Molecular Packing Modes. Part VIII.[1] Crystal and Molecular Structures of But-3-ynoic Acid

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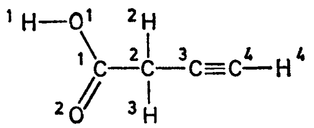
The title compound crystallises in space group $Pca2_1$ with two molecules in the asymmetric unit, the cell having dimensions a = 8·060, b = 4·195, c = 25·433 Å. The phases were determined from a diffractometer data by a multi-solution method and the structure refined by a least-squares procedure to R 0·067 for 968 independent reflections. The bond lengths are C≡C 1·175, 1·179; ≡C–C 1·455, 1·453; C–CO_2H 1·484, 1·506; C=O 1·221, 1·214; C–OH 1·307, 1·259 Å. The C(:O)·C·C⋮C system is *syn*-planar.

The molecules are hydrogen-bonded (O–H ··· O 2·69 and 2·65 Å) in pseudo-centrosymmetric pairs. In the crystal there are no intermolecular ethynyl-H ··· O=C interactions; rather, the acetylenic C–H bond points at the C≡C triple bond, [H ··· C⋮C(midpoint) 3·0 Å]. The C(sp^3)–H ··· bond is directed towards the carbonyl oxygen (C–H ··· O 3·45, and H ··· O 2·6 Å).

But-3-ynoic acid also appears in a pseudo-orthorhombic form showing order–disorder. The relationship of the two forms is discussed.

THE crystal structure analysis of but-3-ynoic acid (I) was undertaken as part of a study on the packing modes of carboxylic acids.



(I) Labelling of atoms in the present analysis. The atoms of the second molecule in the asymmetric unit are primed

EXPERIMENTAL

Crystal Data.—$C_4H_4O_2$, M = 84·4, m.p. 82—84 °C. (i) Orthorhombic form: $a = 8{\cdot}060(1)$, $b = 4{\cdot}195(1)$, $c = 25{\cdot}433(1)$ Å, $U = 850{\cdot}9$ Å^3, $D_m = 1{\cdot}32$, $Z = 8$, $D_c = 1{\cdot}30$, $F(000) = 352$. Space group $Pca2_1$ or $Pcam$ (the former established as correct by the present analysis) from systematic absences $0kl$ for l odd, $h0l$ for h odd. Mo-K_α radiation, $\lambda = 0{\cdot}70926$ Å; μ(Mo-K_α) = 1 cm^{-1}. (ii) Pseudo-orthorhombic form: The cell constants (a_p, b_p, c_p) are given in terms of the $Pca2_1$ form (a, b, c), $a_p = a$, $b_p = b$, $c_p = 2c$, Pseudo-selection rules: $0kl$ $l = 4n$; $h0l$ $h = 2n$, $l = 2n$; hkl $h = 2n$, $l = 2n$; hkl $h = 2n + 1$, $l = 2n$, $l = 2n + 1$.

Crystals were obtained by slow room-temperature evaporation from chloroform solution. The X-ray diffraction photographs showed orthorhombic symmetry, but with systematic absences not matched by any of the orthorhombic space group conditions, and with diffuse streaks along particular reciprocal row-lines. The diffraction spectra with $h = 2n$ were sharp maxima and present for $l = 2n$ only, whereas for $h = 2n + 1$ there were diffuse streaks parallel to c^* and with no restrictions on l. These features indicated pseudo-orthorhombic symmetry and an order–disorder (O/D) structure.

By growing crystals from an unsaturated chloroform solution which was slowly cooled to the temperature of dry ice (−78 °C) eliminated almost completely, in some crystals, the pseudo-orthorhombic diffraction pattern. However, the X-ray photographs still showed diffuse streaks the intensity of which varied from specimen to specimen with some crystals showing little or none. The X-ray spectra possessed mmm symmetry, showed a halving of the c axis of the pseudo-cell, and selection rules consistent with Pca symmetry. The diffraction spectra of this structure and the O/D structure were almost identical for $h = 2n$, and exhibited the same regional variation in intensity along

[1] Part VII, V. Benghiat, L. Leiserowitz, and G. M. J. Schmidt, preceding paper.

c^* for reciprocal lines hkl where $h = 2n + 1$. No observable O/D effects were observed in crystals grown from benzene or light petroleum.

Data Collection.—Lattice constants of the *Pca* structure were determined by a least-squares method from 19 high-order ($2\theta > 120°$) spectra measured on a General Electric diffractometer (Cu-K_α radiation, $\lambda = 1{\cdot}5418$ Å).

As the material tended to deteriorate in air the crystal used for intensity measurements was enclosed in a Lindemann-glass capillary. The specimen, of dimensions 0·34, 0·50, 0·38, and 1·10 mm (bounded by faces 001, 00$\bar{1}$, 010, 0$\bar{1}$0, 0$\bar{1}$2, 01$\bar{2}$, 100, and $\bar{1}$00), was mounted along a^* on an IBM 1800 controlled Siemens three-circle diffractometer.[2] $I(hkl)$ and $I(h\bar{k}l)$ were recorded for $\sin\theta/\lambda \leqq 0{\cdot}65$ with Mo-K_α radiation filtered by a set of balanced zirconium and yttrium metal foils. Our procedure for intensity measurements and data processing,[3] was slightly modified: instead of performing both an intensity and a background ω–2θ scan for each filter (Zr, Y), the background was derived from the first and last four measurements of the intensity profile step-scan. Absorption corrections [4] were applied in the data reduction routine. 968 Independent reflections were recorded of which 175 were treated as unobserved.

