Piezoelectric Quartz Crystal Detection of Benzene Vapour using Chemically Modified Cyclodextrins

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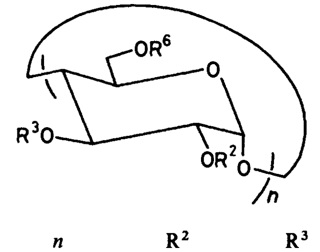
Three chemically modified cyclodextrins have been prepared, characterised by n.m.r. spectroscopy, and studied for their possible rôle as piezoelectric crystal coating detectors towards benzene vapour. 2,6-Per-*O*-methyl-β-cyclodextrin 3-perbenzoate (DMβCD-B_7) is not recommended. 2,6-Per-*O*-(t-butyldimethylsilyl)-α-cyclodextrin (DSαCD) was found to be the best for the *ca.* 0.08—*ca.* 400 mg dm^{-3} range of benzene vapour in air. 2,6-Per-*O*-allyl-α-cyclodextrin (DAαCD) is a possible alternative. Both detector systems function for >20 days. The detectors are selective towards benzene vapour over methane, propane, butane, pentane, ethyne, ammonia, nitrobenzene, and toluene. Toluene gives rise to the most serious interference. For the preferred DSαCD sensor, toluene only gives <20% of the decrease in frequency observed with the corresponding amount of benzene. However, the interference is slightly greater for the DAαCD sensor.

The use of piezoelectric crystals as sorption detectors, in which the crystal is coated with a substrate that will react with or adsorb the material of interest, forms the basis of a highly sensitive technique for the detection of trace amounts of gases and vapours.[1,2] In view of their common occurrence and toxicological concern, the method has been explored for aromatic hydrocarbons. Thus, Karmarkar and Guilbault[3] found a piezoelectric crystal coated with a Nujol–*trans*-chlorocarbonylbis(triphenylphosphine)iridium(I) mixture to be more reactive towards aromatic than towards aliphatic hydrocarbons. 1,3,5-Trimethylbenzene, xylenes, butylbenzene, anisole, and benzaldehyde could all be detected with ease, while hexane, heptane, octane, and cyclohexane could only be detected at high concentrations.[3] Also noteworthy is the fact that toluene in ambient air has been monitored[4] with a portable device based on a piezoelectric quartz crystal coating of Carbowax 550. This coating gave a linear response over the range 30—300 p.p.m. with a reproducibility of >4%. The response time was 30 s and complete reversibility was obtained in <40 s. No interferences were observed from inorganic gases such as carbon monoxide, sulphur dioxide, ammonia, or nitrogen dioxide at 1000 p.p.m. Organic vapours caused some interference but were insignificant at the 5% v/v level. Interference from moisture was eliminated using Nafion tubing. In addition, Edmonds and West,[5] who examined the behaviour of various coatings on 9 MHz AT-cut quartz crystals to chloroform and toluene with regard to various parameters, have reported that Pluronics 64 (a g.l.c. stationary phase material) is the most sensitive coating for ethylbenzene, *o*-xylene, and hexane.

The cyclodextrins are a family of naturally occurring sugars consisting of six or more D-glucose residues joined by α-1,4-linkages to give cyclic compounds. These torus-shaped molecules have been shown[6] to behave as molecular receptors towards a wide variety of guest species, particularly aromatic and aliphatic hydrocarbons, both in aqueous solution and in the solid state. The poor solubility of cyclodextrins in organic solvents has led to a great deal of work being carried out on chemically modified derivatives and an extensive review on the subject has recently been published.[7] We have now prepared two highly lipophilic cyclodextrin derivatives, 2,6-per-*O*-(t-butyldimethylsilyl-α-cyclodextrin (DSαCD) and 2,6-per-*O*-allyl-α-cyclodextrin (DAαCD). In addition, we had already prepared 2,6-per-*O*-methyl-β-cyclodextrin 3-perbenzoate (DMβCD-B_7) as an intermediate in the purification[8] of DMβCD. This paper describes the piezoelectric behaviour of benzene on interaction with these three chemically modified cyclodextrins coated on 9 MHz AT-cut quartz crystals.



	n	R^2	R^3	R^6
αCD	6	H	H	H
DSαCD	6	TBDMS	H	TBDMS
DAαCD	6	$CH_2CH{=}CH_2$	H	$CH_2CH{=}CH_2$
DMβCD	7	Me	H	Me
DMβCD-B_7	7	Me	PhCO	Me

