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Direct Determination of the Crystal Structure of β-Fumaric Acid

BY A. L. BEDNOWITZ*† AND B. POST
Polytechnic Institute of Brooklyn, Brooklyn, N.Y., U.S.A.

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Fumaric acid, $C_4H_4O_4$, normally crystallizes from solution in the form of monoclinic crystals with six molecules per unit cell (α-fumaric acid). Sublimation yields a triclinic polymorph (β-fumaric acid) with $a=5{\cdot}264\pm0{\cdot}003$, $b=7{\cdot}618\pm0{\cdot}003$, $c=4{\cdot}487\pm0{\cdot}002$ Å; the interaxial angles are $\alpha=106{\cdot}85\pm0{\cdot}05$, $\beta=86{\cdot}33\pm0{\cdot}05$ and $\gamma=134{\cdot}94\pm0{\cdot}08°$. There is one molecule per unit cell and the space group is $P\bar{1}$. The structure has been determined from counter data using the symbolic addition phase-determining procedure. The non-hydrogen atoms in the molecule are coplanar within experimental error. The molecules are linked by hydrogen bonds to form chains in the **b** direction. The O–H···O bond lengths are $2{\cdot}673\pm0{\cdot}004$ Å. The central C=C bond is $1{\cdot}315\pm0{\cdot}007$ Å, the carbon to oxygen bonds in the carboxyl group are $1{\cdot}228\pm0{\cdot}004$ and $1{\cdot}289\pm0{\cdot}005$ Å, and the single C–C bond length is $1{\cdot}490\pm0{\cdot}005$ Å.

Introduction

The dicarboxylic acid HOOCCH=CHCOOH occurs in two isomeric forms. The *trans* isomer, fumaric acid (I), normally crystallizes from solution in the form of twinned monoclinic crystals with six molecules per unit cell.‡ A triclinic form, β-fumaric acid, with one molecule per unit cell, can be obtained by sublimation (Roldan, 1965). The *cis* isomer, maleic acid (II), has been studied by Shahat (1952).

The investigation of the crystal structure of β-fumaric acid was undertaken to make possible a comparison of the structures of the *cis* and *trans* isomers as well as the two polymorphic forms of fumaric acid. It also furnished us an opportunity to utilize direct methods to determine the structure.

Experimental

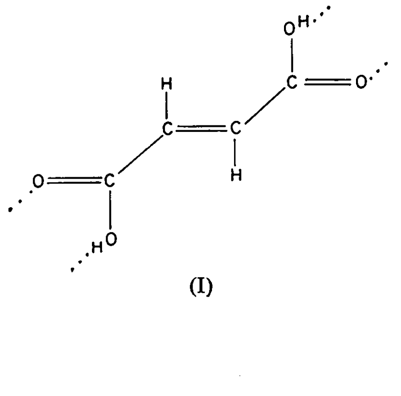
A crystal of β-fumaric acid was prepared by sublimation at 130°C under reduced pressure. A small needle-shaped crystal (0·1 × 0·4 × 0·08 mm) was chosen for study; its unit-cell dimensions were determined with a single-crystal diffractometer using filtered Cu $K\alpha$ radiation. In Table 1, crystal data for β-fumaric acid are compared with corresponding data for the α form (Reis & Schneider, 1928), and for the *cis* isomer, maleic acid (Shahat, 1952).

Table 1. *Crystal data*

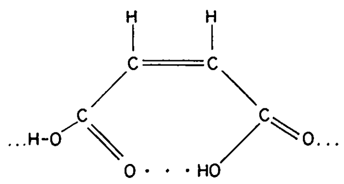
	β-Fumaric* Triclinic	α-Fumaric† Monoclinic	Maleic‡ Monoclinic
Space group	$P\bar{1}$	$P2_1/c$	$P2_1/c$
a	5·264 ± 0·003 Å	7·60 Å	7·47 Å
b	7·618 ± 0·003	15·11	10·15
c	4·487 ± 0·002	6·61	7·65
α	106·85 ± 0·05°	—	—
β	86·33 ± 0·05	111°5′	123·5°
γ	134·94 ± 0·08	—	—
Z	1	6	4
ϱ_x	1·619 g.cm^{-3}	1·631 g.cm^{-3}	1·599 g.cm^{-3}
Mol. Vol.	118·9 Å^3	117·8 Å^3	120·9 Å^3

* This determination.
† Reis & Schneider (1928).
‡ Shahat (1952).

