Molecular Packing Modes. Part VII.[1] Crystal and Molecular Structures of Anhydrous Acetylenedicarboxylic Acid

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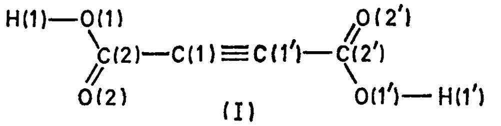
The crystal structure of anhydrous acetylenedicarboxylic acid has been solved from 1031 independent three-dimensional counter data and refined by least-squares methods to R 0·045. Crystals are monoclinic, space group $P2_1/n$, $Z = 4$, unit cell dimensions: $a = 14{\cdot}894$, $b = 6{\cdot}420$, $c = 4{\cdot}862$ Å, $\beta = 90{\cdot}90°$. σ For bond lengths involving heavy atoms only is estimated as 0·002 Å.

The molecule is non-planar: the dihedral angle between the carboxy-groups is 57·8°. The four C–O bond lengths are nearly equal (1·254 ± 0·01 Å). The mean C–C bond length is 1·458 ± 0·001 Å; the experimental value of the –C≡C– bond is short (1·168 Å). The molecular dimensions and packing arrangement are discussed.

THE structure analysis of anhydrous acetylenedicarboxylic acid (I) was undertaken as part of a study on the packing arrangement of carboxylic acids and on the electron-density distribution in the carbon–carbon triple bond.[2] Acetylenedicarboxylic acid was chosen as a compound not containing a C–H group, in which the triple bond provides very similar intramolecular environments for each of the oxygen atoms. In the present paper we discuss the molecular packing arrangement; the bonding electron density has been analysed elsewhere together with similar data on other acetylenic derivatives.[2]



(I)

EXPERIMENTAL

Crystals of the anhydrous, m.p. 175 °C (decomp.), form were grown from nitromethane solution by slow evaporation *in vacuo*. The monoclinic crystals show the {111}, {100}, {101}, and {010} forms. They are extremely hygroscopic; crystal specimens for intensity measurements were enclosed in Lindemann glass capillaries. The cell parameters were computed by a least-squares method from 33 high-angle reflections ($2\theta > 125°$) measured on a G.E. goniostat (Cu-K_α radiation).

Crystal Data.—$C_4H_2O_4$ $M = 114{\cdot}1$. Monoclinic, $a = 14{\cdot}894(1)$, $b = 6{\cdot}420(1)$, $c = 4{\cdot}862(1)$ Å, $\beta = 90{\cdot}90(1)°$, $U = 465{\cdot}1$ Å^3, $Z = 4$, $D_c = 1{\cdot}63$, $F(000) = 232$. Space group $P2_1/n$ from systematic absences: $h0l$ for $h + l$ odd, $0k0$ for k odd. Cu-K_α radiation $\lambda = 1{\cdot}5405$ Å; $\mu(\text{Cu-}K_\alpha) = 13{\cdot}7$ cm^{-1}.

From a crystal mounted along c^*, 1031 independent three-dimensional data including 112 unobserved reflections were collected by the stationary-crystal–stationary-counter method [10 s per reflection, 10 s per background with ω offset by 1°] with nickel-filtered Cu-K_α radiation. The $I(hkl)$ and $I(h\bar{k}l)$ were measured and averaged. Treatment of the data and the weighting scheme have been described previously.[3] Absorption corrections were not applied.

