Electronic Supplementary Material (ESI) for Faraday Discussions.

Electronic Supplementary Information

Repulsion-dispersion parameters for the modelling of organic molecular crystals containing N, O , S and Cl.

Christina-Anna Gatsiou, Claire S. Adjiman, and Constantinos C. Pantelides*

Centre for Process Systems Engineering, Department of Chemical Engineering, Imperial College London, London, SW7 2AZ, UK

E-mail: c.pantelides@imperial.ac.uk

Contents

Calculation of atomic position vectors

Given the fractional coordinates of the $i = 1, \ldots, N_{asym}$ atoms in the asymmetric unit of the experimental crystal, denoted by $Y^{\exp}_{x,i}$,$Y^{\exp}_{y,i}$ and $Y^{\exp}_{z,i}$ and the fractional coordinates of the atoms in the asymmetric unit of the predicted crystal, denoted by $Y^{*}_{x,i}$,$Y^{*}_{y,i}$ and $Y^{*}_{z,i}$ the position vector of any atom i and a reference atom in the asymmetric unit is calculated:

$DO\ i = 1, N_{asym}$

$\delta Y^{\exp}_{x,i} = Y^{\exp}_{x,1} - Y^{\exp}_{x,i}$

$\delta Y^{\exp}_{y,i} = Y^{\exp}_{y,1} - Y^{\exp}_{y,i}$

$\delta Y^{\exp}_{z,i} = Y^{\exp}_{z,1} - Y^{\exp}_{z,i}$

$\delta Y^{*}_{x,i} = Y^{*}_{x,1} - Y^{*}_{x,i}$

$\delta Y^{*}_{y,i} = Y^{*}_{y,1} - Y^{*}_{y,i}$

$\delta Y^{*}_{z,i} = Y^{*}_{z,1} - Y^{*}_{z,i}$

$END\ DO$

The position vectors of each atom $i = 1, \ldots, N_{asym}$ with the reference atom (the first atom in the file) is then compared between the experimental and the predicted structure to give the deviations, denoted by $d_{x,i}$, $d_{y,i}$ and $d_{z,i}$. To correctly calculate these deviations between periodic images we perform a number of checks and readjust the fractional coordinates of the atoms in case it is necessary. Thus:

$DO\ i = 1, N$

$DO\ i = 1, N_{asym}$

$d_{x,i} = \delta Y^{\exp}_{x,i} - \delta Y^{*}_{x,i}$

$$d_{y,i} = \delta Y_{y,i}^{\exp} - \delta Y_{y,i}^{*}$$

$$d_{z,i} = \delta Y_{z,i}^{\exp} - \delta Y_{z,i}^{*}$$

$$IF\ d_{x,i} \geq 0.5\ THEN$$

$$Y_{x,i}^{*} = Y_{x,i}^{*} - 1$$

$$ENDIF$$

$$IF\ d_{y,i} \geq 0.5\ THEN$$

$$Y_{y,i}^{*} = Y_{y,i}^{*} - 1$$

$$ENDIF$$

$$IF\ d_{z,i} \geq 0.5\ THEN$$

$$Y_{z,i}^{*} = Y_{z,i}^{*} - 1$$

$$ENDIF$$

$$IF\ d_{x,i} \leq -0.5\ THEN$$

$$Y_{x,i}^{*} = Y_{x,i}^{*} + 1$$

$$ENDIF$$

$$IF\ d_{y,i} \leq -0.5\ THEN$$

$$Y_{y,i}^{*} = Y_{y,i}^{*} + 1$$

$$ENDIF$$

$$IF\ d_{z,i} \leq -0.5\ THEN$$

$$Y_{z,i}^{*} = Y_{z,i}^{*} + 1$$

$$ENDIF$$

$\delta Y^{\exp}_{x,i} = Y^{\exp}_{x,1} - Y^{\exp}_{x,i}$

$\delta Y^{\exp}_{y,i} = Y^{\exp}_{y,1} - Y^{\exp}_{y,i}$

$\delta Y^{\exp}_{z,i} = Y^{\exp}_{z,1} - Y^{\exp}_{z,i}$

$\delta Y^{*}_{x,i} = Y^{*}_{x,1} - Y^{*}_{x,i}$

$\delta Y^{*}_{y,i} = Y^{*}_{y,1} - Y^{*}_{y,i}$

$\delta Y^{*}_{z,i} = Y^{*}_{z,1} - Y^{*}_{z,i}$

$END\ DO$

$END\ DO$

Lattice energy and sublimation enthalpy relation

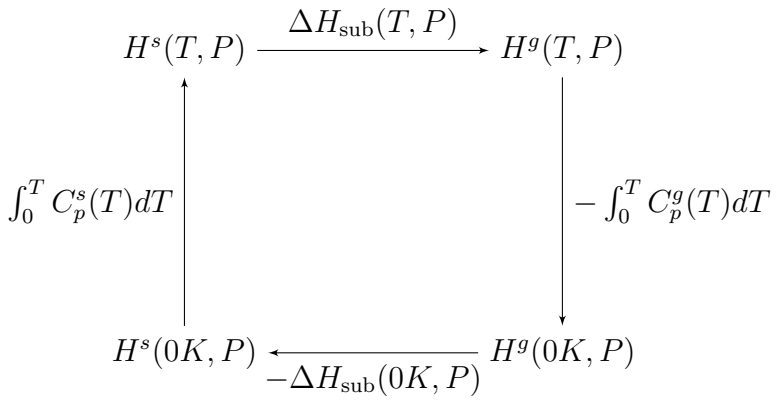


Figure S1: A thermodynamic cycle for adjusting sublimation enthalpies to temperature T

In theory, the molar sublimation enthalpy of a crystal at temperature T and pressure P, ΔH_{sub} is defined as the difference between the enthalpy of the gas phase and the enthalpy

of the solid phase, assuming there are no other phase transitions between the two phases. The enthalpy difference at T and P can be further written as the difference between the internal energy of the gas, U^g, and the internal energy of the solid, U^s, at 0 K and pressure P, the work done by the system against an external pressure at 0K, $PV^g - PV^s$, and the heat involved in a temperature change (from 0 K to T) at constant pressure. Thus:

$$\Delta H_{sub}(T,P) = U^g(T=0K,P) - U^s(T=0K,P) + PV^g - PV^s + \int_0^T C_p^g(T)dT - \int_0^T C_p^s(T)dT \quad (1)$$

where C_p^g and C_p^s are the molar heat capacities at constant pressure of the gas and the crystal respectively.

Since the lattice energy is the energy of formation of the crystal from the gas, $U_{\text{latt}} = U^s - U^g$, Eq. (1) takes the following form:

$$\Delta H_{sub}(T,P) = -U_{\text{latt}}(T=0K,P) + PV^g - PV^s + \int_0^T C_p^g(T)dT - \int_0^T C_p^s(T)dT \quad (2)$$

In Eq. (1) and Eq. (2) the C_p integrals cannot be easily evaluated due to the lack of accurate C_p^g values for the gases and C_p^s values for the condensed phases of many of the compounds considered in this study. Therefore, one usually assumes that the intramolecular vibrations are not influenced by the crystal packing (which is questionable for flexible molecules). If one then approximates the remaining contributions to the specific heat by $6R$ for the crystal and $4R$ for the gas, the last three terms of Eq. (2) are reduced to $-2RT$. If we also assume that the PV^s term is negligible, we obtain Eq. 10.

Local minimization algorithm

A sequential quadratic programming (SQP) algorithm, as implemented in routine E04UCF of the Nag Library[1] is used for the local minimization of the objective function, $R(p)$. The algorithm uses an approximation of the Hessian matrix B of the objective $R(p)$ with

respect to the parameters p. At the start of the minimization, this Hessian approximation is initialized to the unit matrix, I, and at every subsequent iteration, it is updated via the Broyden-Fletcher-Goldfarb-Shanno method (BFGS). The use of the BFGS approximation avoids the evaluation of the second order derivatives of the objective and uses only values of $R(p)$ and the first-order derivatives with respect to the variables. The search direction for the next step is computed by solving the (QP) subproblem and step α is computed from the line search. The algorithm is presented in Figure S2.

In Figure S2, r is the convergence tolerance that is set to 10^{-10} based on the order of magnitude of the gradients and the objective function. According to the convergence criterion, that is also given in Figure S2, gradients of the order of 10^{-3} and a tolerance of 10^{-3} would lead to an early termination of the algorithm. There are certain challenges involved in the local minimization that are important for the progress of the algorithm to the local minima. Firstly, the numerical derivatives of the objective function must be carefully calculated so that they can ensure the progress of the algorithm. Based on calculations of the derivatives performed with different approximation techniques and steps, the method that was found appropriate for our problem was the central-difference method combined with 5% step from a given value of the parameter. Secondly, the different orders of magnitude of the parameters can cause difficulties for some algorithms to converge.[2] In our problem the pre-exponential parameter A_{ij}, the exponential parameter B_{ij} and the attraction parameter C_{ij} are of different units and magnitude that reflect the physical nature of the problem. In order for them to display desirable properties during the minimization process linear transformations of the parameters were used to rescale:

$$p = dy \tag{3}$$

where p are the original parameter and, y the transformed parameter and d is a scaling constant. The scaling constant d is set to a typical value of the parameter. For a variable of

$WHILE\ k < N'\ DO$

0. Initialize

   Specify initial $p^{iter} = p^k$

   Set iteration counter $iter = 0$ and Hessian $\mathrm{B}^{iter} = \mathrm{I}$

   $WHILE\ iter < iter_{max}\ DO$

1. Evaluate objective function and gradients at p^{iter}

   $R(p^{iter})$

   $\nabla R(p^{iter})$

2. Solve the QP subproblem and obtain search direction d^{iter}

   $\min_{\mathrm{d}} \nabla R(p^{iter})^T \mathrm{d} + \frac{1}{2}\mathrm{d}^T \mathrm{B}^{iter} \mathrm{d}$

3. Perform line search

4. Check convergence on sequence of iterates

   $IF\ \alpha\|\mathrm{d}^{iter}\| \leq \sqrt{r}(1 + \|p^{iter}\|)$, go to 9

5. Calculate $\|\nabla R(p^{iter+1})\|$

6. Check convergence on gradients

   $IF\ \|\nabla R(p^{iter+1})\| \leq \sqrt{r}(1 + \max(1 + |R(p^{iter+1})|, \|\nabla R(p^{iter+1})\|))$, go to 9

7. BFGS update to Hessian matrix

8. Set $iter = iter + 1$, go to 2

   $ENDDO$, go to 9

9. Solution found p^{k*}

   $ENDDO$

Figure S2: Local minimization algorithm E04UCF

type A, d is set to 10^3 and for C variable, d_j is set to 10.

Training set data

Table S1: Crystal structures and sublimation enthalpies used for training

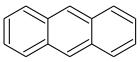
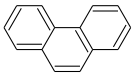
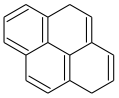
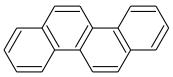
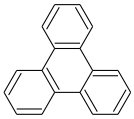
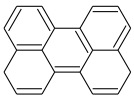
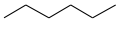
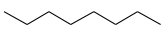
Name	Molecular diagram	CSD code	Space Group	Z	R-factor	T K	$\Delta H_{\mathrm{sub}}^{\mathrm{exp}}(T^{sub})$ kJ mol^{-1}	T^{sub} K
Hexadeutero-benzene		BENZEN06	Pbca	4	3.6	15	44.4 [3]	298.15
Naphthalene		NAPHTA31	P21/a	2	2.34	5	72.7 [4]	298.15
Decadeutero-anthracene		ANTCEN16	P21/a	2	3.2	16	97.9 [5]	298.15
Phenanthrene		PHENAN08	P21	2	4.3	283-303	90.9 [6]	298.15
Pyrene		PYRENE03	P21/a	4	6.3	113	100.3 [7]	298.15
Chrysene		CRYSEN	I2/c	4	8	283-303	123.4 [7]	298.15
Triphenylene		TRIPHE13	P212121	4	3.75	173	120.1 [7]	298.15
Perylene		PERLEN06	P21/c	2	5	200	129.6 [8]	415
n-Pentane		PENTAN01	Pbcn	4	4.02	90	42.0 [9]	143
n-Hexane		HEXANE01	P-1	1	3.42	90	50.8 [9]	178
n-Octane		OCTANE01	P-1	1	4.64	90	68.1 [9]	216
Cubane		CUBANE	R-3r	1	7	283-303	55.2 [10]	298.15

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Table S1 – continued from previous page

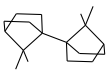
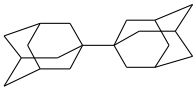
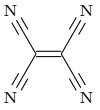
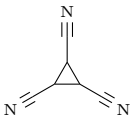
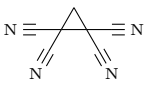
Name	Molecular diagram	CSD code	Space Group	Z	R-factor	T K	$\Delta H_{\mathrm{sub}}^{\mathrm{exp}}(T^{sub})$ kJ mol^{-1}	T^{sub} K
Adamantane		ADAMAN08	P-421c	2	2.4	188	59.0 [11]	298.15
Bicyclopropyl		BCPROP02	Cmca	4	1.94	100		
1-Biapocamphane		BAPOCM10	P-1	1	4	283-303		
1,1'-Biadamantane		BADAMN10	P-1	1	5.2	283-303		
Dideutero-acetylene		ACETYL05	Acam	4	3.67	4	23.5 [11]	145
7,7-Diethynyldispiro(2.0.2.1) heptane		MEYCEY	I2	2	4.9	115		
Ethynylcyclopropane		MEYCIC	Pbca	8	4.84	115		
Cyanogen		CYNGEN	Pcab	4	8.65	283-303	32.4 [12]	224
Dicyanoacetylene		DCYANM	P21/a	2	13	278	44.3 [13]	298.15
Tetracyanoethylene (cubic)		TCYETY01	Im3	6	4.8	283-303	81.2 [14]	298.15
Tetracyanoethylene (monoclinic)		TCYETY	P21/n	2	8.3	283-303		
cis-1,2,3-Tricyanocyclopropane		CYCYPR	R3c	6	2.3	283-303		
1,1,2,2-Tetracyanocyclopropane		TCYCPR01	P212121	4	5.5	283-303		
Triethylenediamine		TETDAM03	P63/m	2	-	283-303	62.2 [15]	298.15
Hexamethylenetetramine		HXMTAM10	I-43m	2	2.8	15	79.6 [16]	298.15

