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

Predicting dielectric constants of pure liquids: fragment-based Kirkwood-Fröhlich model applicable over a wide range of polarity

Supplementary Information

Rémi Bouteloup and Didier Mathieu*

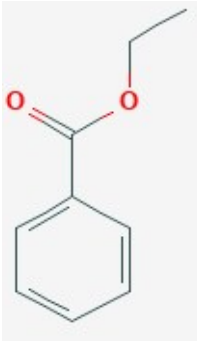
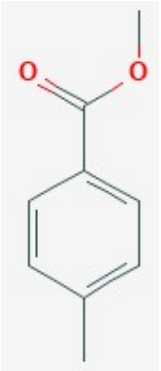
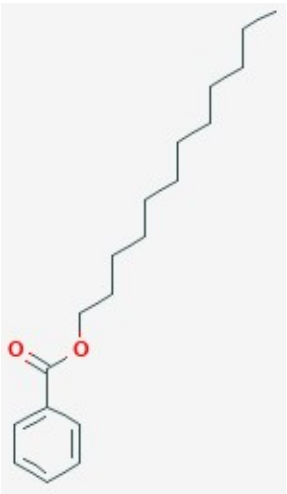
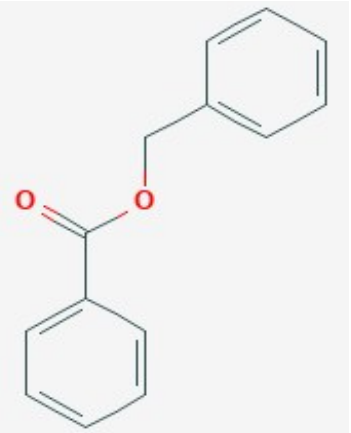
CEA, DAM, Le Ripault, 37260 Monts, France

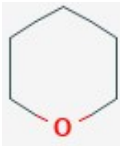
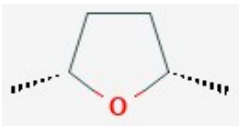
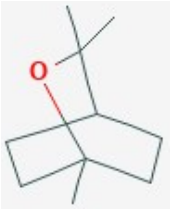
Email: didier.mathieu@cea.fr

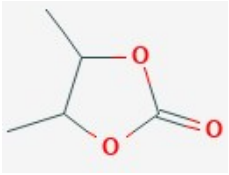
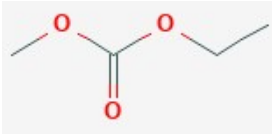
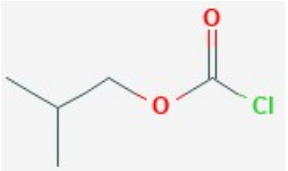
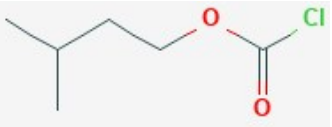
March 11, 2019

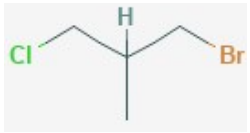
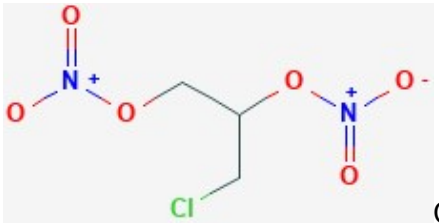
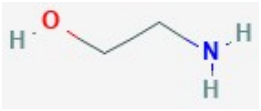
Table S1. Details of the database used to fit and validate the model, along with present predictions for molar volume (V_m), refraction index (n_D), orientational dipolar parameter ($g\mu^2$) and dielectric constant (ε_r). Cf Excel file in Supplementary information to the article.

Figure S1. Further examples of decomposition of molecules into polar fragments, with associated SMARTS codes. In contrast to Figure 7, only real molecules are shown here.

