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Hydrogen Bond Basicity of the Chlorogroup; Hexachlorocyclohexanes as Strong Hydrogen Bond Bases

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A simple chloroalkane or chlorocycloalkane has a very small hydrogen bond basicity, **B** = 0.1 units. Since **B** is often an additive function, it is possible that polychloro-alkanes or -cycloalkanes could have quite large hydrogen bond basicities. Literature data on the 1,2,3,4,5,6-hexachlorocyclohexanes (HCHs) have been analyzed by Abraham's linear free energy relationships to obtain solvation descriptors. These are not extraordinary except for the hydrogen bond basicity, **B**, which is indeed very large. Values of **B** for the HCHs are larger than many functionally substituted aliphatic compounds and as large as that of aliphatic amines. We find that **B** is 0.62−0.72 for the HCHs compared to 0.45 for propanone and 0.70 for ethylamine, the first time that such large hydrogen bond basicities have been identified in compounds with no functional groups. Hydrogen bond basicities are analyzed in order to examine what types of polychlorocompounds give rise to these elevated **B** values.

Introduction

It has been known for some time that simple aliphatic halides are weak hydrogen bond bases. In the present context, 1:1 hydrogen bond complexation constants in solution, eq 1, are the most useful measures of hydrogen bond strength. As long ago as 1962, West et al.[1] measured log *K* values for cyclohexyl halides against phenol in tetrachloromethane solution and found small but significant complexation constants. A few other log *K* values were reported subsequently, [2] and Abraham et al.[3] incorporated chloroalkanes in their 1:1 hydrogen bond basicity scale, β^H_2.

$$\text{B:} + \text{H-A} = \text{B:} \text{ --- } \text{H-A} \qquad (1)$$

A recent paper by Ouvrard et al.[4] lists 1:1 complexation constants for a large number of haloalkanes against 4-fluorophenol in tetrachloromethane solution. These log *K* values can be converted into 1:1 hydrogen bond basicity constants, β^H_2, as previously set out.[3] In Table 1 are collected some values for chloroalkanes,[4] together with values for a number of monofunctional alkanes[3,5] for comparison.

TABLE 1. Some 1:1 Hydrogen Bond Basicities, as β^H_2, and Overall Hydrogen Bond Basicities, B

solute	β^H_2	**B**
alkanes	0.00	0.00
1-chlorobutane	0.15	0.10
1-chloropentane	0.15	0.10
2-chloropropane	0.17	0.12
2-chloro-2-methylpropane	0.18	0.03
1,1-dichloroethane	0.15	0.10
1,2-dichloroethane	0.17	0.11
1,5-dichloropentane	0.22	0.17
chlorocyclohexane	0.18	0.10
hex-1-yne	0.17	0.10
propanone	0.40	0.49
diethyl ether	0.45	0.45
ethylamine	0.70	0.60
triethylamine	0.67	0.79
N,*N*-diethylacetamide	0.77	0.80

Another measure of solute hydrogen bond basicity is the "overall" hydrogen bond basicity, **B**;[6] the differences between the two measures have been discussed at some length.[6,7] Some values of **B** are also given in Table 1; again, they are rather small for chloroalkanes. Thus on both measures, the chloroalkanes are weak hydrogen bond bases, of the same order as alkynes.

In addition to this solution work, Desiraju and Steiner[8] give a number of examples of crystal structures that involve hydrogen bonds to the C−Cl group, mostly but not entirely intramolecular.

