

## Electron Density Distribution in Cumulenes: An X-ray Study of the Complex Allenedicarboxylic Acid–Acetamide (1:1) at $-150^{\circ}\text{C}$

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The crystal structure of the 1:1 complex allenedicarboxylic acid–acetamide was investigated by X-ray ( $\lambda = 0.709 \text{ \AA}$ ) diffraction at  $-150^{\circ}\text{C}$ . The space group is  $C2/c$  with  $Z = 8$  and  $a = 18.962 (4)$ ,  $b = 4.798 (1)$ ,  $c = 21.668 (5) \text{ \AA}$ .  $\beta = 119.01 (3)^{\circ}$ . The dihedral angle between the  $>\text{C}=\text{C}$  moieties of the allene system is  $93.3^{\circ}$ . The conformation of the  $\text{C}^{\beta}=\text{C}^{\alpha}-\text{C}=\text{O}$  system is antiplanar. The molecular electron density distribution was determined by a least-squares procedure. The observed deformation densities in the allene, carboxyl and amide groups are discussed.

### Introduction

A low-temperature X-ray study of the molecular complex allenedicarboxylic acid–acetamide (1:1) was undertaken as part of a study on the electron density distribution in cumulenes, as well as in carboxyl and amide groups. The room-temperature structure of allenedicarboxylic acid–acetamide has been described (Nader, 1976). In this paper we confine ourselves to those features which were not previously discussed.

### Experimental

A single crystal of the complex (1) was mounted on an Enraf–Nonius CAD-3 three-circle diffractometer linked to an IBM 1800 time-sharing computer. The crystal, which was sealed in a capillary of Lindemann glass, was cooled by a stream of cold air (van Bolhuis, 1971). The temperature of the crystal was estimated to be  $-150^{\circ}\text{C}$ . The cell dimensions were derived by a least-squares procedure from high-order reflexions ( $\theta > 20^{\circ}$ ) measured with  $\text{Mo } K\alpha$  radiation. The crystallographic data are given in Table 1. Details on the data collection and processing are given in Table 2. Weights were applied to the reflexion data in a similar manner to that described in the preceding paper (Berkovitch-Yellin & Leiserowitz, 1977).

Table 1. *Crystal data*

m.p.	103–105°C	$\beta$ ( $^{\circ}$ )	119.01 (3)
Space group	$C2/c$	$V$ ( $\text{\AA}^3$ )	1724.3
$a$ ( $\text{\AA}$ )	18.962 (4)	$Z$	8
$b$ ( $\text{\AA}$ )	4.798 (1)	$D_c$ ( $\text{g cm}^{-3}$ )	1.26
$c$ ( $\text{\AA}$ )	21.668 (5)	$\lambda$ ( $\text{Mo } K\alpha_1$ ) ( $\text{\AA}$ )	0.70926

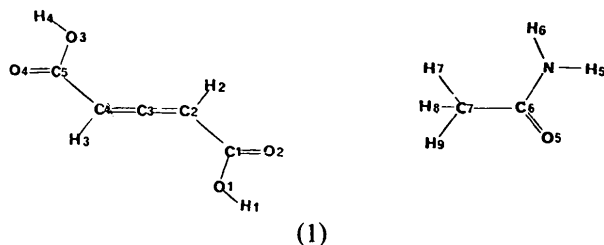


Table 2. *Intensity measurements and processing*

Diffractometer	Nonius CAD-3
Monochromatization	Graphite crystal
Radiation	$\text{Mo } K\alpha$
Minimum and maximum crystal dimensions (mm)	0.3, 0.4
Reciprocal lattice vector parallel to $\phi$ axis	$[\bar{1}11]$
Maximum $\theta$ angle ( $^{\circ}$ )	50
Scanning mode	$\omega/2\theta$
Scan range ( $^{\circ}$ ) excluding the calculated $\alpha_1$ – $\alpha_2$ separation	0.7
$\theta$ step for reflexion scan ( $^{\circ}$ )	0.01
Step-scan time for intensity and background (s)	0.4, 0.2
Number of monitor reflexions	4
Monitor-reflexion interval	100
Number of unique reflexions measured in the range $\theta < 27^{\circ}$	1904
Number of unique reflexions measured in the range $27 < \theta < \theta_{\text{max}}$ (percentage of the total in that range)	2490 (25%)
Number of reflexions measured	11175
Number of unique reflexions	4394
The match $R'^*$ between equivalent reflexions	5.5%
Number of reflexions with $F_o < 0$	295 (6.7%)
Number of reflexions with $F_o^2 < \sigma(F_o^2)$	1305 (29.7%)

\* For definition of  $R'$ , see preceding paper.

## Refinement

The refinement was carried out in essentially three stages, details of which are presented in Table 3.

## Stage a

The starting set of atomic parameters (Nader, 1976) were refined by full-matrix least-squares calculations with free-atom scattering factors. The heavy atoms were treated anisotropically, H isotropically.

## Stage b

In order to reduce the number of refined parameters we treated the thermal motion of the allene skeleton (CH=C=CH) as that of a rigid body (Schomaker & Trueblood, 1968). The other heavy atoms were treated anisotropically, H isotropically.

