## **232.** The Dissociation Constants of Organic Acids. Part XVIII.\* Some Cyclic 1:1-Diacetic Acids.

By WILLIAM L. GERMAN and ARTHUR I. VOGEL.

OF the numerous methods that have been employed for the comparative study of the influence of substituents upon chemical properties with a view to the determination of qualitative values for valency-deflexion angles and also for throwing light upon the structure of ring systems, the two that have been applied to the largest number of substituents are those due to Thorpe and Ingold and their co-workers (J., 1915 et seq.) and to Vogel (J., 1928, 2014). The former depends inter alia upon (i) the stability of the trans-spiro-acid (I) towards hydrochloric acid of various concentrations at different temperatures, and (ii) the tautomeric change between keto-acids of the type (II) and their hydroxy-ring isomerides

$$> \subset \subset_{\text{CH} \cdot \text{CO}_2\text{H}}^{\text{CH} \cdot \text{CO}_2\text{H}} > \subset \subset_{\text{CH}_2 \cdot \text{CO}_2\text{H}}^{\text{CO} \cdot \text{CO}_2\text{H}} > \subset \subset_{\text{CH} \cdot \text{CO}_2\text{H}}^{\text{C}(\text{OH}) \cdot \text{CO}_2\text{H}}$$
 
$$(\text{II.}) \qquad (\text{III.}) \qquad (\text{III.}) \qquad (\text{III.})$$
 
$$(\text{IV.}) > \subset \subset \subset_{\text{CO}_2\text{Et}}^{\text{CN}} \qquad > \subset \subset_{\text{CH}(\text{CN}) \cdot \text{CO}_2\text{Et}}^{\text{C}(\text{OH}) \cdot \text{CO}_2\text{Et}} \qquad (\text{V.})$$

(III). The latter method utilises the yield of the bimolecular compound (V), obtained by the reduction of the unsaturated cyano-ester (IV) with aluminium amalgam in moist ethereal solution, as a basis of comparison. The yields of (V) (compare J., 1931, 1796) for the substituents cyclopentane and 3-methylcyclopentane are 13% and 13% respectively, and for cyclohexane, and 2-,† 3-, and 4-methylcyclohexane the corresponding yields are 6, 2,† 6, and 4% respectively. These figures would suggest that there is no essential difference in the configurations of the cyclopentane and 3-methylcyclopentane rings or between the unsubstituted cyclohexane and the 3- and 4-methylcyclohexane rings and possibly also the 2-methylcyclohexane ring. Desai (J., 1932, 1065), employing the Thorpe-Ingold method, has found a remarkable similarity between the behaviour of the cyclopentane and 3-

<sup>\*</sup> The paper entitled "A New Series of Buffer Mixtures Covering the  $p_{\rm H}$  Range 1 to 6" (Analyst, 1937, 62, 271) is regarded as Part XVII.

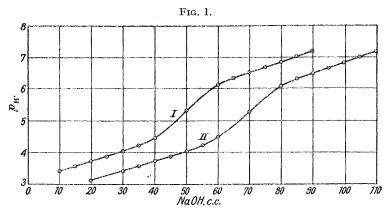
<sup>†</sup> Oommen, Ph.D. Thesis, London, 1929.

methylcyclopentane compounds, but serious differences were encountered between the cyclohexane and the 3- and 4-methylcyclohexane compounds (J., 1932, 1053). Ives, Linstead, and Riley (J., 1932, 1093) suggest, as a result of their determinations of the classical primary dissociation constants of cyclopentane-, cyclohexane-, and 3- and 4methylcyclohexane-1:1-diacetic acids, that the chemical tests employed by Desai are here "misleading if applied as a test for valency deflexion." The three authors state (loc.  $\it cit.$ ) that their determinations of  $K_{1\, {
m class.}}$  for these acids by conductivity "involve certain difficulties of calculation." A method for overcoming all these difficulties and which leads to values of the primary thermodynamic dissociation constants is described in Part XI of this series (J., 1935, 22). In view of the importance of the subject in connexion with the general question of the structure of simple and substituted cyclopentane and cyclohexane rings, measurements have been made of the true primary and secondary ionisation constants of the substituted 1:1-diacetic acids by potentiometric titration, and the distances between the carboxyl groups have been calculated by the methods of Bierrum (Z. physikal. Chem., 1923, 106, 219) (B.) and of Gane and Ingold (J., 1931, 2153, 2160, 2180) (G. & I.). Our results, together with those of Gane and Ingold (J., 1931, 2158) and of Ives, Linstead, and Riley (I. L. & R.), are collected in the following table.

			G. & I.					
	$K_{1  \text{therm}}$ .	$K_{2  \mathrm{therm}}$ .	v (B.)	v (G. & I.)	$K_1 (\mu = 0)$	$K_2 (\mu = 0)$	I. L. & R.	
1: 1-Diacetic acid.	$\times$ 104.	$\times$ 108.	$\times$ 108.	$\times 10^8$ .	× 104.	$\times$ 108.	$K_{1 \text{ class.}} \times 10^4$ .	
cycloPentane		17.0	1.30	3.38	1.66	25.8	1.76	
3-Methyl <i>cyclo</i> pentane		18.2	1.32	3.40				
cycloHexane *		8.26	1.03	3.12	$3 \cdot 34$	9.9	$3 \cdot 23$	
2-Methyl <i>cyclo</i> hexane		13.00	$1 \cdot 16$	3.25	_			
3-Methyl <i>cyclo</i> hexane		8.34	1.04	$3 \cdot 15$		-	3.25	
4-Methyl <i>cyclo</i> hexane	3.23	8.02	1.03	$3 \cdot 13$		_	3.21	

<sup>\*</sup> Jones and Soper (J., 1936, 135) give  $K_{1 \text{therm.}} = 3.25 \times 10^{-4}$  and  $K_{2 \text{therm.}} = 10.85 \times 10^{-8}$ .