Structure Determination.—A first structure model was based on the two outstanding strong reflections (020) and (111), and a planar model of the molecule, the dimensions of which were taken from the structure of acetylenedicarboxylic acid dihydrate;[4] according to the cell constants the hydrogen-bonded acid unit of length 16 Å should lie along a–c (parallel to the intersection of the above strong reflections) and lie with the centres of the hydrogen-bonded dimers across centres of symmetry. This model could not be refined. Instead it followed from the two sharpened Patterson function projections $p^s(x,z)$ and $p^s(x,y)$, computed with coefficients $F^2(hkl)/f^2$, that the molecule was not planar and lay in general positions; the y parameters were determined from a three-dimensional sharpened Patterson map. The molecular model so derived was refined by full-matrix least-squares with isotropic temperature parameters for the carbon and oxygen atoms to R 0·16 and R' 0·08. [$R' = \Sigma w(k^2F_o^2 - |F_c|^2)^2/\Sigma wk^4F_o^4$] for all reflections. The resulting structure consisted of a nearly collinear carbon chain with carboxy-groups making an angle of *ca*. 58° with each other, and being intermolecularly hydrogen-bonded in a pseudocentrosymmetric manner.

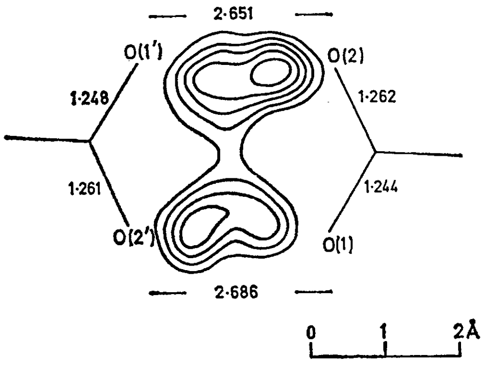


FIGURE 1 Electron-density difference-Fourier synthesis in the plane of the carboxylic acid dimer of acetylenedicarboxylic acid. Interatomic distances (Å) in the dimer are shown. Only positive regions are contoured, the first contour being at 0·1 eÅ^{-3}, with intervals of 0·05 eÅ^{-3}

Although the C–O bond lengths were nearly all equal (1·262, 1·259, 1·268, and 1·266 Å) hydrogen atoms were now attached to the oxygen atoms of the 'longer' C–O bonds (1·262 and 1·268) at a distance of 1 Å. The isotropic refinement of these hydrogen atoms and further anisotropic refinement of the other atoms led to a steep increase in U_H. Next, the two hydrogen atoms were replaced by four 'half-electrons' (labelled $\frac{1}{2}$H) 1 Å from each oxygen along the intermolecular O ··· O vectors. Further refinement led to reasonable values of $U(\frac{1}{2}\text{H})$ (0·04—0·065 Å^2) and O–$\frac{1}{2}$H distances ranging from 0·81—0·95 Å. The final agreement factors for all reflections are R' 0·012 and $R =$

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[1] Part VI, V. Benghiat and L. Leiserowitz, preceding paper.

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

[3] S. E. Filippakis, L. Leiserowitz, and G. M. J. Schmidt, *J. Chem. Soc.* (*B*), 1967, 290.

[4] J. D. Dunitz and J. M. Robertson, *J. Chem. Soc.*, 1947, 148.

0·046. A difference-Fourier synthesis, based on all but the ' half-hydrogen ' atoms, and computed in the plane of the carboxy-dimer (Figure 1) showed a disordered electron-density distribution of the hydrogens.

The scattering factor curves used for carbon and oxygen were taken from ref. 5 and for hydrogen from ref. 6. Observed and calculated structure factors of the final cycle are listed in Supplementary Publication No. SUP 20327 (2 pp., 1 microfiche).*

RESULTS AND DISCUSSION

Table 1 lists the experimental positional and thermal parameters and their estimated standard deviations.

Molecular Dimensions.—The angle between the best planes of the carboxy-groups of acetylenedicarboxylic acid is 57·8°, unlike the crystalline dihydrate in which the molecule is planar. The deviations from the best planes through two carboxy-groups, and the hydrogen-bonded cyclic dimer are listed in Table 2.

