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Synthesis and Structural Characterization of *N*-Phenyl-5-norbornene-2,3-dicarboximide

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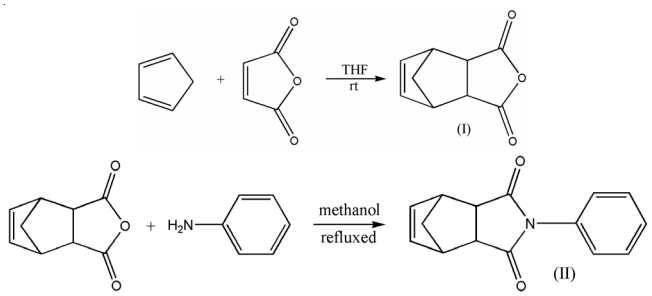
The compound *N*-phenyl-5-norbornene-2,3-dicarboximide ($C_{15}H_{13}NO_2$, M_r = 239.26) was synthesized and characterized by single crystal X-ray diffraction. The crystal belongs to monoclinic, space group P21/c, with a = 9.7534(13), b = 21.395(2), c = 12.0647(14) Å, β = 108.7020(10) °, V = 2384.6(5) Å^3, Z = 8, Dc = 1.333 g/cm^3, λ = 0.71073 Å, μ(MoK$_\alpha$) = 0.089 mm^{-1}, F(000) = 1008. The final refinement gave R = 0.0741, wR (F^2) = 0.1676 for 4,199 observed reflections with I > 2α(I). The structure of the title 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 angles between the pyrrolidine-2,5-dione plane and the aromatic ring are 65.5 (2)° and 54.9 (2)°, respectively in the two molecules.

Keywords: *N*-Phenyl-5-norbornene-2,3-dicarboximide, Synthesis, Structural characterization, X-ray diffraction.

INTRODUCTION

The polymers made of norbornene dicarboximide have good thermal stability and low dielectric constant. They have been used in large-scale integrated circuit[1]. The process of norbornene dicarboximide monomer being synthesized consists of two steps. Norbornene dianhydride was dissolved in toluene and the solution of amine/toluene was dropped into above solution, the reaction of norbornene dianhydride and amine was kept for 3 h at 60 °C, filtered and filter cake dried. And then the above intermediate was added to acetic anhydride containing sodium acetate, the solution was heated to reflux for 4 h, filtered, washed and filter cake dried[2,3].

In this paper, the title compound *N*-phenyl-5-norbornene-2,3-dicarboximide was synthesized in one-pot mode with high yields (**Scheme-I**) and its molecular structure was investigated by X-ray crystallographic techniques.



Scheme-I

EXPERIMENTAL

All the reagents were of AR grade and used without further purification.

The intermediates **I** were prepared according to the literatural report[4]. The synthesis of *N*-phenyl-5-norbornene-2,3-dicarboximide **II** is described as a mixture of exo-bicyclo[2,2,1]hept-5-ene-2,3-dicarboxylic anhydride (0.328 g, 2 mmol) and aniline (0.186 g, 2 mmol) in methanol (8 mL) was stirred for 4 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 6 d.

Data collection and structure determination: A selected crystal of the title 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 11,552 with 4,199 independent ones (R_{int} = 0.1539), of which 325 were observed with I > 2σ(I). Intensities were corrected for Lorentz and polarization effects and empirical absorption and all data were corrected using SADABB[5] program.

The structure was solved by direct methods using SHELXS-97[6] program. 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[7]. The final least-square cycle gave R = 0.0741 and ωR = 0.1676 ($w = 1/[\sigma^2(Fo^2) + (0.0712P)^2 + 0.0000P]$, where $P = (Fo^2 + 2Fc^2)/3$). S = 1.012, $(\Delta\rho)_{min}$ = -0.250 and $(\Delta\rho)_{max}$ = 0.244 e/Å^3.

RESULTS AND DISCUSSION

The atomic coordinates and equivalent isotropic thermal parameters for the non-H atoms in the title 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.

