Combined X-Ray Crystallographic and Infrared and Raman Spectroscopic Study of Hydrogen Bonding Patterns in Keto Acid Phosphoranes

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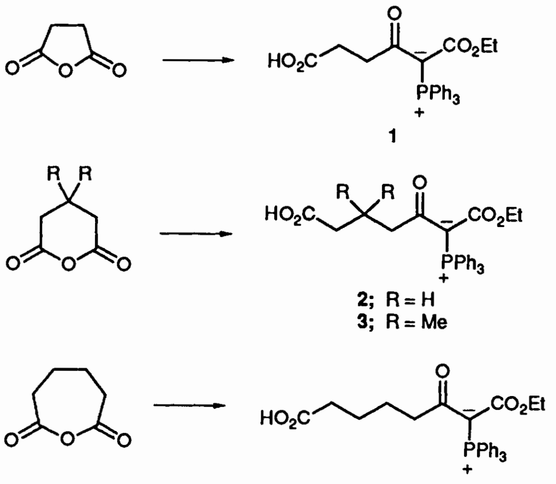
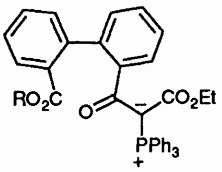
The X-ray crystal structures of 3,3-dimethyl-6-ethoxycarbonyl-5-oxo-6-(triphenylphosphoranylidene)hexanoic acid **3** and 7-ethoxycarbonyl-6-oxo-7-(triphenylphosphoranlylidene)heptanoic acid **4** revealed acid-to-ketone intramolecular and catemeric hydrogen bonding, respectively. Intermolecular hydrogen bonding for the related **1**, **2** and **7** and intramolecular hydrogen bonding for **5** are consistent with the length and substitution of acid to ketone carbon chain. Raman and infrared spectroscopy have also been used to differentiate the centrosymmetric and vibrationally coupled acid to acid dimeric hydrogen bonding of the keto acid phosphorane **1** from the alternative modes of acid to ketone hydrogen bonding found in **2–5** and **7**.

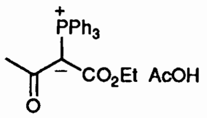
Much effort has gone into understanding the preferences of functional group classes for specific hydrogen bonding patterns in crystalline structures.[1] Indeed, these preferences have been used to establish empirical 'rules' for predicting hydrogen bonding patterns.[1]

Simple crystalline keto carboxylic acids have received little attention with regard to hydrogen bonding patterns but it is known from published X-ray data that in the crystalline state either intermolecular or far less commonly intramolecular hydrogen bonding can occur.[2] Carboxylic acid pairing,[2] the less common acid carboxy-to-ketone catemer,[2,3] and the rare acid carboxy-to-ketone dimer[3] and carboxy-to-ketone intramolecular[2,4] hydrogen bonding have been reported.

For some time we and others have had an interest in phosphoranes of the type **1–5** as intermediates to enol lactones,[5] acetylenes[6] and allenes.[7] We have published the crystal structures of a number of phosphoranes in this area, the succinic anhydride derived **1**,[8] glutaric **2**,[3] diphenic **5**, **6**,[4] acetic anhydride **7**, **8**,[9] and in this paper dimethylglutaric **3** and adipic **4**. In a preliminary communication[3] we reported that the glutaric phosphorane **2** crystallised in both a catemeric and a dimeric acid carboxy-to-ketone hydrogen bonded form. The keto acid phosphorane series represents examples of the four above-mentioned hydrogen bonded classes, the acid-to-acid dimer (aad), *e.g.* **1**, the acid carboxy-to-ketone catemer (akc), *e.g.* **2**, **4**, the acid carboxy-to-ketone intramolecular (aki), *e.g.* **3**, **5** and in addition a fourth, to our knowledge, unique acid carboxy-to-ketone dimer (akd) **2**.




5; R = H
6; R = Me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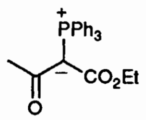
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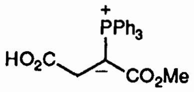
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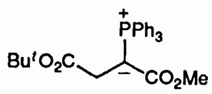
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Discussion

Perspective drawings for **1**(aad), **2**(akd), **3**(aki), **4**(akc), **5**(aki) and **7** are shown with atom labelling in Figs. 1, 2, 4, 5, 7 and 8, respectively. The acid carboxy-to-ketone catemeric hydrogen bonding for **2**(akc) and **4**(akc) is shown in Figs. 3 and 6, respectively, and Tables 1–3 list atomic coordinates and selected bond lengths and angles with standard deviations in parentheses for the previously unreported **3**(aki) and **4**(akc).

The nature of hydrogen bonding in structures of the type **1–5** is dependent on the carbon chain length between the acid and ketone groups as well as the nature of the substitution. The X-ray crystal structure of the keto acid phosphorane with the longest chain length, $HO_2C-(CH)_4-CO-$, **4**(akc) revealed helical catemeric acid carboxy-to-ketone hydrogen bonding (Fig. 6). The ketone O(3) to carboxy O(5a) separation of 2.59 Å is well within hydrogen bonding limits.[10] The solvent of crystallisation was ethyl acetate. X-Ray crystallography of a crystal grown from ethyl acetate–light petroleum gave identical cell parameters to the above determination and hence it is assumed that catemeric hydrogen bonding is also present in this case. The mode of hydrogen bonding in the keto acid phosphoranes seems to be independent of the solvent of crystallisation.[3]

A previously reported crystal structure[8] of **1**(aad) revealed hydrogen bonding between the two carboxy groups forming an

