Molecular Packing Modes. Part XI.[1] Crystal Structures of the 2:1 Complexes of Benzamide with Succinic Acid and Furamide with Oxalic Acid

By **Chi-Min Huang, L. Leiserowitz,*** and (the late) **G. M. J. Schmidt,** Department of Chemistry, Weizmann Institute of Science, Rehovot, Israel

The benzamide–succinic acid adduct (I) crystallises in space group $P2_1/c$, with $Z = 2$ in a unit cell of dimensions: $a = 9{\cdot}194$, $b = 5{\cdot}116$, $c = 19{\cdot}480$ Å, $\beta = 105{\cdot}66°$. The structure was refined from three-dimensional film data to R 0·10 (1441 reflections). The furamide–oxalic acid adduct (II) crystallises in space group $P\bar{1}$, with $Z = 1$ in a unit cell of dimensions: $a = 7{\cdot}459$, $b = 6{\cdot}579$, $c = 8{\cdot}064$ Å, $\alpha = 92{\cdot}19$, $\beta = 95{\cdot}60$, $\gamma = 120{\cdot}29°$. The structure was refined from three-dimensional counter data to R 0·05 (1451 reflections).

Both (I) and (II) form 2:1 molecular-complex units in which the amide and carboxy-groups are linked by cyclic hydrogen-bonded (asymmetric) pairs [(I): O–H ··· O 2·60, N–H ··· O 2·98; (II): O–H ··· O 2·53, N–H ··· O 2·92 Å]. The units of (I) are interlinked, along the 5 Å axis, by amide–amide hydrogen bonds (N–H ··· O 3·02 Å). Those of (II) are joined, along the 6·6 Å axis, by bifurcated N–H ··· O bonds [N–H ··· O(hydroxy) 3·10, N–H ··· O(carbonyl) 2·94 Å] between the furamide and oxalic acid fragments.

THE X-ray structure analyses of the 2 : 1 addition compounds of benzamide with succinic acid (I) and of furamide with oxalic acid (II) were undertaken as part of a study on the molecular packing modes of functional groups. Primary amides and carboxylic acids form crystalline complexes with each other, the molecular association being due to the hydrogen bonding between the carboxy- and amide-groups. We have determined the crystal structures of (I) and (II) in order to reveal the geometry of molecular association.

EXPERIMENTAL

Compound (I).—*Crystal data.* $2(C_7H_7NO),(C_4H_6O_4)$, $M = 360{\cdot}4$. Monoclinic, $a = 9{\cdot}194(1)$, $b = 5{\cdot}116(1)$, $c = 19{\cdot}480(2)$ Å, $\beta = 105{\cdot}66(1)°$, $U = 882{\cdot}1$ Å^3, $D_c = 1{\cdot}36$,

---

[1] Part X, J. Bernstein and L. Leiserowitz, *Israel Chem. Soc.*, 1972, **10**, 601.

$Z = 2$, $D_m = 1{\cdot}36$, $F(000) = 380$. Space group $P2_1/c$. Cu-K_α radiation, $\lambda = 1{\cdot}5418$ Å; $\mu(\text{Cu-}K_\alpha) = 8{\cdot}7$ cm^{-1}.

Monoclinic crystals of benzamide–succinic acid (I), m.p. 126—129 °C, were grown from a slowly cooled solution in nitromethane as needle-like plates elongated along [010], showing well-developed {001} and {100} forms. Cell constants were obtained from a least-squares analysis of high order ($\theta > 65°$) reflections measured on a General Electric goniostat with Cu-K_α radiation.

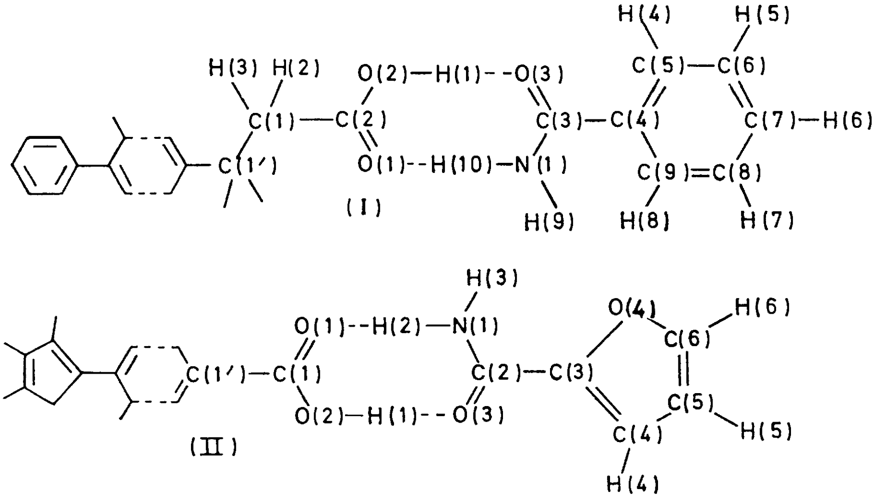
Intensities of the layers $h0$—$4l$, and the $0kl$ zone, were recorded by the equi-inclination Weissenberg technique with Cu-K_α radiation by the multiple-film method. Intensities were estimated visually, and processed for spot extension in nonzero levels,[2] and the Lorentz polarisation factor. The levels were brought to a common scale by the procedure of Rollet and Sparks.[3] The applied weighting scheme $w(hkl)$ has been described elsewhere.[4] 1729 Independent reflections were measured of which 288 were unobserved.

