C5—C6—C7	120.2 (2)	C5—C13—C14	119.2 (2)
C6—C7—C8	121.0 (2)	C10—C13—C14	119.3 (2)
C7—C8—C14	121.1 (2)	C8—C14—C9	123.8 (2)
C11—C9—C14	121.5 (2)	C8—C14—C13	117.4 (2)
C11—C9—C15	119.5 (2)	C9—C14—C13	118.8 (2)
C14—C9—C15	119.0 (2)	C9—C15—O1	116.2 (2)
C12—C10—C13	122.3 (2)	C9—C15—O2	121.4 (2)
C1—C11—C9	123.9 (2)	O1—C15—O2	122.4 (2)
C1—C11—C12	117.5 (2)		

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H···O2$^{\text{i}}$	1.11 (3)	1.54 (3)	2.646 (2)	176 (3)

Symmetry code: (i) $-x, 1-y, 1-z$.

Scan widths were $(1.40 + 0.35\tan\theta)^\circ$ in ω, with a background/scan-time ratio of 0.5. The data were corrected for Lorentz and polarization effects. The Laue group assignment, systematic absences and intensity statistics were consistent with centrosymmetry-indicated space group $P2_1/n$ (No. 14) and since refinement proceeded well, it was adopted. Fourier difference methods were used to locate the H-atom positions. In the later stages of refinement, ring H atoms H1–H8 and H10 were made canonical, with a C—H distance of 0.98 Å and $U_{\text{iso}} = 1.2 \times U_{\text{eq}}$ of the associated C atom. The carboxylic H atom was refined isotropically. The maximum effect of extinction was 7.3% of F_o for $10\bar{5}$. The maximum positive residual peak was located near the midpoint of the C13—C14 bond, with the maximum negative peak located near the center of the central ring.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1991). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1989). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *TEXSAN*.

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Lists of structure factors, least-squares-planes data, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BK1282). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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N-Acetyl-L-glutamic Acid

Allison J. Dobson and Roger E. Gerkin

Department of Chemistry, The Ohio State University, Columbus, Ohio 43210, USA. E-mail: rgerkin@magnus.acs.ohio-state.edu

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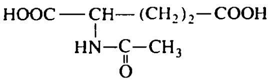
Abstract

In the structure of *N*-acetyl-L-glutamic acid, $C_7H_{11}NO_5$, each molecule is directly hydrogen bonded to four others by a total of six hydrogen bonds. Two carboxylic O atoms and the N atom are donors, while all three acceptors are O atoms. There is also an intramolecular hydrogen bond with the N atom as donor and a carboxylic O atom as acceptor. The carboxyl O and H atoms are ordered. The conformation of the carbon chain with respect to the C3—C4 bond is *trans* as in L-glutamic acid hydrochloride, rather than *gauche* as in the β form of L-glutamic acid.

Comment

This structural study of *N*-acetyl-L-glutamic acid, (I), is one of a continuing series on hydrogen bonding in carboxylic acids. In addition to its two carboxyl groups, this acid has further potential hydrogen-bonding groups, namely the NH group and the carbonyl O atom.



$\mathrm{HOOC{-}CH(NH{-}C({=}O){-}CH_3){-}(CH_2)_2{-}COOH}$

(I)

In the title acid (Figs. 1 and 2), all of the groups mentioned above are indeed involved in hydrogen bonding. Each H atom bonded to a potential hydrogen-bond donor atom (H1, H5 and H6) participates in a single intermolecular hydrogen bond. (In addition, H6 participates in an intramolecular hydrogen bond.) Moreover, each potential acceptor atom that is not already bonded to an H atom (O21, O25 and O5) participates in one intermolecular hydrogen bond. The hydrogen bonding can thus be considered fully developed. Each molecule is directly hydrogen bonded to four other molecules by a total of six hydrogen bonds (Fig. 2). It is of interest that while there are no cyclic dimer hydrogen bonds formed solely by carboxyl groups, there are analogs of them involving the NH group and portions of two carboxyl groups. Geometric details are given in Table 3. Data presented in Tables 2 and 3 for distances and angles involving the carboxylic group atoms show that these O atoms are ordered and that the carboxylic H atoms are also ordered. The dihedral angle between the two carboxyl groups within a molecule in this structure is 79.0 (3)°.

