Tableau 4. *Distances cation–oxygène* (Å) *dans les polyèdres de coordination des cations associés*

Ba–O(*E*21)	2,714 (5)	Ba–O(*W*4)	2,772 (7)
Ba–O(*E*22)	2,749 (7)	Ba–O(*W*3)	2,809 (8)
Ba–O(*E*11)	2,796 (6)	Ba–O(*W*2)	2,877 (7)
Ba–O(*E*32)	2,821 (4)	Ba–O(*W*2)	2,987 (6)
Ba–O(*E*12)	2,922 (6)		
Ag–O(*E*32)	2,445 (5)	Ag–O(*E*32)	2,629 (7)
Ag–O(*E*11)	2,531 (6)	Ag–O(*E*12)	2,706 (5)
Ag–O(*E*22)	2,624 (5)	Ag–O(*W*1)	2,370 (9)

des cations associés qui se développe en une chaîne de direction moyenne **a** − **b**.

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The Molecular Packing Modes and the Hydrogen-Bonding Properties of Amide : Dicarboxylic Acid Complexes

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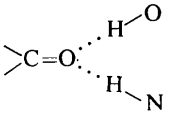
The various possible modes of forming H-bonded complexes of primary and secondary amides with dicarboxylic acids in the crystalline phase have been constructed in terms of: (*a*) O–H···O and N–H···O hydrogen-bond geometry, (*b*) the nature of the residues attached to the amide and carboxyl groups, and (*c*) the commonly occurring crystallographic symmetry elements required to generate hydrogen-bonding arrangements. The existence of these packing modes was corroborated by crystal structure analyses of model compounds. The various observed hydrogen-bonding motifs are compared to determine preferred hydrogen-bond geometries. There is a tendency for a carbonyl O atom which participates in both an N–H···O and O–H···O bond to adopt, the residues permitting, an arrangement where the system



is coplanar with linear hydrogen bonds and C=O···H angles ≃120°. The angular geometry of the complexing O–H···O(amide) bond invariably displays an O(H)···O=C angle ≃120°. The N–H···O (carboxyl) bond shows much greater variation in the N(H)···O=C angle. The O–H···O(amide) distance between amide and carboxyl groups linked by a single hydrogen bond is 2·50 ± 0·02 Å, which is shorter than the average length of the corresponding O–H···O(carboxyl) bond of 2·64 Å. A similar comparison of N–H···O(amide) and N–H···O(carboxyl) bonds shows no systematic differences. The C=O length is, on average, 0·04 Å longer in amides than in carboxylic acids.

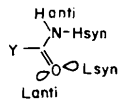
1. Introduction

A systematic study of crystalline molecular complexes formed by a large variety of amides and dicarboxylic acids was undertaken as part of an analysis of the packing modes of H-bonded functional groups. The rationale behind these studies is that much information of chemical interest is imbedded in crystal structures because they represent minimum-energy arrangements and, whereas little can be extracted from a single structure, certain trends become apparent if enough structures are available. Our principal purpose lay in the detection of the primary hydrogen-bonding motifs of the amide : acid complexes as governed by the

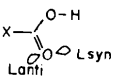
residues attached to the carboxyl and amide groups, and consequently in gaining a deeper understanding of the hydrogen bonds in amides and carboxylic acids and the factors responsible for complexation. This approach is reflected in the general outlay of the paper; first we describe the various packing arrangements in amide:acid complexes, followed by an analysis of their hydrogen-bonding properties.

2. Primary point motifs of amide:acid complexes

The forces responsible for molecular complexation between an amide (1) and a carboxylic acid (2) are mainly due to hydrogen bonds (to be referred to as H-bonds) involving both the N–H and O–H proton donor groups. Possible proton acceptors are the electron lone-pair lobes L of the carbonyl O atoms as depicted in (1) and (2). We shall specify the presumed locations of the two lone-pair lobes L* of the carbonyl O atom as well as the locations of the H atoms by the symbols *syn* and *anti* adopting the following convention: the H atom, or lone-pair lobe, closer to the other hetero-atom of the functional group is designated as H_{syn}, or L_{syn}, while that which is further is labelled H_{anti} or L_{anti}.



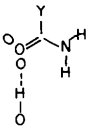
(1)

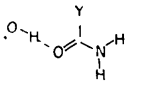


(2)

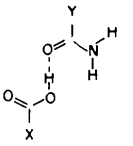
Complexation must be associated with the fact that the amide and carboxyl groups together have an excess of proton acceptors: three proton donors *versus* four proton acceptors. While the H-bond requirements of the amide group are completely satisfied, H_{syn} and H_{anti} are complemented by L_{syn} and L_{anti}, the carboxyl group lacks one proton donor (H_{syn} *versus* L_{syn} and L_{anti}). This deficiency is a necessary but not sufficient requirement for complexation since there are several amide:acid combinations (*e.g.* formamide:succinic acid, and various amides with, for example, fumaric acid) which do not seem to yield complexes. Consequently, it would seem necessary that the lattice energy of the crystalline complex must override that of the individual components.

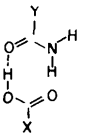
Since the O–H···O bond is significantly shorter and stronger than the N–H···O bond (Pimentel & McClellan, 1960), we shall first consider the possible ways in which O–H···$OCNH_2$ bonds, rather than N–H···OCOH bonds, are formed between the carboxyl and amide groups leading to a set of basic packing motifs. This may be accomplished on the assumption that the O–H proton donor is directed at the acceptor carbonyl O atom along the line of its lone-pair lobe. Since either the L_{syn} or the L_{anti} lobes of (1) may serve as proton acceptors, the O–H group may form two distinct H-bond geometries shown in (3) and (4).

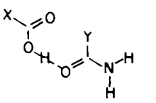

(3)

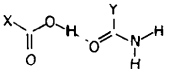

(4)

The relative orientations between the carboxyl and amide groups in (3) and (4) may be varied by rotation about the interlinking O–H···O(amide) bond. We confine ourselves to orientations which lead to coplanar arrangements. Therefore (3) and (4) each yield two motifs, (3*a*) and (3*b*), and (4*a*) and (4*b*) respectively.

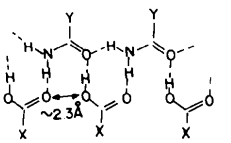

(3*a*)


(3*b*)

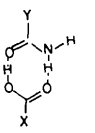

(4*a*)


(4*b*)

The H-bonding schemes in these motifs may be further extended utilizing first the N–H_{syn} proton donor and the available lone-pair lobes of the carbonyl O atoms to form linear N–H···O bonds. This extension precludes the motif (3*a*) since the resulting arrangement (5), which also incorporates a N–H_{anti}···$OCNH_2$ bond, would contain too close a contact of ~2·3 Å between carbonyl and hydroxyl O atoms of neighbouring carboxyl groups. In a similar arrangement (Huang, Leiserowitz & Schmidt, 1973) (see § 3.3.2.1) an O···O contact of not less than 3·6 Å was found. Inserting this distance into motif (5) would induce a pronounced distortion in the whole H-bonding geometry. Motif (3*b*), on the other hand, is satisfactory since it already embodies the N–H_{syn}···O bond yielding the cyclic dimer (6).



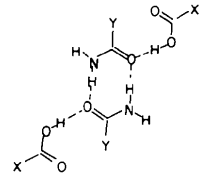
(5)


(6)

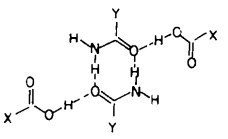
Both motifs (4*a*) and (4*b*) may be extended *via* N–H_{syn}···O bonds by associating the amide groups to form the commonly observed centrosymmetric H-bonded pair, resulting in motifs (7) and (8) respectively.

While it is possible to generate additional H-bonding arrangements from (4*a*) and (4*b*) in which the N–H_{syn} bond interacts with the available L_{anti} lobe of the carboxyl group as shown in (9*a*), (9*b*) and (9*c*), these schemes inhibit the formation of further N–H···O

* The lone-pair lobes are assumed to lie in the plane of the carbonyl system >C=O and make angles of 120° with C=O; *i.e.* the O atom is sp^2 hybridized.

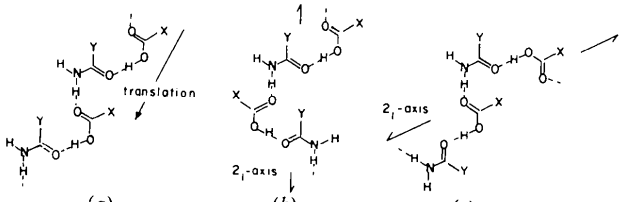


(7)



(8)

bonds since all available lone-pair lobes of the carbonyl O atoms are blocked. Thus motifs (9) may be discarded.



