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The Crystal Structure of Peroxypelargonic Acid

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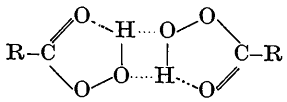
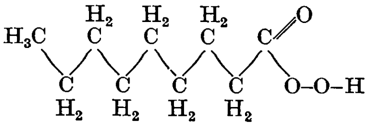
The crystal structure of peroxypelargonic acid, $CH_3[CH_2]_7COOOH$, has been determined from photographic three-dimensional X-ray data. This has established the molecular packing and the hydrogen bonding, which is intermolecular and forms infinite spirals along the twofold screw axes. The –COOO group is planar, with $C=O$ 1·23, C–O 1·35 and O–O 1·44 Å. The C–C bond distances and angles agree with accepted values within the estimated standard deviations of $\sim$ 0·02 Å and 1°.

Introduction

Aliphatic peroxy acids have been known for over a half-century (Swern, 1949), but it is only recently that improved methods of preparation (*cf.* Silbert & Swern, 1959) have made possible the study of the structural characteristics of the peroxycarboxylic acid group. This work has been principally by means of physical chemistry methods and the results have been recently reviewed by Swern & Silbert (1963). Of particular interest is the nature of the hydrogen bonding in these acids, since, unlike normal carboxylic acids, they can theoretically form chelated monomers by intramolecular hydrogen bonding. There is strong evidence, in fact, that in the liquid state the lower member peroxy-acids exist exclusively as such (Giguère & Olmos, 1952). More specifically it has been proposed from dipole moment measurements that the O : C . O . O group is nearly coplanar with the hydrogen atom out of the plane (Rittenhouse, Lobunez, Swern & Miller, 1958), and that in the solid state, the molecules are intermolecularly hydrogen bonded in dimers, or possibly dimers with both intra and intermolecular hydrogen bonding, as in (I) (Swern, Witnauer, Eddy & Parker, 1955).



(I)



(II)

The present structure analysis of peroxypelargonic acid (II) is part of a program using crystal structure analyses as a means to obtaining more conclusive evidence concerning the stereochemistry and the hydrogen-bonding characteristics of the peroxycarboxylic acids in the solid state.

Crystal data

Monoclinic, m.p. 35 °C.

$$a=23\cdot49\pm0\cdot05,\ b=4\cdot80\pm0\cdot05,\ c=9\cdot64\pm0\cdot05\ \text{Å};$$
$$\beta=106\cdot0^\circ\pm0\cdot5^\circ;\ V=1044\ \text{Å}^3;$$
$$D_x=1\cdot11\ \text{g.cm}^{-3},\ D_m=1\cdot11\ \text{g.cm}^{-3}$$

(by flotation in aqueous sodium chloride);

$Z=4$.

Space group $P2_1/c$, from extinctions, $h0l$ absent with l odd, $0k0$ absent with k odd.

The long spacing, $a \sin\beta=22\cdot55$ Å, is in good agreement with the value of 22·53 Å obtained from powder data by Silbert, Siegel & Lutz (1963).

Experimental

The crystals were supplied by Dr D. Swern and Dr L. S. Silbert of the Eastern Regional Research Laboratory, Department of Agriculture. They were soft, thin, colorless plates on (100), which were elongated in the direction of the b axis. Fatty acids generally form poor single crystals which are difficult to manipulate and this compound was no exception. Even the best crystals that could be obtained were of such a quality as to preclude a high precision structure determination. The crystals selected for mounting along the b and c axes were parallelepipeds, approximately 1 mm wide, 0·2 mm thick, and cut to a length of 1 mm. They were sealed into thin-walled glass capillaries. Of this series of acids, ranging from the C_9 to C_{18}, these are the only single crystals we have so far obtained which approach a quality to permit a detailed structure analysis. The X-ray data were recorded on multifilm equi-inclination Weissenberg photographs, with Cu $K\alpha$ radiation. The crystal temperature was maintained at about -30 °C by enclosing the instrument in a cold-box, as described by Allen, McMullan & Jeffrey (1963). Three layers were recorded about the b axis and six layers about the c axis.

