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10-Oxo-10*H*-5λ⁴,10λ⁴-thianthren-5-ylideneamine as a probe for stereochemistry in the formation and amination of fluoro-λ⁶-sulfanenitriles

Takayoshi Fujii,[a,*] Tomoyoshi Takano,[b] Shinsuke Asai,[b] Hiroyuki Morita,[b] Mitsuo Hirata[a] and Toshiaki Yoshimura[b,*]

[a]*Department of Applied Molecular Chemistry, College of Industrial Technology, Nihon University, Izumi-cho, Narashino, Chiba 275-8575, Japan*
[b]*Department of Material Systems Engineering and Life Science, Faculty of Engineering, Toyama University, Gofuku, Toyama 930-8555, Japan*

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Abstract—The fluorination of 10-oxo-10*H*-5λ⁴,10λ⁴-thianthren-5-ylideneamine (**2**) with Selectfluor™ affords 5-fluoro-10-oxo-5,10-dihydro-5λ⁶,10λ⁴-thianthren-5-nitrile (**4**). The amination of **4** with morpholine gives 5-morpholino-10-oxo-5,10-dihydro-5λ⁶,10λ⁴-thianthren-5-nitrile (**5**). The stereochemical course of both reactions has been studied, while the configurations of their products, *cis*-isomer **4** and *trans*-5-morpholino-10-oxo-5,10-dihydro-5λ⁶,10λ⁴-thianthren-5-nitrile (*trans*-**5**) are elucidated by the use of X-ray crystallographic analyses.

1. Introduction

Thianthrene derivatives are one of the most important chemical probes in organic reactions.[1–3] In particular, the oxidation of thianthrene-5-oxide has been used as a mechanistic probe for the assessment of the electronic character of various oxidants.[1,2] Recently, Morita and co-workers have been able to prepare 10-oxo-10*H*-5λ⁴,10λ⁴-thianthren-5-ylideneamine (**2**) by hydrolysis of its *N*-*p*-toluenesulfonyl precursor **1** with concentrated H_2SO_4.[3] Furthermore, the *cis*- and *trans*-isomers of **1** and **2** were separated and their stereochemical interconversions were studied under hydrolytic conditions in acidic media and thermal conditions. Thus, *trans*-**1** or *cis*-**1** was hydrolyzed with concentrated H_2SO_4 to give a mixture of the corresponding *trans*-**2** and *cis*-**2**, in the respective ratio ca. 5:1. In 20% aqueous H_2SO_4 the hydrolysis of *trans*-**2** or *cis*-**2** led to a mixture of the corresponding disulfoxides, indicating that substitution of the NH group with H_2O proceeds through inversion (ca. 86–89%). For the thermal interconversion of **1** and **2**, *cis* derivatives were preferentially formed. The structures of these sulfimides were also determined by X-ray crystallographic analyses.[3]

We have been investigating the syntheses, structures, and reactivities of organic λ⁶-sulfanenitriles bearing an SN triple bond.[4] Particularly, we have succeeded in transforming fluoro-λ⁶-sulfanenitrile to the various substituted λ⁶-sulfanenitriles such as alkoxy-, amino-, imino-, methyl-, and arylsulfanenitriles.[4,5] Quite recently, we have found that several diaryl(fluoro)-λ⁶-sulfanenitriles are prepared by the reaction of *S*,*S*-diarylsulfimides with Selectfluor™ (1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2,2,2]octane bis(tetrafluoroborate) and this reaction allows the first preparation of 5-fluoro-10,10-dioxo-5,10-dihydro-5λ⁶,10λ⁶-thianthren-5-nitrile.[6] We have also shown a new synthetic route for heterocyclic fluoro-λ⁶-sulfanenitrile, due to the fact that conversion of cyclic-*N*-bromosulfimide with the fluoride anion to the corresponding λ⁶-sulfanenitriles is difficult.

