σ-electron *donor*. The π and σ interactions are thus *both favorable* in HC≡CO⁻, leading to a calculated BSE of 225 kJ mol⁻¹. For the double-bonded system CH_2=CHO⁻, as pointed out above, the interaction energy is less sensitive to σ effects, and accordingly, the BSE, though still indicating a strongly stabilizing interaction, is somewhat lower, at 164 kJ mol⁻¹. There is thus a relative stabilization of the HC≡CO⁻ anion by 61 kJ mol⁻¹ (Figure 1).[16]

The combination of the relative destabilization of HC≡COH (by 41 kJ mol⁻¹) and stabilization of HC≡CO⁻ (by 61 kJ mol⁻¹) leads to the greater acidity of HC≡COH compared with CH_2=CHOH (by 101 kJ mol⁻¹). The schematic representation of these results (Figure 1) also presents the acidities of HC≡COH and CH_2=CHOH relative to a common standard, CH_3OH. This shows that HC≡COH and CH_2=CHOH are both substantially more acidic than CH_3OH, largely because of relative stabilization of the conjugate bases (HC≡CO⁻ and CH_2=CHO⁻).

Several important points emerge from this study.

1. The high relative acidity of ethynol (HC≡COH) that is observed in solution is predicted to carry over to the gas phase.

2. The high relative acidity of ethynol may be attributed partly to relative destabilization of neutral ethynol and partly to relative stabilization of the ynolate anion.

3. Acidities calculated for CH_3CHO, CH_2CHOH, CH_2CO, and CH_3OH at the MP4/6-311+G** level are generally somewhat higher than, but in reasonable agreement with, experimental values.

Supplementary Material Available: Table II with calculated total energies and zero-point vibrational energies and Figure 2 with HF/6-31+G* optimized geometries (3 pages). Ordering information is given on any current masthead page.

(16) Note that, in calculating the relative stabilizations, it is necessary for balance to include acetylene (for the triply bonded systems) or ethylene (for the doubly bonded systems); this is done for both the neutrals and anions and therefore, together with CH_3OH on the one hand and $CH_3O⁻$ + H⁺ on the other, provides useful reference levels for comparison purposes.

Synthesis and Structure of Novel Polycyclic Species from Toluene and *m*-Xylene and the Dehalogenation Product of Difluoro(diisopropylamino)borane

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Reaction products obtained from aromatic compounds and the dehalogenated species formed upon treatment of dichloro(diisopropylamino)borane with active metals (Na/K) appear to be formed by carben(oidal) processes.[1-3] Indeed the formation of these polycyclic compounds in some respects resembles the valence isomerization in aromatic compounds which results from a tandem of carbenoid processes in the Katz reaction.[4] However, it differs from the Katz mechanism as hydrogen atom transfer is frequently observed in our reactions.[1,3] The three-dimensional species contain

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(2) Meller, A.; Bromm, D.; Maringgele, W.; Böhler, D.; Elter, G. *J. Organomet. Chem.* **1988**, *347*, 11.
(3) Maringgele, W.; Bromm, D.; Meller, A. *Tetrahedron* **1988**, *44*, 1053.
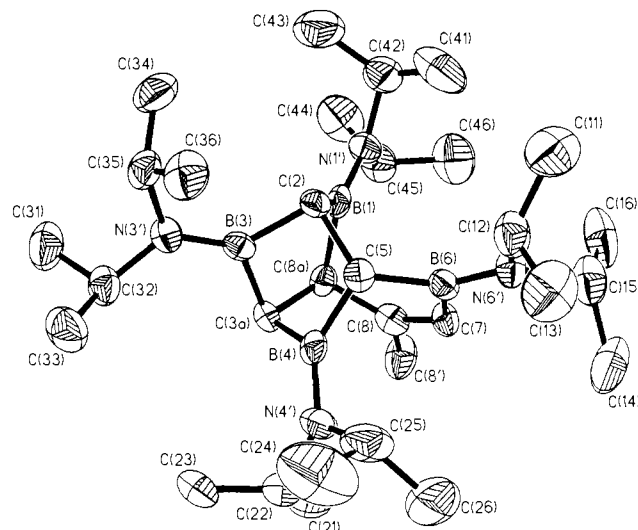(4) Burger, U.; Thorel, P. J.; Mentha, Y. *Chimia* **1987**, *41*, 26.