Although a substantial number of structures involving glutamic acid or *N*-substituted glutamic acid have been determined, none of them provides ideal structural comparisons with this acid for various reasons (for example, protonation of the amino group by one of the carboxyl H atoms in the native acid, very bulky substituent groups or substituent groups with multiple hydrogen-bonding sites of their own). Nonetheless, good comparisons are afforded by neutron-diffraction studies of the β form of both L-glutamic acid (Lehmann, Koetzle & Hamilton, 1972; hereafter LKH) and L-glutamic acid hydrochloride (Sequeira, Rajagopal & Chidambaram, 1972; hereafter SRC). The agreement of comparable non-H-atom bond distances is very good between this study and the two cited studies; the average deviation between LKH and this study is 0.006 (5) Å for six distances, while between this study and SRC, it is 0.008 (9) Å for eight distances. [The C2—N distance (the atomic labeling is as given in Fig. 1 throughout this discussion) is not comparable in either case since nitrogen exists in both as NH_3^+; the C1—O11 and C1—O21 distances are not comparable with those of LKH since there is no carboxyl H atom in the C1 carboxyl group in that case.] Similarly, the average deviation of comparable angles for non-H atoms is 2.0 (4)° for the LKH and present data, and 1.1 (7)° for the SRC and present data. With respect to the LKH angle comparison, it is noteworthy that the C2—C3—C4 and C3—C4—C5 angles differ by 4.3 and 4.9°, respectively, with the present values being 113.5 (2) and 111.2 (2)°, respectively, very close to the value of 112° cited by LKH for C—C—C angles in (unstrained) amino acids. Thus, both the SRC study and this study support the conclusion that these angles are strained in the β form of L-glutamic acid.

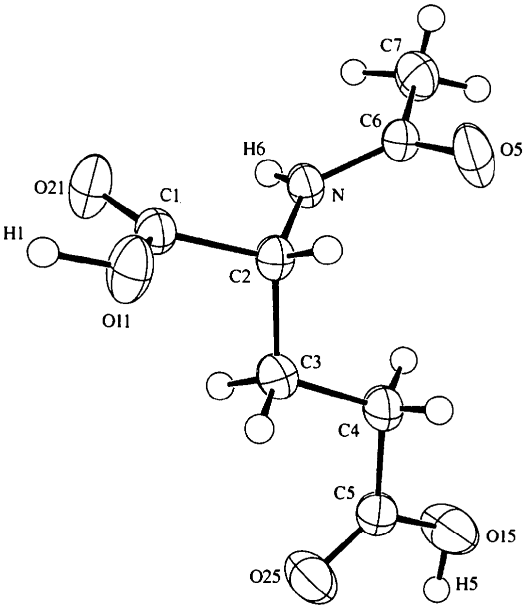


Fig. 1. *ORTEP*II (Johnson, 1976) drawing of *N*-acetyl-L-glutamic acid showing the atomic numbering scheme. Displacement ellipsoids are drawn at 50% probability for all atoms except H atoms, for which they have been set artificially small.

