

Fig. 2. Packing diagram for compound (4).

The cyclopentene ring is almost planar while the five-membered lactone ring exhibits an envelope conformation. The seven-membered ring is in a chair conformation (Toromanoff, 1980).

The coordinates from the X-ray study were used as input for a molecular-mechanics (Allinger & Yuh, 1980) comparison of the C(11) epimers (2) and (3). In (2) the conformation with the hydroxyl hydrogen-bonded to the carbonyl is about 13 kJ mol⁻¹ more stable than the conformer with the hydroxyl rotated in a

nonbonding position. In compound (3) the hydrogen-bonded conformer is only about 0.2 kJ mol⁻¹ more stable. This is due to a steric interaction between the C(13) and C(6) hydrogen atoms in the hydrogen-bonded conformer of (3), and there is little energy gained by intramolecular hydrogen bonding. It is more difficult to rationalize the easier loss of water by (2) to form (1) since the mechanism of dehydration is still not understood completely.

A packing diagram for (4) is given in Fig. 2.

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Structure of Benzamidinium Pyruvate

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Abstract. C₁₀H₁₂N₂O₃, *M_r* = 208.22, monoclinic, *P*2₁/*n*, *a* = 5.756 (3), *b* = 18.994 (13), *c* = 9.766 (8) Å, *β* = 98.53 (5)°, *V* = 1055.9 (1) Å³, *Z* = 4, *D_m* = 1.311 (2), *D_x* = 1.309 (1) Mg m⁻³, λ(Mo Kα) =

0.7107 Å, μ = 0.106 mm⁻¹, *F*(000) = 440, *T* = 296 K, *R* = 0.044 for 1262 unique observed reflections. The structure contains inter- and intramolecular hydrogen bridges between the amidine nitrogens and the carboxy-

lic oxygens. The N...O distances range from 2.779 (3) to 2.899 (3) Å. Intermolecular hydrogen bonds give rise to infinite chains of molecules parallel to the *c* axis. Chains are interconnected by van der Waals forces.

Introduction. Arginine residues participate in the binding sites of some enzymes. Carboxylic substrates are fixed due to an interaction between the carboxyl group of the substrate and the guanidinium group of the amino acid, as suggested by crystallographic studies of carboxypeptidase (Lipscomb, 1973) and lactate dehydrogenase (Adams *et al.*, 1973). The L-arginine dihydrate itself (Karle & Karle, 1964) contains infinite chains of hydrogen bonds linking two N of the guanidino group with two O of COO⁻. The structure of methylguanidinium formate was presented (Bray, Slatery & Russell, 1984) as a simple model of the above mentioned interaction. Besides substituted guanidines, compounds with amidines and isothioureas also exhibit pairing with carboxylic components. The carboxylic part of the benzamidinium pyruvate studied is an important substrate for the enzyme lactate dehydrogenase.

Experimental. Benzamidinium pyruvate was obtained by reaction of benzamidinium chloride (*Organic Syntheses*, 1941) with sodium pyruvate in aqueous solution. Crystals were recrystallized from water/ethanol mixture by slow evaporation at room temperature. The density was determined by flotation in tetrachloromethane/hexane. Crystal of size 0.19 × 0.75 × 0.80 mm, absorption ignored, Syntex P2₁ diffractometer, cell parameters refined from 22 centered reflections, 1875 reflections collected, 0 < 2θ < 50°, *hkl* range: <-6,6>, <0,22>, <0,11>, no significant intensity fluctuation in the three standard reflections (004, 060, 200), 1262 unique observed reflections with *I* > 1.96σ(*I*), the phase problem solved by direct methods, H-atom positions obtained from Δ*F* synthesis, the quantity $\sum w(|F_o| - |F_c|)^2$ minimized by full-matrix least squares, positional and anisotropic thermal parameters of non-H atoms and positional and isotropic thermal parameters of H atoms refined in three blocks, *R* = 0.044, *wR* = 0.047, *w* = 1.6311/[σ²(*F_o*) + 0.0009*F_o*²], (Δ/*σ*)_{max} = 0.05, max. height in the final difference Fourier map 0.13, min. height -0.17 e Å⁻³, SHELX76 (Sheldrick, 1976) - source of the atomic scattering factors, TPLANE (Petříček, 1981), PLUTO (Motherwell, 1976) programs used, EC 1033, ICL 4-72 and IBM 370/135 computers.*

