Pure Component Property Estimation Method of Rarey-Moller

Introduction:

Several pure component property estimation methods were developed within MSc- and PhD-projects in the group of Prof. Ramjugernath at the University of Kwazulu-Natal (UKZN) in Durban, South Africa. The work was closely supervised by Jürgen Rarey within his position as honorary Prof. at UKZN. DDBST GmbH (Oldenburg) supplied data from the DDB and software support. Development was performed using the software-package ARTIST.

This document gives a brief description of the Rarey-Moller method. The various Rarey-Nannoolal methods are covered in a different document.

Since the publication of the method, numerous corrections and improvements were added and the model parameter parameters have been refitted several times during this process. The method as described in the original publication should not be used for components with 3 or more H-bonding groups due to the form of the group-interaction contribution.

Work on the methods is continued and several further methods have been developed but not yet published.

The methods are described in detail in the references below. In addition, short reproductions of the equations and parameter tables for the estimation of the normal boiling point can be found in e.g. “Perry’s Chemical Engineer’s Handbook” or the German “VDI-Wärmeatlas”.

References:

Estimation of Pure Component Properties. Part 1. Estimation of the Normal Boiling Point of Non-Electrolyte Organic Compounds via Group Contributions and Group Interactions	Nannoolal Y., Rarey J., Ramjugernath D., Cordes W.	Fluid Phase Equilib., 226, 1, 45 63 (2004)
Estimation of pure component properties Part 2. Estimation of critical property data by group contribution	Nannoolal Y., Rarey J., Ramjugernath J.	Fluid Phase Equilib., 252, 1-2, 1 27 (2007)
Estimation of pure component properties: Part 3. Estimation of the vapor pressure of non-electrolyte organic compounds via group contributions and group interactions	Nannoolal Y., Rarey J., Ramjugernath D.	Fluid Phase Equilib., 269(1-2), 117-133 (2008)
Estimation of pure component properties. Part 4: Estimation of the saturated liquid viscosity of non-electrolyte organic compounds via group contributions and group interactions	Nannoolal Y., Rarey J., Ramjugernath D.	Fluid Phase Equilib., 281 (2), 97 119 (2009)
Estimation of the vapour pressure of non-electrolyte organic compounds via group contributions and group interactions	**Moller B., Rarey J., Ramjugernath D.**	**J.Mol.Liq., 143, 1, 52 63 (2008)**

The work is based on a previous method by Rarey and Cordes:

A new method for the estimation of the normal boiling	Cordes W., Rarey J.	Fluid Phase Equilib.,

point of non-electrolyte organic compounds		201, 19, 409 433 (2002)

Further published methods are based on a similar approach:

Group Contribution Prediction of Surface Charge Density Profiles for COSMO-RS(Ol)	Mu T., Rarey J., Gmehling J.	AIChE J., 53, 12, 3231 3240 (2007)
Group Contribution Prediction of Surface Charge Density Distribution of Molecules for COSMO-SAC	Mu T., Rarey J., Gmehling J.	AIChE J., 55, 12, 3298 3300 (2009)

Additional methods have been developed but are not yet published. These methods are available via the DDBST-Software ARTIST.

- Activity of Complex Molecules in Water (Solubility, ...) (Moller, Rarey, Ramjugernath)
- Activity of Complex Molecules in Alkanes (Solubility, ...) (Moller, Rarey, Ramjugernath)
- Surface Tension (Olivier, Rarey, Ramjugernath)
- Thermal Conductivity (Govender, Rarey, Ramjugernath)

Group Contribution Scheme and Parameters

Updated parameter table for the vapour pressure method of Moller et al. (Ink No. – the number used in the fragmentation program to identify the group, Size Dep – group values with yes need to be multiplied by the number of heavy atoms in the molecule, Size dependant group constants always have a frequency of 1, Prty – the order in which groups are fragmented – lower numbers first, * - group value only fitted to 1 compound, ** - group value only fitted to 2 compounds)

$$B' = A + \sum v_i dB_i + \frac{1}{2}\sum_i \sum_j \frac{GI_{i-j}}{n \times m}$$

