CCXCV.—*Electrometric Titration Curves of Dibasic Acids. Part II. β-Substituted Glutaric Acids.*

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IN Part I (this vol., p. 1594) we described a preliminary examination into the possibility of obtaining approximate measurements of the distance between the carboxyl groups of dibasic acids by utilising hydrogen-ion activity determinations, during neutralisation with a strong base, in conjunction with Bjerrum's theory respecting the effect of the external field of a pole on the degree of dissociation of another ionising centre situated in the same molecule. It was shown that the results obtained by this method for the distances between the carboxyl groups of normal dibasic acids, are subject to various disturbances, of which probably the most important are the following : (1) the influence of solvation and electrostriction, which, although it interferes with quantitative accuracy, should not, and apparently does not, alter the order of a given series of related substances in respect of the dimension considered; (2) the effect of internally propagated polar influences, which gives rise to larger anomalies the shorter the carbon chain between the carboxyl groups. It was found, furthermore, that the disturbances attributable to internal influences, although large in malonic acid and considerable in succinic acid, became small in glutaric acid and its higher normal homologues, and it was therefore decided to examine a series of substituted glutaric acids in order to ascertain whether the hypothesis of valency deflexion, which has hitherto been successful mainly in explaining chemical relationships, would receive support from physical measurements.*

We have examined glutaric acid, two β-alkylglutaric acids, three ββ-dialkylglutaric acids, and three related ring compounds. The values of the first and second electrometric dissociation constants and the calculated value of the apparent distance *r* (in Ångström units) between the carboxyl groups are shown in the following table :

Substance.	k_1.	k_2.	*r*.
Glutaric acid	$4{\cdot}60 \times 10^{-5}$	$5{\cdot}34 \times 10^{-6}$	9·22
β-Methylglutaric acid	$5{\cdot}77 \times 10^{-5}$	$6{\cdot}28 \times 10^{-7}$	2·27
β-*n*-Propylglutaric acid	$4{\cdot}97 \times 10^{-5}$	$4{\cdot}32 \times 10^{-7}$	2·12
ββ-Dimethylglutaric acid	$2{\cdot}03 \times 10^{-4}$	$5{\cdot}51 \times 10^{-7}$	1·57
ββ-Diethylglutaric acid	$3{\cdot}40 \times 10^{-4}$	$7{\cdot}85 \times 10^{-8}$	1·02
ββ-Di-*n*-propylglutaric acid	$2{\cdot}03 \times 10^{-4}$	$5{\cdot}42 \times 10^{-8}$	1·01
*cyclo*Pentane-1 : 1-diacetic acid	$1{\cdot}68 \times 10^{-4}$	$2{\cdot}63 \times 10^{-7}$	1·40
*cyclo*Hexane-1 : 1-diacetic acid	$3{\cdot}36 \times 10^{-4}$	$1{\cdot}02 \times 10^{-7}$	1·04
*cyclo*Heptane-1 : 1-diacetic acid	$2{\cdot}78 \times 10^{-4}$	$1{\cdot}09 \times 10^{-7}$	1·10

The most remarkable feature presented by these data is the fact that the value for *r* for glutaric acid is so very much greater than for any of the substituted acids. In Part I, it was shown that the normal (unsubstituted) dibasic acids tend to a straight (zig-zag), and not a coiled, configuration, since the apparent distance between the carboxyl groups increases regularly by 1·73 Å.U. for each methylene group in this series of homologues. The value 9·2 Å.U. for glutaric acid is in keeping with this conception, and there appears to be no other way of explaining the much smaller values given by

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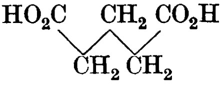
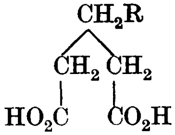
* Spiers and Thorpe (J., 1925, **127**, 538) pointed out the close parallelism between the first dissociation constants (conductivity) of substituted glutaric acids and the tendency to ring-closure of corresponding derivatives, and this, therefore, is the first indication that valency-deflexion may manifest itself in physical properties.

the substitution products than to suppose that the presence of a β-substituent causes the molecule to assume the coiled configuration:





Apart from this unexpected result, the data are in general agreement with the valency-deflexion hypothesis in regard to both the sequence of the compounds and the relative magnitude of the differences in respect of the property under discussion. Thus the value for the β-propyl acid is less than that for the β-methyl derivative; the value for β-ethylglutaric acid was not determined, but it would be expected to approximate closely to the figure for the propyl compound. The distance for the *gem*-dimethyl acid is, however, considerably less than for either of the mono-substituted acids, and this is in conformity both with the spatial theory of valency-deflexion and with the chemical evidence relating to these examples which has been adduced in support of it (Ingold, J., 1921, **119**, 305; 1922, **121**, 2676). Again, both on theoretical grounds and also by analogy with chemical evidence (Deshapande and Thorpe, J., 1922, **121**, 1430; Bains and Thorpe, 1923, **123**, 1206), it would be expected that the distance for the ββ-diethyl acid should be substantially less than for the dimethyl compound, whilst the value for the ββ-di-*n*-propyl derivative should be only very slightly less than for its diethyl analogue. It will be seen that the measurements bear out both these expectations, although the small recorded difference (0·01 Å.U.) between the distances for the diethyl and dipropyl acids cannot be regarded as possessing quantitative significance.

