

The Crystal Structure of Calcium- α -D-glucoisosaccharate and Some Extended Hückel Calculations on α -D-Glucoisosaccharinic Acid

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The crystal structure of Ca- α -D-glucoisosaccharate, $\text{Ca}(\text{C}_6\text{H}_{11}\text{O}_6)_2$, has been refined from three-dimensional X-ray diffraction data by least-squares methods. The crystals are orthorhombic, space group $P2_12_12$, with $a = 19.609$, $b = 6.782$, and $c = 5.782$ Å. The final R index is 0.108. The compound is isostructural with the corresponding strontium salt,¹ which was determined with higher precision ($R = 0.058$). The structure of the α -D-glucoisosaccharate group is not significantly different from that found in the strontium compound and the proposed hydrogen bonds are essentially the same.

Some semiempirical conformational analyses were made on the α -D-glucoisosaccharinic acid using extended Hückel calculations.²⁻⁵ Population analysis and net charges were calculated for the free acid.

In connection with a study on α -D-glucoisosaccharinic acid, X-ray data were collected for the isomorphous strontium and calcium glucoisosaccharates with different techniques.

In both cases the data were collected with a General Electric Single-Crystal Orienter equipped with a scintillation detector and a pulse-height analyser set to collect about 90 % of the $\text{CuK}\alpha$ radiation used. The measuring technique used for the strontium compound was the θ - 2θ scanning technique. It was believed that the peak intensity measurement technique would speed up the data collection. The calcium compound was investigated by this method. In this case, however, it was found necessary to search in 2θ for the maximum intensity positions and no measuring time was saved.

A powder specimen of Ca- α -D-glucoisosaccharate⁶ was kindly supplied by A. Ishizu (*Swedish Forest Products Research Laboratory*). Single crystals suitable for X-ray analysis were obtained by slow cooling of a saturated aqueous solution of the salt. The dimensions of the crystal used were $0.01 \times 0.02 \times 0.06$ mm³ with the long edge parallel to the c axis. Approxi-

mately 91 % of the reflections not systematically absent had observable intensities so that 478 reflections with 2θ less than 102° could be measured. The background was measured 20 seconds at $\pm 1^\circ$ from the 2θ value found for the maximum intensity. The peak intensities were measured 40 seconds. For obtaining integrated intensities a calibration curve was determined. It was based on 15 reflections with increasing 2θ values measured with the $\theta-2\theta$ scanning technique. No corrections of the peak intensities for obtaining integrated intensities were found necessary. L_p and absorption corrections ($\mu = 39 \text{ cm}^{-1}$) were applied to the net intensity counts.

Powder photographs were taken in a Guinier focusing camera using $\text{CuK}\alpha_1$ radiation ($\lambda = 1.54056 \text{ \AA}$) and potassium chloride ($a = 6.2930 \text{ \AA}$) as an internal standard. The unit-cell dimensions refined by least-squares from the X-ray powder pattern are given in Table 1.

Table 1. Crystallographic data of Ca- α -D-glucosaccharate

Lattice constants.	$a = 19.609 \pm 2 \text{ \AA}$ $b = 6.782 \pm 1 \text{ \AA}$ $c = 5.747 \pm 1 \text{ \AA}$
Cell volume	764.3 \AA^3
Density (X-ray)	1.418 g cm^{-3}
Molecules per unit cell	2
Absent reflections	$h00$ with $h = 2n + 1$ and $0k0$ with $k = 2n + 1$
Space group	$P2_12_12$

The positional parameters obtained for the isomorphous strontium compound¹ were used as starting parameters in a full matrix least-squares refinement of the calcium salt structure. The scattering factor curves used were derived from tables given by Freeman.⁷ The real parts of the corrections for anomalous dispersion were included. Attempted least-squares refinements with anisotropic temperature factors for atoms other than calcium did not converge.

Table 2. Final positional and thermal parameters with estimated standard deviations (σ).

