mixture, both obtained from binary data. The agreement between the two solutes and the literature values thus is within the uncertainty in the ideal solubility of the solutes. The remaining systems fail to follow even the less restrictive regular model (*7*).

NOMENCLATURE

ΔE^{ideal} = ideal molar energy of vaporization
ΔG^{E} = molar excess Gibbs free energy of mixing
R = gas constant
T = absolute temperature
V^{0} = molar volume
W = interchange energy, cal. mole^{-1}
W' = interchange energy, cal. ml.$^{-1}$
x = mole fraction
δ = solubility parameter
γ = activity coefficient
ϕ = volume fraction
ϕ^{0} = volume fraction in solute-free mixed solvent

Subscripts

i, j = components i, j
1, 3 = solvents
2 = solute
02 = mixed solvent-solute

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Derivatives of 4,4′-Isopropylidenebis(2,6-dichlorophenol)

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Nine bis esters, six bis ethers, three bis amides, and one bis acid of 4,4′-isopropylidenebis(2,6-dichlorophenol) are described along with their significant infrared spectral data.

THE COMPOUND 4,4′-isopropylidenebis(2,6-dichlorophenol), commonly known as tetrachlorobisphenol A, is easily prepared by chlorination of the parent diphenol (*1*). Although this chlorinated product (m.p. 133-134° C.) is well known to the literature as a flame-retardant epoxy and polycarbonate resin intermediate (*2, 3*), few monomolecular derivatives have been reported.

Nineteen derivatives of tetrachlorobisphenol A have now been prepared and are described in Table I. These include five aromatic and aliphatic carboxylic acid bis esters (I-V), two bis sulfonates (VI and VII), one known bis phosphonate (VIII), one bis thionocarbamate (IX), six aliphatic and arylaliphatic bis ethers (X-XV), three bis amides (XVI-XVIII), and one bis acid (XIX). Pertinent infrared spectral data are recorded in Table II.

EXPERIMENTAL

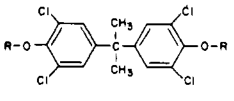
All products were prepared by well established organic chemical processes. The infrared spectral data were obtained on a Beckman Model IR-5, sodium chloride prism, infrared spectrophotometer. Nujol mulls, containing approximately 40% of the compound, were prepared in the usual manner. The spectra were obtained through a film of the mulls (about 10 microns) between sodium chloride salt plates.

Method A. Tetrachlorobisphenol A (0.1 mole) was dissolved in 125 ml. of dry pyridine. The acyl chloride (0.21 mole) was added slowly with stirring while maintaining the temperature at 35° C. over a 15-minute period. The reaction mixture was then heated at 50° to 80° C. for 2 hours, cooled to room temperature, and poured into 500 ml. of ice water with stirring. When the precipitated gummy mass had broken up and become solid, the solid was filtered and washed with 100 ml. of 3% sodium hydroxide solution, then 100 ml. of 3% hydrochloric acid and finally with water. The product was dried and recrystallized from an appropriate solvent.

Method A1. After the reaction mixture was poured into ice water, the pyridine was removed by azeotropic distillation. The gummy mass or solid was removed by decantation and recrystallized from an appropriate solvent.

Method A2. After the reaction mixture was poured into

Table I. Derivatives of 4,4′-Isopropylidenebis (2,6-dichlorophenol)