Experimental

α-Cyclodextrin was purchased from Sigma and, where stated, was dried under high vacuum at 100 °C. t-Butyldimethylsilyl chloride and allyl bromide were purchased from Aldrich and used as received. Pyridine was used from a freshly opened bottle. Dimethylformamide and dimethyl sulphoxide were distilled before use. Column chromatography was performed on Silica gel 60 (Merck 9385). M.p.s were determined with a Reichert hot-stage apparatus and are uncorrected. Microanalyses were carried out by the University of Sheffield Microanalytical Service. Fast-atom bombardment mass spectrometry was performed on a Kratos MS 80 instrument. N.m.r. spectra were recorded on Bruker AM 250 and Bruker WH 400 spectrometers and referenced with respect to tetramethylsilane. The preparation of DMβCD-B_7 has been reported elsewhere.[8]

*2,6-Per-*O*-(t-butyldimethylsilyl)-α-cyclodextrin (DSαCD).*— To a solution of α-cyclodextrin (dry; 3.00 g, 3.1 mmol) in dry DMF (50 ml) and pyridine (10 ml) under nitrogen, t-butyldimethylsilyl chloride (9.0 g, 59.7 mmol, *ca.* 20 equiv.) was added. This mixture was heated with stirring at *ca.* 100 °C for 18 h. After cooling, the solvents were removed under high vacuum. The residue was partitioned between water (150 ml) and hexane (150 ml). The organic phase was retained and washed with hydrochloric acid (0.5M, 150 ml) to remove any further pyridine and then with water (150 ml). After drying ($MgSO_4$) and filtration, the solvent was removed under reduced pressure to leave a powder. This was washed with methanol, air-dried, and finally dried under high vacuum at 80 °C for 6 h, and characterised as 2,6-*per*-O-(*t-butyldimethylsilyl*)-*α-cyclodextrin* (DSαCD) (7.08 g, 3.0 mmol, 97%), m.p. 254—256 °C (Found: C, 55.7; H, 10.0. $C_{108}H_{228}O_{30}Si_{12}$ requires C, 55.4; H, 9.7%); δ_H ($CDCl_3$; 400 MHz) 0.04 (36 H, 2 s, 6-OSiMe$_2$), 0.13 and 0.15 (36 H, 2 s, 2-OSiMe$_2$), 0.88 (54 H, s, 6-OSiBu^t), 0.91 (54 H, s, 2-OSiBu^t), 3.48 (6 H, dd, $J_{3,4}$ 9, $J_{4,5}$ 9 Hz, H-4), 3.55 (6 H, dd, $J_{1,2}$ 3, $J_{2,3}$ 9 Hz, H-2), 3.70 (6 H, dd, $J_{6,6'}$ 11.5, $J_{5,6'}$ 1.5 Hz, H-6′), 3.73 (6 H, m, H-5), 3.95 (6 H, dd, $J_{6,6'}$ 11.5, $J_{5,6}$ 3 Hz, H-6), 3.99 (6 H, dd, $J_{2,3}$ 9, $J_{3,4}$ 9 Hz, H-3), 4.38 (6 H, s, OH), and 4.79 (6 H, d, $J_{1,2}$ 3 Hz, H-1); δ_C($CDCl_3$; 63 MHz) −5.12 (6-OSiMe$_2$), −4.70 and −4.58 (2-OSiMe$_2$), 18.40 (6-OSi*C*Me$_3$), 18.84 (2-OSi*C*Me$_3$), 25.96 (6-OSiC*Me*$_3$), 26.23 (2-OSiC*Me*$_3$), 62.25 (C-6), 71.94 (C-5), 72.35 (C-3), 74.59 (C-2), 82.55 (C-4), and 102.63 p.p.m. (C-1).