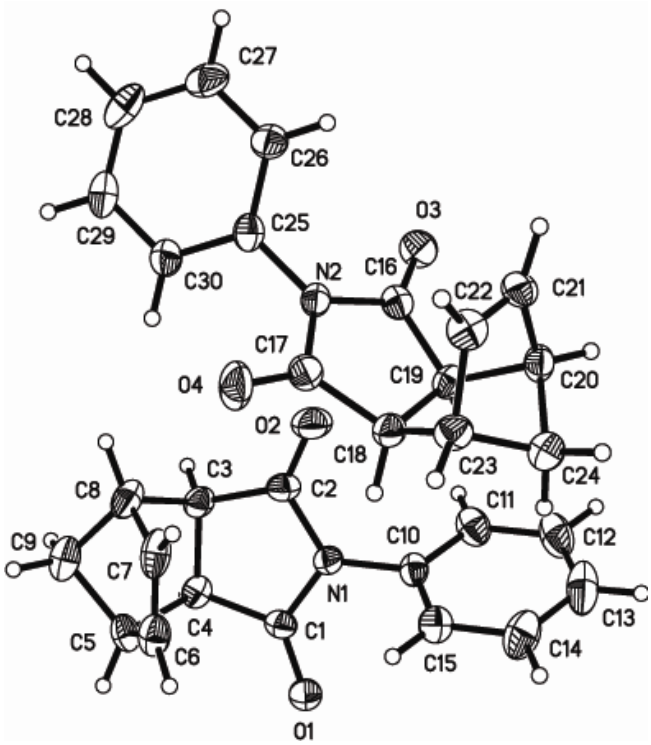


Fig. 1. Molecular structure with atomic numbering scheme

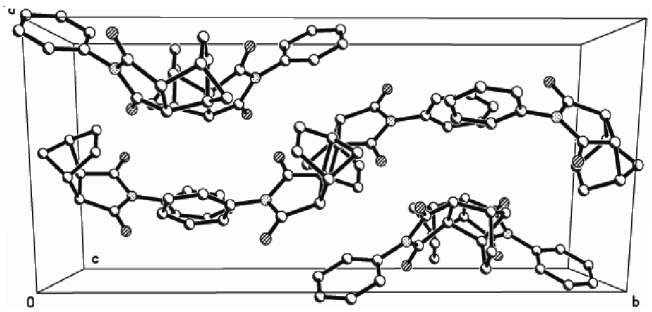


Fig. 2. View of crystal packing down the c-axis

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

Atom	x	y	Z	U(eq)
N(1)	6596(5)	6163(2)	7028(4)	39(1)
N(2)	1684(5)	6382(2)	3806(4)	40(1)
O(1)	8023(4)	6147(2)	8949(4)	58(1)
O(2)	4921(5)	5936(2)	5278(4)	70(1)
O(3)	3110(4)	6564(2)	2652(4)	54(1)
O(4)	559(5)	6451(2)	5210(4)	71(1)
C(1)	7214(6)	5883(3)	8100(5)	41(1)
C(2)	5641(6)	5774(3)	6240(5)	43(2)
C(3)	5630(6)	5163(2)	6796(5)	45(2)
C(4)	6698(6)	5218(2)	8033(5)	41(1)
C(5)	5756(6)	5079(2)	8828(6)	48(2)
C(6)	4719(7)	5610(3)	8649(7)	54(2)
C(7)	3786(7)	5565(3)	7588(7)	58(2)
C(8)	4193(6)	4999(3)	7034(6)	57(2)
C(9)	4764(7)	4575(3)	8095(6)	63(2)
C(10)	6812(6)	6805(3)	6788(5)	41(1)
C(11)	7459(6)	6955(3)	5972(6)	58(2)
C(12)	7630(7)	7579(4)	5743(7)	68(2)
C(13)	7164(8)	8040(4)	6329(8)	79(2)
C(14)	6555(8)	7881(3)	7161(7)	72(2)
C(15)	6368(6)	7262(3)	7387(6)	51(2)
C(16)	2740(6)	6703(3)	3475(5)	40(1)
C(17)	1440(7)	6648(3)	4772(5)	46(2)
C(18)	2387(6)	7197(2)	5147(5)	44(2)
C(19)	3250(6)	7235(2)	4292(5)	40(1)
C(20)	2879(6)	7895(2)	3769(5)	44(2)
C(21)	1301(6)	7885(2)	3045(6)	48(2)
C(22)	554(6)	7846(2)	3770(6)	48(2)
C(23)	1597(6)	7837(2)	4979(5)	46(2)
C(24)	2795(7)	8246(3)	4837(6)	52(2)
C(25)	956(6)	5836(2)	3219(5)	42(2)
C(26)	232(6)	5852(3)	2034(5)	48(2)
C(27)	-421(6)	5334(3)	1489(6)	60(2)
C(28)	-403(7)	4794(3)	2093(8)	67(2)
C(29)	289(7)	4773(3)	3268(7)	60(2)
C(30)	971(7)	5303(3)	3831(6)	49(2)