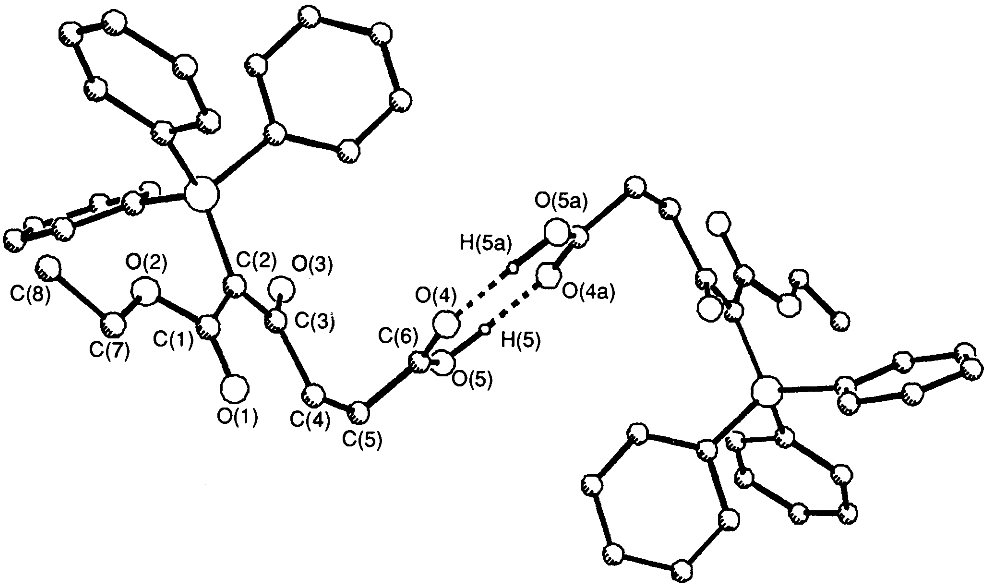

Fig. 1 Perspective view and atom labelling for **1**(aad) showing intermolecular hydrogen bonding

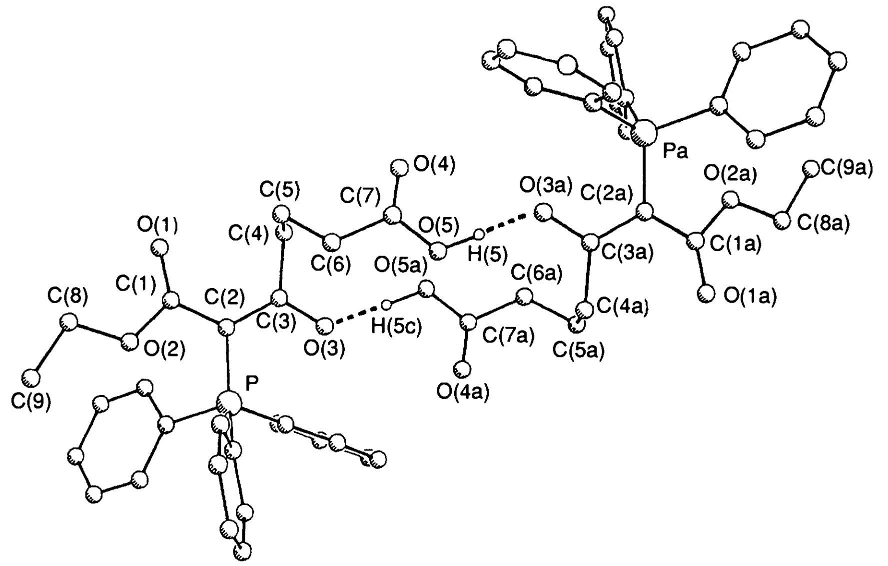

Fig. 2 Perspective view and atom labelling for **2**(akd) showing intermolecular hydrogen bonding

eight-membered ring dimer with an acid carbonyl O(4) to carboxy O(5a) separation of 2.64 Å (Fig. 1). It is clear that crystal packing for the keto acid phosphorane with the shortest carbon chain, $HO_2C-(CH)_2-CO-$, does not favour catemer formation but rather acid-to-acid pairing.

The intermediate carbon chain length, $HO_2C-(CH_2)_3-CO-$, of **2** gave two different modes of hydrogen bonding for independent crystals grown from ethyl acetate.[3] These are the perhaps expected catemeric form (Fig. 3) and a second most unusual acid carboxy-to-ketone dimer resulting in a 16-membered ring (Fig. 2). The ketone O(3) to carboxy O(5a) separation is 2.60 Å for both structures and the O(3)–H(5c)–O(5a) angle is 177.1° for the dimer and 177.5° for the catemer. Two other crystals of **2** and a subsequent crystal recrystallised from ethyl acetate–light petroleum were consistent with the dimeric form. No further examples of the catemeric form were obtained.[3]

The X-ray crystal structure of the keto acid phosphorane **3**(aki), derived from 3,3-dimethylglutaric anhydride and crystallised from ethyl acetate–light petroleum, consists of two well separated crystallographically independent molecules as shown in Fig. 4. Bond angles and lengths are given for both molecules in Table 3. Fig. 4 shows intramolecular acid carboxy-to-ketone hydrogen bonding (aki) resulting in an eight-membered ring. The ketone O(3) to carboxy O(5) separation is 2.55/2.55 Å and the O(3)–H(5)–O(5) angle is 156.7/175.8°. Presumably the dimethyl substitution makes both the catemeric and dimeric crystal packing observed for **2** less favoured. It is well documented that increased acyclic carbon substitution favours cyclisation.[11]

