stable at high pressure (Dachille & Roy, 1960). Because of its relatively easy preparation, it has been used as a model compound for studying the olivine–spinel transition which probably occurs in Fe–Mg silicates in the upper mantle of the earth at depths of ~400 km (Ringwood, 1975). However, there has been some unresolved controversy about the cation distribution in Mg_2GeO_4: Dachille & Roy (1960) show evidence for an inverse distribution, while Tarte (1963), Reinen (1968), and Durif-Verambon, Bertaut & Pauthenet (1956) propose a normal distribution analogous to that in other germanate spinels (Navrotsky, 1973). The cation distribution in silicate and germanate spinels is of interest to geophysics because the configurational entropy arising from a somewhat disordered distribution could have a significant effect on the pressure–temperature slopes of phase transitions in the mantle (Jackson, Liebermann & Ringwood, 1974; Navrotsky & Kasper, 1976) and on the thermodynamics of solid-solution formation in multicomponent silicate and germanate systems (Navrotsky, 1973).

Because of this interest, we have refined the structure of Mg_2GeO_4 using powder neutron diffraction to obtain accurate values of lattice parameters, oxygen position and metal site occupancy.

From the results of this refinement, it is evident that Mg_2GeO_4 spinel is completely normal with an occupancy of germanium ($0{\cdot}00 \pm 0{\cdot}01$) on the octahedral sites. The value of the oxygen positional parameter, $x = 0{\cdot}3758 \pm 0{\cdot}0005$, indicates that the oxygen anion array is nearly perfectly closest-packed with little or no distortion, and is similar to that found, $x = 0{\cdot}375$, for the other normal germanate spinels, Fe_2GeO_4, Co_2GeO_4, and Ni_2GeO_4 (Blasse, 1964).

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Urocanic Acid Dihydrate (4-Imidazoleacrylic Acid Dihydrate)

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Abstract. $C_6H_6N_2O_2.2H_2O$, orthorhombic, $P2_12_12_1$, $a = 9{\cdot}624$ (1), $b = 12{\cdot}881$ (1), $c = 6{\cdot}714$ (1) Å, $Z = 4$, $D_c = 1{\cdot}389$, $D_m = 1{\cdot}391$ (2) g cm^{-3} (at 22 ± 2 °C), FW 174·16, $F(000) = 368$. Intensity data were collected on an automated diffractometer and the structure was solved by direct methods. Full-matrix least-squares refinement yielded an R of 0·038 for 825 observed data. The nearly planar molecules are in the zwitterion form and are organized into stacks in the crystal (the imidazolium ring of one molecule being placed over the carboxylate group of the next). These stacks are held together *via* hydrogen bonding, principally through water molecules, involving all available H atoms.

Introduction. Urocanic acid is a naturally occurring metabolite derived from histidine, and is a major absorber of ultraviolet radiation in epidermal tissues where it undergoes several interesting photochemical reactions (Anglin & Everett, 1964). The compound is found to isomerize and form photodimers in aqueous solution; however, crystals of the dihydrate do not undergo photochemical reaction (Anglin & Batten, 1970).

Urocanic acid (Sigma Chemical Co.) crystallizes from aqueous solution as colorless orthorhombic prisms, elongated along **c**. The space group and approximate cell dimensions of a crystal measuring 0·15 × 0·3 × 0·5 mm were determined from Weissenberg and precession photographs. More accurate cell dimensions were obtained by least-squares refinement of the setting angles for nine Cu $K\alpha_1$ reflections, measured with an Oak Ridge computer-controlled diffractometer (Busing, Ellison, Levy, King & Roseberry, 1968). The density of the crystals was measured by flotation in mixtures of xylene and carbon tetrachloride. Intensity data were collected on the diffractometer with Ni-filtered Cu $K\alpha$ radiation. The intensities of 851 unique reflections with $2\theta < 130°$ were measured with the θ–2θ step-scan technique. Of these, 825 had $I \geq 3\sigma(I)$ and were used in the subsequent analysis. Each intensity was assigned a variance $\sigma^2(I)$ based on counting statistics plus a term $(0{\cdot}04I)^2$, to allow for instrumental scaling errors.

