Dalton Transactions

Cite this: Dalton Trans., 2012, 41, 7485

www.rsc.org/dalton



Role of $p(Z)-\pi(Ar/Nap)$ conjugation in structures of 1-(arylchalcogena)naphthalenes for Z = Te *versus* Se, S and O: experimental and theoretical investigations[†]

Takahito Nakai, Mitsuhiro Nishino, Satoko Hayashi, Masato Hashimoto and Waro Nakanishi*

Received 3rd March 2012, Accepted 13th April 2012 DOI: 10.1039/c2dt30516j

Magnitudes of the $p(Z)-\pi(Ar/Nap)$ conjugation were evaluated for 1-(arylchalcogena)naphthalenes $(1-(ArZ)Nap, 1-(p-YC_6H_4Z)C_{10}H_7; 1 (Z = Te), 2 (Se), 3 (S) and 4 (O))$. Structures of 1 were determined by X-ray analysis for $Y = NMe_2$ (b), OMe (c) and CN (i). For 1b and 1c that have electron donating Y, the Z–C_{Ar} bond is located on the naphthyl plane with Z–C_{Nap} being perpendicular to the aryl plane, which we define as (B: pd). On the other hand, the structure of 1i with electron donating Y is (A: pl), of which Z-CAr is placed almost perpendicular to the naphthyl plane with Z-CNap being located on the aryl plane. Each structure of 1a (Y = H), 1b, 1c, 1d (Me), 1e (F), 1f (Cl), 1g (Br), 1h (COOEt), 1i and 1j (NO₂) was determined by NMR in chloroform-d. Structures of 1 in the solutions are (**B: pd**) for **b**, **c** and e that have electron donating Y, (A: pl) for f-j with electron accepting Y, and in equilibrium between (B: pd) and (A: pl) for a and d of which Y are rather neutral. The results for 2–4 are very similar to those of 1 in solutions. Quantum chemical calculations were performed on 1-4 with Y of a, b' (NH₂), d, f and j. Magnitudes of the p(Z)- $\pi(Ar/Nap)$ conjugation were well-evaluated by NBO (natural bond orbital) analysis. The values were 12.6 and 13.0 kcal mol⁻¹ for the typical forms of (A: pl) and (B: pd) of 1a, respectively, resulting in a much smaller energy difference between the two (0.4 kcal mol^{-1}), which should correspond to the observed result. It is well-demonstrated that the $p(Te)-\pi(Ar/Nap)$ conjugation operates effectively in 1, although the magnitudes increase in the order of Z = Te < Se < S < O. Thermal effect of the Gibbs free energies is shown to play an important role in the energy profiles of 1a-4a.

Introduction

Much attention has been paid to the p– π conjugation of the p(Z)– π (C==C) and p(Z)– π (Ar) types not only for Z of second low elements, but also that of heavier ones.^{1–5} The conjugation will control fine structures⁶ and reactivities of compounds, together with delicate properties of materials, such as electronic absorption–emission energies and NMR chemical shifts. It is of current interest to clarify the factors that control the structures of 1-(arylchalcogena)naphthalenes, especially for the tellurium derivative, as well as selenium,^{2–5,7–18} sulfur¹⁹ and oxygen¹⁹ derivatives [1-(ArZ)Nap, 1-(*p*-YC₆H₄Z)C₁₀H₇: 1 (Z = Te), 2 (Z = Se), 3 (Z = S) and 4 (Z = O); Y = H (a), NMe₂ (b), OMe (c), d (Me), e (F), f (Cl), g (Br), h (COOEt), i (CN) and j (NO₂)]. Chart 1 shows 1-(arylchalcogena)naphthalenes, 1–4.

The p(Se)– π (Ar/Nap) conjugation is well-demonstrated to operate as the factor to determine the fine structures of **2**. The role of p(Te)– π (Ar/Nap) conjugation in **1** should be established in the same accuracy with the unified form to **2**, together with **3** and **4**. Scheme 1 illustrates the p(Z)– π (Ar/Nap) conjugation in **1–4**. However, the role of the p(Te)– π (Ar/Nap) conjugation is unclear yet, including whether it operates well in determining the fine structures of **1**, relative to the case of **2**. It may be the natural consequence of the present situation, since the structures of **1** that were determined by the X-ray crystallographic analysis are seldom found in the literature, to the best of our knowledge. Quantum chemical (QC) calculations have also rarely been



Chart 1 1-(Arylchalcogena)naphthalenes 1-4.

Department of Material Science and Chemistry, Faculty of Systems Engineering, Wakayama University, 930 Sakaedani, Wakayama 640-8510, Japan. E-mail: nakanisi@sys.wakayama-u.ac.jp; Fax: +81 73 457 8253; Tel: +81 73 457 8252

[†] Electronic supplementary information (ESI) available: Cartesian coordinates for optimized structures of **1a–4a**, **1b'–4b'**, **1d–4d**, **1f–4f** and **1j–4j**. CCDC 838257 for **1b**, 838258 for **1c** and 838259 for **1i**. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2dt30516j



Stabilized by Y of acceptors Contributed for Y of donors

Scheme 1 Factors to stabilize (A: pl) and (B: pd) conformations.



Chart 2 Structures of 9-(arylselanyl)anthracenes (5) and 1-(arylselanyl)anthraquinones (6).

performed to clarify the role of the conjugation in the fine structures of **1**.

It is also of current interest for the derivatives of 1–4 to react with metals or halogens yielding complexes with interesting structures and properties.²⁰ The p– π conjugation must serve as one of the basic concepts in chalcogen chemistry. The p(Z)– π (C==C/Ar) conjugation may be believed to decrease swiftly as Z becomes heavier. Therefore, it is necessary to establish a firm basis for the p(Te)– π (C==C/Ar) conjugation. To accomplish this purpose, it is inevitable to determine the structures of 1. However, there must be some impediment, such as the oily nature or unsuitable crystallization of 1, during the X-ray crystallographic analysis for all members in Chart 1.

In such cases, structural determination in solutions becomes very important. Chart 2 illustrates 9-(arylselanyl)anthracenes (5a-5j) and 1-(arylselanyl)anthraquinones (6a-6j), the structures of which have been demonstrated to be all (A: pl) and (B: pd), respectively, in solutions.²¹ Structures of 1a-1j have been determined in solutions employing NMR chemical shifts of 5a-5j and 6a-6j as references, similarly to the case of 2.¹² It would be very useful if the structures of 1-4 could be determined in solutions, since structural determination using NMR must be easier. We are faced with such cases on a daily basis, where the structures are determined in solutions to understand or explain the properties and reactivity of compounds.

Type **A** (abbreviated by **A**), **B** and **C** notation^{11,12,15} is employed here, which has been proposed for the naphthalene system with the planar (**pl**), perpendicular (**pd**) and the nonplanar non-perpendicular (**np**) notation for the aryl group.^{15,16,22} Scheme 2 shows the **A**, **B** and **C** notation exemplified by 8-G-1-XZC₁₀H₆ and the **pl**, **pd** and **np** conformers in C₆H₅ZX. The combined notation will be practically used for the structures of **1**–**4**: a structure of 1-(ArZ)Nap is called (**A**: **pl**) when the Z–C_{Ar} bond is almost perpendicular to the naphthyl plane (**A**), with Z–C_{Nap} being located on the aryl plane (**pl**), whereas it is (**B**: **pd**) if the Z–C_{Ar} bond is almost placed on the naphthyl



Scheme 2 Types A–C in a naphthalene system and pd, pl and np in a benzene system.



Fig. 1 An ORTEP drawing of 1b with atomic numbering scheme for selected atoms (50% probability thermal level).

plane (B) with Z–C_{Nap} being perpendicular to the aryl plane (pd). The C structure and the np conformer are intermediate between A and B and between pd and pl, respectively. The A, B and C structures with the pl, pd and np conformers are closely related to the $p(Z)-\pi(Ar/Nap)$ conjugation in 1–4.

Structures in the solid state are sometimes deformed by the crystal packing effect, so are the solvent effect in solutions. Therefore, QC calculations of a satisfactory level are crucial to establish the role of the p(Te)– π (Ar/Nap) conjugation. QC calculations were performed on 1–4 with Y = H (a), NH₂ (b'), Me (d), Cl (f) and NO₂ (j) at the Møller–Plesset second-order energy correlation (MP2)²³ level using the Gaussian 03 program.²⁴ The thermal effect of the Gibbs free energies was evaluated for 1a–4a through frequency analysis.

Both structures determined experimentally and predicted theoretically were examined and compared carefully. The role of the $p(Te)-\pi(Ar/Nap)$ conjugation in the fine structures of 1 was thus clarified. The results are discussed in relation to the role of such conjugation in 1–4 to draw a conclusion in the unified form for 1–4. QC calculations performed on 1–4 played a very important role for the conclusion, as well as the structural determination.

Results and discussion

Structures of 1-(ArTe)Nap (1) in crystals

1-(Aryltellanyl)naphthalenes of **1b**, **1c** and **1i** were newly prepared according to the method reported earlier for **1a**, **1d–h** and **1j**¹⁹ which are also employed in this work.

Single crystals of **1b**, **1c** and **1i** were obtained *via* slow evaporation of *n*-hexane solutions and one suitable crystal was subjected to X-ray crystallographic analysis for each. Only one type of structure was found for each of them in the crystal. Fig. 1-3 show the structures of **1b**, **1c** and **1i**, respectively. Table 1 collects the selected interatomic distances, angles and torsional angles of **1b**, **1c** and **1i**.



Fig. 2 An ORTEP drawing of 1c with atomic numbering scheme for selected atoms (50% probability thermal level).



Fig. 3 An ORTEP drawing of 1i with atomic numbering scheme for selected atoms (50% probability thermal level).

Intermolecular interactions of **1b**, **1c** and **1i** in the solid state are given in Fig. S1–S3 of the ESI.† Intermolecular interactions are observed between $C_6H_4NMe_2$ in the crystal of **1b** (**B: pd**), while they occur between TeC₆H₄OMe in **1c** (**B: pd**), although one of the H atoms in the naphthyl group participates in the interactions. On the other hand, intermolecular interactions are observed between the naphthyl group and the Te atom in **1i** (**A: pl**). Indeed, each structure could be affected by the crystal packing effect, but the effect is expected not to control the structures of **1b**, **1c** and **1i**. The intermolecular interactions would be the result of their specific structures with the nature of Te and Y.