At room temperatures, the crystals decomposed rapidly in the X-ray beam. At -30 °C, it was possible to record about 250 hours of exposure before severe disintegration occurred. The exposure times were therefore limited to 40 hours per layer, somewhat restricting the number of observed spectra. The number of independent reflections indexed and estimated was 886, of which 197 were unobserved above the background. This is only 31% of those theoretically available with Cu $K\alpha$ radiation. However, the imperfections of the crystals were such that neither longer exposures nor lower temperatures could significantly improve this ratio. The intensities were estimated visually and unobserved reflections were assigned an intensity of 10% of the minimum observable value. The flaking of the crystals was such that the diffraction data exhibited a variety of spot shapes and sizes, making accurate estimation of relative intensities very difficult. The Lorentz and polarization corrections were made with an IBM 1620 computer, using the program of Shiono (1963). Interlayer scaling was carried out by a series of 1620 programs of Beurskens (1964*a*). Owing to variation of spot size and shape, this proved to be rather unreliable, and the layer lines were subsequently rescaled against the calculated structure factors. No corrections for absorption or extinction were applied.

The structure determination

The orientation of the hydrocarbon chain was obvious from the very intense $\bar{5}02$ reflection and general packing considerations. Although several Fourier maps with reasonable appearance for the chain part of the molecule were obtained by trial and error methods, none of these led to a satisfactory solution to the phase problem.

The structure was solved directly by a systematic application of Sayre's equation $s(\mathbf{h}+\mathbf{h}') \sim s(\mathbf{h})s(\mathbf{h}')$, (Sayre, 1952), according to the method of Beurskens (1964*b*), and using a series of IBM 1620 programs for this purpose (Beurskens, 1964*c*). A Wilson plot was used to put the data on an absolute scale and to determine an average atomic temperature factor. The $|F|$'s were converted to normalized structure factors, ($|E|$'s), (Hauptman & Karle, 1953). This method of applying Sayre's equation is based upon the fact that a correct set of signs will give a consistent set of Sayre's relations, and requires no previous knowledge of signs. Three reflections, called the origin set, were arbitrarily given positive signs, in order to fix the origin. Twelve strong reflections were then tentatively assigned positive signs and these reflections were used to generate new reflections with Sayre's equation. The sign dependencies of these new reflections were traced back to the original reflections, to determine whether the arbitrarily chosen signs were actually correct. The criterion for accepting a sign was based on the probability formula of Cochran & Woolfson (1955). Those signs which were shown to be incorrect were reversed and the process was continued, reiteratively. As the signs of more reflections became known, these were used for further generation, by Sayre's equation, until all the strong reflections had been used. The signs of the strong reflections were then correlated with the origin set, for consistency.

The three origin-fixing reflections and the twelve initial reflections are given in Table 1, where the information gained in three cycles of sign generation and sign correlation is shown. At the end of the third cycle, which incorporated all the strong reflections for the profitable use of Sayre's equation, it was found that two of the initial twelve reflections still had unknown signs, but had contributed little to the discovery of new signs, and so these were omitted from further consideration. Six other reflections had successfully been correlated with the origin set, and their signs were therefore uniquely determined. These,

Table 1. *Information about signs obtained in the first three cycles of sign generation and correlation*