The unit-cell dimensions of β-fumaric acid as first reported by Roldan (1965) are: $a=4{\cdot}52\pm0{\cdot}02$, $b=7{\cdot}51\pm0{\cdot}02$, $c=5{\cdot}40\pm0{\cdot}04$ Å, $\alpha=136{\cdot}7\pm0{\cdot}3$, $\beta=110{\cdot}6\pm0{\cdot}3$, $\gamma=72{\cdot}8\pm0{\cdot}3°$, with the needle axis parallel to **b**. The



(I)



(II)

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† Present address: Chemistry Department, Brookhaven National Laboratory, Upton, L.I., New York 11973.

‡ The crystal structure of the *trans* isomer, α-fumaric acid, is being investigated by C. J. Brown of University College, London (Brown, 1965, 1966).

transformation matrix from Roldan's reciprocal axes to those which we used is:

$$\begin{pmatrix} 0 & -1 & -1 \\ 0 & 1 & 0 \\ -1 & 0 & 0 \end{pmatrix}$$

The space group was assumed to be $P\bar{1}$ on the basis of the following considerations: the *trans* isomer of $C_4H_4O_4$ is centrosymmetric; the crystal has one molecule per unit cell, and no piezoelectric effect was detected.

Integrated intensity data were collected with a single-crystal diffractometer. Full data were obtained with Cu $K\alpha$ radiation to an angle of 140° (2θ). Of 480 independent reflections in the experimental range, 410 had measurable intensities.

After correction of the intensity data for Lorentz & polarization effects, a statistical analysis (Wilson, 1942) was carried out to determine a mean temperature factor and an absolute scale factor.

EFACT, a program written in Fortran IV, was used to obtain the normalized structure factors, $|E|$. Hauptman & Karle (1953) found that $<|E|>$ is 0·798 for a centrosymmetric crystal and 0·886 for a noncentrosymmetric crystal. The value we obtained for fumaric acid was 0·82, which lent added support to our assumption that the crystal is centrosymmetric.

Phase determination

The symbolic addition phase-determining procedure (Karle & Karle, 1963) has recently been used in the direct determination of several crystal structures (Karle & Karle, 1964*a*, *b*, 1965; Karle, Britts & Brenner, 1964; Karle, Britts & Gum, 1964; Karle, Karle, Owen & Hoard, 1965; Norment, 1965). In all these cases manual methods were used extensively. The symbolic addition procedure facilitates the use of the Σ_2 relation (1) (Hauptman & Karle, 1953) by introducing symbolic representations for the phases of several key reflections.

$$\Sigma_2\colon\ s(E_{\mathbf{H}}) \simeq s \sum_{\mathbf{K}} E_{\mathbf{K}} E_{\mathbf{H}-\mathbf{K}}\,. \qquad (1)$$

The Σ_2 relation is similar to the relation proposed by Sayre (1952). A similar relation was also used by Zachariasen (1952) in a direct method which incorporated a symbolic procedure, but with an initial set of signs determined from inequalities. The use of the Σ_2 relation is preferable to these alternate procedures. The relation is expressed in terms of normalized structure factors which are independent of unit-cell size and of scattering angle.

In order to minimize the tedious and repetitive aspects of the manual methods, the phase determination was partially automated in the present work. A Fortran IV program, SORTE, was written with simple decision making ability. The computer makes its final phase decisions on the basis of a probability formula derived from equation (3·36) of Hauptman & Karle (1953) and equation (4·12) of Cochran & Woolfson (1955):

$$P_+(E_{\mathbf{H}}) = \tfrac{1}{2} + \tfrac{1}{2}\tanh\left(\frac{\sigma_3}{\sigma_2^{3/2}}\,|E_{\mathbf{H}}| \sum_{\mathbf{K}} E_{\mathbf{K}} E_{\mathbf{H}-\mathbf{K}}\right), \qquad (2)$$

where $\sigma_n = \Sigma_i Z_i^n$, and $P_+(E_{\mathbf{H}})$ is the probability that the sign of $E_{\mathbf{H}}$ is positive. The initial stages of the computation require close examination by the investigator when accepting new signs, but as the number of determined signs increases, the automatic symbolic summation can be relied on to determine additional signs correctly.

The first step in the phase determining process involved the listing of all the Σ_2 interactions among the input reflections. (In order to save time in computing and tabulating, the input was initially limited to $|E| > 1{\cdot}8$). Three reflections with large $|E|$ were chosen, satisfying the requirements of linear independence modulo 2 (Hauptman & Karle, 1953), and having a comparatively large number of Σ_2 interactions. The three reflections were arbitrarily assigned positive phases, thereby fixing the origin. In addition, the symbol *a* was assigned to the sign of $2\bar{6}0$. Several phases were developed manually before beginning the computer calculations. For this purpose only very large triple products were accepted when using the relation

$$s(E_{\mathbf{H}}) \sim s(E_{\mathbf{K}})s(E_{\mathbf{H}-\mathbf{K}})\,. \qquad (3)$$

Phases determined manually by this relation were of course checked later with the Σ_2 relation.