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Table S1 – continued from previous page

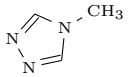
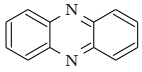
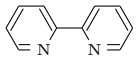
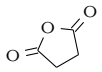
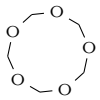
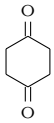
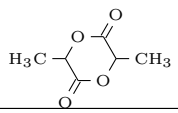
Name	Molecular diagram	CSD code	Space Group	Z	R-factor	T K	$\Delta H_{\mathrm{sub}}^{\mathrm{exp}}(T^{sub})$ kJ mol^{-1}	T^{sub} K
Pyrimidine		PRMDIN01	Pna21	4	4.2	107		
Pyrazine		PYRAZI01	Pmnn	2	4.7	184	56.2 [17]	298.15
1,8-Naphthyridine		NAPTYR11	P21/c	4	4.8	283-303		
4-Methyl-4H-1,2,4-triazole		TELPIJ	Pnma	4	3.52	150		
s-Triazine		TRIZIN01	R-3c	6	4.5	283-303	54.2 [18]	298.15
Phenazine		PHENAZ04	P21/n	2	5.32	283-303	94.3 [19]	354
2,2'-Bipyridyl		BIPYRL04	P21/n	2	2.98	123	81.8 [20]	298.15
1,4-Dioxane		CUKCIU03	P21/n	2	17.84	283-303	35.6 [21]	272
s-Trioxane		TROXAN	R3c	6	6.7	283-303	56.6 [22]	298.15
1,3,5,7-Tetroxocane		TOXOCN	C2/c	4	4.8	283-303	79.6 [23]	298.15
Succinic anhydride		SUCANH12	P212121	4	2.95	100	80.7 [24]	298.15
1,3,5,7,9-Pentoxecane		PTOXEC	Pbcn	4	4.9	283-303	87.9 [25]	298.15
Cyclohexane-1,4-dione		CYHEXO	P21	2	8.1	133	75 [26]	298.15
rac-3,6-Dimethyl-1,4-dioxane-2,5-dione		BICVIS	P21/c	4	3.8	283-303		

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Table S1 – continued from previous page

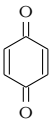
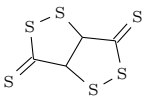
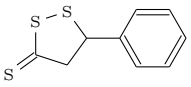
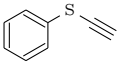
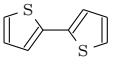
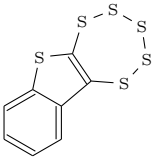
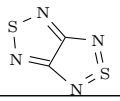
Name	Molecular diagram	CSD code	Space Group	Z	R-factor	T K	$\Delta H_{\mathrm{sub}}^{\mathrm{exp}}(T^{sub})$ kJ mol^{-1}	T^{sub} K
p-Benzoquinone		BNZQUI03	P21/c	2	4.29	173	66.7 [27]	298.15
Furan		FURANE10	P41212	4	6.5	123		
Dideuteroformaldehyde		KEMZIL	P-421c	8	3.1	15		
Dimethylsulfide		PADQAN	P-1	2	2.32	123		
Ethyl methyl sulfide		LIQWEN	P21/c	4	2.79	128		
1,4-Dithiane		DITHAN02	P21/c	2	1.48	100	63.0 [28]	298.15
3H,6H-1,2-Dithiolo(4,3-c)-1,2-dithiol-3,6-dithione		ZAVHAF	P21/c	2	4.6	283-303		
5-Phenyl-3H-1,2-dithiole-3-thione		FABPON11	Pcab	8	2.94	283-303	123.3 [29]	298.15
Ethylene trithiocarbonate		DTOLTO	P21/c	4	4.8	283-303	81.8 [30]	298.15
Phenylthioacetylene		LEVMUU	P21/c	4	4	150		
2,2'-Bithiophene		DTENYL02	P21/c	2	4.6	133	85.2 [31]	298.15
1,3,5-Trithiane		TRITAN03	Pcmn	4	2.5	283-303	93.2 [32]	298.15
Pentathiepino(6,7-b)benzo(d)thiophene (form II)		BAHNUU	P21/n	4	3.21	283-303		
Pentathiepino(6,7-b)benzo(d)thiophene (form I)		BAHNUU01	P21/c	4	3.01	283-303		
[1, 2, 5]thiadiazolo[3,4-c] [1, 2, 5]thiadiazole		BAWHEM01	P21/c	2	4.79	173		

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Table S1 – continued from previous page

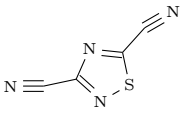
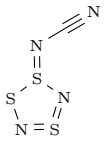
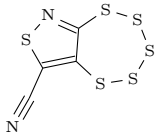
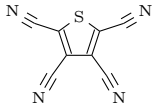
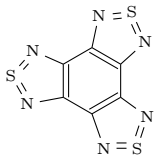
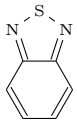
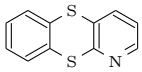
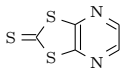
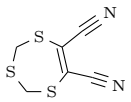
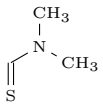
Name	Molecular diagram	CSD code	Space Group	Z	R-factor	T K	$\Delta H_{\mathrm{sub}}^{\mathrm{exp}}(T^{sub})$ kJ mol^{-1}	T^{sub} K
1,2,4-thiadiazole-3,5-dicarbonitrile		CEBYUD	P32	3	3.3	283-303		
1-Cyanoimino-1λ^4,2,4λ^4,3,5-trithiadiazole		GEDHAY	P21/n	4	3.12	283-303		
8-Cyanoisothiazolopentathiepin		ISTZCN10	P21/c	4	5.1	283-303		
Tetracyanothiophene		TCTHPH	Pa	2	10.3	283-303		
Benzo[1,2-c:3,4-c:5,6-c]tris[1,2,5]thiadiazole		EWADAI	Pmn21	2	2.56	173		
Benzo(c)(1,2,5)thiadiazole		BETHAZ01	Pna21	4	2.94	123	70.7[33]	298.15
1-Azathianthrene		CEJSEP	P21/c	4	3.4	163		
[1, 3]Dithiolo[4,5-b]pyrazine-2-thione		DILCOS	Pnma	4	1.74	150		
3,5,7-Trithiacyclo-heptamaleonitrile		HELKEO	I2cb	8	3.72	180		
3,7-Dithia-1,5-diazabicyclo[3.3.1]nonane		DZTNON02	C2/c	4	3.49	120		
N,N-Dimethylthioformamide		KAQPOH	P212121	4	1.95	90		

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Table S1 – continued from previous page

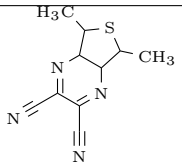
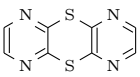
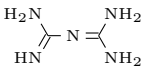
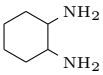
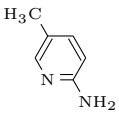
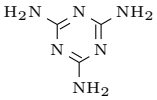
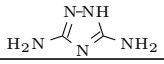
Name	Molecular diagram	CSD code	Space Group	Z	R-factor	T K	$\Delta H_{\mathrm{sub}}^{\mathrm{exp}}(T^{sub})$ kJ mol^{-1}	T^{sub} K
2,3-Dicyano-5,7-dimethylthieno(3,4-b)pyrazine		YIJGAA	P21/m	2	4.2	100		
5,10-Dithia-1,4,6,9-tetra-aza-5,10-dihydroanthracene		WIBWEJ	P21/n	2	2.96	163		
Pyrimidin-2-amine		AMPYRM11	Pbca	8	3.02	90	76.5 [34]	298.15
Biguanide		BIGUAN01	P21/n	4	3.7	283		
Imidazole		IMAZOL06	P21/c	4	2.6	103	81.37 [35]	298.15
Benzimidazole		BZDMAZ02	Pna21	4	2.67	283	101.2 [35]	298.15
Purine		PURINE	Pna21	4	4.8	283		
4-Aminopyridine		AMPYRE	P212121	4	4.9	283	87.1 [34]	298.15
trans-(R,R)-1,2-Diaminocyclohexane		PIWXEY	P21212	2	4.8	220		
1,2,4-Triazole		TRAZOL03	Pbca	8	3	120	83 [36]	298.15
2-Amino-5-methylpyridine		AMMEPY01	P21/c	4	3.65	150		
Melamine		MELAMI06	P21/a	4	4.34	14	123.3 [11]	432
Guanozol		DAMTRZ11	P21/c	4	3.15	200		

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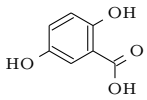
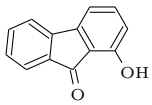
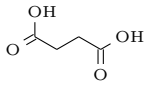
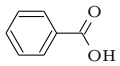
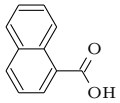
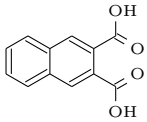
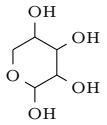
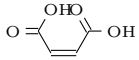
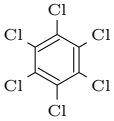
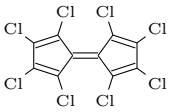
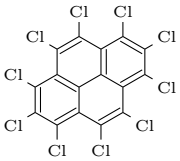
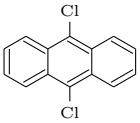
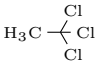
Table S1 – continued from previous page

Name	Molecular diagram	CSD code	Space Group	Z	R-factor	T K	$\Delta H^{\mathrm{exp}}_{\mathrm{sub}}(T^{sub})$ kJ mol^{-1}	T^{sub} K
Methanol		METHOL04	P212121	4	3.38	122		
Butan-2-ol		ZEFPUX	P212121	4	8.05	283		
2-Butyne-1,4-diol		TELXAJ	F2dd	4	3.21	283		
2,5-Dihydroxybenzoic acid		BESKAL04	P21/n	4	4.3	100	130.40 [37]	298.15
rac-trans-1,2-Cyclohexanediol		ZZZKPE03	Pbca	8	3.41	173	85.90 [38]	343
1-Hydroxy-9-fluorenone		BESGEL	P212121	4	3	283		
Dideutero-formic acid		FORMAC02	Pna21	4	7.94	5	60.50 [11]	274.5
Acetic acid		ACETAC07	Pna21	4	3.97	40	67.00 [39]	221.5
Succinic acid		SUCACB03	P21/c	2	2.7	77	123.10 [40]	298.15
Benzoic acid		BENZAC12	P21/n	4	3.63	123	90.00[1]	298.15
1-Naphthoic acid		NAPOAC01	P21/c	4	4.6	283	113.64 [42]	298.15
2,3-Naphthalenedicarboxylic acid		JUBBIR	C2/c	4	3.7	283		
0.8-Deutero-β-L-arabinose		ABINOS02	P212121	4	2.4	123		
cis-Ethene-1,2-dicarboxylic acid		MALIAC12	P21/c	4	3.87	180	105.40 [43]	298.15
cis-Ethene-1,2-dicarboxylic acid		MALIAC13	Pc	2	2.61	180		

Continued on next page

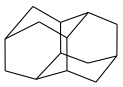
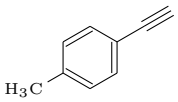
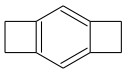
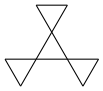
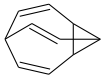
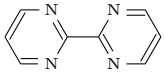
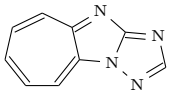
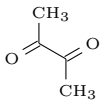
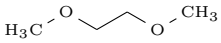
[1]Average of 13 data points [41]

Table S1 – continued from previous page

Name	Molecular diagram	CSD code	Space Group	Z	R-factor	T K	$\Delta H_{\mathrm{sub}}^{\mathrm{exp}}(T^{sub})$ kJ mol^{-1}	T^{sub} K
Hexachlorobenzene		HCLBNZ13	P21/n	2	1.04	100	90.50 [44]	298.15
Perchlorofulvalene		CLFULV01	C2/c	4	3.6	283		
Decachloropyrene		DECPYR10	P21/n	4	3.8	283		
9,10-Dichloroanthracene		DCLANT10	P21/a	4	3	283	113.90 [45]	346.00
1,2-Dichlorobenzene		ABUMIT	P21/n	4	4	223		
Chloromethane		CLMETH03	Cmc21	4	1.28	283	31.60 [46]	151.00
1,1,1-Trichloroethane		MECHLF12	Pnma	4	3.29	220		
1,1-Dichloroethane		RIVDOQ	Pnma	4	2.6	100		
Chloroethane		XAXCOQ03	P21/n	4	5.52	100		
1,2-Dichloroethane		DCLETH02	P21/c	2	1.7	110		
Chloroform		CLFORM03	Pnma	4	1.72	120		