The rigid constraints of the biphenyl group of **5**[4] also facilitates solid state intramolecular acid carboxy-to-ketone hydrogen bonding as evidenced by a ketone O(3) to carboxy O(5) separation of 2.67 Å and an unusually large biphenyl dihedral angle of 99.4° (Fig. 7). In this instance the intramolecular hydrogen bond results in a chiral biphenyl as evidenced by the ^1H NMR spectrum of **5**.[4] The closeness in space of acid carboxy and ketone groups due to the rigid constraints of a molecule does not necessarily result in intramolecular hydrogen bonding. For example, the X-ray crystal structure of *cis*-3-acetyl-2,2-dimethylcyclobutylacetic acid revealed acid carboxy-to-ketone catemeric rather than intramolecular hydrogen bonding.[12]

The acetic anhydride derived keto acid phosphorane **7**[9] represents a related intermolecular association between two different molecules and can be considered as an example of an infinite carbon chain length between the acid and ketone functionalities (Fig. 8).

As with the other phophoranes previously studied, the relatively long[9] P–C(2) bond lengths (Table 3) of 1.767(4)/1.773(4) and 1.762(4) Å for 3(aki) and 4(akc), respectively, and the comparatively short[9] C(1)–C(2) [1.473(7)/1.440(8) Å in 3(aki), 1.439(6) Å in 4(akc)], and C(2)–C(3) [1.404(6)/1.410(8) Å in 3(aki), 1.424(6) Å in 4(akc)] bonds are consistent with extensive phosphorane delocalisation. The bond angles C(1)–C(2)–P, C(1)–C(2)–C(3) and C(3)–C(2)–P are also consistent with a distorted trigonal geometry about C(2) (Table 3).

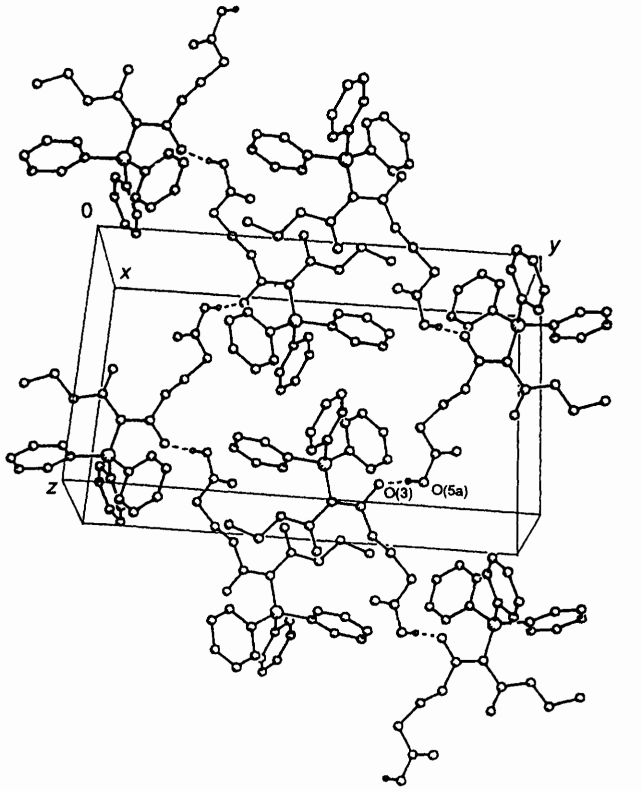

Fig. 3 Packing diagram for 2(akc) showing catemers generated by acid carboxyl to ketone hydrogen bonding

Some deviation from planarity about the resonance-stabilised phosphorane moiety of 1–8, is evident (Table 4). The least deviation is evident when the ketone O(3) is not involved in hydrogen bonding as in 1(aad) and 8. However, when O(3) is involved in hydrogen bonding as in 2–5 and 7 a significant deviation from planarity is apparent (Table 4). The acid-to-methoxycarbonyl intermolecularly hydrogen-bonded phosphorane 9 is also reported to show a greater deviation from planarity than the *tert*-butyl ester analogue 10.[13]

The extent of deviation from planarity about the resonance stabilised phosphorane within the intermolecular hydrogen bonded examples 2, 4 and 7, shows some correlation with increasing carbon chain length between the acid and ketone groups. Intramolecular hydrogen bonding (aki) gives the most significant deviation from planarity, as in 5 and one of the two crystallographically independent molecules of 3 [Fig. 4(*a*)] (see later for supportive infrared evidence). The second molecule of 3 [Fig. 4(*b*)] compensates for the lack of deviation of phosphorane planarity with an almost linear intramolecular hydrogen bond [O(5′)–H(5′)–O(3′) 175.8°]. The unusually large ester carbonyl O(1) deviation for the methyl ester 6 [P–C(2)–C(1)–O(1) 32.1°] is misleading since 6 is unique in that O(1) is *syn* to P.[4] In all the other keto acid phosphoranes O(1) is *anti* to P. The ketone O(3) is *syn* to P in all structures 1–8.