Structure Determination.—Either space group $Pca2_1$ or *Pcam* is compatible with the reflection conditions. This ambiguity was resolved both by packing considerations, indicating the presence of the mirror plane m as unlikely, and by the statistical [5] $N(z)$ test which favoured the non-centrosymmetric space group $Pca2_1$. The structure was solved by an application [6] of the multi-solution phase-determination method [7] based on the tan ϕ formula.[8]

TABLE 1

Initial phase set used for the multi-solution phase determination method

	h	k	l	Phase/radians	E
Origin-defining set	1	1	0	0	3·39
	2	1	0	0	2·63
	6	2	1	$\pi/2$	1·83
Starting phases *	1	1	1	$\pm\pi/6, \pm\pi/2, \pm5\pi/6$	3·13
	2	1	1	$\pm\pi/6, \pm\pi/2, \pm5\pi/6$	2·89
	3	2	2	$\pi/6, \pi/3$	2·10
	3	2	15	$\pm\pi/4, \pm3\pi/4$	2·05

* For implementation of the tan ϕ formula.

Three appropriate phases were assigned to fix the origin. Four additional reflections were chosen each with a set of starting phases (Table 1). Thus, from an initial group of seven given phases, the phase angles of 100 reflections with the highest E values were determined for each of the 288 models. The phases of each of 40 models with the highest figure of merit C[7] were then utilised to generate the phases of 240 reflections. An E-map computed using the phases of the model with the lowest R index (0·33), and which also had the highest C, yielded a structure in which the two molecules of the asymmetric unit formed a pseudo-centrosymmetric hydrogen-bonded pair.

This structure was refined first with individual isotropic thermal parameters, and then with anisotropic thermal parameters. All hydrogen atoms were then inserted at chemically reasonable positions, and their positional and isotropic thermal parameters refined. The final R is 0·067 and R' 0·01 $[R' = \Sigma w(k^2F_o^2 - |F_c|^2)^2/\Sigma wk^4F_o^4]$. A $\delta(xyz)$ synthesis, based on all atoms except the hydroxylic hydrogens, was computed in the plane of the pseudo-centrosymmetric carboxy-dimer (II) to confirm their locations (Figure 1).

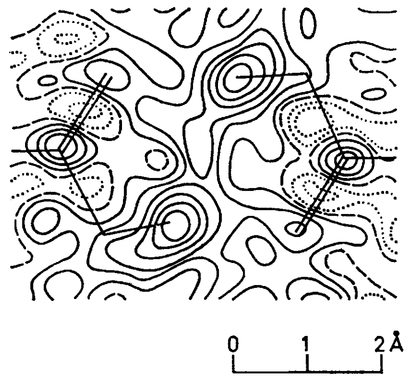
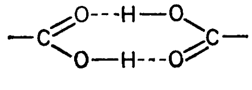


FIGURE 1 Electron density difference synthesis in the plane of the carboxy-dimer. Full, dashed, and dotted lines correspond to positive, zero, and negative contours at intervals of 0·05 Å^{-3}



(II)

The scattering factor curves used for hydrogen, carbon, and oxygen were taken from ref. 9. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20328 (3 pp., 1 microfiche).*

RESULTS AND DISCUSSION

Table 2 lists the positional and thermal parameters and their estimated standard deviations.

Molecular Shape.—The deviations from the best planes through various groups of the two molecules (primed and unprimed) are given in Table 3. The heavy atoms of the carboxy [C·C(OH):O] and propynyl (H·C⋮C·CH$_2$C) groups of each of the two molecules are planar to within 0·017, 0·008, 0·004, and 0·012 Å. The molecules are not completely planar: the dihedral angles between the planes of the carboxy and propynyl groups are 8·3 and 8·8°, and are mostly due to a twist about each C(sp^3)–CO$_2$H bond. Intramolecular repulsive forces between the carbonyl oxygen and the C⋮C triple bond may be responsible for the displacement of the triple bond from the plane of the carboxy-group. In the structure of the related cyanoacetamide,[10] the

* For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. are supplied as full size copies).

[2] L. Leiserowitz, *Z. Krist.*, in the press.

[3] H. Irngartinger, L. Leiserowitz, and G. M. J. Schmidt, *J. Chem. Soc.* (*B*), 1970, 497.

[4] P. Coppens, L. Leiserowitz, and D. Rabinovich, *Acta Cryst.*, 1965, **18**, 1035.

[5] E. R. Howells, D. C. Phillips, and D. Rogers, *Acta Cryst.*, 1950, **3**, 210.

[6] H. W. Kaufman and L. Leiserowitz, *Acta Cryst.*, 1970, *B*, **26**, 422.

[7] G. Germain and M. M. Woolfson, *Acta Cryst.*, 1968, *B*, **24**, 91.

[8] J. Karle and I. L. Karle, *Acta Cryst.*, 1966, **21**, 849.

[9] 'International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962, p. 202.

[10] P. C. Chieh and J. Trotter, *J. Chem. Soc.* (*A*), 1970, 184.

C⋮N bond is also displaced from the amide plane, the torsion angles in the two molecules of the asymmetric unit being 3 and 13° respectively.

