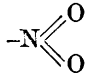
XXIII.—*The Parachor and Chemical Constitution. Part IV. Three-membered and Four-membered Rings.*

By SAMUEL SUGDEN and HENRY WILKINS.

(1) *Three-membered Rings.*

IN the first paper on the parachor (Sugden, J., 1924, **125**, 1180), a provisional value of 22·3 was assigned to the constant for a three-membered ring. This was based upon a misconception of the structure of the nitro-group which has since been cleared up by the discovery of the effect of semipolar double bonds upon the molecular parachor (Sugden, Reed, and Wilkins, J., 1925, **127**, 1525). From the data there discussed it appears probable that the nitro-group has the structure  $-N\begin{smallmatrix}\nearrow O\\ \searrow O\end{smallmatrix}$ and does not contain a three-membered ring. In the present paper, data are given for nine substances which, from chemical evidence, undoubtedly possess a cyclic structure and from which the constant for a three-membered ring can be deduced.

The observed values of the parachors for these substances are in the second column of Table I; the column headed $\Sigma[P]$ gives the sum of the atomic and structural constants, except that for the three-membered ring, so that the effect of this structure is obtained by subtracting $\Sigma[P]$ from $[P]$ obs.

The mean value for the effect of the three-membered ring on the molecular parachor may be taken as 17, which is in good agreement with the figure predicted from the degree of unsaturation in such structures, as discussed later (Section 3). Individual substances give figures diverging by 3—4 units from this mean and such variations require consideration.

In the first place, these differences are much larger than the experimental errors of measurement. The estimated error in the density determinations is 0·1% and in the surface tensions 0·5%; if

TABLE I.

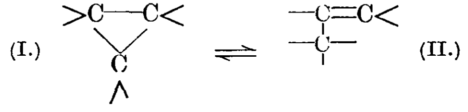
Parachor of Three-membered Rings.

Substance.	[*P*] obs.	$\Sigma[P]$.	Structural constant.	Error of measurement.
1. Ethylene oxide	112·5	98·0	14·5	0·2
2. Epichlorohydrin	193·7	174·2	19·5	0·4
3. Ethyl *cyclo*propane-1 : 1-dicarboxylate	417·1	402·6	14·5	0·8
4. Ethyl *cyclo*propane-1 : 2-dicarboxylate	422·8	,,	20·2	0·8
5. Ethyl *cyclo*propane-1 : 1 : 2 : 2-tetracarboxylate	701·1	688·2	12·9	1·4
6. Ethyl caronate	493·2	479·6	13·6	1·0
Esters of 3-methyl-Δ^2-*cyclo*propene-1 : 2-dicarboxylic acid.				
7. *normal* Methyl ester	371·6	352·6	19·0	0·8
8. ,, Ethyl ,,	450·2	430·6	19·5	0·9
9. *labile* ,, ,,	447·8	430·6	17·2	0·9
		Mean	16·7	

both errors are in the same direction, then (since the fourth root of the surface tension is used) the parachor is uncertain to 0·2% at most. The possible error thus introduced in the determination of the constant for the three-membered ring is given in the last column of Table I; it will be seen that it is much smaller than the differences found in the structural constant.

Further, it does not seem possible to account for these differences by the presence of impurities in some of the substances examined. Nos. 5, 7, and 8 are solids at the ordinary temperature and were recrystallised to constant melting point, whilst Nos. 3 and 4 were esters prepared from recrystallised acids of sharp melting point and boiled within 1°. Of the remaining liquids, epichlorohydrin was available in considerable quantity and was repeatedly dried and fractionated without producing any change in the surface tension or density, and the values found for the latter are in good agreement with those given by previous observers. The figure for ethylene oxide is calculated from the observations of Maass and Boomer (*J. Amer. Chem. Soc.*, 1922, **44**, 1709) on a carefully purified specimen. The esters 4 and 9 were purified by fractional distillation only; they boiled within 1°, and the parachors found for them fall well within the limits of the variation of the constant for a three-membered ring, so that there is no reason to suppose that they are seriously in error.

