Structures and dynamic stereochemistry of 9-arylselanyltriptycenes: X-ray crystallographic, spectroscopic and theoretical investigations†

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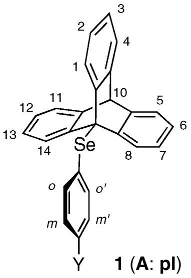
9-(Arylselanyl)triptycenes (**1**: p-YC$_6$H$_4$SeTpc) should supply the planar structure (**pl**) around the p-YC$_6$H$_4$Se (ArSe) group in the ground state, irrespective of the p-Y substituents. **1** with Y = H (**a**), NMe$_2$ (**b**), OMe (**c**), Cl (**d**), CN (**e**) and NO$_2$ (**f**) are prepared. Structures of **1a–d** and **1f** are determined by X-ray analysis and dynamic ^{1}H NMR spectroscopy is applied to **1a**, **1c**, **1e** and **1f**. For convenience of discussion, the structure of **1** is defined as follows: a conformer around the triptycyl group in **1** is called **A** where the Se–C$_{Ar}$ bond is placed in the bisected area between two phenyl planes of the triptycyl group and it is **B** where the bond is on a phenyl plane of the triptycyl group. A conformer for the Ar group is named **pl** where the Se–C$_{Tpc}$ bond is on the Ar plane, while it is **pd** if the bond is perpendicular to the plane. The structure of **1** is confirmed to be (**A**: **pl**) in the ground state by X-ray analysis. **1** (**A**: **pl**) changes to the equivalent one *via* a transition state of **1** (**B**: **pd**) (the gear process). The activation energies are determined by dynamic ^{1}H NMR spectroscopy: the values are 36.4, 41.6, 42.3 and <34 kJ mol^{-1} for **1a**, **1e**, **1f** and **1c**, respectively. The MP2 level of calculations reproduced the observed values: they are evaluated to be 34, 39, 40 and 29 kJ mol^{-1} for **1a**, **1e**, **1f** and **1b′** (Y = NH$_2$), respectively, where **1b′** is employed in place of **1c**. Another process (the isolated rotation process) is also operating for the interconversion of **1** (**A**: **pl**), which proceeds *via* **1** (**A**: **pd**). The activation energies for the process are predicted to be 25, 30, 30 and 20 kJ mol^{-1} for **1a**, **1e**, **1f** and **1b′**, respectively, at the MP2 level. The results demonstrate that (**A**: **pl**) is the global minimum in **1**: the **1** (**A**: **pl**) structure is well established for all Y examined in the ground state.

Introduction

^{77}Se NMR chemical shifts (δ(Se)) are widely applied to determine structures[1–4] and routinely follow reactions,[1,5] since they are sharply sensitive to structural changes in selenium compounds.[1–4] We have pointed out the importance of the orientational effect of p-YC$_6$H$_4$Se (ArSe) on δ(Se) in ArSeR, together with the mechanism, for the better understanding the structures of ArSeR in solutions based on δ(Se).[4] Typical conformers in relation to the orientational effect in ArSeR are planar (**pl**) and perpendicular (**pd**), where the Se–C$_R$ bond in ArSeR is on the Ar plane in **pl** and it is perpendicular to the plane in **pd**.[6,7]

We searched for such selenides that can be the excellent standard of **pl** with a very small temperature dependence of δ(Se).[8,9] 9-(Arylselanyl)triptycenes (**1**: p-YC$_6$H$_4$SeTpc; ArSeTpc) should be an excellent candidate for **pl** around the ArSeC$_{Tpc}$ moiety in the ground state. To employ **1** as the standard for **pl**, it is necessary to establish the stereochemistry containing the structures in the ground state and the thermal behavior of **1**. **1** were prepared for Y = H (**a**), NMe$_2$ (**b**), OMe (**c**), Cl (**d**), CN (**e**) and NO$_2$ (**f**), as shown in Chart 1. The structures are determined by X-ray analysis for **1a–d** and **1f**. Dynamic ^{1}H NMR spectroscopy was applied on **1a**, **1c**, **1e** and **1f**.



1 (A: pl)

	a	b	b′	c	d	e	f
Y =	H	NMe$_2$	NH$_2$	OMe	Cl	CN	NO$_2$

Chart 1 Structure of **1** (**A**: **pl**).

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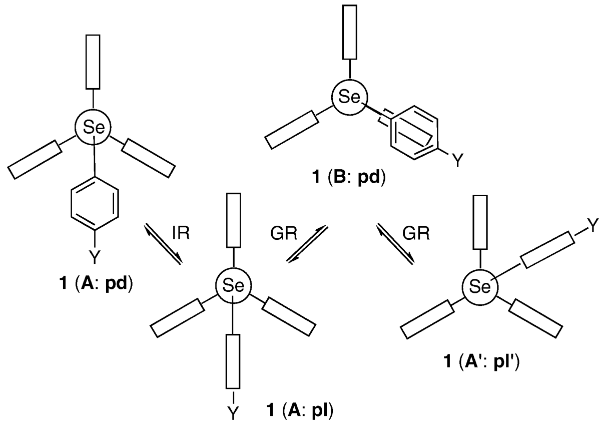
† Electronic supplementary information (ESI) available: ORTEP drawings of **1c** and **1d**. NMR spectra of the aromatic protons of **1a**, **1c** and **1e** in CD$_2$Cl$_2$ at various temperatures. Results of QC calculations on **1a**, **1b′**, **1e** and **1f** for (**A**: **pl**), (**A**: **pd**) and (**B**: **pd**) at the MP2 level. Cartesian coordinates for optimized structures of **1a**, **1b′**, **1e** and **1f**. CCDC reference numbers 704856 for **1a**, 704857 for **1b**, 704858 for **1c**, 704859 for **1d** and 704860 for **1f**. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b817949b



Scheme 1 Interconversion between conformers in **1**.

