

CONFORMATION OF SOME CARBOXYLIC ACIDS AND THEIR DERIVATIVES

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Abstract—The conformation in the crystalline state of some aliphatic carboxylic acids and their derivatives has been analysed. This analysis, based upon the results of structure determinations by means of X-ray diffraction, seems to support the concept that the conformation of a molecule is governed chiefly by intramolecular interactions.

INTRODUCTION

In this article, the rotational arrangement (conformation¹) of substituents about a $C(sp^3)-C(sp^2)$ bond in aliphatic carboxylic acids is discussed. Different groups of these acids pass in review and attention is paid to the conformational aspects as well as to the bond lengths and bond angles of the acetic acid group concerned.

After numerous investigations of the structures of carboxylic acids and their derivatives in the crystalline state by means of X-ray diffraction it is possible to point out some common features in the molecular structures of these compounds. In general the same conformation of a definite molecule is found again and again in crystal structures. This conformational stability is manifest in various structures independent of the space group to which the crystal belongs and of the ionic or molecular character or of the hydrogen bond scheme of the structure. This seems to justify the concept that the realization of a certain conformation in the crystalline state is inherent to the free molecule itself, intramolecular forces dominating over intermolecular interactions.

It is a well-known fact that in the case of a rotation about a $C(sp^3)-C(sp^3)$ bond the energetically most favourable conformation is the staggered one. The $C(sp^3)-C(sp^2)$ conformation in carboxylic acids—the double bonded carboxyl oxygen atom being in an eclipsed position with the α -substituent or β -carbon atom—is compatible with such a staggered conformation if we are to accept Paulings bent bond idea of the double bond.^{2, 3}

Monocarboxylic acids

As may be evident from Table 1, the β -carbon in the acids is fairly coplanar with the atoms of the acetic acid group. The C_3-O_2 distance, being reasonably constant, is no less than about 0.4 Å shorter than a normal van der Waals contact.² Owing to the smaller $O_1C_1C_2$ angle this distance would be greatly decreased if O_1 were in the eclipsed position to the β -carbon atom (approximately 0.15 Å).

¹ E. L. Eliel, *Stereochemistry of Carbon Compounds* Chap. 6; p. 133. McGraw-Hill, N.Y. (1962).

² L. Pauling, *The Nature of the Chemical Bond*. Cornell University Press, N.Y. (1960).

³ L. Pauling, *Proc. Nat. Acad. Sci. U.S.A.* **44**, 211 (1958).

Noteworthy is the difference between the average CCC angle in the carbon chain and the angle $C_1C_2C_3$ that partly determines the $C_3\cdots O_2$ distance: the latter angle is significantly larger than the former.

When no α -substituent and no β -carbon atom is present (acetic acid) one hydrogen atom is found to be in the eclipsed position to the carbonyl oxygen atom.⁴

Dicarboxylic acids

Experimental data of dicarboxylic acids are listed in Table 2. In this series there is a striking alternation in the rotational position of the carboxyl groups with respect to the carbon chain plane, which is reflected in the saw-tooth m.p. curve.⁹ This alternation is the result of the coupling of carboxyl groups, which in the odd members of the series is only possible if the carboxyl groups are rotated several degrees out of the carbon chain.

It is interesting to note the existence of high temperature modifications of the odd members.¹⁶ In these modifications the molecules have lost their symmetry (dyad axis), one carboxyl group being coplanar with the carbon chain plane, whereas the other one, in order to make carboxyl groups couple, makes a yet larger angle with this plane.

The first term of this series, malonic acid¹⁰ has deliberately been left out of Table 2, since the short distance between the terminal groups excludes planarity. A compromise is attained in such a way that one carboxyl group is in the plane of the carbon atoms, the other being turned perpendicular to it.