Ink No	Name	Description	dB_i	Example	Prty	Size Dep	Ref No
-	A	The constant term A	9.47970	-	-	-	-
Aliphatic carbon groups							
1	-CH3	Methyl group attached to a non-aromatic non-electronegative atom	-0.03206	2,2-Dimethylbutane	135	No	101
4	-CH2-	CH2 in a chain	0.07558	n-Butane	141	No	102
5	>CH-	CH in a chain	0.10049	3-Ethylpentane	144	No	103
6	>C<	C in a chain	0.01643	2,2,4-Trimethylpentane	146	No	104
2	-CH3	Methyl group attached to a non-aromatic electronegative atom	0.12260	N-Methylaniline	132	No	105
7	-CH2-	CH2 in a chain attached to an electronegative atom	0.13265	Ethylenediamine	136	No	106
8	-CH<	CH in a chain attached to an electronegative atom	0.13629	5-Ethyl-2-nonanol	137	No	107
9	>C<	C in a chain attached to an electronegative atom	-0.02810	tert-Butanol	138	No	108
29	-CH3	Methyl group attached to a ring carbon	-0.10527	Methylcyclohexane	122	No	109
10	-CH2-	CH2 in a ring	-0.02275	Cyclohexane	143	No	110
11	>CH-	CH in a ring	0.07517	Methylcyclohexane	145	No	111
12	>C<	C in a ring	0.15009	1,1-Dimethylcyclopentane	147	No	112
131	>CH(r) - C(r)<	CH in a ring bonded to a Carbon in a different ring	0.01164	cis-Decahydronaphthalene	110	No	113

136	C(k)-C(r)-3C(r)	Ring carbon attached to 3 other ring carbons and a chain carbon	0.03314	1,3-Dimethyl adamantane	108	No	114
137	C-4C(r)	Ring carbon attached to 4 other ring carbons	0.17291	Spiro[4.5]decane	109	No	115
24	-CH2(r)-en	CH2 in a ring attached to an electronegative carbon	0.08216	1,4-Dioxane	142	No	116
14	>CH-	CH in a ring attached to an electronegative atom	0.13765	Cyclopentanol	139	No	117
15	>C<	C in a ring attached to an electronegative atom	-0.07267	Perfluorocyclopentane	140	No	118
139	C(r)_3C(r)_en	Ring Carbon bonded to 3 other ring carbons and an en atom	-0.00851	1-Nitroadamantane	107	No	119
26	CH2=	Double bonded carbon at the end of a chain/ring	-0.00815	1-Nonene	117	Yes	120
20	-CH=C-	Double bonded carbon in a chain with only 1 carbon neighbour	0.00313	2-Heptene	121	Yes	121
27	-C=C-	Double bonded carbon in a chain with 2 carbon neighbours	0.00711	2-Methyl-2-pentene	118	Yes	122
31	>C=C=C<	C=C=C; cummulated double bonds	0.08052	1,2-Butadiene	112	Yes	123
33	>C=C-C=C<	C=C-C=C (chain); conjugated double bonds (chain)	0.04120	trans-1,3-Pentadiene	114	Yes	124
21	>C=C<	Double bond between carbons in a ring	0.00168	1,3-Cyclopentadiene	123	Yes	125
13	-C=C<	Double bonded carbon in a ring with 2 carbon neighbours	0.02864	1-Methylcyclohexene	120	Yes	126
32	>C=C-C=C<	C=C-C=C (ring); conjugated double bonds (ring)	-0.00190	1,3-Cyclopentadiene	113	Yes	127
