

Hydrogen Bonding. Part 18.† Gas–Liquid Chromatographic Measurements for the Design and Selection of some Hydrogen Bond Acidic Phases Suitable for Use as Coatings on Piezoelectric Sorption Detectors

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A number of involatile liquids based on 4,4'-isopropylidenediphenol (bisphenol-A) or other bisphenols have been prepared as candidate coatings for piezoelectric sorption detectors. The liquids have been used as GLC stationary phases, and gas–liquid partition coefficients of a series of solutes have been obtained for these phases. Application of the linear solvation energy equation below has revealed that two particular liquids (**8** and **9**) possess very large hydrogen bond acidities coupled to rather small hydrogen bond basicities, and hence might be suitable as coatings with selectivity towards solutes that are hydrogen bond bases. One other compound (**10**) is not suitable as a coating because it is a solid at room temperature, but it has very considerable hydrogen bond acidity, and may be suitable as a novel GLC stationary phase. In the linear solution

$$\log K = c + rR_2 + s\pi_2^H + a\alpha_2^H + b\beta_2^H + l \log L^{16}$$

energy equation above, K is the gas–liquid partition coefficient for a series of solutes on a given phase, and the explanatory variables R_2 , π_2^H , α_2^H , β_2^H and $\log L^{16}$ are solute parameters that we have described before. A term by term analysis of the equation can be used to evaluate quantitatively how specific solute–solvent interactions influence the magnitude of the various $\log K$ values.

The concept of piezoelectric sorption detectors, first introduced in 1964 by King¹ using the quartz crystal microbalance (QCM), has proved to be an effective and flexible approach to the design of chemical vapour sensors. A stationary phase coating material is applied to a mass-sensitive piezoelectric device which serves as the resonant element in an oscillator circuit. Changes in the mass of the coating, e.g. by the sorption of a vapour, result in a proportional change in the frequency of the oscillator. The sensitivity and selectivity of the sensor is dependent on the strength and selectivity with which the coating material absorbs the analyte vapour. This concept can be implemented with a variety of other mass-sensitive piezoelectric devices in addition to the QCM, including the surface acoustic wave (SAW) device and the flexural plate wave (FPW) device. The SAW device in particular has received considerable attention in the past decade.^{2–5} The response, δf_v , of such a sensor exposed to a solute vapour concentration C_v is given by eqn. (1)⁴ where δf_s

$$\delta f_v = \delta f_s C_v K / \rho \quad (1)$$

represents the amount of coating on the sensor, ρ is the density of the coating material and K is the gas–liquid partition coefficient, equivalent to the Ostwald solubility coefficient L and defined by eqn. (2). In eqn. (2), C_s is the concentration of

$$K \text{ (or } L) = C_s / C_v \quad (2)$$

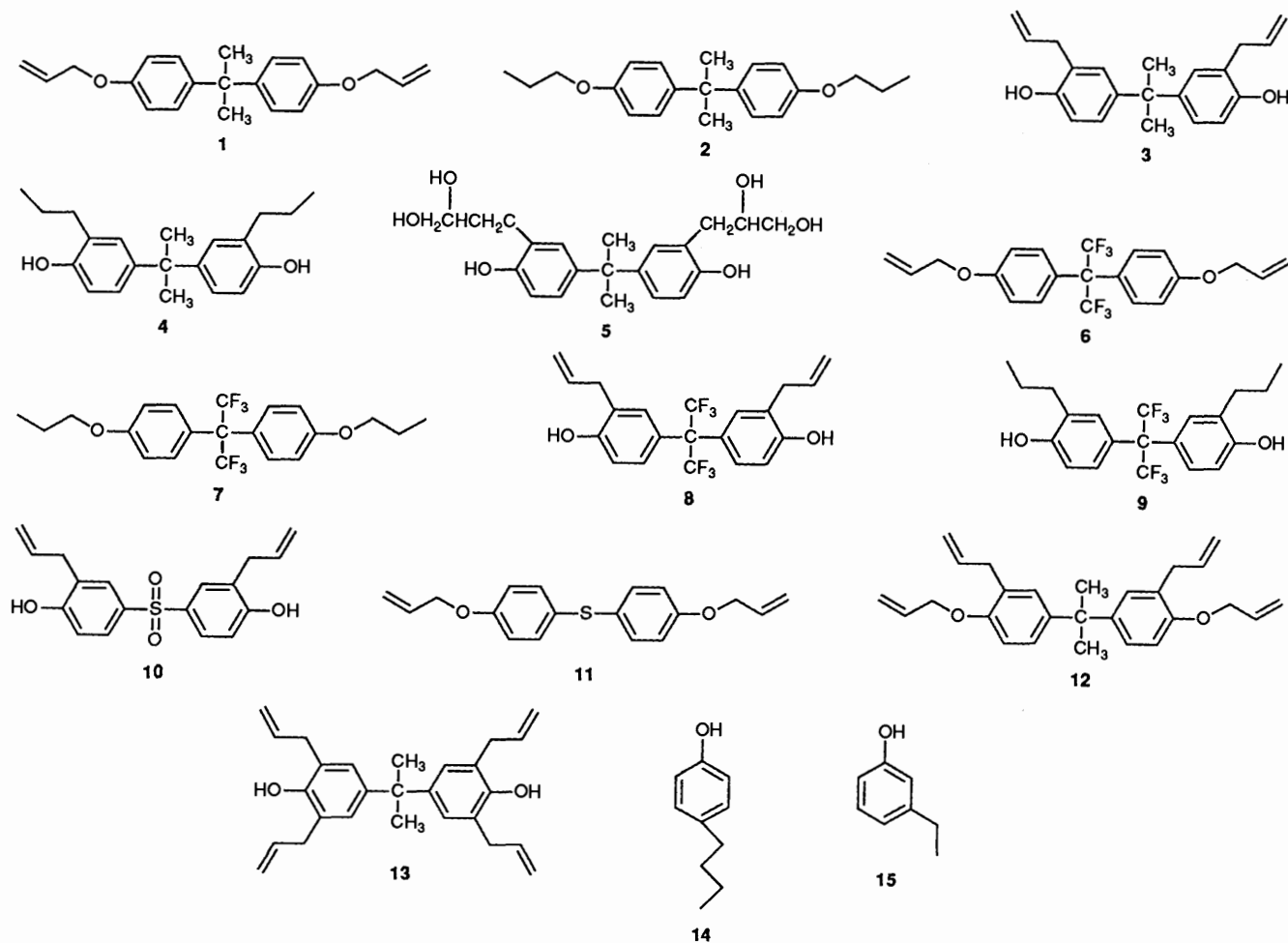
solute in the bulk liquid and C_v is as above. An inherent assumption in the derivation of eqn. (1) is that the response of the sensor is entirely due to mass loading effects. Prior to the

derivation of eqn. (1), the relevance of partition coefficients to QCM and SAW sensor responses had been noted by a number of authors.⁶