TABLE 2

(*a*) Atomic co-ordinates (fractional) and standard deviations referred to axes ***a***, ***b***, ***c***

Atom	*x*	*y*	*z*
O(1)	0·5496(5)	0·9432(10)	0·0396(0)
O(2)	0·3548(4)	0·6146(10)	0·0106(2)
O(1′)	0·2225(6)	0·5560(10)	0·1073(1)
O(2′)	0·4163(4)	0·8841(9)	0·1342(2)
C(1)	0·4735(5)	0·7880(10)	0·0022(3)
C(2)	0·5495(6)	0·8270(13)	−0·0506(2)
C(3)	0·4539(5)	0·6887(11)	−0·0934(3)
C(4)	0·3764(8)	0·5708(16)	−0·1273(3)
C(1′)	0·2969(5)	0·7144(10)	0·1422(2)
C(2′)	0·2195(5)	0·6733(13)	0·1956(2)
C(3′)	0·3133(5)	0·8169(11)	0·2383(3)
C(4′)	0·3885(8)	0·9246(17)	0·2739(3)
H(1)	0·509(11)	0·854(22)	0·072(4)
H(2)	0·666(6)	0·743(11)	−0·049(2)
H(3)	0·579(8)	1·012(14)	−0·053(4)
H(4)	0·318(9)	0·519(17)	−0·157(4)
H(1′)	0·286(7)	0·547(12)	0·077(3)
H(2′)	0·109(7)	0·800(12)	0·191(2)
H(3′)	0·205(6)	0·475(12)	0·203(2)
H(4′)	0·455(8)	1·054(15)	0·300(3)

(*b*) Observed thermal parameters u^{ij} and standard deviations referred to axes ***a***, ***b***, ***c***

Atom	u^{11}	u^{22}	u^{33}
O(1)	0·0912(27)	0·0930(25)	0·0426(21)
O(2)	0·0692(19)	0·1027(24)	0·0471(20)
O(1′)	0·0941(27)	0·0992(27)	0·0510(27)
O(2′)	0·0689(18)	0·0998(24)	0·0484(20)
C(1)	0·0518(23)	0·0496(23)	0·0401(23)
C(2)	0·0675(32)	0·0637(29)	0·0444(24)
C(3)	0·0550(24)	0·0648(27)	0·0392(25)
C(4)	0·0775(36)	0·1024(42)	0·0452(33)
C(1′)	0·0527(23)	0·0491(23)	0·0387(22)
C(2′)	0·0568(28)	0·0602(30)	0·0465(25)
C(3′)	0·0551(26)	0·0703(28)	0·0424(26)
C(4′)	0·0825(37)	0·1096(41)	0·0450(34)

Atom	u^{12}	u^{23}	u^{13}
O(1)	−0·0312(21)	0·0010(21)	−0·0033(18)
O(2)	−0·0276(22)	−0·0103(22)	0·0062(16)
O(1′)	−0·0394(23)	−0·0222(21)	0·0075(19)
O(2′)	−0·0253(20)	−0·0124(22)	0·0047(17)
C(1)	0·0073(19)	−0·0005(20)	−0·0014(20)
C(2)	−0·0057(25)	0·0026(25)	−0·0045(22)
C(3)	0·0016(20)	0·0065(20)	0·0049(21)
C(4)	−0·0096(33)	0·0037(36)	0·0012(29)
C(1′)	0·0079(20)	−0·0046(19)	−0·0080(20)
C(2′)	−0·0061(23)	0·0019(22)	0·0027(22)
C(3′)	0·0060(21)	0·0091(22)	0·0051(22)
C(4′)	−0·0121(37)	−0·0029(34)	−0·0053(29)

Atom	*U*	Atom	*U*
H(1)	0·129(28)	H(1′)	0·045(16)
H(2)	0·042(12)	H(2′)	0·045(13)
H(3)	0·067(22)	H(3′)	0·027(15)
H(4)	0·092(29)	H(4′)	0·053(18)

The C=O bond of the carboxy-group adopts the *s-cis* conformation with respect to the propynyl chain $H_2C{\cdot}C{⋮}C{\cdot}H$, in accordance with the rule [11,12] governing the conformation of the terminal groups of acids, amides, and esters.

Bond Lengths and Angles.—Figure 2 shows the experimental molecular dimensions. The mean σ value for the bond lengths is 0·008 Å, and for angles 0·6°; the corresponding values where one hydrogen atom is involved, are 0·1 Å and 4°. The root-mean-square of the differences between equivalent bonds of the two crystallographically dependent molecules is 0·02 Å and 0·7° for the heavy atoms, and 0·09 Å and 5° where one hydrogen atom is involved.

