

113.8(1)°, also helps to minimize these non-bonded interactions. The bicyclic ammonium ion is hydrogen bonded to the picrate anion; H1...O1 2.03(3) Å and N1—H1...O1 153(2)°. This brings one of the *ortho*-nitro O atoms (O7) into close proximity to one of the methylene H atoms attached to C2; O7...H3A 2.45 Å, within the sum of the van der Waals radii (2.59 Å; Kitaigorodsky, 1973). There is high anisotropic thermal motion of the nitro O atoms; this is consistent with the expected 'soft' torsional motion about the C—N bonds.

Experimental

Crystals of (1) (422–425 K) were grown from ethanol/ether.

Crystal data

C₁₂H₂₆NSi⁺·C₆H₂N₃O₇⁻

M_r = 440.52

Monoclinic

*P*2₁/*c*

a = 11.871(1) Å

b = 21.586(2) Å

c = 8.484(1) Å

β = 102.58(1)°

V = 2121.8(4) Å³

Z = 1

D_x = 1.379 Mg m⁻³

D_m not measured

Mo Kα radiation

λ = 0.71069 Å

Cell parameters from 25 reflections

θ = 12–15°

μ = 0.158 mm⁻¹

T = 293(2) K

Thick plate

0.55 × 0.52 × 0.17 mm

Yellow

Data collection

Enraf–Nonius CAD-4S diffractometer

ω/2θ scans

Absorption correction:

Gaussian (SHELX76; Sheldrick, 1976)

T_{min} = 0.91, *T_{max}* = 0.97

4771 measured reflections

3712 independent reflections

3121 reflections with

I > 2σ(*I*)

R_{int} = 0.025

θ_{max} = 24.96°

h = -14 → 14

k = -25 → 1

l = -1 → 10

3 standard reflections

frequency: 120 min

intensity decay: 0.6%

Refinement

Refinement on *F*²

R[*F*² > 2σ(*F*²)] = 0.050

wR(*F*²) = 0.139

S = 1.034

3712 reflections

384 parameters

All H atoms refined

w = 1/[σ²(*F_o*²) + (0.0791*P*)² + 0.8915*P*]

where *P* = (*F_o*² + 2*F_c*²)/3

(Δ/σ)_{max} = -0.001

Δρ_{max} = 0.422 e Å⁻³

Δρ_{min} = -0.269 e Å⁻³

Extinction correction:

SHELXL93 (Sheldrick, 1993)

Extinction coefficient:

0.0034 (13)

Scattering factors from

International Tables for Crystallography (Vol. C)

C12—Si—C6	105.3(1)	C4—C5—C6	116.0(2)
C11—Si—C6	107.8(1)	C7—C6—N1	107.9(2)
C13—Si—C6	118.2(1)	C7—C6—C5	110.2(2)
C10—N1—C2	109.7(2)	N1—C6—C5	108.4(2)
C10—N1—C6	112.4(2)	C7—C6—Si	113.77(15)
C2—N1—C6	114.3(2)	N1—C6—Si	112.16(13)
C10—N1—H1	107.6(16)	C5—C6—Si	104.27(15)
C2—N1—H1	102.7(16)	C8—C7—C6	114.6(2)
C6—N1—H1	109.6(16)	C7—C8—C9	110.6(2)
C3—C2—N1	111.3(2)	C10—C9—C8	111.8(2)
C2—C3—C4	111.0(2)	N1—C10—C9	111.7(2)
C3—C4—C5	109.3(2)		

The structure was solved by direct methods using SHELXS86 (Sheldrick, 1990). Refinement was performed using SHELXL-93 using anisotropic displacement parameters for all non-H atoms and isotropic displacement parameters for the H atoms. The figure was drawn using ORTEPII (Johnson, 1976) and tables prepared using SHELXL93. All calculations were carried out on a VAXstation 4000VLC computer system.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SX1022). Services for accessing these data are described at the back of the journal.