Atom	x	y	z	B
Ca	0	0	0.2702 ± 8	—
O(0)	0.0598 ± 6	0.171 ± 2	0.971 ± 3	2.2 ± 3
O(1)	0.1579 ± 7	0.262 ± 2	0.815 ± 3	2.8 ± 3
O(2)	0.1059 ± 6	0.158 ± 2	0.394 ± 2	1.5 ± 3
O(2')	0.2148 ± 7	0.947 ± 2	0.197 ± 3	2.9 ± 3
O(4)	0.0889 ± 7	0.751 ± 2	0.160 ± 3	2.3 ± 3
O(5)	0.0285 ± 6	0.781 ± 2	0.585 ± 3	2.7 ± 3
C(1)	0.1203 ± 8	0.208 ± 3	0.985 ± 4	1.6 ± 4
C(2)	0.1529 ± 8	0.251 ± 3	0.225 ± 3	1.2 ± 3
C(2')	0.2227 ± 8	0.149 ± 3	0.249 ± 4	1.4 ± 3
C(3)	0.1613 ± 9	0.471 ± 3	0.294 ± 3	1.9 ± 4
C(4)	0.0957 ± 10	0.595 ± 3	0.326 ± 4	2.3 ± 4
C(5)	0.0886 ± 10	0.660 ± 3	0.570 ± 4	2.3 ± 4

For Ca the anisotropic temperature factor T obtained was
 $T = \exp[-0.0011 h^2 - 0.011 k^2 - 0.003 l^2 + 0.0001 hk]$

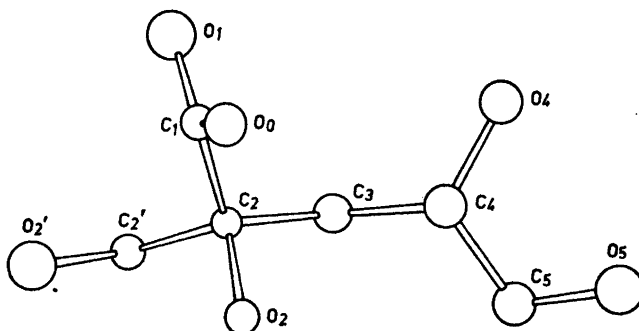


Fig. 1. The structure of the α -D-glucosaccharate group.

In the refinement Hughes' scheme⁸ with $|F_{o, \min}| = 4$ was used to assign weights to the 433 reflections used in the refinement. The measurements of the 26 weakest and 19 of the remaining intensities were obviously in error and these reflections were thus omitted from the least squares calculations. The final value of the residual $R[R = \sum ||kF_o| - |F_c|| / \sum |kF_o|]$ was 0.108. At this stage the shifts in all parameters were less than 1% of their standard deviations. All attempts to refine the hydrogen positions were unsuccessful. The parameters obtained are listed in Table 2.

The structure of the α -D-glucosaccharate group (Fig. 1 and Table 3) is not significantly different from that found in the isomorphous strontium compound. Since the strontium compound is determined with higher precision

Table 3. Interatomic distances (in Å) and angles in the α -D-glucosaccharinic ion with standard deviations.

C(1)–C(2)	1.55 ± 3	O(0)–C(1)–C(2)	$119.9 \pm 1.6^\circ$
C(2)–C(2')	1.54 ± 2	O(1)–C(1)–C(2)	112.9 ± 1.4
C(2)–C(3)	1.55 ± 3	O(0)–C(1)–O(1)	125.0 ± 1.8
C(3)–C(4)	1.55 ± 3	C(1)–C(2)–C(3)	116.9 ± 1.4
C(4)–C(5)	1.47 ± 3	C(1)–C(2)–C(2')	111.2 ± 1.4
		C(1)–C(2)–O(2)	104.3 ± 1.2
C(1)–O(0)	1.21 ± 2	C(2')–C(2)–C(3)	108.4 ± 1.3
C(1)–O(1)	1.28 ± 3	C(2')–C(2)–O(2)	107.7 ± 1.3
C(2)–O(2)	1.48 ± 2	O(2)–C(2)–C(3)	107.9 ± 1.3
C(2')–O(2')	1.41 ± 2	C(2)–C(2')–O(2')	108.6 ± 1.3
C(4)–O(4)	1.43 ± 3	C(2)–C(3)–C(4)	117.7 ± 1.4
C(5)–O(5)	1.44 ± 3	C(3)–C(4)–C(5)	110.8 ± 1.6
		C(3)–C(4)–O(4)	113.5 ± 1.5
O(0)–O(1)	2.21 ± 2	O(4)–C(4)–C(5)	113.9 ± 1.6
O(0)–O(2)	2.60 ± 2	C(4)–C(5)–O(5)	107.8 ± 1.6
O(2)–O(2')	2.81 ± 2		
O(4)–O(5)	2.72 ± 2		