However, the stereochemistry of the formation of fluoro-λ⁶-sulfanenitriles by the reaction of sulfimides with Selectfluor™ and substitution of fluoro-λ⁶-sulfanenitriles with some nucleophiles is completely unknown, due to the lack of a facile preparation of optically active fluoro-λ⁶-sulfanenitriles.[7] It is quite interesting to prepare 5-fluoro-10-oxo-5,10-dihydro-5-λ⁶,10-λ⁴-thianthren-5-nitrile (**4**). We have now investigated (1) reaction of *cis*- and *trans*-10-oxo-10*H*-5λ⁴,10λ⁴-thianthren-5-ylideneamines (**2**) with Selectfluor™ and their stereochemical courses and (2) reaction of 5-fluoro-10-oxo-5,10-dihydro-5λ⁶,10λ⁴-thianthren-5-nitrile (**4**) with morpholine and its stereochemical course.

Keywords: λ⁶-Sulfanenitrile; Sulfimides; Selectfluor™; Thianthrene; Fluorination; Amination; X-ray crystallographic analysis.
* Corresponding authors. Tel.: +81 47 474 2561; fax: +81 47 474 2579 (T.F.); e-mail: t5fujii@cit.nihon-u.ac.jp

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2. Results and discussion

2.1. Reaction of 10-oxo-10*H*-5λ⁴,10λ⁴-thianthren-5-ylideneamine (2) with Selectfluor™

The reaction of *trans*-10-oxo-10*H*-5λ⁴,10λ⁴-thianthren-5-ylideneamine (*trans*-**2**) with Selectfluor™ was carried out at ambient temperature in CH_3CN to give the *cis*-isomer of 5-fluoro-10-oxo-5,10-dihydro-5λ⁶,10λ⁴-thianthren-5-nitrile (**4**) (the SN group and the SO group are in *cis*-relation) and acid salt of starting material *trans*-**2**, in 48 and 43% yields, respectively, together with thianthren-5-oxide in 7% yield (Scheme 1). Neither the corresponding *N*-fluorosulfimide **3** nor the *trans*-isomer of **4** was obtained. The composition of *cis*-**4** was identified by NMR and IR spectroscopies as well as elemental analysis, and its stereochemistry was determined by X-ray crystallographic analysis (Fig. 1 and Table 1). Because of the low relative solubility of *cis*-**2** in CH_3CN, the reaction with Selectfluor™ was carried out at 50 °C. Interestingly, this reaction gave the corresponding *cis*-isomer of **4** and acid salt of *cis*-**2** in 35 and 39% yields, respectively, together with thianthrene-5-oxide, *cis*-, and *trans*-thianthrene-5,10-dioxides in 12, 11, and 2% yields (Scheme 1).

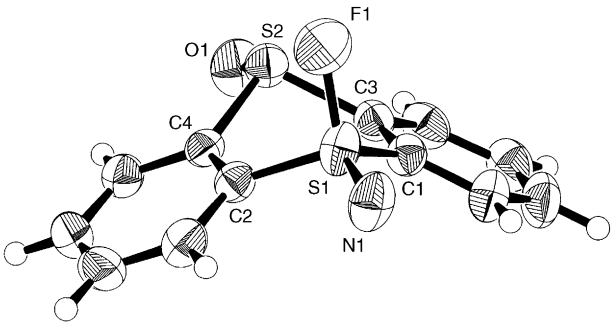


Figure 1. The molecular structure of *cis*-**4**.

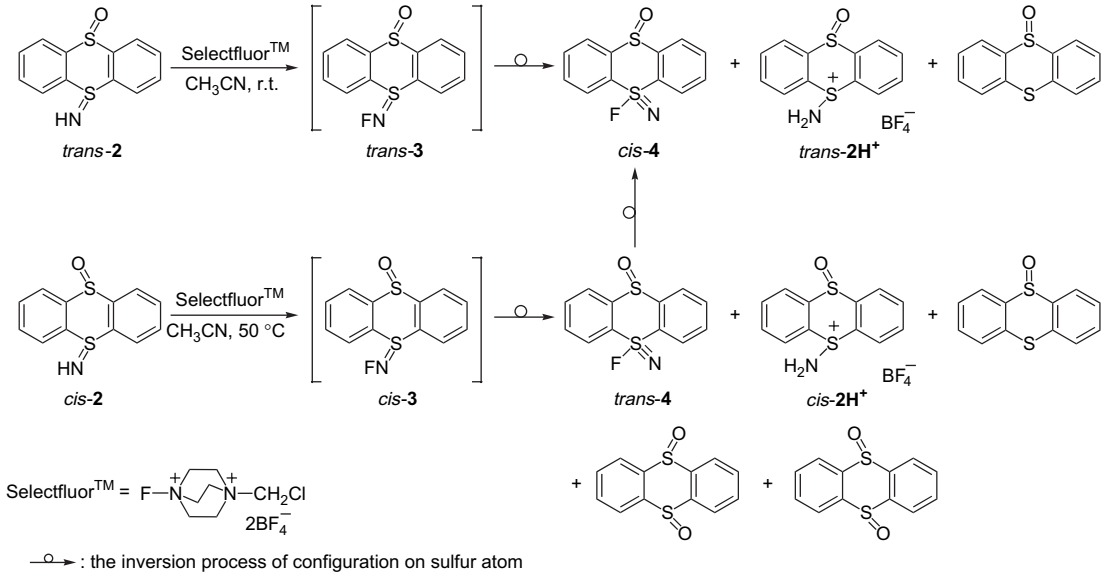
Table 1. Selected bond lengths (Å) and angles (°) for *cis*-**4**[a]

