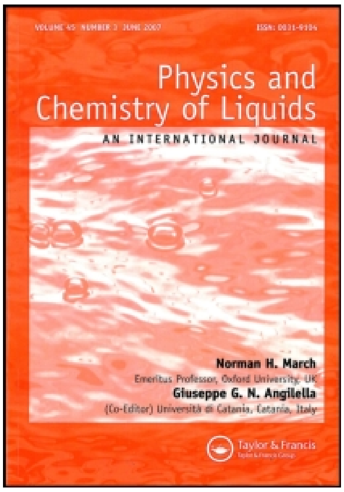

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QUANTITATIVE STRUCTURE-PROPERTY RELATIONSHIPS FOR AQUEOUS SOLUBILITIES OF HALOGENATED AROMATIC COMPOUNDS

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Quantitative structure-property relationships (QSPRs) have been examined for the aqueous solubility of halogenated benzenes, polychlorobiphenyls, polybromobiphenyls, and polychloronaphthalenes at 20 to 25°C. Multiple regression correlations of aqueous mole fraction solubility (X) with molecular size descriptors (molecular weight, total molecular surface area, or various zero-order molecular connectivity indices) and a combined molecular symmetry and structure descriptor ($R *$ Molecular size descriptor) are reported. A generalized correlation takes the form of

$$\log X = a_0 + a_1\,(\text{Molecular size descriptor})^m + a_2(\text{MP} - 25) + a_3(R * \text{Molecular size descriptor})$$

where $1 \leq m \leq 2$, a_i refers to the ith regression coefficient, and R is a molecular redundancy index. The best correlation found, from the standpoint of reduced standard deviations and calculational simplicity, does not contain a melting temperature term ($a_2 = 0$). Derived QSPRs enable estimation of aqueous solubilities based solely on structural information.

KEY WORDS: Molecular connectivity indices; halogenated aromatics; polyhalogenated biphenyls; QSPR; water solubility.

INTRODUCTION

A number of investigators have addressed the problem of correlating and predicting the solubilities of polycyclic aromatic hydrocarbons (PAHs), halogenated benzenes

(HBs), polychlorinated biphenyls (PCBs), polycyclic aromatic hetero-atom compounds, and other organic nonelectrolytes in both aqueous and aqueous-organic solvent media. Development of a model which provides a semi-quantitative means of predicting the solubility of a given PAH or PCB is of importance considering the well-documented carcinogenic activity of these classes of compounds, particularly in light of the frequent danger imposed by the pollution of natural waterways by petroleum hydrocarbons and toxic wastes. Numerous linear and multivariate regression equations have been published expressing the logarithm of the aqueous mole fraction solubility (or molar solubility) as a function of empirically derived quantities such as van der Waals volumes[1-5], total molecular and group surface areas[1-9], molecular weight[2,4], and a variety of other molecular connectivity and topological indices[10-12]. For nonpolar solutes, molecular size descriptors provide a rough measure of the energy required to create a solvent cavity wherein a solute molecule, or possibly, an aggregation of solute molecules would reside. As water is a highly structured solvent, the number of hydrogen bonds that must be broken is directly proportional to the size of the dissolved solute. Secondary considerations involve the energetics of breaking solute-solute interactions, which depends on the types of functional groups present in the molecule, and in the case of crystalline materials, is reflected in the magnitude of the enthalpy of fusion and the melting temperature. These, in turn, are partially correlated with molecular symmetry.

On a more fundamental level, the ability to predict accurately the aqueous solubility of a given molecule will require a more detailed understanding of the exact nature of solute-water interactions at the molecular level than simple molecular-size correlations would be expected to evince. Precise theoretical treatment of the collisional and electrostatic interactions extant in the solution phase, however, proves to be enormously tedious and far too complex to be feasible at the present time. A far simpler approach to this problem, which has found widespread application in environmental sciences, would be to systematically examine quantitative structure-property relationships (QSPRs) between aqueous solubility and measurable/calculable solute properties in hopes of developing better predictive methods with applicability to both nonpolar and polar solutes. Published equations are generally limited in application to a select number of compounds within a narrow family subclass, and little effort is made to extend the derived correlations to the more polar compounds where hydrogen-bonding plays a major role in governing aqueous solubility.

As an initial step in developing a generalized solubility expression, we documented over sixty multiple regression correlations between aqueous mole fractions solubility (X) and molecular size descriptor (total molecular surface area, total group surface area, molecular volume or molecular weight), melting temperature (MP) and a combined molecular symmetry and structure descriptor ($R *$ Molecular size descriptor) for 25 PAHs and 42 HBs[2,4]. A generalized correlation took the form:

$$\log X = a_0 + a_1\,(\text{Molecular size descriptor})^m + a_2(\text{MP} - 25) + a_3(R * \text{Molecular size descriptor}) \qquad (1)$$

where $1 \leq m \leq 2$, a_i refers to the ith regressional coefficient determined via least squares analysis of available experimental solubility data, and R is a molecular redundancy index. Note that in the case of liquid solutes, the breaking of the crystalline lattice is not required and, thus the (MP − 25) correctional term in Eq. 1 is set equal to zero. Table lists a_i coefficients for three of our earlier two-parameter correlations (Eqs. 8, 9, and 11), along with similar equations published in the literature. Also included are the molecular size descriptors employed and statistical correlation coefficients (r^2) and F-values. The generalized correlation expression enables estimation of aqueous PAH and HB solubility to within a factor of two, in most cases using only melting temperatures and structural information as input data. More importantly, the correlations did provide very reasonable predictions for several solutes not included in the original regression analysis and, in the HB study, it was possible to remove the melting temperature term, with only a slight loss in predictive accuracy, in favor of R times the total halogen surface area (TSAX):[4]

$$\log X = -1.61 - 1.49\,(\mathrm{TSA})^2 - 1.59\,(R * \mathrm{TSAX}) \tag{2}$$

$$\mathrm{MSE} = 0.131 \qquad r^2 = 0.993 \qquad F(2, 25) = 1891$$

Successful prediction of PAH and HB solubilities suggests that the generalized correlation expression may be applicable to much larger subsets of aromatic hydrocarbons, and might eventually provide a suitable foundation for estimating the "nonpolar size contributions" to the aqueous solubility of polar, hydrogen-bonding organic solutes. To pursue these ideas further, we extend our previous correlations to include nearly planar polychloronaphthalenes (PCNs), and both polychlorinated (PCBs) and polybrominated biphenyls (PBBs). These three chemical subclasses were selected primarily because: (1) various structural isomers provide the opportunity to study aqueous solubility as a function of molecular symmetry; (2) the substituent groups (which, in this case, are the halogen atoms) are nonpolar in nature and interactions between the dissolved solute and surrounding water molecules should not involve hydrogen bonding; (3) sufficient aqueous solubility data exists so that the PCNs, PCBs, and PBBs can be regressed singly or as one combined data set; (4) x-ray crystallographic data[13–19] reveals that the "interplanar dihedral twist angle" of PCBs/PBBs depends to a large extent on the substitution pattern at the 2, 2′, 6, and 6′ carbon positions; and (5) molecular redundancy indices are extremely sensitive to the molecular configuration assumed. The R value of any given biphenyl derivative having a perpendicular set of phenyl rings will not necessarily be equal to the value based on a planar conformation. It will be informative to ascertain how effective the a_3 (R * Molecular size descriptor) term is in eliminating the a_2 (MP − 25) term and what PCB/PBB conformation is preferred in the molecular redundancy computation.

In addition, we have explored the reasonability of using various molecular connectivity indices as molecular size descriptors. From a computational standpoint, molecular connectivity indices are easier to calculate than surface areas or molecular volumes, and they eliminate all ambiguities regarding which total molecular surface area (TSA) or hydrated molecular surface area (HSA) represents the "best" measure of solute size in aqueous systems. The numerical TSA or HSA value generated from

Table 1 Literature regression equations

Eqn.	Series	Log of	MP-25 x10^{-2}	MW	TSA (planar)	V	Cl n	Const	MSE	r^2	F	Ref.
(8)	HB	X	-1.69 (0.49)	-0.865 (0.310)				-3.24 (0.60)	0.534	0.890	102 (2,25)	4
(9)	HB	X	-1.01 (0.16)		-4.10 (0.32)			1.04 (0.46)	0.151	0.991	1424 (2,25)	4
(10)	HB	S	-1.03		-0.0423			3.30		0.994	(2,32)	1
(11)	HB	X	-1.03 (0.15)			-42.6 (3.1)		-0.01 (0.35)	0.141	0.992	1614 (2.25)	4
(12)	HB	S	-0.95			-0.0482		2.67		0.918	(2,23)	1
(13)	PCB	S					-0.47	-1.40			(1,42)	33
(14)	PCB	S	sub-cooled		-0.0352			4.82	0.370	0.850	(1,165)	9
(15)	PCB	Y	sub-cooled		0.115			-11.687		0.897	412 (1,115)	5
(16)	PCB	X	sub-cooled			0.089		-4.405		0.980	758 (1,115)	5

the number of computational approaches depends on the method used to treat intersecting atomic spheres and how many layers of solvational water molecules are included in the surface area computation.[20–25]

MATERIALS AND METHODS

Mole fraction solubilities at 20 to 25°C for the 42 halogenated benzenes, 167 polychlorobiphenyls, 6 polybromobiphenyls, and 17 polychloronaphthalenes are summarized in Tables 2 to 5. Every effort was made to reference primary literature sources to eliminate any typesetting errors that might be present in published solubility compilations. Unfortunately, compiled values had to be used in a few instances because an original literature source could not be found or was not readily available, although these should be reliable, as most compiling authors critically evaluated their tabulated data against various QSPR correlations. Measured solubility data at 20°C or room temperature was also included so that more isomers could be examined. Errors introduced from using the lower-temperature solubilities are expected to be comparable in magnitude to the standard deviations (maximum error of about ±20%) which were computed whenever multiple, independent literature values were averaged. The numerical values listed for log X represent either a single determination or an arithmetic average, if more than one experimental data point was found in the literature. Any values outside a two standard deviation boundary were rejected from the data set before averaging.