We call the conformers around the Se–C_{Tpc} bond in **1** **A** and **B**: **A** corresponds to a conformer where the Ar group is in the bisected area between two phenyl planes of the triptycyl group and it is **B** if the Ar group is on a phenyl plane of the triptycyl group in **1**. Scheme 1 shows the (**A**: **pl**), (**A**: **pd**) and (**B**: **pd**) conformers, together with the interconversion process in **1**.[10] Isolated rotation (IR) may occur around the Se–C_{Ar} bond, converting (**A**: **pl**) into (**A**: **pd**) and thence into the equivalent form (**A**: **pl**′) by further rotation, where the primes imply the topomeric structures, although (**A**: **pl**′) is not shown in Scheme 1. There are three equivalent conformations in each of (**A**: **pl**) and (**A**: **pd**). Interconversion between (**A**: **pl**) and (**A**′: **pl**′) may occur *via* (**B**: **pd**). This process is referred to as gear rotation (GR). There are three equivalent conformers also in (**B**: **pd**).

Here we discuss the structures of **1** in the ground state based on X-ray crystallographic analysis and dynamic stereochemistry by ^{1}H DNMR spectroscopy. The energy profile of **1** will also be discussed by employing quantum chemical (QC) calculations.

Results and discussion

Structure of 9-(p-YC$_6$H$_4$SeTpc)

X-Ray crystallographic analyses are carried out for suitable single crystals of **1a–d** and **1f**. Whereas only one type of structure corresponds to each of them in the crystals for **1a**, **1c**, **1d** and **1f**, **1b** crystallizes with two symmetrically independent molecules in the asymmetric unit: the two independent molecules are called **1b**$_A$ and **1b**$_B$. Fig. 1–3 show the structures of **1a**, **1b** (**1b**$_A$ and **1b**$_B$) and **1f**, respectively. Those of **1c** and **1d** are shown in the Electronic supplementary information (ESI†) (Fig. S1 and S2, respectively). Table 1 collects the selected interatomic distances, angles and torsional angles of **1a–d** and **1f**, necessary for the discussion.

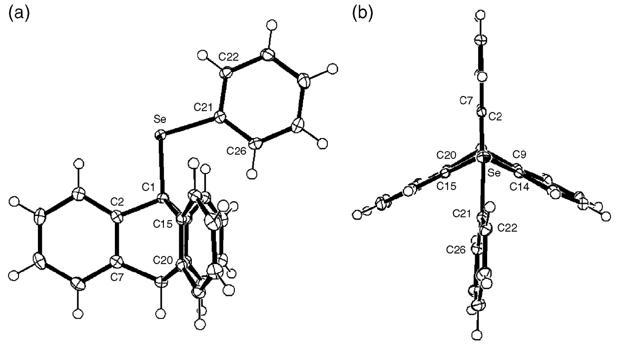


Fig. 1 ORTEP drawing of **1a** with atomic numbering scheme for selected atoms (50% probability thermal level): (a) side view and (b) top view.

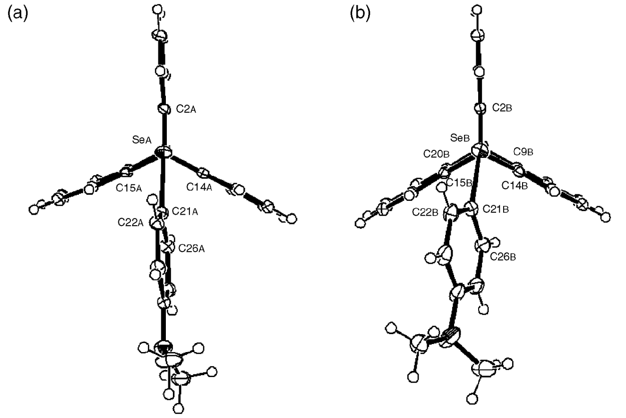


Fig. 2 ORTEP drawing of **1b**$_A$ (a) and **1b**$_B$ (b) with atomic numbering scheme for selected atoms (50% probability thermal level), top view.

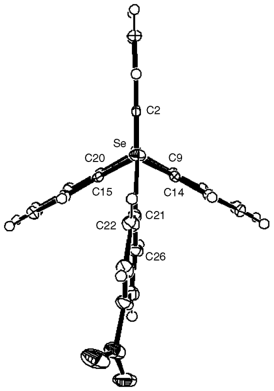


Fig. 3 ORTEP drawing of **1f** with atomic numbering scheme for selected atoms (50% probability thermal level), top view.

The structures of **1a–d** and **1f** are shown to be all (**A**: **pl**) in crystals: the $\angle$C21SeC1C2 values are close to 180° (or −180°). While the Se–C1 lengths are almost constant for the compounds under the measurement conditions, the lengths for Se–C21 of **1d** and **1f** are slightly shorter than those of **1a–c**. The structures are close to C_s symmetry for **1a**, **1d** and **1f** but some deviations are observed for **1b** and **1c**: the magnitudes of $\angle$C1SeC21C22 for the former are 4–6°, whereas those for the latter amount to 10–28°. The crystal packing effect would be responsible for the deviations. The shallow energy surface for **1b** and **1c**, relative to **1a**, **1d** and **1f** would also affect on the observed results. The steric compression seems small for these compounds.

