Supporting Information:

Electron delocalisation in conjugated sulfur heterocycles probed by resonant Auger spectroscopy

Jessica B. Martins,[*,†] Carlos E. V. de Moura,[‡] Gildas Goldsztejn,[¶] Oksana Travnikova,[§,‖] Renaud Guillemin,[§,‖] Iyas Ismail,[§,‖] Loïc Journel,[§,‖] Dimitrios Koulentianos,[§,⊥] Mario Barbatti,[#,@] Alexsandre F. Lago,[△] Denis Céolin,[‖] Maria Luiza M. Rocco,[▽] Ralph Püttner,[††] Maria Novella Piancastelli,[§,‡‡] Marc Simon,[§,‖] and Tatiana Marchenko[*,§,‖]

†*Sorbonne Université, CNRS, UMR 7614, Laboratoire de Chimie Physique-Matière et Rayonnement, F-75005 Paris, France.*

‡*Department of Chemistry and Biochemistry, The Ohio State University, Columbus, Ohio 43210, United States of America.*

¶*ISMO, CNRS, Université Paris-Saclay, 91405 Orsay, France.*

§*Sorbonne Université, CNRS, UMR 7614, Laboratoire de Chimie Physique-Matière et Rayonnement, F-75005 Paris, France.*

‖*Synchrotron SOLEIL, L'Orme des Merisiers, Saint-Aubin, France.*

⊥*Department of Physics, University of Gothenburg, Origovägen 6B, SE-412 96 Gothenburg, Sweden.*

#*Aix-Marseille University, CNRS, ICR, Marseille, France.*

@*Institut Universitaire de France, 75231 Paris, France.*

△*Centro de Ciências Naturais e Humanas, Universidade Federal do ABC (UFABC), 09210-580, Santo André, São Paulo, Brazil.*

▽*Instituto de Química, Universidade Federal do Rio de Janeiro, Rio de Janeiro 21941-909, Brazil.*

††*Fachbereich Physik, Freie Universität Berlin, D-14195 Berlin, Germany.*

‡‡*Department of Physics and Astronomy, Uppsala University, SE-751 20 Uppsala, Sweden.*

E-mail: martinsbjessica@gmail.com; tatiana.marchenko@sorbonne-universite.fr

Table of Contents

1 Atomic coordinates **S-3**

1.1 Thiophene (C_4H_4S) . . . S-3
1.2 Thiazole (C_3H_3NS) . . . S-3
1.3 Thiolane (C_4H_8S): envelope enantiomer (C_S) . . . S-3
1.4 Thiolane (C_4H_8S): twisted enantiomer (C_2) . . . S-4
1.5 Atomic Numbering . . . S-4

2 Molecular Orbitals **S-5**

2.1 Thiophene (C_4H_4S) . . . S-5
2.1.1 Ground State at RHF level . . . S-5
2.1.2 Ground State at CASSCF level . . . S-5
2.1.3 S 1s Excited State B_1 at IS-MCSCF level . . . S-5
2.1.4 S 1s Excited State B_2 at IS-MCSCF level . . . S-5
2.2 Thiazole (C_3H_3NS) . . . S-5
2.2.1 Ground State at RHF level . . . S-5
2.2.2 Ground State at CASSCF level . . . S-5
2.2.3 S 1s Excited State A' at IS-MCSCF level . . . S-6
2.2.4 S 1s Excited State A'' at IS-MCSCF level . . . S-6
2.3 Thiolane (C_4H_8S): envelope enantiomer (C_S) . . . S-6
2.3.1 Ground State at RHF level . . . S-6
2.3.2 Ground State at CASSCF level . . . S-6
2.3.3 S 1s Excited State A'' at IS-MCSCF level . . . S-6
2.3.4 S 1s Excited State A' at IS-MCSCF level . . . S-6
2.4 Thiolane (C_4H_8S): twisted enantiomer (C_2) . . . S-7
2.4.1 Ground State at RHF level . . . S-7
2.4.2 Ground State at CASSCF level . . . S-7
2.4.3 S 1s Excited State B at IS-MCSCF level . . . S-7
2.4.4 S 1s Excited State A at IS-MCSCF level . . . S-7

3 Natural Bond Orbitals Analysis **S-8**

3.1 NBO Results for Thiolane in the envelope enantiomeric form (C_S) . . . S-8
3.2 NBO Results for hyperconjugation interactions . . . S-8
3.3 NBO Orbital Energy Differences . . . S-9
3.4 Off-Diagonal NBO Fock Matrix elements . . . S-10

1 Atomic coordinates

All geometries were optimized at the second-order Møller–Plesset perturbation theory (MP2) level of theory using the aug-cc-pCVTZ-DK. The optimized Cartesian geometry (in Å) is given below.