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TABLE 2. Isomers of 1,2,3,4,5,6-Hexachlorocyclohexane, HCH

isomer	configuration	μ (D)[a]	mp[b]	log P_{oct}	log P_{ben}	log S_{W}
α-HCH	$\alpha,\alpha,\beta,\alpha,\beta,\beta$	2.11	160	3.80	4.15	−5.16
β-HCH	$\alpha,\beta,\alpha,\beta,\alpha,\beta$	0.00	315	3.78	4.17	−6.08
γ-HCH[c]	$\alpha,\alpha,\beta,\alpha,\alpha,\beta$	2.67	113	3.72	4.22	−4.60
δ-HCH	$\alpha,\alpha,\alpha,\beta,\alpha,\beta$	1.92	142	4.14	4.38	−3.97
ϵ-HCH	$\alpha,\alpha,\alpha,\beta,\beta,\beta$	0.00				
η-HCH	$\alpha,\alpha,\alpha,\alpha,\beta,\beta$	1.95				
θ-HCH	$\alpha,\alpha,\alpha,\alpha,\alpha,\beta$	3.21				
ζ-HCH	$\alpha,\alpha,\alpha,\alpha,\alpha,\alpha$	4.49				

[a] Calculated for chair conformations with the smallest number of axial chlorines. [b] In °C. [c] Lindane.

The question we wished to pose is what is the effect of multiple chlorosubstitution on the hydrogen bond basicity of a solute? Suppose we have an alkane with six chloro substituents that do not interact with each other as regards their hydrogen bond basicity. This means that the six substituents will be placed on six different carbon atoms, because two chlorine atoms in the *gem* position will almost certainly interact. A possible candidate is 1,2,3,4,5,6-hexachlorocyclohexane (HCH) of which one isomer, γ-HCH or lindane, is a well-known agrochemical.[9]

The 1:1 hydrogen bond basicity, β^{H}_{2}, may be defined[3,4] through the 1:1 complexation constant for eq 1 with 4-fluorophenol in tetrachloromethane at 298 K, log K (PFP):

$$\beta^{H}_{2} = \frac{1.1 + \log K\,(\text{PFP})}{4.636} \qquad (2)$$

For 1-chlorocyclohexane, Table 1, with $\beta^{H}_{2} = 0.18$, K (PFP) $= 0.54$ dm^{3} mol^{-1}. Then for a polychloroalkane or -cycloalkane with n equivalent chlorosubstituents, K (PFP) is given[10,11] by 0.54n. So for two such substituents on a solute, K (PFP) $= 1.08$ and $\beta^{H}_{2} = 0.24$ (compare values of 0.17 and 0.22 for 1,2-dichoroethane and 1,5-dichloropentane, Table 1). By the same reasoning, six such substituents would give rise to K (PFP) $= 3.24$ and $\beta^{H}_{2} = 0.35$; the latter value still corresponds to a rather weak hydrogen bond base.

The situation with the **B**-descriptor is quite different, for now the **B**-values themselves are additive.[7,10] Thus if chlorocyclohexane has **B** = 0.10, then the various isomers of HCH might be expected to have values of **B** no less than 0.60, which is as much as ethylamine; see Table 1. In Table 2 are listed the isomers of HCH together with a number of properties. The dipole moments, in debyes, were calculated (this work) using Turbomole 5.4 with geometries optimized by Density Functional Theory (DFT) with the default split-valence plus polarization (SVP) basis set and the B-P86 functional.[12] They are given for isomers in the chair conformation with the smallest number of axial chlorine atoms. The water−octanol and water−benzene partition coefficients, expressed as log P_{oct} and log P_{ben} are from the Medicinal Chemistry database,[13] and the other properties are from collections of data.[14−16] Although it is γ-HCH that has been used as an insecticide, it is the β-HCH isomer that seems distinct in its properties, with a very high melting point, mp, and a very low solubility in water, expressed as log S_{W}, where S_{W} is in mol dm^{-3}.

TABLE 3. Coefficients in Eq 3 for Partition between Water and Solvents[a]

solvent	c	e	s	a	b	v
octan-1-ol	0.088	0.562	−1.054	0.034	−3.460	3.814
benzene	0.142	0.464	−0.588	−3.099	−4.625	4.491
hexane	0.361	0.579	−1.723	−3.599	−4.764	4.344
ether	0.255	0.605	−1.096	−0.097	−5.000	4.381
gas phase	−0.994	0.577	2.549	3.813	4.841	−0.869

[a] The final equation is for partition between the gas phase and water.

