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Synthesis and Structural Characterization of *N*-Phenyl-7-oxa-bicyclo[2,2,1]hept-5-ene-2,3-dicarboximide

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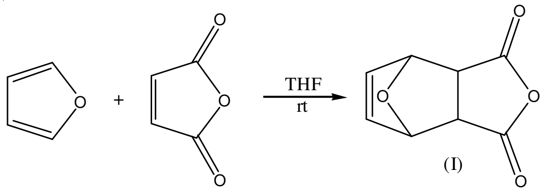
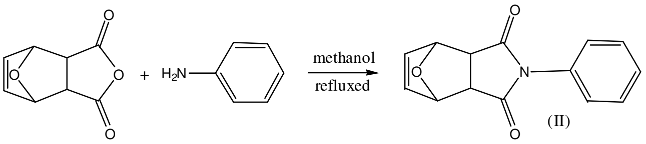
The compound *N*-phenyl-7-oxa-bicyclo[2,2,1]hept-5-ene-2,3-dicarboximide ($C_{14}H_{11}NO_3$, Mr = 241.24) was synthesized and characterized by elemental analysis, ^{1}H NMR spectra, IR spectra and single crystal X-ray diffraction. The crystal belongs to monoclinic, space group $P2_1/c$, with a = 9.4307(7), b = 8.3175(6), c = 14.3592(15) Å, β = 93.6000(10)°, V = 1124.11(17) Å^3, Z = 4, Dc = 1.425 g/cm^3, λ = 0.71073 Å, μ(Mo K_α) = 0.101 mm^{-1}, F(000) = 504. The final refinement gave R = 0.0424, wR(F2) = 0.1058 for 1,975 observed reflections with $I > 2\sigma(I)$. The structure of this compound comprises a racemic mixture of chiral molecules containing four stereogenic centres. X-Ray diffraction analysis reveals that the cyclohexane ring tends towards a boat conformation, the tetrahydrofuran ring and the dihydrofuran ring adopt envelope conformations. The dihedral angle between the pyrrolidine-2,5-dione plane and phenyl plane is 50.4 (2)°.

Key Words: Synthesis, Structural characterization, *N*-Phenyl-7-oxa-bicyclo[2,2,1]hept-5-ene-2,3-dicarboximide.

INTRODUCTION

The imide moiety is an integral structural part of various important bioactive molecules such as fumaramidmycin, granulatimide, isogranulatimide and rebeccamycin. These molecules are reported to exhibit antitumor, antiinflammatory and antimicrobial activities[1-3]. 7-Oxa-bicyclo[2,2,1]hept-5-ene-2,3-dicarboxylic anhydride has been widely employed in clinical practice, as it is less toxic and much easier to be synthesized[4,5]. Its derivatives are also pharmacologically active[6]. Furthermore, 7-oxa-bicyclo[2,2,1]hept-5-ene-2,3-dicarboximide and its *N*-substituent compounds have recently become an intense research topic in heterocyclic chemistry because of their antitumor, antivirus, analgesic, sedative and fungicidal activities[7]. In this paper, the compound *N*-phenyl-7-oxa-bicyclo[2,2,1]hept-5-ene-2,3-dicarboximide was synthesized (**Scheme-I**) and its molecular structure was investigated by elemental analysis, ^{1}H NMR spectra, IR spectra and X-ray crystallographic techniques.





Scheme-I

EXPERIMENTAL

All the reagents were of AR grade and used without further purification. IR spectra (4000-400 cm^{-1}), as KBr pellets, were recorded on a Nicolet FT-IR 510P spectrometer. ^{1}H NMR spectra were measured with a Bruker ALP 80 nuclear magnetic resonance spectrometer (CD_3COCD_3 as solvent, TMS as internal standard).

The intermediate I were prepared according to the literatural report[8]. The synthesis of the title compound II is described below.

