

The Role Played by C–H···O and C–H···N Interactions in Determining Molecular Packing and Conformation

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Abstract

The role played by C–H···O and C–H···N interactions in determining molecular packing and conformation is examined in terms of packing and atom-atom potential-energy calculations for a variety of representative molecular crystals. The Coulomb and van der Waals energy contributions of C(sp³)–H···O, C(sp²)–H···O and C(sp)–H···O interactions in various crystal structures have been analysed. C–H···O,N contacts are instrumental in fixing packing motifs in *N*-methylpropiolamide, substituted quinones, quinone–phenol complexes, α -glycine, pyrazinecarboxamide, uracil, α,β -unsaturated carboxylic acids *R*–CH=CH–CO₂H, barbital–acetamide complex, and ketones. The uncommon antiplanar C=C–C=O conformer in *R*–CH=CH–CO₂H is stabilized through C–H···O interactions.

1. Introduction

C–H···O interactions have long been a subject of controversy. Conclusive crystallographic and spectroscopic evidence for C–H···A interactions exist where A is a strong proton acceptor and the C–H forms part of a haloform molecule or hydrogen cyanide or acetylene derivatives (Sim, 1967). The existence of C–H···O hydrogen bonds had been claimed by a number of workers, notably Sutor (1963), on the basis of short C to O distances of approximately 3.2 Å. Donohue (1968) summarized the evidence in the solid state, for C–H groups which do not appear to be under the influence of activating groups which tend to promote ionization of the H atom. He challenged the existence of such C–H···O bonds, arguing that an O···H distance of 2.4 Å is not presumptive evidence of hydrogen-bond formation and doubted whether many of the short C–H···O distances (H···O 2.2 Å) can be regarded as hydrogen bonds in the same sense that the term is used for O–H···O, N–H···O and N–H···N systems. Recently crystallographic evidence for the existence of C–H···O and C–H···N hydrogen bonds was provided by Taylor & Kennard (1982). By a statistical analysis of 113 neutron diffraction crystal structures, they found that H atoms covalently bound to C have a statistically

significant preference to form intermolecular contacts to O atoms rather than to C or H atoms.

We shall try to establish other criteria for the role played by the C–H···O interaction in formation of the crystal structure, such as whether the motif involving the C–H···O contact repeats itself in a number of different structures and whether the molecule in question could not have adopted a more favourable arrangement or conformation, but for the C–H···O contact. Our analysis is not a statistical overview but a focusing on a variety of representative crystal structures and motifs, incorporating the proton donors C(sp)–H, C(sp²)–H and C(sp³)–H. Our approach will be quantitative, using atom–atom potential-energy calculations. The contributions of the Coulomb (*i.e.* electrostatic) and van der Waals energies were compared for a variety of observed and hypothetical motifs. The electrostatic parameters which were used for the calculations of the Coulomb energies were derived from experimental deformation densities obtained from low-temperature X-ray diffraction data. These include atomic net charges, dipole and quadrupole moments placed at the atomic positions. Details of the method are described elsewhere (Berkovitch-Yellin & Leiserowitz, 1980, 1982).

2. Comparison of $\equiv\text{C}-\text{H}\cdots\text{O}(\text{carboxyl})$, $\equiv\text{C}-\text{H}\cdots\text{O}(\text{amide})$ and $\equiv\text{C}-\text{H}\cdots\text{C}\equiv\text{C}$ interactions

The acetylenic $\equiv\text{C}-\text{H}\cdots\text{O}$ bond has been well established from crystal structure and spectroscopic data. The crystal structure of *N*-methylpropiolamide (Leiserowitz & Tuval, 1978) is an example in which the molecules are so arranged that the O(amide) participates in both N–H···O and C–H···O hydrogen bonds (Fig. 1). In this crystal the C–H···O distance is 3.2 Å, the C–H···O system is linear, the C–O···H angle is 123° and the C–H bond is almost coplanar with the carbonyl system >C=O. In contradistinction, propiolic acid (L. Leiserowitz & I. Olovsson, unpublished results) does not incorporate an analogous motif (Fig. 2); the crystal structure shows hydrogen-bonded dimers interlinked by a C–H···C \equiv C(midpoint) contact of 3.8 Å (H···C \equiv C 2.8 Å) and a nonlinear C–H···O(carbonyl) contact of 3.3 Å (H···O 2.8 Å).

