Carboxy to Ketone Dimeric and Catemeric Hydrogen Bonding in a Keto Acid Phosphorane: X-Ray Structure of 6-Ethoxycarbonyl-5-oxo-6-(triphenylphosphoranylidene)hexanoic Acid

Andrew D. Abell,* John Trent and Ward T. Robinson

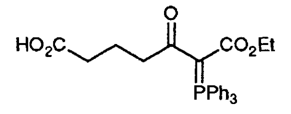
Chemistry Department, University of Canterbury, Christchurch, New Zealand

Single-crystal X-ray crystallography revealed carboxy to ketone catemeric and dimeric hydrogen bonding in separate crystals of the keto acid phosphorane **1**.

Both intermolecular and, much less commonly, intramolecular hydrogen bonding modes are known for simple crystalline keto carboxylic acids.[1] The carboxy group is normally the dominant functionality such that acid to acid eight-membered dimeric ring structures are produced.[1,2] Occasionally ketone involvement to give carboxy to ketone catemers[1] is observed and in a few cases intramolecular carboxy to ketone hydrogen bonding has been reported.[1,3] In this communication we describe two independent crystal structures for the keto acid phosphorane **1**. The results are particularly interesting in that two different hydrogen bonding modes were observed for two independent crystals, one of which was, to our knowledge, a previously unknown mode of carboxy to ketone hydrogen bonded dimerisation.

The keto acid phosphorane **1** was prepared from glutaric anhydride and ethoxycarbonylmethylenetriphenylphosphorane as previously described.[4] X-Ray crystallography of a single crystal of **1** revealed a dimeric hydrogen bonded form as shown in Fig. 1.† Hydrogen bonding between the ketone carbonyl of one molecule and the carboxy group of a second results in an unusual sixteen-membered dimeric ring structure [ketone O(3)–carboxy O(5a) separation is 2.60 Å, O(3)–H(5c)–O(5a) angle is 177.1°].

Fortuitously, a second X-ray structure determination was carried out on another crystal of **1**. The second determination indicated a catemeric hydrogen bonded form of **1**, Fig. 2.† Fig. 3 gives the corresponding packing diagram showing helices generated by the carboxy to ketone hydrogen bonding along a screw axis. The ketone O(3)–carboxy O(5a) separation of 2.60 Å is well within hydrogen bonding limits and the O(3)–H(5c)–O(5a) angle is 177.5°. No other examples of catemeric hydrogen bonding in crystals of **1** were found. In particular,



1

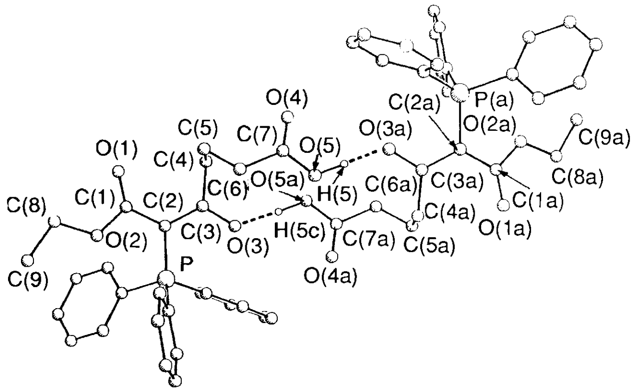


Fig. 1 Perspective view and atom labelling for **1** showing the hydrogen bonded dimer. Hydrogen bonds are indicated. Selected bond lengths (Å) and angles (°): C(1)–O(1) 1.205(3); C(1)–O(2) 1.354(3); C(1)–C(2) 1.456(3); C(2)–P 1.768(2); O(2)–C(3) 1.416(3); C(3)–O(3) 1.253(3); C(7)–O(5) 1.320(3); O(5)–H(5) 1.307(35); H(5)–O(3a) 1.560; O(1)–C(1)–C(2)–P −170.4(2); O(3)–C(3)–C(2)–P −4.3(3); C(1)–C(2)–P 119.5(2); C(1)–C(2)–C(3) 122.8(2); C(3)–C(2)–P 116.9(2).