A number of other features from the X-ray structures of the keto acid phosphoranes are worth noting. The O(4)–C(7)–C(6)–C(5) torsion angle of −98.7°/+99.1° for 3(aki) is consistent with distortion of the synplanar arrangement reported for carboxylic acids,[14] a result of intramolecular hydrogen bonding. The catemeric form of 2(akc) is again unusual in that

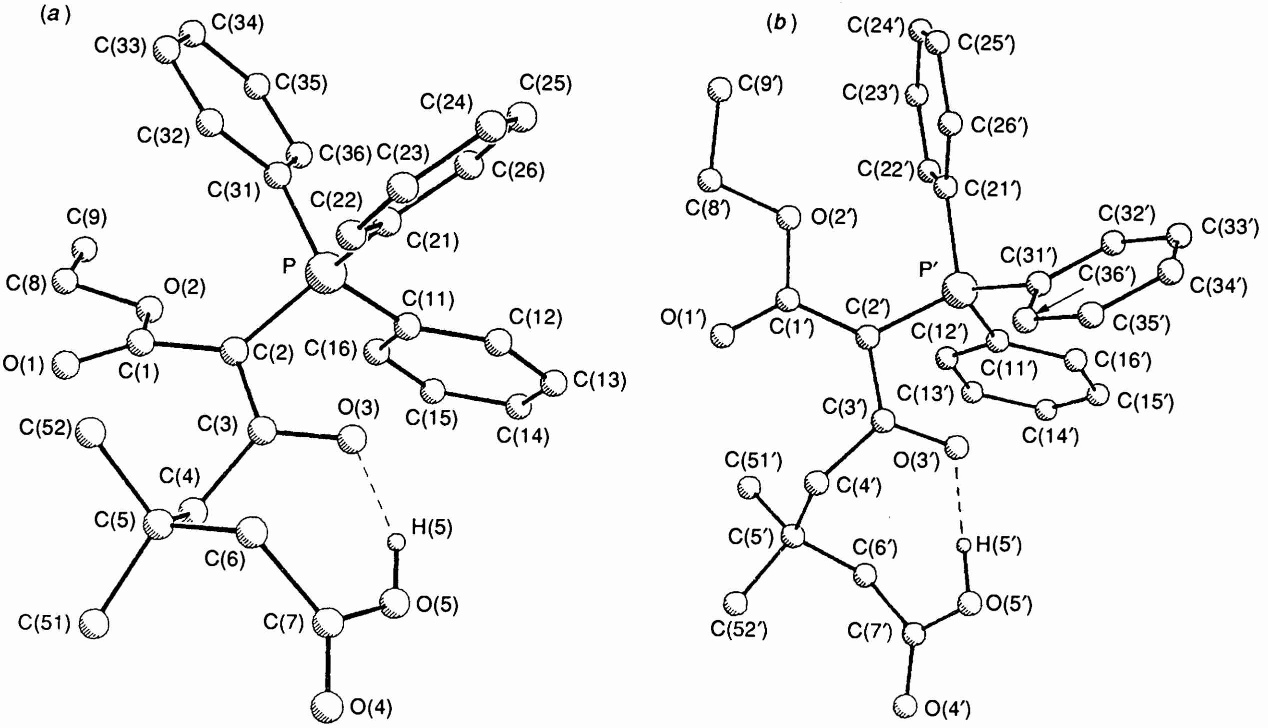

Fig. 4 Perspective view and atom labelling for 3(aki) showing intramolecular hydrogen bonding. Each of the observed two crystallographically independent molecules is shown individually for clarity.

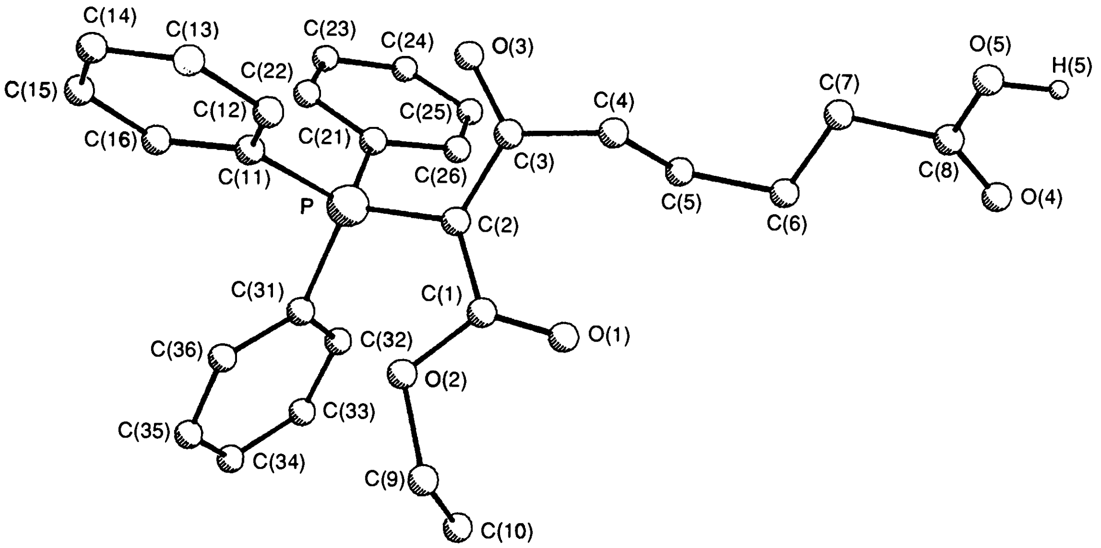

Fig. 5 Perspective view and atom labelling for 4(akc). H(5) was inserted at a calculated position.