It appears that the carbonyl O atom and the $C\equiv C$ triple bond compete for the C-H proton in the crystal structures of propiolic acid and *N*-methylpropiolamide. It is well established that the amide O atom is a far stronger proton acceptor than the corresponding O atom of the carboxyl group. This fact has been demonstrated in the solid, by packing systematics (Leiserowitz & Nader, 1977), electron density mapping (Berkovitch-Yellin, Leiserowitz & Nader, 1977), and atom-atom potential-energy calculations (Berkovitch-Yellin & Leiserowitz, 1982; Berkovitch-Yellin, Ariel & Leiserowitz, 1983). On these premises the distinct difference in C-H...O and C-H...C \equiv C contacts between *N*-methylpropiolamide and propiolic acid may be attributed to the relative proton-acceptor properties of the O(amide) and O(carboxyl) atoms and the C \equiv C bond. From a correlation curve relating the amount of bonding charge and bond length (Berkovitch-Yellin & Leiserowitz, 1977), it was deduced that the excess charge in the C \equiv C bond is approximately 0.4e, which is larger than the net atomic charge of -0.22e on the carbonyl O atom of the carboxyl group (Berkovitch-Yellin & Leiserowitz, 1982) but comparable to the net atomic charge of

-0.38e on the amide O atom (Berkovitch-Yellin & Leiserowitz, 1980).

In order to account for the observed C-H...O and C-H...C \equiv C contacts in the crystal structures of propiolic acid and in *N*-methylpropiolamide, we mapped the electrostatic potential energy around these molecules by placing a positive unit charge at the locus of the points shown in Fig. 3(a). These points represent the nearest approach distances of the acetylenic proton donor to the reference molecule. The potential for propiolic acid (Fig. 3b) demonstrates comparable energies for C-H...C \equiv C(midpoint), and C-H...O interactions, whereas in *N*-methylpropiolamide there is a distinct preference for the C-H...O interaction. These results are completely in agreement with experiment.

3. The C(sp²)-H...O interaction

3.1. Quinones

There are common geometric patterns in several quinone packing arrangements which have been interpreted in terms of C-H...O=C interactions (Bernstein, Cohen & Leiserowitz, 1974). These structures incorporate the motif shown in (1). The C-H...O

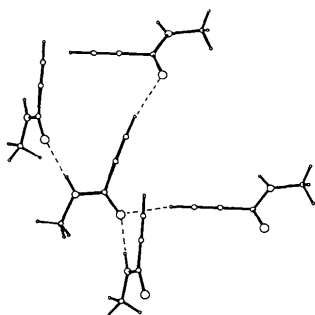


Fig. 1. Arrangement of N-H...O and C-H...O hydrogen bonds in *N*-methylpropiolamide.

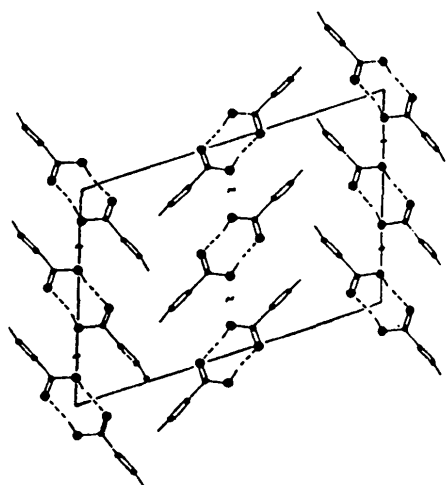


Fig. 2. Propiolic acid. Packing arrangement.