2,6-*Per*-O-*allyl-α-cyclodextrin* (*DAαCD*).—A mixture of barium oxide (6 g, 40 mmol) and barium hydroxide octahydrate (6 g, 20 mmol) was added with stirring to a cooled (ice–water) solution of α-cyclodextrin (1.2 g, 1 mmol) in a mixture of dimethyl sulphoxide (30 ml) and dimethylformamide (30 ml). The suspension was stirred for 15 min and then allyl bromide (15 g, 125 mmol) was added. The mixture was stirred at room temperature for 48 h. Concentrated ammonia solution (25 ml) was added and the mixture was stirred for a further 30 min. Chloroform (100 ml) and hexane (100 ml) were then added and the organic layer was separated, washed with water (5 × 100 ml), and dried (Na_2SO_4). The solvents were removed under reduced pressure. The residue was purified by column chromatography on silica gel using chloroform–ethyl acetate (2:1 v/v) as eluant to give, after recrystallisation (cyclohexane) and drying (12 h, 120 °C, 0.1 mmHg), a crystalline solid (0.88 g, 61%) which was characterised as 2,6-*per*-O-*allyl-α-cyclodextrin* (DAαCD), m.p. >280 °C (Found: C, 59.7; H, 7.5. $C_{72}H_{108}O_{30}$ requires C, 59.5; H, 7.5%); *m/z* (negative ion f.a.b.), 1 451 $[M - H]^-$; δ_H($CDCl_3$; 400 MHz) 3.45 (6 H, dd, $J_{1,2}$ 3.4, $J_{2,3}$ 9.7 Hz, H-2), 3.55 (6 H, dd, $J_{3,4}$ 8.5, $J_{4,5}$ 9.8 Hz, H-4), 3.70 (12 H, d, $J_{5,6}$ 2.9 Hz, H-6), 3.86 (6 H, dt, $J_{4,5}$ 9.9, $J_{5,6}$ 2.8 Hz, H-5), 4.02 (6 H, Y of AMNXY system, $J_{A,Y}$ 6.1, $J_{M,Y}$ and $J_{N,Y}$ 1.3, $J_{X,Y}$ 12.7 Hz, 6-OCH$_X$*H*$_Y$CH$_A$=CH$_M$H$_N$), 4.06 (6 H, X of AMNXY system, $J_{A,X}$ 5.5, $J_{M,X}$ and $J_{N,X}$ 1.4, $J_{X,Y}$ 12.7 Hz, 6-OC*H*$_X$H$_Y$CH$_A$=CH$_M$H$_N$), 4.12 (6 H, dd, $J_{2,3}$ 9.6, $J_{3,4}$ 8.6 Hz, H-3), 4.22 (6 H, Y of AMNXY system, $J_{A,Y}$ 7.0, $J_{M,Y}$ and $J_{N,Y}$ 1.1, $J_{X,Y}$ 12.6 Hz, 2-OCH$_X$*H*$_Y$CH$_A$=CH$_M$H$_N$), 4.44 (6 H, X of AMNXY system, $J_{A,X}$ 5.4, $J_{M,X}$ and $J_{N,X}$ 1.4, $J_{X,Y}$ 12.6 Hz, 2-OC*H*$_X$H$_Y$CH$_A$= CH$_M$H$_N$), 4.72 (6 H, br s, OH), 4.91 (6 H, d, $J_{1,2}$ 3.5 Hz, H-1), 5.18 (6 H, N of AMNXY system, $J_{A,N}$ 10.3, $J_{M,N}$ 1.7, $J_{N,X}$ 1.4, $J_{N,Y}$ 1.3 Hz, 6-OCH$_X$H$_Y$CH$_A$=CH$_M$*H*$_N$), 5.21 (6 H, N of AMNXY system, $J_{A,N}$ 10.3, $J_{M,N}$ 1.5, $J_{N,X}$ 1.4, $J_{N,Y}$ 1.1 Hz, 2-OCH$_X$H$_Y$CH$_A$=CH$_M$*H*$_N$), 5.26 (6 H, M of AMNXY system, $J_{A,M}$ 17.2, $J_{M,N}$ 1.7, $J_{M,X}$ 1.4, $J_{M,Y}$ 1.3 Hz, 6-OCH$_X$H$_Y$CH$_A$= C*H*$_M$H$_N$), 5.29 (6 H, M of AMNXY system, $J_{A,M}$ 17.2, $J_{M,N}$ 1.5, $J_{M,X}$ 1.4, $J_{M,Y}$ 1.1 Hz, 2-OCH$_X$H$_Y$CH$_A$=C*H*$_M$H$_N$), and 5.93 (12 H, 2 × A of AMNXY systems, $J_{A,M}$ 17.2, $J_{A,N}$ 10.3, $J_{A,X}$ 5.4 and 5.5, $J_{A,Y}$ 7.0 and 6.1 Hz, 2- and 6-OCH$_X$H$_Y$C*H*$_A$=CH$_M$H$_N$); δ_C($CDCl_3$; 63 MHz; *J* modulation) 68.7 (C-6), 70.3 (C-5), 72.5 (6-O*C*H$_2$-CH=CH$_2$), 73.1 (2-O*C*H$_2$CH=CH$_2$), 73.6 (C-3), 78.6 (C-2), 83.4 (C-4), 101.4 (C-1), 117.2 (6-OCH$_2$CH=*C*H$_2$), 118.6 (2-OCH$_2$CH=*C*H$_2$), 134.1 (6-OCH$_2$*C*H=CH$_2$), and 134.7 p.p.m. (2-OCH$_2$*C*H=CH$_2$).

