SUPPORTING MATERIAL

Aqueous solubilities of five *N*-(diethylaminothiocarbonyl)benzimido derivatives at *T* = 298.15 K

Bernd Schröder*, Mónia A. R. Martins, João A. P. Coutinho

CICECO, Departamento de Química, Universidade de Aveiro,

3810-193 Aveiro, Portugal

Simão P. Pinho

LSRE/LCM, Escola Superior de Tecnologia e Gestão, Instituto Politécnico de Bragança, 5300-253 Bragança, Portugal

SUPPORTING MATERIAL SM1. Synthesis and characterization

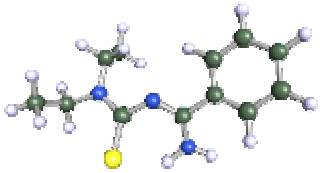
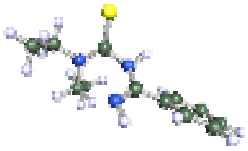
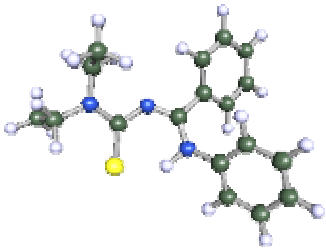
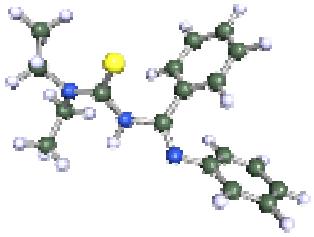
N-(diethylaminothiocarbonyl)benzimide chloride reacts with ammonia or respective primary or secondary amines, in acetone. In the presence of proton trapping reagents and after removal of the precipitated triethylamine hydrochloride and successive recrystallization from ethanol, the respective *N*-thiocarbamoylbenzamidines (**1-4**) were yielded as pale, yellow crystals.

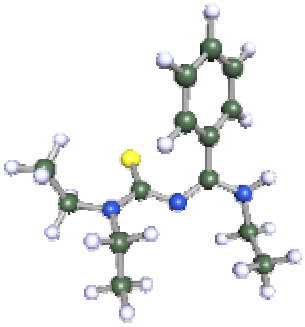
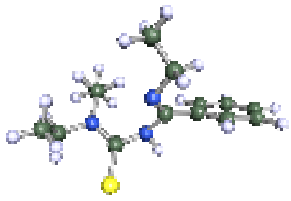
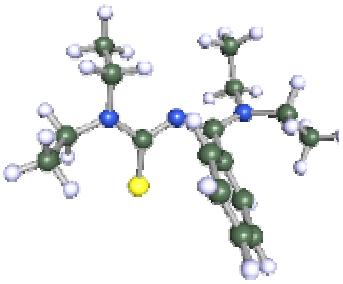
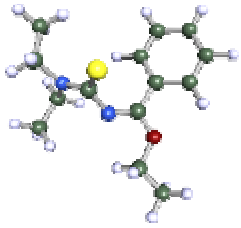
N-(diethylaminothiocarbonyl)benzimidoethylester (**5**): equimolar amounts of sodium ethanoate and *N*-(diethylaminothiocarbonyl)benzimide chloride were dissolved in ethanol. After refluxing and removing the solvent in vacuum, the residue is taken over with 20 cm^3 of H_2O; the precipitating oil crystallizes after applying some friction. Pale yellow crystals of **5** were washed with water and repeatedly recrystallized from *n*-hexane. The samples were characterized by ^{1}H-NMR, IR spectroscopy and elemental analysis. All compounds were further purified by repeated vacuum sublimation. The mole-fraction purity for each sample was estimated to be better than 0.99.

SUPPORTING MATERIAL SM2. Individual experimental aqueous solubility results.

	Solubility ($g \cdot g_{H2O}^{-1}$)				
	1	**2**	**3**	**4**	**5**
	1.261E-04	9.917E-06	1.878E-04	3.212E-04	3.523E-05
	1.275E-04	7.883E-06	1.949E-04	3.254E-04	3.702E-05
	1.284E-04	7.887E-06	1.827E-04	3.140E-04	3.981E-05
	1.258E-04	7.453E-06	1.650E-04	3.194E-04	4.048E-05
	1.267E-04	7.829E-06	1.700E-04	3.050E-04	4.032E-05
	1.307E-04	7.438E-06	1.683E-04	3.061E-04	3.883E-05
	1.280E-04	9.970E-06	1.700E-04	3.305E-04	3.834E-05
	1.361E-04	9.899E-06	1.596E-04	3.356E-04	4.129E-05
	1.339E-04	9.715E-06	1.614E-04	3.297E-04	4.556E-05
	1.298E-04	9.679E-06	1.783E-04	3.069E-04	3.335E-05
	1.305E-04	9.685E-06	1.805E-04	3.026E-04	3.394E-05
	1.273E-04	9.001E-06	1.769E-04	3.002E-04	3.273E-05
	1.274E-04	8.961E-06	1.676E-04	3.116E-04	3.548E-05
	1.249E-04		1.744E-04	3.213E-04	3.099E-05
	1.237E-04		1.756E-04	3.101E-04	
	1.225E-04		1.757E-04	3.185E-04	
	1.269E-04		1.756E-04	3.218E-04	
				3.231E-04	
Average	**1.280E-04**	**8.871E-06**	**1.744E-04**	**3.168E-04**	**3.738E-05**
Standard deviation	3.428E-06	1.021E-06	9.124E-06	1.031E-05	4.001E-06
Uncertainty 95%	**3.598E-06**	**1.071E-06**	**9.575E-06**	**1.082E-05**	**4.199E-06**

