involved in estimating the activity coefficients.

Summary

The solubility of cupric iodate in glycine and in alanine solutions has been determined. The solubility results may be explained by assuming three complex ions, namely, $CuHR^{++}$, CuR^+ and CuR_2. The equilibrium constants for the reaction of cupric ion and the amino acids to form the above complex ions have been evaluated.

DAVIS, CALIFORNIA RECEIVED JUNE 30, 1947

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF EMORY UNIVERSITY]

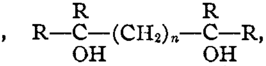
A Study of Organic Parachors. IX. The Additive Nature of Structural Units in the Parachors of Ditertiary Glycols and Chlorides[1,2]

BY THOMAS P. JOHNSTON[3] AND OSBORNE R. QUAYLE

Parachor, first considered primarily an additive property, has been shown to be highly susceptible to minor differences in structure, as, for example, those existing between two isomeric tertiary alcohols. This sensitivity would at first seem to decrease its usefulness as a method of correlating the physical properties of organic compounds with their structure. If such differences are capable of evaluation, however, the parachor immediately becomes a more delicate tool. Results have been obtained with series of tertiary alcohols[4,5] and chlorides[6,7] evaluating the inherent constitutive variations so that the parachor of any tertiary alcohol or chloride having normal alkyl groups may be predicted with reasonable accuracy. These results have been published in the form of tables[5,7] from which reliable theoretical values for such types may be conveniently calculated. It is to be emphasized that the actual value of CH_2 in all cases is considered essentially a constant, 40.0,[8,9] and that constitutive variations are attributed to the alteration of valence forces around the tertiary carbon atom and the attached chlorine or hydroxyl.

The neglect of minor structural effects in the calculation of parachor values is a common cause of considerable deviation between theoretical and calculated values. If structural groups exhibiting constitutive variations can be evaluated, they should in turn be primarily additive in more complex molecules. To test this assumption the parachors of a number of symmetrical ditertiary glycols and chlorides were measured and compared with calculated theoretical values. Parachors for the structural units of each molecule, divided as nearly as possible at the center of symmetry, were calculated and added to obtain the theoretical parachor for the whole molecule. The validity of treating structural units of a complex molecule in an additive manner once the constitutive divergence has been evaluated is upheld by the experimental data presented in this paper.

Ditertiary glycols (Table I) of the general formula,



$R-\overset{R}{\underset{OH}{C}}-(CH_2)_n-\overset{R}{\underset{OH}{C}}-R$, in which R is methyl, ethyl and propyl and n is 2, 4, 7 and 8, were prepared by the standard method of adding the appropriate dibasic ester to the Grignard reagent.[10] The 2,10-, 3,11- and 4,13-diols have not been previously reported in the literature. The yield in the preparation of the 4,13-diol from dimethyl sebacate was least satisfactory; a yield of less than 5% of purified crystals was separated from the predominant viscous non-crystallizable oil. The Grignard addition complexes were hydrolyzed with either saturated aqueous ammonium chloride or cold dilute sulfuric acid, preferably the former. Toluene was the usual solvent for crystallization. These glycols are somewhat more stable than the simple tertiary alcohols in that they all withstand the temperature of boiling toluene and subjection to temperature up to 80° *in vacuo* and at least one, the 3,11-diol, may be distilled without decomposition at a relatively high temperature, about 140° at less than 1 mm. Parachors of only the lower melting glycols were measured, since solid compounds do not lend themselves to ready parachor measurement with the apparatus presently installed in this Laboratory.

The dichlorides (Table I) corresponding to the above ditertiary glycols were in general made by passing dry hydrogen chloride into an anhydrous ether solution of the glycol at a low temperature. A small amount of methanol was added to increase the solubility. After standing twenty-four hours the solvent was removed under reduced pressure

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(1) Presented in part before the Division of Organic Chemistry of the American Chemical Society at the Atlantic City meeting, April 17, 1947.