There are two succinic acid molecules and four benzamide molecules in the unit cell so it was assumed that a centrosymmetric succinic acid was linked to two benzamide molecules *via* hydrogen bonds between the carboxy- and amide-groups as shown in (I). The structure was solved by means of SEARCH[5] with the molecular model (I). SEARCH yielded essentially one trial structure which proved to be correct when tested in a constrained-geometry least-squares programme on 41 low-order reflections. In the refinement only the scale factor and the three Eulerian orientation angles of the planar molecule model were adjusted. After six cycles of refinement R was 0·32.

Individual atomic parameters were then refined by a full-matrix least-squares programme of Busing, Martin, and Levy, the function minimised being $w(k^2F_o^2 - F_c^2)$,[2] with isotropic thermal parameters and fixed hydrogen parameters and finally with anisotropic temperature parameters for all but the hydrogen atoms which were refined isotropically. Refinement was terminated when the shifts were $< 0{\cdot}02\sigma$ for all atoms including hydrogen. The final discrepancy indices for all reflections were R 0·10 and R' $[= \Sigma w(k^2F_o^2 - F_c^2)^2/\Sigma wk^4F_o^4]$ 0·05.

Compound (II).—*Crystal data.* $2(C_5H_5NO_2),(C_2H_2O_4)$, $M = 312{\cdot}2$. Triclinic, $a = 7{\cdot}459(1)$, $b = 6{\cdot}579(1)$, $c = 8{\cdot}064(1)$ Å, $\alpha = 92{\cdot}19(1)$, $\beta = 95{\cdot}60(1)$, $\gamma = 120{\cdot}29(1)°$, $U = 338{\cdot}3$ Å^3, $D_c = 1{\cdot}53$, $Z = 1$, $D_m = 1{\cdot}50$, $F(000) = 162$. Space group $P1$ or $P\bar{1}$ (the latter proved correct by the present analysis). Cu-K_α radiation: $\mu(\text{Cu-}K_\alpha) = 11{\cdot}5$ cm^{-1}.

Triclinic crystals of the 2 : 1 complex of furamide with oxalic acid (II), m.p. 144 °C, were grown from a slowly cooled solution in nitromethane as laths, showing well-developed {001}, {1$\bar{1}$0}, {010}, and {1$\bar{1}\bar{1}$} forms. Cell constants were determined by a least-squares analysis of high-angle ($\theta > 60°$) reflections measured as before.



Labelling of atoms used in the structures analyses

Three-dimensional intensity data of a crystal specimen *ca.* 0·4 × 0·2 × 0·5 mm were collected on a General Electric goniostat with Ni-filtered Cu-K_α radiation according to the stationary-crystal–stationary-counter technique, to a 2θ maximum of 160°. The $I(hkl)$ were corrected for absorption and reduced to $F(hkl)$ by a procedure described elsewhere.[6] 1511 Independent reflections were recorded, of which 60 were treated as unobserved. The weight $w(hkl)$ attached to $F_o(hkl)$ in our least-squares programme was taken equal to $1/\sigma^2(F_o^2)$.

The structure was solved from packing considerations. The molecular model was assumed to consist of an oxalic acid molecule hydrogen-bonded to two furamide molecules *via* the carboxy–amide pairing shown in (II). This molecular complex was assumed to lie in the (102) plane in view of the very high value of $F(102)$. The orientation of the complex unit (II) within this plane was fixed by assuming that these units were interlinked by N–H · · · O hydrogen bonds along the b axis. However, there remained one ambiguity, the direction (positive or negative) of b within the hydrogen-bonded network. Thus we tested both models in a constrained-geometry least-squares programme on 30 low-order reflections in which only the scale factor and the angular orientation parameters (three Eulerian

---

[2] D. C. Phillips, *Acta Cryst.*, 1954, **7**, 746.

[3] J. S. Rollet and R. A. Sparks, *Acta Cryst.*, 1960, **13**, 273.

[4] D. Rabinovich and G. M. J. Schmidt, *J. Chem. Soc.*, 1964, 2030.

[5] D. Rabinovich and G. M. J. Schmidt, *Nature*, 1966, **211**, 1391.