The potentiometric titration curves are shown in Figs. 1 and 2; the abscissæ have been displaced for the different acids in order to avoid overlapping and to emphasise the similar-



I. cycloPentane-1: 1-diacetic acid.

II. 3-Methylcyclopentane-1: 1-diacetic acid.

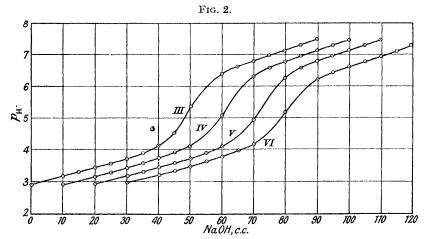
ities in the curves. Our results support the view that the substituted acids closely resemble the parent substances, and provide definite evidence for the current accepted conception of the strainless structure of the cyclopentane and cyclohexane rings.

## EXPERIMENTAL.

Preparation of Materials.—Full details of the preparation of all the acids, except 2-methyl-cyclohexane-1: 1-diacetic acid, have been given by Vogel (J., 1934, 1760); only the methods of further purification are now indicated. All samples were dried in a vacuum desiccator over calcium chloride for several days before use.

cycloPentane-1:1-diacetic acid. Specimen I. A sample which had been recrystallised from dilute alcohol was crystallised from redistilled dioxan (b. p.  $101-103\cdot5^{\circ}$ )-light petroleum

(b. p. 40—60°, AnalaR, sodium-dried), the separated solid well washed with sodium-dried light petroleum (b. p. 40—60°) to remove adhering dioxan, and then dried in a vacuum; m. p. 179°.



III. cycloHexane-1: 1-diacetic acid. V. 3-Methylcyclohexane-1: 1-diacetic acid.

IV. 2-Methylcyclohexane-1: 1-diacetic acid.
VI. 4-Methylcyclohexane-1: 1-diacetic acid.

Specimen II. This was purified through the anhydride and recrystallised from hot water; m. p. 178°.

cycloHexane-1: 1-diacetic acid. Recrystallised from 80% alcohol; m. p. 181°.

2-Methylcyclohexane-1: 1-diacetic acid. 400 C.c. of absolute alcohol were saturated with dry ammonia at - 5° during 5 hours and added to a mixture of 112 g. (1 mol.) of pure 2-methylcyclohexanone, b. p. 164°/770 mm., and 226 g. (2 mols.) of ethyl cyanoacetate contained in a large (1500 c.c.) wide-mouthed glass-stoppered bottle. The whole was kept at 0° for 4 days and then at room temperature for 5 days. A small amount of solid (cyanoacetamide) separated; 2 litres of water were added (the separated solid dissolved), the whole extracted three times with ether, the aqueous layer acidified with hydrochloric acid (to methyl-red), and a further 200 c.c. of concentrated hydrochloric acid added. The separated dicyano-imide was collected after 24 hours and dried at 100° (29·3 g.). The crude substance had m. p. 243°, and m. p. 245° after recrystallisation from 50% alcohol (Kon and Thorpe, J., 1919, 115, 694, give m. p. 245°). 58.4 G. of the finely-powdered dicyano-imide were dissolved in 120 c.c. of cold concentrated sulphuric acid, left for 24 hours, 112 c.c. of water cautiously added, and the whole boiled under reflux for 17 hours. The crude acid which had separated was filtered off after 48 hours, extracted with a saturated solution of sodium bicarbonate, the extract filtered, acidified with concentrated hydrochloric acid, and the solid collected after 24 hours (yield: 46.4 g. after drying at 100°). The acid was recrystallised successively from ether-benzene (2:1) and 50% alcohol; it had

m. p. 152° (Kon and Thorpe, loc. cit., give m. p. 148°).

3-Methylcyclopentane-1: 1-diacetic ucid. This was purified through the anhydride, and recrystallised from chloroform (AnalaR)-light petroleum (b. p. 40—60°, AnalaR, sodium-dried); m. p. 134—135°.

3-Methylcyclohexane-1: 1-diacetic acid. Recrystallised from 50% alcohol; m. p. 142°.

4-Methylcyclohexane-1: 1-diacetic acid. Recrystallised from 50% alcohol; m. p. 160°.

General Technique and Apparatus.—This has already been described (J., 1935, 912, 1628; J. Amer. Chem. Soc., 1936, 58, 1546; Phil. Mag., 1936, 22, 796). All measurements were carried out at  $25^{\circ} \pm 0.01^{\circ}$  with the quinhydrone electrode. Standardisation was effected before and after each titration against at least two independent 0.1N-calomel cells, and also against 0.05M-potassium hydrogen phthalate (the A.R. solid was specially purified for this purpose) and Walpole's standard acetate buffers (18°), appropriate allowance being made for the difference in temperature.

The results were computed as described for maleic acid (*Phil. Mag., loc. cit.*), the large difference in magnitude between  $K_1$  and  $K_2$  permitting the independent evaluation of  $K_1$  class. and  $K_2$  class. All the results are collected in the following tables; the classical values are included to permit comparison with the data in the literature.

