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The Crystal Structure of Sodium Hydrogen Fumarate

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The crystal structure of sodium hydrogen fumarate, $NaC_4H_3O_4$, has been determined using three-dimensional data and least-squares refinements with individual anisotropic temperature factors for each atom, giving $R=0{\cdot}105$. In a triclinic unit-cell in space group $P\bar{1}$ ($a=6{\cdot}62_3$, $b=7{\cdot}94_6$, $c=5{\cdot}34_3$ Å, $\alpha=87{\cdot}8$, $\beta=112{\cdot}8$ $\gamma=98{\cdot}4°$) containing two molecules, fumarate groups are aligned in extensive chains along the [010] axis, adjacent neighbours being linked by H-bonds of 2·51 Å between the oxygen atoms of the contiguous COOH groups. The fumarate group, unlike the fumaric acid molecule, is non-planar and one of the COOH groups is twisted by 40° out of the plane of the rest of the molecule. Na^+–O contacts range from 2·38 to 2·64 Å with a mean value of 2·44 Å, giving a sixfold coordination.

The crystal structure of fumaric acid, $C_4H_4O_4$ has been determined by Brown (1966) and that of β-fumaric acid by Bednowitz & Post (1966) and in both of these structures the fumaric acid molecule is shown to be completely planar. However, Gupta & Roy (1967), Gupta & Sahu (1970), Pedone & Sirigu (1967) show that in the crystal structures of potassium hydrogen fumarate ($KC_4H_3O_4$), 'acid' potassium hydrogen fumarate ($2KC_4H_3O_4+C_4H_4O_4$) and racemic tetracarbonyl(fumaric acid)iron [$Fe(CO)_4$ $(CH.COOH)_2$] respectively, the fumarate groups are far from planar, the departure from planarity being far from nominal. However, the work on the first two structures was confined to projections only while in the last one the fumarate groups form only a small part of a more complex structure. It was, therefore, considered desirable to determine fully the lack of planarity of the fumarate group in the salts of fumaric acid itself. Sodium hydrogen fumarate ($NaC_4H_3O_4$) was chosen for this purpose firstly because it gave good single crystals and secondly because no absorption correction was considered to be necessary and the heavy atom technique could be gainfully employed without the presence of the sodium atom making it difficult to locate the positions of the lighter atoms, as usually happens with structures in which very heavy atoms are present.

Crystal data

The crystals of $Na.C_4H_3O_4$ were grown following methods similar to those described by Gupta & Barnes (1961). The crystals were obtained as small colourless elongated plates with the (100) plane as the plate face, bounded by the edges corresponding to the [001] and [010] axes. Under the polarizing microscope the crystals showed extinction parallel to the long edge [001], when lying on the plate face.

The crystals were shown to be triclinic with

$a=6{\cdot}623_3$ Å $\quad \alpha=87{\cdot}8°$ $\quad \varrho$ calc $=1{\cdot}791$ $g.ml^{-1}$
$b=7{\cdot}946_6$ Å $\quad \beta=112{\cdot}8°$ $\quad \varrho$ obs $=1{\cdot}799$ $g.ml^{-1}$
$c=5{\cdot}343_3$ Å $\quad \gamma=98{\cdot}4°$

$Z=2$
Space group $=P\bar{1}$
Linear absorption coefficient for Cu $K\alpha$ radiation, $\mu=11{\cdot}96$ cm^{-1}.

The lattice parameters were determined from high $\sin\theta$ reflexions on Weissenberg zero-level films on which silver lines were also superposed as internal standards of calibration. Complete three-dimensional data were collected using the equi-inclination Weissenberg technique with a pack of three films for each layer. The total number of non-zero reflexions collected was 600. Others were too weak to be observed. This gives about 5 reflexions for each parameter in a 109 parameter structure (positional, thermal and scale). Intensities were estimated visually using an intensity scale with crystal reflected spots and graded series of exposures. The usual corrections (Lp factor, spot-size and shape) were applied and reflexions brought nearly on an absolute scale using statistical methods. Errors due to absorption were neglected as a very small crystal ($0{\cdot}03\times0{\cdot}02\times0{\cdot}02$ cm) was chosen for collection of the data.

Structure determination

Patterson projections failed to give any clue to the positions of the sodium atoms. Extensive trial and error methods (in all about 400 trials!) proved fruitless, although one or two models looked promising initially but these failed to refine. A three-dimensional Patterson synthesis was then computed which indicated the position of the sodium atom at $x/a=0{\cdot}25$, $y/b=0{\cdot}40$, $z/c=0{\cdot}05$. Once the position of the sodium atom had been fixed, other important vectors around the origin peak gave rough positions for at least three other oxygen atoms. Structure factors readily gave signs for an electron density projection down the [100] axis which was interpreted, giving better positions for all the atoms of the fumarate group. Six Fourier refinement cycles and least-squares refinement cycles gave $R(0kl)=0{\cdot}156$,