1.1 Thiophene (C_4H_4S)

S	0.000000000000	0.000000000000	1.189455000000
C	0.000000000000	1.235991000000	-0.006416000000
C	0.000000000000	0.711333000000	-1.266678000000
C	0.000000000000	-0.711333000000	-1.266678000000
C	0.000000000000	-1.235991000000	-0.006416000000
H	0.000000000000	2.272899000000	0.284702000000
H	0.000000000000	1.315539000000	-2.161781000000
H	0.000000000000	-1.315539000000	-2.161781000000
H	0.000000000000	-2.272899000000	0.284702000000

1.2 Thiazole (C_3H_3NS)

C	-0.029117143510	1.230250919559	0.000000000000
C	-1.294760425589	0.711255592189	0.000000000000
H	0.218944539938	2.290361040790	0.000000000000
H	-2.239936830616	1.257914517777	0.000000000000
S	1.174521703420	-0.009948747855	0.000000000000
C	-0.099748814013	-1.207170769507	0.000000000000
N	-1.321325559214	-0.697522083156	0.000000000000
H	0.070495704022	-2.284659640211	0.000000000000

1.3 Thiolane (C_4H_8S): envelope enantiomer (C_S)

S	-0.586090000000	-1.153394000000	0.000000000000
C	0.264076000000	-0.183227000000	1.281221000000
H	-0.260072000000	-0.302291000000	2.230058000000
H	1.281479000000	-0.562423000000	1.400480000000
C	0.264076000000	1.269039000000	0.776771000000
H	-0.630064000000	1.774248000000	1.143102000000
H	1.128466000000	1.802740000000	1.177625000000
C	0.264076000000	-0.183227000000	-1.281221000000
H	-0.260072000000	-0.302291000000	-2.230058000000
H	1.281479000000	-0.562423000000	-1.400480000000
C	0.264076000000	1.269039000000	-0.776771000000
H	-0.630064000000	1.774248000000	-1.143102000000
H	1.128466000000	1.802740000000	-1.177625000000

1.4 Thiolane (C_4H_8S): twisted enantiomer (C_2)

S	0.000000000000	0.000000000000	-1.234075676045
C	1.330248506536	-0.187406857579	0.013731300901
H	1.644013826977	-1.232183002915	0.049175445674
H	2.185457876429	0.423255850869	-0.283206784382
C	0.722158508350	0.250365611037	1.347262674846
H	1.296525236537	-0.143168850102	2.190247384468
H	0.737037436408	1.342705780907	1.413465437568
C	-0.722158508350	-0.250365611037	1.347262674846
H	-0.737037436408	-1.342705780907	1.413465437568
H	-1.296525236537	0.143168850102	2.190247384468
C	-1.330248506536	0.187406857579	0.013731300901
H	-1.644013826977	1.232183002915	0.049175445674
H	-2.185457876429	-0.423255850869	-0.283206784382

