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Synthesis of 1,3,5,7-Tetra-*tert*-butyl-4,8-diphospha-*s*-indacene

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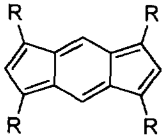
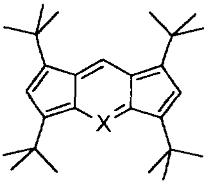
Abstract: 1,3,5,7-Tetra-*tert*-butyl-4,8-diphospha-*s*-indacene, a tricyclic formally antiaromatic heterocycle, has been synthesized and its properties were studied. Copyright © 1996 Elsevier Science Ltd

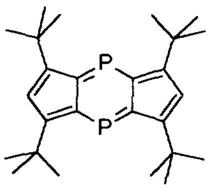
s-Indacene[1] **1**, a tricyclic 12π electron system, has been found to be a touchstone of quantum chemical calculations[2]. In contrast to the unstable parent molecule **1**, the kinetically stabilized tetra-*tert*-butyl derivative **2**[3] could be isolated as a crystalline compound and proved to have nearly equivalent bond lengths along the perimeter and, accordingly, delocalized π electrons despite of its formally antiaromatic character. We were therefore interested in the influence of heteroatoms on the *s*-indacene π perimeter. In our earlier investigations[4] of the 4-aza- and 4-phospha-*s*-indacene derivatives **3** and **4**, respectively, we found only a slight perturbation of the formally antiaromatic π perimeter by replacement of the 4-methine group of the carbocycle **2** by a nitrogen atom, but a stronger deviation in the case of the phospha heterocycle **4**. It was expected that the diphospha-*s*-indacene **5** would exhibit a significant larger perturbation of the *s*-indacene π electron system than found in **3** and **4**. We report herein on the synthesis and properties of the new diphospha heterocycle **5**.



1 (R=H)
2 (R=*t*Bu)

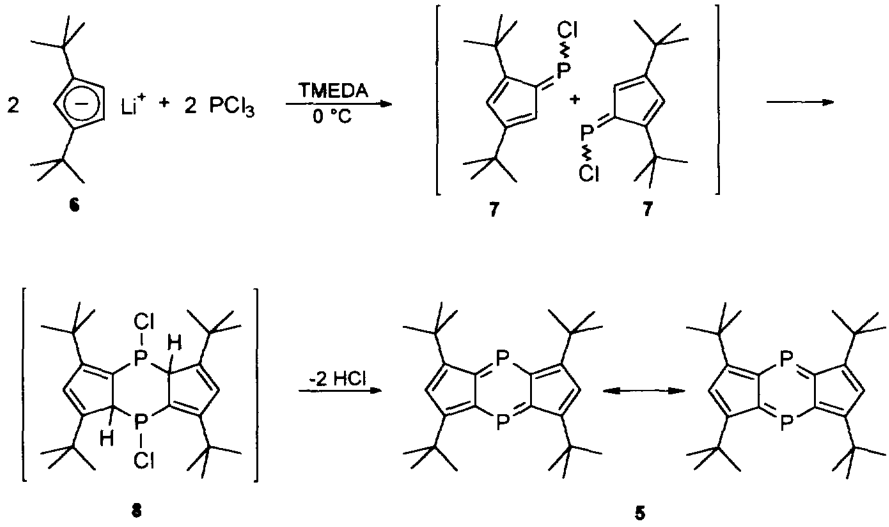


3 (X=N)
4 (X=P)

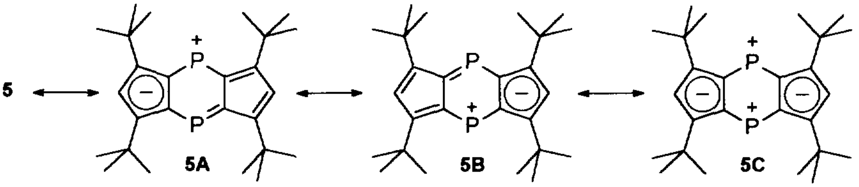


5

Treatment of lithium 1,3-di-*tert*-butylcyclopentadienide **6** with one mole equivalent of phosphorus trichloride in the presence of excess TMEDA at 0 °C leads to a deeply turquoise-coloured suspension, from which up to 8 % of the diphospha-*s*-indacene **5** can be obtained as a blueblack fine crystalline solid which can be recrystallized from anhydrous toluene. The 6-chloro-6-phospha-pentafulvene **7** may be an intermediate, which could dimerize to the tricycle **8**. Subsequent elimination of two mole equivalents of HCl from **8** would give the diphospha heterocycle **5**. In the solid state, **5** can be stored under argon at -30 °C for some weeks without decomposition. In aprotic organic solvents the diphospha-*s*-indacene **5** is only sparely soluble and produces very intense turquoise solutions which decolourize rapidly if even traces of water are present (see below).



