To the 120th anniversary of B.A. Arbuzov

A Comprehensive Study of the Structure and Conformational Behavior of 5-Phenylthianthrenium Triflate

A. S. Novikov[a,b] and M. V. Il'in[a,*]

[a] Institute of Chemistry, St. Petersburg University, St. Petersburg, 199034 Russia
[b] Center NTI "Digital Materials Science: New Materials and Substances", Scientific and Educational Center
"Composites of Russia", Bauman Moscow State Technical University, Moscow, 105005 Russia
*e-mail: m.ilin@spbu.ru

Abstract—This study is focused on the comprehensive structural analysis of 5-phenylthianthrenium triflate, a simplest representative of thianthrenium salts. Combining X-ray diffraction and theoretical investigations it was found that the onium salt has more planar configuration of the fused tricyclic moiety compared to non-functionalized thianthrene and forms intermolecular chalcogen bonds in the solid state. Additionally, quantum-chemical conformational analysis indicated higher thermodynamic stability of the axial conformer of onium salt relatively to the equatorial isomer, which provides insights into its molecular dynamics.

5-Arylthianthrenium salts have emerged as versatile reagents with profound applications in modern synthetic chemistry. Their exceptional reactivity not only facilitates regioselective C–H functionalization, expanding the avenues for direct aromatic modification [1–5], but also positions them as valuable aryne precursors [6, 7]. Additionally, the synergy between 5-arylthianthrenium salts and metallophotoredox catalysis has paved the way for selective C–F bond formation, an advancement with implications in pharmaceuticals and materials science [8]. It should be noted that arylsulfonium salts, which include thianthrenium salts, have proven to be good chalcogen bond donors, which, in turn, find their application in crystal engineering [9–12] and organocatalysis [13–16], which has been extensively studied for the last decade together with many other σ-hole carriers [17–20].

Although the simplest representative of thianthrenium salts, 5-phenylthianthrenium triflate $\mathbf{1}^{OTf}$, has previously been characterized by ^{1}H NMR spectroscopy, mass spectrometry and X-ray diffraction analysis, its structure has not been discussed in detail [8]. The objective of this study was to systematically analyze the structure of $\mathbf{1}^{OTf}$, its intermolecular interactions in the solid state, and to theoretically assess the potential formation of different conformers and structural isomers.

The 5-phenylthianthrenium triflate $\mathbf{1}^{OTf}$ was synthesized according to a previously published procedure [13] with some modifications via arylation of thianthrene by diphenyliodonium triflate in 1,2-dichloroethane at 130°C for 15 min (Scheme 1).

Based on the X-ray diffraction data, the structure of $\mathbf{1}^{OTf}$ seems to be more planar [with a bending angle of 143.21(6)° between two benzo groups] in comparison to thianthrene, which has a bending angle of 128° [21] (Fig. 1). The angle between the S^1–C bond of the phenyl ring and the S^1–S^2 axis is 77.92(5)°, and the length of the S^1–C bond is noticeably longer [$d(S^1-C_{ex}) = 1.810(2)$ Å] than the endocyclic bonds of the same sulfur atom [$d(S^1-C_{en}) = 1.769(2)–1.773(2)$ Å], which in turn are longer than the endocyclic bonds of the unsubstituted sulfur atom [$d(S^2-C_{en}) = 1.755(2)–1.759(2)$ Å].

Scheme 1.

1^{OTf} (90%)
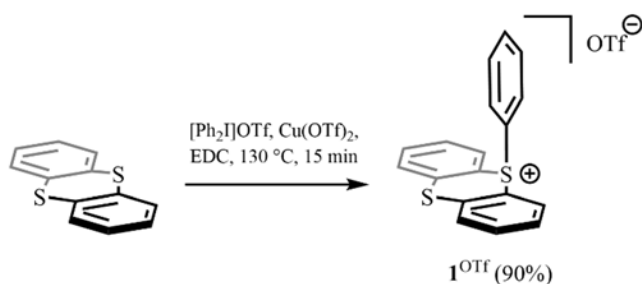
In the structure of 1^{OTf}, the presence of two different types of intermolecular chalcogen bonds leads to the formation of dimers, facilitated by an eight-membered ring involving $S^1{\cdots}O$ interactions. These dimers further assemble into one-dimensional polymer chains through second-type [22] chalcogen bonds (ChBs) formed between $S^2{\cdots}S^2$. Specifically, the S1 atom establishes two chalcogen bonds with triflate anions. The interaction between S^1 and O^1 {$d(S{\cdots}O) = 3.029(1)$ Å; considering $\Sigma_{vdw}(S + O)$ is 3.32 Å [23]} arises due to the interaction through the axial σ-hole of the S atom (opposite side of the phenyl ring). It is important to note that this interaction is shorter than the $d(S^1{\cdots}O^2) = 3.070(1)$ Å, which is formed due to the interaction through the σ-hole opposite to the endocyclic $S^1{\cdots}C$ bond (equatorial σ-hole). Additionally, a short contact exists between S^2 and S^2 {$d(S{\cdots}S)$ 3.232(1) Å; considering $\Sigma_{vdw}(S + S)$ is equal to 3.6 Å [23]}.