Reflection	Original sign assignment	Cycle 1	Cycle 2	Cycle 3	Final possibilities	
					More probable	Less probable
7 4 2	+ ori-	+	+	+	+	+
2 3 4	+ gin	+	+	+	+	+
4 2 3	+ set	+	+	+	+	+
$\bar{2}$ 1 8	(+)	(+)	(+)	omitted		
$\overline{16}$ 3 2	(+)	(+)	(+)†	−	−	−
6 2 2	(+)	(+)	(+)†	(+)	−	+
$\bar{4}$ 1 2	(+)	(+)*	(+)*	(+)*	−	+
$\overline{15}$ 4 2	(+)$^-$	−	−	−	−	−
$\bar{5}$ 0 2	(+)	(+)	(+)†	(+)*	−	+
1 4 4	(+)	(+)	(+)	−	−	−
7 2 2	(+)	−	−	−	−	−
10 2 5	(+)	(+)	(+)	(+)*	−	+
$\bar{4}$ 2 7	(+)	(+)	(+)	−	−	−
$\bar{2}$ 2 7	(+)	(+)	(+)	omitted		
$\overline{12}$ 2 1	(+)	(+)	−	−	−	−

( ) indicates a tentative assignment (sign unknown).
* indicates a correlation with reflection 6 2 2 (positive, if 6 2 2 is positive).
† indicates that reflections $\overline{16}$ 3 2, $\bar{5}$ 0 2, and 6 2 2 do not all have the correct sign.

Table 3(*a*). *The fractional atomic coordinates, isotropic temperature factors and estimated standard deviations*

Atom	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$	B	$\sigma(B)$
O(1)	−0·0172	0·008 Å	−0·108	0·009 Å	−0·190	0·008 Å	3·05 Å^2	0·16 Å^2
O(2)	0·0225	0·008	−0·250	0·009	−0·069	0·008	2·77	0·15
O(3)	0·0865	0·008	0·090	0·009	−0·084	0·008	3·26	0·17
C(1)	0·0759	0·012	−0·125	0·013	−0·027	0·012	2·77	0·23
C(2)	0·1158	0·012	−0·282	0·013	0·096	0·013	3·27	0·26
C(3)	0·1636	0·012	−0·095	0·013	0·192	0·013	3·05	0·25
C(4)	0·2095	0·012	−0·275	0·014	0·302	0·013	3·29	0·26
C(5)	0·2556	0·014	−0·095	0·016	0·409	0·015	4·45	0·32
C(6)	0·3031	0·013	−0·277	0·014	0·515	0·014	3·64	0·27
C(7)	0·3510	0·014	−0·096	0·016	0·623	0·015	4·76	0·32
C(8)	0·3967	0·014	−0·288	0·017	0·728	0·016	4·68	0·34
C(9)	0·4437	0·018	−0·115	0·021	0·839	0·019	6·95	0·45

in turn had initiated the determination of the signs of 166 other reflections. However, the signs of the remaining four initial reflections and 164 reflections generated by them, although correlated among themselves, could only be linked to the origin set by several relations that occurred with low probability. Although these relations suggested a reversal of the signs of these 168 reflections (which meant that the sign of reflection 622, to which they had all been correlated, was actually negative), the evidence was not strong enough to do so with certainty. Therefore, two three-dimensional Fourier E-maps were made, using an IBM 7070 program of McMullan, Chu & Shiono (1962), with the doubtful group of reflections given opposite signs in each case. The less probable combination of signs produced a map with more than the expected number of peaks which could not be fitted to a chemically reasonable structure. The map resulting from a reversal of the dubious signs had the correct number of peaks, three of which were stronger than the others and were identified as oxygen atoms, and nine of which fitted the configuration of an aliphatic carbon chain. Fig. 1 shows the initial three-dimensional Fourier E map and the final three-dimensional Fourier F map.

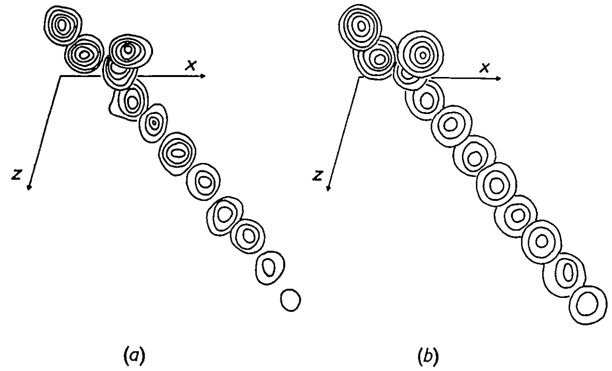


Fig. 1. Structure of peroxypelargonic acid.
(*a*) Initial three-dimensional E Fourier synthesis.
(*b*) Final three-dimensional F Fourier synthesis.