Another possible explanation of these differences is that some of the substances examined exhibit tautomerism and are mixtures of



isomerides having the structures (I) and (II). If this were the case, the structural constant would approach that for a non-polar double bond (23·2) as the proportion of (II) increased. This explanation is excluded, however, for the substances having the structure (II) are in many cases well known and have different properties. Thus the esters 4, 5, and 6 are isomerides of, but not identical with, certain esters of the glutaconic series which have been well characterised.

It is obvious, therefore, that in this series, as in others (compare Sugden and Whittaker, J., 1925, **127**, 1868), the parachor is not strictly an additive function of atomic and structural constants, but that these constants vary slightly from substance to substance. The variation in the constant for the three-membered ring is in harmony with modern views as to the effect of substituents on the stability of rings; in particular, it is interesting to note that the lowest values, corresponding to a lower degree of unsaturation, are given by unsubstituted rings or by those containing a *gem*-group (compare Ingold, J., 1921, **119**, 305).

The figures for the esters of 3-methyl-Δ^2-*cyclo*propene-1 : 2-dicarboxylic acid are of special interest in view of the peculiar type of isomerism exhibited by the derivatives of this acid (Goss, Ingold, and Thorpe, J., 1923, **123**, 327, 3342; 1925, **127**, 460). The parachors found for these substances show clearly that both the normal and labile esters contain a three-membered ring and a non-polar double bond; if the isomerism were due to the presence of a semipolar double bond in either the labile or the normal form, the parachor would have been 25 units lower. This explanation of the remarkable type of isomerism exhibited by these compounds would be compatible with the fact that both forms have been obtained optically active, but is definitely excluded by the data quoted in Table I.

(2) *Four-membered Rings.*

In a previous paper (Sugden, *loc. cit.*), the value 12·0 was allotted to the effect on the parachor on a four-membered ring; this figure was based on observations of the surface tensions of limonene and pinene by Mitchell and Smith (J., 1913, **103**, 489). We have now measured three derivatives of *cyclo*butane with the results shown in Table II. It will be seen that the new data give good confirmation

TABLE II.

	$[P]$ obs.	$\Sigma[P]$.	Four-membered ring.
Ethyl 1-cyano*cyclo*butane-1-carboxylate	360·4	348·8	11·6
Ethyl *cyclo*butane-1 : 1-dicarboxylate	454·1	441·6	12·5
Ethyl *cyclo*butanecarboxylate	309·4	298·8	10·6
		Mean	11·6

of the older value and are also in good agreement with the constant calculated from the degree of unsaturation (see Section 3).

These *cyclo*butane derivatives were prepared by the method of Perkin and Carpenter (J., 1899, **75**, 921), and the esters measured were made *via* the silver salt from specimens of the free acids which had been carefully purified by crystallisation or distillation. The purification of the *cyclo*butane-1 : 1-dicarboxylic acid was effected by a specially devised method (see Experimental). The monocarboxylic ester prepared from this purified acid by the elimination of carbon dioxide and esterification boiled several degrees lower than Perkin and Carpenter's ester (*loc. cit.*), but its purity was confirmed by a determination of its saponification value.

(3) *Structural Constants and Unsaturation.*

It has been suggested in previous communications that the principal factor which determines the value of structural parachors is the intensity of unsaturation. This idea can now be expressed quantitatively, as all the more important constants are known with a fair degree of accuracy.

In Table III, col. 2 gives the number of latent valencies in the structure indicated in col. 1, or the number of hydrogen atoms required to convert each structure into an open-chain saturated compound. Col. 3 gives the number of octets which share this unsaturation, whilst col. 4 gives the ratio x/n, which may be termed the degree of unsaturation. If it is assumed that the structural parachor is proportional to the degree of unsaturation, then, from the experimental value for the double bond (which is based upon the largest number of observations), the parachors for the other structures can be calculated. The numbers thus obtained are in col. 6, and they are seen to be in good agreement with the experimentally determined values in col. 5.