Validation set data

Table S2: Crystal structures and sublimation enthalpies used for validation

Name	Molecular diagram	CSD code	Space Group	Z	R-factor	T K	$\Delta H_{\mathrm{sub}}^{\mathrm{exp}}(T^{sub})$ kJ mol^{-1}	T^{sub} K
Congressane		CONGRS	Pa3	4	11	283-303	95.94 [47]	298.15
4-Ethynyltoluene		AYOJED	P21/n	4	4.65	120		
1,2,4,5-Tetrahydrodicyclobuta (a,d)benzene		BCYBUE01	P-1	1	3.72	103		
Trispiro(2.0.2.0.2.0)nonane		TSCPCP01	P21/n	4	8	96		
Bullvalene		BULVAL03	B21/c	8	2.4	110	71.83 [48]	298.15
Cyclopropane		QQQCIS01	Cmc21	4	1.98	94	29.20 [9]	145
2,2'-Bipyrimidine		BAPJEH01	P21/n	2	4.2	283-303		
1,3,3a,9-Tetra-azacyclopent(a)azuelene		BEBXOV	P21/n	4	4.31	283-303		
Cyanoacetylene		CAACTY	P21/m	2	4.9	283-303	42.26 [49]	264
2,3-Butanedione		CABBIQ01	P21/n	2	8.1	173		
1,2-Dimethoxyethane		NAKWUR	C2/c	4	4.59	183		
4,7-Dioxatricyclo(3.2.1.0^{3,6}) octane		TEMCAP	C2/m	4	3.2	190		

Continued on next page

Table S2 – continued from previous page

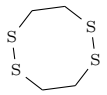
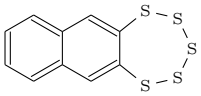
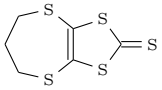
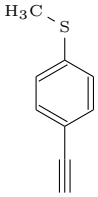
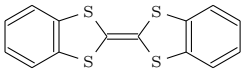
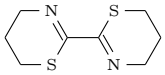
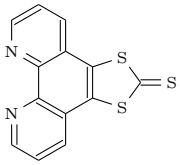
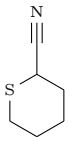
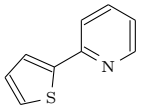
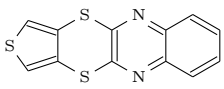
Name	Molecular diagram	CSD code	Space Group	Z	R-factor	T K	$\Delta H^{\mathrm{exp}}_{\mathrm{sub}}(T^{sub})$ kJ mol^{-1}	T^{sub} K
1,2,5,6-Tetrathiacyclo-octane		BIGCID	P21/n	4	3	140		
2,3-(Pentasulfan-1,5-diyl)naphthalene		CEVZEJ	P21/n	4	2.66	123		
4,5-Propylenedithio-1,3- dithiole-2-thione		BEBNOM	P21/c	4	3.64	283-303		
1,4-Dithiacycloheptane		BACYEJ	P212121	4	4.59	283-303		
4-Ethynylthioanisole		AYOJAZ	P212121	4	4.99	120		
Dibenzotetrathiafulvalene		BIRKIW01	P21/c	2	3.6	283-303		
2,2'-Bi-2-thiazine		BARGIK	Pbca	4	1.7	103		
[1, 3]Dithiolo[4,5-f][1, 10]phenanthroline-2-thione		MIHNOI	P21/c	4	4.21	173		
Tetrahydro-2H-thiopyran-2-carbonitrile		ZILZOL	P21/c	4	2.92	173		
2-(2'-Thienyl)pyridine		HABVEL	P212121	4	3.49	193		
Thieno(3',4':5,6)(1,4)dithiino(2,3-b)quinoxaline		WOWFOD	P-1	2	2.86	150		

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Table S2 – continued from previous page

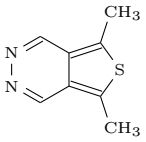
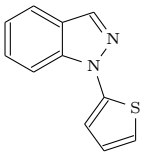
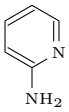
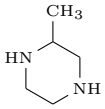
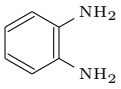
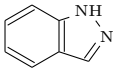
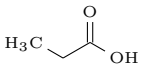
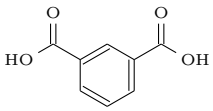
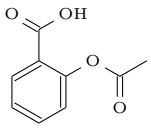
Name	Molecular diagram	CSD code	Space Group	Z	R-factor	T K	$\Delta H^{\mathrm{exp}}_{\mathrm{sub}}(T^{sub})$ kJ mol^{-1}	T^{sub} K
5,7-Dimethylthieno[3,4-d]pyridazine		IRILEB	P21/c	4	3.35	90		
1-(2-Thienyl)-1H-indazole		XOBJAB	P21	2	4.14	150		
Tetrahydro(1,3,4)thiadiazolo(3,4-c)(1,3,4)thiadiazole		OFOHEX	C2/c	4	1.96	100		
2-Aminopyridine		AMPYRD	P21/c	4	3.7	283		
R-(-)-2-methylpiperazine		BILHUB	P21	2	3.53	110		
1,2-Diaminobenzene		BAGFIY	P21/c	4	4	283		
1H-Indazole		INDAZL02	P21	2	4.75	110	91.1 [35]	298.15
Propionic acid		PRONAC	P21/c	4	11.6	178		
Isophthalic acid		BENZDC01	P21/c	4	4.6	283	142 [50]	298.15
2-acetoxybenzoic acid (Aspirin)		ACSALA21	P21/c	4	3.31	90		
2-acetoxybenzoic acid (Aspirin)		ACSALA20	P21/c	4	3.62	120		

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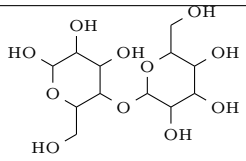
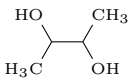
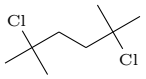
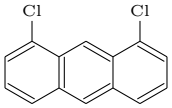
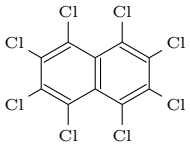
Table S2 – continued from previous page

Name	Molecular diagram	CSD code	Space Group	Z	R-factor	T K	$\Delta H_{\rm sub}^{\rm exp}(T^{sub})$ kJ mol^{-1}	T^{sub} K
β-Lactose		BLACTO02	P21	2	5.8	100		
Butane-2,3-diol		ZEFPAD	P212121	4	4.89	283		
2,5-Dichloro-2,5-dimethylhexane		XOQLAR	P-1	1	2.51	190		
1,8-Dichloroanthracene		ZZZBLP03	Pna21	4	2.8	90		
1,8-Dichloroanthracene		ZZZBLP02	P21/c	4	2.78	100		
Octachloro-naphthalene		OCLNAP10	P21/a	4	7.04	283		

Equilibrium distances and well depths of potentials

Table S3: Equilibrium distances and well depths of twenty four interactions as calculated with FIT, optimized, S-Ab and S-No.

Atom type		FIT		This work		S-Ab		S-No	
i	j	r_{ij}/Å	ϵ_{ij}/kJmol^{-1}	r_{ij}/Å	ϵ_{ij}/kJmol^{-1}	r_{ij}/Å	ϵ_{ij}/kJmol^{-1}	r_{ij}/Å	ϵ_{ij} /kJmol^{-1}
C	C	3.898	-0.398	3.802	-0.323				
C	H$_C$	3.606	-0.143	3.318	-0.230				
H$_C$	H$_C$	3.311	-0.053	3.317	-0.073				
C	N	3.776	-0.360	3.673	-0.529				
N	N	3.662	-0.324	3.730	-0.362				
H$_C$	N	3.493	-0.130	3.718	-0.056				
C	O	3.637	-0.403	3.482	-0.299				
H$_C$	O	3.361	-0.146	3.310	-0.096				
O	O	3.405	-0.400	2.538	-2.712				
C	S	3.987	-0.527	3.664	-0.975	3.967	-0.732	4.176	-0.476
N	S	3.854	-0.483	3.892	-0.488	3.817	-0.686	4.023	-0.444
H$_C$	S	3.673	-0.194	3.697	-0.201	3.607	-0.286	3.829	-0.179
S	S	4.090	-0.687	3.640	-1.990	4.065	-1.270	4.566	-0.507
C	H$_N$	3.087	-0.140	2.900	-0.288				
H$_C$	H$_N$	2.830	-0.052	1.941	-0.401				
N	H$_N$	3.009	-0.122	3.248	-0.041				
H$_N$	H$_N$	2.492	-0.043	3.017	-0.008				
H$_O$	C	3.087	-0.140	3.141	-0.134				
H$_O$	H$_C$	2.830	-0.052	3.530	-0.007				
H$_O$	O	2.906	-0.135	3.153	-0.035				
H$_O$	H$_O$	2.492	-0.043	3.000	-0.007				
C	Cl	3.916	-0.687	3.717	-0.777				
H$_C$	Cl	3.628	-0.245	3.456	-0.522				
Cl	Cl	3.952	-1.153	3.939	-0.990				

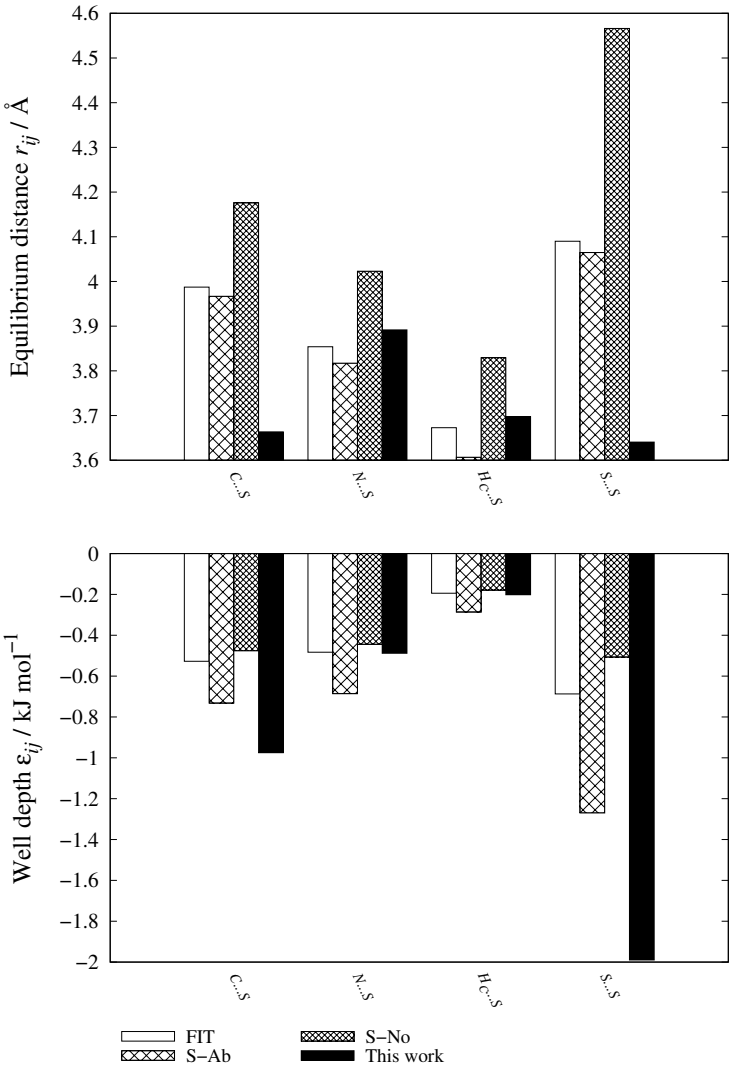


Figure S3: Comparison of equilibrium distances and well depths of 4 interactions as calculated with FIT (white bars) and our new parameter set (black bars). The results for the S-Ab (sparse pattern bars) and S-No (dense pattern bars) parameter sets are also shown.

Crystal packing calculations with FIT, optimized, S-Ab and S-No parameters

Crystal packing results for hydrocarbons

Table S4: Crystal packing results for the hydrocarbon molecules

		unit cell lengths and angles								
Molecule	Refcode	a/Å	b/Å	c/Å	$\alpha/^o$	β /^{o}	$\gamma/^o$	rmsd$_{15}$/Å	Density/g cm^{-3}	ΔH_{sub}/kJ mol^{-1}
Hexadeutero-	BENZEN06 Exp	7.36	9.38	6.70	90	90	90		1.12	44.40

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Table S4 – continued from previous page