1.5 Atomic Numbering

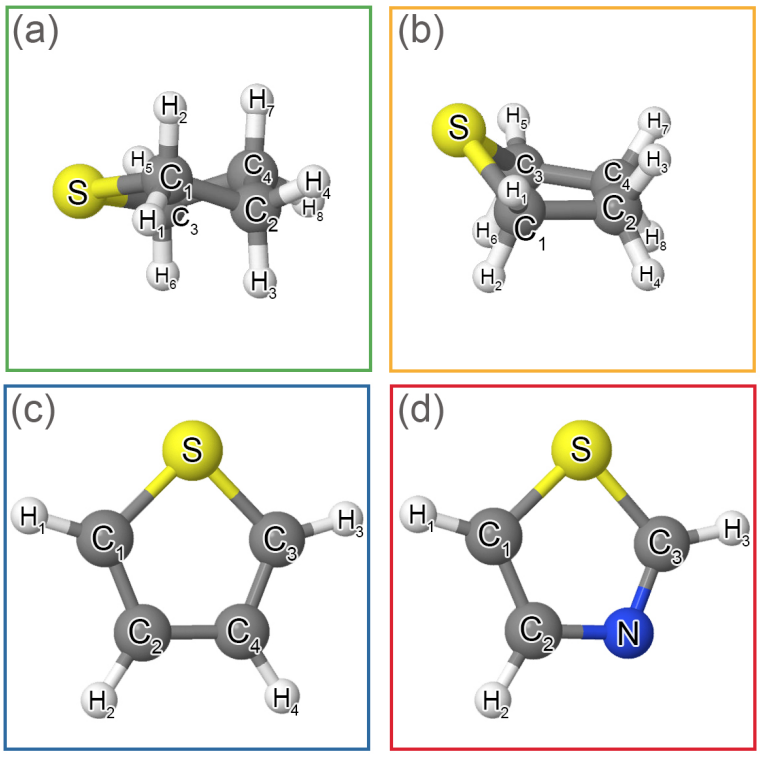

Figure S1: Molecular geometries and atom numbering for thiolane in (a) twisted and (b) envelope conformations, (c) thiophene, and (d) thiazole.

2 Molecular Orbitals

Molecular orbitals, at Restricted Hartree-Fock (RHF) level and natural orbitals, at Complete Active Space Self-Consistent Field (CASSCF) and Inner-Shell Multiconfigurational Self-Consistent Field (IS-MCSCF) level, using the aug-cc-pCVTZ-DK.

2.1 Thiophene (C_4H_4S)

2.1.1 Ground State at RHF level

$1a_1^{(2.0)}$ $1b_2^{(2.0)}$ $2a_1^{(2.0)}$ $3a_1^{(2.0)}$ $2b_2^{(2.0)}$ $4a_1^{(2.0)}$ $3b_2^{(2.0)}$ $1b_1^{(2.0)}$ $5a_1^{(2.0)}$ $6a_1^{(2.0)}$ $4b_2^{(2.0)}$ $7a_1^{(2.0)}$
$5b_2^{(2.0)}$ $8a_1^{(2.0)}$ $6b_2^{(2.0)}$ $9a_1^{(2.0)}$ $10a_1^{(2.0)}$ $2b_1^{(2.0)}$ $11a_1^{(2.0)}$ $7b_2^{(2.0)}$ $3b_1^{(2.0)}$ $1a_2^{(2.0)}$

2.1.2 Ground State at CASSCF level

$1a_1^{(2.0)}$ $1b_2^{(2.0)}$ $2a_1^{(2.0)}$ $3a_1^{(2.0)}$ $2b_2^{(2.0)}$ $4a_1^{(2.0)}$ $3b_2^{(2.0)}$ $1b_1^{(2.0)}$ $5a_1^{(2.0)}$ $6a_1^{(2.0)}$ $4b_2^{(2.0)}$ $7a_1^{(2.0)}$
$5b_2^{(2.0)}$ $8a_1^{(2.0)}$ $6b_2^{(2.0)}$ $9a_1^{(2.0)}$
$10a_1^{(1.996)}$ $2b_1^{(1.982)}$ $11a_1^{(1.976)}$ $7b_2^{(1.970)}$ $3b_1^{(1.951)}$ $1a_2^{(1.919)}$ $4b_1^{(0.089)}$ $2a_2^{(0.057)}$ $8b_2^{(0.033)}$ $12a_1^{(0.026}$

2.1.3 S 1s Excited State B_1 at IS-MCSCF level

$1a_1^{(1.0)}$ $1b_2^{(2.0)}$ $2a_1^{(2.0)}$ $3a_1^{(2.0)}$ $2b_2^{(2.0)}$ $4a_1^{(2.0)}$ $3b_2^{(2.0)}$ $1b_1^{(2.0)}$ $5a_1^{(2.0)}$ $6a_1^{(2.0)}$ $4b_2^{(2.0)}$ $7a_1^{(2.0)}$
$5b_2^{(2.0)}$ $8a_1^{(2.0)}$ $6b_2^{(2.0)}$ $9a_1^{(2.0)}$
$10a_1^{(1.997)}$ $2b_1^{(1.996)}$ $11a_1^{(1.976)}$ $7b_2^{(1.971)}$ $3b_1^{(1.956)}$ $1a_2^{(1.964)}$ $4b_1^{(1.010)}$ $2a_2^{(0.052)}$ $8b_2^{(0.033)}$ $12a_1^{(0.024)}$

