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Bidentate Phosphines of Heteroarenes: 1,9-Bis(diphenylphosphino)-dibenzothiophene and 4,6-Bis(diphenylphosphino)dibenzothiophene[1)]

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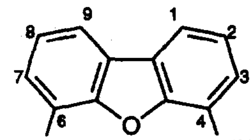
Abstract: **Twofold lithiation of dibenzothiophene with n-butyllithium and N,N,N',N'-tetramethylethylenediamine (TMEDA) in boiling n-heptane followed by reaction with chlorodiphenylphosphine (Ph_2PCl) yielded the title compounds 2 (colourless) and 3 (yellow). Both phosphines were characterised by single crystal X-ray structure analysis and $^{13}C,^{1}H$ shift correlated 2D NMR spectroscopy, based on which our previous assignment of the yellow compound to structure 2 has to be revised.**

Previously we reported the synthesis of 4,6-bis(diphenylphosphino)dibenzofuran (**1**) and 4,6-bis(diphenylphosphino)dibenzothiophene (**2**) via twofold lithiation of the heteroarenes dibenzofuran (**4**) and dibenzothiophene (**5**) by n-butyllithium/TMEDA in n-heptane or n-pentane, respectively, and subsequent reaction of the dilithium compounds with Ph_2PCl.[2)] In the case of **4** the dilithium compound has been characterised by its reaction with ethanol[D] forming [4,6-D_2]dibenzofuran, which has been unambiguously assigned by ^{1}H-NMR and ^{13}C-NMR spectra. For the metalation of **5** we thought that the corresponding proof might be unnecessary, since the formation of 4-lithiodibenzothiophene in the reaction of n-butyllithium with **5** in ether is well established[3,4)] and also the existence of the 4,6-dilithium compound seemed to be proved sufficiently[5)]. Thus, the diphosphine, which we isolated along with 4-diphenylphosphinodibenzothiophene (**6**) from the metalation of **5** in n-pentane using two equivalents of n-butyllithium/TMEDA followed by reaction with Ph_2PCl, was assigned the structure of 4,6-bis-(diphenylphosphino)dibenzothiophene (**2**). The yellow diphosphine (m.p. 228 - 231°C) showed one signal in the ^{31}P-NMR spectrum {CD_2Cl_2, 81 MHz: $\delta = -10.0$ (s)} and one ABC system of twofold intensity at $\delta = 7.88$, 7.57 and 7.41 for three neighbouring protons in the ^{1}H-NMR spectrum (CD_2Cl_2, 200 MHz) in agreement with a symmetric disubstitution in either the dibenzothiophene 4,6- or 1,9-position. The latter possibility seemed to be so improbable that it was not considered seriously. Only the mass spectrum of the compound appeared to be somewhat striking by showing a very low intensity molecular ion peak *m/z* = 552 (1.5%) and the fragment ion peak *m/z* = 475 as the base peak. This had to be attributed to an unusually strong fragmentation [M^+ - 77] by the loss of a phenyl group from the molecular ion. However, last doubts about the structure seemed to be dispelled by the ^{13}C-NMR spectrum ($CDCl_3$, 100 MHz) which was also interpreted in favour of structure **2**[2)].



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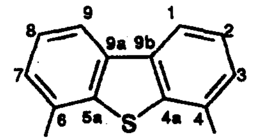

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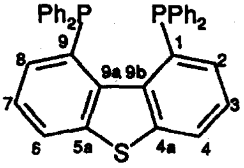

