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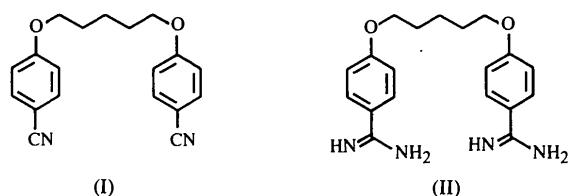
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(I)

(II)

A perspective view of the title molecule showing the atom-numbering scheme is shown in Fig. 1. The molecular dimensions are as expected (Table 2), with aromatic C—C bond lengths ranging from 1.372 (4) to 1.398 (4) Å and non-aromatic C—C bond lengths ranging from 1.497 (3) to 1.518 (3) Å. The two oxybenzonitrile fragments of (I) have approximate C_2 symmetry through atom C(9) of the linking pentanediyl chain, but the structural differences between the two

A Key Intermediate in the Synthesis of Pentamidine: 4,4'-[1,5-Pentanediylbis(oxy)]-bisbenzonitrile

K. Ravikumar,[a] K. Chandra Mohan,[a] Subho Roy[b] and A. K. Singh[b]

[a]*Laboratory of Crystallography, Indian Institute of Chemical Technology, Hyderabad 500 007, India, and* [b]*Bio-Organic Laboratory, Indian Institute of Chemical Technology, Hyderabad 500 007, India*
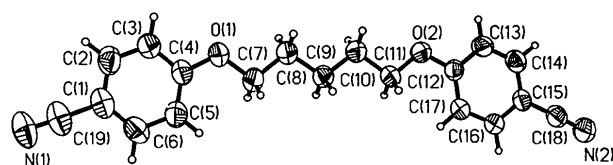
Fig. 1. The molecular structure and atomic numbering scheme of the title compound. The displacement ellipsoids of the C, N and O atoms are drawn at the 50% probability level and H atoms are represented as spheres of arbitrary radii.

Abstract

The title compound, $C_{19}H_{18}N_2O_2$, has an extended conformation at the central pentanediyl chain. The molecule has approximate twofold symmetry through atom C(9). The dihedral angle between the end-to-end phenyl rings is 1.3 (1)°, indicating the overall planarity of the molecule. This facilitates stacking of the phenyl rings in the crystal.

Comment

4,4'-[1,5-Pentanediylbis(oxy)]bisbenzonitrile, (I), is the key intermediate in the synthesis of pentamidine, (II) {4,4'-[1,5-pentanediylbis(oxy)]bisbenzenecarboximidamine}, the drug of choice for the treatment and prevention of TB rhodesiense and TB gambiense infections (Katzung, 1984).
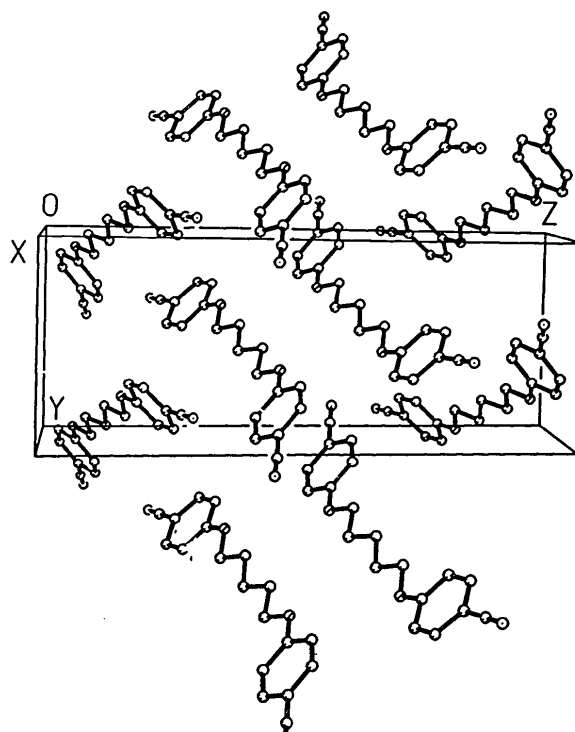

Fig. 2. A view of the crystal packing showing the stacking of the ring systems between inversion-related molecules.

fragments are negligible. The phenyl rings in the molecule are almost in the same plane, the angle between the planes of the rings being 1.3 (1)°. The orientation of the rings with respect to the bridging pentanediyl chain is characterized by the angle between the plane formed by the pentanediyl chain [C(7)–C(11)] and the plane of the phenyl rings, *i.e.* 5.9 (1)° for C(1)–C(6) and 4.8 (1)° for C(12)–C(17).