TABLE 3

Equations of planes in the form $Ax + By + Cz + D = 0$ where *x*, *y*, *z* are fractional atomic co-ordinates; distances (10^3 Å) of relevant atoms from the planes are given in square brackets

Plane (I):
O(1), O(2), C(1)—(4) $\quad -4{\cdot}7140x + 3{\cdot}3771y - 2{\cdot}5250z - 0{\cdot}4203 = 0$
[O(1) 74, O(2) −44, C(1) 4, C(2) −90, C(3) 2, C(4) 55, H(1) −120, H(2) −930, H(3) 400, H(4) 230]

Plane (II):
O(1′), O(2′), C(1′)—(4′) $\quad -4{\cdot}6981x + 3{\cdot}3794y - 2{\cdot}7004z - 0{\cdot}6281 = 0$
[O(1′) −84, O(2′) 41, C(1′) 7, C(2′) 88, C(3′) 17, C(4′) −69, H(1′) −330, H(2′) 1050, H(3′) −540, H(4′) −10]

Plane (III):
O(1), O(2), C(1), C(2) $\quad -4{\cdot}8777x + 3{\cdot}2665y - 4{\cdot}2133z - 0{\cdot}2388 = 0$
[O(1) −6, O(2) −6, C(1) 17, C(2) −5, C(3) 190, C(4) 327, H(1) −240]

Plane (IV):
O(1′), O(2′), C(1′), C(2′) $\quad -4{\cdot}8847x + 3{\cdot}2536y - 4{\cdot}4898z - 0{\cdot}2345 = 0$
[O(1′) 1, O(2′) 1, C(1′) −4, C(2′) 1, C(3′) −182, C(4′) −358, H(1′) −200]

Plane (V): *
O(1), O(2), C(1), C(2), O(1′), O(2′), C(1′), C(2′) $\quad -4{\cdot}8608x + 3{\cdot}2625y - 4{\cdot}5142z - 0{\cdot}2467 = 0$
[O(1) −19, O(2) −13, O(1′) 2, O(2′) 9, C(1) 14, C(2) 9, C(1′) −1, C(2′) 0, H(1) −260, H(1′) −200]

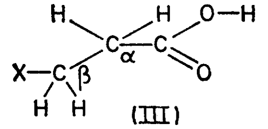
Plane (VI):
C(1)—(4) $\quad 3{\cdot}9944x - 3{\cdot}6093y + 3{\cdot}0227z + 0{\cdot}9464 = 0$
[C(1) 0, C(2) 4, C(3) −8, C(4) 5, H(2) 780, H(3) −550, H(4) −130]

Plane (VII):
C(4′)—(4′) $\quad 3{\cdot}9690x - 3{\cdot}6161y + 3{\cdot}0589z + 0{\cdot}9699 = 0$
[C(1′) 0, C(2′) 5, C(3′) −12, C(4′) 6, H(2′) −910, H(3′) 690, H(4′) −120]

* Hydrogen bonded dimer.

The −C≡C− triple bond lengths (1·175 and 1·179 Å) are shorter than the commonly accepted value (1·206 Å).[13]

The valence angles C_α–C–OH, C_α–C=O, and HO_2-C–C_α–C_β of butynoic acid agree fairly well with the corresponding values in molecules of the type (III)



(III)

[11] L. Leiserowitz and G. M. J. Schmidt, *Acta Cryst.*, 1965, **18**, 1058.

[12] J. D. Dunitz and P. Strickler, ' Structural Chemistry and Molecular Biology,' eds. A. Rich and N. Davidson, Freeman, San Francisco, 1968, p. 595.

[13] *Chem. Soc. Special Publ.*, No. 11, 1958.

(*see* Table 4). The intramolecular O(carbonyl) ··· C_β distance is somewhat shorter in butynoic acid, and in

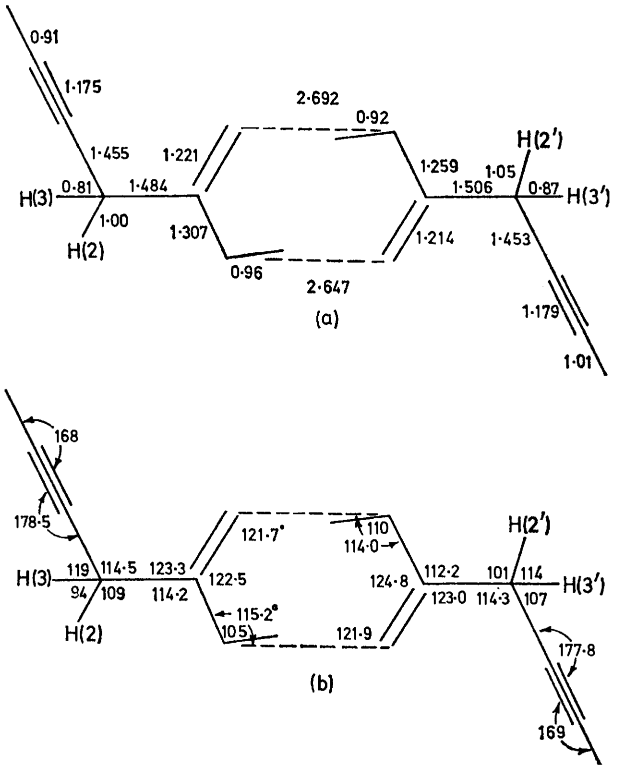


FIGURE 2 (a) Bond lengths (Å) and (b) angles (°) [C(1)–C(2)–H(3) = 107, C(3)–C(2)–H(2) = 112, C(1′)–C(2′)–H(3′) = 112, and C(3′)–C(2′)–H(2′) = 109°]

the related cyanoacetamide[10] than the corresponding distance in the aliphatic acids.[14-18] (Table 4).

packing structure of butynoic acid (*see* Figures 3 and 4). The deviations from $\bar{1}$ symmetry are small according to the molecular co-ordinates of the primed and unprimed atoms. This centrosymmetric character is localised not only in the molecular pair; it describes, in fact,

