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[2.2.2.2]Pagodane: Synthesis and Oxidation of Nonclassical Valence-Isomeric 4C/3e and σ-Bishomoaromatic 4C/2e Ions

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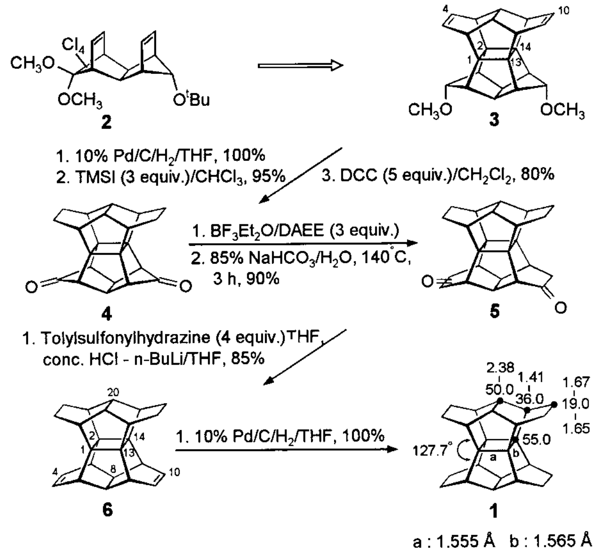
The discovery of a highly persistent 4C/3e radical cation[1] and a σ-bishomoaromatic 4C/2e dication[2] upon oxidation of the [1.1.1.1] pagodane (stationary points on [2 + 1]- and [2 + 0]-cycloaddition reaction coordinates[3,4]) has triggered modifications of the cage skeleton surrounding the central cyclobutane ring; e.g., by functionalization/homologation or by 90° rotation of "half" of the molecular skeletons[1,4−6]—with significant consequences with respect to stability, persistence, and behavior of the respective radical cations and dications.[7,8] This paper deals with the synthesis of the [2.2.2.2]pagodane, its one- and two-electron oxidation,[9] and the nature of the respective ions.

The synthesis of **1** (Scheme 1) follows closely the one developed for 4,9,14,19-tetrafunctionalized pagodanes (original aldol route to dodecahedranes[10]), with the isodrin analogue **2** as starting material. The highly strained, rigid **1** is thermally highly persistent, it melts unchanged at 213 °C. At room temperature, D_{2h} symmetry is manifested by four ^{1}H and ^{13}C NMR signals; in the preliminary X-ray structure the cyclobutane bonds are of similar length. Unfortunately, diene **7** much desired for ESR and CV comparison, could not be obtained from **1**: The sequence of bromine addition/bromine elimination[7] and isomerization by photoinduced electron transfer (PET) proved impossible.