The pentanediyl chain is in an extended *trans* conformation: $-ap$ [O(1)—C(7)—C(8)—C(9) -178.6 (2)°], $+ap$ [C(7)—C(8)—C(9)—C(10) 177.4 (2)°], $+ap$ [C(8)—C(9)—C(10)—C(11) 174.5 (2)°] and $-ap$ [C(9)—C(10)—C(11)—O(2) -176.3 (2)°].

The crystal packing (Fig. 2) is possibly stabilized by van der Waals interactions. Additionally, the phenyl rings tend to stack with each other [the normal distance between the planes of the phenyl rings is 3.736 (2) Å], presumably to improve $\pi \cdots \pi$ interactions. These stacked molecules are inversion related.

Experimental

The title compound was synthesized according to the method of Ashley, Barber, Ewins, Newbery & Self (1942) and recrystallized from ethyl acetate solution.

Crystal data

$C_{19}H_{18}N_2O_2$	Mo $K\alpha$ radiation
$M_r = 306.36$	$\lambda = 0.71073$ Å
Monoclinic	Cell parameters from 25
$P2_1/c$	reflections
$a = 9.163$ (1) Å	$\theta = 8–17°$
$b = 8.370$ (1) Å	$\mu = 0.08$ mm^{-1}
$c = 21.786$ (3) Å	$T = 293$ K
$\beta = 96.95$ (2)°	Cubic
$V = 1658.6$ (4) Å^3	$0.18 \times 0.17 \times 0.14$ mm
$Z = 4$	Transparent
$D_x = 1.227$ Mg m^{-3}	
D_m not measured	

Data collection

Siemens *R3m/V* diffractometer	$R_{int} = 0.010$
eter	$\theta_{max} = 22.5°$
$\omega/2\theta$ scans	$h = 0 \rightarrow 9$
Absorption correction:	$k = 0 \rightarrow 9$
none	$l = -23 \rightarrow 23$
2590 measured reflections	2 standard reflections
2533 independent reflections	monitored every 98
1573 observed reflections	reflections
$[I > 3\sigma(I)]$	intensity decay: $\leq 1\%$

Refinement

Refinement on F	$(\Delta/\sigma)_{max} = 0.001$
$R = 0.043$	$\Delta\rho_{max} = 0.23$ e Å^{-3}
$wR = 0.049$	$\Delta\rho_{min} = -0.18$ e Å^{-3}
$S = 0.93$	Atomic scattering factors
1573 reflections	from *SHELXTL-Plus*
208 parameters	(Sheldrick, 1991)
$w = 1/[\sigma^2(F) + 0.0061F^2]$	