The presence in the crystal of single conformer with an axial arrangement of the phenyl ring stimulated us to theoretically study (i) the possibility of the transition of the phenyl ring to the equatorial position (Scheme 2, route *a*) and (ii) the possibility of transferring the phenyl ring from the S^1 atom to the S^2 atom via intramolecular aromatic nucleophilic substitution (Scheme 2, route *b*). The DFT calculations were carried out based on the experimentally obtained atomic coordinates from the single-crystal X-ray diffraction analysis as input model structures with consequent their full geometry optimization procedure.

The results of calculations of thermodynamic parameters showed that 1_{ax} is a more stable conformer ($\Delta G = 9.4$ kJ/mol for route *a*), which is consistent with the experimental data. In addition, despite the close location of the phenyl ring to the second sulfur atom, which can promote the transfer of phenyl, the energy barrier for such a transformation turned out to be extremely large ($\Delta G^{\neq} = 157.4$ kJ/mol for TS). Although the classical S_NAr mechanism involving the formation of the Meisenheimer complex has been initially supposed, it was found that this pathway is not possible for the studied cation. Instead, a straightforward *syn*-nucleophilic substitution retaining the phenyl aromatic system takes place, which, in turn, can cause the high activation barrier.

In summary, this study elucidates the existence of two different types of intermolecular chalcogen bonds in the crystal structure of 5-phenylthianthrenium triflate. Furthermore, our findings indicate the stability of the axial conformer over the equatorial conformation and highlight the significant energy barrier that hinders intramolecular transfer of the phenyl ring between sulfur atoms. All these
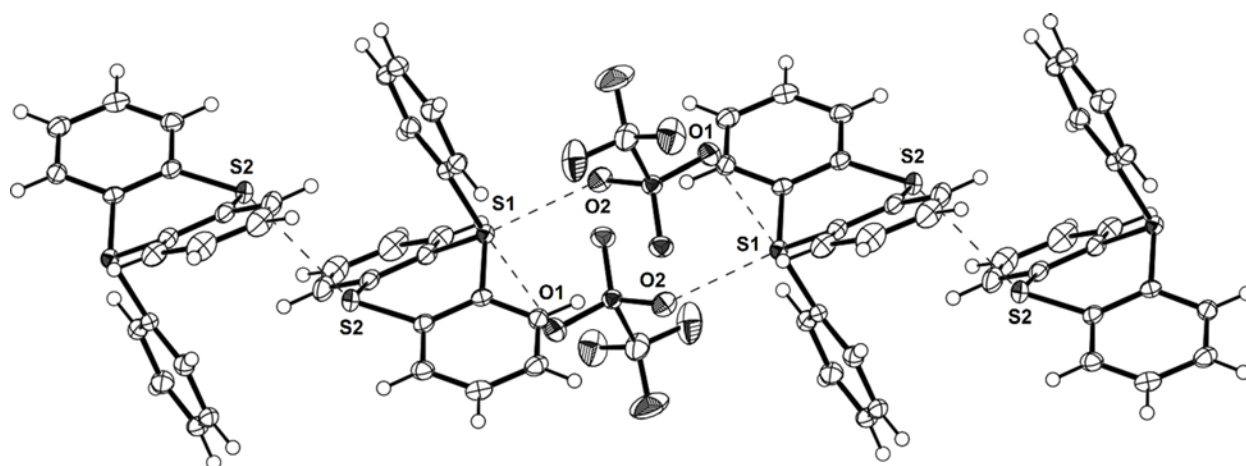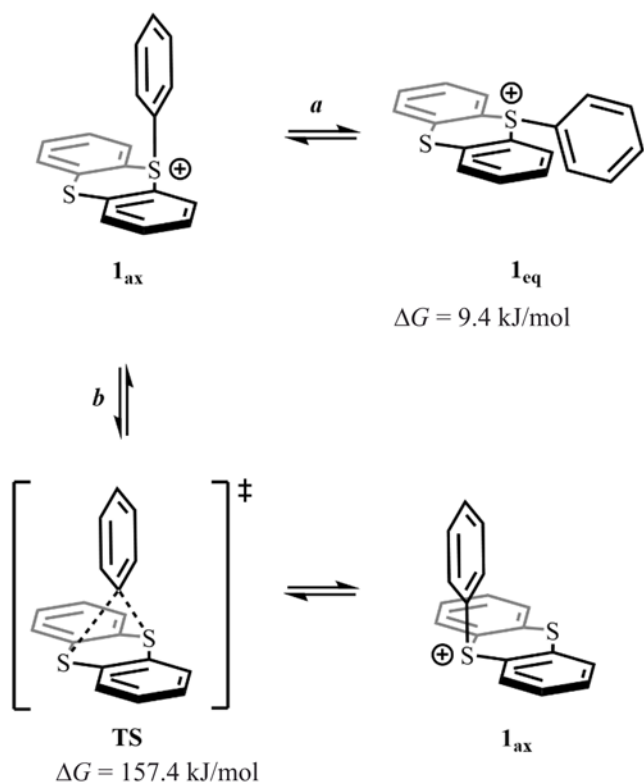