134	>C(r)=C(k)	Carbon in a ring double bonded to a carbon outside the chain	0.01669	beta-Pinene	106	Yes	128
25	CH#	Carbon triple bonded to another carbon at the end of a chain	-0.04184	1-Octyne	124	Yes	129
22	-CtC-	Triple bond between 2 carbons in a chain	-0.01393	2-Heptyne	125	Yes	130
34	-C#C-C#C-	C#C-C#C; conjugated triple bonds	0.00991**	2,4-Hexadiyne	111	Yes	131
Aromatic carbon groups							
3	-CH3	Methyl group attached to an aromatic atom	-0.03718	1-Methyl naphthalene	133	No	201
16	-CH(a)<	CH in an aromatic ring	0.00691	Benzene	128	No	202
17	>C(a)<	C in an aromatic ring	0.13222	Propylbenzene	131	No	203
19	=C(a)<	Aromatic carbon attached to three aromatic neighbours	-0.00328	Naphthalene	116	No	204
132	C(a)-C(r) <	Aromatic carbon bonded to a carbon in a ring	0.08205	1,2,3,4-Tetrahydronaphthalene	129	No	205
133	C(a)-C(a)	2 Aromatic carbons chain bonded	0.15828	Benzidine	130	No	206
135	C(a)-r-C(a)	Aromatic carbon bonded to an aromatic carbon in a ring	-0.10077	9H-Fluorene	115	No	207
138	C(a)-C=	Aromatic carbon attached to a double bonded carbon	0.27831	Divinylbenzene	127	No	208
18	>C(a)<	C in an aromatic ring attached to an electronegative atom	0.24600	Aniline	119	No	209
Fluorine groups							
35	F-	Fluorine attached to nonaromatic carbon	0.01909	1-Fluoropentane	92	No	301
38	F-C-1Halo	Flourine attached to a carbon with one other halogen atom	0.07450	Perfluorocyclopentane	71	No	302
39	F-C-2Halo	Flourine attached to a carbon with two other halogen atoms	0.06602	1,1,1,2-Tetrachloro-2,2-difluoroethane [R112a]	70	No	303
36	F-C=	Fluorine attached to double bonded carbon	0.07029	2-Fluoropropane	69	No	304
148	F-C=(1 Halo)	Flourine attached to a double bonded carbon with one other halogen atom	0.05489	1,1-Difluoroethene	68	No	305
37	F-C(a)	Fluorine attached to aromatic carbon	-0.11552	Fluorobenzene	91	No	306
116	Fe-Si<	Flourine attached to a silicon atom	0.18079	Silicon tetrafluoride	1	No	307
Chlorine groups							
40	Cl-	Chlorine attached to noaromatic carbon	0.02294	Chloroethane	76	No	401
43	Cl-C-1Halo	Chlorine attached to a carbon with one other halogen atom	-0.00101	2-Bromo-2-chloro-1,1,1-trifluoroethane	67	No	402
44	Cl-C-2Halo	Chlorine attached to a carbon with two other halogen atoms	0.02263	1,1,1-Trichloroethane [R140a]	66	No	403
42	Cl-C=	Chlorine attached to double bonded carbon	0.05474	2-Chloro-1,3-butadiene	65	No	404
149	Cl-C=(1 Halo)	Chlorine attached to a double bonded carbon with one othe halogen atom	0.10733	Tetrachloroethylene	64	No	405
41	Cl-C(a)	Chlorine attached to aromatic carbon	-0.24456	Chlorobenzene	77	No	406