(2) The authors wish to express their gratitude to Prof. E. Emmet Reid, research consultant to the department, for his continued interest in the problem and for his several suggestions.

(3) From material to be presented by Thomas P. Johnston to the graduate faculty of Emory University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(4) Owen, Quayle and Beavers, THIS JOURNAL, **61**, 900 (1939).

(5) Quayle and Smart, *ibid.*, **66**, 935 (1944).

(6) Quayle, Owen and Beavers, *ibid.*, **61**, 3107 (1939).

(7) Smart and Quayle, *ibid.*, **67**, 21 (1945).

(8) Mumford and Phillips, *J. Chem. Soc.*, 2112 (1929).

(9) Quayle, Day and Brown, THIS JOURNAL, **66**, 938 (1944).

(10) The glycol in which R is propyl and n is 7 was not isolated; the only attempt to prepare it from dimethyl azelate gave a non-crystallizable oil.

TABLE I

DITERTIARY GLYCOLS AND CHLORIDES

Glycol	M. p., °C.		Empirical formula	Analyses, %				Corresponding dichlorides				
				Carbon		Hydrogen		M. p. of solids, °C.	Refractive index		Analyses, % Cl[b]	
	Found[a]	Lit.		Calcd.	Found	Calcd.	Found		t°	n^t_D	Calcd.	Found
2,5-Dimethyl-2,5-hexanediol[c]	88–89	*d, e, f, g*	$C_8H_{18}O_2$	65.71	65.47	12.41	12.58	64–65[h]				
3,6-Diethyl-3,6-octanediol	66.5–67	66–67.5[i]	$C_{12}H_{26}O_2$	71.23	71.08	12.95	12.88		20	1.4722	29.64	29.69
4,7-Dipropyl-4,7-decanediol	86.5–87	43[j]	$C_{16}H_{34}O_2$	74.36	74.07	13.26	13.35		20	1.4693	24.01	24.18
2,7-Dimethyl-2,7-octanediol[k]	90–90.5	*l, m, n*	$C_{10}H_{22}O_2$	68.91	69.02	12.73	12.71	50–50.5°			33.58	33.55
3,8-Diethyl-3,8-decanediol	71–72	72–73[m]	$C_{14}H_{30}O_2$	72.99	72.85	13.13	13.15		20	1.4720	26.53	26.34
4,9-Dipropyl-4,9-dodecanediol	86–86.5	93[m]	$C_{18}H_{38}O_2$	75.46	75.33	13.37	13.37	29.5–30	30	1.4676	21.93	21.93
2,10-Dimethyl-2,10-undecanediol	67–67.5		$C_{13}H_{28}O_2$	72.16	72.16	13.04	13.10		20	1.4580	28.00	28.06
3,11-Diethyl-3,11-tridecanediol[p]	59.5–60		$C_{17}H_{36}O_2$	74.93	74.91	13.32	13.20		20	1.4726	22.92	22.85
2,11-Dimethyl-2,11-dodecanediol[q]	60.5–61	*r, s*	$C_{14}H_{30}O_2$	72.99	72.80	13.13	13.20	28–29	30	1.4550	26.53	26.34
3,12-Diethyl-3,12-tetradecanediol	60–61	*t, u*	$C_{18}H_{38}O_2$	75.46	75.39	13.37	13.35		20	1.4722	21.93	21.97
4,13-Dipropyl-4,13-hexadecanediol[v]	47.5–48		$C_{22}H_{46}O_2$	77.12	76.83	13.54	13.60		20	1.4709	18.69	18.80