($R = 0.058$) we refer to the paper on the structure of Sr-3-deoxy-2-C-hydroxy-methyl-D-erythro-pentolate (*i.e.* Sr- α -D-glucosaccharate).¹

The dimensions of the coordination polyhedron around each metal ion, a distorted Archimedean antiprism (Table 4), are somewhat decreased in the calcium compound. The average Me—O distance in the calcium salt is thus 0.12 Å less than in the strontium salt. As a result of this the O—O distances

Table 4. Ca—O distances (in Å) and intermolecular O—O distances (in Å) shorter than 3.2 Å. The O—O distances involved in the proposed hydrogen bonding scheme are marked with asterisks. The remaining O—O distances given in the table are all within the coordination polyhedron around calcium.

Ca—O(0)	2.38 ± 2
Ca—O(2)	2.44 ± 1
Ca—O(4)	2.51 ± 1
Ca—O(5)	2.41 ± 2
O(0)—O(4)	3.10 ± 2
O(0)—O(4)	3.15 ± 2
* O(0)—O(5)	2.84 ± 2
* O(1)—O(2)	2.72 ± 2
* O(1)—O(2')	2.79 ± 2
* O(2')—O(4)	2.81 ± 2
O(2)—O(4)	3.09 ± 2
O(2)—O(5)	2.88 ± 2
O(2)—O(5)	3.17 ± 2
O(5)—O(5)	3.18 ± 3

within the coordination polyhedron are somewhat less in the calcium salt. However, all short intermolecular O—O contacts outside the coordination polyhedron remain unchanged. This fact lends strong support to the proposed hydrogen bonding scheme.

EXTENDED HÜCKEL CALCULATIONS

The α -D-glucosaccharate ion shows two distinct structural features which will be briefly discussed here.

1. The intramolecular distance O(0)—O(2) is as short as 2.60 Å. A calculation of a least-squares plane through O(0), O(1), C(1), and C(2) shows that these atoms are without any significant deviation located in a plane. The atom O(2) is removed a very short distance, 0.30 Å, from this plane. This seems to be a common feature of all α -hydroxycarboxylic ions and acids.^{9,10} Therefore, the cation is probably not the cause of the short O(0)—O(2) distance.

2. The carbon chain is twisted at C(4) (*cf.* Fig. 1) and therefore only C(2'), C(2), C(3), and C(4) form a planar zigzag chain. This might be caused by the influence of the cation which is coordinated to O(4) and O(5), but it could also be associated with the fact that C(3) is the only carbon atom which is not bonded to an oxygen atom. The twist may be regarded as a rotation around C(3)—C(4). It may be pointed out that in the arabanate ion¹¹ and in the gluconate ion¹² all the carbon atoms are bonded to oxygen and form planar zigzag chains.

The shape of the anion is influenced by various forces in the crystal structure. Therefore it was considered to be of interest to make a comparison with the geometrical shape of a free acid molecule. By means of the extended Hückel program written by Hoffman¹³ (rewritten by R. Piccioni and modified for CDC 3600 by G. Sperber) it was possible to make some semiempirical conformational analyses of the α -D-glucosiosaccharinic acid. A restriction which must be kept in mind is that the calculations apply to isolated, unsolvated acid molecules. The results obtained may therefore be of limited value but it must be remarked that there are very few ways to bridge the gap between a crystal structure and the corresponding molecular structure of a compound in solution.