(a) (b) (c)

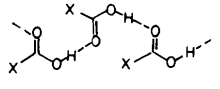
(9) Three unfavourable chain motifs constructed from point motifs (7) and (8).

The remaining primary motifs (6), (7) and (8) may be regarded as *point* motifs, analogous to crystallographic point groups, from which we may develop *space* motifs, analogous to space groups, by interlinking the *point* motifs by H-bonds. In constructing these space motifs use will be made only of the commonly occurring space symmetry elements in organic molecular crystals, *i.e.* translation, glide plane, and twofold screw axis. The existence of these point motifs, and their resulting space motifs, are critically dependent on the steric nature of the amide and acid residues *Y* and *X*. This dependence will now be examined in detail for motifs (7), (8) and (6) in turn.

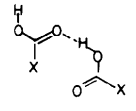
3. Space motifs of the amide : acid complexes

3.1. *Point motif* (7)

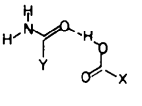
The planar arrangement in point motif (7) induces a close contact between the amide residue *Y* and the carbonyl O atom of the carboxyl group. Therefore the question arises as to the size of the residue *Y* which may be incorporated into motif (7). The answer is provided by the H-bond motif (10) common to formic acid (Holtzberg, Post & Fankuchen, 1953), acetic acid (Nahringbauer, 1970; Jönsson, 1971) and β-tetrolic acid (Benghiat & Leiserowitz, 1972).



(10) Polymeric motif of H-bonded carboxyl groups.



(11*a*)

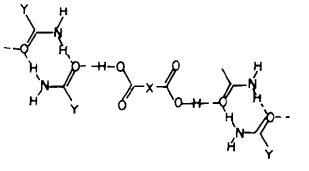


(11*b*)

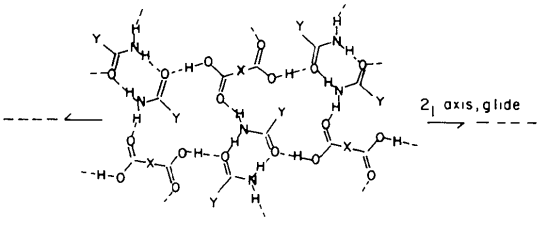
These molecules, $X-CO_2H$, are interlinked by *single* O—H···O bonds in a geometry which strongly resembles that of the O—H···$OCNH_2$ bond in (7). The common features are obvious from (11*a*) and (11*b*). Only these three monocarboxylic acids have been observed incorporating point motif (11), this having been accounted for by the close van der Waals contact *X*···O (Leiserowitz, 1976). By analogy, formamide, acetamide and tetrolamide might be expected to fit into motif (7).

3.1.1. *Twofold screw axis and translation packing*

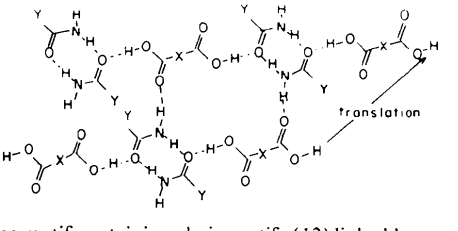
Translation of the point motif (7) generates a one-dimensional space motif (12) in which the two carboxyl groups are linked by C—*X*—C where *X* represents either a chemical bond or a van der Waals contact. These chains (12) may be interlinked only by $N-H_{anti}\cdots$OCOH bonds *via* the L_{anti} lobes of the carboxyl O atoms, in fact the only acceptor lobes available. This may be achieved by a 2_1 axis or a glide, both running parallel to the chain axis or alternatively by translation, yielding space motifs (13) and (14) respectively. An essential difference between (13) and (14) lies in the geometry of their interchain N—H···O bonds.



(12) Chain motif derived from translation linkage of point motifs (7).



(13) Space motif containing chain motifs (12) linked by a 2_1 axis, or glide.



(14) Space motif containing chain motifs (12) linked by translation.

In the 2_1 axis, or glide, space motif (13) the distance between the two carboxyl groups, C—*X*—C, affects the geometry of the interchain N—H···O bond, since its length depends on the length of the 2_1 axis, or glide axis,

which varies with the C–*X*–C distance. Therefore the C–*X*–C distance cannot be longer than 2 Å to accommodate an interchain N–H···O bond of 2·9–3·0 Å. Only oxalic acid satisfies this condition. Furthermore, of the three amides which may fit into the chain (12) only formamide and acetamide may be accommodated into the two-dimensional motif (13); tetrolamide is precluded because of molecular overcrowding.

The C–*X*–C distance imposes no obvious restrictions on the translation space motif (14). However, the short interchain contact between the *Y* groups, determined by the interchain N–H···O distance, probably does not permit the residue *Y* to be bulkier than a H atom, so it would seem that only formamide complexes could pack in this motif.

The 2:1 complex of formamide with oxalic acid (Leiserowitz & Nader, 1977), whose cell constants are listed in Table 1, does not crystallize in the translation space motif (14); rather it appears in the space motif (13) in which the chains (12) are interlinked by a 2_1 axis. The H-bonded system (Fig. 1) contains two striking features: a short O–H···$OCNH_2$ bond of 2·5 Å and a H-bonded network which is not coplanar, but crosslinked by virtue of a tilt of 19° between the chain axis of (12) and the 2_1 axis. Such a crosslinked network cannot be achieved in the glide space motif (13) because the axes of the glide-related chains (12) are parallel, and so would yield a layer structure.

The molecular complex of formamide with formic acid (Nahringbauer & Larsson, 1969), which of course cannot pack in the 2_1 axis motif (13) (the distance C–*X*–C – C–II···II–C > 2 Å), contains two different H-bonded networks, (I) and (II), shown in Fig. 2, both of which resemble the translation motif (14). In (I), the point motifs (7) are interlinked by N–H···O bonds generated by a shallow glide which is almost akin to translation. In (II) the amide groups do not comprise ring dimers as in (I); rather they form H-bonds along a 3·6 Å axis about a twofold screw, an arrangement which is not unique; it appears in the

Table 1. *Cell constants and* H-*bonding motifs of amide:carboxylic acid complexes*

Amide	Carboxylic acid	Amide:acid ratio	Space group	*Z*	*a* (Å)	*b* (Å)	*c* (Å)	*β* (°)	Point motif/space motif
Formamide	Oxalic acid	2:1	$P2_1/c$	2	3·669	11·066	10·314	99·40	(7)/(13)
Acetamide		1:1	$A2/a$	16	20·542	9·079	13·931	112·09	(8)/(16)
α-F-acetamide		2:1	$P2_1/c$	2	4·72	4·83	22·96	108	(17)/(23*c*)
α-Cl-acetamide		2:1	$P2_1/c$	2	4·27	5·20	26·77	108	(17)/(23*c*)
Crotonamide		2:1	$P2_1/c$	4	5·203	12·896	9·310	90·64 92·19	(17)/(18)
Furamide		2:1	$P\bar{1}$	1	7·459	6·578	8·064	95·59 120·29	(17)/(23*c*)
Benzamide		2:1	$P2_1/c$	2	5·13	5·27	30·97	108·6	(17)/(23*a*)
N-Me-formamide		2:1	$P2/c$	4	13·817	3·838	19·860	110·8	(25*b*)/(26)*
N-Me-acetamide		2:1	$P2_1/c$	4	15·23	4·02	19·94	93·2	(25*b*)/(26)*
Crotonamide	Succinic acid	2:1	$P2_1/c$	2	5·14	16·60	9·55	98·5 129·7	(17)/(18)
Furamide		2:1	$P\bar{1}$	1	7·23	9·66	11·81	71·6 111·0	(17)/(23*b*)
Benzamide		2:1	$P2_1/c$	2	9·194	5·116	19·480	105·66	(17)/(23*a*)
Acrylamide	*meso*-DiCl-succinic acid	2:1	$P2_1$	2	5·22	21·65	6·85	109	(17)/(23*a*)
Crotonamide		2:1	*Pbca*	8	20·40	8·69	9·88		
Acrylamide	(±)-DiBr-succinic acid	2:1	$P2_1/c$	4	12·80	13·96	9·33	104	
Acetamide	Maleic acid	1:1	$P2_1$	2	6·09	6·45	10·48	92	
Formamide	Allenedicarboxylic acid	2:1	*Cc* or *C*2/*c*	4	11·78	7·93	10·90	93	
Acetamide		1:1	*C*2/*c*	8	19·017	4·829	21·838	118·69	(8)/(16)
Crotonamide		2:1	$P2_1/c$	4	18·80	18·20	4·52	93·5	
Acetamide	Acetylenedicarboxylic acid	2:1	*Aba*2 or *Acam*	4	13·64	12·86	6·50		
Acrylamide		2:1	*C*2 or *C*2/*m*	4	14·85	6·38	13·40	91	
Tetrolamide		2:1	*C*2/*c*	4	22·279	9·139	6·944	98·51 96·8	(17)/(18)†
Crotonamide	Adipic acid	2:1	$P\bar{1}$	1	8·58	7·96	7·07	116·5 88·0	(17)/(23*b*)
Furamide		2:1	$P2_1/c$	4	6·96	14·36	20·98	123	(17)
Benzamide		2:1	$P2_1/c$	2	5·04	5·34	37·22	91·9	(17)/(23*a*)

* The observed motif in *N*-methylformamide:oxalic acid is very similar to that given in the table (see § 4). The crystal structure of *N*-methylacetamide:oxalic acid has not been solved, yet its H-bonding motif must be almost isostructural with *N*-methylformamide:oxalic acid (see § 4).