The structures of **1b** and **1c** are (**B**: **pd**), which are essentially the same as those of 2c,¹⁵ 3c¹⁹ and 4c,¹⁹ whereas that of **1i** is (**A**: **pl**), which is very close to those of 2f,¹⁵ 2g,¹⁵ 2h,¹⁵ 3g,¹⁹ $4a^{19}$ and $4j^{19}$. The planarity of the naphthyl, *p-N,N*-dimethylaminophenyl, p-anisyl and p-cyanophenyl planes in 1b, 1c and 1i are very good, as shown in Fig. 1–3. The *p-N*,*N*-dimethylaminophenyl plane in 1b and the *p*-anisyl plane in 1c are perpendicular to the naphthyl plane, with the Te-CAr bonds being placed on the naphthyl plane and the Te-C_{Nap} bonds perpendicular to the aryl plane. In the structures of 1b and 1c, torsional angles $C_{11}TeC_1C_{10}$ were 179.70(2)° and 178.50(2)°, torsional angles C1TeC11C12 were 106.37(2)° and 80.27(2)°, and angles C_{Nap}TeC_{Ar} were 99.93(8)° and 97.97(8)°, respectively. On the other hand, the *p*-cyanophenyl plane in 1i was perpendicular to the naphthyl plane, with the Te-CAr bond being perpendicular to the naphthyl plane and the Te-C_{Nap} bond placed on the aryl plane. The torsional angles of $C_{11}TeC_1C_2$ and $C_1TeC_{11}C_{12}$ were $83.32(2)^{\circ}$ and $171.65(2)^{\circ}$, respectively. The angle of C₁TeC₁₁ was 96.32(6)°. The data confirm the (B: pd) structures for 1b and 1c and the (A: pl) structure of 1i.

Table 1Selected interatomic distances, angles and torsional angles of1b, 1c and 1i

| Compound | 1b | 1c | 1i |
|---|------------------|------------|------------|
| Y = | NMe ₂ | OMe | CN |
| Bond distances | (Å) | | |
| TeC ₁ | 2.120(2) | 2.124(2) | 2.1234(17) |
| TeC ₁₁ | 2.100(2) | 2.106(2) | 2.1120(17) |
| Angles (°) | | | |
| $C_1 TeC_{11}$ | 99.93(8) | 97.97(8) | 96.32(6) |
| TeC_1C_2 | 121.42(15) | 121.54(15) | 117.98(13) |
| TeC_1C_{10} | 118.62(15) | 118.28(14) | 121.61(12) |
| $\text{TeC}_{11}C_{12}$ | 119.93(15) | 120.07(16) | 117.87(13) |
| $TeC_{11}C_{16}$ | 121.25(15) | 120.60(15) | 122.50(12) |
| Torsional angles | s (°) | | |
| $C_1 TeC_{11}C_{12}$ | 106.37(2) | 80.27(2) | 171.65(2) |
| $C_1 TeC_{11}C_{16}$ | -84.03(2) | -106.19(2) | -10.95(2) |
| C_{11} Te C_1C_2 | 0.26(2) | -3.76(2) | 83.32(2) |
| C_{11} Te C_1C_{10} | 179.70(2) | 178.50(2) | 94.52(2) |
| $TeC_1C_2C_3$ | -179.10(2) | -176.74(2) | -177.03(2) |
| $\text{TeC}_1 \tilde{\text{C}}_{10} \tilde{\text{C}}_5$ | 179.85(2) | 175.21(2) | 176.37(2) |



Fig. 4 Structures of 1–4 in crystals containing various Y.

Survey of the structures of 1-(ArZ)Nap (1-4) in crystals

Fig. 4 collects together the structures of 1–4 determined in crystals in this work and those reported so far, which are 1b, 1c, 1i, 2c, 2f, 2g, 2h, 3c, 3g, 4a, 4c and 4j.

While electrons in the p-type lone pair orbital of Z (p(Z)) are stabilized through the p(Z)– π (C₆H₄Y) conjugation when the structure is (**A: pl**), the p(Z)– π (Nap) conjugation contributes for (**B: pd**), as illustrated in Scheme 1. The main factor that controls the relative stability between (**A: pl**) and (**B: pd**) depends on the relative contributions between the p(Z)– π (C₆H₄Y) and p(Z)– π (Nap) conjugations. The p(Z)– π (C₆H₄Y) conjugation should be more effective than the p(Z)– π (Nap) conjugation in (**A: pl**) and *vice versa*, as observed.

Table 2 Substituent-induced chemical shifts (δ_{SCS}) of ¹H, ¹³C, ¹²⁵Te and/or ⁷⁷Se of **1** and **2**, together with **5** and **6**

| G 1 | Chemi | cal Shift | | | |
|---|---------------------------------------|-------------------------------|---------------------------------------|---------------------|----------------------------------|
| Compound 1 | $\delta(\mathrm{H}_2)_{\mathrm{S}}$ | $c_{\rm S} = \delta({\rm H})$ | H ₈) _{SCS} | $\delta(C_i)_{SCS}$ | δ (Te) _{SCS} |
| $\mathbf{Y}=\mathbf{H}\left(\mathbf{a}\right)$ | 0.000 | a 0.0 | 000 | 0.00 | 0.00 |
| | (7.972) | r (8. | 135)" | $(114./)^{-1}$ | $(5/0.7)^{2}$ |
| NMe_2 (b) | -0.381 | -0 | .180 | -18.2 | -32.4 |
| $OMe(\mathbf{c})$ | -0.237 | -0 | .119 | -11.8 | -14.6 |
| Me (d) | -0.117 | -0 | .052 | -4.5 | -10.4 |
| F (e) | -0.092 | -0 | .060 | -6.6 | 1.4 |
| Cl (f) | 0.010 | -0 | .025 | -2.2 | 3.6 |
| Br (g) | 0.021 | -0 | .029 | -1.0 | 3.9 |
| CO ₂ Ĕt (h) | 0.174 | 0.0 | 18 | 8.1 | 7.4 |
| CN (i) | 0.236 | 0.0 | 27 | 9.8 | 25.4 |
| $NO_2(\mathbf{j})$ | 0.270 | 0.0 | 33 | 12.0 | 25.5 |
| 2 | $\delta(\mathrm{H}_2)_{\mathrm{SC}}$ | s <i>δ</i> (H | 8)scs | $\delta(C_i)_{SCS}$ | $\delta(\text{Se})_{\text{SCS}}$ |
| $\mathbf{Y} = \mathbf{H} \left(\mathbf{a} \right)$ | 0.000 | 0.00 | 00 | 0.00 | 0.0 |
| | (7.776) ⁶ | ^{<i>i</i>} (8.3 | $(48)^{a}$ | $(131.66)^a$ | $(361.0)^{a}$ |
| NMe_2 (b) | -0.467 | -0. | 088 | -18.15 | -17.2 |
| OMe (c) | -0.277 | -0. | 068 | -11.48 | -6.8 |
| Me (d) | -0.108 | -0. | 021 | -4.37 | -4.8 |
| F (e) | -0.101 | -0. | 053 | -5.98 | -5.0 |
| | 0.003 | -0.0 | 062 | -1.55 | -1.6 |
| $\operatorname{Br}(\sigma)$ | 0.021 | -0.0 | 059 | -0.64 | -17 |
| $CO_{-}Et(\mathbf{h})$ | 0.021 | _0.0 | 068 | 8 17 | 7.0 |
| CN(i) | 0.113 | _0. | 101 | 0.17 | 13.8 |
| $NO(\mathbf{i})$ | 0.115 | -0. | 100 | 12.45 | 18.6 |
| $NO_2(\mathbf{j})$ | 0.125 | =0. | 109 | 12.30 | 18.0 |
| 5 | $\delta(H_1)_{SCS}$ | $\delta(H_{10})_{SCS}$ | $\delta(\mathbf{H}_o)_{\mathrm{SC}}$ | $\delta(C_i)_{SCS}$ | $\delta(\text{Se})_{\text{SCS}}$ |
| Y = H(a) | 0.000 | 0.000 | 0.00 | 0.00 | 0.0 |
| | $(8.884)^{a}$ | $(8.567)^{a}$ | $(7.057)^{a}$ | $(126.57)^{a}$ | $(249.0)^{a}$ |
| NMe ₂ (b) | 0.127 | -0.077 | 0.084 | -8.13 | -21.0 |
| OMe(c) | 0.045 | -0.045 | 0.044 | -3.11 | -12.2 |
| Me(d) | 0.005 | _0.019 | -0.068 | _1.13 | -6.6 |
| $F(\mathbf{a})$ | _0.028 | _0.008 | 0.000 | 1 24 | -3.6 |
| $C1(\mathbf{f})$ | -0.028 | -0.008 | 0.005 | 2.92 | -5.0 |
| CI(I) Dr(r) | -0.073 | 0.008 | -0.075 | 2.03 | 1.5 |
| $\operatorname{Br}(\mathbf{g})$ | -0.084 | 0.010 | -0.137 | 3.94 | 1.0 |
| $CO_2Et(\mathbf{n})$ | -0.106 | 0.071 | -0.01/ | 13.23 | 16.2 |
| CN (1) | -0.186 | 0.060 | -0.028 | 14.89 | 26.2 |
| $NO_2(\mathbf{j})$ | -0.218 | 0.103 | -0.007 | 17.73 | 30.3 |
| 6 | $\delta(\mathrm{H}_2)_{\mathrm{SCS}}$ | $\delta({\rm H_8})_{\rm SCS}$ | $\delta(\mathrm{H}_o)_{\mathrm{SCS}}$ | $\delta(C_i)_{SCS}$ | $\delta(\text{Se})_{\text{SCS}}$ |
| $\mathbf{Y} = \mathbf{H} \left(\mathbf{a} \right)$ | 0.000 | 0.000 | 0.00 | 0.00 | 0.0 |
| | $(7.237)^{a}$ | $(8.352)^{a}$ | $(7.724)^a$ | $(127.44)^{a}$ | $(512.3)^{a}$ |
| NMe_2 (b) | 0.102 | 0.024 | -0.196 | -13.87 | -19.5 |
| OMe (c) | 0.023 | 0.022 | -0.102 | -8.05 | -15.0 |
| Me (d) | 0.024 | 0.013 | -0.128 | -2.06 | -8.9 |
| F (e) | -0.038 | 0.005 | -0.032 | -3.45 | -10.1 |
| Cl(f) | -0.017 | 0.011 | -0.071 | 2.21 | -7.0 |
| Br (g) | -0.012 | 0.010 | -0.144 | 2.21 | -64 |
| $CO_{2}Et(\mathbf{h})$ | -0.052 | 0.016 | 0.046 | 5.26 | 0.0 |
| CN(i) | -0.056 | 0.011 | -0.009 | 5.20 | 8.2 |
| $NO_{1}(\mathbf{i})$ | _0.052 | 0.018 | 0.009 | 5.66 | 2.5 |
| 102 (J) | 0.052 | 0.010 | 0.190 | 5.00 | 4.0 |

^{*a*} δ (H)_{SCS}, δ (C)_{SCS}, δ (Te)_{SCS} and/or δ (Se)_{SCS} are given for 1, 2, 5 and 6, together with δ (H), δ (C), δ (Te) and/or δ (Se) for 1a, 2a, 5a and 6a in parenthesis, measured in chloroform-*d* (0.050 mol L⁻¹) at 24 °C.

