Electronic Supplementary Information

An expanded halogen bonding scale using astatine

Lu Liu, Seyfeddine Rahali, Rémi Maurice, Cecilia Gomez-Pech, Gilles Montavon, Jean-Yves Le Questel, Jérôme Graton, Julie Champion* and Nicolas Galland*

Contents

1. Experimental Procedures

1.1 Chemical materials

All chemicals are commercially available. Unless stated, they are of analytical grade or better. Sodium iodide (Sigma Aldrich), cyclohexane (Sigma Aldrich), heptane (Sigma Aldrich), 70% perchloric acid (Sigma Aldrich), cyclohexanone (Aldrich, 99%), *N,N,N',N'*-tetramethylurea (Acros Organics, 99.0%), dimethyl selenide (Alfa Aesar, 99%), (1*R*)-(–)-thiocamphor (Combi-Blocks, 95%), *N,N,N',N'*-tetramethylthiourea (Alfa Aesar, 98%), *N,N*-dimethylacetamide (Sigma Aldrich, 99.95%) and *N,N*-dimethylcyanamide (Sigma Aldrich, 99%) were used as received, while *N,N*-dimethylthioacetamide (Kodak) was purified by sublimation before using. All solutions were freshly prepared using Milli-Q deionized water and all experiments were performed in air-conditioned laboratories (21 ± 3 °C).

1.2 Production of ^{211}At

^{211}At was produced through the ^{209}Bi(α, 2n)^{211}At nuclear reaction at the ARRONAX cyclotron (Nantes, France). ^{209}Bi targets were irradiated by alpha external beams accelerated and downgraded to 28.6 MeV. After irradiation, astatine was extracted and purified by a dry distillation method[1], and finally was recovered in chloroform with a specific activity close to 500 MBqmL^{-1}.

1.3 Liquid/liquid competition experiments

The liquid/liquid competition method is based on the variation of astatine radioactivity distribution between two immiscible liquid phases as a function of the experimental conditions, to evidence the change of astatine speciation. According to the investigated Lewis base, cyclohexane (for cyclohexanone, dimethyl selenide, *N,N*-dimethylcyanamide, *N,N*-dimethylacetamide) and *N,N,N',N'*-tetramethylthiourea or heptane (for *N,N,N',N'*-tetramethylurea, (1*R*)-(–)-thiocamphor and *N,N*-dimethylthioacetamide) were chosen as organic solvents because they are immiscible in water and were previously used to establish the pK_{BI2} scale.[2] The ligands were initially added in pre-equilibrated (with 0.1 molL^{-1} $HClO_4$) solvent. The aqueous phase was composed of a 0.1 molL^{-1} $HClO_4$ with 0.1 or 0.01 molL^{-1} NaI solution. Astatine was recovered in aqueous medium after back-extractions in 1.5 mL of 0.1 molL^{-1} NaOH solutions, At$^+$ stock solution was then obtained in 0.1 molL^{-1} $HClO_4$/$NaClO_4$ solution (pH = 1.0 ± 0.2, E = 0.60 ± 0.04 *vs*. NHE), in accordance with the established Pourbaix diagram of astatine.[3] The At$^+$ solution was introduced into the I$^-$ one so that the AtI and AtI_2^- species were formed under the applied I$^-$ concentrations.[4] Finally, 2 mL of the organic phase and 4 mL of the aqueous phase were put together in a Pyrex tube (with radioactivity about 1 kBq), and were shaken for 2 hours to reach the reaction equilibrium. The two phases were then separated and 1 mL of aliquot of each phase was taken to measure their radioactivity by a liquid scintillation counter. The pH and the potential of the aqueous solution were systematically measured at equilibrium after separation. In a series of experiments, the NaI concentration was fixed while the initial ligand concentration in the organic phase increased. All experiments were repeated twice under the same experimental conditions with different astatine sources.

1.4 Analytic tools

- Liquid scintillation counting

The radioactivity in solution samples were measured using a Packard 2550 TR/AB Liquid Scintillation analyzer and the Ultima Gold LLT scintillation liquid. The quenching caused by different media was considered to determine the astatine activity (*A*) according to the following equation:

$$A = A_{\mathrm{mes}} \times (8.1063 \times 10^{-10} \times tSIE^3 - 1.7581 \times 10^{-6} \times tSIE^2 + 0.0012 \times tSIE + 0.7299)$$

with A_{mes} being the activity measured by a liquid scintillation counter and *tSIE* being the transformed Spectral Index of External standard defined by the apparatus for counting efficiency determination.

- Total organic carbon measurement

The distribution of ligands in the studied biphasic system was checked with a total organic carbon (TOC) meter (Shimadzu TOC V CSH). The measurements were performed in the same experimental conditions as the liquid/liquid competition experiments, but without the presence of astatine. The organic carbon concentration in the aqueous phase being measured, the ligand concentration can be deduced. The distribution coefficient of ligand (D_1) at equilibrium can be obtained using the following equation:

$$D_1 = \frac{1-2k}{k} \quad (1)$$

with *k* being the fitted slope for the detected ligand concentration in the aqueous phase as a function of the initial ligand concentration in solvent.

- pH / potential measurement

An electrode (Inlab) freshly calibrated with standard pH buffers (pH 4.00 and 7.00, Merck) and a Pt combined redox electrode (Metrohm) calibrated with a redox buffer ($Fe(SCN)_6^{3-}$/$Fe(SCN)_6^{4-}$, 220 mV/Pt/SCE, Radiometer Analytical) were used to measure the pH and the potential E of the aqueous phase at equilibrium, respectively.

1.5 Modeling of experimental data

The distribution ratio of At (*D*) is defined as:

$$D = \frac{A_{org} \times V_{aq}}{A_{aq} \times V_{org}} \quad (2)$$

where V_{org} and V_{aq} represent the volume of organic phase and aqueous phase respectively, and A_{org} and A_{aq} define the total astatine activities in these two phases at equilibrium. Uncertainties associated with D were calculated according to the following equation:

$$\sigma_D = D \times \sqrt{\frac{\sigma^2_{Aorg}}{A^2_{org}} + \frac{\sigma^2_{Aaq}}{A^2_{aq}} + \frac{\sigma^2_{Vorg}}{V^2_{org}} + \frac{\sigma^2_{Vaq}}{V^2_{aq}}} \quad (3)$$

D is plotted as a function of the initial concentration of Lewis base in the organic phase. The objective is to reproduce the experimental curves displaying D variations by a thermodynamic model considering the chemical equilibria occurring in the biphasic system. Under experimental conditions, the equilibrium between AtI and AtI_2^- is ruling the astatine speciation in the aqueous phase. It is described by equation (4), and the associated formation constant was previously determined.[4]

$$AtI + I^- \overset{K}{\rightleftharpoons} AtI_2^- \qquad K = \frac{[AtI_2^-]}{[AtI] \times [I^-]} = 10^{2.7 \pm 0.3} \quad (4)$$

Note that in the analysis, since the ionic strength is nonzero in the aqueous phase, this constant is corrected ("deextrapolated") by the actual ionic strength of the sample using the Davies equation[5].

Between the two phases, the partitions of ligand B and AtI are taken into account *via* equilibria (5) and (6), overlined species relating to the organic phase. D_1 has been determined from TOC measurements ($10^{0.37 \pm 0.02}$ for cyclohexanone, $10^{-0.91 \pm 0.02}$ for *N,N,N',N'*-tetramethylurea, $10^{-0.37 \pm 0.02}$ for *N,N*-dimethylacetamide, $10^{3.61 \pm 0.22}$ for (1*R*)-(–)-thiocamphor, $10^{-0.13 \pm 0.01}$ for *N,N*-dimethylthioacetamide, $10^{-0.37 \pm 0.04}$ for *N,N,N',N'*-tetramethylthiourea and $10^{1.40 \pm 0.16}$ for dimethyl selenide; *N,N*-dimethylcyanamide was found to be totally back-extracted in the aqueous phase), while D_2 is a parameter adjusted during the fitting process.

$$B \overset{D_1}{\rightleftharpoons} \overline{B} \qquad D_1 = \frac{[\overline{B}]}{[B]} \quad (5)$$

$$AtI \overset{D_2}{\rightleftharpoons} \overline{AtI} \qquad D_2 = \frac{[\overline{AtI}]}{[AtI]} \quad (6)$$

In the organic phase, the expected formation of halogen bonded complex is considered *via* equation (7).

$$\overline{B} + \overline{AtI} \overset{K_{BAtI}}{\rightleftharpoons} \overline{BAtI} \qquad K_{BAtI} = \frac{[\overline{BAtI}]}{[\overline{B}] \times [\overline{AtI}]} \quad (7)$$

Based on equilibria (4)–(7), an analytical expression of D was derived as a function of the equilibrium constants and the experimental conditions, denoted model 1.

Model 1
$$D = \frac{D_2 + K_{BAtI} \times D_2 \times [\overline{B}] \times D_1/(D_1+2)}{1 + K \times [I^-]} \quad (8)$$

Model 1 is successfully applied to fit the results for cyclohexanone, *N,N,N',N'*-tetramethylurea and (1*R*)-(–)-thiocamphor. However, the cases of *N,N*-dimethylthioacetamide, dimethyl selenide and *N,N,N',N'*-tetramethylthiourea show a different behavior, already characterized in a previous work.[6] Within the investigated ligand concentration range, the formed complex in the organic phase is also present in the aqueous phase *via* equilibrium (9). Model 2 below considers this additional equilibrium.

$$BAtI \overset{D_3}{\rightleftharpoons} \overline{BAtI} \qquad D_3 = \frac{[\overline{BAtI}]}{[BAtI]} \quad (9)$$

Model 2
$$D = \frac{D_2 + K_{BAtI} \times D_2 \times [\overline{B}] \times D_1/(D_1+2)}{1 + K \times [I^-] + K_{BAtI} \times D_2/D_3 \times [\overline{B}] \times D_1/(D_1+2)} \quad (10)$$

Origin 9.0 was used to fit the experimental data according to the expressions of D in order to determine the unknown parameters. The parameter values and the associated standard errors were determined by the software. The details of determined parameters are presented in Table S2. For each Lewis base, two K_{BatI} values can be obtained by fitting the experimental points corresponding to a given initial I^- concentration with two repetitions, the four values being used to compute an average K_{BAtI} value and the standard deviation.