3

In order to improve the preparation and the yield of **2**, the synthesis was repeated by replacing n-pentane by the higher-boiling n-heptane as solvent in the metalation step since for the reaction of **4** with n-butyllithium/TMEDA, the ratio of mono- and dilithiation was found to depend strongly on the temperature[2)]. To a solution of one equivalent of **5** and two equivalents of TMEDA in n-heptane two equivalents of n-butyllithium in n-hexane were added at 0°C and the yellow-orange solution was subsequently heated to reflux for 30 min. Shortly before reaching the reflux temperature, a yellow solid, presumably consisting of multiply lithiated **5**, started to precipitate from the yellow-orange solution. The subsequent reaction with two equivalents of Ph_2PCl led to a yellowish raw material which was fractionated by repeated crystallisations from mixtures of isopropanol and dichloromethane. In addition to the yellow diphosphine, assigned in our previous work to structure **2**, surprisingly a second diphosphine could be isolated as colourless crystals (m.p. 236 - 237°C). According to the ^{31}P-NMR ($CDCl_3$, 81 MHz) and ^{1}H-NMR spectra ($CDCl_3$, 200 MHz), showing one phophorus signal at $\delta = -9.7$ and one ABC-system of twofold intensity at $\delta = 8.14$, 7.39 and 7.07 for three neighbouring protons, respectively, this newly isolated diphosphine also had to be symmetrically disubstituted either in dibenzothiophene 1,9- or 4,6-position. On comparing the chemical shifts with those of the monosubstituted 4-diphenylphosphinodibenzothiophene (**6**)[2,4], this compound seemed to match even better the 4,6-disubstition pattern of structure **2** than the yellow diphosphine. Therefore, single crystal X-ray structure analyses of both compounds were performed[8,9]. As shown in Figures 1 and 2, the colourless compound is indeed the diphosphine **2** substituted in the dibenzothiophene 4,6-position and the yellow compound is the 1,9-disubstituted isomer **3**. In **2** the dibenzothiophene unit is planar and the distance between the two phosphorus centres is 6.383(1) Å (Figurel). On the other hand, in **3** the close proximity of the two phosphorus centres [P1···P2 3.009(1) Å] causes a considerable distortion of the dibenzothiophene unit and an out-of-plane displacement of the phosphorus atoms: P1 is located 1.117(1) Å below and P2 0.925(1)Å above the average dibenzothiophene plane (Figure 2a,b).

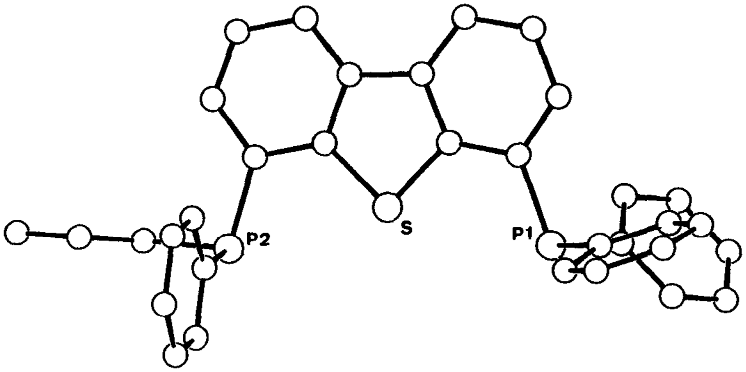

Figure 1: Molecular structure of 4,6-bis(diphenylphosphino)dibenzothiophene (**2**); view onto the dibenzothiophene plane.

The ^{1}H- and ^{13}C-NMR spectra of both isomeric diphosphines **2** and **3** could be assigned by means of ^{13}C,^{1}H shift correlated 2D NMR spectroscopy[6,7]. In the ^{13}C-NMR spectra the multiplets due to coupling with ^{31}P can be analysed as AA'X-systems ($A = A' = {}^{31}P$, $X = {}^{13}C$). In **2** the coupling constant $J_{PP} \equiv 0$ results in doublets of doublets from which the coupling constants J_{PC} and $J_{P'C}$ can be extracted directly. However, in **3** J_{PP} is large compared with J_{PC} and $J_{P'C}$ so that apparent triplets are observed from which only the sum of the couplings $J_{PC+P'C}$ can be obtained. In the UV/Vis spectra (in cyclohexane) of both compounds the absorption bands of the dibenzothiophene unit are shifted to longer wavelengths by 10 to 20 nm for **2** and 20 to 30 nm for **3**. The yellow colour of **3** is caused by the dibenzothiophene α–band at 357 nm tailing to wavelengths of $\lambda > 400$ nm; both the larger spectroscopic shift and the characteristic tailing of the α-band are attributed to the distortion of the dibenzothiophene unit and possibly to a P···P interaction. The latter effect is considered to also cause the unusually strong fragmentation [$M^+ - 77$] which, as mentioned above, is observed in the mass spectrum of the yellow diphosphine[6,7]. Apparently the loss of a phenyl group from the molecular ion of **3** is energetically favoured by the concomitant formation of a P - P bond in the remaining fragment ion *m/z* = 475.