TABLE 4

Valence angles (°), and non-bonded distances (Å) C_β ··· O(carbonyl) in C_β·C_α·CO_2H

Compound	HO–C–C_α	O=C–C_α	C–C_α–C_β	C_β ··· O (carbonyl)
Propionic acid [a]	114	124	113	2·87
Butyric acid [b]	113	124	114	2·82
Valeric acid [c]	117	125	113	2·88
Succinic acid–Benzamide Complex [d]	111·5	125·3	112·7	2·81
β-Succinic acid [e]	112·9	124·5	113·1	2·82
But-3-ynoic acid [f]	114·2	123·5	114·4	2·78
Cyanoacetamide [f,g]		121·0	112·1	2·72

[a] Ref. 14. [b] Ref. 15. [c] Ref. 16. [d] Ref. 17. [e] Ref. 18. [f] Mean values. [g] Ref. 10.

the symmetry of the (001) layer of hydrogen-bonded molecular pairs in the *xy* plane (Figure 3). As the 'inversion centre' of the molecular pair ($x = 0{\cdot}3846$, $y = 0{\cdot}7501$, $z = 0{\cdot}0727$) lies halfway between the *a* glide planes, the pseudo-plane space group, of the (001) layer, regarded as a two-sided plane, is $P12_1/a(1)$.[19]

Short interatomic contacts are listed in Table 5. Along the stack axis *b* the closest contacts are O(carbonyl) ··· O(hydroxy) (3·31 and 3·29 Å), and H(3) ··· C(3) (3·19 and 3·03 Å). Along *x*, the molecular dimer is sandwiched between molecules related by the *a* glide operation such that the dihedral angle between the planes of successive carboxylic acid pairs is 78°. In this approach (Figure 4) the C(sp^3)–H ··· O=C

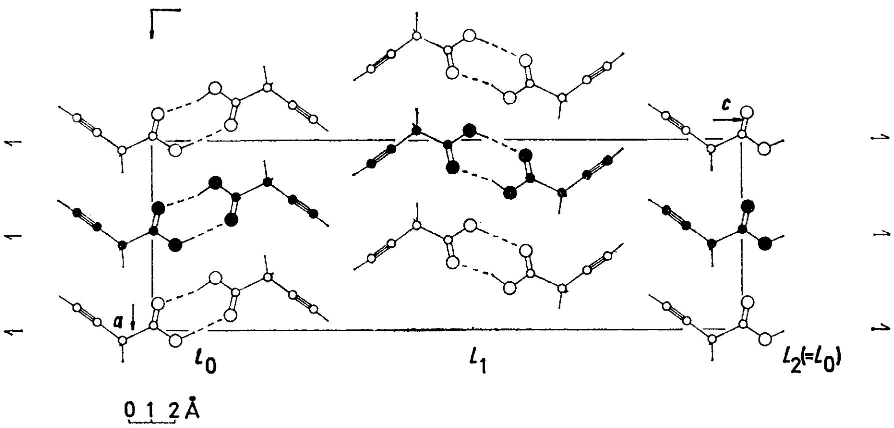


FIGURE 3 Packing arrangement seen along [010]. The (010) layers L_0, L_1, and L_2 each exhibits pseudo $P12_1/a(1)$ symmetry

Packing.—A pseudo-centrosymmetric hydrogen-bonded O–H ··· O dimer is the primary unit of the contact provides the shortest interatomic distances [C–H ··· O 3·45 and 3·44; H ··· O 2·63 and 2·49 Å].

[14] F. J. Strieter, D. H. Templeton, R. F. Scheuerman, and R. L. Sass, *Acta Cryst.*, 1962, **15**, 1233.
[15] F. J. Strieter and D. H. Templeton, *Acta Cryst.*, 1962, **15**, 1240.
[16] R. F. Scheuerman and R. L. Sass, *Acta Cryst.*, 1962, **15**, 1244.
[17] Chi-Min Huang, L. Leiserowitz, and G. M. J. Schmidt, to be published.
[18] J. S. Broadley, D. W. J. Cruickshank, J. D. Morrison, J. M. Robertson, and H. M. M. Shearer, *Proc. Roy. Soc.*, 1959, *A*, **251**, 441.
[19] W. T. Holser, *Z. Krist.*, 1958, **110**, 249; K. Dornberger-Schiff and H. Grell-Niemann, *Acta Cryst.*, 1961, **14**, 167.

The C–H bond points towards the vicinity of the available lone-pair lobe of the carbonyl oxygen and also lies approximately in the plane of the carboxy-group containing this carbonyl oxygen.

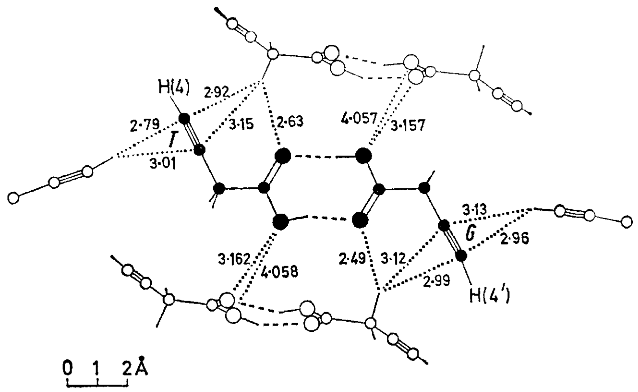


FIGURE 4 Packing arrangement seen along the normal to the best plane through the carboxylic acid dimer of the shaded asymmetric pair. Some short intermolecular contacts (Å) are shown, as well as the ***T*** and ***G*** labels denoting the C·H ··· C⁝C contact types