TABLE III.

Structure.	Latent valencies (x).	Octets (n).	Degree of unsaturation (x/n).	Parachor. Obs.	Parachor. Calc.
Triple bond	4	2	2·000	46·6	46·4
Double bond	2	2	1·000	(23·2)	(23·2)
Three-membered ring	2	3	0·667	17	15·5
Four-membered ring	2	4	0·500	11·6	11·6
Five-membered ring	2	5	0·400	8·5	9·3
Six-membered ring	2	6	0·333	6·1	7·7

EXPERIMENTAL.

In the course of this work new measurements have been made of the surface tension and density of eleven compounds. The surface tensions were determined by the method of maximum bubble pressure (Sugden, J., 1922, **121**, 858; 1924, **125**, 27); the constants for the bubblers used are :

Apparatus	4c.	4d.	5a.	8a.	9a.
r_2 (cm.)	0·139	0·139	0·140	0·206	0·216
A	0·004790	0·007767	0·006805	0·003712	0·00536

Densities were determined by the U-shaped pyknometer previously described (J., 1924, **125**, 1171) and are given in g./c.c. All temperatures recorded were obtained by comparison with a standard thermometer with *N.P.L.* certificate and are corrected for exposed stem.

The tables below are set out in the same manner as in previous papers and do not need further description. The parachor in the last column is calculated by the formula $[P] = \gamma^{\frac{1}{4}}M/(D - d)$, where γ is the surface tension, M the molecular weight, D the density of the liquid, and d the density of the vapour.

Ethylene oxide, C_2H_4O; $M = 44{\cdot}04$. The values of γ, D, and d are taken from the paper of Maass and Boomer (*loc. cit.*).

t.	γ(dynes/cm.).	$(D-d)$ (g./c.c.).	Parachor.
−52·0°	36·4	0·9657	112·0
−43·4	34·8	0·9545	112·1
−26·2	31·9	0·9316	112·4
−15·0	30·3	0·9164	112·7
− 5·0	28·4	0·9027	112·6
5·8	26·8	0·8879	112·9
13·3	25·4	0·8805	112·3
20·0	24·3	0·8679	112·7
		Mean	112·5

Epichlorohydrin, C_3H_5OCl, $M = 92{\cdot}51$, was dried over calcium chloride and boiled at 115° (corr.)/740 mm. Densities determined : $D^{10°}_{4°}$ 1·190, $D^{33°}_{4°}$ 1·161, $D^{55°}_{4°}$ 1·136, $D^{71°}_{4°}$ 1·116, whence $D^{t°}_{4°} = 1{\cdot}202 - 0{\cdot}00119t$. These values are in good agreement with those of Thorpe (J., 1880, **37**, 207).

App.	t.	P.	D.	ϕ.*	γ.	Parachor.
9a	12·5	6939	1·187	1·0250	38·13	193·6
,,	31	6447	1·165	1·0264	35·48	193·7
,,	50·5	5964	1·142	1·0280	32·86	193·9
,,	68·5	5504	1·121	1·0298	30·38	193·7
,,	89	5011	1·096	1·0320	27·72	193·6
					Mean	193·7

* A correction factor, see J., 1924, **125**, 31.

Ethyl cyclo*propane*-1 : 1-*dicarboxylate*, $C_9H_{14}O_4$, $M = 186{\cdot}2$, was prepared *via* the silver salt from purified acid which had been recrystallised from benzene until its melting point was constant. The ester boiled at 218° (corr.)/769 mm. Densities determined :

$D^{15°}_{4°}$ 1·071, $D^{50°}_{4°}$ 1·034, $D^{93°}_{4°}$ 0·988, $D^{139°}_{4°}$ 0·940, whence $D^{t°}_{4°} = 1{\cdot}087 - 0{\cdot}00105t$.

