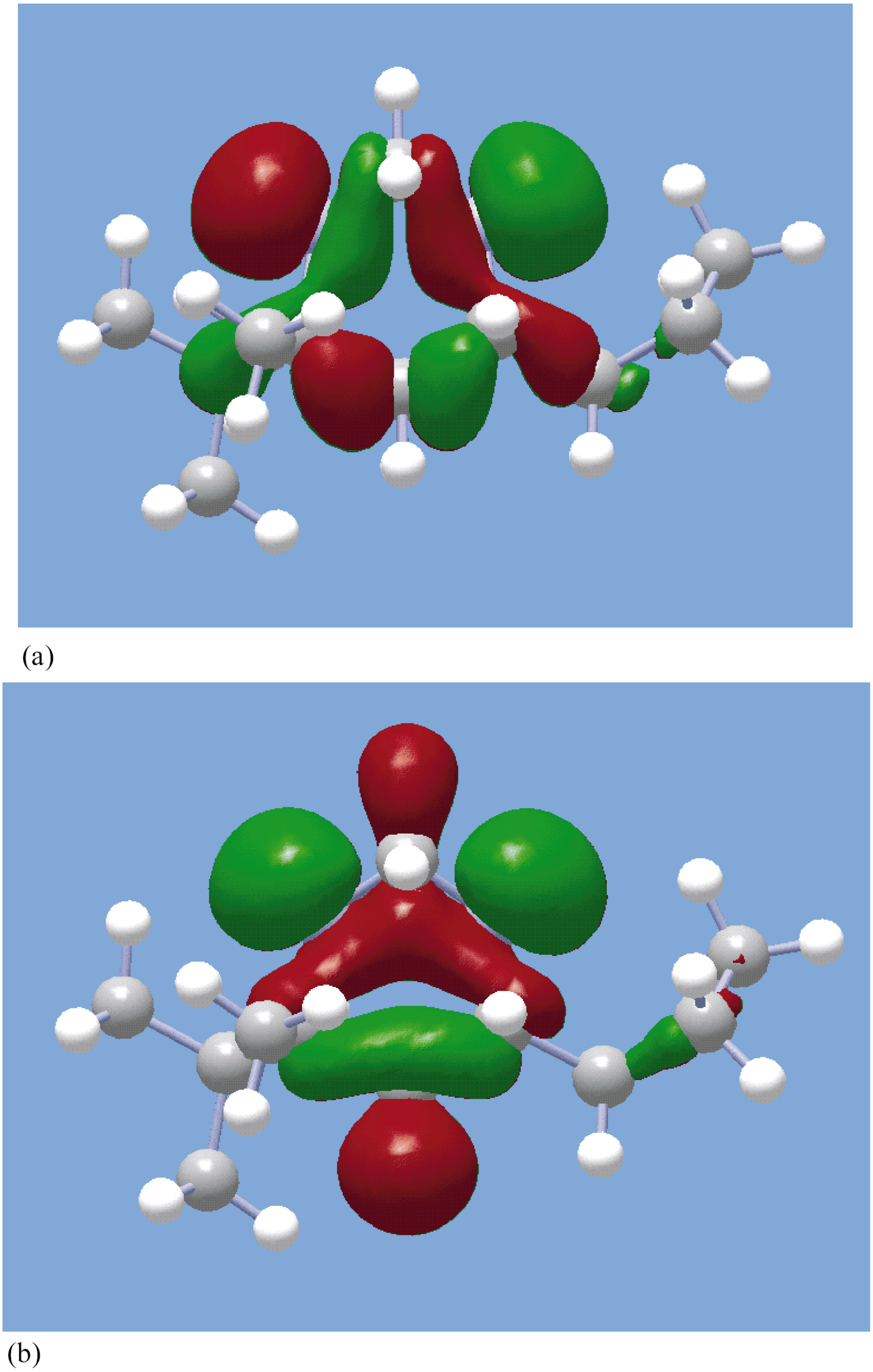


Figure 4. Calculated (a) SOMO of radical cation **4** and (b) HOMO of dication **5**

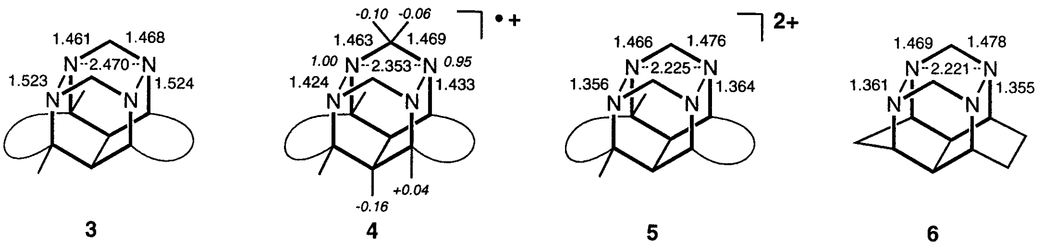


Figure 5. Geometrical parameters (Å) of neutral **3**, radical cation **4**, dication **5** (B3LYP76-31G*) and model system **6** (B3LYP/6-311+G**); calculated hyperfine coupling constants for **4** (mT)

To address the magnetic properties of dication **5**, for the model dication **6** the nucleus independent chemical shift (NICS)[16] in the geometrical centre of the four nitrogen atoms was determined (B3LYP/6-31+G*). The highly negative NICS value of −20.6 is evidence for strong electron delocalisation ('aromaticity'). Artefacts due to a high concentration of electron density at this point are excluded by the NICS value of the triplet state of **6** (−3.6) and the neutral model (+6.5, geometry of the dication retained). In these cases the NICS values are markedly more positive (no 'aromaticity' or even slight 'antiaromaticity').