Table 1. *Observed and calculated structure factors*

h	k	l	/F_o/	/F_c/
0	0	1	12.05	14.02
0	0	2	5.94	7.22
0	0	3	1.97	2.34
0	0	4	4.70	4.46
0	0	5	1.05	0.87
0	0	6	1.85	1.69
0	1	-6	3.94	3.84
0	1	-4	4.80	4.69
0	1	-3	2.63	2.01
0	1	-2	5.03	4.76
0	1	-1	10.38	10.68
0	1	0	8.35	8.25
0	1	1	3.95	4.17
0	1	2	7.79	8.30
0	1	3	16.91	15.87
0	1	4	7.45	8.12
0	1	6	1.26	1.02
0	2	-5	2.85	2.54
0	2	-4	1.95	2.01
0	2	-3	3.14	3.41
0	2	-2	8.45	7.58
0	2	0	1.10	0.42
0	2	1	8.06	7.12
0	2	2	0.92	0.87
0	2	3	12.80	12.08
0	2	4	3.00	2.77
0	2	5	2.20	2.30
0	2	6	2.20	2.13
0	3	-6	2.75	1.95
0	3	-4	13.80	14.96
0	3	-3	2.77	2.45
0	3	-2	13.92	12.96
0	3	-1	7.25	5.37
0	3	0	4.05	2.91
0	3	1	8.88	7.08
0	3	2	3.64	2.87
0	3	3	1.67	1.76
0	3	4	1.60	1.20
0	3	5	1.70	0.84
0	3	6	2.40	3.09
0	4	-4	4.60	5.49
0	4	-3	3.88	3.61
0	4	-2	4.33	4.09
0	4	-1	12.66	12.19
0	4	0	11.90	11.39
0	4	1	6.59	6.50
0	4	2	5.51	5.30
0	4	3	1.14	1.54
0	4	5	1.85	2.19
0	5	-4	2.65	2.96
0	5	-3	2.82	2.50
0	5	-2	1.79	1.11
0	5	-1	13.79	13.01
0	5	0	8.55	7.04
0	5	1	3.19	2.40
0	5	2	4.90	3.33
0	5	3	3.06	3.85
0	5	4	4.60	4.97
0	5	5	1.95	2.36
0	6	-4	3.45	4.00
0	6	-3	3.27	3.75
0	6	-2	1.55	1.07
0	6	-1	2.58	2.72
0	6	0	2.30	1.64
0	6	1	1.05	0.94
0	6	2	6.69	[illegible]
0	6	3	6.37	[illegible]
0	6	4	1.60	2.31
0	7	-4	1.15	0.57
0	7	-3	3.72	4.41
0	7	-2	5.57	[illegible]
0	7	-1	6.90	[illegible]
0	7	1	1.80	1.59
0	7	2	1.70	2.17
0	7	3	3.28	3.28
0	7	4	5.15	4.19
0	8	-3	0.81	1.33
0	8	-2	2.98	2.57
0	8	-1	3.01	3.13
0	8	0	0.70	1.04
0	8	1	4.01	4.05
0	8	2	1.05	0.47
0	8	3	2.30	2.52
0	9	-2	3.31	3.12
0	9	-1	2.66	2.58
0	9	0	4.50	4.42
0	9	1	2.22	0.89
0	9	2	1.25	0.61
0	10	-1	1.67	1.88
0	10	0	3.10	4.03
0	10	1	2.05	5.04
1	-10	-1	2.34	2.00
1	-10	0	4.83	4.86
1	-10	1	2.27	2.38
1	-9	-3	2.07	2.15
1	-9	-1	1.51	1.67
1	-9	0	1.65	0.47
1	-9	2	1.82	0.69
1	-8	-4	1.94	2.07
1	-8	-3	1.64	0.99
1	-8	-1	3.61	3.67
1	-8	0	5.61	5.67
1	-7	-4	2.43	2.45
1	-7	-3	2.13	1.65
1	-7	-2	[illegible]	[illegible]
1	-7	-1	1.10	0.13
1	-7	0	12.71	11.49
1	-7	1	5.11	4.64
1	-7	2	[illegible]	[illegible]
1	-6	-3	[illegible]	[illegible]
1	-6	-2	4.91	4.00
1	-6	-1	[illegible]	0.75
1	-6	0	6.57	6.20
1	-6	1	12.00	11.13
1	-5	-4	5.31	5.61
1	-5	-2	[illegible]	1.59
1	-5	-1	[illegible]	1.49
1	-5	1	12.97	11.15
1	-5	2	1.32	0.44
1	-4	-4	14.29	[illegible]
1	-4	-3	8.60	8.06
1	-4	-2	[illegible]	5.69
1	-4	-1	5.00	[illegible]
1	-4	0	[illegible]	1.40
1	-4	2	[illegible]	3.47
1	-3	-3	[illegible]	[illegible]
1	-3	-2	[illegible]	1.90
1	-3	-1	[illegible]	[illegible]
1	-3	0	3.34	2.98
1	-3	1	3.25	1.95
1	-3	2	4.90	4.16
1	-2	-4	[illegible]	2.06
1	-2	-3	7.62	7.06
1	-2	-2	5.82	5.85
1	-2	-1	14.15	11.72
1	-2	0	6.53	[illegible]
1	-2	1	1.24	0.63
1	-2	2	13.67	13.71
1	-1	-4	1.74	1.82
1	-1	-3	[illegible]	[illegible]
1	-1	-1	[illegible]	2.08
1	-1	0	[illegible]	4.80
1	-1	1	[illegible]	[illegible]
1	-1	2	13.45	[illegible]