It is beyond the scope of this paper to discuss the extended Hückel theory and we refer to the papers by Hoffmann.²⁻⁵

The following parameters were used for the calculations:

	Slater exponent	Coulombic integral (H_{ii})
H(1s)	1.0	-13.60 eV
C(2s)	1.625	-21.34
C(2p)	1.625	-11.54
O(2s)	2.275	-35.30
O(2p)	2.275	-17.91

The resonance integrals H_{ij} ($i \neq j$) were approximated as $H_{ij} = 0.5 K (H_{ii} + H_{jj}) S_{ij}$ with $K = 1.75$ and where S_{ij} is the calculated overlap integral.² The structural parameters used were those of Sr- α -D-glucosiosaccharate. The atomic coordinates used in the calculations are given in Table 5. The

Table 5. Coordinates in Å for α -D-glucosiosaccharinic acid (from Sr- α -D-glucosiosaccharate) used in the extended Hückel calculations.

O(0)	-2.4177	0.1747	-1.3795
O(1)	-0.5315	-0.3467	-2.4636
O(2)	-1.3583	0.0002	0.9816
O(2')	-0.3130	-2.4440	0.0286
O(4)	0.0749	3.4660	-0.9945
O(5)	-0.7146	4.4675	1.4401
C(1)	-1.2013	-0.0794	-1.4129
C(2)	-0.4036	-0.0331	-0.0960
C(2')	0.5064	-1.2694	0.0497
C(3)	0.5044	1.2087	-0.0628
C(4)	-0.2936	2.5368	0.0807
C(5)	-0.0044	3.1909	1.4235
H(0)	-2.98	-0.75	-1.38
H(2)	-0.73	-0.01	1.86
H(2')	0.32	-3.31	0.03
H(4)	-0.16	2.89	-1.87
H(5)	-0.44	5.03	2.32
H(2'1)	1.14	-1.27	0.93
H(2'2)	1.14	-1.27	-0.83
H(3'1)	1.31	-1.18	0.82
H(3'2)	1.31	1.18	-0.94
H(4'1)	-1.37	2.47	0.08
H(5'1)	1.07	3.37	1.42
H(5'2)	-0.26	2.62	2.30

hydrogen atom positions were obtained from geometrical considerations assuming C—H distances of 1.1 Å and O—H distances of 1.0 Å. The calculated net charges and the overlap populations are shown in Figs. 2 and 3, respectively. They show why maxima were obtained in the electron density difference

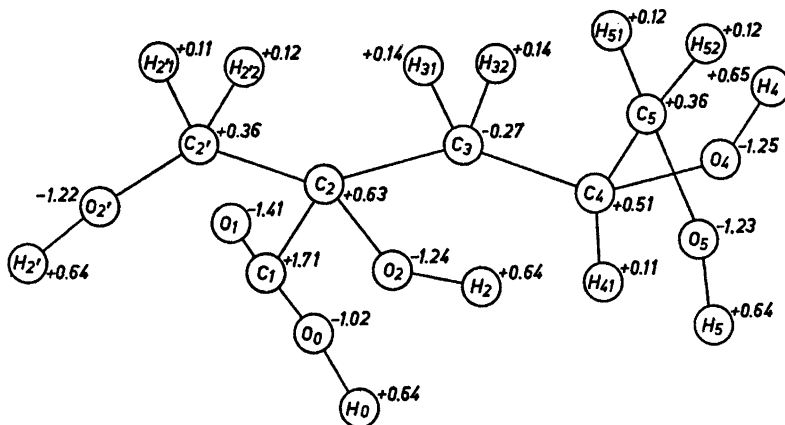


Fig. 2. Calculated net charges (electron units).

