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Linear alignment of four sulfur atoms in bis[(8-phenylthio)naphthyl] disulfide: contribution of linear S_4 hypervalent four-centre six-electron bond to the structure

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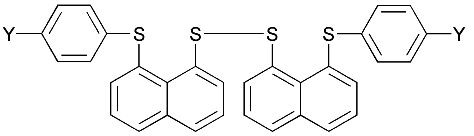
The four sulfur atoms in bis[8-(phenylthio)naphthyl]-1,1′-disulfide are demonstrated to align linearly by the X-ray crystallographic analysis, where the linear S_4 alignment is stabilized by the four-centre six-electron interaction.

We have been highly interested in the nonbonded interactions,[1] especially those leading to linear bonds higher than the three centre-four electron bond (3c–4e),[2] caused by the direct orbital overlaps between nonbonded atoms. The p-type lone pair orbital of Se (n_p(Se)) in R–Se–R′ has been well demonstrated to play an important role in the nonbonded interactions.[3–5] The role of n_p(S) in R–S–R′ in the nonbonded interactions is also of great interest. Here, we report the linear alignment of four sulfur atoms (S_4) in bis[8-(phenylthio)naphthyl]-1,1′-disulfide (**1a**),† demonstrated by the X-ray crystallographic analysis. The linear S_4 alignment is analyzed by the 4c–6e model and the linear form of **1a** is shown to be substantially more stable than the zig-zag conformer, based on the *ab initio* MO calculations. Structures of phenyl *p*,*p*′-dimethoxy and *p*,*p*′-dinitro derivatives of **1a** (**1b** and **1c**, respectively) are essentially the same as that of **1a**, although not shown.



1: Y = H (**a**), OMe (**b**), NO_2 (**c**)

Fig. 1 shows the ORTEP diagram of **1a**. Only one type of structure corresponds to **1a** in the crystal. The two naphthyl planes in **1a** are almost perpendicular to each other. The torsional angle of −89.0° for C(9)–S(2)–S(3)–C(25) is close to those usually observed in ArSSAR′.[6] The rotations around the S(2)–C(9) and S(3)–C(25) bonds are fixed for the S_4 atoms to align linearly: The angles of S(1)–S(2)–S(3) and S(2)–S(3)–S(4) are found to be 168.6 and 166.0°, respectively. The conformations around the outside sulfide S atoms are type **A** and those for the inside disulfide S atoms type **B**: the structure is double type **A**-type **B** pairing in our definition.[3–5] The conformation of each Ph plane is determined so that the corresponding S–C(Nap) bond lies in the Ph plane. The structure of **1** is very close to that of bis[8-(phenylselanyl)naphthyl]-1,1′-diselenide, **2**.[3]

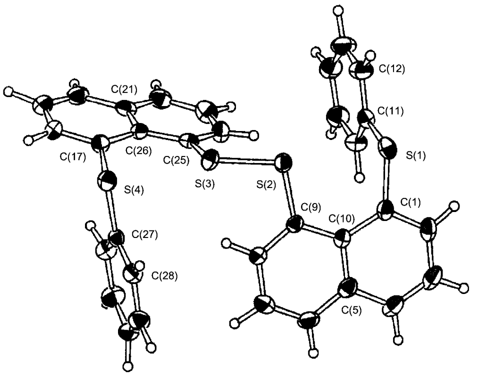
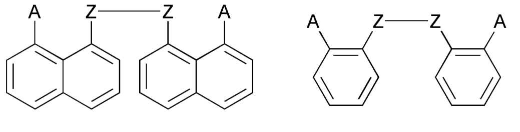


Fig. 1 Structure of **1a**.

Nonbonded r(S(1),S(2)) and r(S(3),S(4)) distances in **1a** are both 2.988(2) Å. The distances are shorter than the sum of van der Waals radii of S atoms (3.70 Å)[7] by 0.71 Å. The n_p(S) orbitals of the outside S atoms must extend toward the area of the σ*(S–S) orbital of the inside disulfide bond since the nonbonded r(S,S) values are so small and the S_4 atoms align linearly. Consequently, the interactions lead to the formation of two nonbonded n_p(S)–σ*(S–S) 3c–4e bonds. The 4c–6e interaction of the n_p(S)–σ*(S–S)–n_p(S) type will be constructed, if the two 3c–4e are effectively connected by the central σ*(S–S) orbital. The 4c–6e would be more stabilized by the two phenyl groups since the electrons of 4c–6e may also delocalize over the phenyl π-orbitals due to the advantageous conformation of the groups in **1a**.