Molecule	Refcode		unit cell lengths and angles						rmsd$_{15}$/Å	Density/g cm^{-3}	ΔH_{sub}/kJ mol^{-1}
			a/Å	b/Å	c/Å	$\alpha/^o$	β /^{o}	$\gamma/^o$			
bezene		FIT	7.46	9.25	7.18	90	90	90	0.268	1.05	42.79
		This work	7.55	9.15	6.71	90	90	90	0.122	1.12	44.98
Naphthalene	NAPHTA31	Exp	8.08	5.93	8.63	90	124.65	90		1.25	72.70
		FIT	8.31	5.70	8.12	90	110.97	90	0.922	1.19	69.26
		This work	7.98	5.50	8.04	90	109.21	90	0.985	1.28	72.25
Decadeutero-	ANTCEN16	Exp	8.37	6.00	11.12	90	125.40	90		1.30	97.90
anthracene		FIT	8.55	6.02	11.08	90	123.13	90	0.241	1.24	95.64
		This work	8.41	5.73	11.13	90	123.58	90	0.222	1.32	98.12
Phenanthrene	PHENAN08	Exp	8.44	6.14	9.44	90	97.96	90		1.22	90.90
		FIT	8.65	6.04	9.39	90	95.48	90	0.189	1.21	91.41
		This work	8.51	5.74	9.38	90	93.52	90	0.420	1.30	94.15
Pyrene	PYRENE03	Exp	13.53	9.16	8.39	90	100.25	90		1.31	100.30
		FIT	12.97	10.00	8.17	90	94.62	90	0.700	1.27	98.97
		This work	12.73	9.90	8.12	90	100.99	90	0.708	1.34	96.95
Chrysene	CRYSEN	Exp	8.39	6.20	25.20	90	116.20	90		1.29	123.40
		FIT	8.49	6.14	25.25	90	114.96	90	0.114	1.27	120.57
		This work	8.32	5.86	25.26	90	115.48	90	0.333	1.36	123.76
Triphenylene	TRIPHE13	Exp	5.27	12.96	16.72	90	90	90		1.33	120.10
		FIT	5.08	13.54	17.10	90	90	90	0.307	1.29	117.36
		This work	5.14	13.04	16.53	90	90	90	0.185	1.37	116.02
Perylene	PERLEN06	Exp	9.76	5.84	10.61	90	96.77	90		1.39	129.60
		FIT	10.15	5.27	11.74	90	101.53	90	0.838	1.36	130.94
		This work	9.90	5.63	10.50	90	96.93	90	0.221	1.44	128.66
n-Pentane	PENTAN01	Exp	4.14	9.03	14.82	90	90	90		0.87	42.00
		FIT	4.24	9.05	15.14	90	90	90.03	0.132	0.82	38.21
		This work	4.22	8.99	15.02	90	90	90.02	0.096	0.84	40.48
n-Hexane	HEXANE01	Exp	4.13	4.70	8.54	83.40	87.27	75.17		0.90	50.80
		FIT	4.27	4.58	8.72	83.16	89.03	77.52	0.262	0.87	48.98
		This work	4.24	4.54	8.70	83.14	89.22	77.71	0.261	0.88	51.37
n-Octane	OCTANE01	Exp	4.19	4.75	11.00	85.11	83.77	74.26		0.91	68.10
		FIT	4.26	4.56	11.16	84.55	85.32	77.88	0.309	0.90	65.36
		This work	4.24	4.52	11.15	84.50	85.45	78.17	0.324	0.91	68.04
Cubane	CUBANE	Exp	5.34	5.34	5.34	72.25	72.25	72.25		1.29	55.20
		FIT	5.34	5.34	5.34	74.96	74.96	74.96	0.301	1.25	60.03
		This work	5.28	5.28	5.28	74.42	74.42	74.42	0.125	1.29	57.35
Adamantane	ADAMAN08	Exp	6.64	6.64	8.92	90	90	90		1.15	59.00
		FIT	6.72	6.72	9.09	90	90	90	0.122	1.10	62.80
		This work	6.74	6.74	8.98	90	90	90	0.093	1.11	61.19
Bicyclopropyl	BCPROP02	Exp	8.85	5.09	11.73	90	90.00	90		1.03	

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Table S4 – continued from previous page

Molecule	Refcode		unit cell lengths and angles						rmsd$_{15}$/Å	Density/g cm^{-3}	ΔH_{sub}/kJ mol^{-1}
			a/Å	b/Å	c/Å	$\alpha/^o$	$\beta/^o$	$\gamma/^o$			
		FIT	9.04	5.24	11.97	90	90.00	90	0.134	0.96	
		This work	9.03	5.15	11.94	90	91.33	90	0.134	0.98	
1-Biapocamphane	BAPOCM10	Exp	6.89	9.51	6.58	112.13	65.84	108.90		1.15	
		FIT	6.86	9.55	6.68	112.50	65.52	108.28	0.100	1.13	
		This work	6.85	9.54	6.71	112.90	64.48	108.71	0.116	1.14	
1,1'-Biadamantane	BADAMN10	Exp	6.53	6.58	10.46	87.50	104.58	119.86		1.20	
		FIT	6.80	6.61	10.62	81.61	108.65	120.99	0.453	1.16	
		This work	6.66	6.64	10.62	86.47	106.42	120.33	0.189	1.16	
Dideutero-	ACETYL05	Exp	6.19	6.00	5.55	90	90	90		0.84	23.50
acetylene		FIT	6.63	6.07	5.45	90	90	90	0.566	0.79	19.15
		This work	6.32	5.73	5.24	90	90	90	0.202	0.91	22.70
7,7-Diethynyldispiro	MEYCEY	Exp	7.34	6.38	9.35	90	95.94	90		1.08	
(2.0.2.1)heptane		FIT	7.58	6.40	9.83	90	95.40	90	0.276	1.00	
		This work	7.54	6.12	9.78	90	93.06	90	0.287	1.05	
Ethynylcyclopropane	MEYCIC	Exp	6.40	9.20	14.61	90	90	90		1.02	
		FIT	6.43	9.90	14.62	90	90	90	0.403	0.94	
		This work	6.36	9.81	13.79	90	90	90	0.398	1.02	
Congressane	CONGRS	Exp	10.11	10.11	10.11	90	90	90		1.21	95.94
		FIT	10.19	10.19	10.19	90	90	90	0.079	1.18	82.45
		This work	10.18	10.18	10.18	90	90	90	0.063	1.19	79.12
4-Ethynyltoluene	AYOJED	Exp	5.90	10.07	11.66	90	102.92	90		1.14	
		FIT	5.80	10.69	12.04	90	103.85	90	0.286	1.06	
		This work	5.63	10.60	11.55	90	103.44	90	0.285	1.15	
1,2,4,5-Tetrahydrodicyclo	BCYBUE01	Exp	5.42	5.52	6.20	106.60	98.05	94.68		1.24	
buta(a,d)benzene		FIT	5.65	5.67	6.21	105.61	96.96	97.09	0.221	1.15	
		This work	5.58	5.63	5.90	103.76	99.28	96.31	0.272	1.23	
Bullvalene	BULVAL03	Exp	6.48	20.58	10.37	90	90.17	90		1.25	71.83
		FIT	6.60	21.09	10.68	90	90.87	90	0.162	1.16	64.72
		This work	6.50	20.81	10.43	90	91.60	90	0.148	1.23	66.37
Cyclopropane	QQQCIS01	Exp	7.97	6.58	5.84	90	90	90		0.91	29.20
		FIT	8.18	6.53	6.31	90	90	90	0.255	0.83	23.86
		This work	8.01	6.68	5.93	90	90	90	0.078	0.88	26.54

Crystal packing results for azahydrocarbons

Table S5: Crystal packing results for the azahydrocarbon molecules

			unit cell lengths and angles								
Molecule	Refcode		a/Å	b/Å	c/Å	$\alpha/^o$	β $/^o$	$\gamma/^o$	$rmsd_{15}$/Å	Density/g cm^{-3}	ΔH_{sub}/kJ mol^{-1}
Cyanogen	CYNGEN	Exp	6.31	7.08	6.19	90	90	90		1.250	32.40
		FIT	5.82	7.40	6.43	90	90	90	0.490	1.247	28.15
		This work	5.81	7.45	6.24	90	90	90	0.476	1.280	32.11
Dicyanoacetylene	DCYANM	Exp	8.93	6.04	3.86	90	99.33	90		1.229	44.25
		FIT	8.51	6.09	3.86	90	98.31	90	0.215	1.277	40.89
		This work	8.62	5.98	3.73	90	97.02	90	0.185	1.325	44.95
Tetracyanoethylene	TCYETY01	Exp	9.74	9.74	9.74	90	90	90		1.383	81.20
		FIT	9.79	9.79	9.79	90	90	90	0.033	1.361	74.40
		This work	9.75	9.75	9.75	90	90	90	0.307	1.378	81.33
Tetracyanoethylene	TCYETY	Exp	7.51	6.21	7.00	90	97.17	90		1.313	
		FIT	7.94	6.05	6.76	90	98.99	90	0.288	1.327	
		This work	7.93	6.02	6.73	90	99.62	90	0.307	1.342	
cis-1,2,3-Tricyano-	CYCYPR	Exp	9.88	9.88	10.42	90.00	90.00	120.00		1.325	
cyclopropane		FIT	10.13	10.13	10.32	89.95	90.05	119.96	0.152	1.272	
		This work	10.08	10.08	10.24	89.95	90.05	119.96	0.130	1.293	
1,1,2,2-Tetracyano-	TCYCPR01	Exp	6.20	6.92	16.13	90	90	90		1.364	
cyclopropane		FIT	6.33	7.07	16.19	90	90	90	0.114	1.305	
		This work	6.27	7.03	16.18	90	90	90	0.085	1.324	
Triethylenediamine	TETDAM03	Exp	6.14	6.14	9.46	90	90	120.00		1.206	62.20
		FIT	6.11	6.11	9.80	90	90	120.01	0.141	1.175	58.86
		This work	6.11	6.12	9.66	90	90	120.01	0.080	1.190	60.84
Hexamethylene-	HXMTAM10	Exp	6.93	6.93	6.93	90	90.00	90.00		1.400	79.60
tetramine		FIT	7.00	7.00	7.00	90	89.99	89.99	0.061	1.360	78.56
		This work	6.94	6.94	6.94	90	89.98	89.99	0.010	1.394	83.16
Pyrimidine	PRMDIN01	Exp	11.56	9.46	3.69	90	90	90		1.318	
		FIT	11.53	9.81	3.68	90	90	90	0.137	1.277	
		This work	11.49	9.77	3.57	90	90	90	0.143	1.326	
Pyrazine	PYRAZI01	Exp	9.33	5.85	3.73	90	90.00	90		1.306	56.20
		FIT	9.69	5.69	3.77	90	90.01	90	0.169	1.281	50.13
		This work	9.68	5.61	3.66	90	90.06	90	0.204	1.335	53.31
1,8-Naphthyridine	NAPTYR11	Exp	6.14	10.41	11.26	90	117.76	90		1.359	
		FIT	6.24	9.99	12.02	90	117.16	90	0.313	1.295	
		This work	6.23	9.76	11.63	90	116.82	90	0.301	1.370	
4-Methyl-4H-	TELPIJ	Exp	10.93	6.46	5.68	90	90	90		1.375	
1,2,4-triazole		FIT	11.41	6.42	5.87	90	90	90	0.191	1.284	
		This work	11.38	6.29	5.84	90	90	90	0.216	1.322	
s-Triazine	TRIZIN01	Exp	9.65	9.65	7.28	90	90.00	120		1.377	
		FIT	9.77	9.77	6.94	90	90.01	120	0.120	1.407	

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Table S5 – continued from previous page

Molecule	Refcode		unit cell lengths and angles a/Å	b/Å	c/Å	$\alpha/^o$	β $/^o$	$\gamma/^o$	$rmsd_{15}$/Å	Density/g cm^{-3}	ΔH_{sub}/kJ mol^{-1}
		This work	9.72	9.72	6.81	90	90.01	120	0.144	1.448	
Phenazine	PHENAZ04	Exp	7.08	5.07	12.79	90	102.34	90		1.333	94.30
		FIT	6.97	5.77	11.36	90	100.62	90	0.747	1.332	93.63
		This work	6.95	5.45	11.45	90	99.12	90	0.631	1.398	94.28
2,2'-Bipyridyl	BIPYRL04	Exp	5.49	6.17	11.61	90	95.28	90		1.326	81.80
		FIT	5.68	6.26	11.62	90	96.19	90	0.169	1.263	79.82
		This work	5.65	6.12	11.41	90	99.05	90	0.246	1.332	83.10
2,2'-Bipyrimidine	BAPJEH01	Exp	3.86	10.80	8.84	90	101.03	90		1.45	
		FIT	4.02	10.93	8.91	90	103.53	90	0.177	1.38	
		This work	3.87	10.93	8.78	90	102.20	90	0.130	1.45	
1,3,3a,9-Tetra-azacyclo	BEBXOV	Exp	3.83	12.93	15.60	90	93.58	90		1.47	
pent(a)azulene		FIT	3.81	13.39	15.55	90	89.35	90	0.283	1.42	
		This work	3.74	13.46	15.21	90	86.35	90	0.433	1.48	
Cyanoacetylene	CAACTY	Exp	6.96	6.30	3.84	90	110.50	90		1.07	42.26
		FIT	7.31	5.74	3.69	90	94.00	90	0.747	1.10	32.75
		This work	7.31	6.00	3.62	90	114.73	90	0.389	1.18	34.77

Crystal packing results for oxohydrocarbons

Table S6: Crystal packing results for the oxohydrocarbon molecules

Molecule	Refcode		unit cell lengths and angles a/Å	b/Å	c/Å	$\alpha/^o$	β $/^o$	$\gamma/^o$	$rmsd_{15}$/Å	Density/g cm^{-3}	ΔH_{sub}/kJ mol^{-1}
1,4-Dioxane	CUKCIU03	Exp	5.66	6.41	5.89	90	98.36	90		1.38	35.60
		FIT	5.90	6.50	6.46	90	99.40	90	0.340	1.20	46.87
		This work	5.77	6.47	6.34	90	100.26	90	0.288	1.26	47.21
s-Trioxane	TROXAN	Exp	9.40	9.40	8.35	90.00	90.00	120.00		1.41	56.57
		FIT	9.46	9.46	8.34	89.99	90.01	120.01	0.079	1.39	49.37
		This work	9.19	9.19	7.97	90.00	90.00	120.01	0.158	1.54	54.39
1,3,5,7-Tetroxocane	TOXOCN	Exp	11.46	4.16	12.23	90.00	108.40	90		1.44	79.60
		FIT	11.68	4.21	11.73	90.03	93.97	90	0.728	1.39	62.78
		This work	11.39	4.02	11.35	90.03	92.01	90	0.808	1.53	69.10
Succinic	SUCANH12	Exp	5.35	6.82	11.56	90	90	90		1.57	80.70
		FIT	5.45	6.97	11.63	90	90	90	0.116	1.50	73.94
		This work	5.30	6.63	11.11	90	90	90	0.182	1.70	82.33
1,3,5,7,9-Pentoxecane	PTOXEC	Exp	8.15	10.67	7.67	90	90	90.00		1.49	87.90
		FIT	8.19	10.70	7.93	90	90	90.14	0.146	1.43	69.68

