Prediction of Subcooled Vapor Pressures of Nonpolar Organic Compounds Using a One-Parameter QSPR

Mima Staikova,[†] Peter Messih,[‡] Ying D. Lei,[†,‡] Frank Wania,[†,‡] and D. James Donaldson*,[†,‡]

Department of Chemistry, University of Toronto, 80 St. George Street, Toronto, Ontario, Canada M5S 3H6, and Department of Physical and Environmental Sciences, University of Toronto at Scarborough, 1265 Military Trail, Toronto, Ontario, Canada M1C 1A4

A previously derived empirical linear relationship between the average polarizability of chlorinated aromatic and aliphatic compounds, α_m, as calculated using density functional theory methods, and their subcooled liquid vapor pressure, log p_L, is tested here for its capability to predict the 25 °C subcooled vapor pressures of a diverse set of nonpolar organic compounds, including 12 brominated benzenes, 13 aromatic hydrocarbons, 10 chlorinated toluenes, 3 hexachlorocyclohexanes, and *p*,*p*′-DDT. A comparison with experimental data shows generally excellent agreement over a 10-order-of-magnitude range in p_L, with an average error of less than 0.5 log unit. Experimental vapor pressure values were taken from the literature or, in the case of the chlorinated toluenes, were determined using gas chromatographic retention times. Remarkably large differences in the experimental octanol−air partition coefficients for the isomers of the hexachlorocyclohexanes were found to correspond to similarly large differences in the out-of-plane polarizabilities of these substances. This work suggests that a single theoretically derived parameter is sufficient to estimate within 1 order of magnitude the volatility of a wide variety of organic compounds whose primary interactions are dispersive in nature. This includes halogenated and nonhalogenated, aromatic, aliphatic and alicyclic, and planar and nonplanar organic substances.

Introduction

An understanding of the important processes governing the transport, distribution, and fate of chemical compounds in the environment is critical for providing meaningful policy advice. The distribution of a compound among the available environmental phases can be modeled using various physicochemical properties that include, among others, the subcooled vapor pressure, p_L, and the octanol−air partition coefficient, K_{OA}. These parameters both relate to equilibrium partitioning between a compound in the gas phase and that compound dissolved in an (assumed liquid) organic matrix. Because the dissolved compound is considered to be in the liquid phase, the subcooled vapor pressures are used for compounds that are solid at the temperature of interest. Experimentally, environmental phase distributions are determined by measuring concentration ratios in the corresponding bulk phases either in the laboratory or in the field. Generally, the procedures are both time-consuming and expensive, and often the experimental methods cannot accurately distinguish congener species with similar physicochemical properties. A reliable theoretical approach, requiring as input only chemical structure data, is clearly an attractive alternative.

Several statistically based methods have been developed to connect physical properties to molecular structures; these are known as quantitative structure−property relationships (QSPR). For recent reviews on QSPRs, the reader is directed to Katritzky et al.[1] and Livingstone[2] as well as references found therein. Several papers have been published in recent years that are particularly dedicated to predictions of vapor pressure and the octanol−air partition coefficient for diverse classes of organic compounds, using computationally derived molecular descriptors. In one such study on predicting vapor pressures, Liang and Gallagher[3] tested several multilinear regressions and artificial neural network analyses with a range of topological and quantum mechanical descriptors derived solely from computations of molecular structure for a set of 479 compounds. They reported their best result (with $r^2 = 0.96$) to be a seven-descriptor linear regression model. Katritzky et al.[4] published a study on vapor pressures and other physicochemical properties using a data set of 411 compounds in which 800 potential descriptors were screened. A five-descriptor equation for vapor pressure with $r^2 = 0.949$ was obtained. Goll et al.[5] used computational methods to link the molecular structures of 352 hydrocarbons and halo-hydrocarbons to their vapor pressures at 25 °C. The best model with a correlation coefficient of $r^2 = 0.98$ relied on seven descriptors. Beck et al.[6] have developed a QSPR model for vapor pressures of organic compounds based on a neural net interpretation of descriptors derived from semiempirical quantum mechanical calculations. McClelland and Jurs[7] presented a model for the prediction of vapor pressures of diverse organic compounds using semiempirically calculated descriptors, which showed improved performance against a model based on topological descriptors. Chalk et al.[8] have presented a temperature-dependent model for vapor pressure based on a feed-forward neural net and descriptors calculated using AM1 semiempirical MO theory. The model is based on a set of 7681 measurements at various temperatures performed on 2349 molecules. Chen et al.[9] have developed QSPR models for subcooled liquid vapor pressures (p_L) of polybrominated diphenyl ether (PBDE) congeners based on quantum chemical descriptors

---

* Corresponding author. E-mail: jdonalds@chem.utoronto.ca.