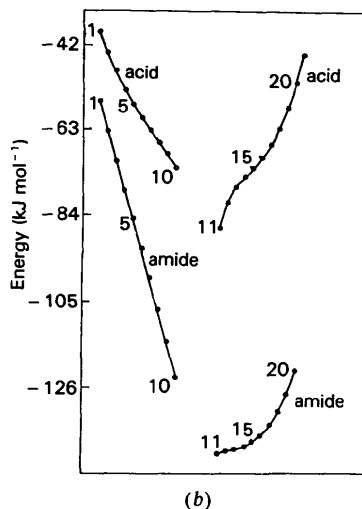
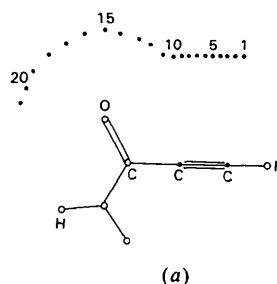
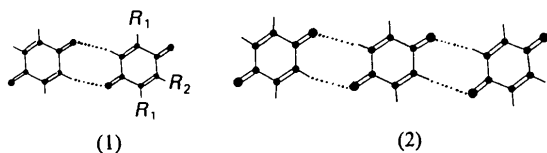


Fig. 3. (a) Discrete points of closest approach of proton donor to *N*-methylpropiolamide and propiolic acid. (b) Electrostatic potential energy (kJ mol⁻¹) at the discrete points of (a).

and $\text{H}\cdots\text{O}$ distances are about 3.5 and 2.5 Å respectively.

In 1,4-benzoquinone (Trotter, 1960) each molecule participates in several $\text{C}-\text{H}\cdots\text{O}$ contacts (Fig. 4), forming a layer structure. Within each layer neighbouring molecules, related by translation along the 6.7 Å axis, are connected by $\text{C}-\text{H}\cdots\text{O}$ contacts of 3.5 Å, as in (1), generating a coplanar ribbon (2). Adjacent ribbons, related by twofold screw axes, are interconnected by $\text{C}-\text{H}\cdots\text{O}$ contacts of 3.38 Å in a triangular pattern linking each molecule of one ribbon to two molecules of the adjacent ribbon.



A strong argument for the role played by $\text{C}-\text{H}\cdots\text{O}$ interactions in determining this layer structure and other layer structures involving benzoquinone molecules is provided by the molecular arrangements in the 1:1 complex between thymine and 1,4-benzoquinone (Sakurai & Okunuki, 1971), in the quinhydrone complex (Sakurai, 1965), in the 1:1 complex of benzoquinone with chlorophenol (Shipley & Wallwork, 1967) and by the observation that tetrafluoro-*p*-benzoquinone (Meresse, Courseille & Chanh, 1974) does not form a layer structure as in 1,4-benzoquinone. The first-mentioned crystal structure contains alternating thymine and benzoquinone layers. The benzoquinone sheet structure in the thymine complex is practically identical with that in the pure benzoquinone crystal structure. Since a sheet of benzoquinone molecules has completely different environments in these two crystal structures, the layer motif must be determined by intralayer, and not interlayer, forces. The quinhydrone complex (Fig. 5) contains alternating ribbons of benzoquinone and of hydroquinone molecules stabilized by $\text{C}-\text{H}\cdots\text{O}(\text{carbonyl})$ and $\text{C}-\text{H}\cdots\text{O}(\text{hydroxyl})$ interactions

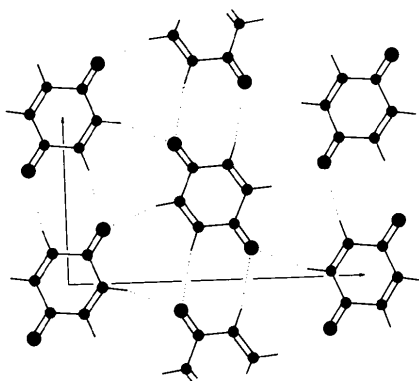


Fig. 4. Benzoquinone. Layer structure. The $\text{C}-\text{H}\cdots\text{O}$ contacts are marked.

respectively. The 1:1 complex of benzoquinone and *p*-chlorophenol (Fig. 6) displays $\text{C}-\text{H}\cdots\text{O}(\text{carbonyl})$ contacts in the ribbon motif (2).