117	Cl-Si<	Chlorine attached to a silicon atom	-0.04326	Trichlorosilane	2	No	407
113	COCl-	Acid Chloride	0.30163	Trichloroacetyl chloride	19	No	408
Bromine groups							
45	Br-	Bromine attached to nonaromatic carbon	-0.06190	1,2-Dibromoethane	78	No	501
144	Br-C-1Halo	Bromine attached to a Carbon with one other halogen atom	0.03436	2-Bromo-2-chloro-1,1,1-trifluoroethane	75	No	502
145	Br-C-2Halo	Bromine attached to a Carbon with two other halogen atom	-0.06034	Tribromomethane [R20B3]	74	No	503
146	Br-C=	Bromine attached to a double bonded carbon	0.12369	Vinyl bromide	73	No	504
46	Br-C(a)	Bromine attached to aromatic carbon	-0.23289	Bromobenzene	79	No	506
118	Br-Si<	Bromine attached to a silicon atom	-0.16653	Silicon tetrabromide	3	No	507
Iodine groups							
47	I-	Iodine attached to carbon	-0.01350	Ethyl iodide	61	No	601
119	I-Si<	Iodine attached to a silicon atom	1.27845**	Triiodomethylsilane	4	No	607
Oxygen groups							
53	-COOH (n=<9)	COOH Group attached to a small molecule (n =< 9)	0.81213	Pentanoic acid	25	Yes	701
155	-COOH (n>9)	COOH Group attached to a large molecule (n > 9)	0.08306	Dodecanoic acid		Yes	702
48	C(a)-COOH	Aromatic COOH	2.35370*	Benzoic acid	24	No	703
49	-OH (n=<4)	OH Group attached to a small molecule (n =< 4)	-0.32187	Ethanol	93	Yes	704
153	-OH (n>4)	OH Group attached to a large molecule (n > 4)	-0.04853	5-Ethyl-2-nonanol		Yes	705
50	C(a)-OH	Aromatic OH	0.68415	2-Naphthol	94	No	706
51	-O-	Ether oxygen	0.10973	Diethyl ether	96	No	707
52	-O-	Aromatic oxygen	0.21686	Furan	95	No	708
54	-COO -	Ester in a chain	0.52436	1,3-Benzenedicarboxylic acid dimethyl ester	26	No	709
55	-COO -	Formic acid ester	0.50096	Formic acid ethyl ester	28	No	710
56	-COO -	Ester in a ring (lactone)	0.49674	gamma-Butyrolactone	27	No	711
57	>C=O	Ketone bonded to aromatic ring	0.11377	Acetophenone	58	No	712
58	>C=O	Ketone	-0.03413	Acetone	59	Yes	713
59	-CHO	Aldehyde in Chain	0.35027	Acetaldehyde	57	No	714
60	-CHO	Aldehyde attached to an aromatic ring	0.25675	Benzaldehyde	56	No	715
61	O=C(-O-)2	Carbonate diester	0.49248	Carbonic acid dimethyl ester	15	No	716
62	-CO-O-CO-	Anhydrides	0.79979	Acetic anhydride	10	No	717
63	-CO-O-CO-	Cyclic anhydrides with double or aromatic bond	0.92784	Maleic anhydride	9	No	718
64	>(OC2)<	Epoxide	-0.05484	Ethylene oxide	54	Yes	719
65	-O-O-	Peroxides	1.72030*	Di-tert.butyl peroxide	34	No	720
66	-OCOO-	Carbonates O-C=O & -O	0.49696	Propylene carbonate	36	No	721
67	>C=O	Carbonyl(C=O) with S attached to Carbon	-0.27172*	Methyl thioacetate	42	No	722
68	>C=O	Urea	0.40287	1,1,3,3-Tetramethyl urea	7	No	723
69	-OCON<	Carbamate	3.64989*	Methyldimethylcarbamate	6	No	724
Nitrogen groups							
70	-CONH<	Amide with no substituents	2.13114*	Acetamide	29	No	801
71	-CONH<	Amide with one substituent attached to the nitrogen	1.54292	N-Methylformamide	11	No	802
72	-CONH<	Amide with two substituents attached to the nitrogen	0.45925	N,N-Dimethylformamide (DMF)	12	No	803
73	OCN-	Isocyanate	0.19590	Isocyanic acid methyl ester	31	Yes	804
141	-OCN(a)	IsoCyanate attached to an aromatic carbon	0.45450	Phenyl isocyanate	30	No	805
74	ONC-	Oxime	2.54770	Methyl ethyl ketoxime	32	No	806
75	NO2-	Nitro group attached to a nonaromatic carbon	0.29689	Nitromethane	21	No	807
76	NO2-	Nitro group attached to an aromatic carbon	0.15037	Nitrobenzene	22	No	808
77	NO2-	Nitrite	-0.32857**	Ethyl nitrite	23	No	809
78	-ON=	Isoxazole O-N=C	0.50042*	5-Methyl-4-nitroisoxazole	51	No	810
79	NO3-	Nitrate	0.79232	Ethylnitrate	14	No	811
80	NH2-	Primary amine attached to nonaromatic carbon/silicon	-0.05227	Ethylenediamine	98	Yes	812
81	NH2-	Primary amine attached to aromatic carbon	0.29860	Aniline	97	No	813
82	-NH-	Secondary amines (chain) attached to carbons/silicons	0.38441	Dibutylamine	102	No	814

