Excitation of 5, 7, and 8 (10^-4 m in degassed CH2Cl2 at room temperature) by a 20-ps laser pulse at 530 nm was used for transient absorption measurements at 820 nm (triplet state absorption; see Ref. [11]) with an apparatus already described.1,12] Simultaneously, time-resolved emission measurements were performed. In 5, emission at 600 nm is completely quenched whereas emission at 660 nm is enhanced as compared to 7 under the same conditions. The formation rate of the triplet state localized on the non-metalated subunit (10^6 s^-1 at room temperature in degassed CH2Cl2) is similar to the decay rate of the singlet state (non-metalated ring). Furthermore, the emission quantum yield at 660 nm and the quantum yield of triplet state generation (absorption at 820 nm) for 5 are roughly twice those for 7, corroborating the data of Table 2 obtained by classical emission spectroscopy. No evidence was obtained for light-induced electron transfer. These observations are in full agreement with the postulated reaction of efficient intramolecular singlet energy transfer from the zinc porphyrin part to the non-metalated ring. 

The present oblique bis-porphyrin may be related to the action center. Energy migration from the special pair to the hypothetical mechanism of the photosynthetic bacterial reaction center. 

Tribenzotriquinacenes with substituents on the central C atom are accessible by double cyclodehydration of the correspondingly substituted 2-benzhydryl-1,3-indandiol.2] The unsubstituted hydrocarbon 2, however, could be obtained only in low yields via this route. Starting from cinnamon, Baker et al.3] synthesized the diquinane ketone 3 in three steps; bromination/dehydrobromination then gave the enone 4 in moderate yield. In our attempts to synthesize 2 and higher benzoannelated centropolyquinanes,4] the ketone 3 and the alcohols 7a, b5] derived therefrom were identified as 8-exo-phenyl stereoisomers on the basis of their mass spectra.4,5 Thus, the cyclodehydration 7 → 2 attempted by Baker et al.3] was doomed to failure for steric reasons. The enone 4, together with the isomer 5,6] is accessible on a preparative scale (overall yield 25%), Scheme 1) by an alternative route involving phenylsulfonylation of 3, oxidation, and thermal elimination of the phenylsulfenyl derivative.6,7] Subsequently, 4 and 5 can be rehydrogenated with palladium on charcoal in dioxide to afford the isomeric diquinane ketone 6 with high selectivity. After reduction to the alcohol 8, bearing an endo-phenyl group, the cyclodehydration to the tricyclic compound 2 occurs readily, as expected. Compound 2 crystallizes from hot xylene as sparingly soluble, colorless, long, hard needles having an unusually high melting point (390°C). The identity of 2 was established on the basis of its analytical5,9] and spectroscopic data.10]

**Tribenzotriquinacene, Dihydrotribenzoaceptalenolide, and the Tribenzocenentalene Radical Anion**

By Dietmar Kueck,* Andreas Schuster, Björk Ohlhorst, Volker Sinnwell, and Armin de Meijere*

Dedicated to Professor Kurt Heyns on the occasion of his 80th birthday

Benzoannelation can increase the stability of cyclically conjugated, nonaromatic hydrocarbons that, owing to unfavorable electron configuration and/or unfavorable HOMO energies, are unstable and therefore highly reactive. To explore this possibility for acepetalene 1, only the dianon of which, 1^**, is so far known,11] we synthesized tribenzoquinacene (tetrahydrotribenzoacepetalenolide) 2 and investigated its deprotonation-dehydrogenation both in solution and in the gas phase.

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Upon treatment of a suspension of 2 in n-hexane with n-butyllithium and potassium tert-amyloxide (molar ratio 1:4.7:2.5), the mixture turns carmine red within 30 min. After 24 h at room temperature and an additional 24 h at reflux temperature, the reaction mixture was filtered under argon. The red-brown solid was washed four times with n-hexane and once with diethyl ether and then dried at 40°C/0.1 torr. In addition to dipotassium dihydrotribenzoacenatalene 92e/2K@ and its trapping product 92f/2K@, the chemical proof for the constitution of 92g/2K@ was accomplished, as for 12g/11 from trapping with chlorotrimethylsilane in n-hexane. The bis(trimethylsilyl)dihydrotribenzoacenatalene 10 (colorless crystals, m.p. 191°C dec.; for spectroscopic data, see Table 1), isolated in 97% yield (based on 2), was much easier to purify than the corresponding parent compound; in addition, 92g/2K@ is markedly more stable than 12g/2K@. The special stabilization of 92g/2K@ is also supported by the fact that it is formed from 10-methyltribenzozenatriquinacene[21] with formal expulsion of methane under the same conditions as it is formed from 2.