A standard method of determining values of K for a series of solutes on a given involatile solvent is to use the latter as the stationary phase in a gas–liquid chromatography (GLC) experiment. Partition coefficients determined in this way have been compared with those calculated *via* eqn. (1) from the responses of SAW sensors coated with the same stationary phase.⁴ This study confirmed the validity of eqn. (1) and the relevance of bulk liquid partition coefficients to SAW vapour sensors. Partition coefficients are also useful because they provide fundamental thermodynamic information on sorption, which can be used to develop linear solvation energy relationships, as we discuss below. The measurement of many partition coefficients for use in developing such relationships is much more convenient by the GLC method than by SAW sensor measurements, since the SAW method requires the generation and individual calibration of a dynamic vapour stream for each partition coefficient to be determined.

One type of sensor coating that is of considerable interest to us is a hydrogen bond acidic phase that will selectively adsorb vapours that are hydrogen bond bases.^{2–4} It would seem relatively straight forward to incorporate simple hydroxy or carboxylic acid groups into a coating material. However, these groups are normally strongly self-associated in condensed phases and so will not give rise to coatings that are very strong hydrogen bond acids. Incorporation of fluorine into aliphatic alcohols leads to materials that are stronger as hydrogen bond acids and weaker as hydrogen bond bases. A number of fluoroalcohol-containing polymers have been synthesised, and we are currently evaluating them by the present procedures. Another possibility, not previously considered, is to synthesise and evaluate involatile liquids that contain the phenolic functional group, and this is the aim of the present work.

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Scheme 1

Bisphenols are readily available as starting materials, and incorporation of alkyl substituents can reduce the melting point and lead to the liquid materials we desire. We stress that we are interested in sensors that respond to vapours rapidly and reversibly, without hysteresis. We have therefore concentrated on non-volatile liquids, as well as amorphous polymers above their glass transition point.

However, we wish not only to synthesise materials for sensor and GLC phases, but also quantitatively to characterise the hydrogen bond acidity of the phase, and to examine the fundamental solute-solvent interactions that influence the ability of solvent phase to absorb given solute vapours. Our method is based on the linear solvation energy eqn. (3) that we

$$\log K = c + rR_2 + s\pi_2^H + a\alpha_2^H + b\beta_2^H + l \log L^{16} \quad (3)$$

have recently developed.⁷⁻¹⁰ In eqn. (3), K (or L) is the gas-liquid partition coefficient for a series of solutes on a given solvent phase, and the explanatory variables are as follows: R_2 is an excess molar refraction;⁷ π_2^H is our new solute dipolarity/polarisability parameter;⁷ α_2^H is the solute hydrogen bond acidity;¹⁰ β_2^H is the solute hydrogen bond basicity;¹⁰ and L^{16} is the solute K or L value on hexadecane at 298 K.⁷⁻⁹ The constants c , r , s , a , b and l in eqn. (3) are found by multiple linear regression analysis, and reflect specific solute-solvent interactions. Thus r shows the ability of the solvent phase to interact with π and n electron pairs. Usually r is positive, but can be negative if the solvent contains fluorine atoms. The s constant relates to dipole/dipole and dipole/induced-dipole interactions;

the a constant to interactions between solute hydrogen bond acid and solvent hydrogen bond base; and the b constant to interactions between solute hydrogen bond base and solvent hydrogen bond acid. Finally, the l constant refers to the ability of a solvent phase to separate adjacent members of a homologous series.⁹

Our second main aim is to understand the various solute-solvent interactions between phenolic solvent phases and various solute vapours in order to acquire fundamental information that can be used in the development of solvent phases in particular separations or selective absorptions.

Experimental

General.—With the exception of two of the phases (**14** and **15**) which are commercially available (and were kindly provided by Synthetic Chemicals Ltd.) all compounds were prepared in house by methods described in refs. 11–14. The compounds were all (with two exceptions: **5** and **10**) clear viscous oils at room temperature (Scheme 1). All coupling constant values J are given in Hz throughout.

*4,4'-Isopropylidenediphenol Diallyl Ether*¹³ (**1**).—A mixture of 4,4'-isopropylidenediphenol (bisphenol-A) (114 g, 0.5 mol), sodium hydroxide (42 g, 1 mol) and propan-1-ol (500 cm³) was heated under reflux until a solution formed, and to this solution was slowly added allyl bromide (100 cm³, 1.16 mol). The resulting solution was refluxed under nitrogen for 9 h, and filtered to remove the precipitated sodium bromide, before

being extracted with dichloromethane (200 cm³). The extract was washed with distilled water (500 cm³), dried, and concentrated on a rotary evaporator (138.8 g, 90%), b.p. 498–503 K/0.02 mmHg (Found: C, 81.6; H, 8.1. Calc. for C₂₁H₂₄O₂: C, 81.8; H, 7.8%; δ_{H} (90 MHz; CDCl₃; standard Me₄Si) 1.65 (6 H, s, 2 × Me), 4.42–4.58 (4 H, dd, 2 × CH₂-O), 5.17–5.54 (4 H, complex m, 2 × =CH₂), 5.87–6.28 (2 H, complex m, J 5, 2 × CH), 6.75–6.92 (4 H, dd, J 9, 2 × Ar-H) and 7.07–7.23 (4 H, dd, J 9, 2 × Ar-H).