The p–π conjugation of the p(Se)–π(C$_6$H$_4$)–p(Y) type should affect the stability of the conformers. Y of acceptors stabilize (**A**: **pl**) through the favorable p–π conjugation,

Table 1 Selected interatomic distances (Å), angles (°) and torsional angles (°) of **1a–d** and **1f**

Compound	**1a**	$\mathbf{1b}_\mathbf{A}$	$\mathbf{1b}_\mathbf{B}$	**1c**	**1d**	**1f**
Y	H	NMe_2	NMe_2	OMe	Cl	NO_2
Se–C1	1.9606(16)	1.953(2)	1.961(2)	1.9603(18)	1.9598(19)	1.958(3)
Se–C21	1.9218(16)	1.921(2)	1.921(2)	1.9228(18)	1.9162(19)	1.902(3)
C21–Se–C1	104.35(7)	103.44(10)	107.42(10)	104.52(7)	105.29(8)	105.31(12)
Se–C21–C22	114.31(12)	114.85(17)	114.53(19)	115.12(13)	114.59(14)	114.1(2)
Se–C21–C26	125.92(13)	126.89(17)	127.14(18)	125.63(14)	125.60(15)	125.7(2)
C21–Se–C1–C2	177.66(10)	−177.68(15)	170.23(14)	−173.82(11)	178.22(12)	177.25(17)
C21–Se–C1–C14	−65.19(12)	−63.88(18)	−72.46(18)	−56.32(14)	−64.45(14)	−65.9(2)
C21–Se–C1–C15	61.10(13)	62.23(17)	53.17(18)	68.28(14)	61.00(15)	59.5(2)
C1–Se–C21–C22	175.91(12)	−175.02(17)	−154.65(18)	168.52(13)	−174.62(14)	−174.4(2)
C1–Se–C21–C26	−4.61(16)	9.5(2)	28.3(2)	−10.32(18)	5.86(18)	4.4(3)
Se–C1–C2–C7	179.55(11)	179.48(15)	179.60 (16)	179.52 (12)	179.74(13)	179.58(18)
Se–C1–C14–C9	−176.44(11)	−176.35(15)	−175.68(16)	−176.70 (12)	−174.95(13)	−175.64(18)
Se–C1–C15–C20	179.28(11)	176.84(15)	174.64(16)	177.18(12)	175.48(13)	175.98(18)

whereas Y of donors will destabilize (**A**: **pl**) through unfavorable interactions between electron rich p(Se) and p(Y). Consequently, the equilibrium between (**A**: **pl**) and (**A**: **pd**) would be facilitated by Y of donors. Therefore, we must carefully examine the structure of **1** having Y of strong donors such as Y = NMe_2. As shown in Fig. 2, the structure of **1b** (Y = NMe_2) is apparently (**A**: **pl**), which strongly suggests that the structure of all members of **1** is (**A**: **pl**). The structures of **1a–d** and **1f** determined by X-ray crystallographic analysis support the (**A**: **pl**) structure of **1** in the ground state for all Y shown in Chart 1.

After confirmation of the **1** (**A**: **pl**) structure in the ground state, the next extension is to clarify the dynamic stereochemistry of **1**.

Dynamic ^{1}H NMR spectroscopy

^{1}H NMR spectra were measured for **1a**, **1c**, **1e** and **1f** at various temperatures in CD_2Cl_2 on a 600 MHz spectrometer for ^{1}H nuclei. Fig. 4 shows the spectra for **1f**, for an example. Fig. 4 also contains the calculated line-shape change of aromatic protons in the triptycyl group for **1f**. The activation energy for rear rotation (GR) is evaluated to be 42.3 kJ mol^{-1} for **1f** by analyzing the temperature dependent ^{1}H NMR spectra shown in Fig. 4. The observed spectra of **1a**, **1c** and **1e** are given in Fig. S3, S4 and S5 of the ESI,† respectively.

Similarly to the case of **1f**, the activation energy for GR of **1e** is evaluated to be 41.6 kJ mol^{-1}. The energy is evaluated to be 36.4 kJ mol^{-1} for GR in **1a** although the signals are not separated completely even at −102 °C. Only the upper limit of the parameter was estimated for **1c** due to the poor signal separation: the upper limit is 34 kJ mol^{-1}. Table 2 summarizes rate constants and free energies of activation for GR in **1**.[11,12] The dynamic spectra demonstrate that the structures of **1a**, **1c**, **1e** and **1f** are all (**A**: **pl**) in the ground state: (**B**: **pd**) appears at the transition state of GR. The activation energies for GR seem all around 30–40 kJ mol^{-1} for **1a–f** (see also Table S2 of the ESI†).

The GR barrier for 9-(phenoxy)triptycene (**2a**: PhOTpc) is reported to be *ca.* 29 kJ mol^{-1}, which is much less than the value of 44.8 kJ mol^{-1} for 9-(benzyl)triptycene (**3a**: $PhCH_2Tpc$).[12] Scheme 2 illustrates the transition states for GR in **1a**, **2a** and **3a**. The low GR barrier in **2a** has been ascribed to the divalency of the oxygen. The eclipsing interaction at the transition states should be considered only between the phenyl group and one of *o*-benzeno bridges in **2a** (**B**: **pd**). However, the eclipsed interaction between the methylene hydrogens and the *o*-benzeno bridges should also be considered in **3a** (**B**: **pd**). The transition state must be more destabilized as the Z–C_{Tpc} bond length becomes shorter. However, the effect in **2a** relative to **3a** is completely overshadowed by the effect of valency in these cases.[12] The GR barrier for PhSeTpc (**1a**) is expected to be less than that for **2a** if the bond length effect is considered (Se in **1a** is divalent). However, the GR barrier for **1a** (36.4 kJ mol^{-1}) is larger than that of **2a**. Mechanisms other than those of the valency and the bond length, such as the angle effect, must also be operating.