[6] S. E. Filippakis, L. Leiserowitz, and G. M. J. Schmidt, *J. Chem. Soc.* (*B*), 1967, 290.

angles) of the planar molecular model (II) were adjusted. After four cycles R was 0·4 and 0·7. The model with the lower R index, and which proved to be the correct structure, was chosen for further refinement.

Next, individual atomic parameters were refined, first with isotropic thermal parameters and fixed hydrogen parameters, and finally with anisotropic parameters for all but the hydrogen atoms which were refined isotropically. Refinement was terminated when the shifts were $< 0{\cdot}05\sigma$ for all atoms. The final agreement factors were R 0·05 and R' 0·02.

The scattering factor curves used for carbon, nitrogen, and oxygen were taken from ref. 7. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20567 (5 pp., 1 microfiche).†

RESULTS AND DISCUSSION

Tables 1 and 2 list the positional and thermal parameters with their estimated standard deviations of (I) and (II). Deviations from some best planes through (I) are given in Table 3(*a*), and those from the best planes of the analogous groups in (II) are listed in Table 3(*b*). Short intermolecular contacts in both structures are listed in Table 4.

TABLE 1

Fractional atomic co-ordinates ($\times 10^4$ for C, N, and O; $\times 10^3$ for H) and standard deviations referred to *a*, *b*, *c*

(*a*) Compound (I)

Atom	*x*	*y*	*z*
O(1)	−2318(3)	−2016(6)	200(1)
O(2)	−2019(4)	1439(6)	906(1)
O(3)	−4627(3)	0503(5)	1136(1)
N(1)	−4808(4)	−3717(7)	808(1)
C(1)	−212(4)	818(8)	287(2)
C(2)	−1618(4)	−114(7)	449(1)
C(3)	−5225(3)	−1651(7)	1128(1)
C(4)	−6454(3)	−2010(6)	1490(1)
C(5)	−6513(4)	−259(8)	2036(2)
C(6)	−7608(5)	−536(10)	2391(2)
C(7)	−8675(5)	−2472(10)	2211(2)
C(8)	−8647(5)	−4161(8)	1665(2)
C(9)	−7535(4)	−3966(8)	1304(2)
H(1)	−297(8)	83(13)	90(3)
H(2)	−32(5)	267(10)	14(2)
H(3)	53(5)	76(8)	70(2)
H(4)	−581(5)	96(8)	214(2)
H(5)	−756(5)	70(9)	268(2)
H(6)	−947(6)	−252(11)	242(3)
H(7)	−944(6)	−552(10)	156(2)
H(8)	−745(5)	−537(10)	98(2)
H(9)	−527(6)	−508(11)	83(2)
H(10)	−385(7)	−328(11)	66(3)

(*b*) Compound (II)

Atom	*x*	*y*	*z*
O(1)	495(1)	2881(1)	88(1)
O(2)	2057(1)	1247(1)	−1208(1)
O(3)	4383(1)	5052(1)	−2440(1)
O(4)	6119(1)	11143(1)	−2509(1)
N(1)	3074(2)	7222(2)	−1416(1)
C(1)	696(2)	1230(2)	−287(1)
C(2)	4403(2)	6958(2)	−2241(1)
C(3)	5961(2)	9025(2)	−2955(1)
C(4)	7306(2)	9305(3)	−4060(2)
C(5)	8374(2)	11750(3)	−4280(2)
C(6)	7615(2)	12771(2)	−3334(2)
H(1)	288(3)	275(3)	−160(2)
H(2)	226(3)	602(4)	−88(2)
H(3)	300(3)	853(4)	−129(3)
H(4)	742(3)	811(4)	−450(3)
H(5)	940(3)	1248(3)	−500(2)
H(6)	794(4)	1437(5)	−309(3)

Molecular Shape.—The complex (I) is non-planar (see Table 3). The heavy-atom skeleton of the succinic acid fragment is almost planar, the carboxy-group being twisted out of the plane of the ethylene chain by 4·4° about the C(1)–C(2) bond. The benzamide fragment is non-planar; the angle between the planes of the phenyl ring and the amide group being 24·2°, as a result of torsion about the exocylic C–C bond. The carboxy–amide pair which links the acid and amide fragments, is not a co-planar system, the angle between the planes of the carboxy- and amide-groups being 19·7°, primarily a result of a twist about the C(1) · · · C(4) vector. The carboxy-group is twisted, with reference to the amide group, in the same direction as the phenyl ring, the angle between their planes being 9·3°.