1	0	-5	[illegible]	[illegible]
1	0	-4	3.12	3.54
1	0	-3	1.50	0.97
1	0	-2	3.75	3.70
1	0	-1	5.12	4.93
1		0	[illegible]	2.32
2	7	-2	6.66	7.39
2	7	-1	1.61	1.37
2	7	0	3.36	3.53
2	8	-2	4.00	3.95
2	8	-1	1.25	1.95
2	8	0	1.47	1.34
2	8	1	3.22	3.48
2	8	2	3.13	3.41
2	9	-2	3.30	2.75
2	9	-1	1.81	1.74
2	9	0	3.49	2.96
2	9	1	1.73	1.13
3	-9	-3	3.10	3.77
3	-9	-2	1.75	1.87
3	-9	0	1.20	0.71
3	-8	-4	3.14	3.29
3	-8	-3	3.40	2.74
3	-8	0	3.55	4.04
3	-8	1	3.85	4.16
3	-7	-5	2.98	2.88
3	-7	-4	1.15	1.46
3	-7	-2	6.34	7.27
3	-7	-1	1.94	0.20
3	-7	0	11.30	11.38
3	-7	1	2.00	2.33
3	-6	-3	1.10	0.97
3	-6	-2	4.04	3.70
3	-6	-1	4.37	4.24
3	-6	0	6.01	5.80
3	-6	1	6.28	6.29
3	-5	-4	4.15	3.77
3	-5	-3	6.50	6.39
3	-5	-2	1.49	1.40
3	-5	0	4.69	4.86
3	-5	1	6.18	6.14
3	-4	-6	3.13	2.85
3	-4	-5	2.26	1.37
3	-4	-4	16.22	16.10
3	-4	-3	1.45	1.77
3	-4	-2	3.47	3.09
3	-4	-1	1.81	1.32
3	-4	0	9.33	9.10
3	-4	1	2.21	1.92
3	-3	-6	2.07	2.05
3	-3	-5	2.85	2.63
3	-3	-3	7.15	7.48
3	-3	-2	7.54	6.33
3	-3	-1	20.10	17.67
3	-3	0	12.88	12.29
3	-2	-6	2.03	1.59
3	-2	-3	8.05	7.66
3	-2	-1	12.66	12.30
3	-2	0	3.05	3.03
3	-1	-6	3.65	3.17
3	-1	-5	2.79	2.57
3	-1	-4	1.92	2.05
3	-1	-3	2.55	2.43
3	-1	1	2.48	2.92
3	-1	2	4.87	4.61
3	0	-6	2.05	2.77
3	0	-5	6.98	7.55
3	0	-4	8.70	7.40
3	0	-3	4.06	3.92
3	0	-2	2.30	2.29
3	0	0	[illegible]	3.77
3	0	1	6.86	6.19
3	0	4	2.75	2.01
3	1	-5	6.18	6.61
3	1	-4	4.41	4.93
3	1	0	8.90	9.17
3	1	1	2.56	2.30
3	1	2	2.33	2.78
3	2	-5	1.62	1.41
3	2	-4	[illegible]	5.31
3	2	-2	6.78	7.70
3	2	-1	13.09	13.51
3	2	0	2.95	2.12
3	2	1	2.06	1.53
3	2	2	4.06	4.43
3	3	-6	3.38	2.68
3	3	-5	4.11	3.96
3	-3	-4	2.55	2.58
3	3	-3	2.95	3.15
3	-3	-1	7.03	7.15
3	3	0	5.10	4.64
3	3	1	8.46	8.05
3	3	2	1.89	1.59
3	4	-4	3.45	3.64
3	4	-3	3.95	4.38
3	4	-2	2.31	2.30
3	4	-1	7.37	7.70
3	4	0	1.61	0.74
3	4	1	3.03	2.57
3	4	2	6.86	7.64
3	5	-5	2.77	2.88
3	5	-4	1.58	2.15
3	5	-3	2.40	2.49
3	5	-1	2.20	0.78
3	5	0	4.62	4.79
3	5	1	4.56	4.77
3	5	2	3.74	3.84
3	6	-5	2.33	3.54
3	6	-4	1.14	1.80
3	6	-3	6.40	[illegible]
3	6	-1	2.18	[illegible]
3	6	0	1.70	1.11
3	6	1	[illegible]	3.10
3	7	-3	1.20	1.35
3	7	-2	4.73	4.87
3	7	-1	[illegible]	3.19
3	7	0	4.89	4.62
3	7	2	2.97	2.02
3	8	-3	2.75	2.59
3	8	-2	[illegible]	3.20
3	8	0	1.45	1.85
3	8	1	1.64	1.80
4	-9	-3	1.47	2.86
4	-9	-1	1.59	1.26
4	-8	-4	2.85	[illegible]
4	-8	-1	2.13	2.33
4	-8	0	3.79	3.87
4	-8	1	1.77	2.14
4	-7	-1	5.54	5.88
4	-7	0	2.55	2.81
4	-7	1	2.73	3.20
4	-6	-5	2.10	1.63
4	-6	-3	2.21	1.99
4	-6	-2	3.46	5.24
4	-6	-1	8.06	8.57
4	-6	0	2.05	1.15
4	-6	1	2.06	2.06
4	-5	-4	4.75	3.82
4	-5	-3	1.82	2.98
4	-5	-2	6.42	6.15
4	-5	-1	2.13	2.22
4	-5	1	1.94	1.89
4	-5	2	5.90	6.84
4	-4	-4	1.10	1.04
4	-4	-3	2.68	2.75
4	-4	-2	2.94	2.26
4	-4	0	3.30	2.42
4	-4	1	7.27	7.41
4	-4	2	1.86	1.84
4	-3	-5	7.66	6.98
4	-3	-4	1.10	1.63
4	-3	-2	3.18	3.44
4	-3	0	1.10	0.76
4	-3	1	3.68	3.72
4	-3	2	5.23	5.83
4	-2	-6	4.48	4.94