In order to verify the role played by $\text{C}-\text{H}\cdots\text{O}$ interactions in stabilizing motifs (1) and (2) and in determining the layer structures of the 1,4-benzoquinones cited above, we calculated the energy of the coplanar dimer (1) (with $R_1 = R_2 = \text{H}$) as a function of molecular displacement along L and M (Fig. 7a). The energy map (Fig. 7b) displays a minimum corresponding to a dimer arrangement (Fig. 7a) similar to that observed in the (substituted) benzoquinone crystal structures which explains the occurrence of (1) for 1,4-benzoquinone and substituted benzoquinones and of the ribbon (2) for 1,4-benzoquinone. Further, we examined the variation in energy of the 1,4-benzoquinone layer (Fig. 4) as a function of the offset along L between adjacent ribbons (2) related originally by twofold screw symmetry (Fig. 8). It is evident that the observed structure corresponds to the energy minimum, where electrostatic forces play the dominant role. We have also calculated the variation in energy as a function of offset between adjacent ribbons (2) related by translation (Fig. 9). The energy minimum corresponds to a layer arrangement (Fig. 9b) in which the interribbon offset provides for a $\text{C}-\text{H}\cdots\text{O}$ interaction; the major contribution to the energy is again electrostatic. The minimum in energy of this layer (Fig. 9a) is comparable to that of the observed layer of benzoquinone (Fig. 8), suggesting that interlayer and not intralayer forces play the deciding role in determining the observed layer structure. It is noteworthy that an arrangement similar to this hypothetical layer, in which the ribbons are related by translation, occurs in the crystal structure of the 1:1 complex of benzoquinone with *p*-chlorophenol (Fig. 6).

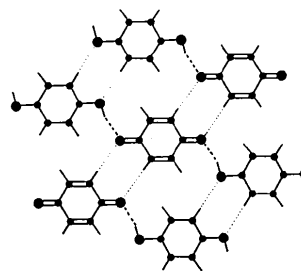


Fig. 5. Triclinic quinhydrone layer structure. $\text{C}-\text{H}\cdots\text{O}(\text{carbonyl})$, $\text{C}-\text{H}\cdots\text{O}(\text{hydroxyl})$ and $\text{O}-\text{H}\cdots\text{O}$ contacts are shown.

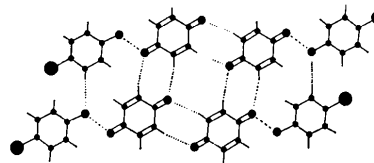


Fig. 6. The complex *p*-chlorophenol:1,4-benzoquinone layer structure. $\text{C}-\text{H}\cdots\text{O}(\text{carbonyl})$, $\text{C}-\text{H}\cdots\text{O}(\text{hydroxyl})$ and $\text{O}-\text{H}\cdots\text{O}$ contacts are shown.

3.2. $C(sp^2)-H\cdots O(\text{carbonyl})$ interaction in carboxylic acids

Qualitative studies of various packing arrangements in carboxylic acids had indicated that attractive C-H...O interactions play an active role in stabilizing certain packing arrangements and in fixing molecular

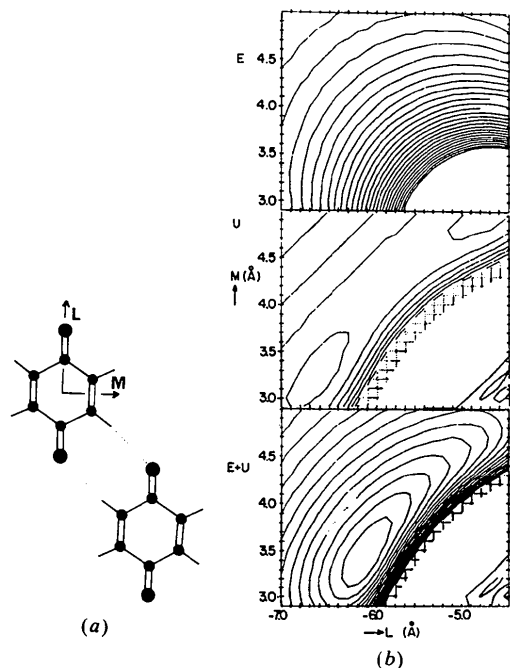


Fig. 7. (a) Arrangement of benzoquinone dimer. (b) Variation of energy of benzoquinone dimer as function of offset along L and M (E Coulomb energy, U van der Waals energy). The minimum is at $l = -6.0$, $m = 3.5$ Å. The observed values are $l = -5.5$, $m = 3.9$ Å.