Where possible, melting temperatures are included in Tables 2 to 5. As the scatter in the data is at times large, a 15°C range for one compound, and we were attempting to find an alternative to the use of the melting temperature, when it is not available, we simply choose a representative value for inclusion in the tables.

As in an earlier paper[2], we define the molecular redundancy index (R) as the following:

$$R = \frac{\sum_{i=1}^{k} n_i \log n_i}{N \log N} \tag{3}$$

where n_i is the number of atoms in the ith atom set, i is the number of different atom sets, and $N = \sum_{i=1}^{k} n_i$ is the total number of atoms in the molecule. Determination of R values is relatively straightforward, particularly in the case of the halogenated benzenes and polychloronaphthalenes, since all atoms are fixed in space by a single, rigid aromatic base ring. Substituted biphenyl derivatives, on the other hand, exhibit free rotation about the lone C—C single bond, and the actual molecular conformation of any given PCB/PBB depends on steric hindrance created by the halogen atom substitution pattern at the 2, 2′, 6 and 6′ carbon positions. X-ray crystallographic data indicates that the parent biphenyl molecule is nearly planar[26], and placement of one, two, or four large chlorine atoms at any of the four positions increases the twist angle from 0° to about 45°, 60°, and 90°, respectively[13–19]. To illustrate calculation of molecular redundancy indices, we consider 2-chlorobiphenyl as a

Table 2a Halogenated benzenes—Summary

Molecular Formula	Name	R	XA	MW	MP[a]
C6H6	Benzene	0.7211	4.0000	78.1	5.5
C6H5F	Fluorobenzene	0.1860	4.1190	96.1	-41.2
C6H5Cl	Chlorobenzene	0.1860	4.2619	112.6	-45.6
C6H5Br	Bromobenzene	0.1860	4.4048	157.0	-30.8
C6H5I	Iodobenzene	0.1860	4.5476	204.0	-31.3
C6H4F2	1,2-Difluorobenzene	0.2789	4.2381	114.1	-34.0
C6H4Cl2	1,2-Dichlorobenzene	0.2789	4.5238	147.0	-17.0
C6H4Br2	1,2-Dibromobenzene	0.2789	4.8095	235.9	7.1
C6H4I2	1,2-Diiodobenzene	0.2789	5.0952	329.9	27.0
C6H4F2	1,3-Difluorobenzene	0.1860	4.2381	114.1	L
C6H4Cl2	1,3-Dichlorobenzene	0.1860	4.5238	147.0	-24.7
C6H4Br2	1,3-Dibromobenzene	0.1860	4.8095	235.9	-7.0
C6H4I2	1,3-Diiodobenzene	0.1860	5.0952	329.9	40.0
C6H4F2	1,4-Difluorobenzene	0.4649	4.2381	114.1	-13.0
C6H4Cl2	1,4-Dichlorobenzene	0.4649	4.5238	147.0	53.1
C6H4Br2	1,4-Dibromobenzene	0.4649	4.8095	235.9	87.3
C6H4I2	1,4-Diiodobenzene	0.4649	5.0952	329.9	131.5
C6H3F3	1,2,3-Trifluorobenzene	0.1860	4.3571	132.1	L
C6H3Cl3	1,2,3-Trichlorobenzene	0.1860	4.7857	181.5	53.5
C6H3Br3	1,2,3-Tribromobenzene	0.1860	5.2143	314.8	87.8
C6H3I3	1,2,3-Triiodobenzene	0.1860	5.6429	455.8	116.0
C6H3F3	1,2,4-Trifluorobenzene	0.0000	4.3571	132.1	L
C6H3Cl3	1,2,4-Trichlorobenzene	0.0000	4.7857	181.5	17.0
C6H3Br3	1,2,4-Tribromobenzene	0.0000	5.2143	314.8	44.5
C6H3I3	1,2,4-Triiodobenzene	0.0000	5.6429	455.8	91.5
C6H3F3	1,3,5-Trifluorobenzene	0.4421	4.3571	132.1	-5.5
C6H3Cl3	1,3,5-Trichlorobenzene	0.4421	4.7857	181.5	63.5
C6H3Br3	1,3,5-Tribromobenzene	0.4421	5.2143	314.8	122.0
C6H3I3	1,3,5-Triiodobenzene	0.4421	5.6429	455.8	184.2
C6H2F4	1,2,3,4-Tetrafluorobenzene	0.2789	4.4762	150.1	L
C6H2Cl4	1,2,3,4-Tetrachlorobenzene	0.2789	5.0476	215.9	47.5
C6H2Br4	1,2,3,4-Tetrabromobenzene	0.2789	5.6190	393.7	62.5
C6H2I4	1,2,3,4-Tetraiodobenzene	0.2789	6.1905	581.7	136.0
C6H2F4	1,2,3,5-Tetrafluorobenzene	0.1860	4.4762	150.1	L
C6H2Cl4	1,2,3,5-Tetrachlorobenzene	0.1860	5.0476	215.9	54.5
C6H2Br4	1,2,3,5-Tetrabromobenzene	0.1860	5.6190	393.7	99.5
C6H2I4	1,2,3,5-Tetraiodobenzene	0.1860	6.1905	581.7	148.0
C6H2F4	1,2,4,5-Tetrafluorobenzene	0.4649	4.4762	150.1	4.0
C6H2Cl4	1,2,4,5-Tetrachlorobenzene	0.4649	5.0476	215.9	140.0
C6H2Br4	1,2,4,5-Tetrabromobenzene	0.4649	5.6190	393.7	182.0
C6H2I4	1,2,4,5-Tetraiodobenzene	0.4649	6.1905	581.7	254.0
C6HF5	Pentafluorobenzene	0.1860	4.5952	168.1	-48.0
C6HCl5	Pentachlorobenzene	0.1860	5.3095	250.3	86.0
C6HBr5	Pentabromobenzene	0.1860	6.0238	472.6	160.5
C6HI5	Pentaiodobenzene	0.1860	6.7381	707.6	172.0
C6F6	Hexafluorobenzene	0.7211	4.7143	186.1	5.3
C6Cl6	Hexachlorobenzene	0.7211	5.5714	284.8	230.0
C6Br6	Hexabromobenzene	0.7211	6.4286	551.5	327.0
C6I6	Hexaiodobenzene	0.7211	7.2857	833.5	350.0
C6H4FI	1-Fluoro-4-iodobenzene	0.1860	4.6667	222.0	-18.0
C6H4ClF	1-Chloro-2-fluorobenzene	0.0000	4.3810	130.6	-43.0
C6H4ClF	1-Chloro-3-fluorobenzene	0.0000	4.3810	130.6	-4.1
C6H4BrF	1-Bromo-2-fluorobenzene	0.0000	4.5238	175.0	L
C6H4BrF	1-Bromo-3-fluorobenzene	0.0000	4.5238	175.0	L
C6H4BrCl	1-Bromo-2-chlorobenzene	0.0000	4.6667	191.5	-12.3
C6H4BrCl	1-Bromo-3-chlorobenzene	0.0000	4.6667	191.5	-21.5
C6H4BrCl	1-Bromo-4-chlorobenzene	0.1860	4.6667	191.5	68.0
C6H4BrI	1-Bromo-4-iodobenzene	0.1860	4.9524	282.9	92.0
C6H4ClI	1-Chloro-2-iodobenzene	0.0000	4.8095	238.5	1.0
C6H4ClI	1-Chloro-3-iodobenzene	0.0000	4.8095	238.5	25.0
C6H4ClI	1-Chloro-4-iodobenzene	0.1860	4.8095	238.5	57.0
C6ClF5	Chloropentafluorobenzene	0.1860	4.8571	202.5	L

a Values averaged from Ref. 71. L = liquid.

b -LX = -(log X). The solubilities were determined between 20 and 30 °C.

c A '@' indicates value used in the solubility prediction for this column.