Table 3(*b*). *The assumed methylene hydrogen atom parameters*

Atom	x	y	z	B
H(2)	0·0948	−0·424	0·151	3·27
H(2′)	0·1296	−0·489	0·072	3·27
H(3)	0·1493	0·098	0·231	3·05
H(3′)	0·1804	0·077	0·140	3·05
H(4)	0·1925	−0·457	0·346	3·29
H(4′)	0·2258	−0·461	0·260	3·29
H(5)	0·2390	0·085	0·454	4·45
H(5′)	0·2712	0·090	0·366	4·45
H(6)	0·2872	−0·460	0·559	3·64
H(6′)	0·3190	−0·460	0·470	3·64
H(7)	0·3358	0·088	0·668	4·76
H(7′)	0·3680	0·086	0·580	4·76
H(8)	0·3794	−0·473	0·768	4·68
H(8′)	0·4124	−0·469	0·681	4·68
H(9)	0·4219	0·064	0·902	6·95
H(9′)	0·4674	0·068	0·782	6·95
H(9″)	0·4749	−0·255	0·911	6·95

The coordinates of the peak positions were determined by the method of Booth (1948) and an initial structure factor calculation yielded an R value of 0·37, for the observed reflections only. On further refinement this proved to be the correct solution to the phase problem. Of the 340 signs determined, only 13, all associated with F's of low magnitudes, were subsequently found to be incorrect.

The structure refinement

Three cycles of isotropic least-squares refinement, with the IBM 7070 program of Carpenter (1963), and a weighting scheme $1/w=2|F_{\min}|+|F|+[2/|F_{\max}|]|F|^2$ reduced R to 0·27. An examination of the observed and calculated structure factors then showed systematic discrepancies due to inaccurate inter-layer scaling. Rescaling with the calculated structure factors reduced R to 0·19. Two more cycles of least-squares refinement reduced R to 0·18, and gave coordinate shifts of less than 0·02 Å, indicating that the original refinement had converged to a nearly correct solution despite the unsatisfactory inter-layer scaling. The largest effect was in the temperature factors, which were reduced by up to 0·5 Å^2. Another least-squares cycle gave coordinate and temperature factor shifts which were less than a quarter of the estimated standard deviations, and the refinement was discontinued.

The hydrogen atom scattering was included with the use of an IBM 7070 program of Shapiro (1962), C–H distances of 1·09 Å and H–C–H angles of 107° being assumed. The agreement for the low-order reflections improved considerably, but the overall R value remained unchanged at 0·18 for the observed reflections only, and $R=0{\cdot}20$, including the unobserved reflections.

Although long chain compounds of this type generally show significant thermal anisotropy, the relatively poor quality and quantity of the diffraction data available from these crystals did not justify further refinement. The final observed and calculated structure factors are given in Table 2.* The final atomic coordinates and individual isotropic temperature factors, along with their estimated standard deviations, are given in Table 3(*a*) and (*b*). The intramolecular distances and angles are given in Tables 4 and 5, and the intermolecular distances less than 4·5 Å in Table 6. The carbon atoms are numbered consecutively from the carboxyl, the carboxyl oxygen is O(3), and the perhydroxy group is C(1)–O(2)–O(1)–H(1). The methylene hydrogen atoms are numbered according to the carbon atoms to which they are attached.