NaOH,		$K_{1  { m elass}}$ .		$K_{1  \rm therm.}$	NaOH,		$K_{2{ m class}}$ .	0	$K_{2  \mathrm{therm.}}$
c.c.	⊅н.	$\times$ 104.	$\mu  imes 10^3$ .		c.c.	⊅н.	$\times 10^7$ .	$\mu  imes 10^3$ .	$\times$ 107.
		сус	loPentane	-1:1-diace	tic Acid (M	$= 186 \cdot 10)$			
Potentio	metric titro	ation of 10	0·00 c.c. o	f 0·005M-a	cid against 0	·009950M-	-sodium h	ydroxide so	lution.
0.00	3.085				50.00	5.281			
10.00	3.382	1.70	1.32	1.63	60.00	6.083		4.03	1.65
15.00	3.531	1.70	1.59	1.62	65.00	6.296	$\substack{2\cdot 10 \\ 2\cdot 15}$	$\substack{4.81\\5.25}$	1.65
20.00	3.680	1.69	$^{1\cdot 87}_{2\cdot 14}$	$1.61 \\ 1.60$	$\begin{array}{c} 70.00 \\ 75.00 \end{array}$	$6.479 \\ 6.638$	2.13 $2.24$	5·25 5·67	1.72
$25.00 \\ 30.00$	$\frac{3.832}{4.000}$	$\substack{1.69\\1.65}$	$\frac{2.14}{2.40}$	1.56	80.00	6.811	2.25	6.08	1.71
35.00	4.142	1.65	2.65	1.56	85.00	6.990	$2.\overline{29}$	6.42	1.73
40.00	4.401	_	_	_	90.00	$7 \cdot 162$	2.60	6.78	(1.95)
			Mea	ın 1·60				Mea	an 1.70
		9 M of h	w.lorrolo.	ntana 1 · 1	diacetic Acid	/M 200	0.94\		
Potentio	metric titu	ation of 10	0.00 cco	f 0.005M-a	cid against 0	·009950M	-sodium h	vdvoxide so	olution.
0.00		atton of 10	0 00 0.0. 0	, 0 000112 11	50.00	5.240		,	
10.00	$\begin{array}{c} 3 \cdot 078 \\ 3 \cdot 382 \end{array}$	1.70	$1.\overline{32}$	1.63	60.00	6.068	_	_	_
15.00	3.531	1.70	1.59	1.62	65.00	6.266	2.25	4.81	1.77
20.00	3.680	1.70	1.87	1.61	70.00	6.447	$2.\overline{31}$	5.25	1.80
25.00	3.833	1.69	$2 \cdot 14$	1.60	75.00	6.607	2.40	5.67	1.84
30.00	4.000	1.65	$2 \cdot 40$	1.56	80.00	6.780	2.41	6.08	1.84
35.00	4.160	1.74	$2 \cdot 65$	1.64	85.00	6.964	2.44	6.42	1.84
40.00	4.451	_	— м.		90.00	$7 \cdot 156$	2.65	6·78	(1·99) an 1·82
			Mea	n 1.61				Mea	an 1.02
		cy	cloHexan	e-1:1-diace	etic Acid (M	= 200.24)	•		
Potentio	metric titr	ation of 10	0.00 c.c. d	f 0.005M-a	cid against 0	0·009919M	-sodium h	ydroxide so	olution.
0.00	2.914		_		50.00	5.377			
10.00	3.178	3.49	1.57	$3 \cdot 34$	60.00	6.376			
15.00	3.306	3.45	1.79	3.29	65.00	6.600	1.036	4.79	0.814
20.00	3.437	3.44	2.02	3.27	70.00	6.787	1.040	5.23	0.808
<b>25</b> ·00	3.553	3.45	2.25	3.27	75.00	6.939	1.097	5.65	0.844
$\begin{array}{c} 30.00 \\ 35.00 \end{array}$	3.721	3.45	2.48	3.26	80·00 85·00	$7.108 \\ 7.301$	$1.109 \\ 1.094$	$6.04 \\ 6.41$	$\begin{array}{c} 0.834 \\ 0.828 \end{array}$
40.00	$3.890 \\ 4.129$	$\begin{array}{c} 3 \cdot 41 \\ 3 \cdot 26 \end{array}$	$\substack{2.65 \\ 2.91}$	$3.21 \ (3.07)$	90.00	7.482		0.41	
40 00	Ŧ 125	3.20		in 3.27	30 00	1 102		Mea	n 0·826
			2.200	0 - 1					
TO 4 41					liacetic Acid			1	. 1 4
					cid against 0	•009915M		ydroxide so	olution.
0.00	2.970	ation of 10 —	0.00 c.c. d —	f 0·005M-a	cid against 0 50.00	0.009915M 5.176		ydroxide so —	olution. —
0·00 10·00	$2.970 \\ 3.208$	ation of 10 	0.00 c.c. c  1.52	f 0·005M-a  2·98	cid against 0 50.00 60.00	5·176 6·183	-sodium h — —	_	_
0·00 10·00 15·00	2.970 $3.208$ $3.338$	3·11 3·10	0.00 c.c. c  1.52 1.76	of 0.005M-a 	cid against 0 50·00 60·00 65·00	5·009915M 5·176 6·183 6·415	-sodium h  1.60		 1·26
0·00 10·00 15·00 20·00	2.970 $3.208$ $3.338$ $3.467$	ation of 10 3·11 3·10 3·13	0·00 c.c. c 	1f 0·005M-a 	cid against 0 50.00 60.00 65.00 70.00	5·176 6·183 6·415 6·596	-sodium h 	$\frac{-}{4\cdot 79}$ $5\cdot 24$	 1·26 1·28
0·00 10·00 15·00 20·00 25·00	2·970 3·208 3·338 3·467 3·606	ation of 10 3.11 3.10 3.13 3.13	$0.00 \ c.c. \ c$ $1.52$ $1.76$ $1.99$ $2.23$		cid against 0 50·00 60·00 65·00 70·00 75·00	5·176 6·183 6·415 6·596 6·761	-sodium h 	$4.79$ $5.24$ $5.65$	1·26 1·28 1·29
0·00 10·00 15·00 20·00	2.970 $3.208$ $3.338$ $3.467$	ation of 10 3·11 3·10 3·13	0·00 c.c. c 	1f 0·005M-a 	cid against 0 50.00 60.00 65.00 70.00	5·176 6·183 6·415 6·596	-sodium h 	$\frac{-}{4\cdot 79}$ $5\cdot 24$	 1·26 1·28