TABLE 5

Interatomic distances (≤3·70 Å)

A(000) * *A*(000)	
O(1) ··· O(2)	2·216
O(1) ··· C(2)	2·345
O(1) ··· H(2)	2·593
O(1) ··· H(3)	2·377
O(1) ··· O(2′)	2·647
O(2) ··· C(2)	2·383
O(2) ··· C(3)	2·780
O(2) ··· C(4)	3·517
O(2) ··· O(1′)	2·692
O(2) ··· H(1′)	1·808
C(1) ··· C(3)	2·470
C(1) ··· H(2)	2·043
C(1) ··· H(3)	1·885
C(3) ··· H(2)	2·055
C(3) ··· H(3)	1·983
O(1′) ··· O(2′)	2·191
O(1′) ··· C(2′)	2·299
O(1′) ··· H(2′)	2·525
O(1′) ··· H(3′)	2·472
O(2′) ··· C(2′)	2·395
O(2′) ··· C(3′)	2·788
A(000) *A*(000)	
O(2′) ··· C(4′)	3·562
C(1′) ··· C(3′)	2·486
C(1′) ··· H(2′)	1·988
C(1′) ··· H(3′)	1·998
C(3′) ··· H(2′)	2·049
C(3′) ··· H(3′)	1·901
A(000) *D*(1̄10)	
O(2) ··· C(1)	3·513
O(2) ··· C(2)	3·450
O(2) ··· H(2)	2·627
C(3) ··· H(2)	3·148
C(4) ··· H(2)	2·920
O(1) ··· O(2′)	3·157
A(000) *D*(1̄20)	
C(3′) ··· H(4′)	3·329
A(000) *A*(01̄0)	
C(3) ··· H(3)	3·185
A(000) *C*(001̄)	
C(4) ··· C(4′)	3·616
H(4) ··· C(3′)	3·131
H(4) ··· C(4′)	2·963
A(000) *A*(010)	
C(2′) ··· H(3′)	3·369
A(000) *A*(010)	
C(3′) ··· H(3′)	3·028
C(4′) ··· H(3′)	3·275
O(2′) ··· O(1′)	3·294
O(2′) ··· H(3′)	3·484
A(000) *D*(010)	
O(1) ··· O(1′)	3·049
O(1) ··· H(1′)	2·965
C(2) ··· C(4)	3·679
C(3) ··· C(4)	3·678
H(1) ··· O(1′)	2·594
H(1) ··· H(1′)	2·799
A(000) *D*(020)	
O(1) ··· O(2)	3·168
O(1) ··· O(1′)	3·053
O(1) ··· C(1′)	3·583
O(2′) ··· C(1′)	3·506
O(2′) ··· C(2′)	3·444
O(2′) ··· H(2′)	2·493
C(3′) ··· H(2′)	3·117
C(4′) ··· H(2′)	2·994
A(000) *B*(121̄)	
C(3) ··· H(4)	3·014
C(4) ··· H(4′)	2·785
H(4) ··· H(4′)	2·787

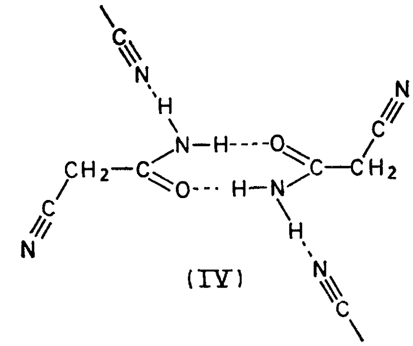
* Co-ordinates of equivalent positions:

A x, y, z
B $-x, -y, \frac{1}{2}+z$
C $\frac{1}{2}-x, y, \frac{1}{2}+z$
D $\frac{1}{2}+x, -y, z$

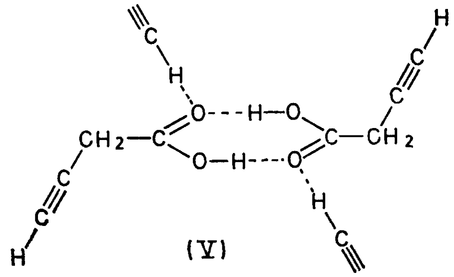
Where *A*(*pqr*) denotes fractional co-ordinates $p+x, q+y, r+z$.

The (001) layers are interlinked along z by contacts in which the acetylenic ≡C–H vector is directed towards the triple bond ⁝C–H ··· C⁝C(midpoint). The crystal structure embodies two types of these ⁝CH ··· C⁝C interactions (Figure 4) C(4′)–H(4′) ··· C(3)⁝C(4) contacts (***T***) about the two-fold screw axis, and C(4)–H(4)- ··· C(3′)⁝C(4′) contacts (***G***) across the c glide plane. The H ··· C⁝C(midpoint) distances are 3·0 and 2·9 Å. The C–H bond, in the ***T*** interaction, points fairly close to the centre of the C⁝C bond; in the ***G*** contact the C–H vector is directed at a region above (or below) the C⁝C bond axis.