2.1.4 S 1s Excited State B_2 at IS-MCSCF level

$1a_1^{(2.0)}$ $1b_2^{(2.0)}$ $2a_1^{(2.0)}$ $3a_1^{(2.0)}$ $2b_2^{(2.0)}$ $4a_1^{(2.0)}$ $3b_2^{(2.0)}$ $1b_1^{(2.0)}$ $5a_1^{(2.0)}$ $6a_1^{(2.0)}$ $4b_2^{(2.0)}$ $7a_1^{(2.0)}$
$5b_2^{(2.0)}$ $8a_1^{(2.0)}$ $6b_2^{(2.0)}$ $9a_1^{(2.0)}$
$10a_1^{(1.999)}$ $2b_1^{(1.993)}$ $11a_1^{(1.983)}$ $7b_2^{(1.985)}$ $3b_1^{(1.945)}$ $1a_2^{(1.897)}$ $4b_1^{(0.106)}$ $2a_2^{(0.059)}$ $8b_2^{(0.995)}$ $12a_1^{(0.037)}$

2.2 Thiazole (C_3H_3NS)

2.2.1 Ground State at RHF level

$1a'^{(2.0)}$ $2a'^{(2.0)}$ $3a'^{(2.0)}$ $4a'^{(2.0)}$ $5a'^{(2.0)}$ $6a'^{(2.0)}$ $7a'^{(2.0)}$ $8a'^{(2.0)}$ $1a''^{(2.0)}$ $9a'^{(2.0)}$ $10a'^{(2.0)}$
$11a'^{(2.0)}$ $12a'^{(2.0)}$ $13a'^{(2.0)}$ $14a'^{(2.0)}$ $15a'^{(2.0)}$ $16a'^{(2.0)}$ $2a''^{(2.0)}$ $17a'^{(2.0)}$ $18a'^{(2.0)}$ $3a''^{(2.0)}$ $4a''^{(2.0)}$

2.2.2 Ground State at CASSCF level

$1a'^{(2.0)}$ $2a'^{(2.0)}$ $3a'^{(2.0)}$ $4a'^{(2.0)}$ $5a'^{(2.0)}$ $6a'^{(2.0)}$ $7a'^{(2.0)}$ $8a'^{(2.0)}$ $1a''^{(2.0)}$ $9a'^{(2.0)}$ $10a'^{(2.0)}$
$11a'^{(2.0)}$ $12a'^{(2.0)}$ $13a'^{(2.0)}$ $14a'^{(2.0)}$ $15a'^{(2.0)}$
$16a'^{(1.996)}$ $2a''^{(1.982)}$ $17a'^{(1.975)}$ $18a'^{(1.969)}$ $3a''^{(1.943)}$ $4a''^{(1.912)}$
$5a''^{(0.093)}$ $6a''^{(0.069)}$ $19a'^{(0.034)}$ $20a'^{(0.026)}$

2.2.3 S 1s Excited State A' at IS-MCSCF level

$1a'^{(1.0)}$ $2a'^{(2.0)}$ $3a'^{(2.0)}$ $4a'^{(2.0)}$ $5a'^{(2.0)}$ $6a'^{(2.0)}$ $7a'^{(2.0)}$ $8a'^{(2.0)}$ $1a''^{(2.0)}$ $9a'^{(2.0)}$ $10a'^{(2.0)}$
$11a'^{(2.0)}$ $12a'^{(2.0)}$ $13a'^{(2.0)}$ $14a'^{(2.0)}$ $15a'^{(2.0)}$
$16a'^{(1.993)}$ $2a''^{(1.992)}$ $17a'^{(1.986)}$ $18a'^{(1.981)}$ $3a''^{(1.936)}$ $4a''^{(1.892)}$
$5a''^{(0.110)}$ $6a''^{(0.072)}$ $19a'^{(0.997)}$ $20a'^{(0.040)}$