The structures determined by X-ray crystallographic analysis and the results of ^{1}H DNMR spectroscopy confirm the **1** (**A**: **pl**) structure in the ground state. Attention was then turned to the energy profiles of the isolated rotation (IR) process in **1** which are not determined by ^{1}H DNMR spectroscopy. QC calculations were thus performed on (**A**: **pl**), (**A**: **pd**) and (**B**: **pd**) for **1a**, **1b′** (*p*-$H_2NC_6H_4SeTpc$), **1e** and **1f**.

QC calculations

QC calculations are performed on **1a**, **1b′**, **1e** and **1f** using the Gaussian 03 program[13] at the density functional theory (DFT) level (B3LYP)[14,15] and the Møller–Plesset second order energy correlation (MP2)[16] level. Calculations at the MP2 level are more reliable relative to those at the DFT level when the transition states are examined. Therefore, results at the MP2 level are employed for the discussion.[17] The (**A**: **pd**) and (**B**: **pd**) structures must correspond to the transition states for the IR and GR processes in **1**, respectively, while (**A**: **pl**) is the ground state. QC calculations support the expectation.

Indeed, the results of QC calculations essentially correspond to those in the gas phase, but the factors to control and/or stabilize the structures in gas phase must also operate in the solid state and in solution. Therefore, it is instructive to consider those predicted by QC calculations, although we

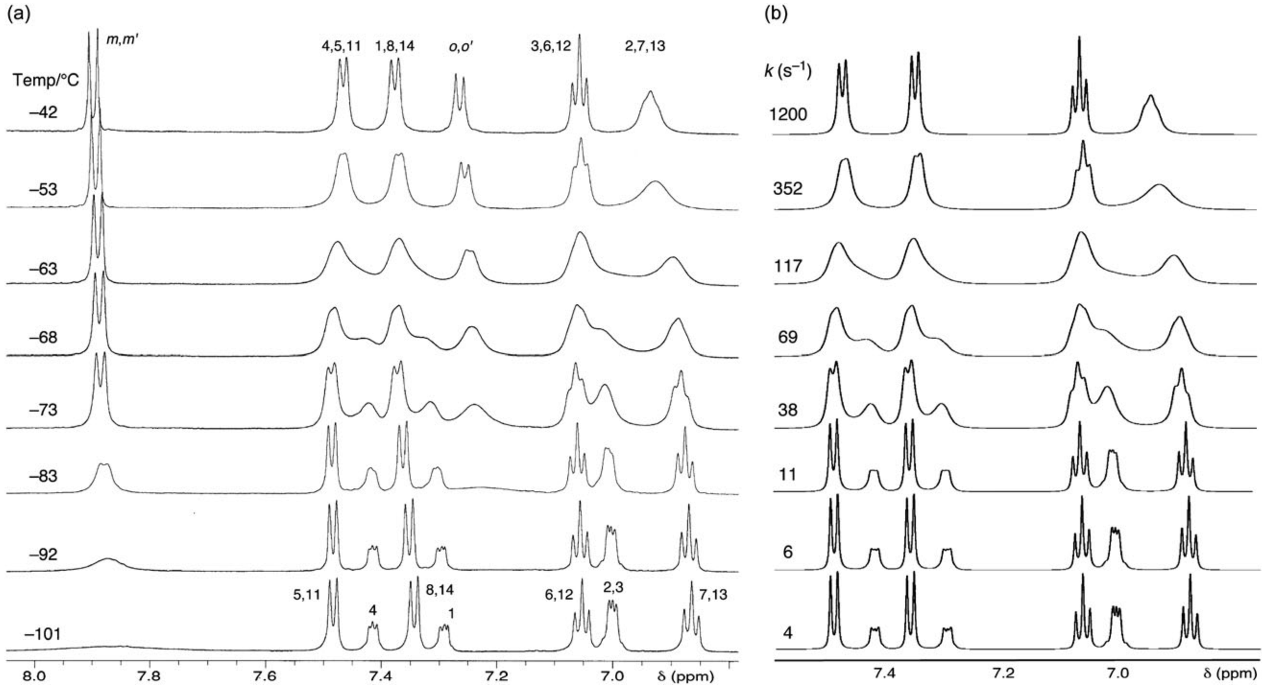
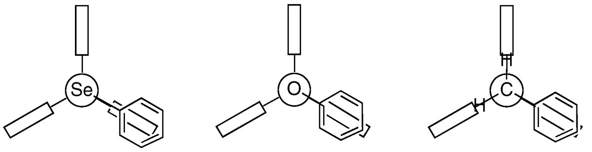


Fig. 4 Observed ^{1}H NMR spectra due to the aromatic proton region of **1f** in CD_2Cl_2 at various temperatures (a) and the calculated spectra with the best-fit rate constants for the aromatic protons of the triptycyl group for the GR process (b).

Table 2 Rate constants and free energies of activation of the GR process in **1**

Compound	Y	k_{GR}/s^{-1}	$\Delta G^{\ddagger}{}_{GR}$/kJ mol^{-1}	T^a/°C
1a	H	*ca.* 90	36.4	−93
1c	OMe	> 100	< 34	−100
1e	CN	*ca.* 84	41.6	−70
1f	NO_2	*ca.* 69	42.3	−68

[a] Coalescence temperature.



