320. *Surface-tension Determinations of Malonic Esters, and the Constitutive Nature of the Parachor.*

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MUMFORD and PHILLIPS have pointed out (J., 1929, 2112) that the parachor does not appear to be such a strictly additive property as is generally assumed; they accordingly suggested that Sugden's atomic and structural parachors be replaced by a fresh series of constants, and, in addition, that due allowance be made for constitutive and strain effects.

It seemed that if such constitutive effects were real, the malonic esters should show variations in parachor depending on the length and nature of the ester chain; further, the substituted alkyl esters should show additional strain effects depending on the number and the nature of the substituted groups. In order to investigate these points and to see if any quantitative relationships existed, the present work was undertaken.

Previous work (Macbeth, J., 1922, **121**, 1116) has shown that the chemical properties of the halogen atom in malonic ester derivatives differ markedly from those of similar atoms in alkyl halides, and it was hoped to measure the parachors of some 20 halogen malonic esters to determine the effect (if any) of the induced positive charge. Up to the present, however, it has not been possible to obtain the degree of purity necessary to give strictly reproducible values of the surface tension with these compounds, and the results are awaiting further confirmation.

EXPERIMENTAL.

The prep. of the esters used will be described elsewhere: they were all liquids. The surface tension was measured by the max. bubble-pressure method of Sugden (J., 1922, **121**, 858; 1924, **125**, 27). The experiments were carried out at 30° in a glass-fronted water-bath in which the cell and the manometer were immersed. The cells were of the type described by Sugden. The manometer fluid was EtOH tinted with magenta.

The rate of bubbling is important. As a bubble forms, the press. diff. increases to a max. and then decreases, at first slowly and finally rapidly as the bubble is detached. These stages can be followed easily with the wider tube, the max. being readily observed. A rate of about one bubble every 4 secs. proved most satisfactory: if the bubbles are formed more rapidly the correct max. is not definite. With the capillary tube, the pressure variation is not so easily followed. Sugden recommends a rate of one bubble per sec., but at this rate the manometer appeared to jump over the max. pressure. Mills and Robinson (J., 1931, 1629), using very fine capillaries, found that better results were obtained by first drawing a rapid stream of bubbles through the tube; in this work, however, capillaries were regarded as dirty if this procedure was necessary to make them work properly.

With liquids such as Hg it is essential that the surface tension be measured in an atmosphere free from aq. vapour: in similar work on ordinary liquids this precaution does not appear to have received attention, but since no appreciable differences were observed when precautions were taken to dry the incoming air in our experiments, it may be concluded that with these liquids the moisture drawn in with the air does not affect the measurement of the surface tension.

Porter (*Phil. Mag.*, 1930, **9**, 1065) has shown that the max. bubble-pressure method may be affected by the contact angle when the bubble breaks from the inside of the tube. Although we made no definite measurements, we found that, with the malonic esters at least, the contact angle appears to be zero.

Degree of Accuracy.—Sugden gives the accuracy of this method as 0·5%. With the compounds studied here the results are concordant to 0·25%, except for a few compounds of higher viscosity where the accuracy fell to 0·33%. The densities, measured in pyknometers of different capacities, were reproducible to at least one part in 1200 parts. Allowing for these variations in the calculation of the parachor, we consider that, as a conservative estimate, the values given below are correct to 0·2%.

The accuracy is also affected by the purity of the compounds. Every care was taken by repeated distillation and by the use of fresh samples to ensure purity. The simple esters gave no trouble, but with one or two of the substituted esters the trace of impurity may decrease the accuracy given above.

Calculations.—The surface tension and parachor were calculated in the usual way. Fractionally distilled C_6H_6 was taken as the standard liquid, the consts. used being $\gamma = 27{\cdot}58$ dynes/cm. and $D^{30°}_{4°} = 0{\cdot}868$. The cell constant was repeatedly checked during the investigation; if any anomalies arose, the cell and the corresponding set of results were rejected.

The factor for converting the press. (in cm. of EtOH) into dynes is 766·5.