† The observed motif in tetrolamide:acetylenedicarboxylic acid is analogous to that given (see § 3.3.1).

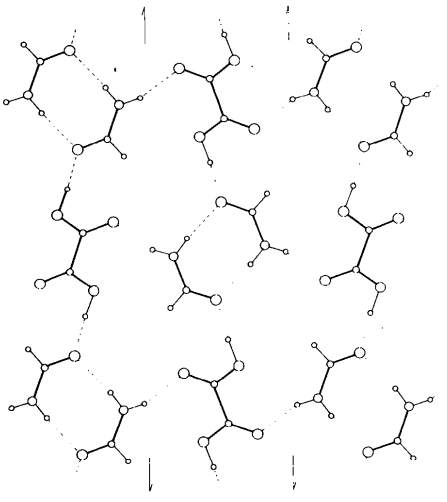


Fig. 1. Formamide:oxalic acid. H-bonding network viewed along **a**.

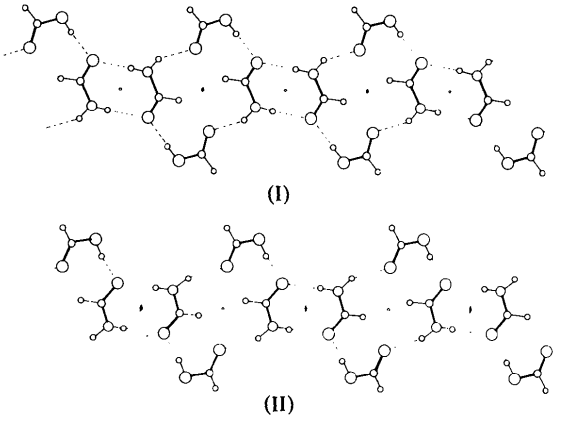


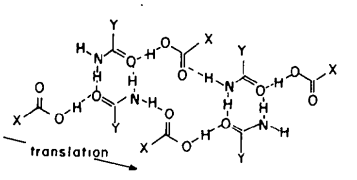
Fig. 2. Formamide:formic acid (Nahringbauer & Larsson, 1969). H-bonding networks (I) and (II) viewed along **b**. In (I) the amide groups form H-bonded rings; in (II) the amide groups are related by a 2_1 axis to form a helical H-bonded system along the short **b** axis of 3·6 Å.

crystal structures of hydroxyurea (Larsen & Jerslev, 1966), isohydroxyurea (Larsen, 1968), and a number of secondary *cis* amides (Leiserowitz & Tuval, 1977).

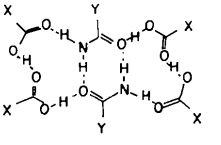
It was argued above that acetamide:oxalic acid could pack in point motif (7) as part of the 2_1 axis space motif (13). The actual structure is quite different displaying the point motif (8). The advantage reaped by acetamide:oxalic acid appearing in point motif (8) is discussed below.

3.2. *Point motif* (8)

A space motif derived from point motif (8) by interlinking the free $N-H_{anti}$ donor with the only available L_{anti} lobe of the carboxyl group would induce close contacts between the residues X and Y as shown in (15). Nevertheless point motif (8) is incorporated into the crystal structures of the 1:1 complexes of acetamide with oxalic acid (Leiserowitz & Nader, 1972) and with allenedicarboxylic acid (Nader, 1977) through an additional carboxyl function, as shown in (16), which bridges the $N-H_{anti}$ proton donor and the available L_{anti} acceptor lobe of the carboxyl group by N–H···OCOH and O–H···OCOH bonds. Characteristic of this point motif in the two complexes are very short O–H···$OCNH_2$ bonds of 2·48 and 2·52 Å.



(15) Space motif containing point motifs (8) linked by translation.



(16) Point motif observed in acetamide:oxalic acid and acetamide:allenedicarboxylic acid.

To accommodate point motif (16) into the crystal structure of acetamide:oxalic acid the less favoured synplanar O=C–C=O conformation of oxalic acid (*i.e.* the torsion angle of O=C–C=O is 0°) is adopted. The structure (Fig. 3) contains acetamide dimers H-bonded to infinite chains of the synplanar oxalic acid molecules linked to each other by *single* O–H···O bonds along a pseudo 2_1 axis* forming a layer. Application of the pseudo 2_1 axis provides the bond linkage between the two 'independent' carboxyl groups in point motif (16) to form the synplanar oxalic acid conformer; indeed it is impossible to construct a H-bond network incorporating (16) with oxalic acid in its stable antiplanar conformation. The question then arises why the acetamide complex does not appear in space motif (13), as does formamide:oxalic acid, in which the oxalic acid is antiplanar. Were acetamide:oxalic acid to pack in motif (13) this postulated arrangement would bear a disadvantage in that the O–H···$OCNH_2$ bond could not be as short as in the observed structure (2·48 Å) because of a close methyl···O(carbonyl) contact [*i.e.* the Y···O contact in (7)]. In the observed structure the length of the O–H···$OCNH_2$ bond, which is part of point motif (8), is not at all affected by the bulkiness of the amide residue Y.

* The structure contains two crystallographically independent oxalic acid molecules related by a pseudo 2_1 axis and two independent acetamide molecules forming the ring dimer.

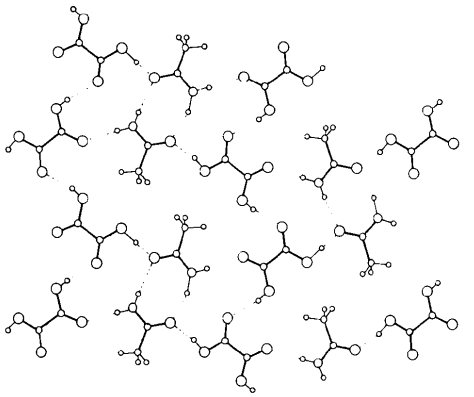
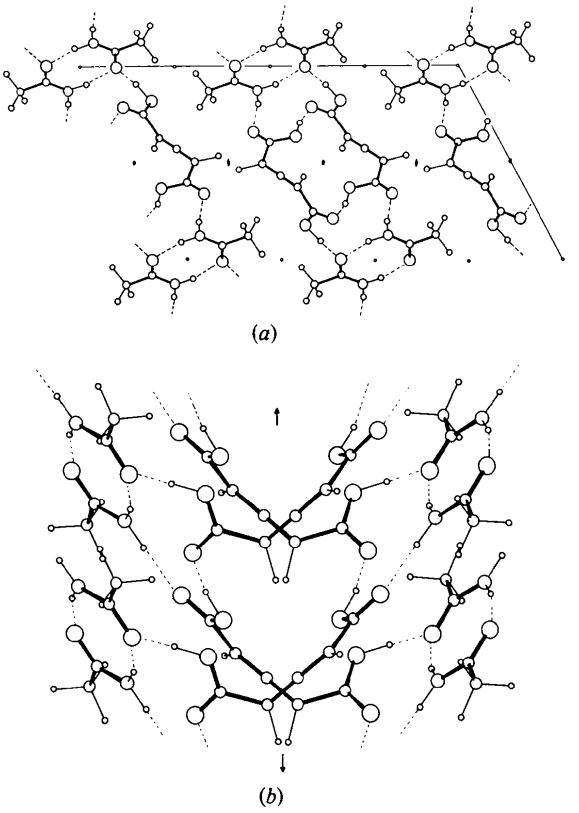


Fig. 3. Acetamide:oxalic acid. H-bonding sheet structure in the *ab* plane.