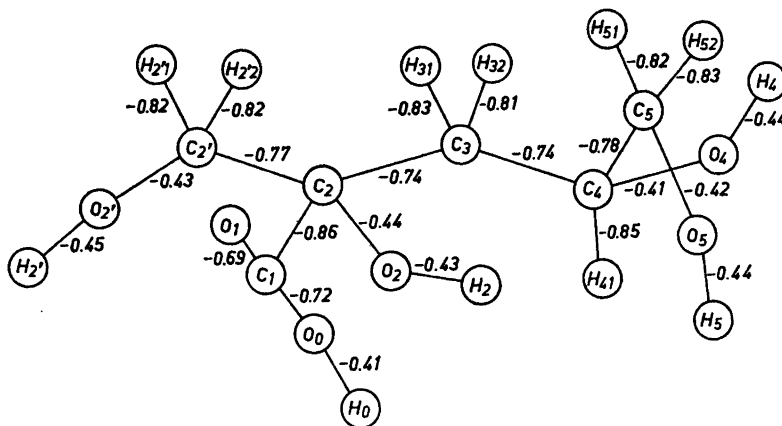


Fig. 3. Calculated overlap populations (electron units).

synthesis for hydrogen bonded to carbon but not for hydrogen bonded to oxygen. It is also evident from the net charges and overlap populations why X-ray analysis, when using atomic scattering functions, should give bond lengths which are too short for C—H and particularly short for O—H bonds.

It has been pointed out by Hoffmann⁵ that the extended Hückel calculations are believed to be reliable if only the orientation of one part of a molecule

Table 6. Observed and calculated structure factors. Reflections marked with an asterisk were not used in the refinement. The columns give $h, k, l, |F_o|$ and $|F_c|$.