Apparatus and Detector Design.—The design of the apparatus and detector used are as previously reported.[9] The piezoelectric crystals were of the 9 MHz AT-cut quartz type with either gold-plated or silver-plated electrodes on both sides (Quartz Crystal Co., Wellington Crescent, New Malden, Surrey*). The crystal was powered by a Weir 400 power supply set at 9 V d.c. The frequency of the vibrating crystal was monitored by a Marconi Type 2431A 200 MHz digital frequency meter. A digital-to-analogue convertor selected the last two digits of the frequency meter output for conversion into an analogue signal to a Bryans model 28000 chart recorder, reading to ±1 Hz. The detector cell incorporating the crystal was based on the double impinger cell design of Karmarkar and Guilbault[10] wherein the gas sample was split into two streams impinging directly on opposite faces of the coated quartz crystal. The perspex-encased cell detector was kept at 25 °C.

Cyclodextrin Coatings.—Coating solutions were 4% (m/v) solutions of chemically modified cyclodextrins in acetone, except for DSαCD when dichloromethane or chloroform were used as solvent. Each of these solutions was brush-coated on the surfaces of the crystal and then dried in a dry air stream until the frequency reached a steady value. In each instance, the coating applied induced a decrease of *ca.* 20 kHz in the basic frequency of the crystal. This was readily removed with acetone or dichloromethane or chloroform as appropriate prior to recoating with fresh solutions.

Test Gas Samples.—Benzene and toluene vapour test samples were obtained with a 10 cm^3 glass syringe from headspaces equilibrated at 25 °C. The benzene and toluene concentrations in the headspace were calculated to be 396 and 144 mg dm^{-3}, respectively, from the equilibrium vapour pressure.[10] Serial dilutions of the headspace samples were made by syringe dilution[11] with dried ambient air (dry air gave ΔF 0 Hz) as described previously.[9] The interferent gases studied were obtained from Speciality Gases Ltd, Hudley House, Bilston. These gases were pure methane, 1.04% propane in air, 10.1% butane in nitrogen, 0.72% pentane, and 0.92% ethyne. Other interferent vapours studied were ammonia and nitrobenzene which were taken from the headspaces of 2M-ammonia solution and pure nitrobenzene, respectively.

Operation of Cyclodextrin-coated Piezoelectric Quartz Crystal Detection Apparatus.—The operation of the piezoelectric quartz crystal detection system is essentially a flow injection analysis involving the gas phase. Gas samples (1 cm^3) were injected into an air stream, dried by passing through silica gel, and carried through the quartz crystal cell at a rate of 20 cm^3 min^{-1} by a Pitman Instruments model 7069 air sampler pump. The cyclodextrin derivatives, when coated on piezoelectric crystals, showed an interaction with benzene corresponding to a decrease in the frequency of oscillation of the crystal. The extent of the decrease was related to the concentration of benzene. In later experiments, the piezoelectric crystal was kept in a hot air oven (80 °C) for 5 min between each set of calibrations.

Results and Discussion

Chemically Modified Cyclodextrins.—Many chemically modified cyclodextrins have been reported[7] but the purity and even the constitution of some of the compounds appears to be questionable. It is essential to work with pure, fully characterised derivatives and the most straightforward to prepare are the symmetrically substituted derivatives. The

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* Piezoelectric crystals are now obtainable from Webster Electronics Ltd., Rosemills, Hortbridge, Ilminster, Somerset TA19 9QA.

