Bond-Stretch Isomers

Evidence for the Coexistence of Two Bond-Stretch Isomers in Solution[**]

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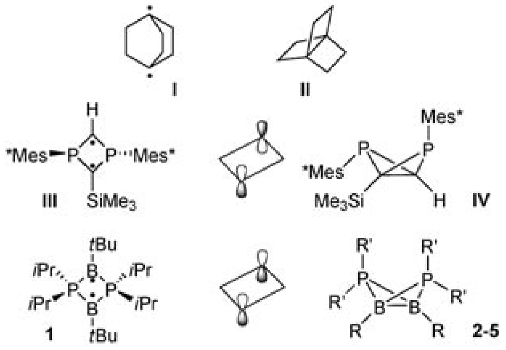
The concept of “bond-stretch isomerism” has been introduced by Stohrer and Hoffmann by using strained tricyclic hydrocarbons (Scheme 1): “In the 2,2,2-system the optimum alignment for through-bond coupling of radical lobes creates the conditions for a new type of isomerism—two stable conformations related by a simple bond stretching. These are



Mes*: $2,4,6\text{-}t\mathrm{Bu}_3\mathrm{C}_6\mathrm{H}_2$
2: R = $2,3,5,6\text{-MeC}_6\mathrm{H}$, R' = iPr; **3**: R = tBu, R' = Ph;
4: R = $2,3,5,6\text{-MeC}_6\mathrm{H}$, R' = Et; **5**: R = R' = Ph

Scheme 1. Some key compounds in the debate on bond-stretch isomerism.

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the normal tricyclic form **II** and the stabilized diradical **I**".[1] The early attempts to characterized bond-stretch isomers either failed or were eventually rejected as crystallographic artifacts, and therefore the existence of bond-stretch isomers became questionable.[2,3] According to the most recent review on this topic,[4] the 1,3-diphosphacyclobutane-2,4-diyl **III** and 1,3-diphosphabicyclo[1.1.0]butane **IV** reported by Niecke et al.[5] are the first and only known stretch isomers that have been isolated and independently characterized. It is important to note that because of a trans-annular anti-bonding π overlap, the thermal ring closure of **III** into **IV** is forbidden. Herein we report the first experimental evidence for the existence of two bond-stretch isomers that features a trans-annular bonding π-overlap, which allows for the thermal ring closure and opening processes.

We have recently reported the synthesis of a 1,3-dibora-2,4-diphosphoniocyclobutane-1,3-diyl **1**,[6–8] as well as several 1,3-dibora-2,4-diphosphoniobicyclo[1.1.0]butanes **2–5**[9] (Scheme 1); they differ by the nature of the boron and phosphorus substituents and therefore are not bond-stretch isomers. Derivatives **1** and **2–5** feature very different spectroscopic properties, which at first glance could be used as a fingerprint for the diradical versus the bicyclic structure. As observed for related carbon-based singlet 1,3-diradicals,[10] compound **1** is strongly colored [λ_{max} (toluene) = 446 nm, $\varepsilon = 2200$], whereas all the derivatives **2–5** are colorless. Because the phosphorus is in a three-membered ring and the boron is tetracoordinated, the ^{31}P and ^{11}B NMR signals for **2–5** appeared at a much higher field than those for **1**.

In the course of a systematic study on the influence of the nature of the substituents on the ground state structure of the PBPB system, we have prepared a derivative that features *iso*-propyl at phosphorus and phenyl groups at boron. This compound has been isolated in 57% yield as very-air-sensitive, but thermally highly stable purple crystals (m.p.: 105 °C). In line with the strong coloration, X-ray diffraction analysis[11] (Figure 1) revealed that in the solid state this compound adopts a very similar structure to that observed for **1**: a planar, almost square PBPB ring, with a very large B–B interatomic distance of 2.57 Å. Interestingly, the phenyl rings are almost coplanar to the PBPB skeleton (torsion angle 13.5°), which suggests some delocalization between the 2p(B) orbitals and the π-ring systems.

