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COMPARATIVE STUDY OF CRYSTAL PACKING IN AMIDO-BENZOIC AND AMIDO-PERBENZOIC ACIDS

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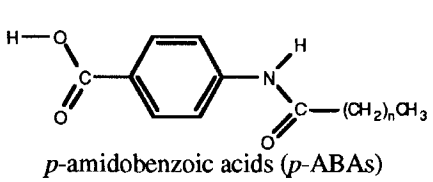
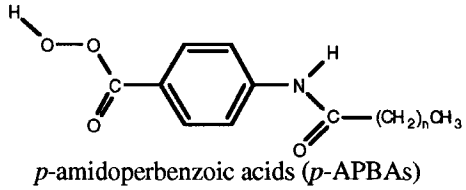
Abstract Hydrogen-bond arrangements in acid and peracid-amides are discussed. The familiar acid dimer motif is observed for these acids and dimers are linked through amide-amide hydrogen-bonds to form ribbon or sheet networks. Peracid dimers are not observed and instead extensive networks are built up from peracid proton to amide carbonyl hydrogen-bonds and amide proton to peracid group hydrogen-bonds. This last interaction can be two-centred involving the peracid carbonyl, or three-centred involving the peracid cabonyl and terminal peroxy oxygen.

INTRODUCTION

In previous communications we have reported on the role of hydrogen-bonding in the crystal packing of a series of *p*-amidobenzoic acids[1,2] (*p*-ABA's), paying particular attention to the influence of alkyl chain length. Here we extend the investigation to consider the packing in the less familiar peroxycarboxylic acid analogs - *p*-amidoperbenzoic acids (*p*-APBA's) - (Figure 1) which possesses an alkyl chain of variable length.



p-amidobenzoic acids (*p*-ABAs)



p-amidoperbenzoic acids (*p*-APBAs)

FIGURE 1 The general molecules studied with variable alkyl chain length 'n'.

Six crystal structures have been determined for the *p*-ABA series, and four in the *p*-APBA series. Unit cell dimensions, space groups and crystal habit are summarised in Table I. [It should be noted that only poor quality crystals could be obtained for *p*-ABA with n = 4. As a result full structure solution could not be made, although the unit cell could be determined.] Extensive hydrogen-bond networks have been identified in each of the acid and peracid structures.

TABLE I Crystal data for the *p*-ABA and *p*-APBA structures.

	n	crystal habit	space group	a/(Å)	b/(Å)	c/(Å)	α/(°)	β/(°)	γ/(°)
p-ABA	0[3]	Plate	$P\bar{1}$	6.986(1)	12.623(1)	5.005(4)	102.58(1)	101.84(1)	83.82(6)
	1*	Rod	$P2_1/n$	5.135(1)	24.556(5)	9.496(2)	90	105.33(3)	90
	2	Plate	$P\bar{1}$	5.120(6)	6.595(2)	15.786(3)	100.98(2)	94.48(5)	98.15(5)
	3[4]	Plate	$P\bar{1}$	5.075(3)	6.601(1)	17.755(4)	81.33(2)	84.08(2)	80.52(3)
	3	Rod	$P2_1/c$	5.081(4)	24.066(6)	9.662(4)	90	82.06(6)	90
	4#	Plate	-	5.067(1)	6.766(4)	18.963(3)	88.08(3)	82.93(2)	79.54(4)
	7	Plate	$P\bar{1}$	5.176(1)	6.731(5)	22.127(17)	92.76(6)	91.14(4)	100.06(4)
p-APBA	0	Rod	Cc	5.054(1)	14.747(5)	12.568(3)	90	92.88(2)	90
	1	Rod	Cc	4.885(1)	15.680(4)	12.793(3)	90	90.21(2)	90
	2	Cuboid	Pbcm	10.750(3)	14.477(6)	6.875(3)	90	90	90
	3	Rod	$P2_1/c$	10.729(5)	14.026(7)	8.654(3)	90	111.59(3)	90

* - acetic acid solvate; # - full structure has not been determined due to poor crystal quality.