1a (**B**: **pd**) **2a** (**B**: **pd**) **3a** (**B**: **pd**)

Scheme 2 Illustration of the transition states for GR in **1a**, **2a** and **3a**.

must consider the crystal packing effect in crystals and the solvent effect in solutions, since they are often larger than the predicted factors.[17]

QC calculations are performed on **1a** employing the 6-311 + G(d) basis sets for Se and the 4-31G basis sets for C and H (basis sets-A) at the MP2 level. Three structures, **1a** (**A**: **pl**), **1a** (**A**: **pd**) and **1a** (**B**: **pd**) of C_s symmetry, are optimized. Frequency analysis is applied on the optimized structures with the same method. Table S1 of ESI† shows the results. Whereas all frequencies are positive for **1a** (**A**: **pl**), only one imaginary frequency is predicted for each of **1a** (**A**: **pd**) and **1a** (**B**: **pd**). The results demonstrate that **1a** (**A**: **pl**), **1a** (**A**: **pd**) and **1a** (**B**: **pd**) of C_s symmetry are the ground state structure, transition state for IR (TS: IR) and (TS: GR), respectively. Therefore, it would be rationalized that the energy profiles of **1a**, **1b′**, **1e** and **1f** can be discussed by assuming (**A**: **pl**), (**A**: **pd**) and (**B**: **pd**) of C_s symmetry as the ground state structures, (TS: IR) and (TS: GR), respectively, except for **1b′** (**A**: **pl**). The ground state of **1b′** (**A**: **pl**) must be of C_1 symmetry.

QC calculations are performed on **1a**, **1b′**, **1e** and **1f**, employing the 6-311 + G(d) basis sets for Se and the 6-31G(d) basis sets for O, N, C and H (basis sets-B) at the MP2 level and results are shown in Table S2 of the ESI.† The results are also illustrated in Fig. 5. (**B**: **pd**) are predicted to be less stable than (**A**: **pl**) by 34, 29, 39 and 40 kJ mol^{-1} for **1a**, **1b′**, **1e** and **1f**, respectively, on the potential energy surface

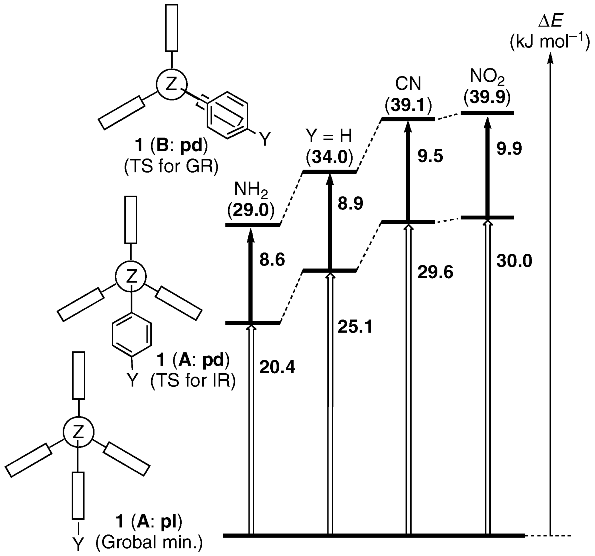


Fig. 5 Energy profiles for the conformers in **1** (values evaluated using basis sets-B at the MP2 level being employed).

when calculated using basis sets-B at the MP2 level. The frequency analysis was unsuccessful due to the memory capacity of our calculation conditions. However, the evaluated values were very close to the observed activation energies for GR of the corresponding compounds, respectively. The evaluated activation energies for GR on the potential energy surface with the calculation method reproduced the observed values for GR.

What is the energy profile of IR? The (**A**: **pd**) structures are predicted to be less stable than (**A**: **pl**) by 25, 20, 30 and 30 kJ mol^{-1} for **1a**, **1b′**, **1e** and **1f**, respectively, when calculated employing the basis sets-B at the MP2 level (see Fig. 5 and Table S2 of the ESI†). The values must correspond to (TS: IR), which are smaller than the corresponding (TS: GR). The activation energies evaluated for IR are expected to be reliable judging from the discussion for the evaluated values in GR with the same method. The results demonstrate that the structures of **1** are (**A**: **pl**) in the ground state, although no experimental data are available for IR.

The evaluated activation energies in both IR and GR processes change depending on Y. However, the energy differences between the two processes ($\Delta\Delta E$ = ΔE(**B**: **pd**) − ΔE(**A**: **pd**)) are very similar to each other irrespective of Y: the differences are 9–10 kJ mol^{-1} when calculated with the basis sets-B at the MP2 level. The $\Delta\Delta E$ values must be equal to ΔE(**B**, **A**) (= E(**B**: **pd**) − E(**A**: **pd**)). Therefore, the results show that the energy differences between (**B**: **pd**) and (**A**: **pd**) are almost constant irrespective of Y. Fig. 5 shows the energy profiles of **1**. It is worthwhile to comment that $\Delta\Delta E$ must contain the intrinsic energy difference between **1** (**B**: **pd**) and **1** (**A**: **pd**): $\Delta\Delta E$ (= ΔE(**B**, **A**)) are almost constant whereas ΔE(**B**: **pd**) (= ΔE(**B**: **pd**) − E(**A**: **pl**)) and ΔE(**A**: **pd**) (= E(**A**: **pd**) − E(**A**: **pl**)) are affected by Y.

Conclusion

9-(Arylselanyl)triptycenes (**1**: p-YC$_6$H$_4$SeTpc) should be excellent candidates for the standard of **pl**. To employ **1** as the standard for **pl**, it is necessary to establish the ground state structures of **1** and the dynamic stereochemistry including the thermal behavior of **1**. Compounds **1** with Y = H (**a**), NMe$_2$ (**b**), OMe (**c**), Cl (**d**), CN (**e**) and NO$_2$ (**f**) were prepared and the structures of **1a–d** and **1f** determined by X-ray analysis. Dynamic ^{1}H NMR spectroscopy was applied on **1a**, **1c**, **1e** and **1f**. **1** (**A**: **pl**) is demonstrated to be more stable than **1** (**B**: **pd**) by 42 kJ mol^{-1} for Y = CN and NO$_2$ and 36 kJ mol^{-1} (or less) for Y = H and OMe. QC calculations well reproduced the experimental results and supported the expectation. **1a** (**A**: **pd**) and **1a** (**B**: **pd**) are evaluated to be less stable than **1a** (**A**: **pl**) by 25 and 34 kJ mol^{-1}, respectively, when calculated at the MP2 level with the basis sets-B. Even for Y of donating NH$_2$ group, **1b′** (**A**: **pd**) and **1b′** (**B**: **pd**) are predicted to be less stable than **1b′** (**A**: **pl**) by 20 and 29 kJ mol^{-1}, respectively, when calculated at the same method. The results strongly support that the structures of **1** are (**A**: **pl**) for all Y examined containing Y = NMe$_2$ and OMe both in crystals and solutions. Consequently, the structures of ArSeR in solution can be analyzed from the viewpoint of the orientational effect employing the set of δ(Se: **1**).