SUPPORTING MATERIAL SM3. COSMO energies of individual most stable conformers of *N*-(diethylaminothiocarbonyl)benzimido derivatives; BP-TZVP and BP-TZVPD-FINE level of theory, in Hartrees. The first column shows the configuration of the respective COSMO conformer, compounds **1**-**3** with respective enamine (**a**) and imino (**b**) tautomers.

	Total energy (gas) [a.u.]		Total energy + OC corr.[a] [a.u.]	
Cpd. conformer	BP-TZVP	BP-TZVPD-FINE	BP-TZVP	BP-TZVPD-FINE
1a				
	-1030.27667	-1030.31121	-1030.29409	-1030.32729
1b				
	-1030.25651	-1030.29185	-1030.27620	-1030.31072
2a				
	-1261.39865	-1261.44312	-1261.41491	-1261.45787
2b				
	-1261.38203	-1261.42720	-1261.40182	-1261.44597
3a				

	-1108.91190	-1108.94928	-1108.93423	-1108.97118
3b				
	-1108.89943	-1108.93667	-1108.91635	-1108.95296
4				
	-1187.55165	-1187.59117	-1187.57176	-1187.61128
5				
	-1128.78306	-1128.82207	-1128.80197	-1128.84029

[a]Correction for remaining outlying charge error.

SUPPORTING MATERIAL SM4a. COSMO-RS dipole moments and first hydrogen bonding moments of *N*-(diethylaminothiocarbonyl)benzimido derivatives; BP-TZVP level of theory, for respective conformers weighed according to Boltzmann distribution.

Cpd.	μ/ D	H-bond moments (accept)	H-bond moments (donor)
1a	6.03	3.34	-3.00
1b	7.34	5.98	-2.25
2a	5.95	2.22	0.00
2b	7.05	3.92	-1.63
3a	8.58	8.13	-2.39
3b	7.30	4.02	-1.45
4	8.93	7.67	0.00
5	7.79	4.26	0.00

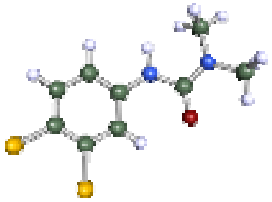
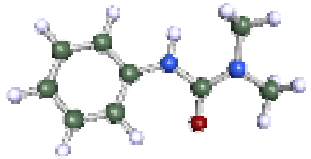
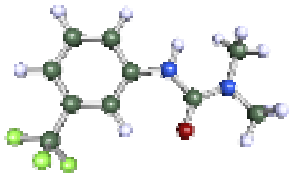
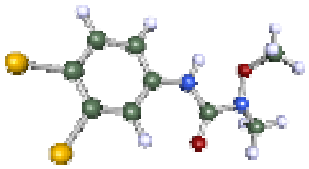
SUPPORTING MATERIAL SM4b. Preliminary COSMO-RS estimates of *p*K data in water

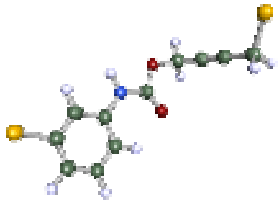
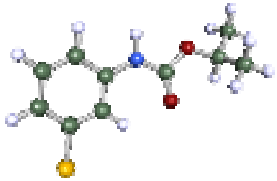
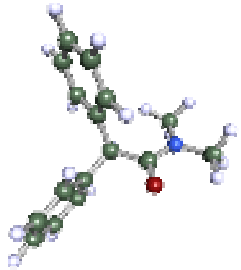
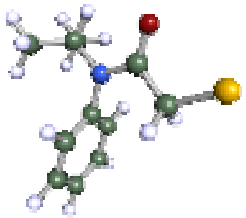
Cpd.	pK_1 (proton gain)	pK_2 (proton loss)
1b	6.66	10.62
2b	3.74	9.63
3a	0.75	13.91
4	0.31	-
5	-	-

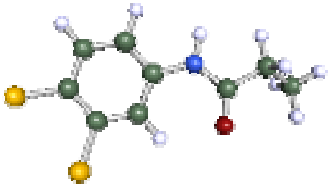
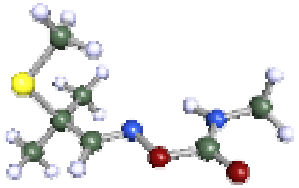
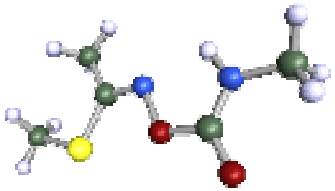
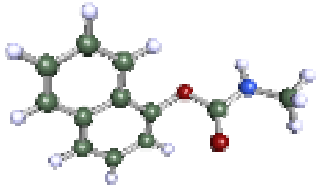
SUPPORTING MATERIAL SM5. Melting points, T_M, Standard Molar Enthalpies of Fusion, $\Delta_{cr}^{l} H_m^o(T_M)$, and Standard Molar Entropies of Fusion, $\Delta_{cr}^{l} S_m^o(T_M)$, of *N*-(diethylaminothiocarbonyl)benzimido derivatives, as reported in Schröder et al. (2011).