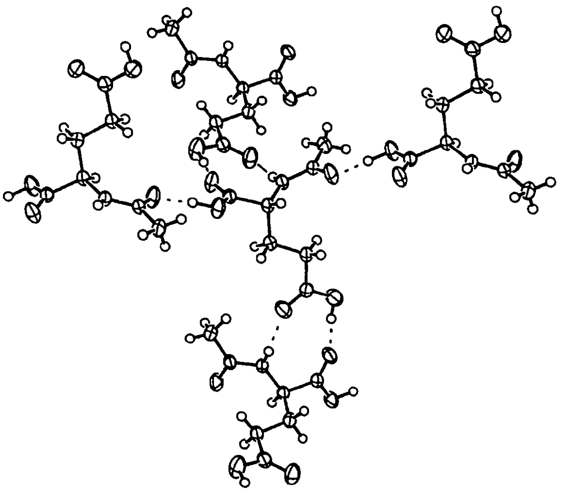


Fig. 2. *ORTEP*II (Johnson, 1976) drawing of a central *N*-acetyl-L-glutamic acid molecule and its four directly hydrogen-bonded neighbors. Displacement ellipsoids are drawn at 50% probability for all atoms except H atoms, for which they have been set artificially small. The six hydrogen bonds involving the central molecule are shown with dashes. The incipient development of a richly three-dimensional network of hydrogen bonds is apparent. In this view, **a** runs approximately into the page, and **b** and **c** lie approximately vertical and horizontal, respectively.

As pointed out by LKH, the major structural difference between the LKH and SRC studies is in the conformation of the C2–C5 chain; with respect to the C3—C4 bond, the LKH structure torsion angle was −73.1 (2)° (*gauche* conformation), whereas in the SRC structure, it was −173.1 (4)° (*trans* conformation). In the present structure, this torsion angle is −176.5 (2)° (*trans* conformation). In this sense, this structure is more nearly like that of the L-glutamic acid hydrochloride than of the native acid.

In this structure, all of the closest intermolecular approaches involve at least one atom involved in hydrogen bonding [C6···H1($\frac{5}{2}-x$, $-y$, $z-\frac{1}{2}$), O25···H7*B*($1-x$, $y-\frac{1}{2}$, $\frac{1}{2}-z$) and O11···H3*A*($1+x$, y,

z)] and fall short of the corresponding Bondi (1964) radius sums by 0.27, 0.26 and 0.15 Å, respectively; moreover, the first two of these approaches occur between atoms in molecules hydrogen bonded to one another.

Experimental

N-Acetyl-L-glutamic acid was obtained from Pfaltz and Bauer Inc. Slow evaporation of an aqueous solution produced crystals of suitable quality.

Crystal data

$C_7H_{11}NO_5$
$M_r = 189.17$
Orthorhombic
$P2_12_12_1$
$a = 4.898\ (1)$ Å
$b = 12.925\ (2)$ Å
$c = 13.875\ (1)$ Å
$V = 878.5\ (3)$ Å^3
$Z = 4$
$D_x = 1.430$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 15.3$–$16.9°$
$\mu = 0.115$ mm^{-1}
$T = 296$ K
Cut rod
0.39 × 0.35 × 0.19 mm
Colorless

Data collection

AFC-5*S* diffractometer
$\omega/2\theta$ scans
Absorption correction: none
2372 measured reflections
1233 independent reflections
989 observed reflections [$I > 3\sigma(I)$]
$R_{\rm int} = 0.019$
$\theta_{\rm max} = 27.5°$

$h = 0 \rightarrow 6$
$k = 0 \rightarrow 16$
$l = -15 \rightarrow 15$
6 standard reflections monitored every 150 reflections intensity decay ±1.6% (average maximum relative intensity)

Refinement

Refinement on F
$R = 0.031$
$wR = 0.039$
$S = 1.66$
989 reflections
163 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F)]$
$(\Delta/\sigma)_{\rm max} = < 0.01$
$\Delta\rho_{\rm max} = 0.22$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.14$ e Å^{-3}

Extinction correction: Zachariasen (1963, 1968)
Extinction coefficient: 27 (9) × 10^{-7}
Atomic scattering factors from Stewart, Davidson & Simpson (1965) for H atoms and Cromer & Waber (1974) for C, N and O atoms