## Stage c

In this stage we introduced the deformation model (Hirshfeld, 1971; Harel & Hirshfeld, 1975) with modified scattering factors and contracted H atoms ( $\zeta = 1.3$ ) (Harel, 1974), and treated  $F(000)$  as an observed quantity with a standard deviation of

$F(000)/100$ . The thermal parameters of the allene skeleton atoms were constrained by the rigid-body treatment, as in stage b.

In defining the deformation model, the molecule was assumed to comprise two identical HC-COOH fragments. This assumption led to sharing of identical deformation coefficients between equivalent atoms. The number of refined deformation parameters was further reduced by taking the carboxyl and amide groups to be symmetric to reflexion in the group plane. For O(2), O(4), O(5) and N a second mirror plane was assumed perpendicular to the first and intersecting in the appropriate C=O or C-N axis. The deformation density at C(3) was assumed to possess 4 symmetry and all the H atoms were assumed to be axially symmetric about their respective bond axes. These assumptions reduced the number of independent deformation parameters to 147. In addition to the various deformation coefficients, four Gaussian exponential parameters (Harel & Hirshfeld, 1975) were refined, one for each atomic type: C, N, O and H.

In the course of the refinement difficulties were encountered especially in the determination of the positional and thermal parameters of the H atoms. The difficulties in deriving accurate H atom parameters from X-ray intensities are well known and stem from the lack of core electrons which are especially sensitive to vibrational smearing. Following the suggestion of Hirshfeld (1976) we fixed the vibration parameters of the H atoms and the X-H lengths ( $X = C, N, O$ ) on external evidence. The values of the vibration components were approximated by the stretching, bending and out-of-plane bending (torsion, rocking) frequencies obtained from spectroscopic studies of acetamide (Davies & Hallam, 1951) and *N*-methylacetamide (Szymanski, 1962). The X-H lengths of the methyl, amide and hydroxyl atoms were fixed at values obtained by neutron diffraction (Pryor & Sanger, 1970; Coppens, Sabine, Delaplane & Ibers, 1969).

Table 3. Three-stage crystal structure refinement

	(a)	(b)	(c)
Total number of parameters	154	142	265
Positional parameters	66	66	45
Thermal parameters	87	75	68
Deformation parameters	—	—	151
Number of reflexions used in the refinement	4356	4356	4393
Effective nuclear charge for H atoms	1.0	1.0	1.3
$R_1$ (omitting unobserved reflexions)	0.082	0.083	0.063
$R_2$ (all reflexions)	0.105	0.106	0.071
$r^*$	0.148	0.149	0.118
Goodness of fit*	3.05	3.08	2.21

\* For definition of  $r$  and goodness of fit see Table 3 in preceding paper.

## Results

The final atomic coordinates are listed in Table 4, and observed bond lengths and angles in Table 5. Some

Table 4. Fractional atomic coordinates and their e.s.d.'s ( $\times 10^4$  for C and  $\times 10^3$  for H)

	x	y	z		x	y	z
C(1)	4041 (1)	1402 (3)	1227 (1)	C(2)	3974 (1)	597 (4)	1857 (1)
C(3)	3674 (1)	2232 (2)	2153 (1)	C(4)	3381 (1)	3810 (3)	2466 (1)
C(5)	3886 (1)	5853 (3)	3022 (1)	C(6)	1144 (1)	-1936 (3)	391 (1)
C(7)	1963 (1)	-3217 (4)	635 (1)	O(1)	3628 (1)	3596 (3)	888 (1)
O(2)	4461 (1)	31 (3)	1048 (0)	O(3)	4649 (1)	5878 (3)	3168 (1)
O(4)	3603 (1)	7388 (3)	3294 (1)	O(5)	918 (1)	129 (5)	11 (1)
N(1)	677 (1)	-3029 (2)	620 (1)	H(1)	380	423	49
H(2)	427 (2)	-171 (7)	212 (1)	H(3)	269 (2)	366 (3)	232 (1)
H(4)	497	757	354	H(5)	85	-464	95
H(6)	12	-230	47	H(7)	198	-530	85
H(8)	242	-187	104	H(9)	207	-339	18