After the second cycle of computation it became evident that an additional symbolic assignment would

Table 2. *Phase assignments for the symbolic addition method*

			Trial phases			
hkl	$\lvert E\rvert$	Assigned symbol	Set 1	Set 2	Set 3*	Set 4
$2\bar{6}0$	3·12	*a*	+	−	−	+
$4\bar{9}1$	3·49	*b*	+	+	−	−
Number of phases determined			339	319	285	289
Number of phases undetermined			0	20	54	50

* The 'correct' set.

$3\bar{6}0$, $2\bar{6}1$ and 212 ($|E| = 3{\cdot}13$, 2·94 and 2·64 respectively) were arbitrarily assigned positive phases to specify the origin.

be necessary; the symbol b was assigned to the sign of $4\bar{9}1$. The initial phase assignments are listed in Table 2. The third cycle indicated that the procedure was operating smoothly, and limitations on the magnitudes of the primary reflections were then relaxed. With each pass through the computer, the amount of input data was increased until values of $|E|$ as low as 0·4 were included.

Since this was our first attempt at using the symbolic addition method, we followed the results rather closely and used many more computer passes than were actually necessary. (Newer versions of the SORTE program have since been written which provide for internal recyling.) We found that an IBM 7040 requires about five minutes per cycle for about 200 reflections in $P\bar{1}$. In this structure determination 339 reflections were analyzed for phase and 285 phases were determined by the symbolic addition method.

In $P\bar{1}$ the choice of positive signs for all symbols will always satisfy the phase relations in (1). This assumption, however, implies that there is a large peak in the electron density at the origin of the unit cell. We may rule this out on physical grounds since there is an even number of atoms in the centrosymmetric unit cell of β fumaric acid.

The correct assignment, $a=-$, $b=-$, was determined readily from an examination of the three ($hk0$) E-factor electron density projections based on the sign combinations of sets 2, 3, and 4 (Table 2). These projections were computed with the aid of a von Eller Photosommateur. Of the 285 signs determined in set 3 (the 'correct' set) only two were later shown to be incorrect and these were associated with E factors of very small magnitudes: 0·56 and 0·47.

Structure refinement

A three-dimensional E-factor Fourier summation was then computed with the use of all 285 terms whose signs had been determined. (The significance of an E-factor Fourier summation has been discussed by Karle, Hauptman, Karle & Wing, 1958). A composite map based on the results of this summation is shown in Fig. 1. Initial coordinates of the non-hydrogen atoms were obtained from this map. The position and thermal parameters of the atoms in Figs. 1 and 2 were refined by a full-matrix least-squares program described by Okaya (1963). In this program $w(F^2_{\text{obs}}-F^2_{\text{calc}})$ is minimized. Errors in atomic coordinates are obtained from inversion of the least-squares matrix. Atomic scattering factors computed by Freeman (1959) were used. Zero weight was assigned to unobserved reflections; constant weight was used for reflections of moderate intensity, and a weight inversely proportional to $|F|^2$ for the strong reflections ($10|F|>100$). The value of the residual, R, was 25% at the start of the first least-squares cycle. After two cycles in which isotropic temperature factors were used, a difference electron density map was computed. This showed the locations of the hydrogen atoms clearly (Fig. 2). At this stage R was 10%.

Anisotropic temperature factors were then used for the carbon and oxygen atoms, and isotropic factors for the hydrogen atoms. In the final cycle, positional

Table 3. *Position and thermal parameters*

Position parameters (e.s.d. × 10⁴)

	x	e.s.d.	y	e.s.d.	z	e.s.d.
C(1)	0·4079	8	0·3804	5	0·4003	7
C(2)	0·4541	8	0·2185	5	0·4495	6
O(1)	0·2716	6	−0·0045	4	0·2567	5
O(2)	0·6842	7	0·3255	4	0·7026	6
H(1)	0·6811	16	0·2417	11	0·7360	14
H(2)	0·2290	8	0·2899	6	0·1853	7

Thermal parameters (× 10⁴)

$$\text{Temperature factor} = \exp\left[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{13}hl+\beta_{23}kl)\right]$$

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	680	256	498	699	105	271
e.s.d.	23	10	18	28	32	22
C(2)	638	235	434	645	147	237
e.s.d.	22	10	17	27	30	21
O(1)	915	260	623	825	−196	101
e.s.d.	21	8	15	23	27	17
C(2)	946	303	594	905	−217	163
e.s.d.	22	9	15	25	28	18