2. Computational Procedures

2.1 Quantum mechanical calculations

The two-component relativistic density functional theory, which was proved to be accurate for investigating At-containing systems,[7,8] requires to replace the orbital representation by spinors that are complex vector functions of two components (2c). The Generalized Kohn-Sham (GKS) method, implemented in the Gaussian 16 rev. A.03 program,[9] takes advantages of relativistic pseudo-potentials containing scalar and spin-dependent terms to treat the electron correlation and the relativistic effects on an equal footing. In this work, we opted for the global hybrid B3LYP and PW6B95 functionals.[10,11] The small core pseudo-potentials ECP*n*MDF with n = 60, 28 and 10 were used for the At, I and Se atoms, respectively.[12,13] Two sets of basis functions were used for describing the explicitly treated electrons. The AVDZ set of double zeta quality, selected solely for the geometry optimizations and subsequent numerical frequency calculations, combines the aug-cc-pVDZ-PP basis sets[12,14] supplemented with two-component extensions for the At[15] and I[16] atoms, the aug-cc-pVDZ-PP basis set for the Se and Br atoms,[14] and the cc-pVDZ basis sets for the remaining atoms,

augmented with diffuse functions for non-H atoms.[17–19] The TZVPD set of triple zeta quality, used solely for single-point energy calculations on previously optimized geometries, combines the dhf-TZVPD-2c basis sets for the At and I atoms,[20] and the def2-TZVP basis sets for the remaining atoms,[21] with diffuse functions being added for non-H atoms.[22] Energies of the halogen bonded complexes were corrected from the basis set superposition error using the counterpoise method.[23]

2.2 Thermodynamic analysis

For each species, its Gibbs free energy is estimated using (i) the energy computed with one DFT functional (B3LYP or PW6B95) and the TZVPD basis set, and (ii) the thermodynamic corrections from the frequency calculation performed with the same functional and the AVDZ basis set. Note that some species exhibit several competitive conformers/isomers (see, for instance, the case of dimethyl sulfide, Fig. S5), their Gibbs free energies have been then evaluated using a Boltzmann distribution:

$$G_{\{x\}} = -RT \sum_{i \in \{x\}} \exp(-G_i/RT) \tag{11}$$

where the summation runs over all the conformers/isomers of the *x* species.

Some of us have previously shown that the equilibrium constants K_{BAtI} can be accurately calculated, provided that isodesmic-like reactions such as (12) are considered to take profit of error cancellations.

$$B_1AtI + B_2 \rightleftharpoons B_1 + B_2AtI \tag{12}$$

When the complexation constant K_{B_1AtI} between AtI and the B_1 Lewis base is accurately known (from experiment), or its value arbitrarily fixed, the computation of the equilibrium constant K_{exc} of the exchange reaction (12) readily leads to the complexation constant of AtI with the B_2 Lewis base according to the equation (13):

$$\log K_{B_2AtI} = \log K_{exc} + \log K_{B_1AtI} \tag{13}$$

The computation of K_{exc} benefits from partial error cancellations between the species belonging to the left-hand side and the right-hand side of reaction (12). Indeed, one may expect the cancellation of bond-by-bond errors in the electron correlation/relativistic terms in the computed $\Delta G^{\circ}_{298}(12)$ free energy. Hence, it becomes possible to predict accurately the trend followed by AtI complexation constants within a series of Lewis bases.

Although the solvents in which the complexation constants are measured (cyclohexane and heptane) are non-polar, aprotic and show very small dielectric constants, we have initially assessed their effects on the computed equilibrium constants for some B···AtI systems. We opted for the implicit solvation model recommended in ref. 24, that is the UAHF-CPCM continuum model applied on HF/AVDZ wave functions for computing the solvation free energies. The influence is negligible on the trend drawn by the AtI complexation constants within the series of studied Lewis bases. For example, the difference between the K_{BAtI} values calculated for the hexamethyl benzene and the diethyl ether, 0.58 log unit at the PW6B95/TZVPD level of theory, is modified by less than 0.01 log unit. Hence, the whole set of computed K_{BAtI} values do not rely on solvation free energies. Note that few additional solvation calculations were performed to assess the influence of water as the solvent.

3. Results

3.1 Competition experiments

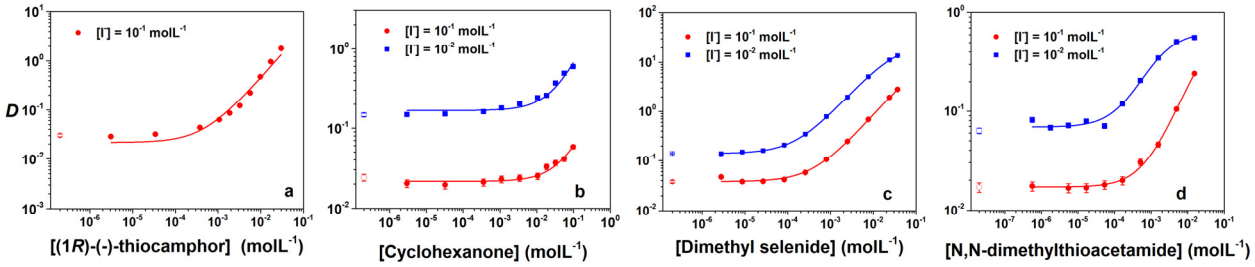


Fig. S1 Astatine distribution ratios between the organic and aqueous phases as functions of the initial ligand concentration in the organic phase and I^- concentration in the aqueous phase. The hollows symbols indicate data without ligand. (a,b) Fitting with model 1 that considers the formation of the 1:1 complex between AtI and ligand in the organic phase. (c,d) Fitting with model 2 that considers additionally the distribution of the 1:1 complex in two phases.

The results of (1*R*)-(–)-thiocamphor with the presence of 0.01 molL^{-1} I^- in the aqueous phase are not repeatable with different astatine sources, for some unclarified reasons. Since unrepeatable behaviors of *D* cannot lead to a reliable analysis, the case of 0.01 M NaI for (1*R*)-(–)-thiocamphor will not be considered. Therefore, the formation constant is obtained by the average value of four repetitions for [I^-] = 0.1 molL^{-1}. Particular attention was paid to the experiments with dimethyl selenide in order to avoid its oxidation into dimethyl selenoxide. First, the ligand solutions were prepared as fresh as possible, leading to a contacting time with the air less than 2 hours before the contact with the aqueous phase for less than 3 hours. Moreover, two series of comparison with non-fresh dimethyl selenide solutions (opened one week earlier) have shown the same results as the fresh solutions. In addition, the oxidation of Me_2Se into Me_2SeO is rather difficult according to the literature, requiring for example "30% aqueous hydrogen peroxide at −10 °C" or "ozone in chloroform at −50 °C".[25] Although OH radical can oxidize dimethyl selenide, leading to various

complexes,[26,27] it is considered unlikely given the low dose of our samples, the short contacting time with astatine solutions and the repeatable results with different astatine sources.

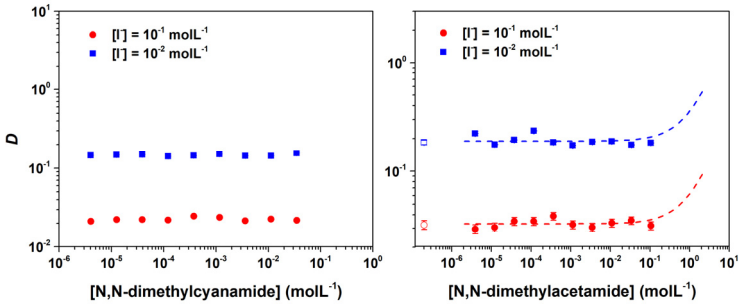


Fig. S2 Astatine distribution ratios between the organic and aqueous phases as functions of the initial ligand concentration in the organic phase and I^- concentration in the aqueous phase. The hollows symbols indicate data without ligand. Dashed lines correspond to the simulation of *D* using model 1 and considering a formation constant of $10^{0.7}$.

For the case of *N,N*-dimethylcyanamide and *N,N*-dimethylacetamide, *D* keeps unchanged within the investigated ligand concentration range. Therefore, we did not evidence the formation of XB between AtI and these ligands. For N,N-dimethylcyanamide, it is because the ligand is totally soluble in the aqueous phase according to the TOC measurements. Therefore, all possible interactions would initially occur in the aqueous phase, and astatine appears not to be extracted into the organic phase. For *N,N*-dimethylacetamide the interaction may be too weak so that the current experimental approach cannot monitor the extraction of AtI into the organic phase. However, assuming that the interaction exists (as a similarity to I_2) and using model 1, we can deduce the equilibrium constant limit. As shown in Fig. S2, the dashed lines are simulations using model 1 and supposing $K_{BAtI} = 10^{0.7}$. The simulated *D* curves present an increase just beyond the studied maximum ligand concentration. Therefore, if the interaction between AtI and *N,N*-dimethylacetamide exists, the real equilibrium constant will not be larger than $10^{0.7}$.

3.2 Formation of XBs in the aqueous phase

The At-mediated XB interactions that we discuss so far occur in an alkane solution because we can distinguish the XB formation from other equilibria of astatine only in the organic phase. However, some BAtI complexes can also be formed in the aqueous phase, according to equation (14).

$$AtI + B \overset{Kw_{BAtI}}{\rightleftharpoons} BAtI \qquad Kw_{BAtI} = \frac{[BAtI]}{[AtI][B]} \tag{14}$$

The cases of *N,N*-dimethylthioacetamide, *N,N,N',N'*-tetramethylthiourea and dimethyl selenide present the possibility to access the formation of XBs in the aqueous phase. From the former analysis, these Lewis bases present solubility in the aqueous phase (D_1 in equation 5), so do the formed XB complexes (D_3 in equation 9). Therefore, the formation constant of BAtI complex in the aqueous phase (Kw_{BAtI}) can be explained by K_{BAtI}, D_1, D_2 (distribution coefficient of AtI) and D_3 as equation (15):

$$Kw_{BAtI} = K_{BAtI} \times \frac{D_1 \times D_2}{D_3} \tag{15}$$

Model 2 of *D* can be rewritten by replacing K_{BAtI} by Kw_{BAtI} and we obtain the model 3 as equation (16).

Model 3
$$D = \frac{D_2 + D_3 \times Kw_{BAtI} \times [\bar{B}]/(D_1+2)}{1 + K \times [I^-] + Kw_{BAtI} \times [\bar{B}]/(D_1+2)} \tag{16}$$

Using model 3 to fit the experimental data for *N,N*-dimethylthioacetamide, *N,N,N',N'*-tetramethylthiourea and dimethyl selenide, we can finally obtain Kw_{BAtI} values while maintaining very good adjustments.

Table S1. Formation constants of AtI with different Lewis bases in the aqueous solution obtained from the distribution ratio measurements.

Lewis base	log Kw_{BAtI}[a]
N,N-dimethylthioacetamide	3.80(63)
Dimethyl selenide	3.82(12)
N,N,N',N'-tetramethylthiourea	4.40(09)

[a] For each Lewis base, two Kw_{BAtI} values can be obtained by fitting the experimental points corresponding to a given initial I^- concentration with two repetitions; the four values are used to compute an average Kw_{BAtI} value and the uncertainties given in parenthesis correspond to two standard deviations.

Despite very limited data, the log Kw_{BAtI} values follow the similar trend as the pK_{BAtI} scale (*N,N*-dimethylthioacetamide ≈ dimethyl selenide < *N,N,N',N'*-tetramethylthiourea). Moreover, the actual XB complexes are significantly stronger in the aqueous solution than the following trihalides formed from AtI: AtI_2^- (log *K* = 2.7 ± 0.3) and $IAtBr^-$ (log *K* = 1.4 ± 0.3).[4]

3.3 Supplementary parameters

Table S2. Adjustable parameters obtained from the fitting of the distribution ratio measurements with different models presented in this work for all experimental data.

