$C_{11}H_{11}ClN_4O$

ketonitrones (1) and 1-alkenyl phenyl ethers (2). The resulting products represented cis/trans mixtures of the corresponding diastereomers of (3). While cyclic nitrones do not present configurational problems, acyclic ketonitrones are known to exist in either E or Z geometric form (Tufariello, 1984). Based on NMR spectral evidence, an E configuration was assigned for the α-substituted ketonitrones (1). An X-ray crystal structure determination of the triazole analog N-[1-(4-chlorophenyl)-2-(1H-1,2,4-triazol-1-yl)ethylidene]-methylamine N-oxide (1a) (Fig. 1) was undertaken in order to firmly establish the configuration of (1) and allow for consistent differentiation between the E and Z isomers of (1) by NMR spectral interpretation.
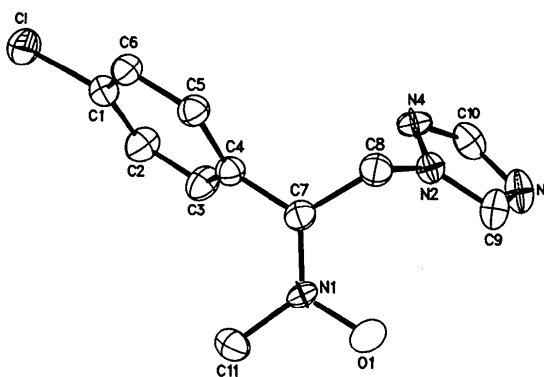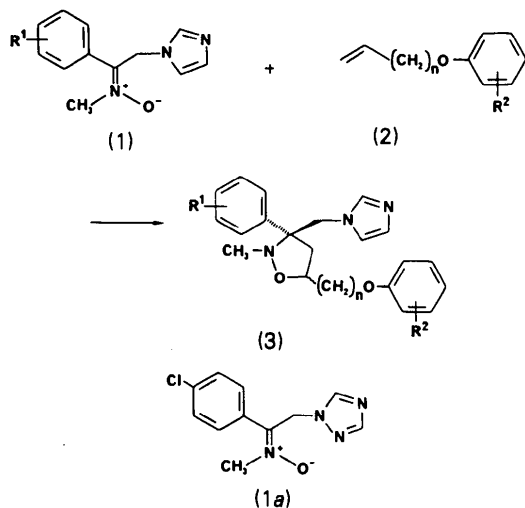

Fig. 1. Drawing of the molecule of (1a) showing the atom-numbering scheme.

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Structure of L-Arginyl-L-aspartic Acid Monohydrate

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Abstract. $C_{10}H_{19}N_5O_5.H_2O$, $M_r = 309.32$, monoclinic, $P2_1$, $a = 8.396$ (2), $b = 8.811$ (2), $c = 9.940$ (2) Å, $\beta = 100.71$ (2)°, $V = 723$ (1) Å^3, $Z = 2$, $D_m = 1.45$, $D_x = 1.42$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0.71073$ Å, $\mu = 1.1$ cm^{-1}, $F(000) = 328$, $T = 293$ K. The final R value for 1289 observed reflections [$I_o \geq 3\sigma(I_o)$] is 0.032. The dipeptide exists as a zwitterion. The peptide bond is planar and the backbone assumes an extended conformation. The two terminal N atoms of the guanidino group are hydrogen bonded to the carbonyl O atom and to one of the terminal carboxyl O atoms of the peptide backbone, a mode of interaction not found in earlier related structures.