The ^{1}H NMR spectrum of **5** shows a singlet at $\delta = 1.42$ for four equivalent *tert*-butyl groups and a signal at $\delta = 5.80$ for 2- and 6-H which is split into a triplet by the two ^{31}P nuclei. The proton resonance for 2- and 6-H experiences a downfield shift of 0.51 *ppm* and 0.26 *ppm* compared with the carbocycle **2** and the mono-phospha-*s*-indacene **4**, respectively, which can be explained by contributions of dipolar mesomeric structures of type **5A**-**5C** to the electronic ground state of **5**. In these structures the formally antiaromatic 12π perimeter is disturbed by the cyclopentadienide partial structures, leading to a decrease of the paratropic ring current and consequently a downfield shift of the ^{1}H NMR signal for 2- and 6-H. Due to the very low solubility of **5** in organic solvents and the sensitivity of these dilute solutions, no convincing ^{13}C NMR spectrum could be recorded so far.



The ^{31}P NMR spectrum of **5** shows one resonance signal at 275.6 *ppm*, *i. e.* accordingly to the proposed mesomeric structures **5A**-**5C** with deshielded phosphorus nuclei at very low field. This implies in comparison with the monophospha-*s*-indacene **4** a downfield shift of about 17 *ppm* and points to even stronger deshielded phosphorus nuclei in **5** than in **4**, but this effect may also be partially attributed to changes in bond angles at the phosphorus atoms in **5** compared to **4**.

The NMR data for **5** imply a D_{2h} symmetry since all *tert*-butyl groups are chemically equivalent, *i. e.* no double bond alternation is observed. Obviously, as has been shown for the 4-aza-*s*-indacene **3** and the 4-phospha-*s*-indacene **5**, the π electrons may be delocalized over the perimeter despite the formally antiaromatic character of the 12π system.

Fig. 1 shows the UV/Vis spectra of the carbocycle **2**, the phospha-*s*-indacene **4** and the diphospha-*s*-indacene **5**. While the UV absorption maximum of **5** at 384 nm is shifted 38 nm bathochromically in comparison with that of **4**, the visible absorption band at 615 nm is not much shifted (5 nm) by the second phosphorus atom in the perimeter but experiences an increase in extinction of about 10 %.

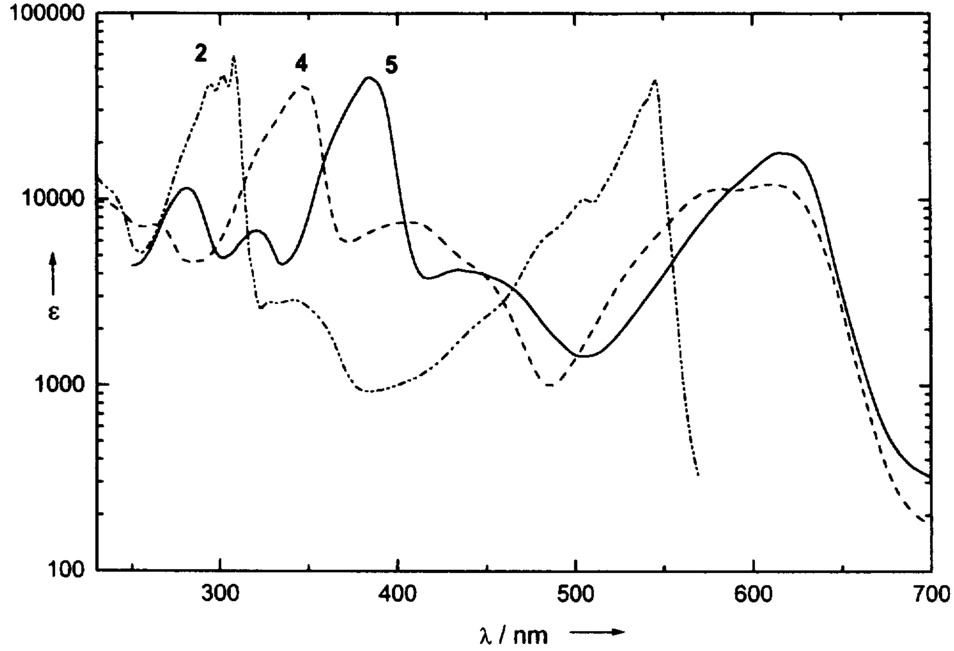


Fig.1. UV/Vis spectra of the *s*-indacenes **2** (*n*-hexane), **4** (CH_2Cl_2) and **5** (CH_2Cl_2).