Discussion of the structure

The arrangement of the molecules is shown in Figs. 2 and 3. The direction of the chain axis is approximately [102]. The chain packing can be referred to the same orthorhombic O′|| subcell with $P2_122$ symmetry as found in oleic acid by Abrahamsson & Ryderstedt-Nahringbauer (1962) and shown in Fig. 6 of that paper. The subcell dimensions are $a_s=8{\cdot}17$, $b_s=4{\cdot}80$, $c_s=2{\cdot}56$ Å. The cross-sectional area per chain is 19·6 Å² and the volume per CH_2 group is 25·1 Å³.

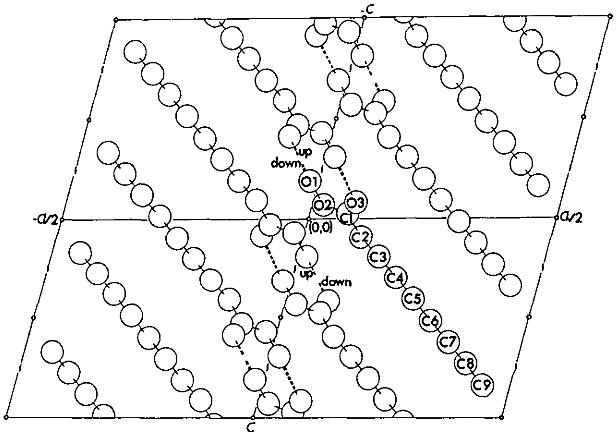


Fig. 2. Structure of peroxypelargonic acid. View of molecules down [*b*].

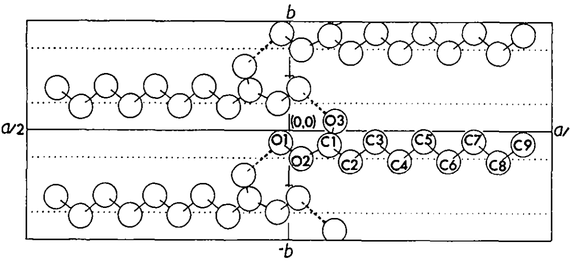


Fig. 3. Structure of peroxypelargonic acid. View down [*c*] of screw-axis related molecules (molecules related by the glide plane have been omitted).

Table 4. *Bond lengths and angles and their estimated standard deviations*

Atom pair	Bond length	σ
O(1)–O(2)	1·442 Å	0·012 Å
O(2)–C(1)	1·348	0·015
O(3)–C(1)	1·231	0·015
C(1)–C(2)	1·494	0·018
C(2)–C(3)	1·536	0·018
C(3)–C(4)	1·552	0·018
C(4)–C(5)	1·536	0·020
C(5)–C(6)	1·557	0·020
C(6)–C(7)	1·565	0·021
C(7)–C(8)	1·560	0·022
C(8)–C(9)	1·547	0·025
O(1) · · · O(3′)	2·744	0·012

Bond angles	Angle	σ
O–O–C	112·0°	0·8°
O–C=O	121·6	1·1
O=C–C	128·2	1·1
O–C–C	110·2	1·0
C(1)–C(2)–C(3)	112·4	1·0
C(2)–C(3)–C(4)	110·0	1·0
C(3)–C(4)–C(5)	111·8	1·1
C(4)–C(5)–C(6)	111·7	1·1
C(5)–C(6)–C(7)	112·2	1·1
C(6)–C(7)–C(8)	110·2	1·2
C(7)–C(8)–C(9)	111·5	1·3

Table 5. *Other intramolecular distances less than* 3·0 Å

Atoms	Distance	Atoms	Distance
O(1) · · · O(3)	2·55 Å	C(2) · · · C(4)	2·53 Å
O(1) · · · C(1)	2·31	C(3) · · · C(5)	2·56
O(2) · · · O(3)	2·25	C(4) · · · C(6)	2·56
O(2) · · · C(2)	2·33	C(5) · · · C(7)	2·59
O(3) · · · C(2)	2·45	C(6) · · · C(8)	2·56
O(3) · · · C(3)	2·92	C(7) · · · C(9)	2·57
C(1) · · · C(3)	2·52		