4,4'-Isopropylidenediphenol Dipropyl Ether¹⁴ (2).—A solution of **1** (6 g, 0.02 mol) in chloroform (25 cm³) was hydrogenated using a 5% palladium on charcoal catalyst (0.2 g) for 3 h until no further uptake of hydrogen was observed. The reaction mixture was filtered, concentrated on a rotary evaporator, and distilled under reduced pressure (5.88 g, 98%), b.p. 463–473 K/0.01 mmHg (Found: C, 80.8; H, 8.9. Calc. for C₂₁H₂₈O₂: C, 80.7; H, 9.0%; δ_{H} (60 MHz; CDCl₃; standard Me₄Si) 0.8–1.8 (6 H, t, J 6, 2 × Me of Prⁿ), 1.4–2.1 (4 H, complex m, J 6, 2 × CH₂), 1.63 (6 H, s, 2 × Me), 3.6–4.0 (4 H, t, J 6, 2 × CH₂), 6.5–6.9 (4 H, dd, J 9, 2 × Ar-H) and 6.93–7.25 (4 H, dd, J 9, 2 × Ar-H).

2,2-Diallyl-4,4'-isopropylidenediphenol¹³ (3).—A solution of **1** (10 g, 0.03 mol) in 2-(2-ethoxyethoxy)ethanol (50 cm³) was heated under nitrogen at 473–478 K for 5 h to undergo the Claisen rearrangement.¹² The solvent was removed by distillation under reduced pressure and the product collected as a slightly viscous, clear liquid distillate (6.50 g, 65%), b.p. 463 K/0.5 mmHg (Found: C, 81.7; H, 8.1. Calc. for C₂₁H₂₄O₂: C, 81.8; H, 7.8%; δ_{H} (90 MHz; CDCl₃; standard Me₄Si) 1.61 (6 H, s, 2 × Me), 3.25–3.45 (4 H, d, J 6.1, CH₂), 4.94 (2 H, s, 2 × OH), 4.98–5.22 (2 H, complex m, 2 × =CH₂), 5.75–6.25 (2 H, complex m, 2 × CH), 6.58–6.80 (2 H, d, J 9.1, 2 × Ar-H) and 6.83–7.08 (4 H, complex m, J 3.2, 4 × Ar-H).

2,2'-Dipropyl-4,4'-isopropylidenediphenol¹⁴ (4).—A solution of **3** (10.15 g, 0.03 mol) in chloroform (200 cm³) was hydrogenated using the procedure outlined for **2** (17.68 g, 87%), b.p. 458 K/0.2 mmHg (Found: C, 80.85; H, 8.9. Calc. for C₂₁H₂₈O₂: C, 80.7; H, 9.0%; δ_{H} (90 MHz; CDCl₃; standard Me₄Si) 0.85–1.00 (6 H, t, J 6.9, 2 × Me of Prⁿ), 1.39–1.80 (4 H, complex m, J 6.9, 2 × CH₂), 1.61 (6 H, s, 2 × Me), 2.44–2.61 (4 H, t, J 6.9, 2 × CH₂-Ar), 4.53 (2 H, s, 2 × OH), 6.59–6.66 (2 H, d, J 6.3, Ar-H), 6.86–6.89 (2 H, d, J 2.3, 2 × Ar-H) and 6.93–6.96 (2 H, d, J 2.3, 2 × Ar-H).

2,2-Bis(2,3-dihydroxypropyl)-4,4'-isopropylidenediphenol (5).—To a solution of **3** (10.15 g, 0.03 mol) in dichloromethane (75 cm³) was added a solution of *m*-chloroperoxybenzoic acid (11.78 g, 0.07 mol) in dichloromethane (120 cm³) whilst maintaining a temperature of 298 K, with cooling as required. The solution was refluxed at 333 K for 12 h, after which it was cooled to room temperature and the excess acid neutralised by addition of 10% aqueous sodium sulphite. The organic phase was separated and successively washed with 5% aqueous sodium hydrogen carbonate, water, and saturated aqueous sodium chloride before being dried and concentrated on a rotary evaporator. To this crude intermediate epoxide (29.65 g) was added aqueous sodium hydroxide (500 cm³, 1.0 mol dm⁻³) and the resulting mixture was refluxed at 373 K for 24 h. Neutralisation by concentrated sulphuric acid precipitated a brown oil which was extracted with a minimum of 96% ethanol, precipitated into vigorously stirred light petroleum (b.p. 60–80 °C), and stirred overnight. The light petroleum was removed by distillation and the residue dried to yield a brown viscous liquid which became a near-glass at room temperature (3.66 g, 30%) (Found: C, 68.8; H, 7.1. Calc. for C₂₁H₂₈O₆: C, 67.0; H, 7.5%; δ_{H} (90 MHz; CD₃OD; standard Me₄Si) 1.58 (6 H, s,

2 × Me + solvent), 2.05–2.16 (4 H, d, J 9.95, 2 × CH₂-Ar), 2.93–3.32 (2 H, complex m, J 9.95, 2 × CH), 3.3 (obscured by solvent) (2 H, s, CH-OH), 3.64–3.69 (4 H, d, J 4.98, 2 × CH₂), 4.8 (obscured by solvent) (2 H, s, 2 × CH₂-OH), 6.53–6.63 (2 H, d, J 8.78, 2 × Ar-H) and 6.91–7.00 (4 H, 2 × d, J 7.61, 4 × Ar-H).

2,2-Bis(4-allyloxyphenyl)hexafluoropropane (6).—To a mixture of 2,2-bis(phenyl)hexafluoropropane (33.6 g, 0.08 mol), distilled water (150 cm³) and sodium hydroxide (12 g) was added tetramethylammonium bromide (1 g) and, slowly, allyl bromide (36.3 g, 0.30 mol). The resulting two-phase solution was reacted at 323–333 K for 20 h until a neutral solution was obtained, then filtered and the toluene removed on a rotary evaporator. The residue was extracted with diethyl ether (50 cm³) and washed with distilled water (2 × 100 cm³). The organic layers were combined, dried, and the ether removed by distillation. The residue, an opaque, viscous oil was rigorously dried (35.51 g, 86%) (Found: C, 60.4; H, 4.4. Calc. for C₂₁H₁₈O₂F₆: C, 60.6; H, 4.4%; δ_{H} (60 MHz; [D₂O]₆]DMSO; standard Me₄Si) 4.45–4.75 (4 H, dd, J 4.8, 2 × CH₂-O), 5.1–5.6 (4 H, complex m, 2 × =CH₂), 5.7–6.4 (2 H, complex m, 2 × CH) and 6.85–7.45 (8 H, 2 × d, J 13.2, 8 × Ar-H).