86	=N-	Secondary amines (chain) attached to one carbons/silicons via double bond	0.82002	N-Benzylidenemethyl amine	105	No	815
93	-NH-	Secondary amines (ring) attached to carbons/silicons	0.54934	Morpholine	101	No	816
94	-NH-	secondary amines attached to aromatic carbons/silicons	0.27388	N-Methylaniline	33	No	817
84	-N<	Tertiary amine attached to carbons/silicons	-0.22854	N,N-dimethylaniline	104	No	818
92	-N<	tertiary amines attached to aromatic carbon	0.05020	N,N-Dimethylaniline	43	No	819
85	>N<	Nitrogen attached to four carbons	-1.16781*	N,N,N',N'-Tetramethylmethylenediamine	35	No	820
140	C2-N-C(r)	Cyclic Tertiary Amines	-0.29163	N-Methylpiperidine	103	No	820
83	N=N	Azene N=N	-0.02889	Azobenzene	50	No	821
130	>N-N<	A hydrazine functional group	0.93778	Hydrazine	49	No	822
143	N-N_C	Hydrazine with 1 carbon neighbours	0.69585	Phenylhydrazine	48	No	823
142	N-N_C2	Hydrazine with 2 carbon neighbours	-0.14041	1,1-Dimethylhydrazine	47	No	824
87	=N-	Aromatic nitrogen in a five-membered ring	0.73215	Oxazole	100	No	825
88	=N-	Aromatic nitrogen in a six-membered ring	0.25193	2-Methylpyridine	99	No	826
89	-CtN (n=<12)	CN Group attached to a small molecule (n =< 12)	-0.04392	Acetonitrile	60	Yes	827
154	-C#N (n>12)	CN Group attached to a large molecule (n>12)	0.07874	Tetradecanenitrile		Yes	828
Sulfur groups							
98	-S-S-	Disulfide	0.00689	Dimethyl disulfide	55	No	902
99	-SH	Thiol or mercaptane attached to carbon	-0.00787	1-Propanethiol	80	No	903
100	-S-	Thioether	-0.06540	Ethyl methyl sulfide	81	No	904
101	-S-	Aromatic thioether	-0.13637	Thiazole	82	No	905
102	-SO2-	Sulfolane O=S=O	-0.37725*	2,4-Dimethylsulfolane	18	No	906
104	-SO2N<	Sulfon amides, attached to N and to S with 2 double bond O	0.17994	N,N-Dimethyl-methanesulfonamide	38	No	908
105	>S=O	Sulfoxide	0.52729*	Dimethyl sulfoxide	40	No	909
106	SCN-	Isothiocyanat	0.01696	Allyl isothiocyanate	20	No	910
107	>SO3	Sulfate with one oxygen replaced by another atom	0.43352*	Benzenesulfonic acid,ethyl ester	39	No	911
Phosphorous groups							
95	P(O)O3-	Phosphate triester	0.65259	Methyl diphenyl phosphate	8	No	1001
96	>P<	Phosphine	-0.04561	Triphenylphosphine	46	No	1002
97	PO3-	Phosphite attached to only 3 Oxygens,PO3	-0.15853*	Triethoxyphosphine	45	No	1003
Metal groups							
108	>Se<	Selenium	0.48426**	Diselenide, diphenyl	52	No	1101
109	AsCl2-	Arsenic dichloride attached to a carbon	0.33997	Methylarsenic dichloride	17	No	1102
110	>Sn<	Stannane with four carbon neighbors	0.13794	Tetramethylstannane	62	No	1103
111	B(O-)3	Boric acid triester	0.46251	Boric acid trimethyl ester	16	No	1104
Germanium groups							
114	GeCl3-	GeCl3 attached to carbon	0.23913	Trichlorosilyl(trichlorogermyl)methane	13	No	1201
115	>Ge<	Germane with four carbon neighbors	0.40216	Tetramethylgermane	63	No	1202
Silicon groups							
120	-SiH3	Silane Group	-0.27218	Butylsilane	84	No	1301
121	-SiH2-	Primary Silicon Group	0.27766	Trisilane	88	No	1302
122	-SiH<	Secondary Silicon Group	-0.27220	Triethylsilane	89	No	1303
123	>Si<	Tertiary Silicon Group	0.09298	Tetraethylsilane	90	No	1304
124	-SiH3	Silane Group attached to an elecromagnetic atom	0.18974	Monochlorosilane	83	No	1305
127	SiH2	SiH2 attached to electronegative atoms	0.21806	Dichlorosilane	85	No	1306
128	SiH	SiH attached to electronegative atoms	0.03309	Trichlorosilane	86	No	1307
125	>Si<	Silicon Atoms bonded to elecromagnetic atoms	0.11733	Tetrachlorosilane	87	No	1308
129	CH3-Si	Methyl group attached to a Silicon atom	-0.03374	Tetramethylsilane	134	No	1309
Special groups							
150	no H	No hydrogen atoms	-0.19495	Perfluoropentane		No	1401
151	one H	one Hydrogen atom	-0.04827	2-Bromo-2-chloro-1,1,1-trifluoroethane		No	1402