It is of interest if the Y dependence in the energy profiles of **1** containing (**A**: **pl**), (**A**: **pd**) and (**B**: **pd**) is a reflection of the p(Se)–π(Ar) conjugation. Investigations into p–π conjugation of the type are in progress.

Experimental

General considerations

Manipulations were performed under a nitrogen or 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 AL-300 spectrometer (^{1}H, 300 MHz; ^{13}C, 75.5 MHz; ^{77}Se, 57.3 MHz) and at various temperatures in CD$_2$Cl$_2$ on a Bruker AVANCE II 600 spectrometer (^{1}H, 600 MHz). The ^{1}H, ^{13}C and ^{77}Se chemical shifts are given in parts per million relative to those of Me$_4$Si, internal CDCl$_3$ in the solvent and external Me$_2$Se, respectively. Flash column chromatography was performed with 300–400 mesh silica gel and basic alumina and analytical thin layer chromatography was performed on precoated silica gel plates (60F-254) with the systems (v/v) indicated.

Syntheses

9-(Phenylselanyl)triptycene (1a). Under an argon atmosphere, to a solution of 9-bromotriptycene[18] (510 mg, 1.50 mmol) in 12 mL of benzene and 40 mL of diethyl ether at 0 °C was added 1.0 mL of n-BuLi (1.62 mmol, 1.62 N). After stirring for 1 h, the fine suspension of 9-triptycyllithium was added to an ethereal solution of 1.0 equiv. benzeneselenobromide. After stirring for 1 h. at 0 °C, the reaction was quenched by acetone (4 mL), and the solvent was removed *in vacuo*. 100 mL of benzene and 6% aqueous solution of hydrochloric acid were added. The organic layer was separated and washed with 50 mL of water, 50 mL of 10% aqueous solution of sodium carbonate, 50 mL of saturated aqueous solution of sodium hydrogen carbonate, 50 mL of water, and dried over sodium sulfate. The crude product was purified by column chromatography (SiO$_2$, benzene–hexane 1 : 2) and recrystallized from dichloromethane and hexane. **1a** was isolated in 32% yield as a colorless solid (195 mg): mp 271.0–272.5 °C; ^{1}H NMR (300 MHz, CDCl$_3$, δ, ppm, TMS) 5.44 (s, 1H), 6.92 (dt, J = 1.4, 7.6 Hz, 3H), 7.01 (dt, J = 1.3, 7.4 Hz, 3H), 7.07–7.11 (m, 3H), 7.16–7.20 (m, 2H), 7.40 (dd, J = 1.2, 7.2 Hz, 3H), 7.54 (d, J = 7.4 Hz, 3H); ^{13}C NMR (75.5 MHz, CDCl$_3$, δ, ppm, TMS) 54.2, 61.0, 123.3 (3C), 124.9 (^3J(Se,C) = 12.1 Hz, 3C), 125.0 (3C), 125.4, 125.8 (3C), 128.7 (*meta*-Ph, 2C), 129.9 (^2J(Se,C) = 15.6 Hz, 2C), 130.7, 144.0 (^2J(Se,C) = 6.2 Hz, 3C), 145.3 (3C); ^{77}Se NMR (57.3 MHz, CDCl$_3$, δ, ppm, Me$_2$Se) 259.0. Anal. Calc. for C$_{26}$H$_{18}$Se, C, 76.28; H, 4.43%. Found: C, 76.42; H, 4.33%.

9-[*p*-(*N*,*N*-Dimethylamino)phenylselanyl]triptycene (1b). Under a nitrogen atmosphere, to a suspension of di-9-triptycyl diselenide[19] (900 mg, 1.38 mmol) and 40 mL of THF at 0 °C was added NaBH$_4$ (110 mg, 2.76 mmol) in small amount of water. A solution of 6.0 equiv. of *p*-(*N*,*N*-dimethylamino)phenyldiazonium chloride was added at 0 °C. If an orange precipitate appeared, $NaBH_4$ (110 mg, 2.76 mmol) in an aqueous THF solution was added to the reaction solution. Dichloromethane (200 mL) and 2% aqueous solution of sodium hydroxide was added. The organic layer was separated and washed with a 10% aqueous solution of sodium carbonate and then a saturated aqueous solution of sodium hydrogen carbonate, and dried over potassium carbonate. The crude product was purified by column chromatography (SiO_2, benzene–hexane 1 : 1 as eluent) and recrystallization from hexane. **1b** was isolated in 6% yield as pale yellow needles (19 mg): mp 227.5–229.0 °C; ^1H NMR (300 MHz, $CDCl_3$, δ, ppm, TMS) 2.87 (s, 6H), 5.42 (s, 1H), 6.55 (d, J = 9.0 Hz, 2H), 6.94 (dt, J = 1.5, 7.5 Hz, 3H), 7.01 (dt, J = 1.3, 7.3 Hz, 3H), 7.10 (d, J = 9.1, 2H), 7.40 (dd, J = 1.3 and 7.1, 3H), 7.60 (d, J = 7.4, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$, δ, ppm, TMS) 40.5 (2C), 54.3, 60.5, 113.4 (2C), 123.1 (3C), 125.0 (3C), 125.1 (3C), 125.1, 125.6 (3C), 131.0 (^2J(Se,C) = 15.3 Hz, 2C), 144.5 (^2J(Se,C) = 6.2 Hz, 3C), 145.4 (3C), 148.6; ^{77}Se NMR (57.3 MHz, $CDCl_3$, δ, ppm, Me_2Se) 238.5. Anal. Calc. for $C_{28}H_{23}NSe$; C, 74.33; H, 5.12; N, 3.10%. Found: C, 74.13; H, 5.11; N, 3.14%.