Figure 1. Structure of **1** (hydrogen atoms omitted) showing 40% probability thermal motion ellipsoids. Selected mean bond distances (Å) are as follows: B–C (mean) = 1.586 (9), N–C (mean) = 1.476 (14), C-(8a)–C(8) = 1.518 (8), C(2)–C(5) = 1.642 (9), B–N (nean) = 1.404 (7), C(3a)–C(8a) = 1.596 (11), C(8)–C(7) = 1.335 (11), C(8)–C(8′) = 1.532 (8).
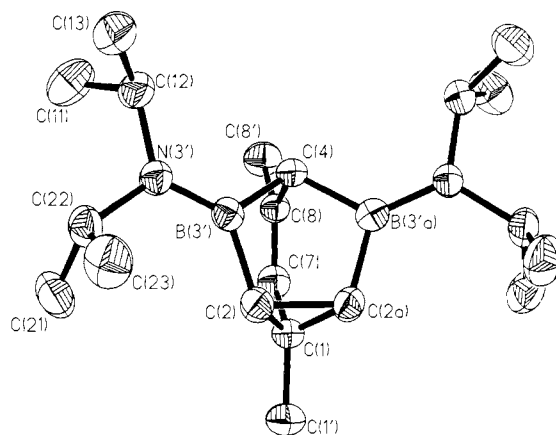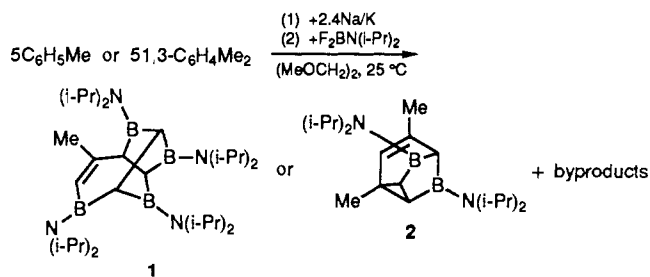

Figure 2. Structure of **2** (hydrogen atoms omitted) showing 40% probability thermal motion ellipsoids. C(1), C(1′), C(7), C(8), C(8′), and C(4) lie on a crystallographic mirror plane. Selected bond distances (Å) are as follows: B(3′)–N(3′) = 1.396 (4), C(4)–C(8) = 1.524 (5), C-(8)–C(7) = 1.329 (6), C(1)–C(2) = 1.520 (4), C(1)–C(1′) = 1.502 (6), N(3)–C(12) = 1.471 (4), B(3′)–C(4) = 1.604 (3), C(8)–C(8′) = 1.506 (4), C(7)–C(1) = 1.487 (4), C(2)–C(2a) = 1.561 (5), C(2)–B(3′) = 1.563 (4), N(3′)–C(22) = 1.485 (3).

Scheme I

only three-coordinated boron and three- or four-coordinated carbon (sp² and sp³ hybridization) and therefore are quite different from carboranes. It has been shown earlier that a *nido*-carborane structure is destabilized by amino substitution at the boron sites, giving a bicyclic structure.[5]

(5) Herberich, G. E.; Ohst, H.; Mayer, H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 969.

The structure of the reaction products of benzene with two and three formal "BN(i-Pr)₂" moieties[2] could be deduced from NMR and mass spectral data. The structure of the product from naphthalene with two formal borene units was finally resolved from spectral data and the hydrolysis products.[1,2] However, NMR spectra of the products of toluene with four added BN(i-Pr)₂ units, **1**, and of *m*-xylene with two additional diisopropylaminoboradiyls, **2**, were too complicated to allow structural assignments. Therefore the structures **1** and **2**, which are obtained according to Scheme I,[6] had to be resolved by X-ray diffraction.[7]

In **1** the aromatic ring is split into C₂ and C₄ units; in **2** the ring has been opened and rearranged with the formation of a cyclopropane ring. In both molecules one C=C double bond is retained. Increased substitution by boron appreciably lengthens the C–C bonds in **1**: C(3a)–C(8a) (1.596 (11)) is substituted by 3B and C(2)–C(5) (1.642 (9) Å) by 4B.