Table 1. Characteristic NMR data for dipotassium dihydrotribenzoacenatalene 92g/2K@ and its trapping product 10. For numbering, see Scheme 1. The cross peaks of magnetically equivalent atoms are not listed separately.

\[ 92g/10: \text{\(\delta = 6.69\)} (2H, X), \text{\(\delta = 5.57\)} (2H, \text{CH\textsubscript{2}}), \text{\(\delta = 4.7\)} (3H, CH\textsubscript{3}), \text{\(\delta = 4.09\)} (2H, \text{CH\textsubscript{2}}), \text{\(\delta = 3.6\)} (2H, CH\textsubscript{2}), \text{\(\delta = 2.8\)} (2H, CH\textsubscript{2}), \text{\(\delta = 2.5\)} (2H, CH\textsubscript{2}). \]

The chemical proof for the constitution of 92g/2K@ was accomplished, as for 12g/11 by trapping with chlorotrimethylsilane in n-hexane. The bis(trimethylsilyl)dihydrotribenzoacenatalene 10 (colorless crystals, m.p. 191°C dec.; for spectroscopic data, see Table 1), isolated in 97% yield (based on 2), was much easier to purify than the corresponding parent compound; in addition, 92g/2K@ is markedly more stable than 12g/2K@. The special stabilization of 92g/2K@ is also supported by the fact that it is formed from 10-methyltribenzozenatriquinacene[21] with formal expulsion of methane under the same conditions as it is formed from 2.

In the gas phase, compound 2 also undergoes ready deprotonation to give the monoanion [2-H]@ under the conditions of negative chemical ionization (NCI).[14,15] Moreover, at low pressure of the reactant gas (i.e., for a higher average excitation of the [2-H]@ ions), predominant formation of [2-H]@ and [2-2H]@ ions is observed, indicating elimination or abstraction of up to three hydrogen atoms (see Fig. 1). Correspondingly, the NCI spectrum of 10-methyltribenzozenatriquinacene[23] is governed by the [M - 2H - CH\textsubscript{3}]@ peak at low reactant gas pressures. Apparently, therefore, the (unsolvated!) radical anion 92g/2 of
trienzoaceptalenene 9 is very stable—in marked contrast to 1. Under identical conditions, triquinacene 11 is deprotonated to the monoanion $\{11-\text{H}\}^-$, but at lower pressure of the reactant gas, only $\{11-2\text{H}\}^{2-}$ (along with a small amount of $\{11-4\text{H}\}^{3-}$, see Fig. 1) is formed. Accordingly, the neutral trienzoaceptalenene 9 must also be appreciably more stable than the parent system 1 and might even be detectable in pure form.

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Electron Densities, Deformation Densities, and Chemical Bonding **

By W. H. Eugen Schwarz,* Klaus Ruedenberg, Lothar Mensching, Lance L. Miller, Petros Valtazanos, and Wolfgang von Niessen

The frequently postulated relationship between electron density and chemical bonding has so far been investigated in two different, although fundamentally related, ways: According to the older method,[1-2] one uses the difference density $\rho_{\text{molecule}} - \rho_{\text{atoms}}$, where $\rho_{\text{molecule}}$ is the electron density of the molecule and $\rho_{\text{atoms}}$ the spherically averaged density of an unperturbed, correctly positioned atom. A chemical bond should be characterized by a positive $\Delta \rho$ between the atoms. According to the more recent method,[3-4] instead of $\Delta \rho$ one uses the second derivative of the molecular density $\nabla^2 \rho_{\text{molecule}}$. Large negative values of $\nabla^2 \rho_{\text{molecule}}$ between two atoms, especially in comparison with the spherically averaged atomic densities, are regarded as an indication of chemical bonding.

The ground states of most atoms with open valence shells, however, are degenerate (e.g., $2p^3$ states for C(1s2s2s2p3) and F(1s2s2s2p5)); that is, their electron density is anisotropic. The electron density of the free atoms can be oriented (e.g., in the $2p^3$ state, see Fig. 1 c) without any increase in energy. Thus, molecules and crystals can be envisioned as consisting of suitably positioned and oriented atoms (whereby, owing to the Heisenberg uncertainty principle, even the positioning of noninteracting atoms requires the zero-point vibrational energy). The positions of the atomic cores along with their