Methodology

To obtain the hydrogen bond basicity, **B**, for the HCHs, it is necessary to obtain various other properties, or descriptors, at the same time. The Abraham method of analysis is based on the two solvation equations, or LFERs, eqs 3 and 4. Here, SP is the dependent variable such as log P_{oct}, and the independent variables are solute properties or descriptors as follows.[5,17,18] **E** is the solute excess molar refractivity in units of (mol cm^{-3})/10, **S** is the solute dipolarity/polarizability, **A** and **B** are the overall or summation hydrogen bond acidity and basicity, **V** is the McGowan characteristic volume in units of (mol cm^{-3})/100, and **L** is the logarithm of the gas-hexadecane partition coefficient:

$$\text{SP} = \text{c} + \text{e}.\mathbf{E} + \text{s}.\mathbf{S} + \text{a}.\mathbf{A} + \text{b}.\mathbf{B} + \text{v}.\mathbf{V} \qquad (3)$$

$$\text{SP} = \text{c} + \text{e}.\mathbf{E} + \text{s}.\mathbf{S} + \text{a}.\mathbf{A} + \text{b}.\mathbf{B} + \text{l}.\mathbf{L} \qquad (4)$$

The method of analysis has been described before.[17,18] In brief, equations on the lines of eqs 3 and 4 are set up for various properties, and the values of the descriptors that best reproduce the properties are taken as those for the solute in question. Some simplification can be obtained, because the descriptor **E** can be estimated by analogy to other compounds, and **V** can easily be calculated;[5,19] the latter is 1.5798 for all the HCHs. The coefficients in eqs 3 and 4 for processes we shall deal with are in Table 3 and Table 4.

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TABLE 4. Coefficients in Eq 4 for Partition between the Gas Phase and Solvents[a]

solvent	c	e	s	a	b	l
octan-1-ol	−0.198	0.002	0.709	3.519	1.429	0.858
benzene	0.107	−0.313	1.053	0.457	0.169	1.020
hexane	0.292	−0.169	0.000	0.000	0.000	0.979
ether	0.245	−0.360	1.079	3.316	0.000	0.889
gas phase	−1.271	0.822	2.743	3.904	4.814	−0.213

[a] The final equation is for partition between the gas phase and water.

TABLE 5. Values of log K^W for Lindane at 298 K

log C_G	log K^W	ref
−7.66	3.06[a]	15
−8.35	3.75[a]	14
−8.52	3.92[a]	16
−8.95	4.35[a]	16
	3.24[b]	14
	3.84[b,c]	16
	3.78[b]	16
	4.00[b,d]	16
	4.09[b]	21
	4.82[b]	13

[a] Using a value of −4.60 for log S_W. [b] Direct values. [c] This is the value given in ref 22. [d] Average value in ref 16.

TABLE 6. Calculation of Solvation Parameters for γ-HCH, Lindane

system	obsd	calc[a]	obsd	calc[b]
log P_{oct}	3.72	3.68	3.72	3.62
log P_{ben}	4.22	4.21	4.22	4.23
log P_{hex}	3.24	3.38	3.24	3.26
log K^W	3.80	3.80	4.10	4.08
log K^{oct}	7.52	7.66	7.82	7.82
log K^{ben}	8.02	8.08	8.32	8.34
log K^{hex}	7.04	7.24	7.34	7.36
log K^W	3.80	3.87	4.10	4.10
GLC, ref 23a	1.735	1.701	1.735	1.738
GLC, ref 23b	2.234	2.068	2.234	2.184
GLC, ref 23c	0.752	0.660	0.752	0.698
GLC, ref 23d	1.007	0.929	1.007	0.957
GLC, ref 23e	1.711	1.731	1.711	1.737
GLC, ref 23f	0.987	0.837	0.987	1.012
GLC, ref 23g	1.333	1.207	1.333	1.289
GLC, ref 23g	0.590	0.550	0.590	0.573
SD		0.107		0.040

[a] With **E** = 1.45, **S** = 0.78, **A** = 0.00, **B** = 0.70, **L** = 7.345, and **V** = 1.5798. [b] With **E** = 1.45, **S** = 0.91, **A** = 0.00, **B** = 0.68, **L** = 7.467, and **V** = 1.5798.

