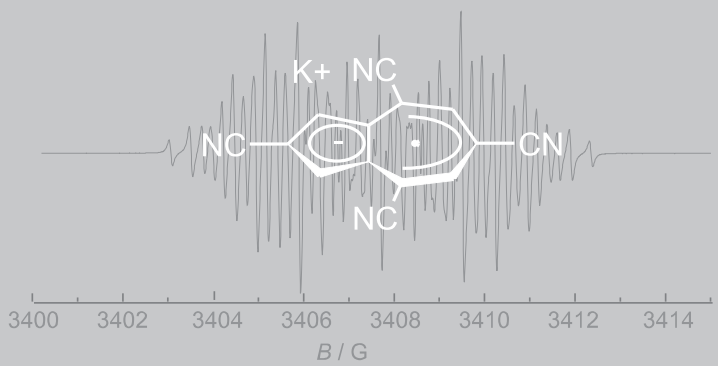
Azulene Renaissance

The highly symmetric 2,4,6,8-tetracyanoazulene is obtained by stepwise substitution of the seven-membered ring of 2-cyanoazulene by nitrile groups.

It joins the series of strong acceptors (TCNE, TCNQ, and DCNQI) of electrically conductive charge-transfer complexes and radical anion salts.



The synthesis and properties of this novel acceptor are reported by K. Hafner et al. on the following pages.

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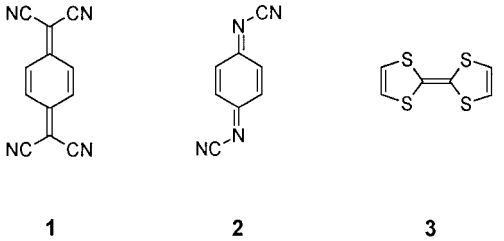
2,4,6,8-Tetracyanoazulene: A New Building Block for "Organic Metals"**

Stefan Schmitt, Martin Baumgarten, Joachim Simon, and Klaus Hafner*

Organic charge-transfer (CT) complexes are being increasingly investigated, both theoretically and experimentally,[1] as their molecular structure allows an easy preparation of single-crystal, well-characterizable compounds with high electric conductivity. The formation of such CT complexes is based on the interaction of an energetically high-lying HOMO (of the donor) with a low-energy LUMO (of the acceptor). Many one-dimensional compounds derived from the acceptors 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ, **1**)[2] and *N*,*N'*-dicyano-*p*-quinodiimine (DCNQI, **2**)[3] as well as the donor tetrathiafulvalene (TTF, **3**; Scheme 1)[4] have already been investigated; superconductivity was proven even for radical ion salts.[5]



Scheme 1. Electron acceptors and donors.

The transfer of free electrons along separated donor or acceptor stacks can formally be understood as "migration of aromaticity".[6] Accordingly, resonance structures with a cyclic electron sextet can be formulated for the radical ions of **1**–**3**. As numerous experimental studies and calculations[7] of the redox characteristics of azulene (**4**)—a bicyclic, non-alternating hydrocarbon—and its derivatives have shown, its radical anion **4A** (cyclopentadienide ion) and cation **4B** (tropylium cation) can be described with an aromatic partial structure (Figure 1). Whereas the donor properties of azulene have been thoroughly investigated,[8] none of its substituted derivatives has been employed so far as an acceptor for the preparation of CT complexes. According to HMO theory, the incorporation of acceptor substituents at the azulene positions with large LUMO coefficients (2-, 4-, 6-, and 8-positions; Figure 1) should lead to a decrease in the energy of the LUMO and consequently to an increased electron affinity.[9]