Experimental. The dipeptide was purchased from Sigma Chemicals and used without further purification. Prismatic crystals of the peptide were grown by diffusing acetone into a solution of 50% water/50% dioxane. The size of the crystal used for X-ray data collection was $0.2 \times 0.2 \times 0.2$ mm. Density was

Table 1. Positional and isotropic thermal parameters with their e.s.d.'s

	x	y	z	$B(\text{Å}^2)$
O1	1·0525 (2)	0·755	−0·0670 (2)	3·16 (5)
O2	0·9329 (2)	0·5935 (3)	0·2188 (2)	3·29 (5)
O3	0·6668 (2)	0·6182 (3)	0·1495 (2)	2·96 (4)
O4	0·8499 (3)	0·8835 (3)	0·3868 (2)	3·89 (6)
O5	0·7585 (2)	1·1207 (3)	0·3451 (2)	2·76 (4)
OW	0·4608 (3)	0·8271 (3)	0·8298 (3)	6·32 (8)
N1	0·9790 (3)	0·8248 (3)	−0·3399 (2)	1·99 (5)
N2	0·7975 (2)	0·8174 (3)	−0·0410 (2)	1·90 (5)
N3	0·4978 (3)	0·6659 (4)	−0·6408 (3)	3·69 (7)
N4	0·3152 (3)	0·6936 (4)	−0·8386 (3)	3·39 (6)
N5	0·2273 (3)	0·6862 (3)	−0·6312 (3)	2·97 (6)
C1	0·8472 (3)	0·7737 (4)	−0·2687 (3)	1·85 (6)
C2	0·9105 (3)	0·7818 (4)	−0·1142 (3)	2·08 (6)
C3	0·8355 (3)	0·8245 (4)	0·1078 (3)	1·79 (6)
C4	0·8089 (3)	0·6648 (3)	0·1646 (3)	2·02 (6)
C5	0·7940 (3)	0·6099 (4)	−0·3094 (3)	2·39 (6)
C6	0·7188 (3)	0·5922 (4)	−0·4594 (3)	2·64 (7)
C7	0·5550 (3)	0·6618 (5)	−0·4946 (3)	4·00 (9)
C8	0·3452 (3)	0·6823 (4)	−0·7031 (3)	2·45 (6)
C9	0·7325 (4)	0·9478 (3)	0·1571 (3)	2·28 (6)
C10	0·7839 (3)	0·9846 (4)	0·3084 (3)	2·25 (6)
H1OW	0·409 (3)	0·879 (4)	0·864 (3)	6 (1)*
H2OW	0·397 (3)	0·770 (4)	0·786 (3)	4·4 (8)*
H1N1	0·941 (3)	0·850 (4)	−0·453 (3)	3·7 (7)*
H2N1	1·069 (3)	0·751 (4)	−0·350 (3)	6·3 (9)*
H3N1	1·032 (3)	0·890 (4)	−0·307 (3)	3·6 (7)*
HN2	0·685 (3)	0·831 (3)	−0·082 (2)	2·0 (6)*
HN3	0·580 (3)	0·658 (3)	−0·692 (3)	2·7 (7)*
H1N4	0·213 (3)	0·711 (3)	−0·892 (3)	3·7 (7)*
H2N4	0·399 (3)	0·692 (4)	−0·887 (3)	5·0 (8)*
H1N5	0·242 (3)	0·673 (3)	−0·525 (3)	4·0 (7)*
H2N5	0·137 (3)	0·685 (3)	−0·674 (3)	3·6 (7)*
HC1	0·754 (2)	0·849 (3)	−0·292 (2)	1·1 (5)*
HC3	0·951 (2)	0·847 (3)	0·130 (2)	1·4 (5)*
H1C5	0·890 (3)	0·549 (3)	−0·286 (3)	2·6 (6)*
H2C5	0·704 (3)	0·589 (3)	−0·250 (2)	2·4 (6)*
H1C6	0·790 (3)	0·632 (3)	−0·527 (2)	2·4 (6)*
H2C6	0·704 (3)	0·500 (4)	−0·480 (3)	5 (1)*
H1C7	0·475 (3)	0·622 (5)	−0·444 (3)	5·4 (9)*
H2C7	0·551 (3)	0·768 (4)	−0·465 (3)	3·6 (7)*
H1C9	0·602 (3)	0·923 (3)	0·130 (3)	3·2 (7)*
H2C9	0·727 (3)	1·024 (4)	0·101 (3)	4·6 (8)*

Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as: $\frac{4}{3}[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

Table 2. Molecular geometry

Numbers in parentheses are e.s.d.'s in the least-significant digits.