The structure was solved by direct methods with the aid of *MULTAN* (Germain, Main & Woolfson, 1971). The two most probable sets of phases each showed two possibilities for the placement of the molecule, all four being in the same orientation. The correct position was selected by least-squares refinement. Subsequently, the translational ambiguity was also resolved by a direct search procedure (Rae, 1977). Full-matrix least-squares refinement with anisotropic thermal parameters proceeded smoothly, and H atoms were placed from a difference map. Final refinement with isotropic thermal parameters for H atoms converged to an R value $(=\Sigma||F_o| - |F_c||/\Sigma|F_o|)$ of 0·038. The standard deviation of an observation of unit weight $[\Sigma w(|F_o| - |F_c|)^2/(n-p)]^{1/2}$, where p is the number of adjusted parameters and n the number of observations, was 2·06. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$, where w is the reciprocal of the estimated variances. The largest parameter shift during the last cycle of refinement was less than half the estimated standard deviation and a final difference map, calculated without H atom contributions, showed no spurious peaks larger than half the height of a H atom (0·3–0·6 e Å^{-3}). An isotropic extinction parameter was included in the final stages of refinement, with the average path length taken to be 0·3 mm (Larson, 1967). All calculations, other than structure solution, were performed with the XRAY 72 system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972).

The final atomic parameters, along with their estimated standard deviations, are given in Table 1.*

Table 1. *Positional parameters* ($\times 10^4$, *for* H $\times 10^3$)

In this and subsequent tables standard deviations in units of the last significant digit are given in parentheses

	x	y	z
C(1)	10563 (2)	5594 (2)	3315 (4)
N(2)	11138 (2)	4679 (2)	3521 (3)
C(3)	10110 (2)	3949 (2)	3671 (4)
C(4)	8877 (2)	4449 (2)	3528 (4)
N(5)	9192 (2)	5489 (1)	3304 (3)
C(6)	7481 (2)	4028 (2)	3555 (3)
C(7)	6318 (2)	4561 (2)	3412 (4)
C(8)	4906 (2)	4074 (2)	3459 (3)
O(1)	3901 (2)	4687 (1)	3510 (4)
O(2)	4795 (2)	3111 (1)	3458 (3)
O(3)	7605 (2)	7221 (1)	3079 (4)
O(4)	3449 (2)	6769 (2)	3560 (4)
H(1)	1105 (3)	623 (2)	315 (4)
H(2)	1200 (3)	455 (2)	355 (4)
H(3)	1040 (3)	321 (2)	383 (4)
H(5)	862 (4)	603 (2)	325 (6)
H(6)	741 (3)	332 (2)	369 (4)
H(7)	634 (3)	532 (2)	331 (4)
H(31)	771 (4)	758 (3)	407 (5)
H(32)	689 (5)	753 (4)	256 (6)
H(41)	402 (4)	718 (3)	298 (5)
H(42)	376 (4)	620 (3)	366 (5)

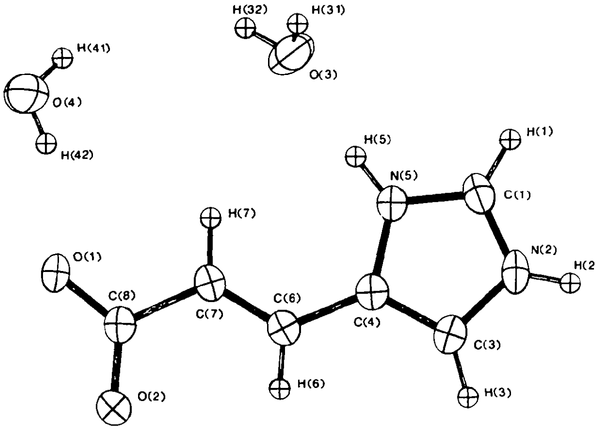

Fig. 1. Projection of the structure onto the (001) plane. The x direction is horizontal and the y direction is vertical.

Discussion. A drawing of the contents of the asymmetric unit, giving the atom-numbering scheme, is shown in Fig. 1. Intramolecular bond distances and angles are given in Table 2. H atoms are found bonded to both N(2) and N(5) and no residual electron density is near O(1) or O(2). Therefore, the imidazole ring is positively charged and the negative charge is distributed over the carboxyl group. This is reflected in the equivalence of bond distances between C(8) and O(1), O(2). The imidazole ring and the carboxyl group are planar, to within ±0·004 Å, with a slight twist in the molecule evident about the C(6)–C(7) double bond.

