ANALYTICAL SCIENCES 2008, VOL. 24

X-ray Structure Analysis Online

Crystal Structure of 2,6-Diisocyano-1,2,3,5,6,7-hexahydro-*s*-indacene-2,6-dicarboxylic Acid Diethylester

P. KUMARADHAS,*† Kundan R. GUPTA,* Sambasivarao KOTHA, Enugurthi BRAHMACHARI,** and K. A. NIRMALA*****

**Department of Physics, Periyar University, Salem–636 011, India*
***Department of Chemistry, Indian Institute of Technology, Powai, Mumbai–400 076, India*
****Department of Physics, Bangalore University, Bangalore–560 056, India*

The title structure, 2,6-diisocyano-1,2,3,5,6,7-hexahydro-*s*-indacene-2,6-dicarboxylic acid diethyl ester is an indane-based amino acid derivative. It crystallizes in the tetragonal space group $I4_1/acd$ with unit cell parameters a=22.868(1)Å, c=14.385(1)Å and V=7522.8(1)Å^3. The residual index of the final refinement is 0.06 for 18734 observed reflections. The five-membered ring is distorted, showing an envelope conformation. The molecular packing is stabilized by C–H···O hydrogen-bonding interactions.

(Received, June 18, 2007; Accepted December 20, 2007; Published on web April 11, 2008)

A peptide backbone conformation or a secondary structure is crucial in the design of peptide-based therapeutics.[1] In this regard, α,α-dialkylated amino acids play an important role in the design of a conformationally restricted peptide.[2,3] Among that, the cyclic α-amino acids are considered to be a special class of α,α-dialkylated amino acids. The title molecule (I) is also one among the α,α-dialkylated amino acids that has been taken to understand its structure and conformational geometry.

The synthesis details of compound (I) are reported in the literature,[4] and it was crystallized from a mixture of petroleum ether and ethyl acetate (9:1) solvents. The crystal data and the structure determination details are summarized in Table 1. The structure was solved by direct methods and refined by a full-matrix least-squares technique. All of the non-hydrogen atoms were refined anisotropically and the H atoms were geometrically fixed and constrained to ride on the parent atom in the model. The atomic coordinates and equivalent isotropic displacement parameters for non-hydrogen atoms are given in Table 2. Selected inter-atomic distances and angles are listed in Table 3.

The asymmetric unit of (I) contains a half of the $C_{20}H_{20}N_2O_4$ unit. This molecule is on the crystallographic center of symmetry, and half of the molecule is independent. The inter-atomic distances and bond angles of (I) reflect the usual geometry of five and six-membered rings. The C–N distances are unequal [C(6)≡N is 1.135(4)Å and C(2)–N is 1.435(4)Å]. One of them was shortened due to the different hybridization *i.e.* *sp* and sp^3, respectively. Specifically, the C(6)≡N distance is much shorter than the reported structures [1.157(2)Å].[6] This difference may be attributed to the different environment. The bond lengths involving C_{sp3} atoms range from 1.543(3) to 1.544(4)Å, for except C(8)–C(9) [1.269(6)Å]. This difference may be due to the large thermal motion of the C(8) and C(9)

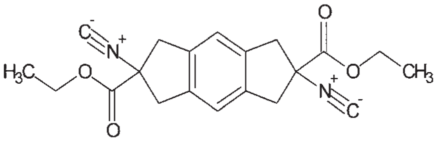

Fig. 1 Chemical structure of the title compound.

Table 1 Crystal data and experimental details

Molecular Formula	$C_{20}H_{20}N_2O_4$
Formula weight	352.38
Temperature	293(2)K
Radiation	Mo K_α
Wavelength	0.71073Å
Crystal system	tetragonal
Space group	$I4_1/acd$ Z = 16
Cell dimensions	a = 22.868(1)Å c = 14.385(1)Å
Volume	7522.8(1)Å^3
Absorption Coefficient	0.088 mm^{-1}
D_c	1.245 Mg m^{-3}
$2\theta_{max}$	52.7°
Crystal size	0.3 × 0.22 × 0.1 mm
F(0 0 0)	2976
$R(F)$ = 0.06	
$wR(F^2)$	0.162
Goodness-of-fit on F^2	1.044
No. of parameters	121
$(\Delta/\sigma)_{max}$	0.001
$(\Delta/\rho)_{max}$	0.26 eÅ^{-3}
$(\Delta/\rho)_{min}$	-0.18 eÅ^{-3}
Measurement	SIEMEN S SMART 1K CCD Area detector
Program System	SHELXS97 and SHELXL97
Structure determination	Direct methods
Refinement	full-matrix
CCDC	663020

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† To whom correspondence should be addressed.
E-mail: kumaradhas@yahoo.com

Table 2 Atomic coordinates (Å × 10^4) and equivalent isotropic displacement parameters of non-hydrogen atoms ($Å^2 \times 10^3$)