TABLE 1

Atomic co-ordinates (fractional) and thermal parameters, with standard deviations in parentheses, referred to axes *a*, *b*, *c*

Atom	x	y	z	10^3U
O(1)	−0·17113(8)	0·36472(22)	0·22691(28)	
O(2)	−0·12761(9)	0·20184(25)	0·61278(28)	
C(2)	−0·11414(10)	0·27853(27)	0·37807(35)	
C(1)	−0·02208(11)	0·26618(32)	0·28113(35)	
C(1′)	0·05140(12)	0·25213(30)	0·20284(36)	
C(2′)	0·14433(10)	0·23261(27)	0·11724(34)	
O(2′)	0·15790(9)	0·13865(22)	−0·10602(29)	
O(1′)	0·20308(8)	0·31023(24)	0·27179(28)	
½H(1)	−0·225(4)	0·368(9)	0·330(11)	65(18)
½H(2)	−0·178(4)	0·223(8)	0·663(10)	41(13)
½H(1′)	0·254(4)	0·319(9)	0·192(11)	65(18)
½H(2′)	0·213(4)	0·142(7)	−0·151(11)	49(18)

Atom	u_{11}	u_{22}	u_{33}
O(1)	0·0371(6)	0·0729(9)	0·0609(8)
O(2)	0·0434(7)	0·0820(10)	0·0626(8)
C(2)	0·0333(8)	0·0497(9)	0·0557(9)
C(1)	0·0360(8)	0·0580(10)	0·0623(11)
C(1′)	0·0364(8)	0·0570(10)	0·0635(11)
C(2′)	0·0324(8)	0·0505(9)	0·0544(9)
O(2′)	0·0406(7)	0·0713(9)	0·0652(8)
O(1′)	0·0355(7)	0·0776(9)	0·0625(8)

Atom	u_{12}	u_{23}	u_{13}
O(1)	0·0093(6)	0·0087(6)	0·0074(5)
O(2)	0·0152(7)	0·0168(7)	0·0168(6)
C(2)	0·0027(6)	−0·0019(7)	0·0090(6)
C(1)	0·0022(7)	0·0024(8)	0·0087(7)
C(1′)	0·0018(7)	0·0011(9)	0·0085(7)
C(2′)	0·0007(6)	0·0037(7)	0·0080(6)
O(2′)	−0·0101(6)	−0·0157(7)	0·0158(6)
O(1′)	−0·0015(6)	−0·0083(7)	0·0042(6)

The observed bond lengths and bond angles are shown in Figure 2. σ Values for the bond lengths involving heavy atoms only and ' half-hydrogens ' are 0·002 and 0·06 Å respectively, a value in accord with the differences between chemically equivalent bond lengths; σ for bond angles not involving hydrogen 0·2°.

The length of the C≡C bond (1·168 Å) is 0·04 Å shorter than the commonly accepted value of 1·206 Å.[7] Electron-density difference-Fourier sections containing the carbon chain C·C⁝C·C (*see* Figure 10 of ref. 2) show excess of density between the single-bonded carbon atoms, and a trough in the centre of the C≡C bond. The ' shortening ' of the triple bond and the (apparent) electron deficiency in the centre of the bond are almost certainly artefacts, for they have been correlated with the neglect of the triple-bond charge density in the least-squares refinement.[2] Indeed, an assumed value of 1·206 Å would also bring the adjoining single bond from 1·458 to 1·439 Å, and thus in line with the bond lengths,

TABLE 2

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 in square brackets

Plane (I):

O(1), O(2), C(1), C(2) $\quad 2{\cdot}9953x + 5{\cdot}6651y + 2{\cdot}0534z - 2{\cdot}0176 = 0$

[O(1) 2, O(2) 2, C(2) −5, C(1) 2, C(1′) −19, C(2′) −27, O(2′) −977, O(1′) 906, ½H(1) 70, ½H(2) 73]

Plane (II):

O(1′), O(2′), C(1′), C(2′) $\quad -1{\cdot}0385x + 5{\cdot}5609y - 2{\cdot}4012z - 0{\cdot}8616 = 0$