0.00 10.00 15.00 20.00 25.00 30.00	2.970 3.208 3.338 3.467 3.606 3.758	ation of 10  3.11 3.10 3.13 3.13 3.12	0·00 c.c. c  1·52 1·76 1·99 2·23 2·47 2·69	1f 0·005M-a 2·98 2·96 2·98 2·96 2·95 2·96	cid against 0 50·00 60·00 65·00 70·00 75·00 80·00	5·176 6·183 6·415 6·596 6·761 6·926	-sodium h 	4·79 5·24 5·65 6·06 6·40 6·76	$\begin{array}{c}\\ 1 \cdot 26\\ 1 \cdot 28\\ 1 \cdot 29\\ 1 \cdot 31\\ 1 \cdot 36\\ (1 \cdot 46) \end{array}$
0.00 10.00 15.00 20.00 25.00 30.00 35.00	2·970 3·208 3·338 3·467 3·606 3·758 3·927	ation of 10  3.11 3.10 3.13 3.13 3.12	0·00 c.c. c  1·52 1·76 1·99 2·23 2·47 2·69	1f 0·005M-a 2·98 2·96 2·98 2·96 2·96 2·95	cid against 0 50·00 60·00 65·00 70·00 75·00 80·00 85·00	5·176 6·183 6·415 6·596 6·761 6·926 7·093	-sodium h 	4·79 5·24 5·65 6·06 6·40 6·76	$\begin{array}{c}\\ 1 \cdot 26\\ 1 \cdot 28\\ 1 \cdot 29\\ 1 \cdot 31\\ 1 \cdot 36 \end{array}$
0.00 10.00 15.00 20.00 25.00 30.00 35.00	2·970 3·208 3·338 3·467 3·606 3·758 3·927	ation of 10  3·11 3·10 3·13 3·13 3·12 3·14	0·00 c.c. a  1·52 1·76 1·99 2·23 2·47 2·69  Mea	96 0.005M-a 2.98 2.96 2.98 2.96 2.95 2.96 2.96 2.96 2.96	cid against 0 50·00 60·00 65·00 70·00 75·00 80·00 85·00 90·00	5·176 6·183 6·415 6·596 6·761 6·926 7·093 7·288	-sodium h	4·79 5·24 5·65 6·06 6·40 6·76	$\begin{array}{c}\\ 1 \cdot 26\\ 1 \cdot 28\\ 1 \cdot 29\\ 1 \cdot 31\\ 1 \cdot 36\\ (1 \cdot 46) \end{array}$
0·00 10·00 15·00 20·00 25·00 30·00 35·00 40·00	2.970 3.208 3.338 3.467 3.606 3.758 3.927 4.134	ation of 10  3·11 3·10 3·13 3·13 3·12 3·14 3-Meti	0·00 c.c. c  1·52 1·76 1·99 2·23 2·47 2·69 — Mea	f 0.005M-a  2.98 2.96 2.98 2.96 2.95 2.96 2.95 2.96 xane-1: 1-a	cid against 0 50.00 60.00 65.00 70.00 75.00 80.00 85.00 90.00	5·176 6·183 6·415 6·596 6·761 6·926 7·093 7·288 (M = 214	-sodium h	4·79 5·24 5·65 6·06 6·40 6·76	1·26 1·28 1·29 1·31 1·36 (1·46) an 1·30
0·00 10·00 15·00 20·00 25·00 30·00 35·00 40·00	2·970 3·208 3·338 3·467 3·606 3·758 3·927 4·134	ation of 10  3·11 3·10 3·13 3·13 3·12 3·14 3-Meti	0·00 c.c. c  1·52 1·76 1·99 2·23 2·47 2·69 — Mea	f 0.005M-a  2.98 2.96 2.98 2.96 2.95 2.96 2.95 2.96 xane-1: 1-a	cid against 0 50.00 60.00 65.00 70.00 75.00 80.00 85.00 90.00  liacetic Acid cid against 0	5·176 6·183 6·415 6·596 6·761 6·926 7·093 7·288 (M = 214 ·009850M-	-sodium h	4·79 5·24 5·65 6·06 6·40 6·76	1·26 1·28 1·29 1·31 1·36 (1·46) an 1·30
0·00 10·00 15·00 20·00 25·00 30·00 35·00 40·00	2·970 3·208 3·338 3·467 3·606 3·758 3·927 4·134	ation of 10  3·11 3·10 3·13 3·13 3·12 3·14     3-Metation of 10	0·00 c.c. c  1·52 1·76 1·99 2·23 2·47 2·69 — Mea	f 0.005M-a  2.98 2.96 2.98 2.96 2.95 2.96 2.95 2.96 xane-1: 1-a	cid against 0 50.00 60.00 65.00 70.00 75.00 80.00 85.00 90.00 liacetic Acid against 0 50.00	5·176 6·183 6·415 6·596 6·761 6·926 7·093 7·288 (M = 214 6·009850M 5·058	-sodium h	4·79 5·24 5·65 6·06 6·40 6·76	1·26 1·28 1·29 1·31 1·36 (1·46) an 1·30
0·00 10·00 15·00 20·00 25·00 30·00 35·00 40·00	2·970 3·208 3·338 3·467 3·606 3·758 3·927 4·134	ation of 10  3·11 3·10 3·13 3·13 3·12 3·14 3-Meti	0·00 c.c. c  1·52 1·76 1·99 2·23 2·47 2·69 — Mea	f 0.005M-a  2.98 2.96 2.98 2.96 2.95 2.96 2.95 2.96 xane-1: 1-a	cid against 0 50.00 60.00 65.00 70.00 75.00 80.00 85.00 90.00  liacetic Acid cid against 0	5·176 6·183 6·415 6·596 6·761 6·926 7·093 7·288 (M = 214 ·009850M-	-sodium h	4·79 5·24 5·65 6·06 6·40 6·76	1·26 1·28 1·29 1·31 1·36 (1·46) an 1·30
0.00 10.00 15.00 20.00 25.00 30.00 35.00 40.00 Potentia	2·970 3·208 3·338 3·467 3·606 3·758 3·927 4·134 ometric titr 2·931 3·168	ation of 10  3·11 3·10 3·13 3·13 3·12 3·14 —  3-Metion of 10  (3·61) 3·49 3·39	0.00 c.c. a  1.52 1.76 1.99 2.23 2.47 2.69 — Mea	f 0.005M-a 2.98 2.96 2.98 2.96 2.95 2.96 2.96 xane-1:1-a f 0.005M-a	cid against 0 50.00 60.00 65.00 70.00 75.00 80.00 85.00 90.00  liacetic Acid cid against 0 50.00 60.00	5·176 6·183 6·415 6·596 6·761 6·926 7·093 7·288 (M = 214 ··009850M- 5·058 6·313	-sodium h	4-79 5-24 5-65 6-06 6-40 6-76 Mes	
