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Crystal Structure of Frozen *o*-Ethoxybenzoic Acid*

By E. M. Gopalakrishna†
Biochemistry Laboratory, National Research Council, Ottawa 7, Ontario, Canada
and L. Cartz‡
Material Science Laboratory, College of Engineering, Marquette University, Milwaukee, Wisconsin 53233, U.S.A.

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o-Ethoxybenzoic acid, $C_2H_5O.C_6H_4.COOH$, an oily liquid at room temperature, crystallizes on cooling below 10°C in the monoclinic space group $P2_1/c$, with $a=7{\cdot}28\pm0{\cdot}01$, $b=15{\cdot}02\pm0{\cdot}02$, $c=16{\cdot}05\pm0{\cdot}02$ Å and $\beta=108{\cdot}27\pm0{\cdot}03°$. The density calculated on the basis of eight molecules per unit cell is 1·325 g.cm^{-3} and the density of the liquid at room temperature is 1·173 g.cm^{-3}. The crystal structure was solved by direct methods using three-dimensional diffractometer data, measured at −10°C. The R index obtained at the end of block-diagonal least-squares refinement is 0·09 for 2469 observed reflections. The bond lengths and bond angles are in good agreement with the usually accepted values. The hydrogen atom in the carboxyl group forms intramolecular hydrogen bonding with the oxygen atom in the ethoxy group. The two independent molecules comprising the asymmetric unit differ only as to the conformation of the ethoxy group. In one molecule it is coplanar with the benzene ring and in the other it is not. The molecules are packed in a layer-like structure with a layer-to-layer distance of 3·6 Å corresponding to half the a-axis translation. There are no unusually short intermolecular contacts.

Introduction

o-Ethoxybenzoic acid (EBA, salicylic acid ethyl ether), $C_2H_5O.C_6H_4.COOH$, is an oily liquid at room temperature with a freezing point of 19·5°C. The crystallization process is rather slow, so that under normal laboratory conditions it is a liquid. Liquid EBA is used as an additive in the zinc oxide–eugenol dental cements (Brauer, 1965, 1967). As part of a general investigation of the formation and hardening mechanism of this cement, the crystal structures of the various components are being investigated (Copeland, Brauer, Sweeney & Forziati, 1955). In particular, the part played by EBA is interesting as it greatly improves the quality of the cement (Brauer, 1965, 1967) and knowledge of its structure could lead to an understanding of the role of EBA in zinc oxide–eugenol dental cements. Fig. 1 shows the stereochemistry of the molecule of EBA and the numbering scheme.

Experimental

Drops of EBA left on a glass plate inside a refrigerator (≃0°C) solidify on cooling into polycrystalline aggregates, consisting of colorless needle-shaped crystals elongated along the a axis. Single crystals suitable for X-ray analysis could be separated and cut to the correct size from these aggregates. The specimen for the diffraction experiments was mounted inside a precooled thin-walled glass capillary, and both ends were sealed with cement. All manipulations in mounting the crystal were carried out inside a refrigerated area to prevent the crystal melting.

The space-group symmetry and the initial lattice parameters were determined from the zero- and first-layer Weissenberg photographs taken about the a and b axes. Final lattice parameters and the intensities were obtained using a General Electric XRD-6 manual single-crystal diffractometer with a scintillation counter. Cu $K\alpha$ radiation was used in both cases. The low-temperature attachment supplied with the Weissenberg camera (Stoe Wissenschaftliche Instrumente, Darmstadt, Germany) was adapted for cooling the crystal in both the Weissenberg and the diffractometer experiments. Using specially designed mounts and nozzles (Gopalakrishna & Cartz, 1969), the full-cassette pictures could be taken rather than the half-cassette pictures possible with the conventional mounting of the low-temperature attachment in the Weissenberg experiments. The temperature of the crystal was measured with a thermocouple placed as near as possible to the crystal, and was −10 ± 4°C.

The systematic absences established the space group as $P2_1/c$. The unit-cell dimensions obtained are $a=7{\cdot}28\pm0{\cdot}01$, $b=15{\cdot}02\pm0{\cdot}02$, $c=16{\cdot}05\pm0{\cdot}02$ Å and $\beta=108{\cdot}27\pm0{\cdot}03°$. The calculated density assuming eight molecules per unit cell is 1·325 g.cm^{-3}, as compared with the measured value of 1·173 g.cm^{-3} for the liquid at room temperature (24°C). The linear absorption coefficient is 5·1 cm^{-1}.

There are two molecules per asymmetric unit. To distinguish them, the atoms belonging to molecule I will have the digit 1 added in the tenth's place of its number and those of the molecule II will have the digit 2; thus C(11) is atom (C1) in molecule I, and C(21)

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‡ To whom all correspondence should be addressed.

Table 1. *Observed and calculated structure factors* (× 10)

An asterisk indicates an unobserved reflection, with $F_{\min}$ given in place of $|F_o|$.

[illegible]

Table 1 (*cont.*)

