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Formation of (1,2-dihydroxynaphth-4-yl)[tris(diethylamino)]phosphonium bromides in the reaction of 1,2-naphthoquinones with tris(diethylamino)phosphine

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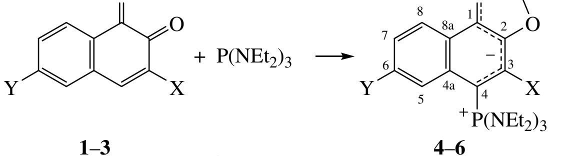
The title reaction leads to the formation of betaines containing a phosphorus–carbon bond, 2-hydroxy-4-[tris(diethylamino)-phosphonium]naphthyl-1-ates, which react with bromine and moist acetone (or hydrogen bromide), as well as diethylammonium chloride, to give (1,2-dihydroxynaphth-4-yl)[tris(diethylamino)]phosphonium bromide derivatives.

ortho-Quinones and their derivatives are of great interest due to their significance in nature. They play an important role in electron transport and possess various kinds of biological activity. They are also used in the synthesis of metal complexes, nitrogen- or oxygen containing heterocycles and in enantioselective synthesis.[1–6]

Trivalent phosphorus compounds are widely used in *ortho*-quinone chemistry, as a rule, for the preparation of pentacoordinated phosphorus derivatives (phosphoranes) or tetracoordinated ones (quasiphosphonium salts having a betaine structure with the P^+–OC bond), which are used in organic synthesis.[7,8] 1,2-Naphthoquinones react with phosphites to form phosphoranes.[7] At the same time, a great number of 1,2-naphthoquinones, especially 4-substituted 1,2-naphthoquinones, exhibit various physiological properties. They can be used as the models of polycyclic carcinogenic hydrocarbons binding by amino acids.[9]

Recently, we have shown that the reaction of 6-bromo-1,2-naphthoquinone with tris(diethylamino)phosphine under mild conditions leads to the formation of 6-bromo-2-hydroxy-4-[tris-(diethylamino)phosphonium]naphthol-1-ate, which easily turns into 4-[tris(diethylamino)phosphoniumbromide]-1,2-naphthoquinone after bromine treatment.[10] We attempted to extend this approach to other 1,2-naphthoquinone derivatives. The use of unsubstituted and 3-halogenated 1,2-naphthoquinones **1**–**3** in these reactions does not change the regiochemistry of phosphorylation, and corresponding betaines **4**, **5**,[†] **6**[‡] are formed in high yields (Scheme 1).

The structure of betaines **4**–**6** was determined by NMR spectroscopy. The singlet at 56.1 ppm in the ^{31}P NMR spectrum corresponds to the phosphorus atom of betaine **4**. There is a broad doublet at 86.01 ppm with $^1J_{PC}$ 223.0 Hz in the ^{13}C NMR spectrum of compound **6** corresponding to the C^4 atom bonded with the phosphorus atom. Despite negative charge delocalization in the ring double bonds system the signals of C^1 and C^2 atoms are quite different (161.43 and 140.84 ppm). The C^1 atom has a more clearly pronounced 'carbonyl' character while the signal of the C^2 atom corresponds to the C^2(OH)=C