S1–F1	1.573(3)	S1–N1	1.436(3)
S1–C1	1.785(3)	S1–C2	1.775(3)
S2–O1	1.484(3)	S2–C3	1.811(3)
S2–C4	1.800(3)		
F1–S1–N1	122.0(2)	F1–S1–C1	102.2(2)
F1–S1–C2	99.4(2)	N1–S1–C1	115.2(2)
N1–S1–C2	114.4(2)	C1–S1–C2	100.3(2)
O1–S2–C3	107.8(2)	O1–S2–C4	108.0(2)
C3–S2–C4	96.6(1)		

[a] The atom-labeling scheme is shown in Figure 1.

To understand this reaction pathway, the conversion into products during the reaction of *cis*- and *trans*-isomers of sulfimides **2** with Selectfluor™ in CH_3CN was followed by time interval ^{19}F NMR spectroscopy (Fig. 2). In the reaction of *trans*-**2** at 23 °C, the ^{19}F NMR peak of Selectfluor™ at δ 46.1 (N–F) gradually diminished and the peak of *cis*-**4** appeared at δ 114.4 (Fig. 2 (left)). At a low temperature (−20 °C), *trans*-**2** slowly reacted with Selectfluor™ to give the same results under the above conditions. Although we were unable to detect *N*-fluorosulfimide **3** by ^{19}F NMR spectroscopy, its analogue, *S*-(4-nitrophenyl)-*S*-phenyl-*N*-fluorosulfimide and its conversion into the corresponding fluoro-λ⁶-sulfanenitrile were observed by ^{19}F NMR spectroscopy as we reported in a preliminary communication.[6] We have also studied on density functional theory (DFT) calculations (B3LYP/6-311++G(3df,2pd)//B3LYP/6-31G(d) level) of *syn*- (12.1 kcal/mol (relative to Me_2FSN): F *syn* with respect to SMe_2) and *anti*-*S*,*S*-dimethyl-*N*-fluorosulfimides (18.0 kcal/mol (relative to Me_2FSN): F *anti* with respect to SMe_2) and fluoro(dimethyl)-λ⁶-sulfanenitrile (0.0 kcal/mol), suggesting that *N*-fluorosulfimides should be converted to thermodynamically stable fluoro-λ⁶-sulfanenitrile.[6] This present reaction would also be relative to the above manner (Scheme 1).

The reaction of *cis*-**2** with Selectfluor™ in CH_3CN was monitored at 50 °C by ^{19}F NMR spectroscopy. The ^{19}F NMR peak of Selectfluor™ at δ 46.1 (NF) gradually reduced, while two resonance signals at δ 114.4 and 117.2 increased (Fig. 2 (right)). The former signal was assigned to that of *cis*-**4**. The



Scheme 1.