(*a*)

(*b*)

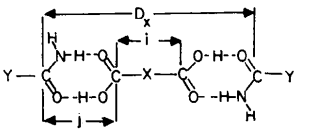
Fig. 4. Acetamide:allenedicarboxylic acid (Nader, 1977). (*a*) Packing arrangement in the *ac* projection. (*b*) The H-bonding layer structure seen perpendicular to the *bc* plane.

Point motif (16) is evident in the H-bond network of acetamide:allenedicarboxylic acid which is a layer structure (Fig. 4*a*). In a manner similar to acetamide:oxalic acid, the allenedicarboxylic acid molecules form infinite chains (Fig. 4*b*) by *single* O–H···O bonds along the 4·5 Å *b* axis. Such chains are made of double-stranded helices. The molecules in each H-bonded strand are related by a twofold screw of repeat **2b** (*i.e.* a combination of the twofold axis and a repeat unit), while the two interwoven strands are related to each other by the twofold axis (Fig. 4*a*). The double-stranded helices are connected to centrosymmetric acetamide pairs by the N–H···OCOH and O–H···$OCNH_2$ bonds inherent in point motif (16). The allenedicarboxylic acid molecule in the complex maintains an overall conformation* similar to that of its parent compound (Leiserowitz & Nader, 1973), in contrast to the oxalic acid complex.

The question arises whether the point motif (16) may be encountered in other systems. It is obvious from the sheet structure of acetamide:oxalic acid (Fig. 3) that an increase in size of the amide residue *Y* will lead to molecular overcrowding. Indeed, F or Cl substitution of one of the methyl H atoms of acetamide leads to a change in packing type. Nevertheless, we envisage molecular complexes with arrangements similar to acetamide:oxalic acid by choosing appropriate *X* and *Y* residues. This may be achieved, for example, by increasing the intramolecular separation between the two carboxyl groups from C–C (oxalic acid) to C–C≡C–C (acetylenedicarboxylic acid).

3.3. *Point motif* (6)

The point motifs (7) and (8), and their corresponding space motifs, impose strict limitations on the sizes of the residues *X* and *Y*. In contrast, point motif (6) obviously has no such restrictions and thus should be commonly observed. Indeed, in the reported monoamides of dicarboxylic acids, *e.g.* fumaramic acid (Benghiat, Kaufman, Leiserowitz & Schmidt, 1972), bromosuccinamic acid (Murakami & Iitaka, 1969), succinamic acid and muconamic acid (Leiserowitz, 1976), the molecules are linked by the carboxyl:amide pair (6). Since this analysis is focused on centrosymmetric dicarboxylic acids point motif (6) develops into a molecular complex (17) with a 2:1 amide:acid composition.



(17) 2:1 amide:acid complex incorporating point motif (6).

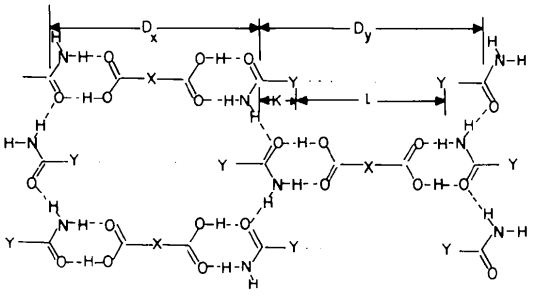
The point motif (17) can be interlinked into a space motif either by an N–H···$OCNH_2$ bond or by an N–H···OCOH bond. This may be accomplished either by translation or by a glide (or 2_1 axis). The latter

* The torsion angle of C–C=C=C–C in allenedicarboxylic acid is ≃90° in both the acetamide complex and the parent compound. The O=C–C=C conformation is antiplanar ($\tau \simeq 180°$) in the parent compound, whereas in the complex τ = 178 and 163° (Nader, 1977).

symmetry, however, permits formation of an extended structure by N–H···$OCNH_2$ bonds only;* translation symmetry imposes no such restrictions.

3.3.1. *Glide packing*

The extended H-bonded system achieved by joining the point motifs (17) by a glide, or 2_1 axis, is shown in (18). This mode of linking amide groups is analogous to that observed in primary amides (Leiserowitz & Schmidt, 1969) where it was shown that, to obtain a sufficiently short, linear, interpair N–H···O bond, the glide plane has to pass close to the amide C atom at an angle approximately perpendicular to the Y–$CONH_2$ bond, and in a direction parallel to the plane of the amide group. This glide† has an axial component of 9·6 ± 0·3 Å.



(18) Space motif generated by linking point motifs (17) by a glide or 2_1 axis.

An examination of space motif (18) reveals a relation between the sizes of the residues X and Y. Firstly, steric contacts arising from the length of the interpair N–H···O bond hardly permit X and Y to extend along the interpair direction and thus X and Y are limited to non-bulky chains (*e.g.* the phenyl ring is most likely excluded). Secondly, the residues X and Y must be of appropriate lengths along the chain direction. This geometric relation between X and Y may be described by two distances D_x and D_y shown in (17) and (18). D_x is the separation between the two amide C atoms in the 2:1 molecular complex, given by $i + 2j$ where i is the intramolecular distance between the two carboxyl C atoms and j is the distance between the amide and carboxyl C atoms of the H-bonded carboxyl:amide pair and thus a constant (= 4·0 Å). D_y is the separation between the two amide C atoms across the residues Y equal to $2k + l$, where k is the length of the residue Y and l is the intermolecular distance between the two Y groups. $D_x + D_y$ is the translation repeat normal to the glide plane in space motif (18). As mentioned above, a linear N–H···O bond of the proper length of 2·9 Å is possible only if the glide plane passes close to the amide C atom, achievable only if $D_x = D_y$.

Such a situation arises for the 2:1 complex of tetrolamide:acetylenedicarboxylic acid (Nader, 1977). Here $D_x \simeq 12{\cdot}1$ Å and $D_y \simeq 12{\cdot}2$ Å ($D_x \simeq i + 8$ Å, $i \simeq 4{\cdot}1$ Å for C–C≡C–C; $D_y = 2k + l$, $k \simeq 4{\cdot}1$ Å for H_3C–C≡C–C and $l \simeq 4$ Å for a $CH_3\cdots H_3C$ contact). The actual structure (Fig. 5) is analogous to the planar space motif (18), the primary difference being that the acetylenedicarboxylic acid does not lie on a centre of inversion but on a twofold axis, so that the acid molecule adopts a synplanar O=C–C≡C–C=O conformation.

The condition $D_x \simeq D_y$ is also satisfied for the 2:1 complex crotonamide:succinic acid ($D_x \sim 3{\cdot}7 + 8{\cdot}0 = 11{\cdot}7$ Å; $D_y \simeq 2 \times 3{\cdot}8 + 4{\cdot}0 = 11{\cdot}6$ Å). The structure exhibits a packing scheme analogous to space motif (18) as indicated by the characteristic glide axis of 9·5 Å (Table 1). Were the complex to adopt the motif (18) in its planar form the translation repeat normal to the glide plane would be $D_x + D_y = 23{\cdot}3$ Å. The actual length of the appropriate b axis, however, is 16·6 Å (Table 1), implying that the plane of the complex unit (17) is not perpendicular to the glide plane, but rather inclined to it at an angle of $\arcsin(b/D_x + D_y) \sim 45°$. Thus the H-bonding scheme of crotonamide:succinic acid is not planar although the spatial relations between the residues X and Y seem to be satisfied. This type of H-bonding arrangement, as viewed along the 9·5 Å glide, is depicted in (19). Were crotonamide:succinic acid to appear in a planar arrangement of (18), the crotonamide molecules interlinked by N–H···O bonds along the glide would be involved in prohibitively short contacts between the NH_2 group and the β-H atom as indicated in (20). A very similar situation has been encountered in the structure of crotonamide itself (Leiserowitz & Schmidt, 1969).