H(1)	$B=7{\cdot}0$ Å²	e.s.d. = 1·7
H(2)	$B=0{\cdot}85$ Å²	e.s.d. = 0·58

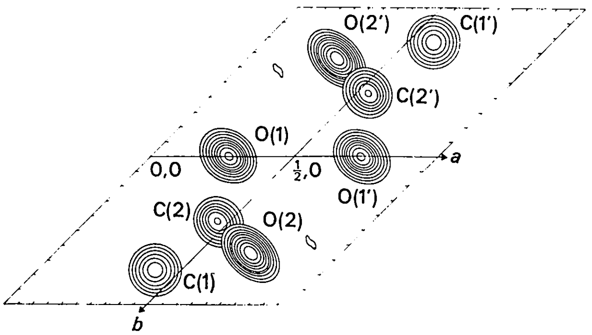

Fig. 1. Composite E-factor map of β-fumaric acid based on directly determined phases.

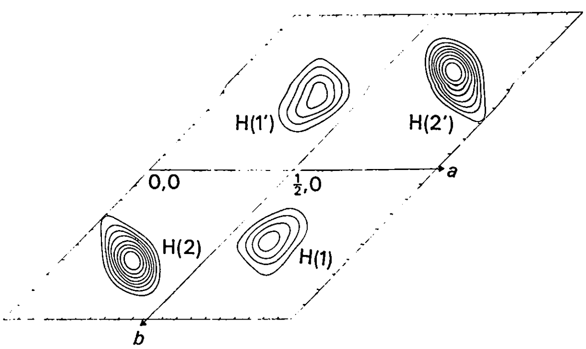

Fig. 2. Composite electron density difference map indicating the location of the hydrogen atoms. Contours at uniform arbitrary intervals.

shifts of the heavy atoms were essentially zero, while the shifts of the hydrogen atoms were less than 0·05 of their estimated standard deviations. The thermal parameters of the non-hydrogen atoms were refined until shifts were negligible compared with the estimated deviations. The final atomic and thermal parameters are listed in Table 3 together with their estimated errors. Observed and calculated structure factors are listed in Table 4. The final residual was 6·2%.

Discussion

Within the limits of experimental error the molecule is planar. The equation of the plane through the non-hydrogen atom positions is:

$$3{\cdot}183x-0{\cdot}004y-2{\cdot}948z=0{\cdot}116\ .$$

All of the non-hydrogen atoms lie within 0·01 Å of this plane.

Table 4. *Observed and calculated structure factors* (× 10)

Asterisks indicate unobserved reflections.