The magic-angle-spinning solid-state NMR spectrum of the purple crystals shows a single ^{31}P signal at $\delta = 5.9$ ppm, which is comparable to that observed for **1** both in solution and in the solid state, thus confirming the diradical structure in the solid state. However, the solution state NMR spectra of the same compound (Figure 2) at room temperature reveal a single ^{31}P signal at $\delta = -28$ ppm and an ^{11}B resonance at $\delta = -9$ ppm, which suggest a different structural preference. These chemical shifts are very comparable to those observed both in solution and in the solid state for the bicyclic derivative **2** (same substituents at the P atom and duryl instead of phenyl at the B atp,). As the ^{31}P chemical shift was found to be temperature dependent and moves towards a lower field as the temperature decreased, these results as a whole suggest a fast interconversion between a diradical structure **6** and the corresponding bicyclic stretch isomer **7**, the latter being favored at higher temperatures. This hypothesis is consistent with the observed changes in the NMR line shape[12] as the solution is cooled. But instead of two slow-exchange P signals, one for **6** and one for **7**, three resonances were observed at −145 °C. The signal at $\delta = 4.0$ ppm can be easily assigned to the open form, **6**, whereas the signals at $\delta =$

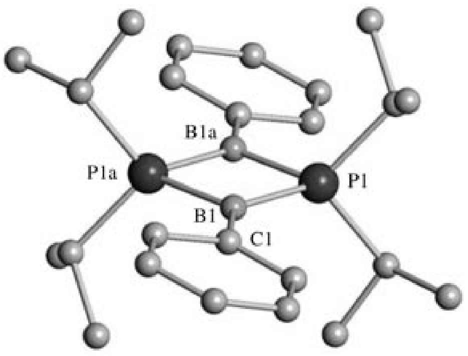

Figure 1. Molecular view of **6** in the solid state (H atoms are omitted). Selected bond lengths: P1–B1, 1.8943 ± 17 Å; P1-B1a, 1.8915 ± 16 Å; B1–C1, 1.557 ± 2 Å; B1-P1-B1a, 85.23 ± 7°, P1-B1-P1a, 94.77 ± 7°, P1-B1-C1, 129.47 ± 11°; P1a-B1-C1, 135.75 ± 12°.

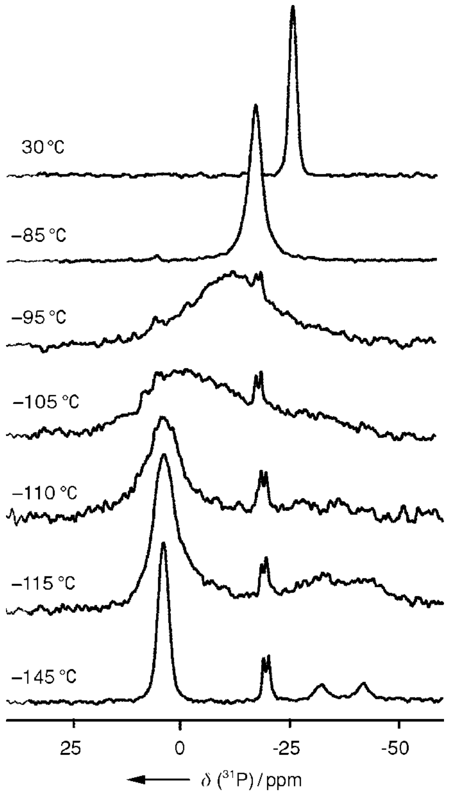

Figure 2. ^{31}P spectra of the interconverting singlet diradical **6** and bicyclic stretch isomers **7** as a function of temperature. Spectra were obtained on a 400 MHz (1 H) Bruker DMX spectrometer equipped with a 5 mm high-resolution double resonance probe and referenced through an external solution of 1% phosphoric acid at 30 °C. The temperature was measured by using an internal probe thermocouple calibrated versus a standard methanol chemical shift thermometer. The signals at −20 ppm are tentatively assigned to impurities.