α -Hydroxycarboxylic acids

The α -hydroxyl group is seen to take over the role from the β -carbon atom such, that this oxygen atom is more or less in the carboxyl group plane (Table 3). The mean value of the $C_3\cdots O_2$ distance is about 0.25 Å lower than a normal van der Waals contact.²

In acids with an asymmetric α -carbon atom the rotational angle of the plane of the carboxyl group with respect to the plane of the carbon chain has been provided with a sign. No significant preference for a definite rotational sense has been found.

⁴ J. A. Kanters and J. Kroon, unpublished work (1965).

⁵ F. J. Strieter and D. H. Templeton, *Acta Cryst.* **15**, 1233 (1962).

⁶ *Ibid.* 1240.

⁷ R. F. Scheuermann and R. L. Sass, *Acta Cryst.* **15**, 1244 (1962).

⁸ G. A. Jeffrey and M. Sax, *Acta Cryst.* **16**, 1196 (1963).

⁹ C. H. MacGillavry, G. Hoogschagen and F. L. J. Sixma, *Rec. Trav. Chim.* **67**, 867 (1948).

¹⁰ J. A. Goedkoop and C. H. MacGillavry, *Acta Cryst.* **10**, 125 (1957).

¹¹ J. S. Broadley, D. W. J. Cruickshank, J. D. Morrison, J. M. Robertson and H. M. M. Shearer, *Proc. Roy. Soc. A*, **250**, 441 (1959).

¹² J. D. Morrison and J. M. Robertson, *J. Chem. Soc.* 987 (1949).

¹³ J. Housty and M. Hospital, *Acta Cryst.* **17**, 1387 (1964).

¹⁴ J. D. Morrison and J. M. Robertson, *J. Chem. Soc.* 993 (1949).

¹⁵ J. D. Morrison and J. M. Robertson, *J. Chem. Soc.* 1001 (1949).

¹⁶ M. I. Kay and L. Katz, *Acta Cryst.* **11**, 289 (1958).

¹⁷ A. J. van Bommel, Thesis, Utrecht (1956).

¹⁸ A. J. J. Sprenkels, Thesis, Utrecht (1956).

¹⁹ G. A. Bootsma and J. C. Schoone, *Acta Cryst.* **22**, 522 (1967).

²⁰ G. S. Parry, *Acta Cryst.* **4**, 131 (1951).

The largest deviation from planarity of the α -hydroxyacetic acid groups was found in tartronic acid.²¹ As in malonic acid, intramolecular steric hindrance prevents the coplanarity of the relevant atoms, the distance between the OH oxygen atoms of the carboxyl groups being 2.92 Å. In fluoromalonic acid²³ the planarity of both fluoroacetic acid groups is much better, however, in spite of the fact that the distance mentioned above (2.92 Å) remains unaltered.

It must be mentioned that in α -hydroxycarboxylic acids a few exceptions have been found to the rule that the double bonded oxygen atom of the carboxyl group is situated at a shorter distance from the α -substituent.¹⁹ The reason for this is not quite clear. A common feature in these acids is the enlargement of the two OCC bond angles at the side of the short contact between the two OH oxygen atoms and the participating in very strong hydrogen bonds.

Salts of α -hydroxycarboxylic acids

In salts the conformation is the same as in the α -hydroxycarboxylic acids. The most peculiar phenomenon is the inequivalency of the two OCC bond angles in the carboxyl group. The enlargement of the angle situated at the side of the α -substituent is significant. Moreover, the differences in the C—O bond lengths also warrant the idea that, here too, the oxygen atom in the bond with the greater double bond character is in an eclipsed position to the aliphatic OH group.

Additional remarks

It should be noted that the preference of the α -OH group over the β -carbon atom for the carboxyl plane has nothing to do with the existence of an intramolecular hydrogen bond. Such a 5-membered ring (the H-atom included) is highly unfavourable:² the distance of the H-atom to the carbonyl oxygen atom is fairly large; even in the most propitious position the hydrogen atom is not very well directed towards the oxygen lone pair electrons and finally a hydrogen bond thus conceived would be far from linear. In tartronic acid, for example, such a bond is completely absent, as appears from X-ray²¹ and IR data, in spite of the fact that the H-atom is not involved in any other hydrogen bond.