H	K	L	FOBS	FCAL
0	0	1	184	-200
	0	2	91	-94
	0	3	26	25
	0	4	19	18
	0	5	7	-1
	1	-5	4	5
	1	-4	18	-16
	1	-3	54	52
	1	-2	80	-73
	1	-1	3*	-0
	1	0	24	20
	1	1	78	81
	1	2	29	-26
	1	3	64	-66
	2	-5	11	9
	2	-4	27	27
	2	-3	33	-30
	2	-2	64	-62
	2	-1	105	101
	2	0	24	-27
	2	1	23	18
	2	2	37	-41
	2	3	17	25
	2	4	5	-4
	3	-5	10	-13
	3	-4	21	22
	3	-3	42	42
	3	-2	123	-121
	3	-1	9	-7
	3	0	137	133
	3	1	24	-20
	3	2	54	-54
	3	3	19	22
	4	-5	16	-17
	4	-4	22	26
	4	-3	16	-19
	4	-2	17	16
	4	-1	44	-42
	4	0	27	23
	4	1	37	39
	4	2	32	-30
	4	3	11	-8
	5	-4	5*	6
	5	-3	15	-16
	5	-2	4*	6
	5	-1	17	-16
	5	0	42	38
	5	1	27	-25
	5	2	5	6
	6	-4	4*	-3
	6	-3	33	34
	6	-2	54	-54
	6	-1	16	16
	6	0	21	20
	-7	0	5	-5
	-7	1	6	-6
	-7	2	6	5
	-7	3	10	10
	-6	-1	31	31
	-6	0	15	14
	-6	1	96	-94
	-6	2	71	70
	-6	3	3*	1
	-6	4	4*	-5
	-5	-2	25	-26
	-5	-1	46	48
	-5	0	21	-19
	-5	1	3*	-0
	-5	2	36	-34
	-5	3	27	27
	-5	4	29	27
	-5	5	37	-37
	-4	-3	22	-23
	-4	-2	37	41
	-4	-1	26	23
	-4	0	62	-65
	-4	1	24	24
	-4	2	26	-24
	-4	3	48	45
	-4	4	35	-33
	-4	5	17	17
	-3	-4	13	14
	-3	-3	41	-41
	-3	-2	12	-8
	-3	-1	144	146
	-3	0	38	-33
	-3	1	230	-222
	-3	2	111	105
	-3	3	54	51
	-3	4	37	-34
	-3	5	4*	4
	-2	-4	16	17
	-2	-3	32	-31
	-2	-2	20	15
	-2	-1	20	-21
	-2	0	129	131
	-2	1	114	-113
	-2	2	61	-55
	-2	3	70	69
	-2	4	12	13
	-2	5	30	-28
	-1	-4	40	-41
	-1	-3	3*	-2
	-1	-2	51	49
	-1	-1	14	10
	-1	0	5	-1
	-1	1	99	-97
	-1	2	91	84
	-1	3	34	-27
	-1	4	8	9
	-1	5	3*	-1
	0	-5	6	6
	0	-4	7	6
	0	-3	34	-37
	0	-2	95	-86
	0	-1	353	379
	0	0	216	-220
	0	1	107	-111
	0	2	50	50
	0	3	30	32
	0	4	8	-7
	1	-5	7	-8
	1	-4	25	25
	1	-3	41	-36
	1	-2	6	5
	1	-1	21	18
	1	0	64	60
	1	1	42	-39
	1	2	73	-76
	1	3	78	78
	1	4	19	-16
	2	-5	2*	7
	2	-4	8	-9
	2	-3	20	-20
	2	-2	46	44
	2	-1	20	-18
	2	0	22	17
	2	1	34	-39
	2	2	27	27
	2	3	7	-6
	3	-5	6	7
	3	-4	13	13
	3	-3	44	-45
	3	-2	3*	4
	3	-1	68	68
	3	0	22	-20
	3	1	45	-43
	3	2	26	24
	3	3	3*	3
	4	-4	12	-12
	4	-3	10	11
	4	-2	20	-18
	4	-1	14	13
	4	0	27	23
	4	1	28	-26
	5	-3	2	7
	5	-2	13	-12
	5	-1	26	24
	5	0	19	-18
2	-8	0	4*	-4
	-8	1	13	-12
	-8	2	26	26
	-8	3	4*	1
	-7	-1	6	-7
	-7	0	8	-7
	-7	1	11	11
	-7	2	15	14
	-7	3	17	-18
	-7	4	8	10
	-6	-2	29	28
	-6	-1	8	7
	-6	0	107	-115
	-6	1	112	109
	-6	2	9	10
	-6	3	24	-25
	-6	4	15	-14
	-6	5	9	11
	-5	-3	19	-20
	-5	-2	40	43
	-5	-1	22	-21
	-5	0	9	-6
	-5	1	50	-47
	-5	2	64	62
	-5	3	37	37
	-5	4	76	-74
	-5	5	29	30
	-4	-4	10	-11
	-4	-3	27	27
	-4	-2	12	12
	-4	-1	56	-57
	-4	0	28	28
	-4	1	31	-28
	-4	2	62	64
	-4	3	52	-50
	-4	4	23	26
	-4	5	11	-11
	-3	-4	20	-20
	-3	-3	3*	1
	-3	-2	88	85
	-3	-1	47	-41
	-3	0	219	-207
	-3	1	153	153
	-3	2	75	73
	-3	3	70	-64
	-3	4	3*	3
	-3	5	3*	-0
	-2	-4	19	-18
	-2	-3	18	14
	-2	-2	13	-10
	-2	-1	81	81
	-2	0	108	-105
	-2	1	51	-51
	-2	2	104	101
	-2	3	6	11
	-2	4	51	-48
	-2	5	13	13
	-1	-5	19	-20
	-1	-4	8	7
	-1	-3	16	14
	-1	-2	3*	1
	-1	-1	2*	0
	-1	0	65	-65
	-1	1	79	78
	-1	2	38	-31
	-1	3	14	13
	-1	4	3*	-3
	0	-5	5*	0
	0	-4	7	-5
	0	-3	35	-31
	0	-2	143	143
	0	-1	126	-119
	0	0	58	-55
	0	1	50	48
	0	2	31	31
	0	3	15	-13
	0	4	19	-15
	1	-5	11	11
	1	-4	18	-16
	1	-3	9	9
	1	-2	3*	4
	1	-1	25	22
	1	0	24	-23
	1	1	57	-53
	1	2	76	77
