Supporting Information

Intermolecular Sulfur•••Oxygen interactions: Theoretical and Statistical Investigations.

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1.Figure S1. A figure showing the result of noncovalent interaction (NCI) analysis on the thiazole and N-methylacetamide model system.

2.Table S1. This table is the comparison of different QM methods with different basis sets. The local Møller-Plesset second-order perturbation theory (LMP2) method reduces the basis set superposition errors that can arise from the canonical MP2 method.[1] The basis sets used were and 6-311++G**[2–5] and aug-cc-pVTZ[6–9].

3.Table S2. This table presents the dipole moments of the three different sulfur-containing aromatic rings.

4.Table S3. A table summarizing the result of distance scan in detail.

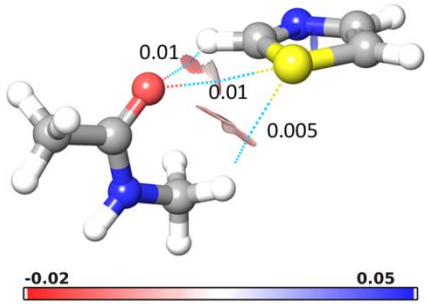

Figure S1. NCI results. When a bonding interaction truly exists between atoms, a bond critical point (where the electron density is a minimum at some point along a line between two atoms, but is a maximum in both directions perpendicular to the bond.) forms between them. The interactions are represented in an NCI plot as small isosurfaces of low density gradient, colored to show that the interactions are favorable. The color gradient from red to blue represents the interaction strength mapped on the isosurfaces (units: electron/bohr**3). The blue isosurface in the direction perpendicular to the thiazole-ring represent the ring critical point.

Table S1. Interaction energies of thiazole-C5 and backbone complex at different levels of theory.

Basis sets	QM Method	Δ E[a](kJ/mol)	dS⋯O(pm)	αC(ar)-S-O,deg	αS-O-C(BB),deg
6-311++G**	B3LYP-D3	-21.5	359	143.0	131.1
	M06-2X-D3	-22.8	306	158.4	136.0
	LMP2[b]	-11.3	349	158.2	115.1
6-31++G**	B3LYP-D3	-21.3	346	150.6	131.3
	M06-2X-D3	-22.6	305	159.4	136.0
aug-cc-PVTZ	M06-2X-D3	-22.4	312	156.8	83.3

[a]. Interaction energies with BSSEs corrected using the counterpoise method. [b]. Bond angles of S⋯O-C(BB) is restricted to 180° in this model system.

Table S2. Dipole moments of the three sulfur-containing aromatic rings.[a]

Dipole	Thiophene	Thiazole	Thiadizole
Dipole (in AU):	0.201	0.678	1.396
Dipole Moments from quantum mechanical wavefunction (Debye)	0.512	1.724	3.548
Dipole Moments from electrostatic potential charges (Debye)	0.453	1.723	3.440

[a]. All dipole moments are calculated at M06-2X-D3/6-31++G** using Jaguar 8.5.

Table S3. The optimal distances, complex formation energies and areas of distance tolerance.

complex	ΔE at optimal distance (kJ/mol)	dS···O/H (pm)	dS···O where ΔE drops 100% (pm)	Areas of tolerance (pm)	
				where ΔE drops below 50%	where ΔE is greater than 11.5 kJ/mol
Thiophene	-23.5	326	273	285-425	284-430
Thiazole-C2	-24.3	320	267	280-430	278-430
Thiazole-C5	-24.1	308	253	266-420	264-420
Thiadiazole	-28.5	304	248	261-430	258-450
MMFF[a]	-10.0	355	302	302-430	N/A
Context	-11.5	240	N/A	N/A	N/A

[a]. The result of distance scan on the thiadiazole model system at MMFF[10–14] level.

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