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Stabilization of *p*-Phenylenebis(*N*-*tert*-butylaminoxyl) Relative to *p*-Benzoquinonediimine *N*,*N*′-Dioxide**

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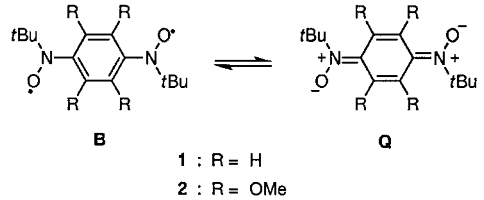
For typically triplet *m*-quinodimethane derivatives,[1, 2] recent theoretical and experimental work revealed that they can have singlet ground states when sterically and/or electronically perturbed.[3–7] We designed the diradical *p*-phenylenebis(*N*-*tert*-butylaminoxyl) **B**, which is expected to be stabilized as the closed-shell *p*-benzoquinonediimine *N*,*N*′-dioxide **Q** (Scheme 1). The synthesis, X-ray crystal structure analysis, and EPR characterization of unsubstituted **1** and its tetramethoxy derivative **2** are reported here.



Scheme 1. Equilibrium between the benzenoid (**B**) and quinonoid forms (**Q**) of **1** and **2**.

The *p* isomers were prepared, analogous to the procedure used to synthesize the triplet *m* isomers,[3] by the oxidation of the corresponding hydroxyamines with Ag_2O. The resulting orange and red powders were crystallized from diethyl ether to give orange prismatic and red bricklike crystals of **1** and **2**, respectively. The X-ray crystal structure analysis (see Experimental Section) of **1** revealed the presence of two pairs of independent molecules A and B in the unit cell. The molecular structures are very similar and have a C_2 symmetry axis at the center of the ring which is nearly coplanar with the planes of the aminoxyl groups (Figure 1, top; Table 1). In the unique molecule of **2** a C_2 axis passes through the midpoints of the C2–C3 and C2*–C3* bonds. The planes of the aminoxyl groups are almost perpenducular to the centeral ring (Figure 1, bottom). Although the two aminoxyl groups in most of the reported *m* isomers have *syn* configuration in the crystal,[2c, 3] the observed *anti* form in **2** can be rationalized

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[**] This work was supported by a Grant-in-Aid for COE Research "Design and Control of Advanced Molecular Assembly Systems" (no. 08CE2005) from the Ministry of Education, Science, Sports, and Culture, Japan.

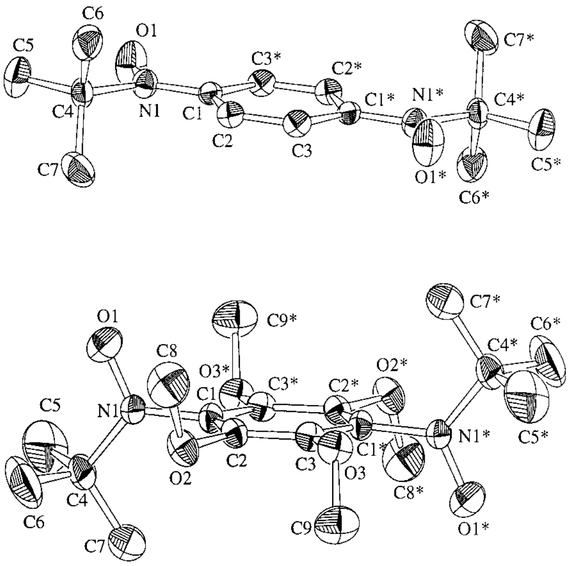

Figure 1. ORTEP drawings (ellipsoids for 50 % probability) of one of the two molecules in **1** (top) and **2** (bottom).

Table 1. Bond lengths, bond angles, and dihedral angle in **1** and **2**.

	1		**2**
	A	B	
bond lengths [Å]			
C2 – C3	1.362	1.358	1.397
C1 – C2	1.423	1.417	1.392
C1 – N1	1.354	1.362	1.428
N1 – O1	1.291	1.287	1.269
bond angles [°]			
C4-N1-O1	115.4	116.1	118.1
dihedral angle [°]			
O1-N1-C1-C2	1.2	3.4	84.5

by aligning the bulky *tert*-butyl groups and the methyl groups of the methoxy substituents alternately up and down out of the plane of the ring to avoid steric congestion. The structural difference between **1** and **2** is best demonstrated by the bond lengths of the six-membered rings (Table 1). Whereas the ring C – C bond lengths are rather uniform in **2**, the C2 – C3 bond length in **1** is clearly shorter than C1 – C2 and close to 1.344 Å for the C – C double bond in *p*-benzoquinone. Consequently, **1** and **2** are concluded to have quinonoid (**Q**) and benzenoid forms (**B**), respectively, in the crystalline state.[8]