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Table S6 – continued from previous page

Molecule	Refcode		unit cell lengths and angles a/Å	b/Å	c/Å	α/^{o}	β /^{o}	γ/^{o}	rmsd$_{15}$/Å	Density/g cm^{-3}	ΔH_{sub}/kJ mol^{-1}
		This work	8.18	10.34	7.71	90	90	90.22	0.140	1.53	71.24
Cyclohexane-1,4-dione	CYHEXO	Exp	6.65	6.21	6.87	90	99.82	90		1.33	75.00
		FIT	6.35	6.78	7.09	90	92.51	90	0.532	1.22	69.56
		This work	6.36	6.57	6.90	90	93.37	90	0.452	1.29	70.74
rac-3,6-Dimethyl-	BICVIS	Exp	8.05	9.09	9.71	90	102.86	90		1.38	
1,4-dioxane-2,5-dione		FIT	7.95	8.76	10.04	90	97.44	90	0.405	1.38	
		This work	7.91	9.06	9.45	90	106.14	90	0.317	1.47	
p-Benzoquinone	BNZQUI03	Exp	5.74	6.77	6.87	90	100.14	90		1.37	66.70
		FIT	5.65	6.74	7.14	90	100.44	90	0.343	1.34	66.18
		This work	5.47	6.62	6.74	90	97.19	90	0.303	1.48	68.00
Furan	FURANE10	Exp	5.69	5.69	11.92	90	90	90		1.17	
		FIT	5.53	5.53	13.19	90	90	90	0.370	1.12	
		This work	5.44	5.44	12.35	90	90	90	0.241	1.24	
Dideutero	KEMZIL	Exp	8.48	8.48	4.46	90	90	90		1.24	
formaldehyde		FIT	9.39	9.39	4.58	90	90	90	0.356	0.97	
		This work	8.66	8.66	4.57	90	90	90	0.172	1.16	
Biacetyl	CABBIQ01	Exp	7.51	5.25	6.55	90	116.10	90		1.23	
		FIT	7.31	5.31	6.53	90	113.39	90	0.188	1.23	
		This work	7.56	4.99	6.47	90	118.08	90	0.237	1.33	
1,2-Dimethoxyethane	NAKWUR	Exp	11.83	4.60	10.29	90	106.32	90		1.11	
		FIT	12.20	4.71	10.38	90	105.86	90	0.156	1.04	
		This work	11.87	4.56	10.44	90	106.24	90	0.067	1.10	
4,7-Dioxatricyclo	TEMCAP	Exp	9.63	6.55	8.47	90	98.86	90		1.41	
(3.2.1.0^3, 6)octane		FIT	9.86	6.64	8.45	90	98.46	90	0.098	1.36	
		This work	9.11	6.68	8.64	90	94.99	90	0.289	1.42	

Crystal packing results for organosulphur compounds

Table S7: Crystal packing results for the organosulphur molecules

Molecule	Refcode		unit cell lengths and angles a/Å	b/Å	c/Å	α/^{o}	β /^{o}	γ/^{o}	rmsd$_{15}$/Å	Density/g cm^{-3}	ΔH_{sub}/kJ mol^{-1}
[1,2,5]thiadiazolo[3,4-C]	BAWHEM01	exp	3.78	10.48	6.32	90	105.76	90		1.99	
[1, 2, 5]thiadiazole		FIT	3.83	10.06	6.75	90	110.68	90	0.292	1.97	
		Williams	3.81	9.93	6.72	90	110.38	90	0.309	2.01	
		Scheraga	4.04	10.11	7.01	90	112.33	90	0.415	1.81	
		This work	3.67	9.99	6.78	90	109.72	90	0.325	2.04	

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Table S7 – continued from previous page

Molecule	Refcode		unit cell lengths and angles						rmsd$_{15}$/Å	Density/g cm^{-3}	ΔH_{sub}/kJ mol^{-1}
			a/Å	b/Å	c/Å	$\alpha/^o$	β /^{o}	$\gamma/^o$			
1,2,4-thiadiazole-	CEBYUD	exp	7.36	7.36	9.11	90	90	120		1.59	
3,5-dicarbonitrile		FIT	7.41	7.41	8.94	90	90	120	0.097	1.60	
		Williams	7.39	7.39	8.92	90	90	120	0.095	1.61	
		Scheraga	7.48	7.48	9.14	90	90	120	0.112	1.53	
		This work	7.40	7.40	8.83	90	90	120	0.13	1.62	
1-Cyanoimino-	GEDHAY	exp	5.45	8.75	11.83	90	99.57	90		1.96	
1^4,2,4^4,3,5-trithiadiazole		FIT	5.63	9.04	11.48	90	96.76	90	0.287	1.88	
		Williams	5.57	8.95	11.40	90	97.29	90	0.231	1.93	
		Scheraga	5.85	9.35	11.67	90	96.38	90	0.412	1.72	
		This work	5.45	8.90	11.55	90	98.06	90	0.158	1.97	
8-Cyanoisothiazolo-	ISTZCN10	exp	16.72	6.24	9.25	90	104.49	90		1.91	
pentathiepin		FIT	16.87	6.15	9.33	90	103.19	90	0.166	1.89	
		Williams	16.78	6.11	9.18	90	103.29	90	0.167	1.95	
		Scheraga	17.34	6.51	9.81	90	105.04	90	0.364	1.67	
		This work	16.34	5.77	8.90	90	101.17	90	0.417	2.16	
Tetracyanothiophene	TCTHPH	exp	13.42	6.56	7.07	90	137.00	90		1.44	
		FIT	13.47	6.61	6.82	90	136.87	90	0.184	1.47	
		Williams	13.45	6.56	6.83	90	136.85	90	0.176	1.48	
		Scheraga	13.53	6.53	6.99	90	137.00	90	0.116	1.45	
		This work	13.36	6.39	7.02	90	137.22	90	0.143	1.50	
Benzo[1,2-c:3,4-c:5,6-c]	EWADAI	exp	14.22	3.68	7.80	90	90	90		2.05	
tris[1,2,5]thiadiazole		FIT	14.21	3.66	7.83	90	90	90	0.106	2.06	
		Williams	14.16	3.65	7.80	90	90	90	0.107	2.08	
		Scheraga	14.54	3.84	7.92	90	90	90	0.205	1.89	
		This work	14.21	3.50	7.86	90	90	90	0.211	2.14	
Benzo(c)(1,2,5)thiadiazole	BETHAZ01	exp	12.57	12.13	3.80	90	90	90		1.56	70.70
		FIT	12.65	12.29	3.81	90	90	90	0.091	1.53	66.02
		Williams	12.60	12.26	3.80	90	90	90	0.082	1.54	74.67
		Scheraga	12.74	12.32	3.92	90	90	90	0.128	1.47	62.73
		This work	12.56	12.26	3.66	90	90	90	0.13	1.61	75.11
1-Azathianthrene	CEJSEP	exp	11.77	6.03	14.15	90	108.51	90		1.52	
		FIT	11.31	6.41	14.09	90	107.49	90	0.448	1.48	
		Williams	11.27	6.34	14.10	90	107.67	90	0.392	1.50	
		Scheraga	11.38	6.56	14.17	90	107.96	90	0.485	1.43	
		This work	11.30	5.87	14.16	90	108.16	90	0.242	1.62	
$[1,3]$-Dithiolo$[4,5-b]$-	DILCOS	exp	11.70	9.79	5.86	90	90	90		1.84	
pyrazine-2-thione		FIT	14.15	10.03	5.05	90	90	90	1.047	1.72	
		Williams	13.95	10.01	5.04	90	90	90	0.996	1.76	
		Scheraga	14.65	10.29	5.15	90	90	90	1.195	1.60	
		This work	13.39	9.82	5.00	90	90	90	0.81	1.88	
3,5,7-Trithiacyclo-	HELKEO	exp	6.74	12.16	20.33	90	90	90		1.60	
heptamaleonitrile		FIT	6.87	12.11	21.31	90	90	90	0.235	1.50	
		Williams	6.78	12.18	20.88	90	90	90	0.125	1.54	
		Scheraga	6.95	12.40	21.49	90	90	90	0.285	1.44	

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Table S7 – continued from previous page

Molecule	Refcode		unit cell lengths and angles						rmsd$_{15}$/Å	Density/g cm^{-3}	ΔH_{sub}/kJ mol^{-1}
			a/Å	b/Å	c/Å	$\alpha/^o$	β /^{o}	$\gamma/^o$			
		This work	6.65	12.15	20.94	90	90	90	0.147	1.57	
	DZTNON02	exp	10.32	8.88	7.56	90	93.30	90		1.23	
3,7-Dithia-1,5-diaza		FIT	11.63	8.82	7.47	90	99.19	90	0.588	1.17	
bicyclo[3.3.1]nonane		Williams	11.43	8.76	7.48	90	98.69	90	0.514	1.19	
		Scheraga	11.87	8.96	7.48	90	98.36	90	0.658	1.37	
		This work	11.18	8.74	7.52	90	98.33	90	0.413	1.48	
	KAQPOH	exp	4.75	5.97	17.02	90	90	90		1.23	
N,N-Dimethylthioformamide		FIT	4.96	6.00	17.01	90	90	90	0.169	1.17	
		Williams	4.91	5.97	16.94	90	90	90	0.135	1.19	
		Scheraga	4.97	6.12	17.38	90	90	90	0.204	1.12	
		This work	4.76	5.94	17.13	90	90	90	0.11	1.22	
2,3-Dicyano-5,7-dimethyl	YIJGAA	exp	4.69	14.80	7.26	90	106.87	90		1.48	
thieno(3,4-b)pyrazine		FIT	4.17	14.84	8.01	90	98.93	90	0.840	1.45	
		Williams	4.17	14.82	8.00	90	99.05	90	0.838	1.46	
		Scheraga	4.22	14.81	8.09	90	99.08	90	0.834	1.42	
		This work	4.14	14.95	7.82	90	101.40	90	1.047	1.50	
5,10-Dithia-1,4,6,9-tetra-aza-	WIBWEJ	exp	3.89	7.87	14.30	90	95.66	90		1.68	
5,10-dihydroanthracene		FIT	3.78	7.98	14.76	90	92.65	90	0.278	1.64	
		Williams	3.77	7.90	14.71	90	92.63	90	0.264	1.67	
		Scheraga	3.92	7.94	14.90	90	92.21	90	0.304	1.58	
		This work	3.64	8.03	14.59	90	96.39	90	0.273	1.73	
Dimethylsulfide	PADQAN	exp	5.62	5.84	6.41	113.16	103.87	94		1.12	
		FIT	6.18	5.67	6.07	108.64	101.82	94	0.424	1.06	
		Williams	6.16	5.62	5.98	108.17	102.09	94	0.44	1.08	
		Scheraga	6.40	5.72	6.12	109.09	101.54	94	0.506	1.00	
		This work	5.76	5.78	6.11	110.80	101.96	93	0.233	1.12	
Ethyl methylsulfide	LIQWEN	exp	5.26	10.72	8.39	90	101.60	90		1.09	
		FIT	5.41	10.92	8.36	90	99.39	90	0.168	1.04	
		Williams	5.37	10.82	8.32	90	99.74	90	0.134	1.06	
		Scheraga	5.48	10.93	8.52	90	100.48	90	0.189	1.01	
		This work	5.38	10.75	8.25	90	98.94	90	0.167	1.07	
1,4-Dithiane	DITHAN02	exp	6.75	5.38	9.97	90	129.84	90		1.43	63.00
		FIT	6.74	5.45	10.37	90	130.27	90	0.198	1.38	55.64
		Williams	6.70	5.39	10.27	90	130.22	90	0.166	1.41	71.53
		Scheraga	6.85	5.53	10.56	90	130.23	90	0.265	1.31	53.33
		This work	6.68	5.40	10.16	90	130.59	90	0.135	1.43	67.24
3H,6H-1,2-Dithiolo(4,4-c)	ZAVHAF	exp	3.89	9.11	10.82	90	98.75	90		2.11	
-1,2-dithiol-3,6-dithione		FIT	3.75	9.62	11.18	90	103.38	90	0.458	2.03	
		Williams	3.70	9.60	11.07	90	102.47	90	0.438	2.08	
		Scheraga	4.07	10.07	11.88	90	103.68	90	0.683	1.69	
		This work	3.39	9.23	10.39	90	100.30	90	0.597	2.49	
5-phenyl-3H-	FABPON11	exp	7.56	12.20	19.94	90	90	90		1.52	123.30
1,2-dithiole-3-thione		FIT	7.51	12.68	19.83	90	90	90	0.272	1.48	84.59

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Table S7 – continued from previous page