2.2.4 S 1s Excited State A'' at IS-MCSCF level

$1a'^{(1.0)}$ $2a'^{(2.0)}$ $3a'^{(2.0)}$ $4a'^{(2.0)}$ $5a'^{(2.0)}$ $6a'^{(2.0)}$ $7a'^{(2.0)}$ $8a'^{(2.0)}$ $1a''^{(2.0)}$ $9a'^{(2.0)}$ $10a'^{(2.0)}$
$11a'^{(2.0)}$ $12a'^{(2.0)}$ $13a'^{(2.0)}$ $14a'^{(2.0)}$ $15a'^{(2.0)}$
$16a'^{(1.991)}$ $2a''^{(1.997)}$ $17a'^{(1.976)}$ $18a'^{(1.972)}$ $3a''^{(1.969)}$ $4a''^{(1.954)}$
$5a''^{(1.01)}$ $6a''^{(0.067)}$ $19a'^{(0.037)}$ $20a'^{(0.025)}$

2.3 Thiolane (C_4H_8S): envelope enantiomer (C_S)

2.3.1 Ground State at RHF level

$1a'^{(2.0)}$ $1a''^{(2.0)}$ $2a'^{(2.0)}$ $3a'^{(2.0)}$ $2a''^{(2.0)}$ $4a'^{(2.0)}$ $3a''^{(2.0)}$ $5a'^{(2.0)}$ $6a'^{(2.0)}$
$7a'^{(2.0)}$ $4a''^{(2.0)}$ $8a'^{(2.0)}$ $9a'^{(2.0)}$ $5a''^{(2.0)}$ $10a'^{(2.0)}$ $11a'^{(2.0)}$ $6a''^{(2.0)}$ $12a'^{(2.0)}$
$7a''^{(2.0)}$ $13a'^{(2.0)}$ $8a''^{(2.0)}$ $9a''^{(2.0)}$ $14a'^{(2.0)}$ $15a'^{(2.0)}$

2.3.2 Ground State at CASSCF level

$1a'^{(2.0)}$ $1a''^{(2.0)}$ $2a'^{(2.0)}$ $3a'^{(2.0)}$ $2a''^{(2.0)}$ $4a'^{(2.0)}$ $3a''^{(2.0)}$ $5a'^{(2.0)}$ $6a'^{(2.0)}$ $7a'^{(2.0)}$
$4a''^{(2.0)}$ $8a'^{(2.0)}$ $9a'^{(2.0)}$ $5a''^{(2.0)}$ $10a'^{(2.0)}$ $11a'^{(2.0)}$ $6a''^{(2.0)}$ $12a'^{(2.0)}$ $7a''^{(2.0)}$ $8a''^{(2.0)}$
$13a'^{(1.999)}$ $9a''^{(1.972)}$ $14a'^{(1.997)}$ $15a'^{(1.976)}$ $10a''^{(0.031)}$ $16a'^{(0.024)}$

2.3.3 S 1s Excited State A'' at IS-MCSCF level

$1a'^{(1.0)}$ $1a''^{(2.0)}$ $2a'^{(2.0)}$ $3a'^{(2.0)}$ $2a''^{(2.0)}$ $4a'^{(2.0)}$ $3a''^{(2.0)}$ $5a'^{(2.0)}$ $6a'^{(2.0)}$ $7a'^{(2.0)}$
$4a''^{(2.0)}$ $8a'^{(2.0)}$ $9a'^{(2.0)}$ $5a''^{(2.0)}$ $10a'^{(2.0)}$ $11a'^{(2.0)}$ $6a''^{(2.0)}$ $12a'^{(2.0)}$ $7a''^{(2.0)}$ $8a''^{(2.0)}$
$13a'^{(1.999)}$ $9a''^{(1.988)}$ $14a'^{(1.999)}$ $15a'^{(1.977)}$ $10a''^{(0.999)}$ $16a'^{(0.035)}$

2.3.4 S 1s Excited State A' at IS-MCSCF level

$1a'^{(1.0)}$ $1a''^{(2.0)}$ $2a'^{(2.0)}$ $3a'^{(2.0)}$ $2a''^{(2.0)}$ $4a'^{(2.0)}$ $3a''^{(2.0)}$ $5a'^{(2.0)}$ $6a'^{(2.0)}$ $7a'^{(2.0)}$
$4a''^{(2.0)}$ $8a'^{(2.0)}$ $9a'^{(2.0)}$ $5a''^{(2.0)}$ $10a'^{(2.0)}$ $11a'^{(2.0)}$ $6a''^{(2.0)}$ $12a'^{(2.0)}$ $7a''^{(2.0)}$ $8a''^{(2.0)}$
$13a'^{(1.999)}$ $9a''^{(1.989)}$ $14a'^{(1.999)}$ $15a'^{(1.988)}$ $10a''^{(0.024)}$ $16a'^{(1.000)}$