Compound No.	R	Method	Yield, %	Recryst. Solvent	M.P., °C.	Formula	Analyses Carbon, % Calcd.	Found	Hydrogen, % Calcd.	Found	Chlorine, % Calcd.	Found
I	*p*-Chlorobenzoyl	A	92	2-Propanol-MEK (1 to 1)	186–188	$C_{29}H_{18}Cl_6O_4$	54.2	54.2	2.82	2.98	33.1	33.4
II	3,4-Dichlorobenzoyl	A1	33	2-Propanol-MEK (1 to 1)	182–185	$C_{29}H_{16}Cl_8O_4$	48.9	49.1	2.26	2.43	39.8	39.7
III	Trichloroacetyl	A	98	Ethyl acetate	201.5–203.5	$C_{19}H_{10}Cl_{10}O_4$	34.7	35.0	1.54	1.96	54.0	54.3
IV	Phenoxyacetyl	A2	25	Skellysolve E	133–136	$C_{31}H_{24}Cl_4O_6$	58.7	58.8	3.81	3.80	22.4	22.5
V	Hexoxycarbonyl	A	91	*n*-Butanol	72–72.5[a]	$C_{29}H_{36}Cl_4O_6$	56.0	56.1	5.83	6.00	22.8	22.9
VI	*p*-Chlorobenzenesulfonyl	A	97	2-Propanol-MEK (1 to 2)	185–188	$C_{27}H_{18}Cl_6O_6S_2$	45.3	...	2.54	...	29.7	29.3[b]
VII	*p*-Acetamidobenzenesulfonyl	A	99	Acetic acid	222–225	$C_{31}H_{26}Cl_4N_2O_8S_2$	49.0	...	3.45	...	18.7	18.9[c]
VIII	Diethoxyphosphinyl[d]	A3	28	Skellysolve C	96–98	$C_{23}H_{30}Cl_4O_8P_2$	43.3	...	4.74	...	22.2	22.2[e]
IX	Diethylthiocarbamoyl	A1	51	2-Propanol	150–155	$C_{25}H_{30}Cl_4N_2O_2S_2$	50.3	...	5.07	...	23.8	24.3[f]
X	Allyl	B	86	MEK	98–101	$C_{21}H_{20}Cl_4O_2$	56.5	56.1	4.52	4.76	31.8	32.1
XI	3-Phenylallyl	B	87	Acetone	143–144.5	$C_{33}H_{28}Cl_4O_2$	66.2	66.6	4.72	4.66	23.7	23.8
XII	*o*-Chlorobenzyl	B	74	2-Propanol	87–88	$C_{29}H_{22}Cl_6O_2$	56.6	56.2	3.60	3.67	34.6	34.9
XIII	*p*-Nitrobenzyl	B	99	2-Propanol-MEK (1 to 2)	175–177.5	$C_{29}H_{22}Cl_4N_2O_6$	54.7	55.2	3.49	3.59	22.3	22.5[g]
XIV	Ethoxycarbonylmethyl	B	75	2-Propanol	115–117	$C_{23}H_{24}Cl_4O_6$	51.3	51.2	4.49	4.51	26.4	26.7
XV	*p*-Chlorophenylcarbonylmethyl	B	87	MEK	151.5–153.5	$C_{31}H_{22}Cl_6O_4$	55.5	55.5	3.30	3.59	31.7	31.5[h]
XVI	Carbamoylmethyl	C	81	Dimethylformamide	226–228	$C_{19}H_{18}Cl_4N_2O_4$	47.5	...	3.78	...	29.5	29.4[i]
XVII	Benzylcarbamoylmethyl	D	75	MEK	209–211	$C_{33}H_{30}Cl_4N_2O_4$	60.0	...	4.58	...	21.5	22.0[j]
XVIII	Diallylcarbamoylmethyl	E	98	2-Propanol	90–92	$C_{31}H_{34}Cl_4N_2O_4$	58.1	58.5	5.35	5.58	22.2	22.2[k]
XIX	Carboxymethyl	F	83	Acetic acid	199–201	$C_{19}H_{16}Cl_4O_6$	47.3	47.4	3.35	3.45	29.4	29.6[l]

[a] Reference (*4*) erroneously reported, m.p., 81–82° C. [b] Sulfur, %: Calcd., 8.96; Found, 9.03. [c] Nitrogen, %: Calcd., 3.68; Found, 3.68. Precipitates with a mole of acetic acid attached. It is lost at 130° to 135° C. [d] Reference (*5*), different preparative method, m.p. 93–94° C. from heptane. [e] Phosphorus, %: Calcd., 9.71; Found, 9.70. [f] Sulfur, %: Calcd., 10.8; Found 10.9. Nitrogen, %: Calcd., 4.70; Found, 4.56. [g] Nitrogen, %: Calcd., 4.40; Found, 4.34. [h] Dry at 120° C. for complete removal of MEK. [i] Nitrogen, %: Calcd., 5.83; Found 5.67. [j] Nitrogen, %: Calcd., 4.24; Found, 4.19. [k] Nitrogen, %: Calcd., 4.38; Found, 4.19. [l] Neutral equivalent: Calcd., 241.1; Found, 243.1.

ice water, the precipitated gummy mass was separated and dissolved in 300 ml. of chloroform. The solution was washed with 3% hydrochloric acid, 3% sodium carbonate solution, and finally with water. The chloroform solution was dried over sodium sulfate, and the solvent was removed by distillation. The residue was extracted with carbon disulfide leaving behind a dark, insoluble unidentified oil. The carbon disulfide extract was evaporated to dryness and the residual product recrystallized from Skellysolve E.

Method A3. After the reaction mixture had been poured into ice water, the precipitated mass was separated by decantation and dissolved in toluene. The toluene solution was extracted with 5% hydrochloric acid, 5% sodium hydroxide solution, and finally with water. The toluene solution was dried over sodium sulfate and evaporated to dryness. The product was recrystallized from Skellysolve C.