0.00 10.00 15.00 20.00 25.00 30.00 35.00 40.00 Potentia 0.00 10.00 10.00 20.00 25.00	2·970 3·208 3·338 3·467 3·606 3·758 3·927 4·134 ometric titr 2·931 3·168 3·300 3·438 3·574	ation of 10  3·11 3·10 3·13 3·13 3·12 3·14 —  3-Methation of 10  (3·61) 3·49 3·39 3·39	0.00 c.c. c  1.52 1.76 1.99 2.23 2.47 2.69 — Mea hylcyclohe 0.00 c.c. c  1.79 2.01 2.24	f 0.005M-a  2.98 2.96 2.98 2.96 2.95 2.96 an 2.96 xane-1:1-a f 0.005M-a  3.32 3.22 3.20	cid against 0 50.00 60.00 65.00 70.00 75.00 80.00 85.00 90.00 liacetic Acid against 0 50.00 60.00 65.00 70.00 75.00	$\begin{array}{c} \text{0-009915M} \\ \text{5-176} \\ \text{6-183} \\ \text{6-415} \\ \text{6-596} \\ \text{6-761} \\ \text{6-926} \\ \text{7-093} \\ \text{7-288} \\ \text{(M} = 214 \\ \text{-009850M} \\ \text{5-058} \\ \text{6-313} \\ \text{6-562} \\ \text{6-756} \\ \text{6-932} \\ \end{array}$	-sodium h		
0.00 10.00 15.00 20.00 25.00 30.00 35.00 40.00 Potentia 0.00 10.00 15.00 20.00 25.00 30.00	2·970 3·208 3·338 3·467 3·606 3·758 3·927 4·134 ometric titr 2·931 3·168 3·300 3·438 3·574 3·719	ation of 10  3·11 3·10 3·13 3·13 3·12 3·14   3-Methation of 10   (3·61) 3·49 3·39 3·39 3·40	0.00 c.c. c  1.52 1.76 1.99 2.23 2.47 2.69 — Mer hylcyclohe 0.00 c.c. c  1.79 2.01 2.24 2.47	f 0.005M-a 2.98 2.96 2.98 2.96 2.95 2.96 an 2.96 xane-1:1-a f 0.005M-a  3.32 3.22 3.20 3.22	cid against 0 50.00 60.00 65.00 70.00 75.00 80.00 85.00 90.00 liacetic Acid cid against 0 50.00 65.00 70.00 75.00 80.00	$\begin{array}{c} \text{0-009915M} \\ \text{5-176} \\ \text{6-183} \\ \text{6-415} \\ \text{6-596} \\ \text{6-761} \\ \text{6-926} \\ \text{7-093} \\ \text{7-288} \\ \text{(M} = 214 \\ \text{0-009850M} \\ \text{5-058} \\ \text{6-313} \\ \text{6-562} \\ \text{6-756} \\ \text{6-932} \\ \text{7-100} \\ \end{array}$	-sodium h		
0.00 10.00 15.00 20.00 25.00 30.00 35.00 40.00 Potentia 0.00 15.00 20.00 25.00 35.00	2·970 3·208 3·338 3·467 3·606 3·758 3·927 4·134 20metric titr 2·931 3·168 3·300 3·438 3·574 3·719 3·890	3-11 3-13 3-13 3-13 3-12 3-14 — 3-Metation of 10 — (3-61) 3-49 3-39 3-39 3-40 3-38	0.00 c.c. a  1.52 1.76 1.99 2.23 2.47 2.69  Mea hylcyclohe 0.00 c.c. a  1.79 2.01 2.24 2.47 2.68	f 0.005M-a  2.98 2.96 2.98 2.96 2.95 2.96 2.96 an 2.96 xane-1:1-a f 0.005M-a  3.32 3.22 3.20 3.22 3.19	cid against 0 50.00 60.00 65.00 70.00 75.00 80.00 85.00 90.00  liacetic Acid against 0 50.00 60.00 65.00 70.00 75.00 80.00 85.00	$\begin{array}{c} \text{0-009915M} \\ \text{5-176} \\ \text{6-183} \\ \text{6-183} \\ \text{6-415} \\ \text{6-596} \\ \text{6-761} \\ \text{6-926} \\ \text{7-093} \\ \text{7-288} \\ \text{(M} = 214 \\ \text{0-009850M-} \\ \text{5-058} \\ \text{6-313} \\ \text{6-562} \\ \text{6-756} \\ \text{6-932} \\ \text{7-100} \\ \text{7-271} \\ \end{array}$	-sodium h		
0.00 10.00 15.00 20.00 25.00 30.00 35.00 40.00 Potentia 0.00 10.00 15.00 20.00 25.00 30.00	2·970 3·208 3·338 3·467 3·606 3·758 3·927 4·134 ometric titr 2·931 3·168 3·300 3·438 3·574 3·719	ation of 10  3·11 3·10 3·13 3·13 3·12 3·14   3-Methation of 10   (3·61) 3·49 3·39 3·39 3·40	0.00 c.c. a  1.52 1.76 1.99 2.23 2.47 2.69	f 0.005M-a  2.98 2.96 2.98 2.96 2.95 2.96 an 2.96 an 2.96  3.32 3.22 3.20 3.22 3.19 3.28	cid against 0 50.00 60.00 65.00 70.00 75.00 80.00 85.00 90.00 liacetic Acid cid against 0 50.00 65.00 70.00 75.00 80.00	$\begin{array}{c} \text{0-009915M} \\ \text{5-176} \\ \text{6-183} \\ \text{6-415} \\ \text{6-596} \\ \text{6-761} \\ \text{6-926} \\ \text{7-093} \\ \text{7-288} \\ \text{(M} = 214 \\ \text{0-009850M} \\ \text{5-058} \\ \text{6-313} \\ \text{6-562} \\ \text{6-756} \\ \text{6-932} \\ \text{7-100} \\ \end{array}$	-sodium h		1·26 1·28 1·29 1·31 1·36 (1·46) an 1·30  blution.  0·845 0·832 0·824 0·825 0·843