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A Putrescine Triamide from *Lilium regale*

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Abstract

The asymmetric unit of the crystals of the synthetic equivalent of the terrestrial natural product (±)-(E)-3-(4-hydroxyphenyl)-N-[4-(3-methyl-2,5-dioxo-1-pyrrolidinyl)butyl]-2-propenamamide, C₁₈H₂₂N₂O₄, contains two independent but structurally similar molecules. The cinnamide, putrescine and succinimide regions of the molecule are each planar but lie almost perpendicular to the adjacent moiety. Hydrogen bonds link the mol-

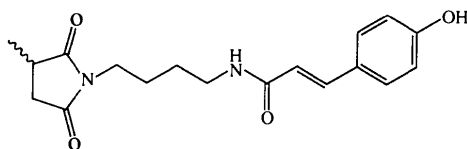
Table 1. Selected geometric parameters (Å, °)

Si—C12	1.856(3)	C2—C3	1.501(4)
Si—C11	1.860(3)	C3—C4	1.505(5)
Si—C13	1.862(3)	C4—C5	1.511(4)
Si—C6	1.947(2)	C5—C6	1.548(3)
N1—C10	1.506(3)	C6—C7	1.534(3)
N1—C2	1.512(3)	C7—C8	1.508(4)
N1—C6	1.544(3)	C8—C9	1.511(4)
N1—H1	0.90(3)	C9—C10	1.507(4)

ecules into infinite sheets characterized by the $R_2^2(18)$ and $R_6^6(62)$ motifs.

Comment

A reinvestigation of the methanolic extract of *Lilium regale* Wilson (Liliaceae), a perennial plant native to China, led to the isolation and characterization of the novel triamide derivative of putrescine (1,4-diaminobutane), (I) (Mimaki & Sashida, 1990). The report also indicated that the bulbs of the genus *Lilium* have been used in traditional Chinese medicine. The occurrence in many higher plants of compounds containing variously hydroxy-substituted cinnamic acids linked to putrescine (generally known as phenolamides or hydroxycinnamic acid amides) is well documented (Mizusaki, Tanabe, Noguchi & Tamaki, 1971; Ganem, 1982; Smith, Negrel & Bird, 1983; Mølgaard & Ravn, 1988). The cinnamides, in general, are of interest because of their diverse biochemical profiles (Sundaramoorthi, Fourrey & Das, 1984) and the role they play in proliferative processes (Bergeron, 1986).



(I)

The synthesis of compound (I) was recently carried out (Kuehne & Hesse, 1993) and the structure of the synthetic product was determined by X-ray diffraction in order to confirm its chemical identity and to establish its spatial structure. Reports of the structures of related

compounds of this type are very scarce, the closest structures being those of three symmetrical dibenzamide derivatives of putrescine (Brisson, Gagné & Brisse, 1989). More distant relatives are the structures of the cyclic spermidine cinnamides, cadabcine (Ahmad, Amber, Arif, Chen & Clardy, 1985), lunarine (Jeffreys & Ferguson, 1970; Tamura & Sim, 1970), caesalpinine A (Mahato, Sahu & Luger, 1983), (+)-(8*S*,13*R*)-cyclo-celabenzine (Schultz & Hesse, 1996*a*) and (+)-(9*S*,13*R*)-isocyclo-celabenzine (Schultz & Hesse, 1996*b*). The structure of pyramidatine, which contains linked cinnamide and putrescine moieties, has been elucidated from NMR measurements (Cordell & Kinghorn, 1991), but it has not been determined crystallographically.

There are two symmetry-independent molecules of compound (I) in the asymmetric unit. The molecules are closely related by a non-crystallographic inversion centre located at 0.745, 0.399, 0.756, with a mean deviation of 0.19 (10) Å. A significant difference in the orientation of the phenyl ring, caused by a twist of 21.2 (8)° about the C3—C4 bond, is the main factor leading to the breakdown of the symmetry relationship. All other torsion angles differ by less than 10°, the largest of these being in the succinimide ring.