H	|FO|	FC
K= 2, L=-12		
3	81	88
4	18*	0
5	18*	7
6	62	63
7	28	-33
8	24	-7
K= 3, L= 12		
0	57	102
1	189	156
2	25	26
3	81	-84
4	25	-22
K= 3, L=-12		
1	80	-76
2	72	64
3	26	-28
4	29	16
5	38	45
6	28	-34
7	16*	-15
K= 4, L= 12		
0	118	-105
1	47	45
2	126	130
3	103	107
4	15	-7
K= 4, L=-12		
1	125	-121
2	166	-148
3	33	-26
4	85	76
5	19*	15
6	32	37
7	22	12
K= 5, L= 12		
0	191	-188
1	67	-70
2	18*	-22
3	17	2
4	64	64
K= 5, L=-12		
1	27	24
2	129	-117
3	149	-133
4	97	-122
5	18*	4
6	57	70
7	36	32
K= 6, L= 12		
0	37	39
1	18*	20
2	107	-109
3	16*	6
4	43	38
K= 6, L=-12		
1	96	88
2	220	196
3	18*	16
4	96	-141
5	96	-112
6	74	-82
7	21	-1
K= 7, L= 12		
0	154	155
1	18*	-1
2	48	-46
3	15*	14
K= 7, L=-12		
1	28	32
2	143	140
3	86	81
4	145	139
5	21	31
6	72	-100
7	51	-59
K= 8, L= 12		
0	51	-52
1	41	-38
2	24	26
3	15	-1
K= 8, L=-12		
1	18*	-1
2	128	-124
3	18*	-4
4	104	115
5	30	43
6	41	49
K= 9, L= 12		
0	18*	-7
1	17*	1
2	57	-64
3	32	-27
K= 9, L=-12		
1	18*	-5
2	68	-71
3	23	-14
4	26	-37
5	22	6
6	19	-4
K= 10, L= 12		
0	80	83
1	27	17
2	19	-18
K= 10, L=-12		
1	33	22
2	51	-45
3	18*	5
4	51	51
5	22	-23
6	28	-34
K= 11, L= 12		
0	24	-18
1	24	16
2	20	17
K= 11, L=-12		
1	17*	-1
2	22	-29
3	45	45
4	16	-4
5	17	-4
K= 12, L= 12		
0	53	50
1	14*	2
K= 12, L=-12		
1	28	-27
2	20	-18
3	16*	-1
4	35	-7
K= 13, L= 12		
0	23	-15
K= 13, L=-12		
1	14	-7
2	15	10
3	18	-1
K= 1, L= 13		
0	40	33
1	97	-98
2	53	49
3	18	10
4	27	20
K= 1, L=-13		
1	120	119
2	51	-75
3	52	-47
4	18*	-11
5	18*	10
6	22	-29
7	30	30
K= 2, L= 13		
0	144	-129
1	52	54
2	18*	-18
3	73	-74
4	53	53
K= 2, L=-13		
1	35	-45
2	37	44
3	69	68
4	40	-33
5	71	-80
6	19	-18
7	31	41
K= 3, L= 13		
0	44	34
1	36	30
2	109	-101
3	35	38
K= 3, L=-13		
1	28	18
2	138	117
3	42	30
4	18*	4
5	21	-23
6	19	-17
7	26	-27
K= 4, L= 13		
0	112	107
1	24	25
2	18*	3
3	19	24
K= 4, L=-13		
1	18*	-14
2	71	62
3	134	112
4	92	97
5	18*	3
6	19	-13
7	22	-5
K= 5, L= 13		
0	18	-13
1	28	-33
2	17	27
3	23	-19
K= 5, L=-13		
1	137	-128
2	144	-131
3	18	11
4	42	52
5	35	47
6	26	28
7	23	8
K= 6, L= 13		
0	35	-39
1	50	-53
2	24	27
3	22	-21
K= 6, L=-13		
1	101	-93
2	18*	0
3	60	-62
4	71	-72
5	18*	-15
6	21	-9
7	28	26
K= 7, L= 13		
0	29	-34
1	62	69
2	16*	12
3	19	-20
K= 7, L=-13		
1	36	37
2	18*	25
3	55	-55
4	60	57
5	19	-26
6	27	-25
K= 8, L= 13		
0	37	-32
1	23	30
2	15*	-6
K= 8, L=-13		
1	41	48
2	54	-86
3	30	31
4	18	8
5	17*	-31
6	36	30
K= 9, L= 13		
0	38	42
1	23	21
2	27	-23
K= 9, L=-13		
1	55	-53
2	19	42
3	27	40
4	51	-60
5	23	-1
6	33	23
K= 10, L= 13		
0	36	36
1	30	-24
K= 10, L=-13		
1	17*	10
2	17	26
3	17*	-19
4	18	11
5	21	14
K= 11, L= 13		
0	28	-21
1	24	19
K= 11, L=-13		
1	17	-11
2	16*	-17
3	16*	18
4	22	-7
5	20	-17
K= 12, L= 13		
0	15	1
K= 12, L=-13		
1	17	7
2	15*	-1
3	16	-1
4	26	-23
K= 13, L=-13		
2	19	17
K= 0, L= 14		
0	47	42
1	92	-96
2	45	45
3	54	-47
K= 0, L=-14		
1	202	192
2	270	-222
3	213	195
4	59	11
5	232	-185
6	138	133
7	53	-47
K= 1, L= 14		
0	112	-107
1	19*	136
2	25	24
3	33	-34
K= 1, L=-14		
1	161	-148
2	44	35
3	206	209
4	179	-175
5	84	106
6	32	48
7	53	-83
K= 2, L= 14		
0	69	-69
1	53	51
2	24	-22
3	53	55
K= 2, L=-14		
1	169	-162
2	93	78
3	75	-80
4	38	-42
5	71	92
6	41	-38
7	26	37
K= 3, L= 14		
0	18*	-24
1	100	-106
2	42	-44
3	20	12
K= 3, L=-14		
1	23	16
2	18*	-4
3	104	-99
4	40	-50
5	21	-18
6	18	-4
7	26	23
K= 4, L= 14		
0	18*	-5
1	19*	16
2	38	-49
3	37	-40
K= 4, L=-14		
1	86	81
2	154	141
3	18*	0
4	18	-19
5	22	-31
6	30	-41
7	21	-11
K= 5, L= 14		
0	124	125
1	17	14
2	63	-67
3	18	11