Scheme 1



According to DFT calculations (B3LYP/6-31G*)[11] (Figures 1 and 2) cleaving of the a bonds in **1** to give diene **7** is thermodynamically more favorable than of the b bonds to give diene **8**. Similarly, the cyclobutanoid "tight" radical cation $\mathbf{1a}^{\bullet+}$ and the "extended" radical cation $\mathbf{7}^{\bullet+}$ are more stable than $\mathbf{1b}^{\bullet+}$ **and** $\mathbf{8}^{\bullet+}$. This is in contrast to the observations with the [1.1.1.1]-/[2.2.1.1]pagodanes.[1,7] Distinction between these radical cations should be possible by ESR spectroscopy: In $\mathbf{1a}^{\bullet+}$ and $\mathbf{7}^{\bullet+}$—with the C_β-H_β bonds lying almost within the nodal planes orthogonal to the a bonds in the SOMO—the H_β hyperfine coupling constant ($a_{H\beta}$) should be vanishingly small. In $\mathbf{1b}^{\bullet+}$ and $\mathbf{8}^{\bullet+}$—with the π-system extending mainly in the direction of the b-bonds—$a_{H\beta}$ should be relatively large (cf. $a_{H\beta} = 1.544$ mT in case of the [1.1.1.1] ion[1]); $a_{H\gamma}$ and $a_{H\gamma'}$ should be larger in $\mathbf{1a}^{\bullet+}$ and $\mathbf{7}^{\bullet+}$ than in $\mathbf{1b}^{\bullet+}$ and $\mathbf{8}^{\bullet+}$. The ESR spectra together with ENDOR and general TRIPLE measurements (Figure 3) indeed confirmed the calculations: The radical cation generated by ^{60}Co irradiation of **1** in a Freon ($CFCl_3$) matrix at −196 °C gives rise to a very narrow ESR signal; the spectral width of the radical cation prepared at −20 °C in fluid solution (CH_2Cl_2, $Tl(CO_2CF_3)_3$) is even less—the assignments as "tight" $\mathbf{1a}^{\bullet+}$ ($d_a \cong 1.75$ Å), with the prominent a_H of 0.582 mT due to the eight symmetry-equivalent γ'-hydrogens, and as "extended" $\mathbf{7}^{\bullet+}$ ($d_a \cong 2.6$ Å), with generally only very small hfc's, were straightforward; still, the D_{2h} symmetries implied are only established within the ESR time scale.

In the multisweep cyclic voltammogram registered at low temperature and a scan rate of 0.5 V/s (Figure 4), the

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(1) Prinzbach, H.; Murty, B. A. R. C.; Fessner, W.-D.; Mortensen, J.; Heinze, J.; Gescheidt, G.; Gerson, F. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 457.

(2) Prakash, G. K. S.; Krishnamurthy V. V.; Herges, R.; Bau, R.; Yuan, H.; Olah, G. A.; Fessner, W.-D.; Prinzbach, H. *J. Am. Chem. Soc.* **1988**, *110*, 7764. Herges, R.; Schleyer, P. v. R.; Schindler, M.; Fessner, W.-D. *J. Am. Chem. Soc.* **1991**, *113*, 3649.

(3) Bauld, N. L. *Tetrahedron* **1989**, *45*, 5307. Roth, H. D. *Top. Curr. Chem.* **1992**, *163*, 131. Jungwirth, P.; Carsky, P.; Bally, T. *J. Am. Chem. Soc.* **1993**, *115*, 5776. Jungwirth, P.; Bally, T. *Ibid.* **1993**, *115*, 5776.

(4) Gescheidt, G.; Herges, R.; Neumann, H.; Heinze, J.; Wollenweber, M.; Etzkorn, M.; Prinzbach, H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1016.

(5) Pracht, T.; Weber, K.; Fritz, H.; Knothe, L.; Prinzbach, H. *J. Chin. Chem. Soc.* **1994**, *41*, 1.

(6) Prinzbach, H.; Wollenweber, M.; Herges, R.; Neumann, H.; Gescheidt, G.; Schmidlin, R. *J. Am. Chem. Soc.* 1**995**, *117*, 1439.

(7) Prinzbach, H.; Gescheidt, G.; Martin, H.-D.; Herges, R.; Heinze, J.; Prakash, G. K. S.; Olah, G. A. *Pure Appl. Chem.* **1995**, *67*, 673. 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.

(8) Trifunac, A. D.; Werst, D. W.; Herges, R.; Neumann, H.; Prinzbach, H.; Etzkorn, M. *J. Am. Chem. Soc.* **1996**, *118*, 9444. Cf. Quin, X.-Z.; Trifunac, A. D.; Eaton, P. E.; Xiong, Y. *Ibid.* **1991**, *113*, 669.

(9) Wahl, F. Dissertation, University of Freiburg, 1993. Etzkorn, M. Dissertation, University of Freiburg, 1998.

(10) Melder, J.-P.; Prinzbach H. *Chem. Ber.* **1991**, *124*, 1271.