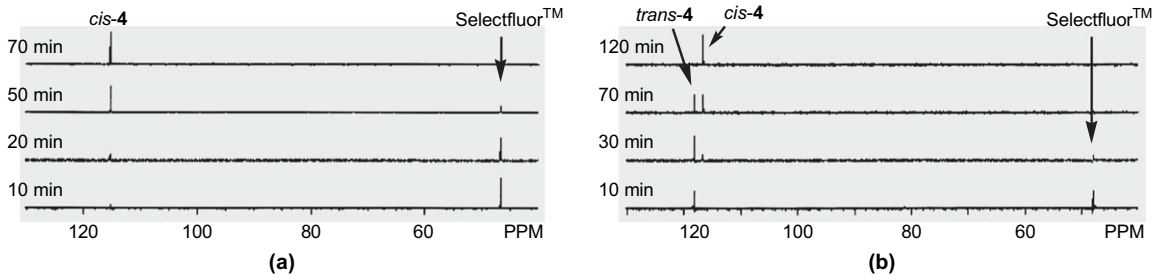


Figure 2. Time course of the change in ^{19}F NMR spectra of the reaction of *trans*- (left) and *cis*-**2** (right) with Selectfluor™ in CD_3CN: (a) rt, (b) 50 °C.

latter peak reached an approximate maximum of 55% of the reaction mixture as determined by the relative integrals of the reaction mixture in ^{19}F NMR spectrum, and then completely disappeared and the spectra changed to that of *cis*-**4**. This intermediate is amenable to detection by ^{19}F NMR spectroscopy, but we could not isolate it from the reaction mixture. The ^{19}F NMR resonance of the latter (δ 118.2) is observed in a similar that of *cis*-fluoro-λ^6-sulfanenitrile *cis*-**4** (δ 115.4) and is shifted to the lower field relative to those of *S*-(4-nitrophenyl)-*S*-phenyl- (δ −125.2)[6] and *S*,*S*-bis(trifluoromethyl)-*N*-fluorosulfimides (δ −50, NF)[8], and hence, the formation of *cis*-isomer of fluoro-λ^6-sulfanenitrile *cis*-**4** can be accounted for the formation of *trans*-**4**, followed by isomerization (Scheme 1).

These results imply that the formation of fluoro-λ^6-sulfanenitrile is as follows. (i) The initial process was that the reaction of sulfimide **2** with Selectfluor™ afforded the corresponding *N*-fluorosulfimide **3** and acid salt of **2**. The fluorination of nitrogen atom in **2** evidently does not involve the inversion process.[3] (ii) The *N*-fluorosulfimide **3** underwent 1,2-migration of fluorine atom yielding the corresponding fluoro-λ^6-sulfanenitrile **4**. This migration (*cis*- and *trans*-**3** to *trans*- and *cis*-**4**, respectively) proceeds via inversion mechanism (Scheme 1). As mentioned above, the DFT calculations predicted that *syn* conformation of *S*,*S*-dimethyl-*N*-fluorosulfimide is more stable than its *anti* conformation by 5.9 kcal/mol.[6] Therefore, *cis-syn* and *trans-syn* isomers of *N*-fluorosulfimide **3** should be converted to the respective *trans*- and *cis*-isomers of fluoro-λ^6-sulfanenitrile **4**, which seem to be formed by a stepwise or a concerted rearrangement.

DFT calculations were performed on the various conformers of *cis*- and *trans*-5-fluoro-10-oxo-5,10-dihydro-5λ^6,10λ^6-thianthren-5-nitriles (*cis*-**4A**, *cis*-**4B**, *trans*-**4A**, and *trans*-**4B**) (Fig. 3). The structures of the four possible conformations were optimized at the B3LYP/6-31G(d) level. All conformers correspond to stable structure. Selected structural parameters of optimized structures are shown in Table 2. The optimized structure of *cis*-**4A** is in good agreement with the experimental structure, except that the calculated S–N and S–F bond lengths are significantly longer than the experimental ones. Such overestimation of S–N and S–F bond lengths by DFT methods has been reported earlier.[9] Calculated relative energies were obtained at the B3LYP/6-311++G(3df,2pd) level using the data from the optimized structures of **4**. Stabilities of **4** are in the order: *cis*-**4A**>*trans*-**4B**>*trans*-**4A**>*cis*-**4B** (Fig. 3). *cis*-**4A** is more stable than *trans*-**4A** and *trans*-**4B** by 7.27 and 5.51 kcal/mol, respectively. These results imply that *trans*-isomer of **4** should be converted to thermodynamically stable *cis*-**4A**.