1–**3**

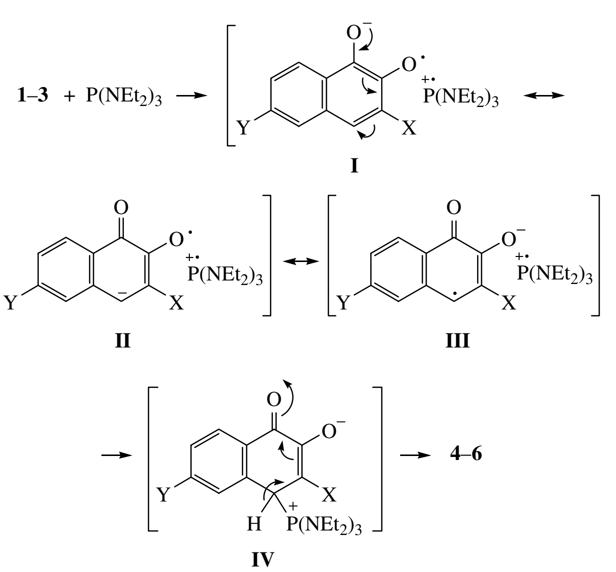
4–**6**

1, **4** X = Y = H
2, **5** X = Br, Y = H
3, **6** X = Cl, Y = Br

Scheme 1

[†] *3-Bromo-2-hydroxy-4-tris(diethylamino)phosphoniumnaphthyl-1-ate* **5**. To a solution of quinone **2** (0.93 g, 3.90 mmol) in dichloromethane (5 ml) with bubbling dry argon, tris(diethylamino)phosphine (1.03 ml, 3.90 mmol) was added dropwise at room temperature. During the addition, the reaction mixture obtained a cerise colour and a strong exothermic effect occurred. After the addition of phosphine, the solvent was removed under reduced pressure and a glass-like residue was treated with light petroleum (10 ml). After a day, the deep-green precipitate formed was separated, washed with acetone and dried to give 1.45 g (79%) of pure compound **5**, mp 163–165 °C. ^{31}P NMR (36.48 MHz, CDCl$_3$) δ_P: 53.3 [m (s)]. IR (Nujol, ν/cm^{-1}): 3454 (br., OH), 1607 (br., C=O), 1553 (C=C), 1496 (C=C), 1405, 1343, 1279, 1237, 1198, 1187, 1157 (P–N), 1113, 1079, 1058, 1031, 1014, 964, 943, 810, 792, 764, 696, 648, 512, 430. Found (%): C, 54.27; H, 7.61; N, 8.18; P, 5.99; Br, 16.41. Calc. for $C_{22}H_{35}BrN_3O_2P$ (%): C, 54.54; H, 7.23; N, 8.68; P, 6.40; Br, 16.53.

[‡] *6-Bromo-3-chloro-2-hydroxy-4-tris(diethylamino)phosphoniumnaphthyl-1-ate* **6**. To a solution of quinone **3** (1.00 g, 3.68 mmol) in dichloromethane (10 ml) with bubbling dry argon, a solution of tris(diethylamino)phosphine (0.97 ml, 3.68 mmol) in dichloromethane (5 ml) was added dropwise (10 °C). During the addition, the reaction mixture obtained a red-maroon colour and a small exothermic effect occurred. After the addition of phosphine, the solvent was removed under reduced pressure and the residue was grinded in diethyl ether. A yellow solid precipitated was filtered off and dried in a vacuum to give 1.65 g (87%) of compound **6**, mp 158–160 °C. ^{31}P NMR (36.48 MHz, CDCl$_3$) δ_P: 45.5 [m (s)]. ^{1}H NMR (600 MHz, CDCl$_3$) δ_H: 1.57 (m, NCMe, $^3J_{HCCH}$ 7.2 Hz), 3.1 (dq, NCH$_2$, $^3J_{PNCH}$ 10.4 Hz, $^3J_{HCCH}$ 7.2 Hz), 7.25 (d, H^8, $^3J_{HCCH}$ 8.8 Hz), 8.30 (d, H^7, $^3J_{HCCH}$ 8.8 Hz), 7.94 (s, H^5). ^{13}C NMR (150.9 MHz, CDCl$_3$) δ_C: 161.43 [br. m (br. d), C^1, $^4J_{PCCCC}$ 2.1–2.3 Hz, $^3J_{HCCC}$ 7.0–7.2 Hz], 140.84 [br. d (br. d), C^2, $^2J_{PCC}$ 13.8–14.0 Hz], 133.40 [br. m (br. d), C^3, $^2J_{PCC}$ 5.0 Hz], 86.01 [br. d (br. d), C^4, $^1J_{PC}$ 223.0 Hz], 126.60 [br. m (br. d), C^{4a}, $^2J_{PCC}$ 8.0–8.4 Hz], 126.06 [ddd (d), C^5, $^3J_{PCCC}$ 6.1 Hz, $^1J_{HC}$ 162.2 Hz, $^3J_{HCCC}$ 4.7 Hz], 121.17 [ddd (s), C^6, $^3J_{HCCC}$ 13.3 Hz, $^2J_{HCC}$ 4.8 Hz, $^2J_{HCC}$ 2.4 Hz], 125.05 [br. dm (br. d), C^7, $^5J_{PCCCCC}$ 2.4 Hz, $^1J_{HC}$ 167.0 Hz], 127.54 [d (s), C^8, $^1J_{HC}$ 164.64 Hz], 124.97 [ddd (d), C^{8a}, $^3J_{PCCC}$ 12.6 Hz, $^3J_{HCCC}$ 6.0 Hz, $^3J_{HCCC}$ 6.0 Hz], 41.96 [tdq (d), NCH$_2$, $^1J_{HC}$ 141.8 Hz, $^2J_{PNC}$ 5.0 Hz, $^2J_{HCC}$ 4.2 Hz], 13.17 [qdm (d), Me, $^3J_{PNCC}$ 3.8 Hz, $^2J_{HCC}$ 3.6 Hz, $^1J_{HC}$ 127.3 Hz]. IR (Nujol, ν/cm^{-1}): 3150–3180 (br., OH), 1597 (C=O), 1578, 1540 (C=C), 1485 (C=C), 1351, 1274, 1238, 1202, 1158 (P–N), 1114, 1070, 1058, 1019, 962, 927, 876, 857, 796, 772, 723, 702, 650, 588, 567, 531, 480.