Table 5. *Uncorrected bond lengths (Å) and bond angles (°) and their e.s.d.'s*

C(1)—C(2) 1.483 (2)	C(1)—O(1) 1.305 (2)	C(1)—O(2) 1.230 (2)
C(2)—C(3) 1.307 (2)	C(3)—C(4) 1.307 (2)	C(4)—C(5) 1.486 (2)
C(5)—O(3) 1.323 (3)	C(5)—O(4) 1.218 (2)	C(6)—N(1) 1.316 (3)
C(6)—O(5) 1.251 (2)	C(7)—C(6) 1.508 (1)	C(2)—H(2) 1.20 (2)
C(4)—H(3) 1.19 (2)	C(7)—H(7) 1.10	C(7)—H(8) 1.10
C(7)—H(9) 1.10	O(1)—H(1) 1.10	O(3)—H(4) 1.10
N(1)—H(5) 1.00	N(1)—H(6) 1.00	
C(2)—C(1)—O(1) 115.5 (2)	C(2)—C(1)—O(2) 120.5 (1)	
O(1)—C(1)—O(2) 123.9 (2)	C(1)—C(2)—C(3) 123.3 (1)	
C(1)—C(2)—H(2) 116.7 (10)	C(3)—C(2)—H(2) 120.0 (10)	
C(2)—C(3)—C(4) 178.2 (1)	C(3)—C(4)—C(5) 122.2 (1)	
C(3)—C(4)—H(3) 120.6 (8)	C(5)—C(4)—H(3) 117.2 (8)	
C(4)—C(5)—O(3) 113.6 (1)	C(4)—C(5)—O(4) 121.9 (1)	
O(3)—C(5)—O(4) 124.4 (1)	O(5)—C(6)—N(1) 120.8 (2)	
H(7)—C(7)—H(8) 110.1 (1)	H(7)—C(7)—H(9) 110.1 (2)	
H(8)—C(7)—H(9) 110.1 (2)	C(1)—O(1)—H(1) 111.7 (10)	
C(5)—O(3)—H(4) 113.5 (10)	C(6)—N(1)—H(5) 122.1 (1)	
C(6)—N(1)—H(6) 122.1 (1)	H(5)—N(1)—H(6) 115.7 (2)	

short intermolecular contacts are given in Table 6. The deviations from the best planes of various parts of both molecules are given in Table 7.\*

### Discussion

#### Molecular shape

The carbon skeleton C—C=C=C—C adopts a conformation in keeping with allene systems; the angle between the planes of the two C=C moieties of the allene skeleton is 93.3°, compared with 90° in allene itself (Almenningen, Bastiansen & Trætteberg, 1959). The conformation of the two carboxyl groups with respect to their attached allene system is such that the two C=C—C=O groups are almost antiplanar. The torsion angles of C(3)=C(2)—C(1)=O(2) and

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32753 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.




Table 6. *Intermolecular contacts (Å)*

See Table 9 in preceding paper for definition of five-digit code.

Symmetry operations					
01	$x, y, z$	05	$\frac{1}{2} - x, \frac{1}{2} - y, -z$		
02	$-x, y, \frac{1}{2} - z$	06	$x, -y, \frac{1}{2} + z$		
03	$-x, -y, -z$	07	$\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$		
04	$\frac{1}{2} + x, \frac{1}{2} + y, z$	08	$\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$		
C(1)···H(4)	64502	2.58	C(1)···O(3)	65502	3.06
C(1)···O(5)	55505	3.15	C(1)···H(9)	54505	3.17
C(1)···O(3)	64502	3.43	C(2)···H(4)	65402	2.93
C(2)···O(3)	54501	3.36	C(2)···C(5)	54501	3.46
C(2)···O(3)	64502	3.48	C(2)···C(2)	65502	3.52
C(3)···C(5)	54501	3.51	C(3)···O(4)	54501	3.44
C(4)···O(4)	54507	3.36	C(4)···O(4)	54501	3.49
C(5)···O(2)	66502	3.43	C(5)···H(2)	56501	2.76
C(5)···H(5)	56507	2.96	C(5)···N(1)	55507	3.23
O(4)···N(1)	55507	3.32	C(6)···H(1)	55505	2.50
C(6)···H(6)	55503	3.01	C(6)···O(2)	54505	3.13
C(6)···O(4)	54507	3.37	C(6)···O(1)	55505	3.41
C(7)···H(1)	55505	2.96	C(7)···O(1)	54501	3.31
C(7)···O(2)	54505	3.43	O(1)···O(5)	55505	2.51
O(1)···H(4)	65502	2.94	O(1)···H(9)	56501	2.99
O(1)···O(3)	65502	3.09	O(1)···H(7)	56501	3.16
O(1)···H(9)	55505	3.19	O(1)···O(2)	56501	3.41
O(2)···H(6)	55504	2.51	O(2)···O(3)	64502	2.63
O(2)···H(5)	55504	2.75	O(2)···H(9)	54505	2.96
O(2)···N(1)	55504	3.02	O(2)···O(5)	55505	3.06
O(2)···O(3)	65502	3.29	O(2)···O(4)	64502	3.47
O(3)···H(2)	66502	2.82	O(3)···O(5)	55508	3.52
O(3)···H(6)	55507	3.13	O(3)···N(1)	55507	3.52
O(4)···H(5)	56507	2.03	O(4)···H(3)	55507	2.41
O(4)···H(7)	56507	2.90	O(4)···N(1)	56507	3.02
O(4)···N(1)	56507	3.02	O(4)···N(1)	55507	3.32
O(4)···O(5)	55507	3.55	O(5)···H(1)	55505	1.58
O(5)···H(6)	55503	2.02	O(5)···H(4)	45408	3.08
O(5)···H(7)	56501	3.10	O(5)···O(5)	55503	3.51
N(1)···N(1)	54503	3.27	N(1)···H(6)	54503	3.10
H(1)···H(6)	55504	2.75	H(1)···H(9)	55505	2.64
H(1)···H(9)	54505	3.18	H(1)···H(4)	65502	2.77
H(1)···H(8)	55505	3.18	H(2)···H(4)	64502	2.51
H(2)···H(2)	65502	2.66	H(2)···H(4)	54501	2.76
H(3)···H(3)	54507	2.89	H(3)···H(3)	55507	2.89
H(3)···H(7)	56501	2.91	H(4)···H(5)	56507	2.78