Isomer **1** is EPR-silent in solution and in the crystal from room temperature down to cryogenic temperatures, and shows two sharp singlets at $\delta = 7.40$ and 1.68 in the ^{1}H NMR spectrum. In contrast, an EPR spectrum of **2** in toluene shows a broad signal ($\Delta H_{pp} = 30$ G) with five peaks overlapping as shoulders ($g = 2.006$ and $a_N/2 = 6.8$ G). In the solid state, a single EPR line is observed with $\Delta H_{pp} = 18$ G. In frozen toluene, **2** shows a set of signals characteristic of a triplet state with $|D/hc| = 0.013$ cm^{-1} together with one signal due to a $\Delta m_S = \pm 2$ transition at $g = 4$. By applying a point-dipole approximation to the $|D/hc|$ value, the average distance between the radical centers was estimated to be 5.78 Å; this is in adequate agreement with the value of 6.36 Å observed between the radical centers ($r_{N1N1^*-O1O1^*}$) by X-ray analysis. The dependence of the intensity I of the triplet signal at $g = 4$ on the temperature T between 10 and 100 K was determined by a plot of I versus $1/T$. Below 20 K there is a deviation downward from the linear relationship, indicating that the triplet and singlet states are nearly degenerate. Furthermore, the singlet state is the ground state, and the excited triplet state is higer in energy by 20 cal mol^{-1} or less. The molar paramagnetic susceptibility χ_{mol} of a crystalline sample of **2** was measured with a SQUID magnetometer/susceptometer in the temperature range of 2 – 300 K. The $\chi_{mol}T$ values above 60 K were constant at 0.73 emu K mol^{-1} and decreased below 60 K with decreasing temperature to become nearly zero at 2 K. The observed temperature profile reveals that a singlet ground state is present. The values above 60 K are in good agreement with theoretical value of 0.75 emu K mol^{-1} calculated for a diradical having degenerate singlet – triplet states or isolated spins. A Bleaney – Bowers equation for an singlet – triplet model[9] fit the experimental data reasonably well to give a singlet ground state; the lowest excited triplet lies 14.7 ± 0.12 cal mol^{-1} higher in energy.[10]

The UV/Vis spectra of **1** and **2** in CH_2Cl_2 measured at room temperature were completely different from each other. Strong and broad absorptions were observed at $\lambda_{max} = 404$ nm ($\varepsilon = 8.8 \times 10^4$) for **1** ($\lambda_{max} = 403$ nm ($\varepsilon = 6.6 \times 10^4$) for the *N-sec*-butyl derivative[11a]) due to the quinonoid form and at $\lambda_{max} = 483$ nm ($\varepsilon = 550$) for **2** due to the *N*-arylaminoxyl radical.

All this information leads to the conclusion that **1** has only the **Q** form[11] in solution as well as in the crystalline state. The energy gained by aromatization does not appear to be enough to stabilize the **B** form. In the *p* isomer, which has no barrier to rotation about the C1 – N1 bond, the planar structures **1**-**Q** and **1**-**B** should be considered as resonance hybrids rather than isomers in the equilibrium shown in Scheme 1; this equilibrium is predominantly directed to the **1**-**Q** form. Isomer **2**, which has a large torsion angle, has only the **B** form in solution as well as in the solid state. Therefore, the stability of the **B** form in solution depends on the magnitude of the torsion of the aminoxyl radicals; the **B** form can only be stabilized when there is a barrier to acheiving the coplanar structure.[12] The analogous 2,5-dimethoxy-*p*-phenylenebis(aminoxyl) diradical, which is expected to have a much lower barrier to rotation than **1**, has the **Q** form in the solid state, but is able to equilibrate between the **B** and **Q** forms in solution and is EPR-active.[12, 13]

In summary, stabilization of the diradical **B** form relative to the **Q** form has been achieved by steric effects in the case of the *p* isomer. Subtle changes in the total number of electrons[14] as well as electronic and steric effects of the substituents are concluded to tune the **B** – **Q** equiliblium and similar tautomerisms.