Structures of 1-(ArTe)Nap (1) in solutions

NMR chemical shifts were measured at 400 MHz for **1a–1j** in chloroform-*d* (0.050 mol L⁻¹) at 24 °C.²⁵ Table 2 summarizes the selected substituent induced chemical shifts (SCS) of $\delta(H_n)_{SCS}$, $\delta(C_i)_{SCS}$ and $\delta(Te)_{SCS}$ for **1**, where H_n stand for H at

the *n*-position and C_i for the *ipso*-carbon as shown in Chart 1. Table 2 also contains $\delta(H_n)_{SCS}$, $\delta(C_i)_{SCS}$ and $\delta(Se)_{SCS}$ for 2, 5 and 6 (see Charts 1 and 2).²¹ NMR chemical shifts measured from TMS for the parent compounds (Y = H: 1a, 2a, 5a and 6a) are given in parenthesis. Those of 3 and 4 are given in Table S1 of the ESI.[†]

Fine structures of 1a–1j in chloroform-*d* solutions were determined employing NMR chemical shifts of 5a–5j and 6a–6j as references, *via* those of 2a–2j.^{13,21} The strategy to determine the structures of 1–4 in solutions was as follows: structures of 1–4 should be (A: pl) in solutions for those with arbitrary substituents, Y_s, Y_t and Y_u, if plots of δ_{SCS} in 1–4 *versus* δ_{SCS} in 5 give a very good correlation for those with Y_s, Y_t and Y_u, since the structures of 5 are (A: pl) for all Y in solutions. Similarly, those with Y_s, Y_t and Y_u should be (B: pd) in solutions if a very good correlation is obtained for those with Y_s, Y_t and Y_u in the plot of δ_{SCS} in 1–4 *versus* δ_{SCS} in 6, since the structures of 6 are all (B: pd) in solutions.

Confirmation of the structures for 2a-2j in solutions

It seems complex to discuss the structures of 1–4 in solutions in the unified form, at first glance. Therefore, compounds containing the most similarities are examined first: 2, 5 and 6 are the nice candidates to be discussed first, since they are all organic selenium compounds. Structures of 1–4 in solutions were determined as follows. (1) Fine structures⁶ of 2a–2j were established in solutions first, employing the NMR data of 5a–5j and 6a–6j as references. (2) Fine structures of 1a–1j in solutions were confirmed next, employing the NMR data of 2a–2j as references. (3) Then, fine structures of 3 and 4 in solutions are discussed similarly.

The $\delta(C_i)_{SCS}$ values of **2** ($\delta(C_i: \mathbf{2})_{SCS}$) were plotted *versus* $\delta(C_i: \mathbf{5})_{SCS}$ and $\delta(C_i: \mathbf{6})_{SCS}$. Fig. 5a and b show the plots, respectively. The plots are analyzed for Y separately by three groups: Y = H (**a**) and Me (**d**) make a group (G(**l**)), Y = NMe₂ (**b**), OMe (**c**) and F (**e**) make the second group (G(**m**)) and Y = Cl (**f**), Br (**g**), COOEt (**h**), CN (**i**) and NO₂ (**j**) belong to the third one (G(**n**)). The correlations are excellent and are given in the entries 1–4 in Table 3. The (*a*, R^2) values in Fig. 5a are (1.300, 0.9998) for G(**m**) and (0.932, 0.9997) for G(**n**), whereas the values in Fig. 5b are (1.167, 0.9999) for G(**m**) and (3.527, 0.973) for G(**n**).

The (a, R^2) values change depending on whether the mechanisms are similar or different.^{21*a*} For the plots of $\delta(C_i: 2)_{SCS}$ *versus* $\delta(C_i: 5)_{SCS}$ in Fig. 5a, the *a* value for G(n) (0.932) is substantially closer to 1.0, relative to that for G(m) (1.300), whereas that for G(m) (1.167) is much closer to 1.0, relative to G(n) (3.527), in the plot of $\delta(C_i: 2)_{SCS}$ versus $\delta(C_i: 6)_{SCS}$ (Fig. 5b). Data for G(l) somewhat deviate from the correlations both in Fig. 5a and b. The results are well-explained by assuming that the structures of 2 are (A: pl) for G(n), (B: pd) for G(m) and in equilibrium between (A: pl) and (B: pd) for G(l).

The $\delta(H_2; 2)_{SCS}$ values should correspond to $\delta(H_1; 5)_{SCS}$ for $G(\mathbf{n})$ and $\delta(H_2; 2)_{SCS}$ would do to $\delta(H_2; 6)$ for $G(\mathbf{m})$. $\delta(H_2; 2)_{SCS}$ are plotted *versus* $\delta(H_1; 5)$ and $\delta(H_2; 6)_{SCS}$, which are drawn in Fig. S4 in the ESI.[†] Correlations for $G(\mathbf{n})$ and $G(\mathbf{m})$ of the plots are given in entries 5–8 in Table 3. The results for $\delta(H_2; 2)_{SCS}$ support the above conclusion that the structures



Fig. 5 Plots of $\delta(C_i: 2)_{SCS}$ versus $\delta(C_i: 5)_{SCS}$ (a) and $\delta(C_i: 2)_{SCS}$ versus $\delta(C_i: 6)_{SCS}$ (b). Plots are analyzed by three groups, G(1), G(m) and G(n), and drawn as black circle, red triangle and blue rectangle, respectively.

of **2** are (A: pl) for G(n) and (B: pd) for G(m), with equilibrium between (A: pl) and (B: pd) for G(l).

The $\delta(\text{Se})_{\text{SCS}}$ values must also be a good measure to determine the fine structures of **2** in solutions. Fig. S5a and b in the ESI† show the plots of $\delta(\text{Se: 2})_{\text{SCS}}$ versus $\delta(\text{Se: 5})_{\text{SCS}}$ and $\delta(\text{Se: 6})_{\text{SCS}}$, respectively. The correlation for G(n) in the plot of $\delta(\text{Se: 2})_{\text{SCS}}$ versus $\delta(\text{Se: 5})_{\text{SCS}}$ is given in entry 9 in Table 3. The good correlation for G(n) supports the above conclusion of (A: pl) for G(n: 2). Data of 2e in G(m) deviate from the correlation line of 2b and 2c in the plot of $\delta(\text{Se: 2})_{\text{SCS}}$ versus $\delta(\text{Se: 5})_{\text{SCS}}$ (see entry 10 in Table 3), which may show some equilibrium between (B: pd) and (A: pl) for 2e. Correlations in the plot of $\delta(\text{Se: 2})_{\text{SCS}}$ versus $\delta(\text{Se: 6})_{\text{SCS}}$ are given in entries 11 and 12 in Table 3. The behavior of $\delta(\text{Se: 2})_{\text{SCS}}$ essentially support the (A: pl) structure for G(n) and (B: pd) for G(m) with equilibrium between (A: pl) and (B: pd) for G(l) in 2.

After confirmation of the structure of 2 in solutions separately by Y, the next extension is to determine the structures of 1, 3 and 4 in solutions, based on NMR parameters.

Structural determination of 1, 3 and 4 in solutions

What are the similarities and differences in the structures of 1–4? $\delta(C_i)_{SCS}$ are discussed first. Fig. 6 shows the plots of $\delta(C_i: 1, 3)_{SCS}$ and $4)_{SCS}$ versus $\delta(C_i: 2)_{SCS}$. They gave excellent correlations with no deviations, which are given in entries 13–15 in Table 3. The results support that the structures of 1–4 are essentially (B: pd) for G(m), (A: pl) for G(n) and in the equilibrium between the two for G(I). Slopes for the correlations in 1 and 3 are very close to 1.0, but that of 4 is much smaller, which suggests that the structural features in 1–3 are more similar to each other, compared to the case of 4.

To understand the structure of 1 in solutions in more detail, $\delta(H_2; 1)_{SCS}$ were plotted *versus* $\delta(H_2; 2)_{SCS}$. Fig. S6 in the ESI[†]

Table 3 Correlations in the plots of $\delta(H)_{SCS}$, $\delta(C)_{SCS}$, $\delta(Se)_{SCS}$ and/or $\delta(Te)_{SCS}$ for 1–6 analyzed separately mainly by three groups^a