2 0 0	401	502	6 1 0	285	333	0 2 0	681	695	1 3 0	182	145
4 0 0	404	458	8 1 0	290	319	1 2 0	331	356	2 3 0	252	235
6 0 0	107	87	9 1 0	517	534	2 2 0	185	189	3 3 0	291	250
8 0 0	260	235	11 1 0	78	61	3 2 0	630	651	4 3 0	355	368
10 0 0	350	359	12 1 0	368	369	4 2 0	741	712	5 3 0	312	318
12 0 0	325	316	13 1 0	96	85	5 2 0	196	199	6 3 0	195	195
14 0 0	229	193	14 1 0	165	166	6 2 0	287	332	7 3 0	257	198
16 0 0	270	300	15 1 0	236	236	7 2 0	438	455	* 8 3 0	41	34
18 0 0	281	278	16 1 0	193	210	* 8 2 0	47	170	9 3 0	265	187
* 1 0 1	948	735	* 17 1 0	229	211	9 2 0	377	251	* 10 3 0	37	6
* 2 0 1	332	255	* 18 1 0	17	30	10 2 0	311	316	11 3 0	289	304
3 0 1	350	299	19 1 0	157	146	12 2 0	100	79	12 3 0	156	170
4 0 1	118	118	0 1 1	450	466	13 2 0	67	48	13 3 0	267	244
5 0 1	185	178	1 1 1	166	163	14 2 0	240	223	14 3 0	47	32
6 0 1	58	61	2 1 1	267	401	15 2 0	76	78	15 3 0	202	192
7 0 1	173	152	3 1 1	163	196	16 2 0	231	234	* 16 3 0	37	8
8 0 1	225	219	4 1 1	635	634	17 2 0	53	82	* 17 3 0	17	48
9 0 1	682	670	5 1 1	97	94	18 2 0	166	167			
10 0 1	298	275	6 1 1	224	227	0 2 1	210	222	0 3 1	76	45
11 0 1	261	268	7 1 1	220	215	1 2 1	460	416	1 3 1	65	125
12 0 1	32	89	8 1 1	470	435	2 2 1	133	144	2 3 1	384	365
13 0 1	309	350	9 1 1	253	238	3 2 1	123	148	3 3 1	168	147
14 0 1	214	210	10 1 1	386	375	4 2 1	331	328	4 3 1	437	418
* 15 0 1	24	15	11 1 1	138	149	5 2 1	621	628	5 3 1	141	170
16 0 1	162	171	12 1 1	55	98	6 2 1	76	104	6 3 1	241	238
17 0 1	64	49	13 1 1	88	61	7 2 1	469	441	7 3 1	151	135
18 0 1	67	89	14 1 1	290	269	8 2 1	168	117	8 3 1	246	247
19 0 1	288	265	15 1 1	55	30	9 2 1	166	203	10 3 1	244	248
			16 1 1	94	109	10 2 1	120	122	11 3 1	170	129
* 0 2 0	897	595	17 1 1	71	41	11 2 1	130	136	15 3 1	107	147
* 1 2 0	24	60	18 1 1	129	175	12 2 1	137	146	16 3 1	196	209
* 2 2 0	521	405	19 1 1	55	41	13 2 1	232	237	* 17 3 1	146	75
3 2 0	280	250				14 2 1	104	118			
4 2 0	244	249	0 1 2	76	46	15 2 1	132	128	0 3 2	212	201
5 2 0	134	165	* 1 1 2	601	447	16 2 1	152	126	1 3 2	372	399
6 2 0	532	522	2 1 2	259	230	17 2 1	184	155	2 3 2	123	123
7 2 0	246	296	3 1 2	649	569	18 2 1	73	90	3 3 2	448	408
8 2 0	214	233	4 1 2	448	393				4 3 2	249	275
10 2 0	162	167	5 1 2	332	487	* 0 2 2	538	458	5 3 2	155	155
11 2 0	95	72	6 1 2	90	72	1 2 2	343	295	6 3 2	218	234
12 2 0	375	356	7 1 2	85	59	2 2 2	488	439	7 3 2	160	158
* 13 0 2	29	4	8 1 2	323	315	3 2 2	350	349	8 3 2	168	134
14 2 0	321	327	9 1 2	425	429	4 2 2	360	371	11 3 2	178	137
* 15 0 2	33	0	10 1 2	104	79	5 2 2	64	41	13 3 2	100	150
16 0 2	251	191	11 1 2	115	130	6 2 2	88	63	14 3 2	71	104
17 0 2	215	214	12 1 2	115	102	7 2 2	50	38	15 3 2	207	218