Experimental Section

1:[11] *p*-Dibromobenzene (1.0 g, 4.23 mmol) in Et_2O was lithiated with a 1.64 M solution of *tert*-butyllithium (10 mL, 16.4 mmol) at −78 °C and then treated with 2-methyl-2-nitrosopropane (0.92 g, 10.6 mmol). The reaction mixture was stirred for 1 h at −78 °C and then left overnight at room temperature. The crude hydroxyamine, containing a small amount of the corresponding oxidized product, was obtained as a pale yellow solid (1.05 g, ca. 60 % yield). This solid (0.53 g, 2.1 mmol) was oxidized without further purfication with freshly prepared Ag_2O (1.42 g) in CH_2Cl_2 to afford an orange precipitate (0.21 g, 0.84 mmol, 40%). Recrystallization from Et_2O gave **1** as orange prisms. M.p. 200–202 °C, ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 7.40$ (*s*, 4H), 1.68 (*s*, 18H); FAB-MS (*m*-nitrobenzyl alcohol matrix): *m*/*z* 252 $[M^+ + 2]$; elemental analysis calcd for $C_{14}H_{22}N_2O_2$: C 67.17, H 8.86, N 11.19; found: C 67.22, H 8.85, N, 11.17. Crystal data: $C_{14}H_{22}N_2O_2$, $M_r = 250.34$, monoclinic, space group $P2_1/c$ (no. 14) $a = 10.572(1)$, $b = 11.829(2)$, $c = 11.658(2)$ Å, $\beta = 96.720(8)°$, $V = 1447.9(3)$ Å^3, $T = 296$ K, $Z = 4$, $\rho_{calcd} = 1.148\ g\,cm^{-3}$, $\mu(Cu_{K\alpha}) = 6.16\ cm^{-1}$; of 2417 total reflections, 2281 were independent; $R = 0.081$ and $R_w = 0.100$ for 1754 reflections with $I > 3\sigma(I)$.[15]

2: 1,2,4,5-Tetramethoxybenzene (1.0 g, 5.3 mmol) in Et_2O (60 mL) was lithiated with a 1.6 M solution of *n*-butyllithium (19.3 mL, 32.0 mmol) in the presence of TMEDA (7.7 g, 66 mmol) at −78 °C and then treated with 2-methyl-2-nitrosopropane (5.5 g, 63.2 mmol). The reaction mixture was stirred for 1 h at −78 °C and then left overnight at room temperature. The crude hydroxyamine, containing a small amount of the corresponding diradical, was obtained as a brown solid (0.44 g, ca. 23% yield) and oxidized as for **1**. Recrystallization from Et_2O gave **2** as red bricklike crystals. M.p. 252 °C; FAB-MS (*m*-nitrobenzyl alcohol matrix): *m*/*z* 372 $[M^+ + 2]$; elemental analysis calcd for $C_{18}H_{30}N_2O_6$: C 58.36, H 8.16, N 7.56; found: C 58.61, H 8.13, N 7.50. Crystal data: $C_{18}H_{30}N_2O_6$, $M_r = 370.44$, triclinic, space group $P\bar{1}$ (no. 2) $a = 19.087(2)$, $b = 19.288(2)$, $c = 6.261(2)$ Å, $\alpha = 92.89(2)$, $\beta = 106.48(2)$, $\gamma = 86.48(2)°$, $V = 504.4(2)$ Å^3, $T = 296$ K, $Z = 1$, $\rho_{calcd} = 1.217\ g\,cm^{-}$, $\mu(Cu_{K\alpha}) = 7.55\ cm^{-1}$; of 1604 total reflections, 1493 were independent; $R = 0.071$ and $R_w = 0.084$ for 1240 reflections with $I > 3\sigma(I)$. The structure was solved by direct methods, and the refinement converged with the full-matrix least-squares method of the TEXSAN program (version 1.6, Molecular Structure Corporation).[15]

Received: December 8, 1997 [Z11239IE]
German version: *Angew. Chem.* **1998**, *110*, 1645–1647

Keywords: aminoxyls · aromaticity · magnetic properties · quinonediimines · radicals

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Adaptation of the Barton Reaction to Carborane Chemistry: The Synthesis and Reactivity of 2-Hydroxyimino-1-hydroxymethylnona-*B*-methyl-1,12-dicarba-*closo*-dodecaborane(12)**

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M. Frederick Hawthorne*

In memory of Sir Derek H. R. Barton

Recently, we reported the synthesis of deca-*B*-methyl-1,12-dicarba-*closo*-dodecaborane(12) (**1**) by electrophilic methylation of 1,12-dicarba-*closo*-dodecaborane(12) with methyl trifluoromethanesulfonate (methyltriflate). Permethylated 1,12-dicarba-*closo*-dodecaborane(12) (**2**) was obtained by a similar method from 1,12-dimethyl-1,12-dicarba-*closo*-dodecaborane(12).[1] Since this initial report, preparations of other permethylated polyhedral boranes have appeared.[2, 3] These results, and those to follow, establish “camouflaged” carboranes (and similarly constituted polyhedral boranes) as a new branch of polyhedral borane chemistry with compounds that show novel structure–reactivity relationships and new applications in chemistry. Species **1** and **2** provide a unique hydrocarbon surface due to their methyl substituents. This lipophilic surface offers excellent solubility and improved stability and, most importantly, it allows chemical transformations at the boron cluster surface which are independent

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[**] This work was supported by the National Science Foundation (grant CHE9314037).