| Entries | Y | x | а | b | R^2 | $\mathbf{G}(x)$ | Structure |
|---------|---|--|--------|-------|--------|---------------------|------------------|
| 1 | $\delta(C_i; 2)_{SCS}$ | $\delta(C_i: 5)_{SCS}$ | 1.300 | -7.54 | 0.9998 | G(m) | (B: pd) |
| 2 | $\delta(C_i; 2)_{SCS}$ | $\delta(C_i; 5)_{SCS}$ | 0.932 | -4.25 | 0.9997 | G(n) | (A: pl) |
| 3 | $\delta(C_i; 2)_{SCS}$ | $\delta(C_i; 6)_{SCS}$ | 1.167 | -2.00 | 0.9999 | $G(\mathbf{m})$ | (B: pd) |
| 4 | $\delta(C_i; 2)_{SCS}$ | $\delta(C_i: 6)_{SCS}$ | 3.527 | -8.98 | 0.973 | $G(\mathbf{n})$ | (A: pl) |
| 5 | $\delta(H_2; 2)_{SCS}$ | $\delta(H_1: 5)_{SCS}$ | -1.862 | -0.15 | 0.9999 | $G(\mathbf{m})$ | (B: pd) |
| 6 | $\delta(H_2; 2)_{SCS}$ | $\delta(H_1: 5)_{SCS}$ | -1.897 | -0.13 | 0.992 | G(n) | (A: pl) |
| 7 | $\delta(H_2; 2)_{SCS}$ | $\delta(H_2; 6)_{SCS}$ | -2.053 | -0.17 | 0.994 | $G(\mathbf{m})$ | (B: pd) |
| 8 | $\delta(H_2; 2)_{SCS}$ | $\delta(H_2; 6)_{SCS}$ | -5.374 | -0.06 | 0.908 | G(n) | (A: pl) |
| 9 | $\delta(\text{Se: 2})_{\text{SCS}}$ | $\delta(\text{Se: 5})_{\text{SCS}}$ | 0.673 | -2.98 | 0.990 | $G(\mathbf{n})$ | (A: pl) |
| 10 | $\delta(\text{Se: 2})_{\text{SCS}}$ | $\delta(\text{Se: 5})_{\text{SCS}}$ | 1.182 | 7.62 | | $G(\mathbf{m}^*)^b$ | (B: pd) |
| 11 | $\delta(\text{Se: 2})_{\text{SCS}}$ | $\delta(\text{Se: 6})_{\text{SCS}}$ | 1.050 | 5.74 | 0.986 | $G(\mathbf{n})$ | (A: pl) |
| 12 | $\delta(\text{Se: 2})_{\text{SCS}}$ | $\delta(\text{Se: 6})_{\text{SCS}}$ | 2.311 | 27.87 | | $G(\mathbf{m}^*)^b$ | (B: pd) |
| 13 | $\delta(C_i: 1)_{SCS}$ | $\delta(C_i: 2)_{SCS}$ | 1.007 | -0.21 | 0.990 | AÌÌ | · · / |
| 14 | $\delta(C_i: 3)_{SCS}$ | $\delta(C_i: 2)_{SCS}$ | 0.972 | -0.09 | 0.998 | All | |
| 15 | $\delta(C_i: 4)_{SCS}$ | $\delta(C_i: 2)_{SCS}$ | 0.572 | -0.48 | 0.992 | All | |
| 16 | $\delta(H_2: 1)_{SCS}$ | $\delta(\mathrm{H}_2; 2)_{\mathrm{SCS}}$ | 0.789 | -0.01 | 0.999 | G(m) | (B: pd) |
| 17 | $\delta(H_2: 1)_{SCS}$ | $\delta(\mathrm{H}_2; 2)_{\mathrm{SCS}}$ | 2.147 | -0.01 | 0.983 | $G(\mathbf{n})$ | (A: pl) |
| 18 | $\delta(\mathrm{H}_2:3)_{\mathrm{SCS}}$ | $\delta(\mathrm{H}_2; 2)_{\mathrm{SCS}}$ | 1.044 | 0.00 | 0.999 | $G(\mathbf{m'})^c$ | (B: pd) |
| 19 | $\delta(\mathrm{H}_2:3)_{\mathrm{SCS}}$ | $\delta(\mathrm{H}_2; 2)_{\mathrm{SCS}}$ | 2.156 | 0.01 | 0.989 | $G(\mathbf{n'})^d$ | (A: pl) |
| 20 | $\delta(H_2: 4)_{SCS}$ | $\delta(\mathrm{H}_2; 2)_{\mathrm{SCS}}$ | 0.227 | 0.00 | 0.999 | $G(\mathbf{m'})^c$ | (B: pd) |
| 21 | $\delta(H_2: 4)_{SCS}$ | $\delta(H_2: 2)_{SCS}$ | 1.467 | -0.01 | 0.982 | $G(\mathbf{n'})^d$ | (A: pl) |
| 22 | δ (Te: 1) _{SCS} | $\delta(\text{Se: 2})_{\text{SCS}}$ | 1.812 | -1.68 | 0.990 | | |
| | | | | | | | |

^{*a*} G(l) with Y = H (a) and Me (d); G(m) with Y = NMe₂ (b), OMe (c) and F (e); G(n) of Y = Cl (f), Br (g), COOEt (h), CN (i) and NO₂ (j). ^{*b*} G(m*) of Y = NMe₂ (b) and OMe (c). ^{*c*} G(m') with Y = H (a), OMe (c) and Me (d). ^{*d*} G(n') with Y = Cl (f), Br (g), COOEt (h) and NO₂ (j).

shows the plot. The plot was analyzed by three groups; $G(\mathbf{m})$ and $G(\mathbf{n})$ with the equilibrium nature for $G(\mathbf{l})$. The correlations are given in entries 16 and 17 in Table 3. Different correlations are recorded for $G(\mathbf{m})$ and $G(\mathbf{n})$ in this case. This must be the reflection of the different anisotropic effect at H_2 from SeC₆H₄Y-*p* and TeC₆H₄Y-*p* in (**B**: **pd**) and (**A**: **pl**), together with the bond lengths. The results are also consistent with the conclusion of the (**A**: **pl**) structure for $G(\mathbf{n})$ and (**B**: **pd**) for $G(\mathbf{m})$ with the equilibrium for $G(\mathbf{l})$ in **1** and **2**.

The structures of **3** and **4** were similarly examined as discussed in **1**. $\delta(H_2: 3 \text{ and } 4)_{SCS}$ were plotted *versus* $\delta(H_2: 2)_{SCS}$



Fig. 6 Plots of $\delta(C_i)_{SCS}$ of **1**, **3** and **4** versus $\delta(C_i: \mathbf{2})_{SCS}$. G(**1**), G(**m**) and G(**n**) are drawn in black, red and blue, respectively.



Fig. 7 A plot of δ (Te: 1)_{SCS} versus δ (Se: 2)_{SCS}.

 Table 4
 Structures of 1–4 in solutions^a

(see Fig. S7 in the ESI[†]). The plots should be analyzed by three groups of G(l), G(m) and G(n). However, the plots were analyzed as two correlations with G(m') of Y = H (a), OMe (d) and Me (a) and G(n') of Y = Cl (f), Br (g), COOEt (h) and NO₂ (j) due to a lack of data for NMe₂, F and CN. The correlations are given in entries 18–21 in Table 3. The relations in the structures of **3** and **4** *versus* **2** are similar to the case of **1** *versus* **2**.

 δ (Te: 1)_{SCS} are plotted *versus* δ (Se: 2)_{SCS}. Fig. 7 shows the results. The correlation was also good, as shown in entry 22, although data for Y = F, Cl, Br and NO₂ are omitted from the correlation line. Firm standards for δ (Te)_{SCS} seem necessary for the final conclusion based on δ (Te)_{SCS}.²⁶ The Te derivatives of **5** and **6** would be the candidates for the standards. Table 4 summarizes the structures of **1–4** determined in the solutions using NMR.

After determination of the fine structures of 1-4, in crystals and solutions, the next extension is to clarify the energy profiles of 1-4 on the basis of the theoretical background.

QC calculations on 1-(ArZ)Nap (1-4)

Structures and energies evaluated on the basis of QC calculations correspond to those in the gas phase, so do the nature of interactions. We must be careful when structures, energies and profiles are discussed on the basis of QC calculations, since other factors, such as the crystal packing effect in crystals and the solvent effect in solutions, would be stronger than those predicted by QC calculations. However, factors to stabilize the structures in the gas phase must also operate in solid states and solutions, which enable us to clarify the nature of interactions by the careful comparison of the calculated results with the observed ones.

Z-dependence in structures of 1-(PhZ)Nap (1a-4a)

The **pl**, **pd** and **np** conformations of the aryl group will change depending on the **A**, **B** and **C** structures for the naphthyl group in **1a–4a**. Therefore, the discussion on the basis of the theoretical calculations of **1a–4a** is focused on the **A**, **B** and **C** structures for the naphthyl group, first. Tables 5 and 6 collect the optimized structures for **1a** and **2a**, respectively, confirmed by the frequency analysis. Those for **3a** and **4a** are collected in Tables S2 and S3 in the ESI,† respectively. Energies on the potential energy surface are given by *E* and the energy differences on the potential energy surface from a standard are by ΔE . Those with thermal correction to Gibbs free energy are denoted by E_{GF} and ΔE_{GF} respectively. While **A** is the global minimum, **B'** is the local minimum for each of **1a–4a** on the energy surface. The **B'**

| Z/Y | NMe ₂ (b) | OMe (c) | Me (d) | Н (a) | F (e) | Cl/Br (f/g) | CO ₂ Et (h) | CN (i) | NO ₂ (j) |
|--------|----------------------------------|---------------------|-----------|-------------------|----------------------|----------------|---------------------------------|-----------|------------------------|
| Te (1) | (B: pd) | (B: pd) | Eq. | Eq. | $(\mathbf{B: pd})^b$ | (A: pl) | (A: pl) | (A: pl) | (A: pl) |
| Se (2) | (B: pd) | (B: pd) | Eq. | Eq. | $(\mathbf{B: pd})^b$ | (A: pl) | (A: pl) | (A: pl) | (A: pl) |
| S (3) | (B: pd) | (B: pd) | Eq. | Eq. | $(\mathbf{B: pd})^b$ | (A: pl) | (A: pl) | (A: pl) | (A: pl) |
| O (4) | (B: pd) | (B: pd) | Eq. | Eq. | $(\mathbf{B: pd})^b$ | (A: pl) | (A: pl) | (A: pl) | (A: pl) |

^a Eq. means that the structure is in equilibrium. ^b It could be somewhat in equilibrium with (A: pl).