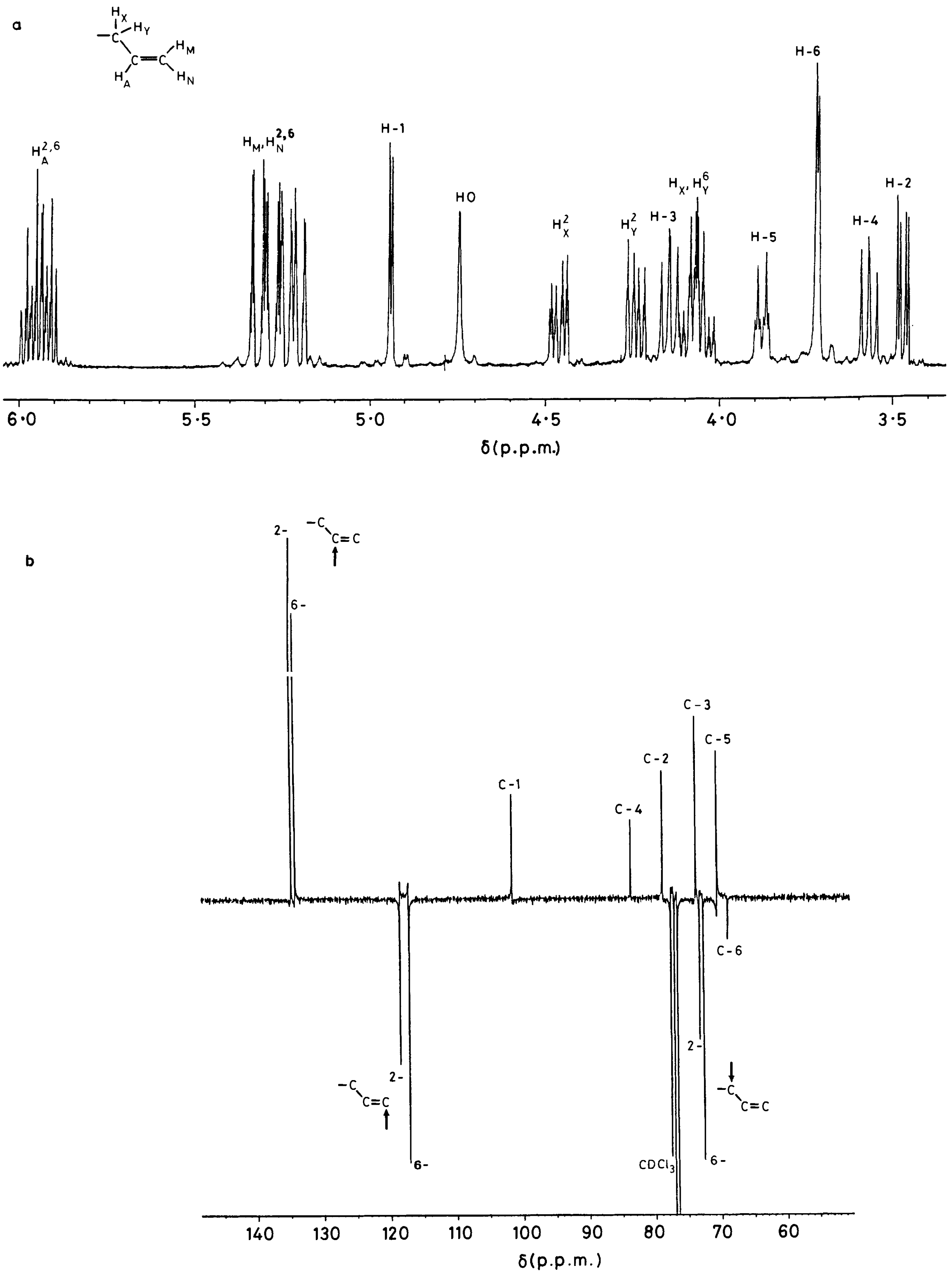

Figure 1. a, ^1H N.m.r. spectrum of DAαCD (400 MHz; $CDCl_3$; Me_4Si); b, ^{13}C n.m.r. spectrum of DAαCD (63 MHz; $CDCl_3$; *J* modulation)

Table 1. Response (ΔF/Hz) to benzene vapour (1 cm^3) by DAαCD coated on quartz crystal (gold electrodes)

	[Benzene]/mg dm^{-3}				
Day	396	48.4	5.90	0.72	0.088
1	401	132	34	7	3
2	344	142	38	8	3
4	297	118	27	15	4
6	278	119	26	9	2
*					
7	316	125	27	4	2
8	276	164	27	6	2
*					
10	365	187	37	7	2
*					
15	355	166	39	6	2
*					
18	300	133	32	9	3
*					
20	273	162	38	7	2

* Piezoelectric crystal placed in hot air oven (80 °C) for 5 min. For day 1 to day 6 $\log (\Delta F/\text{Hz}) = 1.08 + 0.591 \log ([\text{Benzene}]/\text{mg dm}^{-3})$ (r 0.998, s.d. 0.0395).

synthesis and complete characterisation of 2,6-per-*O*-methyl-β-cyclodextrin 3-perbenzoate (DMβCD-B$_7$) has recently been reported.[8]

2,6-Per-*O*-(t-butyldimethylsilyl)-α-cyclodextrin (DSαCD) was prepared from α-cyclodextrin (αCD) employing a modification of the method used by Bender *et al.*[12] who reported a 60% yield after chomatographic separation. A simplified work-up procedure involving partitioning between water and hexane afforded a remarkable 97% yield of analytically pure product without the necessity of resorting to chromatography. This product was fully characterised by ^{1}H and ^{13}C n.m.r. spectroscopy. C-3 and C-5, which had not been previously assigned, were distinguished on the basis of selective heteronuclear decoupling experiments. Furthermore, the protons and the carbon atoms associated with the 2- and 6-*O*-silyl groups were distinguished on the basis of n.O.e. difference spectroscopy and selective heteronuclear decoupling experiments, confirming the previous assignments.

