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Tetra-*tert*-butylpyrazole and Tetra-*tert*-butylthiophene

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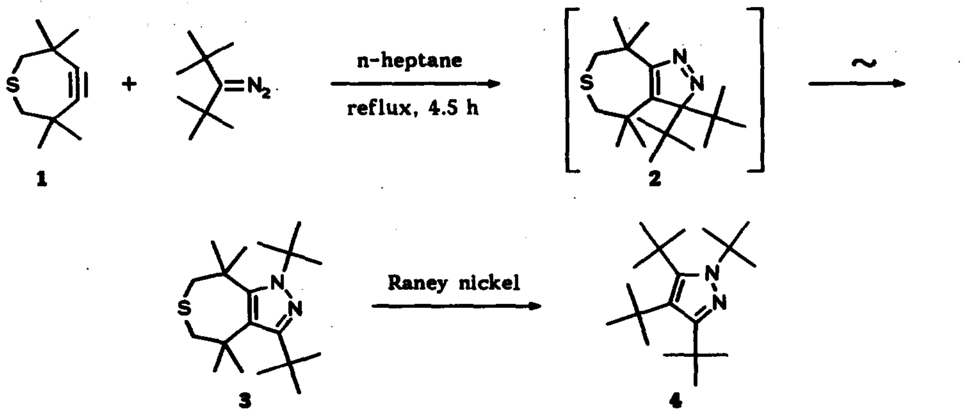
Abstract: Tetra-*tert.*butylpyrazole (4) and tetra-*tert.*butylthiophene (11) were prepared starting from the seven membered cycloalkyne 1 and a reductive desulfurization in the last step. Some reactions of 4 and 11 are described. X-ray structural analyses of 11 and the corresponding S,S-dioxide were carried out.

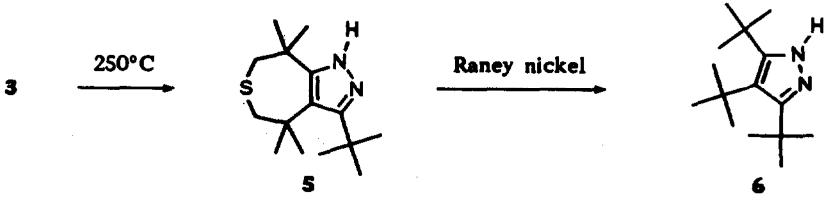
The influence of several *tert.*butyl groups on the structural parameters, the spectroscopic properties and the reactivity of aromatic compounds have been the subject of many publications.[1] Whereas 3,4- and 3,5-di-*tert.*butylpyrazole[2,3] and all possible di-*tert.*butylthiophenes are known,[4] tetra-*tert.*-butylpyrazole (4) and tetra-*tert.*butylthiophene (11)[5] could not be synthesized.

In our synthetic approach to 4 and 11 we made use of the angle strained thiacycloheptyne 1,[6] which has a very reactive triple bond connected to two masked *tert.*butyl groups.