Size dependant group constants				
170	Alkenes group constant	-0.03682	No	2001
171	Alkynes group constant	0.58091	No	2002
172	Ketone group constant	0.71842	No	2003
173	Epoxy group constant	0.70573	No	2004
174	IsoCyanate group constant	-0.45738	No	2005
175	Short OH group constant (n=<4)	6.27492	No	2006
176	Long OH group constant (n>4)	5.24404	No	2007
177	Primary amine group constant	0.84041	No	2008
179	Short CN group constant (n=<12)	0.56132	No	2010
180	Long CN group constant (n>12)	-1.04824	No	2011
181	Short COOH group constant (n=<9)	-2.57882	No	2012
182	Long COOH group constant (n>9)	3.92182	No	2013
Group interactions				
200	Alcohol - Alcohol Interaction	-4.71956	No	3001
201	Alcohol - 1 Amime Interaction	-3.88115	No	3002
202	Alcohol - 2 Amine Interaction	-8.95373	No	3003
203	Alcohol - Thiol Interaction	-10.16458*	No	3004
205	Alcohol - Ether Interaction	-14.35895	No	3006
207	Alcohol - Ester Interaction	-20.46935	No	3008
208	Alcohol - Ketone Interaction	-20.17369**	No	3009
210	Alcohol - Cyan Interaction	1.28492*	No	3011
220	1 Amime - 1 Amime Interaction	10.17517	No	3021
221	1 Amime - 2 Amine Interaction	-2.35759**	No	3022
224	1 Amime - Ether Interaction	4.87158	No	3025
226	1 Amime - Ester Interaction	-17.71899*	No	3027
230	1 Amime - Aromatic O Interaction	-10.30558*	No	3031
232	1 Amime - Alcohol (a) Interaction	33.03490*	No	3033
237	1 Amime - Nitro(a) Interaction	5.60601	No	3038
239	2 Amine - 2 Amine Interaction	-2.61666**	No	3040
242	2 Amine - Ether Interaction	-0.38331*	No	3043
257	Thiol - Thiol Interaction	3.76376	No	3058
267	Thiol - Alcohol (a) Interaction	2.97641*	No	3068
274	Carboxy - Carboxy Interaction	-61.22494	No	3075
286	Carboxy - Aromatic S Interaction	-50.44323*	No	3087
290	Ether - Ether Interaction	0.39710	No	3091
291	Ether - Epox Interaction	11.11875	No	3092
292	Ether - Ester Interaction	1.12699	No	3093
293	Ether - Ketone Interaction	-16.97401	No	3094
294	Ether - ThioEther Interaction	-13.78509*	No	3095
295	Ether - Cyan Interaction	1.38626	No	3096
298	Ether - Alcohol (a) Interaction	-12.48454	No	3099
299	Ether - Aldehyde Interaction	-2.94131	No	3100
303	Ether - Nitro(a) Interaction	-2.64771**	No	3104
304	Ether - Iso Cyan(a) Interaction	-32.29329*	No	3105
305	Epox - Epox Interaction	-8.30210*	No	3106
319	Ester - Ester Interaction	0.80055	No	3120
320	Ester - Ketone Interaction	0.00307	No	3121
322	Ester - Cyan Interaction	4.79222	No	3123
323	Ester - Aromatic O Interaction	12.27720*	No	3124
324	Ester - 6 N Ring Interaction	34.90694**	No	3125
325	Ester - Alcohol (a) Interaction	-25.39290*	No	3126
326	Ester - Aldehyde Interaction	1.20149*	No	3127
332	Ketone - Ketone Interaction	0.47824	No	3133
334	Ketone - Cyan Interaction	12.53967*	No	3135
344	ThioEther - ThioEther Interaction	-5.49026*	No	3145
355	Cyan - Cyan Interaction	3.87689	No	3156