Method B. Tetrachlorobisphenol A (0.05 mole), anhydrous potassium carbonate (0.12 mole), potassium iodide (0.12 mole), the active organic chloride (0.12 mole for XI, XII, XIII and XIV) or bromide (0.12 mole for X and XV), and 200 ml. of methyl ethyl ketone were stirred and refluxed for 9 hours. The reaction mixture was cooled to 25° C., and

Table II. Infrared Spectral Data (Nujol Mulls)

Compound	Functional Group Absorption, Microns
Tetrachlorobisphenol A (R = Hydrogen)	2.98 S (OH)
I	5.70 S (C=O), 5.21 W (1,4-disubstd. phenyl)
II	5.69 S (C=O)
III	5.60 S (C=O)
IV	5.52 S and 5.57 S (C=O)[a]
V	5.63 S (C=O)
VI	5.17 W (1,4-disubstd. phenyl), 8.38 S and 8.45 M (SO_3)
VII	2.97 W (NH), 5.95 M (Amide I), 8.34 M and 8.48 S (SO_3)
VIII	7.79 S ($P \rightarrow O$), 9.3–9.8 S (POC aliphatic), 10.1–10.8 S (POC aromatic)
IX	8.9–9.5 S (C=S)
X	3.24 W ($H_2C=$), 6.05 (C=C)
XI	6.05 W (C=C), 10.36 S (trans olefin), 13.35 M and 14.36 M (monosubstd. phenyl)
XII	13.17 S (1,2-disubstd. phenyl)
XIII	5.17 W (1,4-disubstd. phenyl), 6.59 S and 7.42 S (NO_2)
XIV	5.67 S (C=O), 8.25 S (C—O)
XV	5.88 S (C=O), 5.20 W and 12.05 S (1,4-disubstd. phenyl)
XVI	2.94 M (NH_2), 5.98 S (Amide I), 6.42 W (Amide II)
XVII	3.0 W (NH), 6.01 S (Amide I), 6.49 M (Amide II), 13.52 M and 14.20 M (monosubstd. phenyl)
XVIII	3.24 W ($H_2C=$), 6.02 S (Amide I), 6.07 M (C=C)
XIX	3.0–4.0 M, 5.76 S, 5.84 S, 7.90 S, 10.5–11.0 W (COOH)

[a] 2% $CHCl_3$ solution shows strong, sharp carbonyl band at 5.55 microns with spur at 5.63 microns.

100 ml. of water were added with stirring. The top oil layer was separated, washed with 10% sodium hydroxide solution, and finally with water. The methyl ethyl ketone solution was then dried over sodium sulfate and evaporated to dryness. The residual product was recrystallized from an appropriate solvent.

In the case of the bis 3-phenylallyl and *p*-chlorophenylcarbonylmethyl derivatives (XI and XV), some of the product precipitated on cooling and adding the water. The precipitated material was filtered out and the water-methyl ethyl ketone filtrate processed in the usual manner. The residual material from evaporation of the dried methyl ethyl ketone solution was added to the precipitated product for recrystallization.

Method C. Compound XIV (10.8 grams, 0.02 mole), concentrated ammonium hydroxide solution (50 grams, 0.8 mole as NH_3), and 50 ml. of ethanol were stirred and heated at 50° C. for 1 hour and then stirred for one week at 25° C. The product was filtered, washed with water, dried, and recrystallized from *N,N*-dimethylformamide.

Method D. Compound XIV (10.8 grams, 0.02 mole), benzylamine (26.7 grams, 0.25 mole), and ammonium chloride (1 gram) were refluxed at 185° C. for 1 hour. The reaction mixture was cooled to 25° C. and the product separated by filtration, washed with 3% hydrochloric acid, then with water, dried, and recrystallized from methyl ethyl ketone.

Method E. Tetrachlorobisphenol A (36.6 grams, 0.1 mole), *N,N*-diallylchloroacetamide (38.2 grams, 0.22 mole), anhydrous potassium carbonate (30.4 grams, 0.22 mole), potassium iodide (36.5 grams, 0.22 mole), and 200 ml. of methyl ethyl ketone were stirred and refluxed for 10 hours. The reaction mixture was cooled, and 100 ml. of water were added. The top oil layer was separated and extracted twice with 50 ml. of 10% sodium hydroxide solution and finally with 100 ml. of salt water. The solution was dried over sodium sulfate, and the solvent was removed by distillation under reduced pressure (final conditions: 70° C. at 25 mm.). After the product had cooled and the container was scratched, the compound solidified and was recrystallized from 2-propanol.

Method F. Compound XIV (10.8 grams, 0.02 mole), 20 ml. of ethanol, and 20 ml. of 25% sodium hydroxide solution were refluxed for 6 hours with stirring. Water (200 ml.) was then added and the reaction mixture heated to dissolve the solids. The solution was acidified, while it was stirred, to a pH of 4 with 5% hydrochloric acid; after it cooled to 25° C., the solid product was filtered. The material was then dissolved in 200 ml. of 5% sodium bicarbonate solution. After it was filtered, the solution was slowly dropped into 200 ml. of 4% hydrochloric acid with stirring. The product was separated by filtration and recrystallized from glacial acetic acid.

Attempts to prepare XIX from chloroacetic acid in pyridine as well as under Schotten-Baumann conditions failed.

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