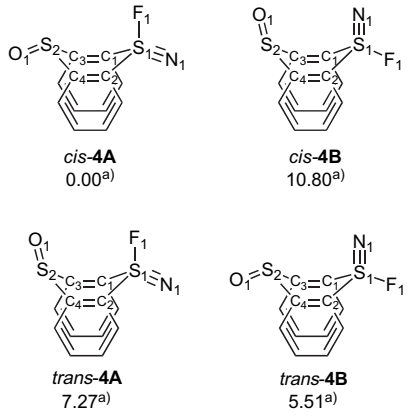


Figure 3. Calculated relative energies of **4**. a) B3LYP/6-311++G(3df,2pd)//B3LYP/6-31G(d), ZPE corrected values (kcal/mol).

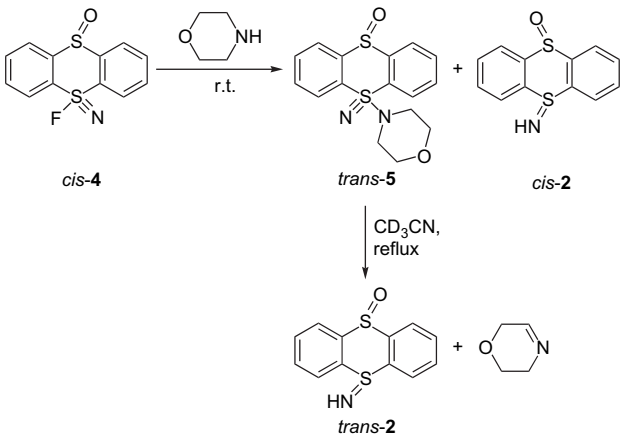
Table 2. Optimized geometries for *cis*- and *trans*-**4A** and -**4B**[a]

	cis-**4A**	*cis*-**4B**	*trans*-**4A**	*trans*-**4B**
Bond lengths (Å)				
S1–F1	1.708	1.715	1.679	1.706
S1–N1	1.462	1.462	1.462	1.464
S1–C1	1.811	1.819	1.813	1.815
S1–C2	1.811	1.819	1.813	1.815
S2–O1	1.509	1.508	1.506	1.509
S2–C3	1.833	1.829	1.832	1.832
S2–C4	1.833	1.829	1.832	1.832
Bond angles (°)				
F1–S1–N1	120.6	117.3	119.7	118.6
F1–S1–C1	93.7	93.0	95.3	94.8
F1–S1–C2	93.7	93.0	95.3	94.8
N1–S1–C1	120.7	122.4	119.6	121.4
N1–S1–C2	120.7	122.4	119.6	121.4
C1–S1–C2	101.3	101.2	102.2	99.6
O1–S2–C3	107.6	108.5	109.9	107.9
O1–S2–C4	107.6	108.5	109.9	107.9
C3–S2–C4	95.7	97.5	97.0	96.0

[a] Calculated at the B3LYP/6-31(d) level. The atom-labeling scheme is shown in Figure 3.

2.2. Reaction of *cis*-5-fluoro-10-oxo-5,10-dihydro-5λ^6,10λ^4-thianthren-5-nitrile (*cis*-**4**) with morpholine

The reaction of *cis*-**4** with a large excess of morpholine at room temperature gave the *trans*-isomer of 5-morpholino-10-oxo-5,10-dihydro-5λ^6,10λ^4-thianthren-5-nitrile (*trans*-**5**) in 56% yield (Scheme 2). The structure of *trans*-**5** was determined by X-ray crystallography (Fig. 4 and Table 3). In this reaction, an unexpected *cis*-10-oxo-10*H*-5λ^4,10λ^4-thianthren-5-ylideneamine (*cis*-**2**) was also obtained in 40% yield.



Scheme 2.