DISCUSSION OF STRUCTURES

General Packing in Acids and Peracids

Very little has been reported on the hydrogen-bonding within peracid crystal structures compared to the much studied acids[5]. Three uncharged peracid crystal structures were found by a recent search of the Cambridge Structural Database[6] - *p*-nitroperbenzoic acid[7], *o*-nitroperbenzoic acid[8] and peroxypelargonic acid[9]. While in similar acids (*p*-nitrobenzoic acid[10] and *o*-nitrobenzoic acid[11]) hydrogen-bonding produces the familiar centrosymmetric 8-membered ring dimer motif, ring dimers are not found the peracid structures. Peracid to peracid hydrogen-bonds are formed, however, between molecules related by a two-fold screw or glide operation to form chains of molecules. The interaction is either two-centred with the peracid carbonyl oxygen acting as the lone acceptor (as shown schematically in Figure 2a) or three-centred with both the carbonyl oxygen and terminal peroxy oxygen acting as hydrogen-bond acceptors (Figure 2b).

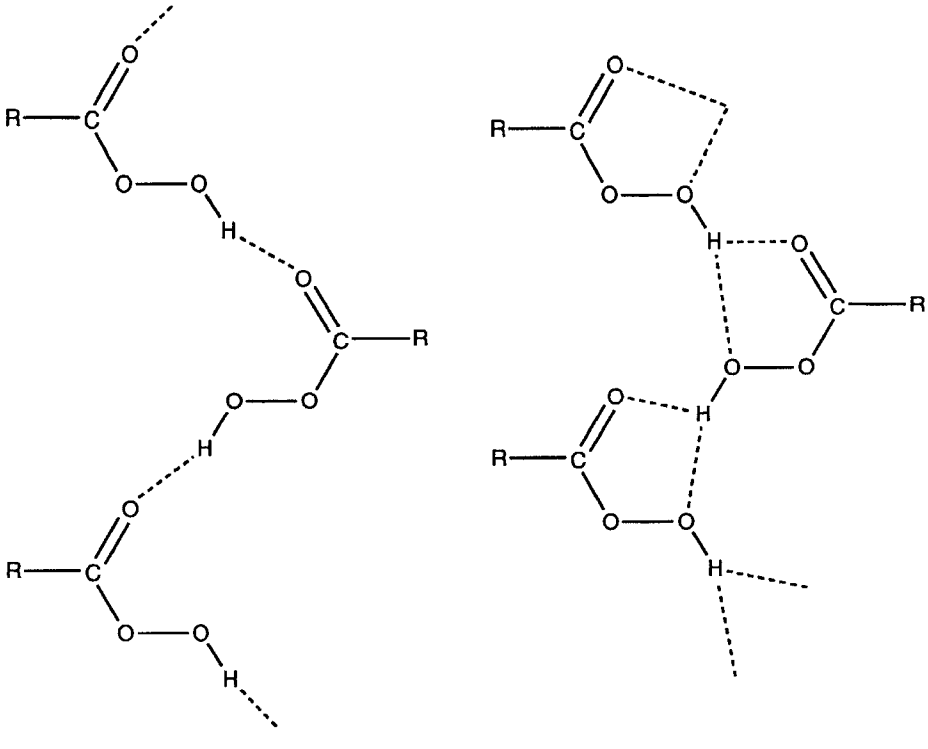
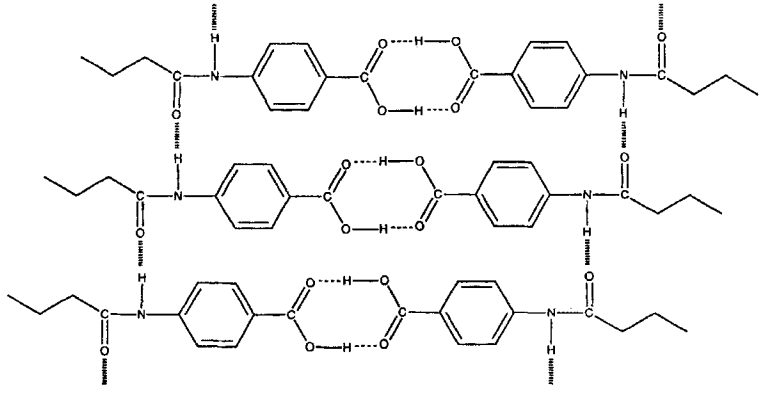