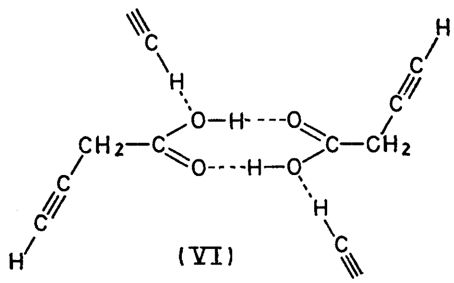
The specific and attractive nature of this ⁝C–H ··· C⁝C interaction may be gauged from the fact that the crystal structure of butynoic acid does not incorporate ethynyl-H ··· O contacts; whether butynoic acid can indeed form an acceptable structure with ⁝C–H ··· O contacts is a question we shall consider by examining the packing mode of an analogous compound, cyanoacetamide.[10]



(IV)



(V)



(VI)

The structure (IV) consists of hydrogen-bonded dimers where the available N–H bond is linked to a cyano-group.

If butynoic acid adopts the isostructural arrangements [(V) and (VI)], the group –C≡N ··· H–N (⋮N ··· HN 3·14 Å) is replaced by –C⋮C–H ··· O (⋮CH ··· O 3·2—3·4 Å).[20] Arrangement (V) contains a ⋮C–H ··· O(carbonyl) interaction and requires an antiplanar conformation of the O⁚C·CH$_2$·C⋮CH group; the (preferred) synplanar conformation embodies a ⋮C–H ··· O (hydroxy) interaction (VI). The latter CH ··· O–C interaction is probably less favourable than CH ··· O⁚C; it is nevertheless observed in the crystal structure of Laurencin,[21] where the ethynyl hydrogen bond is directed midway between two ether oxygens (bifurcated C–H ··· O bond) of an adjacent molecule but does not approach an (available) carbonyl oxygen. In the absence (so far) of either (V) or (VI), we conclude tentatively that the C(sp^3)–H ··· O(carbonyl) and ≡C–H ··· C⋮C(midpoint) interactions in the observed structure override the ethynyl-H ··· O forces in the hypothetocal arrangements (V) and (VI).

The Pseudo-orthorhombic (O/D) *Structure*.—The selection rules governing the diffraction spectrum of the pseudo-orthorhombic O/D structure may be interpreted by assuming every fourth (001) layer of the $Pca2_1$ structure to be displaced by $a/2$. Although these rules may be easily derived from the co-ordinates of the equivalent positions of this postulated cell (Table 6),

TABLE 6

Co-ordinates of the equivalent positions of the postulated model of the pseudo-orthorhombic cell, and the (001) layers L_i (Figure 5) which correspond to these equivalent positions

(001) Layer	Equivalent positions	
L_0	$x, y, z;$	$\frac{1}{2} + x, -y, z$
L_1	$\frac{1}{2} - x, y, \frac{1}{4} + z;$	$-x, -y, \frac{1}{4} + z$
L_2'	$\frac{1}{2} + x, y, \frac{1}{2} + z;$	$x, -y, \frac{1}{2} + z$
L_3	$\frac{1}{2} - x, y, \frac{3}{4} + z;$	$-x, -y, \frac{3}{4} + z$

we shall adopt the following procedure to show the compatibility of the suggested model.

The consecutive (001) layers [with pseudo $P12_1/a(1)$ symmetry] of the refined $Pca2_1$ structure are labelled L_0, L_1, L_2, L_3 [$L_i = L_{i+2}$, see Figure 3] and construct a pseudo-orthohombic arrangement (Figure 5), which consists of layers L_0, L_1, L_2', L_3, where L_2' is the L_2 layer displaced by $a/2$.

The sets L_0 and L_2' contribute to $F(hkl)$ for $h + l = 2n$, and L_1 and L_3 contribute to $F(hkl)$ for $l = 2n$, from which we deduce that this structural model complies with the conditions for hkl of the pseudo-orthorhomic cell.

$$hkl:\ h = 2n,\ l = 2n \qquad (1)$$

$$hkl:\ h = 2n + 1,\ l = 2n,\ l = 2n + 1. \qquad (2)$$

The intensity diffraction pattern of the pseudo-cell for hkl, $h = 2n$ is the same as that of the $Pca2_1$ form, which is in keeping with the postulated structure, as this reflection set is unaffected by any layer displacement of $a/2$. The model consisting of layers L_0, L_1, L_2', L_3', where both L_2 and L_3 are displaced by $a/2$, is ruled out for the systematic absences would be hkl : $h + l = 2n + 1$. The postulated structure L_0, L_1, L_2', L_3 is supported by a comparison of the variation of the calculated structure factors of the $11l$ reflection set with the observed $11l$ intensities (Table 7).