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

Bond	Length (Å)	Bond	Angle (º)
N(1)-C(2)	1.376(7)	C(2)-N(1)-C(1)	112.4(5)
N(1)-C(1)	1.377(7)	C(2)-N(1)-C(10)	123.4(5)
N(1)-C(10)	1.433(7)	C(1)-N(1)-C(10)	123.9(4)
N(2)-C(17)	1.385(7)	C(17)-N(2)-C(16)	112.3(5)
N(2)-C(16)	1.399(7)	C(17)-N(2)-C(25)	124.1(5)
N(2)-C(25)	1.429(7)	C(16)-N(2)-C(25)	123.6(5)
O(1)-C(1)	1.213(6)	O(1)-C(1)-N(1)	124.1(5)
O(2)-C(2)	1.199(6)	O(2)-C(2)-N(1)	123.5(5)
O(3)-C(16)	1.198(6)	C(7)-C(6)-C(5)	108.2(6)
O(4)-C(17)	1.219(7)	C(6)-C(7)-C(8)	107.0(5)
C(5)-C(9)	1.527(8)	C(8)-C(9)-C(5)	93.4(4)
C(6)-C(7)	1.315(9)	O(3)-C(16)-N(2)	124.0(5)
C(8)-C(9)	1.521(8)	O(4)-C(17)-N(2)	123.9(5)
C(20)-C(24)	1.516(8)	C(22)-C(21)-C(20)	107.3(5)
C(21)-C(22)	1.308(8)	C(21)-C(22)-C(23)	107.7(5)
C(23)-C(24)	1.513(8)	C(23)-C(24)-C(20)	93.7(4)

The asymmetric unit of the title compound contains two molecules. The structure of the title compound 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 cyclopentene ring and the cyclopentane ring adopt envelope conformations. The dihedral angles between the pyrrolidine-2,5-dione plane and the aromatic ring are 65.5 (2)° and 54.9 (2)°, respectively in

the two molecules. In one molecule, the mean planes C3/C4/C5/C8 and C5/C6/C7/C8 form dihedral angles of 59.7 (3) and 52.0 (3)º, respectively with the mean plane C5/C8/C9. While in another one, the mean planes C18/C19/C20/C23 and C20/C21/C22/C23 form dihedral angles of 60.7 (3) and 51.8 (3)º, respectively with mean plane C20/C23/C24.

As seen from Table-2, the bond lengths and bond angles are as expected. In 7-bicyclo(2,2,1)hept-5-ene-2,3-dicarboximide group, C6-C7 and C6-C7 double bond lengths are 1.315(9) Å and 1.308(8) Å, respectively. The other C-C bonds are normal single bonds with bond lengths of 1.488(8)-1.558(8) Å. The crystal structure is stabilized by a strong π-π stacking interactions from the existence of benzene ring[8].

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