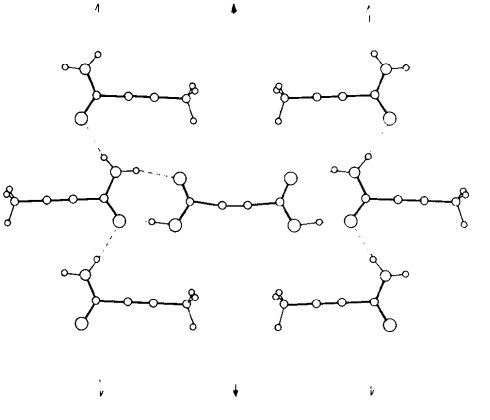
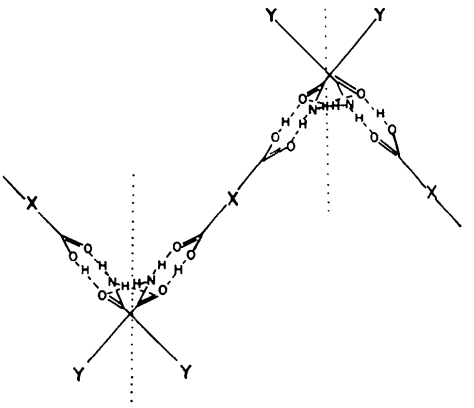


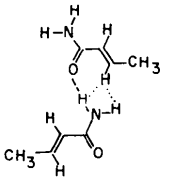
Fig. 5. Tetrolamide:acetylenedicarboxylic acid (Nader, 1977). H-bonding sheet structure.

* An extended arrangement wherein interpair N–H···OCOH bonds are interlinked by glide symmetry cannot be achieved. This may be seen by constructing hypothetical models.

† This N–H···O bond may also be achieved *via* a 2_1 axis, imposing requirements similar to that of the glide; the 2_1 axis must pass through the Y–$CONH_2$ bond and be in the plane of the amide group.



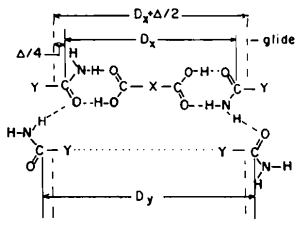
(19) View of space motif (18) along the glide axis in which the amide plane makes a shallow tilt of ~45° with the glide plane.



(20)

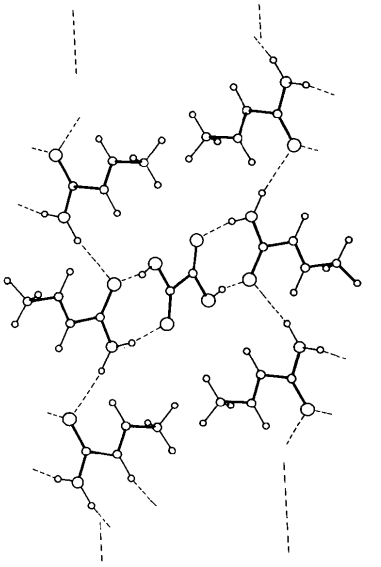
In general the condition $D_x = D_y$ is rarely satisfied, leaving the two alternatives $D_x < D_y$ and $D_x > D_y$ to be considered.

Given $D_x < D_y$, $= \Delta$ say, the separation between the adjacent glide planes in (18) $= D_x + \Delta/2$, so that the glide plane would pass through the H_2NOC-Y bond at a distance of $\Delta/4$ from the amide C atom as shown in (21). An appreciable deviation Δ would induce too long an interpair N—H···O bond. This situation exists for the 2:1 complex of crotonamide:oxalic acid (Leiserowitz & Nader, 1977). Here the estimated mismatch between D_x and D_y (9·5 *versus* 11·6 Å) is 2 Å. Yet this complex crystallizes in the glide motif (18) (Fig. 6*a*). The packing scheme in Fig. 6(*b*), viewed along the H-bonding glide axis, shows how the mismatch Δ is compensated. The complex unit (17) is not inclined at a steep angle to the glide plane but at a shallow angle of 40° which serves to bring the glide-related amide groups into close proximity, yielding a normal N—H···O bond of 2·95 Å.

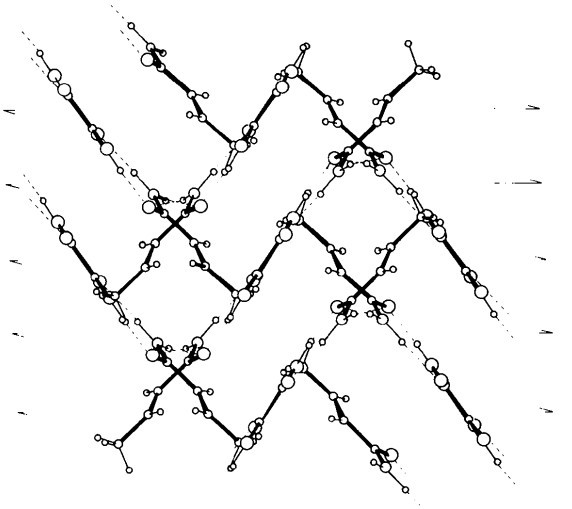


(21) Space motif (18) in which $D_y > D_x$.

In the event where $D_x > D_y = \Delta$ the glide planes in (18) pass through the C=O and C—N amide bonds at a distance of $\Delta/4$ from the C atom as shown in (22). The glide operation yields a geometrically unsatisfactory interpair N—H···O bond if $\Delta/4$ is of appreciable length (*i.e.* 0·5 Å). This N—H···O bond geometry cannot be improved by varying the tilt of the complex unit with respect to the glide plane, unlike the prior condition D_x

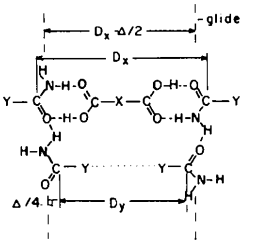


(*a*)



(*b*)

Fig. 6. Crotonamide:oxalic acid. (*a*) H-bonding network viewed along **a**. (*b*) Packing arrangement in the *ab* projection.

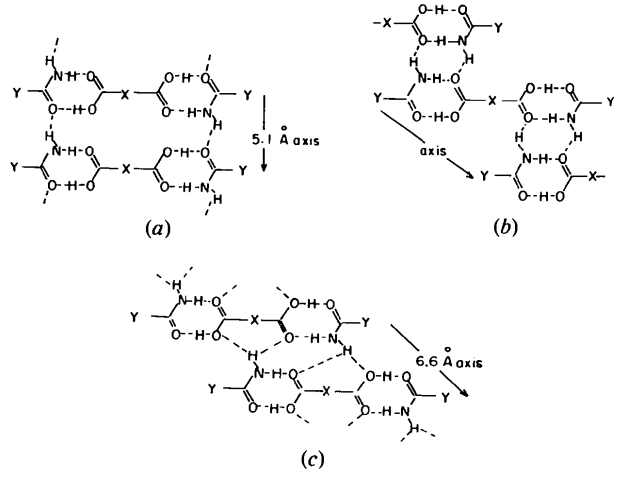


(22) Space motif (18) in which $D_x > D_y$.

$< D_y$. This point is illustrated by the example of the 2:1 complex crotonamide:adipic acid ($D_x \simeq 14{\cdot}6$, $D_y \simeq 11{\cdot}6$ Å) for which $\Delta \simeq 3$ Å, too large a mismatch to permit the glide space motif (18). This is indeed supported by the cell constants (Table 1). Applying the same arguments we rule out packing motif (18) for a number of 2:1 complexes such as fluoro- and chloroacetamide with oxalic acid, supported again by their cell constants (Table 1).

3.3.2. *Translation packing*

All the previously discussed space motifs impose rather severe constraints on the sizes of residues X and Y. These restrictions may be partially overcome by interlinking the complex units (17) by translation in three distinct ways, shown in (23*a*), (23*b*) and (23*c*).



(*a*) (*b*) (*c*)

(23) Three modes of interlinking point motifs (17) by translation.

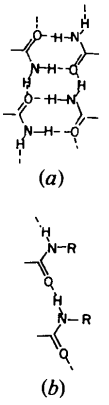
The packing mode (23*a*) exhibits an interpair N–H···$OCNH_2$ bond between amide groups along a 5·1 Å axis. The same type of linkage is frequently encountered in both primary and secondary amides, as shown in (24*a*) and (24*b*). In space motif (23*b*) an interpair N–H···OCOH linkage occurs between amide and carboxyl groups. The interpair N–H···O geometries in (23*a*) and (23*b*) resemble one another; their overall packing structures, however, differ completely and thus their relative merits should depend on the sizes of X and Y. A significant crystallographic distinction between the two space motifs is provided by the translation axis; in (23*a*) it is of constant value (5·1 Å), whereas in (23*b*) it varies according to the length of C–X–C and must always be appreciably longer than in (23*a*).

The packing mode (23*c*) contains interpair N–H··· O(carboxyl) bonds which are bifurcated; both the carbonyl and the hydroxyl O atoms act as proton acceptors. Such a H-bond is possible if the intramolecular separation C–X–C between the two carboxyl groups is sufficiently short, which is satisfied only in oxalic acid. The length of the translation axis in these oxalic acid complexes is a constant ≃6·6 Å.