2,6-Per-*O*-allyl-α-cyclodextrin (DAαCD) was prepared according to the method used[13] to prepare the β-cyclodextrin (βCD) analogue. A solution of αCD in DMSO–DMF (1 : 1) was treated with BaO–Ba(OH)$_2$·8H$_2$O (1 : 1) and an excess of allyl bromide. Column chromatography on silica gel yielded DAαCD which was shown to be the symmetrically 2- and 6-*O*-substituted compound by ^{1}H and ^{13}C n.m.r. spectroscopy. A detailed interpretation of the n.m.r. spectra is given in the Experimental section and the spectra are reproduced in Figure 1.

The glucosidic ring protons were assigned on the basis of a series of homonuclear decoupling experiments. The assignment of the two different kinds of allyl group to the 2- and 6-positions can be made on the basis of several pieces of evidence, the most important of which are: (i) benzylation of the 3-OH groups causes[14] a large (0.4 p.p.m.) shift to lower frequency of the resonances associated with the allylic protons of the 2-*O*-allyl groups and no change in the chemical shifts of the 6-*O*-allyl protons and (ii) 2-per-*O*-allyl-6-per-*O*-(t-butyldimethylsilyl)-α-cyclodextrin (ASαCD),[15] allylated at only the 2-position, has chemical shifts for the allyl group protons identical with those assigned for the 2-*O*-allyl groups in DAαCD. All the resonances in the ^{13}C n.m.r. spectrum were assigned on the basis of a series of selective heteronuclear decoupling experiments once the ^{1}H n.m.r. spectrum had been fully assigned.

Table 2. Response (ΔF/Hz) to benzene vapour (1 cm^3) by DMβCD-B$_7$ coated on quartz crystal (gold electrodes)

	[Benzene]/mg dm^{-3}			
Day	396	48.4	5.90	0.72
1	164	83	15	2
2	125	62	12	2
3	62	30	11	4
4	65	31	9	3

Table 3. Response (ΔF/Hz) to benzene vapour (1 cm^3) by freshly prepared DSαCD coated on quartz crystal (gold electrodes)

	[Benzene]/mg dm^{-3}					
Day	396	48.4	5.90	0.72	0.088	0.011
1	743	394	169	61	21	12
2	754	319	62	17	4	0
6	613	239	67	21	6	2
7	394	178	43	10	3	0
10	397	216	51	12	5	2
17	373	199	45	16	5	2
20	366	184	47	14	2	0

It should be noted that DAαCD was found to decompose (possibly polymerise) upon standing in air for several months and was therefore stored under nitrogen at −20 °C. Under these conditions, it was found to be stable for at least a year.

Principles of Piezoelectric Crystal Detection.—The quantifying principle of piezoelectric crystal detection lies in the increased mass resulting from the sorption of the anolyte by the coating on the crystal leading to a decrease in the frequency of vibration. The frequency change, ΔF/Hz, is governed by the Sauerbrey equation (1) where F/MHz is the initial frequency of

$$\Delta F = -2.3 \times 10^6 F^2 \Delta m/A \qquad (1)$$

the quartz crystal, Δm/g is the mass sorbed, and A/cm^2 is the area of the coating. Although equation (1) can be simplified to (2) where C is the anolyte concentration (mg dm^{-3} or μg dm^{-3} or

$$\Delta F = KC \qquad (2)$$

g dm^{-3}) and K is a constant to include other terms and a factor to convert the mass of analyte sorbed into its gas-phase concentration, the actual slopes of frequency decrease *versus* concentration graphs are lower than those deduced[9,16] from equation (1). This means that actual sensitivities are better than predicted. This has been corrected partially by modifying the syringe dilution procedure[9] used in this work. Although other more intransigent factors remain, a relationship of the type of equation (2) exists for practical purposes between ΔF and C and forms the basis of the data presented in this investigation.

Calibration Tests for Different Cyclodextrin Coatings.—Table 1 shows calibration data over 20 days for benzene vapour detection with a coating of DAαCD. The coating was overloaded with benzene at 396 mg dm^{-3}. After calibration set 6 (Table 1), the piezoelectric crystal was placed in a hot air oven (80 °C) for 5 min, when the response to benzene was restored. This was again done after calibration set 8 and adopted as a ritual prior to each subsequent calibration set. These data and the good benzene desorption characteristics (Figure 2a) indicate that DAαCD is a promising piezoelectric crystal detector coating for benzene.