From C(3) to C(9), the carbon atoms are coplanar. The equation to this plane with reference to the crystallographic axes is

$$0{\cdot}774X-0{\cdot}003Y-0{\cdot}822Z=1{\cdot}430\ .$$

The maximum deviation from this plane is 0·02 Å. Within experimental error, this plane is perpendicular

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Table 6. *Intermolecular distances less than* 4·5 Å

The column headings indicate the symmetry relationship between the atoms

Atom pair	Distance (Å) Translation (on *b*)	Center of symmetry	Screw axis	Glide plane
O(1)–O(1)		3·67	2·88	
O(1)–O(2)	4·31	3·06, 3·99	2·86, 3·84	4·08
O(1)–O(3)		3·46	2·74	
O(1)–C(1)		3·02	3·56, 3·67	
O(1)–C(2)		3·29, 3·99	4·26	4·23
O(1)–C(3)		3·57	4·12	
O(2)–O(2)		3·07, 3·08	3·68	
O(2)–O(3)	3·52	3·38	4·32	
O(2)–C(1)	4·37	3·26, 4·04		
O(2)–C(2)		3·90, 4·09		4·37
O(3)–C(1)	3·82	4·24		
O(3)–C(2)	3·45			3·65
O(3)–O(3)		2·92		3·96, 3·99
O(3)–C(4)				3·68
C(1)–C(1)		3·93		
C(1)–C(2)	4·25			4·02
C(1)–C(3)				4·05
C(1)–C(4)				3·95
C(2)–C(3)	4·09			4·37
C(2)–C(4)				4·04
C(2)–C(5)				4·20
C(3)–C(4)	4·14			4·23
C(3)–C(5)				4·19
C(3)–C(6)				4·14
C(4)–C(5)	4·14			4·26
C(4)–C(6)				3·99
C(4)–C(7)				4·19
C(5)–C(6)	4·13			4·28
C(5)–C(7)				4·27
C(5)–C(8)				4·19
C(6)–C(7)	4·14			4·28
C(6)–C(8)				3·99
C(6)–C(9)				4·14
C(7)–C(8)	4·07			4·26
C(7)–C(9)				4·17
C(8)–C(9)	4·18		4·28	4·22
C(9)–C(9)			4·27	

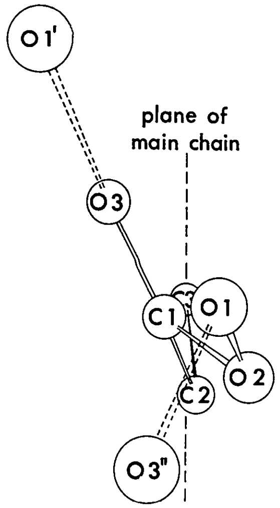

Fig. 4. Stereochemistry of peroxyacid group in peroxypelargonic acid. Viewed along the direction of the aliphatic chain.

to (010), and makes an angle of 58° with (100), which is the plane of the crystal flakes. At C(3), the chain twists; the C(3)–C(2) and C(2)–C(1) bonds make angles of 4° and 8° respectively with the plane of the main chain in opposite directions. The O=C–O plane is 34° to the C(3) to C(9) plane. This stereochemistry is illustrated in Fig. 4.