Compound	T_M / K	$\Delta_{cr}^{l} H_m^o(T_M)$ / kJ·mol^{-1}	$\Delta_{cr}^{l} S_m^o(T_M)$ / J·K^{-1}·mol^{-1}
1	371.42 ± 0.26	27.18 ± 0.28	73.2 ± 0.8
2	374.88 ± 0.17	29.37 ± 0.32	78.4 ± 0.9
3	383.36 ± 0.30	32.74 ± 0.40	85.3 ± 1.0
4	334.77 ± 0.12	25.58 ± 0.27	76.4 ± 0.8
5	350.34 ± 0.26	34.39 ± 0.39	98.2 ± 1.1

SUPPORTING MATERIAL SM6. Urea-based pesticides. Physico-chemical property data as compiled in Mackay et al. (2006). The first column shows the configuration of the encountered most stable COSMO conformer.

	Cpd.	Chemical name	CAS No.	Sum formula	Molar mass / g·mol^{-1}
	Diuron **	3-(3,4-dichlorophenyl)-1,1-dimethylurea	330-54-1	$C_9H_{10}Cl_2N_2O$	233.093
	Fenuron **	1,1-dimethyl-3-phenylurea	101-42-8	$C_9H_{12}N_2O$	164.203
	Fluometuron **	*N*,*N*-dimethyl-*N*'-(3-trifluoromethyl)-phenylurea	2164-17-2	$C_{10}H_{11}F_3N_2O$	232.201
	Linuron **	3-(3,4-dichlorophenyl)-1-methoxy-1-methylurea	330-55-2	$C_9H_{10}Cl_2N_2O_2$	249.093

	Barban **	4-chlorobut-2-ynyl-3-chlorocarbanilate	101-27-9	$C_{11}H_9Cl_2NO_2$	258.101
	Chlorpropham **	isopropyl 3-chlorocarbanilate	101-21-3	$C_{10}H_{12}ClNO_2$	213.661
	Diphenamid **	*N,N*-dimethyldiphenylacetamide	957-51-7	$C_{16}H_{17}NO$	239.312
	Propachlor **	2-chloro-*N*-(1-methylethyl)-*N*-phenylacetamide	1918-16-7	$C_{11}H_{14}ClNO$	211.688

	Propanil **	*N*-(3,4-dichlorophenyl)-propionamide	709-98-8	$C_9H_9Cl_2NO$	218.080
	Aldicarb *	2-methyl-2-(methylthio)-propionaldehyde O-(methylcarbamoyl) oxime	116-06-3	$C_7H_{14}N_2O_2S$	190.263
	Methomyl *	*S*-methyl-*N*-(methylcarbamoyloxy) thioacetimidate	16752-77-5	$C_5H_{10}N_2O_2S$	162.210
	Carbaryl *	naphthalen-1-yl methylcarbamate	63-25-2	$C_{12}H_{11}NO_2$	201.221

* insecticide; ** herbicide

	p_S / Pa	p_L / Pa	c_S / mol·m^{-3}	c_L / mol·m^{-3}	log K_{OW}	log K_{AW}	log K_{OC}
Diuron	0.000092	0.0019	0.172	3.63	2.78	-6.56	2.6
Fenuron	0.0267	0.305	23.14	264.7	0.98	-6.33	1.43
Fluometuron	0.000067	0.00161	0.388	9.292	2.42	-7.16	2.24
Linuron	0.000897[a]	0.00162[a]	0.301	1.449	3	-4.52	2.91
Barban	0.00005	0.00016	0.043	0.1362	2.68	-6.33	2.66
Chlorpropham	0.0116[b]	0.0165[b]	0.417	0.6	3.51	-6.01	2.8
Diphenamid	0.000004	0.0000495	1.087	13.46	1.92	-8.83	2.31
Propachlor	0.03	0.0958	2.834	9.055	2.18	-5.35	1.9
Propanil	0.005	0.023	0.917	4.218	3.07	-5.66	2.17
Aldicarb	0.004	0.0216	31.54	170	1.1	-7.29	1.48
Methomyl	0.0067	0.0229	358	1223	0.6	-8.12	1.3[c]
Carbaryl	0.000027	0.000383	0.596	8.56	2.36	-7.74	2.36

[a]Recommended vapour pressure data are known to be subject to large error. Here, data from US EPA EPISuite 4.1 (2012) were used instead.