There is little difference between gold and silver quartz

Table 4. Piezoelectric crystal (gold electrodes) response towards benzene vapour for coatings of DAαCD and DSαCD prepared from material following 8 weeks storage at 4 °C

	Frequency change (Hz)											
	DAαCD				DSαCD							
[Benzene vapour]/mg dm^{-3}	Day 1	2	4	6	Day 1	2	4	6	7	9	20	25
396	214	183	147	160	528	536	528	530	532	531	460	431
48.4	111	100	109	79	215	229	214	228	224	214	157	131
5.9	25	46	24	21	55	58	54	32	55	53	42	40
0.72	7	12	6	6	16	19	18	18	18	14	7	8
0.088	1	2	1	1	4	4	5	5	5	5	2	2

Table 5. Piezoelectric crystal (gold electrodes) response by interferents (1 cm^3 samples) for coating of DAαCD, DSαCD, and DMβCD-B$_7$

Sample and concentration (in air unless stated)	Coating material DAαCD	DSαCD	DMβCD-B$_7$	No. of calibrations
Methane pure	0	0	0	5
Propane 1%	3	3	3	5
Butane 10% in nitrogen	18	9	5	4
Pentane 0.72%	11	2	2	5
Ethyne 0.92% in nitrogen	6	2	2	4
Nitrobenzene (head space vapour at 25 °C)	8	14	21	5
Ammonia 32 mg dm^{-3}	35*	66	100	3
Toluene 144 mg dm^{-3}	114	64	43	4
Toluene 17.5 mg dm^{-3}	37	16	8	4
Toluene 2.1 mg dm^{-3}	7	4	0	4

* Poor reversibility.

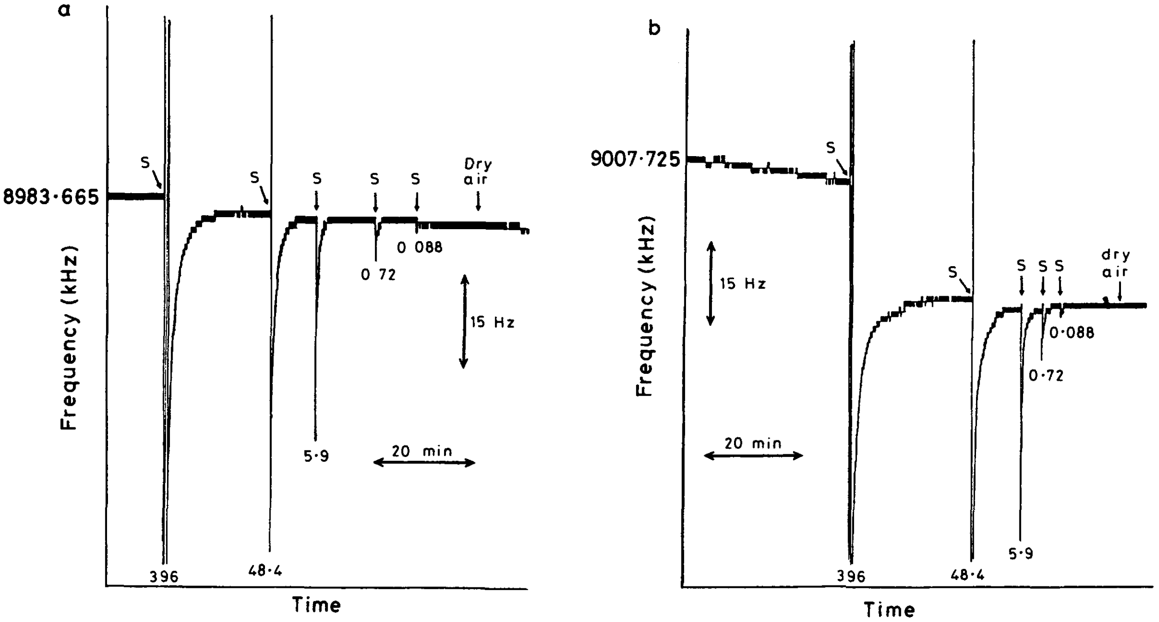

Figure 2. Typical recorder traces of calibration of benzene vapour using two different quartz crystals (gold electrodes) coated with DAαCD. Sample size 1 cm^3. Numbers on peaks are benzene concentration (mg dm^{-3})

crystals (D and E in Figure 3). The remaining chemically modified cyclodextrins were then investigated as alternative coatings to try and improve upon DAαCD (Figure 3). DMβCD-B$_7$ exhibited lower sensitivity to benzene (F in Figure 3 and Table 2) and the response quickly faded (Table 2). On the other hand, DSαCD coatings showed a considerable improvement in sensitivity over DAαCD. The sensitivity remained high for the first seven days, after which it dropped: even then, it was still better than DAαCD to beyond day 20 (A—C in Figure 3 and Table 3).