Molecules with benzoate fragment [COC(=O)c1ccccc1]			
Ethyl benzoate	Methyl 4-methylbenzoate	Dodecyl benzoate	Benzyl benzoate
			

Molecules with cyclic ether fragment [COC]			
Tetrahydropyran	cis-2,5-Dimethyltetrahydrofuran	Eucalyptol	Oxirane
			

Molecules with cyclic and aliphatic carbonate [COC(=O)OC] fragments and with chlorocarbonate [COC(=O)Cl] fragments			
2,3-butylene carbonate	Ethyl methyl carbonate	Isobutyl chlorocarbonate	3-Methyl-1-butyl chlorocarbonate
			

Molecules with more than one polar fragment	
3-Bromo-1-chloro-2-methylpropane 	- One chlorine fragment [C-Cl] - One bromine fragment [C-Br]
Monomethyl adipate 	- One ether fragment [COC(C)=O] One carboxylic fragment [CC(=O)O]
 Clonitrate	- One chlorine fragment [C-Cl] - Two nitrate fragments –O–NO_2 [CO[N+](=O)[O-]] -
Ethanolamine 	- One hydroxyl fragment [C-OH] - One primary amine fragment [C-NH2]

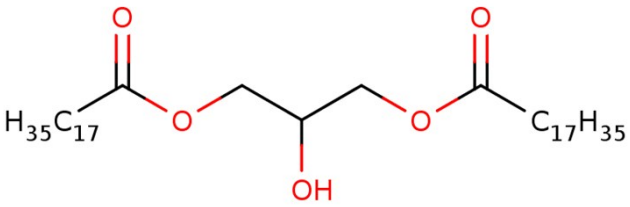
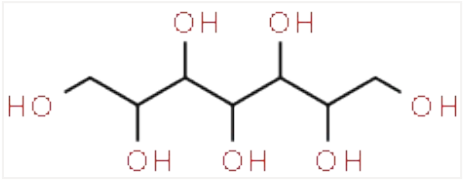
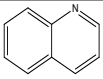
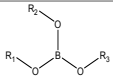
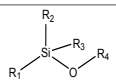
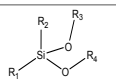
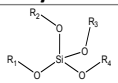
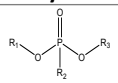
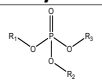
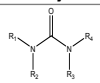
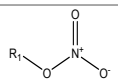
1,2,3-Propanetriol-1,3-distearate 	- One hydroxyl fragment [C-OH] Two ether fragment [COC(C)=O]
Glucoheptitol 	- Seven hydroxyl fragment [C-OH]

Table S2. Values (in D^2) of the transferable additive fragment contributions $(g\mu^0_i)^2$ to the molecular orientational dipolar parameter $g\mu^2$. TR and TE refer respectively to the number of compounds that exhibit the corresponding fragment in the training and test sets. In addition, "R" denotes sp3 carbon atoms, and "size" indicates that the parameter does not depend on the size of the associated ring.

Polar fragment	$g\mu^2_i$	TR	TE	Polar fragment	$g\mu^2_i$	TR	TE	Polar fragment	$g\mu^2_i$	TR	TE
 **Pyrazine**	0.28	3	0	 **Pyridine**	4.84	6	3	 **Quinoline**	4.10	3	2
 **Pyridine-1-oxide**	17.91	3	1	 **Borate**	0.52	3	4	 **Silane**	0.12	3	0
 **Oxysilane**	1.31	5	2	 **Dioxysilane**	1.78	4	2	 **Trioxysilane**	2.51	5	2
 **Tetraoxysilane**	2.74	3	3	 **Phosphonate**	8.64	10	7	 **Phosphate**	12.74	4	0
 **Urea**	15.31	3	1	 **Carbamate**	7.68	3	0	 **Fluorobenzene**	2.08	4	1
 **Chlorobenzene**	2.19	4	4	 **Bromobenzene**	1.91	4	3	 **Nitrobenzene**	15.14	4	1
 **Nitro**	12.68	5	3	 **Nitrate**	8.90	3	1	 **Nitrite**	5.61	5	3