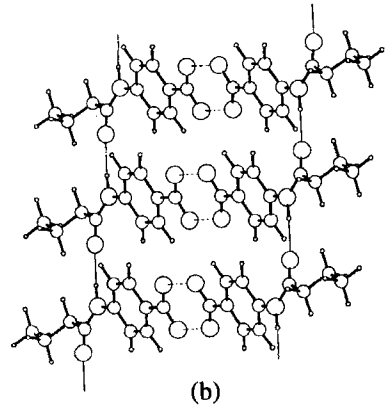
FIGURE 2 Hydrogen-bond motifs in peracids: (a) chain formed through a two-centred interaction, (b) chain formed through a three-centred interaction.

p-ABA

An inspection of Table I shows that two types of crystal have been grown for the members of this series of acids - plates and rods. Each of the crystal structures determined for the plate-like crystals were found to be isostructural in $P\bar{1}$ with an increase in the long axis dimension as the value of 'n' increases. Figure 3a is a schematic representation of the hydrogen-bonding within these structures, and Figure 3b demonstrates the arrangement for *p*-ABA n = 2. There are two types of hydrogen-bond. Carboxylic acid groups are hydrogen-bonded to give the familiar 8-membered ring dimer motif. These are then related by translation along the a-axis and linked by linear amide-amide hydrogen-bonds to produce a ribbon-type network. This type of packing appears suitable for any value of 'n'.



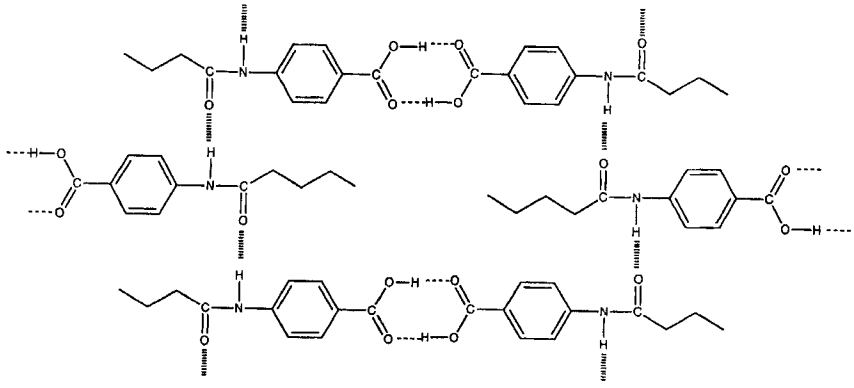
(a)



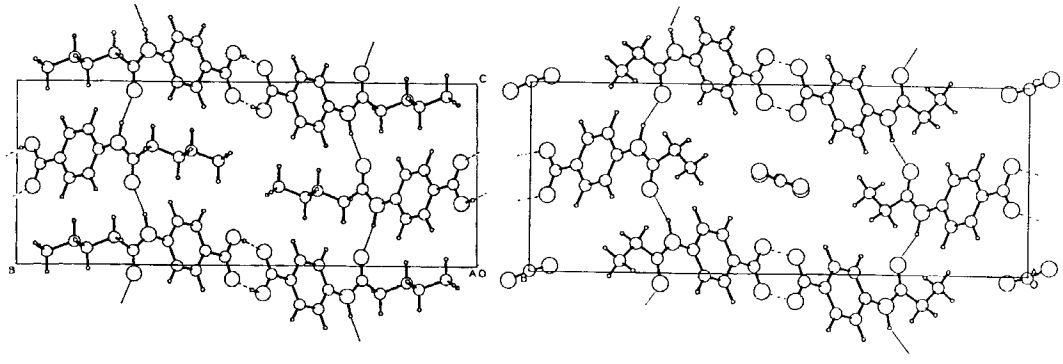
(b)

FIGURE 3 (a) Schematic representation of the hydrogen-bonding in the *p*-ABA ribbon-type structures and (b) the packing diagram for *p*-ABA n = 2.