(a) Bond distances (Å)

O1—C2	1·221 (4)	N4—C8	1·327 (4)
O2—C4	1·249 (3)	N5—C8	1·324 (5)
O3—C4	1·245 (3)	C1—C2	1·531 (4)
O4—C10	1·244 (4)	C1—C5	1·542 (5)
O5—C10	1·282 (4)	C3—C4	1·548 (4)
N1—C1	1·490 (4)	C3—C9	1·526 (4)
N2—C2	1·336 (4)	C5—C6	1·517 (4)
N2—C3	1·455 (3)	C6—C7	1·486 (4)
N3—C7	1·444 (4)	C9—C10	1·520 (4)
N3—C8	1·324 (3)		

(b) Bond angles (°)

C2—N2—C3	121·4 (3)	O2—C4—C3	116·7 (2)
C7—N3—C8	125·8 (3)	O3—C4—C3	117·1 (2)
N1—C1—C2	108·2 (2)	C1—C5—C6	113·7 (3)
N1—C1—C5	111·3 (2)	C5—C6—C7	112·8 (3)
C2—C1—C5	109·7 (2)	N3—C7—C6	111·5 (3)
O1—C2—N2	125·2 (2)	N3—C8—N4	117·9 (3)
O1—C2—C1	120·6 (3)	N3—C8—N5	120·4 (3)
N2—C2—C1	114·2 (2)	N4—C8—N5	121·7 (2)
N2—C3—C4	108·2 (2)	C3—C9—C10	113·3 (2)
N2—C3—C9	109·1 (2)	O4—C10—O5	124·7 (3)
C4—C3—C9	113·7 (2)	O4—C10—C9	118·7 (3)
O2—C4—O3	126·2 (3)	O5—C10—C9	116·7 (2)

(c) Torsion angles (°; average e.s.d. 0·3°)

N1—C1—C2—N2	ψ_1	146·8	C6—C7—N3—C8	χ^4	−161·0
C2—N2—C3—C4	φ_2	−89·2	C7—N3—C8—N5	χ^{51}	−4·7
C1—C2—N2—C3	ω	−177·8	C7—N3—C8—N4	χ^{52}	175·7
N1—C2—C5—C6	χ^1	−64·2	N2—C3—C9—C10	χ^1	−169·5
C1—C5—C6—C7	χ^2	−71·4	C3—C9—C10—O4	χ^{21}	−28·1
C5—C6—C7—N3	χ^3	170·4	C3—C9—C10—O5	χ^{22}	150·4

(d) Hydrogen-bond distances and angles (Å, °; average e.s.d.'s 0·01 Å, 5°)

A—H···B	A···B	A—H···B	Unit-cell translation of atom B			Symmetry code
N1—H1···O4	2·78	168	0	0	−1	i
N1—H2···O5	2·85	173	−2	0	0	ii
N1—H3···O2	2·69	154	−2	1	0	ii
N2—H···OW	2·88	172	0	0	−1	i
N3—H···O3	2·76	156	0	0	−1	i
N4—H1···O1	2·91	155	−1	0	−1	i
N4—H2···O3	3·05	137	0	0	−1	i
N5—H1···O5	2·88	169	−1	0	0	ii
N5—H2···O2	2·76	157	−1	0	−1	i
OW—H1···O3	2·80	137	−1	1	−1	ii
OW—H2···O5	2·92	174	−1	0	−1	ii

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

measured by flotation. The cell parameters were initially determined from Weissenberg photographs and were later refined on a CAD-4 diffractometer using 25 reflections, θ range 4–15°. Three-dimensional intensity X-ray data were collected up to $\theta = 25°$ using ω–2θ scans. Three standard reflections during the data collection showed little variation in their intensities, showing that the crystal was stable to X-rays. The ranges of the indices were $h = -10$ to 10, $k = 0$ to 10 and $l = 0$ to 11. A total of 1289 reflections were considered observed [$I_o \geq 3\sigma(I_o)$] out of 1612 collected. Lorentz and polarization corrections were applied but no absorption correction was made. The structure was solved using MULTAN82 (Main et al., 1982). Non-H atoms were refined anisotropically using full-matrix refinement methods. All the H atoms were located from difference Fourier maps and refined isotropically. The y coordinate of O1 was fixed to locate the origin. Final $R = 0.032$ and $wR = 0.026$ where the weight $w = 1/\sigma(F_o)^2$. The function minimized was $w(|F_o| - |F_c|)^2$. The average shift to e.s.d. was 0·08. The highest peak in the difference Fourier maps was 0·13 e Å^{-3}. Atomic