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)*

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

	x	y	z	U_{eq}
O(1)	1.4197 (2)	−0.0782 (2)	0.1505 (1)	0.073 (1)
O(2)	0.6678 (2)	0.1798 (2)	0.0455 (1)	0.064 (1)
N(1)	2.1123 (3)	−0.0548 (3)	0.2912 (1)	0.096 (1)
N(2)	0.0558 (3)	0.6102 (3)	0.0668 (1)	0.090 (1)
C(1)	1.8416 (3)	−0.0571 (3)	0.2409 (1)	0.068 (1)
C(2)	1.8009 (3)	−0.1687 (2)	0.1943 (2)	0.076 (1)
C(3)	1.6591 (3)	−0.1710 (3)	0.1656 (1)	0.072 (1)
C(4)	1.5557 (3)	−0.0638 (3)	0.1819 (1)	0.060 (1)
C(5)	1.5964 (3)	0.0494 (4)	0.2274 (1)	0.071 (1)
C(6)	1.7387 (3)	0.0515 (4)	0.2572 (1)	0.075 (1)
C(7)	1.3105 (3)	0.0399 (3)	0.1592 (1)	0.061 (1)
C(8)	1.1761 (3)	0.0033 (3)	0.1152 (1)	0.062 (1)
C(9)	1.0548 (2)	0.1247 (3)	0.1198 (1)	0.055 (1)
C(10)	0.9181 (3)	0.0979 (3)	0.0743 (1)	0.061 (1)
C(11)	0.7992 (2)	0.2140 (3)	0.0864 (1)	0.058 (1)
C(12)	0.5476 (3)	0.2724 (3)	0.0513 (1)	0.052 (1)
C(13)	0.4211 (3)	0.2345 (3)	0.0124 (1)	0.063 (1)
C(14)	0.2943 (3)	0.3209 (3)	0.0146 (1)	0.063 (1)
C(15)	0.2922 (3)	0.4479 (3)	0.0560 (1)	0.053 (1)
C(16)	0.4190 (3)	0.4845 (3)	0.0948 (1)	0.063 (1)
C(17)	0.5463 (3)	0.3983 (3)	0.0929 (1)	0.060 (1)
C(18)	0.1606 (3)	0.5386 (3)	0.0607 (1)	0.065 (1)
C(19)	1.9921 (3)	−0.0549 (4)	0.2698 (1)	0.078 (1)

Table 2. *Selected geometric parameters (Å, °)*

O(1)–C(4)	1.354 (3)	O(1)–C(7)	1.435 (3)
O(2)–C(11)	1.437 (3)	O(2)–C(12)	1.366 (3)
N(1)–C(19)	1.143 (4)	N(2)–C(18)	1.152 (4)
C(1)–C(19)	1.445 (4)	C(7)–C(8)	1.497 (3)
C(8)–C(9)	1.518 (3)	C(9)–C(10)	1.517 (3)
C(10)–C(11)	1.507 (4)	C(15)–C(18)	1.440 (4)
C(4)–O(1)–C(7)	119.1 (2)	C(11)–O(2)–C(12)	117.0 (2)
C(2)–C(1)–C(6)	119.6 (2)	C(2)–C(1)–C(19)	118.8 (3)
C(6)–C(1)–C(19)	121.6 (3)	O(1)–C(4)–C(3)	115.4 (2)
O(1)–C(4)–C(5)	125.0 (2)	O(1)–C(7)–C(8)	107.9 (2)
C(7)–C(8)–C(9)	111.9 (2)	C(8)–C(9)–C(10)	114.3 (2)
C(9)–C(10)–C(11)	110.3 (2)	O(2)–C(11)–C(10)	109.4 (2)
O(2)–C(12)–C(13)	115.9 (2)	O(2)–C(12)–C(17)	124.2 (2)
C(14)–C(15)–C(16)	119.1 (2)	C(14)–C(15)–C(18)	121.6 (2)
C(16)–C(15)–C(18)	119.2 (2)	N(2)–C(18)–C(15)	177.4 (3)
N(1)–C(19)–C(1)	178.1 (3)		

The H atoms were located from difference Fourier maps. They were positioned geometrically and included as riding atoms with fixed isotropic displacement parameters in the structure-factor calculations.

Data collection: *P3 Diffractometer Program* (Siemens, 1991). Cell refinement: *P3 Diffractometer Program*. Data reduction: *SHELXTL-Plus* (Sheldrick, 1991). Program(s) used to solve structure: *SHELXTL-Plus*. Program(s) used to refine structure: *SHELXTL-Plus*. Molecular graphics: *SHELXTL-Plus*. Software used to prepare material for publication: *PARST* (Nardelli, 1983).