The lessons from this study: (i) as in the ions **B** and **D** enforced proximity as in **1** allows the observation of a novel bonding situation, and (ii) to realise the bonding motif **F**, very strict, preparatively hardly accessible, geometrical and stereoelectronic prerequisites will have to be met.

Acknowledgements

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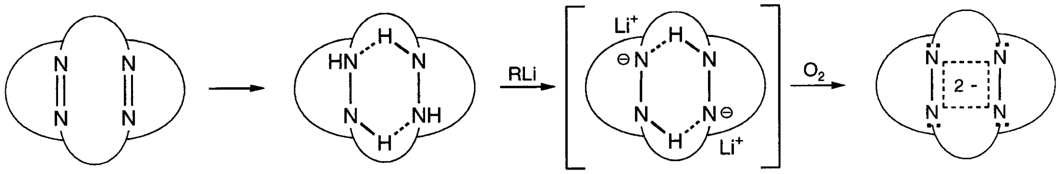
References

1. (a) Exner, K.; Fischer, G.; Bahr, N.; Beckmann, E.; Lugan, M.; Yang, F.; Rihs, G.; Keller, M.; Hunkler, D.; Knothe, L.; Prinzbach, H. *Eur. J. Org. Chem.* **2000**, 763. (b) Exner, K.; Fischer, G.; Lugan, M.; Fritz, H.; Hunkler, D.; Keller, M.; Knothe, L.; Prinzbach, H. *Eur. J. Org. Chem.* **2000**, 787.
2. (a) Exner, K.; Hunkler, D.; Gescheidt, G.; Prinzbach, H. *Angew. Chem., Int. Ed.* **1998**, *37*, 1910. (b) Exner, K.; Vögtle, M.; Prinzbach, H.; Grossmann, B.; Heinze, J.; Liesum, L.; Bachmann, R.; Schweiger, A.; Gescheidt, G. *J. Am. Chem. Soc.*, in press. It was recently found that the 4N/6e dianions **B** (X = N) are also generated through metallation of the bishydrazines (prepared by hydrogenation of the bisdiazenes **A** (X = N)) and oxidation (Geier, J.; Kegel, M.; Vögtle, M.; Exner, K.; Prinzbach, H., to be published).



3. Exner, K.; Prinzbach, H.; Gescheidt, G.; Großmann, B.; Heinze, J. *J. Am. Chem. Soc.* **1999**, *121*, 1964.
4. Prakash, G. K. S.; Fessner, W.-D.; Olah, G. A.; Lutz, G.; Prinzbach, H. *J. Am. Chem. Soc.* **1989**, *111*, 746.

5. *Aromaticity and Antiaromaticity*; Minkin, V. I.; Glukhovtsev, M. N.; Simkin, B. Y., Eds.; Wiley: New York, 1994; p. 243. Schleyer, P. v. R.; Jiao, H. *Pure Appl. Chem.* **1996**, *68*, 209–218.
6. Exner, K.; Großmann, B.; Gescheidt, G.; Heinze, J.; Keller, M.; Bally, T.; Bednarek, P.; Prinzbach, H. *Angew. Chem., Int. Ed.* **2000**, *39*, 1455.
7. Exner, K. Dissertation, University of Freiburg, 1998.
8. (a) Nelsen, S. In *Studies of Organic Molecules*; Liebmann, J. F.; Greenberg, A., Eds. Molecular structure and energetics. VCH: Weinheim, 1986; Vol. 3, p. 1–56. (b) Nelsen, S. F. In *The Chemistry of the Hydrazo, Azo and Azoxy Groups*; Patai, S., Ed.; Wiley: New York, 1997; Chapter 6.
9. Nelsen, S. F.; Hintz, P. J. *J. Am. Chem. Soc.* **1972**, *94*, 7108.
10. Nelsen, S. F.; Hintz, P. J.; Buschek, J. M.; Weisman, G. R. *J. Am. Chem. Soc.* **1975**, *97*, 4933.
11. Since with increasing concentration of **2** its oxidation becomes irreversible (CV) with concomitant formation of **3**, $\mathrm{CH}_2^{\bullet+}$ transfer from **2**$^{\bullet+}$ to **2** to form **1** and **5** is assumed. According to B3LYP/6-31G* calculations this process is exothermic by -32.2 kcal mol^{-1}.[7]
12. (a) Nelsen, S. F.; Chang, H.; Wolff, J.; Adamus, J. *J. Am. Chem. Soc.* **1993**, *115*, 12276. (b) Simonet, J.; Gueguen-Simonet, N. In *The Chemistry of the Hydrazo, Azo and Azoxy Groups*; Patai, S., Ed.; Wiley: New York, 1997; Chapter 12.
13. For geometry optimisation: Gaussian 94, Revision E.2, Gaussian Inc., Pittsburgh PA, 1995. For TD-DFT calculations: Gaussian 98, Revision A.6, Gaussian Inc., Pittsburgh, PA, 1998.
14. Note that the 'inverse symmetry breaking' effect of DFT as applied to radical cations (Bally, T.; Sastry, G. N. *J. Phys. Chem.* **1997**, *201*, 7923) does not hamper the correct description of delocalised radical cations of type **B**, **D** and **F**.
15. Bader, R. F. W. *Atoms in Molecules—A Quantum Theory*; The International series on monographs in chemistry, Vol. 22, Calderon Press: Oxford, 1995. EXTREME of the AIMPAC-program packet was used.
16. Schleyer, P. v. R.; Maerker, C.; Dransfeld, A.; Jiao, H.; Stewart, J. P. *J. Am. Chem. Soc.* **1996**, *118*, 6317.