TABLE 2

Observed thermal parameters * ($\times 10^4$ for C, N, and O; $\times 10^3$ for H) and their standard deviations (Å^2)

(*a*) Compound (I)

Atom	u_{11}	u_{22}	u_{33}	u_{12}	u_{23}	u_{13}
O(1)	590(28)	516(20)	653(18)	−268(16)	−219(16)	434(14)
O(2)	599(19)	492(21)	811(22)	−211(17)	−291(17)	474(17)
O(3)	523(16)	291(17)	816(21)	−99(14)	−114(14)	442(15)
N(1)	575(21)	304(21)	634(22)	−107(18)	−133(15)	433(18)
C(1)	389(18)	320(26)	410(18)	−114(18)	−054(16)	190(15)
C(2)	413(18)	244(20)	382(16)	−71(18)	−009(14)	147(14)
C(3)	332(15)	249(20)	390(16)	−21(16)	−005(13)	136(13)
C(4)	360(16)	216(19)	321(15)	17(15)	−001(13)	111(12)
C(5)	411(19)	364(23)	437(18)	−66(19)	−128(17)	187(15)
C(6)	595(26)	477(28)	440(19)	12(22)	−141(20)	260(18)
C(7)	597(27)	541(29)	493(22)	−23(23)	028(19)	344(19)
C(8)	570(20)	349(24)	635(24)	−127(21)	−074(19)	402(21)
C(9)	436(20)	340(22)	448(18)	−44(18)	−063(17)	256(16)

Atom	*U*	Atom	*U*
H(1)	57(20)	H(6)	45(16)
H(2)	25(12)	H(7)	34(13)
H(3)	15(11)	H(8)	25(12)
H(4)	16(11)	H(9)	37(17)
H(5)	17(11)	H(10)	51(17)

(*b*) Compound (II)

Atom	u_{11}	u_{22}	u_{33}	u_{12}	u_{23}	u_{13}
O(1)	546(6)	381(5)	739(9)	278(4)	154(4)	329(5)
O(2)	502(6)	389(5)	700(7)	272(4)	158(4)	290(5)
O(3)	622(7)	410(5)	819(8)	296(5)	177(5)	401(6)
O(4)	565(6)	379(5)	558(6)	233(4)	76(4)	188(4)
N(1)	519(7)	395(6)	649(8)	258(5)	114(5)	259(5)
C(1)	389(6)	360(6)	507(7)	217(5)	78(5)	111(5)
C(2)	423(6)	384(6)	479(6)	215(5)	58(5)	126(5)
C(3)	413(7)	373(6)	488(7)	199(5)	62(5)	84(5)
C(4)	531(8)	545(9)	656(9)	300(7)	155(7)	261(7)
C(5)	518(8)	597(9)	683(9)	249(7)	253(7)	254(7)
C(6)	590(9)	418(7)	662(9)	186(7)	149(6)	156(7)

Atom	*U*	Atom	*U*
H(1)	35(5)	H(4)	48(6)
H(2)	28(4)	H(5)	35(5)
H(3)	48(6)	H(6)	59(7)

* Debye–Waller factor is defined as $\exp[-2\pi^2\sum_i\sum_j a_i^* a_j^* h_i h_j u_{ij}]$ for the C, N, and O atoms, and $\exp[-8\pi^2 U\sin^2\theta/\lambda^2]$ for hydrogen.

The oxalic acid fragment, of (II), is planar to within 0·002 Å; the furamide molecule is non-planar, the

---

† For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. are sent as full size copies).

[7] 'International Tables for X-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962, p. 202.

TABLE 3

Equations of planes in the form $Ax + By + Cz + D = 0$ where x, y, z are fractional co-ordinates; distances (10^3 Å) of relevant atoms from the planes are given in square brackets

(*a*) Compound (I)

Plane (I): C(1), C(2), C(1′), C(2′)
$-3{\cdot}3626x + 3{\cdot}0978y - 11{\cdot}3330z = 0$
[O(1) −72, O(2) 98, H(2) 774, H(3) −740]

Plane (II): C(1), C(2), O(1), O(2)
$-3{\cdot}2661x + 2{\cdot}8025y - 12{\cdot}3378z + 0{\cdot}0562 = 0$
[C(1) 1, C(2) −2, O(1) 1, O(2) 1, C(3) −93, N(1) −414, O(3) 306, H(1) 140]

Plane (III): C(3), C(4), N(1), O(3)
$-4{\cdot}3043x + 1{\cdot}2333y - 13{\cdot}4836z - 0{\cdot}5219 = 0$
[C(3) 2, C(4) −1, N(1) −1, O(3) −1, O(1) −42, O(2) −697, H(9) 0, H(10) −160]

Plane (IV): C(2), C(3), N(1), O(1)—(3)
$-3{\cdot}4397x + 2{\cdot}0619y - 13{\cdot}6976z + 0{\cdot}0665 = 0$
[C(2) −16, C(3) −23, N(1) −154, O(1) 173, O(2) −184, O(3) 204, C(1) −85, C(4) −170, H(1) 20, H(9) −310, H(10) −190]