A small amount of residual electron density suggests the presence of conformational disorder at C15 and C35 in the succinimide rings, although attempts to model the disorder were unsuccessful. The unusual shortness of the C15—C18 and C35—C38 bonds, as well as the differences in the torsion angles around the succinimide ring, probably result from the inadequately modelled disorder. All other geometric parameters have normal values and the molecules adopt a straight-chain conformation rather than a twisted or folded form.

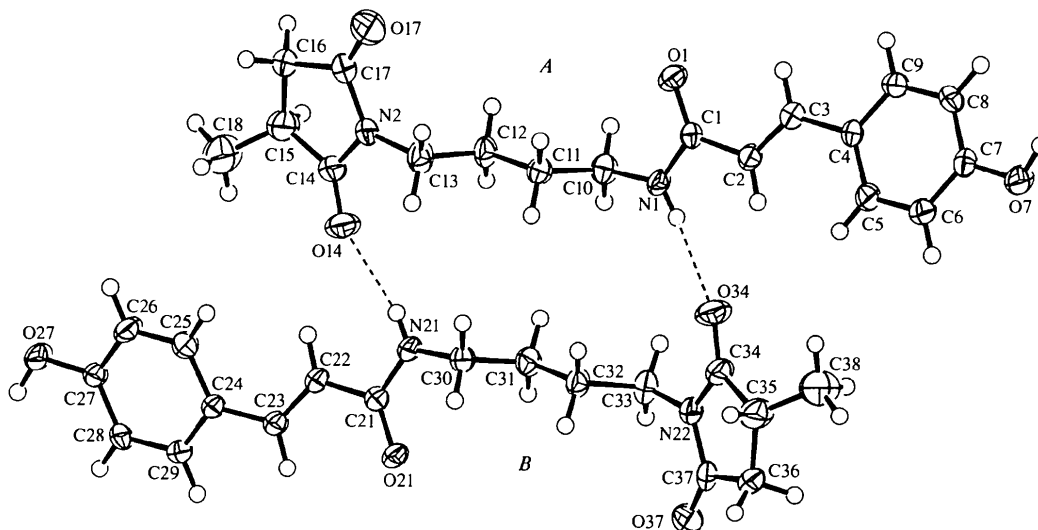


Fig. 1. The asymmetric unit of compound (I) showing the atom-labelling scheme and the $R_2^2(18)$ ring motif formed by the N—H...O hydrogen bonds. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented by spheres of arbitrary size. Molecule *B* is shown in the symmetry position $1 - x, 1 - y, 1 - z$.

The molecules have three roughly planar sections, the plane of each section being almost perpendicular to that of the adjacent section. The first section contains all atoms of the cinnamide moiety from N1 through to the hydroxy group. The r.m.s. deviation from this plane in molecule *A* (data for molecule *B* follows in parentheses) is 0.074 Å (0.081 Å) and the maximum deviation from the plane is 0.174 (2) Å for atom N1 [0.125 (3) Å, C25]. The second planar section is the putrescine moiety, including the two N atoms, with an r.m.s. deviation from the plane of 0.054 Å (0.066 Å) and a maximum deviation of 0.076 (2) Å for atom N2 [0.105 (2) Å, N21]. The succinimide ring, including the O atoms, forms the third planar section with an r.m.s. deviation from the plane of 0.060 Å (0.046 Å) and a maximum deviation of 0.122 (3) Å for atom C16 [0.092 (4) Å, C35]. The cinnamide plane makes an angle of 74.5 (2)° [81.2 (2)°] with the putrescine plane and the latter makes an angle of 83.3 (2)° [84.0 (2)°] with the succinimide plane. The deviation from planarity of the succinimide ring is towards a half-chair conformation twisted on C15 and C16 (C35 and C36) with pseudorotation parameters, *P* and τ_m (Rao, Westhof & Sundaralingam, 1981), of 69 (1) and 13.6 (3)°, respectively [63 (2) and 8.3 (3)°].