For the calc. of the corresponding theoretical parachors, the constants both of Sugden ("Parachor and Valency," p. 38) and of Mumford and Phillips (*loc. cit.*) were utilised for the sake of comparison. The latter involve certain constitutive correction factors, and of these − 3 units for each C═O group, and − 3 units for each branching chain (as, *e.g.*, in each of the *iso*-esters) have been incorporated into the calcs. No correction is introduced in any of our tables for the attachment of the two ·CO_2R groups to the central C atom; this is discussed later (p. 2261).

Cell constants.

Cell.	Press., cm.	Radius of wide tube.	A.
A	5·395	0·1845	0·006501
B	5·934	0·1845	0·005923
C	5·669	0·1765	0·006200

Table I.

Unsubstituted malonic esters, $CH_2(CO_2R)_2$.

							[*P*], calc.*		Diff.*	
R =	*M.*	$D^{30°}_{4°}$.	Cell.	Press. (cm.).	γ.	[*P*], obs.	(1).	(2).	(1).	(2).
Methyl	132·1	1·1447	B	7·724	35·90	282·5	280·8	281·2	+ 1·7	+ 1·3
Ethyl	160·1	1·0445	A	5·966	30·56	360·4	358·8	361·2	+ 1·6	− 0·8
n-Propyl	188·1	0·9980	A	5·702	29·22	438·2	436·8	441·2	+ 1·4	− 3·0
*iso*Propyl	188·1	0·9807	C	5·521	26·97	437·1	436·8	435·2	+ 0·3	+ 1·9
n-Butyl	216·2	0·9735	A	5·583	28·61	513·8	514·8	521·2	− 1·0	− 7·4
*iso*Butyl	216·2	0·9632	A	5·265	27·02	511·8	514·8	515·2	− 3·0	− 3·4
*iso*Amyl	244·2	0·9505	A	5·307	27·21	586·9	592·8	595·2	− 5·9	− 8·3
n-Octyl	328·3	0·9121	A	5·488	28·08	828·7	826·8	835·2	+ 1·9	− 6·5
*cyclo*Hexyl	268·2	1·0570	A	7·018	35·83	620·5	614·6	621·2	+ 5·9	− 0·7
2-Methyl*cyclo*-hexyl	296·2	1·0263	A	6·609	33·77	695·6	692·6	701·2	+ 3·0	− 5·6
3-Methyl*cyclo*-hexyl	296·2	1·0167	A	6·281	32·13	693·7	692·6	701·2	+ 1·1	− 7·5
4-Methyl*cyclo*-hexyl	296·2	1·0154	A	6·277	32·10	694·4	692·6	701·2	+ 1·8	− 6·8

* (1) From Sugden's constants; (2) from Mumford and Phillips's constants.

The papers of Morgan and Chazal (*J. Amer. Chem. Soc.*, 1913, **35**, 1821) and of Morgan and Kramer (*ibid.*, p. 1834) contain data for the surface tension of the malonates. These figures have been recalculated by the method of Harkins and Brown (*ibid.*, 1919, **41**, 499) (see also "Parachor and Valency," p. 13). The parachor values so obtained are 281·8 for the Me ester (compare 282·5 in Table I), 361·9 for the Et ester (compare 360·4), and 583·6 for the *l*-amyl ester (compare 586·9 for the *iso*amyl ester).

In the last two cols. of Table I the differences between the obs.

and the calc. parachors are given, (1) the Sugden and (2) the Mumford and Phillips consts. respectively being used. Although the average difference of the values calc. from Sugden's constants is less than with Mumford and Phillips's figures, the fact that the former variations are of an irregular nature precludes the introduction of a regular constitutive correction factor. The Mumford and Phillips differences, on the other hand, although somewhat greater, show a deviation in one direction, indicating a common depressive constitutive effect. In the unsubstituted malonic esters, in general, the depression increases with the length of the alkyl chain, and in conformity, those compounds whose chains are of comparable length, such as the *n*-propyl and *iso*butyl, or the *n*-butyl and the *iso*amyl, show approximately the same depression. The effect appears to reach a limiting value with the *n*-butyl group, for the obs. result (— 7 units) is also obtained approximately in the case of the *iso*amyl and octyl esters.