	1	3	26	-21
	2	-4	4	-5
	2	-3	16	15
	2	-2	13	-11
	2	-1	16	14
	2	0	31	-26
	2	1	24	22
	2	2	7	-6
	3	-4	12	-13
	3	-3	3*	5
	3	-2	22	23
	3	-1	11	-11
	3	0	24	-22
	3	1	19	18
	4	-3	4*	-6
	4	-2	3*	5
	4	-1	9	10
	4	0	14	-15
3	-9	2	47	-50
	-8	-1	3*	-5
	-8	0	14	-12
	-8	1	35	38
	-8	2	3*	-0
	-8	3	30	-32
	-8	4	4*	0
	-7	-2	4*	-3
	-7	-1	6	-6
	-7	0	11	13
	-7	1	13	15
	-7	2	22	-24
	-7	3	11	13
	-7	4	8	-8
	-6	-3	17	16
	-6	-2	3*	3
	-6	0	121	116
	-6	1	9	7
	-6	2	51	-46
	-6	3	20	-19
	-6	4	27	26
	-6	5	6	5
	-5	-3	28	28
	-5	-2	21	-20
	-5	-1	3*	-2
	-5	0	39	-38
	-5	1	75	75
	-5	2	34	35
	-5	3	111	-109
	-5	4	52	50
	-5	5	4*	4
	-4	-4	10	12
	-4	-3	3*	3
	-4	-2	30	-29
	-4	-1	23	22
	-4	0	27	-23
	-4	1	64	63
	-4	2	56	-58
	-4	3	33	32
	-4	4	18	-17
	-4	5	3*	2
	-3	-4	4*	3
	-3	-3	32	31
	-3	-2	25	-22
	-3	-1	101	-98
	-3	0	111	112
	-3	1	51	53
	-3	2	76	-74
	-3	3	3*	4
	-3	4	3*	4
	-2	-4	11	10
	-2	-3	8	-8
	-2	-2	32	31
	-2	-1	53	-52
	-2	0	22	-20
	-2	1	76	80
	-2	2	5	2
	-2	3	57	-56
	-2	4	18	20
	-1	-4	3*	1
	-1	-3	3*	-0
	-1	-2	7	6
	-1	-1	32	-31
	-1	0	45	43
	-1	1	25	-23
	-1	2	13	12
	-1	3	3*	-4
	0	-4	12	-13
	0	-3	45	48
	0	-2	51	-50
	0	-1	8	-8
	0	0	23	23
	0	1	16	17
	0	2	13	-11
	0	3	18	-14
	1	-4	4	7
	1	-3	3*	-1
	1	-2	5	5
	1	-1	3*	-4
	1	0	29	-28
	1	1	57	52
	1	2	24	-20
	2	-3	6	-6
	2	-2	10	10
	2	-1	16	-15
	2	0	13	14
	2	1	5	-4
4	-9	1	56	-60
	-9	2	10	10
	-9	3	23	25
	-8	-1	10	-8
	-8	0	38	36
	-8	1	6	-5
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	-8	3	6	8
	-8	4	44	45
	-7	-2	3*	-4
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	-7	0	13	13
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	-7	3	11	-11
	-7	4	8	6
	-6	-3	4*	3
	-6	-2	55	-51
	-6	-1	88	82
	-6	0	7	-6
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	-6	2	17	-17
	-6	3	35	36
	-6	4	4*	4
	-5	-3	16	-15
	-5	-2	3*	5
	-5	-1	22	-20
	-5	0	50	48
	-5	1	20	22
	-5	2	102	-107
	-5	3	64	62
	-5	4	4*	6
	-4	-3	9	-10
	-4	-2	13	13
	-4	-1	18	-18
	-4	0	45	44
	-4	1	46	-45
	-4	2	28	29
	-4	3	18	-19
	-4	4	3*	5
	-3	-4	6	8
	-3	-3	9	-7
	-3	-2	31	-31
	-3	-1	46	50
	-3	0	19	18
	-3	1	50	-48
	-3	2	3*	6
	-3	3	6	4
	-2	-4	4*	-5
	-2	-3	12	11
	-2	-2	20	-17
	-2	0	31	36
	-2	1	3*	-1
	-2	2	42	-41
	-2	3	22	22
	-1	-4	3*	0
	-1	-3	4*	5
	-1	-2	12	-14
	-1	-1	21	20
	-1	0	15	-13
	-1	1	9	9
	-1	2	4*	-4
	0	-3	17	-20
	0	-2	5	5
	0	-1	5	6
	0	0	6	6
	0	1	5	-4
	1	-2	4*	1
	1	-1	5*	-12
5	-9	0	54	-51
	-9	1	15	14
	-9	2	28	27
	-8	-1	26	23
	-8	0	10	-8
	-8	2	13	14
	-8	3	51	50
	-7	-2	4*	4
	-7	-1	13	9
	-7	0	15	-17
	-7	1	9	11
	-7	2	9	-10
	-7	3	4*	9
	-6	-2	45	43
	-6	-1	16	-14
	-6	0	19	-19
	-6	1	11	-9
	-6	2	31	30
	-6	3	4*	2
	-5	-3	3	6
	-5	-2	10	-9
	-5	-1	20	19
	-5	0	19	11
	-5	1	68	-69
	-5	2	56	55
	-5	3	4*	2
	-4	-3	7	6
	-4	-2	12	-11
	-4	-1	23	25
	-4	0	31	-28
	-4	1	20	21
	-4	2	16	-14
	-4	3	4	6
	-3	-3	8	-8
	-3	-2	14	18
	-3	-1	3*	3
	-3	0	17	-20
	-3	1	3*	7
	-3	2	3*	0
	-2	-2	3*	1
	-2	-1	10	11
	-2	0	4*	-1
	-2	1	21	-20
	-1	-1	4	-6
	-1	0	4*	5
6	-8	0	20	-17
	-8	1	10	11
	-8	2	38	38
	-7	-1	11	-9
	-7	0	7	7
	-7	1	7	-6
	-7	2	7	8
	-6	-1	3*	-2
	-6	0	6	-4
	-6	1	15	16
	-6	2	3*	1
	-5	-1	8	6
	-5	0	34	-32
	-5	1	32	35
	-4	-1	12	-14
	-4	0	13	13
	-4	1	9	-8