2,2-Bis(4-propoxyphenyl)hexafluoropropane¹⁴ (7).—A solution of **6** (3 g, 0.01 mol) and chloroform (200 cm³) was hydrogenated in the manner described previously with 5% palladium on charcoal catalyst (0.5 g) for 5 h, filtered, concentrated on a rotary evaporator, and rigorously dried (2.97 g, 98%) (Found: C, 60.15; H, 5.5. Calc. for C₂₁H₂₂O₂F₆: C, 60.0; H, 5.3%; δ_{H} (60 MHz; CDCl₃; standard Me₄Si) 0.8–1.2 (6 H, t, J 6.6, 2 × Me), 1.4–2.15 (4 H, complex m, J 6, 2 × CH₂), 3.7–4.1 (4 H, t, J 4.5, 2 × CH₂-O), 7.05–7.4 (4 H, d, J 9, 4 × Ar-H) and 6.6–7.0 (4 H, dd, J 9, 4 × Ar-H).

2,2-Bis(3-allyl-4-hydroxyphenyl)hexafluoropropane (8).—Compound **6** (7.05 g, 0.02 mol) was heated at 473–478 K for 24 h and distilled under reduced pressure to yield a straw-coloured viscous oil (6.6 g, 88%) (Found: C, 60.4; H, 4.4. Calc. for C₂₁H₁₈O₂F₆: C, 60.6; H, 4.4%; δ_{H} (60 MHz; CDCl₃; standard Me₄Si) 3.2–3.5 (4 H, d, J 6, 2 × CH₂-Ar), 4.8–5.5 (4 H, complex m, 2 × =CH₂), 5.2 (2 H, s, 2 × OH), 5.5–6.3 (2 H, complex m, 2 × CH), 6.7–6.85 (2 H, dd, J 12, 2 × Ar-H) and 6.9–7.25 (4 H, complex m, 4 × Ar-H).

2,2-Bis(4-hydroxy-3-propylphenyl)hexafluoropropane (9).—A solution of **8** (6 g, 0.01 mol) and chloroform (500 cm³) was hydrogenated in the usual manner using a 5% palladium on charcoal catalyst (0.5 g) for 3.5 h, filtered, concentrated on the rotary evaporator, and rigorously dried to yield an opaque, viscous oil (5.82 g, 96%) (Found: C, 59.7; H, 5.3. Calc. for C₂₁H₂₂O₂F₆: C, 60.0; H, 5.3%; δ_{H} (300 MHz; CDCl₃; standard Me₄Si) 0.87–0.92 (6 H, t, J 2.4, 2 × Me), 1.54–1.62 (4 H, complex m, J 2.5, 2 × CH₂), 2.52–2.57 (4 H, t, J 2.5, 2 × CH₂-Ar), 5.30 (2 H, s, OH), 6.71–6.75 (2 H, d, J 2.8, 2 × Ar-H) and 7.12–7.15 (4 H, 2 d, J 3, 4 × Ar-H).

Bis(3-allyl-4-hydroxyphenyl)sulphone¹¹ (10).—To a mixture of 4,4'-sulphonyldiphenol (25 g, 0.1 mol), toluene (150 cm³), sodium hydroxide (12 g) and distilled water (150 cm³) was added tetramethylammonium bromide (1 g) and, slowly, allyl bromide (36.3 g, 0.30 mol). The resulting two-phase solution was reacted at 323–333 K for 15 h until a neutral solution was obtained and the toluene was removed by steam distillation to yield a white solid, the bis(allyl ether) (m.p. 416–418 K). A solution of this bis(allyl ether) (15 g, 0.05 mol) in octan-1-ol (50 cm³) was heated at 481 K for 30 h to undergo the Claisen rearrangement. After conclusion of the rearrangement, the

phenolic product was extracted with an aqueous solution of 48% (w/w) sodium hydroxide (50 cm³), treated with activated charcoal, and neutralised using dilute hydrochloric acid to produce a tan-coloured solid. The crude **10** was recrystallised twice (ethanol-water, 50:50) to produce white needles (12.75 g, 85%) (Found: C, 65.4; H, 5.3. Calc. for C₁₈H₁₈O₄S: C, 65.43; H, 5.49%); δ_{H} (60 MHz; [²H₆]DMSO; standard Me₄Si) 3.15–3.40 (4 H, d, *J* 6.0, 2 × CH₂), 4.75–5.20 (4 H, complex m,

2 × =CH₂), 5.5–6.2 (2 H, complex m, 2 × CH), 6.75–7.10 (2 H, d, *J* 3.0, 2 × Ar-H), 7.30–7.55 (2 H, dd, *J* 3.0, 2 × Ar-H), 7.55–7.70 (2 H, dd, *J* 12.0, 2 × Ar-H) and 10.45 (2 H, s, 2 × OH).

4,4'-Thiodiphenol Diallyl Ether (11).—To a mixture of 4,4'-thiodiphenol (80.59 g, 0.26 mol), toluene (600 cm³), and sodium hydroxide (48 g), were added tetramethylammonium bromide (4 g), and, slowly, allyl bromide (14.52 g, 0.12 mol). The resulting mixture was reacted at 323–333 K under nitrogen for 20 h before being filtered, the organic phase separated, and the toluene removed by distillation. The residue was extracted with diethyl ether, washed with dilute hydrochloric acid, and distilled water until the washings were neutral. The diethyl ether was removed on a rotary evaporator, and the product, an amber oil, rigorously dried (88.14 g, 80%) (Found: C, 72.2; H, 6.3. Calc. for C₁₈H₁₈O₂S: C, 72.5; H, 6.1%); δ_{H} (60 MHz; CDCl₃; standard Me₄Si) 4.25–4.55 (4 H, dd, *J* 6, 2 × CH₂-Ar), 4.7–5.5 (4 H, complex m, 2 × =CH₂), 5.5–6.4 (2 H, complex m, 2 × CH), 6.5–6.8 (4 H, dd, *J* 10.5, 4 × Ar-H) and 7.05–7.3 (4 H, dd, *J* 10.5, 4 × Ar-H).

