ORGANIC LETTERS

2005
Vol. 7, No. 9
1861−1863

Perchloro-2,5,8-triazaphenalenyl Radical

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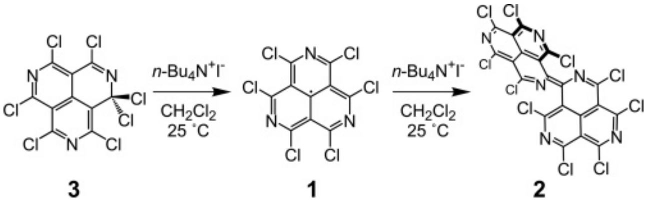
Received March 16, 2005

ABSTRACT



The unusually stable perchloro-2,5,8-triazaphenalenyl radical 1 and its twisted dechlorinated dimer 2 were synthesized and characterized by ESR spectroscopy and X-ray crystallography. The X-ray structure of dimer 2 shows that the double bond connecting the two triazaphenalene systems is strongly twisted. Dimer 2 has a dramatic color shift from the solid state to solution, which may be due to a change of the twisting angle between both states.

Neutral π-radicals such as the phenalenyl radicals have received much attention in the field of molecular materials.[1] The phenalenyl radical and its derivatives were predicted as potential neutral organic molecular conductors by Haddon.[2] Several stable phenalenyl radical derivatives have been reported, e.g., the 2,5,8-tri-*tert*-butyl-phenalenyl, perchlorophenalenyl, and 2,5,8-tri-*tert*-butyl-1,3-diazaphenalenyl radicals.[3] A remarkable bistable spirobiphenalenyl radical was obtained by linking two phenalenyl units through a boronate bridge.[3d−f] The perchlorophenalenyl radical is paramagnetic at most temperature ranges.[3b] On the other hand, the 2,5,8-tri-*tert*-butylphenalenyl and 2,5,8-tri-*tert*-butyl-1,3-diazaphenalenyl radicals form strongly antiferromagnetically coupled π-dimers in the solid state.[3a,c]

We have proposed using the 2,5,8-triazaphenalenyl radical system as a novel bridging ligand for building ferromagnetic materials.[4] We report here on the synthesis and magnetic properties of the first 2,5,8-triazaphenalenyl radical derivative, the perchloro-2,5,8-triazaphenalenyl radical **1** (PTAZ).

The PTAZ radical **1** was synthesized in five steps from diethyl 1,3-acetonedicarboxylate (Scheme 1):[5] Condensation with triethyl orthoformate in the presence of urea as an NH_3 source (xylene, 3 h, reflux) resulted in the formation of diethyl 4-oxo-1,4-dihydro-3,5-pyridinedicarboxylate (**4**) in 92% yield. After failure to condense pyridone **4** directly with malononitrile, it was converted with $POCl_3$ to diethyl 4-chloro-3,5-pyridine dicarboxylate (**5**),[6] which reacted with the potassium salt of malononitrile to give product **6** in 50% yield. Compound **6** underwent chlorination and cyclization in one pot by solid-state reaction with PCl_5 and $Me_4N^+Cl^-$ to afford 1,1,3,4,6,7,9-heptachloro-2,5,8-triazaphenalene (**3**)

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(1) For a recent overview, see: *Magnetic Properties of Organic Materials* Lathi, P. M., Ed.; Marcel Dekker: New York, 1999; pp 1−728.

(2) Haddon, R. C. *Nature* **1975**, *256*, 394−396.

(3) (a) Goto, K.; Kubo, T.; Yamamoto, K.; Nakasuji, K.; Sato, K.; Shiomo, D.; Takeji, T.; Kubota, M.; Kobayashi, T.; Yakusi, K.; Ouyang, J. *J. Am. Chem. Soc*. **1999**, *121*, 1619−1620. (b) Koutentis, P.; Chen, Y.; Cao, Y.; Best, T.; Itkis, M.; Beer, L.; Oaklay, R.; Cordes, A.; Brock, C.; Haddon, R. *J. Am. Chem. Soc*. **2001**, *123*, 3864−3871. (c) Morita, Y.; Aoki, T.; Fukui, K.; Nakazawa, S.; Tamaki, K.; Suzuki, S.; Fuyuhiro, A.; Yamamoto, K.; Sato, K.; Shiomi, D.; Naito, A.; Takui, T.; Nakasuji, K. *Angew. Chem., Int. Ed*. **2002**, *41*, 1793−1796. (d) Itkis, M. E.; Chi, X.; Cordes, A. W.; Haddon, R. C. *Science* **2002**, *296*, 1443−1445. (e) Miller, J. S. *Angew. Chem., Int. Ed.* **2003**, *42*, 27−29. (f) Liao, P.; Itkis, M. E.; Oakley, R. T.; Tham, F. S.; Haddon, R. C. *J. Am. Chem. Soc*. **2004**, *126*, 14297−14302.