Fig. 1. Representations of 1^{OTf} crystal structure visualizing intermolecular ChBs.

Scheme 2.

1_{ax} 1_{eq}

$\Delta G = 9.4$ kJ/mol

TS 1_{ax}

$\Delta G = 157.4$ kJ/mol

observations might be useful for further study on catalytic activity of chalcogen bond donors.

EXPERIMENTAL

Electrospray ionization (ESI) mass spectra were obtained on Bruker maXis spectrometer equipped with an ESI source. The instrument was operated in positive ion mode using an *m/z* range of 50−1200. The nebulizer and drying gas flows were set to 1.0 bar and 4.0 L/min, respectively. For high resolution electrospray ionization (HRESI+), the studied compounds were dissolved in MeOH. ^{1}H and ^{13}C{^{1}H} NMR spectra were measured on a Bruker Avance 400 spectrometer in $(CD_3)_2CO$ at 298 K; the residual solvent signal was used as the internal standard. Melting points were determined using a Stuart SMP30 instrument.

X-Ray diffraction studies. Crystallographic data for crystal 1^{OTf} grown from $(CD_3)_2CO$ were obtained using a SuperNova, Single source at offset/far, HyPix3000 diffractometer, which is equipped with a monochromatic micro-focus CuK_α X-ray source. The crystal was maintained at 100 K during the data collection. Crystal structure was solved using the ShelXT [24] structure solution program and refined using the ShelXL [24] structure refinement program incorporated in the Olex2 [25] software package. All crystallographic data for this work can be obtained free of charge from the Cambridge Crystallographic Database (CCDC 2290261).

Computational details. The full geometry optimization procedure for all model structures was carried out at the ωB97XD/6-31+G* level of theory with the help of the Gaussian-09 software package [26]. No symmetry restrictions were applied during the geometry optimization procedure. The Hessian matrices were calculated analytically for all optimized model structures to prove the location of the correct minimum or saddle point on the potential energy surface (no imaginary frequencies or only one imaginary frequency corresponding to transition state were found, respectively).