Lewis base	$[I^-]$ ($molL^{-1}$)	log K_{BAtI} [a]	log Kw_{BAtI} [a]	D_2 [a]	D_3 [a]
Cyclohexanone	0.01	1.78 ± 0.14	/	0.12 ± 0.06	/
		1.75 ± 0.10	/	0.08 ± 0.04	/
	0.1	1.40 ± 0.10	/	0.37 ± 0.04	/
		1.52 ± 0.08	/	0.14 ± 0.04	/
N,N,N',N'-tetramethylurea	0.01	1.95 ± 0.10	/	-0.19 ± 0.02	/
		2.00 ± 0.04	/	-0.19 ± 0.02	/
	0.1	1.51 ± 0.10	/	0.16 ± 0.02	/
		1.58 ± 0.12	/	0.16 ± 0.02	/
(1*R*)-(–)-thiocamphor	0.1	3.29 ± 0.24	/	0.11 ± 0.22	/
		3.31 ± 0.38	/	0.14 ± 0.34	/
		3.28 ± 0.34	/	0.16 ± 0.30	/
		3.13 ± 0.18	/	0.22 ± 0.16	/
Dimethyl selenide	0.01	3.78 ± 0.04	/	-0.02 ± 0.04	1.38 ± 0.12
		3.80 ± 0.02	/	0.01 ± 0.00	1.40 ± 0.04
		/	3.78 ± 0.04	-0.02 ± 0.02	1.38 ± 0.06
		/	3.88 ± 0.18	0.00 ± 0.00	1.36 ± 0.14
	0.1	3.43 ± 0.12	/	0.30 ± 0.08	1.38 ± 0.72
		3.39 ± 0.06	/	0.38 ± 0.08	1.37 ± 0.68
		/	3.75 ± 0.36	0.30 ± 0.04	1.38 ± 0.34
		/	3.86 ± 0.08	0.36 ± 0.02	1.32 ± 0.08
N,N-dimethyl thioacetamide	0.01	4.31 ± 0.14	/	-0.30 ± 0.04	-0.20 ± 0.04
		4.23 ± 0.20	/	-0.17 ± 0.06	-0.12 ± 0.08
		/	4.08 ± 0.14	-0.30 ± 0.04	-0.20 ± 0.04
		/	4.05 ± 0.22	-0.17 ± 0.06	-0.12 ± 0.08
	0.1	3.64 ± 0.06	/	0.04 ± 0.02	-0.06 ± 0.14
		3.44 ± 0.06	/	0.19 ± 0.02	0.05 ± 0.28
		/	3.61 ± 0.18	0.04 ± 0.02	-0.06 ± 0.14
		/	3.46 ± 0.32	0.19 ± 0.02	0.05 ± 0.28
N,N,N',N'-tetramethylthiourea	0.01	5.80 ± 0.06	/	-0.04 ± 0.04	1.01 ± 0.04
		5.85 ± 0.06	/	-0.04 ± 0.04	1.01 ± 0.08
		/	4.38 ± 0.10	-0.04 ± 0.04	1.01 ± 0.06
		/	4.43 ± 0.10	-0.04 ± 0.04	1.01 ± 0.06
	0.1	5.60 ± 0.04	/	0.19 ± 0.02	1.08 ± 0.16
		5.52 ± 0.04	/	0.27 ± 0.04	0.98 ± 0.18
		/	4.34 ± 0.16	0.19 ± 0.02	1.08 ± 0.14
		/	4.44 ± 0.20	0.27 ± 0.04	0.98 ± 0.18

[a] Uncertainties correspond to two standard errors.

3.4 Theoretical calculations

Table S3. Calculated distances and angles of interaction, At–I distances and their variations upon complexation, for the most stable complex formed with the 16 ligands, at the PW6B95/AVDZ level of theory.

Ligand	Atomic site (B)	$d_{B\cdots At}$ (Å)	r_{XB} [a]	$\Theta_{B\cdots At-I}$ (°)	d_{At-I} (Å)	Δd_{At-I} (Å)
Cyclohexanone	O sp^2	2.721	0.769	179.3	2.898	0.028
N,*N*,*N*',*N*'-tetramethylurea	O sp^2	2.644	0.747	177.6	2.909	0.039
(1R)-(-)-thiocamphor	S sp^2	2.964	0.776	179.8	2.946	0.076
N,*N*-dimethyl thioacetamide	S sp^2	2.978	0.780	178.3	2.948	0.078
N,*N*,*N*',*N*'-tetramethylthiourea	S sp^2	2.966	0.776	176.4	2.962	0.092
Dimethyl selenide	Se sp^3	3.073	0.784	176.3	2.946	0.077
Toluene	C sp^2	3.187	0.857	173.7	2.892	0.022
Ethyl butanoate	O sp^2	2.792	0.789	179.8	2.885	0.016
Hexamethyl benzene	C sp^2	3.121	0.839	172.2	2.899	0.029
Diethyl ether	O sp^3	2.810	0.794	175.8	2.891	0.021
Diethyl methylphosphonate	O sp^2	2.667	0.754	178.7	2.899	0.029
Tributyl phosphate	O sp^2	2.676	0.756	178.4	2.900	0.030
Triphenylphosphine sulfide	S sp^2	2.989	0.783	179.1	2.952	0.082
Dibutyl sulfoxide	O sp^2	2.588	0.731	179.8	2.923	0.053
Diethyl sulfide	S sp^3	2.985	0.782	175.5	2.938	0.069
Tributylphosphine oxide	O sp^2	2.572	0.726	178.8	2.923	0.053

[a] Normalized interaction distance $r_{XB} = d_{int}/(r_B + r_{At})$; r_B and r_{At} are the van der Waals radii of the two involved atoms in the XB interaction.[28]

Table S4. Measured distances and angles of interaction for crystallographic complexes formed between I_2 and representative compounds of four sulphur, one selenide, and one oxygenated ligands. These data have been found in the Cambridge structural database, their corresponding refcodes being specified.[29]

Ligand	Representative (CSD refcode)	$d_{B\cdots I}$ (Å)	r_{XB} [a]	$\Theta_{B\cdots I-I}$ (°)
N,*N*-dimethyl thioacetamide	*N*-methyl-thiocaprolactam (TCAPLI)	2.687	0.711	176.2
N,*N*,*N*',*N*'-tetramethylthiourea	Thiourea (LOPQEM)	2.503	0.662	176.0
Dimethyl selenide	Dimethyl selenide (RIZMES)	2.768	0.713	174.3
Diethyl ether	1,4-dioxane (QOJKEF)	2.808	0.802	178.7
Triphenylphosphine sulfide	Triphenylphosphine sulfide (TPHPSI10)	2.729	0.722	175.3
Diethyl sulfide	1,4-dithiane (DTHINI)	2.870	0.759	177.9

[a] Normalized interaction distance $r_{XB} = d_{int}/(r_B + r_I)$; r_B and r_I are the van der Waals radii of the two involved atoms in the XB interaction.[28]

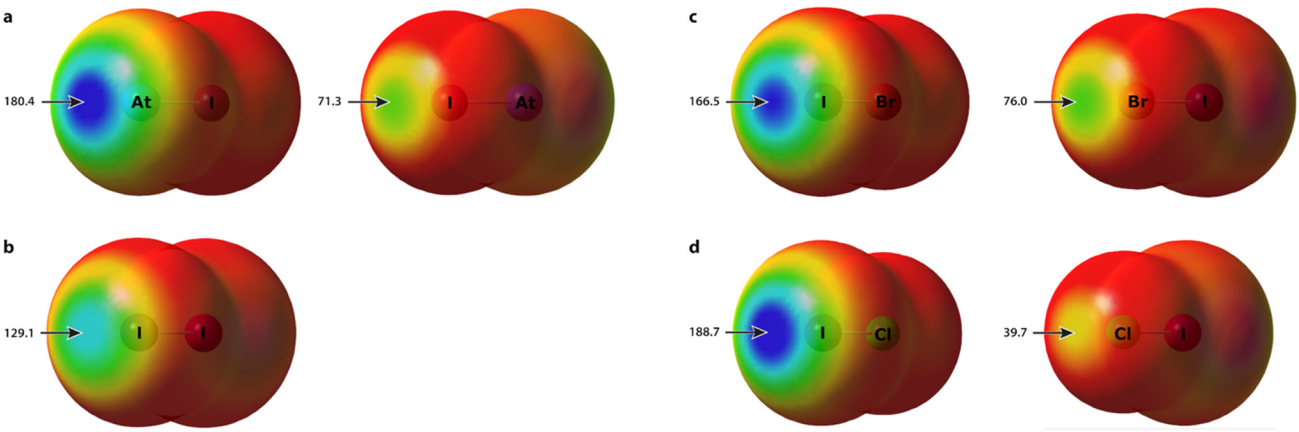


Fig. S3 Molecular electrostatic potential calculated at the PW6B95/TZVPD level of theory for (a) AtI, (b) I_2, (c) IBr and (d) ICl. The molecular surfaces were defined by isovalue of the electron density of 0.001 e $bohr^{-3}$, and the $V_{S,max}$ values are given in kJ mol^{-1}. Colour code: from red (most negative values) to blue (most positive values).

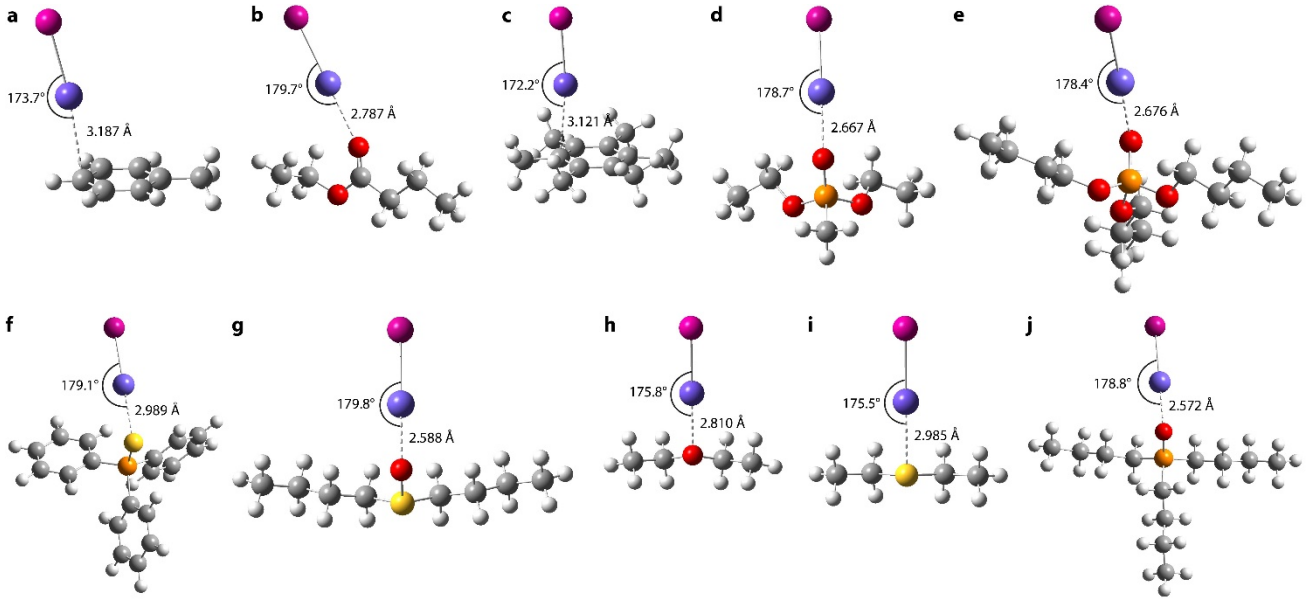
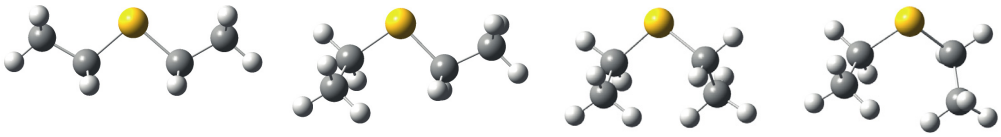