[b]Extrapolated from Rordorf (1989), as reported in Mackay et al. (2006).

[c]The data from Schüürmann et al. (2006) was chosen.

SUPPORTING MATERIAL SM7. Melting points, T_M, Standard Molar Enthalpies of Fusion, and solid solubilities, at T = 298.15 K, of urea-based pesticides, as compiled in Mackay et al. (2006), in comparison with COSMO-RS results, at the BP-TZVP level of theory.

	$\Delta^1_{cr}H^o_m(T_M)$ / kJ·mol^{-1}	T_M / K	log S_S / mol·L^{-1}	
			Experimental	BP-TZVP
Diuron	33.89	431.15	-3.764	-4.137
Fenuron	24.267	405.15	-1.636	-2.183
Fluometuron	29.706	437.15	-3.411	-3.458
Linuron	28.66	366.15	-3.521	-4.013
Barban	26.8	348.15	-4.367	-4.388
Chlorpropham	16	314.15	-3.380	-3.481
Diphenamid	27.405	408.15	-2.964	-3.562
Propachlor	27.614	350.15	-2.548	-2.352
Propanil	15.3	365.15	-3.038	-2.827
Aldicarb	25.94	372.15	-1.501	-1.641
Methomyl	22.267	351.15	-0.446	-0.608
Carbaryl	24.27	418.15	-3.225	-3.106
			σ^a	0.25

[a] $\sigma = \frac{1}{N_C}\sum_{i=1}^{N_C}\left|\log S_{S,Exp} - \log S_{S,Calc}\right|$ with σ the standard error**,** and N_C the number of compounds.

SUPPORTING MATERIAL SM8. Physico-chemical properties of the title compounds, at T = 298.15 K, as derived from COSMO-RS, at the BP-TZVP level of theory, at T = 298.15 K.

	log K_{AW}	log K_{OW} (wet)	log K_{OW} (dry)	log K_{OC}	log K_{OA}
1	-7.34	2.69	2.62	2.52	9.96
2	-7.69	4.43	4.47	3.48	12.16
3	-8.81	2.92	2.81	2.64	11.62
4	-7.91	3.50	3.38	2.70	11.29
5	-6.49	3.95	3.94	2.79	10.43

SUPPORTING MATERIAL SM9. Physico-chemical properties of some structurally related urea pesticides, at T = 298.15 K, as derived from COSMO-RS, at the BP-TZVP level of theory, at T = 298.15 K.

	log K_{AW}	log K_{OW} (wet)	log K_{OW} (dry)	log K_{OC}	log K_{OA}
Diuron	-7.49	2.62	2.54	2.98	10.03
Fenuron	-6.84	1.45	1.28	1.96	8.12
Fluometuron	-6.28	2.41	2.30	3.00	8.58
Linuron	-6.01	3.33	3.30	3.05	9.31
Barban	-6.44	3.88	3.94	4.01	10.38
Chlorpropham	-4.67	3.75	3.77	3.08	8.44
Diphenamid	-7.37	2.94	2.78	2.65	10.15
Propachlor	-6.06	2.29	2.13	2.40	8.20
Propanil	-6.34	2.84	2.79	2.98	9.13
Aldicarb	-6.94	1.42	1.19	1.53	8.13
Methomyl	-7.77	0.54	0.29	1.39	8.05
Carbaryl	-7.08	2.23	2.12	2.50	9.19

SUPPORTING MATERIAL SM10. Deviation of predicted physico-chemical properties of urea-based herbicides from experiment, at T = 298.15 K, as derived from COSMO-RS, at the BP-TZVP level of theory.

	(Experimental – COSMO-RS)						
	log p_S / Pa	log p_L / Pa	log S_S / mol·L^{-1}	log S_L / mol·L^{-1}	log K_{OW} (wet)	log K_{AW}	log K_{OC}
Diuron	1.20	0.68	0.37	-0.14	0.16	0.93	-0.38
Fenuron	1.06	1.00	0.55	0.49	-0.47	0.51	-0.53
Fluometuron	-0.52	-0.80	0.05	0.07	0.01	-0.87	-0.76
Linuron	2.09	1.62	0.49	0.33	-0.33	1.49	-0.14
Barban	0.19	0.02	0.02	-0.10	-1.20	0.12	-1.35
Chlorophoram	-0.18	-0.17	0.10	0.12	-0.24	-1.35	-0.28
Diphenamid	-0.66	-0.86	0.60	0.59	-1.02	-1.46	-0.34
Propachlor	0.56	0.35	-0.20	-0.37	-0.11	0.71	-0.50
Propanil	0.52	0.70	-0.21	0.00	0.23	0.68	-0.81
Aldicarb	-0.20	-0.37	0.14	-0.16	-0.32	-0.35	-0.05
Methomyl	-0.07	-0.12	0.16	0.26	0.06	-0.36	-0.09
Carbaryl	-0.58	-0.65	-0.12	0.01	0.13	-0.67	-0.14
σ[a]	0.54	0.48	0.25	0.22	0.36	0.79	0.45

[a] $\sigma = \frac{1}{N_C}\sum_{i=1}^{N_C}\left|\log X_{Exp} - \log X_{Calc}\right|$ with σ the standard error of logarithmic quantity X , and N_C the number of compounds.