Table 5 Selected structural information and energies of optimized structures of $1-(PhTe)C_{10}H_7$ (1a) at the MP2 level^a

| Structure | Α | TS- AB' ^b | B ′ ^c | $\mathbf{B_o}^d$ |
|---|------------|-----------------------------|-------------------------|------------------|
| E (au) | -7226.8627 | -7226.8604 | -7226.8613 | -7226.8613 |
| ΔE (kJ mol ⁻¹) | 0.0^e | 5.9 | 3.5 | 3.6 |
| $r(\text{Te}, \text{C}_1)$ (Å) | 2.1097 | 2.1177 | 2.1207 | 2.1206 |
| $r(Te, C_{11})$ (Å) | 2.1121 | 2.1097 | 2.1042 | 2.1042 |
| $\angle C_1 \text{Te} C_{11}$ (°) | 95.63 | 94.22 | 95.82 | 95.84 |
| $\angle C_{10}C_1TeC_{11}$ (°) | 62.92 | 120.07 | 174.68 | 180.00 |
| $\angle C_1 TeC_{11}C_{12}$ (°) | 38.15 | -54.75 | -88.08 | -89.94 |
| v_1^{f} (sym) (cm ⁻¹) | 22.2 (A) | -11.7 (A) | 4.5 (A) | -306.4 (A") |
| v_2^{g} (sym) (cm ⁻¹) | 26.6 (A) | 16.5 (A) | 30.1 (Å) | -1.2 (A'') |
| $ZC^{h}(au)$ | 0.2275 | 0.2269 | 0.2273 | 0.2260 |
| GF^{i} (au) | 0.1831 | 0.1839 | 0.1814 | 0.1838 |
| $E_{\rm GF}^{j}$ (au) | -7226.6796 | -7226.6765 | -7226.6799 | -7226.6775 |
| $\Delta E_{\rm GF}$ (kJ mol ⁻¹) | 0.0^e | 8.0 | -0.8 | 5.4 |

^{*a*} The basis sets of the (7433111/743111/74111/2 + 1s1p1d1f) type were employed for Te with the 6-31G(d,p) basis sets for C and H. ^{*b*} Transition state between **A** and **B'**. ^{*c*} Closer to **B**. ^{*d*} Corresponding to higher TS with two imaginary frequencies. ^{*e*} Taken as the standards for the energies. ^{*f*} Lowest frequency obtained by the frequency analysis. ^{*g*} Second-lowest frequency obtained by the frequency analysis. ^{*k*} Zero-point correction. ^{*i*} Thermal correction to Gibbs free energy at 298.15 K. ^{*j*} Sum of electronic and thermal Gibbs free energies at 298.15 K.

Table 6 Selected structural information and energies of $1-(PhSe)C_{10}H_7$ (2a) at the MP2 level^a

| Structure | Α | TS- AB ′ ^b | B' | TS- B'B' | $\mathbf{B_o}^d$ |
|--|------------|------------------------------|------------|-----------------|------------------|
| E (au) | -3015.0774 | -3015.0751 | -3015.0751 | -3015.0750 | -3015.0750 |
| ΔE (kJ mol ⁻¹) | 0.0^e | 5.9 | 5.9 | 6.2 | 6.4 |
| $r(Se, C_1)$ (Å) | 1.9191 | 1.9293 | 1.9297 | 1.9298 | 1.9298 |
| $r(Se, C_{11})$ (Å) | 1.9231 | 1.9181 | 1.9164 | 1.9145 | 1.9144 |
| $\angle C_1 SeC_{11}$ (°) | 98.11 | 97.31 | 97.89 | 99.04 | 99.05 |
| $\angle C_{10}C_1SeC_{11}$ (°) | 66.59 | 136.92 | 150.23 | 179.35 | 180.00 |
| $\angle C_1 SeC_{11}C_{12}$ (°) | 40.31 | -66.86 | -73.16 | -91.33 | -90.71 |
| v_1^{f} (sym) (cm ⁻¹) | 25.1 (A) | -7.3 (A) | 6.3 (A) | -8.3 (A) | -375.7 (A'') |
| v_2^{g} (sym) (cm ⁻¹) | 27.5 (A) | 25.5 (A) | 29.6 (Á) | 29.7 (A) | -9.0 (A'') |
| ZC^{h} (au) | 0.2282 | 0.2279 | 0.2281 | 0.2283 | 0.2266 |
| GF^{i} (au) | 0.1849 | 0.1864 | 0.1835 | 0.1870 | 0.1853 |
| $E_{\rm GF}^{j}$ (au) | -3014.8925 | -3014.8887 | -3014.8917 | -3014.8880 | -3014.8897 |
| $\Delta_{\rm GF} ({\rm kJ \ mol}^{-1})$ | 0.0^e | 10.1 | 2.2 | 11.9 | 7.7 |

^{*a*} The 6-311+G(3d) basis sets were employed for Se with the 6-31G(d,p) basis sets for C and H. ^{*b*} Transition state between **A** and **B'**, where **B'** is very close to **C'**. ^{*c*} Transition state between **B'** and the topological isomer. ^{*d*} Corresponding to higher TS with two imaginary frequencies. ^{*e*} Taken as the standards for the energies. ^{*j*} Lowest frequency obtained by the frequency analysis. ^{*g*} Second-lowest frequency obtained by the frequency analysis. ^{*k*} Zero-point correction. ^{*i*} Thermal correction to Gibbs free energy at 298.15 K. ^{*j*} Sum of electronic and thermal Gibbs free energies at 298.15 K.

notation is employed instead of **B** for **1a–4a**, since **B** becomes closer to **C** for Y of non-H in **1–4**. The structure should be called **B'** and it is convenient when the structures of **1–4** are discussed in a unified form. Structures are also optimized assuming the C_s symmetry with $\angle C_{10}C_1ZC_{11} = 180.00^\circ$ for **1a–4a**, which are called **B**₀. Structures converged to **B'**, when optimizations are started around **B**₀ for **1a–4a**. Tables 5 and 6 contain the data for **A**, **B'** and **B**₀, together with the transition state between **A** and **B'** (TS-**AB'**).

The **B**_o structure is not the transition state between **B'** and the topological isomer, since it has two imaginary frequencies for each of **1a–4a**. The transition state of TS-**B'B'** was optimized for each of **2a** and **4a**, of which $\angle C_{10}C_1ZC_{11}$ is about 179.4°. However, the transition state of TS-**B'B'** was not optimized for **1a** and **3a**. The transition state was converged to TS-**AB'**, even when the optimization is started from $\angle C_{10}C_1ZC_{11}$ of around 179.4° for **1a** and **3a**.

Fig. 8a and b show the energy profiles for **1a-4a**, evaluated on the potential energy surface and those with the thermal correction to Gibbs free energy at 298.15 K, respectively. The energy difference between **B'** and **A** ($\Delta E(\mathbf{B'A}) = E(\mathbf{B'}) - E(\mathbf{A})$) in **4a** is predicted to be 1.4 kJ mol⁻¹. The results are in accordance with the observed structure of **4a** in crystals (see Fig. 4). The $\Delta E(\mathbf{B'A})$ values becomes larger and up to 6–7 kJ mol⁻¹ for **2a** and **3a**. It seems difficult to examine the predicted values, since the structures of **1a–3a** are not determined by the X-ray crystallographic analysis, due to the oily nature around room temperature. It seems somewhat strange, since the energy level of TS-**AB'** is predicted to be very close to that of **B'** for **2a**.

On the other hand, the energy profiles become reasonable if the thermal correction by the Gibbs free energy at 298.15 K is taken into account. The $\Delta E_{GF}(\mathbf{B'A})$ values are predicted to be -1.0-2.5 kJ mol⁻¹ for **1a-4a**, which support the equilibrium between **A** and **B'** in solutions. They could be observed for both **A** and **B'** in crystals. The predicted energy barriers for TS-**AB'** and TS-**B'B'** are 4–12 kJ mol⁻¹ for **1a-4a**, which separate **A** and **B'** reasonably. Namely, the energy profiles on the energy potential surface are well-improved by the thermal energy of the Gibbs free energy for **1a-4a**, although the effect on TS-**B'B'** could not be clarified for **1a** and **3a**.



Fig. 8 Energy profiles for 1a–4a evaluated on the potential energy surface (a) and considering the Gibbs free energy at 298 K (b).

The $\angle C_{10}C_1ZC_{11}$ values of **A** in **1a–4a** are 62.92°, 66.59°, 67.48° and 77.82°, respectively. The values increase monotonically in the order of **1a** (Z = Te) < **2a** (Se) < **3a** (S) < **4a** (O). The order seems inverse to the C–Z bond lengths. The π - π interaction may occur more easily between naphthyl and phenyl planes as the C–Z bond becomes longer, as shown by the $\angle C_{10}C_1ZC_{11}$ values. The $\angle C_{10}C_1ZC_{11}$ values of **B'** are 174.68°, 150.23°, 163.18° and 149.70° for **1a–4a**, respectively, and those of TS-**AB'** are 120.07°, 136.93°, 136.38° and 115.92°, respectively. It seems difficult to explain the trends.

Compilation of these results suggests that the structures of minima and the transition states would change depending on the electronic environment around Z. This consideration led us to clarify the structures and energy profiles in more detail for 1-4 that have Y of non-H.

Features in structures of 1-(p-YC₆H₄Z)Nap (1-4)

The A_o structure was obtained by optimizing partially with the torsional angles being fixed at $\angle C_1ZC_{11}C_{12} = 0.00^\circ$, similar to the case of B_o of which $\angle C_{10}C_1ZC_{11}$ is fixed at 180.00°. The A_o and B_o structures were calculated for 1–4 with Y of H (a), NH₂ (b'), Me (d), Cl (f) and NO₂ (j), for a better understanding of the p– π conjugation. Table 7 collects the results of calculations for 1 and 2. Those for 3 and 4 are given in Table S4 of the ESI.†

The $\angle C_{10}C_1ZC_{11}$ and $\angle C_1ZC_{11}C_{12}$ values will change depending on Z and Y (see Scheme 3). Fig. 9a and b show the plots of $\angle C_{10}C_1ZC_{11}$ and $\angle C_1ZC_{11}C_{12}$ versus Y, respectively, separately by the types of structures. The $\angle C_{10}C_1ZC_{11}$ values of A are 62.5-64.8°, 66.0-68.3°, 67.0-69.3° and 75.8-80.3° for 1-4, respectively (see Table 7). The values are rather constant or increase slightly as the accepting ability of Y becomes larger. On the other hand, the $\angle C_{10}C_1ZC_{11}$ values of **B'** change dramatically depending on Y, as shown in Fig. 9a (and Table 7). The B' structures are (very) close to B_o for 1b'-4b'. However, $\angle C_{10}C_1ZC_{11}$ decreases as the accepting ability of Y increases. In this process, B' converges to A via C at 3f, 1j, 2j and 4j. The results strongly support the observed results in solutions: the A structure is predicted for 1-4 with Y of accepting ability stronger than Cl. The change of $\angle C_1 Z C_{11} C_{12}$ is well-correlated to that of $\angle C_{10}C_1ZC_{11}$, as shown in Fig. 9b.

What are the energy profiles of 1 and 2 with Y of a, b', d, f and j? The energy differences between the $p(Z)-\pi(C_6H_4Y)$ and $p(Z)-\pi(Nap)$ conjugations $(\Delta E_{p\pi}Z:Y) = E(p(Z)-\pi(Nap)) - E(p(Z)-\pi(C_6H_4Y)))$ can be roughly estimated through the energy differences between A_0 and B_0 . However, we must be careful when the energy profiles are examined, since the data in Table 7 are evaluated on the energy potential surface. How can the thermal effect be incorporated? The thermal effect could be approximately incorporated by employing the values given in Fig. 8b as the standard for 1a-4a, if the thermal effect on Y is not so different in A and B and the related structures. Fig. 10a and b draw the relative values of $\Delta E_{p\pi}(Z:Y)$ for those between A_0 and B_0 , and between A and B', respectively.