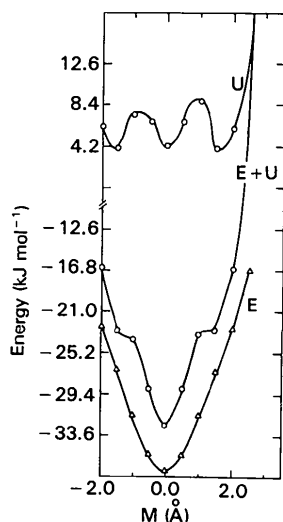
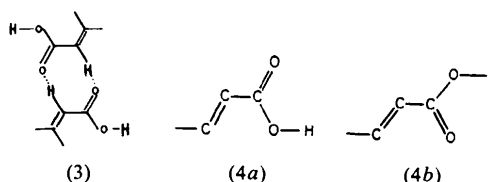


Fig. 8. Benzoquinone. Variation in energy of ribbons (2) interrelated by 'twofold screw' symmetry as a function of the offset between ribbons from the observed structure ($m = 0$). The separation of ribbons along L was kept at the observed distance of $l = 6.2$ Å (see Fig. 4).

conformation (Leiserowitz, 1976). These deductions were put on a sound footing by energy calculations (Berkovitch-Yellin & Leiserowitz, 1982); It was demonstrated that motif (3), incorporated in several crystal structures, is stabilized by C-H...O interactions. This motif is possible only if the carboxyl moiety $\text{CH}=\text{CH}-\text{CO}_2\text{H}$ exhibits the antiplanar $\text{CH}=\text{CH}-\text{C}=\text{O}$ conformation (4a), as against the synplanar conformation (4b) which is preferred in terms of intramolecular forces. It was found that all crystal structures which exhibit the antiplanar conformer (4a) incorporate the C-H...O(carbonyl) contact (3). Thus it was deduced that this conformer is stabilized by these interactions.



This deduction was examined in detail for fumaric acid, which exhibits an antiplanar $\text{C}=\text{C}-\text{C}=\text{O}$ con-

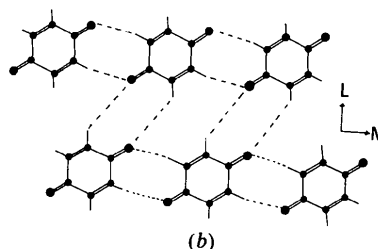
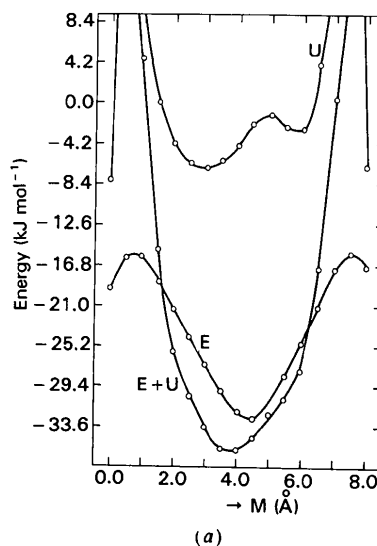
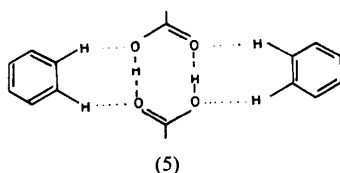


Fig. 9. Benzoquinone. (a) The variation in energy of ribbons (2) related by translation as a function of offset along M . The separation between ribbons along L is 6.5 Å, which was found to correspond to the minimum energy. (b) Arrangement which corresponds to the minimum energy ($l = 6.5$, $m = 4$ Å).

formation in the layer structure shown in Fig. 10. To establish the role played by the C-H...O interactions the energy of the layer was calculated as a function of offset between adjacent hydrogen-bonded chains. The resulting energy minimum corresponds to the observed offset which is determined mainly by Coulomb forces. A similar calculation was carried out for the hypothetical synplanar conformer. Here the arrangement corresponding to the energy minimum incorporates a C-H...O(hydroxyl) contact, instead of the C-H...O(carbonyl) contact, and is 4.6 kJ mol^{-1} less stable than the observed layer structure. We concluded that in this system CH...O(carbonyl) interactions determine both the molecular conformation and the offset between the hydrogen-bonded chains.