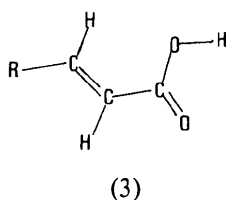
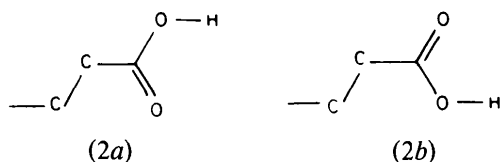
C(3)=C(4)—C(5)=O(4) are 166.0 and 178.4° respectively. The significant deviation from antiplanarity of the former is probably due to H-bonding and is discussed later.

Table 7. *Deviations from best planes*

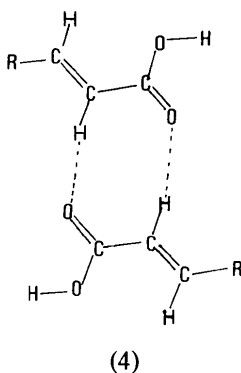
Group	Equation of the plane	$\left(\frac{\sum \Delta^2}{n-1}\right)^{1/2}$ *
C(2)—C(1) 	$-11.0292x - 2.7849y - 4.6893z + 5.4209 = 0$	0.002
C(5)—C(4) 	$-2.9531x - 3.3026y + 15.0634z - 1.4610 = 0$	0.007
C(7)—C(6) 	$-0.2536x - 2.9448y - 14.8193z + 0.0400 = 0$	0.003
Acetamide dimer	$-0.0039x - 2.9827y + 14.8467z - 1.4894 = 0$	0.018

\*  $\sum \Delta^2$  is the sum of the squares of the deviations (Å) from the best plane of the  $n$  atoms forming the plane.

The conformational features of the carboxyl group, as well as of esters, have been analysed by a number of workers (e.g. Leiserowitz & Schmidt, 1965; Dunitz & Strickler, 1968; Einspahr & Donohue, 1973; Leiserowitz, 1976). In  $\alpha,\beta$ -saturated carboxylic acids  $R-CH_2-CH_2-CO_2H$  the synplanar  $C^\beta-C^\alpha-C=O$  arrangement (2a) is adopted without any known exceptions. The synplanar rule does not apply to the  $\alpha,\beta$ -unsaturated acids  $R-CH=CH-CO_2H$ ; several molecules exhibit the antiplanar form (3).

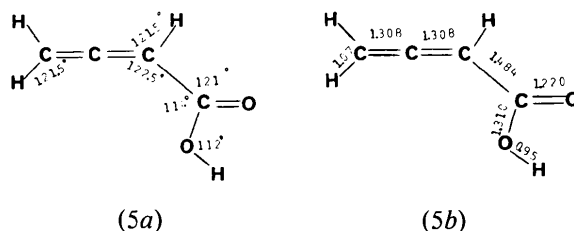


It was shown (Leiserowitz, 1976) that all those molecules which exist in the antiplanar form have similar packing environments about their carboxyl groups and that their antiplanar  $C=C-C=O$  conformations are probably induced by intermolecular forces. Specifically, these intermolecular forces comprise  $C-H \cdots O(\text{carbonyl})$  interactions, the motif of which is shown in (4).

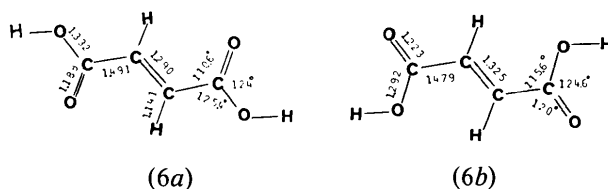


In contrast to  $R-CH=CH-CO_2H$ , allenedicarboxylic acid adopts the antiplanar conformation in both its own structure (Leiserowitz & Nader, 1973) and in its complex with acetamide. These results suggest that the preference for the antiplanar conformer is due to intramolecular forces. In order to corroborate this suggestion, we computed the energy difference

between the two possible conformations in allene-monocarboxylic acid,  $H_2-C=C-CO_2H$ , by *ab initio* molecular orbital calculations with a STO-31G extended basis set and the GAUSSIAN 70 program (Hehre, Lathan, Ditchfield, Newton & Pople, 1970).