The crystal structure of a second polymorphic form for *p*-ABA n = 3 has been determined from rod-like crystals, in space group $P2_1/c$. The hydrogen-bonding arrangement is shown schematically in Figure 4a and in the packing diagram Figure 4b. Carboxylic acid dimers are again formed, as are the linear amide-amide hydrogen-bonds, however this time linking molecules related by a c-glide. The network produced is a two-dimensional sheet rather than a ribbon. This type of hydrogen-bond arrangement appears only possible for this particular value of n. Larger chains cannot fit in the space created by the network and smaller chains leave a void space. The second situation can be satisfied, however, if the void can be filled with solvent, as was found for the *p*-ABA n = 1 acetic acid solvate structure, shown in Figure 4c.



(a)



(b) (c)

FIGURE 4 (a) Schematic representation of the hydrogen-bonding in the *p*-ABA sheet-type structures, (b) the packing diagram for *p*-ABA n = 3. and (c) the packing diagram for *p*-ABA n = 1 acetic acid solvate.

p-APBA

In the *p*-APBA series the hydrogen-bond motifs and packing arrangements have been found to be very different to those of the *p*-ABA series. As in the comparison of nitroperbenzoic and nitrobenzoic acids, the most notable difference between the *p*-ABA and *p*-APBA structures is that 10-membered ring peracid dimers are not observed. Instead each hydrogen-bond network involves peracid to amide and amide to peracid interactions.

For *p*-APBA n = 0 and 1 (which are isostructural) the network involves two types of hydrogen-bond. Firstly each molecule is hydrogen-bonded to two others to form a chain by the interaction of a peracid proton with an amido carbonyl oxygen atom between molecules related by translation in both a and b (C-centering). Each molecule in the chain is hydrogen-bonded to a further two other molecules by the interaction of an amido proton with a peracid group between molecules related by a c-glide. This interaction is of the three centred type (i.e. Figure 2b). The hydrogen-bond network is three dimensional, as is illustrated by the partial packing diagram for *p*-APBA n = 0 in Figure 5.

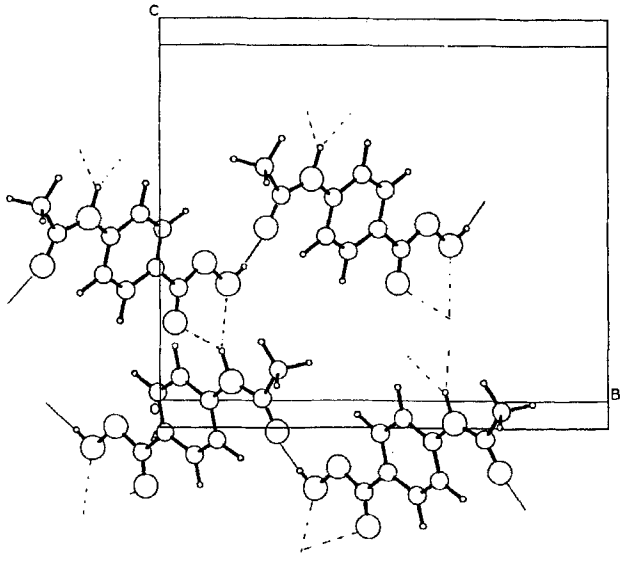
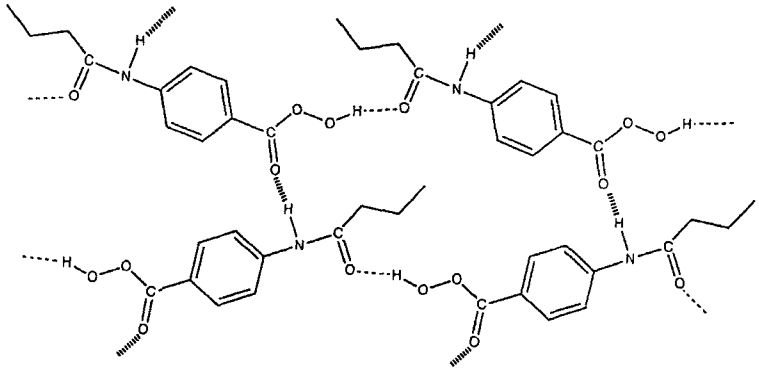