According to the elementary form of the deflexion hypothesis, the distance *r* for *cyclo*pentanediacetic acid would be expected to be slightly greater than that for the *gem*-dimethyl analogue; chemical evidence, however, indicates that it might be slightly smaller (Becker and Thorpe, J., 1920, **117**, 1579), and it would be possible to reconcile this discrepancy by means of a minor modification of the theory, provided that the value for the *cyclo*pentane acid is definitely greater than that for its open-chain analogue having the same number of carbon atoms, *viz.*, the diethyl acid. The data now recorded show that the distance for the *cyclo*pentane acid is actually slightly less than that for the *gem*-dimethyl acid, in agreement with the chemical indications, and is considerably greater than that for the *gem*-diethyl acid as theory requires. The distance for the *cyclo*hexane acid should, of course, be less than for either the *gem*-dimethyl or the *cyclo*pentane acid (Beesley, Ingold, and Thorpe, J., 1915, **107**, 1080), and the measurements illustrate this. Finally, according to Baker and Ingold's conception (J., 1923, **123**, 122) of the influence of large rings in producing valency-deflexion, the value for *cyclo*heptanediacetic acid should be between the values for the *cyclo*hexane and *cyclo*pentane acids, since the maximum deflexion occurs with *cyclo*hexane. This also is shown by the data now submitted, and corresponds with the evidence already obtained by the study of *spiro*-compounds (*idem, ibid.*; Baker, J., 1925, **127**, 1678).

In conclusion, then, it may be stated that the measurements here recorded justify the suggestion of Ingold and Thorpe (this vol., p. 1318) that a study of the dissociation constants of β-substituted glutaric acids would confirm all the main features of the hypothesis of valency-deflexion by means of which for some 13 years past they have interpreted chemical relationships. Furthermore, it will be seen that where unexpected chemical observations have suggested modifications of the original hypothesis, the physical measurements confirm the modifications.

EXPERIMENTAL.

The substituted glutaric acids were prepared by known methods and carefully purified * by repeated crystallisations before use. The hydrogen potential measurements were carried out and standardised and the results calculated exactly as described in Part I, and in this connexion we have again to thank Messrs. W. R. Atkin and F. C. Thompson for the loan of their apparatus. The temperature was in all cases 25°.

β-*Methylglutaric acid.* Original concentration 0·00675*M*; NaOH equivalent to 0·002567 g. $Na^{\cdot}$/c.c.; equivalent titre 18·15 c.c.

Titre.	p_H.	Titre.	p_H.	Titre.	p_H.	Titre.	p_H.
0·00	3·253	4·97	4·199	11·53	5·029	16·65	5·929
0·34	3·361	5·88	4·333	12·56	5·164	17·24	6·169
0·77	3·442	6·76	4·446	13·50	5·291	17·59	6·392
1·14	3·531	7·62	4·550	14·40	5·432	17·89	6·754
1·71	3·658	8·55	4·664	14·99	5·533	18·03	7·083
2·28	3·773	9·50	4·772	15·53	5·636	18·08	7·269
3·06	3·913	10·52	4·905	16·09	5·767	18·10	7·684
3·99	4·058						

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* Since acids, which appear pure as judged by ordinary standards, may contain a non-acidic impurity which "poisons" the electrodes, causing instability in the null-points, it is desirable to include washing the sodium salts with acetone in the scheme of purification.

β-n-*Propylglutaric acid.* Original concentration 0·004768*M*; NaOH equivalent to 0·002567 g. Na˙/c.c.; equivalent titre 12·82 c.c.

Titre.	p_{H}.	Titre.	p_{H}.	Titre.	p_{H}.	Titre.	p_{H}.
0·00	3·331	2·98	4·188	7·01	4·947	10·70	5·713
0·31	3·450	3·61	4·320	7·60	5·056	11·24	5·875
0·74	3·599	4·24	4·440	8·24	5·177	11·65	6·037
1·26	3·764	5·08	4·598	8·88	5·301	12·02	6·223
1·82	3·920	5·63	4·696	9·51	5·430	12·42	6·535
2·46	4·071	6·31	4·821	10·10	5·557	12·66	6·912

ββ-*Dimethylglutaric acid.* Original concentration 0·007995*M*; NaOH equivalent to 0·002567 g. Na˙/c.c.; equivalent titre 21·50 c.c.