2,2'-Diallyl-4,4'-isopropylidenediphenol Diallyl Ether (12).—To a solution of **3** (51 g, 0.165 mol), sodium hydroxide (14 g, 0.34 mol) and propan-1-ol (500 cm³) was slowly added allyl bromide (35.04 cm³, 0.405 mol). After being refluxed under nitrogen for 30 h the cool, neutral solution was filtered and concentrated on a rotary evaporator. The residue was extracted with dichloromethane (200 cm³), washed well with water, and rigorously dried. The dichloromethane was removed by distillation to yield an amber oil (54.49 g, 85%) (Found: C, 83.3; H, 8.3. Calc. for C₂₇H₃₂O₂: C, 83.5; H, 8.3%); δ_{H} (300 MHz; CDCl₃; standard Me₄Si) 1.61 (6 H, s, 2 × Me), 3.35–3.37 (4 H, d, 2 × CH₂-Ar), 4.42–4.45 (4 H, d, 2 × CH₂-O), 4.94–5.03 (4 H, complex m, 2 × =CH₂), 5.17–5.40 (4 H, 2 d, 2 × =CH₂), 5.91–6.03 (4 H, complex m, 4 × CH), 6.66–6.78 (2 H, dd, 2 × Ar-H) and 6.91–7.12 (4 H, 2 dd, 4 × Ar-H).

2,2',6,6'-Tetrallyl-4,4'-isopropylidenediphenol (13).—Ether **11** (8.47 g, 0.02 mol) was refluxed under nitrogen at 473 K for 5 h to undergo the Claisen rearrangement. The phenolic product was rigorously dried to yield a viscous amber oil (7.62 g, 90%) (Found: C, 83.2; H, 8.3. Calc. for C₂₇H₃₂O₂: C, 83.5; H, 8.3%); δ_{H} (300 MHz; CDCl₃; standard Me₄Si) 1.60 (6 H, s, 2 × Me), 3.31–3.33 (8 H, d, *J* 2.1, 4 × CH₂), ≈5 (obscured) (2 H, s, 2 × OH), 5.04–5.10 (8 H, complex m, 4 × =CH₂), 5.88–5.99 (4 H, complex m, 4 × CH) and 6.85 (4 H, s, 4 × Ar-H).

Density Measurements.—All of the liquid stationary phases that required density determination (compounds **14** and **15** are well documented) are quite viscous materials; several are indeed

Table 1 Physical characteristics of stationary phases

Compound	<i>M_r</i>	$\rho^a/\text{g cm}^{-3}$	B.p. (mmHg)/K	M.p./K
1	308.42	1.022 ^b	493.2 (0.05)	—
2	312.45	1.109 ^b	463.2–493.2 (0.01)	—
3	308.42	1.078 ^b	463.2 (0.5)	—
4	312.45	1.060 ^b	458.2 (0.2)	—
5	376.45	solid	—	458.2
6	416.37	1.332 ^b	—	—
7	420.39	1.445 ^b	403.2 (0.025)	—
8	416.37	1.405 ^b	—	—
9	420.39	1.382 ^b	458.2 (0.015)	—
10	330.41	solid	—	(416.2–418.2)
11	298.41	1.194 ^b	—	—
12	388.55	1.111 ^b	—	—
13	388.55	1.144 ^b	—	—
14	150.21	0.978 ^c	521.2 (760) ^d	—
15	122.17	1.001 ^c	491.2–492.2 (760) ^d	—

^a Density of stationary phase at 298.2 K. ^b Density determined using bulb with calibrated stem. ^c Density taken as supplied. ^d Source: *Catalogue Handbook of Fine Chemicals*, Aldrich Chemical Co., 1986–1987.

Table 2 Stationary phases used in the GLC experiments

	Loading (%)	Support ^a	<i>T</i> /K
1	10.50	Chrom. 750	298.2
2	14.65	Chrom. 750	298.2
3	10.02	Chrom. 750	298.2
4	10.12	Chrom. 750	298.2
5	9.96	Chrom. 750	298.2
6	13.00	Chrom. WHP	298.2
7	12.00	Chrom. WHP	298.2
8	11.30	Chrom. 750	298.2
9	10.56	Chrom. WHP	298.2
10	11.00	Chrom. WHP	448.2
11	11.00	Chrom. WHP	298.2
12	11.10	Chrom. WHP	298.2
13	15.00	Chrom. WHP	298.2
14	10.20	Chrom. 750	298.2
15	11.49	Chrom. DMCS	298.2

^a Mesh size was always 60–80 BS.

Table 3 Absolute log *L* values for alkanes at 298 K

Alkane	1	2	3	4	6	7	8	9	10^a	11	12	13	14	15
C5	1.410	2.323	—	—	—	1.822	—	—	—	1.767	2.345	—	1.647	—
C6	1.974	2.827	—	—	—	2.345	—	—	—	2.345	2.854	1.763	2.136	—
C7	2.467	3.338	1.006	—	2.454	2.853	2.126	1.972	—	2.810	3.336	2.255	2.619	—
C8	2.920	3.820	1.544	1.067	2.902	3.366	2.544	2.496	—	3.270	3.795	2.760	3.119	2.231
C9	3.420	4.304	2.072	1.649	3.371	3.867	3.005	3.026	—	3.748	4.266	3.231	3.550	2.689
C10	3.883	4.824	2.628	2.189	3.788	—	3.454	3.425	—	—	—	3.703	3.950	3.137
C11	—	—	3.089	2.819	4.186	—	3.912	3.890	—	—	—	—	4.280	3.557
C12	—	—	3.565	3.404	—	—	—	—	—	—	—	—	—	4.013
C13	—	—	4.064	3.962	—	—	—	—	1.029	—	—	—	—	—
C14	—	—	—	—	—	—	—	—	1.258	—	—	—	—	—
C16	—	—	—	—	—	—	—	—	1.652	—	—	—	—	—
C18	—	—	—	—	—	—	—	—	2.038	—	—	—	—	—
C20	—	—	—	—	—	—	—	—	2.401	—	—	—	—	—
C22	—	—	—	—	—	—	—	—	2.782	—	—	—	—	—

^a Measurements taken at 448 K.

