

## Hydrogen bonding

# XXI. Solvation parameters for alkylaromatic hydrocarbons from gas–liquid chromatographic data

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### ABSTRACT

The truncated solvation equation

$$\log SP = c + rR_2 + l \log L^{16}$$

has been applied to numerous sets of gas–liquid chromatographic (GLC) data for alkylaromatic hydrocarbons on non-polar stationary phases. Here  $SP$  can be  $V_G$  or can be the relative retention time, and the retention index  $I$  can in this context be used in place of  $\log SP$ .  $R_2$  is the solute excess molar refraction, easily obtained from refractive index. A set of solutes of known  $\log L^{16}$  is used to set up the equation and then values of  $\log L^{16}$  can be back-calculated for other solutes;  $L^{16}$  is originally defined as the solute gas–liquid partition coefficient on hexadecane at 25°C. Through the above equation  $\log L^{16}$  values were calculated for 190 solutes. Once  $\log L^{16}$  is known, the reduced equation

$$\log SP = c + s\pi_2^H + l \log L^{16}$$

can be applied to GLC data on polar stationary phases, and the dipolarity/polarizability parameter  $\pi_2^H$  obtained by back-calculation in a similar way. Values of  $\pi_2^H$  for 120 solutes are listed. It is shown that *n*-alkyl substituents affect the  $\pi_2^H$  value only slightly, but *ortho* substituents considerably increase  $\pi_2^H$ , e.g., benzene (0.52), toluene (0.52), *o*-xylene (0.56), 1,2,3-trimethylbenzene (0.61), 1,2,3,4-tetramethylbenzene (0.65), pentamethylbenzene (0.66), hexamethylbenzene (0.72).

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### INTRODUCTION

Previously, we have shown that the general solvation equation

$$\log SP = c + rR_2 + s\pi_2^H + a\alpha_2^H + b\beta_2^H + l \log L^{16} \quad (1)$$

can be used to characterize all types of gas–liquid chromatographic (GLC) stationary phases, ranging from non-polar hydrocarbons to liquid salts [1–3], and also polymers [4] and not too volatile, non-polymeric liquids [5]. In eqn. 1,  $\log SP$  is a retention property for a series of solutes on a given stationary

phase, such as the retention volume as  $\log V_G$  or the gas–liquid partition coefficient as  $\log L$ , but not the retention index  $I$ . The explanatory variables are solute properties as follows:  $R_2$  is the solute excess molar refraction [6],  $\pi_2^H$  is the solute dipolarity/polarizability [1],  $\alpha_2^H$  and  $\beta_2^H$  are the solute hydrogen-bond acidity and basicity [1] and  $L^{16}$  is the solute gas–liquid partition coefficient on hexadecane at 25°C [7]. Note that in eqn. 1,  $\pi_2^H$ ,  $\alpha_2^H$  and  $\beta_2^H$  are “effective” or “summation” values, appropriate to the situation in which a monomeric solute molecule is surrounded by a large excess of solvent molecules.

The constants in eqn. 1 are found by the method of multiple linear regression analysis, and serve to

characterize the particular stationary phase under investigation. Eqn. 1 can also be used to correlate a series of  $I$  values, but the constants thus obtained are not characteristic constants for the particular stationary phase. As we shall see, however, the use of  $I$  values can lead to equations that are useful in other ways.

The generality of eqn. 1 depends on the availability of the various solute parameters used as explanatory variables. We have set out an extensive table of these parameters, but the large majority of solutes therein were aliphatic rather than aromatic. In order to extend our data base of solutes, so as to make eqn. 1 more general, we now set out the determination of relevant parameters for aromatic hydrocarbons, especially the key parameter  $\pi_2^H$ .

As the solutes with which we shall deal are all non-hydrogen-bonded acids, the term  $a\alpha_2^H$  in eqn. 1 will be redundant. Further, all the stationary phases we shall investigate will be either neutral or hydrogen-bonded bases. They will not be hydrogen-bonded acids and so the  $b\beta_2^H$  term in eqn. 1 is also redundant, leaving

$$\log SP = c + rR_2 + s\pi_2^H + l\log L^{16} \quad (2)$$

The excess molar refraction,  $R_2$ , can be obtained from the liquid refractive index, or can easily be estimated, so that there are only two unknown parameters,  $\pi_2^H$  and  $\log L^{16}$ , for any solute in eqn. 2.

Our method is thus to set up equations for a series of known solutes on a non-polar phase, where the  $s\pi_2^H$  term will either be zero or small, and then for any other solute knowing  $\log SP$  and  $R_2$  a value of  $\log L^{16}$  can be obtained by back-calculation. Once  $\log L^{16}$  is known, the only other required parameter is  $\pi_2^H$ . Now, if an equation can be constructed for known solutes on a polar phase, where the  $s$ -constant is very large, then for any other solute  $\pi_2^H$  can be back-calculated, knowing  $\log SP$ ,  $R_2$  and  $\log L^{16}$ . Unlike the situation with characteristic constants,  $\log SP$  in the above method can now be the retention index  $I$ . Indeed, many of the equations we shall use will be in terms of  $I$ , or of  $I/10$ , which for our purpose is slightly more convenient.

## RESULTS

There is a very large amount of literature data, mostly as retention index values, for aromatic

hydrocarbons on non-polar phases such as squalane and other hydrocarbons [8–16] and poly(methylsiloxanes) such as OV-101 [14,17–20]. Most results are at temperatures around 100°C, where the  $s\pi_2^H$  term in eqn. 2 is negligible. Then the correlation equation reduces to

$$\log SP = c + rR_2 + l\log L^{16} \quad (3)$$

where  $SP = V_G$  or the relative retention time  $t(\text{rel})$ , or to

$$I = c' + r'R_2 + l'\log L^{16} \quad (4)$$

where  $I$  is the retention index. The constants in eqn. 4 will not correspond to those in eqn. 3, but this does not matter as far as the back-calculation of  $\log L^{16}$  is concerned.

Results of the back-calculations are summarized in Table I, where S.D. is the standard deviation in  $\log L^{16}$  over the various determinations, and No. is the number of determinations. In a few instances, notably with benzene, there are slight differences between the squalane and the siloxane values, but we take the overall average as the obtained value. For a few solutes, it is possible to compare the overall average in Table I with our directly determined  $\log L^{16}$  values on hexadecane [7] (see Table II). There is good agreement between the two sets of values, and if the new values were to replace the old set in any correlation equation, alterations in the equations would be insignificant. Typical equations used to back-calculate  $\log L^{16}$  are for squalane at 96°C [11]

$$I/10 = 7.604 + 4.189R_2 + 19.747\log L^{16} \quad (5)$$

$$n = 67, \quad R = 0.9996, \quad \text{S.D.} = 0.377$$

and for OV-101 at 100°C [18]

$$I/10 = 6.418 + 5.915R_2 + 19.979\log L^{16} \quad (6)$$

$$n = 42, \quad R = 0.9992, \quad \text{S.D.} = 0.482$$

where  $n$  is the number of solutes,  $R$  is the overall correlation coefficient and S.D. is the standard deviation in  $I/10$ . As a rough indication of the error in the back-calculated  $\log L^{16}$  values we can take the overall standard deviation divided by the particular constant, in this instance S.D./ $l$ . Expected errors in  $\log L^{16}$  are thus estimated to be around 0.02 log units, in agreement with the various S.D. values given in Table I. Values of  $R_2$  needed in the back-calculations are also given in Table I.