Molecule	Refcode		unit cell lengths and angles						rmsd$_{15}$/Å	Density/g cm^{-3}	ΔH_{sub}/kJ mol^{-1}
			a/Å	b/Å	c/Å	$\alpha/^o$	β /^{o}	$\gamma/^o$			
		Williams	7.47	12.63	19.70	90	90	90	0.252	1.50	106.56
		Scheraga	7.80	12.77	20.43	90	90	90	0.368	1.37	76.45
		This work	6.99	12.38	19.70	90	90	90	0.396	1.64	115.24
Ethylene	DTOLTO	exp	8.64	7.18	9.23	90	100.06	90		1.61	81.80
trithiocarbonate		FIT	8.20	7.72	9.20	90	101.17	90	0.361	1.58	55.98
		Williams	8.10	7.68	9.02	90	100.24	90	0.362	1.64	78.52
		Scheraga	8.48	8.15	9.28	90	98.00	90	0.569	1.43	50.03
		This work	8.13	7.21	9.00	90	103.07	90	0.277	1.76	81.71
Phenyl-	LEVMUU	exp	5.74	7.53	16.01	90	94.30	90		1.29	
thioacetylene		FIT	5.68	7.69	16.48	90	92.78	90	0.199	1.24	
		Williams	5.70	7.60	16.43	90	91.86	90	0.184	1.25	
		Scheraga	5.69	7.99	16.42	90	96.52	90	0.449	1.20	
		This work	5.45	7.41	16.46	90	93.52	90	0.249	1.34	
2,2'-Bithiophene	DTENYL02	exp	7.73	5.73	8.93	90	106.72	90		1.46	85.20
		FIT	7.81	5.65	9.20	90	107.63	90	0.154	1.43	71.77
		Williams	7.89	5.64	8.95	90	107.24	90	0.13	1.45	86.87
		Scheraga	8.13	5.79	8.95	90	108.05	90	0.256	1.38	69.84
		This work	7.32	5.49	9.15	90	105.46	90	0.33	1.56	89.71
1,35-Trithiane	TRITAN03	exp	5.26	7.67	14.03	90	90	90		1.62	93.20
		FIT	5.34	7.52	14.70	90	90	90	0.214	1.56	57.39
		Williams	5.27	7.41	14.71	90	90	90	0.246	1.60	79.76
		Scheraga	5.43	7.53	15.93	90	90	90	0.505	1.41	50.46
		This work	5.29	7.37	13.90	90	90	90	0.198	1.70	82.76
Pentathiepino(6,7-b)benzo-	BAHNUU	exp	9.00	10.12	12.12	90	93.89	90		1.77	
(d)thiophene(Form II)		FIT	9.20	10.35	12.31	90	102.01	90	0.511	1.69	
		Williams	9.12	10.28	12.10	90	100.99	90	0.44	1.74	
		Scheraga	9.84	10.05	12.75	90	85.28	90	0.857	1.55	
		This work	8.55	10.22	11.95	90	100.92	90	0.485	1.89	
Pentathiepino(6,7-b)benzo-	BAHNUU01	exp	4.47	13.51	18.05	90	94.59	90		1.79	
(d)thiophene(Form I)		FIT	4.33	13.67	18.57	90	93.06	90	0.237	1.77	
		Williams	4.29	13.57	18.43	90	93.15	90	0.237	1.82	
		Scheraga	4.69	14.21	18.30	90	92.95	90	0.386	1.60	
		This work	3.94	13.28	18.61	90	94.61	90	0.538	2.00	
1,2,5,6-Tetrathiacyclo-	BIGCID	exp	6.47	13.76	8.71	90	103.60	90		1.63	
octane		FIT	6.69	13.85	8.84	90	100.24	90	0.308	1.52	
		Williams	6.63	13.76	8.76	90	101.97	90	0.214	1.57	
		Scheraga	6.94	13.99	9.32	90	104.16	90	0.389	1.40	
		This work	6.52	13.66	8.53	90	99.70	90	0.304	1.63	
2,3-(Pentasulfan-1,5-diyl)	CEVZEJ	exp	7.06	24.25	7.06	90	113.92	90		1.72	
naphthalene		FIT	7.46	24.42	7.11	90	116.59	90	0.304	1.64	
		Williams	7.53	24.01	6.99	90	117.00	90	0.390	1.69	
		Scheraga	7.32	26.09	7.28	90	115.14	90	0.315	1.51	
		This work	6.88	24.03	7.06	90	115.90	90	0.270	1.81	

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Table S7 – continued from previous page

Molecule	Refcode		unit cell lengths and angles						rmsd$_{15}$/Å	Density/g cm^{-3}	ΔH_{sub}/kJ mol^{-1}
			a/Å	b/Å	c/Å	$\alpha/^o$	$\beta/^o$	$\gamma/^o$			
4,5-Propylenedithio-	BEBNOM	exp	4.66	10.98	18.10	90	90.15	90		1.71	
1,3-dithiole-2-thione		FIT	4.85	10.84	18.08	90	93.55	90	0.254	1.67	
		Williams	4.74	10.84	18.01	90	93.13	90	0.204	1.71	
		Scheraga	4.83	11.67	18.81	90	88.35	90	0.374	1.49	
		This work	4.58	10.55	17.72	90	97.78	90	0.445	1.87	
1,4-Dithia-	BACYEJ	exp	5.41	10.88	11.39	90	90	90		1.33	
cycloheptane		FIT	5.38	11.11	11.47	90	90	90	0.104	1.30	
		Williams	5.34	11.04	11.38	90	90	90	0.092	1.33	
		Scheraga	5.50	11.34	11.53	90	90	90	0.187	1.24	
		This work	5.29	10.94	11.37	90	90	90	0.095	1.36	
4-Ethynylthioanisole	AYOJAZ	exp	5.65	7.27	19.53	90	90	90		1.23	
		FIT	5.76	7.40	19.69	90	90	90	0.239	1.17	
		Williams	5.75	7.36	19.65	90	90	90	0.215	1.18	
		Scheraga	5.77	7.40	19.90	90	90	90	0.231	1.16	
		This work	5.55	7.09	19.41	90	90	90	0.195	1.29	
Dibenzotetra-t	BIRKIW01	exp	12.08	3.96	14.55	90	114.36	90		1.60	
thiafulavalene		FIT	12.59	3.76	14.80	90	115.58	90	0.319	1.60	
		Williams	12.54	3.73	14.74	90	115.32	90	0.334	1.62	
		Scheraga	12.68	3.92	15.26	90	117.83	90	0.359	1.51	
		This work	12.26	3.56	14.34	90	112.97	90	0.48	1.75	
2,2'-Bi-2-thiazine	BARGIK	exp	9.65	13.03	7.30	90	90	90		1.45	
		FIT	9.70	13.37	7.57	90	90	90	0.195	1.35	
		Williams	9.67	13.30	7.52	90	90	90	0.154	1.38	
		Scheraga	9.74	13.51	7.59	90	90	90	0.236	1.33	
		This work	9.59	13.38	7.39	90	90	90	0.152	1.40	
$[1,3]$Dithiolo$[4,5-f]$	MIHNOI	exp	3.85	10.30	28.55	90	91.51	90		1.68	
$[1,10]$phenanthroline-2-thione		FIT	3.76	10.36	29.33	90	89.23	90	0.279	1.67	
		Williams	3.75	10.33	29.16	90	89.39	90	0.27	1.68	
		Scheraga	3.91	10.46	29.39	90	89.67	90	0.25	1.58	
		This work	3.57	10.25	29.17	90	91.34	90	0.354	1.78	
Tetrahydro-2H-thiopyran-	ZILZOL	exp	7.19	6.75	13.72	90	99.17	90		1.29	
2-carbonitrile		FIT	7.13	6.91	13.89	90	99.00	90	0.127	1.25	
		Williams	7.11	6.88	13.84	90	99.02	90	0.118	1.26	
		Scheraga	7.20	6.93	13.99	90	98.47	90	0.151	1.22	
		This work	7.11	6.88	13.70	90	99.00	90	0.114	1.28	
2-(2'-Thienyl)pyridine	HABVEL	exp	5.77	8.79	15.70	90	90	90		1.35	
		FIT	5.76	9.00	15.43	90	90	90	0.156	1.35	
		Williams	5.75	8.98	15.37	90	90	90	0.157	1.35	
		Scheraga	5.82	9.08	15.46	90	90	90	0.183	1.30	
		This work	5.57	8.85	15.08	90	90	90	0.226	1.44	
Thieno(3',4':5,6)(1,4)dithiino	WOWFOD	exp	6.88	9.36	9.51	101.96	95.96	104.09		1.59	
(2,3-b)quinoxaline		FIT	7.07	9.48	9.46	100.28	93.20	107.94	0.34	1.55	
		Williams	7.06	9.45	9.40	99.92	94.42	108.60	0.348	1.57	

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Table S7 – continued from previous page

Molecule	Refcode		unit cell lengths and angles a/Å	b/Å	c/Å	$\alpha/^o$	β $/^o$	$\gamma/^o$	$rmsd_{15}$/Å	Density/g cm^{-3}	ΔH_{sub}/kJ mol^{-1}
		Scheraga	7.16	9.58	9.61	100.37	95.29	106.58	0.285	1.48	
		This work	6.72	9.31	9.33	99.71	94.57	107.88	0.338	1.68	
5,7-Dimethylthieno	IRILEB	exp	6.94	14.20	8.13	90	105.76	90		1.42	
$[3,4-d]$pyridazine		FIT	7.06	14.24	8.38	90	107.06	90	0.208	1.36	
		Williams	7.04	14.21	8.36	90	106.93	90	0.198	1.36	
		Scheraga	7.15	14.32	8.41	90	107.37	90	0.221	1.33	
		This work	6.84	14.08	8.28	90	105.34	90	0.269	1.42	
1-(2-Thienyl)-1H-indazole	XOBJAB	exp	6.45	7.27	10.41	90	105.81	90		1.41	
		FIT	6.69	7.16	11.09	90	111.46	90	0.338	1.35	
		Williams	6.73	7.19	10.55	90	107.75	90	0.243	1.37	
		Scheraga	6.67	7.25	11.18	90	112.31	90	0.45	1.33	
		This work	6.55	6.85	11.22	90	112.92	90	0.499	1.43	
Tetrahydro(1,3,4)thiadiazolo	OFOHEX	exp	12.16	4.79	10.76	90	102.05	90		1.61	
(3,4-c)(1,3,4)thiadiazole		FIT	12.42	4.89	11.20	90	103.21	90	0.179	1.49	
		Williams	12.35	4.84	11.16	90	102.98	90	0.152	1.52	
		Scheraga	12.80	4.97	11.25	90	102.71	90	0.239	1.41	
		This work	12.12	4.86	10.99	90	102.28	90	0.102	1.56	

Crystal packing results for amines and imidazoles

Table S8: Crystal packing results for the amine and imidazole molecules

Molecule	Refcode		unit cell lengths and angles a/Å	b/Å	c/Å	$\alpha/^o$	β $/^o$	$\gamma/^o$	$rmsd_{15}$/Å	Density/g cm^{-3}	ΔH_{sub}/kJ mol^{-1}
Pyrimidin-2-amine	AMPYRM11	exp	10.86	5.62	14.83	90	90	90		1.40	76.50
		FIT	10.76	5.45	15.76	90	90	90	0.258	1.37	76.69
		This work	10.77	5.39	15.31	90	90	90	0.202	1.42	82.49
Biguanide	BIGUAN01	exp	9.52	5.06	10.00	90	102.95	90		1.43	
		FIT	9.38	5.10	9.10	90	105.45	90	0.405	1.60	
		This work	9.53	5.11	9.12	90	105.82	90	0.401	1.57	
Imidazole	IMAZOL06	exp	7.57	5.37	9.79	90	119.08	90		1.30	81.37
		FIT	7.60	5.37	9.82	90	116.60	90	0.136	1.26	68.53
		This work	7.75	4.97	9.91	90	117.75	90	0.248	1.34	72.55
Benzimidazole	BZDMAZ02	exp	13.49	6.81	6.94	90	90	90		1.23	101.20
		FIT	14.24	6.61	7.01	90	90	90	0.247	1.19	81.80
		This work	13.27	6.63	7.00	90	90	90	0.208	1.28	87.53
Purine	PURINE	exp	15.55	9.37	3.66	90	90	90		1.49	
		FIT	15.63	9.42	3.69	90	90	90	0.236	1.47	
		This work	15.55	9.46	3.58	90	90	90	0.232	1.52	

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Table S8 – continued from previous page

Molecule	Refcode		unit cell lengths and angles						rmsd$_{15}$/Å	Density/g cm^{-3}	ΔH_{sub}/kJ mol^{-1}
			a/Å	b/Å	c/Å	$\alpha/^o$	β /^{o}	$\gamma/^o$			
4-Aminopyridine	AMPYRE	exp	5.57	7.32	12.12	90	90	90		1.26	87.10
		FIT	5.33	7.40	12.28	90	90	90	0.205	1.29	76.46
		This work	5.17	7.24	12.22	90	90	90	0.261	1.37	83.01
trans-(R,R)-1,2-Diaminocyclohexane	PIWXEY	exp	5.25	8.47	7.70	90	90	90		1.11	
		FIT	5.18	8.05	8.25	90	90	90	0.375	1.10	
		This work	5.17	8.05	8.05	90	90	90	0.306	1.13	
1,2,4-Triazole	TRAZOL03	exp	9.76	9.35	6.99	90	90	90		1.44	83.00
		FIT	9.85	9.59	6.97	90	90	90	0.151	1.40	68.32
		This work	9.86	9.46	6.86	90	90	90	0.141	1.43	71.93
2-Amino-5-methylpyridine	AMMEPY01	exp	10.35	5.84	10.74	90	117.27	90		1.24	
		FIT	9.48	5.98	12.01	90	120.35	90	0.581	1.22	
		This work	9.47	5.88	11.93	90	121.65	90	0.64	1.27	
Melamine	MELAMI06	exp	10.43	7.46	7.24	90	113.30	90		1.62	123.30
		FIT	10.35	7.09	7.20	90	111.20	90	0.215	1.70	131.56
		This work	10.35	7.12	7.20	90	111.46	90	0.202	1.70	134.67
Guanozol	DAMTRZ11	exp	10.64	4.30	10.81	90	118.78	90		1.52	
		FIT	10.41	3.88	11.12	90	118.60	90	0.373	1.67	
		This work	10.43	3.89	11.14	90	118.41	90	0.364	1.66	
2-Aminopyridine	AMPYRD	exp	11.71	5.67	7.59	90	95.55	90	1.25		
		FIT	11.67	5.67	7.57	90	100.39	90	1.27	0.325	
		This work	11.52	5.51	7.35	90	97.96	90	1.35	0.276	
R-(-)-2-methylpiperazine	BILHUB	exp	5.21	8.47	7.21	90	105.36	90	1.08		
		FIT	5.17	8.29	7.24	90	104.74	90	1.11	0.102	
		This work	5.13	8.19	7.20	90	104.47	90	1.14	0.149	
1,2-Diaminobenzene	BAGFIY	exp	10.32	7.54	7.72	90	99.98	90	1.21		
		FIT	10.14	7.75	7.29	90	99.36	90	1.27	0.306	
		This work	10.04	7.57	7.25	90	100.58	90	1.33	0.298	
1H-Indazole	INDAZL02	exp	7.43	5.75	7.63	90	118.46	90	1.37		91.10
		FIT	8.08	5.57	8.53	90	127.15	90	1.28	0.574	79.65
		This work	7.73	5.43	8.20	90	123.70	90	1.37	0.377	86.19