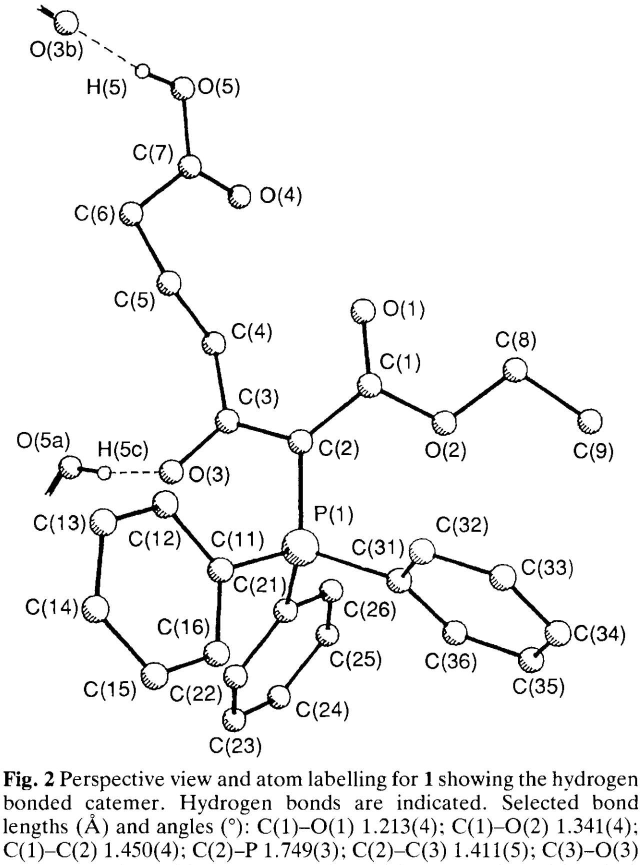


Fig. 2 Perspective view and atom labelling for **1** showing the hydrogen bonded catemer. Hydrogen bonds are indicated. Selected bond lengths (Å) and angles (°): C(1)–O(1) 1.213(4); C(1)–O(2) 1.341(4); C(1)–C(2) 1.450(4); C(2)–P 1.749(3); C(2)–C(3) 1.411(5); C(3)–O(3) 1.254(4); C(7)–O(5) 1.318(4); O(5)–H(5) 0.855(51); H(5)–O(3b) 1.751; O(1)–C(1)–C(2)–P −154.8(3); O(3)–C(3)–C(2)–P 3.1(5); C(1)–C(2)–P 124.2(3); C(1)–C(2)–C(3) 123.7(2); C(3)–C(2)–P 112.0(2).

---

† *Crystal data* for the dimer of **1** $C_{27}H_{27}O_5P$; crystal dimensions 0.4 × 0.4 × 0.4 mm; M = 462.49, monoclinic, space group $C2/c$, a = 17.541(10), b = 9.045(5), c = 29.711(20) Å, β = 95.03(5)°, U = 4666.6 Å^3, Z = 8, D_c = 1.32 g cm^3, $F(000)$ = 1952, μ = 1.48 cm^{-1}. Using 1.6° ω-scans at a scan rate of 7.32° min^{-1}, 4597 unique reflections were collected in the range of $4 < 2\theta < 45°$ and 3133 of these having $I > 3\sigma(I)$ were used in the structural analysis, R = 0.047, R_w = 0.050.

Crystal data for the catemer of **1**: $C_{27}H_{27}O_5P$; crystal dimensions 0.44 × 0.22 × 0.056 mm; monoclinic, space group $P2_1/n$, a = 9.563(5), b = 19.576(10), c = 13.207(9) Å, β = 109.15(4)°, U = 2335.7 Å^3, Z = 4, D_c = 1.32 g cm^{-3}, $F(000)$ = 976, μ = 1.48 cm^{-1}. Using 1.2° ω-scans at a scan rate of 4.88° min^{-1}, 5375 unique reflections were collected in the range of $4 < 2\theta < 45°$ and 3788 of these having $I > 3\sigma(I)$ were used in the structural analysis, R = 0.065, R_w = 0.065.