Fig. S4 Calculated structures at the PW6B95/AVDZ level of theory for the most stable conformer of each species corresponding to the interaction between AtI and toluene (a), ethyl butanoate (b), hexamethyl benzene (c), diethyl methylphosphonate (d), tributyl phosphate (e), triphenylphosphine sulfide (f), dibutyl sulfoxide (g), diethyl ether (h), diethyl sulfide (i) and tributylphosphine oxide (j). Atom's colour code: purple for At, pink for I, red for O, yellow for S, orange for P, grey for C and white for H.



14.6% (12.4%) | 60.2% (63.8%) | 10.1% (15.1%) | 15.2% (8.7%)

Fig. S5 Calculated structures of the conformers for the dimethyl sulfide at the PW6B95/AVDZ level of theory. Boltzmann populations calculated at the PW6B95/TZVPD level of theory are given in percentage (for comparison, the ones at the B3LYP/TZVPD level of theory are indicated in parentheses). Atom's colour code: yellow for S, grey for C and white for H.

3.5 Supplementary structures

Cartesian coordinates (in angstroms) calculated at the PW6B95/AVDZ level of theory for the most stable conformer of each species, the Boltzmann populations come from the PW6B95/TZVPD calculations.

Dimethyl selenide, pop=100%

Se	0.0000000000	0.0000000000	0.5826402543
C	-1.4554707326	0.0000000000	-0.7154250221
H	-1.4104540708	0.8976307433	-1.3374552299
H	-1.4104540708	-0.8976307433	-1.3374552299
H	-2.3892066927	0.0000000000	-0.1473585878
C	1.4554707326	0.0000000000	-0.7154250221
H	1.4104540709	0.8976307433	-1.3374552298
H	2.3892066927	0.0000000000	-0.1473585877
H	1.4104540709	-0.8976307433	-1.3374552298

Atl--dimethyl selenide, pop=100%

Se	-0.3817254271	-3.0614178296	-0.0000692258
C	0.8709339901	-3.3699225404	-1.4613981709
H	1.7203303313	-2.6903624137	-1.3637920229
H	1.1963280651	-4.4125971292	-1.4464985186
H	0.3331842824	-3.1605265337	-2.3885992770
C	0.8709105014	-3.3696208970	1.4613018363
H	1.7202570523	-2.6900140583	1.3636213438
H	0.3331183617	-3.1601322893	2.3884572257
H	1.1963692484	-4.4122761660	1.4465615187
At	-0.162513584	0.0042483184	0.0000211578
I	0.2351732387	2.9236410866	0.0003941330

Dibutyl sulfoxide, pop=39.1%

S	-0.4575303410	0.5687668985	-0.0000000001
O	-1.6002460256	-0.4535020350	-0.0000000002
C	0.6531871118	0.0770142347	1.3681218802
H	1.5467094906	0.7098233174	1.3007057173
H	0.9309493001	-0.9664694709	1.1793488661
C	0.6531871122	0.0770142347	-1.3681218800
H	1.5467094910	0.7098233174	-1.3007057169
H	0.9309493004	-0.9664694709	-1.1793488658
C	-0.0607062460	0.2299233360	2.6973053792
H	-1.0038929575	-0.3275765019	2.6487281152
H	-0.3246044543	1.2844464490	2.8534195043
C	-0.0607062452	0.2299233360	-2.6973053792
H	-1.0038929568	-0.3275765019	-2.6487281154
H	-0.3246044535	1.2844464490	-2.8534195043
C	0.7761527444	-0.2667978252	-3.8690065596
H	1.7271686864	0.2819851348	-3.8977983006
H	1.0358812725	-1.3204246093	-3.7022366457
C	0.7761527433	-0.2667978252	3.8690065598
H	1.7271686853	0.2819851348	3.8977983011
H	1.0358812715	-1.3204246093	3.7022366460
C	0.0610283165	-0.1214872033	5.2031016391
H	-0.8762956821	-0.6885744677	5.2098031135
H	0.6806892218	-0.4877267689	6.0276295084
H	-0.1827851308	0.9271454237	5.4074802887
C	0.0610283180	-0.1214872033	-5.2031016391
H	0.6806892235	-0.4877267689	-6.0276295082
H	-0.8762956806	-0.6885744677	-5.2098031138
H	-0.1827851292	0.9271454237	-5.4074802888

Atl--dibutyl sulfoxide, pop=42.2%

S	0.8093698427	-3.6752584152	-0.1270017303
O	1.2721607438	-2.1894977853	-0.2003154654
C	-0.4096795400	-3.7519598276	1.2277461717
H	-0.7621875164	-4.7900102504	1.2545098542
H	-1.2404414620	-3.0950021439	0.9450709335
C	-0.3408492085	-3.9091464677	-1.5232819586
H	-0.6945406331	-4.9444958676	-1.4492455247
H	-1.1827940826	-3.2266500430	-1.3589906017
C	0.2215032062	-3.3212410499	2.5379021069
H	0.6452271636	-2.3180622406	2.4088431910
H	1.0561765471	-3.9896169957	2.7863175620
C	0.3560776804	-3.6285697694	-2.8408514450
H	0.7756969385	-2.6160176558	-2.8058670576
H	1.2001891193	-4.3184988646	-2.9696546331
C	-0.5974105902	-3.7509422765	-4.0230165960
H	-1.0276604172	-4.7611229984	-4.0422397808
H	-1.4376281767	-3.0602076722	-3.8767592802
C	-0.7900682275	-3.3109636258	3.6773083331
H	-1.2236180158	-4.3136105060	3.789927992
H	-1.6199798172	-2.6437620189	3.4116775336
C	-0.1766965221	-2.8656580779	4.9952381817
H	0.2314183913	-1.8524030467	4.9154538231
H	-0.9222088797	-2.8643626073	5.796032459
H	0.6386631960	-3.5325388555	5.2971264004
C	0.0821541952	-3.4568075414	-5.350848404
H	-0.6225103446	-3.5488007058	-6.1827420131
H	0.4886674348	-2.4398978047	-5.3666812906
H	0.9096461852	-4.1513919581	-5.5338440813
At	-0.4099239095	-0.2288780979	-0.3544263092
I	-2.3032983808	1.9912113098	-0.5286480606

Triphenylphosphine sulfide, pop=100%

P	0.0000000003	0.0000000005	0.8257210186
S	0.0000000003	0.0000000005	2.7988085469
C	-0.5487625338	-2.7217166191	0.7816452861
H	-1.0066966049	-2.5212484386	1.7471458257
C	-0.5507365147	-4.0030754560	0.2437004305
H	-1.0312294761	-4.8139234935	0.7847492601
C	0.0696107980	-4.2494481817	-0.9781355320
H	0.0730756029	-5.2537487297	-1.3938545604
C	0.6955123600	-3.2120288122	-1.6613570294
H	1.1914060723	-3.4032706934	-2.6093260469
C	0.6966339443	-1.9263902892	-1.1287363983
H	1.1990773189	-1.1227115413	-1.6600361874
C	0.0694852023	-1.6781401851	0.0929117948
C	-1.4880546325	0.7788941431	0.0929117948
C	-2.0826944672	1.8361006054	0.7816452861
H	-1.6801168947	2.1324490540	1.7471458257
C	-3.1913967808	2.4784895415	0.2437004305
H	-3.6533652992	3.3000326711	0.7847492601
C	-3.7149354764	2.0644393723	-0.978135532
H	-4.5864176665	2.5635890373	-1.3938545604
C	-3.1294547291	1.0036830346	-1.6613570294
H	-3.5430219126	0.6698474228	-2.6093260469
C	-2.0166199002	0.3598924526	-1.1287363983
H	-1.5718353754	-0.4770756477	-1.6600361874
C	1.4185694310	0.8992460434	0.0929117948
C	1.3199859567	1.5664978379	-1.1287363983
H	0.3727580572	1.5997871904	-1.6600361874
C	2.4339423699	2.2083457790	-1.6613570294
H	2.3516158411	2.7334232720	-2.6093260469
C	3.6453246792	2.1850088108	-0.9781355320
H	4.5133420644	2.6901596938	-1.3938545604
C	3.7421332963	1.5245859159	0.2437004305
H	4.6845947761	1.5138908237	0.7847492601
C	2.6314570017	0.8856160151	0.7816452861
H	2.6868135004	0.3887993860	1.7471458257

Atl--triphenylphosphine sulfide, pop=100%

P	-0.2520959541	0.2021119255	2.2102622010
S	-0.5693497236	0.3254292483	0.2285316215
C	1.9909433262	1.7629329015	2.6848071985
H	1.3357703230	2.6031756252	2.4693308517
C	3.3357018433	1.9801103206	2.9515355467
H	3.7290842323	2.9928129442	2.9505391369
C	4.1778046495	0.9013579527	3.2114115308
C	3.6754379066	-0.3948387013	3.2010993902
H	4.3334942451	-1.2386094208	3.3876427356
C	2.3284961081	-0.6197401191	2.9366119821
H	1.9430463451	-1.6347522762	2.9126336839
C	1.4828097181	0.4614839115	2.6870616690
C	-1.2130832039	1.4819704018	3.0892106801
C	-2.3612781100	2.0052918902	2.4974107798
H	-2.6375795979	1.6927867328	1.4939713560
C	-3.1353765090	2.9302181694	3.1891347368
H	-4.0278197573	3.339479636	2.7238916432
C	-2.7663818484	3.3329292997	4.4685257503
H	-3.3716551970	4.0580991373	5.0058914308
C	-1.6180505674	2.8129302607	5.0587023210
H	-1.3228960436	3.1319289114	6.0545378229
C	-0.8401031441	1.8883836189	4.3723602403
H	0.0649655918	1.4980546962	4.8302285125
C	-0.7664188075	-1.3963672573	2.9228298658
C	-0.5047032484	-1.6716393909	4.2673402778
H	0.0440778540	-0.9590170572	4.8780152382
C	-0.9375622741	-2.8675532872	4.8240551150
H	-0.7300716962	-3.0835942636	5.8684206061
C	-1.6319823486	-3.7880835120	4.0423633359
H	-1.9667479638	-4.7253329282	4.4787652134
C	-1.8932628296	-3.5117777303	2.7053163528
H	-2.4292287561	-4.2312615878	2.0929084613