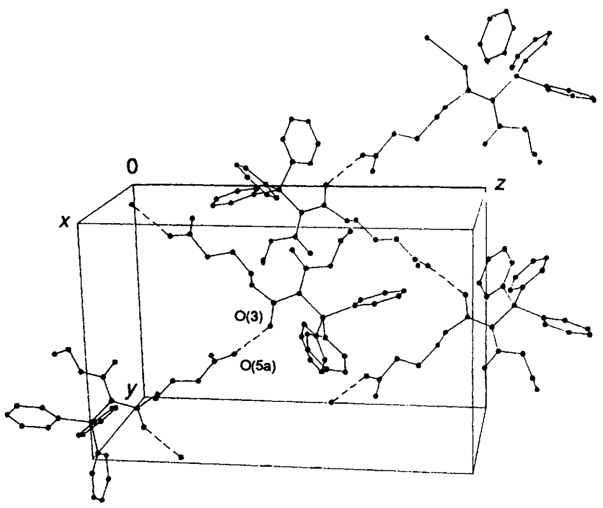

Fig. 6 Packing diagram for 4(akc) showing helices generated by acid carboxy-to-ketone hydrogen bonding

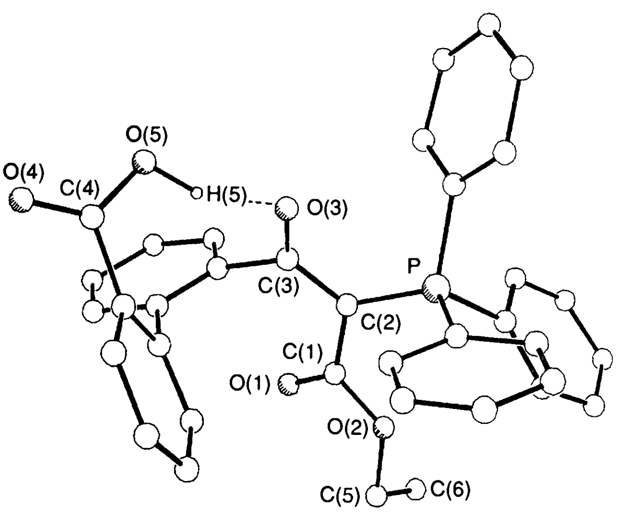

Fig. 7 Perspective view and atom labelling for 5(aki) showing intramolecular hydrogen bonding

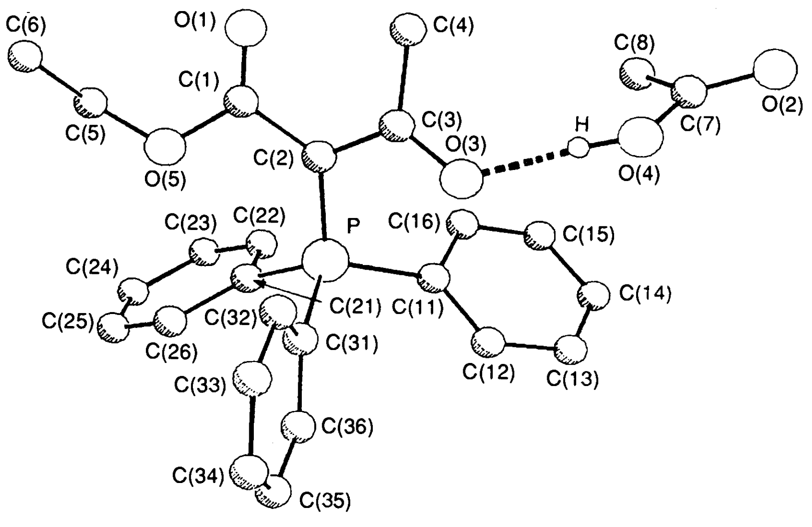

Fig. 8 Perspective view and atom labelling for 7 showing intermolecular hydrogen bonding

Table 1 Atom coordinates (× 10^4) for **3**(aki)

Atom	*x*	*y*	*z*
P	4 384(1)	7 199(1)	5 982(1)
O(1)	3 779(3)	5 724(3)	8 558(2)
O(2)	2 664(3)	6 187(2)	7 272(2)
O(3)	6 503(3)	5 912(2)	6 627(2)
O(4)	9 720(3)	4 098(3)	8 294(3)
O(5)	8 488(3)	4 775(2)	7 081(2)
C(1)	3 688(4)	6 041(3)	7 733(3)
C(2)	4 638(4)	6 279(3)	7 093(3)
C(3)	5 774(4)	5 722(3)	7 269(3)
C(4)	6 168(4)	4 866(3)	8 158(3)
C(5)	7 021(4)	4 993(3)	8 799(3)
C(6)	8 121(4)	5 331(3)	8 317(3)
C(7)	8 853(4)	4 671(4)	7 904(4)
C(8)	1 626(4)	6 176(5)	7 838(4)
C(9)	634(5)	6 379(5)	7 287(5)
C(12)	5 347(2)	6 864(2)	4 469(2)
C(13)	5 397	6 473	3 809
C(14)	4 566	5 950	3 782
C(15)	3 684	5 817	4 416
C(16)	3 633	6 208	5 076
C(11)	4 465	6 731	5 103
C(22)	6 117(3)	7 951(2)	6 460(2)
C(23)	6 855	8 604	6 281
C(24)	6 854	9 317	5 403
C(25)	6 114	9 377	4 704
C(26)	5 377	8 725	4 884
C(21)	5 378	8 011	5 762
C(32)	2 774(2)	8 373(2)	6 552(2)
C(33)	1 680	8 920	6 577
C(34)	780	9 050	5 961
C(35)	975	8 633	5 318
C(36)	2 068	8 086	5 293
C(31)	2 968	7 956	5 909
C(51)	7 393(4)	4 018(3)	9 599(3)
C(52)	6 407(4)	5 732(3)	9 175(3)
H(5)	7 625(21)	5 211(23)	9 175(24)
P′	11 796(1)	1 494(1)	8 113(1)
O(1)′	9 278(3)	1 560(2)	9 893(2)
O(2)′	11 079(3)	1 828(2)	9 865(2)
O(3)′	10 202(3)	682(2)	7 700(2)
O(4)′	6 843(3)	454(2)	6 702(2)
O(5)′	8 729(3)	59(2)	7 060(2)
C(1)′	10 217(4)	1 572(3)	9 532(3)
C(2)′	10 535(4)	1 300(3)	8 770(3)
C(3)′	9 841(4)	888(3)	8 386(3)
C(4)′	8 679(4)	624(3)	8 762(3)
C(5)′	7 591(4)	1 334(3)	8 180(3)
C(6)′	7 639(4)	1 525(3)	7 146(3)
C(7)′	7 690(4)	647(3)	6 944(3)
C(8)′	10 743(4)	2 189(4)	10 572(4)
C(9)′	11 817(5)	2 304(5)	10 948(4)
C(12)′	10 485(3)	3 067(2)	6 759(2)
C(13)′	10 130	3 684	5 856
C(14)′	10 648	3 487	5 125
C(15)′	11 520	2 674	5 296
C(16)′	11 875	2 057	6 198
C(11)′	11 358	2 253	6 930
C(22)′	12 561(3)	3 078(2)	8 149(2)
C(23)′	13 264	3 514	8 481
C(24)′	14 118	2 954	9 172
C(25)′	14 268	1 959	9 531
C(26)′	13 564	1 523	9 199
C(21)′	12 711	2 082	8 508
C(32)′	13 834(3)	436(2)	7 747(2)
C(33)′	14 589	−408	7 812
C(34)′	14 282	−1 291	8 313
C(35)′	13 219	−1 329	8 749
C(36)′	12 464	− 485	8 685
C(31)′	12 771	398	8 184
C(51)′	7 433(4)	2 308(3)	8 257(3)
C(52)′	6 535(4)	879(4)	8 578(3)
H(5)′	9 245(32)	314(31)	7 283(31)