[a] All m. p.'s reported in this paper uncorrected. [b] Empirical formula same as that of glycol except replacement of 2 OH by 2 Cl. [c] Only appreciably water-soluble member of series. Anhydrous ethyl acetate was solvent for final crystallization. Corresponding di-chloride can be purified by sublimation by warming under reduced pressure and/or crystallization from methanol. Pleasant odor. [d] 92–93°, Zelinsky, *Ber.*, **35**, 2139 (1902), and Pace, *C. A.*, **22**, 3890 (1928). [e] 88.5–89°, Pogorzelski. *Chem. Zentr.*, **75**, I, 578 (1904). [f] 89°, Harries and Turk, *Ann.*, **343**, 364 (1905). [g] 92°, Bruylants, *Chem. Zentr.*, **80**, II, 797 (1909). [h] Pogorzelski, *Chem. Zentr.*, **70**, I, 773 (1899) reported m. p. 64°; Henry, *Compt. rend.*, **143**, 497 (1906), 66–67°. [i] Zal'kind and Buistryakov, *C. A.*, **9**, 2511 (1915). [j] Dupont, *Compt. rend.*, **156**, 1623 (1913). [k] Few drops of methanol added to toluene as solvent for crystallization to increase solubility. Corresponding dichloride was crystallized from methanol. Slight odor. [l] 88–89°, Michiels, *C. A.*, **7**, 3602 (1913), and Zal'kind and Aizikovich, *ibid.*, **31**, 4283 (1937). [m] 92°, Bouvet, *Bull. soc. chim.*, **17**, 202 (1915). [n] 94°, Zelinski, see *C. A.*, 9, 2639 (1915). [o] Reference[m] reported m. p. 49°. [p] B. p. about 139–142° at < 1 mm. [q] Crystallized from toluene to which pyridine in ratio of 1 drop per 10 cc. was added. [r] 62°, Petrov and Sanin, *C. A.*, **34** 4054 (1940). [s] 57.5–58°. Kislovskaya, *ibid.*, **8**, 1422 (1914). [t] 72.5°. reference [r]. [u] 59°, Landa and Habada, *C. A.*, **31**, 1757 (1937). [v] Crystallized from pet. ether.

and the dichloride or its chloroform solution dried over sodium sulfate and sodium carbonate. Further purification can be effected by a modification of the method of Whitmore and Williams.[11] The following dichlorides were prepared: 2,5-dichloro-2,5-dimethylhexane, 3,6-dichloro-3,6-diethyloctane, 4,7-dichloro-4,7-dipropyldecane, 2,7-dichloro-2,7-dimethyloctane, 3,8-dichloro-3,8-diethyldecane, 4,9-dichloro-4,9-dipropyldodecane, 2,10-dichloro-2,10-dimethylundecane, 3,11-dichloro-3,11-diethyltridecane, 2,11-dichloro-2,11-dimethyldodecane, 3,12-dichloro-3,12-diethyltetradecane, 4,13-dichloro-4,13-dipropylhexadecane.

Average over-all yields were about 75%; the average yield exclusive of those purified by sulfuric acid was about 85%. Only the 2,5- and 2,7-dichlorides have been previously reported.[12] These dichlorides should be kept anhydrous and cold to prevent decomposition over an extended period of time.

The parachors of all the above dichlorides and five of the glycols have been measured (Table II). Surface tensions were determined by the maximum bubble pressure method, the apparatus used being a modification of that of Sugden.[5] The type of pycnometer employed in the determination of density was designed for volatile liquids[13] but has been found satisfactory for the rather viscous dichlorides and even for the melts of the low-melting solids. The experimental precision in the measurement of surface tension was estimated to be not less than one part in five hundred, the more precise values being attainable at the lower temperatures. The over-all precision in the determination of the parachor was approximately one part in two thousand. It is recognized that the lack of direct methods of purification, the measurement of surface tension and density at relatively high temperatures and the inherent instability of tertiary chlorides especially at elevated temperatures have undoubtedly tended to increase the experimental error. It is felt, however, that definite conclusions concerning the problem as stated above may be derived from the experimental data obtained.