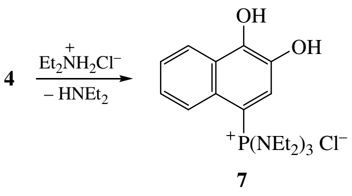
Scheme 2

fragment. The regiochemistry of phosphorylation was confirmed by the multiplicity of C^3, C^{4a} and C^{8a} signals. The signals of C^3 and C^{4a} atoms appear as doublets with coupling constant from phosphorus ($^2J_{PCC}$ 5.0 and 8.0 Hz, respectively) in the ^{13}C-{^{1}H} NMR spectrum and the signal of C^{8a} as a broad doublet with the greater value of coupling constant from phosphorus ($^3J_{PCCC}$ 12.6 Hz).

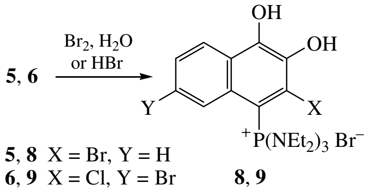
The possible mechanism of the process is presented in Scheme 2. The first stage of the reaction probably includes one-electron transfer from the phosphorus atom to the *ortho*-quinone molecule to form ion–radical pair **I**. The structures **II** and **III** with different localization of negative charge and a lone electron in the naphthalene moiety can be proposed as the resonance structures of the intermediate. The localization of a lone electron in the 4-position of a naphthalene nucleus probably decreases the energy because of conjugation with the benzene ring. Then, the recombination of electrons takes place in radical-ion **III** to form a P–C bond (structure **IV**). The following proton transfer with an electron density redistribution gives the final reaction products: phosphonium betaines **4**–**6**. The closely related processes of one-electron transfer were investigated earlier by ESR spectroscopy with the example of the reaction of substituted 1,2-benzoquinone derivatives with triaminophosphines, which leads to the formation of λ^5-1,3,2-dioxaphospholanes.[11,12] The suggested mechanism is in accordance with an intense colour change in the reactions.

The diethylammonium chloride treatment of betaine **4** leads to the formation of dihydroxynaphthylphosphonium salt **7**[§] (Scheme 3).

In contrast to our previous result,[10] the dihydroxynaphthylphosphonium salts **8**,[¶] **9**[††] were obtained by bromination followed by isolation from moist acetone or hydrogen bromide treatment of compounds **5**, **6** in hexane (Scheme 4).



Scheme 3



Scheme 4

The structure of phosphonium salts **7**–**9** was confirmed by ^{31}P, ^{1}H and ^{13}C NMR spectroscopy. The signals with δ_P 45–51 ppm in the ^{31}P-{^{1}H} NMR spectra correspond to compounds **7**–**9**. The signal at 105.31 ppm with the direct coupling constant $^1J_{PC}$ 155.0 Hz in the ^{13}C-{^{1}H} NMR spectrum belongs to the C^4 of compound **7**. In the ^{13}C NMR spectrum, the C^1 atom signal is a doublet of doublets of doublets with coupling constants from two protons at C^3 and C^8 atoms and from phosphorus ($^4J_{PCCCC}$ 3.3 Hz, $^3J_{HC^8CC}$ 4.0–5.0 Hz, $^3J_{HC^3CC}$ 7.0–8.0 Hz), while the signal of the C^2 atom is presented as a doublet of doublets with the greater value of the coupling constants $^3J_{PCCC}$ 21.2 Hz. There are signals of only three carbon atoms bonded with protons [126.06 (C^5), 125.05 (C^7) and 127.54 ppm (C^8)] in the ^{13}C-{^{1}H} NMR spectrum of compound **9**. It shows that the bromination of the naphthalene system does not take place. Two signals at 146.64 and 136.97 ppm corresponding to the C^1 and C^2 atoms confirm the presence of a dihydroxybenzene fragment in compound **9**. The intense absorption band at 3150–3180 cm^{-1} in the IR spectrum of this compound corresponds to the bond vibration of hydroxyl groups connected with the aromatic ring. The structure of compounds **7**, **9** was also confirmed by single crystal X-ray diffraction (Figures 1 and 2).[‡‡] The phosphorus atom has a distorted tetrahedral configuration in both molecules. Note that, due to the