2.4 Thiolane (C_4H_8S): twisted enantiomer (C_2)

2.4.1 Ground State at RHF level

$1a^{(2.0)}$ $1b^{(2.0)}$ $2a^{(2.0)}$ $3a^{(2.0)}$ $2b^{(2.0)}$ $4a^{(2.0)}$ $3b^{(2.0)}$ $5a^{(2.0)}$ $4b^{(2.0)}$ $6a^{(2.0)}$ $5b^{(2.0)}$ $7a^{(2.0)}$
$6b^{(2.0)}$ $8a^{(2.0)}$ $7b^{(2.0)}$ $9a^{(2.0)}$ $10a^{(2.0)}$ $8b^{(2.0)}$ $9b^{(2.0)}$ $11a^{(2.0)}$ $12a^{(2.0)}$ $10b^{(2.0)}$ $13a^{(2.0)}$ $11b^{(2.0)}$

2.4.2 Ground State at CASSCF level

$1a^{(2.0)}$ $1b^{(2.0)}$ $2a^{(2.0)}$ $3a^{(2.0)}$ $2b^{(2.0)}$ $4a^{(2.0)}$ $3b^{(2.0)}$ $5a^{(2.0)}$ $4b^{(2.0)}$ $6a^{(2.0)}$ $5b^{(2.0)}$ $7a^{(2.0)}$
$6b^{(2.0)}$ $8a^{(2.0)}$ $7b^{(2.0)}$ $9a^{(2.0)}$ $10a^{(2.0)}$ $8b^{(2.0)}$ $9b^{(2.0)}$ $11a^{(2.0)}$
$10b^{(1.999)}$ $12a^{(1.997)}$ $13a^{(1.975)}$ $11b^{(1.972)}$ $12b^{(0.031)}$ $14a^{(0.026)}$

2.4.3 S 1s Excited State B at IS-MCSCF level

$1a^{(1.0)}$ $1b^{(2.0)}$ $2a^{(2.0)}$ $3a^{(2.0)}$ $2b^{(2.0)}$ $4a^{(2.0)}$ $3b^{(2.0)}$ $5a^{(2.0)}$ $4b^{(2.0)}$ $6a^{(2.0)}$ $5b^{(2.0)}$ $7a^{(2.0)}$
$6b^{(2.0)}$ $8a^{(2.0)}$ $7b^{(2.0)}$ $9a^{(2.0)}$ $10a^{(2.0)}$ $8b^{(2.0)}$ $9b^{(2.0)}$ $11a^{(2.0)}$
$10b^{(1.999)}$ $12a^{(1.999)}$ $13a^{(1.976)}$ $11b^{(1.987)}$ $12b^{(0.999)}$ $14a^{(0.038)}$

2.4.4 S 1s Excited State A at IS-MCSCF level

$1a^{(1.0)}$ $1b^{(2.0)}$ $2a^{(2.0)}$ $3a^{(2.0)}$ $2b^{(2.0)}$ $4a^{(2.0)}$ $3b^{(2.0)}$ $5a^{(2.0)}$ $4b^{(2.0)}$ $6a^{(2.0)}$ $5b^{(2.0)}$ $7a^{(2.0)}$
$6b^{(2.0)}$ $8a^{(2.0)}$ $7b^{(2.0)}$ $9a^{(2.0)}$ $10a^{(2.0)}$ $8b^{(2.0)}$ $9b^{(2.0)}$ $11a^{(2.0)}$
$10b^{(2.000)}$ $12a^{(1.999)}$ $13a^{(1.987)}$ $11b^{(1.989)}$ $12b^{(0.024)}$ $14a^{(1.00)}$

3 Natural Bond Orbitals Analysis

Calculations were done using the Inner-Shell approach for Restricted Open-Shell Hartree-Fock method (IS-ROHF). The basis set aug-cc-pCVTZ-DK and 4^{th} order Douglas-Kroll-Hess (DKH) relativistic corrections were applied.