Crystal packing results for carboxylic acids and alcohols

Table S9: Crystal packing results for the carboxylic acid and alcohol molecules

Molecule	Refcode		unit cell lengths and angles						rmsd$_{15}$/Å	Density/g cm^{-3}	ΔH_{sub}/kJ mol^{-1}
			a/Å	b/Å	c/Å	$\alpha/^o$	β /^{o}	$\gamma/^o$			
Methanol	METHOL04	exp	4.65	4.93	9.04	90	90	90		1.03	
		FIT	4.51	6.36	7.85	90	90	90	0.857	0.95	

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Table S9 – continued from previous page

Molecule	Refcode		unit cell lengths and angles						$rmsd_{15}$/Å	Density/g cm^{-3}	ΔH_{sub}/kJ mol^{-1}
			a/Å	b/Å	c/Å	$\alpha/^o$	$\beta/^o$	$\gamma/^o$			
		This work	4.24	5.92	8.17	90	90	90	0.575	1.04	
Butan-2-ol	ZEFPUX	exp	5.06	5.22	16.05	90	90	90		1.16	
		FIT	5.88	5.15	16.41	90	90	90	0.748	0.99	
		This work	5.90	4.96	16.39	90	90	90	0.875	1.03	
2-Butyne-1,4-diol	TELXAJ	exp	4.33	7.97	26.89	90	90	90		1.23	
		FIT	4.34	8.91	25.16	90	90	90	0.473	1.18	
		This work	4.21	8.26	24.83	90	90	90	0.435	1.33	
2,5-Dihydroxybenzoic acid	BESKAL04	exp	5.56	4.87	23.36	90	93.45	90		1.62	130.40
		FIT	5.43	5.02	23.51	90	94.27	90	0.165	1.60	105.47
		This work	5.26	4.77	23.08	90	93.40	90	0.293	1.77	120.07
rac-trans-1,2-Cyclohexanediol	ZZZKPE03	exp	8.42	7.80	19.30	90	90	90		1.22	85.90
		FIT	8.14	8.11	19.40	90	90	90	0.247	1.21	80.99
		This work	8.16	7.68	19.58	90	90	90	0.241	1.26	87.55
1-Hydroxy-9-fluorenone	BESGEL	exp	11.67	15.41	5.20	90	90	90		1.39	
		FIT	11.69	15.66	5.19	90	90	90	0.102	1.37	
		This work	11.21	15.91	4.92	90	90	90	0.351	1.49	
Dideutero-formic acid	FORMAC02	exp	10.24	3.52	5.36	90	90	90		1.58	60.50
		FIT	10.50	3.61	5.35	90	90	90	0.121	1.51	44.57
		This work	9.82	3.39	4.84	90	90	90	0.323	1.90	62.06
Acetic acid	ACETAC07	exp	13.15	3.92	5.76	90	90	90		1.34	67.00
		FIT	13.45	3.92	5.91	90	90	90	0.117	1.28	52.72
		This work	13.04	3.78	5.65	90	90	90	0.112	1.43	61.93
Succinic acid	SUCACB03	exp	5.46	8.77	5.00	90	93.29	90		1.64	123.10
		FIT	5.30	8.90	5.20	90	93.90	90	0.249	1.60	107.19
		This work	5.09	8.35	4.97	90	95.91	90	0.402	1.86	133.6
Benzoic acid	BENZAC12	exp	5.42	5.04	21.63	90	96.14	90		1.38	90.00
		FIT	5.34	5.13	22.29	90	93.16	90	0.199	1.33	78.88
		This work	5.21	4.98	21.56	90	92.25	90	0.228	1.45	85.54
1-Naphthoic acid	NAPOAC01	exp	6.91	3.84	30.96	90	92.04	90		1.39	113.64
		FIT	7.07	3.73	31.09	90	92.58	90	0.187	1.40	105.40
		This work	7.07	3.59	30.62	90	93.48	90	0.430	1.48	105.60
2,3-Naphthalenedicarboxylic acid	JUBBIR	exp	5.09	19.22	9.55	90	93.81	90		1.54	
		FIT	4.98	19.35	9.60	92.25	95.72	90.49	0.267	1.56	
		This work	4.77	19.20	9.25	92.03	98.73	89.88	0.537	1.72	
0.8-Deutero--L-arabinose	ABINOS02	exp	6.43	19.48	4.78	90	90	90		1.67	
		FIT	6.54	17.47	5.60	90	90	90	0.868	1.56	
		This work	6.19	17.01	5.41	90	90	90	0.750	1.75	
cis-Ethene-1,2-dicarboxylic acid	MALIAC12	exp	7.48	10.09	7.55	90	124.42	90		1.64	105.40
		FIT	7.61	10.26	7.40	90	125.47	90	0.256	1.64	88.92

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Table S9 – continued from previous page

Molecule	Refcode		unit cell lengths and angles						rmsd$_{15}$/Å	Density/g cm^{-3}	ΔH_{sub}/kJ mol^{-1}
			a/Å	b/Å	c/Å	$\alpha/^o$	β /^{o}	$\gamma/^o$			
		This work	7.31	9.84	7.29	90	130.78	90	0.530	1.94	111.29
cis-Ethene-1,2-dicarboxylic acid	MALIAC13	exp	3.69	7.48	8.59	90	102.22	90		1.66	
		FIT	3.74	7.69	8.32	90	100.69	90	0.189	1.64	
		This work	3.49	7.38	7.75	90	98.56	90	0.434	1.95	
Propionic acid	PRONAC	exp	4.04	9.06	11.00	90	91.25	90		1.22	
		FIT	4.09	9.33	10.76	90	89.50	90	0.392	1.20	
		This work	3.98	9.31	10.34	90	86.38	90	0.487	1.29	
Isophthalic acid	BENZDC01	exp	3.76	16.36	11.70	90	90.30	90		1.53	142
		FIT	3.78	16.55	11.67	90	87.19	90	0.246	1.51	118.74
		This work	3.75	16.24	11.04	90	82.29	90	0.588	1.66	132.13
2-acetoxybenzoic acid (Aspirin)	ACSALA21	exp	11.27	6.55	11.27	90	95.93	90		1.45	
		FIT	11.22	6.78	11.32	90	95.68	90	0.174	1.40	
		This work	10.97	6.73	10.95	90	97.67	90	0.29	1.50	
2-acetoxybenzoic acid (Aspirin)	ACSALA20	exp	12.36	6.53	11.50	90	112.44	90		1.40	
		FIT	12.00	6.71	11.47	90	111.81	90	0.193	1.40	
		This work	11.46	6.64	11.16	90	109.70	90	0.369	1.50	
β-Lactose	BLACTO02	exp	4.93	13.27	10.78	90	91.55	90		1.61	
		FIT	5.39	15.53	9.14	90	96.19	90	1.828	1.49	
		This work	6.16	13.41	10.31	90	95.04	90	1.537	1.34	
Butane-2,3-diol	ZEFPAD	exp	5.05	9.42	10.25	90	90.00	90		1.23	
		FIT	5.41	9.56	10.45	90	90.00	90	0.32	1.11	
		This work	5.22	9.38	10.39	90	90.00	90	0.204	1.18	

Crystal packing results for chlorohydrocarbons

Table S10: Crystal packing results for the chlorohydrocarbon molecules

Molecule	Refcode		unit cell lengths and angles						rmsd$_{15}$/Å	Density/g cm^{-3}	ΔH_{sub}/kJ mol^{-1}
			a/Å	b/Å	c/Å	$\alpha/^o$	β /^{o}	$\gamma/^o$			
Hexachlorobenzene	HCLBNZ13	exp	7.97	3.76	14.69	90	92.46	90		2.15	90.50
		FIT	8.27	3.74	14.78	90	88.62	90	0.502	2.07	94.81
		This work	8.07	3.64	14.93	90	91.32	90	0.192	2.16	90.04
Perchlorofulvalene	CLFULV01	exp	15.00	7.91	11.81	90	103.38	90		1.97	
		FIT	14.90	8.17	11.78	90	104.10	90	0.152	1.93	
		This work	15.14	7.60	11.89	90	105.82	90	0.231	2.04	
Decachloropyrene	DECPYR10	exp	21.46	7.49	10.80	90	92.80	90		2.09	
		FIT	21.57	8.30	10.66	90	94.27	90	0.529	1.91	
		This work	21.19	7.54	11.21	90	90.06	90	0.735	2.03	

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Table S10 – continued from previous page

Molecule	Refcode		unit cell lengths and angles						rmsd$_{15}$/Å	Density/g cm^{-3}	ΔH_{sub}/kJ mol^{-1}
			a/Å	b/Å	c/Å	$\alpha/^o$	$\beta/^o$	$\gamma/^o$			
9,10-Dichloroanthracene	DCLANT10	exp	7.04	17.95	8.61	90	102.97	90		1.55	113.90
		FIT	7.05	18.22	8.78	90	103.85	90	0.138	1.50	105.20
		This work	6.62	18.17	8.71	90	104.26	90	0.283	1.62	113.90
1,2-Dichlorobenzene	ABUMIT	exp	3.95	10.63	15.27	90	97.00	90		1.54	
		FIT	3.92	10.72	15.61	90	96.71	90	0.111	1.50	
		This work	3.80	10.53	15.28	90	100.26	90	0.252	1.62	
Chloromethane	CLMETH03	exp	6.02	4.83	7.04	90	90	90		1.64	31.60
		FIT	6.44	5.26	8.09	90	90	89.1	0.479	1.23	22.70
		This work	6.18	5.08	7.85	90	90	88.97	0.349	1.36	31.60
1,1,1-Trichloroethane	MECHLF12	exp	11.55	8.01	5.87	90	90	90		1.63	
		FIT	11.39	7.91	5.90	90	90	90	0.111	1.67	
		This work	11.08	7.82	5.80	90	90	90	0.212	1.77	
1,1-Dichloroethane	RIVDOQ	exp	7.75	9.34	5.86	90	90	90		1.55	
		FIT	7.83	9.59	5.90	90	90	90	0.139	1.48	
		This work	7.64	9.34	5.79	90	90	90	0.103	1.59	
Chloroethane	XAXCOQ03	exp	5.28	9.82	6.77	90	98.07	90		1.23	
		FIT	5.51	10.24	6.69	90	97.82	90	0.199	1.14	
		This work	5.46	10.03	6.40	90	97.33	90	0.204	1.23	
1,2-Dichloroethane	DCLETH02	exp	4.82	5.35	8.15	90	102.26	90		1.60	
		FIT	4.83	5.50	8.54	90	101.06	90	0.195	1.48	
		This work	4.67	5.44	8.44	90	100.31	90	0.173	1.56	
Chloroform	CLFORM03	exp	7.44	9.46	5.80	90	90	90		1.94	
		FIT	7.48	9.49	5.98	90	90	90	0.146	1.87	
		This work	7.34	9.32	5.95	90	90	90	0.157	1.95	
2,5-Dichloro-2,5-dimethylhexane	XOQLAR	exp	5.91	5.98	8.38	91.03	105.76	118.99		1.24	
		FIT	5.90	6.22	8.33	92.95	104.40	120.47	0.207	1.22	
		This work	5.82	6.15	8.23	93.06	103.76	120.73	0.249	1.27	
1,8-Dichloroanthracene	ZZZBLP03	exp	15.33	3.86	18.09	90	90	90		1.53	
		FIT	15.85	3.89	18.36	90	90	90	0.234	1.45	
		This work	15.56	3.85	17.73	90	90	90	0.311	1.54	
1,8-Dichloroanthracene	ZZZBLP02	exp	19.01	3.86	15.14	90	107.41	90		1.55	
		FIT	19.56	3.86	15.82	90	108.72	90	0.316	1.45	
		This work	18.97	3.77	15.47	90	105.92	90	0.187	1.54	
Octachloro-naphthalene	OCLNAP10	exp	19.58	7.29	9.80	90	111.76	90		2.07	
		FIT	19.53	7.60	9.75	90	111.69	90	0.228	2.00	
		This work	19.55	7.05	9.76	90	111.14	90	0.192	2.14	

Structural performance of FIT, optimized parameters, S-Ab and S-No

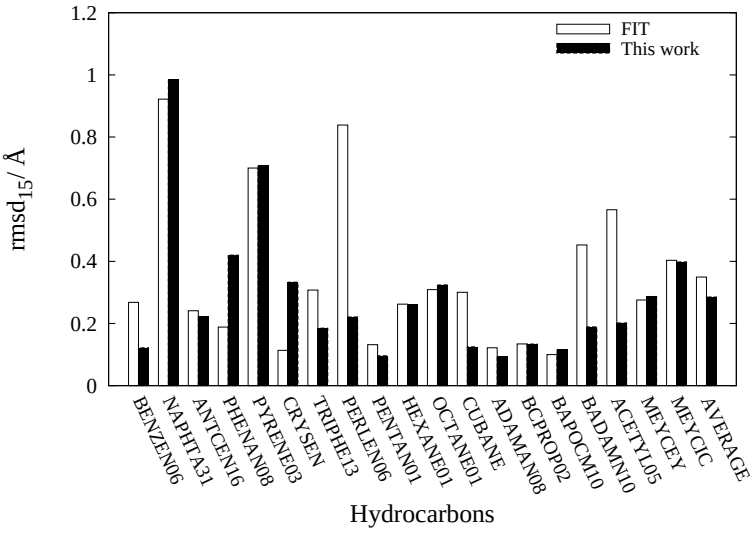

Figure S4: Structural performance of optimized parameters and FIT parameters for hydrocarbons. Rmsd_{15} between experimental and predicted structures given with empty columns for FIT parameters (▭) and black for optimized parameters (▬).