SUPPORTING MATERIAL SM11. Hybrid air-water partition coefficient.

	$\log K_{AW(exp)}$ [a]
1	-7.69
2	-8.97
3	-9.68
4	-8.57
5	-7.51

[a]Calculated according to eq. 3 with COSMO-RS vapour pressures.

SUPPORTING MATERIAL SM12. Environmental model as proposed by Gouin et al. (2000). The environment is modelled as volumes of air, water, and octanol, where octanol represents the organic fraction appearing in soils and sediments. Octanol is considered to be the best surrogate for organic matter, with correlations between the octanol-water and organic carbon-water partition coefficients readily available.

The environmental volumes of air (10^{14} m^3) and water ($2 \cdot 10^{11}$ m^3) as applied in the Equilibrium Criterion (EQC) (Mackay et al., 1996) evaluative model are used directly. These represent volumes corresponding to an area of 100 000 km^2, a height of the atmospheric column of 1000 m, while 10% of the area is covered by water to a depth of 20 m, the resting area covered with soil having a depth of 10 cm and a sediment layer of 1 cm thickness.

Volumes of soil and sediment are converted to corresponding volumes of octanol using eq. 1:

$$V_{\text{octanol}} = V_{\text{soil}} \Phi \cdot 0.35 \rho_{\text{soil}} \qquad \text{(eq. 1)}$$

where Φ is fraction of organic carbon in the soil (0.02) and ρ_{soil} is the soil density, assumed to be 2.4 $g \cdot cm^{-3}$. V_{soil} corresponds to $9 \cdot 10^9$ m^3, which gives V_{octanol} of $151 \cdot 10^6$ m^3, assuming $K_{\text{OC}} = 0.35 K_{\text{OW}}$ (Seth et al., 1999). It needs to be kept in mind that this assumption is fairly applicable for non-polar compounds; in the case of the polar title compounds, it is likely to be less appropriate, so it is used as a first approximation (Goss and Schwarzenbach, 2001). In the case of the sediment layer, a similar approach is assumed, with Φ is 0.04, ρ_{soil} is 2.4 $g \cdot cm^{-3}$ and V_{sediment} corresponding to 10^8 m^3, giving an equivalent volume of octanol of V_{octanol} is $3.4 \cdot 10^6$ m^3. The ratio between air:water:octanol volumes is roughly 650000:1300:1 (with octanol equivalents originating to 97.8% from soil and to 2.2% from sediment).

At equilibrium, the total mass of chemical, M, is distributed as described by eqs. 2 and 3:

$$M = V_{\text{W}} c_{\text{W}} + V_{\text{A}} c_{\text{A}} + V_{\text{O}} c_{\text{O}} \qquad \text{(eq. 2)}$$

$$M = c_{\mathrm{W}}(V_{\mathrm{W}} + K_{\mathrm{AW}}V_{\mathrm{A}} + K_{\mathrm{OW}}V_{\mathrm{O}}) \qquad \text{(eq. 3)}$$

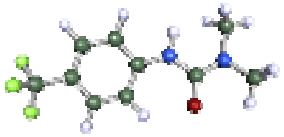
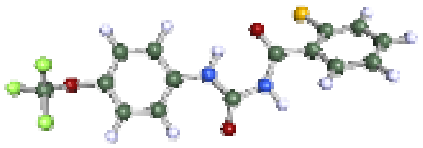
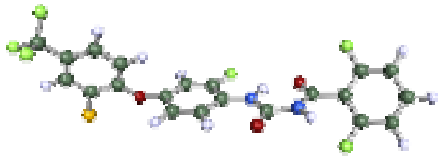
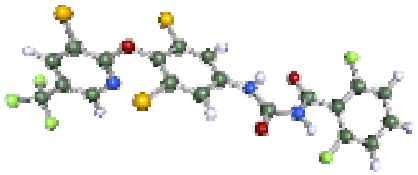
with V the volume in m^3, c the concentration in $g \cdot m^{-3}$, K_{AW} the air-water partition coefficient and K_{OW} the octanol-water partition coefficient. The subscripts A, W, and O are referring to the air, water, and octanol compartment, respectively. The mass fractions of the chemical in each medium can be obtained through eq. 4:

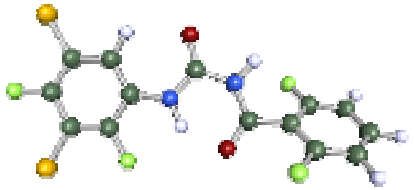
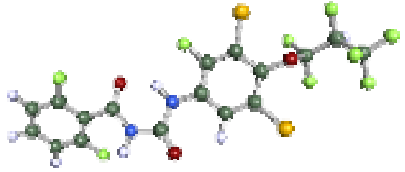
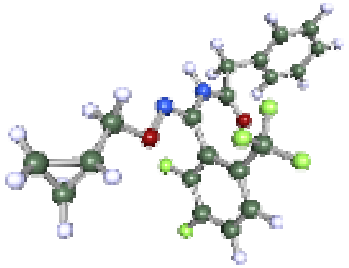
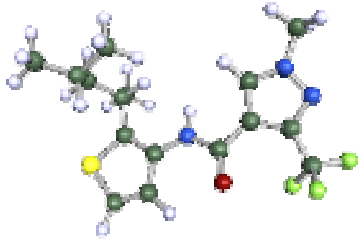
$$F_i = V_{\mathrm{i}}K_{\mathrm{iW}} / (K_{\mathrm{WW}}V_W + K_{\mathrm{AW}}V_A + K_{\mathrm{OW}}V_{\mathrm{O}}) \qquad \text{(eq. 4)}$$

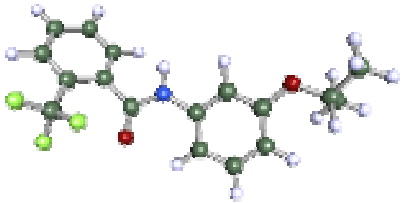
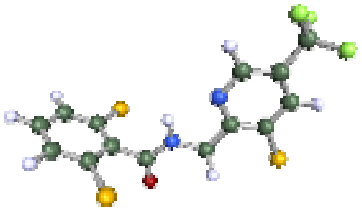
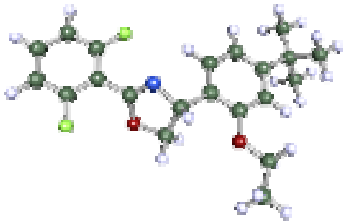
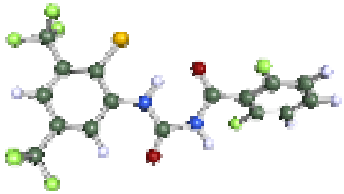
where i is A, W, or O, and K_{WW} is 1.0.

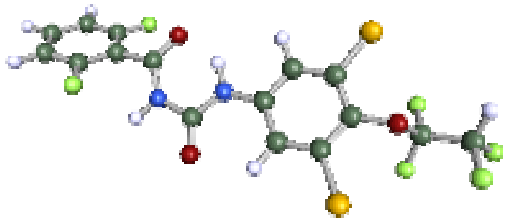
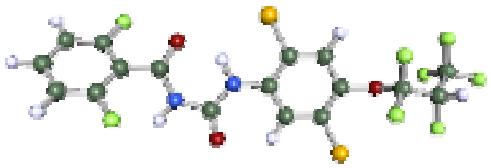
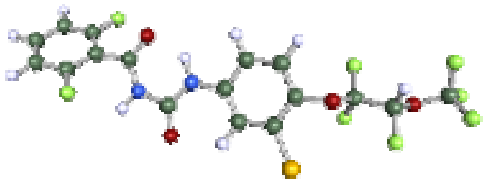
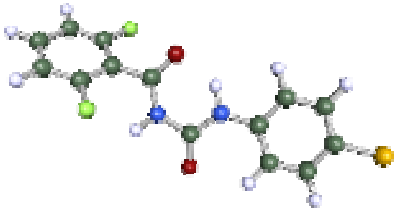
From this approach, the plot of log K_{AW} vs. log K_{OW} was prepared, as given in Figure 5.

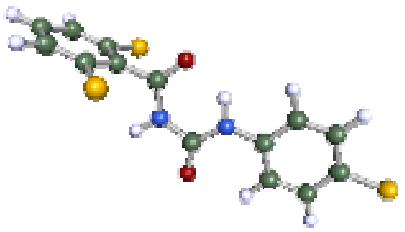
SUPPORTING MATERIAL SM13. Set of modern fluorinated pesticides. The first column shows the configuration of the encountered most stable COSMO conformer. Second table shows physico-chemical property data of diflubenzuron as compiled in Mackay et al. (2006).

	Cpd.	Chemical name	CAS No.	Sum formula	Molar mass / g.mol^{-1}
	Parafluron **	1,1-dimethyl-3-(α,α,α-trifluoro-p-tolyl)urea	7159-99-1	$C_{10}H_{11}F_3N_2O$	232.202
	Triflumuron *	2-chloro-*N*-[[[4-(trifluoromethoxy)phenyl]amino]carbonyl]benzamide	64628-44-0	$C_{15}H_{10}ClF_3N_2O_3$	358.700
	Flufenoxuron *	*N*-[[[4-[2-chloro-4-(trifluoromethyl)phenoxy]-2-fluorophenyl]amino]carbonyl]-2,6-difluorobenzamide	101463-69-8	$C_{21}H_{11}ClF_6N_2O_3$	488.767
	Chlorfluazuron *	*N*-[[[3,5-dichloro-4-[[3-chloro-5-(trifluoromethyl)-2-pyridinyl]oxy]phenyl]amino]carbonyl]-2,6-difluorobenzamide	71422-67-8	$C_{20}H_9Cl_3F_5N_3O_3$	540.655