C	-1.4619596175	-2.3152116807	2.1416681134
H	-1.6575119491	-2.0905732327	1.0967114869
At	1.2947635320	-1.8758643873	-0.5563705293
I	3.1273611119	-4.0702532512	-1.2914138003
H	5.2313623461	1.0729824908	3.4150617315

***N,N,N',N'*-tetramethylurea, pop=100%**

C	0.0000000000	0.0000000001	-0.5605852132
O	0.0000000000	0.0000000003	-1.7858049845
N	-0.1048383246	-1.1670082657	0.1726299075
N	0.1048383246	1.1670082657	0.1726299079
C	-0.6516031569	1.3696668261	1.3926910962
H	-1.4580916772	2.0957537446	1.2175488967
H	-1.1069883254	0.4354150748	1.7207129305
H	-0.0148621441	1.7576949538	2.1977345839
C	0.3537332120	2.3718026390	-0.589244514
H	1.0421236036	2.1512070809	-1.4045654751
H	-0.5700266285	2.7837781627	-1.0205135689
H	0.7981894619	3.1221368119	0.0727186959
C	-0.3537332120	-2.3718026390	-0.5892445147
H	-0.7981894619	-3.1221368120	0.0727186949
H	-1.0421236036	-2.1512070805	-1.4045654757
H	0.5700266285	-2.7837781624	-1.0205135698
C	0.6516031569	-1.3696668266	1.3926910958
H	1.1069883254	-0.4354150754	1.7207129304
H	0.0148621441	-1.7576949545	2.1977345833
H	1.4580916772	-2.0957537450	1.2175488961

AtI--*N,N,N',N'*-tetramethylurea, pop=100%

C	0.1672680000	-0.2777570000	0.5514450000
O	0.2653890000	-0.4834040000	1.7765310000
N	0.4884180000	-1.2581450000	-0.3431850000
N	-0.2646950000	0.9156940000	0.0509820000
C	0.2202790000	1.4670240000	-1.1987500000
H	0.6792150000	2.4435730000	-1.0035720000
H	0.9806680000	0.8161370000	-1.6305340000
H	-0.5881890000	1.6081050000	-1.9268710000
C	-0.8858980000	1.8630980000	0.9540110000
H	-1.3040310000	1.3300160000	1.8073990000
H	-0.1654080000	2.6055180000	1.3202180000
H	-1.6890110000	2.3854050000	0.4230100000
C	1.1614450000	-2.4353200000	0.1691070000
H	1.7605270000	-2.8739420000	-0.6346910000
H	1.8138700000	-2.1542880000	0.9948440000
C	-0.2305570000	-1.4446040000	-1.5886450000
H	-1.0187930000	-0.6985650000	-1.6890240000
H	0.4353920000	-1.3812750000	-2.4576710000
H	-0.6995630000	-2.4362110000	-1.5888370000
At	1.9451370000	0.8876550000	3.2890400000
I	3.8852930000	2.3487240000	4.8900600000
H	0.4460340000	-3.1864950000	0.5288090000

***N,N,N',N'*-tetramethylthiourea, pop=100%**

C	-0.0000000000	0.0000000000	0.5936520000
S	0.0000000000	0.0000000000	2.2717050000
N	0.0611010000	-1.1530150000	-0.1407610000
N	-0.0611010000	1.1530150000	-0.1407610000
C	0.6878980000	1.2968760000	-1.3782870000
H	1.4283550000	2.0980490000	-1.2603620000
H	1.2195490000	0.3739770000	-1.6083780000
H	0.0362210000	1.5546320000	-2.2221940000
C	-0.3574280000	2.4047890000	0.5231480000
H	-1.1593590000	2.2594570000	1.2469690000
H	0.5177900000	2.7983240000	1.0572920000
H	-0.6723350000	3.1270540000	-0.2365890000
C	0.3574280000	-2.4047890000	0.5231480000
H	0.6723350000	-3.1270540000	-0.2365890000
H	1.1593590000	-2.2594570000	1.2469690000
H	-0.5177900000	-2.7983240000	1.0572920000
C	-0.6878980000	-1.2968760000	-1.3782870000
H	-1.2195490000	-0.3739770000	-1.6083780000
H	-0.0362210000	-1.5546320000	-2.2221940000
H	-1.4283550000	-2.0980490000	-1.2603620000

AtI--*N,N,N',N'*-tetramethylthiourea, pop=100%

C	2.9227850000	0.0191510000	-0.1211550000
N	2.7318500000	1.2458370000	-0.6591150000
N	3.6901040000	-0.0554890000	0.9876960000
C	4.7784910000	0.8751050000	1.2382050000
H	5.6854010000	0.2980970000	1.4478890000
H	4.9551060000	1.4895970000	0.3557370000
H	4.5772940000	1.5253290000	2.0971730000
C	3.6959080000	-1.2434320000	1.8224410000
H	2.7107540000	-1.7076600000	1.8121210000
H	4.4342310000	-1.9742340000	1.4713580000
H	3.9498430000	-0.9408760000	2.8426190000
C	2.2714030000	1.4053140000	-2.0261220000
H	2.6655770000	2.3524910000	-2.4074290000
H	2.6384750000	0.5822130000	-2.6376960000
H	1.1760810000	1.4263760000	-2.0785980000
C	2.5522450000	2.4222370000	0.1791500000
H	2.5194230000	2.1335140000	1.2293100000
H	3.3467890000	3.1619940000	0.0280990000
H	1.5913640000	2.8816580000	-0.0769370000
S	2.2375290000	-1.3883750000	-0.8100930000
At	-0.5397770000	-0.4987010000	-0.2698850000
I	-3.2537440000	0.4560830000	0.4332620000

Diethyl ether, pop = 47.4 %

O	0.0000000000	0.0000000000	0.2727665065
C	-1.1732237498	0.0000000000	-0.5108070912
C	1.1732237498	0.0000000000	-0.5108070912
C	-2.3725313323	0.0000000000	0.4043631319
C	2.3725313323	0.0000000000	0.4043631319
H	-1.1816883732	0.8875214287	-1.1656057834
H	-1.1816883732	-0.8875214287	-1.1656057834
H	1.1816883732	0.8875214287	-1.1656057834
H	1.1816883732	-0.8875214287	-1.1656057834
H	-3.2961768158	0.0000000000	-0.1829825218
H	3.2961768158	0.0000000000	-0.1829825218
H	-2.3669445227	-0.8872823412	1.0443664162
H	-2.3669445227	0.8872823412	1.0443664162
H	2.3669445227	0.8872823412	1.0443664162
H	2.3669445227	-0.8872823412	1.0443664162

AtI--diethyl ether, pop=27.8%

O	-0.1219300000	-2.8443600000	0.0000000000
C	0.4894100000	-3.3534500000	1.1848200000
C	0.4894100000	-3.3534500000	-1.1848200000
C	-0.3564900000	-3.0035600000	2.3825900000
C	-0.3564900000	-3.0035600000	-2.3825900000
H	0.5788500000	-4.4443400000	1.0816400000
H	1.5062800000	-2.9424100000	1.2767400000
H	0.5788500000	-4.4443400000	-1.0816400000
H	1.5062800000	-2.9424100000	-1.2767400000
H	0.0964900000	-3.4242100000	3.2856300000
H	0.0964900000	-3.4242100000	-3.2856300000
H	-0.4333800000	-1.9203900000	2.5143300000
H	-1.3642100000	-3.4147700000	2.2745200000
H	-1.3642100000	-3.4147700000	-2.2745200000
H	-0.4333800000	-1.9204000000	-2.5143300000
At	0.0149000000	-0.0377700000	0.0000000000
I	0.3658600000	2.8318600000	0.0000000000

Diethyl sulfide, pop = 60.2 %

C	-0.3183900000	2.5421500000	-0.0806600000
C	-0.6047100000	1.0865000000	0.2385600000
S	0.8503400000	0.0663000000	-0.1663000000
C	0.3087600000	-1.5479100000	0.4784900000
C	-0.7994400000	-2.2090900000	-0.3199400000
H	-1.4682900000	0.7344000000	-0.3347400000
H	-0.8254700000	0.9594900000	1.3048800000
H	0.0208700000	-1.4175500000	1.5283400000
H	1.2137700000	-2.1640700000	0.4678400000
H	-1.1913800000	3.1595500000	0.1552700000
H	-1.0387800000	-3.1918600000	0.1033300000
H	0.5311700000	2.9129700000	0.5011300000
H	-0.0875400000	2.6741700000	-1.1426500000
H	-1.7159900000	-1.6111100000	-0.3071700000
H	-0.4977700000	-2.3458600000	-1.3625100000

AtI--diethyl sulfide, pop=40.6%

C	-0.0962135300	3.0387473500	2.7168466600
C	-0.7936131600	3.3027833300	1.3970350300
S	0.3415141400	2.9969657100	0.0000000000
C	-0.7936131600	3.3027833300	-1.3970350300
C	-0.0962135300	3.0387473500	-2.7168466600
H	-1.1233420200	4.3444040300	1.3218394800
H	-1.6632392400	2.6494877600	1.2685386800
H	-1.1233420200	4.3444040300	-1.3218394800
H	-1.6632392400	2.6494877600	-1.2685386800
H	-0.7850271000	3.2400698900	3.5428520100
H	-0.7850271000	3.2400698900	-3.5428520100
H	0.2253050600	1.9951114100	2.7896972100
H	0.7804741800	3.6819269500	2.8396666300
H	0.7804741800	3.6819269500	-2.8396666300
H	0.2253050600	1.9951114100	-2.7896972100
At	0.2217601600	0.013881630	0.0000000000
I	-0.1278535700	-2.9037274600	0.0000000000