Table 2 Atom coordinates (× 10^4) for **4**(akc)

Atom	*x*	*y*	*z*
P	−101(1)	177(1)	4199(1)
O(1)	−313(4)	3061(3)	5019(2)
O(2)	144(4)	2454(2)	3954(2)
O(3)	449(3)	−141(2)	5595(1)
O(4)	−2318(4)	3969(3)	7975(2)
O(5)	−331(4)	3564(4)	8366(2)
C(1)	−122(5)	2309(4)	4636(2)
C(2)	−88(5)	1200(3)	4822(2)
C(3)	143(5)	821(3)	5504(2)
C(4)	−24(5)	1532(4)	6121(2)
C(5)	−1498(5)	1742(5)	6279(3)
C(6)	−1702(7)	2657(7)	6801(4)
C(7)	−1160(7)	2512(7)	7441(4)
C(8)	−1315(6)	3462(5)	7940(3)
C(9)	−115(6)	3509(4)	3673(3)
C(10)	−1527(6)	3650(5)	3525(4)
C(11)	1554(4)	−301(4)	4000(2)
C(12)	2612(5)	84(4)	4392(2)
C(13)	3897(4)	−265(4)	4270(2)
C(14)	4119(5)	−1018(4)	3764(3)
C(15)	3078(5)	−1382(4)	3363(3)
C(16)	1802(5)	−1029(4)	3473(3)
C(21)	−1167(4)	−898(3)	4497(2)
C(22)	−2255(5)	−666(4)	4916(2)
C(23)	−3146(5)	−1447(4)	5084(3)
C(24)	−2991(5)	−2465(4)	4833(2)
C(25)	−1914(5)	−2709(4)	4429(2)
C(26)	−1014(5)	−1926(4)	4256(3)
C(31)	−876(5)	539(4)	3381(2)
C(32)	−2248(5)	506(4)	3319(3)
C(33)	−2839(6)	720(5)	2692(3)
C(34)	−2090(6)	978(4)	2131(3)
C(35)	−724(6)	1027(4)	2185(3)
C(36)	−100(5)	796(3)	2807(2)

it too has a large O(4)–C(7)–C(6)–C(5) torsion angle (49.8°). The corresponding torsion angles for **1**(aad) −20.6°, **2**(akd) 17.6° and **4**(akc) −147.6° are closer to the normal synplanar arrangement. The expected[14] synplanar geometry for the carboxy group (HO–CO–) is apparent in the structures of **1**(aad), **2**(akd) and **4**(akc), while the much less common antiplanar arrangement is apparent for the intramolecular hydrogen bonded **3** and **5** and more surprisingly for **7** and **2**(akc) (the synplanar geometry is observed for other reported examples of acid to ketone catemeric hydrogen bonding[2]).

Solid-state infrared spectroscopy has been used to determine crystalline hydrogen bonding modes where hydrogen bonding produces frequency shifts for both the ketone and the carboxylic acid carbonyls.[2] Problems have been encountered with this approach since other factors such as strain and conjugation can contribute to frequency shifts. Recently, a comparison of infrared and Raman spectroscopy has been used to determine the solid state hydrogen bonding patterns in carboxylic acids.[2] We chose to study the infrared and Raman spectra of the keto acid phosphoranes **1–5** and **7** since they represent a closely related series of keto carboxylic acids that give predictable modes of hydrogen bonding. In the past isolated examples and comparisons of structurally dissimilar compounds have been used to rationalise the mode of hydrogen bonding adopted by keto carboxylic acids.

A summary of the solid-state infrared and Raman carbonyl stretching frequencies for the keto acid phosphoranes **1–5** and **7** is given in Table 5. The ketone carbonyl and the acid hydroxy, but not the acid carbonyl, are involved in hydrogen bonding in all but **1**(aad). The acid carbonyl stretching frequency for **1**(aad) is observed at 1705 cm^{-1}, consistent with a normal acid to acid dimer,[12,15] while the same absorption for **2–5** and **7** is observed at a higher frequency but still lower than in gas-phase acid monomers.[12] The conjugated ketone and ester carbonyl stretching frequencies for **1**(aad), **2**(akd), **4**(akc) and **7** are coincident. The intramolecular hydrogen bonding (aki) in **3** and **5** disrupts the extended phosphorane conjugation (see earlier for a discussion of this point). A carbonyl absorption shift towards 1700 cm^{-1} results and hence three distinct carbonyl absorptions are observed. Consistent with this is the fact that the ester and ketone carbonyl stretching frequencies are coincident at 1670 cm^{-1} for **6**[4] which can not display intramolecular hydrogen bonding.