Synthesis of 1^{OTf}. $Cu(OTf)_2$ (7 mg, 0.02 mmol) was added to the stirred solution of diphenyliodonium triflate (167 mg, 0.390 mmol) and thianthrene (101 mg, 0.466 mmol) in 1,2-dichloroethane (3 mL) and the resulting mixture was stirred at 130°C for 15 min. After that the solvent was evaporated in vacuum at 50°C and the crude material was crystallized using EtOAc (2 mL), filtered off, washed with EtOAc (2×1 mL) and dried at 65°C in air. Yield 90% (153 mg), colorless crystalline solid, mp 202–205°C (decomp.). ^{1}H NMR spectrum (400.13 MHz), δ, ppm: 8.60 d (2H, Ar, $^3J_{HH}$ = 7.9 Hz), 8.01 d. d (2H, Ar, $^3J_{HH}$ = 7.9 Hz), 7.92 t. d (2H, Ar, $^3J_{HH}$ = 7.7, $^4J_{HH}$ = 1.3 Hz), 7.84 t. d (2H, Ar, $^3J_{HH}$ = 7.7, $^4J_{HH}$ = 1.3 Hz), 7.60–7.56 m (1H, Ar), 7.51–7.47 m (2H, Ar), 7.25–7.23 (m, 2H, Ar). ^{13}C{^{1}H} NMR spectrum (101.61 MHz), δ_C, ppm: 136.5, 135.4, 135.2, 132.8, 130.6, 130.5, 130.0, 128.0, 124.4, 119.0 (Ar), 121.5 q (CF$_3$, $^1J_{CF}$ = 322.3 Hz). Mass spectrum (HRMS ESI-TOF), *m/z*: 293.0460 (calcd for $C_{18}H_{13}S_2^+$: 293.0454).

ACKNOWLEDGMENTS

FUNDING

CONFLICT OF INTEREST

The authors declare no conflict of interest.

REFERENCES

1. Alvarez, E.M., Plutschack, M.B., Berger, F., and Ritter, T., *Org. Lett.,* 2020, vol. 22, p. 4593. https://doi.org/10.1021/acs.orglett.0c00982

2. Tian, Z.Y., Lin, Z.H., and Zhang, C.P., *Org. Lett.,* 2021, vol. 23, p. 4400. https://doi.org/10.1021/acs.orglett.1c01322

3. Zhao, B., Wang, Q., Zhu, T., Feng, B., and Ma, M., *Org. Lett.,* 2022, vol. 24, p. 5608. https://doi.org/10.1021/acs.orglett.2c02328

4. Zhang, J. and Wu, X.F., *Org. Lett.,* 2023, vol. 25, p. 2162. https://doi.org/10.1021/acs.orglett.3c00792

5. Zhang, J., Wang, L.C., Bao, Z.P., and Wu, X.F., *Chem. Sci.,* 2023, vol. 14, p. 7637. https://doi.org/10.1039/d3sc02402d

6. Roberts, R.A., Metze, B.E., Nilova, A., and Stuart, D.R., *J. Am. Chem. Soc.,* 2023, vol. 145, p. 3306. https://doi.org/10.1021/jacs.2c13007

7. Gu, X.-W., Zhao, Y.-H., and Wu, X.-F., *Green Chem.,* 2023, vol. 25, p. 6282. https://doi.org/10.1039/d3gc02052e

8. Li, J., Chen, J., Sang, R., Ham, W.S., Plutschack, M.B., Berger, F., Chabbra, S., Schnegg, A., Genicot, C., and Ritter, T., *Nat. Chem.,* 2020, vol. 12, p. 56. https://doi.org/10.1038/s41557-019-0353-3

9. Gleiter, R., Haberhauer, G., Werz, D.B., Rominger, F., and Bleiholder, C., *Chem. Rev.,* 2018, vol. 118, p. 2010. https://doi.org/10.1021/acs.chemrev.7b00449

10. Scilabra, P., Terraneo, G., and Resnati, G., *Acc. Chem. Res.,* 2019, vol. 52, p. 1313. https://doi.org/10.1021/acs.accounts.9b00037

11. Ho, P.C., Szydlowski, P., Sinclair, J., Elder, P.J., Kubel, J., Gendy, C., Lee, L.M., Jenkins, H., Britten, J.F., Morim, D.R., and Vargas-Baca, I., *Nat. Commun.,* 2016, vol. 7, p. 11299. https://doi.org/10.1038/ncomms11299

12. Kremer, A., Fermi, A., Biot, N., Wouters, J., and Bonifazi, D., *Chem. Eur. J.,* 2016, vol. 22, p. 5665. https://doi.org/10.1002/chem.201504328

13. Il'in, M.V., Novikov, A.S., and Bolotin, D.S., *J. Org. Chem.,* 2022, vol. 87, p. 10199. https://doi.org/10.1021/acs.joc.2c01141