App.	*t*.	*P*.	*D*—*d*.	ϕ.	γ.	Parachor.
4c	25	6430	1·061	1·0155	31·28	415·1
9a	75	4712	1·008	1·0313	26·05	417·4
4c	110	4633	0·971	1·0197	22·62	418·3
9a	134	3641	0·946	1·0380	20·25	417·6
4c	153	3780	0·925	1·0230	18·52	417·7
9a	164	3141	0·914	1·0425	17·55	417·1
4c	189	3156	0·887	1·0264	15·52	416·7
					Mean	417·1

Ethyl cyclo*propane*-1 : 2-*dicarboxylate*, $C_9H_{14}O_4$, *M* = 186·2, was twice distilled under diminished pressure; the specimen used boiled at 106·5—107·5° (corr.)/11 mm. Densities determined : $D^{13°}_{4°}$ 1·062, $D^{54°}_{4°}$ 1·020, $D^{81°}_{4°}$ 0·993, whence $D^{t°}_{4°} = 1{\cdot}075 - 0{\cdot}00101t$.

App.	*t*.	*P*.	*D*.	ϕ.	γ.	Parachor.
5a	11	4810	1·064	1·0210	33·41	420·9
8a	14	8802	1·061	1·0168	33·22	421·3
5a	54	4154	1·020	1·0233	28·92	423·4
8a	71	7215	1·003	1·0194	27·29	424·3
5a	90	3607	0·984	1·0258	25·17	423·9
					Mean	422·8

Ethyl cyclo*propane*-1 : 1 : 2 : 2-*tetracarboxylate*, $C_{15}H_{22}O_8$, *M* = 330·2, was recrystallised from ligroin and melted sharply at 43° (corr.). Densities determined : $D^{57°}_{4°}$ 1·117, $D^{69°}_{4°}$ 1·104, $D^{77°}_{4°}$ 1·096, $D^{83·2°}_{4°}$ 1·090, whence $D^{t°}_{4°} = 1{\cdot}176 - 0{\cdot}00104t$.

App.	*t*.	*P*.	*D*.	ϕ.	γ.	Parachor.
5a	76	4170	1·097	1·0250	29·08	699·0
,,	97	3876	1·075	1·0264	27·08	700·8
,,	122	3537	1·049	1·0282	24·75	702·2
,,	152	3127	1·018	1·0308	21·93	702·2
					Mean	701·1

Ethyl caronate (*ethyl* trans-3 : 3-*dimethyl*cyclo*propane*-1 : 2-*dicarboxylate*), $C_{11}H_{18}O_4$, *M* = 214·2, was prepared from recrystallised caronic acid and absolute alcohol and boiled at 244° (corr.)/762 mm. Densities determined : $D^{11°}_{4°}$ 1·035, $D^{30·5°}_{4°}$ 1·015, $D^{53°}_{4°}$ 0·992, $D^{71°}_{4°}$ 0·973, whence $D^{t°}_{4°} = 1{\cdot}046 - 0{\cdot}00103t$.

App.	*t*.	*P*.	*D*.	ϕ.	γ.	Parachor.
4d	12	3965	1·034	1·0245	31·56	491·0
,,	34	3662	1·011	1·0260	29·19	492·5
,,	54	3395	0·990	1·0275	27·10	493·7
,,	63·5	3258	0·981	1·0283	26·02	493·1
,,	75	3128	0·969	1·0291	25·00	494·3
,,	93·5	2890	0·950	1·0309	23·15	494·6
					Mean	493·2

normal *Methyl* 3-*methyl*-Δ^2-cyclo*propene*-1 : 2-*dicarboxylate*, $C_8H_{10}O_4$, *M* = 170·1. White crystals, m. p. 33—34° (corr.). Densities determined : $D^{39°}_{4°}$ 1·123, $D^{57°}_{4°}$ 1·103, $D^{71°}_{4°}$ 1·087, $D^{91°}_{4°}$ 1·064, whence $D^{t°}_{4°} = 1{\cdot}169 - 0{\cdot}00115t$.