The molecular geometry for the antiplanar conformation (5a,b) was taken from the crystal structure of allenedicarboxylic acid-acetamide averaging over the two independent carboxyl groups. This molecular geometry compares favourably with that observed in allenedicarboxylic acid itself (Leiserowitz & Nader, 1973). Regarding the angular geometry of the hypothetical synplanar form, the  $C-C-O$  angles do not necessarily remain constant upon change of conformation. Thus, the  $C-C-O$  angles, for the synplanar form ( $C-C-OH$   $109^\circ$ ,  $C-C=O$   $126.4^\circ$ ), were obtained from a comparison of the differences in the pertinent bond angles of fumaric acid ( $HO_2C-CH=CH-CO_2H$ ), which is observed in the crystal phase in both synplanar (Gorres, McAfee & Jacobson, 1975) and antiplanar (Brown, 1966; Bednowitz & Post, 1966) forms with lengths and angles as shown in (6a) and (6b). Thus the  $C-C-OH$  and



$C-C=O$  angles of the synplanar conformer used in the computation were  $109.0$  (i.e.  $114.0 - 5.0^\circ$ ) and  $126.4$  (i.e.  $121.0 + 5.4^\circ$ ) respectively. The resulting  $O-C=O$  angle is  $126.6^\circ$ . The antiplanar form was found to be more stable by an insignificant amount,  $0.01 \text{ kcal mol}^{-1}$ ; in comparison a similar computation performed on acrylic acid,  $H_2C=CHCO_2H$ , incorporating bond lengths and angles as found in the syn- and antiplanar forms of fumaric acid, yielded a more stable synplanar conformer by a significant amount,  $0.5 \text{ kcal mol}^{-1}$ . The latter result is in accordance with the observation that the synplanar  $C=C-C=O$  conformer is preferred in the  $\alpha,\beta$ -unsaturated carboxylic acids  $R-CH=CH-CO_2H$  (Leiserowitz, 1976). As a further test of the energy difference between the syn- and antiplanar

forms of allenemonocarboxylic acid, the molecular energies were computed varying the  $\text{C}-\text{C}-\text{O}$  and  $\text{C}-\text{C}=\text{O}$  angles and keeping the  $\text{O}-\text{C}=\text{O}$  angle fixed at the derived value of  $124.6^{\circ}$  for the synplanar form, and at the observed value of  $125.0^{\circ}$  for the antiplanar form. The stable conformers were obtained at  $\text{C}-\text{C}-\text{OH}$  and  $\text{C}-\text{C}=\text{O}$  angles of  $110.5$  and  $124.9^{\circ}$  for the synplanar form, and  $113.5$  and  $121.5^{\circ}$  for the antiplanar form. These angles do not differ appreciably from the observed values of the antiplanar form, and from the derived values of the synplanar form. However, a reversal in conformational stability was obtained; the synplanar form was found to be more stable by  $0.1$  kcal mol $^{-1}$ . This value is appreciably less than the  $0.5$  kcal mol $^{-1}$  difference computed for acrylic acid. Although this computation does not prove that the observed preference for the antiplanar conformer is due to intramolecular forces, it does demonstrate that the energy difference between the two conformers of allenemonocarboxylic acid is small.

Deviations from planes involving carboxyl groups are insignificant for the C, O and N atoms (Table 7). In carboxyl group  $\text{C}-\text{C}-\text{O}(1)\text{O}(2)$  the hydroxyl H atom lies  $0.13$  Å from the best plane through the carboxyl group. This O-H forms a short  $\text{O}-\text{H}\cdots\text{OCNH}_2$  contact in which the O acceptor atom lies  $0.44$  Å from the best plane of the carboxyl group (Table 7) to which it is H-bonded (Fig. 1). Therefore it appears that the O-H bond is turned out of the plane of its carboxyl group to form a more linear  $\text{O}-\text{H}\cdots\text{O}$  bond. In a similar manner the hydroxyl H(4) deviates  $0.08$  Å from the best plane of its carboxyl group  $\text{C}-\text{C}-\text{O}(3)\text{O}(4)$  so

as to make a more linear  $\text{O}-\text{H}\cdots\text{O}(2)$  bond with the O(2) acceptor which lies  $0.45$  Å from the plane.

The heavy-atom skeleton of the amide system is planar (Table 7); the amide H atoms deviate from this plane on the average by  $0.006$  Å.

The methyl group adopts a conformation such that the torsion angle  $\text{H}(8)-\text{C}(7)-\text{C}(6)-\text{N}$  is  $12.4^{\circ}$ . This conformation in which  $\text{H}-\text{C}-\text{C}-\text{N}$  is almost synplanar, seems to be preferred in acetamides  $\text{CH}_3-\text{C}(\text{O})-\text{NH}-\text{R}$  (Hagler, Leiserowitz & Tuval, 1976).

#### Packing arrangement and molecular dimensions

The packing is dictated by H bonds involving the carboxyl and amide groups (Nader, 1976). The H-bond parameters of the low-temperature structure are shown in Fig. 1.

A comparison of the two chemically equivalent moieties  $\text{C}=\text{C}-\text{CO}_2\text{H}$  leads to scatters of  $0.007$  Å and  $0.75^{\circ}$  in bond lengths and angles. These appear to be significantly higher than the average estimated standard deviations ( $0.002$  Å and  $0.15^{\circ}$ ) determined from the least-squares analysis. The difference in bond lengths and angles between the two 'chemically equivalent' moieties of  $\text{C}=\text{C}-\text{CO}_2\text{H}$  resides mainly in the carboxyl group; comparing only the  $\text{C}=\text{C}-\text{C}$  bonds of the two moieties we obtain scatters of  $0.002$  Å and  $0.5^{\circ}$  which compare more favourably with the least-squares result. The question then arises whether the differences in bond lengths of the two carboxyl groups are significant and may be associated with their different H-bonding arrangements.