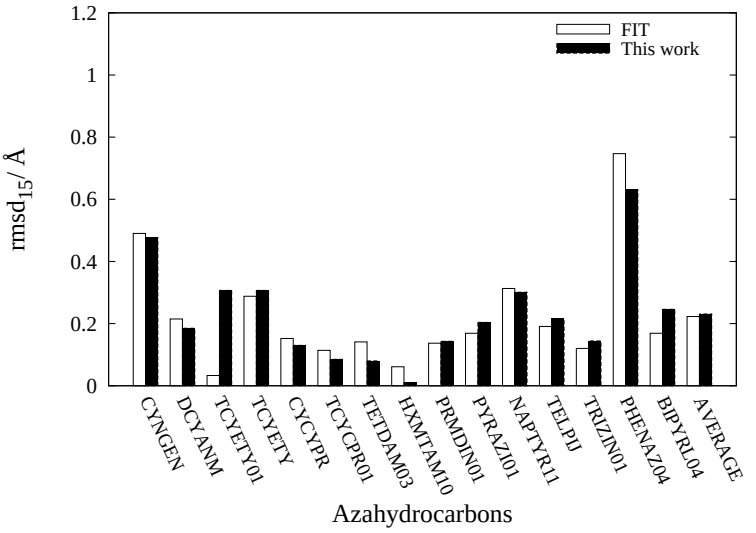

Figure S5: Structural performance of optimized parameters and FIT parameters for azahydrocarbons. Rmsd_{15} between experimental and predicted structures given with empty columns for FIT parameters (▭) and black for optimized parameters (▬).

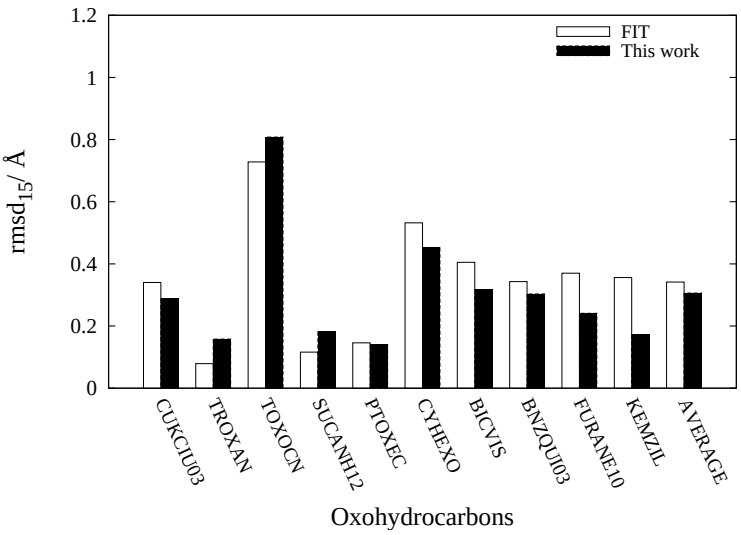

Figure S6: Structural performance of optimized parameters and FIT parameters for oxohydrocarbons. Rmsd_{15} between experimental and predicted structures given with empty columns for FIT parameters (▭) and black for optimized parameters (■).

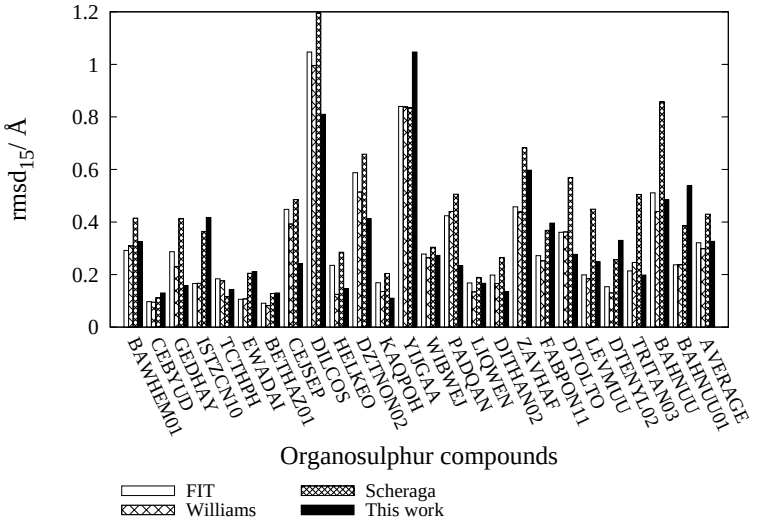

Figure S7: Rmsd_{15} between experimental and predicted structures of the training set of organosulphur compounds calculated for FIT, S-Ab, S-No and optimized parameters.

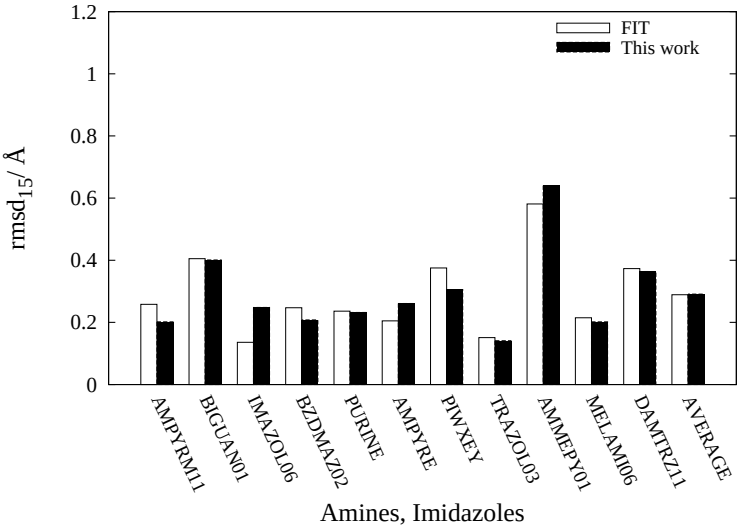

Figure S8: Structural performance of optimized parameters and FIT parameters for amines and imidazoles. Rmsd_{15} between experimental and predicted structures given with empty columns for FIT parameters (▭) and black for optimized parameters (▬)

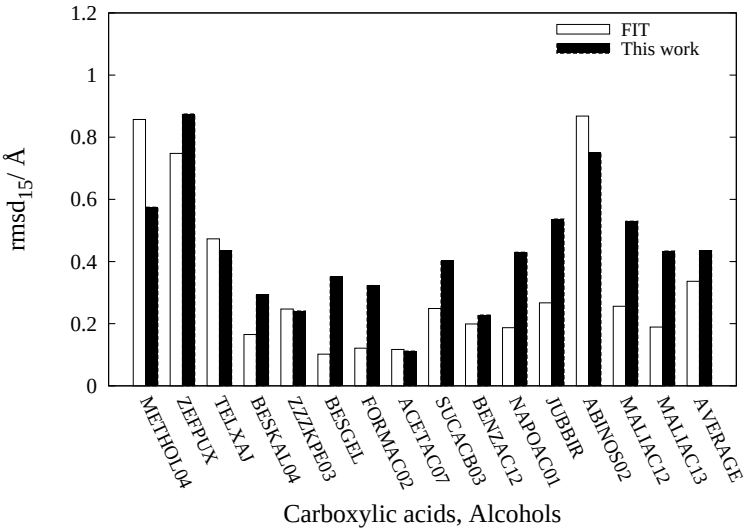

Figure S9: Structural performance of optimized parameters and FIT parameters for carboxylic acids and alcohols. Rmsd_{15} between experimental and predicted structures given with empty columns for FIT parameters (▭) and black for optimized parameters (▬)

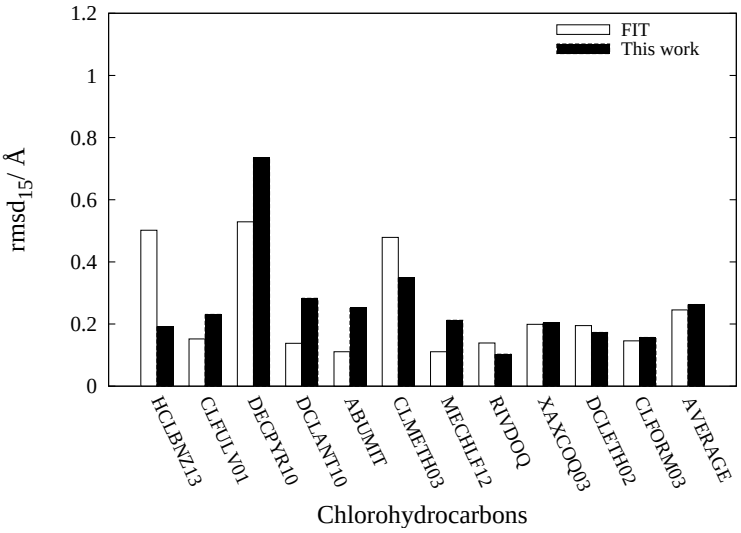

Figure S10: Structural performance of optimized parameters and FIT parameters for chlorohydrocarbons. Rmsd_{15} between experimental and predicted structures given with empty columns for FIT parameters (▭) and black for optimized parameters (▬)

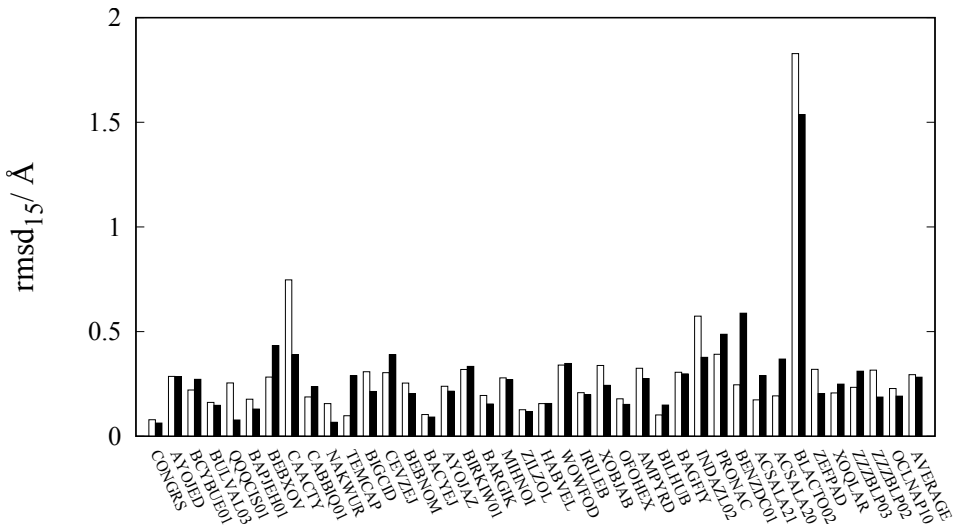

Figure S11: Structural performance of optimized parameters and FIT parameters for the validation set. Rmsd_{15} between experimental and predicted structures given with empty columns for FIT parameters and black for optimized parameters

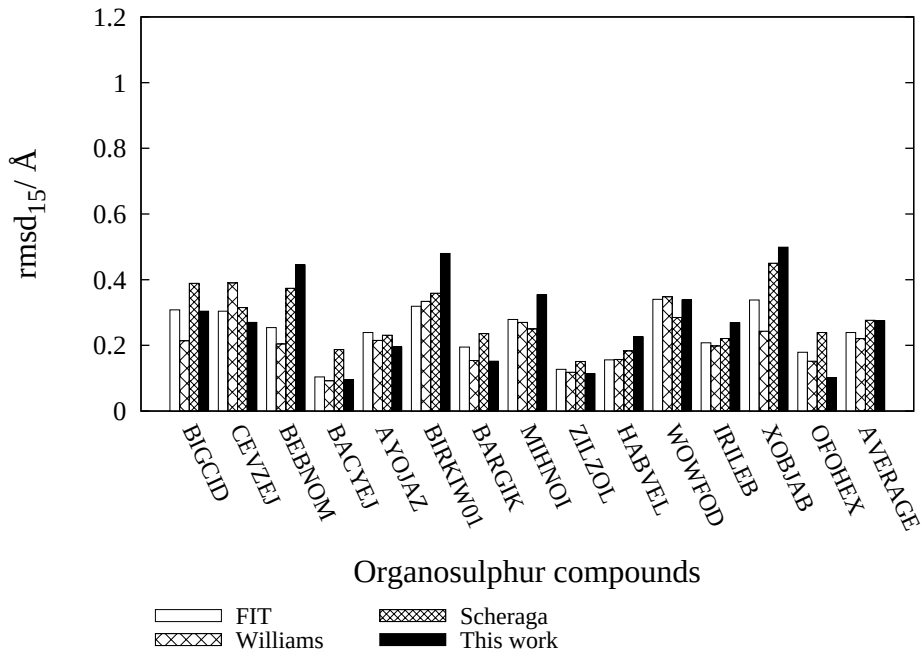

Figure S12: $Rmsd_{15}$ between experimental and predicted structures of the validation set of organosulphur compounds calculated for FIT, S-Ab, S-No and optimized parameters.

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