Table 2b Halogenated benzenes—Summary

Name	n obs	-LX[b] avg	SD	-LX[c] (eq 36)	-LX (eq 37)	Ref.
Benzene	19	3.38	0.016	3.20@	3.11	31,34,35,36,37,38,39,40,41,42,43,44,45,46,47,48,49,50,51
Fluorobenzene	3	3.53	0.006	3.56@	3.47	31,52,53
Chlorobenzene	11	4.17	0.105	3.97@	3.89	30,31,34,41,43,50,53,54,55,56,57
Bromobenzene	6	4.30	0.044	4.37@	4.29	31,34,39,43,53,66
Iodobenzene	5	4.69	0.107	4.75@	4.68	31,43,52,53,55
1,2-Difluorobenzene	1	3.74		3.90@	3.82	31
1,2-Dichlorobenzene	7	4.83	0.133	4.69@	4.62	30,31,48,53,56,58,59
1,2-Dibromobenzene	1	5.24		5.43@	5.37	31
1,2-Diiodobenzene	1	5.99		6.13@	6.07	31
1,3-Difluorobenzene	1	3.74		3.90@	3.82	31
1,3-Dichlorobenzene	8	4.79	0.033	4.69@	4.62	30,31,46,48,50,56,58,59
1,3-Dibromobenzene	1	5.12		5.43@	5.37	31
1,3-Diiodobenzene	1	6.31		6.13@	6.07	31
1,4-Difluorobenzene	1	3.71		3.90@	3.82	31
1,4-Dichlorobenzene	9	5.00	0.032	4.96@	4.88	31,34,43,48,53,54,58,60,61
1,4-Dibromobenzene	2	5.81		6.04@	5.95	31,53
1,4-Diiodobenzene	2	7.05		7.16@	7.06	31,53
1,2,3-Trifluorobenzene	0			4.24	4.16	
1,2,3-Trichlorobenzene	6	5.77	0.151	5.65@	5.57	30,31,50,56,61,62
1,2,3-Tribromobenzene	0			7.02	6.94	
1,2,3-Triiodobenzene	0			8.25	8.17	
1,2,4-Trifluorobenzene	0			4.24	4.16	
1,2,4-Trichlorobenzene	6	5.38	0.078	5.37@	5.31	30,31,50,56,59,63
1,2,4-Tribromobenzene	1	6.24		6.40@	6.36	31
1,2,4-Triiodobenzene	0			8.01	7.94	
1,3,5-Trifluorobenzene	0			4.24	4.16	
1,3,5-Trichlorobenzene	5	6.23	0.170	5.74@	5.67	30,31,50,56,62
1,3,5-Tribromobenzene	2	7.34		7.35@	7.26	31,71
1,3,5-Triiodobenzene	0			8.91	8.80	
1,2,3,4-Tetrafluorobenzene	0			4.56	4.49	
1,2,3,4-Tetrachlorobenzene	5	6.15	0.196	6.01@	5.96	30,31,50;56,62
1,2,3,4-Tetrabromobenzene	0			7.67	7.62	
1,2,3,4-Tetraiodobenzene	0			9.56	9.49	
1,2,3,5-Tetrafluorobenzene	1	4.05		4.56	4.49	4
1,2,3,5-Tetrachlorobenzene	7	6.52	0.089	6.30@	6.23	30,31,48,50,56,58,62
1,2,3,5-Tetrabromobenzene	0			8.03	7.96	
1,2,3,5-Tetraiodobenzene	0			9.68	9.60	
1,2,4,5-Tetrafluorobenzene	1	4.12		4.56	4.49	4
1,2,4,5-Tetrachlorobenzene	6	7.15	0.357	7.13@	7.03	30,31,50,56,64,65
1,2,4,5-Tetrabromobenzene	1	8.72		8.84	8.73	31
1,2,4,5-Tetraiodobenzene	0			10.71	10.59	
Pentafluorobenzene	0			4.88	4.81	
Pentachlorobenzene	6	7.23	0.212	7.22@	7.15	30,31,48,50,58,62
Pentabromobenzene	0			9.47	9.38	
Pentaiodobenzene	0			10.93	10.86	
Hexafluorobenzene	0			5.19	5.12	
Hexachlorobenzene	7	9.18	0.456	9.20@	9.07	30,31,50,67,68,69,70
Hexabromobenzene	1	11.48		11.88	11.73	64
Hexaiodobenzene	0			13.61	13.47	
1-Fluoro-4-iodobenzene	1	4.87		5.06	5.00	4
1-Chloro-2-fluorobenzene	1	4.16		4.30	4.23	4
1-Chloro-3-fluorobenzene	1	4.09		4.30	4.23	4
1-Bromo-2-fluorobenzene	1	4.44		4.69	4.62	4
1-Bromo-3-fluorobenzene	1	4.41		4.69	4.62	4
1-Bromo-2-chlorobenzene	1	4.93		5.06	5.00	31
1-Bromo-3-chlorobenzene	1	4.95		5.06	5.00	31
1-Bromo-4-chlorobenzene	1	5.37		5.48	5.40	31
1-Bromo-4-iodobenzene	1	6.30		6.44	6.35	31
1-Chloro-2-iodobenzene	1	5.28		5.43	5.37	31
1-Chloro-3-iodobenzene	1	5.29		5.43	5.37	31
1-Chloro-4-iodobenzene	1	5.77		5.74	5.67	31
Chloropentafluorobenzene	0			5.55	5.49	

[a] Values averaged from Ref. 71. L = liquid.

[b] -LX = -(log X). The solubilities were determined between 20 and 30 °C.

[c] A '@' indicates value used in the solubility prediction for this column.

Table 3a Polychlorinated biphenyls—Summary

NUM[a]	NAME	R	XA	MW	MP[b]
0	BIPHENYL	0.3873	7.6667	154.211	71.0
1	2-CHLOROBIPHENYL	0.0815	7.9286	188.656	34.0
2	3-CHLOROBIPHENYL	0.0815	7.9286	188.656	16.5
3	4-CHLOROBIPHENYL	0.1631	7.9286	188.656	77.7
4	2,2'-DICHLOROBIPHENYL	0.2242	8.1905	223.101	60.5
5	2,3-DICHLOROBIPHENYL	0.0815	8.1905	223.101	28.0
6	2,3'-DICHLOROBIPHENYL	0.0000	8.1905	223.101	Oil
7	2,4-DICHLOROBIPHENYL	0.0815	8.1905	223.101	24.3
8	2,4'-DICHLOROBIPHENYL	0.0815	8.1905	223.101	40.5
9	2,5-DICHLOROBIPHENYL	0.0815	8.1905	223.101	23.0
10	2,6-DICHLOROBIPHENYL	0.1631	8.1905	223.101	35.5
11	3,3'-DICHLOROBIPHENYL	0.2242	8.1905	223.101	29.0
12	3,4-DICHLOROBIPHENYL	0.0815	8.1905	223.101	49.5
13	3,4'-DICHLOROBIPHENYL	0.0815	8.1905	223.101	Oil
14	3,5-DICHLOROBIPHENYL	0.1631	8.1905	223.101	36.0
15	4,4'-DICHLOROBIPHENYL	0.3873	8.1980	223.101	148.5
16	2,2',3-TRICHLOROBIPHENYL	0.0000	8.4524	257.546	28.5
17	2,2',4-TRICHLOROBIPHENYL	0.0000	8.4524	257.546	.
18	2,2',5-TRICHLOROBIPHENYL	0.0000	8.4524	257.546	43.5
19	2,2',6-TRICHLOROBIPHENYL	0.0815	8.4524	257.546	.
20	2,3,3'-TRICHLOROBIPHENYL	0.0000	8.4524	257.546	42.0
21	2,3,4-TRICHLOROBIPHENYL	0.0815	8.4524	257.546	101.5
22	2,3,4'-TRICHLOROBIPHENYL	0.0815	8.4524	257.546	73.1
23	2,3,5-TRICHLOROBIPHENYL	0.0815	8.4524	257.546	41.0
24	2,3,6-TRICHLOROBIPHENYL	0.0815	8.4524	257.546	.
25	2,3',4-TRICHLOROBIPHENYL	0.0000	8.4524	257.546	.
26	2,3',5-TRICHLOROBIPHENYL	0.0000	8.4524	257.546	40.3
27	2,3',6-TRICHLOROBIPHENYL	0.0815	8.4524	257.546	.
28	2,4,4'-TRICHLOROBIPHENYL	0.0815	8.4524	257.546	56.0
29	2,4,5-TRICHLOROBIPHENYL	0.0815	8.4524	257.546	78.5
30	2,4,6-TRICHLOROBIPHENYL	0.1631	8.4524	257.546	62.5
31	2,4',5-TRICHLOROBIPHENYL	0.0815	8.4524	257.546	67.0
32	2,4',6-TRICHLOROBIPHENYL	0.1631	8.4524	257.546	.
33	2',3,4-TRICHLOROBIPHENYL	0.0000	8.4524	257.546	65.5
34	2',3,5-TRICHLOROBIPHENYL	0.0815	8.4524	257.546	58.0
35	3,3',4-TRICHLOROBIPHENYL	0.0000	8.4524	257.546	62.0
36	3,3',5-TRICHLOROBIPHENYL	0.0815	8.4524	257.546	.
37	3,4,4'-TRICHLOROBIPHENYL	0.0815	8.4524	257.546	87.3
38	3,4,5-TRICHLOROBIPHENYL	0.1631	8.4524	257.546	.
39	3,4',5-TRICHLOROBIPHENYL	0.1631	8.4524	257.546	88.0
40	2,2',3,3'-TETRACHLOROBIPHENYL	0.2242	8.7143	291.991	120.9
41	2,2',3,4-TETRACHLOROBIPHENYL	0.0000	8.7143	291.991	.
42	2,2',3,4'-TETRACHLOROBIPHENYL	0.0000	8.7143	291.991	69.0
43	2,2',3,5-TETRACHLOROBIPHENYL	0.0000	8.7143	291.991	.
44	2,2',3,5'-TETRACHLOROBIPHENYL	0.0000	8.7143	291.991	46.8
45	2,2',3,6-TETRACHLOROBIPHENYL	0.0000	8.7143	291.991	.
46	2,2',3,6'-TETRACHLOROBIPHENYL	0.0815	8.7143	291.991	.
47	2,2',4,4'-TETRACHLOROBIPHENYL	0.2242	8.7143	291.991	83.0
48	2,2',4,5-TETRACHLOROBIPHENYL	0.0000	8.7143	291.991	66.0
49	2,2',4,5'-TETRACHLOROBIPHENYL	0.0000	8.7143	291.991	67.8
50	2,2',4,6-TETRACHLOROBIPHENYL	0.0815	8.7143	291.991	.
51	2,2',4,6'-TETRACHLOROBIPHENYL	0.0815	8.7143	291.991	.
52	2,2',5,5'-TETRACHLOROBIPHENYL	0.2242	8.7143	291.991	88.0
53	2,2',5,6'-TETRACHLOROBIPHENYL	0.0815	8.7143	291.991	103.7
54	2,2',6,6'-TETRACHLOROBIPHENYL	0.3873	8.7143	291.991	198.0
55	2,3,3',4-TETRACHLOROBIPHENYL	0.0000	8.7143	291.991	.
56	2,3,3',4'-TETRACHLOROBIPHENYL	0.0000	8.7143	291.991	96.5
57	2,3,3',5-TETRACHLOROBIPHENYL	0.0000	8.7143	291.991	.
58	2,3,3',5'-TETRACHLOROBIPHENYL	0.0815	8.7143	291.991	128.3
59	2,3,3',6-TETRACHLOROBIPHENYL	0.0000	8.7143	291.991	.
60	2,3,4,4'-TETRACHLOROBIPHENYL	0.0815	8.7143	291.991	142.0
61	2,3,4,5-TETRACHLOROBIPHENYL	0.0815	8.7143	291.991	92.3
62	2,3,4,6-TETRACHLOROBIPHENYL	0.0815	8.7143	291.991	.
63	2,3,4',5-TETRACHLOROBIPHENYL	0.0815	8.7143	291.991	104.0
64	2,3,4',6-TETRACHLOROBIPHENYL	0.0815	8.7143	291.991	.
65	2,3,5,6-TETRACHLOROBIPHENYL	0.1631	8.7143	291.991	79.0