[†] Department of Chemistry, University of Toronto.

[‡] Department of Physical and Environmental Sciences, University of Toronto at Scarborough.

10.1021/je049732n CCC: $30.25

by the use of partial least-squares regression. The same research group in the same manner has developed models for the prediction of octanol−air partition coefficients for polychlorinated biphenyls (PCBs),[10] PBDEs,[11] and polychlorinated dibenzo-dioxins and dibenzo-furans.[12]

Our approach has been somewhat different in scope and philosophy. An examination of the types of intermolecular interaction responsible for condensation suggests that for compounds that do not exhibit specific interactions (strong dipolar interactions or hydrogen bonding) with themselves or with 1-octanol, $\log p_L$ and $\log K_{OA}$ should each be related to the molecular polarizability and perhaps also to multipole moments, such as the dipole, quadrupole, and hexapole moments. In a recent paper,[13] we demonstrated that for several classes of nonpolar chlorinated compounds (chlorobenzenes, chlorinated naphthalenes, chlorinated aliphatic compounds, and PCBs) a simple relationship does exist between the measured (experimental) 25 °C values of $\log p_L$ or $\log K_{OA}$ and the average molecular polarizability α_m. Including the dipole and quadrupole moments was found to be unnecessary to give a very good description of the relationship.

In that paper, we give thermochemical reasons for why such a simple relationship is expected for nonpolar compounds that interact nonspecifically. In the case of vapor pressure, the Clausius−Clapeyron equation gives

$$\ln \frac{P_2}{P_1} = \frac{\Delta H_{vap}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \qquad (1)$$

where ΔH_{vap} is assumed to be temperature-independent. Using the standard thermodynamic reference standard state of 1 bar (= 10^5 Pa exactly) for P_1, T_1 becomes the normal boiling point T_b, and the vapor pressure at 298 K may be expressed as

$$\ln P_{298} = \frac{\Delta H^\circ_{vap}}{R}\left(\frac{1}{T_b} - \frac{1}{T_{298}}\right) \qquad (2)$$

At the equilibrium normal boiling point, $\Delta H^\circ_{vap} = T_b \Delta S^\circ_{vap}$. For compounds without specific intermolecular interactions, Trouton's rule states that ΔS°_{vap} should be approximately 85 J K^{-1} mol^{-1}. Substituting for ΔH°_{vap} and ΔS°_{vap} and using common logarithms, we obtain an expression for the vapor pressure in the Antoine form ($\log P(T) = A - B/T$), commonly reported in the literature as

$$\log P_{298} = \frac{\Delta H^\circ_{vap}\Delta S^\circ_{vap}}{2.303 R \Delta H^\circ_{vap}} - \frac{\Delta H^\circ_{vap}}{2.303(R)298} = 4.44 - \frac{\Delta H^\circ_{vap}}{5706} \qquad (3)$$

where P_{298} is expressed in bar and ΔH°_{vap} is in J·mol^{-1}.

In the above equation, ΔH°_{vap} represents the standard enthalpy difference between the liquid and vapor states and is essentially given by the change in standard internal energy ΔU°_{vap} since the $\Delta(pV)$ component of ΔH°_{vap} is expected to be very small. At a fixed temperature (298 K), ΔU°_{vap} reflects the total self-solvation energy of a compound. This is essentially just the sum of the intermolecular interaction energies between the compound and its nearest neighbors. For compounds such as those considered here, the intermolecular interactions are predominantly dispersive and therefore are expected to depend on the molecular polarizability of the compound. This quantity is a measure of a molecule's ability to respond to an electric field and to acquire a transient electric dipole moment. Variations in vapor pressure among a group of nonspecifically interacting compounds may thus be expected to reflect variations in the molecular polarizability. Similar arguments may be made concerning the octanol−air partition coefficient.