Tributyl phosphate, pop = 82.8 %

P	0.0197500000	0.0105400000	0.6039400000

O	-0.2719700000	0.0881600000	2.0669000000
O	-0.9660900000	-0.9182500000	-0.2707900000
O	1.4688500000	-0.5644000000	0.1935800000
O	-0.0241700000	1.4037200000	-0.2065300000
C	-1.3666000000	-2.1837500000	0.2940400000
H	-0.5225800000	-2.8801000000	0.2172000000
H	-1.6051400000	-2.0389200000	1.3532700000
C	-2.5595800000	-2.6918500000	-0.4784800000
H	-2.2938400000	-2.7565200000	-1.5410200000
C	-3.0323900000	-4.0480700000	0.0254900000
H	-3.2798800000	-3.9737800000	1.0926000000
H	-2.2083400000	-4.7701900000	-0.0468700000
C	2.6089100000	-0.1032200000	0.9509500000
H	2.7782300000	0.9542300000	0.7124100000
H	2.3812600000	-0.1919500000	2.0176400000
C	3.8031100000	-0.9428100000	0.5658700000
H	4.6386000000	-0.6387900000	1.2106600000
C	4.2011000000	-0.8114300000	-0.8969300000
H	3.3472700000	-1.0893000000	-1.5249200000
H	4.4123800000	0.2440000000	-1.1157100000
C	-1.0892500000	2.3247200000	0.1065200000
H	-2.0155500000	1.9497700000	-0.3457200000
H	-1.2195300000	2.3592400000	1.1935800000
C	-0.7242600000	3.6790800000	-0.4508400000
H	0.2195500000	4.0055300000	0.0035000000
C	-1.8110600000	4.7142500000	-0.1975100000
H	-1.9966200000	4.7904600000	0.8819600000
H	-2.7526900000	4.3698100000	-0.6452500000
H	-0.5398800000	3.5823000000	-1.5280600000
H	-3.3707800000	-1.9573600000	-0.3994900000
H	3.5883300000	-1.9920500000	0.8060800000
C	-1.4564200000	6.0855200000	-0.7511700000
H	-2.2527000000	6.8107600000	-0.5565900000
H	-0.5363600000	6.4680800000	-0.2951300000
H	-1.2984800000	6.0438200000	-1.8347600000
C	5.4084800000	-1.6625500000	-1.2562400000
H	5.6749600000	-1.5496800000	-2.3118900000
H	6.2840600000	-1.3826700000	-0.6587600000
H	5.2088700000	-2.7249700000	-1.0748900000
C	-4.2366900000	-4.5722700000	-0.7410500000
H	-4.5563300000	-5.5473700000	-0.3603600000
H	-5.0862000000	-3.8851800000	-0.6569800000
H	-4.0059200000	-4.6875300000	-1.8060900000

Atl--tributyl phosphate, pop = 39.7 %

C	3.1272693200	1.7085185000	4.1514318100
C	3.1402773600	0.6335001800	3.0760149000
C	1.7923153100	-0.0574442500	2.9241724400
C	1.8238803700	-1.1224660300	1.8567737100
O	0.5067861200	-1.7219047800	1.7656040100
P	-0.0135327800	-2.2581491000	0.3504841600
O	0.2401930700	-1.3459435200	-0.8259638000
O	0.6602133200	-3.7046476100	0.2158474100
C	0.5651427300	-4.3913934100	-1.0559689700
C	1.5296750800	-5.5508894000	-1.0371779700
C	1.4789326200	-6.3535886000	-2.3298492600
C	2.4474169700	-7.5260158400	-2.3289771500
O	-1.5518179300	-2.5962844700	0.6446787700
C	-2.4978206200	-1.4983240700	0.6661576900
C	-3.8577034700	-2.0585270700	0.9994476700
C	-4.9234779600	-0.9721921300	1.0463748300
C	-6.3021592400	-1.5202107200	1.3799758700
At	0.0811620000	1.3236038000	-0.7317958600
I	-0.0815426000	4.2129285000	-0.5480273500
H	-0.4677306400	-4.7355674600	-1.1825082400
H	0.8018715100	-3.6815199200	-1.8551797900
H	1.2926613700	-6.1965668700	-0.1826992800
H	1.7021704700	-5.6929681500	-3.1777938100
H	0.4568715400	-6.7214042900	-2.4897761400
H	-2.1725161400	-0.7696096300	1.4180401900
H	-2.4909829600	-1.0136431600	-0.3159479300
H	-4.6390908700	-0.2152322800	1.7887359300
H	-4.9576519200	-0.4530745100	0.0797891300
H	2.5319243500	-1.9214336800	2.1012174300
H	2.0916126900	-0.6963570900	0.8838347700
H	1.0227414100	0.6782645900	2.6602628900
H	3.4267005800	1.0800817500	2.1149684700
H	3.9102530400	-0.1136205500	3.3106791400
H	1.4891856000	-0.5129064100	3.8750612000
H	2.5433722000	-5.1654737100	-0.8725351500
H	-4.1224381600	-2.8146346000	0.2499336500
H	4.1054853700	2.1907795900	4.2404371100
H	2.3908674600	2.4856274500	3.9195998800
H	2.8715518200	1.2850741400	5.1292683700
H	-7.0491569500	-0.7211477800	1.4083117200
H	-6.6254527400	-2.2547150300	0.6338655400
H	-6.3035033700	-2.0151002600	2.3575897700
H	2.3917128800	-8.0864543400	-3.2671687700
H	3.4805751300	-7.1830636700	-2.2046033400
H	2.2254401500	-8.2196924300	-1.5103930400
H	-3.8016714300	-2.5750512700	1.9654247400

Diethyl methylphosphonate, pop = 43.4 %

P	0.6102916308	-1.2653682273	0.0000000003
O	-0.8141258420	-1.7373985305	-0.0000000004
O	1.0108573320	-0.3640882954	-1.3036000962
O	1.0108573307	-0.3640882954	1.3036000971
C	-0.0064234669	0.4426380091	-1.9259329567
H	-0.0763367183	1.3929056171	-1.3816841043
H	-0.9667493979	-0.0763690133	-1.8451223814
C	-0.0064234687	0.4426380091	1.9259329567
H	-0.9667493996	-0.0763690133	1.8451223805
H	-0.0763367196	1.3929056171	1.3816841042
C	1.9262672581	-2.4810711552	0.0000000009
H	1.8285440226	-3.1005113914	-0.8936201886
H	1.8285440217	-3.1005113914	0.8936201903
H	2.8930429256	-1.9731788040	0.0000000014
C	0.3846386728	0.6736999419	-3.3631734685
H	-0.3599357920	1.3117094616	-3.8501470520
H	0.4365123249	-0.2748524983	-3.9055295779
H	1.3592469041	1.1664902595	-3.4275705788
C	0.3846386696	0.6736999419	3.3631734689
H	-0.3599357956	1.3117094616	3.8501470517
H	1.3592469009	1.1664902595	3.4275705801
H	0.4365123212	-0.2748524983	3.9055295783

Atl--diethyl methylphosphonate, pop = 51.3 %

P	0.4783725584	-3.1433659858	-0.0349624548
O	1.3634962747	-1.9203536248	0.0679198514
O	-0.6445448698	-3.2198919017	1.1379178848
O	-0.3391368967	-3.2918910470	-1.4254036319
C	-0.9331288229	-2.0539466707	1.9455624492
H	-1.4727452482	-1.3242737361	1.3309098424
H	0.0102682132	-1.5988056462	2.2610367767
C	-1.1571596776	-2.1891568093	-1.8757819057
H	-0.5421620877	-1.2840694984	-1.9117897811
H	-1.9651538680	-2.0370524173	-1.1500429332
C	1.3205451114	-4.7175908697	0.0509173284
H	1.8952442182	-4.7512375764	0.9784956607
H	1.9930161932	-4.8025840003	-0.8050138947
H	0.5853607461	-5.5245185294	0.0339195130
C	-1.7612665176	-2.4999970696	3.1211423667
H	-2.0062194037	-1.6328161734	3.7421486827
H	-1.2106141959	-3.2206483267	3.7325513434
H	-2.6941964770	-2.9639842424	2.7886121701
C	-1.7047163192	-2.5380864922	-3.2342693446
H	-2.3346515733	-1.7192940904	-3.5951070305
H	-2.3089934783	-3.4484273957	-3.1877271335
H	-0.8918251017	-2.6914757924	-3.9493854248
At	1.1408025810	0.7371975633	0.0136474054
I	0.83613518880	3.6194408055	-0.0352977182

Hexamethyl benzene, pop = 100 %

C	0.9912180800	-0.9912180800	-0.0099879500
C	1.3540290800	0.3628110000	0.0099879500
C	0.3628110000	1.3540290800	-0.0099879500
C	-0.9912180800	0.9912180800	0.0099879500
C	-1.3540290800	-0.3628110000	-0.0099879500
C	-0.3628110000	-1.3540290800	0.0099879500
C	2.0557575000	-2.0557575000	-0.0921042100
H	2.9376401300	-1.6964075000	-0.6267473000
H	1.6964075000	-2.9376401300	-0.6267473000
H	2.3909985100	-2.3909985100	0.8987715700
C	2.8082169700	0.7524594700	0.0921042100
H	3.3922747300	0.0003119300	0.6267473000
H	2.9379520600	1.6958672300	0.6267473000
H	3.2661647000	0.8751662000	-0.8987715700
C	0.7524594700	2.8082169700	-0.0921042100
H	0.0003119300	3.3922747300	-0.6267473000
H	1.6958672300	2.9379520600	-0.6267473000
H	0.8751662000	3.2661647000	0.8987715700
C	-2.0557575000	2.0557575000	0.0921042100
H	-2.3909985100	2.3909985100	-0.8987715700
H	-1.6964075000	2.9376401300	0.6267473000
H	-2.9376401300	1.6964075000	0.6267473000
C	-2.8082169700	-0.7524594700	-0.0921042100
H	-3.3922747300	-0.0003119300	-0.6267473000
H	-3.2661647000	-0.8751662000	0.8987715700
H	-2.9379520600	-1.6958672300	-0.6267473000
C	-0.7524594700	-2.8082169700	0.0921042100
H	-0.8751662000	-3.2661647000	-0.8987715700
H	-1.6958672300	-2.9379520600	0.6267473000

H	-0.0003119300	-3.3922747300	0.6267473000

AtI--hexamethyl benzene, pop = 100 %

C	1.3860721500	3.0007095100	0.0000000000
C	0.7179212000	2.7979711700	-1.2170661300
C	-0.6470504000	2.4756645400	-1.2203456200
C	-1.3293947000	2.2966712100	0.0000000000
C	-0.6470504000	2.4756645400	1.2203456200
C	0.7179212000	2.7979711700	1.2170661300
C	2.8220843400	3.4560163200	0.0000000000
H	3.0452102500	4.0648046100	-0.8782338500
H	3.0452102500	4.0648046100	0.8782338500
H	3.5251038600	2.6126410200	0.0000000000
C	1.4759464700	2.8779380000	-2.5169468200
H	2.5307579700	2.6354967400	-2.3776129200
H	1.0809720200	2.1688946300	-3.2473622900
H	1.4263329800	3.8765215200	-2.9703051700
C	-1.4079265300	2.3592530200	-2.5142944300
H	-2.4047515500	2.7981612200	-2.4235081100
H	-0.9013159700	2.8762061200	-3.3297123600
H	-1.5427273500	1.3128701100	-2.8193759300
C	-2.7950552900	1.9439827500	0.0000000000
H	-3.4257512500	2.8427787600	0.0000000000
H	-3.0669740200	1.3547310300	-0.8779812800
H	-3.0669740200	1.3547310300	0.8779812800
C	-1.4079265300	2.3592530200	2.5142944300
H	-2.4047515500	2.7981612200	2.4235081100
H	-1.5427273500	1.3128701100	2.8193759300
H	-0.9013159700	2.8762061200	3.3297123600
C	1.4759464700	2.8779380000	2.5169468200
H	1.4263329800	3.8765215200	2.9703051700
H	1.0809720200	2.1688946300	3.2473622900
H	2.5307579700	2.6354967400	2.3776129200
At	-0.2428356000	-0.6294773600	0.0000000000
I	0.3869024800	-3.4593152600	0.0000000000