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7β-Hydroxy-7α-(3-propargyl)-3-methyl-spiro[5.5]undec-2-en-1-one

S. Lakshmi,[a] K. Subramanian,[a] G. Koellner,[b] Th. Steiner[b] and K. Rajagopalan[c]

[a]*Department of Physics, Anna University, Madras 25, India,* [b]*Institut fur Kristallographie, Freie Universitat Berlin, Takustraße 6, D-14159 Berlin, Germany, and* [c]*Department of Organic Chemistry, University of Madras, Madras, India*

Abstract

The title compound, $C_{15}H_{20}O_2$, contains two six-membered rings, one of which is in a chair conformation while the other assumes an envelope shape. The molecules form dimers which are connected by C—H···O hydrogen bonds donated by the propargyl residue. The hydrogen-bonding pattern is composed of finite cooperative C≡C—H···O—H···O≡C chains.

Comment

Terminal alkynes of the present type are used as starting materials for the synthesis of steroids (Nasipuri, 1992). The crystal structure of the title compound, (I), was determined to study the intermolecular contacts of the propargyl residue, which is usually involved in C—H···*X* hydrogen bonding if suitable acceptors, *X*, are available (Desiraju, 1991).

(I)
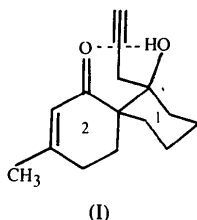
Compound (I) crystallizes in a non-centrosymmetric space group with a pair of enantiomeric molecules (*A*, *B*) per asymmetric unit. For molecule *A*, the molecular conformation and the atomic numbering scheme are shown in Fig. 1. Ring 1 is in a chair conformation and Ring 2 adopts an envelope shape. The ring-puckering parameters (following Cremer & Pople, 1975) for Rings 1 and 2 of both molecules are given in Table 3. The hydroxy group forms an intermolecular hydrogen bond to O=C with O···O = 2.668 (4) Å (Table 4). Molecules *A* and *B* form a pseudo-centrosymmetric dimer, with a non-crystallographic centre of symmetry at x/a = 0.123 (3), y/b = 0.519 (6), z/c = 0.344 (6). The molecules are connected by mutual C—H···O hydrogen bonds donated by the propargyl residues and accepted by the hydroxy groups (Fig. 2) (H···O ≃ 2.37 Å, for normalized H-atom positions). Within this dimer, the two molecules are tilted with respect to each other, so that true centrosymmetry is disturbed [this is reflected in non-zero dihedral angles between corresponding molecular planes; *e.g.* the least-squares-planes through rings 1(*A*) and 1(*B*) form an angle of 7.0 (2)°, and those through rings 2(*A*) and 2(*B*) form an angle of 8.8 (2)°].
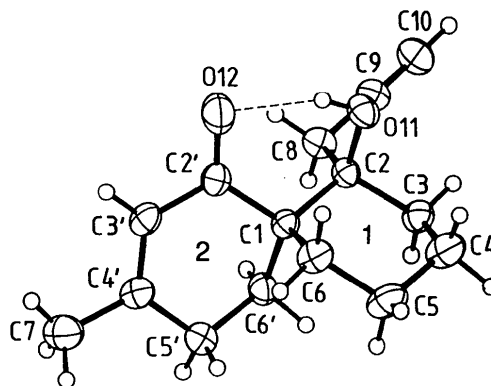

Fig. 1. Molecular structure and atomic numbering scheme of molecule *A*. Displacement ellipsoids are drawn at the 30% probability level.
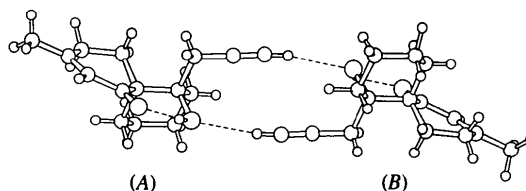

Fig. 2. The pseudo-centrosymmetric dimer formed by molecules *A* and *B*. Hydrogen bonds are shown as dashed lines.

The hydrogen bonds form finite cooperative C≡C—H···O—H···O=C chains (Figs. 2 and 3), which constitutes a stronger hydrogen-bonding pattern than isolated O—H···O and C—H···O hydrogen bonds. We