TABLE I  
 CALCULATED VALUES OF LOG  $L^{16}$ 

Solute	<i>R</i>	Squalane average	S.D.	No.	Siloxane average	S.D.	No.	Overall average	S.D.	No.
Benzene	0.610	2.778	0.003	8	2.803	0.002	4	2.786	0.013	12
Toluene	0.601	3.325	0.005	8	3.326	0.007	4	3.325	0.006	12
Ethylbenzene	0.613	3.774	0.003	8	3.785	0.004	5	3.778	0.006	13
<i>o</i> -Xylene	0.663	3.944	0.003	8	3.931	0.003	5	3.939	0.007	13
<i>m</i> -Xylene	0.623	3.850	0.003	8	3.821	0.005	5	3.839	0.016	13
<i>p</i> -Xylene	0.613	3.845	0.004	8	3.829	0.003	5	3.839	0.009	13
<i>n</i> -Propylbenzene	0.604	4.220	0.003	8	4.246	0.005	5	4.230	0.014	13
Isopropylbenzene	0.602	4.075	0.003	8	4.099	0.005	5	4.084	0.012	13
1,2,3-Trimethylbenzene	0.728	4.571	0.005	8	4.554	0.010	5	4.565	0.011	13
1,2,4-Trimethylbenzene	0.677	4.456	0.005	8	4.417	0.009	5	4.441	0.021	13
1,3,5-Trimethylbenzene	0.649	4.371	0.005	8	4.301	0.006	5	4.344	0.036	13
2-Ethyltoluene	0.680	4.346	0.004	8	4.348	0.005	5	4.346	0.004	13
3-Ethyltoluene	0.630	4.276	0.006	8	4.273	0.003	5	4.275	0.005	13
4-Ethyltoluene	0.630	4.292	0.004	8	4.283	0.002	5	4.289	0.005	13
<i>n</i> -Butylbenzene	0.600	4.722	0.005	8	4.746	0.007	4	4.730	0.013	12
Isobutylbenzene	0.580	4.493	0.005	8	4.525	0.004	2	4.500	0.014	10
<i>sec.</i> -Butylbenzene	0.603	4.489	0.005	8	4.533	0.008	5	4.506	0.023	13
<i>tert.</i> -Butylbenzene	0.619	4.400	0.009	8	4.439	0.008	4	4.413	0.021	12
1,2-Diethylbenzene	0.688	4.721	0.005	6	4.749	0.006	4	4.732	0.015	10
1,3-Diethylbenzene	0.637	4.676	0.009	8	4.701	0.010	5	4.686	0.016	13
1,4-Diethylbenzene	0.645	4.732	0.007	8	4.732	0.006	5	4.732	0.006	13
1,2,4,5-Tetramethylbenzene	0.739	5.048	0.009	7	5.008	0.009	6	5.029	0.022	13
1,2,3,5-Tetramethylbenzene	0.748	5.074	0.009	7	5.027	0.017	6	5.052	0.027	13
1,2,3,4-Tetramethylbenzene	0.794	5.179	0.009	7	5.171	0.019	4	5.176	0.013	11
2- <i>n</i> -Propyltoluene	0.664	4.757	0.008	8	4.781	0.010	5	4.766	0.015	13
3- <i>n</i> -Propyltoluene	0.624	4.707	0.006	6	4.713	0.004	5	4.710	0.006	11
4- <i>n</i> -Propyltoluene	0.623	4.735	0.006	8	4.733	0.002	5	4.734	0.005	13
2-Isopropyltoluene	0.669	4.611	0.006	6	4.635	0.015	5	4.622	0.016	11
3-Isopropyltoluene	0.621	4.556	0.011	7	4.555	0.015	5	4.556	0.012	12
4-Isopropyltoluene	0.607	4.593	0.008	7	4.584	0.011	5	4.590	0.010	12
1,2-Dimethyl-3-ethylbenzene	0.742	4.951	0.005	4	4.936	0.003	2	4.946	0.009	6
1,2-Dimethyl-4-ethylbenzene	0.685	4.880	0.003	6	4.860	0.007	3	4.873	0.011	9
1,3-Dimethyl-2-ethylbenzene	0.757	4.866	0.006	4	4.865	0.011	2	4.866	0.007	6
1,3-Dimethyl-4-ethylbenzene	0.690	4.852	0.007	6	4.834	0.008	3	4.846	0.011	9
1,3-Dimethyl-5-ethylbenzene	0.653	4.774	0.006	4	4.741	0.008	3	4.760	0.018	7
1,4-Dimethyl-2-ethylbenzene	0.693	4.824	0.005	6	4.826	0.013	3	4.824	0.007	9
<i>n</i> -Pentylbenzene	0.594	5.225	0.016	4	5.254		1	5.230	0.019	5
Isopentylbenzene	0.574	5.053	0.004	2	5.097		1	5.068	0.026	3
<i>sec.</i> -Pentylbenzene	0.600	4.937	0.009	4				4.937	0.009	4
<i>tert.</i> -Pentylbenzene	0.620	4.890	0.011	3	4.965		1	4.909	0.038	4
Pentamethylbenzene	0.850	5.795	0.013	4	5.805	0.019	2	5.798	0.014	6
2- <i>n</i> -Butyltoluene	0.652	5.261		1	5.292		1	5.276	0.022	2
3- <i>n</i> -Butyltoluene	0.617				5.216		1	5.216		1
4- <i>n</i> -Butyltoluene	0.621	5.234		1	5.248		1	5.241	0.010	2
3- <i>sec.</i> -Butyltoluene	0.613				4.963		1	4.963		1
4- <i>sec.</i> -Butyltoluene	0.613	5.011	0.001	2	4.998		1	5.006	0.007	3
2- <i>tert.</i> -Butyltoluene	0.670	4.998	0.001	2				4.998	0.001	2
3- <i>tert.</i> -Butyltoluene	0.630	4.826	0.006	3				4.826	0.006	3
4- <i>tert.</i> -Butyltoluene	0.620	4.922	0.008	3	4.939		1	4.926	0.011	4
1-Ethyl-2- <i>n</i> -propylbenzene	0.660	5.144	0.001	2	5.176		1	5.154	0.019	3
1-Ethyl-3- <i>n</i> -propylbenzene	0.622	5.110	0.000	2	5.137		1	5.119	0.016	3
1-Ethyl-4- <i>n</i> -propylbenzene	0.625	5.174	0.007	3	5.205		1	5.182	0.016	4

(Continued on p. 232)

TABLE I (continued)