Table 1. GC-Derived Vapor Pressures p_{GC} and Subcooled Liquid Vapor Pressures p_L for the Chlorotoluenes

compound	n	p_{GC}/Pa	$\log(p_L/\text{Pa})$
3-monochlorotoluene	3	101.5 ± 3.6	2.53 ± 0.09
4-monochlorotoluene	3	101.2 ± 3.2	2.53 ± 0.09
2,3-dichlorotoluene	3	17.6 ± 0.1	1.73 ± 0.07
2,4-dichlorotoluene	3	22.4 ± 0.4	1.84 ± 0.07
2,5-dichlorotoluene	3	21.8 ± 0.1	1.83 ± 0.07
2,6-dichlorotoluene	3	21.8 ± 0.2	1.83 ± 0.07
3,4-dichlorotoluene	3	17.6 ± 0.1	1.73 ± 0.07
2,3,6-trichlorotoluene	3	4.24 ± 0.01	1.08 ± 0.05
2,4,5-trichlorotoluene	3	4.63 ± 0.09	1.12 ± 0.05
α,2,6-trichlorotoluene	3	3.20 ± 0.01	0.95 ± 0.05

The relationships we derived using this approach are[13]

$$\log p_L = -(0.340 \pm 0.005)\alpha_m + (6.70 \pm 0.10) \qquad (4)$$

$$\log K_{OA} = (0.334 \pm 0.005)\alpha_m + (0.188 \pm 0.11) \qquad (5)$$

These one-parameter QSPR equations fit the vapor pressure ($N = 124$) and K_{OA} data ($N = 82$) with high accuracy: $r^2 = 0.98$ in each case. This result, though very promising, is based on a limited number of compound classes: chlorinated aromatic and aliphatic compounds only. The object of the present work is to test the predictive ability of these equations against consistent, high-quality, experimentally determined p_L data, which had not been used in the original work. We choose several additional classes of compounds whose p_L values have been reported:[14−23] polycyclic aromatic hydrocarbons (PAHs); brominated benzenes; α-, β-, and γ-hexachlorocyclohexanes (HCHs); *p,p′*-DDT; and chlorinated toluenes, whose subcooled vapor pressures have not been previously reported. We have measured these for a set of 12 chlorinated toluenes and report the values here. In addition, we explore the ability of the equations to predict observed differences in $\log K_{OA}$ among isomers of the HCHs.[22] As discussed in ref 22, these differences are currently not described well by QSPR predictions based on linear solvation energy relationships.

Methods

Quantum Chemical Calculations. In ref 13, we present full details concerning the type of calculations performed here. The molecular polarizability of each compound studied here was calculated using density functional theory methods utilizing the Gaussian 98 suite of programs.[25] The calculations were carried out by first optimizing the geometry of all compounds using the smaller 6-31G(d,p) basis set and then using the optimized geometries as starting points to reoptimize with the 6-311G(d,p) basis set at the DFT(B3LYP) level of theory. Diffuse functions were not included in the calculations because their inclusion has been shown to give little improvement of the calculated values but increases the demand for computational resources.[26,27]

The average polarizability used here was calculated as the average of the three geometric components

$$\alpha_m = \frac{\alpha_{xx} + \alpha_{yy} + \alpha_{zz}}{3}$$

with the values determined here reported in Table 1. For some planar compounds, it is also of interest to consider the Cartesian components separately. The α_{zz} component of the polarizability describes the electron density out-of-plane, whereas the α_{xx} and α_{yy} components, which we combine into $\alpha_{xy} = (\alpha_{xx} + \alpha_{yy})/2$, describe the electron density in-plane. In the Gaussian 98 output, the polarizability tensor is given in atomic units a_0^3. To be compatible with the other units used throughout this work, the polarizability is converted to Å^3 (1 Å = 10^{-10} m).

Experimental Determination of p_{L} Values of Several Chlorinated Toluenes. The 25 °C subcooled liquid vapor pressures for 12 chlorinated toluenes were measured using the GC retention time method as described in detail by Bidleman[16] and as improved upon by Hinckley et al.[17] This method allows the relatively rapid determination of the temperature-dependent vapor pressure of a large number of compounds. Small quantities of the substance are sufficient, and high purity is not required. For the determination of the vapor pressure of the chlorinated toluenes, hexachlorobenzene (HCB) was employed as a standard reference compound, and the calibration was based on known vapor-pressure values for the chlorobenzenes.