−32.2 and −41.8 ppm could not be readily explained and prompted us to perform ab initio calculations.[13]

For the planar structure, local minima that correspond to eight different arrangements of the isopropyl groups, including the crystallographically observed conformer **6**, were found. The calculated ^{31}P NMR chemical shift (+6.0 ppm) agrees well with both the solid-state and the low-temperature liquid-state NMR data. For the bicyclic structures, ten local minima were found, among them **7a** and **7b** were the lowest and equivalent in energy (Figure 3). Due to the presence of two inequivalent phosphorous nuclei, AX systems are calculated at $\delta = -36.3$ and −43.1, and −31.9 and −40.3 ppm, for **7a** and **7b**, respectively. The observed signals of equal intensity and line width at $\delta = -32.2$ and −41.8 ppm fit well with a rapid low-temperature interconversion between **7a** and **7b**, although the participation of other conformers that preserves the AX system cannot be excluded.

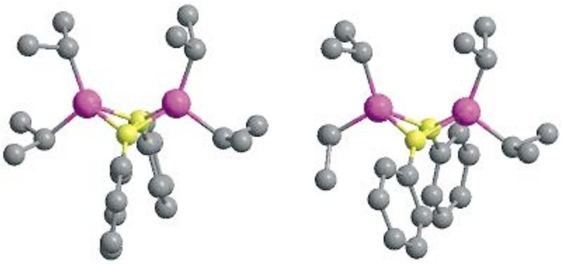

Figure 3. Optimized structures of the two most-stable bicyclic conformers **7a** and **7b**.

As the temperature is raised above −145 °C, the singlet diradical and bicyclic bond-stretch isomers exchange. Initially, the signals at high field broaden more rapidly due to the inequivalent exchange, which favors **6** over **7** by a 3:1 ratio at −145 °C. Rates extracted from the line width of the diradical peak in the initial broadening regime (from −145 to −110 °C) give a free energy of activation[14] of 6.6 ± 1.8 kcal mol^{-1} at −130 °C for the pathway between **6** and **7**. The transition through intermediate exchange (−110 to −85 °C) is somewhat convoluted as the equilibrium constant **6**/**7** also changes dramatically in this region with preference switching from **6** to the bicyclic forms **7** (1:2 at −85 °C). Above −65 °C, only a single fast-exchange resonance is observed with a temperature-dependent chemical shift that reflects the changing populations of the bond-stretch isomers, which reaches a **6**/**7** ratio of 1:7 at room temperature. We can extract a free-energy difference between the stretch isomers from these data by using a three-site exchange model, which gives $\Delta H = 1.4 \pm 0.2$ kcal mol^{-1} (**6** being the most stable isomer) and $\Delta S = 7.2 \pm 1.6$ cal mol^{-1} K. Although, ab initio calculations of the energy difference between the biradical and bicyclic forms favor the bicyclic isomer by 0.8 kcal mol^{-1}, this discrepancy is within the limit of error expected for such a comparison.

We note the excellent agreement of the limiting chemical shifts for the diradical **6** and bicyclic forms **7** with the related compounds **1** and **2**, respectively, as well as the agreement with the ab initio calculated shifts. These results give us confidence that the observed dynamic NMR behavior is not due to isopropyl group rotations[15] within the planar bond-stretch form **6**. This conclusion is confirmed by variable-temperature UV/Vis spectroscopy,[16] which also tracks the population shift from the colorless bicyclic form **7** to the colored diradical species **6** as the temperature is decreased (Figure 4).

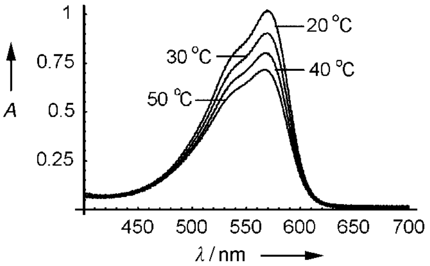

Figure 4. UV/Vis spectra showing the preference for the colored open form **6** over the colorless bicyclic form **7** as the temperature is lowered.