Plane (V): C(4)—(9)
$-3{\cdot}9598x + 3{\cdot}1338y - 10{\cdot}1652z - 0{\cdot}4178 = 0$
[C(4) −7, C(5) 10, C(6) −5, C(7) −5, C(8) 9, C(9) −3, C(3) −13, N(1) −501, O(3) 417, H(4) 10, H(5) 80, H(6) 80, H(7) −10, H(8) −160]

(*b*) Compound (II)

Plane (I): C(1), O(1), O(2), C(1′), O(1′), O(2′)
$4{\cdot}0633x - 0{\cdot}8839y + 6{\cdot}0075z = 0$
[C(1) 2, O(1) −1, O(2) 0, H(1) −30]

Plane (II): C(1′), N(1), C(1)—(3), O(1)—(3)
$3{\cdot}9820x - 0{\cdot}6084y + 5{\cdot}9635z - 0{\cdot}0093 = 0$
[C(1′) −40, C(1) 22, C(2) −16, C(3) 53, O(1) 65, O(2) 13, O(3) −26, N(1) −70, H(1) 10, H(2) −10, H(3) −100]

Plane (III): C(3)—(6), O(4)
$4{\cdot}7707x - 1{\cdot}5606y + 5{\cdot}5031z + 0{\cdot}1965 = 0$
[C(2) −22, C(3) 5, C(4) −5, C(5) 2, C(6) 1, O(3) 157, O(4) −4, N(1) −244, H(4) −10, H(5) −20, H(6) 40]

furan ring being twisted out of the plane of the amide group by 17·4° about the exocyclic C–C bond. The hydrogen-bonded carboxy-amide pair is almost coplanar, the angle between the planes of the amide- and the carboxy-groups being 3°.

With regard to the conformation of the furamide molecule, the endocyclic C=C double-bond and the carbonyl C=O bond adopt the cisoid conformation about the exocyclic C–C bond, in contrast to the crystal molecular structures of furoic acid[8] and furan-αα′-dicarboxylic acid[9] in which the conformations are transoid. An *anti*-planar conformation of C=C–C=O in furamide would lead to a fairly short intramolecular H · · · H contact.

Bond Lengths and Angles.—The experimental bond lengths and angles of (I) are shown in Figure 1, the mean σ values being 0·005 Å and 0·3°. The corresponding values where one hydrogen atom is involved, are 0·04 Å and 3°.

Figure 2 shows the experimental bond lengths and angles in (II). The mean of the σ value of the bond lengths is 0·002 Å, and of angles 0·1°; the corresponding values where one hydrogen is involved, are 0·03 Å and 1°.

Molecular Packing.—Benzamide and succinic acid form a centrosymmetric 2 : 1 complex unit (I) *via* the hydrogen-bond pairing of their carboxy- and amide-groups (see Figure 3). These complex units are interlinked, along the 5 Å axis, by N–H · · · O bonds between the benzamide molecules (Figure 3). Interatomic distances and angles of the hydrogen-bonded network are also shown in Figure 3. The amide groups, joined by hydrogen bonds along the 5 Å axis, are not coplanar, rather their planes are offset by 1·2 Å. The separation between the phenyl rings, along this axis, is 3·1 Å as the ring is twisted 24° away from the plane of the amide group. Crystalline benzamide[10,11] shows very similar structural features as the benzamide component of (I), namely, the molecules are linked along a 5 Å axis by N–H · · · O bonds between amide groups the planes of which are offset by 1·2 Å, and the phenyl ring is twisted 26° out of the plane of the amide group. The twist angle of 26° in benzamide represents the balance between the probable loss of hydrogen-bond energy implied in the offset of 1·2 Å of the amide planes along the 5 Å axis, and the resistance to further torsion with possible loss of conjugation and

TABLE 4

Short intermolecular contacts (Å) *

(*a*) Compound (I)

$H(6)\cdots H(7^{I})$	2·64	$O(1)\cdots H(10^{VI})$	1·98
$O(1)\cdots H(8^{II})$	2·63	$O(2)\cdots O(3^{VI})$	2·60
$O(1)\cdots H(9^{II})$	2·96	$O(3)\cdots H(1^{VI})$	1·71
$N(1)\cdots N(1^{II})$	3·34	$C(5)\cdots H(8^{VII})$	3·20
$C(5)\cdots H(4^{III})$	3·01	$O(3)\cdots N(1^{VII})$	3·02
$C(9)\cdots H(3^{IV})$	3·04	$O(2)\cdots O(1^{VII})$	3·60
$O(1)\cdots O(3^{V})$	3·36	$H(2)\cdots H(2^{VIII})$	2·56
$O(1)\cdots C(3^{V})$	3·48	$C(1)\cdots H(7^{IX})$	3·05
$C(9)\cdots H(2^{V})$	3·05	$O(2)\cdots H(7^{IX})$	2·83
$O(1)\cdots N(1^{VI})$	2·98	$H(3)\cdots H(7^{IX})$	2·53