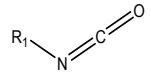
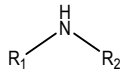
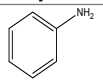
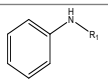
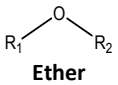
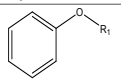
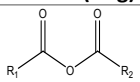
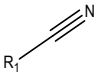
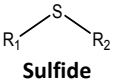
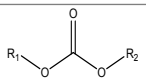
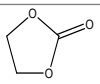
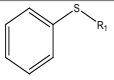
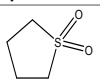
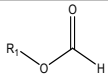
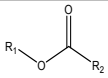
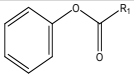
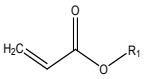
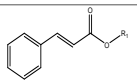
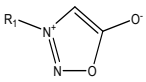
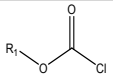
 **Isocyanate**	8.04	3	2	 **Amine**	1.90	15	7	 **N-Amine**	1.10	4	3
 **Aniline**	2.26	4	2	 **N-Aniline**	2.69	3	0	 **N,N-Amine**	0.49	4	1
 **Ether**	1.74	9	5	 **N,N-Aniline**	1.99	4	1	 **Anisole**	1.43	5	4
 **Ether (ring)**	3.13	3	3	 **Ketone (ring)**	8.27	8	4	 **Aldehyde**	7.09	5	1
 **Ketone**	9.44	12	11	 **Anhydride**	12.28	3	1	 **Carboxylic acid**	0.78	22	13
 **Thiol**	2.33	12	4	 **Nitrile**	12.13	12	5	 **Sulfide**	2.55	4	0
 **Carbonate**	0.89	3	0	 **Carbonate (ring)**	36.41	3	3	 **Thioanisole**	1.92	3	0
 **N,N-Formamide**	19.04	3	2	 **N,N-Amide**	22.02	5	10	 **Sulfoxide**	24.50	4	4
 **Sulfone**	29.59	8	6	 **Sulfolane**	22.57	3	0	 **Phenyl sulfone**	30.15	3	0
 **Formate**	3.51	5	4	 **Carboxylate**	2.95	77	27	 **Lactone**	20.28	4	0
 **Benzoate**	3.33	9	5	 **Phenyl carboxylate**	2.35	5	4	 **Acrylate**	3.25	3	0
 **Phosphine-oxide**	37.49	4	2	 **Phosphine sulfide**	42.81	4	4	 **Cinnamate**	3.71	6	3
 **Sydnone**	50.82	4	3	 **Oxazolidine-2-one**	31.24	3	0	 **N-Oxazolidine-2-one**	41.89	4	0
 **Chloroformate**	5.82	3	1	**Trichloroacetate**	5.59	3	2	**Chlorocarboxylate**	7.14	3	0
Bromocarboxylate	5.94	3	1	**Phtalate**	6.61	3	3	**Salicylate**	4.43	5	0
Phenol	3.49	12	2	**Alcohol**	9.19	6	104				

Table S3. Values of the linear parameters A and B (in D^2) required to evaluate $(g\mu^0_i)^2$ from equation (6), taking into account the number of hydrogen atoms on an adjacent carbon atom in a position. Like for Table S2, TR and TE refer respectively to the number of compounds that exhibit the corresponding fragment in the training and test sets.

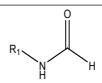
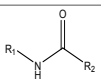
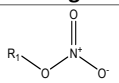
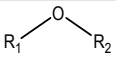
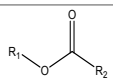
Fragment	A	B	TR	TE	Fragment	A	B	TR	TE
 **Fluor**	-0.64	3.46	6	0	 **Brome**	-1.19	5.97	27	7
 **Chlore**	-1.02	5.83	20	5	 **Iode**	-0.94	4.88	16	4
 **N-Formamide**	16.90	22.18	3	0	 **N-Amide**	8.12	69.27	10	6

Table S4. Values of the interaction parameters T_i (dimensionless) needed to evaluate $(g\mu_i)^2$ from equation (5) in cases where δ_i is non-zero and must be calculated using equation (7). TR refers to the number of compounds that exhibit the corresponding fragment in the training and set.

Polar fragment	Ti	TR	Polar fragment	Ti	TR	Polar fragment	Ti	TR
 **Amine**	0.41	2	 **Thiol**	-0.41	3	 **Nitrate**	-0.05	5
 **Chlore**	-0.50	12	 **Brome**	-0.73	19	 **Ether**	-0.10	2
 **Ketone***	-0.12	3	 **Acid***	1.59	2	 **Carboxylate**	-0.22	20
 **Nitrile**	0.03	7	 **Alcohol**	-0.35	17			