It can be concluded that the order of stability of the bond-stretch isomers **6** and **7** is strongly entropy driven. The diradical isomer with the coplanar phenyl group has fewer degrees of freedom than the bicyclic isomers in which free rotation of the phenyl groups and inversion at boron are both allowed. This is certainly a unique example of a reaction in which the breaking of a σ-bond is induced by decreasing the temperature and the bond formation is entropically favored. It is noteworthy that the B−B interatomic distance between **6** [257 (exp), 258 pm (calcd)] and **7** [186 pm (calcd)] varies by 40%. Combined with the phenomenon of temperature-dependent interconversion, these results open interesting perspectives for "molecular muscles"[17] as well as electrical switch devices.[18]

Experimental Section

All manipulations were performed under argon by using standard Schlenk techniques. Dry, oxygen-free solvents were employed.

Synthesis of [(iPr)$_2$PB(Cl)Ph]$_2$: (iPr)$_2$PSiMe$_3$ (3.05 g, 16.05 mmol) was added to a solution of commercially available PhBCl$_2$ (2.55 g, 16.05 mmol) in toluene (30 mL) at −80 °C. The reaction mixture was heated overnight at 100 °C. All the volatile products were removed under vacuum. Single crystals were obtained by cooling a saturated solution of product in toluene to −30 °C. m.p.: 268 °C, decomp; ^{13}C{^{1}H} NMR (125.8 MHz, CDCl$_3$): $\delta = 132.9$, 127.7, 126.8 (s, C$_{\text{aro}}$), 24.4 (pseudo-t, $J_{\text{PC}} = 15.2$ Hz, PCH), 21.4 (s, CHCH_3), 20.3 ppm (s, CHCH_3), *ipso*-C atoms are not observed; ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 7.72$ (d, $^3J_{\text{HH}} = 6.0$ Hz, 4H, Ph-*o*-CH), 7.23 (m, 6H, Ph-*m*,*p*-CH), 3.02 (m, 4H, P*C*H), 1.28 (dd, $J_{\text{HP}} = 13.8$ Hz, $^3J_{\text{HH}} = 7.2$ Hz, 12H, CHCH_3), 0.75 ppm (dd, $J_{\text{HP}} = 13.8$ Hz, $^3J_{\text{HH}} = 7.2$ Hz, 12H, CHCH_3); ^{31}P{^{1}H} (CDCl$_3$) $\delta = -5.2$ ppm; ^{11}B{^{1}H} (CDCl$_3$) $\delta = -1$ ppm.

Synthesis of derivative **6**/**7**: A freshly prepared solution of Li-naphtalene (6.4 mL, 0.8 M, thf) was added dropwise to a toluene solution (15 mL) of [(iPr)$_2$PB(Cl)Ph]$_2$ (2.5 mmol) at −80 °C. The reaction mixture was warmed to room temperature and stirring was maintained for about 30 minutes. The solvents were immediately removed under vacuum and the residue was dissolved in pentane (30 mL). Salts were removed by filtration and pentane was removed under vacuum. Naphtalene was sublimed by heating to 80 °C under vacuum for 30 minutes. Purple single crystals (57% yield) were obtained by cooling saturated solutions of product in pentane to −30 °C. m.p.: 105 °C; ^{13}C{^{1}H} NMR (125.8 MHz, C$_7$D$_8$): $\delta = 143.8$ (br, *i*-C_{aro}), 136.3, 128.5, 126.3 (s, C_{aro}), 28.6 (pseudo-t, $J_{PC} = 22$ Hz, PCH), 21.4 ppm (s, $CHCH_3$); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.48$ (d, $^3J_{HH} = 7.2$ Hz, 4H, Ph-*o*-CH), 7.01 (pseudo-t, $^3J_{HH} = 7.2$ Hz, 4H, Ph-*m*-CH), 6.89 (t, $^3J_{HH} = 7.2$ Hz, 2H, Ph-*p*-CH), 1.73 (d. sept., $J_{HP} = 4.2$ Hz, $^3J_{HH} = 7.2$ Hz, 4H, PCH), 0.80 ppm (dd, $J_{HP} = 16.5$ Hz, $^3J_{HH} = 7.2$ Hz, 24H, $CHCH_3$).

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