9-(*p*-Methoxyphenylselanyl)triptycene (1c). Following the procedure used for the preparation of **1a**, **1c** was obtained in 21% yield as colorless prisms: mp 192.0–193.0 °C; ^1H NMR (300 MHz, $CDCl_3$, δ, ppm, TMS) 3.72 (s, 3H), 5.44 (s, 1H), 6.71 (d, J = 9.0 Hz, 2H), 6.94 (dt, J = 1.4, 7.5 Hz, 3H), 7.02 (dt, J = 1.3, 7.4 Hz, 3H), 7.13 (d, J = 9.0 Hz, 2H), 7.40 (dd, J = 1.3, 7.2 Hz, 3H), 7.55 (d, J = 7.5 Hz 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$, δ, ppm, TMS) 54.3, 55.2, 60.9, 114.7 (2C), 120.4, 123.3 (3C), 124.9 (^3J(Se,C) = 11.5 Hz, 3C), 125.0 (3C), 125.7 (3C), 131.1 (^2J(Se,C) = 15.7 Hz, 2C), 144.2 (3C), 145.4 (3C), 157.8; ^{77}Se NMR (57.3 MHz, $CDCl_3$, δ, ppm, Me_2Se) 247.7. Anal. Calc. for $C_{27}H_{20}OSe$: C, 73.80; H, 4.59%. Found: C, 73.92; H, 4.63%.

9-(*p*-Chlorophenylselanyl)triptycene (1d). Following the procedure used for the preparation of **1a**, **1d** was obtained in 15% yield as colorless solid: mp 237.0–238.0 °C; ^1H NMR (300 MHz, $CDCl_3$, δ, ppm, TMS) 5.45 (s, 1H), 6.95 (dt, J = 1.4, 7.6 Hz, 3H), 7.04 (dt, J = 1.2, 7.4 Hz, 3H), 7.10 (s, 4H), 7.42 (dd, J = 1.2, 7.2 Hz, 3H), 7.48 (d, J = 7.5 Hz, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$, δ, ppm, TMS) 54.2, 61.3, 123.4 (3C), 124.6 (^3J(Se,C) = 12.5 Hz, 3C), 125.1 (3C), 125.9 (3C), 128.9 (2C), 128.9, 131.2 (^2J(Se,C) = 16.2 Hz, 2C), 131.4, 143.6 (^2J(Se,C) = 6.2 Hz, 3C), 145.3 (3C); ^{77}Se NMR (57.3 MHz, $CDCl_3$, δ, ppm, Me_2Se) 262.7. Anal. Calc. for $C_{26}H_{17}ClSe$, C, 70.36; H, 3.86%. Found: C, 70.48; H, 3.81%.

9-(*p*-Cyanophenylselanyl)triptycene (1e). Following the procedure used for the preparation of **1b**, **1e** was obtained in 24% yield as colorless solid: mp 252.0–253.5 °C; ^1H NMR (300 MHz, $CDCl_3$, δ, ppm, TMS) 5.48 (s, 1H), 6.95 (dt, J = 1.3, 7.5 Hz, 3H), 7.06 (dt, J = 1.1, 7.5 Hz, 3H), 7.26 (d, J = 9.0 Hz, 2H), 7.36 (d, J = 8.8 Hz, 2H), 7.43 (d, J = 7.5 Hz, 3H), 7.44 (dd, J = 1.2, 7.2 Hz, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$, δ, ppm, TMS) 54.1, 62.0, 108.9, 118.8, 124.3 (3C), 125.1 (3C), 126.2 (3C), 130.5 (^2J(Se,C) = 16.2 Hz, 2C), 131.8 (^3J(Se,C), 5.0 Hz, 2C), 138.6, 143.2 (3C), 145.2 (3C); ^{77}Se NMR (57.3 MHz, $CDCl_3$, δ, ppm, Me_2Se) 287.6. Anal. Calc. for $C_{60}H_{46}N_2Se_2$ (**1e** × 2 and cyclohexane), C, 75.62; H, 4.87; N, 2.94%. Found: C, 75.67; H, 4.84; N, 2.88%.

9-(*p*-Nitrophenylselanyl)triptycene (1f). Under a nitrogen atmosphere, to a suspension of di-9-triptycyl diselenide[17] (500 mg, 0.75 mmol) in ethanol (15 mL) at 0 °C was added $NaBH_4$ (270 mg, 6.78 mmol). *p*-Nitroiodobenzene was added to the reaction mixture. After refluxing for 3 h, the reaction mixture was poured into 100 g of ice-water. The precipitate was separated by using suction filtration. The crude product was purified by column chromatography (SiO_2, benzene–hexane 1 : 1) and recrystallized from dichloromethane and cyclohexane. **1f** was isolated in 57% yield as a bright yellow