The unexpected formation of **3** prompted us to study the twofold lithiation of dibenzothiophene (**5**) in more detail. After treating **5** with two equivalents of each n-butyllithium and TMEDA for different times at various temperatures, the lithium compounds formed were characterised by their reaction with ethan[D]ol and subsequent investigation of the deuterated **5** by MS, ^{1}H-NMR and ^{13}C-NMR spectroscopy. Whereas at 0°C essentially only monometalation with formation of the 4-lithiodibenzothiophene is observed, increasing yields of a mixture of 4,6- and 1,9 dilithiodibenzothiophene in a nearly constant ratio of ca. 3:1 is obtained in the temperature range from room to reflux temperature[10]. Based on these observations we conclude that after the first lithiation in the dibenzothiophene 4-position, the second lithiation step results in a ca. 3:1 mixture of the 4,6- and the 1,4- (and/or 4,9-) dilithium derivatives, from which the latter isomerise by intermolecular transmetalation into the thermodynamically more favoured 1,9-isomer[11].

1,9-disubstituted dibenzothiophenes have been recently obtained in moderate yields by ring contraction of 4,6-disubstituted thianthrene-5-oxides[12]. The results presented here demonstrate that such sterically crowded 1,9-disubstituted dibenzothiophenes can also be obtained directly by the twofold lithiation of **5** and subsequent reaction of the 1,9-dilithiodibenzothiophene with electrophiles.

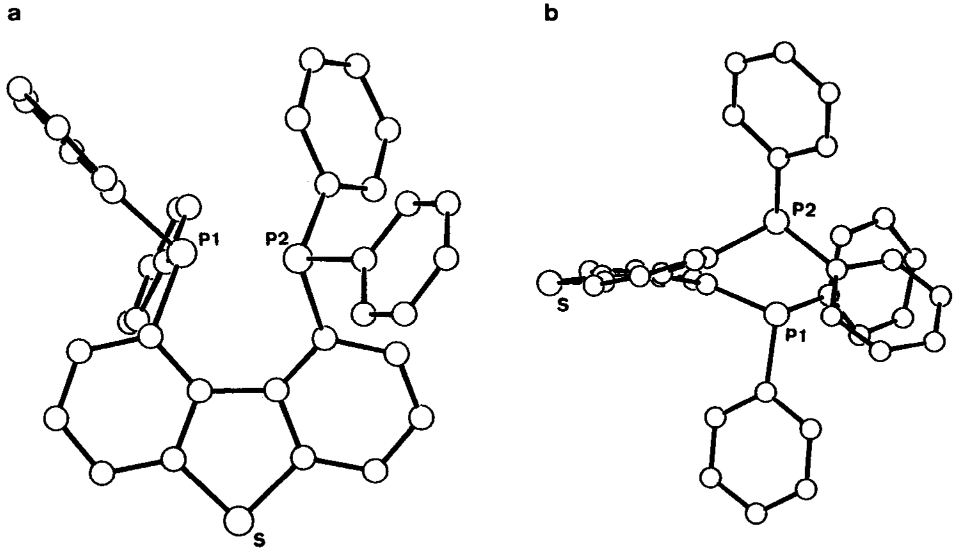

Figure 2: Molecular structure of 1,9-bis(diphenylphosphino)dibenzothiophene (**3**); **a**: view onto the dibenzothiophene plane; **b**: side view.

References and Notes:

1) Phosphine ligands, 3; for part 2 see ref.[2].

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4) 4-Diphenylphosphinodibenzothiophene (**6**), obtained from 4-lithiodibenzothiophene and Ph_2PCl, has been characterised by single crystal X-ray structure analyses of two metal complexes as well as the uncomplexed ligand; Bucknor, S.M.; Draganjac, M.; Rauchfuss, T.B.; Ruffing, C.J.; Fultz, W.C.; Rheingold, A.L. *J. Am. Chem. Soc.* **1984**, *106*, 5379-5381. Robinson, P.D.; Dunkerton, L.V.; Pandey, A.; Hinckley, C.C. *Acta Crystallogr., Sect. C.*, **1989**, *45*, 587-591.

