Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information for "The halogen bond in thiirane□ClF: An example of a Mulliken inner complex"

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Computational Details

Geometry optimisations and single-point energy calculations were carried out at the CCSD(T)-F12b[1] level of theory with the 3C(FIX) ansatz using the MOLPRO package of *ab initio* programs.[2] For the geometry optimisations the basis set used was aug-cc-pV(T+d)Z,[3] which includes an additional 'tight'-d function for Cl and S, and is equivalent to aug-cc-pVTZ for all other elements in the current investigation.[4] Additional single point energy calculations on these optimised geometries were carried out using the aug-cc-pV(Q+d)Z basis in order to estimate the complete basis set limit *via* extrapolation (see below). The implementation of the explicitly correlated coupled cluster method in MOLPRO uses a number of auxiliary basis sets to speed up integral evaluation; the cc-pV*n*Z/JKFIT[5] set was used for the Fock matrix, aug-cc-pV*n*Z/MP2FIT[6] for the two-electron repulsion integrals and aug-cc-pV*n*Z/OPTRI[7] in the CABS[8] procedure for many-electron integrals arising from F12 theory. The geminal Slater exponent was set to 1.2 a_0^{-1} for the TZ calculations and 1.4 a_0^{-1} for QZ. The basis set extrapolation used a Schwenke-type formula:[9]

$$E_{\mathrm{CBS}} = \left(E_{\mathrm{QZ}} - E_{\mathrm{TZ}}\right)F + E_{\mathrm{TZ}} \ .$$

As they converge at different rates, the CCSD-F12b (F = 1.416422) and (T) correlation energies (F = 1.663388) were extrapolated separately.[10] Counterpoise correction was used in the calculation of the resulting interaction energies,[11] where the monomers are frozen in their interacting geometries. The sum of the results was then added to the Hartree-Fock/aug-cc-pV(Q+d)Z energy, including CABS relaxation.

NBO charge/population analysis calculations were carried out using the NBO6[12] program interfaced to MOLPRO, with an MP2/aug-cc-pV(T+d)Z wavefunction. NBO second order perturbation theory analysis was carried out at the same level of theory, but using the NBO6 program interfaced to Gaussian09.[13] The SAPT[14] calculations used the SAPT2+(3)δMP2/aug-cc-pV(T+d)Z level,[15] which includes a counterpoise corrected MP2 level correction to the induction contribution that has recently been shown to work well for a large number of non-covalent interactions.[15] All SAPT calculations were carried out with the Psi4 (beta 5) program,[16] using density fitting and MP2 natural orbitals.[17] The individual SAPT terms were collected into the so-called chemist's grouping:

$$E_{\mathrm{electrostatic}} = E^{(10)}_{\mathrm{elst}} + E^{(12)}_{\mathrm{elst,\,resp}} + E^{(13)}_{\mathrm{elst,\,resp}}$$

$$E_{\mathrm{exchange}} = E^{(10)}_{\mathrm{exch}} + E^{(11)}_{\mathrm{exch}} + E^{(12)}_{\mathrm{exch}}$$

$$E_{\mathrm{induction}} = E^{(20)}_{\mathrm{ind,\,resp}} + E^{(20)}_{\mathrm{exch\text{-}ind,\,resp}} + E^{(30)}_{\mathrm{ind}} + E^{(30)}_{\mathrm{exch\text{-}ind}} + {}^{t}E^{(22)}_{\mathrm{ind}} + {}^{t}E^{(22)}_{\mathrm{exch\text{-}ind}} + \delta E^{(3)}_{\mathrm{HF}} + \left[\delta E_{\mathrm{MP2}}\right]$$

$$E_{\mathrm{dispersion}} = E^{(20)}_{\mathrm{disp}} + E^{(30)}_{\mathrm{disp}} + E^{(21)}_{\mathrm{disp}} + E^{(22)}_{\mathrm{disp}} + E^{(20)}_{\mathrm{disp\text{-}exch}}$$

The SAPT charge transfer energy was evaluated using the method of Stone and Misquitta, where the induction (and exchange-induction) term in the monomer basis is subtracted from that in the dimer basis.[18] The δE_{MP2} correction was not applied to any energies in this step.

NBO Atomic natural charges (NPA)

Atom	Thiirane□ClF	Thiirane□HCl	Oxirane□ClF	Oxirane□HCl
[S,O]	0.29054	0.11877	–0.51284	–0.52041
C[a]	–0.46139	–0.46475	–0.08517	–0.08750
H[b]	0.23344	0.21648	0.18673	0.18331
H[c]	0.22222	0.22284	0.18364	0.18789
[Cl,H]	0.17525	0.24642	0.34148	0.27683
[F,Cl]	–0.45433	–0.31434	–0.39904	–0.32384

[a] Both C atoms are equivalent by symmetry.
[b] Two H atoms equivalent.
[c] Two H atoms equivalent.