Solute	<i>R</i>	Squalane average	S.D.	No.	Siloxane average	S.D.	No.	Overall average	S.D.	No.
1-Ethyl-2-isopropylbenzene	0.658	4.943	0.001	2	5.012		1	4.966	0.040	3
1-Ethyl-3-isopropylbenzene	0.625	4.935	0.001	2	4.966	0.013	2	4.951	0.020	4
1-Ethyl-4-isopropylbenzene	0.626	5.039	0.001	2	5.018	0.008	2	5.028	0.013	4
1,2-Dimethyl-3- <i>n</i> -propylbenzene	0.750				5.373		1	5.373		1
1,2-Dimethyl-4- <i>n</i> -propylbenzene	0.690				5.282		1	5.282		1
1,3-Dimethyl-2- <i>n</i> -propylbenzene	0.757				5.263		1	5.263		1
1,3-Dimethyl-4- <i>n</i> -propylbenzene	0.690				5.259	0.010	2	5.259	0.010	2
1,3-Dimethyl-5- <i>n</i> -propylbenzene	0.653				5.169	0.013	2	5.169	0.013	2
1,4-Dimethyl-2- <i>n</i> -propylbenzene	0.693				5.237	0.007	2	5.242		1
1,2-Dimethyl-4-isopropylbenzene	0.690				5.150	0.011	2	5.150	0.010	2
1,3-Dimethyl-4-isopropylbenzene	0.695				5.102	0.008	2	5.102	0.008	2
1,3-Dimethyl-5-isopropylbenzene	0.658				5.007	0.003	2	5.007	0.003	2
1,4-Dimethyl-2-isopropylbenzene	0.698				5.079	0.011	2	5.079	0.011	2
1,2-Diethyl-3-methyltoluene	0.740				5.338		1	5.338		1
1,2-Diethyl-4-methylbenzene	0.720				5.190		1	5.190		1
1,3-Diethyl-4-methylbenzene	0.708				5.241	0.007	2	5.241	0.007	2
1,3-Diethyl-5-methylbenzene	0.665				5.075	0.062	3	5.075	0.062	3
1,4-Diethyl-2-methylbenzene	0.708				5.221		1	5.221		1
1,2,3-Trimethyl-4-ethylbenzene	0.800				5.594		1	5.594		1
1,2,3-Trimethyl-5-ethylbenzene	0.760				5.452		1	5.452		1
1,2,4-Trimethyl-3-ethylbenzene	0.800				5.559		1	5.559		1
1,2,5-Trimethyl-3-ethylbenzene	0.760				5.407		1	5.407		1
1,3,5-Trimethyl-2-ethylbenzene	0.760				5.402		1	5.402		1
<i>n</i> -Hexylbenzene	0.591	5.707	0.006	3	5.758		1	5.720	0.026	4
Hexamethylbenzene	0.950	6.538		1	6.576		1	6.557	0.027	2
1,2-Di- <i>n</i> -propylbenzene	0.665	5.492		1				5.492		1
1,3-Di- <i>n</i> -propylbenzene	0.625	5.514		1	5.546		1	5.530	0.023	2
1,4-Di- <i>n</i> -propylbenzene	0.620	5.601		1	5.605		1	5.603	0.003	2
1,2-Diisopropylbenzene	0.665	5.149	0.002	2	5.253		1	5.183	0.060	3
1,3-Diisopropylbenzene	0.605	5.148	0.006	4	5.213	0.006	2	5.170	0.034	6
1,4-Diisopropylbenzene	0.616	5.319	0.010	4	5.309	0.011	2	5.315	0.010	6
1- <i>n</i> -Propyl-2-isopropylbenzene	0.665				5.394		1	5.394		1
1- <i>n</i> -Propyl-3-isopropylbenzene	0.616				5.408		1	5.408		1
1- <i>n</i> -Propyl-4-isopropylbenzene	0.618	5.453		1	5.447		1	5.450	0.004	2
1,2-Dimethyl-3- <i>n</i> -butylbenzene	0.750				5.858		1	5.858		1
1,2-Dimethyl-4- <i>n</i> -butylbenzene	0.690				5.762		1	5.762		1
1,2-Dimethyl-4- <i>sec.</i> -butylbenzene	0.690				5.542		1	5.542		1
1,2-Dimethyl-4- <i>tert.</i> -butylbenzene	0.690				5.452		1	5.452		1
1,3-Dimethyl-4- <i>n</i> -butylbenzene	0.695				5.736		1	5.736		1
1,3-Dimethyl-4- <i>sec.</i> -butylbenzene	0.695				5.482		1	5.482		1
1,3-Dimethyl-5- <i>n</i> -butylbenzene	0.640				5.640		1	5.640		1
1,3-Dimethyl-5- <i>sec.</i> -butylbenzene	0.640				5.391		1	5.391		1
1,3-Dimethyl-5- <i>tert.</i> -butylbenzene	0.640	5.292	0.010	2				5.292	0.010	2
1,4-Dimethyl-2- <i>n</i> -butylbenzene	0.690				5.707		1	5.707		1
1,4-Dimethyl-2- <i>sec.</i> -butylbenzene	0.695				5.447		1	5.447		1
1-Methyl-2- <i>n</i> -pentylbenzene	0.650	5.735		1	5.740		1	5.738	0.004	2
1-Methyl-3- <i>n</i> -pentyltoluene	0.620				5.672		1	5.672		1
1-Methyl-4- <i>n</i> -pentylbenzene	0.620	5.727		1	5.702		1	5.715	0.018	2
1-Ethyl-2- <i>n</i> -butylbenzene	0.650	5.598		1				5.598		1
1-Ethyl-3- <i>n</i> -butyltoluene	0.620				5.602		1	5.602		1
1-Ethyl-4- <i>n</i> -butylbenzene	0.620	5.681		1	5.657		1	5.669	0.017	2
1-Ethyl-2- <i>sec.</i> -butylbenzene	0.650				5.380		1	5.380		1

TABLE I (continued)