14. Benz, S., Lopez-Andarias, J., Mareda, J., Sakai, N., and Matile, S., *Angew. Chem. Int. Ed.,* 2017, vol. 56, p. 812. https://doi.org/10.1002/anie.201611019

15. Zhu, H., Zhou, P. P., and Wang, Y., *Nat. Commun.,* 2022, vol. 13, p. 3563. https://doi.org/10.1038/s41467-022-31293-5

16. Sysoeva, A.A., Novikov, A.S., Il'in, M.V., and Bolotin, D.S., *Catal. Sci. Technol.,* 2023, vol. 13, p. 3375. https://doi.org/10.1039/d3cy00071k

17. Cavallo, G., Metrangolo, P., Milani, R., Pilati, T., Priimagi, A., Resnati, G., and Terraneo, G., *Chem. Rev.,* 2016, vol. 116, p. 2478. https://doi.org/10.1021/acs.chemrev.5b00484

18. Gilday, L.C., Robinson, S.W., Barendt, T.A., Langton, M.J., Mullaney, B.R., and Beer, P.D., *Chem. Rev.,* 2015, vol. 115, p. 7118. https://doi.org/10.1021/cr500674c

19. Il'in, M.V., Sysoeva, A.A., Novikov, A.S., Bolotin, D.S., *J. Org. Chem.,* 2022, vol. 87, p. 4569. https://doi.org/10.1021/acs.joc.1c02885

20. Sysoeva, A.A., Novikov, A.S., Il'in, M.V., Suslonov, V.V., and Bolotin, D.S., *Org. Biomol. Chem.,* 2021, vol. 19, p. 7611. https://doi.org/10.1039/d1ob01158h

21. Rowe, I. and Post, B., *Acta Crystallogr.* 1958, vol. 11, p. 372. https://doi.org/10.1107/s0365110x58000992

22. Bolotin, D.S., Il'in, M.V., Suslonov, V.V., and Novikov, A.S., *Symmetry* 2020, vol. 12, p. 637. https://doi.org/10.3390/sym12040637

23. Bondi, A., *J. Phys. Chem. (A)*, 1964, vol. 68, p. 441. https://doi.org/10.1021/j100785a001

24. Sheldrick, G.M., *Acta Crystallogr. (A)*, 2015, vol. 71, p. 3. https://doi.org/10.1107/S2053273314026370

25. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J., Howard, J.A.K., and Puschmann, H., *J. Appl. Crystallogr.*, 2009, vol. 42, p. 339. https://doi.org/10.1107/S0021889808042726

26. Frisch, M.J., Trucks, G.W., Schlegel, H.B., Scuseria, G.E., Robb, M.A., Cheeseman, J.R., Scalmani, G., Barone, V., Petersson, G.A., Nakatsuji, H., Li, X., Caricato, M., Marenich, A.V., Bloino, J., Janesko, B.G., Gomperts, R., Mennucci, B., Hratchian, H.P., Ortiz, J.V., Izmaylov, A.F.,

Sonnenberg, J.L., Williams, Ding, F., Lipparini, F., Egidi, F., Goings, J., Peng, B., Petrone, A., Henderson, T., Ranasinghe, D., Zakrzewski, V.G., Gao, J., Rega, N., Zheng, G., Liang, W., Hada, M., Ehara, M., Toyota, K., Fukuda, R., Hasegawa, J., Ishida, M., Nakajima, T., Honda, Y., Kitao, O., Nakai, H., Vreven, T., Throssell, K., Montgomery, J.A., Jr., Peralta, J.E., Ogliaro, F., Bearpark, M.J., Heyd, J.J., Brothers, E.N., Kudin, K.N., Staroverov, V.N., Keith, T.A., Kobayashi, R., Normand, J., Raghavachari, K., Rendell, A.P., Burant, J.C., Iyengar, S.S., Tomasi, J., Cossi, M., Millam, J.M., Klene, M., Adamo, C., Cammi, R., Ochterski, J.W., Martin, R.L., Morokuma, K., Farkas, O., Foresman, J.B., and Fox, D.J., Gaussian 16 Rev. C.01, Wallingford, CT, 2016.

Publisher's Note. Pleiades Publishing remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.