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[§] *(1,2-Dihydroxynaphth-4-yl)[tris(diethylamino)]phosphonium chloride* **7**. To a solution of quinone **1** (3.00 g, 20.0 mmol) in dichloromethane (20 ml) with bubbling dry argon, diethylammonium chloride (2.19 g, 20.0 mmol) was added and then hexaethyltriamidophosphite (6.06 ml, 20.0 mmol) was added dropwise at room temperature. After a day, the solvent was removed under reduced pressure and the residue was dissolved in ethanol (10 ml). After a week, the brown solid precipitated was filtered off and crystallised from benzene–hexane–ethanol (5:5:1) to give 5.94 g (67%) of compound **7**, mp 232 °C. For spectral characteristics of **7** see Online Supplementary Materials.

[¶] *(3-Bromo-1,2-dihydroxynaphth-4-yl)[tris(diethylamino)]phosphonium bromide* **8**. To a solution of compound **5** (1.45 g, 3.01 mmol) in 5 ml of dichloromethane–hexane (5:1) with bubbling dry argon, a solution of bromine (0.16 ml, 3.01 mmol) in hexane (5 ml) was added dropwise at room temperature. After a day, the red-brown precipitate formed was filtered off, dried in a vacuum and crystallised from acetone to give 1.30 g (74%) of compound **8** as white plates, mp 185–188 °C. ^{31}P NMR (36.48 MHz, [^{2}H$_6$]DMSO) δ_P: 48.2 [m (s)]. ^{1}H NMR (600 MHz, [^{2}H$_6$]DMSO) δ_H: 8.19 (d, H^5, $^3J_{HCCH}$ 8.3 Hz), 7.70 (dt, H^6, $^3J_{HCCH}$ 6.6 Hz, $^4J_{HCCCH}$ 1.3 Hz), 7.67 (br. t, H^7, $^3J_{HCCH}$ 6.6 Hz), 8.34 (d, H^8, $^3J_{HCCH}$ 7.7 Hz), 3.22 (dq, NCH$_2$, $^3J_{HCCH}$ 7.1 Hz, $^2J_{PCH}$ 10.9 Hz), 1.23 (t, NCMe, $^3J_{HCCH}$ 7.0 Hz). ^{13}C NMR (150.9 MHz, [^{2}H$_6$]DMSO) δ_C: 147.20 [br. s (s), C^1], 138.25 [d (d), C^2, $^3J_{PCCC}$ 14.4 Hz], 125.50 [d (d), C^3, $^2J_{PCC}$ 5.5 Hz], 109.18 [dd (d), C^4, $^1J_{PC}$ 157.4 Hz, $^3J_{HCCC}$ 3.7 Hz], 131.33 [ddd (d), C^{4a}, $^2J_{PCC}$ 7.8 Hz, $^3J_{HCCC}$ 7.2 Hz, $^3J_{HCCC}$ 7.6 Hz], 125.53 [ddd (d), C^5, $^3J_{HCCC}$ 4.8 Hz, $^3J_{HCCC}$ 6.7 Hz, $^1J_{HC}$ 159.1 Hz], 126.47 [dd (s), C^6, $^1J_{HC}$ 163.5 Hz, $^3J_{HCCC}$ 8.1 Hz], 127.21 [dd (s), C^7, $^1J_{HC}$ 162.3 Hz, $^3J_{HCCC}$ 8.2 Hz], 123.31 [ddd (s), C^8, $^1J_{HC}$ 163.5 Hz, $^3J_{HCCC}$ 7.4 Hz], 125.38 [ddd (d), C^{8a}, $^3J_{PCCC}$ 12.6 Hz, $^3J_{HCCC}$ 5.4 Hz, $^3J_{HCCC}$ 6.6 Hz], 42.61 [dt (d), NCH$_2$, $^1J_{HC}$ 138.6 Hz, $^2J_{PNC}$ 3.6 Hz], 13.69 [dq (s), NCMe, $^1J_{HC}$ 126.7 Hz, $^2J_{HCC}$ 2.7 Hz]. IR (Nujol, ν/cm^{-1}): 3095 (OH), 1701, 1577 (C=C), 1499 (C=C), 1344, 1313, 1218, 1203, 1159 (P–N), 1111, 1035, 1015, 993, 970, 805, 772, 707, 679, 662, 641, 627, 481, 443.