5) The reaction of **5** with a fourfold excess of n-butyllithium in di-n-butyl ether followed by reaction with dimethyl sulphate has been reported to yield 15% of 4,6-dimethyldibenzothiophene along with a material assumed to be 4-methyldibenzothiophene: Gerdil, R.; Lucken, E.A.C. *J. Am. Chem. Soc.* **1965**, *87*,

213-217. The product obtained from the reaction of **5** with a fourfold excess of n-butyllithium in diethyl ether and subsequent reaction with deuterium oxide has been shown by mass spectrometry to contain 68% of $[D_1]$- and 22% of $[D_2]$dibenzothiophene from which the latter compound was presumed to be 4,6-disubstituted: Meyerson, S.; Fields, E.K. *J. Org. Chem.* **1968**, *33*, 847-848.

6) Yellow crystals, previously assigned$^{2)}$ to structure **2**, now assigned to structure **3**: m.p. 228 - 231°C. – ^{1}H NMR (CD_2Cl_2, 25°C, 200 MHz): δ = 7.88, 7.57, 7.41 [ABCXX′ with X and X′= ^{31}P, J_{AB} = 1.2, J_{AC} = 7.8, J_{BC} = 7.6, $\Sigma J_{BX(X')}$ = 3.2, $J_{CX} \approx$ 0 Hz, each 2H for 4-, 6-H, 2-, 8-H, 3-, 7-H], 7.25 - 7.20 [m, 20H, phenyl H]. – ^{31}P NMR (CD_2Cl_2, 25°C, 81 MHz): δ = - 10.0 (s). – ^{13}C NMR ($CDCl_3$, 30°C, 100 MHz, analysed by ^{13}C,^{1}H shift correlated 2D NMR spectroscopy): δ [multiplicity with respect to $^1J_{CH}$, coupling to ^{31}P with apparent multiplicity ("m")] = 140.5 [s, $J_{PC+P'C}$ = 31.3 Hz ("t"), C-9a, -9b], 140.2 [s, $J_{PC+P'C}$ = 9.0 Hz ("t"), C-4a, -5a], 140.0 [s, $J_{PC+P'C}$ = 0.6 Hz ("d"), phenyl C_{ipso}], 135.4 [s, $J_{PC+P'C}$ = 12.5 Hz ("t"), C-1, -9], 135.0 [d, $^1J_{CH}$ = 163 Hz, $J_{PC+P'C}$ = 1,8 Hz ("t"), C-2, -8], 133.0 [d, $^1J_{CH}$ = 160 Hz, $J_{PC+P'C}$ = 21.0 Hz ("t"), phenyl C_{ortho}] 127.8 [d, $^1J_{CH}$ = 160 Hz, $J_{PC+P'C}$ = 6.7 Hz ("t"), phenyl C_{meta}] 127.6 [d, $^1J_{CH}$ = 160 Hz, phenyl C_{para}], 126.4 [d, $^1J_{CH}$ = 163 Hz, C-3, -7], 123.4 [d, $^1J_{CH}$ = 163 Hz, C-4, -6]. – MS (70 eV): *m/z* (%) = 553 (0.6), 552 (1.5) [M^+], 476 (33), 475 (100) [M^+ - Ph], 398 (3.5) [M^+ - 2 Ph], 367 (1.3) [M^+ - Ph_2P], 321 (18), 289 (9), 276 (8), 258 (5), 244 (4), 213 (3), 183 (12), 152 (1), 107 (1), 77 (2), 51 (2).