A Hewlett-Packard 5890 gas chromatograph equipped with flame ionization (FID) and electron capture detectors (ECD) was used to determine the isothermal retention times of the chlorinated toluenes and benzenes relative to that of HCB on a 1-m-long DB-1 column (0.32-mm i.d., 0.25-μm film thickness, J & W Scientific, Folsom, CA) for five to six temperatures in the range of 40 to 110 °C. The injector and detector were kept at 250 °C, the carrier gas had a flow rate of approximately 4 mL/min, and the split ratio was 1:10. GC-derived vapor pressures p_{GC} were calculated using the expression

$$\ln (p_{\mathrm{GC}}/\mathrm{Pa}) = (\Delta_{\mathrm{vap}}H/\Delta_{\mathrm{vap}}H_{\mathrm{ref}}) \ln(p_{\mathrm{Lref}}/\mathrm{Pa}) + C \qquad (6)$$

where p_{Lref} and $\Delta_{\mathrm{vap}}H_{\mathrm{ref}}$ refer to the liquid-phase vapor pressure at 25 °C and the enthalpy of vaporization of HCB. The enthalpies of vaporization are assumed to be constant over the temperature range from 25 °C to the temperatures of the retention time measurements. The enthalpy ratio $\Delta_{\mathrm{vap}}H/\Delta_{\mathrm{vap}}H_{\mathrm{ref}}$ and the constant C were obtained by regressing $\ln(t_{\mathrm{R}}/t_{\mathrm{R_{ref}}})$ at each temperature against $\ln(p_{\mathrm{L_{ref}}}/\mathrm{Pa})$ at that temperature using

$$\ln \frac{t_{\mathrm{R}}}{t_{\mathrm{R_{ref}}}} = \left(1 - \frac{\Delta_{\mathrm{vap}}H}{\Delta_{\mathrm{vap}}H_{\mathrm{ref}}}\right) \ln(p_{\mathrm{L_{ref}}}/\mathrm{Pa}) - C \qquad (7)$$

Equation 6 assumes that the infinite dilution activity coefficients in the DB-1 stationary phase are the same for both the analyte and the standard reference compound HCB. Because this is an approximation, p_{GC} is not necessarily identical to p_{L}, and a calibration with chlorobenzenes was performed. GC-derived vapor pressures, p_{GC}, for 10 chlorinated benzenes were determined and regressed against the subcooled liquid vapor pressure of these substances derived from the literature. This procedure gave a calibration equation with $r^2 = 0.99$:

$$\log(p_{\mathrm{L}}/\mathrm{Pa}) = (1.06 \pm 0.04) \log(p_{\mathrm{GC}}/\mathrm{Pa}) + (0.42 \pm 0.05) \qquad (8)$$

Using eq 8 and the average p_{GC} for the chlorotoluenes from three replicate injections, we calculated the 25 °C log p_{L} of the chlorotoluenes. These are given in Table 1. The uncertainty in p_{GC} is very small because of the high precision of gas chromatographic retention time measurements, so the uncertainty of the p_{L} values is dominated by the standard error of the regression coefficients in eq 8.

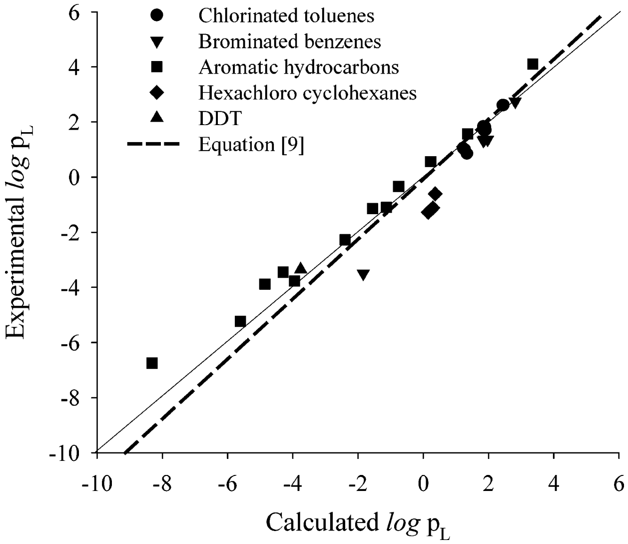

Figure 1. Test of the predictive ability of the one-parameter QSPR given in Staikova et al.[13] The points show the predicted and measured values of the vapor pressure; the solid line shows the 1:1 relationship; and the dashed line is given by eq 9.