* Roman numeral superscripts refer to the molecules in the following equivalent positions relative to the reference molecule at x, y, z:

(*a*) Benzamide—succinic acid

I $-2 + x, \frac{1}{2} + y, \frac{1}{2} - z$
II $-1 - x, -1 - y, -z$
III $-1 + x, -\frac{1}{2} + y, \frac{1}{2} - z$
IV $-1 + x, y, z$
V $-1 - x, -y, -z$
VI x, y, z
VII $x, 1 + y, z$
VIII $-x, 1 - y, -z$
IX $1 + x, 1 + y, z$

(*b*) Compound (II)

$O(1)\cdots C(6^{I})$	3·30	$O(3)\cdots H(6^{III})$	3·00
$O(1)\cdots O(4^{I})$	3·33	$O(3)\cdots H(4^{IV})$	2·89
$O(1)\cdots N(1^{II})$	2·92	$C(3)\cdots C(6^{V})$	3·52
$O(1)\cdots H(2^{II})$	2·05	$H(4)\cdots H(5^{VI})$	2·64
$O(2)\cdots O(3^{II})$	2·53	$O(1)\cdots O(1^{VII})$	3·23
$O(3)\cdots H(1^{II})$	1·59	$O(1)\cdots N(1^{VII})$	2·94
$O(2)\cdots N(1^{III})$	3·10	$O(1)\cdots H(3^{VIII})$	2·60
$O(2)\cdots O(4^{III})$	3·33	$C(1)\cdots C(3^{VIII})$	3·50
$O(2)\cdots H(3^{III})$	2·23	$O(2)\cdots C(2^{VIII})$	3·36
$O(3)\cdots C(6^{III})$	3·53	$O(1)\cdots H(6^{IX})$	2·74
$O(3)\cdots O(4^{III})$	3·41	$N(1)\cdots O(4^{IX})$	3·20

Equivalent positions:

I $-1 + x, -1 + y, z$
II x, y, z
III $x, -1 + y, z$
IV $-x, -y, -1 - z$
V $1 - x, 2 - y, -1 - z$
VI $2 - x, 2 - y, -1 - z$
VII $-x, 1 - y, -z$
VIII $1 - x, 1 - y, -z$
IX $1 - x, 2 - y, -z$

---

[8] P. Hudson, *Acta Cryst.*, 1962, **15**, 919.

[9] E. Martuscelli and C. Pedone, *Acta Cryst.*, 1968, *B*,**24**, 175.

[10] B. R. Penfold and J. C. B. White, *Acta Cryst.*, 1959, **12**, 130.

[11] L. Leiserowitz and G. M. J. Schmidt, *J. Chem. Soc.* (*A*), 1969, 2372.

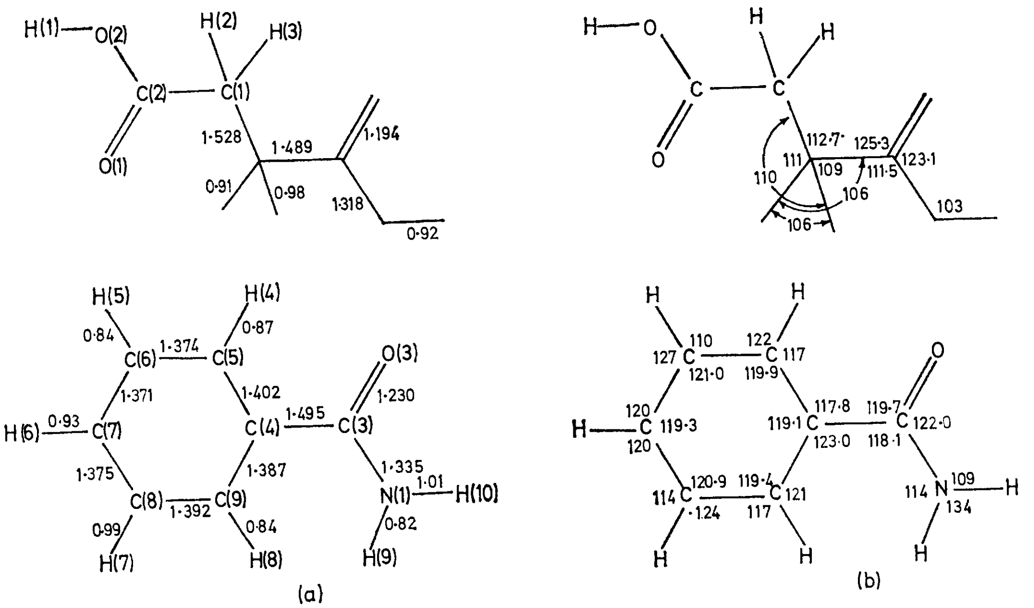


Figure 1 (a) Bond lengths (Å), and (b) bond angles (°) in (I)