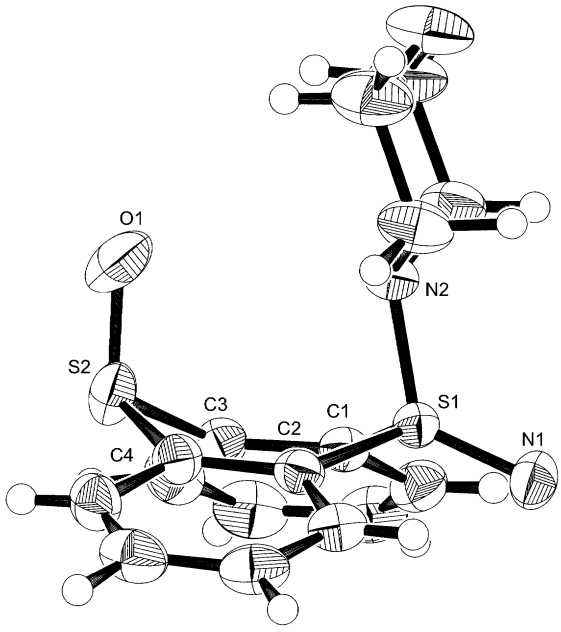


Figure 4. The molecular structure of *trans*-**5**.

We have already reported that diphenyl(piperidino)-λ^6-sulfanenitrile decomposes to the corresponding diphenylsulfimide and 3,4,5,6-tetrahydropyridine.[5a] Therefore, thermal stabilities of *trans*-**5** were examined. When *trans*-**5** was refluxed in CD_3CN, the retention product *trans*-**2** was obtained together with 3,6-dihydro-2*H*-[1,4]oxazine (Scheme 2). However, *trans*-**5** was stable under the above reaction conditions. These results suggest that the formation of *cis*-sulfimide *cis*-**2** is probably due to the concurrent electron-transfer reduction of the starting material *cis*-**4** and the substitution of S–F to S–N$(CH_2)_2$O involves the inversion process through an S_N2 or an addition–elimination mechanism.

2.3. X-ray crystallographic analysis of *cis*-5-fluoro-10-oxo-5,10-dihydro-5λ^6,10λ^4-thianthren-5-nitrile (*cis*-4) and *trans*-5-morpholino-10-oxo-5,10-dihydro-5λ^6,10λ^4-thianthren-5-nitrile (*trans*-5)

The detailed structural analyses of *cis*-**4** and *trans*-**5** were performed by X-ray crystallographic analyses. Selected bond lengths and angles of *cis*-**4** and *trans*-**5** are collected in Tables 1 and 3, respectively. The ORTEP drawings of *cis*-**4** and *trans*-**5** are depicted in Figures 1 and 4, respectively.

Table 3. Selected bond lengths (Å) and angles (°) for *trans*-**5**[a]

S1–N1	1.464(2)	S1–N1	1.690(2)
S1–C1	1.807(2)	S1–C2	1.809(2)
S2–O1	1.490(2)	S2–C3	1.790(2)
S2–C4	1.802(2)		
N1–S1–N2	123.5(1)	N1–S1–C1	116.9(1)
N1–S1–C2	116.4(1)	N2–S1–C1	97.90(9)
N2–S1–C2	97.23(9)	C1–S1–C2	105.0(10)
O1–S2–C3	108.4(1)	O1–S2–C4	109.9(1)
C3–S2–C4	98.1(1)		

[a] The atom-labeling scheme is shown in Figure 4.

The X-ray structure of *cis*-**4** shows two independent molecules with nearly identical bond lengths and angles (an ORTEP drawing and the selected bond lengths and angles of one of the two independent molecules). The thianthrene ring system is found in the boat configuration. The nitrogen or oxygen bonded to sulfur assumes a pseudoequatorial position in the six-membered ring, whereas the fluorine bonded to sulfur assumes a pseudoaxial position. The S1–N1 and S1–F1 bond lengths (1.436(3) and 1.573(3) Å) in *cis*-**4** are much closer to those of 5-fluoro-10,10-dioxo-5,10-dihydro-5λ^6,10λ^6-thianthren-5-nitrile (S–N; 1.435(2) Å, S–F; 1.584(2) Å).[6]

The crystal lattice of *trans*-**5** consists of morpholino-λ^6-sulfanenitrile and $CHCl_3$ molecule. The distance between the nitrogen and carbon atoms is 3.067(4) Å. This value is significantly shorter than the sum of the van der Waals radii (3.39 Å) of the two elements[10] and is indicative of the N⋯H–C hydrogen bond. In the conformation of *trans*-**5**, the morpholino group and oxygen atom at S1 and S2 atoms lie in a pseudoaxial position, while the nitrogen atom at S1 atom is in a pseudoequatorial position. The S1–N1 bond length of 1.464(2) Å in *trans*-**5** is very close to that of 2,2-biphenylylene(phenyl)-λ^6-sulfanenitrile (1.470(2) Å),[5e] but significantly longer than that of fluorosulfanenitrile *cis*-**4**, which would be due to the influence of the electronegativity of substituents at S atom. The S1–N2 bond length (1.690(2) Å) is significantly shorter than the sum of the covalent radii of S and N (1.74 Å),[10] suggesting the polarization of the S1–N2 bond.