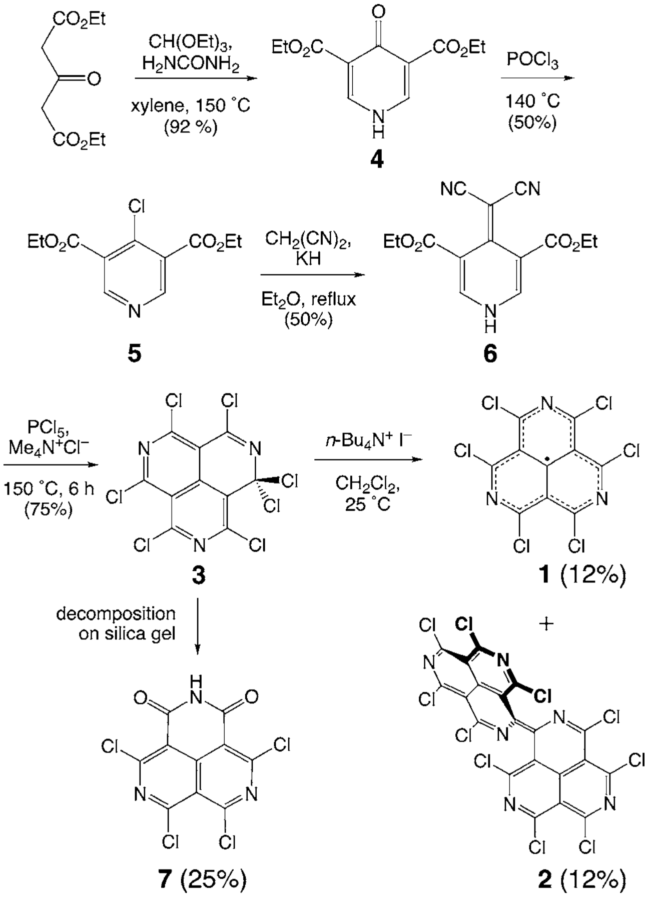
(4) Zheng, S.; Lan, J.; Khan, S.; Rubin, Y. *J. Am. Chem. Soc*. **2003**, *125*, 5786−91.

(5) See Supporting Information.

(6) Barluenga, J.; Gonzalez, F.; Carlon, R.; Fustero, S. *J. Org. Chem.* **1991**, *56*, 6751−6754.

10.1021/ol050570+ CCC: \$30.25

Scheme 1. Synthesis of the PTAZ radical **1**



(75% yield) as a rather moisture-sensitive compound readily undergoing decomposition to imide **7** in solution. Compound **3** is rapidly reduced with n-$Bu_4N^+I^-$ in CH_2Cl_2 to the perchloro-2,5,8-triazaphenalenyl radical **1** and varying amounts of its dechlorinated dimer **2**. The PTAZ radical **1**, as an iminium chloride and phenalenyl radical, is unusually stable and lends itself to purification by normal procedures. Both dark blue compounds can be separated without noticeable decomposition by column chromatography (SiO_2, CH_2Cl_2/hexanes 2:1) and are much less sensitive to hydrolysis than compound **3**.

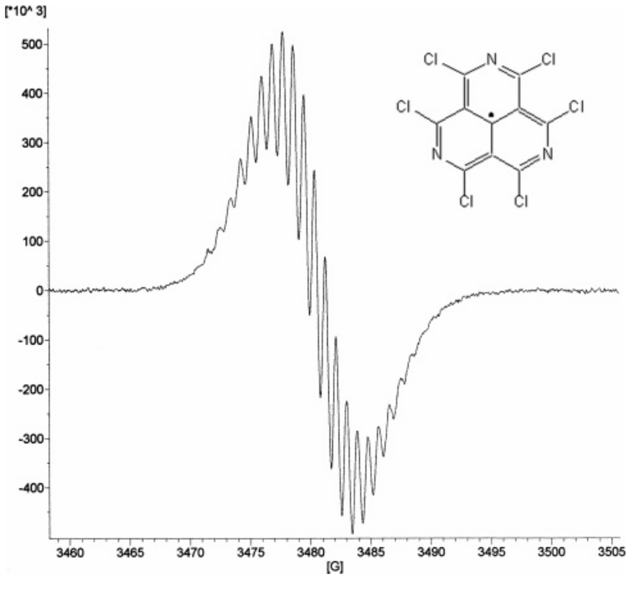


Figure 1. ESR spectrum of the PTAZ radical **1**.