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
O11	1.2679 (4)	−0.0634 (1)	0.3903 (1)	0.0433 (5)
O21	0.9375 (4)	0.0537 (1)	0.3935 (1)	0.0444 (4)
O15	0.4417 (5)	−0.2964 (2)	0.0819 (1)	0.0610 (6)
O25	0.5580 (4)	−0.3282 (1)	0.2330 (1)	0.0557 (5)
O5	1.1376 (4)	0.0208 (1)	0.0648 (1)	0.0487 (5)
N	0.8769 (4)	0.0384 (1)	0.1962 (1)	0.0289 (5)
C1	1.0708 (5)	−0.0107 (2)	0.3514 (1)	0.0294 (5)
C2	1.0143 (4)	−0.0439 (2)	0.2480 (1)	0.0276 (4)
C3	0.8441 (5)	−0.1438 (2)	0.2518 (2)	0.0349 (5)
C4	0.7543 (6)	−0.1821 (2)	0.1530 (2)	0.0355 (6)
C5	0.5760 (5)	−0.2754 (2)	0.1614 (2)	0.0352 (6)
C6	0.9489 (5)	0.0656 (2)	0.1072 (1)	0.0314 (5)
C7	0.7883 (7)	0.1509 (2)	0.0613 (2)	0.0445 (7)

Table 2. *Geometric parameters (Å, °)*

O5—C6	1.239 (3)	C4—C5	1.493 (3)
N—C2	1.449 (3)	C6—C7	1.497 (3)
N—C6	1.332 (3)	C1—O11	1.299 (3)
C1—C2	1.523 (3)	C1—O21	1.209 (3)
C2—C3	1.538 (3)	C5—O15	1.313 (3)
C3—C4	1.522 (3)	C5—O25	1.209 (3)
C2—N—C6	122.0 (2)	N—C6—C7	116.7 (2)
N—C2—C1	110.1 (2)	C2—C1—O11	112.2 (2)
N—C2—C3	112.5 (2)	C2—C1—O21	123.5 (2)
C1—C2—C3	107.6 (2)	O11—C1—O21	124.2 (2)
C2—C3—C4	113.5 (2)	C4—C5—O15	113.3 (2)
C3—C4—C5	111.2 (2)	C4—C5—O25	124.2 (2)
O5—C6—N	121.0 (2)	O15—C5—O25	122.5 (2)
O5—C6—C7	122.3 (2)		

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H···A	D—H	H···A	D···A	D—H···A
O11—H1···O5$^{\rm i}$	1.00 (4)	1.53 (4)	2.527 (2)	173 (4)
O15—H5···O21$^{\rm ii}$	0.92 (4)	1.80 (4)	2.705 (3)	167 (4)
N—H6···O25$^{\rm iii}$	0.82 (3)	2.10 (3)	2.911 (3)	171 (3)
N—H6···O21	0.82 (3)	2.63 (3)	2.761 (2)	90 (2)

Symmetry codes: (i) $\frac{5}{2} - x, -y, \frac{1}{2} + z$; (ii) $1 - x, y - \frac{1}{2}, \frac{1}{2} - z$; (iii) $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$.

Scan widths were $(1.20 + 0.35\tan\theta)°$ in ω, with a background/scan-time ratio of 0.5. The data were corrected for Lorentz and polarization effects. The Laue group assignment, systematic absences and the lack of centrosymmetry indicated by the intensity statistics led to unique assignment of the space group as $P2_12_12_1$ (No. 19) and since refinement proceeded well, it was adopted. Fourier difference methods were used to locate the initial H-atom positions. The maximum effect of extinction was 4.7% of F_o for 121. The maximum peak in the final difference map occurred ~0.9 Å from O25 and the maximum negative peak occurred ~0.8 Å from O25.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1991). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1989). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *TEXSAN*.

It is a pleasure to acknowledge the partial support provided to AJD by a National Needs Fellowship. We thank Dr J. C. Gallucci for help of various sorts. The diffractometer was purchased with funds provided in part by an NIH grant.