The C–C distances from C(2) to C(9) range from 1·54 to 1·57 Å, and the variations from the mean of 1·55 Å are not significant. The C–C–C angles vary from 110·0° to 112·4° and the variations from the mean of 111·1° are not significant. The C(1) to C(2) bond is 1·49 Å, in agreement with the expected value for an sp^3–sp^2 bond. The stereochemistry of the peroxycarboxylic acid group is shown in Fig. 5. It is coplanar within the accuracy of the analysis and O(1), O(3) are *cis* with respect to the bond O(1)–O(2). The greatest deviation from the best plane through C(1), O(1), O(2), O(3) is 0·03 Å. This is consistent with the C(1)–O(2) bond length, which is less than that of a single-bond, and corresponds to the same degree of double-bond character as found in the normal carboxylic acids. The O–O distance of 1·44 Å is not significantly different from that of 1·49 Å found in the crystal structure of hydrogen peroxide, (Abrahams, Collins & Lipscomb, 1951) and 1·47 ± 0·02 and 1·49 ± 0·01 Å in the gas molecules, as observed by electron diffraction (Giguère & Schomaker, 1943) and by infrared spectra (Bain & Giguère, 1955) respectively. The accuracy of these bond length measurements is insufficient to reveal any weakening of the peroxy linkage due to intramolecular hydrogen bonding such as is suggested by Swain, Silbert & Miller (1964) on the basis of their recent thermochemical measurements.

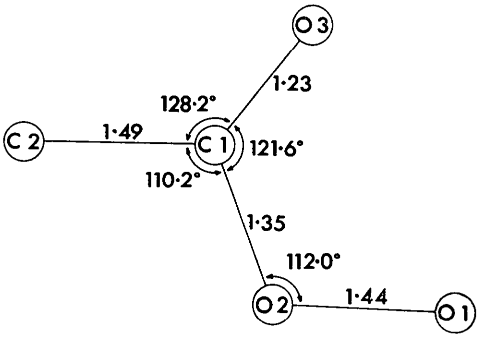

Fig. 5. Bond distances and angles in the peroxyacid group in peroxypelargonic acid.

The molecules are hydrogen-bonded in infinite spirals about the screw axes. The intermolecular O(1) · · · O(3′) distance between screw-related molecules is 2·74 Å and makes an angle of 120° with O(1)–O(2). The dihedral angle between the planes containing the atoms C(1)O(2)O(1) and O(2)O(1)O(3′) is 133°. This is approximately the dihedral angle of the perhydroxy group, if it is assumed that the hydrogen atom is not far removed from the line of the hydrogen-bonded oxygen atoms, O(1) and O(3'), (*cf.* Sax, Beurskens & Chu, 1965). This angle is considerably greater than the 91° observed in H_2O_2 by neutron diffraction (Busing & Levy, 1958), but close to that of 130° in $H_2O_2.2H_2O$ (Olovsson & Templeton, 1960). Because of this dihedral angle, the peroxycarboxylic acid molecules have a definite sense and in this structure there are adjacent hydrogen-bonded spirals of left and right handed molecules, which are related by the centers of symmetry, (*cf.* Jeffrey, McMullan & Sax, 1964).

The intramolecular $O(1) \cdots O(3)$ distance is 2·55 Å, and is at an angle of 60° to the O(2)–O(1) bond. This non-bonding distance could be increased by rotation of O(1) about the O(2)–C(1) bond. The coplanarity of the peroxy-acid group suggests that the van der Waals repulsion energy of the two oxygen atoms along $O(1) \cdots O(3)$ is small compared with that required for rotation about the C(1)–O(2) partial double bond. Any proton interaction in this direction can be excluded, since it is almost diametrically on the opposite side of O(1) to the intermolecular hydrogen bond. On the basis of thermochemical data, Swain, Silbert & Miller (1964) have postulated the formation of intramolecular hydrogen bonding in the peroxy fatty acids in the liquid phase and, furthermore, that this bonding may weaken the O–O bond. Inter- and intramolecular hydrogen bonding will be mutually incompatible in most molecular arrangements and it is not surprising that the sterically more favored intermolecular bonding takes precedence in the condensed phase. We have observed no evidence of a second crystalline phase of peroxypelargonic, and, unlike the normal aliphatic acid, the formation of hydrogen-bonded dimers is not a particularly likely configuration. Thus on melting or dissolution in a non-polar solvent, the hydrogen-bonded spiral chains will disrupt into shorter chains and single molecules with no particular concentration of dimers, and according to the dipole moment and thermochemical evidence cited above, the hydrogen bonding will correspondingly change from inter- to intramolecular.

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