Table 3a (*continued*)

NUM[a]	NAME	R	XA	MW	MP[b]
66	2,3',4,4'-TETRACHLOROBIPHENYL	0.0000	8.7143	291.991	127.3
67	2,3',4,5-TETRACHLOROBIPHENYL	0.0000	8.7143	291.991	.
68	2,3',4,5'-TETRACHLOROBIPHENYL	0.0815	8.7143	291.991	.
69	2,3',4,6-TETRACHLOROBIPHENYL	0.0815	8.7143	291.991	.
70	2,3',4',5-TETRACHLOROBIPHENYL	0.0000	8.7143	291.991	104.0
71	2,3',4',6-TETRACHLOROBIPHENYL	0.0815	8.7143	291.991	.
72	2,3',5,5'-TETRACHLOROBIPHENYL	0.0815	8.7143	291.991	106.0
73	2,3',5',6-TETRACHLOROBIPHENYL	0.1631	8.7143	291.991	.
74	2,4,4',5-TETRACHLOROBIPHENYL	0.0815	8.7143	291.991	125.0
75	2,4,4',6-TETRACHLOROBIPHENYL	0.1631	8.7143	291.991	.
76	2',3,4,5-TETRACHLOROBIPHENYL	0.0815	8.7143	291.991	.
77	3,3',4,4'-TETRACHLOROBIPHENYL	0.2242	8.7143	291.991	183.0
78	3,3',4,5-TETRACHLOROBIPHENYL	0.0815	8.7143	291.991	.
79	3,3',4,5'-TETRACHLOROBIPHENYL	0.0815	8.7143	291.991	119.5
80	3,3',5,5'-TETRACHLOROBIPHENYL	0.3873	8.7143	291.991	164.0
81	3,4,4',5-TETRACHLOROBIPHENYL	0.1631	8.7143	291.991	.
82	2,2',3,3',4-PENTACHLOROBIPHENYL	0.0000	8.9762	326.437	119.7
83	2,2',3,3',5-PENTACHLOROBIPHENYL	0.0000	8.9762	326.437	.
84	2,2',3,3',6-PENTACHLOROBIPHENYL	0.0000	8.9762	326.437	.
85	2,2',3,4,4'-PENTACHLOROBIPHENYL	0.0000	8.9762	326.437	.
86	2,2',3,4,5-PENTACHLOROBIPHENYL	0.0000	8.9762	326.437	99.9
87	2,2',3,4,5'-PENTACHLOROBIPHENYL	0.0000	8.9762	326.437	112.3
88	2,2',3,4,6-PENTACHLOROBIPHENYL	0.0000	8.9762	326.437	99.9
89	2,2',3,4,6'-PENTACHLOROBIPHENYL	0.0815	8.9762	326.437	.
90	2,2',3,4',5-PENTACHLOROBIPHENYL	0.0000	8.9762	326.437	.
91	2,2',3,4',6-PENTACHLOROBIPHENYL	0.0000	8.9762	326.437	.
92	2,2',3,5,5'-PENTACHLOROBIPHENYL	0.0000	8.9762	326.437	.
93	2,2',3,5,6-PENTACHLOROBIPHENYL	0.0815	8.9762	326.437	.
94	2,2',3,5,6'-PENTACHLOROBIPHENYL	0.0815	8.9762	326.437	.
95	2,2',3,5',6-PENTACHLOROBIPHENYL	0.0000	8.9762	326.437	99.2
96	2,2',3,6,6'-PENTACHLOROBIPHENYL	0.0815	8.9762	326.437	.
97	2,2',3',4,5-PENTACHLOROBIPHENYL	0.0000	8.9762	326.437	81.5
98	2,2',3',4,6-PENTACHLOROBIPHENYL	0.0815	8.9762	326.437	.
99	2,2',4,4',5-PENTACHLOROBIPHENYL	0.0000	8.9762	326.437	.
100	2,2',4,4',6-PENTACHLOROBIPHENYL	0.0815	8.9762	326.437	.
101	2,2',4,5,5'-PENTACHLOROBIPHENYL	0.0000	8.9762	326.437	77.0
102	2,2',4,5,6'-PENTACHLOROBIPHENYL	0.0815	8.9762	326.437	.
103	2,2',4,5',6-PENTACHLOROBIPHENYL	0.0815	8.9762	326.437	.
104	2,2',4,6,6'-PENTACHLOROBIPHENYL	0.1631	8.9762	326.437	.
105	2,3,3',4,4'-PENTACHLOROBIPHENYL	0.0000	8.9762	326.437	103.0
106	2,3,3',4,5-PENTACHLOROBIPHENYL	0.0000	8.9762	326.437	.
107	2,3,3',4',5-PENTACHLOROBIPHENYL	0.0000	8.9762	326.437	.
108	2,3,3',4,5'-PENTACHLOROBIPHENYL	0.0815	8.9762	326.437	.
109	2,3,3',4,6-PENTACHLOROBIPHENYL	0.0000	8.9762	326.437	.
110	2,3,3',4',6-PENTACHLOROBIPHENYL	0.0000	8.9762	326.437	.
111	2,3,3',5,5'-PENTACHLOROBIPHENYL	0.0815	8.9762	326.437	.
112	2,3,3',5,6-PENTACHLOROBIPHENYL	0.0815	8.9762	326.437	.
113	2,3,3',5',6-PENTACHLOROBIPHENYL	0.0815	8.9762	326.437	.
114	2,3,4,4',5-PENTACHLOROBIPHENYL	0.0815	8.9762	326.437	98.5
115	2,3,4,4',6-PENTACHLOROBIPHENYL	0.0815	8.9762	326.437	.
116	2,3,4,5,6-PENTACHLOROBIPHENYL	0.1631	8.9762	326.437	123.0
117	2,3,4',5,6-PENTACHLOROBIPHENYL	0.1631	8.9762	326.437	.
118	2,3',4,4',5-PENTACHLOROBIPHENYL	0.0000	8.9762	326.437	111.5
119	2,3',4,4',6-PENTACHLOROBIPHENYL	0.0815	8.9762	326.437	.
120	2,3',4,5,5'-PENTACHLOROBIPHENYL	0.0815	8.9762	326.437	76.9
121	2,3',4,5',6-PENTACHLOROBIPHENYL	0.1631	8.9762	326.437	.
122	2',3,3',4,5-PENTACHLOROBIPHENYL	0.0815	8.9762	326.437	.
123	2',3,4,4',5-PENTACHLOROBIPHENYL	0.0815	8.9762	326.437	.
124	2',3,4,5,5'-PENTACHLOROBIPHENYL	0.0815	8.9762	326.437	.
125	2',3,4,5,6'-PENTACHLOROBIPHENYL	0.1631	8.9762	326.437	.
126	3,3',4,4',5-PENTACHLOROBIPHENYL	0.0815	8.9762	326.437	.
127	3,3',4,5,5'-PENTACHLOROBIPHENYL	0.1631	8.9762	326.437	.
128	2,2',3,3',4,4'-HEXACHLOROBIPHENYL	0.2242	9.2381	360.882	150.0
129	2,2',3,3',4,5-HEXACHLOROBIPHENYL	0.0000	9.2381	360.882	84.9
130	2,2',3,3',4,5'-HEXACHLOROBIPHENYL	0.0000	9.2381	360.882	.

(*continued*)