Results and Discussion

The average molecular polarizabilities (α_{m}) and the vapor pressure values calculated from α_{m} using eq 4 ($\log p_{\mathrm{L}}^{\mathrm{calcd}}$) and, where available, experimental vapor pressure values ($\log p_{\mathrm{L}}^{\mathrm{exptl}}$) for all of the compounds considered here are presented in Table 2. The comparison of $\log p_{\mathrm{L}}^{\mathrm{calcd}}$ and $\log p_{\mathrm{L}}^{\mathrm{exptl}}$ in Figure 1 suggests that for $\log p_{\mathrm{L}} > -6$ the $\log p_{\mathrm{L}}^{\mathrm{calcd}}$ value obtained with eq 4 is quite close to the experimental values. In fact, using eq 4 for the $N = 32$ compounds with a known experimental vapor pressure gives a standard error (taken to be $\sum \log p_{\mathrm{L}}^{\mathrm{exptl}} - \log p_{\mathrm{L}}^{\mathrm{calcd}})^2/N - 1)^{1/2}$) of 0.7 log unit. The elimination of hexabromobenzene and the HCH compounds from consideration gives a standard error of 0.5 log unit. We had earlier noted[13] similarly good agreement for a set of 124 chlorinated organic compounds spanning the range of $\log p_{\mathrm{L}} = -2.5$ to $+5.7$. There, the best fit between $\log p_{\mathrm{L}}^{\mathrm{calcd}}$ and $\log p_{\mathrm{L}}^{\mathrm{exptl}}$ was

$$\log p_{\mathrm{L}}^{\mathrm{calcd}} = 0.92 \log p_{\mathrm{L}}^{\mathrm{exptl}} + 0.079 \qquad (9)$$

This regression line is included in Figure 1. At first, the strong predictive ability of eq 4 might seem surprising, given its simplicity. However, we have restricted our consideration to organic compounds whose intermolecular interactions are dominated by dispersion forces. As we discuss at some length in Staikova et al.,[13] for such compounds the variability in the enthalpy of vaporization is expected to be dominated by the variability in the molecular polarizability, hence trends in vapor pressure should follow trends in that parameter. This is clearly the case for the compounds considered here, which include various aromatic hydrocarbons, chlorinated aliphatics and aromatics, and brominated benzenes. The subcooled vapor pressures even of organic compounds with reasonable dipole moments are well described using polarizability alone, as illustrated here for the chlorotoluenes and further documented in ref 13.

We stressed previously[13] that the variability in vapor/condensed-phase partitioning between different classes of

Table 2. Average Molecular Polarizability α_m, Experimental and Predicted (Using Equation 4) 25 °C Subcooled Liquid Vapor Pressures, and Discrepancies between Predicted and Experimental Values for Several Chlorinated Toluenes, Brominated Benzenes, Polycyclic Aromatic Hydrocarbons, and Chlorinated Pesticides

compound	α_m	$\log p_L^{exptl}$	$\log p_L^{calcd}$	exptl − calcd	exptl − calcd^2
2-chlorotoluene	2.39		2.49		
3-chlorotoluene	2.48	2.53	2.46	0.07	0.0049
4-chlorotoluene	2.54	2.53	2.44	0.09	0.0081
2,3-dichlorotoluene	4.08	1.73	1.91	−0.18	0.0324
2,4-dichlorotoluene	4.30	1.84	1.84	0	0
2,5-dichlorotoluene	4.29	1.83	1.84	−0.01	0.0001
2,6-dichlorotoluene	4.15	1.83	1.89	−0.06	0.0036
3,4-dichlorotoluene	4.22	1.73	1.86	−0.13	0.0169
3,5-dichlorotoluene	4.34		1.83		
2,3,6-trichlorotoluene	5.98	1.08	1.27	−0.15	0.0225
2,4,5-trichlorotoluene	6.12	1.12	1.22	−0.10	0.0100
A,2,6-trichlorotoluene	5.75	0.95	1.34	−0.39	0.1521
1-bromobenzene	1.40	2.74[19]	2.82	−0.08	0.0064
1,2-dibromobenzene	13.90	1.36[20]	1.97	−0.61	0.3721
1,3-dibromobenzene	14.20	1.36[20]	1.87	−0.51	0.2601
1,4-dibromobenzene	14.30	1.33[19]	1.84	−0.51	0.2601
1,2,3-tribromobenzene	16.57		1.07		
1,2,4-tribromobenzene	16.95		0.94		
1,3,5-tribromobenzene	17.17		0.86		
1,2,3,4-tetrabromobenzene	19.44		0.09		
1,2,3,5-tetrabromobenzene	19.73				
1,2,4,5-tetrabromobenzene	19.81				
pentabromobenzene	22.41				
hexabromobenzene	25.12	−3.5[21]	−1.84	−1.66	2.7556
benzene	9.81	4.1[15]	3.36	0.74	0.5476
naphthalene	15.72	1.57[14]	1.36	0.21	0.045
biphenyl	19.05	0.56[14]	0.22	0.34	0.11
phenanthrene	23.03	−1 × 10[14]	−1.13	0.03	0.001
anthracene	24.30	−1.14[14]	−1.56	0.42	0.18
pyrene	26.77	−2.27[14]	−2.40	−0.14	0.018
chrysene	31.33	−3.77[14]	−3.95	0.18	0.033
1,2-benzanthracene	32.35	−3.45[14]	−4.30	−0.85	0.72
2,3,5-trimethylnaphthalene	21.93	−0.34[14]	−0.76	0.42	0.18
3,4-benzopyrene	36.19	−5.23[14]	−5.60	0.38	0.14
9-phenylanthracene	33.99	−3.88[14]	−4.86	0.97	0.95
9,10-diphenylanthracene	44.18	−6.75[14]	−8.32	1.57	2.5
α-HCH	18.63	−0.61[22]	0.366	−0.98	0.95
β-HCH	19.26	−1.28[22]	0.152	−1.43	2.05
γ-HCH	18.84	−1.12[22]	0.293	−1.41	2.00
p,*p*′-DDT	30.76	−3.35[23]	−3.76	0.41	0.17