3.1 NBO Results for Thiolane in the envelope enantiomeric form (C_S)

Table S1: Results from Second-order Perturbation Theory Analysis of Fock Matrix in NBO Basis. Stabilisation energies $\Delta E^{(2)}$ for the hyperconjugation interactions in eV. Symmetrically equivalent NBO interactions are omitted due to redundancy.

Molecule	NBO Orbital		Stabilisation Energy $\Delta E^{(2)}$				
	Donor	Acceptor	Ground	S $1s^{-1}\sigma^*$	S $2p_x^{-1}p_z^{-1}\sigma^*$	S $2p_x^{-1}p_y^{-1}\sigma^*$	S $2p_y^{-1}p_z^{-1}\sigma^*$
Thiolane	σ_{C1-H1}	σ^*_{S-C1}	0.02	0.07	0.20	0.28	0.26
envelope	σ_{C1-C2}	σ^*_{S-C1}	<0.01	0.05	0.14	0.13	0.12
C_4H_8S (C_s)	σ_{C2-C4}	σ^*_{S-C1}	0.16	0.18	0.25	0.25	0.26

3.2 NBO Results for hyperconjugation interactions

Table S2: Results from the Second-order Perturbation Theory Analysis of Fock Matrix in NBO Basis. Stabilisation energies $\Delta E^{(2)}$ for the hyperconjugation interactions in eV. Symmetrically equivalent NBO interactions are omitted due to redundancy.

Molecule	NBO Orbital		Stabilisation Energy $\Delta E^{(2)}$				
	Donor	Acceptor	Ground	S $1s^{-1}\sigma^*$	S $2p_x^{-1}p_z^{-1}\sigma^*$	S $2p_x^{-1}p_y^{-1}\sigma^*$	S $2p_y^{-1}p_z^{-1}\sigma^*$
Thiophene C_4H_4S	np_S (sp^2)	σ^*_{C1-C2}	0.14	0.13	0.09	0.10	0.09
Thiazole	np_S (sp^2)	σ^*_{C1-C2}	0.12	0.12	0.08	0.09	0.08
C_3H_3NS	np_S (sp^2)	σ^*_{C3-N}	0.14	0.10	0.07	0.07	0.07
Thiolane C_4H_8S (C_2)	np_S (sp^2)	σ^*_{C1-C2}	0.06	0.05	0.03	0.03	0.03
Thiolane C_4H_8S (C_s)	np_S (sp^2)	σ^*_{C1-C2}	0.05	0.04	0.02	0.02	0.02

3.3 NBO Orbital Energy Differences

Table S3: Orbital Energy Differences ($\epsilon_a - \epsilon_d$) for the Second-order Perturbation Theory Analysis of Fock Matrix in NBO Basis (in Hartree). Symmetrically equivalent NBO interactions are omitted due to redundancy.

Molecule	NBO Orbital		Orbital Energy Differences $\epsilon_a - \epsilon_d$				
	Donor	Acceptor	Ground	S $1s^{-1}$V	S $2p_x^{-1}p_z^{-1}$V	S $2p_x^{-1}p_y^{-1}$V	S $2p_y^{-1}p_z^{-1}$V
Thiophene C_4H_4S	np_S	π^*_{C1-C2}	0.48	0.65	0.84	0.83	0.84
	π_{C3-C4}	π^*_{C1-C2}	0.53	0.50	0.52	0.52	0.52
	σ_{C1-H1}	σ^*_{S-C1}	1.19	1.05	0.97	0.97	0.96
	σ_{C1-C2}	σ^*_{S-C1}	1.42	1.27	1.20	1.20	1.19
	σ_{C2-H2}	σ^*_{S-C1}	1.16	1.02	0.93	0.92	0.92
Thiazole C_3H_3NS	np_S	π^*_{C1-C2}	0.58	0.68	0.86	0.86	0.87
	np_S	π^*_{C3-N}	0.46	0.58	0.75	0.75	0.76
	π_{C3-N}	π^*_{C1-C2}	0.58	0.56	0.58	0.58	0.57
	π_{C1-C2}	π^*_{C3-N}	0.51	0.45	0.45	0.45	0.45
	σ_{C1-H1}	σ^*_{S-C1}	1.20	1.04	0.97	0.96	0.96
	σ_{C3-H3}	σ^*_{S-C3}	1.18	1.00	0.91	0.90	0.90
	σ_{C1-C2}	σ^*_{S-C1}	1.42	1.27	1.21	1.21	1.21
	σ_{C3-N}	σ^*_{S-C3}	1.54	1.35	1.26	1.26	1.24
	σ_{C2-H2}	σ^*_{S-C1}	1.17	1.02	0.94	0.93	0.93
	np_N	σ^*_{S-C3}	0.98	0.81	0.72	0.71	0.70
Thiolane twisted C_4H_8S (C_2)	σ_{C1-H1}	σ^*_{S-C1}	1.07	0.93	0.85	0.92	0.76
	σ_{C1-C2}	σ^*_{S-C1}	1.19	1.04	0.96	1.01	0.88
	σ_{C2-H4}	σ^*_{S-C1}	1.06	0.91	0.80	0.73	0.73
Thiolane envelope C_4H_8S (C_s)	σ_{C1-H1}	σ^*_{S-C1}	1.08	0.94	0.86	0.81	0.76
	σ_{C1-C2}	σ^*_{S-C1}	1.19	1.04	0.96	0.92	0.88
	σ_{C2-C4}	σ^*_{S-C1}	1.06	0.91	0.80	0.76	0.73