Table 3a *(continued)*

NUM[a]	NAME	R	XA	MW	MP[b]
131	2,2',3,3',4,6-HEXACHLOROBIPHENYL	0.0000	9.2381	360.882	.
132	2,2',3,3',4,6'-HEXACHLOROBIPHENYL	0.0000	9.2381	360.882	.
133	2,2',3,3',5,5'-HEXACHLOROBIPHENYL	0.2242	9.2381	360.882	128.5
134	2,2',3,3',5,6-HEXACHLOROBIPHENYL	0.0815	9.2381	360.882	99.9
135	2,2',3,3',5,6'-HEXACHLOROBIPHENYL	0.0000	9.2381	360.882	.
136	2,2',3,3',6,6'-HEXACHLOROBIPHENYL	0.2242	9.2381	360.882	114.3
137	2,2',3,4,4',5-HEXACHLOROBIPHENYL	0.0000	9.2381	360.882	77.5
138	2,2',3,4,4',5'-HEXACHLOROBIPHENYL	0.0000	9.2381	360.882	81.0
139	2,2',3,4,4',6-HEXACHLOROBIPHENYL	0.0000	9.2381	360.882	.
140	2,2',3,4,4',6'-HEXACHLOROBIPHENYL	0.0815	9.2381	360.882	70.2
141	2,2',3,4,5,5'-HEXACHLOROBIPHENYL	0.0000	9.2381	360.882	.
142	2,2',3,4,5,6-HEXACHLOROBIPHENYL	0.0815	9.2381	360.882	135.5
143	2,2',3,4,5,6'-HEXACHLOROBIPHENYL	0.0815	9.2381	360.882	.
144	2,2',3,4,5',6-HEXACHLOROBIPHENYL	0.0000	9.2381	360.882	.
145	2,2',3,4,6,6'-HEXACHLOROBIPHENYL	0.0815	9.2381	360.882	.
146	2,2',3,4',5,5'-HEXACHLOROBIPHENYL	0.0000	9.2381	360.882	.
147	2,2',3,4',5,6-HEXACHLOROBIPHENYL	0.0815	9.2381	360.882	.
148	2,2',3,4',5,6'-HEXACHLOROBIPHENYL	0.0815	9.2381	360.882	.
149	2,2',3,4',5',6-HEXACHLOROBIPHENYL	0.0000	9.2381	360.882	Oil
150	2,2',3,4',6,6'-HEXACHLOROBIPHENYL	0.0815	9.2381	360.882	.
151	2,2',3,5,5',6-HEXACHLOROBIPHENYL	0.0815	9.2381	360.882	100.5
152	2,2',3,5,6,6'-HEXACHLOROBIPHENYL	0.1631	9.2381	360.882	.
153	2,2',4,4',5,5'-HEXACHLOROBIPHENYL	0.2242	9.2381	360.882	103.5
154	2,2',4,4',5,6'-HEXACHLOROBIPHENYL	0.0815	9.2381	360.882	Oil
155	2,2',4,4',6,6'-HEXACHLOROBIPHENYL	0.3873	9.2381	360.882	112.5
156	2,3,3',4,4',5-HEXACHLOROBIPHENYL	0.0000	9.2381	360.882	.
157	2,3,3',4,4',5'-HEXACHLOROBIPHENYL	0.0815	9.2381	360.882	.
158	2,3,3',4,4',6-HEXACHLOROBIPHENYL	0.0000	9.2381	360.882	.
159	2,3,3',4,5,5'-HEXACHLOROBIPHENYL	0.0815	9.2381	360.882	.
160	2,3,3',4,5,6-HEXACHLOROBIPHENYL	0.0815	9.2381	360.882	98.5
161	2,3,3',4,5',6-HEXACHLOROBIPHENYL	0.0815	9.2381	360.882	.
162	2,3,3',4',5,5'-HEXACHLOROBIPHENYL	0.0815	9.2381	360.882	.
163	2,3,3',4',5,6-HEXACHLOROBIPHENYL	0.0815	9.2381	360.882	88.1
164	2,3,3',4',5',6-HEXACHLOROBIPHENYL	0.0815	9.2381	360.882	.
165	2,3,3',5,5',6-HEXACHLOROBIPHENYL	0.1631	9.2381	360.882	.
166	2,3,4,4',5,6-HEXACHLOROBIPHENYL	0.1631	9.2381	360.882	162.5
167	2,3',4,4',5,5'-HEXACHLOROBIPHENYL	0.0815	9.2381	360.882	.
168	2,3',4,4',5',6-HEXACHLOROBIPHENYL	0.1631	9.2381	360.882	110.5
169	3,3',4,4',5,5'-HEXACHLOROBIPHENYL	0.3873	9.2381	360.882	201.5
170	2,2',3,3',4,4',5-HEPTACHLOROBIPHENYL	0.0000	9.5000	395.327	135.0
171	2,2',3,3',4,4',6-HEPTACHLOROBIPHENYL	0.0000	9.5000	395.327	122.3
172	2,2',3,3',4,5,5'-HEPTACHLOROBIPHENYL	0.0000	9.5000	395.327	.
173	2,2',3,3',4,5,6-HEPTACHLOROBIPHENYL	0.0815	9.5000	395.327	.
174	2,2',3,3',4,5,6'-HEPTACHLOROBIPHENYL	0.0000	9.5000	395.327	130.6
175	2,2',3,3',4,5',6-HEPTACHLOROBIPHENYL	0.0000	9.5000	395.327	.
176	2,2',3,3',4,6,6'-HEPTACHLOROBIPHENYL	0.0000	9.5000	395.327	.
177	2,2',3,3',4',5,6-HEPTACHLOROBIPHENYL	0.0815	9.5000	395.327	.
178	2,2',3,3',5,5',6-HEPTACHLOROBIPHENYL	0.0815	9.5000	395.327	.
179	2,2',3,3',5,6,6'-HEPTACHLOROBIPHENYL	0.0815	9.5000	395.327	.
180	2,2',3,4,4',5,5'-HEPTACHLOROBIPHENYL	0.0000	9.5000	395.327	114.5
181	2,2',3,4,4',5,6-HEPTACHLOROBIPHENYL	0.0815	9.5000	395.327	.
182	2,2',3,4,4',5,6'-HEPTACHLOROBIPHENYL	0.0815	9.5000	395.327	152.5
183	2,2',3,4,4',5',6-HEPTACHLOROBIPHENYL	0.0000	9.5000	395.327	.
184	2,2',3,4,4',6,6'-HEPTACHLOROBIPHENYL	0.0815	9.5000	395.327	.
185	2,2',3,4,5,5',6-HEPTACHLOROBIPHENYL	0.0815	9.5000	395.327	148.5
186	2,2',3,4,5,6,6'-HEPTACHLOROBIPHENYL	0.1631	9.5000	395.327	.
187	2,2',3,4',5,5',6-HEPTACHLOROBIPHENYL	0.0815	9.5000	395.327	.
188	2,2',3,4',5,6,6'-HEPTACHLOROBIPHENYL	0.1631	9.5000	395.327	.
189	2,3,3',4,4',5,5'-HEPTACHLOROBIPHENYL	0.0815	9.5000	395.327	178.0
190	2,3,3',4,4',5,6-HEPTACHLOROBIPHENYL	0.0815	9.5000	395.327	117.0
191	2,3,3',4,4',5',6-HEPTACHLOROBIPHENYL	0.0815	9.5000	395.327	.
192	2,3,3',4,5,5',6-HEPTACHLOROBIPHENYL	0.1631	9.5000	395.327	.
193	2,3,3',4',5,5',6-HEPTACHLOROBIPHENYL	0.1631	9.5000	395.327	.
194	2,2',3,3',4,4',5,5'-OCTACHLOROBIPHENYL	0.2242	9.7619	429.772	159.0
195	2,2',3,3',4,4',5,6-OCTACHLOROBIPHENYL	0.0815	9.7619	429.772	.

Table 3a (*continued*)

NUM[a]	NAME	R	XA	MW	MP[b]
196	2,2',3,3',4,4',5',6-OCTACHLOROBIPHENYL	0.0000	9.7619	429.772	.
197	2,2',3,3',4,4',6,6'-OCTACHLOROBIPHENYL	0.2242	9.7619	429.772	132.0
198	2,2',3,3',4,5,5',6-OCTACHLOROBIPHENYL	0.0815	9.7619	429.772	.
199	2,2',3,3',4,5,6,6'-OCTACHLOROBIPHENYL	0.0815	9.7619	429.772	.
200	2,2',3,3',4,5',6,6'-OCTACHLOROBIPHENYL	0.0815	9.7619	429.772	.
201	2,2',3,3',4',5,5',6-OCTACHLOROBIPHENYL	0.0815	9.7619	429.772	.
202	2,2',3,3',5,5',6,6'-OCTACHLOROBIPHENYL	0.3873	9.7619	429.772	161.0
203	2,2',3,4,4',5,5',6-OCTACHLOROBIPHENYL	0.0815	9.7619	429.772	.
204	2,2',3,4,4',5,6,6'-OCTACHLOROBIPHENYL	0.1631	9.7619	429.772	.
205	2,3,3',4,4',5,5',6-OCTACHLOROBIPHENYL	0.1631	9.7619	429.772	.
206	2,2',3,3',4,4',5,5',6-NONACHLOROBIPHENYL	0.0815	10.0238	464.217	206.0
207	2,2',3,3',4,4',5,6,6'-NONACHLOROBIPHENYL	0.0815	10.0238	464.217	.
208	2,2',3,3',4,5,5',6,6'-NONACHLOROBIPHENYL	0.1631	10.0238	464.217	182.7
209	2,2',3,3',4,4',5,5',6,6'-DECACHLOROBIPHENYL	0.3873	10.2857	498.662	310.0

a Ballschmitter number.
b Melting points taken from Ref. 78, 90, 91, or from the general literature.
c ~LX = ~(log X). Solubilities determined between 20 and 25 °C.
d A '@' indicates the compound was used in the solubility prediction for this column.
Oils are treated as liquids.

representative example. In the case of a planar 2-chlorobiphenyl molecule, none of the carbon and hydrogen atoms are truly equivalent, and $R = 22 \log 1/(22 \log 22) = 0$. Rotation of the two phenyl rings by a full 90 degrees to the so-called "perpendicular structure" increases the topological symmetry considerably:

$$R = \frac{4(2 \log 2) + 14 \log 14}{22 \log 22} = 0.0815 \tag{4}$$

because the $(2', 6')$ and $(3', 5')$ carbon and hydrogen atom ordered pairs become equivalent, ie, $C_{2'} = C_{6'}$, $H_{2'} = H_{6'}$, etc. Tabulated R values listed in Table 3 were computed assuming perpendicular benzene rings. It should be noted though, that both sets of R values were tried in the initial regression analysis. The planar geometry proved unsuccessful and was quickly abandoned, as this computation resulted in smaller or zero R values for a number of fairly high melting temperature PCBs such as 2,2′,3,3′,4,4′,5,5′,6-nonachlorobiphenyl (MP = 206°C), 2,2′,3,4,4′,5,6′-heptachlorobiphenyl (MP = 152.5°C) and 2,2′3,4,5,5′6-heptachlorobiphenyl (MP = 148.5°C).