(6) For the preparation of **1**, 1,3,4,6-tetrakis(diisopropylamino)-8-methyl-1,2,3,3a,4,5,6,8a-octahydro-2,5-cyclo[1,3]diborolo[4,5-*d*]diborepin, and **2**, 3,5-bis(diisopropylamino)-1,8-dimethyl-3,5-diboratricyclo[2.2.2.0²,⁶]-oct-7-en, respectively, 1.2 mol of Na/K alloy (1:3, 6.9 g of Na + 35.2 g of K) are dispersed in a solution of 2.5 mol of the aromatic compound (230 g of toluene or 260 g of *m*-xylene and 750 mL of dimethoxyethane (DME)). 0.5 mol (74.5 g) of F₂BN(i-Pr)₂ is slowly added with vigorous stirring to this dispersion, and the temperature of the reaction mixture rises to about 35 °C. Stirring is continued for 2 days at room temperature until the alloy solidifies. Then 3.5 g of potassium are added, and stirring is continued 2 more days at reflux temperature. Insoluble materials (alloy and salts) are removed by filtration under N₂ pressure. Solvent and unreacted aromatic compounds are distilled off under reduced pressure. The reaction with toluene delivers 91.5 g of raw products (red oil). High vacuum distillation gives 32.8 g of a yellow oil, bp 90–160 °C/0.01 mbar, which contains mainly C₇H₈·2BN(i-Pr)₂ and C₇H₈·3BN(i-Pr)₂. Short-path distillation of the residue at 165 °C/0.001 mbar delivers 20.7 g of a highly viscous yellow oil which consists mainly of **1**. The substance shows a tendency to crystallize if it is held at 50 °C. By crystallization from acetone about 10 g of colorless crystals with mp 152 °C are obtained. Anal. Calcd for C₃₁H₆₄B₄N₄ (536.13): C, 69.45; H, 12.03; B, 8.07; N, 10.45. Found, MS (FI and EI) 536 (100%): C, 69.52; H, 11.96; B, 8.11; N, 10.41. NMR (only assigned signals are given) δ¹¹B 46.2 (h/2 840 Hz); δ¹H 1.91 (d, ⁴*J*_{HH} 1.1 Hz, CH₃ pos. 8), 5.52 (br, pos. 7); δ¹³C 31.78 (CH₃ pos. 8), 128.3 (pos. 8), 162.3 (pos. 7). The reaction with *m*-xylene upon distillation over a 20-cm Vigreux column along with a lower boiling fraction delivers 12.6 g of a colorless oil (bp 101 to 115 °C/0.01 mbar) which solidifies on standing. Recrystallization from acetone gives colorless needles mp 132–133 °C. Anal. Calcd for C₂₀H₃₈B₂N₂ (328.15): C, 73.24; H, 12.91; B, 6.59; N, 8.54. Found, MS (FI and EI) 328 (100): C, 73.37; H, 11.62, B, 6.67; N, 8.50. NMR δ¹¹B 42.6; δ¹H 0.62 (d, ⁴*J*_{H₂/₆H₄} 1.7 Hz pos. 8'), 1.36 (s, 3 H, CH₃ pos. 1'), 1.70 (d, 3 H, *J*_{H₈'H₇} 1.5 Hz, CH₃ pos. 8'), 1.71 (d of t, ⁴*J*_{H₄H₇} 1.5 Hz, ⁴*J*_{H₄H₂/₆} 1.7 Hz pos. 4), 5.27 (d of q, ⁴*J*_{H₇H₈'} 1.5 Hz, ⁴*J*_{H₇H₄} 1.5 Hz pos. 7); i-Pr (C22) 3.72 (sept), 1.11 + 1.09 (d, ³*J*_{HH} 6.9 Hz); i-Pr (12) 3.58 (sept), 1.20 + 1.22 (d, ³*J*_{HH} 6.9 Hz); δ¹³C 22.93 (pos. 8'), 25.23 (pos. 1'), 30.89 (br, pos. 2/6), 33.80 (pos. 1), 37.09 (br, pos. 4), 120.72 (pos. 7), 136.17 (pos. 8); i-Pr (C22) 46.81, 24.12, 24.33; i-Pr (C12) 48.43, 23.35, 23.58. Assignments have been made for ¹H by selective decoupling and for ¹³C by C–H ¹*J*-correlation and C–H long-range correlation. The numbering (pos.) follows the nomenclature, and in case of the CH₃– and i-Pr groups the numbering correlates with that of Figure 2.