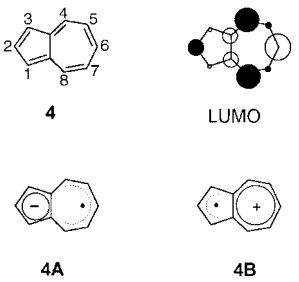
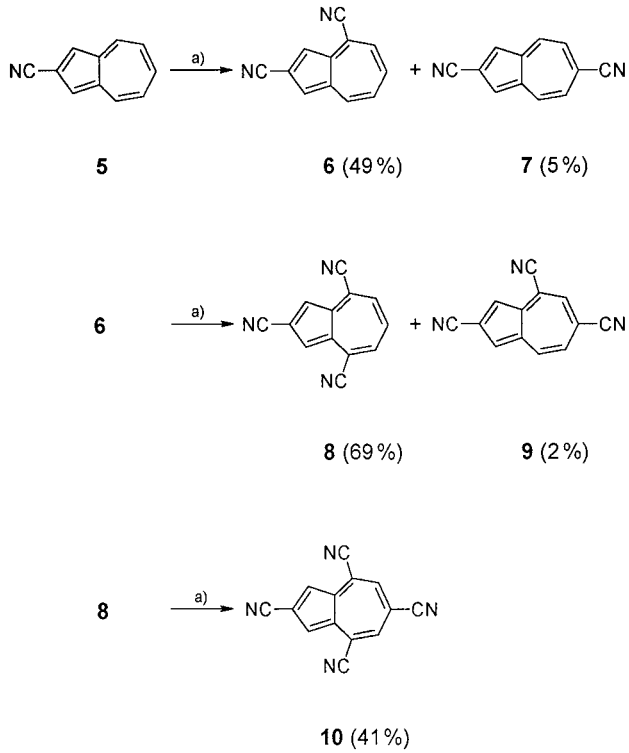


Figure 1. Schematic representation of the radical anion **4A** and the radical cation **4B** as well as the LUMO coefficients of azulene (**4**).

We report here on the synthesis of 2,4,6,8-tetracyanoazulene (TCNA, **10**) and the di- and tricyanoazulenes **6**–**9** (Scheme 2) as well as their chemical and physical properties. Our special interest was focused on the electron affinity of these new π acceptors and their tendency to form CT complexes.



Scheme 2. Synthesis of azulenenitriles **6**–**10**. a) 1. KCN/DMF; 2. 2N AcOH; 3. *p*-chloranil.

In contrast to azulene (**4**), which can be attacked only by strong nucleophiles such as alkali organometallic compounds at the 4- or 8- and 6-positions,[10] azulenes with acceptor substituents on the five-membered ring react with cyanide ions in dimethylformamide (DMF) already at room temperature to form σ adducts.[11] After hydrolysis with 2N AcOH and dehydrogenation with *p*-chloranil, these adducts can be converted into 4-, 8-, and 6-cyanoazulenes as blue or green needles. 2,4,6,8-Tetracyanoazulene (**10**) was thus obtained from 2-cyanoazulene (**5**)[12] by repeated nucleophilic addition and dehydrogenation.[13] The ratios of regioisomers are in agreement with findings by McDonald et al.,[14] according to which the reaction of azulenes with nucleophiles affords mixtures of regioisomers providing an attack at one of these positions is not favored because of steric or electronic reasons. Owing to the differences in symmetry, differentiation between

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compounds **6** and **7** as well as between **8** and **9** is possible by ^{1}H NMR spectroscopy (Scheme 2).

Characteristic for the substitution at an electron-deficient position of the seven-membered ring by a nitrile group is a bathochromic shift of the long-wave absorption of approximately 50 nm in the electron spectrum of azulenes **6**–**10**. This suggests a decrease in the energy of the LUMO. Additional information on the energy of the frontier orbitals as well as the electron affinity of compounds **6**, **8**, and **10** was obtained by cyclic voltammetry studies. These indicate that the formation of the radical anions and the paratropic dianions is completely reversible (Figure 2). A comparison of the half-wave potentials for the first reduction of **6**, **8**, and **10** shows