We also consider, as part of this QSPR study, the zero-order molecular connectivity index (χVO), which is calculated from a hydrogen suppressed molecular graph:

$$\chi VO = \sum_{i=1}^{k} (\delta_i^v)^{-1/2} \tag{5}$$

and $\delta_i^V = (Z^V - h)/(Z - Z^v - 1)$ where h is the count of hydrogen atoms, Z^V is the count of valence electrons and Z is the count of total electrons[27,28]. We felt the calculated progression in size of the halogen atoms, especially when bonded to an aromatic carbon atom, was more regular than that described by Eq. 5 and developed

Table 3b Polychlorinated biphenyls--Summary

NUM^a	n obs	-LX^c avg	SD	-LX^d (eq 58)	Ref.
0	11	6.09	0.039	6.54@	30,37,43,60,64,72,73,74,75,76,77
1	5	6.29	0.065	6.68@	30,33,69,78,79
2	5	6.72	0.292	6.68@	33,69,77,78,79
3	6	6.96	0.087	6.84@	33,69,77,78,79,80
4	5	7.13	0.214	7.67@	33,69,78,79,81
5	2	7.01		7.38@	78,79
6	2	7.17		7.22@	79,82
7	6	7.11	0.167	7.38@	33,77,78,79,81,82
8	5	7.14	0.200	7.38@	33,69,78,79,83
9	4	7.10	0.233	7.38@	30,69,79,81
10	5	7.11	0.345	7.54@	5,30,78,79,81
11	2	7.87		7.67@	79,81
12	1	8.13		7.38@	79
13	1	8.14		7.38@	79
14	1	8.48		7.54@	79
15	6	8.30	0.142	8.00@	69,77,78,79,81,84
16	2	7.76		7.86@	79,82
17	2	7.99		7.86	79,82
18	5	7.66	0.294	7.86@	69,79,81,82,83
19	2	7.58		8.04	79,82
20	0			7.86	
21	1	7.92		8.04@	79
22	2	7.77		8.04@	79,82
23	0			8.04	
24	2	8.13		8.04	79,82
25	2	8.35		7.86	79,82
26	3	7.88	0.130	7.86@	79,81,82
27	1	8.56		8.04	82
28	5	8.07	0.226	8.04@	5,69,78,79,81
29	4	8.06	0.109	8.04@	30,69,77,79
30	4	7.98	0.339	8.21@	30,79,81,85
31	3	8.08	0.143	8.04@	5,64,79
32	1	7.95		8.21	79
33	3	8.08	0.157	7.88@	78,79,82
34	1	8.04		8.04@	79
35	0			7.88	
36	1	9.20		8.04	79
37	3	8.80	0.450	8.04@	78,79,82
38	0			8.21	
39	0			8.21	
40	5	8.51	0.383	8.95@	78,79,81,82,86
41	1	8.75		8.50	79
42	2	8.56		8.50@	79,82
43	1	7.97		8.50	87
44	5	8.24	0.263	8.50@	77,78,79,82,86
45	2	8.10		8.50	79,86
46	3	8.12	0.074	8.66	79,82,86
47	4	8.51	0.330	8.95@	5,78,79,86
48	3	8.77	0.199	8.50@	79,82,88
49	4	8.59	0.400	8.50@	30,79,82,86
50	1	8.68		8.66	79
51	1	8.39		8.66	79
52	6	8.57	0.343	8.95@	5,78,79,81,83,86
53	3	8.36	0.181	8.66	79,81,82
54	3	8.95	0.929	9.28@	5,79,81
55	0			8.50	
56	1	8.21		8.50	79
57	0			8.50	
58	0			8.66	
59	0			8.50	
60	2	8.37		8.66@	79,86
61	5	8.98	0.150	8.66@	30,69,77,79,81
62	0			8.66	
63	2	8.65		8.66	79,82
64	2	8.50		8.66	79,82
65	1	8.99		8.83@	79

Table 3b (*continued*)

NUM^a	n obs	$-LX^c$ avg	SD	$-LX^d$ (eq 58)	Ref.
66	4	8.42	0.179	8.50@	78,79,82,86
67	1	8.87		8.50	79
68	0			8.66	
69	1	9.01		8.66	79
70	3	8.42	0.196	8.50@	78,79,86
71	1	8.76		8.66	79
72	0			8.66	
73	0			8.83	
74	3	8.48	0.256	8.66@	79,82,86
75	2	8.68		8.83	79,81
76	1	8.45		8.66	79
77	6	10.27	0.193	8.95@	5,33,69,79,81,89
78	0			8.66	
79	0			8.66	
80	2	10.28		9.28@	79,81
81	0			8.83	
82	2	8.67		9.08	82,86
83	2	8.70		9.08	82,86
84	2	8.55		9.08	79,82
85	3	8.97	0.368	9.08	79,82,86
86	3	9.20	0.453	9.08@	69,77,79
87	6	9.33	0.385	9.08@	33,69,78,79,82,86
88	1	9.17		9.08@	69
89	1	8.52		9.25	79
90	1	9.56		9.08	79
91	2	8.79		9.08	79,82
92	1	9.56		9.08	79
93	1	9.14		9.25	79
94	0			9.25	
95	1	8.94		9.08	79
96	0			9.25	
97	3	8.98	0.461	9.08@	79,82,86
98	1	9.14		9.25	79
99	3	9.10	0.522	9.08	79,82,86
100	3	8.83	0.543	9.25	64,79,86
101	10	9.14	0.323	9.08@	30,69,78,79,81,82,83,84,86,89
102	0			9.25	
103	1	9.20		9.25	79
104	1	9.06		9.41	81
105	1	9.26		9.08@	79
106	1	9.42		9.08	79
107	1	9.08		9.08	82
108	0			9.25	
109	0			9.08	
110	3	8.91	0.437	9.08	79,82,86
111	0			9.25	
112	1	9.51		9.25	79
113	1	9.69		9.25	79
114	2	9.21		9.25@	79,82
115	1	9.70		9.25	79
116	5	9.50	0.260	9.41@	5,30,69,79,81
117	1	9.62		9.41	79
118	2	9.10		9.08@	79,82
119	1	9.65		9.25	79
120	0			9.25	
121	1	9.66		9.41	79
122	1	9.15		9.25	82
123	1	9.16		9.25	79
124	1	9.05		9.25	82
125	0			9.41	
126	0			9.25	
127	0			9.41	
128	5	10.01	0.773	10.09@	30,69,79,82,86
129	6	9.81	0.629	9.63@	33,69,79,81,82,86
130	1	9.54		9.63	82

(*continued*)

Table 3b *(continued)*

NUM^a	n obs	-LX^c avg	SD	-LX^d (eq 58)	Ref.
131	2	9.72		9.63	79,82
132	1	9.39		9.63	79
133	0			10.09	
134	4	9.90	0.726	9.80@	33,69,79,82
135	1	9.56		9.63	79
136	5	9.54	0.547	10.09@	30,78,82,86,89
137	3	9.58	0.607	9.63@	79,82,86
138	3	9.55	0.520	9.63@	79,82,86
139	0			9.63	
140	1	9.98		9.80	79
141	3	9.56	0.544	9.63	79,82,86
142	0			9.80	
143	1	9.87		9.80	79
144	2	9.48		9.63	79,86
145	0			9.80	
146	3	9.63	0.613	9.63	79,82,86
147	0			9.80	
148	1	8.73		9.80	79
149	3	9.36	0.274	9.63@	79,82,86
150	0			9.80	
151	3	9.34	0.294	9.80@	79,82,86
152	0			9.96	
153	9	9.95	0.500	10.09@	5,69,79,81,82,83,84,85,86
154	1	10.01		9.80@	79
155	5	10.22	0.333	10.41@	5,30,69,79,81
156	2	9.81		9.63	79,82
157	0			9.80	
158	2	9.81		9.63	79,82
159	0			9.80	
160	0			9.80	
161	0			9.80	
162	0			9.80	
163	3	9.80	0.367	9.80@	33,77,79
164	1	10.01		9.80	79
165	0			9.96	
166	0			9.96	
167	1	9.95		9.80	79
168	0			9.96	
169	1	10.60		10.41@	79
170	2	10.05		10.15@	79,86
171	3	10.07	0.384	10.15@	30,79,82
172	3	10.02	0.719	10.15	79,82,86
173	1	9.72		10.32	82
174	3	9.83	0.435	10.15@	79,82,86
175	3	9.80	0.546	10.15	79,82,86
176	2	9.73		10.15	79,82
177	3	9.79	0.333	10.32	79,82,86
178	3	9.76	0.501	10.32	79,82,86
179	2	9.61		10.32	79,86
180	3	10.03	0.709	10.15@	79,82,86
181	1	10.71		10.32	79
182	1	10.42		10.32@	79
183	2	10.12		10.15	79,82
184	0			10.32	
185	5	10.20	0.579	10.32@	69,78,79,82,86
186	0			10.48	
187	2	10.01		10.32	79,86
188	1	10.23		10.48	79
189	1	10.46		10.32@	79
190	1	10.64		10.32@	79
191	1	10.84		10.32	79
192	1	10.84		10.48	79
193	1	10.84		10.48	79
194	3	10.60	0.869	11.10@	5,69,79
195	2	10.44		10.81	79,86

Table 3b (*continued*)

NUM[a]	n obs	-LX[c] avg	SD	-LX[d] (eq 58)	Ref.
196	2	10.54		10.65	79,86
197	1	10.84		11.10@	79
198	1	11.16		10.81	79
199	1	10.84		10.81	79
200	1	10.94		10.81	79
201	2	10.46		10.81	79,86
202	4	11.00	0.199	11.43@	69,78,79,89
203	1	11.24		10.81	79
204	1	11.22		10.98	79
205	1	11.44		10.98	79
206	4	11.70	0.311	11.28@	5,69,79,89
207	1	11.82		11.28	79
208	2	11.90		11.44@	30,79
209	5	12.62	0.598	12.34@	5,30,69,79,89

a Ballschmitter number.
b Melting points taken from Ref. 78, 90, 91, or from the general literature.
c -LX = -(log X). Solubilities determined between 20 and 25 °C.
d A '@' indicates the compound was used in the solubility prediction for this column.
Oils are treated as liquids.

another index:

$$\chi A = \sum_{i=1}^{k} (PQ_i/\delta_i^V) \tag{6}$$

where PQ_i is the principal quantum number of atom i and δ_i is the number of valence electrons belonging to atom i minus the number of hydrogen atoms bonded to atom i[29]. For 2-chlorobiphenyl, the summation:

$$\chi A = \frac{(9)(2)}{3} + \frac{(3)(2)}{4} + \frac{(1)(3)}{7} = 7.9286 \tag{7}$$

would extend over the nine carbon atoms ($PQ_C = 2$) with $\delta^V = 3$ counted valence electrons, three carbon atoms with $\delta^V = 4$, and the single chlorine atom ($PQ_{Cl} = 3$) having a valence of seven, $\delta^V = 7$.