K= 5, L=-14		
1	18*	14
2	18*	-9
3	16*	21
4	53	113
5	17*	14
6	28	-40
7	25	-23
K= 6, L= 14		
0	55	58
1	17*	-11
2	38	35
K= 6, L=-14		
1	32	37
2	122	-118
3	18*	2
4	25	22
5	17*	5
6	56	85
K= 7, L= 14		
0	25	-26
1	50	52
2	36	36
K= 7, L=-14		
1	22	-27
2	66	65
3	44	45
4	86	-108
5	16*	23
6	37	45
K= 8, L= 14		
0	28	-25
1	16*	11
2	31	-24
K= 8, L=-14		
1	67	-65
2	39	46
3	58	-63
4	17	-9
5	16*	35
6	34	-50
K= 9, L= 14		
0	35	35
1	18	-2
K= 9, L=-14		
1	51	48
2	21	24
3	46	-51
4	16*	10
5	23	-26
K= 10, L= 14		
0	18	-29
1	16	10
K= 10, L=-14		
1	16*	2
2	16*	-5
3	16	16
4	22	20
5	19	1
K= 11, L= 14		
0	17	-6
K= 11, L=-14		
1	25	25
2	17	-17
3	20	-22
4	23	23
K= 12, L=-14		
2	21	-15
K= 1, L= 15		
0	18*	-2
1	17*	11
2	16*	-9
K= 1, L=-15		
1	18*	0
2	30	-36
3	18*	-31
4	19*	10
5	21	21
6	23	32
7	24	-26
K= 2, L= 15		
0	18*	-12
1	19	-23
2	15*	1
K= 2, L=-15		
1	35	42
2	18*	-5
3	29	-34
4	39	-66
5	17*	11
6	16*	-4
7	21	-15
K= 3, L= 15		
0	18*	-1
1	30	-28
2	18	-9
K= 3, L=-15		
1	69	71
2	51	58
3	18*	12
4	18*	17
5	17*	17
6	24	-41
K= 4, L= 15		
0	49	52
1	56	83
2	21	15
K= 4, L=-15		
1	19*	-9
2	31	-26
3	18*	6
4	19*	34
5	17*	17
6	24	6
K= 5, L= 15		
0	17*	-6
1	18	-13
2	23	24
K= 5, L=-15		
1	39	-32
2	46	-44
3	26	-31
4	19	-15
5	21	-41
6	15	-12
K= 6, L= 15		
0	28	-24
1	35	-35
2	29	-25
K= 6, L=-15		
1	17*	7
2	18*	-16
3	26	35
4	21	15
5	16*	-29
6	21	-4
K= 7, L= 15		
0	32	36
1	15*	7
K= 7, L=-15		
1	17*	-9
2	17*	-9
3	17*	18
4	23	-26
5	15*	28
6	24	24
K= 8, L= 15		
0	28	-25
1	18	-12
K= 8, L=-15		
1	23	11
2	35	38
3	16*	-17
4	22	-18
5	19	6
K= 9, L= 15		
0	14*	12
K= 9, L=-15		
1	20	15
2	27	24
3	18	14
4	22	25
5	17	-11
K= 10, L=-15		
1	25	-19
2	18	13
3	17	10
4	22	25
K= 0, L= 16		
0	28	25
1	16*	-10
2	25	-24
K= 0, L=-16		
1	21	23
2	18*	1
3	26	-42
4	41	58
5	41	72
6	20	-12
K= 1, L= 16		
0	17*	1
1	20	24
2	23	18
K= 1, L=-16		
1	18*	-1
2	19	-31
3	21	-37
4	17*	2
5	16	-35
6	21	24
K= 2, L= 16		
0	17*	16
1	18	18
K= 2, L=-16		
1	17*	17
2	18*	18
3	18*	-15
4	17*	-21
5	18	-61
6	20	5
K= 3, L= 16		
0	17*	22
1	15*	6
K= 3, L=-16		
1	47	44
2	22	28
3	40	44
4	17*	9
5	16*	-16
6	21	3
K= 4, L= 16		
0	16*	-11
1	15	-8
K= 4, L=-16		
1	17*	-17
2	17*	-12
3	29	33
4	17*	-10
5	16*	10
6	20	13
K= 5, L= 16		
0	17	10
1	14*	1
K= 5, L=-16		
1	17*	4
2	24	29
3	17*	17
4	22	-17
5	15*	8
6	17	-3
K= 6, L= 16		
0	23	-18
1	18	-19
K= 6, L=-16		
1	25	-27
2	16*	-14
3	16*	10
4	29	28
5	15*	30
K= 7, L= 16		
0	14*	5
K= 7, L=-16		
1	26	-26
2	27	-35
3	27	-35
4	21	-7
5	14*	-11
K= 8, L= 16		
0	16	8
K= 8, L=-16		
1	16	-11
2	15*	0
3	15*	1
4	17	-41
K= 9, L=-16		
1	32	36
2	23	22
3	14	-11
K= 1, L= 17		
0	15	22
1	15	-1
K= 1, L=-17		
1	16*	5
2	17*	5
3	17*	-17
4	16*	-5
5	15*	-10
6	20	-12
K= 2, L= 17		
0	19	22
1	20	10
K= 2, L=-17		
1	16*	10
2	17*	26
3	17*	21
4	16*	18
5	15*	-6
K= 3, L= 17		
0	15	-14
K= 3, L=-17		
1	20	-32
2	16	-16
3	16*	-3
4	16*	8
5	15*	25
K= 4, L= 17		
0	14*	-6
K= 4, L=-17		
1	16*	5
2	16*	-4
3	35	-52
4	15*	-17
5	14*	-6
K= 5, L= 17		
0	19	14
K= 5, L=-17		
1	15*	62
2	16*	2
3	15*	-2
4	15*	0
5	15	-19
K= 6, L= 17		
0	14	-6
K= 6, L=-17		
1	16	1
2	15*	12
3	24	38
4	22	1
K= 7, L=-17		
1	17	2
2	17	12
3	21	17
4	19	8
K= 0, L= 18		
0	13	1
K= 0, L=-18		
1	23	-26
2	18	17
3	15	-8
4	15*	1
5	52	37
K= 1, L=-18		
1	15*	1
2	15*	-12
3	15*	-40
4	15*	10
5	13*	1
K= 2, L=-18		
1	14*	13
2	15*	2
3	15*	-2
4	14*	1
5	13	-5
K= 3, L=-18		
1	14	20
2	14*	-7
3	15*	-9
4	14*	17
K= 4, L=-18		
1	14	-11
2	17	-31
3	14*	18
4	17	-15
K= 5, L=-18		
2	14	30
3	15	-7

