Are the Silyl Group Hydrogens in peri-Substituted-9-Silyltriphyenes Engaged in Blue-Shifting Hydrogen Bonds?

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In this supplementary material, $^1$H NMR characteristics at room temperature of 1,4-dichloro-, 1,4-dibromo-, and 1,4-dimethyl-9-silyltriphyene, 1, 2 and 3, respectively, are given. Moreover, $^1$H COSY spectrum of 3 documenting the occurrence of J-couplings between the silyl and methyl group protons is shown.

Fig. S1. Labelling of the skeleton positions in 1-3.

Experimental details

1,4-dichloro-, 1,4-dibromo-, and 1,4-dimethyl-9-silyltriphyene, 1, 2, and 3, respectively, were synthesized by adapting the literature procedures. The details of these rather cumbersome syntheses will be published elsewhere. The structures of the compounds...
were confirmed by room-temperature $^1$H NMR spectra (500 MHz, CDCl$_3$, δ, see Fig. S1 for the position labelling); 1: 4.45 (1H, br s, SiH$_2$H), 4.98 (2H, br s, SiHH$_2$), 5.970 (1H, s, C10-H), 6.900 (1H, d, C2-H or C3-H), 6.955 (1H, d, C3-H or C2-H), 7.07 - 7.11 (4H, m, C6-H, C7-H, C12-H, C13-H), 7.46 - 7.49 (2H, m, C5-H, C11-H), 7.60 - 7.63 (2H, m, C8-H, C14-H); 2: 4.50 (1H, br s, SiHH$_2$), 5.18 (2H, br s, SiHH$_2$), 6.030 (1H, s, C10-H), 7.04 (1H, d, J = 8.60 Hz, C2-H or C3-H), 7.07 (1H, d, J = 8.60 Hz, C3-H or C2-H), 7.09 - 7.14 (4H, m, C6-H, C7-H, C12-H, C13-H), 7.49 - 7.52 (2H, m, C5-H, C11-H), 7.65 - 7.69 (2H, m, C8-H, C14-H); 3: 2.49 (3H, s, C3-CH$_3$), 2.64 (3H, s, C2-CH$_3$), 4.75 (3H, br s, SiH$_3$), 5.66 (1H, s, C10-H), 6.65 (1H, d, J = 7.80 Hz, C2-H or C3-H), 6.72 (1H, d, J = 7.8 Hz, C3-H or C2-H), 7.01 - 7.06 (4H, m, C6-H, C7-H, C12-H, C13-H), 7.38 - 7.43 (2H, m, C5-H, C11-H), 7.54 - 7.59 (2H, m, C8-H, C14-H).

For 3, the assignments of both the methyl- and peri-protons' resonances were made on the basis of the difference NOE experiments at room temperature, with irradiation of the silyl protons' signal. The COSY-LR spectrum of 3 was measured on a Bruker Avance II 300 MHz spectrometer at room temperature. Further details are given in Ref. 7.
Fig. S2. $^1$H (300 MHz) COSYLR spectrum of 3, measured at room temperature. The SiH$_3$ resonance appears as the small, broad peak at 4.75 ppm. The coupling to the methyl protons is represented by the crosspeak at F1=2.65 ppm and F2 = 4.75 ppm.