(7) Crystal data for C₃₁H₆₄B₄N₄ (**1**) at 20 °C: *a* = 12.518 (9) Å, *b* = 19.426 (10) Å, *c* = 19.357 (10) Å, *β* = 129.31 (4)°, *V* = 3642 (6) Å³, *Z* = 4, *d*_calcd = 0.98 g cm⁻³, space group *P*2₁/*c*. A total of 6360 reflections were measured by using a real-time profile-fitting procedure on a Stoe–Siemens AED. After merging equivalents, 2438 data with *F* > 3σ(*F*) were used for all calculations (all programs written by author G.M.S.). Final residuals *R* = 0.114, *R*_w = 0.081. Crystal data for C₂₀H₃₈B₂N₂ (**2**) at 20 °C: *a* = 6.456 (3) Å, *b* = 21.850 (17) Å, *c* = 8.139 (6) Å, *β* = 112.57 (5)°, *V* = 1060 (2) Å³, *Z* = 2, *d*_calcd = 1.03 g cm⁻³, space group *P*2₁/*m*. 3936 data were measured, after merging 1161 with *F* > 3σ(*F*) used for all calculations. Final residuals *R* = 0.060, *R*_w = 0.057. A riding model with idealized hydrogen geometry was employed for H-atom refinement in both structures.

Resonance Raman Spectrum of the Lowest Triplet State of Zinc(II) Tetraphenylporphyrin

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Porphyrin-based macrocycles in low-energy excited electronic states are involved in a number of important biological processes, including excitation energy transfer and charge separation. To gain insight into the detailed mechanisms by which the excited macrocycles perform their functions, knowledge of the conformation and electronic structure of the participating electronic state is needed. Previous resonance Raman investigations of metalloporphyrin excited states have focused on d,d states.[2] Here, we report the time-resolved resonance Raman (TR³) spectrum of the lowest π,π* triplet state of Zn(II) tetraphenylporphyrin (ZnTPP). The number of observed vibrational bands is consistent with a lowering of the point group symmetry of the porphyrin core (excluding phenyl rings) from the D_{4h} symmetry of the ground electronic state, which we attribute to the Jahn–Teller effect previously predicted for the T₁ state.[3] In addition, the electronic excitation appears to be localized on the porphyrin ring alone and does not extend to the phenyl rings.

Figure 1 shows the TR³ spectrum (1150–1650 cm⁻¹) from T₁ of ZnTPP in tetrahydrofuran (Figure 1a) and methylcyclohexane (Figure 1b).[4] The T₁ state was populated with a ~10-ns pulse of 532-nm radiation and probed with a second ~10-ns pulse with a wavelength (460 nm) chosen to coincide with the maximum of the triplet–triplet absorption curve.[5] Bands are observed at the same frequencies in the two solvents. From the absence of observable scattering at 1551 cm⁻¹, where the ground state (S₀) exhibits a strong band (Figure 1c), we conclude that all the labeled peaks in the TR³ spectra are attributable to scattering from the T₁ state of ZnTPP.

Consistent with this assignment are the kinetics of the recovery of the ground-state spectrum. With increasing time delay between laser pulses, the intensities of the T₁ bands decrease and those of the S₀ bands increase, yielding a time constant of several hundred microseconds. This decay time is shorter than the triplet lifetime obtained optically,[6] owing to triplet–triplet annihilation processes[5b,7] that occur for the more concentrated samples required for the resonance Raman experiment.

Analysis of the TR³ spectrum yields information on the structure of the porphyrin in the triplet excited state. The two

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(4) The pump pulse was the second harmonic from a Quanta-Ray Nd: YAG laser. The probe pulse was obtained from a Quanta-Ray dye laser pumped by a second Nd:YAG laser. The time delay between pulses was controlled by a Stanford Research Corp. digital delay generator, which triggered both lasers. Photons scattered from the excited state were collected in a SPEX Triplemate monochromator and detected with a PAR 1420 intensified diode array detector. A low-temperature (−80 °C) backscattering apparatus was used to obtain the T₁ spectra. The spectral resolution was approximately 8 cm⁻¹. Samples were degassed to prevent quenching of the triplet state. The integrity of all samples was monitored by UV–vis spectra obtained before and after irradiation, which establish that none of the peaks in Figure 1 are due to decomposition products.

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(6) Triplet lifetime is 1.2 ms at 300 K and 26 ms at 77 K in methylcyclohexane, as reported in the following: Darwent, J.; Douglas, P.; Harriman, A.; Porter, G.; Richoux, M.-C. *Coord. Chem. Rev.* **1982,** *44,* 83–126.

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