App.	t.	P.	D.	ϕ.	γ.	Parachor.
4d	42	4460	1·121	1·0237	35·46	370·3
,,	63	4138	1·097	1·0250	32·94	371·4
,,	81	3863	1·076	1·0262	30·79	372·4
,,	95	3632	1·060	1·0275	28·98	372·3
					Mean	371·6

normal *Ethyl* 3-*methyl*-Δ^2-cyclo*propene*-1 : 2-*dicarboxylate*, $C_{10}H_{14}O_4$, M = 198·1. White crystals, m. p. 38—39° (corr.). Densities determined : $D_{4°}^{44·5°}$ 1·038, $D_{4°}^{60·5°}$ 1·024, $D_{4°}^{81·5°}$ 1·001, whence $D_{4°}^{t°} = 1·084 - 0·00100t$.

App.	t.	P.	D.	ϕ.	γ.	Parachor.
4d	41·5	3947	1·042	1·0248	31·42	450·1
,,	51	3803	1·033	1·0255	30·33	450·1
,,	62	3653	1·022	1·0263	29·12	450·2
,,	77·5	3448	1·007	1·0275	27·52	450·6
					Mean	450·2

labile *Ethyl* 3-*methyl*-Δ^2-cyclo*propene*-1 : 2-*dicarboxylate*, $C_{10}H_{14}O_4$, M = 198·1. This ester was prepared by distilling the normal ester at atmospheric pressure (compare Goss, Ingold, and Thorpe, *loc. cit.*). Considerable decomposition and gas evolution took place; the distillate fractionated under diminished pressure gave a 50% yield of an oil, b. p. 155—156° (corr.)/19 mm., which was regarded as the labile ester. Densities determined : $D_{4°}^{23°}$ 1·072, $D_{4°}^{40·5°}$ 1·054, $D_{4°}^{64·5°}$ 1·029, whence $D_{4°}^{t°} = 1·096 - 0·00103t$.

App.	t.	P.	D.	ϕ.	γ.	Parachor.
4d	26	4275	1·069	1·0235	33·98	447·5
,,	50	3911	1·045	1·0252	31·13	447·8
,,	77	3507	1·017	1·0273	27·99	448·0
					Mean	447·8

Ethyl 1-*cyano*cyclo*butane*-1-*carboxylate*, $C_8H_{11}O_2N$, M = 153·1. The crude ester was prepared by the condensation of cyanoacetic ester and trimethylene bromide (Perkin and Carpenter, *loc. cit.*); the yield was low in the first runs, but was raised to 67% by using alcohol dried with the aluminium–mercury couple. The crude ester (b. p. 99—102°/14 mm.) was partly hydrolysed with a slight excess of methyl-alcoholic potash, and the free cyano-acid recrystallised twice from benzene; it then melted sharply at 67—68° (corr.). From this, the ethyl ester was prepared *via* the silver salt and boiled at 215·5—216° (corr.)/762 mm. Densities determined : $D_{4°}^{13·5°}$ 1·045, $D_{4°}^{43°}$ 1·015, $D_{4°}^{70·5°}$ 0·988, $D_{4°}^{92°}$ 0·966, whence $D_{4°}^{t°} = 1·058 - 0·000995t$.