Effect of Storage of Chemically Modified Cyclodextrin Materials.—Stocks of the chemically modified cyclodextrins were stored in closed containers in a refrigerator at 4 °C for 8

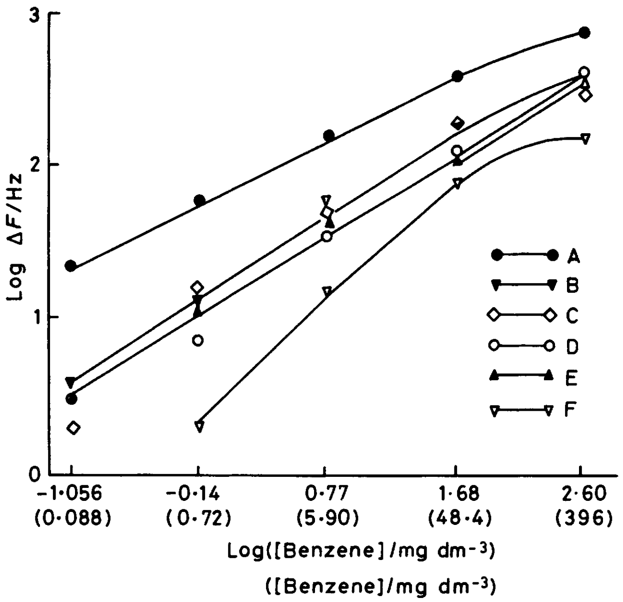

Figure 3. Calibrations of piezoelectric quartz crystals for benzene vapour, illustrating the effect of different coatings and different electrodes fitted to the crystal (gold unless otherwise stated). **A**, DSαCD coating (day 1); **B**, DSαCD coating (day 7); **C**, DSαCD coating (day 20); **D**, DAαCD coating (day 1); **E**, DAαCD coating (silver electrode; day 1); electrode; day 1); **F**, DMβCD-B_7 coating (day 1)

weeks. DAαCD and DSαCD were coated on piezoelectric crystals which were tested for their response to benzene vapour (Table 4). It was observed that DAαCD lost a greater proportion of its sensitivity towards benzene vapour than was the case for DSαCD. Also, the sensitivity of the DSαCD after storage was more consistent than for the freshly prepared material (Table 4 compared with Table 3). It is, therefore, recommended that DSαCD is preferred for its better storage quality and overall performance.

Chemical Interferences.—DAαCD, DSαCD, and DMβCD-B_7 were also evaluated for selectivity purposes with a wide range of organic vapours and the data obtained are summarised in Table 5. There were no significant interferences from low relative molecular mass alkane gases but pentane registered higher than background readings for DAαCD. Ethyne also gave low readings. More surprising are the low readings for nitrobenzene which might have been expected to interact with the chemically modified cyclodextrins. Ammonia registered significant readings for both DAαCD and DSαCD, while readings were higher still for DMβCD-B_7 which has been discounted as a suitable sensor for benzene. However, while DSαCD and DMβCD-B_7 registered quick reversibility for the sensor (<2 min for the 66 Hz ΔF and 100 Hz ΔF, respectively, to fall to zero), DAαCD only recovered 10 Hz of the 35 Hz ΔF caused by the 32 mg dm^{-3} ammonia sample. Toluene is a significant interferent for both DAαCD and DSαCD, although the material registers lower readings for DSαCD than for DAαCD (Table 5). There is somewhat less interference of DMβCD-B7. However, coupled with the greater sensitivity of DSαCD for benzene, toluene interference is less serious for this superior sensor.

Conclusions. A fresh range of possible piezoelectric crystal detector coatings for detecting gases and vapours have been described in this paper. The chemically modified cyclodextrins prepared and studied herein demonstrate that these molecular receptors can be selective and reversible in their response to volatile organic compounds and that the resulting sensors can have reasonable lifetimes. Thus, 2,6-per-*O*-t-butyldimethylsilyl-α-cyclodextrin (DSαCD) is shown to behave as a highly suitable piezoelectric crystal sensor for benzene vapour. The less stable 2,6-per-*O*-allyl-α-cyclodextrin (DAαCD) provides a possible alternative piezoelectric crystal detector coating for sensing benzene vapour.

Acknowledgements

We are grateful for the award of the Alderman Lewis Morgan Studentship (to C. S. I. L.), a Johnson Matthey Studentship (to D. C. M.), and S.E.R.C. CASE Studentship (to R. Z.), and a Leverhulme Research Fellowship (to J. F. S.). The joint research programme was made possible as a result of generous support from the S.E.R.C. Chemistry Committee under the auspices of their initiative on Chemical Sensors.

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Received 23rd *February* 1987; *Paper* 7/343