h	k	l	/F_o/	/F_c/
1	0	1	7.90	8.35
1	0	2	4.32	3.72
1	0	4	1.85	1.42
1	0	5	7.80	7.88
1	1	-3	1.72	1.45
1	1	-2	12.24	11.34
1	1	-1	17.38	18.07
1	1	0	8.05	9.24
1	1	1	1.38	1.65
1	1	2	2.23	2.89
1	2	-4	1.94	2.45
1	2	-3	3.53	3.51
1	2	-2	19.26	19.04
1	2	-1	13.10	12.78
1	2	0	7.46	7.98
1	2	1	4.68	4.49
1	2	2	8.47	9.24
1	3	-4	2.00	2.36
1	3	-2	8.12	7.27
1	3	-1	4.23	4.34
1	3	0	9.75	8.45
1	3	1	21.10	22.35
1	3	2	5.20	4.25
1	4	-3	1.56	1.59
1	4	-2	4.08	3.62
1	4	-1	6.30	6.04
1	4	0	2.23	2.09
1	4	1	2.21	2.75
1	4	2	10.32	10.07
1	5	-4	1.74	1.71
1	5	-3	2.78	2.14
1	5	-2	2.24	2.29
1	5	-1	7.81	7.56
1	5	0	6.44	5.73
1	5	1	1.74	1.16
1	5	2	5.00	4.99
1	6	-3	8.87	9.30
1	6	-2	1.77	0.78
1	6	-1	13.29	12.76
1	6	0	3.49	2.86
1	7	-3	2.62	3.32
1	7	-2	5.40	5.48
1	7	-1	5.68	5.03
1	7	0	8.74	8.30
1	7	2	6.00	6.41
1	8	-4	2.20	1.88
1	8	-2	2.93	3.72
1	8	-1	1.00	0.87
1	8	0	4.09	[illegible]
1	8	1	3.54	[illegible]
1	9	-2	2.10	2.29
1	9	-1	2.26	2.17
1	9	0	1.92	2.00
1	9	1	2.54	2.41
2	-10	-1	6.07	5.43
2	-10	0	1.70	1.59
2	-9	-3	2.85	2.72
2	-9	-1	1.90	1.15
2	-9	0	3.04	3.25
2	-9	1	4.21	3.82
2	-8	0	7.49	7.77
2	-7	-6	6.83	7.28
2	-7	-4	3.72	3.38
2	-7	-2	3.30	3.26
2	-7	-1	2.92	3.10
2	-7	0	4.16	4.16
2	-7	1	6.48	6.41
2	-7	2	1.68	0.81
2	-6	-3	5.29	5.11
2	-6	-2	9.22	9.20
2	-6	-1	5.56	5.09
2	-6	0	1.76	0.74
2	-6	1	2.07	0.93
2	-6	2	4.58	[illegible]
2	-5	-3	3.47	4.52
2	-5	-2	[illegible]	7.11
2	-5	-1	1.57	1.49
2	-5	0	1.79	1.18
2	-5	1	[illegible]	[illegible]
2	-5	2	6.31	7.10
2	-4	-4	1.49	[illegible]
2	-4	-3	2.70	[illegible]
2	-4	-2	4.95	[illegible]
2	-4	-1	3.49	[illegible]
2	-4	0	6.92	6.99
2	-4	1	14.65	13.48
2	-3	-6	[illegible]	4.57
2	-3	-4	1.04	1.45
2	-3	-2	3.10	2.60
2	-3	-1	[illegible]	7.86
2	-3	1	6.22	[illegible]
2	-2	-4	1.69	1.82
2	-2	-3	[illegible]	10.04
2	-2	-2	[illegible]	10.17
2	-2	-1	7.41	6.96
2	-2	0	1.61	0.69
2	-2	1	4.97	4.58
2	-2	2	2.61	[illegible]
2	-1	-6	[illegible]	1.60
2	-1	-4	2.10	2.41
2	-1	-3	23.45	20.34
2	-1	-2	3.95	2.45
2	-1	0	4.90	3.69
2	-1	1	14.23	13.82
2	-1	2	[illegible]	[illegible]
2	0	-5	[illegible]	1.95
2	0	-3	4.00	4.31
2	0	-2	[illegible]	[illegible]
2	0	-1	[illegible]	[illegible]
2	0	0	37.60	[illegible]
2	0	1	[illegible]	4.39
2	0	2	[illegible]	[illegible]
2	0	3	[illegible]	1.75
2	0	4	[illegible]	3.56
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2	1	-3	[illegible]	[illegible]
2	1	0	[illegible]	7.46
2	1	1	[illegible]	[illegible]
2	1	2	5.45	5.55
2	[illegible]	[illegible]	[illegible]	[illegible]
2	2	-4	[illegible]	[illegible]
2	2	-3	[illegible]	[illegible]
2	2	-2	[illegible]	[illegible]
2	2	-1	[illegible]	[illegible]
2	2	0	[illegible]	3.15
2	2	1	[illegible]	[illegible]
2	2	[illegible]	[illegible]	[illegible]
2	3	[illegible]	[illegible]	4.11
2	3	-4	[illegible]	[illegible]
2	3	[illegible]	[illegible]	13.51
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2	3	0	1.70	[illegible]
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2	3	[illegible]	[illegible]	[illegible]
2	[illegible]	-4	[illegible]	[illegible]
2	4	[illegible]	[illegible]	[illegible]
2	4	[illegible]	[illegible]	[illegible]
2	4	-1	[illegible]	[illegible]
2	4	0	[illegible]	[illegible]