It is obvious from Fig. 1 that the H-bond contacts of the two carboxyl groups differ significantly. The moot point is to what extent do these differences affect the  $\text{C}=\text{O}$  and  $\text{C}-\text{O}(\text{H})$  lengths of the two carboxyl groups. A similar H-bonding motif to Fig. 1 is found in oxalic acid-acetamide (Leiserowitz & Nader, 1972), shown in Fig. 2, which also displays bond lengths and H-bond distances. This structure, which was measured at room temperature, does not exhibit any significant differences in bond length between the two carboxyl groups which are differently H-bonded. It is also noteworthy that no significant differences were observed in the room-temperature structure of allenedicarboxylic acid-acetamide (Nader, 1976). Consequently, it remains an open question whether the differences in bond lengths between the two carboxyl groups in the low-temperature structure of allenedicarboxylic acid-acetamide are significant and are associated with differences in H-bonding. It is probable that the bond lengths obtained from the low-temperature structure are more reliable, primarily because of the far greater number of reflexions measured ( $4393$ ,  $d_{\text{max}}^* = 2.158$  vs  $2137$ ,  $d_{\text{max}}^* = 1.324$ ). Moreover, non-spherical electron density distributions were taken into account in the low-temperature study, in contrast to the room-

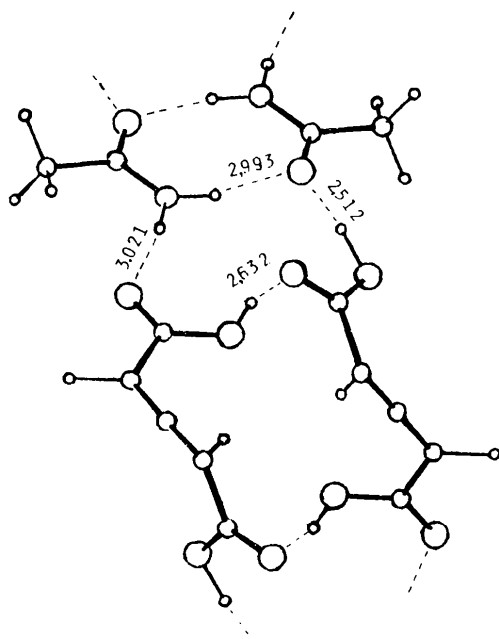


Fig. 1. The H-bonding motif in allenedicarboxylic acid-acetamide.

temperature studies of both allenedicarboxylic acid-acetamide and oxalic acid-acetamide. The effect of H-bonding on the bond lengths of some carboxylic acids and acetamides was summarized by Beagley (1975); there is a pronounced shortening of 0.04 Å of the carboxyl C–OH length on formation of a H-bond. In the allenedicarboxylic acid complex the C–OH bond which participates in the very short OH...OCNH<sub>2</sub> bond of 2.51 Å is 0.018 Å shorter than the C–OH bond whose O–H group participates in a relatively longer OH...OCOH bond of 2.63 Å.

The C=O length of the amide group (1.250 Å) is longer than that of the carboxyl groups (1.217, 1.230 Å). This is significant, for similar differences have been observed in a number of other crystal structures containing both functional groups (e.g. Huang, Leiserowitz & Schmidt, 1973; Benghiat, Kaufman, Leiserowitz & Schmidt, 1972).

### Charge deformation maps

Electron density difference maps were obtained by plotting the sum of the deformation functions around each atom with coefficients determined by the least-squares refinement (Hirshfeld, 1971; Harel & Hirshfeld, 1975). The deformation maps show accumulation of charge between bonded atoms and distinct electron density maxima at sites predicted on the basis of *sp*<sup>2</sup> hybridization of the O atoms of allenedicarboxylic acid-acetamide, namely, at lone pairs around the O atoms. The atomic centres are in troughs of negative density indicating migration of charge from

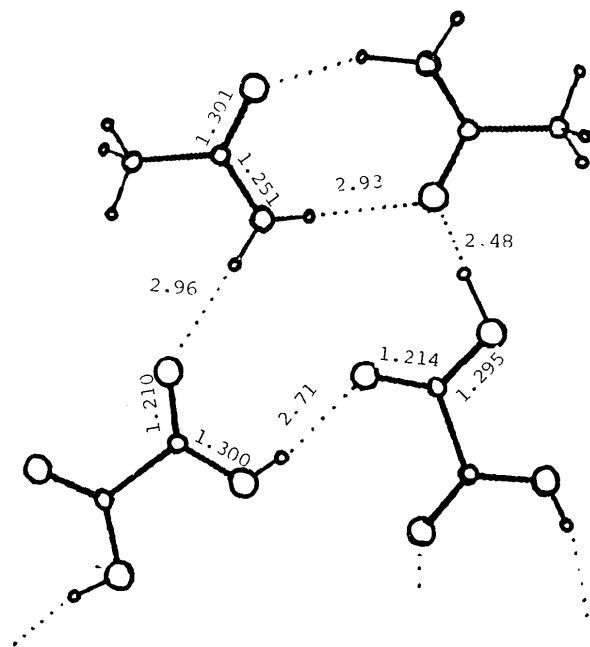


Fig. 2. The H-bonding motif in oxalic acid-acetamide (Leiserowitz & Nader, 1972).

the close vicinity of the atoms to the bonds and lone pairs, owing to the formation of a molecule. The H atoms, forming one bond peak, but also contracted owing to the formation of an X–H bond, show a dipolar pattern of angular polarization superimposed on pronounced radial contraction.