Solute	<i>R</i>	Squalane average	S.D.	No.	Siloxane average	S.D.	No.	Overall average	S.D.	No.
1-Ethyl-3- <i>sec.</i> -butyltoluene	0.620				5.347		1	5.347		1
1-Ethyl-4- <i>sec.</i> -butyltoluene	0.620				5.422		1	5.422		1
1-Ethyl-4- <i>tert.</i> -butylbenzene	0.620	5.363	0.001	2				5.363	0.001	2
1,2,3-Triethylbenzene	0.780				5.683		1	5.683		1
1,2,4-Triethylbenzene	0.715	5.585	0.005	2	5.589		1	5.586	0.004	3
1,3,5-Triethylbenzene	0.672	5.504	0.004	3	5.520	0.001	2	5.510	0.009	5
1,2,3-Trimethyl-5- <i>n</i> -propylbenzene	0.760				5.882		1	5.882		1
1,2,3-Trimethyl-5-isopropylbenzene	0.760				5.717		1	5.717		1
1,2,4-Trimethyl-3- <i>n</i> -propylbenzene	0.800				5.969		1	5.969		1
1,2,4-Trimethyl-5-isopropylbenzene	0.750				5.653		1	5.653		1
1,2,5-Trimethyl-3- <i>n</i> -propylbenzene	0.760				5.872		1	5.872		1
1,3,5-Trimethyl-2- <i>n</i> -propylbenzene	0.760				5.802		1	5.802		1
<i>n</i> -Heptylbenzene	0.577	6.219		1				6.219		1
1-Methyl-2- <i>n</i> -hexylbenzene	0.647	6.218		1				6.218		1
1-Methyl-4- <i>n</i> -hexylbenzene	0.618	6.219		1				6.219		1
1-Ethyl-2- <i>n</i> -pentylbenzene	0.647	6.069		1				6.069		1
1-Ethyl-4- <i>n</i> -pentylbenzene	0.618	6.162		1				6.162		1
1- <i>n</i> -Propyl-2- <i>n</i> -butylbenzene	0.647	5.955		1				5.955		1
1- <i>n</i> -Propyl-4- <i>n</i> -butylbenzene	0.618	6.105		1				6.105		1
<i>n</i> -Octylbenzene	0.579	6.714		1				6.714		1
1,2-Di- <i>n</i> -butylbenzene	0.642	6.409		1				6.409		1
1,4-Di- <i>n</i> -butylbenzene	0.611	6.612		1				6.612		1
1,4-Diisobutylbenzene	0.610	6.091		1				6.091		1
1,4-Di- <i>sec.</i> -butylbenzene	0.612	6.073		1				6.073		1
1,4-Di- <i>tert.</i> -butylbenzene	0.616	5.956		1				5.956		1
1- <i>n</i> -Butyl-4-isobutylbenzene	0.611	6.353		1				6.353		1
1- <i>n</i> -Butyl-4- <i>sec.</i> -butylbenzene	0.612	6.347		1				6.347		1
1- <i>n</i> -Butyl-4- <i>tert.</i> -butylbenzene	0.613	6.280		1				6.280		1
1-Isobutyl-4- <i>sec.</i> -butylbenzene	0.611	6.081		1				6.081		1
1-Isobutyl-4- <i>tert.</i> -butylbenzene	0.613	6.004		1				6.004		1
1- <i>sec.</i> -Butyl-4- <i>tert.</i> -butylbenzene	0.614	6.004		1				6.004		1
1-Methyl-2- <i>n</i> -heptylbenzene	0.642	6.714		1				6.714		1
1-Methyl-4- <i>n</i> -heptylbenzene	0.611	6.728		1				6.728		1
1-Ethyl-2- <i>n</i> -hexylbenzene	0.642	6.547		1				6.547		1
1-Ethyl-4- <i>n</i> -hexylbenzene	0.611	6.664		1				6.664		1
1- <i>n</i> -Propyl-2- <i>n</i> -pentylbenzene	0.642	6.418		1				6.418		1
1- <i>n</i> -Propyl-4- <i>n</i> -pentylbenzene	0.611	6.653		1				6.653		1
<i>n</i> -Nonylbenzene	0.578	7.212		1				7.212		1
1-Methyl-2- <i>n</i> -octylbenzene	0.640	7.209		1				7.209		1
1-Ethyl-2- <i>n</i> -heptylbenzene	0.637	7.040		1				7.040		1
1- <i>n</i> -Propyl-2- <i>n</i> -hexylbenzene	0.637	6.892		1				6.892		1
1- <i>n</i> -Butyl-2- <i>n</i> -pentylbenzene	0.637	6.862		1				6.862		1
1-Methyl-3,5-di- <i>tert.</i> -butylbenzene	0.616	7.099		1				7.099		1
1,3,5-Triisopropylbenzene	0.627	5.999	0.011	3	6.104		1	6.025	0.053	4
<i>n</i> -Decylbenzene	0.579	7.708		1				7.708		1
1-Methyl-2- <i>n</i> -nonylbenzene	0.636	7.705		1				7.705		1
1-Ethyl-2- <i>n</i> -octylbenzene	0.635	7.532		1				7.532		1
1- <i>n</i> -Propyl-2- <i>n</i> -heptylbenzene	0.635	7.379		1				7.379		1
1- <i>n</i> -Butyl-2- <i>n</i> -hexylbenzene	0.635	7.333		1				7.333		1
1,2-Di- <i>n</i> -pentylbenzene	0.635	7.317		1				7.317		1
1,2,4,5-Tetraisopropylbenzene	0.726	6.559		1				6.559		1
Styrene	0.849	3.865	0.002	2	3.840		1	3.856	0.014	3

(Continued on p. 234)

TABLE I (continued)

Solute	<i>R</i>	Squalane average	S.D.	No.	Siloxane average	S.D.	No.	Overall average	S.D.	No.
$\alpha$ -Methylstyrene	0.847	4.300	0.004	2	4.278		1	4.292	0.013	3
<i>trans</i> - $\beta$ -Methylstyrene	0.913	4.486	0.018	2				4.486	0.018	2
2-Methylstyrene	0.915	4.358	0.005	2	4.342		1	4.352	0.010	3
3-Methylstyrene	0.866	4.390	0.003	2	4.346		1	4.375	0.025	3
4-Methylstyrene	0.871	4.399	0.005	2				4.399	0.005	2
2,4-Dimethylstyrene	0.913	4.913	0.001	2				4.913	0.001	2
Phenylethyne	0.679	3.692	0.005	2				3.692	0.005	2
Allylbenzene	0.717	4.126	0.003	2	4.157		1	4.136	0.018	3
Naphthalene	1.340	5.160	0.004	3	5.163	0.001	2	5.161	0.003	5
1-Methylnaphthalene	1.344	5.756	0.007	2	5.821	0.082	2	5.789	0.061	4
2-Methylnaphthalene	1.304	5.774	0.001	2	5.768	0.095	2	5.771	0.055	4
1,2-Dimethylnaphthalene	1.431				6.398		1	6.398		1
1,3-Dimethylnaphthalene	1.387				6.326		1	6.326		1
1,4-Dimethylnaphthalene	1.400				6.339		1	6.339		1
1,5-Dimethylnaphthalene	1.369				6.447		1	6.447		1
1,6-Dimethylnaphthalene	1.369				6.280		1	6.280		1
1,7-Dimethylnaphthalene	1.369				6.264		1	6.264		1
1,8-Dimethylnaphthalene	1.400				6.496		1	6.529	0.047	2
2,3-Dimethylnaphthalene	1.431				6.291	0.062	2	6.291	0.062	2
2,6-Dimethylnaphthalene	1.329				6.226	0.024	2	6.226	0.024	2
2,7-Dimethylnaphthalene	1.329				6.228		1	6.228		1
2-Ethylnaphthalene	1.371				6.140		1	6.140		1
2,3,6-Trimethylnaphthalene	1.429				6.856		1	6.856		1
1-Allylnaphthalene	1.474				6.556		1	6.556		1
Tetrahydronaphthalene	0.891	5.183	0.005	3	5.234	0.037	2	5.203	0.034	5
1,2-Dihydronaphthalene	1.093	5.119	0.004	2	5.151		1	5.130	0.019	3
Indene	1.001	4.546	0.001	2	4.572	0.018	2	4.559	0.018	4
1-Methylindene	0.980	4.737	0.018	2				4.737	0.018	2
2-Methylindene	1.123	4.735	0.002	2				4.735	0.002	2
3-Methylindene	1.123	5.041	0.004	2				5.041	0.004	2
5-Ethylindene	1.000	5.498		1				5.498		1
Indane	0.829	4.574	0.003	3	4.614	0.013	2	4.590	0.023	5
1-Methylindane	0.804	4.823		1				4.823		1
2-Methylindane	0.694	4.812		1				4.812		1
4-Methylindane	0.820	5.138		1				5.138		1
5-Methylindane	0.820	5.103		1				5.103		1
1,2-Dimethylindane	0.820	5.155	0.003	2				5.155	0.003	2

Of the 190  $\log L^{16}$  values in Table I, about 60 are averages of three or more values, and can be regarded as reasonably precise. The remaining values could be expected to alter slightly if further data were forthcoming, but we believe such alteration would be minimal.