[O(1) 799, O(2) −1078, C(2) −102, C(1) −34, C(1′) 0, C(2′) 0, O(2′) 0, O(1′) 0, ½H(1′) 185, ½H(2′) 70]

Plane (III):

O(1), O(2), C(1), C(2), O(1′), O(2′), C(1′), C(2′) * $\quad -1{\cdot}9576x + 5{\cdot}6266y - 2{\cdot}2431z - 0{\cdot}7668 = 0$

[O(1) −37, O(2) −71, C(2) −3, C(1) 104, C(1′) 96, C(2′) −4, O(2′) −58, O(1′) −29]

* Hydrogen-bonded carboxy-dimer.

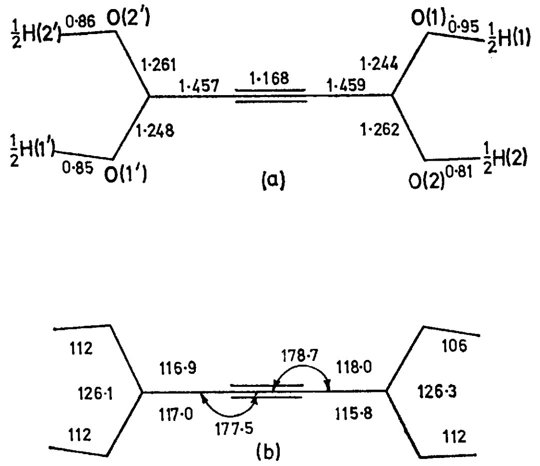

FIGURE 2 (a) Bond lengths (Å) and (b) bond angles (°)

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

[5] J. Berghuis, IJ. M. Haanappel, M. Potters, B. O. Loopstra, C. H. MacGillavry, and A. L. Veenendaal, *Acta Cryst.*, 1955, **8**, 478.

[6] R. McWeeny, *Acta Cryst.*, 1951, **4**, 513.

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

determined by microwave analysis, in propynal[8] (C≡C 1·215, and C–C 1·444 Å).

The C–O bonds are almost equal in length, a result compatible with the refined parameters of the four 'half-electrons' attached to the oxygen atoms [O—$\frac{1}{2}$H: 0·95, 0·81, 0·85, 0·86 Å; $U^2(\frac{1}{2}\text{H})$: 0·065, 0·041, 0·065, 0·049 Å^2]. However, there appear to be small and consistent differences in the molecular parameters of the hydrogen-bonded pair. Firstly, the bonds C(2)–O(2) and C(2′)–O(2′), which are related to each other by the pseudo-inversion centre of the cyclic dimer, are equal in length to within 0·001 Å, and are 0·015 Å longer than the C(2)–O(1) and C(2′)–O(1′) bonds which themselves match to within 0·002 Å from their mean. Secondly, the two 'half-hydrogens' [$\frac{1}{2}$H(2) and $\frac{1}{2}$H(2′)] attached to the 'longer' C–O bonds have the lower temperature factors (0·041, 0·049 < 0·065, 0·065 Å^2) which is consistent with their somewhat higher electron-density peaks of the $\delta(x,y,z)$ synthesis (Figure 1).

TABLE 3

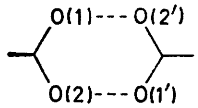
Interatomic distances (Å)