3.4 Off-Diagonal NBO Fock Matrix elements

Table S4: Off-Diagonal NBO Fock Matrix elements for the Second-order Perturbation Theory Analysis of Fock Matrix in NBO Basis (in Hartree). Symmetrically equivalent NBO interactions are omitted due to redundancy.

Molecule	NBO Orbital		Off-Diagonal NBO Fock Matrix elements F_{da}				
	Donor	Acceptor	Ground	S $1s^{-1}V$	S $2p_x^{-1}p_z^{-1}V$	S $2p_x^{-1}p_y^{-1}V$	S $2p_y^{-1}p_z^{-1}V$
Thiophene C_4H_4S	np_S	π^*_{C1-C2}	0.127	0.075	0.060	0.060	0.064
	π_{C3-C4}	π^*_{C1-C2}	0.112	0.100	0.092	0.093	0.093
	σ_{C1-H1}	σ^*_{S-C1}	< 0.010	0.037	0.059	0.063	0.063
	σ_{C1-C2}	σ^*_{S-C1}	< 0.010	0.027	0.051	0.047	0.049
	σ_{C2-H2}	σ^*_{S-C1}	0.067	0.072	0.079	0.082	0.082
Thiazole C_3H_3NS	np_S	π^*_{C1-C2}	0.121	0.074	0.061	0.061	0.065
	np_S	π^*_{C3-N}	0.146	0.086	0.074	0.075	0.080
	π_{C3-N}	π^*_{C1-C2}	0.134	0.134	0.132	0.132	0.133
	π_{C1-C2}	π^*_{C3-N}	0.103	0.067	0.062	0.063	0.063
	σ_{C1-H1}	σ^*_{S-C1}	0.014	0.035	0.057	0.061	0.061
	σ_{C3-H3}	σ^*_{S-C3}	0.027	0.048	0.068	0.072	0.077
	σ_{C1-C2}	σ^*_{S-C1}	< 0.010	0.031	0.055	0.051	0.052
	σ_{C3-N}	σ^*_{S-C3}	< 0.010	0.034	0.054	0.050	0.051
	σ_{C2-H2}	σ^*_{S-C1}	0.063	0.066	0.074	0.076	0.071
	np_N	σ^*_{S-C3}	0.112	0.117	0.131	0.136	0.136
Thiolane twisted C_4H_8S (C_2)	σ_{C1-H1}	σ^*_{S-C1}	0.019	0.040	0.063	0.069	0.067
	σ_{C1-C2}	σ^*_{S-C1}	0.012	0.036	0.058	0.056	0.056
	σ_{C2-H4}	σ^*_{S-C1}	0.058	0.064	0.072	0.073	0.074
Thiolane envelope C_4H_8S (C_s)	σ_{C1-H1}	σ^*_{S-C1}	0.018	0.038	0.063	0.068	0.067
	σ_{C1-C2}	σ^*_{S-C1}	0.011	0.034	0.056	0.055	0.056
	σ_{C2-C4}	σ^*_{S-C1}	0.056	0.061	0.068	0.070	0.074