In these back-calculations of  $\log L^{16}$ , standard known values of  $\log L^{16}$  are available, either from previous determinations as shown in Table II or from the *n*-alkanes used to obtain the *I* values.

However, if we wish to use eqn. 2 to back-calculate  $\pi_2^H$  values, it is essential to have a reasonable number of values already available as standards. We therefore set up a number of regression equations using data that included aromatic hydrocarbons together with a variety of other solutes of known [1]  $\pi_2^H$  values. We used the results of Langer and co-workers [21,22] on polyaromatic hydrocarbons [21] and dialkyl tetrachlorophthalate esters [22], and also several other series [19,23,24].

TABLE II  
COMPARISON OF OVERALL AVERAGE LOG  $L^{16}$  VALUES IN TABLE I WITH DIRECTLY DETERMINED VALUES

Solute	Table I	Direct values <sup>a</sup>
Benzene	2.786	2.803
Toluene	3.325	3.344
<i>o</i> -Xylene	3.939	3.937
<i>m</i> -Xylene	3.839	3.864
<i>p</i> -Xylene	3.839	3.858
<i>n</i> -Propylbenzene	4.230	4.221

<sup>a</sup> Ref. 7.

Results of these preliminary regressions are given in Table III. A typical equation, using Langer and Purnell's [21] results on 7,8-benzoquinoline at 110°C is given as

$$\log V_G^0 = -0.582 + 1.119 \pi_2^H + 0.622 \log L^{16} \quad (7)$$

$$n = 30, \quad R = 0.9980, \quad \text{S.D.} = 0.029$$

We can estimate the expected error in back-calculated  $\pi_2^H$  values as S.D./ $s$ , i.e.  $0.029/1.119 = 0.026$  units. For the seventeen solutes listed in Table III, the average of the S.D. ( $\pi_2^H$ ) values is 0.012 units.

We can now use these seventeen aromatic solutes

TABLE III  
PRELIMINARY CALCULATIONS OF  $\pi_2^H$

Solute	Overall average	S.D.	No.
Benzene	0.515	0.011	16
Toluene	0.514	0.010	16
Ethylbenzene	0.511	0.012	16
<i>o</i> -Xylene	0.559	0.007	16
<i>m</i> -Xylene	0.519	0.010	16
<i>p</i> -Xylene	0.515	0.013	16
<i>n</i> -Propylbenzene	0.496	0.012	13
Isopropylbenzene	0.488	0.017	14
1,2,3-Trimethylbenzene	0.610	0.019	15
1,2,4-Trimethylbenzene	0.552	0.012	16
1,3,5-Trimethylbenzene	0.505	0.027	13
2-Ethyltoluene	0.546	0.007	12
3-Ethyltoluene	0.500	0.016	12
4-Ethyltoluene	0.499	0.005	12
<i>n</i> -Butylbenzene	0.493	0.009	12
<i>tert.</i> -Butylbenzene	0.475	0.016	12

as standards to construct final equations for the back-calculation of  $\pi_2^H$ , using polar phases where the  $s$  constant is large. As we have seen, the magnitude of  $s$  is not the only factor that determines the expected error in  $\pi_2^H$ , and we have restricted our analysis to equations in which S.D./ $s$  is  $\leq 0.02$  units. Most of our final equations relate to Carbowaxes at various temperatures [14–16,25,26] or to a variety of dialkyltetrachloro- or -tetrabromophthalates [26–28], but a number of other phases [29–33] were also used. A typical equation is for the 35 aromatic solutes on di-*n*-propyl tetrachlorophthalate at 90°C [26], where, with no omissions, we find for log  $t$  relative to *n*-propylbenzene

$$\log t(\text{rel}) = -3.433 + 1.640 \pi_2^H + 0.618 \log L^{16} \quad (8)$$

$$n = 35, \quad R = 0.9986, \quad \text{S.D.} = 0.018$$

Although eqn. 8 is suitable for the calculation of  $\pi_2^H$  values, with S.D./ $s = 0.011$  units, it is of course unsuitable as a general solvation equation because of the limited range of the explanatory variables.

Our final set of 123 calculated  $\pi_2^H$  values is given in Table IV, together with the number of equations used, the standard deviation in  $\pi_2^H$ , and the maximum and minimum values of  $\pi_2^H$  obtained as a result of the back-calculations. We also list the maximum deviation (Max – Min) and in the final column give the  $\pi_2^H$  value we select. For a few cases, shown in parentheses, the selected value is not exactly the same as the calculated value. We shall deal with these later. These most recent values of  $\pi_2^H$  in Table IV are in good agreement with those we have listed previously [1], although in a few instances, *e.g.*, *o*-xylene and 1,2,3-trimethylbenzene, our new values are higher than the old values. Where there are differences, the new values are to be preferred.

In general, the back-calculation method works very well. For the solutes where the number of equations used is two or more, the S.D. in  $\pi_2^H$  averages out to 0.009, and the average value of Max – Min is 0.024 units. We can therefore claim that the final  $\pi_2^H$  values are precise to *ca.* 0.01 unit. However, such precision disguises the fact that any individual determination may be subject to much larger errors. Thus, for the typical case of *n*-propylbenzene, the spread of results ranges from 0.511 to 0.483 units, and in the atypical case of benzene from 0.547 to 0.495 units. We therefore suggest that