Results and Discussion

We deal first with lindane, γ-HCH, for which more data is available than for the other isomers. Values of log P_{oct} and log P_{ben} are in Table 2, and values are also available[13] for other partitions; water−hexane (log P_{hex} = 3.24) and water−ether (log P_{ether} = 2.00). We consider the latter value as far too small to be realistic, and hence it was not used. The gas−water partition coefficient, K^W, is an important parameter, and can be obtained either by direct analysis or by combining the solubility in water at 298 K with the saturated vapor concentration, C_G, also at 298 K, since $K^W = S_w/C_G$. The water solubility of lindane seems well established, three reference databases[14−16] all giving log S_W = −4.60, but this is not the case for vapor pressure (from which C_G is calculated). Mackay[16] gives two sets of vapor pressure/temperature equations that yield log C_G = −8.52 and −8.95, while other values are −7.66[15] and −8.35[14] (the latter has been corrected from −8.65 at 293 K). The log C_G value of −8.52 as reported by Boehncke et al.[20] is probably the most reliable value. The range of log K^W is therefore from 3.06 to 4.35 depending on the vapor pressure used. Reported direct values are 3.24,[14] from 3.78 to 4.00,[16] and 4.09.[21] A recently suggested value is 3.84;[22] a comparison is given in Table 5.

The value of log K^W is not only important in its own right, but also because log K^W can be combined with any water−solvent partition coefficient, as log P, to yield the corresponding partition from the gas phase to the solvent, K^S, eq 5. Thus for lindane, eq 5 yields partitions from the gas phase to (wet) octanol, benzene, and hexane. However, all these values of log K^S depend on the value used for log K^W. Fortunately, independent data are available through gas−liquid chromatography on phases that we have characterized through eq 4.[23] This helps greatly in selection of a value for log K^W.

$$\log K^S = \log P + \log K^W \tag{5}$$

We have a total of sixteen equations for the calculation of the unknown descriptors **S**, **A**, **B** and **L**, but before we can proceed, we have to choose a value for log K^W. The average of all the values collected in Table 5 is 3.80, and so we carried out calculations on this basis; see Table 6. With **S** = 0.78, **A** = 0.00, **B** = 0.70, and **L** = 7.345, we were able to reproduce the sixteen dependent variables with SD = 0.107 units. However, by inspection, the various log K^S values were not compatible with the GLC data, i.e., the log K^W value of 3.80 leads to an inconsistency. By trial and error, we examined the effect of changing the value of log K^W initially used. A value of 4.10 gave the smallest SD value of only 0.040, using **S** = 0.91, **A** = 0.00, **B** = 0.68, and **L** = 7.467 as descriptors, see Table 6. Our “best” value of 4.10 for log K^W is within the quoted range, is compatible with the GLC data, and is identical with that obtained by Pirrone et al.,[21] and so we suggest this as the most reasonable value. The corresponding value for log C_G is −8.70, based on log S_W = −4.60; this value of −8.70 is also well within the range of quoted values; see Table 5.

For α-HCH, data for only the water−solvent partitions recorded in Table 1 are available, but GLC data are also available.[23] Values[14] of log S_W = −5.16 and log C_G = −8.62 lead to log K^W = 3.46, as compared to values from direct measurements of 3.36,[14] 3.51,[22] and 3.80.[21] We chose a value of 3.80 as the basis for our calculations,