The two independent molecules, *A* and *B*, are linked into *AB* pairs by intermolecular hydrogen bonds between the amide N—H group of each molecule and one of the O atoms of the succinimide ring of the other molecule. This results in a closed loop of hydrogen bonds with the graph set $R_2^2(18)$ (Bernstein, Davis, Shimoni & Chang, 1995). The hydroxy group of molecule *A* forms an intermolecular hydrogen bond with the amide O atom of an adjacent molecule *A* (Fig. 2). This interaction links the type *A* molecules into infinite one-dimensional

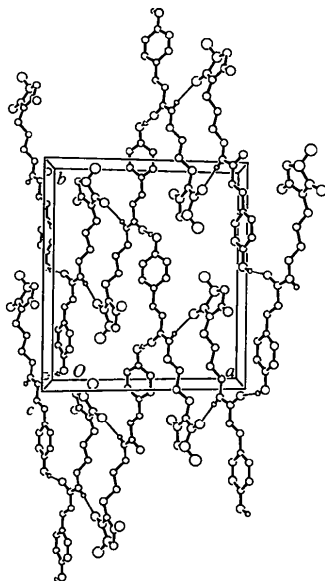


Fig. 2. The crystal packing of compound (I) viewed down the *c* axis, showing the infinite sheets and the $R_2^2(18)$ and $R_6^6(62)$ ring motifs formed by the hydrogen bonds.

chains running parallel to the *y* axis; graph set $C(10)$. The type *B* molecules form the same type of chains. The combination of all hydrogen-bonding interactions links the molecules into infinite two-dimensional sheets which lie normal to the $[20\bar{1}]$ direction and can be described by two ring graph sets. The $R_2^2(18)$ motif described above links molecules *A* and *B*, while a larger $R_6^6(62)$ motif involves six molecules and both types of hydrogen bond. The large rings can be thought of as distorted hexagons, each side of which edge shares with an adjacent ring, thereby forming infinite sheets based on a honeycomb pattern.

Experimental

Compound (I) was prepared according to the method of Kuehne & Hesse (1993). Suitable crystals were obtained by recrystallization from methanol.

Crystal data

C₁₈H₂₂N₂O₄
 $M_r = 330.38$
 Monoclinic
 $P2_1/c$
 $a = 16.488$ (7) Å
 $b = 18.221$ (3) Å
 $c = 11.670$ (8) Å
 $\beta = 103.76$ (4)°
 $V = 3405$ (3) Å³
 $Z = 8$
 $D_x = 1.289$ Mg m⁻³
 D_m not measured

Data collection

Rigaku AFC-5R diffractometer
 ω - 2θ scans
 Absorption correction: none
 6535 measured reflections
 6000 independent reflections
 3235 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.056$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.064$
 $wR(F^2) = 0.224$
 $S = 1.235$
 5696 reflections
 451 parameters
 H atoms: see below
 $w = 1/[\sigma^2(F_o^2) + (0.0771P)^2 + 1.7795P]$
 where $P = (F_o^2 + 2F_c^2)/3$

Mo $K\alpha$ radiation

$\lambda = 0.71069$ Å
 Cell parameters from 25 reflections
 $\theta = 17.0$ – 19.5 °
 $\mu = 0.0915$ mm⁻¹
 $T = 173$ (1) K
 Prism
 $0.50 \times 0.20 \times 0.15$ mm
 Colourless

$\theta_{max} = 25$ °

$h = -19 \rightarrow 19$

$k = 0 \rightarrow 21$

$l = 0 \rightarrow 13$

3 standard reflections every 150 reflections
 intensity decay: insignificant

$(\Delta/\sigma)_{max} = 0.001$

$\Delta\rho_{max} = 0.732$ e Å⁻³

$\Delta\rho_{min} = -0.391$ e Å⁻³

Extinction correction: none

Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. Selected geometric parameters (Å, °)