is atom C(1) in molecule II. When referring to an atom without distinction, the tenth's place will have either a 0 or a blank (see Fig. 1.) The hydrogen atoms on C(8) and C(9) have a further digit. Thus, H(218) is the hydrogen atom H(208) attached to C(8) in molecule I, H(228) being the corresponding hydrogen atom in molecule II.

Intensities were collected by the stationary crystal/stationary counter method using balanced Ross filters and counting the intensity for each reflection for ten sec with each filter. The crystal used was 0·3 × 0·3 × 0·5 mm in size and was mounted with its *a* axis parallel to the φ-axis of the instrument. Intensities of all the 3111 non-equivalent reflections with $2\theta \le 136°$ were measured. Of these, 2469 reflections had net intensities greater than twice their respective standard deviations. The remaining 642 reflections were treated as unobserved.

Structure analysis

After the usual corrections were made for the Lorentz and polarization effects, the normalized structure factors, *E*, were calculated (Karle & Hauptman, 1953). No absorption corrections were applied. The signs were determined for all the reflections whose *E* values were greater than or equal to 1·5 by the symbolic-addition method making use of the $\sum_2$ relationship.

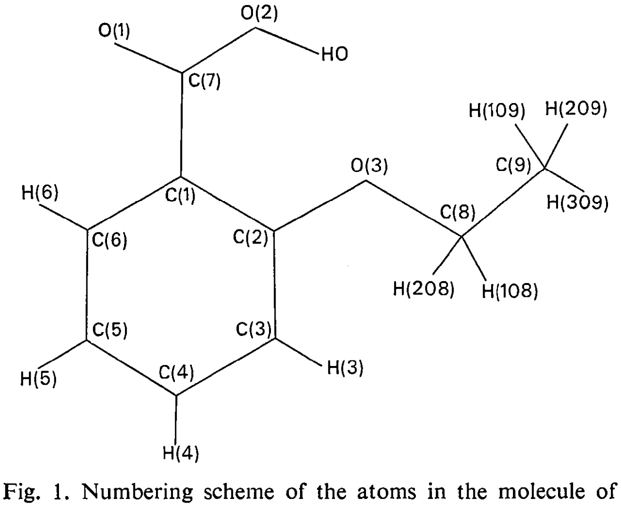


Fig. 1. Numbering scheme of the atoms in the molecule of ethoxybenzoic acid.

The derivation of the signs of the *E*'s was carried out using the symbolic-addition (centrosymmetric) program (Hall & Ahmed, 1968). The origin was fixed by assuming the signs for a set of three linearly independent reflections with large *E* values and evaluating the signs for all other reflections with $E \ge 1·5$. Using the signs so obtained, and with the *E*'s as Fourier coefficients, a Fourier map was computed. The peaks in this map were consistent with the broad features observed in the sharpened Patterson map, which indicated that the molecules are stacked very nearly parallel to the $(20\bar{1})$ plane. However, the map could not be interpreted to yield the complete structure. Eleven peaks from this map, which gave reasonable bond distances and bond angles, were selected. Structure factors were calculated using these peaks, and the set of signs obtained was refined by using the tangent formula, with the restriction that the phase angle could be either 0 or π. The tangent refinement of the phases was carried out using the direct-phasing method (centrosymmetric and non-centrosymmetric) program (Huber & Brisse, 1970). The *E* map calculated with this set of signs yielded the complete structure without any ambiguity.

The structure-factor calculation with the set of atomic positions derived from the *E* map gave an *R* value of 30%, which was reduced to 18% after four cycles of least-squares refinement using isotropic temperature factors. Three cycles of further refinement using anisotropic temperature factors brought down the *R* value to 11%. A difference map calculated at this stage using only the reflections with $\sin^2\theta < 0·5$ showed the positions of all twenty hydrogen atoms. On including the hydrogen atoms with isotropic temperature factors in the structure-factor least-squares refinement, the *R* value finally came down to 9·2%. At

Table 2. *Fractional atomic coordinates and anisotropic temperature factors*

(*a*) Carbon and heavier atoms

The temperature factor is

$$\exp\left[-2\pi^2\left\{U(11)h^2a^{*2}+U(22)k^2b^{*2}+U(33)l^2c^{*2}+U(23)klb^*c^*+U(13)hla^*c^*+U(12)hka^*b^*\right\}\times10^{-3}\right]$$

where *h*, *k* and *l* are the Miller indices.

B (iso) are the isotropic temperature factors obtained before introducing anisotropic temperature factors.