2	4	1	[illegible]	[illegible]
2	4	[illegible]	[illegible]	[illegible]
2	5	[illegible]	[illegible]	[illegible]
2	[illegible]	-3	[illegible]	[illegible]
2	[illegible]	[illegible]	[illegible]	[illegible]
2	[illegible]	-1	6.96	6.94
2	[illegible]	0	8.22	8.20
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[illegible]	[illegible]	0	[illegible]	[illegible]
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4	-2	0	1.00	0.33
4	-2	1	2.98	2.64
4	-1	-6	1.79	2.50
4	-1	-5	3.75	3.59
4	-1	0	6.85	6.25
4	-1	1	6.98	6.50
4	-1	2	4.22	4.62
4	0	-6	1.15	1.28
4	0	-5	3.84	4.24
4	0	-4	1.00	1.32
4	0	-2	14.05	12.61
4	0	-1	11.18	9.83
4	0	0	13.30	11.66
4	0	1	3.93	3.51
4	0	2	7.93	7.83
4	1	-5	3.58	3.29
4	1	-4	1.85	2.32
4	1	-2	7.16	7.76
4	1	1	6.53	5.93
4	2	-5	5.21	5.39
4	2	-4	2.20	2.18
4	2	-1	4.28	3.97
4	2	0	5.85	5.76
4	[illegible]	1	5.19	4.83
4	3	-6	3.98	4.16
4	3	-5	3.64	3.37
4	3	-4	7.50	7.98
4	3	-2	9.70	9.18
4	3	0	1.10	1.11
4	3	2	1.90	2.19
4	4	-4	[illegible]	2.07
4	4	0	5.00	4.71
4	4	1	[illegible]	2.33
4	4	[illegible]	3.07	3.69
4	5	-5	1.62	1.81
4	5	-4	2.55	2.68
4	5	-1	1.61	1.69
4	[illegible]	0	4.15	4.33
4	[illegible]	1	2.56	2.07
4	6	-5	[illegible]	2.14
4	6	-1	2.15	2.48
4	6	1	2.73	2.18
4	6	2	1.90	0.79
4	7	-4	0.55	0.41
4	7	-2	3.34	4.19
4	7	-1	2.15	2.66
4	7	0	1.70	2.17
4	7	1	1.30	0.67
4	8	-2	2.21	2.40
5	-8	-4	1.65	2.80
5	-8	-3	2.32	3.41
5	-8	-1	3.90	4.22
5	-7	-2	3.69	4.32
5	-7	0	6.35	7.85
5	-6	-5	1.00	1.05
5	-6	0	3.40	3.20
5	-6	1	3.00	2.96
5	-5	-5	0.76	0.82
5	-5	-3	5.66	6.38
5	-5	-2	3.38	3.39
5	-5	0	2.45	2.90
5	-5	1	2.41	1.85
5	-4	-6	3.69	3.78
5	-4	-5	2.96	2.77
5	-4	-4	9.29	9.82
5	-4	-3	1.81	2.03
5	-4	-2	5.64	5.62
5	-4	0	4.40	4.44
3	-4	1	3.53	3.05
5	-3	-6	2.66	2.45
5	-3	-5	1.45	1.42
5	-3	-3	7.24	6.89
5	-3	0	7.90	7.74
5	-3	1	4.07	4.58
5	-2	-6	1.25	1.24
5	-2	-5	1.00	1.17
5	-2	-3	6.38	5.70
5	-2	0	2.70	3.00
5	-2	1	3.30	2.58
5	-1	-6	4.22	4.17
5	-1	-5	2.30	1.99
5	-1	0	1.10	0.97
5	-1	1	3.10	2.86
5	0	-2	4.33	2.34
5	0	-1	3.10	1.83
5	0	0	2.95	2.58
5	0	1	3.05	3.02
5	1	-5	3.00	2.92
5	1	-1	4.65	4.55
5	1	0	5.50	5.19
5	1	1	2.92	2.21
5	2	-5	1.75	1.59
5	2	-1	5.63	5.81
5	2	0	[illegible]	4.65
5	2	1	1.37	1.14
5	3	-6	2.66	2.81
5	3	-1	[illegible]	2.80
5	3	1	3.38	3.49
5	4	-5	1.45	1.16
5	4	-2	3.45	4.80
5	4	-1	3.13	3.14
5	4	0	1.95	1.99
5	4	1	2.29	2.83
5	4	2	2.72	2.96
5	5	-5	2.95	2.40
5	5	-1	2.03	0.95
5	5	0	1.00	1.08
5	5	1	4.04	3.89
5	6	-3	3.56	3.86
5	6	-1	6.48	5.99
5	6	0	1.10	1.46
5	6	1	2.87	3.07
5	7	-1	1.14	1.49
6	-7	-4	2.56	2.77
6	-7	0	1.20	0.56
6	-6	-5	1.28	1.37
6	-6	0	2.45	3.20
6	-5	0	1.45	1.69
6	-4	0	1.10	1.00
6	-4	1	2.48	2.93
6	-3	-6	1.45	1.19
6	-3	-5	4.87	4.90
6	-3	1	2.53	2.98
6	-3	2	3.22	3.40
6	-2	-6	1.85	2.06
6	-2	-5	3.04	3.45
6	-2	0	1.70	1.76
6	-2	1	2.03	0.82
6	-1	-5	2.05	2.89
6	-1	0	2.95	3.05
6	-1	1	1.73	1.74
6	-1	2	1.34	2.28
6	0	0	4.50	4.12
6	0	2	4.75	3.58
6	1	0	1.10	0.78
6	2	0	3.90	4.01
6	3	-2	4.33	4.77
6	3	0	1.45	1.35
[illegible]	4	[illegible]	[illegible]	2.12
7	-3	0	[illegible]	2.28
7	-3	1	3.18	3.17
7	-2	1	3.21	2.43
7	-1	0	1.00	1.41
7	-1	1	2.73	2.41
7	0	0	1.20	1.17
7	0	1	1.20	1.08
7	1	0	1.45	1.91
7	1	1	[illegible]	1.36
7	2	0	2.30	[illegible]