compounds is not well predicted by changes in molecular mass. Although this parameter can be reasonably well correlated with $\log p_L$ and $\log K_{OA}$ for a single class of compounds (e.g., the chlorinated benzenes), different linear regressions are obtained when considering several compound classes. This is seen in the present work as well: even though the dibrominated benzenes and chrysene, for example, each have a molecular mass of approximately 230 g mol^{-1}, their vapor pressures differ by more than 5 orders of magnitude. This difference is well predicted using eq 4, however. Hexabromobenzene, with a molecular weight of more than twice that of chrysene, has a similar vapor pressure; again, this is well predicted using the respective polarizabilities in eq 4.

The different octanol−air partitioning exhibited by the various isomers of the HCHs provides a stringent test of the predictive ability of a QSPR method. In particular, the α and γ isomers that are, respectively, the major constituent and primary insecticide in technical HCH show quite different air/condensed phase partitioning behavior from that of the β isomer.[22,24] In Table 2 and Figure 1, it may be seen that the calculated values of $\log p_L$ somewhat overestimate the experimental values but correctly predict the relative ordering. This overestimate may be a limitation of some calculations with a large number of chlorine atoms. The prediction of p_L for hexachlorobenzene, reported in ref 13, also somewhat overestimates the experimental value, though the value for hexachloroethane is well predicted. Table 3 displays the calculated and experimental values of $\log K_{OA}$, adjusted by Xiao et al.[22] Here, the differences among the three isomers are much more apparent: the β isomer has an air−octanol partitioning coefficient that is about an order of magnitude larger than that of the γ isomer, which is larger in turn than that of the α isomer. The use of eq 5 to calculate $\log K_{OA}$ tends to underestimate the experimental value, but as with the use of eq 4 for calculating vapor pressures, it does capture the trend correctly.

Table 3. Average and Out-of-Plane Polarizabilities α_m and α_{zz}, Experimentally Derived Values for $\log K_{OA}$[22] at 25 °C and, $\log K_{OA}$ Predicted Using α_m and Equation 5 or α_{zz} and Equation 10 for Three HCH Isomers

compound	α_m	α_{zz}	log K_{OA}^{exptl}	log K_{OA}^{calcd} (α_m)	log K_{OA}^{calcd} (α_{zz})
α-HCH	18.63	24.77	7.46	6.89	4.12
β-HCH	19.26	12.78	8.74	7.12	6.14
γ-HCH	18.84	19.38	7.84	6.97	5.00

In ref 13, we discussed the use of the in-plane and out-of-plane components of the polarizability to predict $\log K_{OA}$ and $\log p_L$ for the planar chloroaromatic compounds. It was found that whereas the average polarizability proved to be the best descriptor for considering all of the compounds investigated there the out-of-plane component of the polarizability gave marginally better results for the planar compounds. In Table 3, we also show the calculated log K_{OA} values using the out-of-plane polarizability in the expression

$$\log K_{OA} = 1.53\alpha_{zz} - 3.58 \qquad (10)$$

which we determined for the planar chloroaromatics.[13] Although the values of K_{OA} are now seriously underestimated, the trend is very well captured by use of the out-of-plane component alone. It is perhaps worth noting that, of course, all three isomers have identical molecular mass; QSPRs using mass as a descriptor are bound to fail at predicting the trends captured here.