A sample calculation of the theoretical value for a parachor, that of 3,8-dichloro-3,8-diethyldecane, follows in which values for the structural units (tertiary chlorides) are taken from the table published by Smart and Quayle[7]; the atomic parachor of hydrogen used (15.5) is that reported by Quayle, Day and Brown[9]: (2 × ethylethylethylchloromethane) − (2 × hydrogen) = parachor of 3,8-dichloro-3,8-diethyldecane. (2 × 338.8) − (2 × 15.5) = 646.6. This method is based upon the assumption that, once evaluated, the parachors of the component groups may be added to ascertain the parachor for the larger molecule. In the compounds in which functional groups are separated by a small number of carbon atoms, a new constitutive factor involving the influence of one functional group on the other was recognized as a possibility. Thus in cases where *n* is 2, deviations from the calculated parachor were anticipated since no appraisal of this new constitutive effect has been included. It would be expected that the observed parachor would be less than the calculated value. This is evident in the data of Table III.

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[11] Whitmore and Williams, THIS JOURNAL, **55**, 406 (1933).

[12] See references under Table I.

[13] Lipkin, Davison, Harvey and Kurtz, *Ind. Eng. Chem., Anal. Ed.*, **16**, 55 (1944).

TABLE II

PARACHOR DATA OF DITERTIARY GLYCOLS AND CHLORIDES

Compound	Temp., °C.	Density, g./ml.	Surface tension,[a] dynes/cm.	Parachor
3,6-Diol	70	0.8985	27.12	513.9
	75	.8946	26.73	514.2
	80	.8904	26.20	514.1
3,11-Diol	65	.8796	29.61	722.5
	70	.8755	29.31	724.1
	75	.8713	28.89	725.0
2,11-Diol	65	.8676	29.79	620.3
	70	.8641	29.39	620.7
	75	.8602	28.99	621.4
3,12-Diol	65	.8767	30.05	765.0
	70	.8725	29.63	766.0
	75	.8684	29.24	767.1
4,13-Diol	60	.8643	28.32	914.5
	65	.8602	27.98	916.0
	70	.8566	27.62	916.9
2,5-Di-Cl	70	.9543	24.13	425.3
	75	.9496	23.59	425.1
3,6-DiCl	25	.9995	31.32	566.2
	35	.9917	30.40	566.5
	50	.9799	29.03	566.7
4,7-Di-Cl	25	.9580	29.85	720.6
	35	.9505	28.95	720.7
	50	.9391	27.63	721.0
2,7-Di-Cl	55	.9496	26.39	504.0
	60	.9448	26.08	505.1
	65	.9407	25.63	505.1
	70	.9362	25.19	505.3
3,8-Di-Cl	25	.9799	32.16	649.5
	35	.9723	31.21	649.8
	50	.9614	29.84	649.8
4,9-Di-Cl	25	.9488	30.72	802.4
	35	.9417	29.82	802.5
	45	.9342	28.90	802.6
	55	.9269	28.03	802.7
2,10-Di-Cl	25	.9519	30.32	624.3
	35	.9439	29.44	625.0
	50	.9322	28.11	625.5
3,11-Di-Cl	25	.9599	32.59	770.0
	35	.9530	31.75	770.2
	50	.9424	30.44	771.1
2,11-Di-Cl	25	.9451	30.76	666.0
	35	.9370	29.86	666.8
	45	.9296	28.99	667.2
	55	.9220	28.11	667.5
3,12-Di-Cl	25	.9540	32.89	811.7
	35	.9467	31.99	812.4
	50	.9364	30.70	812.9
4,13-Di-Cl	25	.9318	31.51	964.9
	35	.9248	30.69	965.8
	50	.9146	29.40	966.2

[a] Mean probable error not over ±0.03.

The parachor of the compound cited above calculated from values of Mumford and Phillips[8] for the individual atoms includes a strain constant (−3.0) for secondary branching of the carbon chain, which was not considered to vary with the length of the chain involved: Parachor of $C_{14}H_{28}Cl_2 = (14 \times 9.2) + (28 \times 15.4) + (2 \times 55.0) + (2 \times -3.0) = 664.0$.

TABLE III

COMPARISON OF EXPERIMENTAL AND CALCULATED PARACHORS

The experimental parachor at 25° is given in all cases in which such measurement was possible. Experimental values listed for glycols were obtained by extrapolation to 25°.