Lists of structure factors, least-squares-planes data, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: FG1211). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Zachariasen, W. H. (1968). *Acta Cryst.* **A24**, 212–216.

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The Donor–Acceptor Complex between 4,6,8-Trimethylazulene and Picric Acid

Christian Näther, Claudia Arad and Hans Bock

Institut für Anorganische Chemie der Universität Frankfurt, Marie-Curie-Strasse 11, 60439 Frankfurt/Main, Germany.
E-mail: chris@bock.anorg.chemie.uni-frankfurt.de

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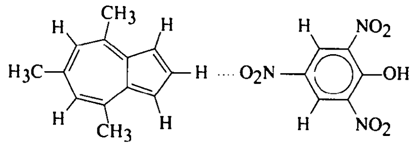
Abstract

Slow cooling of an equimolar mixture of 4,6,8-trimethylazulene and picric acid (2,4,6-trinitrophenol) in ethanol yields crystals of an 1:1 donor–acceptor complex, $C_{13}H_{14}.C_6H_3N_3O_7$, the structure of which has been determined by X-ray diffraction at 200 K. The donor and acceptor molecules alternate in mixed stacks along the [001] direction. All geometric parameters of the donor as well as the acceptor molecules are comparable to those in isolated 4,6,8-trimethylazulene and picric acid.

Comment

The structure of the title compound, (I), has been determined as part of a study of geometric perturbations on the formation of electron donor–acceptor complexes (Bock, Sievert, Schödel & Kleine, 1996; Bock, Ziemer, Näther, Schödel, Kleine & Sievert, 1996; Bock, Seitz, Sievert, Kleine & Bats, 1996; Bock, Rauschenbach, Näther, Kleine & Bats, 1996). In addition, the sodium metal reduction of azulene has been investigated (Bock, Arad, Näther & Göbel, 1996). 4,6,8-Trimethylazulene was selected for co-crystallization with picric acid because azulene tends to be disordered in the solid state (Kovats, Günthard & Plattner, 1955; Robertson, Shearer, Sim & Watson, 1962) even in its molecular complexes (Hanson, 1965).



(I)

The crystal structure of the title complex contains mixed stacks of alternating donor and acceptor molecules, which are often observed in π-molecular complexes such as picric acid:anthracene (Herbstein & Kaftory, 1976) or picric acid:naphthalene (Banerjee & Brown, 1985; Yamaguchi, Goto, Takayanagi & Ogura, 1988). Between the stacks, which are oriented parallel to [001], short intermolecular contacts of 2.500 (2) Å are observed between the H5 atom of 4,6,8-trimethylazulene and the O4 atom of the picric acid. Each molecule is enclosed in a quasi-hexagonal environment. The angles between the molecular mean planes of the 4,6,8-trimethylazulene and picric acid molecules are 4.38 (3) and 9.44 (3)°, however, due to the non-parallel arrangement, the interplanar distances need additional specification. The calculated distances between the reference plane of the 4,6,8-trimethylazulene molecule and the centroid of the six-membered ring of picric acid are 3.35 (1) [interplanar angle = 4.38 (1)°] and 3.50 (1) Å [interplanar angle = 9.44 (12)°], and indicate only a weak 'molecule pairing' within the stacks, in which the orientation of picric acid alternates with a periodicity of about 14 Å. It has been shown (Herbstein, 1971; Herbstein & Kaftory, 1975) that equimolar π-molecular complexes with stack-axis lengths of about 7 Å can be sorted into groups of quasi-isomorphous structures. In addition, only a few compounds exhibit periodicities of about 14 Å, *e.g.* pyrene:picryl chloride, triphenylene:picryl chloride and triphenylene:picryl bromide (Herbstein & Kaftory, 1975). The title complex represents another example of this structure type.

Neither the donor 4,6,8-trimethylazulene nor the acceptor picric acid exhibit significant distortions of their structures attributable to complex formation, presumably as a result of the relatively large donor and acceptor molecules. Smaller acceptor molecules such as bromine

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