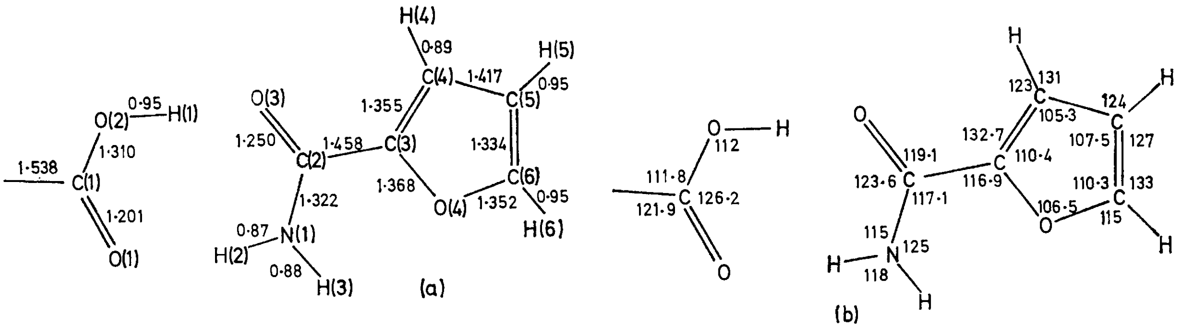


Figure 2 (*a*) Bond lengths (Å) and (b) bond angles (°) in (II)

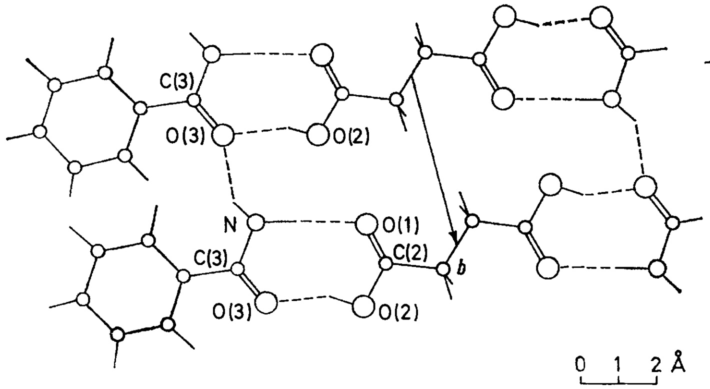


Figure 3 Packing arrangement of the hydrogen-bonded molecules seen normal to the planes of the succinic acid molecule in (I). Distances (Å) and angles of the hydrogen-bonded system are: O(2) · · · O(3) 2·60, N · · · O(1) 2·98, N · · · O(3) 3·02, O(1) · · · O(2) 3·60; C(3)–O(3) · · · O(2) 126·4°, C(2)–O(2) · · · O(3) 116·3°, C(3)–N · · · O(1) 107·6°, C(2)–O(1) · · · N 117·6°, C(3)–N · · · O(3) 133·0°, C(3)–O(3)- · · · N 150·1°

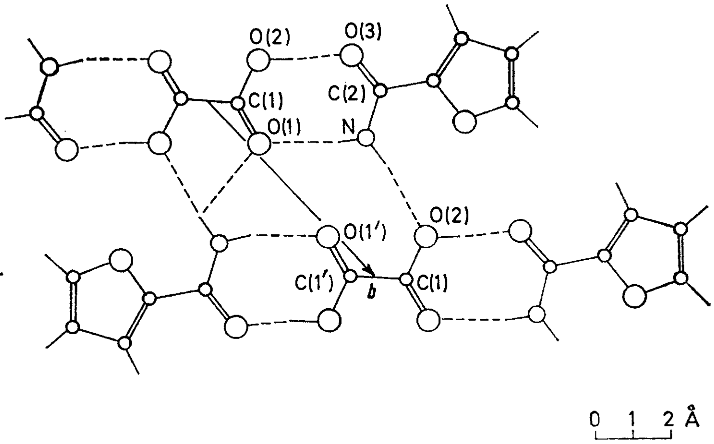


Figure 4 Packing arrangement of the hydrogen-bonded molecules seen normal to the plane of the oxalic acid molecule in (II). Distances (Å) and angles of the hydrogen-bonded system are: O(2) · · · O(3) 2·53, N · · · O(1) 2·92, N · · · O(1′) 2·94, N · · · O(2) 3·10; C(1)–O(2) · · · O(3) 117·5°, C(2)–O(3)- · · · O(2) 126·1°, C(1)–O(1) · · · N 116·3°, C(2)–N · · · O(1) 109·1°, C(2)–N · · · O(2) 131·7°, C(2)–N · · · O(1′) 176·0°, C(1)–O(2) · · · N 123·0°, C(1′)–O(1′) · · · N 127·2°

inefficient packing of molecules normal to the overall benzamide plane.[11]