Atom	*x*	*y*	*z*	U_{eq}
O(1)	9877(1)	-1136(1)	268(2)	107(1)
O(2)	9632(1)	-984(1)	1725(2)	126(1)
N	9060(1)	-410(1)	-371(2)	84(1)
C(1)	8490(1)	-608(1)	1010(2)	68(1)
C(2)	9102(1)	-459(1)	621(2)	68(1)
C(3)	9243(1)	150(1)	1023(2)	76(1)
C(4)	8645(1)	418(1)	1137(2)	62(1)
C(5)	8217(1)	-13(1)	1134(2)	57(1)
C(6)	9015(2)	-354(2)	-1152(3)	128(2)
C(7)	9580(1)	-902(1)	830(2)	78(1)
C(8)	10132(2)	-1346(3)	2040(4)	179(3)
C(9)	10022(3)	-1608(3)	2798(4)	189(3)
C(10)	8500(1)	1000(1)	1250	70(1)
C(11)	7631(1)	131(1)	1250	59(1)

Table 3 Selected bond distances (Å) and angles (˚)

O(1)–C(7)	1.182(3)	N–C(2)–C(1)	108.6(2)
O(2)–C(7)	1.307(4)	C(7)–C(2)–C(1)	115.7(2)
O(2)–C(8)	1.484(4)	N–C(2)–C(3)	108.3(2)
N–C(6)	1.135(4)	C(7)–C(2)–C(3)	112.1(2)
N–C(2)	1.435(4)	C(1)–C(2)–C(3)	104.6(2)
C(1)–C(5)	1.509(3)	C(4)–C(3)–C(2)	102.6(2)
C(1)–C(2)	1.543(3)	C(10)–C(4)–C(5)	121.1(2)
C(2)–C(7)	1.521(4)	C(10)–C(4)–C(3)	128.4(2)
C(2)–C(3)	1.544(4)	C(5)–C(4)–C(3)	110.5(2)
C(3)–C(4)	1.508(3)	C(11)–C(5)–C(4)	120.7(2)
C(4)–C(10)	1.381(3)	C(11)–C(5)–C(1)	129.0(2)
C(4)–C(5)	1.389(3)	C(4)–C(5)–C(1)	110.4(2)
C(5)–C(11)	1.388(3)	O(1)–C(7)–O(2)	123.9(3)
C(8)–C(9)	1.269(6)	O(1)–C(7)–C(2)	125.4(3)
C(10)–C(4)^{i}	1.381(3)	O(2)–C(7)–C(2)	110.7(2)
C(11)–C(5)^{i}	1.388(3)	C(9)–C(8)–O(2)	111.9(4)
		C(4)–C(10)–C(4)^{i}	118.4(3)
C(7)–O(2)–C(8)	116.7(3)	C(5)^{i} –C(11)–C(5)	118.2(3)
C(6)–N–C(2)	177.6(3)		
C(5)–C(1)–C(2)	102.7(2)		
N–C(2)–C(7)	107.3(2)		

(i) *x*–3/4, *y*+3/4, –*z*+1/4

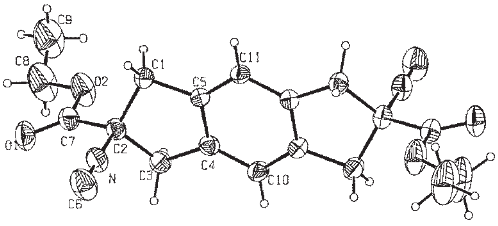

Fig. 2 The molecular structure of the title compound, showing 50% probability displacement ellipsoids and arbitrary spheres for the H atoms.

atoms. The carbonyl bonds fall into three categories: C$_{sp3}$–O single bonds [C(8)–O(2): 1.484(4)Å], C$_{sp2}$–O single bonds [C(7)–O(2): 1.307(4)Å] and C=O double bonds [C(7)=O(1): 1.182(3)Å]. The values of the torsion angles of the isocyano group and the acetate group at C(2) and C(7) have a staggered orientation, since the torsion angle N–C(2)–C(7)–O(2) is –178.2(3);˚ whereas the torsion angle, C(3)–C(2)–C(7)–O(1) [–115.6(3)˚], shows a partially eclipsed form at the C(2) and C(7) atoms. The torsion angles of C(8)–O(2)–C(7)–O(1) [6.3(6)˚] and N–C(2)–C(7)–O(1) [3.2(4)˚] clear the eclipsed form at that center.

The molecular packing is stabilized by C–H···O hydrogen-bonding interactions. Figure 2 depicts the C–H···O interaction between the carbonyl group with the adjacent cyclopentane group of the adjacent molecule. This intermolecular interaction forms a centrosymmetric dimer in the crystal. The C(3)–H(3)···O(1) hydrogen-bond parameters are C(3)···O(1)ii: 3.55(4), H(3B)···O(1): 2.59(2)Å and the angle is 168.3(2).˚
[Symmetry code(ii): –*x*+2, –*y*, –*z*]

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