Compound	Parachor Exp.	Parachor Calcd.	JQ[a] % dev.	Previous calcd. values % Dev. (uncor.)[b] %	Previous calcd. values Dev. (cor.)[c]
3,6-Diol	511.2[d]	519.8	1.7	5.6	4.5
3,11-Diol	712.1	708.9	−0.45	3.9	3.1
2,11-Diol	615.9	603.0	−2.1	0.67	−0.31
3,12-Diol	756.6	748.0	−1.1	3.1	2.3
4,13-Diol	906.1	903.2	−0.32	3.7	3.1
2,5-Di-Cl	425.2[e]	427.8	0.61	1.1	−0.28
3,6-Di-Cl	566.2	575.2	1.6	4.2	3.1
4,7-Di-Cl	720.6	731.4	1.5	4.0	3.2
2,7-Di-Cl	505.2[f]	502.8	−0.48	0.95	−0.24
3,8-Di-Cl	649.5	646.6	−0.48	3.1	2.4
4,9-Di-Cl	802.4	802.8	0.05	3.4	2.7
2,10-Di-Cl	624.3	620.7	−0.58	0.91	−0.05
3,11-Di-Cl	770.0	764.5	−0.71	2.6	1.8
2,11-Di-Cl	666.0	660.2	−0.87	0.60	−0.30
3,12-Di-Cl	811.7	804.0	−0.95	2.3	1.5
4,13-Di-Cl	964.9	961.6	−0.34	2.6	2.0
Average % deviation,					
glycols			1.1	3.4	2.7
chlorides			0.74	2.3	1.6
omitting n = 2, glycols			1.0	2.8	2.2
chlorides			0.56	2.1	1.4
Algebraic sum % dev.					
glycols			−2.3	17.0	12.7
chlorides			−0.65	25.8	15.8
omitting n = 2, glycols			−4.0	11.4	8.2
chlorides			−4.4	16.5	9.8

[a] Based on tables of references (5) and (7). Fourth CH_2 in longest alkyl group of dichlorides taken as 39.5 instead of devious 38.6. [b] Derived from atomic constants only with no correction for branching of chain. [c] Mumford and Phillips' correction for branching of chain used. [d] 5° increment taken as 0.3. [e] Average of 70 and 75°. [f] Average of 60, 65 and 70°.

In Table III the experimental parachors are compared with values calculated as in the above examples and also with values based simply on Mumford and Phillips' atomic parachors with no correction for branching.

It should be pointed out that while the use of an average correction value or strain constant greatly reduces the total deviation in a series, it does not distinguish between two isomers both with the same type of branching. Such isomers always differ from each other. It is seen from Table III that for the five glycols reported the average deviation between calculated and observed values is 1.1%; the minimum, 0.3%; the maximum, 2.1%. Strictly additive values give an average deviation of 3.4%, a minimum of 0.7% and a maximum of 5.6%. The application of an average correction for secondary branching gives an average deviation of 2.7%, a minimum of 0.3% and a maximum of 4.5%. For the eleven dichlorides reported the average deviation between the observed and predicted values is 0.7%; the minimum, 0.05%; the maximum, 1.6%. Strictly additive values give an average deviation of 2.3%, a minimum of 0.6% and a maximum of 4.2%. The application of an average correction for branching gives an average deviation of 1.6%, a minimum of 0.05% and a maximum of 3.2%. Exclusive of dichlorides in which the number of separating methylene groups is two, the average deviation is 0.6% for the parachors in which individual constitutive values are included, whereas the average deviation is 1.4% for parachors in which an average correction is applied.

Experimental

The ditertiary glycols and chlorides were all prepared by standard methods. Detailed procedures are given below for two typical examples.