Following the computation and tabulation of the molecular and thermodynamic input data (listed in Tables 2 to 5) multiple regression analysis was performed using the SAS® package. In this study, the logarithm of aqueous solubility (log X) was examined in relation to various calculated molecular size descriptors, molecular weight (MW), XVO, XA, $1/XA$, and ln XA. Additional terms included the thermodynamic (MP − 25) and symmetry (R) correction terms along with various geometric combinations of the symmetry and molecular size descriptors. Regression equations were limited to contain no more than three terms.

Table 4 Polybrominated biphenyls—Summary

Molecular Formula	NAME	R	XA	MW	MP[a]	n obs	-LX[b] avg	-LX (eq 58)	-LX (eq 59)	Ref.
C12H9Br	4-BROMOBIPHENYL	0.1631	8.0714	233.11	91.2	1	7.29	7.23	7.22	85
C12H8Br2	4,4'-DIBROMOBIPHENYL	0.3873	8.4762	312.00	163.0	1	9.48	8.72	8.74	92
C12H7Br3	2,4,6-TRIBROMOBIPHENYL	0.1631	8.8810	390.90	65.5	1	9.11	9.20	9.20	92
C12H6Br4	2,2',5,5'-TETRABROMOBIPHENYL	0.2242	9.2857	469.80	143.5	1	9.80	10.18	10.19	92
C12H5Br5	2,2',4,5,5'-PENTABROMOBIPHENYL	0.0000	9.6905	548.69	157.0	1	10.83	10.52	10.49	85
C12H4Br6	2,2',4,4',6,6'-HEXABROMOBIPHENYL	0.3873	10.0952	627.59	175.9	1	10.74	12.02	12.06	92

[a] Melting point value for 4-Bromobiphenyl taken from Ref. 71, for 4,4' & 2,4,6 & 2,2'5,5' from Ref. 93, for 2,2',4,5,5' from Ref. 50, for 2,2',4,4',6,6' from Ref. 92.

[b] -LX = -(log X). Solubilities determined at 25 °C.

Table 5 Halogenated naphthalenes—Summary

Molecular Formula	Name	R	XA	MW	MP[a]	n obs	-LX[b] avg	SD	-LX[c] (eq 76)	Ref.
C10H8	Naphthalene	0.4530	6.3333	128.13	80.6	6	5.35	0.016	5.24@	43,45,73,74,77,94
C10H7Cl	1-Chloronaphthalene	0.0000	6.5952	162.62	-3.0	1	6.49		6.76@	95
C10H7Cl	2-Chloronaphthalene	0.0000	6.5952	162.62	59.0	1	6.99		6.76@	95
C10H6Cl2	1,2-Dichloronaphthalene	0.0000	6.8571	197.06	35.5	1	7.90		7.73@	95
C10H6Cl2	1,4-Dichloronaphthalene	0.2398	6.8571	197.06	70.0	1	7.54		7.46@	95
C10H6Cl2	1,5-Dichloronaphthalene	0.2398	6.8571	197.06	107.0	1	7.44		7.46@	95
C10H6Cl2	1,8-Dichloronaphthalene	0.2132	6.8571	197.06	88.8	1	7.26		7.49@	95
C10H6Cl2	2,3-Dichloronaphthalene	0.2398	6.8571	197.06	120.0	1	7.10		7.46@	95
C10H6Cl2	2,8-Dichloronaphthalene	0.2132	6.8571	197.06	115.0	1	7.66		7.73@	95
C10H5Cl3	1,3,7-Trichloronaphthalene	0.0000	7.1190	231.51	112.8	1	8.30		8.63@	95
C10H5Cl3	2,3,6-Trichloronaphthalene	0.0000	7.1190	231.51	90.5	1	8.88		8.63@	95
C10H4Cl4	1,2,3,4-Tetrachloronaphthalene	0.2398	7.3810	265.95	197.0	2	9.52		9.18@	64,95
C10H4Cl4	1,2,3,5-Tetrachloronaphthalene	0.0000	7.3810	265.95	141.0	1	9.60		9.47@	95
C10H4Cl4	1,3,5,7-Tetrachloronaphthalene	0.2398	7.3810	265.95	179.5	1	9.56		9.18@	95
C10H4Cl4	1,3,5,8-Tetrachloronaphthalene	0.0000	7.3810	265.95	131.0	1	9.25		9.47@	95
C10H4Cl4	1,4,6,7-Tetrachloronaphthalene	0.2398	7.3810	265.95	139.0	1	9.26		9.18@	95
C10Cl8	Octachloronaphthalene	0.4530	8.4286	403.73	200.3	1	11.44		11.66@	95
C10H7Br	1-Bromonaphthalene	0.0000	6.7381	221.10	56.0	1	6.09		7.30	75

[a] Values from Ref. 96 except for Bromonaphthalene, which was from 71.

[b] -LX = -(log X). Solubilities determined between 20 and 25 °C.

[c] A '@' indicates value used in the solubility prediction for this column.

RESULTS AND DISCUSSION

Correlations (Eqs. 17–78) exhibiting significant statistical merit are presented in Tables 6 to 9. The criteria employed in the decision to report a given correlation were: first, the equations reported were required to exhibit favorable standard deviation(s) and correlation coefficients and second, that the 95 percent confidence interval of the individual regression coefficients could not be inordinately large with respect to the coefficients themselves. The simple linear regressions involving only the single R or $R * XA$ term are presented for completeness as $r^2 \leq 0.40$ shows that neither term contributes appreciably to the overall aqueous solubility. In many instances, regression statistics could be favorably affected by augmentation of the data set to include additional compounds. However, in the interests of evaluating the effectiveness of the molecular and thermodynamic descriptors as predictive tools, we elected to determine regression coefficients based on only 42 HBs, 79 PCBs (denoted by the @ symbol in Tables 2 to 5) and 17 PCNs respectively. These linear and multivariate correlations were, in turn, utilized to predict mole fraction solubilities of the remaining compounds. Out of curiosity, we did regress smaller (27 HBs) and larger (166 PCBs) data sets and the derived correlations were nearly identical to ones presented in Tables 7 and 8 (see Eqs. 36 vs 37 and Eqs. 59 vs. 60).

Comparison between experimental and calculated values are listed in the next to last columns of Tables 2 to 5 for select equations. Careful examination of these four tables reveals that the derived correlations provide very reasonable estimates for the majority of compounds considered, with predictive values falling within one or two standard deviations of the computed averages. Uncertainties associated with the smaller mole fraction solubilities are believed to be on the order of $\Delta \log X = \pm 0.477$ (or less) based on inter-laboratory comparisons of duplicate values for identical compounds. As an example, the experimental values of Miller *et al*[30] for several chlorobenzenes differ from published solubility data of Yalkowsky and co-workers[31]

Table 6 Formula weight—Regression equations

Eqn.	Series	MW	MP-25	CONST	MSE	r^2	F (P, Q)
(17)	Halogenated Benzenes	-0.016 (0.001)		-2.113 (0.295)	0.747	0.791	155 (1,41)
(18)			-0.023 (0.002)	-4.777 (0.126)	0.737	0.797	161 (1,41)
(19)		-0.009 (0.001)	-0.013 (0.002)	-3.132 (0.224)	0.468	0.920	231 (2,40)
(20)	Polyhalogenated Biphenyls	-0.014 (0.001)		-4.628 (0.255)	0.606	0.793	310 (1,81)
(21)			-0.020 (0.002)	-7.457 (0.149)	0.784	0.653	152 (1,81)
(22)		-0.010 (0.001)	-0.009 (0.001)	-5.188 (0.231)	0.503	0.859	243 (2,80)
(23)	Chlorinated Naphthalenes	-0.023 (0.002)		-3.077 (0.386)	0.413	0.927	189 (1,15)
(24)			-0.022 (0.005)	-6.353 (0.470)	0.984	0.582	20.9 (1,15)
(25)		-0.022 (0.003)	-0.000 (0.003)	-3.105 (0.450)	0.427	0.927	88.4 (2,14)

Table 7 Halogenated benzenes—Regression equations

Eqn.	MP-25 x10^{-2}	R	RXA	XA	LXA	1/XA	XVO	CONST	MSE	r^2	F (P, Q)
(26)	-2.289 (0.180)							-4.78 (0.13)	0.734	0.798	162 (1,41)
(27)		-3.679 (1.091)						-4.60 (0.35)	1.447	0.217	11 (1,41)
(28)			-0.932 (0.183)					-4.38 (0.30)	1.280	0.387	26 (1,41)
(29)				-3.497 (0.127)				11.16 (0.61)	0.370	0.949	761 (1,41)
(30)					-17.229 (0.720)			21.33 (1.12)	0.423	0.933	573 (1,41)
(31)						83.056 (4.134)		-23.07 (0.88)	0.497	0.908	404 (1,41)
(32)							-0.728 (0.032)	-0.62 (0.22)	0.442	0.927	522 (1,41)
(33)	-0.796 (0.089)			-2.602 (0.124)				7.15 (0.57)	0.216	0.983	1156 (2,40)
(34)		-1.216 (0.231)		-3.310 (0.105)				10.58 (0.48)	0.288	0.970	643 (2,40)
(35)			-0.261 (0.046)	-3.182 (0.111)				9.98 (0.51)	0.280	0.971	680 (2,40)
(36)	-0.976 (0.089)				-12.072 (0.514)			13.53 (0.78)	0.182	0.985	768 (2,24)
(37)	-0.931 (0.075)				-12.228 (0.520)			13.84 (0.79)	0.194	0.986	1441 (2,40)
(38)		-1.500 (0.243)			-16.203 (0.548)			20.10 (0.84)	0.307	0.966	546 (2,40)
(39)			-0.323 (0.047)		-15.423 (0.557)			18.91 (0.84)	0.289	0.970	637 (2,40)
(40)	-1.066 (0.071)					56.286 (2.405)		-17.07 (0.53)	0.195	0.986	1427 (2,40)
(41)		-1.788 (0.274)				77.766 (3.025)		-21.51 (0.66)	0.350	0.955	427 (2,40)
(42)			-0.388 (0.051)			73.323 (2.967)		-20.54 (0.66)	0.322	0.962	510 (2,40)
(43)	-0.898 (0.109)						-0.519 (0.032)	-1.74 (0.19)	0.273	0.973	719 (2,40)