3.3.2.1. *Space motif* (23*a*). The space motif (23*a*) is strongly indicated for the three molecular complexes of benzamide with oxalic, succinic, and adipic acid (Huang, 1969) since all exhibit 5·1 Å axes (Table 1). Indeed, this mode has been proved for benzamide:succinic acid (Huang, Leiserowitz & Schmidt, 1973) (Fig. 7). For the two remaining complexes the alternative modes (23*b*) and (23*c*) are ruled out by their cell constants since none of their translation axes, and combinations thereof, are compatible with the axial lengths required by (23*b*) and (23*c*).*

A unique feature of the benzamide:succinic acid structure is the non-planarity of its H-bonded carboxyl:amide pair (6). The distortion comprises a twist of 20° between the planes of the amide and carboxyl groups about the N–H···OCOH bond. Such a pronounced distortion is not evident in other structures which contain the carboxyl:amide pair (6). The angle between the planes of the amide and carboxyl groups in the structures of fumaramic acid (Benghiat, Kaufman, Leiserowitz & Schmidt, 1972), furamide:oxalic acid (Huang, Leiserowitz & Schmidt,

* Motif (23*b*) would demand interpair repeat distances ~8·2 and 11·8 Å for the oxalic and adipic acid complexes respectively; (23*c*), which is possible only for the oxalic acid complex, requires a 6·6 Å axis.



(*a*)

(24*a*) Primary amide dimers H-bonded by translation.

(*b*)

(24*b*) Secondary amides H-bonded by translation.

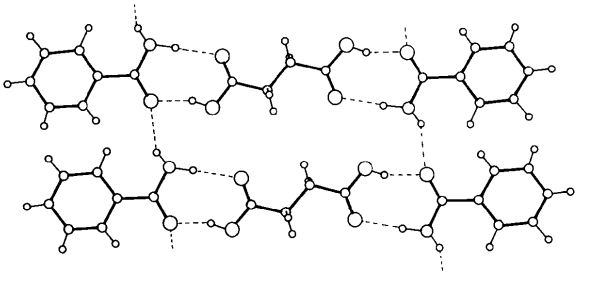


Fig. 7. Benzamide:succinic acid (Huang, Leiserowitz & Schmidt, 1973). H-bonding along the 5·2 Å translation axis.

1973), and tetrolamide:acetylenedicarboxylic acid (Nader, 1977) are 0·5, 3 and 10·0° respectively. As a result of this distortion in benzamide:succinic acid a separation of 3·6 Å is achieved between the carbonyl and hydroxyl O atoms of the carboxyl groups related by the 5·2 Å axis. Were the carboxyl:amide pair (6) coplanar, this O···O separation would be ≃3·0 Å. Thus it was deduced (Huang *et al.*, 1973) that O···O lone-pair repulsions do not permit an approach less than 3·6 Å between two O atoms of neighbouring carboxyl groups arranged in such a way that their lone-pair lobes are partially directed towards each other.

3.3.2.2. *Space motif* (23*b*). No detailed crystal structure analysis of a molecular complex embodying space motif (23*b*) has yet been undertaken. Nevertheless, the evidence for the existence of this motif in the crystal structures of furamide:succinic acid and crotonamide:apidic acid (Huang, 1969) is indisputable. Both are triclinic ($P\bar{1}$) containing one complex unit (17) per unit cell (Table 1). Therefore interpair N—H···O bonds can be formed only *via* translation. Space motif (23*a*) is ruled out by the absence of 5·1 Å axes. Incorporating furamide:succinic acid and crotonamide:adipic acid into motif (23*b*) with reasonable distances and angles (Fig. 8*a* and *b*) yields axial repeats of 9·6 and 10·9 Å respectively, in excellent agreement with the corresponding axial lengths b = 9·7 Å and $|b + c|$ = 11·2 Å (Table 1).

3.3.2.3. *Space motif* (23*c*). The precise packing of motif (23*c*), with its characteristic 6·6 Å axis, follows from the crystal structure of furamide:oxalic acid (Huang, Leiserowitz & Schmidt, 1973) (Fig. 9). The interpair N—H···O bond is bifurcated, since the N—H group straddles the carbonyl and hydroxyl O atoms of oxalic acid with distances N···O(hydroxyl) 3·10 Å and N···O(carbonyl) 2·94 Å. This H-bond system is similar to that observed in azodicarbonamide (Bryden, 1961), which is bifurcated with N—H···N and N—H···O bonds.

The motif (23*c*) in all likelihood appears in the isomorphous crystal structures of fluoroacetamide:oxalic acid and chloroacetamide:oxalic acid although their crystal structures have not yet been determined and their cell dimensions (Table 1) do not unambiguously identify their H-bond space motifs. While the vectors **a** + **b** for both compounds are of the proper length of 6·7 Å for space motif (23*c*) the 4·80 Å axis of the fluoro derivative, and particularly the 5·20 Å axis of the chloro derivative, imply that these two structures might, however, belong to space motif (23*a*). On scrutiny the 4·8 Å axis of the fluoro compound seems too short for an interpair N—H···O bond. Fluoroacetamide itself (Hughes & Small, 1962) exhibits a 5·15 Å axis motif (24*a*) with an interpair N—H···O distance of 2·88 Å. Were the fluoroacetamide complex to form the interpair N—H···O bond along the 4·8 Å axis, the resulting N···O distance would be appreciably shorter than 2·88 Å. Moreover, the average value of this H-bond translation axis in (24*a*) for 23 primary amide structures (Leiserowitz & Schmidt, 1969) is 5·12 Å with a scatter [$= (\Sigma \Delta^2/23 - 1)$] of 0·07 Å and thus is significantly longer than 4·8 Å. Consequently fluoroacetamide:oxalic acid undoubtedly does not appear in the motif (23*a*), but crystallizes in motif (23*c*) forming the bifurcated N—H···O bond along the 6·7 Å axis. Since both the F and Cl complexes appear to be isomorphous we conclude that chloroacetamide:oxalic acid features the same H-bond scheme, despite its 5·2 Å axis.

3.3.2.4. *Comparison of the three translational modes.* The existence of the three translation modes of N—H···O bonding between complex units (17) raises the question of their relative merits. The packing mode (23*a*) suffers from the disadvantage of a non-planar carboxyl:amide pair (6) apparently induced by O···O lone-pair repulsions. These O···O contacts are absent in space motif (23*b*), and therefore one may query why the benzamide complexes with oxalic, succinic,

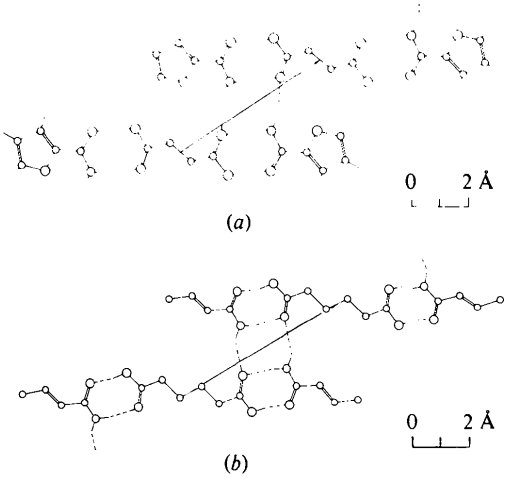


Fig. 8. H-bonding translation motif (23*b*) postulated for (*a*) furamide:succinic acid, (*b*) crotonamide:adipic acid, yields axial repeats of 9·6 and 10·9 Å respectively.

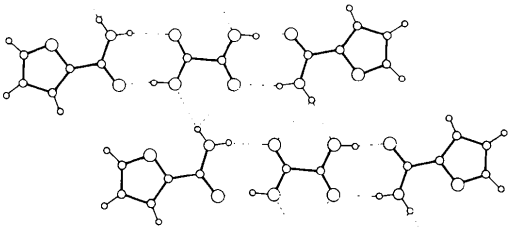


Fig. 9. Furamide:oxalic acid (Huang, Leiserowitz & Schmidt, 1973). H-bonding arrangement along the 6·6 Å axis.