* Lists of structure factors, anisotropic thermal parameters, least-squares-planes details, H-atom coordinates and bond distances and angles involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44170 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Final coordinates (× 10⁴) for non-H atoms and their equivalent isotropic thermal parameters (× 10⁴)

$$U_{eq} = (U_{11} + U_{22} + U_{33} + 2U_{13}\cos\beta)/3$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i> (Å ²)
O(1)	2030 (3)	1751 (1)	4527 (1)	616 (6)
O(2)	2167 (3)	2059 (1)	2352 (1)	717 (6)
O(3)	6051 (3)	1274 (1)	2420 (2)	930 (8)
N(1)	-1582 (3)	2801 (1)	4663 (2)	537 (6)
N(2)	-1553 (3)	2989 (1)	2375 (2)	547 (6)
C(1)	2934 (4)	1749 (1)	3444 (2)	481 (7)
C(2)	5215 (4)	1331 (1)	3465 (2)	541 (8)
C(3)	6331 (5)	1006 (2)	4787 (3)	860 (12)
C(4)	-2344 (4)	3153 (1)	3532 (2)	442 (7)
C(5)	-4057 (3)	3728 (1)	3540 (2)	434 (10)
C(6)	-5806 (4)	3686 (1)	4377 (2)	514 (7)
C(7)	-7385 (4)	4226 (1)	4371 (2)	598 (9)
C(8)	-7249 (4)	4819 (1)	3573 (2)	629 (9)
C(9)	-5510 (5)	4866 (1)	2756 (2)	652 (10)
C(10)	-3928 (4)	4326 (1)	2733 (2)	563 (6)

Table 2. Bond distances (Å) and angles (°)

C(5)-C(6)	1.390 (3)	C(10)-C(5)-C(4)	120.7 (2)
C(6)-C(7)	1.370 (3)	C(6)-C(5)-C(4)	120.3 (2)
C(7)-C(8)	1.379 (3)	C(5)-C(4)-N(1)	121.0 (2)
C(8)-C(9)	1.372 (3)	C(5)-C(4)-N(2)	119.8 (2)
C(9)-C(10)	1.374 (3)	N(1)-C(4)-N(2)	119.2 (2)
C(10)-C(5)	1.391 (3)	O(1)-C(1)-O(2)	126.0 (2)
C(5)-C(4)	1.472 (3)	O(1)-C(1)-C(2)	117.1 (2)
C(4)-N(1)	1.310 (3)	O(2)-C(1)-C(2)	116.9 (2)
C(4)-N(2)	1.317 (3)	C(1)-C(2)-O(3)	119.2 (2)
O(1)-C(1)	1.246 (2)	C(1)-C(2)-C(3)	119.0 (2)
O(2)-C(1)	1.241 (2)	O(3)-C(2)-C(3)	121.8 (2)
C(1)-C(2)	1.532 (3)		
C(2)-O(3)	1.196 (3)		
C(2)-C(3)	1.488 (4)		

Hydrogen bonds

Intermolecular		Intramolecular	
N(1)...O(1)	2.898 (3)	N(1)...O(2 ⁱ)	2.837 (2)
N(2)...O(2)	2.779 (3)	N(2)...O(1 ⁱⁱ)	2.824 (2)

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

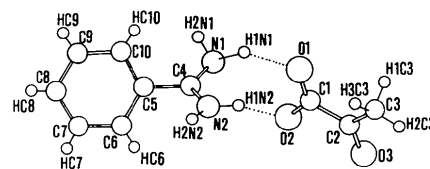


Fig. 1. Perspective view of the molecule with atom numbering.