Table 8 Polychlorinatedbiphenyls—Regression equations

Eqn.	MP-25 $\times 10^{-2}$	R	RXA	XA	LXA	1/XA	TSA (nonplanar)^a	CONST	MSE	r^2	F (P, Q)
(44)	-1.882 (0.176)							-7.60 (0.16)	0.837	0.593	114 (1,78)
(45)		-2.160 (1.218)						-8.69 (0.20)	1.286	0.039	3.1 (1,78)
(46)			-0.333 (0.132)					-8.60 (0.19)	1.261	0.075	6.3 (1,78)
(47)				-2.230 (0.087)				10.78 (0.77)	0.425	0.895	664 (1,78)
(48)					-19.820 (0.771)			34.21 (1.68)	0.426	0.894	660 (1,78)
(49)						175.1 (6.911)		-28.82 (0.79)	0.432	0.892	641 (1,78)
(50)							-0.038 (0.001)	1.14 (0.38)	0.411	0.902	716 (1,78)
(51)	-0.533 (0.110)			-1.871 (0.106)				7.98 (0.89)	0.374	0.920	440 (2,77)
(52)		-1.731 (0.355)		-2.215 (0.076)				10.84 (0.68)	0.374	0.920	441 (2,77)
(53)			-0.193 (0.040)	-2.184 (0.077)				10.56 (0.68)	0.374	0.920	440 (2,77)
(54)	-0.552 (0.108)				-16.554 (0.925)			27.50 (1.96)	0.371	0.921	450 (2,77)
(55)		-1.862 (0.347)			-19.714 (0.663)			34.17 (1.44)	0.367	0.923	460 (2,77)
(56)			-0.207 (0.039)		-19.418 (0.667)			33.55 (1.45)	0.366	0.923	461 (2,77)
(57)	-0.578 (0.107)					145.2 (8.092)		-25.01 (0.97)	0.370	0.922	452 (2,77)
(58)		-1.993 (0.343)				174.5 (5.814)		-28.52 (0.66)	0.363	0.924	469 (2,77)
(59)			-0.240 (0.033)			170.7 (4.589)		-28.07 (0.51)	0.364	0.899	726 (2,164)
(60)			-0.221 (0.038)			171.6 (5.846)		-28.20 (0.67)	0.363	0.924	469 (2,77)
(61)	-0.537 (0.104)						-0.0320 (0.0017)	-0.09 (0.41)	0.356	0.927	490 (2,77)

a values taken from Ref. 50.

Table 9 Halogenated naphthalenes—Regression equations

Eqn.	MP-25 x10^{-2}	R	RXA	XA	LXA	1/XA	XVO	CONST	MSE	r^2	F (P, Q)
(62)	-2.164							-6.35	0.984	0.582	21
	(0.473)							(0.47)			(1,15)
(63)		-0.588						-8.12	1.520	0.004	0.1
		(2.357)						(0.51)			(1,150
(64)			-0.227					-7.96	1.498	0.034	0.5
			(0.315)					(0.50)			(1,15)
(65)				-2.993				12.96	0.413	0.927	189
				(0.218)				(1.54)			(1,15)
(66)					-22.054			34.89	0.358	0.945	256
					(1.378)			(2.69)			(1,15)
(67)						160.82		-31.04	0.313	0.958	340
						(8.723)		(1.24)			(1,15)
(68)							-0.742	-1.83	0.413	0.927	189
							(0.054)	(0.48)			(1,15)
(69)	-0.044			-2.955				12.73	0.427	0.927	88
	(0.033)			(0.365)				(2.36)			(2,14)
(70)		1.668		-3.132				13.69	0.324	0.958	159
		(0.518)		(0.176)				(1.23)			(2,14)
(71)			0.245	-3.219				14.29	0.314	0.960	169
			(0.071)	(0.178)				(1.24)			(2,14)
(72)	0.044				-22.334			35.40	0.371	0.945	120
	(0.291)				(2,331)			(4.36)			(2,14)
(73)		1.408			-22.812			36.16	0.284	0.967	207
		(0.453)			(1.125)			(2.19)			(2,14)
(74)			0.205		-23.326			37.15	0.278	0.969	218
			(0.062)		(1.137)			(2.20)			(2,14)
(75)	0.098					165.33		-31.76	0.322	0.958	160
	(0.254)					(14.740)		(2.27)			(2,14)
(76)		1.139				164.69		-31.76	0.260	0.973	250
		(0.411)				(7.388)		(1.06)			(2,14)
(77)			0.164			167.56		-32.17	0.256	0.974	258
			(0.057)			(7.50)		(1.09)			(2,14)
(78)	-0.044						-0.732	-1.87	0.427	0.927	88
	(0.332)						(0.090)	(0.59)			(2,14)

by as much as a factor of 3 or 0.477, when expressed as log X. Compound purity, equilibration time, and analysis method differ amongst the various research groups and there is no compelling reason to presume that any reported value is necessarily more reliable than another. Longer equilibration times followed by repetitive measurements would normally ensure that equilibrium was achieved. Even this standard practice may not be without question, in light of a recent study by Kim and Saleh[32], which suggests that tetrachlorobenzenes can undergo chlorine atom exchange reactions when dissolved in aqueous solutions. This latter claim is stated for informational purposes so that other researchers will be aware of this possibility. Interestingly, none of the research groups which measured the solubilities listed in Tables 2 to 5 reported the appearance of additional chlorobenzene, PCB, etc. isomers in their published articles. One would naturally assume that if the exchange reaction were to occur during the normal equilibration time, researchers would be able to observe several compounds in their chromatographic/spectrophotometric analysis, and that such unusual behavior would be noted at the time the solubility data was originally published.

Inspection of Tables 7 to 9 further reveals that the better two parameter correlations either combine the melting temperature contribution with a molecular size descriptor:

$$\text{Log } X = 13.84 - 12.228 \ln XA - 0.00931\,(\text{MP} - 25) \qquad \text{(Eq. 37)}$$

$$\text{MSE} = 0.194 \quad r^2 = 0.986 \quad F(2, 40) = 1441$$

$$\text{Log } X = 27.50 - 16.554 \ln XA - 0.00552\,(\text{MP} - 25) \qquad \text{(Eq. 54)}$$

$$\text{MSE} = 0.370 \quad r^2 = 0.921 \quad F(2, 77) = 451$$

$$\text{Log } X = -31.76 + 165.33\,(1/XA) + 0.00098\,(\text{MP} - 25) \qquad \text{(Eq. 74)}$$

$$\text{MSE} = 0.322 \quad r^2 = 0.958 \quad F(2, 14) = 160$$

or contain both molecular redundancy and molecular size terms:

$$\text{Log } X = -28.20 + 171.6\,(1/XA) - 0.221\, R * XA \qquad \text{(Eq. 60)}$$

$$\text{MSE} = 0.363 \quad r^2 = 0.924 \quad F(2, 77) = 469$$

$$\text{Log } X = -32.17 + 167.56\,(1/XA) + 0.164\, R * XA \qquad \text{(Eq. 77)}$$

$$\text{MSE} = 0.256 \quad r^2 = 0.974 \quad F(2, 14) = 258$$

Very little predictive accuracy is lost in replacing the (MP − 25) term with an easily calculable $R * XA$ structural parameter. In the case of the PCN compounds, the correlation coefficient increases slightly from $r^2 = 0.958$ (Eq. 75) to $r^2 = 0.974$ (Eq. 77). The data sets do contain a sufficient number of crystalline solutes so that removal of the (MP − 25) term is statistically significant. Seventy-three solid PCBs and sixteen solid PCNs were used in the regression analysis. From a thermodynamic standpoint, the melting temperature term is required to properly describe the solubility of crystalline compounds. Elimination of this term should not be construed as a complete departure from thermodynamics, but rather, an attempt to predict a compound's melting temperature contribution to solubility from structural information, thereby replacing a_2 (MP − 25) in our generalized correlation expression with a linear combination of molecular descriptors. Predictive expressions requiring *a priori* knowledge of the compound's melting temperature are of no use, if the required information is not readily available, as must be apparent by the large number of absent melting temperatures in Table 3. Equations 60 and 77, on the other hand, require only structural information, which can be estimated by assuming either a rigid and planar structure (PCNs) or two perpendicular phenyl rings (PCBs).

Results from the present study confirm that our generalized correlation expression does take the form:

$$\log X = a_0 + a_1\,(\text{Molecular size descriptor})^m + a_2(\text{MP} - 25) + a_3\,(R * \text{Molecular size descriptor}) \qquad (1)$$

(with the principal quantum number modified molecular connectivity index (XA) being another viable molecular size descriptor. The correlations listed in Tables 6 to 9 are specific one and two-parameter expressions derived from our generalized form. As one might surmise from this study, the selection of predictive expression depends, to a large extent, on the predictive accuracy desired and the effort that one is willing to spend.

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