	Teflubenzuron *	*N*-[[(3,5-dichloro-2,4-difluorophenyl)amino]carbonyl]-2,6-difluorobenzamide	83121-18-0	$C_{14}H_6Cl_2F_4N_2O_2$	381.109
	Noviflumuron *	*N*-[[[3,5-dichloro-2-fluoro-4-(1,1,2,3,3,3-hexafluoropropoxy)phenyl]amino]carbonyl]-2,6-difluorobenzamide	121451-02-3	$C_{17}H_7Cl_2F_9N_2O_3$	529.141
	Cyflufenamid ***	(Z)-*N*-[α-(cyclopropylmethoxyimino)-2,3-difluoro-6-(trifluoromethyl)benzyl]-2-phenylacetamide	180409-60-3	$C_{20}H_{17}F_5N_2O_2$	412.353
	Penthiopyrad ***	(RS)-*N*-[2-(1,3-dimethylbutyl)-3-thienyl]-1-methyl-3-(trifluoromethyl)pyrazole-4-carboxamide	183675-82-3	$C_{16}H_{20}F_3N_3OS$	359.410

	Flutolanil ***	*N*-[3-(1-methylethoxy)phenyl]-2-(trifluoromethyl)benzamide	66332-96-5	$C_{17}H_{16}F_3NO_2$	323.310
	Fluopicolide ***	2,6-dichloro-*N*-[3-chloro-5-(trifluoromethyl)-2-pyridylmethyl]benzamide	239110-15-7	$C_{14}H_8Cl_3F_3N_2O$	383.580
	Etoxazole *	(RS)-5-tert-butyl-2-[2-(2,6-difluorophenyl)-4,5-dihydro-1,3-oxazol-4-yl]phenetole	153233-91-1	$C_{21}H_{23}F_2NO_2$	359.410
	Bistrifluron *	*N*-[[[2-chloro-3,5-bis(trifluoromethyl)phenyl]amino]carbonyl]-2,6-difluorobenzamide	201593-84-2	$C_{16}H_7ClF_8N_2O_2$	446.680

	Hexaflumuron *	*N*-[[[3,5-dichloro-4-(1,1,2,2-tetrafluoroethoxy)phenyl]amino]carbonyl]-2,6-difluorobenzamide	86479-06-3	$C_{16}H_8Cl_2F_6N_2O_3$	461.143
	Lufenuron *	*N*-[[[2,5-dichloro-4-(1,1,2,3,3,3-hexafluoropropoxy)phenyl]amino]carbonyl]-2,6-difluorobenzamide	103055-07-8	$C_{17}H_8Cl_2F_8N_2O_3$	511.150
	Novaluron *	*N*-[[[3-chloro-4-[1,1,2-trifluoro-2-(trifluoromethoxy)ethoxy]phenyl]amino]carbonyl]-2,6-difluorobenzamide	116714-46-6	$C_{17}H_9ClF_8N_2O_4$	492.705
	Diflubenzuron*	1-(4-chlorophenyl)-3-(2,6-difluoro-benzol) urea	35367-38-5	$C_{14}H_9ClF_2N_2O_2$	310.683

	Dichlorobenzuron (*)	2,6-dichloro-*N*-[(4-chlorophenyl)carbamoyl]benzamide	35409-97-3	$C_{14}H_9Cl_3N_2O_2$	343.592

* insecticide; ** herbicide; *** fungicide

	p_S / Pa	p_L / Pa	c_S / mol·m^{-3}	c_L / mol·m^{-3}	log K_{OW}	log K_{AW}	log K_{OC}
Diflubenzuron	0.00000012	0.0000131	0.000257	0.0281	3.88[a]	-6.73	3.01

[a]The data of Sotomatsu et al. (1987) was chosen here. The recommended value of log K_{OW} = 0.78 does not seem plausible, with respect to the recommended value of log K_{OC}.

SUPPORTING MATERIAL SM14. The table summarizes predictions of environmental properties of the set of fluorinated pesticides, as obtained with COSMO-RS, at the BP-TZVP level of theory.

	COSMO-RS			
Trivial name	$\log K_{AW}$	$\log K_{OW}$(wet)	$\log K_{OW}$(dry)	$\log K_{OA}$
Parafluron	-6.44	2.31	2.20	8.64
Trimefluor	-6.48	3.32	3.25	9.73
Flufenoxuron	-7.82	6.55	6.64	14.46
Chlorfluazuron	-8.60	6.99	7.10	15.71
Teflubenzuron	-6.07	5.05	5.11	11.18
Noviflumuron	-6.35	6.43	6.54	12.90
Cyflufenamid	-6.51	5.06	5.08	11.59
Penthiopyrad	-7.44	4.44	4.42	11.86
Flutolanil	-6.79	4.48	4.49	11.27
Fluopicolide	-7.44	4.21	4.15	11.59
Etoxazole	-6.25	6.36	6.39	12.64
Bistrifluron	-5.07	5.70	5.79	10.85
Hexaflumuron	-7.36	5.70	5.78	13.14
Lufenuron	-6.57	6.44	6.55	13.12
Novaluron	-6.57	6.39	6.49	13.06
Diflubenzuron	-6.96	3.95	3.96	10.92
Dichlorbenzuron	-7.65	4.61	4.64	12.29

SUPPORTING MATERIAL SM15. Outcome of the screening exercise of the title compounds with PBT-profiler (PBT Profiler, 2015).