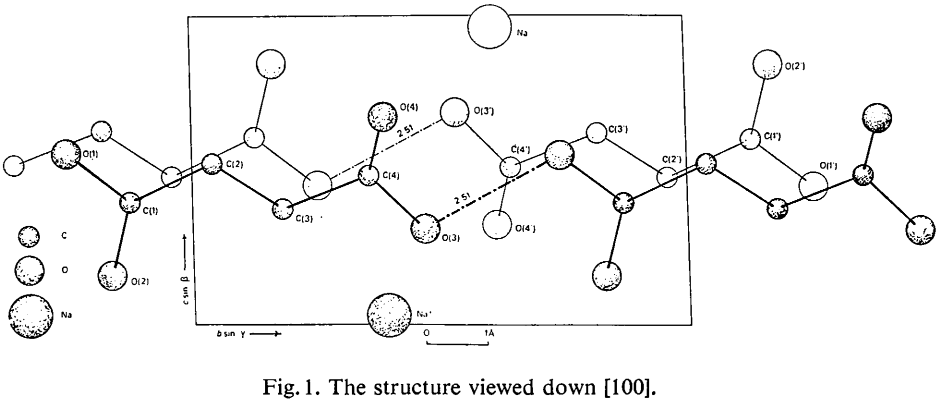

Fig. 1. The structure viewed down [100].

Table 2. *Final positional coordinates*

	X	$\sigma(X)$	Y	$\sigma(Y)$	Z	$\sigma(Z)$
Na^+	1·5606 Å	0·0021 Å	3·1206 Å	0·0020 Å	0·1607 Å	0·0038 Å
O(1)	2·2226	0·0036	−3·7055	0·0040	3·6600	0·0066
O(2)	1·0303	0·0036	−3·0656	0·0040	1·3667	0·0064
O(3)	1·7899	0·0036	2·0177	0·0038	2·3731	0·0066
O(4)	1·9154	0·0037	1·1531	0·0038	4·4871	0·0066
C(1)	1·6129	0·0052	−2·8291	0·0056	2·7305	0·0094
C(2)	1·7237	0·0053	−1·4652	0·0054	3·3409	0·0092
C(3)	1·6214	0·0051	−0·3667	0·0052	2·5378	2·0090
C(4)	1·8232	0·0053	0·9713	0·0054	3·2459	0·0094

Table 3. *Thermal parameters*

From the expression $T=\exp\left[-(b_{11}h^2+b_{22}k^2+b_{33}l^2+b_{23}kl+b_{31}hl+b_{12}hk)\right]$.

	b_{11}	b_{22}	b_{33}	b_{23}	b_{31}	b_{12}
Na^+	0·01916	0·00602	0·01098	0·00138	0·01236	0·00735
O(1)	0·01815	0·00246	0·01276	0·00562	0·01290	0·00074
O(2)	0·02212	0·00289	0·00714	−0·00367	0·00199	0·00743
O(3)	0·02310	0·00260	0·01595	0·00811	0·02096	0·00545
O(4)	0·02288	0·00331	0·01515	−0·00351	0·01540	0·00568
C(1)	0·01663	0·00200	0·02318	0·00341	0·00241	0·00471
C(2)	0·01533	0·00259	0·01615	−0·00391	0·00667	0·00153
C(3)	0·01086	0·00500	0·01394	−0·00401	0·00407	0·00785
C(4)	0·01057	0·00364	0·02053	0·00031	0·00282	0·00086

$R(h0l)=0{\cdot}175$, $R(hk0)=0{\cdot}182$. At this stage, a least-squares refinement using three-dimensional data and individual anisotropic temperature factors for each atom and unit weights for the reflexions was undertaken. This gave $R=0{\cdot}108$. Correction for extinction following the method of Srinivasan (1959) finally gave $R=0{\cdot}105$. The list of calculated and observed structure factors is given in Table 1. The atomic scattering factors given in *International Tables for X-ray Crystallography* (1962) were used throughout. Reflexions not observed are excluded from the list. The contributions of the hydrogen atoms are not included as they were not accurately located even in a difference synthesis (sodium, carbon and oxygen atom contributions subtracted).