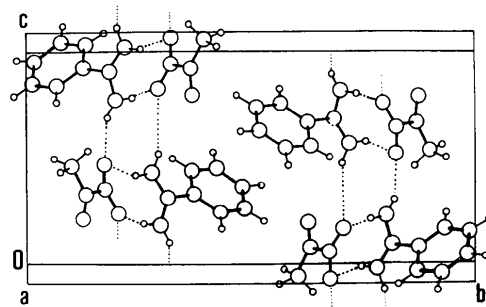


Fig. 2. The unit-cell contents. Dashed lines indicate the hydrogen bonding.

Discussion. The atomic coordinates and thermal parameters of the non-H atoms are given in Table 1. Fig. 1 depicts a perspective view of the molecule with its atom numbering. The unit-cell contents are presented in Fig. 2. The interatomic bond distances and angles are summarized in Table 2. The most conspicuous features of the structure are two inter- and two intramolecular symmetrically independent hydrogen bridges between the amidine nitrogens and the carboxylic oxygens. The intramolecular bridges are realized through H1N1 and H1N2 and intermolecular contacts are mediated by H2N1 and H2N2 hydrogens. Intermolecular hydrogen bonds give rise to infinite chains of molecules parallel to the *c* direction and thus form the arrangement of the structure. The chains are interconnected by van der Waals forces. A comparison of the N...O contacts in the title compound with the structures of methylguanidinium formate and L-arginine dihydrate shows no significant differences in bond lengths. Atoms of the amidine group (H1N1, N1, C4, N2 and H1N2) are situated nearly in one plane with a maximum deviation of 0.032 (2) Å for N2. This plane deviates from that of the benzene ring by 35.2 (3)°. The torsion angle C6—C5—C4—N2 is 35.1° and C10—C5—C4—N1 is 36.5 (2)°. The differences between N1...O1 and N2...O2 distances are due to the influence of the C2=O3 group in the pyruvic acid moiety. The same

effect is probably responsible for the mutual orientation of amidine and carboxylic planes. The angle between the H1N1, N1, C4, N2, H1N2 and the H1N1, O1, C1, O2, H1N2 planes is 5.6 (3)°. The torsion angles O3—C2—C1—O2 and O3—C2—C1—O1 are 5.8 (3) and 5.2 (2)° respectively.

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Structure of 3'-O-Acetyl-2'-deoxyadenosine

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Abstract. C₁₂H₁₅N₅O₄, *M_r* = 293.3, monoclinic, *P*2₁, *a* = 8.363 (9), *b* = 7.33 (1), *c* = 11.52 (1) Å, β = 106.8 (9)°, *U* = 676 Å³, *Z* = 2, *D_x* = 1.44 Mg m⁻³, Mo *Kα* radiation, λ = 0.71069 Å, μ = 0.7 mm⁻¹, *F*(000) = 308, *T* = 293 K, *R* = 0.044 for 1901 unique observed [*F* > 3σ(*F*)] reflections. The molecule is *anti*, with χ(C4—N9—C1'—O4') = -165.7 (3)°, has sugar pucker ₃*E*, with *P* = 197°, and C4'—C5' conformation of +*sc* (*gauche-gauche*). The structure has base-paired symmetry-related molecules, with hydrogen bonds between the 6-amino group and N1 and N7. The structure differs from that of 3'-*O*-acetyladenosine [Rao & Sundaralingam (1970). *J. Am. Chem. Soc.* **92**,

4963–4970] in which there is no interbase hydrogen bonding. The base-pair shows a propeller twist, defined as the angle between the base planes about a line joining them, of 28°. There is also a hydrogen bond between N3 and O5' of a symmetry-related molecule, similar to that found for 3'-*O*-acetyladenosine, with N...O = 2.811 (4), N...H = 1.847 Å and N...H—O = 153.2 (2)°.

Introduction. The structural study was undertaken in continuation of our studies of acetylated nucleosides, induced base-pairing and studies of propeller-twisting in mononucleoside crystals.