7) Colourless crystals, assigned to structure **2**: m.p. 236 - 237°C. – ^{1}H NMR ($CDCl_3$, 25°C, 200 MHz): δ = 8.14, 7.39, 7.07 [ABCX with X = ^{31}P, J_{AB} = 8.0, J_{AC} = 1.1, J_{BC} = 7.3, $J_{AX} \approx$ 0.5, $J_{BX} \approx$ 0.5, J_{CX} = 4.8 Hz, each 2H for 1-, 9-H, 2-, 8-H, 3-, 7-H], 7.28 - 7.15 [m, 20H, phenyl H]. – ^{31}P NMR ($CDCl_3$, 25°C, 81 MHz): δ = - 9.7 (s). – ^{13}C NMR ($CDCl_3$, 30°C, 75 MHz, analysed by ^{13}C,^{1}H shift correlated 2D NMR spectroscopy): δ [multiplicity with respect to $^1J_{CH}$, coupling to ^{31}P with multiplicity (m)] = 146.1 [s, $J_{PC} \approx$ 29.9, $J_{P'C} \approx$ 6.3 Hz (dd), C-4a, -5a], 135.4 [s, $J_{PC} \approx$ 6.3, $J_{P'C} \approx$ 2.2 Hz (dd), C-9a, -9b], 135.3 [s, $J_{PC} \approx$ 9.4 Hz (d), phenyl C_{ipso}], 133.8 [d, $^1J_{CH}$ = 162, $J_{PC} \approx$ 19.4 Hz (d), phenyl C_{ortho}], 131.54 [s, $J_{PC} \approx$ 12.1 Hz (d), C-4, -6], 131.49 [d, $^1J_{CH}$ n.d. (overlapping signals), C-3, -7], 128.9 [d, $^1J_{CH}$ = 162 Hz, phenyl C_{para}], 128.5 [d, $^1J_{CH}$ = 160, $J_{PC} \approx$ 7.1 Hz (d), phenyl C_{meta}], 124.8 [d, $^1J_{CH}$ = 160, $J_{PC} \approx$ 0.9 Hz (d), C-2, -8], 122.1 [d, $^1J_{CH}$ = 160, $J_{PC} \approx$ 1.0 Hz (d), C-1, -9]. – MS (70 eV): *m/z* (%) = 554 (12), 553 (32), 552 (100) [M^+], 475 (3) [M^+ - Ph], 395 (2), 367 (4) [M^+ - Ph_2P], 365 (8), 289 (10), 276 (11), 258 (3), 257 (4), 213 (3), 197 (4), 183 (17), 152 (1), 107 (2), 77 (2), 51 (2).

8) Crystal structure analysis of **2**, $C_{36}H_{26}P_2S$, MW = 552.6, crystal size 0.28 x 0.39 x 0.32 mm, a = 14.689(1), b = 12.091(1), c = 16.196(2) Å, β = 90.53(1)°, V = 2876.4 Å^3, d_{calc} = 1.28 g cm^{-3}, μ = 2.39 cm^{-1}, F(000) = 1152 e, Z = 4, crystal system monoclinic, space group $P2_1/c$(No.14), Enraf-Nonius-CAD4-diffractometer, λ = 0.71069 Å, 10466 measured reflections ($\pm h, \pm k, +l$), $[(\sin \theta)/\lambda]_{max}$ 0.65 Å^{-1}, 6563 independent and 5011 observed reflections [$I \geq 2\sigma(I)$], 352 refined parameters, heavy-atom method, H-atom positions were calculated and kept fixed in the final least-squares-refinement, R = 0.039, R_w = 0.046 [$w = 1/\sigma^2 (F_o)$], max. residual electron density 0.21 eÅ^{-3}.

9) Crystal structure analysis of **3**, $C_{36}H_{26}P_2S$, MW = 552.6, crystal size 0.07 x 0.21 x 0.25 mm, a = 10.801(2), b = 11.002(1), c = 13.694(1) Å, α = 93.78(1)°, β = 106.58(1)°, γ = 112.08(1)°, V = 1417.5 Å^3, d_{calc} = 1.29 g cm^{-3}, μ = 2.43 cm^{-1}, F(000) = 576 e, Z = 2, crystal system triclinic, space group $P\bar{1}$ (No.2), Enraf-Nonius-CAD4-diffractometer, λ = 0.71069 Å, 6720 measured reflections ($\pm h, \pm k, +l$), $[(\sin \theta)/\lambda]_{max}$ 0.65 Å^{-1}, 6448 independent and 4392 observed reflections [$I \geq 2\sigma(I)$], 352 refined parameters, heavy-atom method, H-atom positions were calculated and kept fixed in the final least-squares-refinement, R = 0.047, R_w = 0.048 [$w = 1/\sigma^2 (F_o)$], max. residual electron density 0.30 eÅ^{-3}.

10) Details will be given in an extended paper on the multiple lithiation of dibenzothiophene (**5**).

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