The final positional coordinates for the atoms and their standard deviations obtained from the last cycle of least-squares refinement are given in Table 2 and the vibrational parameters in Table 3.

Intermolecular and intramolecular distances and bond angles

Table 4 gives the bond lengths and their e.s.d's (the atom numbering scheme is shown in Fig. 1) and Table 5 gives the bond angles in the molecule. These are similar to those found for the fumarate group in a number of salts of fumaric acid: rubidium hydrogen fumarate (Gupta & Roy, 1969), potassium hydrogen fumarate (Gupta & Roy, 1967), acid potassium hydrogen fumarate (Gupta & Sahu, 1969). Table 6 gives the intermolecular contacts up to 4·0 Å between neighbouring molecules, where the primed atoms indicate those derived from the unprimed atoms by the operation of a centre of symmetry, and a symbol such as *a*O(1), *etc.* indicates the oxygen atom O(1) in the neighbouring molecule, obtained by a unit **a** translation of O(1), and so on. Table 7 gives Na^+–O distances in the crystal up to 2·7 Å.

Table 4. *Bond lengths*

	Bond length l	Deviation Δl
C(1)–C(2)	1·488 Å	0·008 Å
C(1)–O(1)	1·287	0·009
C(1)–O(2)	1·274	0·010
C(2)–C(3)	1·327	0·009
C(3)–C(4)	1·489	0·009
C(4)–O(3)	1·332	0·008
C(4)–O(4)	1·227	0·011

Table 5. *Bond angles*

	Angle	Deviation
O(1)–C(1)–O(2)	123·53°	0·53°
O(1)–C(1)–C(2)	115·60	0·57
O(2)–C(1)–C(2)	121·23	0·77
C(1)–C(2)–C(3)	121·80	0·62
C(2)–C(3)–C(4)	118·57	0·70
C(3)–C(4)–O(3)	114·18	0·62
C(3)–C(4)–O(4)	125·50	0·60
O(3)–C(4)–O(4)	119·98	0·57

Table 6. *Intermolecular contacts less than* 4 Å

	Intermolecular distance	
Oxygen–oxygen		
O(1)——$_{-b}$O(3)	2·51 Å	... Hydrogen bond
O(1)——$_{-a,\,-2b}$O(2′)	3·42	
O(1)——$_{-b}$O(3′)	3·19	
O(1)——$_{-b}$O(4)	3·17	
O(1)——$_{c}$O(2)	3·78	
O(1)——$_{-2b,\,c}$O(1′)	3·30	
O(2)——$_{-b}$O(3)	3·10	
O(2)——$_{-2b}$O(1′)	3·63	
O(2)–$_{-a,\,-2b,\,-c}$O(2′)	3·16	

Table 6 (*cont.*)

	Intermolecular distance
O(3)————${}_{-c}$O(4)	3·42
O(3)————${}_{-b}$O(2′)	3·51
O(3)—${}_{-a,\ -b,\ -c}$O(2′)	3·92
O(4)————${}_{-b,\ c}$O(1′)	3·59
O(4)———${}_{-a,\ -b}$O(2′)	3·61
Carbon–carbon	
C(1)————${}_{-b}$C(4′)	3·71
C(1)———${}_{-a,\ -2b}$C(1′)	3·63
C(2)————${}_{-b}$C(3′)	3·73
C(3)————${}_{-b}$C(4′)	3·51
C(3)————${}_{-b}$C(3′)	3·22
Carbon–oxygen	
C(1)————${}_{-b}$O(3′)	3·12
C(2)————${}_{c}$O(2)	3·93
C(2)————${}_{-b}$O(3′)	3·40
C(3)————${}_{-b}$O(3′)	3·69
C(3)————${}_{-b}$O(4′)	3·12
C(3)————${}_{-c}$O(4)	3·76
C(4)————${}_{-b}$O(2′)	3·85

Table 7. Na^+–O *distances less than* 2·7 Å

		Distance
Na^+———	${}_{b,\ -c}$O(1)	2·38 Å
	${}_{b}$O(2)	2·40
	O(3)	2·38
	${}_{-c}$O(4)	2·38
	${}_{-b}$O(1′)	2·64
	${}_{-a,\ -b,\ -c}$O(2′)	2·44
Average value		2·44

Discussion of the structure

Fig. 1 shows the structure projected down the [100] axis and Fig. 2 shows a three-dimensional view of the contents of a unit cell viewed from the direction of the [100] axis. In the crystal, the molecules are linked together by short hydrogen bonds of 2·51 Å to form extensive chains parallel to the [010] axis. These chains run roughly at $\frac{1}{4}a$ and $\frac{3}{4}a$ in the unit cell. There are weak intermolecular contacts between the atoms of different chains at van der Waals distances ranging from 3·13 to 3·93 Å.

An interesting feature of the hydrogen bonds is that they are between two oxygen atoms of the COOH groups, both of which are of the type (OH) where, presumably, one of the hydrogen atoms has been replaced by a sodium ion, leaving behind a negatively charged oxygen ion which becomes the acceptor and the oxygen atom of the nearest OH group serves as the donor for the formation of the hydrogen-bond.