The N–H $\cdots$ O geometry of (I) along the translation axis (Figure 3) is consistent with the observed pattern of N–H $\cdots$ O (carbonyl) hydrogen bonding[11] insofar as the N $\cdots$ H vector points toward the region where one would expect the electron lone-pair lobe of the carbonyl oxygen to lie. The carboxy-amide pair is distorted, the twist angle between the planes of the carboxy- and amide-groups being as large as 19·7°. The mean deviation of the oxygen and nitrogen atoms from the best plane through this system is 0·18 Å (Table 3). By way of comparison, the carboxy-amide pair of (II) is planar to within 0·07 Å (Table 3), with a twist angle of 3° between the planes of the carboxy- and amide-groups. In the crystal structure of fumaramic acid[12] ($HO_2C{\cdot}CH{:}CH{\cdot}CONH_2$), where the carboxy- and amide-groups are linked to each other to form the cyclic asymmetric pair as in (I) and (II), the dihedral angle between the two planes (carboxy and amide) is 0·5°, and the system is planar to within 0·07 Å.

The torsional distortion of the hydrogen-bonded pair of (I) is due to intermolecular forces. In order to determine their nature we construct the 'ideal' coplanar hydrogen-bonded pair, by bringing the plane of the succinic acid molecule into coincidence with that of the amide group, and consider the changes induced in the intermolecular contacts along the 5 Å axis. Although the offset between the planes of the neighbouring succinic acid molecules along the 5 Å axis is reduced from 3·0 Å (observed) to 1·2 Å in the hypothetical structure the ethylene chains would not be overcrowded in this model structure, for the intermolecular distance between the methylene hydrogens would be 2·9 Å. Moreover, in the crystal structure of adipamide,[13] the almost planar molecules are hydrogen-bonded (N–H $\cdots$ O) along a 5 Å axis with an offset between their carbon sheets of only 0·4 Å. Let us now consider the contact between the carboxy-groups along the 5 Å axis. The O(1) $\cdots$ O(2) separation, observed value 3·6 Å (see Figure 3 and Table 4) would be 3·0 Å, *i.e.* the observed interpair N–H $\cdots$ O distance, in the model arrangement.

Now an O $\cdots$ O contact of 3·1 ± 0·1 Å would not be unusual,[9,14] since the van der Waals radius of oxygen is reported[15] to be 1·4 Å. However, assuming that the van der Waals interaction between two oxygen atoms is dependent upon their direction of approach, and that the atoms O(1) and O(2) are respectively sp^2 and sp^3 hybridised, then the lone-pair lobes of O(1) and O(2), which would be partially directed towards each other in the hypothetical structure, are further removed from each other in the observed structure by virture of the 20° twist of the carboxy-group. We therefore tend to the view that the torsional distortion of the carboxy–amide pair is induced by intermolecular oxygen lone-pair–lone-pair repulsions.

In the crystal structure of (II) the oxalic acid is hydrogen-bonded to two furamide molecules *via* the carboxy–amide pairing (see Figure 4), a pattern identical to that in (I). These complex units (II) are interlinked, along the *b* axis, by N–H $\cdots$ O hydrogen bonds between furamide and oxalic acid fragments; in contradistinction to the packing motif in (I) in which the units are joined by amide–amide hydrogen bonds. The interatomic distances, and angles of the hydrogen-bonded network of (II) are shown in Figure 4. The N–H $\cdots$ O hydrogen bond interlinking the units of (II) appears to be bifurcated; the nitrogen atom straddles the oxygens of the oxalic acid with the N $\cdots$ H vector pointing along the bisectrix of the C–O(2)–H angle. The N $\cdots$ O(2) distance is 3·10 Å. The N–H proton also lies close to the available lone-pair lobe of the carbonyl oxygen O(1), the N $\cdots$ O(1) distance being 2·94 Å. Indeed, this hydrogen-bond network is similar to that of the (bifurcated) hydrogen-bonded system in azodicarboxamide.[11,16]

[2/1101 *Received*, 15*th May*, 1972]

---

[12] V. Benghiat, H. W. Kaufman, L. Leiserowitz, and G. M. J. Schmidt, *J.C.S. Perkin II*, 1972, 1758.

[13] M. Hospital and J. Housty, *Acta Cryst.*, 1966, **20**, 626.

[14] C. J. Brown, *Acta Cryst.*, 1966, **21**, 1.

[15] L. Pauling, 'The Nature of the Chemical Bond,' 3rd edn. Cornell University Press, Ithaca, New York, 1960, p. 260.

[16] J. H. Bryden, *Acta Cryst.*, 1961, **14**, 61.