Several substituted benzoic acids exhibit motif (5). The question as to whether this motif is stabilized by C-H...O interactions was considered by energy calculations. It was demonstrated that van der Waals forces, and not Coulomb forces, play the primary role in stabilizing motif (5) (Berkovitch-Yellin & Leiserowitz, 1982).



3.3. Can $C(sp^2)\text{-H}\cdots\text{O}$ or $C(sp^2)\text{-H}\cdots\text{N}$ interactions induce less favourable hydrogen-bonding arrangements?

We shall now examine the crystal structures of the β and δ forms of 2-pyrazinecarboxamide which incorporate long $\text{NH}\cdots\text{O}$ bonds, and that of uracil which contains an irregular $\text{N-H}\cdots\text{O}$ hydrogen-bond arrangement.

2-Pyrazinecarboxamide crystallizes in four modifications, α , β , γ and δ (Tamura, Kuwano & Sasada, 1961). The α form (Takaki, Sasada & Watanabe, 1960) contains two types of cyclic hydrogen-bonded pairs, $\text{N-H}\cdots\text{O}$ bonds of 2.90 \AA and $\text{N-H}\cdots\text{N}$ bonds of 3.14 \AA , as shown in (6).

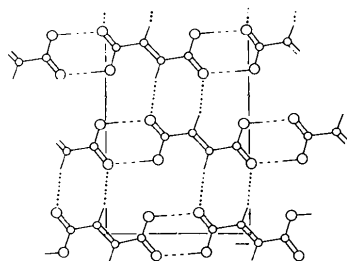
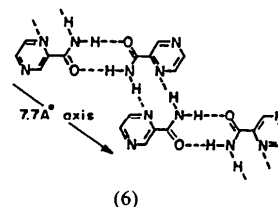
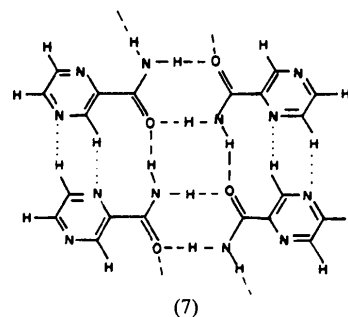


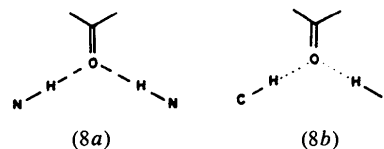
Fig. 10. Fumaric acid layer structure.



The β and δ forms exhibit hydrogen-bonding motifs which are similar to each other and exemplified in (7). In the β form (Rø & Sørum, 1972a) the cyclic hydrogen-bonded pairs ($\text{N-H}\cdots\text{O}$ 2.9 \AA) are inter-linked by $\text{N-H}\cdots\text{O}$ bonds of 3.24 \AA and $\text{C-H}\cdots\text{N}$ contacts of 3.38 \AA . In the δ form (Rø & Sørum, 1972b) the corresponding $\text{N-H}\cdots\text{O}$ and $\text{C-H}\cdots\text{N}$ distances are 3.48 and 3.40 \AA . These results suggest that the pronounced stretchings of the $\text{N-H}\cdots\text{O}$ bonds in the β and δ forms are compensated by the presence of interactions involving the $\text{C-H}\cdots\text{N}$ contacts of 3.4 \AA . Furthermore, we may, by analogy, regard a $\text{C-H}\cdots\text{N}$ or $\text{C-H}\cdots\text{O}$ interaction as not insignificant if the $\text{C}\cdots\text{O}$ or $\text{C}\cdots\text{N}$ distance is $0.2\text{--}0.3 \text{ \AA}$ longer than 3.2 \AA . Such a long contact would hardly have been considered as constituting a significant $\text{C-H}\cdots\text{N}$ or $\text{C-H}\cdots\text{O}$ interaction if just distance criteria were paramount.