0.00 10.00 15.00 20.00 25.00 30.00 35.00 40.00 Potentia 0.00 15.00 20.00 25.00 35.00	2·970 3·208 3·338 3·467 3·606 3·758 3·927 4·134 20metric titr 2·931 3·168 3·300 3·438 3·574 3·719 3·890	3-11 3-13 3-13 3-13 3-12 3-14 	0.00 c.c. a  1.52 1.76 1.99 2.23 2.47 2.69 — Mea hylcyclohe 0.00 c.c. a  1.79 2.01 2.24 2.47 2.68 2.90 Mea	f 0.005M-a  2.98 2.96 2.98 2.96 2.95 2.96 2.96 an 2.96 xane-1:1-a f 0.005M-a  3.32 3.22 3.22 3.19 3.28 an 3.23	cid against 0 50.00 60.00 65.00 70.00 75.00 80.00 85.00 90.00  diacetic Acid cid against 0 50.00 60.00 65.00 70.00 75.00 80.00 85.00 90.00	$\begin{array}{c} \text{0-009915M} \\ \text{5-176} \\ \text{6-183} \\ \text{6-415} \\ \text{6-596} \\ \text{6-761} \\ \text{6-926} \\ \text{7-093} \\ \text{7-288} \\ \text{(M} = 214 \\ \text{0-009850M} \\ \text{5-058} \\ \text{6-313} \\ \text{6-562} \\ \text{6-756} \\ \text{6-932} \\ \text{7-100} \\ \text{7-271} \\ \text{7-435} \\ \end{array}$	-sodium h		
0·00 10·00 15·00 20·00 25·00 30·00 35·00 40·00 Potentio 0·00 10·00 15·00 20·00 20·00 35·00 40·00	2·970 3·208 3·338 3·467 3·606 3·758 3·927 4·134 2·931 3·168 3·300 3·438 3·574 3·719 3·890 4·090	ation of 10	0.00 c.c. a  1.52 1.76 1.99 2.23 2.47 2.69 — Mea hylcyclohe 0.00 c.c. a  1.79 2.01 2.24 2.47 2.68 2.90 Mea	f 0.005M-a  2.98 2.96 2.98 2.96 2.95 2.96 an 2.96 an 2.96  xane-1:1-a  3.32 3.22 3.20 3.22 3.19 3.28 an 3.23  xane-1:1-a	cid against 0 50.00 60.00 65.00 70.00 75.00 80.00 85.00 90.00  liacetic Acid cid against 0 50.00 65.00 70.00 75.00 80.00 80.00 80.00 80.00	$\begin{array}{c} \text{0-009915M} \\ \text{5-176} \\ \text{6-183} \\ \text{6-415} \\ \text{6-596} \\ \text{6-761} \\ \text{6-926} \\ \text{7-093} \\ \text{7-288} \\ \text{(M} = 214 \\ \text{0-009850M} \\ \text{5-058} \\ \text{6-313} \\ \text{6-562} \\ \text{6-756} \\ \text{6-932} \\ \text{7-100} \\ \text{7-271} \\ \text{7-435} \\ \text{(M} = 214 \\  \end{array}$	-sodium h		
0·00 10·00 15·00 20·00 25·00 30·00 35·00 40·00 Potentio 0·00 10·00 15·00 20·00 20·00 35·00 40·00	2·970 3·208 3·338 3·467 3·606 3·758 3·927 4·134 2·931 3·168 3·300 3·438 3·574 3·719 3·890 4·090	ation of 10	0.00 c.c. a  1.52 1.76 1.99 2.23 2.47 2.69 — Mea hylcyclohe 0.00 c.c. a  1.79 2.01 2.24 2.47 2.68 2.90 Mea	f 0.005M-a  2.98 2.96 2.98 2.96 2.95 2.96 an 2.96 an 2.96  xane-1:1-a  3.32 3.22 3.20 3.22 3.19 3.28 an 3.23  xane-1:1-a	cid against 0 50.00 60.00 65.00 70.00 75.00 80.00 85.00 90.00  diacetic Acid cid against 0 50.00 60.00 65.00 70.00 75.00 80.00 85.00 90.00	$\begin{array}{c} \text{0-009915M} \\ \text{5-176} \\ \text{6-183} \\ \text{6-415} \\ \text{6-596} \\ \text{6-761} \\ \text{6-926} \\ \text{7-093} \\ \text{7-288} \\ \text{(M} = 214 \\ \text{0-009850M} \\ \text{5-058} \\ \text{6-313} \\ \text{6-562} \\ \text{6-756} \\ \text{6-932} \\ \text{7-100} \\ \text{7-271} \\ \text{7-435} \\ \text{(M} = 214 \\  \end{array}$	-sodium h		
0.00 10.00 15.00 20.00 25.00 30.00 35.00 40.00 Potentia 0.00 15.00 20.00 25.00 30.00 40.00	2·970 3·208 3·338 3·467 3·606 3·758 3·927 4·134 ometric titr 2·931 3·168 3·300 3·438 3·574 3·719 3·890 4·090	3-11 3-10 3-13 3-13 3-13 3-12 3-14 3-Methation of 10 (3-61) 3-39 3-39 3-40 3-38 3-48 4-Methation of 10	0.00 c.c. c  1.52 1.76 1.99 2.23 2.47 2.69 — Mea hylcyclohe 0.00 c.c. c  1.79 2.01 2.24 2.47 2.68 2.90 Mea hylcyclohe 0.00 c.c. c	f 0.005M-a 2.98 2.96 2.98 2.96 2.95 2.96 2.96 an 2.96 an 2.96 3.32 3.22 3.22 3.20 3.22 3.19 3.28 an 3.23 xane-1:1-a f 0.005M-a	cid against 0 50.00 60.00 65.00 70.00 75.00 80.00 85.00 90.00 liacetic Acid against 0 50.00 65.00 70.00 85.00 90.00 liacetic Acid against 0 50.00 65.00 70.00 85.00 90.00	5·176 6·183 6·415 6·596 6·761 6·926 7·093 7·288 (M = 214 0·09850M 5·058 6·313 6·562 6·756 6·932 7·100 7·271 7·435 (M = 214 0·09850M 4·937	-sodium h	4-79 5-24 5-65 6-06 6-40 6-76 Mes  ydroxide so  4-73 5-23 5-59 5-98 6-35 Mea	