Table 4 Log *L* values for solutes at 298 K

Solute	1	2	3	4	6	7	8	9	10 ^a	11	12	13	14	15
2,2,4-Trimethylpentane	2.400	3.247	—	—	2.359	2.857	—	1.729	—	2.654	3.227	1.929	2.578	1.687
Cyclohexane	2.384	3.236	—	—	2.315	2.754	2.130	1.795	—	2.694	3.248	2.147	2.494	1.699
Dichloromethane	2.366	2.967	—	—	2.089	2.393	1.890	1.871	—	2.677	2.972	2.098	2.167	1.549
Trichloromethane	2.696	3.404	—	—	2.419	2.775	2.064	2.107	—	3.029	3.402	2.493	2.562	1.930
Tetrachloromethane	2.649	3.397	—	—	2.463	2.866	2.160	2.126	—	2.942	3.446	2.422	2.621	1.908
1,2-Dichloroethane	2.928	3.608	1.862	0.859	2.655	2.992	2.604	2.499	—	3.258	3.599	2.760	2.832	2.204
2-Chloro-2-methylpropane	2.046	2.766	—	—	2.025	2.406	—	1.649	—	2.455	2.826	1.739	2.136	1.454
Benzene	2.832	3.533	1.655	0.589	—	3.063	2.513	2.545	—	3.156	3.549	2.684	2.771	2.079
Toluene	3.313	4.040	2.225	1.266	3.157	3.597	3.100	3.161	—	3.654	4.039	3.179	3.269	2.564
Butylbenzene	—	—	—	—	—	—	—	—	1.183	—	—	—	—	—
Chlorobenzene	3.733	4.480	2.750	1.758	3.522	3.971	3.472	3.501	—	4.101	4.441	3.590	3.656	2.966
Diethyl ether	—	2.741	1.707	0.589	—	—	—	—	—	—	—	—	3.118	—
Anisole	—	—	—	2.570	—	—	—	—	1.344	—	—	—	4.247	—
Propan-2-one	2.507	3.018	2.479	1.452	2.585	2.825	4.039	4.232	—	2.997	2.876	2.711	3.580	2.986
Butan-2-one	2.932	3.540	2.895	1.915	3.016	3.294	4.452	4.732	—	3.460	3.364	3.151	3.979	3.389
Pentan-2-one	—	—	3.322	2.405	—	—	—	—	1.582	—	—	—	—	—
Octan-2-one	—	—	—	—	—	—	—	—	2.170	—	—	—	—	—
Nonan-2-one	—	—	—	—	—	—	—	—	2.015	—	—	—	—	—
Decan-2-one	—	—	—	—	—	—	—	—	2.197	—	—	—	—	—
Methyl formate	1.859	—	—	—	1.951	2.141	2.661	—	—	2.241	2.454	1.983	2.379	1.809
Ethyl formate	—	—	1.905	0.830	—	—	—	—	—	—	—	—	—	—
Methyl acetate	2.458	3.057	2.283	1.209	2.579	2.770	3.735	—	—	2.930	3.002	2.672	3.171	2.672
Ethyl acetate	—	—	2.577	1.830	—	—	—	—	—	—	—	—	—	—
Propyl acetate	—	—	3.242	2.448	—	—	—	—	—	—	—	—	—	—
Ethyl propanoate	—	—	3.115	2.353	—	—	—	—	—	—	—	—	—	—
Methyl pentanoate	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Acetonitrile	2.644	3.110	2.417	—	2.610	2.748	—	—	—	3.051	—	—	3.303	—
Benzonitrile	—	—	—	—	—	—	—	—	2.102	—	—	—	—	—
Ethylamine	—	—	1.748	—	—	—	4.035	—	—	—	—	—	—	—
Propylamine	2.537	—	—	—	—	—	—	—	2.167	—	—	—	—	—
Triethylamine	—	—	—	—	3.573	—	—	—	—	—	—	—	—	—
Aniline	—	—	—	—	—	—	—	—	2.453	—	—	—	—	—
4-Methylpyridine	—	—	—	—	—	—	—	—	2.700	—	4.887	—	4.580	—
Nitromethane	3.041	—	—	—	—	—	—	—	—	—	—	—	—	—
Nitroethane	3.381	3.805	—	—	3.214	3.399	3.655	3.807	—	3.685	—	3.130	—	—
Methanol	1.997	2.605	2.123	0.982	1.951	2.224	3.184	3.258	—	2.602	2.319	2.279	2.983	2.596
Ethanol	2.342	3.000	2.485	1.548	2.338	2.552	3.597	3.782	—	2.976	2.664	2.624	3.411	3.025
Propan-1-ol	2.877	3.501	2.992	2.042	2.792	3.046	4.115	4.286	—	3.439	3.181	3.088	3.816	3.483
Propan-2-ol	2.571	3.178	2.659	1.617	2.525	—	3.997	—	—	3.111	2.876	2.746	—	3.253
Butan-1-ol	3.338	4.025	3.591	2.691	3.294	3.594	4.459	4.787	1.687	3.957	3.671	3.583	4.214	3.952
Butan-2-ol	2.989	3.657	3.114	2.135	2.967	—	4.499	—	—	3.577	3.358	3.220	—	3.656
<i>tert</i> -Butyl alcohol	—	3.284	—	—	2.666	2.948	—	4.101	—	3.210	2.959	2.795	—	3.346
Pentan-1-ol	—	4.544	3.708	3.311	3.753	4.087	4.859	5.287	1.912	4.470	4.174	4.084	4.625	4.400
Hexan-1-ol	—	—	4.301	3.891	—	—	—	—	—	—	—	—	—	—
Heptan-1-ol	—	—	—	—	—	—	—	—	2.323	—	—	—	—	—
Octan-1-ol	—	—	—	—	—	—	—	—	2.512	—	—	—	—	—
2,2,2-Trifluoroethanol	2.157	2.873	—	1.155	2.178	2.309	2.238	2.075	—	2.639	2.634	2.003	2.464	2.046
Hexafluoroisopropanol	2.458	3.241	—	—	2.644	2.688	2.130	1.515	—	2.924	2.872	2.154	2.975	2.116
Prop-2-en-1-ol	—	—	—	—	—	—	3.874	—	—	—	—	—	—	—