Intensity data were collected at 148 K on a Nicolet R3m four-circle diffractometer, graphite monochromatized Mo-Kα radiation (λ 0.7107 Å) being used. The structures were solved by direct methods (SHELXTL version 4.1). 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. Data were corrected for Lorentz and polarization effects but not for absorption. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

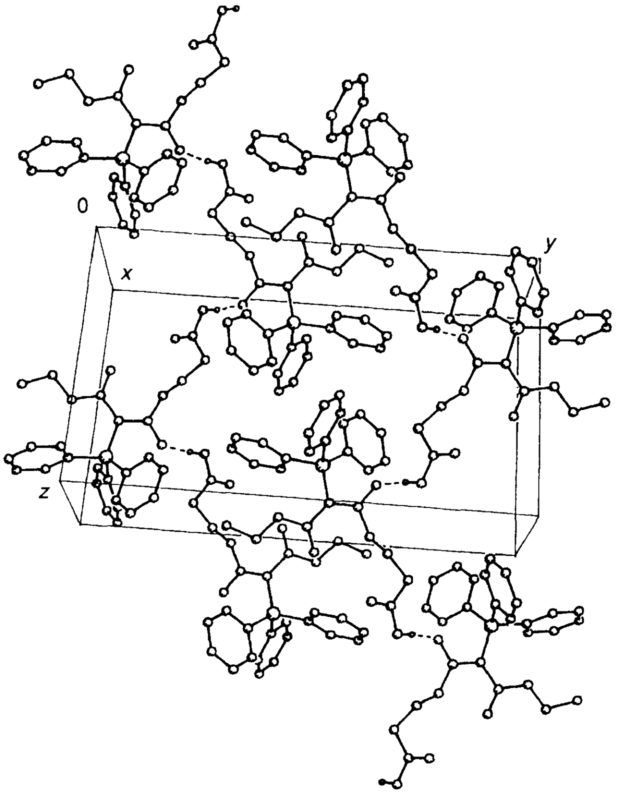


Fig. 3 Packing diagram for the catemer form of **1** showing the helices generated by carboxy to ketone hydrogen bonding

the unit cell determination for two subsequent crystals of **1** were consistent with dimeric hydrogen bonding. Dimeric hydrogen bonding was also observed in a crystal grown from ethyl acetate-light petroleum. As pointed out by a referee, the keto group of **1** to which hydrogen bonding occurs in both structures is part of a ketophosphorane. A significant contribution from the canonical form $Ph_3P^+C(CO_2Et)=CR-O^-$ might therefore be expected to enhance hydrogen-bonding basicity.

In addition to the hydrogen bonding information the X-ray crystallography revealed the following information. The expected synplanar C(5)–C(6)–C(7)=O(4) arrangement is apparent in both crystal structures while in the dimer **1** adopts a synplanar geometry for the carboxy group [H(5)–O(5)–C(7)–O(4)] and in the catemer the less common antiplanar geometry.[2] An extended delocalised system for the stabilised phosphorane is also evident in both structures (see bond angles and lengths in Figs. 1 and 2) as is the normal propeller arrangement for the triphenylphosphoranylidene group. The X-ray crystallography of a number of related keto-acid phosphoranes is currently under investigation to gain further understanding into the mode of keto-acid hydrogen bonding.

Received, 25th September 1990; Com. 0/04330C

References

1 For leading references see P. A. Vanderhoff, R. A. Lalancette and H. W. Thompson, *J. Org. Chem.*, 1990, **55**, 1696.
2 L. Leiserowitz, *Acta Crystallogr., Sect. B*, 1976, **32**, 775.
3 A. D. Abell, K. B. Morris and V. McKee, *Aust. J. Chem.*, 1990, **43**, 765.
4 A. D. Abell and R. A. Massy-Westropp, *Aust. J. Chem.*, 1982, **35**, 2077.