357	Cyan - 6 N Ring Interaction	6.79035**	No	3158
368	Aromatic O - Aldehyde Interaction	1.94212*	No	3169
371	Aromatic O - 5 N Ring Interaction	-0.78283*	No	3172
374	6 N Ring - 6 N Ring Interaction	1.43116	No	3175
375	6 N Ring - Alcohol (a) Interaction	-17.96727*	No	3176
382	Alcohol (a) - Alcohol (a) Interaction	-0.52433	No	3183
389	Aldehyde - Aldehyde Interaction	7.87563*	No	3190
395	Iso Cyan - Iso Cyan Interaction	-102.82720*	No	3196
401	Aromatic S - 5 N Ring Interaction	-2.84572**	No	3202
404	5 N Ring - 5 N Ring Interaction	-21.83168*	No	3205
407	Nitro(a) - Nitro(a) Interaction	-9.95224	No	3208
408	Nitro(a) - Iso Cyan(a) Interaction	357.52880	No	3209

Treatment of Non-Additive Behavior of Hydrogen-Bonding Groups

In case of groups that can act as H-bond donors or acceptors, adding a further group of this type often results in competitive effects between different H-bonding sites that lead to non-additivity of the effect of these groups on the physical property to be estimated.

A well-known case is the occurrence of multiple alcohol-groups in one molecule. The table below lists the groups considered to be non-additive:

Groups considered to be non-additive (group-ID(s) given in brackets)

A	Alcohol (-OH) (34,35,36,37)	J	Sulfide (-S(na)-) (54)	M	Primary Amine (-NH_2) (40, 41)
B	Phenol (-OH(a)) (37)	K	Aromatic Sulphur (-S(a)-) (56)	N	Secondary Amine (>NH) (42,97)
C	Carboxylic Acid (-COOH) (44)	L	Thiol (-SH) (53)	O	Isocyanate (-OCN) (80)
D	Ether (-O-) (38)			P	Cyanide (-CN) (57)
E	Epoxide (>(OC2)<) (39)			Q	Nitrate (69)
F	Ester (-COOC-) (45,46,47)			R	Aromatic N in 5-ring (=N(a)-(r5)) (66)
G	Ketone (-CO-) (51,92)			S	Aromatic N in 6-ring (=N(a)-(r6)) (67)
H	Aldehyde (-CHO) (52,90)				
I	Aromatic Oxygen (-O(a)-) (65)				

Special group interaction parameters c_{ij} were regressed to account for this behavior. It should be noted that not in every combination this effect is of importance.

Interaction groups are listed in the table under “Group Contribution Scheme and Parameters” above.

Model Equations

In the model developed by Nannoolal et al. the C-parameter in Eq. 1 was set to $T_b / 8$. This model works well for most compounds except alcohols and carboxylic acids, for this reason a correction term was added here resulting in:

$$\ln\left(\frac{P}{1atm}\right) = B' \frac{T - T_b}{T - C(T_b)} + D' \ln\left(\frac{T}{T_b}\right) \qquad (1)$$

For all compounds that do not contain an aliphatic alcohol group or a carboxylic acid group, D' is set to zero. While the value of C was simply assumed to be $T_b / 8$ in the model of Nannoolal et al., the following function was found to give better representation of both large and small molecules:

$$C(T_b) = -2.65 + \frac{T_b^{1.485}}{135} \tag{2}$$

The advantage of this C-parameter correlation is that it not only provides a better representation of the data but also improves the group contribution estimation of B'. Both B' and D' in Eq. (1) are calculated from group contribution. Due to significant intercorrelation simultaneous regression of B' and the group increments for D' was required.

In order to account for the size dependence a new group (with a frequency of 1) was added to all alkene and alkyne compounds and the following size dependent contribution scheme was used:

$$B' = A + \sum_i \nu_i dB_i + \sum_j n_j \nu_j dB_j + \sum_k dB_k + GI \tag{3}$$

The subscript i covers all normal (size independent) groups, the subscript j covers all size dependent (e.g. alkene) groups and subscript k is for the size dependent group constants and therefore does not have a frequency term. For example if a molecule has 3 alkene and 2 alkyne groups there will be only be two size dependant groups, one for the alkene groups and one for the alkyne groups (i.e. $\sum_k dB_k = dB_{alkyne} + dB_{alkene}$).

The group interaction term in Eq. 3 is calculated via:

$$GI = \sum_i \sum_j \frac{GI_{i-j}}{m \times n} \tag{4}$$

with GI_{i-j} group interaction contribution between group i and group j [K] ($C_{i-i} = 0$),
n number of atoms (except hydrogen),
m total number of interaction groups in the molecule

$$D' = D + \frac{\nu_{OH} dE_{OH}}{n_a} + \frac{\nu_{OH-OH} dE_{OH-OH}}{\nu_{OH} \times n_a} \tag{1}$$

where
ν_{OH} number of OH groups
n_a number of heavy (non-hydrogen) atoms
D, dE_{OH}, $dE_{OH\text{-}OH}$ group contribution values
$\nu_{OH\text{-}OH}$ "on-off" group interaction frequency