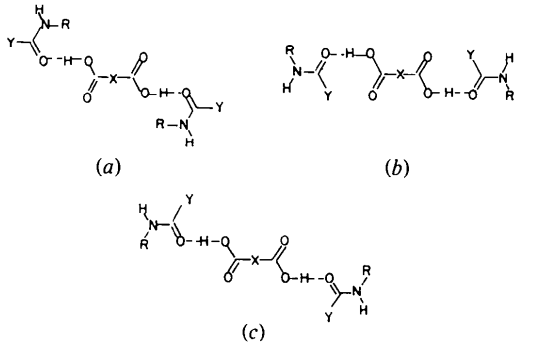
and adipic acid do not adopt this motif instead of (23*a*). It is obvious that such hypothetical arrangements would induce very short intermolecular contacts between the benzamide ring and the carboxylic acid molecule along the H-bond axis. However, we are not certain of the distortions the amide and acid molecules would undergo to relieve the repulsive contacts and how the energy of such a motif would compare with that of the alternative motif (23*a*). Perhaps a more satisfactory approach to this question lies in examining the effect of substituting the bulky phenyl residue by a smaller group, *e.g.* furan or allyl. Indeed furamide:succinic acid and crotonamide: adipic acid both appear in space motif (23*b*) rather than (23*a*) implying that of the two packing arrangements the former is probably preferred, steric factors permitting.

The preference of space motif (23*c*) over that of (23*a*) and (23*b*) in oxalic acid complexes is probably due to the bifurcated N—H···O bonds in (23*c*).

4. Point and space motifs of secondary amide:dicarboxylic acid complexes

The principles applied in constructing the possible modes of H-bonding between secondary amides *Y*—CONH*R* and dicarboxylic acids are similar to those adopted in generating the point and space motifs involving the primary amides.

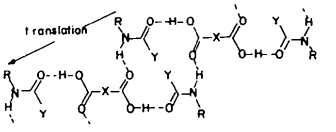
Three cardinal modes (25*a*), (25*b*) and (25*c*) of forming O—H···OCNH*R* bonds may be envisaged.* It is evident that motif (25*a*) may be discarded in view of the too short contact between the OH group and the residue *R*. Motif (25*b*), which is analogous to (7) in the primary amide series, obviously cannot accommodate a bulky *Y* residue. Motif (25*c*), which is analogous to (8) in the primary amides, has no such restrictions.



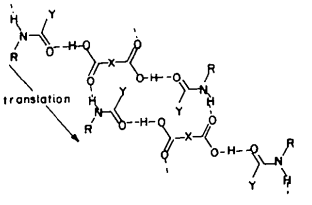
(25) Three possible point motifs linking secondary amides with dicarboxylic acids.

* Only the synplanar O=C—N—*R* conformation is considered in deriving the motifs since this is the conformer invariably found in crystalline secondary amides.

The point motifs (25*b*) and (25*c*) may each be interlinked by N—H···OCOH bonds, *via* translation to generate the one-dimensional space motifs (26) and (27). As planar arrangements these two motifs suffer from the shortcoming of very close contacts.

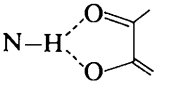


(26) Space motif containing point motifs (25*b*) linked by translation.



(27) Space motif containing point motifs (25*c*) linked by translation.

The H-bond arrangement in *N*-methylformamide: oxalic acid (Leiserowitz & Nader, 1977) (Fig. 10) mostly resembles (26). Its geometry is characterized by a linear and short O—H···OCNH bond of 2·475 Å and a bifurcated H-bonded system



which is approximately coplanar with N···O distances of 2·96 and 3·09 Å. The *N*-methylformamide and carboxyl groups, linked by the O—H···OCNH bond into a point motif akin to (25*b*), are not coplanar, the angle between them being 57°. It is by virtue of this non-planarity that repulsive contacts are avoided between the point motifs (25*b*), which are interlinked by the bifurcated N—H···O bonds *via* a shallow glide, which may be regarded as a pseudo translation in view of the short *b* axis of 3·8 Å (Table 1). The shallow glide performs the role of bringing the N—H bond, which is not coplanar with the oxalic acid molecule in point motif (25*b*), into approximate coplanarity with the oxalic acid molecule to which it is linked by a bifurcated H-bond.

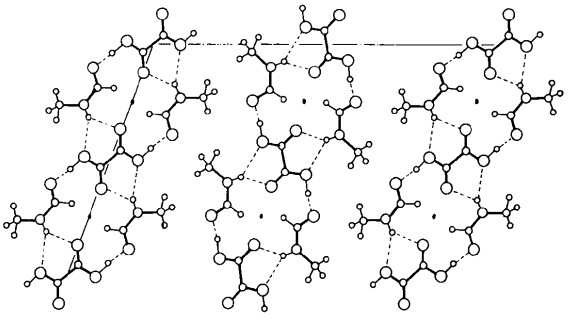


Fig. 10. *N*-Methylformamide:oxalic acid. H-bonding arrangement in the *ac* projection.

Table 2. H-*bonding parameters of amide:carboxylic acid complexes*

d is the *X*–(H)···O distance (Å); α is the *X*–H···O angle (°); β is the C=O···(H)*X* angle (°).

	O–H···O bonds				N–H···O bonds					References
	single O–H···OCNH	ring O–H···OCNH	single O–H···OCOH	ring $N–H_{syn}$···OCNH	ring $N–H_{syn}$···OCOH	$N–H_{anti}$···OCNH	$N–H_{anti}$···OCOH	Bifurcated N–H (O_1(carbonyl), O_2(hydroxyl))		
	d α β	*d* α β	*d* α β	*d* α β	*d* α β	*d* α β	*d* α β	d_1 α_1 β_1	d_2 α_2 β_2	
Formamide: oxalic acid	2·52 173 116·5	—	—	2·99 173 119·4	—	—	2·95 162 133·1	—	—	
Acetamide: oxalic acid*	2·48 167 128·5	—	2·71 168 129·6	2·93 161 124·8	—	—	2·96 173 139·6	—	—	
Acetamide: allenedicarboxylic acid	2·52 169 127·0	—	2·66 157 121·2	3·01 171 127·4	—	—	3·05 177 133·0	—	—	Nader (1977)
Crotonamide: oxalic acid	—	2·61 170 126·7	—	—	3·00 170 115·5	2·95 171 129·0	—	—	—	
Tetrolamide: acetylenedicarboxylic acid	—	2·56 168 116·8	—	—	2·93 163 116·1	2·87 168 112·2	—	—	—	Nader (1977)
Furamide: oxalic acid	—	2·53 170 126·1	—	—	2·92 172 119·2		—	2·91 104 127·2	3·10 172 123·0	Huang, Leiserowitz & Schmidt (1973)
Benzamide: succinic acid	—	2·60 173 126·4	—	— —	2·98 160 117·6	3·02 142 150·1	—	—	—	Huang, Leiserowitz & Schmidt (1973)
N-Methylformamide: oxalic acid*	2·48 174 115·3	—	—	—	—	—	—	2·96 144 129	3·09 143 125	
Formamide: formic acid†	2·60 2·58 174 172 113·0 114·5	—	—	2·99 2·93 176 177 116·8 122·7	—	—	2·95 2·87 151 140 136·0 138·7	—	—	Nahringbauer & Larsson (1969)
Fumaramic acid‡	—	2·66 180 125·6	—	—	2·84 171 120·9	2·94 163 113·6	—	—	—	Benghiat *et al.* (1972)
2,5-Pyridinedicarboxylic acid: dimethylformamide $+H_2O$	2·52	—	—							Ito, Kashino & Haisa (1976)

* Average values of two independent parameters for acetamide:oxalic acid and *N*-methylformamide:oxalic acid.
† Values are given for the two different H-bonding networks (I) and (II) shown in Fig. 2.
‡ Fumaramic acid is not a molecular complex yet it is relevant since it contains the carboxyl:amide ring (6).

N-Methylacetamide:oxalic acid is almost isostructural with the *N*-methylformamide analogue as is evident from their cell constants (Table 1). This is in contradiction with what is found in the analogous primary amide series because acetamide:oxalic acid is not isostructural with formamide:oxalic acid, as discussed in § 3.2.2. The latter complex has a point motif (7) which is analogous to (25*b*), but in a planar arrangement. Since in the secondary amide series the amide group is not coplanar with the oxalic acid molecule in (25*b*), *N*-methylacetamide may easily be inserted into motif (25*b*) without incurring a close $C-CH_3\cdots O{=}COH$ contact and thus a short O–H···O(amide) bond may be formed.

5. H-bonding properties

The systematics of the packing of the amide:acid complexes, and their H-bond lengths and angles (Table 2) may provide a fuller understanding of the H-bonding properties of amides and acids and of the factors responsible for their complexation.

According to a study on the packing modes of primary amides $Y-CONH_2$ (Leiserowitz & Schmidt, 1969), a carbonyl O atom which participates in *two* N–H···O bonds tends to adopt, the residue *Y* permitting, the motif (28) which is coplanar and contains two linear N–H···O bonds symmetrically disposed about the carbonyl bond with C=O···N angles $\simeq 120°$.