O7—C7	1.366 (4)	O27—C27	1.360 (4)
N1—C1	1.343 (5)	N21—C21	1.341 (5)
N1—C10	1.458 (4)	N21—C30	1.450 (5)
N2—C14	1.385 (5)	N22—C34	1.373 (5)

N2—C17	1.388 (5)	N22—C37	1.389 (5)
N2—C13	1.469 (4)	N22—C33	1.469 (5)
C1—C2	1.479 (5)	C21—C22	1.481 (5)
C2—C3	1.329 (5)	C22—C23	1.324 (5)
C3—C4	1.474 (5)	C23—C24	1.465 (5)
C14—C15	1.523 (6)	C34—C35	1.537 (6)
C15—C16	1.530 (6)	C35—C36	1.535 (6)
C15—C18	1.428 (6)	C35—C38	1.452 (6)
C14—C15—C16	103.6 (4)	C34—C35—C36	102.0 (3)
C2—C3—C4—C5	-7.3 (6)	C22—C23—C24—C25	13.9 (6)
C1—N1—C10—C11	-92.0 (4)	C21—N21—C30—C31	-91.8 (4)
C14—N2—C13—C12	89.1 (5)	C34—N22—C33—C32	82.7 (4)

Table 2. Hydrogen-bonding geometry (\AA , $^\circ$)

D—H...A	D—H	H...A	D...A	D—H...A
O7—H7...O1 ⁱ	0.89 (4)	1.83 (4)	2.679 (4)	160 (4)
N1—H1...O34 ⁱⁱ	0.81 (4)	2.31 (4)	3.078 (4)	160 (4)
O27—H27...O21 ⁱⁱⁱ	0.90 (5)	1.78 (5)	2.671 (4)	173 (4)
N21—H21...O14 ⁱⁱⁱ	0.81 (4)	2.18 (4)	2.971 (4)	168 (3)

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

The *BUNYIP* program (Hester & Hall, 1995) indicated that the two independent molecules in the asymmetric unit are closely related by a centre of inversion. Tests for overlooked superlattice reflections and transformations of the unit-cell parameters confirmed that additional crystallographic symmetry is not present. All H atoms were initially located in a difference electron-density map. The positions and isotropic displacement parameters of those attached to N and O atoms were refined freely. The positions of the H atoms bonded to C atoms were geometrically optimized and allowed to ride on their parent atoms with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. Methyl groups were treated as rotating rigid groups with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$. A total of 304 reflections with $F_o^2 < -2\sigma(F_o^2)$ were excluded during refinement.

The two largest peaks of residual electron density (0.73 and 0.59 e \AA^{-3}) are located within 1.1 \AA of C15 and C35 and their positions suggest conformational disorder of the five-membered ring in each independent molecule. Attempts to refine C15 and C35 as disordered atoms, even with bond-length and similarity restraints, produced unsatisfactory results. The unusually short bond lengths for C15—C18 and C25—C38 are probably the result of the inadequately modelled disorder.

Data collection: *MSCIAFC Diffractometer Control Software* (Molecular Structure Corporation, 1991). Cell refinement: *MSCIAFC Diffractometer Control Software*. Data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1989). Program(s) used to solve structure: *SHELXS86* direct methods (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *SHELXL93*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: AB1491). Services for accessing these data are described at the back of the journal.

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Photoproducts Derived from 9-Substituted Dibenzobarrelenes

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Abstract

Irradiation of 11,12-dibenzoyl-9,10-dihydro-9-hydroxy-methyl-9,10-ethenoanthracene, (1a), and 11,12-dibenzoyl-9,10-dihydro-9-methoxy-9,10-ethenoanthracene, (1b),