3. Conclusion

In the study of stereochemistry of formation of fluoro-λ^6-sulfanenitriles by the reaction of sulfimides with Selectfluor™, we investigated the fluorination of 10-oxo-10*H*-5λ^4,10λ^4-thianthren-5-ylideneamine (**2**). The *cis*- and *trans*-**2** reacted with Selectfluor™ to give a *cis*-isomer of 5-fluoro-10-oxo-5,10-dihydro-5λ^6,10λ^4-thianthren-5-nitrile (**4**), which is determined by X-ray crystallographic analysis. Inspection of the present results shows that the reaction proceeds through the mechanism outlined in Scheme 1. The initial product, *N*-fluorosulfimide **3** undergoes 1,2-migration of fluorine atom yielding the corresponding fluoro-λ^6-sulfanenitrile **4** via inversion process. In addition, *trans*-isomer of **4** should be converted to thermodynamically stable *cis*-**4**.

Further, the reaction of *cis*-**4** with morpholine gave the *trans*-isomer of 5-morpholino-10-oxo-5,10-dihydro-5λ^6,10λ^4-thianthren-5-nitrile (*trans*-**5**), indicating that substitution of fluorine with morpholine proceeds through inversion. The structure of *trans*-**5** was determined by X-ray crystallography, which reveals that **5** is a new type of heterocyclic amino-λ^6-sulfanenitrile.

4. Experimental

4.1. General

NMR spectra were obtained on a JEOL-JNM 400 NMR spectrometer and calibrated by the use of tetramethylsilane (TMS) as an internal reference. Chemical shifts (δ) were measured in parts per million, and coupling constants (J values) were in hertz (Hz). Mass spectra were recorded on a JEOL-JMS 700 mass spectrometer. Infrared spectra (IR) were recorded on a Horiba FT-710 spectrometer. Melting point was measured on a Yanaco Mp-J3 melting point apparatus. Elemental analyses were performed on a Yanaco MT-5 CHN CORDER. The X-ray crystallographic analyses were performed on a Rigaku AFC7R four-circle diffractometer using graphite monochromated Mo Kα radiation at 296 K.

All reagents and solvents were obtained commercially and were further purified by general methods when necessary. *cis*- and *trans*-10-Oxo-10*H*-5λ^4,10λ^4-thianthren-5-ylideneamines (**2**) were prepared according to the method reported in our previous articles.[3]

4.1.1. Reaction of 2 with Selectfluor™. Selectfluor™ (85 mg, 0.24 mmol) was added to a solution of *trans*-**2** or *cis*-**2** (100 mg, 0.40 mmol) in CH_3CN (100 ml) at ambient temperature or 50 °C. When the reaction was completed (monitored by TLC), the solution was poured into ice-water and then extracted with $CHCl_3$, and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure to afford *cis*-5-fluoro-10-oxo-5,10-dihydro-5λ^6,10λ^4-thianthren-5-nitrile (*cis*-**4**) and acid salt of *trans*-**2** or *cis*-**2** together with thianthren-5-oxide and/or *cis*- and *trans*-thianthrene-5,10-dioxides, which were identified by comparison with authentic samples[2a].

cis-**4**: mp 198–200 °C (decomp.); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77–7.87 (m, 4H), 8.16 (dd, 2H, J_1=7.6 Hz, J_2=1.2 Hz, 2H), 8.43 (dd, 2H, J_1=7.6 Hz, J_2=1.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 125.3, 127.3, 131.1, 133.6, 134.1 (d, J_{CF}=25 Hz), 145.4 (d, J_{CF}=2.5 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ 114.4; IR (KBr) 1379 cm^{-1} (SN), 1087 (SO); FAB (*m*/*z*) 266 (M^++1). Calcd for $C_{12}H_8FNOS_2$: C, 54.32; H, 3.04; N, 5.28. Found: C, 54.56; H, 3.12; N, 5.33.