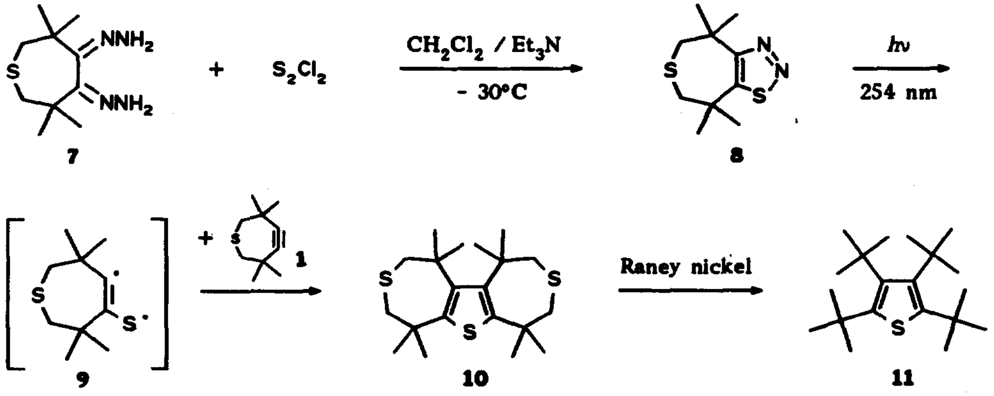


1 **2** **3** **4**

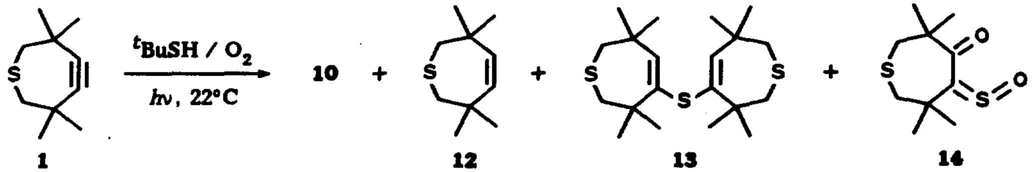
Reaction of 1 with di-*tert*.butyldiazomethane (n-heptane, reflux, 4.5 h) afforded the pyrazole 3 in 92% yield; the formation of 3 is explained by a migration of a *tert*.butyl group in 2, which is a plausible intermediate. Reductive desulfurization with Raney nickel (dioxane, 100°C, 7 h) gave 4 in 95% yield.[7] On sublimation (250°C) 3 loses isobutene to yield 5 (77%), which can be desulfurized with Raney nickel to 3,4,5-tri-*tert*.butylpyrazole (6).[8]



For the synthesis of tetra-*tert*.butylthiophene (11) diradical 9, which was generated by photolysis of 8, was trapped by 1; thiadiazole 8 was prepared from the dihydrazone 7[6] with S_2Cl_2 in 45% yield. On irradiation of a suspension of 8 in excess 1 the thiophene 10 was obtained in 94% yield; selective reductive desulfurization with Raney nickel afforded 11 (53%) as the main product.[9]

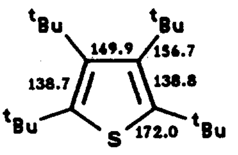


The thiophene 10 was also isolated as a by-product (14%) in the reaction of 1 with *tert*.butanethiol and oxygen on irradiation with a high pressure mercury lamp (10 min); the main products were the alkene 12 (20%), 13 (27%), and the sulfine 14 (15%).[10] Recently, 10 was observed in a reaction of 1 with a 1,2-dithietane.[11]

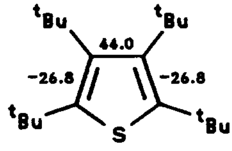


An X-ray crystal structural analysis of 11 was carried out at -110°C; the bond lengths and bond angles are given below. The five membered ring is not planar any more, the torsional angle C_2-C_3-C_4-C_5 amounts to 16.2°; the torsional angles between the *tert*.butyl groups are much larger: 44° between the 3- and 4-, and 26.8° between the 2- and 3-*tert*.butyl groups. Thus, most of the strain is released by reduction of the interactions between adjacent *tert*.butyl groups through change of torsional angles and an elongation of the $C_{thiophene}$-$C_{tert.butyl}$ bonds.[12]

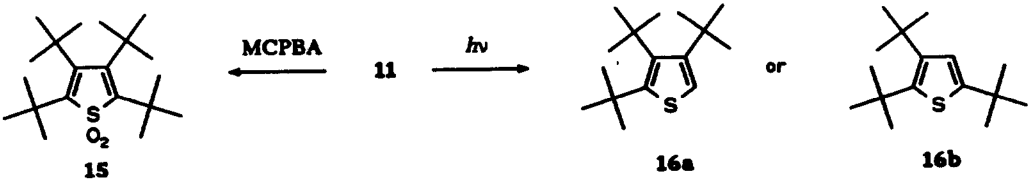
bond lengths:



torsional angles:

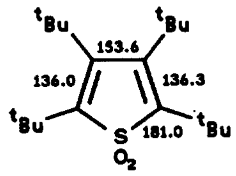


On photolysis of 11 in benzene (60 h, λ>300 nm) loss of isobutene occurs and a tri-*tert*.butylthiophene was isolated in 44% yield; an unequivocal decision between the two alternatives, 2,3,4- (**16a**) and 2,3,5-tri-*tert*.butylthiophene (**16b**), could not be made based on the presently available spectroscopic data.[13]

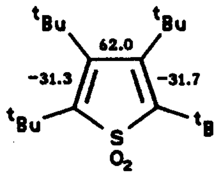


Oxidation of 11 with m-chloroperbenzoic acid in CH_2Cl_2 (1 h, 20°C) gave the 2,3,4,5-tetra-*tert*.butylthiophene-S,S-dioxide (15) in 75% yield.[14]

bond lengths:



torsional angles:



The X-ray crystal structural analysis (-110°C) of the non-aromatic 15 shows a much higher bond alternation than in 11 (C_3-C_4 153.6, C_2-C_3 136.0 pm); in addition the torsional angle between the *tert*.butyl groups at C_3 and C_4 is increased to 62.0°. The larger torsional angles compared to the corresponding ones in 11 are a consequence of the larger size of the SO_2-group.[15]

These results demonstrate the potential of angle strained cyclic systems, i.e. cycloalkynes or cyclobutadienes, for the synthesis of five- and six-membered aromatic systems with four vicinal *tert*.butyl groups.[17-19] Tetra-*tert*.butylfuran has been obtained previously via this route;[18] experiments to prepare tetra-*tert*.butylpyrrole from 1 are in progress.