$A(000)$ * $A(000)$	
O(1) ··· O(2)	2·236
O(1) ··· C(1)	2·320
O(1) ··· C(1′)	3·397
O(2) ··· C(1)	2·307
C(1) ··· O(2′)	3·400
C(1) ··· O(1′)	3·367
C(1′) ··· O(2′)	2·319
C(1′) ··· O(1′)	2·310
O(2′) ··· O(1′)	2·237
C(2) ··· O(2′)	3·440
C(2) ··· O(1′)	3·401
C(2) ··· H(1′)	2·588
C(2) ··· H(2′)	2·624
$A(000)$ $\bar{A}(001)$	
O(2) ··· O(2′)	3·282
O(2) ··· O(1′)	3·522
C(2′) ··· H(2)	3·153
O(2′) ··· H(2)	3·180
O(1′) ··· H(2)	3·459
$A(000)$ $B(000)$	
O(1′) ··· H(1)	3·120
$A(000)$ $A(010)$	
O(1) ··· C(2′)	3·109
O(1) ··· O(2′)	3·249
O(1) ··· O(1′)	3·229
O(1) ··· H(1′)	3·119
O(1) ··· H(2′)	3·247
$A(000)$ $\bar{B}(000)$	
O(1′) ··· O(1′)	3·509
O(1′) ··· H(1′)	3·331
O(1′) ··· H(2′)	3·070
$A(000)$ $B(\bar{1}0\bar{1})$	
O(1) ··· O(1′)	3·089
O(1) ··· H(1′)	3·051
$A(000)$ $B(\bar{1}00)$	
O(1) ··· C(2′)	3·423
O(1) ··· O(2)	2·686
O(1) ··· O(1)	3·457
O(1) ··· H(1′)	2·801
O(1) ··· H(2′)	1·833
O(2) ··· C(2′)	3·424
O(2) ··· O(2′)	3·505
O(2) ··· O(1′)	2·651
O(2) ··· H(1′)	1·821
O(2) ··· H(2′)	2·859
$A(000)$ $\bar{A}(011)$	
O(1) ··· O(1′)	3·250
O(2) ··· C(2′)	3·870
O(2) ··· O(1′)	3·378
C(2) ··· O(1′)	3·420
O(1′) ··· H(1)	2·848
O(1′) ··· H(2)	3·037
$A(000)$ $A(001)$	
O(1′) ··· H(2′)	3·010
$A(000)$ $\bar{B}(0\bar{1}0)$	
C(2′) ··· O(1′)	3·574
C(2′) ··· H(1′)	3·191
O(2′) ··· O(1′)	3·357
O(2′) ··· H(1′)	3·150
$A(000)$ $A(00\bar{1})$	
O(1) ··· O(2)	3·240
O(1) ··· H(2)	2·891
O(2′) ··· O(1′)	3·299
$A(000)$ $B(00\bar{1})$	
C(2′) ··· H(1)	2·499
C(2′) ··· H(2)	2·667
O(2′) ··· H(1)	1·778
O(2′) ··· H(2)	2·893
O(1′) ··· H(1)	2·673
O(1′) ··· H(2)	1·868
$A(000)$ $\bar{A}(000)$	
O(1) ··· O(2′)	3·219
O(2) ··· O(2′)	3·320
O(1) ··· H(2′)	3·334
O(2) ··· H(2′)	3·386
C(2) ··· O(2′)	3·053
C(2) ··· H(2′)	3·263
C(1) ··· O(2′)	3·394
$A(000)$ $\bar{A}(001)$	
O(2) ··· C(1′)	3·249
O(2) ··· C(2′)	3·095

* Co-ordinates of equivalent positions:

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

A_{pqr} Denotes fractional co-ordinates $p+x, q+y, r+z$.



(II)

Packing.—The structure consists of hydrogen-bonded chains lying parallel to the [10$\bar{1}$] *n* glide direction

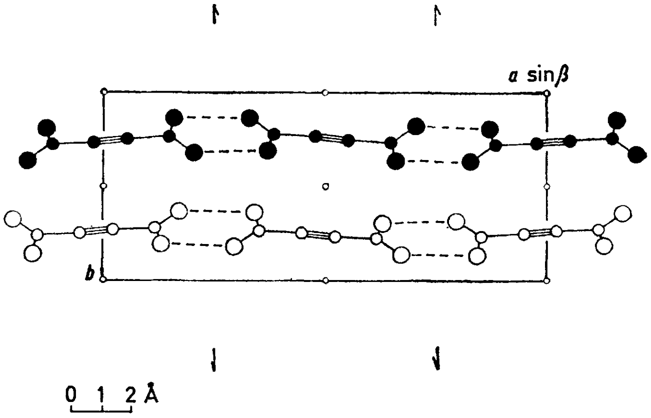


FIGURE 3 Packing arrangement seen along [001]