The $\Delta E_p \pi(Z:Y)$ values between $\mathbf{A_o}$ and $\mathbf{B_o}$ are all about -5 kJ mol^{-1} for 1-4 when Y of **b'**. The values become monotonically larger as the accepting ability of Y increases and finally (over) +5 kJ mol⁻¹ at Y of **j**. The trend in $\Delta E_p \pi(Z:Y)$ between **A** and **B'** is essentially the same as those between $\mathbf{A_o}$ and $\mathbf{B_o}$, although $\Delta E_p \pi(Z:Y)$ for Z = S and Se with Y of **b'** seems smaller, which must be due to the employed standard values of 2.2–2.5 kJ mol⁻¹, instead of -1 kJ mol^{-1} , for the compounds. Very large values are predicted for **3f** and **1j–4j**, which arise from the structural convergence to **A** in the compounds. The results demonstrate that the p– π conjugation operates effectively for Z of heavier atoms, such as Se and Te, as well as O and S.

After clarification of the energy profiles of 1–4, the role of the $p(Z)-\pi(Ar/Nap)$ conjugation in the fine structures is next examined employing NBO analysis.

p(Z)-π(Ar/Nap) conjugations in 1–4 evaluated by NBO

NBO (natural bond orbital)²⁷ analysis was applied to \mathbf{A}_{o} and \mathbf{B}_{o} of **1a–4a**, **1b'**, **1d**, **1f** and **1j**. However, the (**A**: **pl**)_o and (**B**: **pd**)_o notation is employed here, instead of \mathbf{A}_{o} and \mathbf{B}_{o} , respectively, since it is inevitable to define the conformation around the p-YC₆H₄Z group to evaluate the p(Z)– π (Ar/Nap) conjugation. Magnitudes of the p– π conjugation of the n_p (Z) $\rightarrow \pi^*$ (Nap) and n_p (Z) $\rightarrow \pi^*$ (Ar) types were evaluated for Z = Te, Se, S and O in **1–4**.

Such $p-\pi$ conjugation can be obtained as the CT interactions of which magnitudes are evaluated as the second order perturbation of the Fock matrix in NBO. For each donor NBO (i) and acceptor NBO (j), the stabilization energy E(2) associated with

| Table 7 | Selected structural information and energies of 1 and 2 that have p-Y of NH ₂ (b'), Me (d), H (a), Cl (f) and NO ₂ (j) calculated at the MP2 |
|----------------------|--|
| level ^{a,b} | |

| Compound/Y = | NH ₂ (b ′) | Me (d) | Н (а) | Cl (f) | $NO_{2}\left(\mathbf{j}\right)$ |
|---|-------------------------------|-----------------|------------|--------------------|---------------------------------|
| 1: 1-(<i>p</i> -YC ₆ H ₄ Te)C ₁₀ H ₇ | | | | | |
| $\angle C_{10}C_1 \text{Te}C_{11} (\mathbf{A}) (^{\circ})$ | 63.26 | 62.51 | 62.92 | 63.10 | 64.83 |
| $\angle C_1 \text{Te} C_{11} C_{12} (\mathbf{A}) (^{\circ})$ | 53.71 | 40.40 | 38.15 | 36.84 | 26.87 |
| $\angle C_{10}C_1 \text{Te}C_{11} (\mathbf{B'}) (^{\circ})$ | 178.25 | 176.61 | 174.68 | 171.31 | 64.83 ^c |
| $\angle C_1 \text{Te} C_{11} C_{12} (\mathbf{B'}) (^\circ)$ | -90.08 | -88.91 | -88.08 | -86.01 | 26.88^{c} |
| $\angle C_{10}C_1 \text{Te}C_{11} (\mathbf{A_0}) (^{\circ})$ | 72.91 | 72.97 | 73.13 | 73.03 | 73.13 |
| $\angle C_1 \text{Te} C_{11} C_{12} (\mathbf{A}_0) (^\circ)$ | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| $\angle C_{10}C_1 \text{Te}C_{11} (\mathbf{B}_0) (^{\circ})$ | 180.00 | 180.00 | 180.00 | 180.00 | 180.00 |
| $\angle C_1 \text{Te} C_{11} C_{12} (\mathbf{B}_0) (^\circ)$ | -90.09 | -89.62 | -89.92 | -89.99 | -90.11 |
| $E(\mathbf{A})^d$ (au) | -7282.0654 | -7266.0487 | -7226.8627 | -7685.8835 | -7430.8558 |
| $\Delta E(\mathbf{A})^{e}$ (kJ mol ⁻¹) | as 0.0 | as 0.0 | as 0.0 | as 0.0 | as 0.0 |
| $\Delta E(\mathbf{B'})^e$ (kJ mol ⁻¹) | 0.5 | 2.9 | 3.5 | 4.3 | 0.0^c |
| $\Delta E(\mathbf{A_0})^e$ (kJ mol ⁻¹) | as 0.0 | as 0.0 | as 0.0 | as 0.0 | as 0.0 |
| $\Delta E(\mathbf{B}_{0})^{e}$ (kJ mol ⁻¹) | -4.1 | 0.0 | 0.9 | 1.9 | 6.5 |
| 2 : $1 - (p - YC_6H_4Se)C_{10}H_7$ | | | | | |
| $\angle C_{10}C_1SeC_{11}(A)(^{\circ})$ | 65.99 | 66.23 | 66.59 | 66.88 | 68.28 |
| $\angle C_1 SeC_{11}C_{12}(A)(^{\circ})$ | 50.41 | 42.40 | 40.31 | 39.09 | 29.05 |
| $\angle C_{10}C_1SeC_{11}$ (B') (°) | 173.37 | 155.90 | 150.24 | 93.99 ^c | 68.28° |
| $\angle C_1 \text{SeC}_{11} C_{12} (\mathbf{B'}) (^\circ)$ | -88.34 | -77.59 | -73.16 | 47.39^{c} | 29.05^{c} |
| $\angle C_{10}C_1SeC_{11}(\mathbf{A_0})(^\circ)$ | 75.28 | 75.51 | 75.69 | 75.64 | 75.77 |
| $\angle C_1 SeC_{11}C_{12} (\mathbf{A_0}) (^{\circ})$ | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| $\angle C_{10}C_1SeC_{11}(\mathbf{B}_0)(^\circ)$ | 180.00 | 180.00 | 180.00 | 180.00 | 180.00 |
| $\angle C_1 \text{SeC}_{11} C_{12} (\mathbf{B}_0) (^\circ)$ | -90.92 | -90.47 | -90.71 | -90.77 | -90.86 |
| $E(\mathbf{A})^d$ (au) | -3070.2797 | -3054.2633 | -3015.0774 | -3474.0982 | -3219.0709 |
| $\Delta E(\mathbf{A})^{e}$ (kJ mol ⁻¹) | as 0.0 | as 0.0 | as 0.0 | as 0.0 | as 0.00 |
| $\Delta E(\mathbf{B'})^e$ (kJ mol ⁻¹) | 3.1 | 5.5 | 5.9 | 4.1^{f} | 0.0^{c} |
| $\Delta E(\mathbf{A_o})^e$ (kJ mol ⁻¹) | as 0.0 | as 0.0 | as 0.0 | as 0.0 | as 0.0 |
| $\Delta E(\mathbf{B_0})^e \text{ (kJ mol}^{-1})$ | -1.9 | 2.4 | 3.4 | 4.5 | 9.4 |

^{*a*} The basis sets of the (7433111/743111/7411/2 + 1s1p1d1f) type were employed for Te with the 6-31G(d,p) basis sets for C and H. ^{*b*} A stationary point was not obtained for typical **B**. ^{*c*} The value is almost the same if the thermal effect is considered, but it becomes -8.4 kJ mol^{-1} if the solvent effect is calculated by the IPCM method. ^{*d*} $\Delta E = E(\mathbf{A}) - E(\mathbf{B})$. ^{*e*} **A**. ^{*f*} **A**'.



Scheme 3 Structures of A and B with atomic numbering used for the torsional angles.

delocalization was estimated by eqn (1), where q_i is the donor orbital occupancy, ε_j and ε_i are diagonal elements (orbital energies) and F(i, j) is the off-diagonal NBO Fock matrix element.

$$E(2) = \Delta E_{ij} = q_i F(i,j)^2 / (\varepsilon_j - \varepsilon_i)$$
(1)

Table 8 collects the results at the MP2 level. Donor orbitals of NBO (*i*) in **1–4** correspond to $n_p(Z)$, where Z = Te, Se, S and O, respectively. On the other hand, acceptor orbitals of NBO (*j*) depend on the structures of **1–4**. While a $\sigma^*(C_1 = C_2)$ in the naphthyl group acts as NBO (*j*) for each (**B**: **pd**)_o in the calculations, NBO (*j*) will be a $\sigma^*(C_{11} = C_{12})$ in the aryl groups for (**A**: **pd**)_o, as shown in Scheme 3. The *E*(2) values for [(**A**: **pl**)_o; (**B**: **pd**)_o] are evaluated as [12.58; 13.00], [17.70; 18.45], [24.02; 25.43] and [30.64; 33.55] in kcal mol⁻¹ for **1a–4a**, respectively. The results show that the p– π conjugation of the $n_p(Z) \rightarrow \pi^*(\text{Ar}/\text{Nap})$ types operates effectively, even for Z = Te, although the

magnitudes increase in the order of Z = Te < Se < S < O. It is worthwhile to note that the $\Delta E(2)$ values (= $E(2: (\mathbf{B}: \mathbf{pd})_{o}) - E(2: (\mathbf{A}: \mathbf{pl})_{o}))$ decrease to 0.42, 0.75, 1.41 and 2.91 kcal mol⁻¹ for **1a**-**4a**, respectively. The $\Delta E(2)$ values control the appearance of (**A**: **pl**)_o or (**B**: **pd**)_o in crystals and the predominance in equilibrium in solutions, although other factors, such as the crystal packing effect in crystals, solvent effect in solutions and the steric effect in the conformers must be taken into account. The Y dependence of $\Delta E(2)$ is also of very interest. The values are evaluated to be 1.75, 0.78, 0.42, -0.05 and -2.32 kcal mol⁻¹ for **1b'**, **1d**, **1a**, **1f** and **1j**, respectively. The values decrease in the order of Y = NH₂ (**b'**) > Me (**d**) > H(**a**) > Cl(**f**) > NO₂(**j**). The results of NBO explain the experimentally observed ones well.