(11) Gaussian 92, Revision B: Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Repogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. Gaussian, Inc., Pittsburgh, PA, 1992. Spin projection method: Schlegel, H. B. *J. Chem. Phys.* **1986**, *84*, 4530. Geometry optimizations were performed using the symmetry constraints indicated. The minima could not be checked by a fequency analysis because of the size of the systems. At the semiempirical PM3 level the radical cation structures are true minima with a distortion of the rectangular 4C/3e system toward a trapezoid geometry being the lowest (positive) normal mode. Such a distortion of the pagodane radical cation structures could also be excluded at the UHF und UB3LYP level, corresponding structures upon optimization adopt the more symmetrical rectangular geometry.

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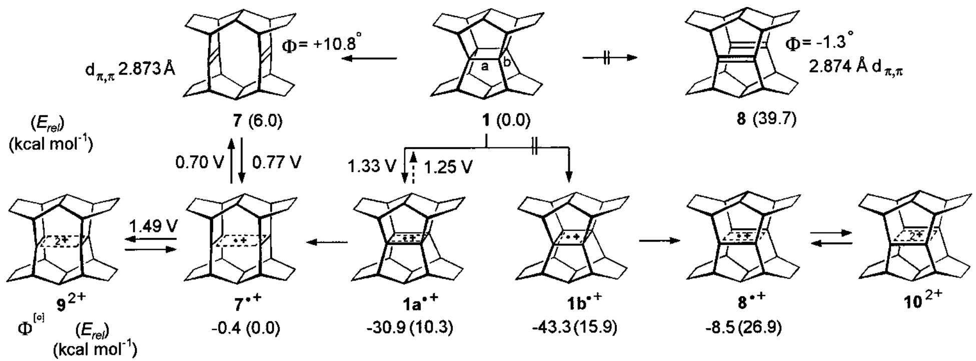

		exp.	B3LYP	6-31G*		exp.	B3LYP	6-31G*		B3LYP		B3LYP
d_a :			2.646	2.510			1.757	1.750		1.503		1.380
d_b :			1.385	1.362			1.505	1.490		1.743		2.619
$a_{H\beta}$:	$7^{\bullet+}$	0.011	- 0.002	+0.007	$1a^{\bullet+}$	0.060	-0.031	-0.031	$1b^{\bullet+}$	+1.658	$8^{\bullet+}$	+1.148
$a_{H\gamma}$:		0.034	- 0.039	- 0.038		0.060	-0.034	-0.035		+0.002		-0.022
$a_{H\gamma'}$:		+0.011	+0.164	+0.186		0.582	+0.627	+0.575		+0.038		+0.002
$a_{H\gamma''}$:		- 0.167	- 0.167	- 0.152		<0.05	+0.018	+0.026		-0.040		+0.086

Figure 1. Selected structural data (Φ: outside (+)/ inside (−) pyramidalization of the central carbons), relative energies (B3LYP/6-31G*),[11] oxidation/reduction potentials (V), and experimental and calculated hfc's (mT).

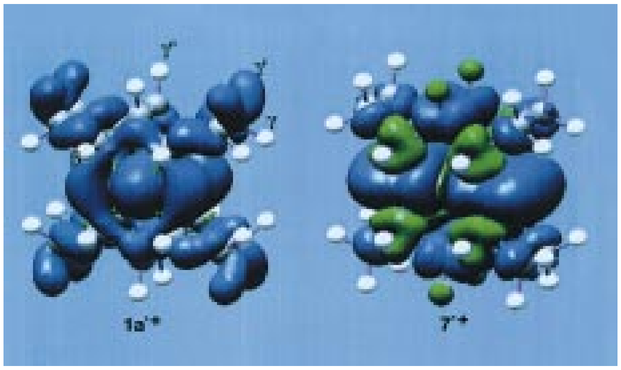

Figure 2. Spin density plots (B3LYP/6-31G*) (isosurface at 0.0015).