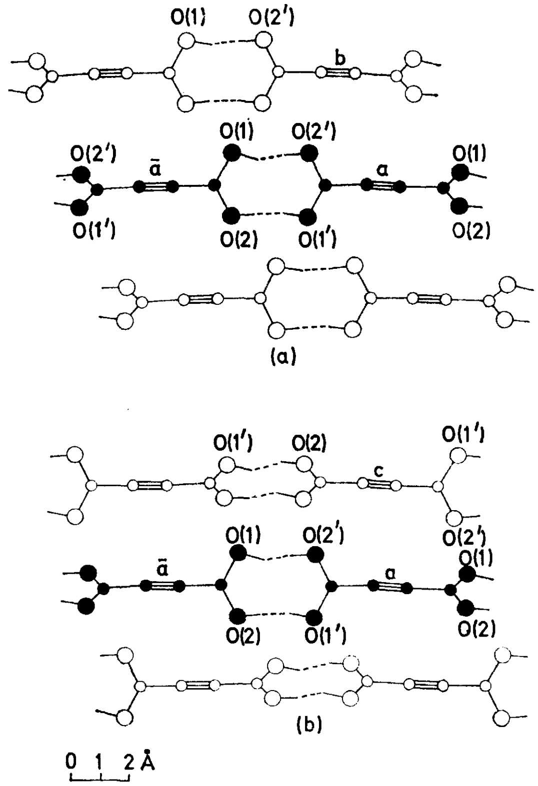


FIGURE 4 Packing arrangement of molecular dimers related by (a) the *c* translation, and (b) centre of inversion, seen normal to the plane of the shaded carboxylic acid dimer. The general positions of molecules *a*, *ā*, *b*, and *c* are x, y, z; $\frac{1}{2}-x, \frac{1}{2}+y, -\frac{1}{2}+z$; $x, y, -1+z$; and $-x, -y, -z$

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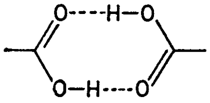
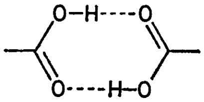
[8] C. C. Costain and J. R. Morton, *J. Chem. Phys.*, 1959, **31**, 389.

(Figures 3 and 4). The carboxylic acid pairs (II) which are formed *via* the *n* glide symmetry operation, are nearly coplanar (Table 2) since, first, the molecular chain (C·C⋮C·C) is almost parallel to $[10\bar{1}]$ at height $y = \frac{1}{4}$ (*n* glide plane at $y = \frac{1}{4}$), and, secondly, the planes of the attached carboxy-groups make angles with the glide plane which are approximately equal in magnitude and opposite in sign (+28·1, −35·9°). The dihedral angle between the best planes of the carboxy-groups in the dimer is 8·6°.

The 'half-hydrogens' and the approximately equal C–O bond lengths suggest either considerable proton tautomerism within the cyclic dimer, or oriențional disorder whereby the carboxy-dimer exists in either of the two equivalent orientations (III) and (IV). The mean O–H···O distance is 2·668 Å, which is 0·01 Å longer than the unsymmetric O–H···O(carbonyl) hydrogen bond of the β-form of tetrolic acid.[1] This result seems then to be incompatible with the existence of a symmetric O···H···O hydrogen bond in acetylenedicarboxylic acid, and so we adopt the view that the carboxy-dimer is orientationally disordered in the crystal lattice.



(III)



(IV)

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[1/1290 *Received*, 26*th July*, 1971]