How do $n_p(Z)$ interact effectively with π -orbitals of naphthyl and aryl groups in (**A**: **pl**) and (**B**: **pd**)? Such interactions can be exemplified by the HOMO of **1a**. Fig. 11 shows the HOMO of **1a** for (**A**: **pl**)_o and (**B**: **pd**)_o. As shown in Fig. 11, $n_p(Te)$ of the HOMOs for (**A**: **pl**)_o and (**B**: **pd**)_o in **1a** are placed on the naphthyl and phenyl planes, respectively. This means that $n_p(Te)$ of the HOMO extends easily over $\pi^*(Ph)$ in (**A**: **pl**)_o and π^* -(Nap) in (**B**: **pd**)_o. The results show that the $n_p(Te) \rightarrow \pi^*(Ar)$ interaction contributes predominantly in (**A**: **pl**)_o, while $n_p(Te) \rightarrow \pi^*(Nap)$ is in (**B**: **pd**)_o. The results for (**A**: **pl**) and (**B**: **pd**) are essentially the same as those for (**A**: **pl**)_o and (**B**: **pd**)_o, respectively, although these are not shown.

While the $\angle C_{10}C_1\text{Te}C_{11}$ and $\angle C_1\text{Te}C_{11}C_{12}$ values were predicted to be 73.13° and 0.00°, respectively, for **1a** (A: **pl**)_o, the



Fig. 9 Structural changes in 1–4 along with $Y = NH_2$, Me, H, Cl and NO_2 in $\angle C_{10}C_1ZC_{11}$ (a) and in $\angle C_1ZC_{11}C_{12}$ (b).

values changed to 62.92° and 38.15°, respectively, for the fully optimized structure of **1a** (**A**: **np**). The HOMO would extend over both $\pi^*(\text{Ph})$ and $\pi^*(\text{Nap})$ in **1a** (**A**: **np**). However, the $\angle C_{10}C_1\text{Te}C_{11}$ and $\angle C_1\text{Te}C_{11}C_{12}$ values were experimentally determined to be 94.52(2)° and -10.95(2)°, respectively, for **1i**. The structure of **1i** can be well-described by (**A**: **pl**)_o, as shown in Fig. 3. Consequently, the p– π conjugation operates practically in **1** and controls the fine structures of **1**.

The crystal packing effect would deform the molecular structures in crystals and the solvent effect affects on the relative stabilities of conformers. Therefore, we must be careful when phenomena arising from weak interactions are analyzed with causality. The over-estimation of weak interactions in the MP2 calculations must also be considered when such phenomena are calculated at the MP2 level, although this level is highly reliable.²⁸

Structural determinations in solutions were successfully performed on **2** employing NMR data of **5** and **6**. Similar determinations in solutions were also successful in **1**. However, some deviations were detected when $\delta(\text{Te})_{\text{SCS}}$ were plotted *versus* $\delta(\text{Se:})_{\text{SCS}}$, employing the same structures for the Te and Se derivatives. Sets of standards for $\delta(\text{Te})_{\text{SCS}}$ are inevitably similar to the case of $\delta(\text{Se:})_{\text{SCS}}$. The Te analogues of **5** and **6** (**5'** and **6'**, respectively) would be the candidates for the standards. Such investigations on $\delta(\text{Te})_{\text{SCS}}$ are in progress, although the accurate estimation of the relativistic effect on $\delta(\text{Te})$ must also be necessary to accomplish the purpose.



Fig. 10 The $\Delta E_p \pi(Z : Y)$ values between type \mathbf{A}_o and type \mathbf{B}_o (a) and between type \mathbf{A} and type $\mathbf{B'}$ (b). The thermal effect is contained in (b), which is evaluated employing $\Delta E_p \pi(Z : H)$ given in Fig. 8b.

Conclusion

1-(Arylchalcogena)naphthalenes $[1-(p-YC_6H_4Z)C_{10}H_7:$ 1 (Z = Te), 2 (Z = Se), 3 (Z = S) and 4 (Z = O)] must be the key compounds to generate specific structures, to design particular kinds of interactions and to create delicate properties in materials for the derivatives of 1-4. Reactions of the derivatives with metals and/or halogens must also be of much interest. To determine the fine structures and to clarify the factors that control the fine structures of 1–4 is the first step for a better understanding of the compounds. The p- π conjugation of the p(Z)- π (Ar/Nap) type is the most significant factor to control the structures of 1-4. The role of $p(Te) - \pi(Ar/Nap)$ conjugation is established as the factor to control the fine structures of **1** in the same accuracy for 2-4 in the unified form, after determination of the fine structures of 1 in crystals and solutions. NMR chemical shifts of 9-(arylselanyl)anthracenes (5) and 1-(arylselanyl)anthraquinones (6) serve as the sets of standards for **pl** and **pd**, respectively, in solutions. However, we encountered some specific observations in 1 relative to the case of 2. The discrepancy between δ (Te) in 1 and $\delta(Se)$ in 2 seems not be eliminated unless the behavior of δ (Te) in 1 is clarified by using the sets of standards. The Te derivatives of 5 and 6 (5' and 6', respectively) will be the candidates for the standard compounds, although preparations of 5' and 6' are still in progress.

QC calculations supplied the crucial information for the energy profiles of 1-4. The energy profiles become much more

| Compound | Structure | NBO (i) | NBO (j) | $E(2)^e$ | $\Delta E(2)^e$ | E(i,j) ^f | F(i,j) ^f |
|----------|---------------------------------|-------------------------------|---|----------|-----------------|---------------------|---------------------|
| 1a | (A: pl) _o | $n_{\rm p}({\rm Te})$ | $\sigma^*(C_{11} = C_{12}: Ph)$ | 12.58 | 0.00 | 0.46 | 0.074 |
| 1b' | $(\mathbf{A: pl})_{o}$ | $n_{\rm p}({\rm Te})$ | $\sigma^*(C_{11} = C_{12}: Ar)$ | 11.23 | 0.00 | 0.46 | 0.070 |
| 1d | $(\mathbf{A: pl})_{o}$ | $n_{\rm p}({\rm Te})$ | $\sigma^*(C_{11} = C_{12}: Ar)$ | 12.24 | 0.00 | 0.46 | 0.073 |
| 1f | $(\mathbf{A: pl})_{o}$ | $n_{\rm p}^{\rm P}({\rm Te})$ | $\sigma^*(C_{11} = C_{12}: Ar)$ | 12.92 | 0.00 | 0.46 | 0.074 |
| 1j | $(\mathbf{A: pl})_{o}$ | $n_{\rm p}({\rm Te})$ | $\sigma^*(C_{11} = C_{12}: Ar)$ | 15.02 | 0.00 | 0.46 | 0.079 |
| 1a | $(\mathbf{B}:\mathbf{pl})_{o}$ | $n_{\rm p}({\rm Te})$ | $\sigma^*(C_1 = C_2: Nap)$ | 13.00 | 0.42 | 0.48 | 0.075 |
| 1b' | $(\mathbf{B}:\mathbf{pl})_{o}$ | $n_{\rm p}({\rm Te})$ | $\sigma^*(C_1 = C_2: Nap)$ | 12.98 | 1.75 | 0.48 | 0.075 |
| 1d | $(\mathbf{B}; \mathbf{pl})_{0}$ | $n_{\rm p}^{\rm P}({\rm Te})$ | $\sigma^*(C_1 = C_2: Nap)$ | 13.02 | 0.78 | 0.48 | 0.075 |
| 1f | $(\mathbf{B}; \mathbf{pl})_{0}$ | $n_{\rm p}^{\rm P}({\rm Te})$ | $\sigma^*(C_1 = C_2: Nap)$ | 12.87 | -0.05 | 0.48 | 0.075 |
| 1j | $(\mathbf{B}; \mathbf{pl})_{0}$ | $n_{\rm p}^{\rm P}({\rm Te})$ | $\sigma^*(C_1 = C_2: Nap)$ | 12.70 | -2.32 | 0.49 | 0.074 |
| 2a | $(\mathbf{A}; \mathbf{pl})_{0}$ | $n_{\rm p}({\rm Se})$ | $\sigma^*(C_{11} = \tilde{C}_{12}; Ph)$ | 17.70 | 0.00 | 0.49 | 0.090 |
| 2a | $(\mathbf{B}; \mathbf{pl})_{0}$ | $n_{\rm p}({\rm Se})$ | $\sigma^*(C_1 = C_2: Nap)$ | 18.45 | 0.75 | 0.51 | 0.091 |
| 3a | $(\mathbf{A}; \mathbf{pl})_{0}$ | $n_{\rm p}({\rm S})$ | $\sigma^*(C_{11} = \tilde{C}_{12}; Ph)$ | 24.02 | 0.00 | 0.51 | 0.106 |
| 3a | $(\mathbf{B}; \mathbf{pl})_{0}$ | $n_{\rm p}^{\rm P}({\rm S})$ | $\sigma^*(C_1 = C_2: Nap)$ | 25.43 | 1.41 | 0.53 | 0.109 |
| 4a | $(\mathbf{A: pl})_{o}$ | $n_{\rm p}({\rm O})$ | $\sigma^*(C_{11} = C_{12}: Ph)$ | 30.64 | 0.00 | 0.68 | 0.138 |
| 4a | $(\mathbf{A: pl})_{o}$ | $n_{\rm p}^{\rm r}({\rm O})$ | $\sigma^*(C_1 = C_2: Nap)$ | 33.55 | 2.91 | 0.70 | 0.143 |

Table 8 Results of NBO analysis for the $n_p(Z) \rightarrow \pi^*(Ar/Nap)$ conjugation in (A: pl)_o and (B: pd)_o of 1a–4a, 1b', 1d, 1f and 1j^{*a,b,c,d*}

^{*a*} G(l) with Y = H (a) and Me (d); G(m) with Y = NMe₂ (b), OMe (c) and F (e); G(n) of Y = Cl (f), Br (g), COOEt (h), CN (i) and NO₂ (j). ^{*b*} G(m^{*}) of Y = NMe₂ (b) and OMe (c). ^{*c*} G(m') with Y = H (a), OMe (c) and Me (d). ^{*d*} G(n') with Y = Cl (f), Br (g), COOEt (h) and NO₂ (j). ^{*f*} In kcal mol⁻¹. ^{*f*} In au.