0.00 10.00 15.00 20.00 25.00 30.00 35.00 40.00 10.00 10.00 20.00 25.00 30.00 35.00 40.00	2.970 3.208 3.338 3.467 3.606 3.758 3.927 4.134 metric titr 2.931 3.168 3.300 3.438 3.574 3.719 3.890 4.090	ation of 10  3·11 3·10 3·13 3·13 3·12 3·14 —  3-Methation of 10  —  (3·61) 3·49 3·39 3·40 3·38 3·48  4-Methation of 10  —  3·38 3·48	0.00 c.c. a  1.52 1.76 1.99 2.23 2.47 2.69 — Mea hylcyclohe 0.00 c.c. a  1.79 2.01 2.24 2.47 2.68 2.90 Mea hylcyclohe hylcyclohe 0.00 c.c. a	f 0.005M-a 2.98 2.96 2.98 2.96 2.95 2.96 an 2.96 xane-1:1-a f 0.005M-a 3.32 3.22 3.20 3.22 3.19 3.28 an 3.23 xane-1:1-a f 0.005M-a	cid against 0 50.00 60.00 65.00 70.00 75.00 80.00 85.00 90.00 liacetic Acid cid against 0 50.00 65.00 70.00 85.00 90.00 liacetic Acid cid against 0 50.00 65.00 70.00 85.00 90.00 liacetic Acid cid against 0 50.00 60.00	5·176 6·183 6·415 6·596 6·761 6·926 7·093 7·288 (M = 214 ··009850M 5·058 6·313 6·562 6·756 6·932 7·100 7·271 7·435 (M = 214 ··009850M	-sodium h		
0.00 10.00 15.00 20.00 25.00 30.00 35.00 40.00 10.00 15.00 20.00 25.00 30.00 35.00 40.00	2·970 3·208 3·338 3·467 3·606 3·758 3·927 4·134 20metric titr 2·931 3·168 3·300 3·438 3·574 3·719 3·890 4·090 20metric titr 2·941 3·184 3·213	ation of 10  3·11 3·10 3·13 3·13 3·12 3·14   3-Methation of 10   (3·61) 3·49 3·39 3·39 3·40 3·38 3·48  4-Methation of 10   3·38 3·34	0.00 c.c. a  1.52 1.76 1.99 2.23 2.47 2.69 — Mea hylcyclohe 0.00 c.c. a  1.79 2.01 2.24 2.47 2.68 2.90 Mea hylcyclohe 0.00 c.c. a	f 0.005M-a  2.98 2.96 2.98 2.96 2.95 2.96 an 2.96 xane-1:1-a f 0.005M-a  3.32 3.22 3.20 3.22 3.19 3.28 an 3.23 xane-1:1-a f 0.005M-a	cid against 0 50.00 60.00 65.00 70.00 75.00 80.00 85.00 90.00 liacetic Acid against 0 50.00 65.00 70.00 85.00 90.00 liacetic Acid against 0 50.00 65.00 65.00 60.00 60.00 65.00	0-009915M 5-176 6-183 6-415 6-596 6-761 6-926 7-093 7-288 (M = 214 0-009850M 5-058 6-313 6-562 6-756 6-932 7-100 7-271 7-435 (M = 214 0-009850M 4-937 6-257 6-584	-sodium h		
0.00 10.00 15.00 20.00 25.00 30.00 35.00 40.00 10.00 15.00 20.00 20.00 40.00 Potential 0.00 10.00 10.00 10.00 10.00 10.00 10.00 10.00 10.00 10.00 20.00	2.970 3.208 3.338 3.467 3.606 3.758 3.927 4.134 2.931 3.168 3.300 3.438 3.574 3.719 3.890 4.090 2.941 3.184 3.213 3.438	ation of 10	0.00 c.c. a  1.52 1.76 1.99 2.23 2.47 2.69 — Mea hylcyclohe 0.00 c.c. a  1.79 2.01 2.24 2.47 2.68 2.90 Mea hylcyclohe 0.00 c.c. a	f 0.005M-a  2.98 2.96 2.98 2.96 2.95 2.96 an 2.96 an 2.96 3.32 3.22 3.20 3.22 3.20 3.22 3.19 3.28 an 3.23 xane-1:1-a  f 0.005M-a  3.32 3.19 3.23 3.19 3.21	cid against 0 50.00 60.00 65.00 70.00 75.00 80.00 85.00 90.00  liacetic Acid cid against 0 50.00 65.00 70.00 80.00 85.00 90.00  liacetic Acid against 0 50.00 60.00 80.00 85.00 90.00	$\begin{array}{c} \text{0-009915M} \\ \text{5-176} \\ \text{6-183} \\ \text{6-415} \\ \text{6-596} \\ \text{6-761} \\ \text{6-926} \\ \text{7-093} \\ \text{7-288} \\ \text{(M} = 214 \\ \text{0-009850M} \\ \text{5-058} \\ \text{6-313} \\ \text{6-562} \\ \text{6-756} \\ \text{6-932} \\ \text{7-100} \\ \text{7-271} \\ \text{7-435} \\ \text{(M} = 214 \\ \text{0-009850M} \\ \text{4-937} \\ \text{6-584} \\ \text{6-772} \\ \end{array}$	-sodium h		