^a At 448 K.

very viscous. This precluded the use of a density bottle or a pycnometer tube. Instead, the densities of the materials were measured by using a glass bulb (5 cm³) with a calibrated vertical stem (15 cm). The bulb was weighed before and after careful addition of each liquid and left for some time in a thermostatted bath at various temperatures. The level to which the meniscus rose was noted on the calibrated stem at each temperature. After thorough cleaning of the density bulb (with methanol and chloroform) and drying, doubly-distilled deionised water was carefully added with a dropping pipette, and the density bulb replaced in the thermostatted bath. At each temperature previously used to measure the level of the stationary phase meniscus the level of the water meniscus was adjusted to that of the stationary phase by addition or removal by pipette. At each temperature the density bulb was removed from the thermostatted bath sealed with a rubber cap, the external surface thoroughly cleaned and dried, and the density bulb (containing water) weighed. Using the known density of water at each temperature¹⁵ the volume of the stationary phase (and hence

its density) was calculated from the known weight in the density bulb. To reduce possible errors, the stem of the density bulb was filled quite high up (whilst allowing for expansion at higher temperatures) and as large a bulb as possible was used (within the restriction of limited quantities of compound available). Results are in Table 1.

Gas-Liquid Chromatography.—Gas partition coefficients (*L* or *K*) were obtained using the methodology described before.¹⁶ The stationary phase loadings and the inert supports used are given in Table 2. The instrument used was a Perkin-Elmer F11, equipped with a liquid thermostat bath (± 0.05 K) and Negretti and Zambra flow controllers. Flow rates were obtained by extinguishing the flame and attaching the outlet nitrogen gas to a soap bubble meter. Whilst this is not as satisfactory as using a thermal conductivity meter, it sufficed for the present purpose. Absolute values of log *L* were determined for alkanes, Table 3, and log *L* values for various other solutes were then obtained from relative retention values, Table 4. The absolute values were

Table 5 Regression analysis of the log *K* values at 298 K using eqn. (3)^a

Phase	<i>c</i>	<i>r</i>	<i>s</i>	<i>a</i>	<i>b</i>	<i>l</i>	<i>n</i> ^b	<i>R</i> ^c	SD ^d
1	-0.51	-0.07	1.36	1.21	0.83	0.931	32	0.9934	0.02
	0.08	0.08	0.06	0.06	0.07	0.022			
2	0.26	-0.01	0.99	1.39	0.70	0.967	32	0.9984	0.04
	0.04	0.04	0.03	0.04	0.03	0.011			
3	-2.00	-0.92	2.24	2.79	2.41	0.975	30	0.9891	0.13
	0.16	0.18	0.17	0.21	0.21	0.032			
4	-3.36	-1.20	1.88	2.84	2.86	1.186	29	0.9931	0.12
	0.16	0.14	0.17	0.16	0.17	0.031			
6	-0.34	-0.46	1.22	1.06	1.16	0.882	31	0.9963	0.05
	0.06	0.06	0.05	0.06	0.05	0.016			
7	-0.16	-0.23	1.01	1.04	1.14	0.956	29	0.9963	0.05
	0.06	0.06	0.05	0.06	0.06	0.018			
8	-0.58	-0.48	1.04	0.89	4.56	0.863	27	0.9937	0.11
	0.14	0.12	0.12	0.13	0.12	0.034			
9	-1.21	-0.38	1.38	0.71	5.31	0.984	28	0.9887	0.18
	0.23	0.22	0.20	0.25	0.19	0.057			
10 ^e	-1.09	0.53	(0)	0.59	3.27	0.353	20	0.9031	0.24
	0.39	0.22		0.41	0.45	0.047			
11	-0.18	0.00	1.18	1.50	1.33	0.931	31	0.9946	0.07
	0.07	0.08	0.06	0.07	0.06	0.022			
12	0.39	0.08	1.01	0.82	0.36	0.923	31	0.9968	0.05
	0.06	0.06	0.06	0.06	0.05	0.018			
13	-0.75	0.07	1.14	1.28	1.89	0.934	30	0.9890	0.10
	0.11	0.11	0.10	0.11	0.10	0.032			
14	-0.06	-0.56	0.91	1.40	2.76	0.846	32	0.9862	0.14
	0.12	0.15	0.16	0.15	0.15	0.034			
15	-1.08	-0.20	0.87	1.80	3.42	0.899	29	0.9924	0.11
	0.13	0.13	0.14	0.13	0.11	0.031			

^a Second row for each phase represents standard deviations in the constants. ^b Number of solutes used. ^c Overall correlation coefficient. ^d Overall standard deviation. ^e At 448 K.

corrected for the pressure drop across the column¹⁶ and for gas imperfections,¹⁶ but the latter were trivial. Values of *L* were obtained from V_G using the equation $L = V_G \rho$ where ρ is the stationary phase density at the column temperature.

Discussion

Thirteen materials have been prepared and tested. Of these, compounds **3**, **4**, **8**, **9** and **13** are phenols that are liquid at room temperature and which are therefore possible hydrogen bond acidic phases for use as coatings. We also include two simple phenols, **14** and **15**, for purposes of comparison. The non-acidic compounds are of unusual structure as regards GLC stationary phases, and so we tested these liquids as well (compounds **1**, **2**, **6**, **7**, **11** and **12**). Compounds **5** and **10** are solid at room temperature. We examined **5** briefly, but since it did not exhibit any remarkably strong acidic behaviour we did not pursue this further. Compound **10** was tested at 448 K, *ca.* 30 K above its m.p., as we felt that it might prove to be a useful GLC stationary phase. The corresponding bis(3-propyl) compound would have been even more interesting, but we were unable to hydrogenate **10** to the bis(3-propyl) derivative.