Fig. 11 Orbital interactions in 1a. The HOMOs of $(A:\,pl)_{o}$ (a) and $(B:\,pd)_{o}$ (b).

reasonable if corrected thermally by the Gibbs free energy evaluated at 298.15 K, although those on the potential energy surface must also be intrinsic. Magnitudes of the $p(Z)-\pi(Ar/Nap)$ conjugation were well-evaluated by NBO analysis. The $p(Z)-\pi(Ar/Nap)$ conjugation is demonstrated to operate effectively for Z = Te, as well as Z = O, S and Se. The substituent effect on the $p(Te)-\pi(Ar/Nap)$ conjugation in 1 substantially explains the observed results. Such conjugation in 1a can be imaged well by examining how HOMO of $n_p(Te)$ extends over $\pi(Ar)$ and $\pi(Nap)$ in the structures of (A: pl)_o and (B: pd)_o, although they are typical conformers in 1a. The results of the calculations show a guideline to analyze the interactions containing heavier atoms. Interactions with heavier atoms could be analyzed similarly to the cases with usual atoms for those of the p- π conjugation.

Experimental section

General considerations

Manipulations were performed under an argon atmosphere with standard vacuum-line techniques. Glassware was dried at 130 °C overnight. Solvents and reagents were purified by standard procedures as necessary. The melting points were determined on a Yanako MP-S3 melting point apparatus and are uncorrected. NMR spectra were recorded at 25 °C on a JEOL JNM-ECA 400 spectrometer (¹H, 400 MHz; ¹³C, 100 MHz: ¹²⁵Te, 126 MHz) in CDCl₃ solution. The ¹H, ¹³C and ¹²⁵Te chemical shifts are given

in parts per million relative to those of Me₄Si, internal CDCl₃ in the solvent and external Me₂Te, respectively. Flash column chromatography was performed with 300–400 mesh silica gel and analytical thin layer chromatography was performed on precoated silica gel plates (60F-254) with the systems (ν/ν) indicated.

1-[*p*-(*N*,*N*-Dimethylamino)phenyltellanyl]naphthalene (1b)

Under a nitrogen atmosphere, to a suspension of 1,1'-diphenyl ditelluride (1.00 g, 1.96 mmol) and 40 mL of THF at 3-5 °C was added NaBH₄ (0.30 g, 7.85 mmol) in a small amount of water. A solution of 6.0 equiv. of p-(N,N-dimethylamino)phenyldiazonium chloride was added at 3–5 °C. Benzene (200 mL) was added. The organic layer was separated and washed with 10% aqueous solution of sodium bicarbonate and saturated aqueous solution of sodium hydrogen carbonate and dried over sodium sulfate. The crude product was purified by flash column chromatography (SiO₂, benzene as eluent) and recrystallization from *n*-hexane. **1b** was isolated in 28% yield as yellow needles (410 mg): mp 84.5–85.5 °C; ¹H NMR (400 MHz, CDCl₃, δ, ppm, TMS) 2.97 (s, 6H), 6.62 (d, J = 8.9 Hz, 2H), 7.20 (dd, J = 7.3 Hz and 8.0 Hz, 1H), 7.45–7.54 (m, 2H), 7.59 (dd, J = 1.0Hz and 7.1 Hz, 1H), 7.69–7.74 (m, 3H), 7.78 (dd, J = 1.6 Hz and 7.7 Hz, 1H), 7.96 (dd, J = 1.0 Hz and 8.1 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃, δ, ppm, TMS) 40.1 (2C), 96.5, 113.7 (2C), 119.7, 126.0, 126.4, 127.8, 128.6, 130.1, 133.6, 134.6, 135.2, 141.6 (${}^{2}J(\text{Te},\text{C}) = 23.0 \text{ Hz}$, 2C), 150.5; ${}^{125}\text{Te}$ NMR (126 MHz, CDCl₃, δ , ppm, Me₂Te) 538.3. Anal. calc. for C₁₈H₁₇NTe; C, 57.66; H, 4.57; N, 3.74%. Found: C, 57.61; H, 4.53; N, 3.70%.

1-(p-Fuluorophenyltellanyl)naphthalene (1e)

Under a nitrogen atmosphere, to a solution of 1-bromonaphthalene (1.50 g, 4.83 mmol) in 20 mL of THF at -78 °C was added 3.1 mL of *n*-BuLi (5.05 mmol, 1.65 N). After being stirred for

0.5 h, a THF solution of 1.0 equiv. of phenyltellanylbromide was added to the 1-naphthyllithium solution. After being stirred for 2 h at -78 °C, the reaction was guenched by 4 mL of acetone. The crude product was purified by flash column chromatography (SiO₂, *n*-hexane) and recrystallized from *n*-hexane. Compound 1e was isolated in 22% yield as a pale yellow oil (368 mg): ¹H NMR (400 MHz, CDCl₃, δ , ppm, TMS) 6.89 (t, J = 8.9 Hz, 2H), 7.28 (dd, J = 7.1 Hz and 8.1 Hz, 1H), 7.47–7.54 (m, 2H), 7.63 (dd, J = 5.6 Hz and 8.8 Hz, 1H), 7.78–7.85 (m, 2H), 7.88 (dd, J = 1.1 Hz and 7.1 Hz, 1H), 8.08 (d, J = 7.6 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃, δ , ppm, TMS) 108.1 (${}^{4}J(C,F) = 2.9 \text{ Hz}$), 116.9 (${}^{2}J(C,F) = 21.1 \text{ Hz}$, 2C), 117.9, 126.3, 126.5, 127.0, 128.8, 129.4; 131.3, 133.7, 135.6, 138.1, 140.0 (${}^{3}J(C,F) = 7.7$ Hz, 2C), 162.9 (${}^{1}J(C,F) = 247.2$ Hz); 125 Te NMR (126 MHz, CDCl₃, δ , ppm, Me₂Te) 572.1. Anal. calc. for C₁₆H₁₁FTe; C, 54.93; H, 3.17%. Found: C, 54.88; H, 3.19%.

1-(p-Cyanophenyltellanyl)naphthalene (1i)

Following the procedure used for the preparation of **1b**, **1i** was obtained in 46% yield as colorless solid: mp 64.9–65.9 °C; ¹H NMR (400 MHz, CDCl₃, δ , ppm, TMS) 7.29 (d, J = 8.2 Hz, 2H), 7.38 (dd, J = 7.2 Hz and 8.1 Hz, 1H), 7.42 (d, J = 8.2 Hz, 2H), 7.48–7.56 (m, 2H), 7.85 (dd, J = 1.5 Hz and 6.9 Hz, 1H), 7.97 (d, J = 8.1 Hz, 1H), 8.16 (dd, J = 2.5 Hz and 6.5 Hz, 1H), 8.21 (dd, J = 1.0 Hz and 7.0 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃, δ , ppm, TMS) 110.3, 116.0, 118.7, 124.5, 126.6, 126.7, 127.7, 129.0, 131.2, 132.2 (2C), 132.3, 133.7, 135.0 (²*J*(Te,C) = 26.0 Hz, 2C), 135.9, 141.6; ¹²⁵Te NMR (126 MHz, CDCl₃, δ , ppm, Me₂Te) 596.1. Anal. calc. for C₁₇H₁₁NTe; C, 57.21; H, 3.11; N, 3.92%. Found: C, 57.16; H, 3.19; N, 3.88%.

X-ray structure determination

Single crystals of 1b, 1c and 1i were obtained from solutions of *n*-hexane after slow evaporation of the solvent at room temperature. Diffraction data for 1b, 1c and 1i were performed at 93(2) K with the use of a RIGAKU CCD SATURN 724 diffractometer with a graphite-monochromated MoK α radiation source (λ = 0.71073 Å). The structures were solved by direct methods (SHELXS-97)²⁹ and refined by full-matrix least-square methods on F^2 for all reflections (SHELXL-97),³⁰ with all non-hydrogen atoms anisotropic and all hydrogen atoms isotropic. For 1b, the structure analysis is based on 3447 observed reflections with $I > 2.00\sigma(I)$ and 249 variable parameters; colorless prisms, 93(2) K, monoclinic, space group $P2_1/n$ (#14), a = 7.437(4) Å, b =19.619(9) Å, c = 10.378(5) Å, $\beta = 95.950(8)^{\circ}$, V = 1506.1(13)Å³, Z = 4, R = 0.0311, $R_{\rm W} = 0.0458$, GOF = 0.974. For **1c** the structure analysis is based on 2976 observed reflections with $I > 2.00\sigma(I)$ and 228 variable parameters; colorless prisms, 93(2) K, monoclinic, space group $P2_1/c$ (#14), a = 7.741(3) Å, b =22.180(9) Å, c = 8.551(4) Å, $\beta = 109.847(6)^{\circ}$, V = 1381.0(10)Å³, Z = 4, R = 0.0245, $R_W = 0.0659$, GOF = 1.125. For **1i**, the structure analysis is based on 2914 observed reflections with $I > 2.00\sigma(I)$ and 216 variable parameters; colorless prisms, 93(2) K, monoclinic, space group $P2_1/c$ (#14), a = 14.8180(13) Å, b =5.5614(5) Å, c = 16.5413(12) Å, $\beta = 96.886(5)^{\circ}$, V = 1353.3(2)Å³, Z = 4, R = 0.0209, $R_W = 0.0525$, GOF = 1.079. CCDC

838257 for **1b**, CCDC 838258 for **1c** and CCDC-838259 for **1i** contain the supplementary crystallographic data for this paper.⁺

QC calculations

1a–4a, **1b'–4b'**, **1c–4c**, **1f–4f** and **1j–4j** were optimized and the frequency analysis was performed on the optimized structures using the Gaussian 03 program.²⁴ The Møller–Plesset second-order energy correlation (MP2) level was applied to the calculations²³ with the 6-311+G(3d) basis sets³¹ for O, S and Se, the (7433111/743111/7411/2 + 1s1p1d1f) basis sets³² for Te and with the 6-31G(d,p) basis sets for C and H.

Acknowledgements

This work was partially supported by a Grant-in-Aid for Scientific Research (Nos. 19550041 and 20550042) from the Ministry of Education, Culture, Sports, Science and Technology, Japan. The support of the Wakayama University Original Research Support Project Grant and the Wakayama University Graduate School Project Research Grant is also acknowledged.

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