18 0 2	197	183	13 1 2	243	252	8 2 2	249	253	16 3 2	58	64
			14 1 2	255	247	9 2 2	74	62			
* 1 0 3	726	533	15 1 2	205	184	10 2 2	259	296	0 3 3	124	139
* 2 0 3	444	328	16 1 2	150	123	11 2 2	140	177	1 3 3	186	147
3 0 3	239	221	17 1 2	128	103	12 2 2	115	87	2 3 3	214	201
* 4 0 3	41	4	18 1 2	93	117	14 2 2	88	83	3 3 3	110	171
5 0 3	468	468				16 2 2	209	218	4 3 3	302	295
6 0 3	76	23	0 1 3	267	234				5 3 3	162	156
7 0 3	76	85	1 1 3	112	87	0 2 3	295	225	6 3 3	119	100
8 0 3	101	125	2 1 3	258	230	1 2 3	232	207	7 3 3	156	152
9 0 3	107	119	3 1 3	291	295	2 2 3	119	85	8 3 3	287	290
10 0 3	90	57	4 1 3	640	546	3 2 3	191	173	9 3 3	149	106
* 11 0 3	73	10	5 1 3	78	73	4 2 3	146	127	10 3 3	314	315
12 0 3	73	45	6 1 3	188	197	5 2 3	120	177	11 3 3	191	101
13 0 3	283	283	7 1 3	133	128	6 2 3	195	199	12 3 3	199	223
14 0 3	71	83	8 1 3	343	312	7 2 3	148	169	13 3 3	87	65
15 0 3	93	87	10 1 3	133	131	8 2 3	74	69	* 14 3 3	29	54
16 0 3	247	223	11 1 3	178	186	9 2 3	203	215			
			12 1 3	60	64	10 2 3	64	60			
* 0 0 4	325	252	13 1 3	212	186	11 2 3	211	231	0 3 4	185	155
1 0 4	175	135	14 1 3	256	245	12 2 3	317	351	1 3 4	141	118
* 2 0 4	115	5	15 1 3	82	111	13 2 3	163	146	2 3 4	220	209
3 0 4	105	113	16 1 3	128	134	15 2 3	157	117	3 3 4	238	210
4 0 4	233	235							4 3 4	94	56
5 0 4	182	147	0 1 4	251	191	0 2 4	208	182	5 3 4	90	102
6 0 4	314	265	1 1 4	196	187	1 2 4	143	133	* 6 3 4	158	77
7 0 4	320	276	2 1 4	307	249	2 2 4	239	217	7 3 4	170	221
8 0 4	110	118	* 3 1 4	322	252	3 2 4	76	79	8 3 4	121	67
* 9 0 4	33	48	4 1 4	198	186	4 2 4	191	191	9 3 4	204	200
10 0 4	50	52	* 5 1 4	325	238	5 2 4	152	142	10 3 4	91	120
11 0 4	160	157	6 1 4	201	179	6 2 4	80	116	11 3 4	248	210
12 0 4	47	49	* 7 1 4	37	60	7 2 4	105	108			
13 0 4	109	108	8 1 4	132	123	8 2 4	188	185	0 3 5	149	109
14 0 4	287	276	9 1 4	198	176	9 2 4	91	75	1 3 5	186	172
			10 1 4	64	33	10 2 4	210	218	2 3 5	188	215
0 0 5	379	259	11 1 4	130	113	11 2 4	113	144	3 3 5	123	146
1 0 5	71	38	12 1 4	97	108	12 2 4	149	176	4 3 5	188	176
* 2 0 5	29	58	13 1 4	127	152						
4 0 5	197	175				0 2 5	464	368	* 0 4 0	525	449
5 0 5	397	339	0 1 5	129	156	* 1 2 5	303	221	1 4 0	380	334
6 0 5	141	148	1 1 5	184	151	2 2 5	207	193	2 4 0	204	176
7 0 5	295	247	2 1 5	252	198	3 2 5	274	235	* 3 4 0	33	81
			3 1 5	193	192	4 2 5	156	138	* 4 4 0	24	76
			4 1 5	153	140	5 2 5	153	175	5 4 0	71	65
1 1 0	361	431	5 1 5	126	94	6 2 5	64	77	6 4 0	510	521
2 1 0	435	513	6 1 5	173	175	7 2 5	64	77	7 4 0	121	158
3 1 0	388	398	7 1 5	137	165	8 2 5	90	118	8 4 0	196	164
4 1 0	562	571	8 1 5	160	138				9 4 0	120	123
5 1 0	595	572							10 4 0	74	48