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TABLE 7. Solvation Parameters for HCHs

solute	**E**	**S**	**A**	**B**	**L**	**V**
α-HCH	1.45	0.73	0.00	0.71	7.317	1.5798
β-HCH	1.45	0.88	0.00	0.69	7.493	1.5798
γ-HCH	1.45	0.91	0.00	0.68	7.467	1.5798
δ-HCH	1.45	0.94	0.00	0.63	7.626	1.5798
ϵ-HCH	1.45	(0.93)	0.00		7.802	1.5798
n-HCH	1.45		0.00			1.5798
θ-HCH	1.45		0.00			1.5798
ζ-HCH	1.45		0.00			1.5798

TABLE 8. Values of B for Chlorocompounds

solute	**B**	solute	**B**
γ-HCH	0.68	trichloromethane	0.02
1,2-dichloroethane	0.10	1,1,1-trichloroethane	0.09
1,2-dichloropropane	0.17	allyl chloride	0.05
1,2,3-trichloropropane	0.32	hexachloroethane	0.00
cis-1,2-dichloroethene	0.05	hexachlorobenzene	0.00
trans-1,2-dichloroethene	0.05	*p,p*′-DDT	0.28
dichloromethane	0.05	heptachlor	0.58
1,1-dichloroethane	0.10	dieldrin	0.65

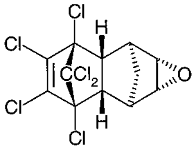

FIGURE 1. Dieldrin

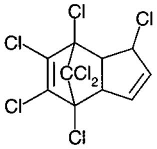

FIGURE 2. Heptachlor

because this appeared compatible with the various GLC data. The situation with δ-HCH is unsatisfactory. The only water−solvent partitions are those in Table 2, and there is only one recorded value[14] for log K^W, 4.75, which seems too large by comparison with values for α-HCH and γ-HCH. Indeed, use of the 4.75 value leads to very poor agreement between calculated and observed values. A value of 4.0 for log K^W brings about better agreement and leads to an SD of 0.137 between observed and calculated SP values. This smaller value for log K^W also leads to descriptors that are more compatible with those for α-HCH and γ-HCH. We have left β-HCH until last, because some of the properties listed in Table 2 seem quite out of line. The position as regards data is exactly the same as for δ-HCH; once again, the given value for log K^W, 4.52,[14] seems very high. A much better fit is obtained if log K^W is taken as 4.10, with an SD of 0.062 over 12 equations. A summary of the suggested solvation descriptors for the HCHs is in Table 7. The sets of descriptors are remarkably similar; there is nothing exceptional about γ-HCH, even though it has been widely used as an insecticide. Neither are the descriptors for β-HCH very different from those of the other isomers, although some physicochemical properties of β-HCH are considerably different, for example, mp, water solubility, and vapor pressure. However, these properties are functions of the crystal energy that cancels out when transfers between solvents are considered.

The **E**- and **S**-values of the HCHs are not exceptional. It is clear from Table 2 that there is no direct connection between the **S**-values and calculated dipole moments; hence the **S**-values must depend significantly on dipolarizabilities or other higher order effects.

The large values of **L** (7.32−7.80) are again not exceptional for aliphatic compounds with six chlorine atoms. What is very remarkable are the very large **B**-values for the HCHs (0.63−0.71). Simple aliphatic compounds with ether, carbonyl, or ester functional groups have hydrogen bond basicities that are considerably smaller; see Table 1. The HCHs can be regarded as reasonably strong hydrogen bond bases, comparable in strength to aliphatic amines and not far short of amides.

This strong hydrogen bond basicity is exactly as expected if the **B**-descriptor is additive. If a monochloroalkane or monochlorocycloalkane has **B** = 0.107−0.117, for example, then simple addition of basicity will yield **B** = 0.64−0.70 for a hexachlorocompound. However, it must be stressed that these calculations refer to substituted alkanes or cycloalkanes with no chlorine atoms in the *gem*-configuration. This can be illustrated by a survey of **B**-values for chlorocompounds of various types as shown in Table 8. Whereas 1,2,3-trichloropropane has **B** = 0.32 (0.106 per chlorine atom), the trichlorocompound 1,1,1-trichloroethane has **B** = 0.10, and hexachloroethane has **B** = 0. A chlorosubstituent in the vinyl position, as in the dichloroethenes, does not confer any hydrogen bond basicity on a solute.