4.1.2. Reaction of *cis*-4 with morpholine. Fluorosulfanenitrile *cis*-**4** (265 mg, 1 mmol) was dissolved in moropholine (3 ml) for 2 h at ambient temperature. The solution was poured into ice-water and then extracted with $CHCl_3$, and dried over anhydrous Na_2SO_4. After the solvent was removed under reduced pressure, the residue was chromatographed ($CHCl_3$–CH_3OH=16:1) through a column packed with silica gel to afford *trans*-5-morpholino-10-oxo-5,10-dihydro-5λ^6,10λ^4-thianthren-5-nitrile (*trans*-**5**, 196 mg, 59%) and *cis*-**2** (98 mg, 40%).

trans-**5**: mp 153–154 °C (decomp.); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.07 (t, J=4.6 Hz, 4H), 3.71 (t, J=4.6 Hz, 4H), 7.73–7.82 (m, 4H), 8.01 (dd, 2H, J_1=7.4 Hz, J_2=1.2 Hz, 2H), 8.42 (dd, 2H, J_1=7.4 Hz, J_2=1.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 44.7, 66.1, 129.1, 131.2, 132.4, 132.7, 139.2, 140.9; IR (KBr) 1321 cm^{-1} (SN), 1098 (SO); FAB (*m*/*z*) 333 (M^++1). Calcd for $C_{16}H_{16}N_2O_2S_2$: C, 57.81; H, 4.85; N, 8.43. Found: C, 57.59; H, 4.82; N, 8.12.

4.1.3. X-ray crystal structure analysis of *cis*-4. The single crystals were obtained by recrystallization from $CHCl_3$–*n*-hexane. Diffraction data were measured with ω–2θ scan technique at 296 K on a Rigaku AFC7R diffractometer using graphite monochromated Mo Kα radiation (λ=0.7107 Å). A total of 6966 reflections were collected. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods (SIR 92)[11] and expanded using Fourier techniques (DIRDIF)[12]. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on 4365 observed reflections ($I>3.00\sigma(I)$) and 307 variable parameters converged with the unweighted and weighted agreement factors equal to $R=(\Sigma||Fo|-|Fc||)/(\Sigma|Fo|)=0.054$; $R_w=[(\Sigma\omega(|Fo|-|Fc|)^2/\Sigma\omega Fo^2)]^{1/2}=0.088$. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.90 and −0.39 e$^-$/Å^3, respectively. All calculations were performed using the teXsan crystallographic software package of Molecular Structure Corporation (1985) and (1999). Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 600495 for compound *cis*-**4**.

4.1.4. X-ray crystal structure analysis of *trans*-5. The single crystals were obtained by recrystallization from $CHCl_3$–*n*-hexane. Diffraction data were measured with ω–2θ scan technique at 296 K on a Rigaku AFC7R diffractometer using graphite monochromated Mo Kα radiation (λ=0.7107 Å). A total of 5724 reflections were collected. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods (SIR 92)[11] and expanded using Fourier techniques (DIRDIF)[12]. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on 4065 observed reflections ($I>3.00\sigma(I)$) and 303 variable parameters converged with the unweighted and weighted agreement factors equal to $R=(\Sigma||Fo|-|Fc||)/(\Sigma|Fo|)=0.043$; $R_w=[(\Sigma\omega(|Fo|-|Fc|)^2/\Sigma\omega Fo^2)]^{1/2}=0.063$. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.54 and −0.63 e$^-$/Å^3, respectively. All calculations were performed using the teXsan crystallographic software package of Molecular Structure Corporation (1985) and (1999). Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 600496 for compound *cis*-**5**.

4.1.5. Ab initio calculation of 4. The geometries of *cis*-**4A** and -**4B** and *trans*-**4A** and -**4B** were optimized by the use of the Gaussian 98 program at B3LYP/6-31(d) levels of density

functional theory.[13] The relative energies of the optimized structures of **4** were carried out with B3LYP/6-311++G(3df,2pd).

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