Toluene, pop = 100 %

C	0.0054364700	-0.9121878700	0.0000000000
C	1.1990940300	-0.1915950800	0.0000000000
C	1.1990055500	1.2006595800	0.0000000000
C	-0.0033038900	1.8978049300	0.0000000000
C	-1.2033313200	1.1913698700	0.0000000000
C	-1.1958113100	-0.1979977600	0.0000000000
H	2.1451479700	-0.7297482000	0.0000000000
H	2.1427336600	1.7403490100	0.0000000000
H	-0.0074629900	2.9845924500	0.0000000000
H	-2.1499494400	1.7260959400	0.0000000000
H	-2.1394106700	-0.7407626400	0.0000000000
C	0.0010171200	-2.4138510200	0.0000000000
H	-0.5160676000	-2.8087549800	-0.8811819500
H	1.0193941500	-2.8119809900	0.0000000000
H	-0.5160676000	-2.8087549800	0.8811819500

AtI--toluene, pop = 50.3 %

C	-1.1107878700	3.8012243600	-0.0169164800
C	-0.4764982700	3.6201804900	1.2171130000
C	0.8163020000	3.1223466800	1.2930300100
C	1.5111980900	2.7942461800	0.1257479600
C	0.8896407000	2.9721208800	-1.1115863100
C	-0.4086590600	3.4723326200	-1.1753229600
H	-1.0089305100	3.8719158100	2.1319287100
H	1.2910330300	2.9905044800	2.2616573600
H	2.5364868200	2.4369961100	0.1790691800
H	1.4230988700	2.7317634100	-2.0276599700
H	-0.8846853800	3.6065973700	-2.1440945000
C	-2.5169991300	4.3193619300	-0.0808704500
H	-3.2257891900	3.5670984800	0.2829621700
H	-2.6400995700	5.2091466700	0.5443351300
H	-2.7992592700	4.5764240300	-1.1050434000
At	0.402391370	-0.1890412400	-0.0437224600
I	-0.3989821600	-2.9667655800	0.0347321900

Cyclohexanone, pop = 98.1%

C	-0.3072352937	0.9856667047	1.2553969461
C	0.0360829768	1.7769047532	-0.0000000016
C	-0.3072352937	0.9856667024	-1.2553969479
C	0.4077805824	-0.3685894273	-1.2749479636
C	0.4077805824	-0.3685894249	1.2749479643
H	1.4919381214	-0.1998470455	-1.3505712031
H	0.1032738053	-0.9870670573	-2.1222617249
H	-0.4975978578	2.7336487646	-0.0000000025
H	1.1093560702	2.0147452345	-0.0000000019
H	-1.391890691	0.8194671836	-1.2951642134
H	-0.0445764024	1.5523674906	-2.1549162494
H	1.4919381214	-0.1998470430	1.3505712035
H	0.1032738053	-0.9870670534	2.1222617267
H	-1.391890691	0.8194671860	1.2951642119
H	-0.0445764024	1.5523674946	2.1549162465
C	0.1621184656	-1.1400463430	0.0000000011
O	-0.2130987491	-2.2928333175	0.0000000021

AtI--cyclohexanone, pop = 96.9%

C	0.5322800000	-0.9424700000	1.1851300000
C	0.2027200000	-2.1100000000	0.2651400000
C	0.3212700000	-1.7023600000	-1.1970000000
C	-0.5811000000	-0.5055900000	-1.5178700000
C	-0.3654800000	0.2671400000	0.9001000000
H	-1.6320500000	-0.8078200000	-1.4028700000
H	-0.4441500000	-0.1397100000	-2.5374600000
H	0.8701200000	-2.9523400000	0.4751900000
H	-0.8193800000	-2.4594900000	0.4671400000
H	1.3625200000	-1.4368600000	-1.4205700000
H	0.0617100000	-2.5358300000	-1.8572100000
H	-1.4048900000	0.0096100000	1.1497900000
H	-0.0844500000	1.1397700000	1.4945400000
H	1.5812200000	-0.6506400000	1.0469900000
H	0.4231800000	-1.2298900000	2.2353600000
C	-0.3441000000	0.6268800000	-0.5578200000
O	-0.1393200000	1.7610300000	-0.9623500000
At	0.3477500000	4.0631700000	0.4045300000
I	0.8797500000	6.5299100000	1.8292300000

Tributylphosphine oxide, pop = 36.9 %

C	1.0450142282	0.6919760803	-1.4472924108
H	0.3659208259	1.5456845660	-1.3261105915
H	2.0688933966	1.0845986313	-1.4066343352
C	0.8052858903	-0.0251507880	-2.7698089433
H	1.4154477639	-0.9364748196	-2.7953828854
H	-0.2426871842	-0.3517212224	-2.8269735601
C	1.1230786623	0.8400900419	-3.9817607602
H	2.1731468919	1.1556332244	-3.9270250617
H	0.5251151101	1.7605044859	-3.9372348665
C	0.8698163195	0.1269368371	-5.3004855579
H	1.1118224733	0.7685589482	-6.1536637519
H	-0.1812749332	-0.1697945385	-5.3930820373
H	1.4791844362	-0.7802181170	-5.3798596067
C	-0.8375104314	-1.0181223268	0.0000000000
H	-0.9214786114	-1.6726680535	-0.8758794052
H	-0.9214786114	-1.6726680535	0.8758794052
C	-1.9308180969	0.0417414748	0.0000000000
H	-1.8203961811	0.6921393280	-0.8786320931
H	-1.8203961811	0.6921393280	0.8786320931
C	-3.3322936830	-0.5557006291	0.0000000000
H	-3.4426896481	-1.2065118442	-0.8771614925
H	-3.4426896481	-1.2065118442	0.8771614925
C	-4.4279915816	0.4983193944	0.0000000000
H	-5.4216387985	0.0395327120	0.0000000000
H	-4.3573131908	1.1413287291	-0.8847858883
H	-4.3573131908	1.1413287291	0.8847858883
C	1.0450142282	0.6919760803	1.4472924108
H	2.0688933966	1.0845986313	1.4066343352
H	0.3659208259	1.5456845660	1.3261105915
C	0.8052858903	-0.0251507880	2.7698089433
H	-0.2426871842	-0.3517212224	2.8269735601
H	1.4154477639	-0.9364748196	2.7953828854
C	1.1230786623	0.8400900419	3.9817607602
H	0.5251151101	1.7605044859	3.9372348665
H	2.1731468919	1.1556332244	3.9270250617
C	0.8698163195	0.1269368371	5.3004855579
H	1.4791844362	-0.7802181170	5.3798596067
H	-0.1812749332	-0.1697945385	5.3930820373
H	1.1118224733	0.7685589482	6.1536637519
O	1.8987780711	-1.5548753987	0.0000000000
P	0.8910780051	-0.4166981914	0.0000000000

AtI--tributylphosphine oxide, pop = 14.4 %

C	1.0249020006	-2.1157929705	1.4834457946
P	-0.0639900437	-2.1603713667	0.0245154598
O	-1.0995016903	-1.0135912696	0.0228678943
C	0.2564330007	-2.0291796289	2.7971100236
C	1.1744857323	-1.8470417163	3.9981822690
C	0.4133226958	-1.7584865300	5.3110678705
C	-0.9313656556	-3.7607188877	0.0060212995
C	-0.0472881495	-4.9956039433	-0.1192389277
C	-0.8506364238	-6.2900925503	-0.1065501591
C	0.0214671981	-7.5283129344	-0.2371982873
C	1.0348783809	-2.1030094827	-1.4252536499
C	0.2859313739	-2.2284422014	-2.7468467717
C	1.1900219074	-2.0203120988	-3.9543975275
C	0.4479755638	-2.1515085214	-5.2746626974
H	1.6844707742	-2.9922038041	1.4550556743

H	1.6606138976	-1.2301542902	1.3550173404
H	-0.4482507432	-1.1903414593	2.7410948144
H	-0.3496066088	-2.9347331802	2.9363322474
H	1.7697607072	-0.9365667872	3.8529411525
H	1.8900073237	-2.6794255260	4.0383290480
H	1.0954196288	-1.6228246409	6.1558812403
H	-0.1681971673	-2.6694670974	5.4934939350
H	-0.2834134292	-0.9132617171	5.3043189407
H	-1.5306532802	-3.7904569281	0.9236357466
H	-1.6443627246	-3.6973493606	-0.8244862423
H	0.6839675066	-5.0200039287	0.6996002606
H	0.5335736920	-4.9438071476	-1.0500010121
H	-1.4317862170	-6.3406282244	0.8232165751
H	-1.5835457892	-6.2631003337	-0.9232406036
H	-0.5822105256	-8.4407371621	-0.2245673049
H	0.7416336737	-7.5931762802	0.5862443080
H	0.5877547996	-7.5157413196	-1.1752996625
H	1.5494946064	-1.1352519190	-1.3630896421
H	1.7995569742	-2.8828553541	-1.3184641404
H	-0.1839040530	-3.2198230339	-2.8136659288
H	-0.5302811668	-1.4959585358	-2.7661318009
H	2.0149992960	-2.7443969146	-3.9179206339
H	1.6509770251	-1.0268664698	-3.8849087840
H	-0.3613436302	-1.4165532167	-5.3453489508
H	0.0041616124	-3.1479301318	-5.3817532444
H	1.1192801752	-1.9921282649	-6.1239410227
At	-0.2595207491	1.3999024503	0.3119428004
I	0.7517281043	4.1207832453	0.65665230160

Ethylbutanoate, pop = 24.7 %

C	-0.5855022000	3.6879818200	0.0000000000
H	-1.2321400200	3.7166333900	-0.8847510900
H	0.0189775100	4.6001865900	0.0000000000
H	-1.2321400200	3.7166333900	0.8847510900
C	0.2953026200	2.4490302700	0.0000000000
H	0.9568173200	2.4520155300	-0.8731908000
H	0.9568173200	2.4520155300	0.8731908000
C	-0.5159225700	1.1660891200	0.0000000000
H	-1.1798266900	1.1125083400	-0.8723156700
H	-1.1798266900	1.1125083400	0.8723156700
C	0.3328922100	-0.0741786600	0.0000000000
O	1.5405121900	-0.0978413300	0.0000000000
O	-0.4226316400	-1.1863559000	0.0000000000
C	0.3080339600	-2.4258725900	0.0000000000
H	0.9551847700	-2.4467535300	0.8825639900
H	0.9551847700	-2.4467535300	-0.8825639900
C	-0.6952753200	-3.5490132700	0.0000000000
H	-0.1706344700	-4.5093929400	0.0000000000
H	-1.3328468000	-3.5042009600	0.8877620200
H	-1.3328468000	-3.5042009600	-0.8877620200