Although Fig. 3 is essentially a projection of the unit-cell contents onto the *bc* plane, it does show clearly the arrangement of the molecules in space. Intermolecular contacts between non-bonded atoms are normal; the shortest intermolecular contact between non-bonded oxygen atoms is 3·13 Å (between oxygen atoms in adjacent layers).

Bond lengths in fumaric and maleic acids are shown in Table 5. The very small differences between the 'single' and 'double' carbon–carbon bonds in maleic acid as compared with corresponding ones in fumaric acid should be noted. Maleic acid is essentially planar and a very short intramolecular O–H···O bond (2·46 Å) results in what resembles a distorted six-membered ring system. The essential equivalence of single and double carbon–carbon bond lengths may reflect aromatic character resulting from this ring-like structure.* In both forms of fumaric acid the 'single' and 'double' carbon–carbon bond lengths are normal.

Table 5. *Bond lengths in fumaric and maleic acids*

	β-Fumaric*	α-Fumaric†	Maleic‡
C–C	1·490 ± 0·005 Å	1·46 Å	1·44, 1·465 Å
C=C	1·315 ± 0·007	1·34	1·43
C–OH	1·289 ± 0·005	1·29	1·275, 1·275
C=O	1·228 ± 0·004	1·23	1·20, 1·21
O···HO	2·673 ± 0·004	2·68	2·46, 2·75

* This determination.
† Brown (1965).
‡ Shahat (1952).

In β-fumaric acid intermolecular hydrogen bonds lead to the formation of chains of dimers approximately parallel to (010). In maleic acid there are both intermolecular and intramolecular hydrogen bonds; the latter are very short (2·46 Å); the former are relatively long (2·75 Å). The lengths of the hydrogen bonds in fumaric acid (2·67 Å) fall between these extremes.

The atomic temperature factors and the estimated standard deviations of the coordinates of the hydrogen atoms involved in hydrogen bonds in fumaric acid are substantially greater than those of the methylene hydrogen atoms. This is clearly shown in Fig. 2.

The O–H–O bond length (2·673 ± 0·004 Å) and the C–O–O angle (111·2 ± 0·4°) are normal for carboxylic

Table 6. *Dimensions and orientations of atomic thermal ellipsoids*

R.M.S. components of thermal displacements along principal axes (Å).

	Principal axes		
	R_1	R_2	R_3
C(1)	0·13	0·20	0·23
C(2)	0·13	0·19	0·21
O(1)	0·13	0·21	0·29
O(2)	0·12	0·20	0·29

Angles (°) between the principal axes and the axes of a Cartesian system defined by: $X_1 = C(1) \rightarrow C(2)$; $X_2 = (X_1) \times [O(1) \rightarrow O(2)]$; and $X_3 = (X_1) \times (X_2)$.

	X_i	R_1	R_2	R_3
C(1)	1	176	93	87
	2	93	84	173
	3	93	6	84
C(2)	1	173	96	86
	2	93	100	170
	3	97	12	100
O(1)	1	165	105	90
	2	91	87	176
	3	105	15	86
O(2)	1	177	88	87
	2	93	88	177
	3	88	3	89