Table 3 Crystallographic data for **1a–d** and **1f**

	1a	**1b**	**1c**	**1d**	**1f**
Empirical formula	$C_{26}H_{18}Se$	$C_{28}H_{23}NSe$	$C_{27}H_{20}OSe$	$C_{26}H_{17}ClSe$	$C_{26}H_{17}NO_2Se$
M_r	409.36	452.43	439.39	443.81	454.37
	Colorless plate	Yellow needle	Colorless needle	Colorless plate	Pale yellow plate
T/K	233	233	233	233	233
Crystal system	Monoclinic	Triclinic	Monoclinic	Orthorhombic	Orthorhombic
Space group	$P2_1/n$ (#14)	$P\bar{1}$ (#2)	$P2_1/n$ (#14)	$Pbca$ (#61)	$Pbca$ (#61)
a/Å	9.8178(5)	9.6439(4)	11.5331(11)	11.8868(6)	7.9805(4)
b/Å	15.3715(7)	11.2233(5)	14.2581(14)	13.9067(7)	14.0346(7)
c/Å	12.2627(6)	20.4121(8)	12.4437(12)	22.8836(11)	34.5168(18)
α/°		74.692(1)			
β/°	91.809(1)	87.418(1)	91.798(1)		
γ/°		77.850(1)			
V/Å^3	1849.69(16)	2082.08(15)	2045.2(3)	3782.8(3)	3866.0(3)
Z	4	4	4	8	8
D_c/g cm^{-3}	1.470	1.443	1.427	1.559	1.561
F(000)	832	928	896	1792	1840
Reflections observed [$I > 2\sigma(I)$]	4133	8849	4570	4302	4416
Parameters	244	545	263	253	271
R_1 [$I > 2\sigma(I)$]	0.0243	0.0340	0.0283	0.0269	0.0385
R_1 [all data]	0.0310	0.0420	0.0365	0.0369	0.0542
wR_2 [$I > 2\sigma(I)$]	0.0600	0.0933	0.0732	0.0733	0.0968
wR_2 [all data]	0.0632	0.0980	0.0772	0.0855	0.1117
Goodness-of-fit on F^2	1.024	1.074	1.064	1.131	1.170

solid (394 mg): mp 293.0–294.0 °C; ^{1}H NMR (300 MHz, CDCl$_3$, δ, ppm, TMS) 5.49 (s, 1H), 6.96 (dt, J = 1.3, 7.6 Hz, 3H), 7.07 (dt, J = 1.2, 7.4 Hz, 3H), 7.32 (d, J = 9.1 Hz, 2H), 7.41–7.47 (m, 6H), 7.95 (d, J = 9.1 Hz, 2H); ^{13}C NMR (75.5 MHz, CDCl$_3$, δ, ppm, TMS) 54.1, 62.2, 123.4 (2C), 123.7 (3C), 124.3 (3C), 125.1 (3C), 126.2 (3C), 130.3 (^2J(Se,C) = 16.2 Hz, 2C), 141.3, 143.0 (3C), 145.2 (3C), 145.7; ^{77}Se NMR (57.3 MHz, CDCl$_3$, δ, ppm, Me$_2$Se) 292.6. Anal. Calc. for C$_{26}$H$_{17}$NO$_2$Se, C, 68.73; H, 3.77; N, 3.08%. Found: C, 68.72; H, 3.91; N, 3.11%.

X-Ray structure determination. Single crystals of **1a** were obtained from solutions of *n*-hexane–ethyl acetate (2 : 1, v/v) after slow evaporation of the solvent at room temperature, **1b**, **1c** and **1f** from solutions of *n*-hexane–dichloromethane (2 : 1, v/v) and **1d** from solutions of cyclohexane. Diffraction data were collected on a Bruker Apex-II CCD diffractometer equipped with a graphite-monochromated Mo-Kα radiation source (λ = 0.71070 Å). The structures were solved by direct methods (SHELXS-97),[20] and refined by full-matrix least-square methods on F^2 for all reflections (SHELXL-97)[21] with all non-hydrogen atoms anisotropic and all hydrogen atoms isotropic. Table 3 lists the parameters for **1a–d** and **1f**.

Analysis of ^{1}H DNMR. The temperature-dependent spectra of the aromatic protons of **1e** and **1f** (and **1a**) were analyzed using an NMR simulation program, *gNMR*[22] (see Fig. 4, for example).

QC calculations. QC calculations are performed on **1a**, **1b′**, **1e** and **1f** using the Gaussian 03 program.[13] The Møller–Plesset second order energy correlation (MP2)[16] level is also applied with the 6-311+G(d) basis sets for Se and the 4-31G basis sets for C and H (basis sets-A). The 6-311+G(d) basis sets for Se and the 6-31G(d) basis sets for C and H (basis sets-B) are also employed for the calculations at the MP2 level. The density functional theory (DFT) level of the Becke three-parameter hybrid functional combined with the Lee–Yang–Parr correlation functional (B3LYP)[14,15] is also applied with the 6-311+G(d) basis sets being employed for Se and the 6-311G(d,p) basis sets for C and H.

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9 Sets of δ(Se) in 9-(arylselanyl)anthracenes (**I**: *p*-YC$_6$H$_4$SeAtc), δ(Se: **I**) and 1-(arylselanyl)anthraquinones (**II**: *p*-YC$_6$H$_4$SeAtq), δ(Se: **II**), are demonstrated to be the standards of **pl** and **pd**, respectively, based on the theoretical and experimental investigations. Although the temperature dependence of δ(Se) is very small in **II** (**B**: **pd**), that in **I** (**A**: **pl**) is not so small, which may show that the structure of **I** (**A**: **pl**) is unstable relative to that of **II** (**B**: **pd**). See, (*a*) W. Nakanishi, S. Hayashi, D. Shimizu and M. Hada, *Chem.–Eur. J.*, 2006, **12**, 3829–3846; (*b*) S. Hayashi and W. Nakanishi, *Bioinorg. Chem. Appl.*, 2006, 1–13, DOI: 10.1155/BCA/2006/79327.

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