AtI--ethylbutanoate, pop = 21.2 %

C	-2.7358368500	-5.7616800300	0.0000000000
H	-2.4800630400	-6.3555328700	-0.8849563500
H	-3.8197664700	-5.6141719700	0.0000000000
H	-2.4800630400	-6.3555328700	0.8849563500
C	-2.0060337800	-4.4283129900	0.0000000000
H	-2.2970656200	-3.8354229700	-0.8738790200
H	-2.2970656200	-3.8354229700	0.8738790200
C	-0.4979120400	-4.6019173400	0.0000000000
H	-0.1592026800	-5.1757313700	-0.8719236500
H	-0.1592026800	-5.1757313700	0.8719236500
C	0.2565230800	-3.3050156300	0.0000000000
O	-0.2702459700	-2.2086100300	0.0000000000
O	1.5738194000	-3.4917674700	0.0000000000
C	2.3986951300	-2.3058858600	0.0000000000
H	2.1490443300	-1.7126172000	0.8852494600
H	2.1490443300	-1.7126172000	-0.8852494600
C	3.8363902900	-2.7502214000	0.0000000000
H	4.4868400300	-1.8707151600	0.0000000000
H	4.0615127000	-3.3467840600	0.8884091700
H	4.0615127000	-3.3467840600	-0.8884091700
At	-0.1467281700	0.5802811000	0.0000000000
I	-0.0296764100	3.4633938800	0.0000000000

***N,N*-dimethyl thioacetamide, pop = 100 %**

C	-0.2554463515	-0.5468923915	-0.2652748899
S	0.8320360495	-1.5700261598	-1.0117270144
N	-0.0417392198	0.7765614204	-0.1756871303
C	-0.9459366825	1.7161342601	0.4587285845
H	-1.2745860591	2.4705475969	-0.2659802648
H	-1.8239196878	1.2132653701	0.8554188568
H	-0.4373353044	2.2305125937	1.2827990324
C	1.1661198185	1.3507912327	-0.7396454669
H	2.0520706609	0.9062543411	-0.2757002631
H	1.2209909430	1.1445259618	-1.8130564048
H	1.1527373957	2.4284767846	-0.5653829172
C	-1.5229885661	-1.0925230860	0.3353804134
H	-1.5751028250	-0.8890995710	1.4114774848
H	-2.4099753305	-0.6497479652	-0.1329004077
H	-1.5439424909	-2.1689058180	0.1798868071

IAt--*N,N*-dimethyl thioacetamide, pop = 88.7 %

C	0.3355750082	0.3343838353	0.0000001583
N	-0.8720389768	-0.2305581832	-0.0000000344
C	-2.1222463640	0.5108186520	0.0000001502
H	-2.7057648039	0.2487734755	0.8891023974
H	-1.9475226319	1.5829622607	0.0000000089
H	-2.7057650941	0.2487733176	-0.8891018542
C	-1.0037681442	-1.6791095818	-0.0000003865
H	-0.5198907713	-2.1040567451	-0.8846533272
H	-0.5198907626	-2.1040571778	0.8846523413
H	-2.0649446889	-1.9309119155	-0.0000004394
C	0.4269754524	1.8299142229	0.0000006238
H	-0.0600243224	2.2504359338	-0.8865161706
H	-0.0600248101	2.2504354212	0.8865173893
H	1.4715081991	2.1351978508	0.0000009766
S	1.7138249050	-0.6394905682	-0.0000001177
I	6.7110558246	2.5437383678	-0.0000002575
At	4.2017568209	0.9970843240	-0.0000001641

(1*R*)-(–)-thiocamphor, pop = 100 %

C	-0.8622313206	0.9195282460	0.0562574602
C	0.6666910845	0.9230601329	-0.0206364918
C	0.1262170159	3.1245726621	0.1257588814
C	-1.1944053613	2.3926107432	0.1384310193
H	-1.3515099338	0.4541531349	-0.8051012489
H	-1.2460530529	0.4094574901	0.9454952498
C	1.0333154292	2.1118061464	0.8987766527
C	1.0301662859	1.4429288610	-1.4175423887
H	2.0964585636	1.3258091493	-1.6285171691
H	0.4882269904	0.9018145677	-2.1982986052
C	0.6228869626	2.9308716282	-1.3373046778
H	1.4710652869	3.6009381028	-1.510215504
H	-0.1544906426	3.2076270599	-2.0541075614
H	1.1304616355	-0.0308005822	0.2461297557
S	-2.6847963497	3.0437074553	0.2110272256
C	0.0989819993	4.5573927709	0.5912313665
H	-0.5733939479	5.1521870540	-0.0329900538
H	-0.2658781368	4.6320722079	1.6199944272
H	1.0997322662	4.9977815858	0.5386088539
C	2.5128108857	2.4764617072	0.8750714471
H	2.6981806676	3.3641474690	1.4885281692
H	3.1048460974	1.6583798139	1.3001260055
H	2.8963980551	2.6782085484	-0.1271102545
C	0.6118852390	1.9274569901	2.3543179886
H	-0.4628831093	1.7691580456	2.4753680003
H	1.1348861610	1.0739486658	2.7989877303
H	0.8766467592	2.8139279539	2.9398358321

IAt--(1*R*)-(–)-thiocamphor, pop = 99.1 %

C	-0.6853200000	-1.4366900000	0.1014100000
C	0.8334100000	-1.3021400000	0.241200000
C	0.2105200000	0.6049800000	-0.8281200000
C	-1.0581900000	-0.1681900000	-0.6108400000
H	-1.0140800000	-2.3170700000	-0.4619600000
H	-1.2120500000	-1.4829100000	1.0613800000
C	1.0044600000	0.2185800000	0.4663900000
C	1.4158200000	-1.5132600000	-1.1616100000
H	2.5056300000	-1.5894200000	-1.1385900000
H	1.0393700000	-2.4326600000	-1.6176700000
C	0.9477500000	-0.2469500000	-1.9095900000
H	1.7854200000	0.3439700000	-2.2922500000
H	0.2931300000	-0.4591000000	-2.7587100000
H	1.2637500000	-1.9400600000	1.0170200000
C	0.0662800000	2.0651100000	-1.1740100000
H	-0.4852900000	2.1927200000	-2.1097900000
H	-0.4790600000	2.6065100000	-0.395400000
H	1.0513800000	2.5249400000	-1.2958400000
C	2.4535300000	0.6891300000	0.4465500000
H	2.5043600000	1.7771100000	0.5549500000
H	2.9952300000	0.2532900000	1.2927500000
H	2.9892400000	0.4192500000	-0.4655600000
C	0.3499700000	0.7401600000	1.7428900000
H	-0.7200200000	0.5241700000	1.8036800000
H	0.8328800000	0.304500000	2.6234600000
H	0.4658800000	1.8265100000	1.8110200000
S	-2.5554300000	0.3013200000	-1.0796800000
At	-4.3582400000	-1.8960300000	-0.2372500000
I	-6.1501600000	-4.0744800000	0.6113700000

References

1 S. Lindegren, T. Bäck and H. J. Jensen, *Appl. Radiat. Isot.*, 2001, **55**, 157–160.

2 C. Laurence, J. Graton, M. Berthelot and M. J. El Ghomari, *Chem. - A Eur. J.*, 2011, **17**, 10431–10444.

3 J. Champion, C. Alliot, E. Renault, B. M. Mokili, M. Chérel, N. Galland and G. Montavon, *J. Phys. Chem. A*, 2010, **114**, 576–582.

4 N. Guo, D.-C. Sergentu, D. Teze, J. Champion, G. Montavon, N. Galland and R. Maurice, *Angew. Chemie Int. Ed.*, 2016, **55**, 15369–15372.

5 B. J. Colston and V. J. Robinson, *J. Environ. Radioact.*, 1995, **29**, 121–136.

6 N. Guo, R. Maurice, D. Teze, J. Graton, J. Champion, G. Montavon and N. Galland, *Nat. Chem.*, 2018, **10**, 428–434.

7 A. V. Mitin and C. van Wüllen, *J. Chem. Phys.*, 2006, **124**, 064305.

8 D.-D. Yang and F. Wang, *Phys. Chem. Chem. Phys.*, 2012, **14**, 15816.

9 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji and E. Al., *Gaussian 16 Rev. A.03*, Wallingford, CT, 2016.

10 P. J. Stephens, F. J. Devlin, C. F. Chabalowski and M. J. Frisch, *J. Phys. Chem.*, 1994, **98**, 11623–11627.

11 Y. Zhao and D. G. Truhlar, *J. Phys. Chem. A*, 2005, **109**, 5656–5667.

12 K. A. Peterson, B. C. Shepler, D. Figgen and H. Stoll, *J. Phys. Chem. A*, 2006, **110**, 13877–13883.

13 K. A. Peterson, *J. Chem. Phys.*, 2003, **119**, 11099–11112.

14 K. A. Peterson, D. Figgen, E. Goll, H. Stoll and M. Dolg, *J. Chem. Phys.*, 2003, **119**, 11113–11123.

15 J. Champion, M. Seydou, A. Sabatié-Gogova, E. Renault, G. Montavon and N. Galland, *Phys. Chem. Chem. Phys.*, 2011, **13**, 14984.

16 M. K. Armbruster, W. Klopper and F. Weigend, *Phys. Chem. Chem. Phys.*, 2006, **8**, 4862–4865.

17 D. E. Woon and T. H. Dunning, *J. Chem. Phys.*, 1993, **98**, 1358–1371.

18 T. H. Dunning, *J. Chem. Phys.*, 1989, **90**, 1007–1023.

19 R. A. Kendall, T. H. Dunning and R. J. Harrison, *J. Chem. Phys.*, 1992, **96**, 6796–6806.

20 F. Weigend and A. Baldes, *J. Chem. Phys.*, 2010, **133**, 174102.

21 F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3297.

22 D. Rappoport and F. Furche, *J. Chem. Phys.*, 2010, **133**, 134105.

23 S. F. F. Boys and F. Bernardi, *Mol. Phys.*, 1970, **19**, 553–566.

24 D.-C. Sergentu, G. David, G. Montavon, R. Maurice and N. Galland, *J. Comput. Chem.*, 2016, **37**, 1345–1354.

25 F. Ogura, T. Otsubo, T. Wirth and Z. A. Khan, in *Encyclopedia of Reagents for Organic Synthesis*, John Wiley & Sons, Ltd, Chichester, UK, 2008.

26 L. Wang and A. Tang, *Chem. Phys.*, 2011, **382**, 98–103.

27 R. Atkinson, S. M. Aschmann, D. Hasegawa, E. T. Thompson-Eagle and W. T. Frankenberger, *Environ. Sci. Technol.*, 1990, **24**, 1326–1332.

28 M. Mantina, A. C. Chamberlin, R. Valero, C. J. Cramer and D. G. Truhlar, *J. Phys. Chem. A*, 2009, **113**, 5806–5812.

29 C. R. Groom, I. J. Bruno, M. P. Lightfoot and S. C. Ward, *Acta Crystallogr. Sect. B Struct. Sci. Cryst. Eng. Mater.*, 2016, **72**, 171–179.