It should be noted that all of the results reported here, both experimental and calculated, are given for 25 °C. Of course, environmental phase partitioning rarely occurs at this convenient temperature, so for maximum utility, the temperature dependence of the predicted values of K_{OA} and p_L is required. Because the temperature dependence of the molecular polarizability is likely to be small, at least over the range of environmental temperatures of interest on earth, a comparison of eq 3 with eq 4 suggests that a predictive equation for p_L would have a somewhat different constant term (arising from the T-dependence of the entropy of vaporization) and a coefficient of α that is scaled by a different temperature: $0.340T/298$. We are exploring this avenue to obtain more general expressions for prediction.

For now, we suggest that eq 4 will provide good 25 °C predictions for other compounds in the classes considered here, in particular, for brominated aromatic and aliphatic compounds and for any chlorinated aromatic compounds not considered thus far. Furthermore, given that the results of ref 13 were as promising for K_{OA} as for p_L, we suggest that octanol−air partition coefficients (often less widely available than vapor pressures) will also be well predicted using eq 5. We have demonstrated this in the case of the HCH isomers. It will be of great interest to explore the utility of such simple predictive equations for other compounds of current interest, such as PBDEs. Work in this direction will commence shortly.

Conclusions

We have measured the subcooled vapor pressures of a set of 10 chlorinated toluenes and report the values here. Using these and literature values of the subcooled vapor pressures of the brominated benzenes and several aromatic hydrocarbons, we have tested the predictive ability of the approach outlined in Staikova et al.[13] Equation 4, presented here, provides very good predictions of the experimental log p_L for a wide range of compounds whose primary interactions are dispersive in nature. The standard error of predictions based on eq 4 amounts to only 0.5 log unit over a range of more than 10 orders of magnitude in vapor pressure. Although this amounts to a factor of 3 in the absolute values, for compounds whose vapor pressures are not known a prediction to better than an order of magnitude is a significant achievement. The discrepancies that appear for log $p_L^{\text{exptl}} < -6$ may be due to errors in the (very difficult) experimental determinations or a deficiency in the basis set used here. Because the discrepancies occur only for larger compounds containing many heavy atoms (especially halogens), a larger basis set might be necessary to provide accurate polarizabilities in these cases.