The difference density in the plane of the allene system is shown in Fig. 3. A comparison between the electron density distributions in the two adjacent C=C bonds of the allene system indicates that the charge density in the >C=C bond extends more along the direction perpendicular to the plane of >C=C than along its in-plane direction. This electron density distribution implies that the charge densities in adjacent double bonds are mutually perpendicular, a feature displayed most convincingly in the structure of tetraphenylbutatriene (Berkovitch-Yellin & Leiserowitz, 1977).

The electron density distribution of the carboxyl group exhibits many features observed in other electron density studies, both theoretical (Hagler & Lapicciarella, 1976) and experimental (Coppens, Sabine, Delaplane & Ibers, 1969; Hecht & Hirshfeld, 1976; Griffin & Coppens, 1975). However, on close comparison there are several features which do not match well. Therefore we tend to the view that only gross features of the electron density distributions in the carboxyl and amide groups should be regarded as significant.

The section through the plane of the H-bonded acetamide dimer (Fig. 4) displays the following important features; it contains maxima (*L*) lying ~0.6 Å from the O atom where the angle *L*–O=C ≈ 100°. These maxima, commonly designated as the lone-pair electrons, lie approximately along the line of the X–H...O bonds. A section (Fig. 5) perpendicular to the plane of the amide system and passing through the two maxima of the lone-pair electrons of the amide O atom does not display two distinct lone-pair lobes. Rather, the distribution appears to be almost cylindrical in shape.

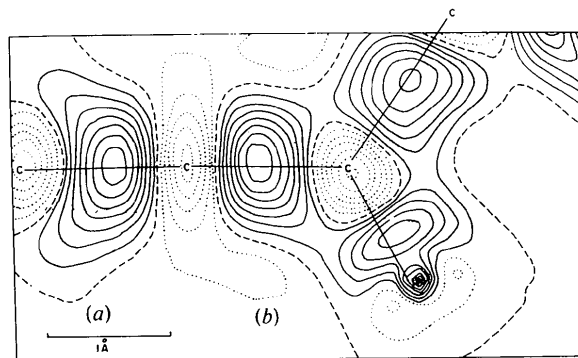


Fig. 3. Deformation density in the allene system (C=C=C<). Peaks (*a*) and (*b*) are two perpendicular sections of the deformation density in the allene C=C bond. (*a*) is perpendicular to and (*b*) is in the plane of C=C<. Contour interval 0.1 eÅ<sup>-3</sup>. Zero contours broken, negative contours dotted.

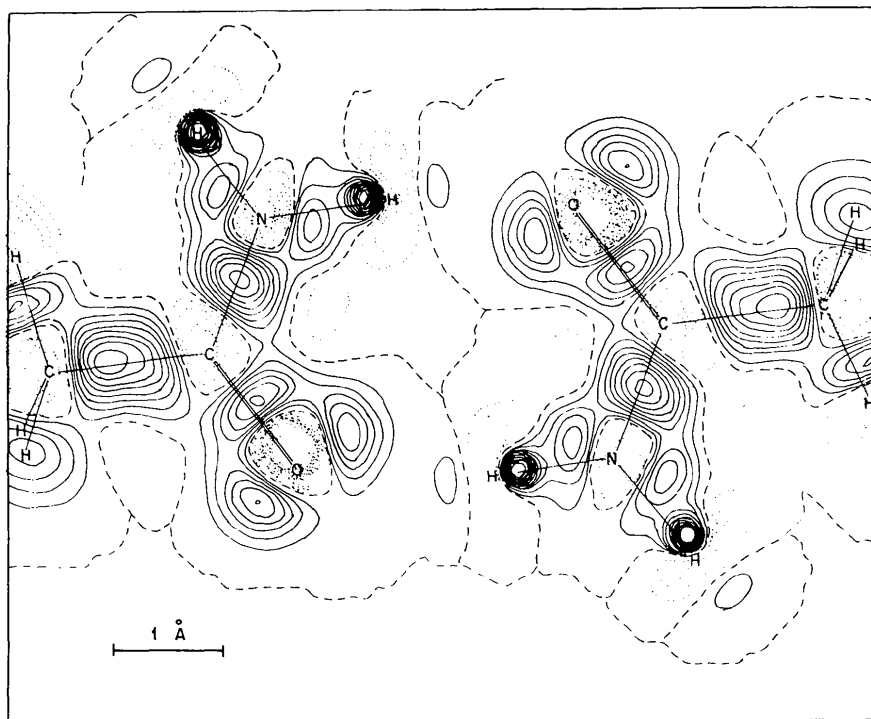


Fig. 4. Deformation density section through the plane of a H-bonded acetamide dimer. Contours as in Fig. 3.