A mixture of exo-7-oxa-bicyclo[2,2,1]hept-5-ene-2,3-dicarboxylic anhydride (0.332 g, 2 mmol) and *o*-aminobenzoic acid aniline (0.186 g, 2 mmol) in methanol (5 mL) was stirred for 5 h at room temperature and then refluxed for 1 h. After cooling the precipitate was filtered and dried, the title compound was obtained. The crude product of 20 mg was dissolved in methanol of 10 mL. The solution was filtered to remove impurities and then the filtrate was left for crystallization at room temperature. The single crystal suitable for X-ray determination was obtained by evaporation from the methanol solution after 5 d.

Data collection and structure determination: A selected crystal of the present compound was mounted on a SMART CCD diffractometer. The reflection data were measured at 298 K, using a graphite monochromator MoK$_\alpha$ (λ = 0.71073 Å) radiation with an ω-2θ scan mode. The total reflections were 5454 with 1975 independent ones (R_{int} = 0.0452), of which 1210 were observed with $I > 2\sigma(I)$. Intensities were corrected for Lorentz and polarization effects and empirical absorption and all data were corrected using SADABB program[9].

The structure was solved by direct methods using SHELXS-97 program[10]. All the non-hydrogen atoms were refined on F^2 anisotropically by full-matrix least squares method. All hydrogen atoms were placed in the geometrically calculated positions. The contributions of these hydrogen atoms were included in the structurefactor calculations. The atomic scattering factors and anomalous dispersion corrections were taken from International Table for X-ray crystallography[11]. The final least-square cycle gave R = 0.0424 and ωR = 0.1058 ($w = 1/[\sigma^2(Fo^2) + 0.0398P^2 + 0.2186P]$, where $P = (Fo^2 + 2Fc^2)/3$). S = 1.015, $(\Delta/\sigma)_{max}$ = 0.000, $(\Delta\rho)_{min}$ = -0.168 and $(\Delta\rho)_{max}$ = 0.176 e/Å^3.

RESULTS AND DISCUSSION

The atomic coordinates and equivalent isotropic thermal parameters for the non-H atoms in the present compound are given in Table-1 and the selected bond distances and bond angles in Table-2. A displacement ellipsoid plot with atomic numbering scheme is shown in Fig. 1 and a perspective view of the crystal packing in the unit cell in Fig. 2.

TABLE-1
ATOMIC COORDINATES (× 10^4) AND
THERMAL PARAMETERS (Å^2 × 10^3)

Atom	x	y	Z	U (eq)
N(1)	3972(2)	7227(2)	3058(1)	38(1)
O(1)	5491(2)	6248(2)	1998(1)	60(1)
O(2)	3073(2)	8397(2)	4344(1)	56(1)
O(3)	6283(2)	5569(2)	4443(1)	50(1)
C(1)	5303(2)	6952(3)	2713(2)	41(1)
C(2)	6427(2)	7614(3)	3393(2)	38(1)
C(3)	5618(2)	8233(3)	4213(1)	39(1)
C(4)	4075(2)	8009(3)	3916(2)	40(1)
C(5)	2685(2)	6594(3)	2628(2)	36(1)
C(6)	1814(2)	5690(3)	3160(2)	45(1)
C(7)	605(3)	4992(3)	2740(2)	54(1)
C(8)	271(3)	5199(3)	1803(2)	56(1)
C(9)	1142(3)	6100(3)	1280(2)	52(1)
C(10)	2354(3)	6807(3)	1687(2)	43(1
C(11)	7304(2)	6222(3)	3854(2)	46(1)
C(12)	8383(3)	6949(3)	4542(2)	52(1)
C(13)	7656(3)	7443(3)	5242(2)	53(1)
C(14)	6130(2)	7010(3)	4982(2)	46(1)

In the infrared spectrum, the broad absorption at 1775 and 1684 cm^{-1} is assigned to the stretching vibration of ν(C=O) of carbonyl group. The compound exhibits characteristic strong bands at 3075 ν(Ar-H), 1600 ν(C=C), 1198 ν(C-O-C). ^{1}H NMR δ: 7.65 (d, 2H, 2ArH), 7.26 (m, 2H, 2ArH), 7.03 (m, 1H, ArH), 5.81 (m, 2H, 2CH), 4.65 (m, 2H, 2CH), 3.10 (m, 2H, 2CH). Anal. calcd. (%) for $C_{14}H_{11}NO_3$: C 69.71, H 4.56, N 5.81. Found (%): C 69.79, H 4.63, N 5.72.