Table 6. Continued.

*11 4 0	37	29	11 4 2	53	55	6 5 0	253	217	0 5 3	150	168
12 4 0	226	239	12 4 2	296	283	7 5 0	120	92	2 5 3	173	192
13 4 0	119	130	13 4 2	85	93	8 5 0	373	340	3 5 3	145	155
14 4 0	132	159	14 4 2	175	167	9 5 0	253	225	4 5 3	162	172
0 4 1	167	156	0 4 3	131	163	10 5 0	164	166	5 5 3	123	158
1 4 1	231	203	1 4 3	236	233	11 5 0	107	99	6 5 3	121	133
2 4 1	170	145	**2 4 3	37	57	12 5 0	69	77	7 5 3	60	86
3 4 1	164	172	3 4 3	184	164	**13 5 0	24	20	8 5 3	147	151
4 4 1	327	341	4 4 3	190	179	0 5 1	155	162	0 6 0	206	109
5 4 1	166	193	5 4 3	160	155	1 5 1	188	197	1 6 0	190	153
6 4 1	195	197	6 4 3	149	147	2 5 1	163	152	2 6 0	96	155
7 4 1	166	196	7 4 3	273	280	3 5 1	80	103	3 6 0	212	159
** 8 4 1	29	35	8 4 3	108	114	4 5 1	141	139	** 6 6 0	24	13
9 4 1	80	96	9 4 3	147	116	** 6 5 1	41	120	7 6 0	71	71
10 4 1	155	173	11 4 3	99	125	7 5 1	183	190			
11 4 1	171	201	12 4 3	130	138	8 5 1	224	172	0 6 1	94	87
12 4 1	44	73				9 5 1	188	158	1 6 1	83	92
13 4 1	241	238	0 4 4	160	141	10 5 1	250	223	2 6 1	134	80
14 4 1	53	68	1 4 4	121	103	11 5 1	146	128	3 6 1	164	158
15 4 1	168	168	2 4 4	149	141	12 5 1	200	172	4 6 1	83	126
			3 4 4	55	73				5 6 1	185	213
0 4 2	352	354	**4 4 4	41	39	0 5 2	76	53	** 6 6 1	24	30
1 4 2	147	141	5 4 4	204	185	1 5 2	82	60	7 6 1	136	164
2 4 2	188	171	6 4 4	202	194	** 2 5 2	17	85	8 6 1	119	119
3 4 2	295	284	7 4 4	141	163	3 5 2	204	194			
4 4 2	100	101	8 4 4	153	176	4 5 2	112	122	0 6 2	53	61
5 4 2	179	178				5 5 2	219	118	1 6 2	143	183
6 4 2	245	253	1 5 0	290	350	6 5 2	144	155	** 2 6 2	37	51
7 4 2	151	175	2 5 0	64	71	7 5 2	312	287	3 6 2	211	250
8 4 2	153	119	3 5 0	241	259	8 5 2	188	164	** 5 6 2	129	51
9 4 2	132	105	4 5 0	176	213	9 5 2	147	159	6 6 2	164	167
10 4 2	60	53	5 5 0	55	34	10 5 2	196	189			

is varied, or where the arguments are concerned with the electron distribution. Therefore, we have made some calculations for different conformations of the acid.

The carboxylic group was rotated around the C(1)—C(2) bond and the total energies calculated are plotted in Fig. 4. The minimum point is located about 18° from the position obtained in the crystal structure and corresponds to an almost planar group C(1), O(0), O(1), C(2), O(2). The deviation from a planar group is only 2° . Thus, the calculations show no tendency for the free acid to increase the short O(0)—O(2) distance by rotation of the carboxylic group. It should be stressed that the absolute values of the calculated energies are not to be relied upon. However, it seems probable that the energy involved in hydrogen bonding (in solution or in crystal structures) is too small to explain the configuration of the plane group.

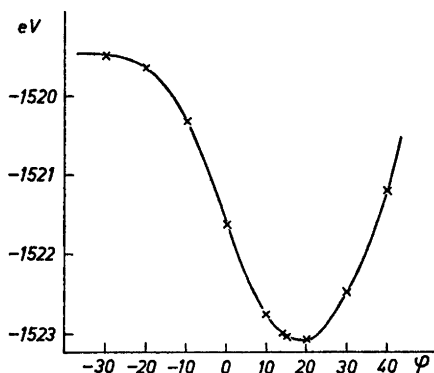


Fig. 4. Calculated total energy plotted as a function of rotation angle, φ , around the C(1)—C(2) bond. The φ -value 0° corresponds to the orientation found in the crystal structure.

Finally the C(3)—C(4) bond was rotated 75° in order to obtain a planar staggered zigzag chain. The calculated total energy was -1520.82 eV. This is 0.81 eV more than the energy calculated from the crystal structure parameters. Furthermore, it is notable that C(3) is the only carbon atom with a calculated negative net charge. Therefore, it is not improbable that the carbon chain remains twisted at C(4) in the solvated acid.

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