	x/*a*	*y*/*b*	*z*/*c*	*U*(11)	*U*(22)	*U*(33)	*U*(23)	*U*(13)	*U*(12)	*B*(iso)
C(11)	0·3763 (5)	0·2151 (3)	0·2332 (3)	39 (2)	45 (2)	64 (2)	0 (4)	29 (4)	−7 (3)	3·1
C(12)	0·3498 (5)	0·3069 (3)	0·2274 (3)	41 (2)	44 (2)	63 (2)	8 (4)	26 (3)	−9 (3)	3·2
C(13)	0·3477 (6)	0·3562 (3)	0·3004 (3)	59 (2)	47 (2)	66 (3)	−5 (4)	28 (4)	−3 (4)	3·7
C(14)	0·3730 (6)	0·3144 (3)	0·3795 (3)	59 (3)	66 (3)	67 (3)	2 (5)	24 (4)	1 (4)	4·4
C(15)	0·3995 (7)	0·2241 (3)	0·3877 (3)	70 (3)	70 (3)	65 (3)	26 (5)	29 (5)	2 (5)	4·6
C(16)	0·4013 (6)	0·1756 (3)	0·3147 (3)	57 (2)	47 (2)	80 (3)	28 (4)	23 (4)	7 (4)	4·1
C(17)	0·3773 (6)	0·1572 (3)	0·1601 (3)	60 (2)	48 (2)	82 (3)	5 (4)	51 (5)	−8 (4)	3·9
C(18)	0·2916 (7)	0·4392 (3)	0·1371 (3)	72 (3)	38 (2)	74 (3)	9 (4)	46 (5)	−4 (4)	3·9
C(19)	0·2765 (7)	0·4628 (3)	0·0437 (3)	85 (3)	53 (3)	83 (3)	23 (5)	44 (5)	1 (5)	4·8
O(11)	0·4155 (6)	0·0788 (2)	0·1690 (3)	133 (3)	41 (2)	98 (3)	−0 (3)	85 (5)	21 (4)	5·6
O(12)	0·3309 (7)	0·1911 (2)	0·0789 (2)	156 (4)	51 (2)	73 (2)	−1 (3)	92 (5)	10 (4)	5·5
O(13)	0·3245 (4)	0·3443 (2)	0·1462 (2)	76 (2)	38 (1)	66 (2)	7 (3)	51 (3)	2 (3)	3·6
C(21)	0·8749 (5)	0·2589 (3)	0·2787 (3)	36 (2)	55 (2)	61 (2)	13 (4)	13 (3)	−7 (3)	3·3
C(22)	0·8603 (5)	0·2499 (3)	0·1895 (3)	43 (2)	48 (2)	62 (2)	8 (4)	8 (4)	−10 (3)	3·3
C(23)	0·8304 (6)	0·3232 (3)	0·1350 (3)	58 (2)	57 (3)	70 (3)	20 (4)	14 (4)	−0 (4)	3·8
C(24)	0·8139 (7)	0·4048 (3)	0·1676 (3)	62 (3)	58 (3)	77 (3)	32 (5)	15 (5)	0 (4)	5·0
C(25)	0·8231 (7)	0·4154 (3)	0·2550 (3)	62 (3)	50 (3)	91 (4)	2 (5)	16 (5)	13 (4)	4·8
C(26)	0·8560 (6)	0·3434 (3)	0·3107 (3)	51 (2)	55 (2)	76 (3)	2 (4)	22 (4)	14 (4)	4·0
C(27)	0·9088 (6)	0·1851 (3)	0·3434 (3)	49 (2)	62 (3)	71 (3)	15 (4)	17 (4)	−7 (4)	4·1
C(28)	0·8195 (7)	0·1493 (4)	0·0668 (3)	79 (3)	76 (3)	59 (3)	−11 (5)	15 (5)	5 (5)	4·6
C(29)	0·7984 (11)	0·0509 (4)	0·0543 (4)	157 (6)	65 (3)	79 (4)	−42 (6)	26 (8)	9 (7)	6·3
O(21)	0·9248 (6)	0·1957 (3)	0·4208 (2)	103 (3)	91 (3)	64 (2)	31 (4)	52 (4)	27 (4)	5·8
O(22)	0·9264 (6)	0·1039 (2)	0·3145 (2)	124 (3)	48 (2)	79 (2)	19 (3)	26 (4)	−14 (4)	5·1
O(23)	0·8794 (5)	0·1660 (2)	0·1607 (2)	88 (2)	49 (2)	59 (2)	−2 (3)	11 (3)	1 (3)	4·0

Table 2 (*cont.*)

(*b*) Fractional atomic coordinates and isotropic temperature factors for hydrogen atoms

	x/a	y/b	z/c	B(Å^2)
H(13)	0·332 (6)	0·419 (3)	0·296 (3)	2·3 (9)
H(14)	0·370 (6)	0·352 (3)	0·437 (3)	2·1 (9)
H(15)	0·440 (8)	0·190 (4)	0·441 (4)	5·8 (14)
H(16)	0·425 (6)	0·114 (3)	0·318 (3)	2·8 (10)
H(118)	0·406 (6)	0·474 (3)	0·185 (3)	2·5 (9)
H(218)	0·162 (6)	0·453 (3)	0·148 (3)	3·7 (11)
H(119)	0·249 (7)	0·531 (3)	0·044 (3)	4·7 (12)
H(219)	0·130 (10)	0·435 (5)	0·017 (5)	9·8 (22)
H(319)	0·420 (7)	0·449 (3)	0·034 (3)	3·9 (11)
H(10)	0·297 (7)	0·259 (4)	0·086 (3)	5·4 (13)
H(23)	0·804 (8)	0·318 (4)	0·074 (4)	6·2 (15)
H(24)	0·794 (6)	0·457 (3)	0·124 (3)	3·6 (10)
H(25)	0·795 (7)	0·477 (3)	0·283 (3)	4·2 (12)
H(26)	0·856 (8)	0·347 (4)	0·378 (4)	7·1 (16)
H(128)	0·664 (9)	0·180 (4)	0·045 (4)	8·2 (18)
H(228)	0·936 (9)	0·177 (4)	0·036 (4)	7·9 (18)
H(129)	0·778 (10)	−0·003 (5)	0·100 (5)	10·2 (21)
H(229)	0·765 (8)	0·030 (4)	−0·007 (4)	6·4 (15)
H(329)	0·970 (10)	0·049 (5)	0·060 (5)	11·8 (22)
H(20)	0·918 (11)	0·097 (5)	0·241 (5)	10·1 (24)

this stage all the shifts were less than one fourth of their corresponding estimated standard deviations. The atomic scattering factors used in the calculation of the structure factors were taken, for carbon and oxygen atoms, from *International Tables for X-ray Crystallography* (1962) and those for hydrogen atoms from Stewart, Davidson & Simpson (1965). Least-squares refinement was carried out using block-diagonal matrices, a 9×9 matrix for each atom with anisotropic temperature factors and a 4×4 matrix for each atom with isotropic temperature factor. A weighting scheme with