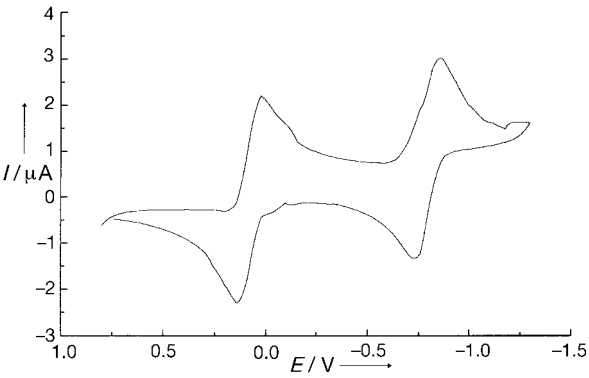


Figure 2. Cyclic voltammogram of **10** (nBu$_4$NPF$_6$, 10^{-4} M, CH_2Cl_2, 25 °C, 100 mV s^{-1}, working electrode: Pt disk, counter electrode: Pt plate (1 cm^2), reference electrode: saturated calomel electrode (SCE)).

that the half-wave potential increases with rising substitution at the electron-deficient positions of the seven-membered ring (Table 1). These data are in agreement with a resonance stabilization of the negative charge and the unpaired electron by the cyano groups.

Table 1. First and second half-wave potentials of azulenenitriles **6**, **8**, and **10**.

Compd	E_1 [mV]	E_2 [mV]
6	– 765	– 1631
8	– 320	– 1240
10	80	– 795

First indications for the ability of **10** to form colored CT complexes were provided by UV/Vis studies on solutions of **10** and *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine (TMPD) in dichloromethane or acetonitrile (Figure 3). Whereas in dichloromethane two unstructured, concentration-dependent CT bands at 513 and 1200 nm appear in addition to the characteristic absorptions of **10** between 600 and 950 nm, in acetonitrile absorption bands are observed that indicate the presence of the Wurster radical TMPD$^{\bullet+}$ and thus indicate a complete charge transfer.

The concentration of CT complexes in solution and the degree of charge transfer are determined with the complex-formation constant and with the difference in potentials

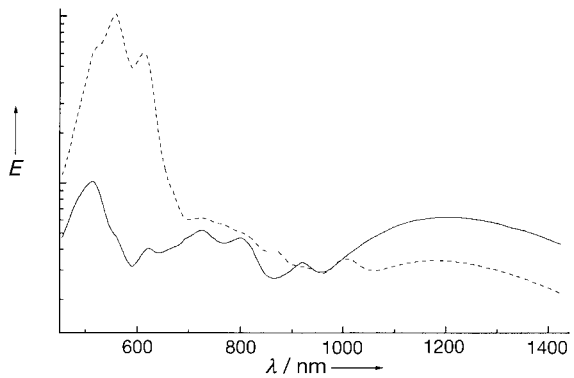
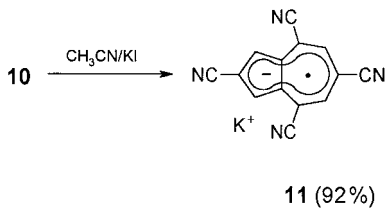


Figure 3. UV/Vis spectra of **10**/TMPD in CH_2Cl_2 (——) and CH_3CN (– – –). The extinction E is given in arbitrary units.

between the acceptor and donor. Consequently, a more positive reduction or oxidation potential leads to a stronger saltlike character and therefore to lower solubility in organic solvents.[15] The reaction of **10** with an excess of potassium iodide in acetonitrile yields the potassium salt of the radical anion **11** as a green powder; it is stable in solution and in the solid state at room temperature as well as in the presence of oxygen, and dissolves in polar solvents with an intense violet color (Scheme 3).



Scheme 3. Synthesis of the radical anion salt **11**.

The UV/Vis spectrum of **11** in acetonitrile shows three absorption maxima at $\lambda = 489$, 517 and 554 nm together with a broad band of low extinction with characteristic fine structure between 600 and 1100 nm. Information on the distribution of the spin density at the individual positions was anticipated from the distances of the corresponding multiplets in the ESR spectrum. Numerous lines (about 100) appear in the ESR spectrum (Figure 4a); however, owing to the small width of