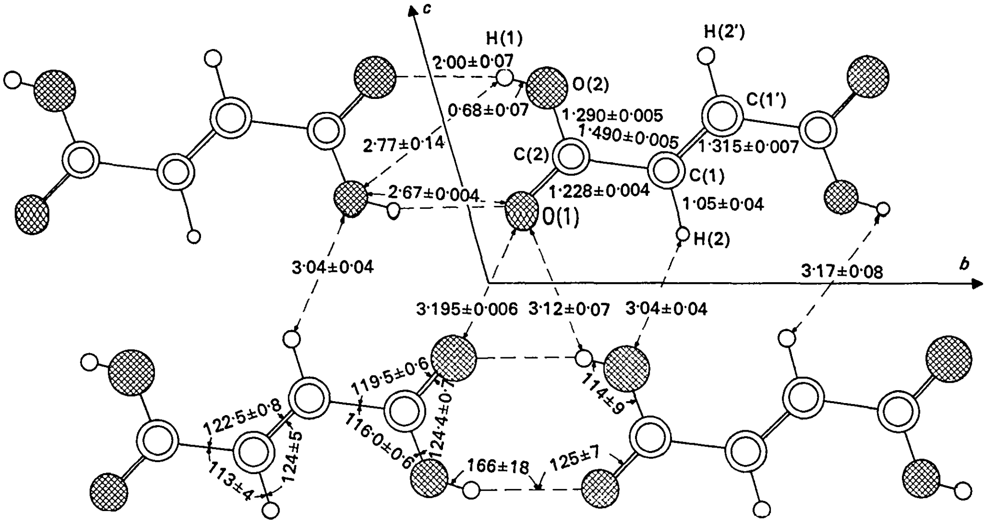

Fig. 3. Inclinographic projection of the crystal structure.

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* The referee has correctly noted that there is no indication of aromatic character in the C=O and C–OH bond lengths in the six-membered systems. A redetermination of the crystal structure of maleic acid appears to be called for to check on these bond lengths and the very short O–H···O bond.

hydrogen bonds. The molecular chains in β-fumaric acid which are due to hydrogen bond formation are similar to those formed in a number of dicarboxylic acids (Pimentel & McClellan, 1960).

The atomic thermal motions are given in Table 6. These are best described in terms of orthogonal axes, X_1 and X_3, lying in the plane of the molecule and X_2, perpendicular to the molecular plane. In all cases, the amplitudes of motion of the non-hydrogen atoms are smallest in the molecular plane in directions within a few degrees of the $C(1) \rightarrow C(2)$ vector. These are therefore almost parallel to the direction along which chains of hydrogen bonded molecules are oriented. The largest thermal motions are in all cases perpendicular to the molecular plane.

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Die Kristallstruktur von Tetrastickstofftetraselenid N_4Se_4

VON HARTMUT BÄRNIGHAUSEN UND TASSILO VON VOLKMANN
Chemisches Laboratorium der Universität Freiburg, 78 *Freiburg* (*Breisgau*), *Albertstrasse* 21, *Deutschland*

UND JOCHEN JANDER
Anorganisch-Chemisches Laboratorium der Technischen Hochschule München, 8 *München* 2, *Arcisstrasse* 21, *Deutschland*

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The crystal structure of N_4Se_4 (space group $C2/c$; $a=9{\cdot}65$, $b=9{\cdot}73$, $c=6{\cdot}47$ Å, $\beta=104{,}9°$) was solved by means of a three-dimensional Patterson synthesis using integrated equi-inclination Weissenberg photographs taken with Cu $K\alpha$ radiation. Least-squares refinement of the positional and individual isotropic thermal parameters led to a final reliability index of 10·2% for the 546 observed reflexions. Although N_4Se_4 and the well-known sulphur analogue N_4S_4 are not isostructural, both compounds have the same cage-like molecular structure with the approximate symmetry $\bar{4}2m$. The spatial arrangement of the N_4Se_4 molecules may be roughly considered as a body-centred cubic lattice of spheres, whereas for N_4S_4 a cubic close-packing was found.

Einleitung

Das vor über hundert Jahren von Wöhler & Espenschied (1859) entdeckte, zu heftigen Explosionen neigende Stickstoffselenid der Bruttoformel NSe ist die einzige bisher bekannte Verbindung zwischen Selen und Stickstoff. Obwohl eine strukturelle Analogie zum intensiv untersuchten Tetrastickstofftetrasulfid N_4S_4 nahelag, konnten weder aus dem chemischen Verhalten noch aus dem IR-Spektrum beweiskräftige Schlüsse zugunsten der tetrameren Formel N_4Se_4 gezogen werden (Jander & Doetsch, 1960). Auch eine kryoskopische Molekulargewichtsbestimmung war nicht möglich, da sich trotz weitgespannter Suche kein einziges Lösungsmittel für Stickstoffselenid finden liess. Ebensowenig konnten strukturelle Hinweise aus dem von Jander & Doetsch (1962) näher untersuchten Reaktionsverlauf der bewährten, auf der Ammonolyse von