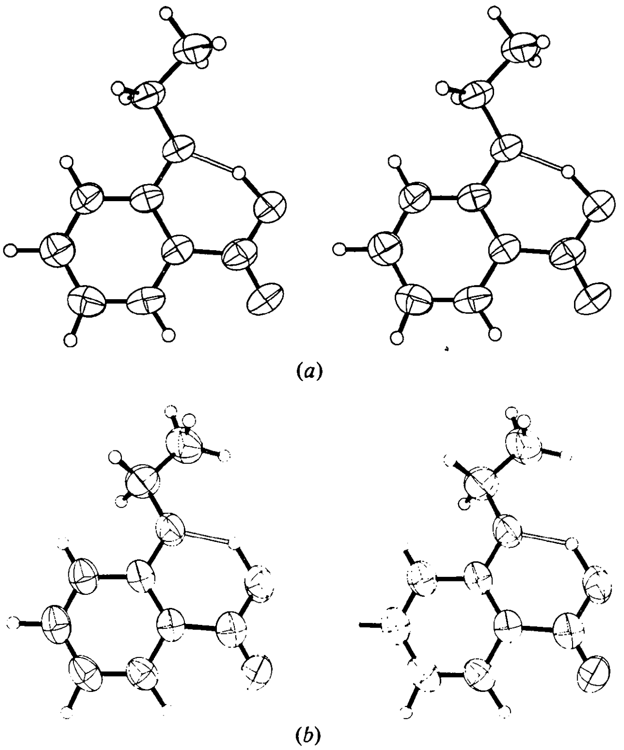
$$\text{weight} = 1 \text{ if } F(\text{obs}) \le 20$$

and

$$\text{weight} = 20/F(\text{obs}),\ F(\text{obs}) > 20$$

was used in the final stages of the refinement. The structure factors were calculated for the unobserved reflections in each cycle of the refinement and only those unobserved reflections whose F(calc) were greater than the corresponding threshold values were included in the least-squares sums and in the R value. The estimated standard deviations were obtained from the inverse of the block-diagonal matrices.

Table 1 lists the observed and the calculated structure factors (the values listed are ten times their absolute values). The positional and temperature parameters obtained at the end of the final refinement are given in Table 2.



(*a*)

(*b*)

Fig. 2. Stereoscopic view of the two symmetry-unrelated molecules: (*a*) Molecule I, (*b*) Molecule II.

Discussion

Stereoscopic plots of each of the two symmetry-unrelated molecules are given in Fig. 2. Bond lengths and bond angles are given in Fig. 3. The estimated standard deviations are given in parentheses and refer to the least significant digit in the values given. The value obtained for any particular bond length or bond angle in one molecule does not differ from that obtained in the other molecule by more than four times the e.s.d. As such, these differences are probably not significant. The bond distances in the central part of the molecule are all very close to expected values, whereas bonds further from the center are all systematically shorter. The average bond lengths of 1·393 Å for C(6)–C(1), 1·400 Å for C(1)–C(2) and 1·385 Å for C(2)–C(3) are very close to the value of 1·395 ± 3 Å expected for the C–C bond in aromatic rings (*International Tables for X-ray Crystallography*, 1962). The bond length of 1·474 Å for C(1)–C(7) is very close to the theoretical value of 1·477 Å quoted by Dewar & Schmeising (1959) and by Cruickshank & Sparks (1960) for the sp^2 single bond between trigonally linked carbon atoms. The C(2)–C(3) bond length with a value of 1·370 Å is also in agreement with the expected value of 1·36 Å (*International Tables for X-ray Crystallography*, 1962). All the above bond lengths are in the central part of the molecule. The other bond lengths are shorter than the usually accepted values, the shortening being conspicuously large at the extremes of the molecule. A considerable part of the bond-length shortening appears to be due to the thermal librational motion of the molecules. This is evident from the isotropic temperature factors obtained at the end of the first stage of the least-squares refinement before the introduction of anisotropic temperature factors. These are given in the last column of Table 2(*a*). The temperature factors are smaller for atoms closer to the center of the molecule, and increase with the distance from the center. This is true for both molecules I and II. The bond length which is shortened most is C(8)–C(9) and the effect is greater in molecule II, where the temperature factors of the two atoms are larger than those in molecule I. An attempt was made to correct the bond lengths for librational motion effects using the *MGTLS* program by Schomaker & Trueblood (1968). Table 3 lists the corrected and uncorrected bond lengths. Although the corrections by this method are in the right direction, they appear to be too small. This may be because the corrections have been calculated on the assumption that the whole molecule is rigid, whereas the substituent groups may really be moving relative to the aromatic ring.

Table 3. *Bond lengths* (Å) *before and after correction for thermal motion*

	Molecule I		Molecule II	
	Un-corrected	Corrected	Un-corrected	Corrected
C(1)–C(2)	1·391	1·395	1·409	1·414
C(2)–C(3)	1·389	1·396	1·381	1·388
C(3)–C(4)	1·377	1·380	1·353	1·357
C(4)–C(5)	1·371	1·373	1·392	1·397
C(5)–C(6)	1·382	1·388	1·376	1·380
C(6)–C(1)	1·395	1·400	1·391	1·397
C(1)–C(7)	1·463	1·471	1·485	1·493
O(1)–C(7)	1·208	1·211	1·221	1·223
O(2)–C(7)	1·340	1·343	1·325	1·331
O(3)–C(2)	1·377	1·382	1·363	1·370
C(8)–O(3)	1·445	1·449	1·453	1·457
C(8)–C(9)	1·509	1·515	1·493	1·499

The values obtained for bond lengths involving hydrogen atoms are all reasonable, except for C(29)–H(329), in molecule II, which seems to be erroneous with a value of 1·23 Å. All the other C–H and O–H bond lengths are between 0·93 and 1·13 Å.

The bond angle C(7)–C(1)–C(2), with an average value of 125·2°, seems to be highly strained because of the steric hindrance between the two adjacent substituent groups. The bond angles involving hydrogen atoms in the ethoxy groups appear to be highly erroneous, which may again be because of large temperature factors of the atoms concerned. All the other bond angles are reasonable.

Fig. 4 shows the packing of the molecules in a unit cell as seen along the *a* axis in stereo. This and the diagrams in Fig. 2 were drawn using the *ORTEP* program by Johnson (1965). The molecules are packed in layers approximately parallel to the (20$\bar{1}$) plane, with a layer-to-layer distance of 3·6 Å. The *a*-axis translation corresponds to twice this distance.