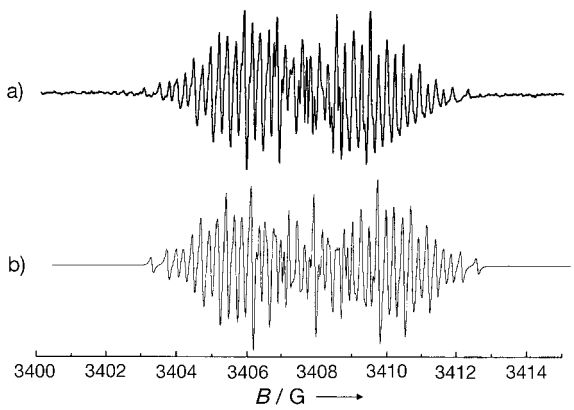


Figure 4. ESR spectra of **11**: a) in CH_3CN; b) simulated.

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the signal, they could not be assigned. The proton hyperfine coupling constants of 0.95 and 0.45 G were clearly determined with the ENDOR technique. The nitrogen coupling constants could be established from these by computer simulation[16] (Figure 4b). As expected, large spin densities resulted for the 2-, 4-, 6-, and 8-positions, and small spin densities for the 1/3- and 5/7-positions (Figure 5). The g value of 2.0027 also suggests only small spin densities at the nitrogen centers, since nitrogen-centered radicals are typically characterized by large deviations in the g value of the free electron, which are caused by an increase in the spin-orbit coupling value.

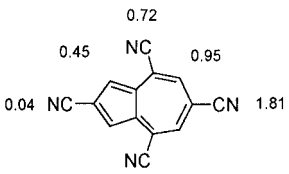
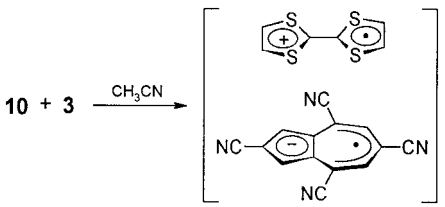


Figure 5. Nitrogen and proton hyperfine coupling constants [G] of **11**.

Prompted by these findings, it appeared interesting to investigate whether an aprotic, dipolar solvent could also increase the charge transfer of organic donors. In fact, combining solutions of **10** and **3** in acetonitrile provides the CT complex **12** as a microcrystalline powder; the 1:1 ratio of the components was confirmed by elemental analysis.[13] Complex **12** has a conductivity of 1–3 S cm^{-1}, as determined by a two-point powder measurement (Scheme 4).[17]



12 (80 %)

Scheme 4. Synthesis of a CT complex from **10** and **3**.

In accordance with the changed bond character of **11** and **12** as compared to **10**, a characteristic decrease in the CN wavenumber, which is often used as a measure of charge transfer, is observed in the respective IR spectra.

Experimental Section

Standard procedure for the preparation of azulenenitriles: Under an atmosphere of pure nitrogen, the azulene (1.0 mmol) substituted with an acceptor group at the five-membered ring and potassium cyanide (72 mg, 1.1 mmol) are dissolved in anhydrous DMF (10 mL) and stirred at room temperature until the solution turns colorless (ca. 12 h). After subsequent hydrolysis with 2 N acetic acid (1 mL), the mixture is poured into a saturated solution of NaCl (100 mL) and extracted with dichloromethane (3 × 50 mL). The organic layer is dried with magnesium sulfate, filtered, and treated with *p*-chloranil (245 mg, 1.0 mmol). After 16 h at room temperature the solvent is removed in vacuo, and the residue subjected to chromatography on silica gel. Unchanged *p*-chloranil and starting material can be recovered in early fractions, and then the desired azulene products substituted at the 4-, 6-, and/or 8-position are isolated.

6: M.p. 174–176 °C; ^{1}H NMR (300 MHz, CD_2Cl_2, 25 °C, TMS): $\delta = 7.46$ (t, ^3J(H,H) = 9.8 Hz, 1 H, 7-H), 7.51 (d, ^3J(H,H) = 9.9 Hz, 1 H, 5-H), 7.70 (d, ^4J(H,H) = 1.6 Hz, 1 H, 1-H), 7.75 (t, ^3J(H,H) = 9.1 Hz, 1 H, 6-H), 7.85 (d, ^4J(H,H) = 1.2 Hz, 1 H, 3-H), 8.47 (d, ^3J(H,H) = 9.3 Hz, 1 H, 8-H); IR (KBr): $\tilde{\nu} = 2229$ cm^{-1} (CN); UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 257 (3.94), 295 (4.24), 307 (sh, 4.02), 348 (3.13), 362 (3.19), 367 (3.16), 379 (3.12), 597 (sh, 2.18), 636 (2.29), 689 (2.27), 758 nm (1.93); MS (70 eV): m/z (%): 178 (100), 151 (19) $[M - HCN]^+$.