The perchloro-2,5,8-triazaphenalenyl radical **1** was characterized by ESR (Figure 1) and mass spectroscopy. The g-factor for the PTAZ radical **1** at 20 °C in CH_2Cl_2 is 2.0059, slightly larger than that of a carbon-based radical, due to spin density partially delocalized over the chlorine substituents. The well-resolved ESR spectrum derives from hyperfine interactions of the free electron with chlorine and nitrogen isotopes. Line shape analysis gives hyperfine coupling constants of $a(^{35}Cl) = 0.89$ G, $a(^{37}Cl) = 0.74$ G, and $a(N) = 1.8$ G. In the high-resolution mass spectrum (EI), the experimental isotopic distribution pattern is exactly the same as the theoretical pattern.[5]

The magnetic susceptibility of PTAZ (**1**) was studied by SQUID magnetometry in an applied field of 1 kOe (Figure 2) from 2−300 K. The susceptibility data were fit to the modified Curie−Weiss equation $\chi(T) = \chi_0 + C/(T - \theta)$. The fit gives the parameters χ_0, C, and θ: χ_0 reflects a T-independent contribution ($3.7 \pm 0.2 \times 10^{-4}$ emu/mol); the Curie constant C gives an effective moment $\mu_{eff} = 0.46 \pm 0.09\ \mu_B$; and the Weiss temperature $\theta = -2.01 \pm 0.16$ K. Qualitatively, the fit accounts for the temperature dependence of χ over the whole temperature range, and the small value of θ indicates that the overall coupling is weakly antiferromagnetic. The small value of C indicates that the radical **1** tends to form a π-dimer in the solid state in a fashion similar to the 2,5,8-tri-*tert*-butylphenalenyl, 2,5,8-tri-*tert*-butyl-1,3-diazaphenalenyl, and 1,3,2-dithiazolyl radicals, to quench paramagnetism.[3a,c,7] The abnormal deviation from the fit

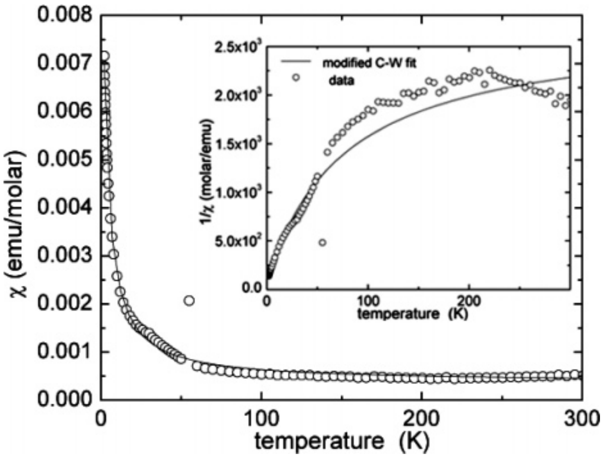


Figure 2. Temperature dependence of the magnetic susceptibility of PTAZ radical **1**.

above 210 K reflects a phase transition, which is likely due to the dissociation of the π-dimer pair of radical **1**.

The formation of compound **2** by dimerization of radical **1** and subsequent dechlorination is induced by excess of n-$Bu_4N^+I^-$. The lesser steric hindrance of the PTAZ radical **1** over that of the perchlorophenalenyl radical[3b] is partially at the origin of this higher reactivity, but the irreversible dechlorination step to the C═C bonded dimer is ensured by conjugate iodide reduction.

Single crystals of dimer **2** were obtained by recrystallization from CH_2Cl_2/n-hexane at −10 °C.[8] The X-ray structure (Figure 3) indicates that the C(1)−C(1A) double bond between the two triazaphenalenyl units, at 1.373 Å, is significantly distorted and bent, while being slightly elongated compared to a normal C═C bond (1.32 Å) due to steric repulsion between the phenalenyl units. While the naphthyridine moieties in dimer **2** remain planar, the two bonded six-membered rings are strongly bent: The torsional angle N(3)−C(1)−C(2)−C(3) is −150°, 30° away from planar. This distortion is even more apparent in the cell packing structure,[5] in which dimer **2** stacks in columns of this "butterfly-shaped" molecule. There are significant $\pi-\pi$ stacking contacts (3.60 Å average C−C distance) within the stacks and close Cl−Cl contacts between molecular stacks.