TABLE IV  
CALCULATED VALUES OF  $\pi_2^H$

Solute	No.	Average	S.D.	Max	Min	Max - Min	Taken value
Benzene	26	0.520	0.014	0.547	0.495	0.052	0.52
Toluene	26	0.520	0.008	0.533	0.503	0.030	0.52
Ethylbenzene	26	0.511	0.007	0.527	0.501	0.026	0.51
<i>o</i> -Xylene	25	0.565	0.011	0.585	0.542	0.043	0.56
<i>m</i> -Xylene	25	0.523	0.006	0.535	0.515	0.020	0.52
<i>p</i> -Xylene	25	0.521	0.016	0.551	0.503	0.048	0.52
<i>n</i> -Propylbenzene	26	0.500	0.008	0.511	0.483	0.028	0.50
Isopropylbenzene	26	0.487	0.011	0.515	0.465	0.050	0.49
1,2,3-Trimethylbenzene	21	0.613	0.011	0.633	0.591	0.042	0.61
1,2,4-Trimethylbenzene	24	0.563	0.011	0.588	0.548	0.040	0.56
1,3,5-Trimethylbenzene	25	0.520	0.012	0.536	0.489	0.047	0.52
2-Ethyltoluene	22	0.553	0.007	0.563	0.536	0.027	0.55
3-Ethyltoluene	22	0.510	0.012	0.527	0.490	0.037	0.51
4-Ethyltoluene	21	0.509	0.006	0.518	0.499	0.019	0.51
<i>n</i> -Butylbenzene	26	0.505	0.011	0.521	0.484	0.037	0.51
Isobutylbenzene	15	0.471	0.010	0.495	0.456	0.039	0.47
<i>sec.</i> -Butylbenzene	17	0.480	0.004	0.488	0.471	0.017	0.48
<i>tert.</i> -Butylbenzene	16	0.489	0.007	0.500	0.473	0.027	0.49
1,2-Diethylbenzene	15	0.540	0.009	0.549	0.527	0.022	0.54
1,3-Diethylbenzene	16	0.506	0.009	0.522	0.487	0.035	0.50
1,4-Diethylbenzene	16	0.505	0.009	0.516	0.488	0.028	0.50
1,2,4,5-Tetramethylbenzene	17	0.604	0.013	0.625	0.584	0.041	0.60
1,2,3,5-Tetramethylbenzene	17	0.610	0.010	0.629	0.592	0.037	0.61
1,2,3,4-Tetramethylbenzene	17	0.656	0.018	0.685	0.623	0.062	0.65
2- <i>n</i> -Propyltoluene	14	0.541	0.006	0.547	0.525	0.022	0.54
3- <i>n</i> -Propyltoluene	10	0.505	0.003	0.509	0.499	0.010	0.50
4- <i>n</i> -Propyltoluene	16	0.503	0.004	0.515	0.499	0.016	0.50
2-Isopropyltoluene	10	0.529	0.012	0.536	0.498	0.038	0.53
3-Isopropyltoluene	14	0.497	0.007	0.512	0.485	0.027	0.49
4-Isopropyltoluene	12	0.490	0.009	0.509	0.474	0.035	0.49
1,2-Dimethyl-3-ethylbenzene	10	0.607	0.008	0.615	0.594	0.021	0.61
1,2-Dimethyl-4-ethylbenzene	16	0.558	0.010	0.579	0.542	0.037	0.56
1,3-Dimethyl-2-ethylbenzene	8	0.596	0.006	0.606	0.587	0.019	0.60
1,3-Dimethyl-4-ethylbenzene	16	0.554	0.006	0.563	0.543	0.020	0.55
1,3-Dimethyl-5-ethylbenzene	12	0.517	0.013	0.530	0.490	0.040	0.52
1,4-Dimethyl-2-ethylbenzene	16	0.553	0.008	0.572	0.537	0.035	0.55
<i>n</i> -Pentylbenzene	9	0.508	0.013	0.533	0.489	0.044	0.51
Isopentylbenzene	3	0.501	0.000	0.501	0.501	0.000	0.50
<i>sec.</i> -Pentylbenzene	1	0.467					0.48
<i>tert.</i> -Pentylbenzene	5	0.492	0.009	0.509	0.486	0.023	0.49
Pentamethylbenzene	6	0.662	0.013	0.681	0.650	0.031	0.66
2- <i>n</i> -Butyltoluene	1	0.512					(0.54)
4- <i>n</i> -Butyltoluene	3	0.498	0.002	0.500	0.496	0.004	0.50
3- <i>tert.</i> -Butyltoluene	1	0.500					0.50
4- <i>tert.</i> -Butyltoluene	2	0.495	0.001	0.496	0.494	0.002	0.50
1-Ethyl-2- <i>n</i> -propylbenzene	1	0.546					(0.53)
1-Ethyl-4- <i>n</i> -propylbenzene	3	0.491	0.003	0.494	0.488	0.006	0.49
1,3-Diethyl-5-methylbenzene	1	0.542					0.52
<i>n</i> -Hexylbenzene	5	0.502	0.010	0.513	0.491	0.022	0.50
1-Methyl-2- <i>n</i> -pentylbenzene	1	0.536					0.54
1-Methyl-4- <i>n</i> -pentylbenzene	3	0.500	0.004	0.503	0.495	0.008	0.50
1-Ethyl-2- <i>n</i> -butylbenzene	1	0.535					0.53



TABLE IV (continued)