Steric hindrance will also decrease the acceptor potentialities of the carboxyl oxygen atom that is at a short distance from the α -substituent or the β -carbon atom. One of the two lone pairs of this carboxyl oxygen atom is directed backwards and has its greatest electron density in the plane of the carboxyl group where the α -substituent or the β -carbon atom is also situated. Thus it seems unprofitable for this lone pair to become involved in a hydrogen bond, the α -substituent or the β -carbon atom preventing any oxygen atom from coming into closer contact with the carbonyl oxygen atom in that direction.

In conclusion the statement seems justified that from the point of view of hydrogen bonding the coplanarity of the acetic acid group with the α -substituent or the β -carbon atom is unfavourable. All the more reason to disparage intermolecular interactions when considering the conformation of the compounds discussed above.

²¹ B. P. van Eijck, J. A. Kanters and J. Kroon. *Acta Cryst.* **19**, 435 (1965).

²² L. Golic and J. C. Speakman. *J. Chem. Soc.* 2521 (1965).

²³ J. A. Kanters, J. Kroon, G. Roelofsens and J. A. Vliegthart, to be published (1967).

²⁴ J. Kroon, A. F. Peerdeeman and J. M. Bijvoet. *Acta Cryst.* **19**, 293 (1965).

²⁵ R. H. Colton and D. E. Henn. *Acta Cryst.* **18**, 820 (1965).

TABLE I. SOME MOLECULAR DATA OF MONOCARBOXYLIC ACIDS

Compound	Ref.	Dihedral angle between $C_1O_1O_2$ and $C_1C_2C_3$	Non-bonding distance C_3-O_2	Bond lengths		Stand dev. bond lengths		Bond angles		Stand dev. bond angles
				C_1-O_1	C_1-O_2	$O_1C_1O_2$	$O_2C_1C_2$	$C_1C_2C_3$	$C_2C_3C_4$	
Propionic acid	5	12	2.84 Å	1.31 Å	1.23 Å	0.01 Å	114	124	114°	1.0°
Butyric acid	6	0	2.83	1.32	1.20	0.02	113	124	114	1.5
Valeric acid	7	2	2.87	1.35	1.26	0.02	117	125	113	1.5
<i>cis</i> -n.1.-8.9	8	5	2.85	1.30	1.24	0.005	114	122	115	0.5
Methylene-hepta decanoic acid										
Mean		5	2.85	1.32	1.23		114	124	114	1.10

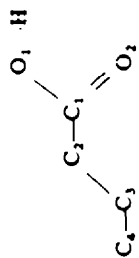


TABLE 2. SOME MOLECULAR DATA OF DICARBOXYLIC ACIDS

Compound	Ref.	Dihedral angle between $C_1O_1O_2$ and $C_1C_2C_3$	Non-bonding distance		Bond lengths		Stand dev.		Bond angles		Stand dev. bond angles
			C_3-O_2	C_3-O_1	C_1-O_1	C_1-O_2	bond lengths	$O_1C_1C_2$	$O_2C_1C_2$	$C_1C_2C_3$	
(even members)											
β -Succinic acid	11	10	2.83	1.31 Å	1.24 Å	0.01 Å	113°	124°	113°	—	1.0°
Adipic acid	12	11	2.79	1.29	1.24	0.04	114	120	115	112	3.0
Suberic acid	13	8	2.84	1.36	1.22	0.01	114	121	115	116	1.0
Sebacic acid	14	6	2.84	1.26	1.24	0.04	116	119	119	114	3.0
Mean		9	2.83	1.30	1.24		114	121	115	113	
(odd numbers)											
β -Glutaric acid	15	24	2.92	1.30	1.23	0.03	114	124	116	109	2.0
β -Pimelic acid	9	23	2.83	1.32	1.25	0.03	110	121	115	112	2.0
α -Pimelic acid	16	37	2.93	1.26	1.24	0.03	118	121	116	111	2.0
(high temp. mod.)		3	2.86	1.34	1.20		114	126	115	110	
Mean		22	2.88	1.30	1.23		114	123	116	110	