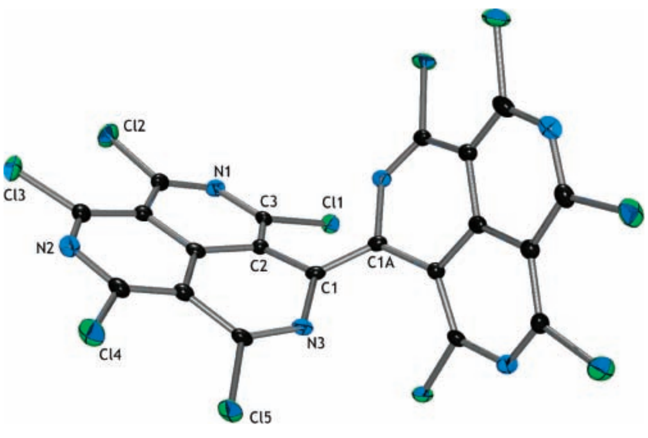


Figure 3. X-ray crystal structure of dimer **2**.

Interestingly, dimer **2** is reddish in the crystal but turns immediately deep blue upon dissolution, as seen from a very strong broad band centered at 680 nm (ϵ 12 700).[5] This color change may be due to an increase of bond distortion in solution or even free rotation of the strained, central C═C bond. Although the latter cannot be confirmed by ESR, which is silent and possibly due to a ground-state singlet biradical,[9] there is similar precedent in bianthrones,[10] octachlorofulvalene,[11] and perchlorobifluorenylidene.[12] These systems either undergo strong color change upon conformational or bond isomerization[13] or are deeply colored in the ground state. Both arise from the lowering of the HOMO−LUMO energy separation occurring upon axial distortion/elongation of a C═C bond.

Cyclic voltammography of PTAZ radical **1**, as well as its dimer **2** (CH_2Cl_2, 0.1 M n-$Bu_4N^+PF_6^-$, Ag wire as a pseudoreference, vs Fc/Fc^+), shows that the chlorine substituents and nitrogen atoms substantially increase the electron affinity of these compounds, for example, compared to 2,5,8-tri-*tert*-butylphenalenyl.[3a] Radical **1** has a reversible reduction wave at −0.25 V (vs Fc/Fc^+) and an irreversible oxidation wave at 1.10 V. Dimer **2** shows two reduction waves at −0.31 and −0.64 V, respectively, but no oxidation wave between 0 and +1.5 V. This shows that dimer **2** can successively accept two electrons to generate a radical anion and dianion to relieve strain in the bridging double bond.

Further derivatization of chlorinated precursor **3** with aryl and alkynyl groups, as well as with fluorine-, sulfur-, and oxygen-based substituents, is being investigated to further stabilize the triazaphenalenyl radical system and to promote formation of transition metal complexes.

Acknowledgment. We thank Dr. Richard Stevens and Prof. Kym F. Faull for their generous efforts with the mass spectra (NIH S10RR15952) and NSF for grants CHE-0080942 (Y.R.), CHE-9871332 (X-ray), and CHE-9974928 (NMR).

Supporting Information Available: Experimental section and crystallographic data (CIF) for compounds **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(7) Barclay, T.; Cordes, A.; George, N.; Haddon, R.; Itkis, M.; Mashuta, M.; Oakley, R.; Patenaude, G.; Reed, R.; Richardson, J.; Zhang, H. *J. Am. Chem. Soc*. **1998**, *120*, 352−360.

(8) Compound **2** ($C_{20}Cl_{10}N_6$; $M_r = 678.76$) crystallized in the monoclinic space group $P2/c$ with cell dimensions of $a = 8.7677(14)$ Å, $b = 4.8934(8)$ Å, $c = 25.862(4)$ Å, $V = 1107.0(3)$ Å^3, and an occupation of $Z = 2$ in the unit cell. Data were collected at 100 K on a Bruker Smart 1000 CCD diffractometer using graphite-monochromated Mo Kα radiation, to a maximum $2\theta = 56.66°$, giving 6676 unique reflections; the structure was solved by direct methods and refined with full matrix least squares, yielding $R = 0.0419$, $R_w = 0.0987$ for 2638 independent reflections with $I > 2\sigma(I)$, R_w (all data) = 0.1039.

(9) Dimer **7** is also diamagnetic in the solid state from 2 to 350 K.

(10) Biedermann, P.; Stezowski, J.; Agranat, I. *Eur. J. Org. Chem.* **2001**, 15−34 and references therein.

(11) Ammon, H. L.; Wheeler, G. L.; Agranat, I. *Tetrahedron* **1973**, *29*, 2695−2698.

(12) Molins, E.; Miravitlles, C.; Espinosa, E.; Ballester, M. *J. Org. Chem.* **2002**, *67*, 7175−7178.

(13) Feringa, B. L.; van Delden, R. A.; Koumura, N.; Geertsema, E. M. *Chem. Rev.* **2000**, *100*, 1789−1816.