Literature Cited

(1) Katritzky, A. R.; Petrukhin, R.; Tatham, D.; Basak, S.; Benfenati, E.; Karelson, M.; Maran, U. Interpretation of quantitive structure-property and -activity relationships. *J. Chem. Inf. Comput. Sci.* **2001**, *41*, 679−685.
(2) Livingstone, D. J. The characterization of chemical structures using molecular properties. A survey. *J. Chem. Inf. Comput. Sci.* **2000**, *40*, 195−209.
(3) Liang, C. K.; Gallagher, D. A. QSPR prediction of vapor pressure from solely theoretically derived descriptors. *J. Chem. Inf. Comput. Sci.* **1998**, *38*, 321−324.
(4) Katritzky, A. R.; Wang, Y.; Sild, S.; Tamm, T.; Karelson, M. QSPR studies on vapor pressure, aqueous solubility, and the prediction of water-air partition coefficients. *J. Chem. Inf. Comput. Sci.* **1998**, *38*, 720−725.
(5) Goll, E. S.; Jurs, P. C. Prediction of vapor pressures of hydrocarbons and halohydrocarbons from molecular structure with a computational neural network model. *J. Chem. Inf. Comput. Sci.* **1999**, *39*, 1081−1089.
(6) Beck, B.; Breindl, A.; Clark, T. QM/NN QSPR models with error estimation: Vapor pressure and Log P. *J. Chem. Inf. Comput. Sci.* **2000**, *40*, 1046−1051.
(7) McClelland, H. E.; Jurs, P. C. Quantitative structure-property relationships for the prediction of vapor pressures of organic compounds from molecular structures. *J. Chem. Inf. Comput. Sci.* **2000**, *40*, 967−975.
(8) Chalk, A. J., Beck, B., Clark, T. 2001. A temperature-dependent quantum mechanical/neural net model for vapor pressure. *J. Chem. Inf. Comput. Sci.* **2001**, *41*, 1053−1059.
(9) Chen, J. W.; Yang, P.; Chen, S.; Quan, X.; Yuan, X.; Schramm, K. W.; Kettrup, A. Quantitative structure-property relationships for vapor pressures of polybrominated diphenyl ethers. *SAR QSAR Environ. Res.* **2003**, *14*, 97−111.
(10) Chen, J. W.; Xue, X. Y.; Schramm, K. W.; Quan, X.; Yang, F. L.; Kettrup, A. Quantitative structure-property relationships for octanol-air partition coefficients of polychlorinated biphenyls. *Chemosphere* **2002**, *48*, 535−544.
(11) Chen, J. W.; Harner, T.; Yang, P.; Quan, X.; Chen, S.; Schramm, K. W.; Kettrup, A. Quantitative predictive models for octanol-air partition coefficients of polybrominated diphenyl ethers at different temperatures. *Chemosphere* **2003**, *57*, 577−584.
(12) Chen, J. W.; Harner, T.; Schramm, K. W.; Quan, X.; Xue, X. Y.; Wu, W. Z.; Kettrup, A. Quantitative relationships between molecular structures, environmental temperatures and octanol-air partition coefficients of PCDD/Fs. *Sci. Total Environ.* **2002**, *300*, 155−166.
(13) Staikova, M.; Wania, F.; Donaldson, D. J. Molecular polarizability as a single- parameter predictor of vapor pressures and octanol-air partitioning coefficients of nonpolar compounds: *a priori* approach and results. *Atmos. Environ.* **2004**, *38*, 213−225.
(14) Lei, Y. D.; Chankalal, R.; Chan, A.; Wania, F. Supercooled Liquid Vapor Pressures of the Polycyclic Aromatic Hydrocarbons. *J. Chem. Eng. Data* **2002**, *47*, 801−806.
(15) Mackay, D.; Shiu, W.-Y.; Ma, K.-C. *Physical-Chemical Properties and Environmental Fate Handbook*; Chapman & Hall/CRCnetBase: Boca Raton, FL, 1999 (CD-ROM).
(16) Bidleman, T. F. Estimation of Vapor Pressures for Nonpolar Organic Compounds by Capillary Gas Chromatography. *Anal. Chem.* **1984**, *56*, 2490−2496.
(17) Hinckley, D. A.; Bidleman, T. F.; Foreman, W. T.; Tuschall, J. R. Determination of Vapor Pressures for Nonpolar and Semipolar Organic Compounds from Gas Chromatographic Retention Data. *J. Chem. Eng. Data* **1990**, *35*, 232−237.
(18) Mackay, D.; Bobra, A. M.; Chan, D. W.; Shiu, W. Y. Vapor pressure correlation for low-volatility environmental chemicals. *Environ Sci. Technol.* **1982**, *16*, 645−649.
(19) Stephenson, R. M.; Malanowski, S. *Handbook of the Thermodynamics of Organic Compounds*; Elsevier: New York, 1987.
(20) Sage, G. W.; Michalenko, E. M.; Basu, D. K.; Hill, A.; Aronson, D. Solvents 3. Volume 5 of *Handbook of Environmental Fate and Exposure Data for Organic Chemicals*; Howard, P. H., Ed.; SRC Handbooks Series; CRC/Lewis Publishers: Boca Raton, FL, 1997.
(21) Yamasaki, H.; Kuwata, K.; Kuge, Y. Determination of vapor pressure of polycyclic aromatic hydrocarbons in the subcooled liquid phase and their adsorption on airborne particulate matter. *Nippon Kagaku Kaishi* **1984**, 1324−1329 (in Japanese).
(22) Xiao, H.; Li, N.; Wania, F. Compilation, Evaluation, and Selection of Physical−Chemical Property Data for α-, *β*-, and *γ*-Hexachlorocyclohexane *J. Chem. Eng. Data* **2004**, *49*, 173−185.
(23) Hornsby, A. G.; Wauchope, R. D.; Herner, A. E. *Pesticide Properties in the Environment*; Springer-Verlag: New York, 1996.
(24) Shoeib, M.; Harner, T. Using measured octanol-air partition coefficients to explain environmental partitioning of organochlorine pesticides. *Environ. Toxicol. Chem.* **2002**, *21*, 984−990.
(25) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi,

J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.

(26) Heard, G. L.; Boyd, R. J. Calculation of Quadrupole Moments of Polycyclic Aromatic Hydrocarbons: Applications to Chromatography. *J. Phys. Chem. A* **1997**, *101*, 5374−5377.

(27) Hernandez-Trujillo, J.; Vela, A. Molecular Quadrupole Moments for the Series of Fluoro- and Chlorobenzenes. *J. Phys. Chem.* **1996**, *100*, 6524−6530.

Received for review July 20, 2004. Accepted December 20, 2004. We are grateful to the Canadian Chlorine Coordinating Committee, the Natural Sciences and Engineering Research Council of Canada, and the Canadian Foundation for Climate and Atmospheric Science for funding.

JE049732N