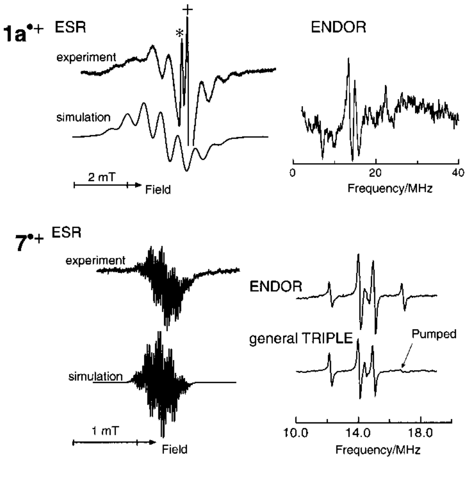

Figure 3. ESR, ENDOR, and general TRIPLE spectra of $1a^{\bullet+}$ ($CFCl_3$ matrix, −196 °C, ^{60}Co) and $7^{\bullet+}$ (CH_2Cl_2, −20 °C, $Tl(CF_3CO_2)_3$); simulations with the data of Figure 1. The marked signals in the spectrum of $1a^{\bullet+}$ stem from paramagnetic impurities in the quartz tube and presumably from $7^{\bullet+}$ present in low concentration, respectively.

inflection at 1.33 V marks the oxidation $1 \rightarrow 1a^{\bullet+}$ (half-life ca. 10^{-1} s), which very rapidly[8] expands into $7^{\bullet+}$. The latter is oxidized (1.49 V) to what is most probably the σ-bishomoaromatic dication 9^{2+} (ECE). Reduction leads via $7^{\bullet+}$ (0.70 V) to diene **7**, which then is oxidized (0.77 V) to $7^{\bullet+}$.[12] The reduction peak at 1.22 V presumably manifests the reduction of still present $1a^{\bullet+}$ to **1** (under modified conditions a shoulder at ca. 1.4 V is probably due to the reduction $9^{2+} \rightarrow 7^{\bullet+}$). Only very slowly does a side reaction build up (reduction peak at ca. 0.1 V). For the [1.1.1.1]-/[2.2.1.1]-pagodanes a second reversible oxidation wave had not been observed.[7]

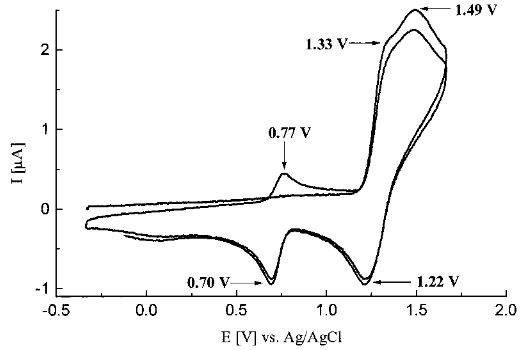

Figure 4. Multisweep cyclic voltammogram (CH_2Cl_2, 0.1 M $TBAPF_6$, 0.5 V/s, vs Ag/AgCl, −50 °C); peak potentials (V).

With a significant persistence of a dication, presumably 9^{2+}, being disclosed and with experimental structural data for a σ-bishomoaromatic dication still lacking, activities are being directed at the generation and spectroscopic characterization of 9^{2+} to its interception as access to the diene **7** (and its ions) and to its isolation with the help of an appropriate counterion.

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Supporting Information Available: Experimental procedures and spectral data of the new products of Scheme 1 (IR, ^1H, ^{13}C NMR, MS) (4 pages).

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[12] The half-wave potential of diene **7** (0.73 V) nicely corresponds to that of a recently published, structurally similar [4]beltene derivative ($d_{\pi,\pi}$ = 2.92 Å, $E_{1/2}$ = 1.27 V, correction for the anhydride ring ca. 0.4 V): Grimme, W.; Geich, H.; Lex, J.; Heinze, J. *J. Chem. Soc., Perkin Trans. 2* **1997**, 1955.