App.	t.	P.	D.	ϕ.	γ.	Parachor.
4d	13·5	4495	1·045	1·0219	35·68	358·1
,,	46	4011	1·012	1·0237	31·88	359·5
,,	57	3887	1·001	1·0242	30·92	360·7
,,	69·5	3673	0·989	1·0253	29·26	360·1
,,	84·5	3495	0·974	1·0262	27·86	361·1
,,	111·5	3128	0·947	1·0285	24·99	361·5
,,	126·5	2936	0·932	1·0299	23·49	361·7
					Mean	360·4

Ethyl cyclo*butane*-1 : 1-*dicarboxylate*, $C_{10}H_{16}O_4$, $M = 200{\cdot}2$. The crude cyano-ester on complete hydrolysis gave a mixture of the required dibasic acid and malonic acid derived from unchanged cyanoacetic ester. This mixture was difficult to separate by crystallisation from any solvent, but the malonic acid was removed completely in the following manner. The mixed acids were dissolved in excess of 5% ammonia, and barium chloride solution was added until no further precipitate was produced. The precipitate of barium malonate was filtered off, and the filtrate, after acidification and extraction with ether, gave nearly pure *cyclo*butane-1 : 1-dicarboxylic acid, which, after one crystallisation from benzene, melted at 156·5° (corr.). From this, the ester was prepared *via* the silver salt; b. p. 228·5—229·5° (corr.)/755 mm. Densities determined: $D_{4^\circ}^{15 \cdot 5^\circ}$ 1·054, $D_{4^\circ}^{51 \cdot 5^\circ}$ 1·017, $D_{4^\circ}^{79^\circ}$ 0·990, $D_{4^\circ}^{99^\circ}$ 0·969, whence $D_{4^\circ}^{t^\circ} = 1{\cdot}070 - 0{\cdot}00102t$.

App.	t.	P.	D.	ϕ.	γ.	Parachor.
4d	15	4086	1·054	1·0243	32·51	453·5
,,	49	3601	1·0195	1·0266	28·70	454·4
,,	81	3157	0·987	1·0294	25·24	454·5
					Mean	454·1

Ethyl cyclo*butanecarboxylate*, $C_7H_{12}O_2$, $M = 128{\cdot}1$. The pure dicarboxylic acid lost carbon dioxide smoothly at 185—190° and gave a good yield of the monobasic acid, b. p. 190—192° (corr.)/762 mm. The ethyl ester prepared *via* the silver salt was repeatedly fractionated and boiled at 152—154° (corr.)/756 mm. (Perkin and Carpenter give 159—162°). The purity of the ester was therefore checked by a determination of its equivalent by hydrolysis with potash (Found: 127·0. Calc.: 128·1). Densities determined: $D_{4^\circ}^{31^\circ}$ 0·956, $D_{4^\circ}^{45 \cdot 5^\circ}$ 0·941, $D_{4^\circ}^{60^\circ}$ 0·927, $D_{4^\circ}^{74 \cdot 5^\circ}$ 0·911, whence $D_{4^\circ}^{t^\circ} = 0{\cdot}988 - 0{\cdot}00103t$.

App.	t.	P.	D.	ϕ.	γ.	Parachor.
4d	19·5	3766	0·968	1·0242	29·96	309·5
,,	47·5	3335	0·939	1·0265	26·58	309·6
,,	70	3016	0·916	1·0286	24·10	309·8
,,	90·5	2707	0·895	1·0311	21·68	308·8
					Mean	309·4

Summary.

1. The "structural" parachor for a three-membered ring is found to be 17; individual substances show variations of a few units from this value.

2. Both the normal and the labile forms of esters of 3-methyl*cyclo*propenedicarboxylic acid contain a non-polar double bond.

3. The value for a four-membered ring is shown to be 11·6.

4. Structural parachors are proportional to the degree of unsaturation of the multiple bond or ring structure concerned.

The authors wish to express their thanks to Prof. C. K. Ingold, F.R.S., for the loan of substances 4, 5, 7, and 8 in Table I, and to Mr. R. G. Atkinson for a specimen of synthetic caronic acid. One of us (S. S.) is also indebted to the Research Fund Committee of this Society for a grant which has partly defrayed the cost of this investigation.

BIRKBECK COLLEGE (UNIVERSITY OF LONDON),
LONDON, E.C. 4.
[*Received, November 6th*, 1926.]