References and Notes

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7. Data of **4**: m.p. 74°C (EtOH); MS (70eV): m/e 292 (3%, M^+); ^{1}H-NMR ($CDCl_3$, 270 MHz): δ = 1.37, 1.42, 1.47, 1.55 (4s, 9H each, CH_3); ^{13}C-NMR ($CDCl_3$, 15.08 MHz): δ = 32.3, 33.0 (3C each, CH_3), 35.0 (6C, CH_3), 32.8, 35.5 (1C each, $\underline{C}_q$-CH_3), 63.7 (N-$\underline{C}(CH_3)_3$), 130.3 ($C_{\beta\ ring}$) 149.3, 153.9 (1C each, $C_{\alpha\ ring}$). One missing $\underline{C}_q$-CH_3 signal is probably hidden under one of the CH_3 signals.
8. Data of **6**: m.p. 137°C (n-hexane); MS (70eV): m/e 236 (16%, M^+); ^{1}H-NMR ($CDCl_3$, 270 MHz): δ = 1.47 (s, 18H, CH_3), 1.50 (s, 9H, CH_3); ^{13}C-NMR ($CDCl_3$, 15.08 MHz): δ = 32.4 (6C, C_α-$C(\underline{C}H_3)_3$), 35.0 (3C, C_β-$C(\underline{C}H_3)_3$), 31.1 (1C, C_β-$\underline{C}(CH_3)_3$), 34.4 (2C, C_α-$\underline{C}(CH_3)_3$), 124.6 (1C, $C_{\beta\ ring}$), 152.2 (2C, $C_{\alpha\ ring}$).
9. Data of **11**: m.p. 79°C (EtOH); MS (70eV): m/e 308 (20%, M^+) : ^{1}H-NMR ($CDCl_3$, 270 MHz): δ = 1.42, 1.46 (2s, 18H each, CH_3); ^{13}C-NMR ($CDCl_3$, 67.88 MHz): δ = 35.5, 35.9 (6C each, CH_3), 37.5, 37.7 (2C each, $\underline{C}_q$-CH_3), 145.3, 146.3 (2C each, C_{ring}).
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11. Nicolaou, K. C.; DeFrees, S. A.; Hwang, C.-K.; Stylianides, N.; Carroll, P. J.; Snyder, J. P. *J. Am. Chem. Soc.* **1990**, *112*, 3029-3039. We found a m.p. of 179-180°C for **10**.
12. Crystallographic data: a = 886.2 (8), b = 973.0 (6), c = 1206.4 (15) pm; α = 99.10 (8), β = 90.51 (8), γ = 111.96 (7)°; triclinic space group $P\bar{1}$; Z = 2; D (calc.) = 1.07 Mg/m^3. R = 0.044, R_w = 0.066.[16]
13. Data of **16** (**a** or **b**): m.p. 42°C (CH_3OH); MS (70eV): m/e = 252 (21%, M^+); ^{1}H-NMR ($CDCl_3$, 270 MHz): δ = 1.34, 1.44, 1.53 (3s, 9H each, CH_3), 6.76 (s, 1H, ring); ^{13}C-NMR ($CDCl_3$, 67.88 MHz): δ = 33.4, 33.7, 34.0 (3C each, CH_3), 34.9, 35.7 (1C each, $\underline{C}_q$-CH_3), 125.2 (1C, $C_{t\ ring}$), 143.6, 145.2, 148.2 (1C each, $C_{q\ ring}$). One missing $\underline{C}$q-CH_3 signal is probably hidden under one of the CH_3 signals.
14. Data of **15**: m.p. 149-150°C (petrolether 60/70); MS (70eV): m/e 340 (2.3%, M^+) ; ^{1}H-NMR ($CDCl_3$, 270 MHz): δ = 1.46, 1.52 (2s, 18H each, CH_3); ^{13}C-NMR ($CDCl_3$, 67.88 MHz): δ = 31.5, 33.9 (6C each, CH_3), 36.8, 39.3 (2C each, $\underline{C}_q$-CH_3), 146.4, 154.9 (2C each, C_{ring}).
15. Crystallographic data: a = 872.4 (9), b = 2295.8 (6), c = 1081.6 (10) pm; β = 113.35 (8)°; monoclinic space group Cc; Z = 4; D (calc.) = 1.13 Mg/m^3. R = 0.045, R_w = 0.061.[16]
16. Details of the X-ray structural analyses are available from Fachinformationszentrum Energie, Physik, Mathematik, D-7514 Eggenstein-Leopoldshafen 2, with reference to registration number CSD-56317.
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