In the crystal structure of uracil (Stewart & Jensen, 1967) one carbonyl O atom participates in two $\text{N-H}\cdots\text{O}$ hydrogen bonds, (8a), and the other, (8b), makes short contacts of 3.35 \AA with two C-H bonds. This arrangement is not in keeping with the observed tendency of the maximum number of potential hydrogen-bonding acceptor groups to participate in hydrogen bonds (Etter, 1982; Berkovitch-Yellin *et al.*, 1983). A more homogeneous hydrogen-bonded structure could have been formed were both carbonyl O atoms to participate in $\text{N-H}\cdots\text{O}$ bonds, as in 5-flourouracil (Fallon, 1973) or 6-azauracil (Singh & Hodgson, 1974), suggesting that the observed structure of uracil is stabilized by the contributions of the two $\text{C-H}\cdots\text{O}$ interactions.



4. The C(sp³)-H...O contact

4.1. Glycine

α -Glycine (Legros & Kvick, 1980) crystallizes in the centrosymmetric monoclinic space group $P2_1/n$ ($a = 5.18$, $b = 11.8$, $c = 5.45$ Å, $\beta = 112^\circ$). As shown in Fig. 11, the molecules form hydrogen-bonded layers parallel to the ac plane, in which they are related to each other by translation only. Each layer is interlinked to its neighbour on one side across centres of inversion by N-H...O bonds (H...O 2.05 Å) giving a centrosymmetric bilayer, and by an n glide to its other neighbour, by C-H...O contacts of 3.25 Å (H...O 2.4 Å).

Given the centrosymmetric bilayer which incorporates intralayer N-H...O bonds, the question we address ourselves to is the role the C-H...O contact plays in determining the juxtaposition between bilayers. We calculated the various contributions to the energy of interaction of two glycine molecules forming the C-H...O contact. The electrostatic parameters for glycine were derived from an experimental deformation density distribution of crystalline glycine (Legros & Kvick, 1980). The total energy (electrostatic E + van der Waals U) is -14 kJ mol⁻¹.

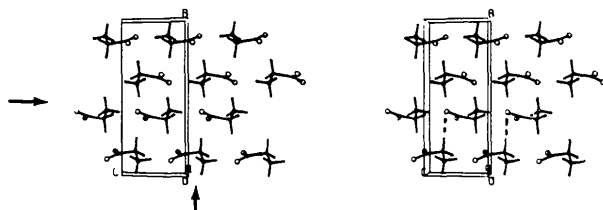


Fig. 11. The α form of glycine. Packing arrangement. The C-H...O contacts are marked. The horizontal arrow indicates the array of glide-related molecules, and the vertical arrow the donor molecule.

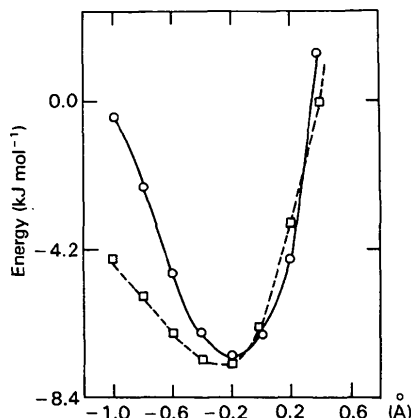


Fig. 12. The α form of glycine. The interaction energy between one glycine donor molecule and an array of glide-related molecules along the c axis. Open circles for the whole glycine molecule as donor, open squares for only the C-H group as donor.

Of this sum the contributions arising from interaction between only the C-H group of the proton-donor molecule and the whole acceptor molecule are $E = -13$ kJ mol⁻¹ and $U = 4$ kJ mol⁻¹, yielding a total of -9 kJ mol⁻¹. Thus the contribution of the C-H...O interaction is significant. The total energy of interaction between a C-H donor glycine molecule, and an array of glide-related molecules along the c axis (marked in Fig. 11) was calculated as a function of offsetting this array of molecules along c , for the donor glycine molecule as a whole and for its C-H moiety only. The resulting energy curves, shown in Fig. 12, are very similar, indicating that the C-H...O interaction determines to a large extent the interbilayer arrangement. The energy of an alternative packing arrangement, in which the bilayers are related by translation, was checked as a function of the offset and separation between bilayers: it yielded a similar interbilayer arrangement incorporating approximately linear C-H...O contacts.