Table 3 Selected bond lengths/Å and angles/° for **3**(aki) and **4**(akc)

	3(aki)[a]	**4**(akc)
Bond lengths		
P–C(2)	1.767(4)/1.773(4)	1.762(4)
C(1)–C(2)	1.473(7)/1.440(8)	1.439(6)
C(1)–O(1)	1.203(6)/1.216(6)	1.226(7)
C(1)–O(2)	1.361(6)/1.347(7)	1.360(6)
C(2)–C(3)	1.404(6)/1.410(8)	1.424(6)
C(3)–O(3)	1.280(5)/1.282(6)	1.258(5)
C(3)–C(4)	1.515(5)/1.524(6)	1.501(6)
C(4)–C(5)	1.544(8)/1.556(5)	1.539(7)
C(5)–C(6)	1.542(6)/1.546(7)	1.544(10)
C(6)–C(7)	1.530(8)/1.506(8)	1.368(10)
C(7)–C(8)		1.543(10)
C(7)–O(4)	1.208(6)/1.207(7)	
C(7)–O(5)	1.327(7)/1.335(5)	
C(8)–O(4)		1.196(7)
C(8)–O(5)		1.296(7)
O(5)–H(5)	0.932(24)/0.932(51)	
O(3)–H(5)[b]	1.670/1.618	
O(3)–O(5)[c]	2.553/2.549	2.59
Bond angles		
C(1)–C(2)–P	122.1(3)/126.4(4)	122.3(3)
C(1)–C(2)–C(3)	122.8(3)/124.8(4)	124.1(4)
C(3)–C(2)–P	114.7(3)/108.7(4)	113.1(3)
C(2)–C(1)–O(1)	126.2(5)/125.7(5)	127.0(4)
C(2)–C(1)–O(2)	111.0(4)/114.5(4)	111.6(4)
C(2)–C(3)–O(3)	118.4(3)/119.8(4)	119.4(4)
O(3)–C(3)–C(4)	117.8(4)/116.2(5)	119.2(4)
C(3)–C(4)–C(5)	116.4(4)/113.8(3)	111.7(4)
C(4)–C(5)–C(6)	113.1(4)/113.8(4)	112.7(5)
C(5)–C(6)–C(7)	115.0(5)/114.0(3)	116.2(7)
C(6)–C(7)–O(4)	122.3(5)/123.0(4)	
C(6)–C(7)–O(5)	115.9(4)/117.2(4)	
C(6)–C(7)–C(8)		115.1(7)
C(7)–C(8)–O(4)		122.2(5)
C(7)–C(8)–O(5)		113.4(5)
C(7)–O(5)–H(5)	123.9(26)/106.1(27)	
O(5)–H(5)–O(3)	156.7/175.8	
C(3)–O(3)–H(5)	152.6/144.7	
Torsion angles		
P–C(2)–C(1)–O(1)	−149.9(5)/168.9(3)	168.2(5)
P–C(2)–C(3)–O(3)	−0.9(7)/2.9(4)	7.5(6)
O(4)–C(7)–C(6)–C(5)	−98.7(6)/99.1(5)	
O(4)–C(8)–C(7)–C(6)		−147.6(6)
O(1)–C(1)–C(2)–C(3)	38.5(9)/−6.6(6)	−20.9(9)
O(3)–C(3)–C(2)–C(1)	171.3(5)/179.2(3)	−164.2(5)

[a] Two crystallographically independent molecules (′ values given second). [b] Hydrogen bond. [c] Non-bonded interatomic distance.

Table 5 Solid-state infrared (KBr) and Raman (glass capillary) carbonyl stretching frequencies for the keto acid phosphoranes **1**–**5** and **7**

	Infrared/cm^{-1} [a]		Raman/cm^{-1} [a]		
Compound	Acid	Ketone/ester	Acid	Ketone/ester	Δ/cm^{-1} for acid
1(aad)	1705	1666	1660	1660[b]	45
2(akd)	1723	1670	1721	1667[b]	2
3(aki)	1726	1675, 1687	1723	1665, 1682	3
4(akc)	1719	1677	1716	1671[b]	3
5(aki)	1731	1657, 1689	1726	1655, 1689	5
7	1735	1676	1727	1674[b]	8

[a] Frequencies ±3 cm^{-1}. [b] Acid/ketone/ester carbonyl stretching frequencies coincide.

For the centrosymmetric carboxylic acid dimer **1**(aad) the vibrational coordinates of the acid carbonyl groups within the hydrogen bonded ring should couple to give a symmetric, Raman-active mode and an antisymmetric, infrared active mode. The coupling of the two carbonyls depends on both the symmetry and the alignment of the vibrational modes. The centrosymmetric eight-membered ring of **1**(aad) would be anticipated to give strong coupling, and indeed we observe a frequency difference of some 45 cm^{-1} (Table 5).

For the low-symmetry, crystalline keto acid phosphoranes **3**(aki), **4**(akc), **5**(aki) and **7**, the acid carbonyl stretching frequencies in the Raman spectra are very similar to those in the infrared spectra (Table 5). In each of these systems, the ketone carbonyl and acid hydroxy are involved in intermolecular catenation or intramolecular hydrogen bonding and vibrational coupling between the acid carbonyl groups should be weak due to both asymmetry and poor alignment.