The solute parameters used in this work were taken from our previous compilation,¹⁰ except for some log L ¹⁶ values that were listed before.^{7,8,16} Summaries of the regression equations based on eqn. (3) are given in Table 5. These regression

equations are nearly all reasonably good, and enable phases to be selected for possible use in SAW devices, as well as allowing the calculation of solute-solvent interaction energies.

The two phenols derived from bisphenol-A, **3** and **4**, have quite an affinity for solute hydrogen bond bases, with *b* constants of 2.4 and 2.9, respectively. These are, however, no more than the *b* constants for the simple phenols **14** and **15**, *viz.* 2.8 and 3.4 units. However, **3** and **4** both have very large *l* constants and hence will separate adjacent members of an homologous series much better than will **14** or **15**, which might be an advantage. The two most acidic liquid phases we have succeeded in making are the fluorinated phenols **8** and **9** with very large *b* constants of 4.6 and 5.3, respectively. Furthermore, both **8** and **9** have rather small *a* constants and so will be very selective towards solutes that are hydrogen bond bases. Since both **8** and **9** have quite large *l* constants, these two phases could prove very useful as coating materials in chemical sensors, phase **9** pure and phase **8** possibly as a copolymer. Hence we have succeeded in one of our main aims, namely to devise an involatile liquid phase with a high hydrogen bond acidity, that will selectively absorb challenge vapours that are hydrogen bond bases.

Of the other phases that we have tested, only **10** has any outstanding characteristics that might be utilised in any way. Although **10** is a solid at room temperature, we found that it is a very strong hydrogen bond acid above its m.p., *i.e.* at 448 K.

Table 6 A breakdown of $\log K$ values for some solutes with phases **9**, **15** and DMF, using the solvation eqn. (3)

Phase	c	rR_2	$s\pi_2^H$	$\alpha\alpha_2^H$	$b\beta_2^H$	$l \log L^{16}$	
						Disp. ^a	Cavity ^a
Solute: butan-2-one							
9	-1.21	-0.06	0.97	0.00	2.71	5.35	-3.10
15	-1.08	-0.03	0.61	0.00	1.74	4.90	-2.84
DMF	-0.24	0.01	1.58	0.00	0.00	4.50	-2.61
Solute: butan-1-ol							
9	-1.21	-0.09	0.58	0.26	2.55	5.69	-3.13
15	-1.08	-0.04	0.37	0.67	1.64	5.20	-2.86
DMF	-0.24	0.02	0.95	1.61	0.00	4.78	-2.63
Solute: 1,2-dichloroethane							
9	-1.21	-0.15	0.88	0.07	0.58	5.07	-2.54
15	-1.08	-0.08	0.56	0.18	0.38	4.63	-2.32
DMF	-0.24	0.03	1.45	0.44	0.00	4.27	-2.14

^a These have been calculated as in ref. 17, so that they total the $l \log L^{16}$ term.

Now since the hydrogen bond constants a and b usually decrease markedly with temperature, the observed b constant of 3.3 at 448 K might well correspond to a hydrogen bond acidity even larger than those of **8** or **9** at 298 K. Certainly, **10** (or derivatives of **10**) might be a useful addition to the complement of GLC stationary phases, bearing in mind that no strongly acidic phase is commercially available. Unfortunately, we were unable to hydrogenate **10** to the corresponding propyl derivative.

It is of some interest to compare the magnitude of solute-solvent interactions involving the phenolic compounds we have studied with those for other types of solvent. We have previously⁸ analysed solute-solvent interactions for a number of amides at 298 K, but since the solvation equation that we used included our old π_2^H parameter rather than the new π_2^H , we have re-determined the solvation equation for *N,N*-dimethylformamide (DMF) as an example [eqn. (4)]. In Table

$$\log K (\text{DMF}) = -0.24 + 0.08R_2 + 2.26\pi_2^H + 4.36\alpha_2^H + 0.827 \log L^{16}$$

$$n = 55 \quad R = 0.9929 \quad \text{SD} = 0.159 \quad (4)$$

6 we set out a term by term analysis of $\log K$ values for three typical solutes in phases **9** and **15**, and also in DMF. We can dissect the $l \log L^{16}$ term into a general dispersion interaction term and a cavity term using the analysis of Abraham and Fuchs.¹⁷ Although only approximate, in that the relative proportions are taken as being the same in the solvent hexadecane at 298 K, this dissection will still allow a comparison to be made of the relative importance of polar and hydrogen bond terms, with general dispersion interactions. In all cases, as we have found before,⁸ the dispersion interaction term makes a much larger positive contribution to $\log K$ than do any of the other interaction terms.

With a solute such as butan-2-one ($\pi_2^H = 0.70$, $\alpha_2^H = 0$ and $\beta_2^H = 0.51$)¹⁰ there are significant dipolar interactions with all three phases, and large hydrogen bond interactions with the phenolic solvents of type solute base-solvent acid. The

solute butan-1-ol is interesting, as it has both hydrogen bond acidity and basicity ($\pi_2^H = 0.42$, $\alpha_2^H = 0.37$ and $\beta_2^H = 0.48$). With the phenolic solvents, interactions of the type solute base-solvent acid are much larger than those involving solute acid-solvent base. With DMF only the latter can take place giving rise to a large $\alpha\alpha_2^H$ term. Of course, with a solute such as 1,2-dichloroethane, dipole/dipole effects are larger than any hydrogen bond interactions simply because both α_2^H and β_2^H are small ($\pi_2^H = 0.64$, $\alpha_2^H = 0.10$ and $\beta_2^H = 0.11$).¹⁰

Our method of analysis of $\log K$ values through the solvation eqn. (3) is therefore not only of value in the selection of phases for chemical sensors or for other particular uses, but also results in a better understanding of the mode of action of such phases through the determination of individual solute-solvent interaction terms.

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