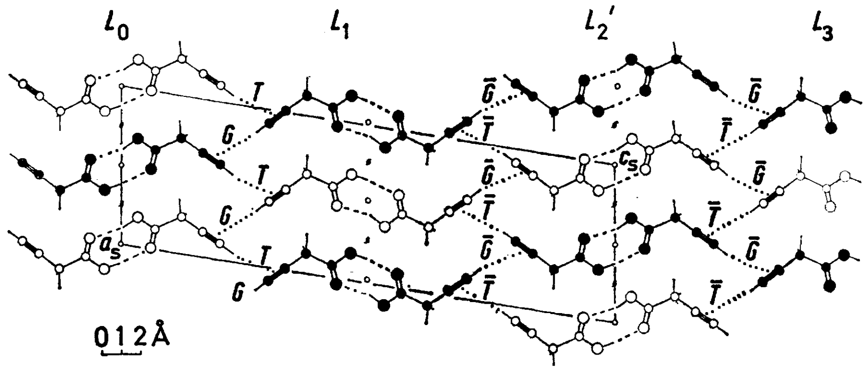


FIGURE 5 Postulated packing arrangement of the pseudo-orthorhombic structure including the outline of the pseudomonoclinic cell ($a_sb_sc_s$) for the $L_0L_1L_2'$ layers as seen along [010]. The T and $\bar{T}$, and G and $\bar{G}$ ·C⋮C·H ··· C⋮C contacts

TABLE 7

The $11l$ (l = 0—20) reflection set of the pseudo-orthorhombic cell listing the calculated structure factors of the model $L_0L_1L_2'L_3$ and the observed $11l$ film intensities

$h = 1, k = 1$ l	$\|F_c\|$	I	$h = 1, k = 1$ l	$\|F_c\|$	I
0	126	s	11	14	w
1	136	s	12	6	w
2	56	s	13	24	w
3	105	s	14	35	m
4	28	m	15	34	m
5	41	m	16	61	s
6	57	m	17	34	s
7	2	w	18	54	s
8	33	w	19	21	m
9	13	vw	20	30	m
10	1	vw			

s = Strong, m = medium, w = weak, v = very.

The O/D structure involving (001) layer misregistry of the pseudo-cell would induce streaking along c^* for reciprocal rods hkl where $h = 2n + 1$.

The displacement of the L_2 layer by $a/2$ does not

[20] G. A. Sim, *Ann. Rev. Phys. Chem.*, 1967, **18**, 57.
[21] A. F. Cameron, K. K. Cheung, G. Ferguson, and J. M. Robertson, *J. Chem. Soc.* (*B*), 1969, 559.

bring about drastic changes in the interlayer ($L_1 \ldots L_2 \ldots L_3$) contacts. The effect is rather one of replacing a ***T*** type C–H · · · C≡C contact (Figure 4) by an interaction labelled $\bar{\boldsymbol{G}}$, as its geometry closely resembles the G type C–H · · · C≡C contact; similarly, the ***G*** contact is converted into a $\bar{\boldsymbol{T}}$ type. The relationship between the contact types ***T*** and $\bar{\boldsymbol{T}}$, and ***G*** and $\bar{\boldsymbol{G}}$, upon displacement of an (001) layer by $a/2$ is shown as follows.

Let us construct a subcell a_s, b_s, c_s (Figure 5) comprising the layer set L_0, L_1, L_2' of the pseudo-orthorhombic cell a_p, b_p, c_p. The transformation is: $a_s = a_p$, $b_s = b_p$, and $c_s = \frac{1}{2}a_p + \frac{1}{2}c_p$.

If the origin (000) of this subcell is fixed in the layer L_0 at the centre of the refined molecular dimer whose co-ordinates in the pseudo-orthorhombic cell are $x_p = 0{\cdot}3846$, $y_p = 0{\cdot}7501$, $z_p = 0{\cdot}0727/2$.

Therefore the transformation relating the co-ordinates $x_py_pz_p$ and $x_sy_sz_s$ is:

$$\begin{bmatrix} -1 & 0 & 1 \\ 0 & 1 & 0 \\ 2 & 0 & 0 \end{bmatrix} \begin{bmatrix} x_p & -0{\cdot}3846 \\ y_p & -0{\cdot}7501 \\ z_p & -0{\cdot}0364 \end{bmatrix} = \begin{bmatrix} x_s \\ y_s \\ z_s \end{bmatrix}$$

The molecular dimer, with the 'inversion centre' at $x_py_pz_p = \frac{1}{2} + 0{\cdot}3846$, $2 - 0{\cdot}7501$, $\frac{1}{4} + 0{\cdot}0364$ (layer L_1, Figure 5), has co-ordinates $x_sy_sz_s$ of 0·0192, 0·4987, 0·4616 in the subcell. As this point lies close to 0, $\frac{1}{2}$, $\frac{1}{2}$ we may regard the subcell as pseudo-monoclinic $P2_1/a$ (Figure 5), and so the layer set L_0, L_1, L_2' comprises a pseudo-centrosymmetric group.

Consequently the ***T*** and ***G*** type C–H · · · C≡C contacts linking the layers L_0 and L_1 are matched by a set of 'centrosymmetrically related' $\bar{\boldsymbol{T}}$ and $\bar{\boldsymbol{G}}$ contacts linking layers L_1 and L_2' (Figure 5).

A fundamental difference between the $Pca2_1$ and the (postulated) pseudo-orthorhombic structures lies in the distribution of these ***T*** and ***G*** contacts. In the former structure the molecules are linked, along z, by chains of ***T·T·T·T·T·*** and ***G·G·G·G·G·*** contacts which alternate in the x direction; in the postulated pseudo-orthorhombic structure these respective chains are replaced by $\boldsymbol{T{\cdot}T{\cdot}\bar{G}{\cdot}\bar{G}{\cdot}T{\cdot}T{\cdot}\bar{G}{\cdot}\bar{G}{\cdot}}$ and $\boldsymbol{GG{\cdot}\bar{T}\bar{T}{\cdot}GG{\cdot}\bar{T}\bar{T}{\cdot}}$ contacts.

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