0·00	2·914	4·30	3·573	9·48	4·527	16·02	6·245
0·20	2·962	4·76	3·642	10·00	4·697	17·00	6·393
0·62	3·026	5·28	3·713	10·49	4·892	18·00	6·559
1·20	3·116	5·90	3·802	10·97	5·095	19·02	6·767
1·77	3·209	6·51	3·901	11·50	5·299	20·00	7·033
2·40	3·299	7·10	4·002	11·98	5·457	21·23	7·827
2·79	3·355	7·78	4·120	12·98	5·708	21·27	7·910
3·30	3·432	8·50	4·266	14·01	5·912	21·60	9·562
3·80	3·503	8·96	4·381	15·00	6·083	21·63	9·731

ββ-*Diethylglutaric acid.* Original concentration 0·00545*M*; NaOH equivalent to 0·002567 g. Na˙/c.c.; equivalent titre 14·65 c.c.

0·00	2·942	3·82	3·578	7·20	5·090	10·58	7·017
0·30	2·985	4·30	3·675	7·40	5·443	11·44	7·210
0·98	3·084	4·89	3·810	7·60	5·748	12·19	7·406
1·50	3·167	5·41	3·950	8·02	6·139	12·99	7·626
1·85	3·225	5·81	4·076	8·42	6·362	13·62	7·878
2·28	3·294	6·22	4·233	9·00	6·587	14·54	8·758
2·80	3·384	6·59	4·435	9·80	6·819	14·86	9·850
3·42	3·498	6·95	4·743				

ββ-*Dipropylgluratic acid.* Original concentration 0·0005455*M*; NaOH equivalent to 0·0003671 g. Na˙/c.c.; equivalent titre 10·25 c.c.

0·00	3·612	3·00	4·106	4·80	5·095	6·90	7·001
0·31	3·664	3·51	4·255	5·42	6·139	7·43	7·169
0·75	3·713	4·00	4·441	5·62	6·359	8·02	7·369
1·30	3·790	4·40	4·677	5·95	6·592	9·76	8·100
1·89	3·884	4·60	4·839	6·40	6·821	10·74	9·317
2·51	4·005						

cyclo*Pentane*-1 : 1-*diacetic acid.* Original conc. 0·003421*M*; NaOH equivalent to 0·002567 g. Na˙/c.c.; equivalent titre 9·20 c.c.

0·00	3·186	3·01	4·091	5·40	5·961	7·51	6·824
0·25	3·239	3·30	4·211	5·62	6·077	7·82	6·945
1·50	3·602	3·60	4·358	5·92	6·217	8·10	7·084
1·79	3·688	3·90	4·531	6·22	6·344	8·40	7·246
2·10	3·783	4·20	4·782	6·53	6·461	8·98	7·852
2·40	3·880	4·40	4·992	6·86	6·582	9·35	9·696
2·71	3·982	4·60	5·249	7·20	6·707		

cyclo*Hexane*-1 : 1-*diacetic acid.* Original conc. 0·002232*M*; NaOH equivalent to 0·002567 g. $Na^{\cdot}$/c.c.; equivalent titre 6·00 c.c.

Titre.	p_H.	Titre.	p_H.	Titre.	p_H.	Titre.	p_H.
0·25	3·200	1·78	3·798	3·43	6·239	5·88	8·311
0·60	3·327	1·96	3·901	3·80	6·548	6·02	9·059
0·90	3·429	2·25	4·088	4·10	6·747	6·16	9·798
1·30	3·584	3·17	5·863	4·39	6·921		

cyclo*Heptane*-1 : 1-*diacetic acid.* Original conc. 0·000733*M*; NaOH equivalent to 0·0003671 g. $Na^{\cdot}$/c.c.; equivalent titre 13·8 c.c.

0·00	3·455	4·03	3·979	7·68	6·122	11·50	7·275
0·31	3·502	4·61	4·094	8·10	6·324	12·00	7·386
0·68	3·546	5·20	4·247	8·62	6·552	12·52	7·530
1·23	3·602	5·82	4·474	9·22	6·729	12·99	7·674
1·86	3·672	6·30	4·747	9·68	6·854	13·94	8·029
2·28	3·722	6·75	5·010	10·31	7·000	14·34	8·300
2·82	3·790	7·00	5·570	10·93	7·144	14·52	8·445
3·40	3·873	7·32	5·892				

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