Mumford and Phillips (*loc. cit.*) state that "the attachment of two or more halogen or other negative groups to the same carbon atom is also attended by a well-defined decrease in parachor. The contraction is variable depending on the size and polarity of the atoms and groups concerned, but on the average, $—CHX_2$ groups ($X = Cl$, CN, CO_2R, OR, etc.) have a parachor three units less, $—CX_3$ groups six units less, than those calculated additively." No allowance for such a correction has been made by us in the calc. of the Mumford and Phillips parachors set out in Table I: and it would therefore appear that the depressions recorded are simply particular cases of this general rule. With the *cyclo*hexyl malonates the depression is zero for the simplest member, but has a common value (— 6 to — 7) for the three methyl derivatives: it would thus appear that the effect of side-chain attachment to each polymethylene ring introduces a constitutive strain effect of the same order as that observed in the case of the branching of open chains. In other cases, the "variable" nature of the contraction is very pronounced, being approximately zero for the methyl and ethyl esters and increasing with the length of the alkyl chain up to a limiting value; the change may be ascribed to particular packings of the carbalkoxy-groups.

With certain other dibasic acids there is a similar and even greater lowering of the parachors of the esters. From the surface-tension figures of Morgan and co-workers (*locc. cit.*), and with the corrections already indicated, the parachors of the four compounds shown below have been calculated:

Compound.	[*P*].	[*P*] obs. — [*P*] calc. Sugden.	 M. & P.
Ethyl phthalate	490·0	— 2·7	— 4·1
Amyl phthalate	702·7	— 24·0	— 25·4
Amyl succinate	622·3	— 9·5	— 11·6
Amyl malate	629·9	— 21·9	— 19·9

They all show depressions, some of which are distinctly abnormal; but a repetition of the measurements is desirable before discussing them.

TABLE II.

Substituted malonic esters.

Malonate.	[*P*], obs.	[*P*] calc.		[*P*] obs. − [*P*] calc.	
		Sugden.	M. & P.	Sugden.	M. & P.
Methyl methyl-	321·0	319·8	321·2	+ 1·2	− 0·2
Methyl dimethyl-	354·0	358·8	361·2	− 4·8	− 7·2
Methyl ethyl-	364·2	358·8	361·2	+ 5·4	+ 3·0
Methyl *n*-propyl-	393·3	397·8	401·2	− 4·5	− 7·9
Methyl *iso*propyl-	390·6	397·8	398·2	− 7·2	− 7·6
Methyl *n*-butyl-	432·5	436·8	441·2	− 4·3	− 8·7
Methyl *iso*amyl-	470·7	475·8	478·2	− 5·1	− 7·5
Ethyl ethyl-	434·8	436·8	441·2	− 2·0	− 6·4
Ethyl diethyl-	506·5	514·8	521·2	− 8·3	− 14·7
Ethyl ethyl*iso*amyl-	619·3	631·8	638·2	− 12·5	− 18·9

The results obtained with the substituted esters (Table II) show clearly that the constitutive effect, particularly in the case of the disubstituted compounds, cannot be neglected. Discussion of the values will be limited to the differences shown in the last column of the table. The monosubstituted esters (with the exception of the first and third) still show some variation from the theoretical even after corrections of − 3 units have been made for chain branching at the central carbon in the alkyl group and for the *gem*-dicarbalkoxy-groups. The work of Ingold and Thorpe (J., 1921, **119**, 306, *et seq.*) on the deviation of the angle between the valencies in carbon compounds may be considered in connexion with the deviations observed in the parachors of the substituted malonic esters : the substitution of a hydrogen atom of the methylene group would cause a decrease in the angle between the carbalkoxy-groups, and a correction factor which was unnecessary in the case of a simple ester becomes apparent on substitution. The effect is, as expected, much more pronounced in the case of the disubstituted esters.

Gane and Ingold (J., 1931, 2166), from conductivity determinations, have deduced the distance between the two carboxyl groups in a series of substituted malonic acids. The decrease in distance between the two groups is evidently connected with the decrease in the parachor of the esters, but nothing more than a general statement is possible on account of the rather uncertain effect of the ester radical.

Sulphonal and trional, which present somewhat similar structural features, $CRR(SO_2Et)_2$, both show a parachor much below the calculated value (Freiman and Sugden, J., 1928, 266); and the introduction of the common correction factors (Mumford and Phillips, *loc. cit.*) does not remove the discrepancy in the results.

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