The equations of the least-squares planes are given in Table 4, the deviations from these in Table 5, and the dihedral angles in Table 6. In both molecules I and II, the benzene rings are planar within experimental error. In molecule I, the COOH group is rotated by 7·2° from the plane of the benzene ring. The ethoxy group is almost parallel to the benzene ring, the angle be-

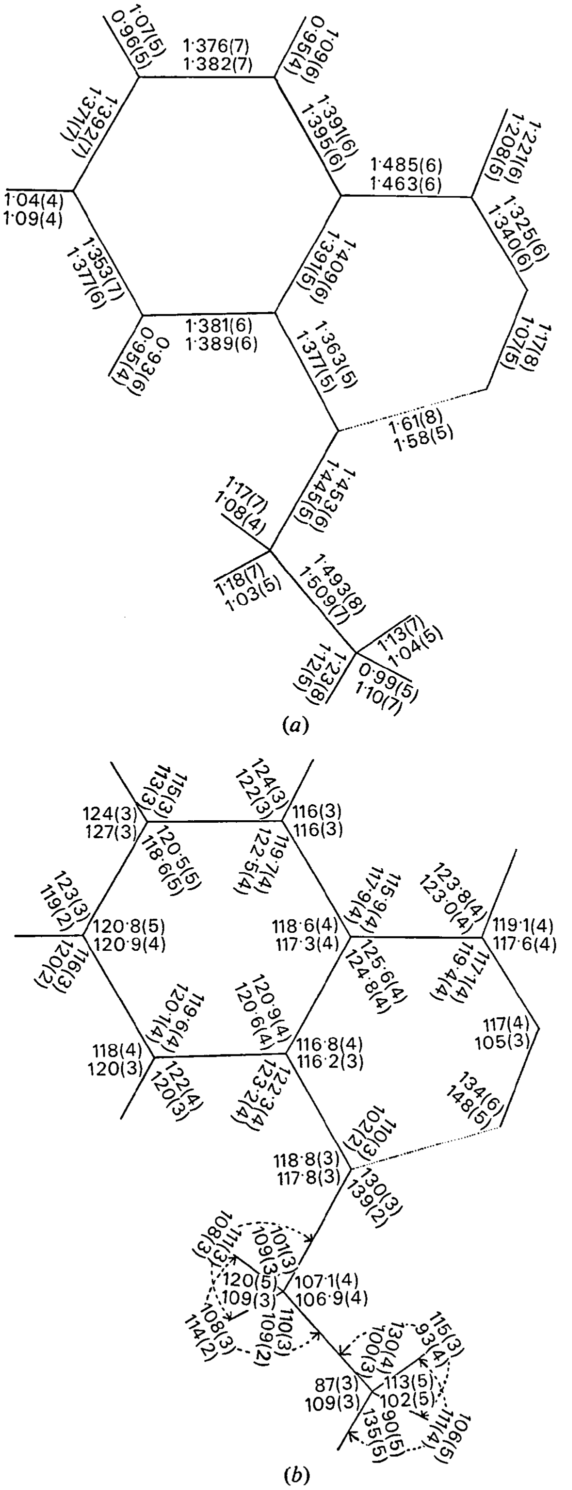


Fig. 3. (*a*) Bond lengths (Å). (*b*) Bond angles (°). The two values marked for each of these correspond to the values for molecules I and II. The lower value refers to molecule I and the upper value to molecule II.

tween them being only 2·7°. The atoms of molecule II deviate more from planarity. The COOH group in this case is almost coplanar with the benzene ring, the angle between them being 1·9°, whereas the mean plane of the atoms of the ethoxy group is inclined at 16·5° to the benzene ring. C(28) and C(29) are displaced 0·35 and 0·68 Å respectively from the mean plane of the benzene ring. The ethoxy group of molecule I is constrained on either side by neighboring molecules. In molecule II, the ethoxy group has greater freedom of movement. As a consequence, the atoms C(28) and C(29) deviate much more from the mean plane of the rest of the molecule. They also have larger thermal motions.

Table 4. *Least-squares planes*

The equations of the least-squares planes are of the form $lX+mY+nZ=P$ relative to the crystal axes, where X, Y, Z and P are in Å.

Plane	Atoms included	l	m	n	P
A I	C(11), C(12), C(13), C(14), C(15) and C(16)	0·9616	0·1315	0·2409	2·7879
B I	C(17), O(11) and O(12)	0·9679	0·2080	0·1411	2·7141
C I	O(13), C(18) and C(19)	0·9477	0·1559	0·2783	2·9683
A II	C(21), C(22), C(23), C(24), C(25) and C(26)	0·9620	0·1352	0·2371	6·3070
B II	C(27), O(21) and O(22)	0·9683	0·1428	0·2049	6·2029
C II	O(23), C(28) and C(29)	0·9971	0·0665	0·0371	5·5026

Table 5. *Perpendicular distances* (Å) *from the mean planes*

The atoms included in the calculation of the mean plane are marked with an asterisk.

Plane A I		Plane A II	
C(11)	0·001*	C(21)	−0·004*
C(12)	−0·001*	C(22)	0·006*
C(13)	0·001*	C(23)	0·000*
C(14)	−0·001*	C(24)	−0·009*
C(15)	0·001*	C(25)	0·011*
C(16)	−0·001*	C(26)	−0·004*
C(17)	0·023	C(27)	−0·012
C(18)	0·039	C(28)	0·345
C(19)	−0·010	C(29)	0·678
O(11)	−0·079	O(21)	−0·051
O(12)	0·186	O(22)	−0·006
O(13)	0·006	O(23)	0·007
H(13)	−0·020	H(23)	0·120
H(14)	0·014	H(24)	−0·028
H(15)	−0·150	H(25)	0·119
H(16)	−0·041	H(26)	0·075
H(10)	0·296	H(20)	−0·023

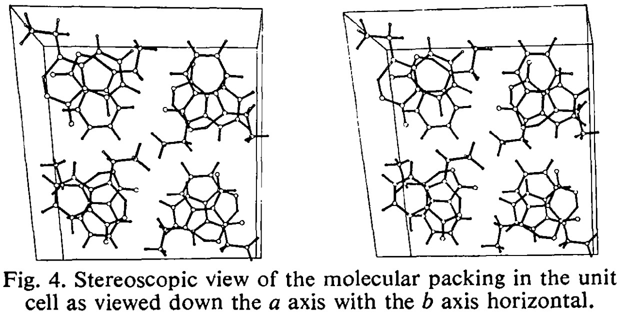
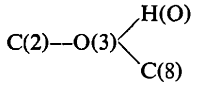


Fig. 4. Stereoscopic view of the molecular packing in the unit cell as viewed down the *a* axis with the *b* axis horizontal.