As could be expected from the ylidic mesomeric structures **5A**-**5C**, the diphospha-*s*-indacene **5** readily adds two mole equivalents of water resulting in quantitative yields of 1,3,5,7-tetra-*tert*-butyl-3a*H*,7a*H*-4,8-diphospha-*s*-indacene-4,8-dioxide **10** as colourless microcrystalline needles. Presumably the phosphinous acid **9** is formed initially which rearranges to the *sec*-phosphine oxide **10**. The ^1H, ^{13}C and ^{31}P NMR data indicate that

10 must have a centre of symmetry or a twofold axis normal to the molecular plane. For steric reasons it is most likely that the six membered ring adopts a chair conformation giving rise to a C_i symmetric molecule.

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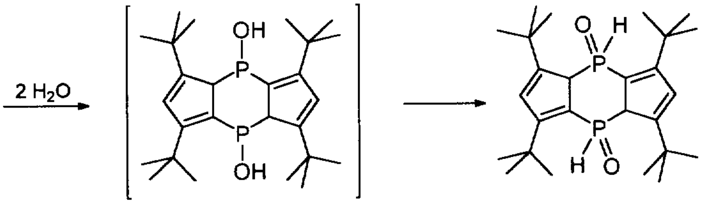

9 **10**

Tab. 1: Physical data of compounds **5**, **10**[5,6]

5: blueblack fine crystals, m.p. 223-225 °C (decomp.), MS (70 eV): *m/z* (%): 412 (100) [M^-], 397 (48) [M^+-Me], 355 (49) [M^+-*t*Bu], 57 (42) [*t*Bu^+]; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.42$ (s, 36H, 4 *t*Bu, 5.80 (t, ^4J(P-H) = 3.5 Hz, 2H, 2- and 6-H); ^{31}P NMR (121.5 MHz, $CDCl_3$): $\delta = 275.6$; UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 281 nm (4.06), 320 (3.84), 384 (4.66), 433 (3.63), 615 (4.25), 760 (2.48) (sh), 917 (2.26) (sh).

10: colourless microcrystalline needles, m. p. 209-210 °C, MS (70 eV): *m/z* (%): 448 (43) [M^+], 433 (22) [M^+-Me], 57 (100) [*t*Bu^+]; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.35$ (s, 18H, 1- and 5-*t*Bu or 3- and 7-*t*Bu), 1.38 (s, 18H, 1- and 5-*t*Bu or 3- and 7-*t*Bu), 4.80 (ddd, ^2J(P-H) = 27.6 Hz, ^3J(H-H) = 5.8 Hz, ^3J(P-H) = 2.5 Hz, 2H, 3a-H and 7a-H), 6.16 (dd, ^1J(P-H) = 518.1 Hz, ^3J(H-H) = 5.8 Hz, 2H, 4-H and 8-H), 6.56 (dd, ^3J(P-H) = 3.9 Hz, ^3J(P-H) = 1.7 Hz, 2H, 2-H and 6-H); ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta = 30.25$ (d, ^4J(P-C) = 3 Hz, 1- and 5-$C(\underline{C}H_3)_3$), 31.19 (s, 3- and 7-$C(\underline{C}H_3)_3$), 34.10 (s, 1- and 5-$\underline{C}(CH_3)_3$ or 3- and 7-$\underline{C}(CH_3)_3$), 35.92 (br. s, 1- and 5-$\underline{C}(CH_3)_3$ or 3- and 7-$\underline{C}(CH_3)_3$), 57.06 (dd, ^1J(P-C) = 51 Hz, ^2J(P-C) = 13 Hz, C-3a and C-7a), 121.79 (d, ^1J(P-C) = 111 Hz, C-4a and C-8a), 130.94 (dd, ^3J(P-C) = 14 Hz, ^3J(P-C) = 3 Hz, C-2 and C-6), 165.51 (m, C-3 and C-7), 171.73 (dd, ^2J(P-C) = 8 Hz, ^3J(P-C) = 8 Hz, C-1 and C-5); ^{31}P NMR (121.5 MHz, $CDCl_3$): $\delta = 19.4$; UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 240 nm (3.92), 308 (4.07).

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REFERENCES AND NOTES

Dedicated to Professor Siegfried Hünig, Würzburg, on the occasion of his 75th birthday.

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5. The compounds **5** and **10** gave correct elemental analyses.

6. ^{1}H- and ^{13}C NMR spectra are referred to tetramethylsilane as internal standard. For ^{31}P NMR spectra 85 % phosphoric acid was used as external standard.

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