TABLE-2
SELECTED BOND LENGTHS (Å) AND BOND ANGLES (º)

Bond	Length (Å)	Bond	Angle (º)
N(1)-C(4)	1.392(3)	C(4)-N(1)-C(1)	112.05(19)
N(1)-C(1)	1.397(3)	C(4)-N(1)-C(5)	124.43(18)
N(1)-C(5)	1.427(3)	C(1)-N(1)-C(5)	123.07(18)
O(1)-C(1)	1.205(3)	C(11)-O(3)-C(14)	95.49(17)
O(2)-C(4)	1.203(2)	O(1)-C(1)-N(1)	124.4(2)
O(3)-C(11)	1.428(3)	O(2)-C(4)-N(1)	124.3(2)
O(3)-C(14)	1.439(3)	–	–

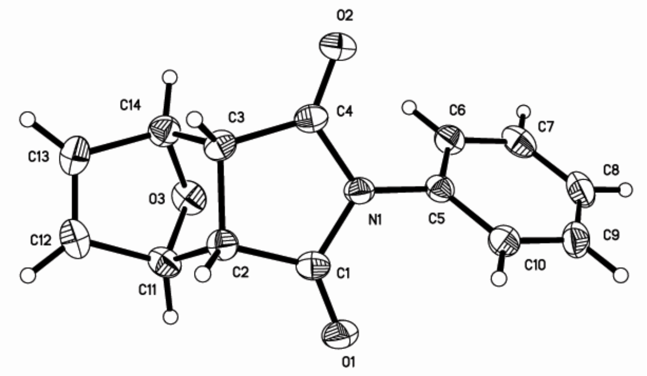


Fig. 1. Molecular structure with atomic numbering scheme

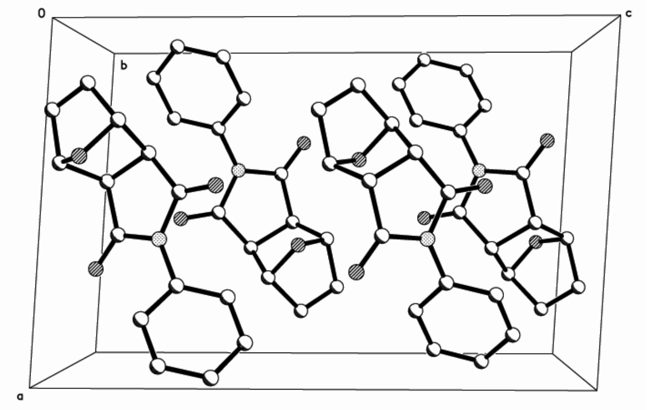


Fig. 2. View of crystal packing down the b-axis

The structure of II (**Scheme-I**) comprises a racemic mixture of chiral molecules containing four stereogenic centres. As seen from Fig. 1, the cyclohexane ring tends towards a boat conformation and the tetrahydrofuran ring and the dihydrofuran ring adopt envelope conformations. The dihedral angle between the pyrrolidine-2,5-dione plane and the aromatic ring is 50.4 (2)º. As seen from Table-2, the bond lengths and bond angles are as expected. And they are comparable to those in the similar compounds[12,13]. In 7-oxabicyclo(2,2,1)hept-5-ene-2,3-dicarboximide group, the C-C bonds lengths [1.501(3)-1.555(3) Å], except C12-C13 double bond length [1.317(3) Å], are longer than the normal single bond length. The degree of lengthening of the C-C bonds in II is in good agreement with that of corresponding C-C bonds in *N*-methyl-7-oxabicyclo(2,2,1)hept-5-ene-2,3-exo- dicarboximide[12] and exo-4-[(4-bromophenyl)amino]-10-oxa-4-azatricyclo

(5,2,1,02,6)dec-8-ene-3,5-dine[13]. The crystal structure is stabilized by a strong π-π stacking interactions from the existence of the benzene ring[14].

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