Table 6. *Dihedral angles*

Plane 1	Plane 2	Angle
A I	*A* II	0·3°
A I	*B* I	7·2
A II	*B* II	1·9
A I	*C* I	2·7
A II	*C* II	16·5

In spite of the ethoxy groups assuming different conformations with respect to the rest of the molecule, the fold angle has very similar values in both molecules.



In molecule I it is 12·0° and in molecule II it is 14·2°. This fold angle is the angle between the two mean planes of the atoms C(2), C(3) and C(8) as one group and the atoms C(2), O(3) and H(O) as another.

There are no unusually short intermolecular contacts in this structure. There are only two distances not involving hydrogen atoms that are shorter than 3·5 Å: 3·467 Å between C(15) and C(27) and 3·166 Å between C(18) and O(22). There are fifteen intermolecular contacts less than 3·0 Å between hydrogen atoms and either carbon or oxygen atoms, of which three are slightly less than 2·5 Å. All these distances are given in Table 7. None of them is significantly less than the corresponding van der Waals distance when considered in the light of their e.s.d.'s. The distance between O(2) and O(3) is 2·553 Å and that between O(3) and H(O) is 1·59 Å.

Table 7. *Intermolecular contacts*

Atom 1	Atom 2	N_{eqv}*	Cell*			Distance (Å)
C(15)	C(27)	1	−1	0	0	3·467 (7)
C(18)	O(22)	2	1	0	0	3·166 (6)
C(14)	H(128)	−2	0	0	−1	2·83 (7)
C(19)	H(24)	−1	1	1	0	2·84 (4)
O(11)	H(229)	−1	1	0	0	3·00 (6)
O(11)	H(13)	2	1	−1	0	2·97 (4)
O(11)	H(118)	2	1	−1	0	2·78 (4)
O(11)	H(25)	2	1	−1	0	2·46 (5)
O(12)	H(228)	1	−1	0	0	2·75 (7)
O(12)	H(14)	−2	0	0	−1	2·48 (4)
C(24)	H(218)	1	1	0	0	2·75 (5)
O(21)	H(119)	2	1	0	0	2·91 (5)
O(21)	H(219)	−2	1	0	0	2·65 (7)
O(21)	H(23)	−2	0	0	0	2·87 (6)
O(21)	H(228)	−2	0	0	0	2·65 (7)
O(22)	H(218)	2	1	−1	0	2·48 (5)
O(22)	H(24)	2	2	−1	0	2·95 (5)

* N_{eqv} and Cell specify the Atom 2 with respect to Atom 1. $N_{\text{eqv}}=1$, -1, 2 and -2 refer to the equivalent positions x, y, z; $-x, -y, -z$; $-x, \frac{1}{2}+y, \frac{1}{2}-z$; $x, \frac{1}{2}-y, \frac{1}{2}+z$ respectively. Cell refers to unit translations along the crystallographic axes.

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The Crystal Structure of Ammonium Hydrogen Terephthalate

By R. E. Cobbledick and R. W. H. Small

Chemistry Department, The University, Lancaster, England

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The crystal structure of ammonium hydrogen terephthalate, $NH_4^+C_6H_4COOHCOO^-$, has been determined using three-dimensional X-ray data measured with a proportional counter. The space group is $C2/c$ with four molecules in the monoclinic unit cell. Positional and anisotropic thermal vibrational parameters have been refined by the method of least-squares giving a final conventional R value of 0·076. The crystal structure consists of chains of centrosymmetric terephthalate ions linked by short hydrogen bonds across centres of symmetry (O···O distance of 2·51 Å) and these chains are linked *via* the ammonium ions to form a three-dimensional hydrogen-bonding network. The carboxyl groups are twisted 9° out of the plane of the benzene ring to form hydrogen bonds with the ammonium ions. Bond lengths for the terephthalate ion have been corrected for librational motion and are C–C (carboxylate) = $1·495 \pm 0·004$, C–O = $1·237 \pm 0·004$, C–O = $1·310 \pm 0·004$, C–C = $1·386 \pm 0·005$, C–C = $1·409 \pm 0·005$ and C–C = $1·374 \pm 0·005$ Å.

Experimental

A sample of ammonium hydrogen terephthalate was prepared by the dropwise addition of aqueous ammonia to a solution of terephthaloyl chloride in pyridine. Plate-shaped crystals were grown by recrystallization from an aqueous solution of dimethylformamide. Composition of the crystals was confirmed by quantitative elemental analysis and mass spectrometry.

Weissenberg photographs showed the crystals to be monoclinic and the systematically absent reflexions, hkl for $(h+k)=2n+1$, $h0l$ for $l=2n+1$, indicated the space group to be Cc or $C2/c$. The space group was later assumed to be $C2/c$ on the evidence of a centric distribution of the three-dimensional intensities (Howells, Phillips & Rogers, 1950). Cell dimensions were determined by a least-squares fit to θ values of a number of reflexions measured on a three-circle diffractometer (Small & Travers, 1961) using Cu $K\alpha$ radiation ($\lambda = 1·5418$ Å). The density was measured by flotation using a mixture of chlorobenzene and carbon tetrachloride. Crystal data are shown in Table 1.

Table 1. *Crystal data*

$C_8H_9NO_4$

$a = 18·913 \pm 0·004$ Å

$b = 3·801 \pm 0·001$

$c = 11·460 \pm 0·002$

$\beta = 97·44 \pm 0·04°$

$V = 816·99$ Å^3

$Z = 4$

$D_{obs} = 1·472$ g.cm^{-3}

$D_{calc} = 1·489$

Determination and refinement of the structure

A total of 891 integrated intensities ($833 > 1\sigma$) with $\sin \theta/\lambda < 0·642$ Å^{-1} were measured using the three-circle diffractometer. Corrections were applied to the intensities for the absorption of X-rays using the program *ABSCOR* on the Chilton ATLAS computer.