The infrared and Raman frequencies obtained from a single crystal of the acid carboxy-to-ketone hydrogen-bonded dimer of **2**(akd) differ by only 2 cm^{-1}. The poor coupling of the same order of magnitude as that found in the non-centrosymmetric catemeric species, is a consequence of vibrational alignment and the separation (7.379 Å) of the acid carbonyls O(4) and O(4a). A sample of a population of crystalline **2** gave identical acid carbonyl stretching frequencies by infrared and Raman spectroscopy to the single dimeric crystal. It is unclear as to the catemeric content of this sample. Unfortunately the Raman and infrared spectra of a single crystal of the catemeric form of **2** could not be obtained.

Experimental

Infrared spectra were recorded on a BIO RAD FTS 40 spectrophotometer. Raman spectra were recorded using a Spectra-physics 171 argon-ion laser (excitation at 488.0 nm)

Table 4 Magnitude[a] of O(1), O(3) and P deviation from planarity/° for the stabilised phosphoranes **1**–**8**

	No H-bonding to O(3)			Intermolecular H-bonding				Intramolecular H-bonding	
Torsion angle	**8**[9]	**1**(aad)[8]	**6**[4]	**2**(akd)[3]	**2**(akc)[3]	**4**(akc)	**7**[9]	**3**(aki)[b]	**5**(aki)[4]
O(1)–C(1)–C(2)–C(3)	3.1	20.5	29.9	20.3	28.5	20.9	26.3	38.5/6.6	22.9
P–C(2)–C(1)–O(1)	9.5	6.4	32.1	9.6	25.2	11.8	27.3	30.1/11.1	18.2
O(3)–C(3)–C(2)–C(1)	4.5	15.4	2.2	14.7	0.2	15.8	7.3	8.7/0.8	30.1
P–C(2)–C(3)–O(3)	1.1	2.8	0.1	4.3	3.1	7.5	8.3	0.9/2.9	10.9
Average	4.6	11.3	16.1	12.2	14.3	14.0	17.3	19.6/5.4	20.5

[a] Calculated from respective torsion angles. [b] Two crystallographically independent molecules (′ values given second).

and a SPEX 1403 double monochromator. The keto acid phosphoranes 3(aki)[5b] and 4(akc)[7b] were prepared as reported.

Crystal Data for 3(*aki*).—Crystallised from ethyl acetate, $C_{29}H_{31}O_5P$. Crystal dimensions 0.5 × 0.4 × 0.3 mm. M = 490.5, triclinic, space group $P\bar{1}$, a = 11.678(7), b = 15.505(9), c = 15.845(9) Å, α = 66.80(5), β = 87.59(5), γ = 78.57(5)°, V = 2582(3) Å^3, Z = 4, D_c = 1.26 g cm^{-3}, $F(000)$ = 1040. Using 1.4° ω-scans at a scan rate of 4.88° min^{-1}, 9058 unique reflections were collected in the range $4 < 2\theta < 50°$ and 5305 of these having $I > 3\sigma(I)$ were used in the structural analysis, R = 0.070, R_W = 0.053. Intensity data were collected at 148 K on a Nicolet R3m four-circle diffractometer, graphite monochromatised Mo-Kα radiation (λ = 0.7107 Å) being used. Data were corrected for Lorentz and polarisation effects but not for absorption.

Crystal Data for 4(*akc*).—Crystallised from ethyl acetate, $C_{28}H_{29}O_5P$. Crystal dimensions 0.6 × 0.6 × 0.8 mm. M = 476.5, orthorhombic, space group $P2_12_12_1$, a = 10.073(2), b = 12.557(2), c = 19.370(5) Å, V = 2450(1) Å^3, Z = 4, D_c = 1.29 cm^{-3}, $F(000)$ = 1007. Using 1.5° ω-scans at a scan rate of 5.86° min^{-1}, 2448 unique reflections were collected in the range $4 < 2\theta < 50°$ and 1995 of these having $I > 3\sigma(I)$ were used in the structural analysis. Data were recorded at 160 K on a Nicolet R3m four-circle diffractometer using Mo-Kα radiation (λ = 0.7107 Å). The refinement converged with R = 0.053 and R_W = 0.057. The data were corrected for Lorentz and polarisation effects and an absorption correction was applied based on φ-scan data (T_{max} = 85%, T_{min} = 82%). The cell parameters determined for 4(akc) crystallised from ethyl acetate–light petroleum were consistent with those for 4(akc) crystallised from ethyl acetate.

Structure Analysis and Refinement.—The structures were solved by direct methods (SHELXTL version 4.1).[16] The phenyl groups of 3(aki) were refined as rigid rings and all hydrogen atoms were inserted at calculated positions except for the hydrogen bonded H(5), which was located from a difference Fourier map and inserted at that position. All hydrogen atoms were inserted at calculated positions for 4(akc).

Tables of hydrogen-atom coordinates and anisotropic thermal parameters have been deposited with the Cambridge Crystallographic Data Centre (CCDC).*

Acknowledgements

The authors are grateful to the following University of Canterbury staff: Dr. W. T. Robinson (Department of Chemistry) for his assistance with the X-ray crystallography, Dr. B. E. Williamson (Department of Chemistry) and Dr. R. W. Syme (Department of Physics) for assistance with the Raman spectroscopy.

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Paper 0/04982D
Received 5*th November* 1990
Accepted 26*th February* 1991

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* For details of the CCDC deposition scheme, see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 2*, 1991, issue 1.