[††] *(6-Bromo-3-chloro-1,2-dihydroxynaphth-4-yl)[tris(diethylamino)]phosphonium bromide* **9**. To a solution of compound **6** (1.65 g, 2.90 mmol) in hexane (20 ml) with bubbling dry argon, a solution of bromine (0.15 ml, 2.90 mmol) in hexane (5 ml) was added dropwise at room temperature. After two days, the bright red precipitate formed was filtered off, dried in a vacuum and crystallised from damp acetone–light petroleum (2:1) to give 1.51 g (79%) of compound **9** as a white powder, mp 198–200 °C. For spectral characteristics of **9** see Online Supplementary Materials.

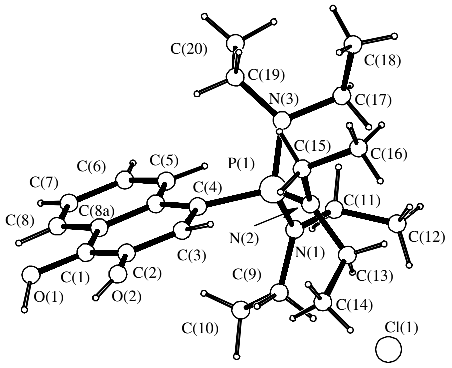

Figure 1 Molecular geometry of **7** in a crystal. Selected bond lengths (Å): P(1)–N(1) 1.623(3), P(1)–N(2) 1.644(3), P(1)–N(3) 1.626(3), P(1)–C(4) 1.799(4), O(1)–C(1) 1.368(4), O(2)–C(2) 1.372(4), C(1)–C(2) 1.362(6), C(1)–C(8a) 1.414(5), C(2)–C(3) 1.402(5), C(3)–C(4) 1.388(5), C(4)–C(4a) 1.419(6), C(4a)–C(8a) 1.437(5); selected bond angles (°): C(1)–C(2)–C(3) 119.7(3), C(2)–C(3)–C(4) 122.4(4), C(3)–C(4)–C(4a) 119.1(3), C(4)–C(4a)–C(5) 124.9(3), C(4)–C(4a)–C(8a) 118.0(3), O(1)–C(1)–C(2) 123.8(3), O(1)–C(1)–C(8a) 116.0(4), O(2)–C(2)–C(1) 125.4(3), O(2)–C(2)–C(3) 114.9(3), N(1)–P(1)–N(2) 107.1(2), N(1)–P(1)–N(3) 112.4(2), N(1)–P(1)–C(4) 110.6(2), N(2)–P(1)–N(3) 110.2(2), N(2)–P(1)–C(4) 110.6(2), N(3)–P(1)–C(4) 105.9(2), P(1)–C(4)–C(3) 116.9(3), P(1)–C(4)–C(4a) 123.6(2).

introduction of a bulky chlorine atom in the 3-position of 1,2-dihydroxynaphthalene ring, the bond angle P(1)C(4)C(3) increases in passing from **7** to **9**, while the P(1)C(4)C(4a) angle decreases. The P(1)–C(4) bond length also increases slightly on going from **7** to **9**.

In conclusion, note that the reaction of 1,2-naphthoquinones with tris(diethylamino)phosphine followed by the treatment of obtained betaines **4**–**6** with bromine (or hydrogen halogenide) is a versatile approach to the synthesis of 4-phosphorus-containing 1,2-dihydroxynaphthalenes **7**–**9**.