4.2. Acetamide, acetic acid and the acetyl group

The C-H groups of acetamide appear to participate in C-H...O interactions. This interaction was indirectly suggested (Berkovitch-Yellin & Leiserowitz, 1980) by a comparison of the isomorphous crystal structures of urea-barbital (Gartland & Craven, 1974) and acetamide-barbital (Hsu & Craven, 1974). Urea forms a bifurcated bond (2.95, 3.16 Å) with an O atom of barbital (Fig. 13a). Acetamide makes similar contacts in which an acetamide C-H...O contact of length 3.45 Å replaces a urea N-H...O bond (Fig. 13b). This hypothesis was substantiated by calculation which yielded a Coulomb energy of -9 kJ mol⁻¹ for a C...O separation of 3.3 Å.

Acetic acid (Nahringbauer, 1970) appears in a hydrogen-bonding chain motif which incorporates the pseudo centrosymmetric dimer (9) in which the O-H...O bond, of length 2.63 Å, is complemented by a C-H...O contact of 3.43 Å. We found by calculation (Berkovitch-Yellin & Leiserowitz, 1982) that the energy of this dimer is -18 kJ mol⁻¹, almost 70% of which is due to Coulomb forces. The energy of acetic acid in a 'normal' centrosymmetric dimer (10) is -27 kJ mol⁻¹. Ascribing half of this energy to each O-H...O bond, it appears that the C-H...O interaction contributes 4 kJ mol⁻¹ to the stabilization of the observed dimer (9).

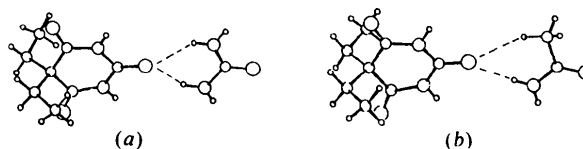
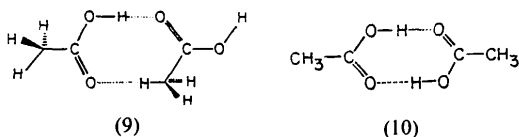


Fig. 13. Hydrogen-bonding motifs of (a) barbital:urea complex, and (b) barbital:acetamide complex.



Analogous arrangements to the dimer motif (10) have been found in two 4-acetylbiphenyl derivatives (Sutherland & Hoy, 1968, 1969) depicted in Fig. 14 and in the host-guest crystalline complexes of deoxycholic acid with methyl alkyl ketones $\text{CH}_3\text{-CO-(CH}_2)_n\text{-CH}_3$. In these complexes (Popovitz-Biro, Chang, Tang, Shochet, Lahav & Leiserowitz, 1980) the guest ketone molecules form cyclic pairs in the chiral inclusion channels, for ethyl methyl ketone and methyl pentyl ketone, with $\text{C}\cdots\text{O}$ distances of 3.7 Å.

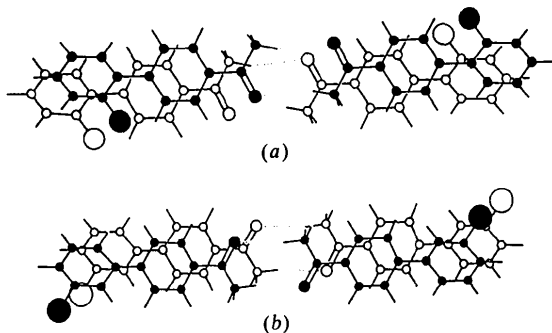


Fig. 14. Part of a stack of dimers of 4-acetylbiphenyl derivatives. (a) 4-Acetyl-2'-chlorobiphenyl. (b) 4-Acetyl-3'-bromobiphenyl [H atoms of the CH_3 group of (b) were not reported].

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