In this laboratory such hydrogen bonds have been observed and reported earlier in compounds such as $2KC_4H_3O_4+C_4H_4O_4$ (Gupta & Sahu, 1970), $KC_4H_3O_4$ (Gupta & Roy, 1967), and $RbC_4H_3O_4$ (Gupta & Roy, 1969). A similar situation was reported by Speakman (1949) and Bacon & Curry (1957) in the crystal structure of potassium hydrogen bisphenylacetate, $(C_4H_5CH_2OO)_2HK$.

The angle $\mathrm{C}\overset{\mathrm{O---H---O}}{\diagup}$ from this work is 113·4°, *i.e.* near to the expected tetrahedral value.

Na^+–O *contacts*

Each Na^+ ion in the crystal is surrounded by six oxygen atoms of six different molecules at Na^+–O distances ranging from 2·38 to 2·64 Å with an average of 2·44 Å. The metal ion is sandwiched between the layers of the fumarate group. The oxygen atoms surrounding the sodium ion form a distorted octahedron.

Non-planarity of the molecule

Another interesting feature of the structure is that fumarate groups in this structure are definitely not planar. The equations to the best plane containing atoms O(1), C(1) and O(2) and the rest of the atoms [C(2), C(3), C(4), O(3) and O(4)] in the molecule are given below.

$x+0{\cdot}200\,y-0{\cdot}704\,z+0{\cdot}230=0$ [atoms O(1), C(1) and O(2)],

$x-0{\cdot}050\,y+0{\cdot}317\,z-1{\cdot}302=0$ (rest of the atoms).

The deviations of the atoms from these planes together with their standard deviations are given in Table 8.

Table 8. *Deviations of atoms from the best planes with e.s.d.'s*

	Deviation	E.s.d.
O(3)	0·017 Å	0·003 Å
O(4)	−0·017	0·003
C(2)	0·032	0·005
C(3)	−0·044	0·004
C(4)	0·018	0·005

The orientation of the molecule with respect to an orthogonal set of axes is given in Table 9 where *l*, *m* and *n* represent the direction cosines of the normal to the given plane. The orthogonal axes are so chosen that **b**′ coincides with **b**, **a**′ is orthogonal to the **b** axis in the *ab* plane and **c**′ is perpendicular to **a** and **b**.

The lack of planarity in the fumarate molecule is definitely confirmed in this structure. The structure determination of the fumaric acid molecule by Brown (1966) and of *β*-fumaric acid by Bednowitz & Post (1966) has shown an absence of conjugation in the C–CH=CH–C bond system and the central C=C bond to be a real double bond. This, therefore, leaves scope for the COOH group to twist around the single C–C bond, presumably for packing of the molecule in the unit cell and for the balancing of opposite charges locally.

The difference Fourier synthesis

With a view to locating the hydrogen atoms a three-dimensional difference Fourier synthesis was calculated

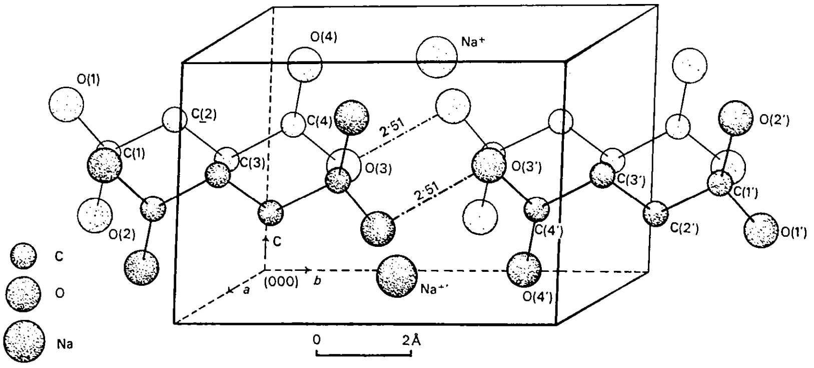

Fig. 2. A three-dimensional view of structure.

Table 9. *Direction cosines of the normals to the planes*

		l	m	n
(i)	Normal to the plane of O(1), C(1) and O(2)	0·8333	0·1667	−0·0587
(ii)	Normal to the plane of O(3), C(4) and O(4)	0·9434	−0·0250	0·3255
(iii)	Normal to the plane of C(2), C(3), C(4), O(3) and O(4)	0·9524	−0·0479	0·3019

Table 10. *Observed and calculated hydrogen positional parameters*

	From difference Fourier			Calculated		
	x/a	y/b	z/c	x/a	y/b	z/c
H(1)	0·300	0·417	0·625	0·310	0·415	0·580
H(2)	0·300	−0·167	0·813	0·300	−0·175	0·800
H(3)	0·200	−0·042	0·250	0·200	−0·035	0·250

using all the observed reflexions, the contributions of only the oxygen, carbon and sodium atoms having been subtracted from the observed structure factors. The difference map showed maxima at the expected hydrogen atom positions and it also contained some spurious peaks. The positional parameters for hydrogen atoms as located from the difference synthesis and the expected positions calculated with an assumed value of 1·08 Å for the C–H (or O–H) distance are given in Table 10.

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