7: M.p. 225 °C (subl.); ^{1}H NMR (300 MHz, CD_2Cl_2, 25 °C, TMS): $\delta = 7.47$ (d, ^3J(H,H) = 10.3 Hz, 1 H, 7-H and 5-H), 7.68 (s, 1 H, 1-H and 3-H), 8.38 (d, ^3J(H,H) = 10.4 Hz, 1 H, 4-H and 8-H); IR(KBr): $\tilde{\nu} = 2227$ cm^{-1} (CN); UV/Vis (CH_2Cl_2):λ_{max} (lg ε) = 281 (4.76), 327 (sh, 3.49), 338 (3.68), 351 (3.85), 362 (sh, 3.70), 368 (4.06), 603 (sh, 2.55), 646 (2.70), 702 (2.68), 775 nm (2.32); MS (70 eV): m/z (%): 178 (100), 151 (26) $[M - HCN]^+$.

8: M.p. 264–265 °C; ^{1}H NMR (300 MHz, CD_2Cl_2, 25 °C, TMS): $\delta = 7.75$ (d, ^3J(H,H) = 10.2 Hz, 1 H, 5-H and 7-H), 7.93 (t, ^3J(H,H) = 9.4 Hz, 1 H, 6-H), 8.10 (s, 1-H and 3-H); IR (KBr): $\tilde{\nu} = 2227$ cm^{-1} (CN); UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 269 (4.33), 291 (sh, 4.21), 302 (4.30), 311 (4.32), 324 (sh, 4.00), 360 (3.30), 377 (3.39), 395 (3.17), 639 (sh, 2.30), 684 (2.44), 752 (2.42), 840 nm (2.01); MS (70 eV): m/z (%): 203 (100), 176 (15) $[M - HCN]^+$.

9: M.p. 268 °C (subl.); ^{1}H NMR (300 MHz, CD_2Cl_2, 25 °C, TMS): $\delta = 7.67$ (s, 1 H, 5-H), 7.71 (d, ^3J(H,H) = 10.2 Hz, 1 H, 7-H), 7.85 (s, 1 H, 3-H), 7.97 (s, 1 H, 1-H), 8.50 (d,^3J(H,H) = 9.7 Hz, 1 H, 8-H); IR (KBr):$\tilde{\nu} = 2222$ cm^{-1} (CN); UV/Vis(CH_2Cl_2): λ_{max} (lg ε) = 295 (4.72), 353 (3.54), 371 (3.75), 389 (3.87), 637 (sh, 2.49), 684 (2.63), 752 (2.61), 838 nm (2.21); MS (70 eV): m/z (%): 203(100), 176 (21) $[M - HCN]^+$.

10: M.p. 348 °C (decomp); ^{1}H NMR (300 MHz, CD_2Cl_2, 25 °C, TMS): $\delta =$ 7.94 (s, 2 H, 5-H and 7-H), 8.24 (s, 2 H, 1-H and 3-H); IR(KBr): $\tilde{\nu} =$ 2235 cm^{-1} (CN); UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 277 (4.45), 306 (4.78), 366 (3.60), 385 (3.83), 404 (3.82), 675 (sh, 2.49), 725 (2.63), 802 (2.58), 912 nm (2.19); MS (70 eV): m/z (%): 228 (100), 201 (20) $[M - HCN]^+$.

11: M.p. 281 °C (decomp); IR (KBr): $\tilde{\nu} = 2197$ cm^{-1} (CN); UV/Vis (CH_3CN): λ_{max} = 247, 306, 325 (sh), 364, 380, 399, 410 (sh), 462 (sh), 489, 517, 554, 687, 753, 864, 1000 nm.