2,10-Dimethyl-2,10-undecanediol.—Thirty-two grams of dimethyl azelate (0.15 mole) in 170 cc. of dry ether was added dropwise under moderate reflux to methylmagnesium iodide prepared by the addition of 46 cc. of methyl iodide in 60 cc. of dry ether to 17.4 g. of magnesium in 170 cc. of dry ether.[14] The addition mixture was warmed under gentle reflux over a water-bath for two hours (with agitation if possible) after all the ester had been added. It was then allowed to cool and was hydrolyzed by working into the mass saturated aqueous ammonium chloride solution until separation of a supernatant ether layer occurred.[15] The ether layer was decanted and the hydrolysis mass washed several times with small portions of ether. (If a red color due to iodine develops, it may be removed by washing with 5% aqueous thiosulfate solution.) The combined ether extracts were dried over Drierite. Most of the ether was removed from the extract by distillation. Final traces of ether and other volatiles were removed by heating up to 70° under reduced pressure. On cooling the residue readily crystallized to a red-brown solid. The first series of crystallizations from toluene gave 29 g. of slightly brown solid (91% crude). After four recrystallizations 24 g. (75%) of colorless, odorless crystals, m. p. 67–67.5°, was obtained.

2,10-Dichloro-2,10-dimethylundecane.—Ten grams of 2,10-dimethyl-2,10-undecanediol was dissolved in 162 cc. of anhydrous ether (8% solution) to which was added 30 cc. of methanol.[16] The temperature was maintained between −10 and −20° by an ice–salt-bath. Anhydrous hydrogen chloride was bubbled through with mechanical agitation until the solution was saturated or nearly so (twenty hours). After standing overnight in an ice-salt mixture the reaction mixture was concentrated by drawing dry air through under reduced pressure. Evaporation was continued in a large test-tube until the mixture became cloudy, at which point it was allowed to settle into two layers. The top ether layer was pipetted into a cold glass-stoppered bottle. The above extraction was repeated twice with small volumes of cold ether. The combined ether extracts were aerated further to remove as much of the remaining hydrogen chloride as possible, a small volume of chloroform was added and the solution was dried in the cold over 1:1 sodium sulfate and carbonate for twenty-four hours. Nine and six-tenths grams of oil with slight odor and color was recovered from the filtered chloroform solution by aeration as described above. Further evaporation and extraction of the original reaction residue gave 1.3 g. of brown oil for a total yield of 11.2 g. of crude dichloride (96%). The first fraction was further purified by the following general procedure. Ten cc. (9.6 g.) of the 2,10-dichloride was dissolved in 15 cc. of chloroform. The chloroform solution and 5 cc. of concentrated sulfuric acid were cooled to −15° in separate small glass-stoppered bottles, mixed and shaken thoroughly at intervals in the cold for twenty minutes. The mixture was allowed to stand in an ice–salt-bath for twenty-five minutes before the chloroform layer was pipetted off, centrifuged five to ten minutes, dried twenty-four hours in the cold over sodium sulfate–carbonate mixture and concentrated by aeration under reduced pressure as above. This final evaporation of solvent required about four hours toward the end of which a water-bath at 45° was applied. The yield of dried and filtered, colorless and odorless oil was 8.6 g. (74% over-all).

Summary

Three new ditertiary glycols and nine new ditertiary chlorides have been prepared.

The parachors of a number of ditertiary glycols and chlorides have been measured and shown to compare satisfactorily with predicted values.

These results indicate that large structural units after evaluation may be treated in general in an additive manner in predicting the parachor of a large molecule. As expected the agreement is closer when the functional groups are separated by four or more carbon atoms.

EMORY UNIVERSITY, GA.
RECEIVED JULY 31, 1947

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[14] Good mechanical agitation is essential since the Grignard addition products of dibasic esters of high molecular weight tend to separate as tough solid masses and stop the stirrer.

[15] Hydrolysis procedure outlined by Fieser, "Experiments in Organic Chemistry," 2nd ed., D. C. Heath and Co., New York, N. Y., 1941, p. 410.

[16] Concentration of solution and volume of methanol added was varied according to the solubility of a particular glycol at low temperatures.