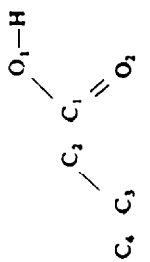


TABLE 3. SOME MOLECULAR DATA OF 3-HYDROXYCARBOXYLIC ACIDS

Compound	Ref.	Dihedral angle between $C_1O_1O_2$ and $C_1C_2O_3$		Non-bonding distance O_3-O_2	Bond lengths		Stand dev. bond lengths	Bond angles		Stand dev. bond angles
		$C_1O_1O_2$	and $C_1C_2O_3$		C_1-O_1	C_1-O_2		$O_1C_1C_2$	$O_2C_1C_2$	
Ammonium hydrogen-D-tartrate	17	- 9°		2.71 Å	1.34 Å	1.21 Å	0.005 Å	113°	124°	0.5°
Ammonium hydrogen-DL-tartrate	18	- 8		2.79	1.28	1.24	0.02	108	126	1.5
Mesotartaric acid	19	-10		2.60*	1.28	1.21	0.01	114	121	1.0
(monoclin. 1 aq.)		- 8		2.65	1.30	1.22		111	124	
Mesotartaric acid	19	+ 4		2.64	1.32	1.20	0.01	111	124	1.0
(triclinic 1 aq.)		- 7		2.63	1.32	1.21		111	124	
Mesotartaric acid	19	+10		2.60	1.31	1.22	0.02	113	122	1.5
(triclinic anh.)		+10		2.68	1.34	1.21		113	124	
DL-Tartaric acid	20	- 4		2.69	1.30	1.21	0.03	115	122	2.0
		+15		2.69	1.37	1.25		115	120	
Tartaric acid	21	-16		2.68	1.31	1.21	0.005	114	120	0.5
		-18		2.75	1.30	1.22		112	122	
Rubidium bisglycolate	22	7		2.76	1.31	1.21	0.015	112	125	1.0
Mean		- 3 abs. 10		2.69	1.31	1.22		112	123	

* In this case the value of the distance O_3-O_2 is given (see text).

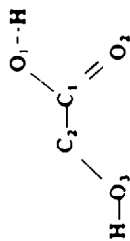


TABLE 4. SOME MOLECULAR DATA OF SALTS OF α -HYDROXYCARBOXYLIC ACIDS

Compound	Ref.	Dihedral angle between $C_1O_1O_2$ and $C_1C_2O_3$		Non-bonding distance C_3-O_3		Bond lengths C_1-O_1 C_1-O_2		Stand dev. bond lengths		Bond angles $O_1C_1C_2$ $O_2C_1C_2$		Stand dev. bond angles
		+	-	\AA	\AA	\AA	\AA	\AA	$^\circ$	$^\circ$		
Ammonium hydrogen-D-tartrate	17	+ 4		2.69	1.26	1.26	1.26	0.005	117	118	118	0.5
Ammonium hydrogen-DL-tartrate	18	+ 6		2.73	1.26	1.21	1.26	0.02	115	118	118	1.5
Lithium ammonium-DL-tartrate	18	+ 7		2.61	1.26	1.25	1.26	0.02	120	116	116	1.5
Lithium ammonium-D-tartrate	18	+ 9		2.55	1.29	1.26	1.26	0.01	117	117	118	1.0
Potassium mesotartrate dihydrate	24	- 11		2.62	1.31	1.26	1.26	0.02	117	116	118	1.5
Rubidium hydrogen bisglycollate	22	- 7		2.70	1.30	1.30	1.27	0.015	117	117	123	1.0
Lithium glycollate monohydrate	25	0		2.66	1.26	1.24	1.22	0.01	116	115	120	1.0
Mean		0	abs. 6	2.66	1.28	1.26	1.26		117	117	119	