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* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32544 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

The dihedral angle between the two planes is 7·3°, while the torsion angle C(4)–C(6) → C(7)–C(8) is 177·2°. The distances and angles in the imidazole and carboxyl portions of the molecule are very similar to those found in protonated histidine species (Bennett, Davidson, Harding & Morelle, 1970; Donohue & Caron, 1964), while the distances and angles involving C(6) and C(7) are representative of double-bonded systems conjugated to aromatic rings.

Table 2. *Bond distances* (Å) *and angles* (°)

(*a*) Involving non-hydrogen atoms (e.s.d.'s are 0·003 Å and 0·2°)

C(1)–N(2)	1·310	N(5)–C(1)–N(2)	109·2
N(2)–C(3)	1·368	C(1)–N(2)–C(3)	108·7
C(3)–C(4)	1·354	N(2)–C(3)–C(4)	107·5
C(4)–N(5)	1·382	C(3)–C(4)–N(5)	106·1
N(5)–C(1)	1·326	C(4)–N(5)–C(1)	108·4
C(4)–C(6)	1·450	N(5)–C(4)–C(6)	124·6
C(6)–C(7)	1·316	C(3)–C(4)–C(6)	129·3
C(7)–C(8)	1·497	C(4)–C(6)–C(7)	126·3
C(8)–O(1)	1·249	C(6)–C(7)–C(8)	123·5
C(8)–O(2)	1·246	C(7)–C(8)–O(1)	116·0
		C(7)–C(8)–O(2)	119·7
		O(1)–C(8)–O(2)	124·3

(*b*) Involving hydrogen atoms (e.s.d.'s are 0·05 Å)

C(1)–H(1)	0·95	C(7)–H(7)	0·98
N(2)–H(2)	0·85	O(3)–H(31)	0·81
C(3)–H(3)	0·99	O(3)–H(32)	0·87
N(5)–H(5)	0·89	O(4)–H(41)	0·85
C(6)–H(6)	0·92	O(4)–H(42)	0·80

The hydrogen-bonding parameters are given in Table 3, where it can be seen that all available H atoms participate in hydrogen bonds to O atoms. The *a* axis translation is, in part, defined by the hydrogen bond N(2)–H(2)···O(1) involving urocanic acid molecules in a head-to-tail arrangement. The structure is maintained in the *y* and *z* directions by hydrogen bonding through a sheet of water molecules, O(3) and O(4). The urocanic acid molecules also associate, *via* the 2_1 axis parallel to *z*, in a stacking arrangement in which the positively charged imidazole ring of one molecule is over the negatively charged carboxyl group of another molecule. This arrangement is illustrated in Fig. 2. The distance between the centers of the double bonds C(6)–C(7) is 3·988 Å, whereas the mean molecular planes are separated by $\frac{1}{2}c$ (3·357 Å). This separation of the double bonds is near the limit of distances (3·6–4·1 Å) where photodimerization has been found to take place in crystals of related compounds (Schmidt, 1964),

Table 3. *Distances* (Å) *and angles* (°) *in the hydrogen bonds D*–H–*A*

Donor *D*	Acceptor *A*	In molecule at	Distance *D*–*A*	Distance H–*A*	Angle
N(2)	O(1)	$1+x, y, z$	2·660	1·84	163
N(5)	O(3)	x, y, z	2·708	1·82	174
O(3)	O(2)	$1-x, \frac{1}{2}+y, \frac{1}{2}-z$	2·778	1·91	174
O(3)	O(4)	$\frac{1}{2}+x, 1\frac{1}{2}-y, 1-z$	2·728	1·94	164
O(4)	O(2)	$1-x, \frac{1}{2}+y, \frac{1}{2}-z$	2·771	1·92	176
O(4)	O(1)	x, y, z	2·717	1·95	161