In order to elucidate the nature of 4c–6e of the linear S_4 atoms in **1**, *ab initio* MO calculations are performed on di(naphthyl)-1,1′-disulfide (**3**) and bis[8-(methylthio)naphthyl]-1,1′-disulfide (**4**), using the Gaussian 98[8] program. The 6–311+G(d) basis sets are employed for S and the 6–31G(d) for H and C at the DFT (B3LYP) level. Linear and zig-zag conformers are optimized to be stable.‡ Natural charges (*Qn*)[9] of atoms are also calculated for the optimized structures. Table 1 collects the results.[10] Molecular orbitals are also depicted on the optimized structures.[11] HOMO-2 of **4** (linear) is shown in Fig. 2.



2 (Z = Se, A = SePh)
3 (Z = S, A = H)
4 (Z = S, A = SMe)

5 (Z = S, A = H)
6 (Z = S, A = SMe)

As shown in Table 1, the zig-zag conformer of **3** (**3** (zig-zag)) is evaluated to be more stable than **3** (linear) by 14.7 kJ mol^{-1}

Table 1 Calculated energies (*E*) and natural charges (*Qn*) for linear and zig-zag conformers of **3** and **4** at the DFT (B3LYP) level[a]

Compd	*E*/au	*Qn*(^{1}S)	*Qn*(^{8}S)
3 (linear)	−1566.9983	0.1469	(0.2442)[b]
3 (zig-zag)	−1567.0039	0.1025	(0.2496)[b]
Δ(**3**)[c]	0.0056[d]	0.0444	(−0.0054)[b]
4 (linear)	−2442.0293	0.1334	0.2446
4 (zig-zag)	−2442.0268	0.1285	0.2123
Δ(**4**)[c]	−0.0025[e]	0.0049	0.0323
ΔΔ[f]	−0.0081[g]	−0.0395	(0.0377)[b]

[a] The 6–311+G(d) basis sets are employed for S and the 6–31G(d) for H and C. [b] Value for ^{8}H of **3**. [c] *P* (linear) − *P* (zig-zag) where *P* = *E* and *Qn*. [d] 14.7 kJ mol^{-1}. [e] −6.6 kJ mol^{-1}. [f] Δ(**4**) − Δ(**3**). [g] −21.3 kJ mol^{-1}.

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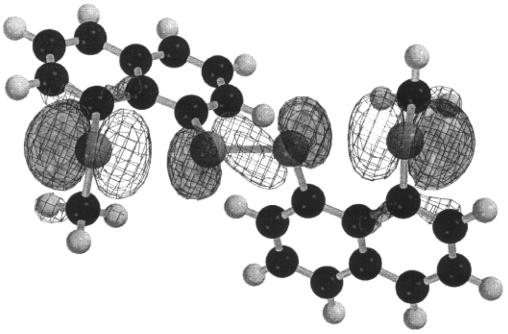

Fig. 2 HOMO-2 of **4** (linear), which corresponds to ψ_3 of S_4 4c–6e.