An aromatic chlorosubstituent also confers no hydrogen bond basicity on a solute. Thus hexachlorobenzene has **B** = 0.00; see Table 8. In the important class of polychlorobiphenyls (PCBs), the **B**-value of biphenyl itself (0.32) is reduced by chlorosubstitution. For example, **B**-values are as follows:[24] 4,4′-dichlorobiphenyl (0.16), 2,2′,3,3′,5,5′-hexachorobiphenyl (0.10), and decachlorobiphenyl (0.00).

The effect of the large hydrogen bond basicity on the properties of lindane can be illustrated with reference to log P_{oct} values; these depend markedly on solute **B**- and **V**-values, through the terms −3.460 **B** and 3.814 **V**; see Table 3. The six chlorosubstituents in hexachlorobenzene reduce the **B**-value from 0.14 in benzene to 0.00 in hexachlorobenzene, and then the effect of increase in volume leads to a very large increase in log P_{oct} from 2.13 to 5.37 log units. However, the six chlorosubstituents in lindane increase the **B**-value from 0.00 in cyclohexane to 0.68 in lindane, thus counteracting the effect of the large increase in volume and leading to only a very small increase in log P_{oct} from 3.44 to 3.72 log units.

The effect of type of chlorosubstituent on the overall solute hydrogen bond basicity can be illustrated by reference to the solute dieldrin (Figure 1), which has six chlorosubstituents. We find that **B** = 0.65 by the same procedure as shown for lindane. Dieldrin contains the 1,2-dichloroethene moiety (**B** = 0.05) and a 1,3-epoxide (**B** = 0.40). The *gem*-dichloro group will have **B** = 0.10, to leave just two chlorocycloalkane substituents each with **B** = 0.10 units. The combined **B**-value is 0.75, quite close to our determined value (0.65). Heptachlor (Figure 2) is another highly chlorinated cycloalkane with **B** = 0.58.

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[24] Abraham, M. H.; Al-Hussaini, A. J. M. Unpublished work.

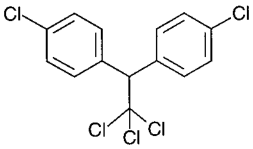

FIGURE 3. *p,p′*-DDT

We can carry out a similar sum: 1,2-dichloroethene (0.05), *gem*-dichloro (0.10), and allyl chloride (0.05) add up to 0.20 to leave two saturated chlorosubstituents each contributing 0.19 to **B**. The latter is larger than usual, but the general trend is observed. Finally we consider *p,p′*-DDT (Figure 3) with **B** = 0.28. Our summation will include the CCl_3 group (0.09) and two "chlorobenzene" groups (0.07 each) giving **B** = 0.23, in reasonable agreement with the experimental value of 0.28.

Thus if due regard is given to the type of chlorosubstituent, the hydrogen bond basicity of polychlorocompounds can be understood, even the very large basicity of the hexachlorocyclohexanes that have no functional group. This basicity arises from the presence of six noninteracting aliphatic chlorosubstituents that each contribute about 0.11 units to **B**. The present results also unravel the difficulty of Gibb et al.,[25]who find that haloadamantyl compounds can take part in hydrogen bonding, although as Gibb et al.[25] believe "...evidence for hydrogen bonds to halogens is weak." We show that there is considerable evidence for such hydrogen bonding and that aliphatic chlorocompounds can be strong hydrogen bond bases by virtue of their hydrogen bond capability.

An advantage of the Abraham method of assigning physicochemical parameters to solutes, is that data from a large number of apparently unrelated processes can be assessed, and inconsistencies in the experimental data can be uncovered.

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Supporting Information Available: Optimized coordinates and energies from the dipole moment calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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[25] Gibb, C. L. D.; Stevens, E. D.; Gibb, B. C. *J. Am. Chem. Soc.* **2001**, *123*, 5849−5850.