Solute	No.	Average	S.D.	Max	Min	Max—Min	Taken value
1-Ethyl-4- <i>n</i> -butylbenzene	3	0.489	0.004	0.492	0.485	0.007	0.49
1,2-Di- <i>n</i> -propylbenzene	1	0.528					0.53
1,3-Diisopropylbenzene	2	0.460	0.017	0.472	0.448	0.024	(0.48)
1,4-Diisopropylbenzene	6	0.476	0.015	0.503	0.459	0.044	0.47
1- <i>n</i> -Propyl-4-isopropylbenzene	3	0.470	0.007	0.474	0.462	0.012	0.47
1,3-Dimethyl-5- <i>tert.</i> -butylbenzene	2	0.513	0.028	0.532	0.493	0.039	0.51
1,3,5-Triethylbenzene	2	0.501	0.013	0.510	0.492	0.018	0.50
Hexamethylbenzene	4	0.719	0.009	0.726	0.707	0.019	0.72
<i>n</i> -Heptylbenzene	1	0.484					0.48
1-Methyl-2- <i>n</i> -hexylbenzene	1	0.529					0.53
1-Methyl-4- <i>n</i> -hexylbenzene	3	0.502	0.007	0.506	0.494	0.012	0.50
1-Ethyl-2- <i>n</i> -pentylbenzene	1	0.529					0.53
1-Ethyl-4- <i>n</i> -pentylbenzene	3	0.493	0.007	0.497	0.485	0.012	0.49
1- <i>n</i> -Propyl-2- <i>n</i> -butylbenzene	1	0.510					0.51
1- <i>n</i> -Propyl-4- <i>n</i> -butylbenzene	3	0.481	0.009	0.488	0.470	0.018	0.49
<i>n</i> -Octylbenzene	1	0.482					0.48
1-Methyl-2- <i>n</i> -heptylbenzene	1	0.522					0.52
1-Methyl-4- <i>n</i> -heptylbenzene	2	0.504	0.005	0.507	0.500	0.007	0.50
1-Ethyl-2- <i>n</i> -hexylbenzene	1	0.520					0.52
1-Ethyl-4- <i>n</i> -hexylbenzene	3	0.489	0.007	0.497	0.484	0.013	0.49
1- <i>n</i> -Propyl-2- <i>n</i> -pentylbenzene	1	0.502					0.50
1- <i>n</i> -Propyl-4- <i>n</i> -pentylbenzene	3	0.444	0.007	0.449	0.436	0.013	(0.48)
1,2-Di- <i>n</i> -butylbenzene	1	0.518					(0.50)
1,4-Di- <i>n</i> -butylbenzene	3	0.479	0.009	0.485	0.468	0.017	0.48
1,4-Diisobutylbenzene	3	0.414	0.014	0.427	0.400	0.027	0.41
1,4-Di- <i>sec.</i> -butylbenzene	3	0.432	0.010	0.440	0.421	0.019	0.43
1,4-Di- <i>tert.</i> -butylbenzene	3	0.439	0.004	0.443	0.435	0.008	0.44
1- <i>n</i> -Butyl-4-isobutylbenzene	3	0.444	0.011	0.452	0.431	0.021	0.44
1- <i>n</i> -Butyl-4- <i>sec.</i> -butylbenzene	3	0.456	0.011	0.464	0.443	0.021	0.46
1- <i>n</i> -Butyl-4- <i>tert.</i> -butylbenzene	3	0.456	0.006	0.462	0.450	0.012	0.46
1-Isobutyl-4- <i>sec.</i> -butylbenzene	3	0.420	0.015	0.433	0.404	0.029	0.42
1-Isobutyl-4- <i>tert.</i> -butylbenzene	3	0.424	0.010	0.433	0.413	0.020	0.42
1- <i>sec.</i> -Butyl-4- <i>tert.</i> -butylbenzene	3	0.439	0.010	0.445	0.427	0.010	0.44
<i>n</i> -Nonylbenzene	1	0.477					0.48
1-Methyl-2- <i>n</i> -octylbenzene	1	0.520					0.52
1-Ethyl-2- <i>n</i> -heptylbenzene	1	0.520					0.52
1- <i>n</i> -Propyl-2- <i>n</i> -hexylbenzene	1	0.498					0.50
1- <i>n</i> -Butyl-2- <i>n</i> -pentylbenzene	1	0.501					0.50
1-Methyl-3,5-di- <i>sec.</i> -butylbenzene	3	0.471	0.007	0.475	0.463	0.012	0.47
1,3,5-Triisopropylbenzene	1	0.398					0.40
<i>n</i> -Decylbenzene	1	0.469					0.47
1-Methyl-2- <i>n</i> -nonylbenzene	1	0.509					0.51
1-Ethyl-2- <i>n</i> -octylbenzene	1	0.509					0.51
1- <i>n</i> -Propyl-2- <i>n</i> -heptylbenzene	1	0.492					0.49
1- <i>n</i> -Butyl-2- <i>n</i> -hexylbenzene	1	0.493					0.49
1,2-Di- <i>n</i> -pentylbenzene	1	0.496					0.49
1,2,4,5-Tetraisopropylbenzene	3	0.394	0.029	0.417	0.362	0.055	0.39
Styrene	7	0.649	0.011	0.674	0.642	0.032	0.65
$\alpha$ -Methylstyrene	2	0.643	0.014	0.653	0.633	0.020	0.64
<i>trans</i> - $\beta$ -Methylstyrene	1	0.721					0.72
Allylbenzene	1	0.596					0.60
Naphthalene	6	0.917	0.018	0.937	0.885	0.052	0.92
1-Methylnaphthalene	3	0.895	0.006	0.899	0.889	0.010	0.90

(Continued on p. 238)

TABLE IV (continued)

Solute	No.	Average	S.D.	Max	Min	Max - Min	Taken value
2-Methylnaphthalene	3	0.881	0.001	0.882	0.880	0.002	0.88
1,2-Dimethylnaphthalene	2	0.920	0.004	0.923	0.917	0.005	0.92
1,3-Dimethylnaphthalene	2	0.921	0.001	0.922	0.920	0.002	0.92
1,4-Dimethylnaphthalene	2	0.906	0.004	0.909	0.903	0.006	0.91
1,5-Dimethylnaphthalene	2	0.871	0.003	0.873	0.869	0.004	0.87
1,6-Dimethylnaphthalene	3	0.912	0.005	0.916	0.907	0.009	0.91
1,7-Dimethylnaphthalene	2	0.894	0.004	0.896	0.891	0.005	0.89
1,8-Dimethylnaphthalene	2	0.909	0.001	0.910	0.908	0.002	0.91
2,3-Dimethylnaphthalene	3	0.945	0.009	0.953	0.935	0.018	0.94
2,6-Dimethylnaphthalene	3	0.911	0.003	0.914	0.908	0.006	0.91
2,7-Dimethylnaphthalene	2	0.911	0.001	0.911	0.910	0.001	0.91
Tetrahydronaphthalene	6	0.646	0.047	0.699	0.591	0.108	0.65
Indene	1	0.768					0.77
Indane	7	0.624	0.031	0.656	0.579	0.077	0.62
1-Methylindane	3	0.621	0.004	0.625	0.618	0.007	0.62
2-Methylindane	3	0.603	0.002	0.604	0.600	0.004	0.60
4-Methylindane	3	0.671	0.009	0.680	0.663	0.017	0.67
5-Methylindane	3	0.644	0.006	0.650	0.639	0.011	0.64

whenever possible, back-calculated solvation parameters are obtained from several equations and not just one.

We have just enough results in Table IV to reach a number of general conclusions as to structural effects on  $\pi_2^H$ . The effect of chain length of alkyl groups is very small. Thus, from benzene to *n*-hexylbenzene,  $\pi_2^H$  decreases from 0.52 to 0.50 units. Beyond this, we have only one determination for each *n*-alkylbenzene and so we cannot make any definitive comment; even so, reduction of  $\pi_2^H$  to 0.47 in the case of *n*-decylbenzene does show that after the first one or two members in any homologous series  $\pi_2^H$  is approximately constant.

A much greater variation in  $\pi_2^H$  is shown by positional isomers. In general, *o*-dialkyl groups have  $\pi_2^H$  about 0.035 units larger than the corresponding *m*- or *p*-dialkyl groups. This seems to extend to any di-*n*-alkyl-substituted benzene, and probably also to di-*sec*-alkylbenzenes, although unfortunately lack of data prevents any discussion of the *tert*-alkyl substituents. The tri- and tetramethylbenzenes follow this trend almost exactly, and even pentamethylbenzene ( $\pi_2^H = 0.66$ , calc. 0.66) and hexamethylbenzene ( $\pi_2^H = 0.72$ , calc. 0.73) obey the rule when the number of *ortho* interactions is taken as four and six, respectively.

However, values of  $\pi_2^H$  for tri- and tetrasubstituted benzenes involving *sec*-alkyl or *tert*-alkyl groups are appreciably less than calculated using the 0.035 unit rule for *ortho* groups. Thus, 1,2,4,5-tetramethylbenzene ( $\pi_2^H = 0.60$ , calc. 0.59) shows the predicted elevation of  $\pi_2^H$ , but we find that 1,2,4,5-tetraisopropylbenzene has a lower  $\pi_2^H$  value than benzene itself, *viz.*, 0.39 units only. Clearly, more than one factor is at work with these complicated substituted benzenes.