0.00 10.00 15.00 20.00 25.00 30.00 35.00 40.00 10.00 10.00 20.00 25.00 30.00 40.00 Potential 0.00 10.00 10.00 10.00 10.00 20.0	2·970 3·208 3·338 3·467 3·606 3·758 3·927 4·134 ***metric titr 2·931 3·168 3·300 3·438 3·574 3·719 3·890 4·090 ***metric titr 2·941 3·184 3·213 3·438 3·577	ation of 10  3·11 3·10 3·13 3·13 3·12 3·14   3-Methation of 10  (3·61) 3·39 3·49 3·39 3·40 3·38 3·48  4-Methation of 10  3·38 3·34 3·38 3·34 3·38	0.00 c.c. c  1.52 1.76 1.99 2.23 2.47 2.69 — Mea hylcyclohe 0.00 c.c. c  1.79 2.01 2.24 2.47 2.68 2.90 Mea hylcyclohe 0.00 c.c. c  1.555 1.77 2.01 2.24	f 0.005M-a 2.98 2.96 2.98 2.96 2.95 2.96 2.96 an 2.96 xane-1:1-a 3.32 3.22 3.22 3.19 3.28 an 3.23 xane-1:1-a f 0.005M-a 3.32 3.19 3.28 3.19 3.28 3.19 3.28 3.19 3.28	cid against 0 50.00 60.00 65.00 70.00 75.00 80.00 85.00 90.00 liacetic Acid against 0 50.00 65.00 70.00 85.00 90.00 liacetic Acid against 0 50.00 65.00 70.00 85.00 90.00 liacetic Acid against 0 50.00 60.00 65.00 70.00 70.00 75.00	0-009915M 5-176 6-183 6-415 6-596 6-761 6-926 7-093 7-288 (M = 214 0-009850M 5-058 6-313 6-562 6-756 6-932 7-100 7-271 7-435 (M = 214 0-009850M 4-937 6-584 6-772 6-946	-sodium h		
0.00 10.00 10.00 10.00 15.00 20.00 25.00 30.00 40.00   Potentia 0.00 15.00 20.00 25.00 30.00 35.00 40.00   Potentia 0.00 10.00 15.00 20.00 25.00 30.00 35.00 40.00	2.970 3.208 3.338 3.467 3.606 3.758 3.927 4.134 bmetric titr 2.931 3.168 3.300 3.438 3.574 3.719 3.890 4.090 bmetric titr 2.941 3.184 3.213 3.438 3.577 3.715	ation of 10  3·11 3·10 3·13 3·13 3·12 3·14 —  3-Methation of 10  — (3·61) 3·49 3·39 3·40 3·38 3·48  4-Methation of 10  — 3·38 3·48  4-Methation of 10  — 3·38 3·48	0.00 c.c. a  1.52 1.76 1.99 2.23 2.47 2.69 — Mea hylcyclohe 0.00 c.c. a  1.79 2.01 2.24 2.47 2.68 2.90 Mea hylcyclohe 0.00 c.c. a  1.55 1.77 2.01 2.24 2.47	f 0.005M-a 2.98 2.96 2.98 2.96 2.95 2.96 an 2.96 an 2.96 3.32 3.22 3.20 3.22 3.19 3.28 an 3.23 xane-1:1-a f 0.005M-a 3.32 3.28 3.19 3.28 3.19 3.21 3.18 3.26	cid against 0 50.00 60.00 65.00 70.00 75.00 80.00 85.00 90.00 liacetic Acid cid against 0 50.00 65.00 70.00 85.00 90.00 liacetic Acid cid against 0 50.00 65.00 75.00 80.00 60.00 65.00 70.00 75.00 80.00 80.00	5·176 6·183 6·415 6·596 6·761 6·926 7·093 7·288 (M = 214 ··009850M 5·058 6·313 6·562 6·756 6·932 7·100 7·271 7·435 (M = 214 ··009850M 4·937 6·257 6·584 6·772 6·946 7·113	-sodium h		
0.00 10.00 15.00 20.00 25.00 30.00 35.00 40.00 10.00 10.00 20.00 25.00 30.00 40.00 Potential 0.00 10.00 10.00 10.00 10.00 20.0	2·970 3·208 3·338 3·467 3·606 3·758 3·927 4·134 ***metric titr 2·931 3·168 3·300 3·438 3·574 3·719 3·890 4·090 ***metric titr 2·941 3·184 3·213 3·438 3·577	ation of 10  3·11 3·10 3·13 3·13 3·12 3·14   3-Methation of 10  (3·61) 3·39 3·49 3·39 3·40 3·38 3·48  4-Methation of 10  3·38 3·34 3·38 3·34 3·38	0.00 c.c. c  1.52 1.76 1.99 2.23 2.47 2.69 — Mea hylcyclohe 0.00 c.c. c  1.79 2.01 2.24 2.47 2.68 2.90 Mea hylcyclohe 0.00 c.c. c  1.555 1.77 2.01 2.24	f 0.005M-a 2.98 2.96 2.98 2.96 2.95 2.96 2.96 an 2.96 xane-1:1-a 3.32 3.22 3.22 3.19 3.28 an 3.23 xane-1:1-a f 0.005M-a 3.32 3.19 3.28 3.19 3.28 3.19 3.28 3.19 3.28	cid against 0 50.00 60.00 65.00 70.00 75.00 80.00 85.00 90.00 liacetic Acid against 0 50.00 65.00 70.00 85.00 90.00 liacetic Acid against 0 50.00 65.00 70.00 85.00 90.00 liacetic Acid against 0 50.00 60.00 65.00 70.00 70.00 75.00	0-009915M 5-176 6-183 6-415 6-596 6-761 6-926 7-093 7-288 (M = 214 0-009850M 5-058 6-313 6-562 6-756 6-932 7-100 7-271 7-435 (M = 214 0-009850M 4-937 6-584 6-772 6-946	-sodium h		
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## SUMMARY.

- (1) The thermodynamic primary and secondary dissociation constants of *cyclo*pentane-, 3-methyl*cyclo*pentane-, 2-methyl*cyclo*hexane-, 3-methyl*cyclo*hexane- and 4-methyl*cyclo*hexane-1:1-diacetic acids have been determined by potentiometric titration with the quinhydrone electrode at 25°.
- (2) The intercarboxylic distances have been evaluated by the methods of Bjerrum and of Gane and Ingold. The results support the view that the *cyclo*pentane and *cyclo*hexane rings in these compounds are all strainless.

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