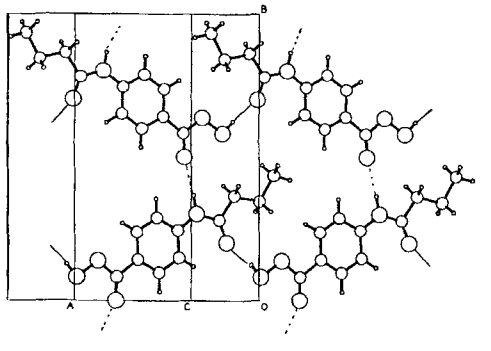
FIGURE 5 Packing diagram for *p*-APBA n = 0. The amido proton to peracid hydrogen-bond can be seen to be three-centred.

Peracid proton to amide carbonyl oxygen hydrogen-bonds are also formed in the structures of *p*-APBA n = 2 and 3, but this time between molecules related by translation along the a-axis only, linking these molecules into chains. The amido proton is hydrogen-

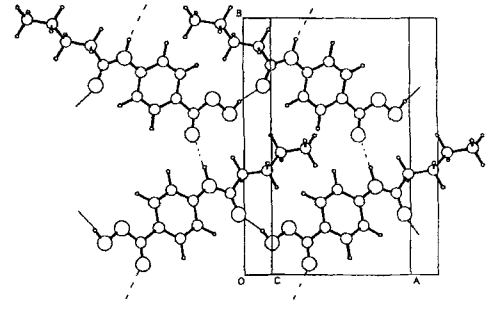
bonded to a peracid carbonyl oxygen between molecules related by a b-glide in n = 2 and the two-fold screw in n = 3. The interaction is two-centred (i.e Figure 2a). The hydrogen-bond networks for these two structures are two-dimensional. Figure 6a illustrates the arrangement schematically, while Figures 6b and 6c are the packing diagrams for n = 2 and 3 respectively.



(a)



(b)



(c)

FIGURE 6 (a) Schematic representaion of the hydrogen-bond network found in the sheet-like arrangements of *p*-APBA n = 2 and 3, (b) and (c) the partial packing diagrams for *p*-APBA n = 2 and 3 respectively. The amido proton to peracid group hydrogen-bond can be seen to be two-centred.

Packing of the Alkyl Chain in *p*-ABA's and *p*-APBA's

It has been demonstrated that for the *p*-ABA's there exists a hydrogen-bond ribbon arrangement that can be adopted by any chain length. Also it was found that a combination of similar hydrogen-bond motifs can produce a sheet arrangement. This second network, however, produces a void space which can only be suitably filled at a value of n = 3, and for smaller values of 'n' when included solvent is incorporated into the lattice.

Although the specific hydrogen-bond motifs and packing arrangements of the *p*-APBA's are very different to the *p*-ABA's, the general patterns do produce a cavity in which the alkyl chains are located. The 'ideal' arrangement appears to be when n = 2. Structure solution showed each of the heavy atoms to be sitting on special positions, making the molecule planar. The cavity made by the hydrogen-bond network of such planar molecules is exactly filled by the alkyl chain when n = 2 (Figure 6b). For different values of 'n' subtle modifications are made to keep the basic arrangement. When n = 3, the molecules are not completely planar and so the cavity is slightly larger and the extra carbon in the chain can be accommodated without having to sit far out of the mean plane of the sheet (Figure 6c). Smaller chain lengths, such as when n = 0 and 1, are accommodated by reducing the size of the cavity by making the amide proton to peracid group hydrogen-bond three-centred. The effective size of the cavity in which the alkyl chain is located is also reduced in these two structures by allowing the cavity to extend infinitely parallel to the a-axis.

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