(28)

Electron density maps about the carbonyl O atom, as determined from the diffraction analyses of a number of carbonyl systems such as cyanuric acid (Verschoor & Keulen, 1971) (combined X-ray and neutron study at −170 °C) and diketopiperazine (Harel & Hirshfeld, 1977) (X-ray study at −150 °C) display, fairly convincingly, two lone-pair lobes of the O atom in the plane of the carbonyl system C=O at approximately 0·6 Å from the O atom and making an angle of about 110° with the C=O bond. Combining these findings with the favoured geometry of motif (28) suggests that in the preferred H-bonded system the *two* N–H proton donors are directed towards the acceptor O atom approximately along the line of its lone-pair lobes.

The same angular properties as deduced for the N–H···O bonded motif (28) also seem to prevail for the O–H···OCOH bond present in carboxylic acids. Here the carbonyl O atom participates in only *one* H-bond.* A study of the packing modes of carboxylic acids (Leiserowitz, 1976) appears to have provided ample evidence that the O–H···O=C< system is coplanar with an angle C=O···(H)O $\simeq 120°$.

5.1 *Preferred geometry of the* H-*bonded* C(=O)(H–O)(H–N) *system*

The amide:acid complexes follow a trend similar to the primary amides insofar as a carbonyl O atom which participates in *two* H-bonds N–H···O and O–H···O, tends to adopt, the residues *Y* and *X* permitting, a motif (29) whose geometry is analogous to the N–H···O bonded system (28). The justification of the preferences for motif (29) is based primarily on the observation that those complexes which tend to incorporate (29) [namely, formamide:formic acid, formamide:oxalic acid, acetamide:oxalic acid, acetamide:allenedicarboxylic acid, tetrolamide:acetylenedicarboxylic acid, crotonamide:oxalic acid, crotonamide:succinic acid] appearing in space motifs (13), (16) and (18) could as well exist in a translation space motif, *e.g.* (23*b*). In the translation packing the N–H···O bond along the translation axis is non-linear with a C=O···N angle $\simeq 150°$. Thus the translation modes (23*a*), (23*b*) are inferior to (13), (16) or (18). It is noteworthy that most of the complexes which appear in the translation modes (23) cannot, on steric grounds, fit into any of the preferred motifs. As to the relative merits of the preferred motifs (13), (16), and (18), their H-bonding geometries do not permit a clear distinction.

(29)

5.2. H-*bonding lengths*

The O–H···OCNH bond has proved to be surprisingly short in most of the complexes (Table 2), particularly where the amide and carboxyl groups are linked by a *single* H-bond as in point motifs (7), (8), and (25*b*). Its length is 2·50 ± 0·02 Å for formamide:oxalic acid, acetamide:oxalic acid, acetamide:allenedicarboxylic acid, and 2,5-pyridine dicarboxylic acid:dimethylformamide + H_2O (Ito, Kashino & Haisa, 1976), and *N*-methylformamide:oxalic acid. Only in formamide:formic acid were relatively long O–H···O bonds of 2·58 and 2·60 Å found (Table 2).

* It does not necessarily follow that the preferred geometry of a *single* H-bond about a carbonyl O atom is the same as for a double H-bonded carbonyl group, *i.e.* the angle C=O···H–*X* for single O–H···O or N–H···O bonds may not preferentially be ~120°.

The O–H···$OCNH_2$ bond shows much greater variation in length when it forms part of the cyclic carboxyl:amide pair (6). Furamide:oxalic acid and tetrolamide:acetylenedicarboxylic acid form short O–H···O bonds of 2·53 and 2·56 Å whereas in crotonamide:oxalic acid and benzamide:succinic acid these distances are 2·61 and 2·60 Å. Moreover, the structures of fumaramic acid (Benghiat, Kaufman, Leiserowitz & Schmidt, 1972) and of 2-bromosuccinamic acid (Murakami & Iitaka, 1969) both contain the carboxyl:amide pair (6) with O–H···$OCNH_2$ bonds of 2·66 and 2·57 Å respectively. Thus it may be concluded that only those motifs containing a single O–H···OCNH bond, namely point motifs (7), (8) and (25*b*), lead, with only one exception, to the formation of exceptionally short (and therefore strong) O–H···O bonds. Therefore a preference of these motifs over the cyclic structure (6) seems to exist.

There appears to be no obvious distinction in length between dimeric and single O–H···O bonds of carboxylic acids. The average length of the single O–H···O bond of 2·65 Å (Table 3) matches the O–H···O distance of 2·64 Å of a large variety of cyclic dimers (Leiserowitz, 1976). Consequently, there seems to be little doubt that the single O–H···OCNH bond is distinctly shorter than the single or dimeric O–H···OCOH bond. An analogous comparison of N–H···$OCNH_2$ and N–H···OCOH lengths, both for intra- and interpair motifs, does not appear to display any significant pattern (Table 2).

5.3. *The* C=O *length in amides and acids*

In the context of the findings on O–H···OCOH and O–H···OCNH lengths it is significant that the C=O

Table 3. O–H···O *distances* (Å) *between carboxyl groups linked by single* O–H···O *bonds*

Compound	O–H···O distance	Reference
Formic acid	2·58	Holtzberg, Post & Fankuchen (1953)
Acetic acid	2·631	Jönsson (1971)
β-Tetrolic acid	2·655	Benghiat & Leiserowitz (1972)
Maleic acid	2·643	James & Williams (1974)
Cyclopropane-1,1-dicarboxylic acid	2·641	Meester, Schenk & MacGillavry (1971)
Bicyclo[2.2.2]octa-2,5-diene-2,3-dicarboxylic acid	2·590	Hechtfischer, Steigemann & Hoppe (1970)
	2·585	
D-Tartaric acid	2·707	Okaya, Stemple & Kay (1966)
α-Oxalic acid	2·702	Derissen & Smit (1974)
Acetamide:oxalic acid	2·71	
Acetamide:allenedicarboxylic acid	2·66	Nader (1977)

Table 4. *Bond lengths* (Å) *and angles* (°) *of amide and carboxyl groups*

	Amide group			Carboxyl group			
Compound	C=O	C–N	O=C–N	C=O	C–OH	O=C–O	References
Formamide:formic acid	1·251*	1·312	124·6	1·202*	1·320	125·4	Nahringbauer & Larsson (1969)
Formamide:oxalic acid	1·246	1·298	123·9	1·203	1·302	125·8	
N-Methylformamide:oxalic acid	1·234*	1·296	124·7	1·194*	1·295	125·9	
Acetamide:oxalic acid	1·251*	1·301	120·0	1·212†	1·298	126·2	
Acetamide:allenedicarboxylic acid	1·255	1·305	120·8	1·222*	1·294	124·2	Nader (1977)
Tetrolamide:acetylenedicarboxylic acid	1·248	1·313	123·2	1·204	1·297	126·4	Nader (1977)
Crotonamide:oxalic acid	1·255	1·324	121·7	1·201	1·307	126·1	
Furamide:oxalic acid	1·250	1·322	123·6	1·201	1·310	126·2	Huang, Leiserowitz & Schmidt (1973)
Benzamide:succinic acid	1·230	1·335	122·0	1·194	1·318	123·1	Huang, Leiserowitz & Schmidt (1973)
Fumaramic acid	1·247	1·323	122·6	1·209	1·310	124·0	Benghiat *et al.* (1972)
Acetamide (orthorhombic)	1·260*	1·334	123·1				Hamilton (1965)
Acetamide (rhombohedral)	1·241	1·324	122·6				Denne & Small (1971)
Benzamide	1·249	1·342	122·1				Blake & Small (1972)
α- and β-oxalic acid				1·214*	1·298	126·8	Derissen & Smit (1974)
Allenedicarboxylic acid				1·222*	1·293	124·3	Leiserowitz & Nader (1973)

* Mean values of two independent groups.
† Mean values of four independent groups.

length is, on average, 0·04 Å longer in amides than in acids (1·25 *versus* 1·21 Å) (Table 4). This implies that the carbonyl O atoms of the two groups have different electron density distributions and therefore different proton acceptor properties, the amide carbonyl group probably being the stronger acceptor. This statement is also borne out by the fact that in the complexes it is the amide O atom which participates in two H-bonds rather than the carboxyl O atom. The only exception is space motif (23*b*).

5.4. *The bifurcated* N–H···O *bond*

A bifurcated N–H···O bond occurs in the oxalic acid complexes which appear in space motifs (23*c*) and (26). On inspection it would seem that the bifurcated N–H···O system could have been avoided by formation of a single N–H···O(carbonyl) bond. Thus we conclude, tentatively, that the bifurcated N–H···O bond is preferred over the single N–H···O(carbonyl) bond.

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