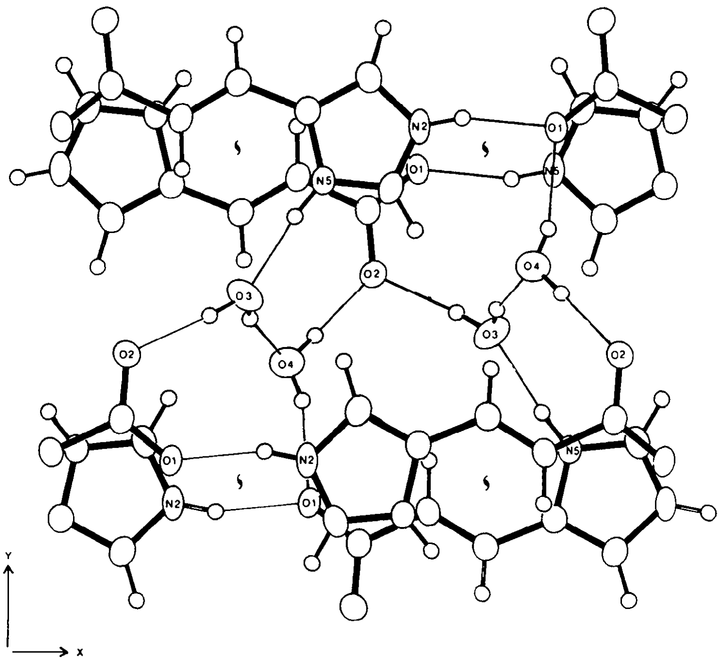

Fig. 2. Illustration of the stacking produced by the 2_1 axis parallel to *z*. Closest approaches are: O(1)–C(1), 3·29 Å; C(8)–C(1), 3·32 Å; and C(7)–N(5), 3·32 Å.

and may explain the stability of crystals of urocanic acid dihydrate when exposed to ultraviolet irradiation.

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9-Isopropylxanthene

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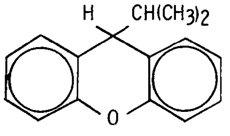
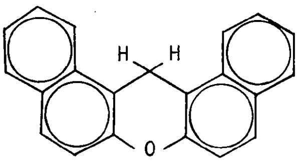
Abstract. $C_{16}H_{16}O$, orthorhombic, $Pca2_1$, $Z = 4$, $M_r = 224 \cdot 30$, $a = 16 \cdot 389$ (2), $b = 5 \cdot 789$ (1), $c = 13 \cdot 005$ (4) Å, $D_x = 1 \cdot 207$, $D_m = 1 \cdot 22$ g cm^{-3} (by flotation); λ(Mo $K\alpha$) = 0·7107 Å, μ(Mo $K\alpha$) = 0·786 cm^{-1}; final R = 0·065. The isopropyl substituent is in the boat–axial conformation.

Introduction. Samples of 9-isopropylxanthene (I) were obtained through the courtesy of Dr Andrew L. Ternay Jr of the Chemistry Department of the University of Texas at Arlington. Single crystals in the form of clear prisms were grown from an ethanol solution. The unit-cell parameters were obtained by measuring the 2θ values of 10 reflections. The space group, $Pca2_1$ or $Pcam$, was deduced from systematic absences ($0kl$ absent with l odd and $h0l$ absent with h odd). The intensity data were collected on a Picker FACS-1 automatic diffractometer at the Lyndon B. Johnson Space Center, NASA, Houston, Texas, with a crystal approximately 0·37 × 0·75 × 0·37 mm. A $\theta/2\theta$ scanning mode, with graphite-monochromated Mo $K\alpha$ radiation, was used to measure 1145 independent reflections with 2θ values below 50°; of these, 699 were considered as observed by the criterion $I > 2 \cdot 0\sigma(I)$, where $\sigma(I)$ was determined from counting statistics. The intensity data were reduced to structure factors by the application of Lorentz and polarization factors; no absorption corrections were applied.



(I)



(II)

The structure was determined by the application of direct methods with the weighted multisolution tangent-refinement technique (Germain, Main & Woolfson, 1971). The correct space group was shown to be $Pca2_1$, as was also shown by the noncentrosymmetric distribution of normalized structure factors. The ratios between $\langle E \rangle$, $\langle E^2 \rangle$, and $\langle E^2 - 1 \rangle$ are 0·872, 1·010, and 0·810 respectively. The E map calculated from 132 reflections with $|E| \geq 1 \cdot 5$ showed the positions of all non-hydrogen atoms. The refinement was carried out by the full-matrix least-squares method with isotropic temperature factors, and by the block-diagonal least-squares method with anisotropic temperature factors. The z coordinate of the O atom was held constant during the refinement. Only four of the H positions were located on a difference Fourier synthesis and the rest were calculated with reasonable bond lengths and bond angles with respect to the atoms to which they are bonded. In the final refinements, the positional parameters of the H atoms were refined, but their