Optimised geometries

CCSD(T)-F12b/aug-cc-pV(T+d)Z optimised geometries from MOLPRO:

Thiirane□ClF:

9

CCSD(T)-F12B/AVTZ+D ENERGY=-1035.69345044

S	1.3441975452	-0.4290048683	0.0000000000
C	1.4292092994	1.2292635659	0.7407555412
C	1.4292092994	1.2292635659	-0.7407555412
H	0.5160372615	1.5117139725	1.2478434962
H	2.3566950759	1.4395846375	1.2553129151
H	0.5160372615	1.5117139725	-1.2478434962
H	2.3566950759	1.4395846375	-1.2553129151
Cl	-1.1365254215	-0.5227422038	0.0000000000
F	-2.8543463972	-0.4529332793	0.0000000000

Thiirane□HCl:

9

CCSD(T)-F12B/AVTZ+D ENERGY=-936.60578351

S	-1.2062862599	0.8026999473	0.0000000000
C	-1.2080310969	-0.8607450475	0.7406689795
C	-1.2080310969	-0.8607450475	-0.7406689795
H	-2.1243664165	-1.1198565624	-1.2527629857
H	-0.2877751560	-1.1287262874	-1.2435049960
H	-0.2877751560	-1.1287262874	1.2435049960
H	-2.1243664165	-1.1198565624	1.2527629857
H	1.0442218567	0.6180923762	0.0000000000
Cl	2.2258767420	0.0710184713	0.0000000000

Oxirane□ClF:

9

CCSD(T)-F12B/AVTZ+D ENERGY=-713.05549502

O	-0.8901774938	-1.1253244879	0.0000000000
C	-0.0176370668	-2.0058521037	0.7317370939
C	-0.0176370668	-2.0058521037	-0.7317370939
H	0.7821590547	-1.4997546518	1.2583626585
H	-0.5338064496	-2.7920990048	1.2672407785
H	0.7821590547	-1.4997546518	-1.2583626585
H	-0.5338064496	-2.7920990048	-1.2672407785
Cl	0.0251472051	1.0746265714	0.0000000000
F	0.7492262120	2.5614684369	0.0000000000

Oxirane□HCl:

9

CCSD(T)-F12B/AVTZ+D ENERGY=-613.97408789

O	0.9977426480	0.0000000000	-0.7781675103
C	1.5579625206	-0.7314170737	0.3286154689
C	1.5579625206	0.7314170737	0.3286154689
H	2.4668283799	1.2674240244	0.0884179582
H	0.8259971970	1.2563381812	0.9310545530
H	0.8259971970	-1.2563381812	0.9310545530
H	2.4668283799	-1.2674240244	0.0884179582
H	-0.7550032963	0.0000000000	-0.5094601895
Cl	-1.9474555466	0.0000000000	0.0168857400

Absolute energies

Absolute CCSD(T)-F12b energies (hartree) obtained directly from MOLPRO.

Thiirane□ClF:
TZ = -1035.693450
QZ = -1035.727135
Thiirane TZ dimer basis = -476.230268
Thiirane QZ dimer basis = -476.243514
ClF TZ dimer basis = -559.443061
ClF QZ dimer basis = -559.462873
Thiirane TZ own basis = -476.229996
Thiirane QZ own basis = -476.243442
ClF TZ own basis = -559.442642
ClF QZ own basis = -559.462673

Thiirane□HCl:
TZ = -936.605784
QZ = -936.627789
Thiirane TZ dimer basis = -476.230476
Thiirane QZ dimer basis = -476.243725
HCl TZ dimer basis = -460.365311
HCl QZ dimer basis = -460.373851
Thiirane TZ own basis = -476.230214
Thiirane QZ own basis = -476.243654
HCl TZ own basis = -460.365004
HCl QZ own basis = -460.373730

Oxirane□ClF:
TZ = -713.055495
QZ = -713.090915
Oxirane TZ dimer basis = -153.597220
Oxirane QZ dimer basis = -153.612413
ClF TZ dimer basis = -559.446246
ClF QZ dimer basis = -559.466174
Oxirane TZ own basis = -153.597088
Oxirane QZ own basis = -153.612361
ClF TZ own basis = -559.445898
ClF QZ own basis = -559.466002

Oxirane□HCl:
TZ = -613.974088
QZ = -613.998005
Oxirane TZ dimer basis = -153.597272
Oxirane QZ dimer basis = -153.612442
HCl TZ dimer basis = -460.365290
HCl QZ dimer basis = -460.373823
Oxirane TZ own basis = -153.597088
Oxirane QZ own basis = -153.612361
HCl TZ own basis = -460.364965

HCl QZ own basis = -460.373692

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