12: M.p. 256 °C (decomp); IR (KBr): $\tilde{\nu} = 2201$ cm^{-1} (CN).

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Effect of Chain Length on the Adsorption Behavior of *n*-Alkanes in Ferrierite

Willy J. M. van Well, Xavier Cottin, Jan W. de Haan, Rutger A. van Santen, and Berend Smit*

Zeolites are microporous crystalline materials that are used as catalysts in petrochemical applications because of their acidity and stability.[1] At present there are more than a hundred types of zeolites, each with characteristic pore sizes and pore topologies. One important aim of zeolite science is to use these differences to tune the selectivity of a given reaction.[2] To arrive at a rational design, it is essential to have an understanding on the molecular level of the behavior of the sorbates in the pores of these zeolites.[3] Currently such information is mainly obtained from computer simulations. For example, recent Monte Carlo calculations have allowed many predictions to be made about the behavior of *n*-alkanes in zeolites,[4–8] in particular regarding the preferential adsorption sites of *n*-alkanes in zeolites. To the best of our knowledge, none of these predictions have been confirmed experimentally, since direct information on the siting of *n*-alkanes is difficult to obtain.

Here we present work on the siting of *n*-alkanes in the zeolite ferrierite (FER). FER has ten-ring channels which are interconnected by cages with eight-ring windows. The use of this zeolite as an isomerization catalyst for the production of isobutene, an intermediate in the production of methyl *tert*-butyl ether (MTBE, considered to be an environmentally beneficial fuel), has been studied extensively.[9,10] The comparison of the performance of FER and other zeolites as catalysts for the isomerization of *n*-butene has been mainly focused on the dimensions of the ten-ring channels.[9] We now find that the characteristic pore topology is an important factor as well. One of the questions still open pertains to the distribution of the molecules over these ten- and eight-ring channels.

To study this distribution, we investigated the siting of *n*-alkanes in FER by means of Monte Carlo simulations and ^{13}C NMR spectroscopy. For the simulations we assumed that the zeolite is rigid, and the *n*-alkanes were modeled with a united atom representation; that is, CH_3 and CH_2 groups are considered as "united atoms". Fixed bond lengths, bond angles, and torsion potentials were used.[11] Details on the simulation techniques have already been described.[5,12] The results of Monte Carlo simulations (Figure 1) indicate a surprising effect of the chain length. *n*-Alkanes with more than five carbon atoms prefer the ten-ring channels for all loadings; these molecules are too large to fit into the eight-ring channels. At low loadings propane and butane are distributed over the ten-ring and eight-ring channels. While propane prefers adsorption in the eight-ring channel, butane adsorbs preferentially in the ten-ring channel. The adsorption of pentane is at low loading limited to the ten-ring channel, and adsorption in the eight-ring channel occurs only at higher loadings. These simulations show that the adsorption behavior of even simple *n*-alkanes is quite complex and depends strongly on the chain length. One of the purposes of the present work was to present experimental evidence that the above prediction is indeed correct.

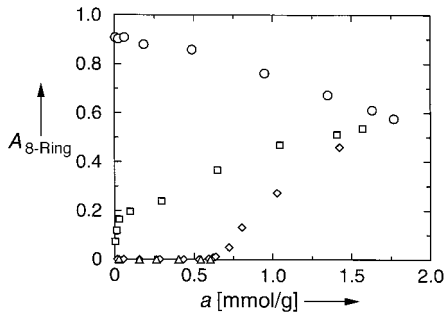

Figure 1. Fraction $A_{8\text{-Ring}}$ of the molecules adsorbed in the eight-ring channels as a function of the loading a. The data were obtained from computer simulations with the configurational-bias Monte Carlo method at 333 K. ○ propane, □ butane, ◇ pentane, △ hexane.

An obvious experimental technique to investigate the siting of hydrocarbons in zeolites is ^{13}C NMR spectroscopy. The chemical shifts of *n*-alkanes depend on the local environment

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