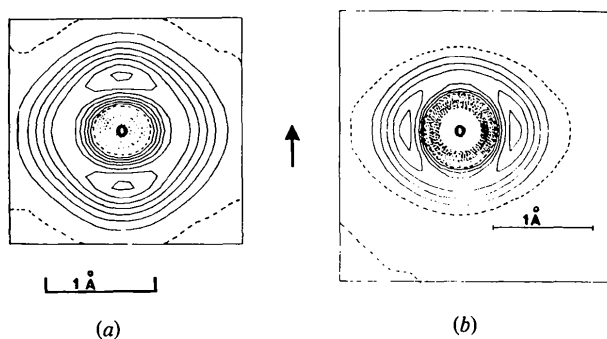
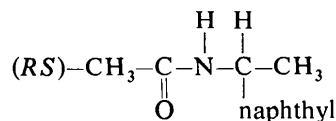


Fig. 5. Deformation density sections perpendicular to (a) the amide group and (b) the carboxyl group through the lone-pair maxima. The arrow indicates the direction perpendicular to (a) the amide group and (b) the carboxyl group.

The section through the plane of the carboxyl group (Fig. 6) displays an electron density distribution about the carbonyl O atom which is similar to that of the amide O atom. The density distribution of the lone-pair lobes of the carbonyl O atom of the carboxyl group differs somewhat from that of the amide O atom. The section through the lone-pair maxima perpendicular to the plane of the carboxyl group (Fig. 5) shows that the lone-pair maxima lie in the plane of the carbonyl system. This is in contrast to what is found in the amide system. Whether this is a significant difference between the amide and the carboxyl atoms is open to question.

In this context it is noteworthy that there are other distinct differences between the amide and carboxyl C=O bonds: in bond length (amide: 1.25 Å, acid: 1.22 Å), in the average lengths of the single O-H...OCNH and O-H...OCOH bonds (amide: 2.50 Å, acid: 2.64 Å) (Leiserowitz & Nader, 1977) and in IR stretching frequencies (amide: 1650–1620  $\text{cm}^{-1}$ , acid: 1725–1690  $\text{cm}^{-1}$ ). There also appear to be differences in the H-bonding acceptor properties of both O atoms; while the carbonyl O atom of the carboxyl group almost invariably forms H-bonds in which the X-H bond lies in the plane of the carbonyl system  $\text{>C=O}$  to which it is H-bonded (Leiserowitz, 1976), there are several amide crystal structures in which the N-H bond is directed towards the carbonyl O atom of the molecule to which it is H-bonded from well above the plane of the carbonyl system  $\text{>C=O}$ . These include *N*-methylpropiolamide,  $\text{H-C}\equiv\text{C-CO-NHCH}_3$  (Leiserowitz & Tuval, 1977),



(Leiserowitz & Weinstein, 1976) and particularly urea (Caron & Donohue, 1969). This may imply more-localized lone-pair density peaks lying in the plane of the carbonyl system in acids, than in amides.

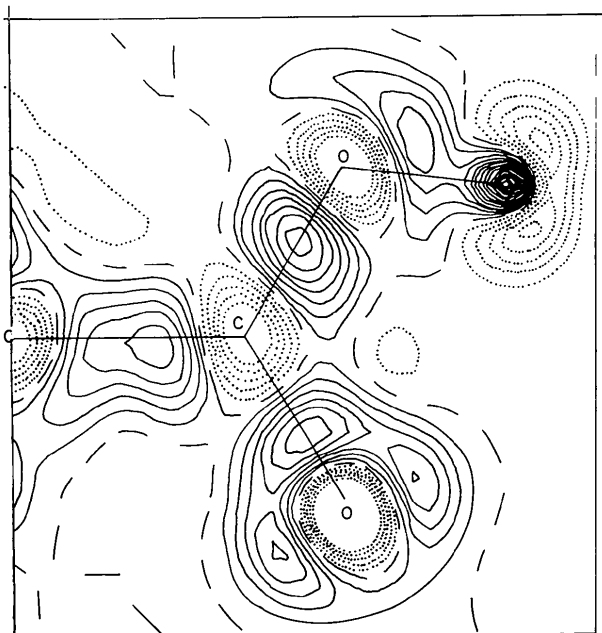


Fig. 6. Section through the plane of the carboxyl group. Contours as in Fig. 3.

The deformation density near the hydroxyl O atom (Fig. 6) seems to be at fault. In oxalic acid dihydrate (Coppens *et al.*, 1969), in a bicyclobutanedicarboxylic acid derivative (Hecht & Hirshfeld, 1976) and in a theoretical difference density map of acetic acid (Hagler & Lapicciarella, 1976) the lone-pair peak of the hydroxyl O atom is located almost on the bisector of the C—O—H bond at the back of the hydroxyl O atom and in the plane of the carboxyl group. In the carboxyl group (Fig. 6) the deformation density around the hydroxyl O atom is not resolved into a lone-pair lobe and an O—H bonding density peak but appears as one merged peak.

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