For the simpler benzene derivatives, the very regular pattern of  $\pi_2^H$  enables us to identify outliers to the general trend. These are solutes where our suggested value in Table IV is in parentheses and is significantly different to the determined value. Thus, in the series of 1-methyl-2-*n*-alkylbenzenes we have for the variation of the 2-*n*-alkyl group, methyl 0.56, ethyl 0.55, *n*-propyl 0.54, *n*-butyl 0.51, *n*-pentyl 0.54 and *n*-hexyl 0.53. Clearly, the value of 0.51 for 1-methyl-2-*n*-butylbenzene is too low, and we suggest in Table IV a value of 0.54 units. There are a few other cases shown in Table IV where similar reasoning leads to alternative suggested values.

We have listed in Table I the  $R_2$  and  $\log L^{16}$  values for alkyl aromatics and in Table IV the new  $\pi_2^H$  values that we have calculated. As  $\alpha_2^H$  is zero for the solutes that we are considering, the only remaining

TABLE V  
VALUES OF  $\beta_2^H$  FOR AROMATIC HYDROCARBONS

Solute	A <sup>a</sup>	B <sup>b</sup>	C <sup>c</sup>	D <sup>d</sup>	Taken
Benzene	0.15	0.15	0.13	0.15	0.14
Toluene	0.14	0.12	0.14	0.15	0.14
Ethylbenzene	0.15	0.14	0.15	0.17	0.15
<i>n</i> -Propylbenzene		0.13	0.16	0.18	0.15
<i>n</i> -Butylbenzene		0.11	0.16	0.18	0.15
Isobutylbenzene			0.10	0.16	0.15
<i>n</i> -Pentylbenzene		0.07	0.17	0.18	0.15
<i>n</i> -Hexylbenzene		0.04	0.17	0.18	0.15
<i>n</i> -Octylbenzene		0.10			0.15
<i>n</i> -Decylbenzene		0.09			0.15
<i>n</i> -Dodecylbenzene	0.17				0.15
Isopropylbenzene	0.16	0.14	0.16	0.21	0.16
<i>sec.</i> -Butylbenzene			0.17	0.23	0.16
<i>tert.</i> -Butylbenzene	0.15	0.16	0.18	0.27	0.16
<i>o</i> -Xylene	0.16	0.15	0.16	0.16	0.16
<i>m</i> -Xylene	0.18	0.13	0.15	0.16	0.16
<i>p</i> -Xylene	0.18	0.14	0.16	0.16	0.16
2-Ethyltoluene		0.18	0.21	0.23	0.18
4-Ethyltoluene		0.15	0.22	0.24	0.18
4-Isopropyltoluene		0.16	0.22	0.30	0.19
1,2,3-Trimethylbenzene		0.16	0.20	0.20	0.19
1,2,4-Trimethylbenzene		0.15	0.18	0.18	0.19
1,3,5-Trimethylbenzene	0.20	0.21	0.21	0.22	0.19
1,2,4,5-Tetramethylbenzene	0.20	0.16			0.19
1,2,3,5-Tetramethylbenzene	0.17	0.16			0.19
1,2,3,4-Tetramethylbenzene		0.18			0.19
Pentamethylbenzene	0.20	0.17			0.20
Hexamethylbenzene	0.22	0.26			0.21
Indane		0.13	0.21	0.15	0.16
Indene		0.20			0.18
Styrene	0.18	0.13	0.14	0.20	0.18
$\alpha$ -Methylstyrene	0.15	0.19	0.17	0.24	0.18
Biphenyl	0.20	0.24	0.18	0.24	0.20
Naphthalene	0.21	0.19	0.16	0.21	0.20
1-Methylnaphthalene	0.22	0.19	0.20	0.22	0.20
2-Methylnaphthalene	0.23	0.15			0.20
1,2-Dimethylnaphthalene		0.21			0.20
1,3-Dimethylnaphthalene		0.18			0.20
1,4-Dimethylnaphthalene		0.19			0.20
1,5-Dimethylnaphthalene		0.19			0.20
1,7-Dimethylnaphthalene		0.17			0.20
2,3-Dimethylnaphthalene	0.22	0.19			0.20
2,6-Dimethylnaphthalene	0.22	0.20			0.20
2-Ethyl-naphthalene		0.19			0.20
Allylbenzene		0.22			0.22
Phenylethyne		0.25			0.24

<sup>a</sup> Values from 1:1 complexation constants in tetrachloromethane [35].

<sup>b</sup> From a regression of water-octanol partition coefficients for aromatics [34].

<sup>c</sup> From a regression of air-water partition coefficients, all solutes [34].

<sup>d</sup> From a regression of water-hexadecane partition coefficients, all solutes [34].

solvation parameter is  $\beta_2^H$ . We have listed already [1] a number of  $\beta_2^H$  values for alkyl aromatics, either obtained by the back-calculation method [34] or deduced from the 1:1 complexation constants for hydrogen bonding in carbon tetrachloride as set out in detail before [35]. We can extend and update this list, as shown in Table V, where we have enough  $\beta_2^H$  values to predict a number of outstanding values with some confidence. In Table V the solutes are ordered by the increasing number of alkyl substituents, to show the regular increase in  $\beta_2^H$ . Using values in Table V that have been determined, we can deduce that any *n*-dialkylbenzene will have a  $\beta_2^H$  of 0.18 and any *n*-trialkylbenzene a value of 0.19 units: the only possible exceptions are compounds with di-*tert*-butyl groups, for which we have no data. The results in Table V now complete the entire set of solvation parameters for about 120 alkyl aromatic solutes, and so greatly extend the scope of application of the general solvation eqn. 1.

Finally, we discuss briefly the effects of structure on the solvation parameters. As found before [1], branching in an alkyl chain always results in a decrease in  $\log L^{16}$ . Oddly enough, polysubstituted isomers always have a larger  $\log L^{16}$  value than does the monosubstituted isomer, e.g., the trimethylbenzenes all have larger  $\log L^{16}$  values than *n*-propylbenzene. However, there is little that is exceptional with the values of  $\log L^{16}$  in Table I. The  $\beta_2^H$  values (or more correctly the  $\Sigma\beta_2^H$  values) in Table V are also unexceptional; increasing alkyl substitution in the benzene ring slightly increases the hydrogen-bond basicity, as expected from the small negative Hammett  $\sigma$  constants for alkyl groups. However, structural effects on the polarizability parameter  $\pi_2^H$  are not easily interpreted, especially the marked increase in  $\pi_2^H$  with *ortho*-alkyl groups. It is well known that *ortho*-methyl groups in the benzene ring suffer restricted rotation, as shown by thermodynamic [36] and spectroscopic evidence [37], including  $^{13}\text{C}$  NMR studies [38], but why this should lead to an increase in polarizability is not clear. Baudour and Sanquer [39] have suggested that in 1,2,4,5-tetramethylbenzene the two sets of *ortho*-methyl groups are "wagging" above and below the plate of the benzene ring. This could possibly give rise to a local or instantaneous dipole moment that could lead to increased polarizability. What our results do show, however, is that it is very difficult to

predict values of  $\pi_2^H$  for new systems, and that for the time being they must be based on experimental results.

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