	Smiles	half-life [d]				% in each medium				BCF	Fish ChV / mg·L^{-1}
		water	soil	sediment	air	water	soil	sediment	air		
1	S=C(N(CC)CC)NC(c1ccccc1)=N	38	75	340	0.1	13	85	2	0	13	13
2	CCN(CC)C(=S)NC(=NC1=CC=CC=C1)C2=CC=CC=C2	38	75	340	0.1	7	59	34	0	740	0.094
3	S=C(N=C(c1ccccc1)N(CC))N(CC)CC	38	75	340	0.1	14	81	4	0	220	0.065
4	S=C(N=C(c1ccccc1)N(CC)CC)N(CC)CC	38	75	340	0.092	15	76	9	0	630	0.019
5	S=C(N=C(c1ccccc1)OCC)N(CC)CC	38	75	340	0.17	18	80	2	0	310	0.24

SUPPORTING MATERIAL SM16. PBT profiler colour code with respect to assumed threshold values (PBT Profiler, 2015).

Environmental Compartment	Half-Life		
	Not Persistent	Persistent	
Water	**< 2 months** (< 60 days)	**>= 2 months** (>= 60 days)	**> 6 months** (> 180 days)
Soil	**< 2 months** (< 60 days)	**>= 2 months** (>= 60 days)	**> 6 months** (> 180 days)
Air	**<= 2 days**		**> 2 days**
Sediment	**< 2 months** (< 60 days)	**>= 2 months** (>= 60 days)	**> 6 months** (> 180 days)
Bioconcentration Factor			
Not Bioaccumulative		Bioaccumulative	
< 1,000		**> = 1,000**	**> = 5,000**
Fish ChV / mg·L^{-1}			
Not Toxic		Toxic	
> 10 mg·L^{-1} or no effects at saturation		**< 10 mg·L^{-1}**	**< 0.1 mg·L^{-1}**

References

Goss, K.-U., Schwarzenbach, R.P., 2001. Linear Free Energy Relationships Used To Evaluate Equilibrium Partitioning of Organic Compounds. Environ. Sci. Technol. 35, 1–9. doi:10.1021/es000996d

Gouin, T., Mackay, D., Webster, E., Wania, F., 2000. Screening Chemicals for Persistence in the Environment. Environ. Sci. Technol. 34, 881–884. doi:10.1021/es991011z

Mackay, D., Di Guardo, A., Paterson, S., Cowan, C.E., 1996. Evaluating the environmental fate of a variety of types of chemicals using the EQC model. Environ. Toxicol. Chem. 15, 1627–1637. doi:10.1002/etc.5620150929

Mackay, D., Shiu, W.Y., Ma, K.-C., Lee, S.C., 2006. Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals, Volume II, 2^{o} ed. Taylor & Francis Group/CRC Press.

PBT Profiler, http://www.pbtprofiler.net, as accessed 29/07/2015.

Rordorf, B.F., 1989. Prediction of vapor pressures, boiling points and enthalpies of fusion for twenty-nine halogenated dibenzo-p-dioxins and fifty-five dibenzofurans by a vapor pressure correlation method. Chemosphere 18, 783–788. doi:10.1016/0045-6535(89)90196-3

Schröder, B., Gomes, L.R., Low, J.N., Santos, L.M.N.B.F., Rodrigues, A.S.M.C., 2011. Structure and solid–liquid phase transition thermodynamics of N-(diethylaminothiocarbonyl)benzimido derivatives. J. Mol. Struct. 1004, 257–264. doi:http://dx.doi.org/10.1016/j.molstruc.2011.08.014

Schüürmann, G., Ebert, R.-U., Kühne, R., 2006. Prediction of the Sorption of Organic Compounds into Soil Organic Matter from Molecular Structure. Environ. Sci. Technol. 40, 7005–7011. doi:10.1021/es060152f

Seth, R., Mackay, D., Muncke, J., 1999. Estimating the Organic Carbon Partition Coefficient and Its Variability for Hydrophobic Chemicals. Environ. Sci. Technol. 33, 2390–2394. doi:10.1021/es980893j

Sotomatsu, T., Nakagawa, Y., Fujita, T., 1987. Quantitative structure-activity studies of benzoylphenylurea larvicides. Pestic. Biochem. Physiol. 27, 156–164. doi:10.1016/0048-3575(87)90042-3

US EPA EPISuite 4.1, US EPA. (2012). Estimation Programs Interface Suite™ for Microsoft® Windows, v 4.11. United States Environmental Protection Agency, Washington, DC, USA.