scattering factors were taken from International Tables for X-ray Crystallography (1974). All the computations were performed on a PDP 11/44 computer using the structure determination package supplied by Enraf–Nonius (1979). The final positional and isotropic thermal parameters are given in Table 1 and the bond lengths and angles, conformational angles (IUPAC–IUB Commission on Biochemical Nomenclature, 1970) and the hydrogen-bonding details are listed in Table 2.* The molecular structure and atomic numbering are shown in Fig. 1. The packing of molecules down the b axis is shown in Fig. 2.
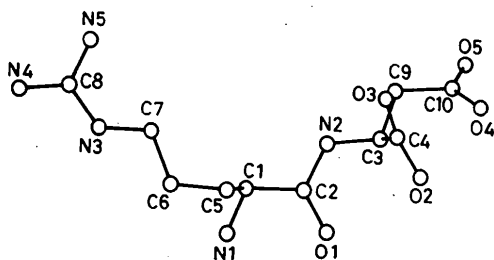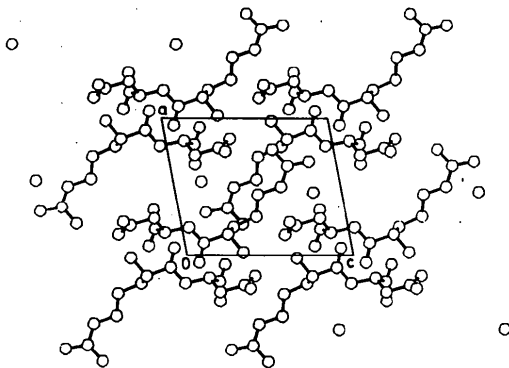
Fig. 1. Molecular structure and atomic numbering.

Fig. 2. View of crystal packing along the b axis.

Related literature. The guanidino group N atoms N4 and N5 interact directly with the peptide backbone O atoms O1 and O2 in contrast with the crystal structure

of the dihydrated form of the peptide (Ramakrishnan & Viswamitra, 1988). The side-chain conformation of arginine has $\chi^1 = -64.2°$ and $\chi^2 = -71.4°$, predicted as a possible geometry (Ponnuswamy & Sasisekharan, 1971) but not seen in earlier arginine crystal structures (Pandit, Seshadri & Viswamitra, 1983; Bhat & Vijayan, 1977).

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The Structure of 1-Benzylidene-2,3-diphenylindene

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Abstract. $C_{28}H_{20}$, $M_r = 356.47$, $P2_1/c$, $a = 10.948$ (2), $b = 19.856$ (6), $c = 10.173$ (1) Å, $\beta = 117.40$ (1)°, $V = 1963.3$ (7) Å^3, $Z = 4$, $D_x = 1.206$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 0.34$ cm^{-1}, $F(000) = 752$, $T = 298$ (2) K, $R = 0.043$ for 2705 unique observed reflections. The indene portion of the molecule exhibits a small fold of 2.6 (1)° between the fused rings. Lengths and angles within the indene fragment are normal and vary according to hybridization. The five-membered ring is planar (r.m.s.d.=0.01 Å) as are all six-membered rings. The C=C double bond linking the benzyl group to the five-membered ring is clearly defined by bond length [1.345 (2) Å] and geometry. The benzyl group is related *cis* to the C atom at the fused ring juncture and oriented away from the adjacent phenyl group. Conjugation does not extend beyond the indene fragment to include the phenyl groups. All three pendent phenyl rings are canted 47–57° with respect to the five-membered ring in a paddle-wheel arrangement.

Experimental. The title compound was isolated as an unexpected side product from the reaction of elemental

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