[= Δ_E (**3**) = E (**3** (linear)) − E (**3** (zig-zag))]. **4** (linear) becomes more stable than **4** (zig-zag): Δ_E (**4**) = −6.6 kJ mol^{-1}. The contribution of linear S_4 4c–6e for the naphthalene system is estimated by $\Delta\Delta_E$ = Δ_E (**4**) − Δ_E (**3**), which is −21.3 kJ mol^{-1}. The results show that the two S atoms at the 8,8′-positions in **4** stabilize the linear conformer containing S_4 4c–6e by 21.3 kJ mol^{-1}. The direction of charge transfer (CT) in S_4 4c–6e of the $n_p(S) \rightarrow \sigma^*(S–S) \leftarrow n_p(S)$ type is rationalized by analyzing Qn (S). While Δ_{Qn} (**3**) [= Qn (**3** (linear)) − Qn (**3** (zig-zag))] for ^{1}S is 0.044, Δ_{Qn} (**4**) = 0.005 for ^{1}S. Therefore, $\Delta\Delta_{Qn}$ = Δ_{Qn} (**4**) – Δ_{Qn} (**3**) = −0.039 for ^{1}S. However, $\Delta\Delta_{Qn}$ = 0.038 for ^{8}S, although H atoms are placed at 8,8′-positions in **3**, instead of S atoms in **4**. The results are the reflection of CT from ^{8}S to ^{1}S in the formation of **4** (linear). They are well explained by the CT of the $n_p(S) \rightarrow \sigma^*(S–S) \leftarrow n_p(S)$ direction. HOMO-2 of **4** (linear) shown in Fig. 2 clearly corresponds to ψ_3 of S_4 4c–6e, which also supports the 4c–6e nature of the S_4 in **4** (linear). These results well demonstrate the contribution of 4c–6e of linear S_4 atoms to the structure of **1**.

It is worthwhile to comment on the effect of crystal packing. Both linear and zig-zag structures are reported for substituted diphenyl disulfides. The structure depends on the substituents at not only *ortho*[12] but also *meta* and/or *para* position(s).[6] The through-bond interaction plays an important role in determining the structures[13] but the contribution of the crystal packing effect may also be important in the benzene systems. On the other hand, the structures of **1** must be mainly stabilized by 4c–6e of linear S_4 since the nonbonded S–S distances in the naphthalene system are shorter than those of the benzene system. *Ab initio* MO calculations are also performed on **5** and **6**,[14] similarly to the cases of **3** and **4**. The results support that the contribution of linear S_4 4c–6e is larger for the naphthalene system than the benzene system.[15] The structures of **1b** and **1c** are also of the linear type and not changed depending on the substituents, which is another support for the contribution of the 4c–6e on the structure of **1**.

An advanced study on the nature of 4c–6e is in progress in our laboratory. Details will be reported elsewhere.

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Notes and references

† Elemental analyses were satisfactory for **1a**. Yield 68%, mp 170.2 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.02 (d, J = 7.1 Hz, 4H), 7.12 (t, J = 7.9 Hz, 4H), 7.21 (t, J = 7.3 Hz, 4H), 7.45 (d, J = 7.7 Hz, 2H), 7.63 (d, J = 8.0 Hz, 2H), 7.67 (dd, J = 1.1 and 7.7 Hz, 2H), 7.86 (dd, J = 1.5 and 7.2 Hz, 2H), 7.90 (dd, J = 1.4 and 8.2 Hz, 2H); ^{13}C NMR ($CDC1_3$: 75.5 MHz) δ 125.5, 125.8, 125.9, 126.3, 127.1, 127.4, 128.5, 129.0, 131.4, 133.9, 134.6, 136.4, 138.5, and 140.0; Crystal data for **1a**: $C_{32}H_{22}S_4$, M_r = 534.77, monoclinic, space group $P2_1/a$ (No. 14), a = 10.420(4), b = 24.167(5), c = 10.622(4) Å, β = 106.52(3)°, V = 2564(1) Å^3, Z = 4, D_c = 1.385 g cm^{-3}, Mo-Kα radiation, λ = 0.71069 Å, μ = 3.91 cm^{-1}, T = 298 K; 6372 reflections were collected, 6054 were unique, R_{int} 0.061; final refinement to convergence on F^2 with all non-H atoms anisotropic and all H atoms modeled isotropically gave R = 0.056 (F, 2502 obs. data only) and R_w = 0.085 (F^2, all data), GOF = 1.16, 338 refined parameters; max./min. residual electron density: 0.33/−0.51 e Å^{-3}. CCDC reference number 188993. See http://www.rsc.org/suppdata/cc/b2/b206137f/ for crystallographic data in CIF or other electronic format.

‡ The notation of linear (4c–6e) and zig-zag conformers are also applied to **3** and **5**, where A = H.

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