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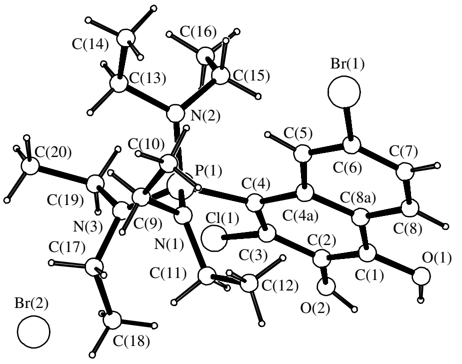

Figure 2 Molecular geometry of **9** in a crystal. Selected bond lengths (Å): O(1)–C(1) 1.342(9), O(2)–C(2) 1.368(9), Cl(1)–C(3) 1.723(8), P(1)–C(4) 1.820(8), Br(1)–C(6) 1.917(8), P(1)–N(1) 1.640(7), P(1)–N(2) 1.641(7), P(1)–N(3) 1.633(7); selected bond angles (°): O(1)–C(1)–C(2) 124.6(7), O(1)–C(1)–C(8a) 114.8(8), C(8)–C(8a)–C(1) 119.5(8), O(2)–C(2)–C(1) 124.4(7), O(2)–C(2)–C(3) 116.3(7), C(2)–C(3)–Cl(1) 115.6(6), C(4)–C(3)–Cl(1) 120.6(6), P(1)–C(4)–C(3) 124.7(6), P(1)–C(4)–C(4a) 118.6(6), N(2)–P(1)–N(3) 106.2(4), N(1)–P(1)–N(3) 107.5(4), N(1)–P(1)–N(2) 115.0(3), N(3)–P(1)–C(4) 121.7(4), N(2)–P(1)–C(4) 105.9(4), N(1)–P(1)–C(4) 101.1(4).

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2007.05.018.

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[‡‡] *The X-ray investigations of compounds* **7**, **9** were carried out at 20 °C. Crystals of compound **7** ($C_{22}H_{37}ClN_3O_2P$) are triclinic, $a = 9.258(5)$, $b = 10.939(5)$ and $c = 12.251(9)$ Å, $\alpha = 80.91(5)°$, $\beta = 82.52(5)°$, $\gamma = 80.39(4)°$, $V = 1200(1)$ Å^3, $Z = 2$, $d_{calc} = 1.22$ g cm^{-3}, space group $P\bar{1}$. Crystals of compound **9** ($C_{22}H_{35}Br_2ClN_3O_2P$) are triclinic, $a = 9.346(3)$, $b = 11.317(3)$ and $c = 13.533(3)$ Å, $\alpha = 88.65(3)°$, $\beta = 75.54(3)°$, $\gamma = 70.94(3)°$, $V = 1307.4(6)$ Å^3, $Z = 2$, $d_{calc} = 1.52$ g cm^{-3}, space group $P\bar{1}$. Cell parameters and intensities of 4267 for **7** and 5231 for **9** independent reflections, from which 2659 for **7** with $I \geq 3\sigma$ and 2009 for **9** with $I \geq 2\sigma$, were measured on an Enraf-Nonius CAD-4 diffractometer in the $\omega/2\theta$-scan mode, $\theta \leq 74.21°$ for **7** and ω-scan, $\theta \leq 74.20°$ for **9** (Cu$K\alpha$ radiation, graphite monochromator). The intensity falling was not observed at three control measurements. Empirical absorption correction was applied ($\mu_{Cu} = 22.26$ cm^{-1} for **7**; $\mu_{Mo} = 56.37$ cm^{-1} for **9**). The structures of **7**, **9** were solved by direct methods using the SIR program.[13] All non-hydrogen atoms were refined anisotropically for **7** using the MOLEN[14] package and for **9** using the WinGX package.[15] The hydrogen atoms were solved from difference Fourier maps and its contribution on structural factors was included with fixed positional and isotropic thermal parameters for **7** in the last cycle and were refined as riding atoms for **9**. The final residuals were $R = 0.052$, $R_w = 0.063$ for **7** and $R = 0.065$, $R_w = 0.113$ for **9**. All figures were made using the program PLATON.[16] Cell parameters, data collection and data reduction were performed on an Alpha Station 200 computer using the MOLEN[14] program.

Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). These data can be obtained free of charge *via* www.ccdc.cam.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or deposit@ccdc.cam.ac.uk). Any request to the CCDC for data should quote the full literature citation and CCDC reference numbers 622311 and 622312 for **7** and **9**, respectively. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2007.