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Supramolecular structure of 5-methyl-5-phenyl hydantoin and hydrogen-bonding patterns in 5,5′-substituted hydantoins

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ABSTRACT

The crystal structure of heterocyclic compound 5-methyl-5-phenyl hydantoin has been determined from X-ray single crystal structural characterization. This material crystallizes in the orthorhombic system and noncentrosymmetric space group P21 (N°4). The crystal packing is governed by N–H···O hydrogen bond-type intermolecular interactions, forming chains and edge-fused 12-membered rings with graph-set C(4) C(5) C22(8) R33(12) in a similar hydrogen-bonding pattern of another chiral 5,5′-substituted hydantoins.

KEYWORDS

Hydantoin compounds; crystal structure; hydrogen-bond patterns

1. Introduction

Hydantoins, or imidazolidine-2,4-diones, are a five-member heterocycle ring containing a reactive cyclic urea nucleus. This heterocycle represents a significant molecular template in combinatorial chemistry libraries [1,2], principally because of the four possible substitution points. From structural point of view hydantoin structural motif is suitable to form excellent supramolecular architectures through hydrogen bonds, which play a key role in molecular recognition and crystal engineering [3] with applications in drug and pharmaceuticals design [4]. It is generally accepted that the probability of formation of a supramolecular motif increases proportionally to the number of involved hydrogen bonds [5]. The hydantoin core possesses two donors groups (N-H) and two acceptor groups (C =O) and are susceptible to form excellent supramolecular architectures through hydrogen bonds. In organic compounds these interactions, or supramolecular synthons, usually are of the type N–H···O, N–H···N, O–H···O, or O–H···N.

Hydantoin compounds forms a large group of derivatives widely applied in medicine and pharmacy because of their varied range of therapeutic properties [6–8]. In particular, the hydantoins substituted at the 5-position, like Norantoin (3-methyl-5-phenyl hydantoin), Mepheenytoin (5-ethyl-3-methyl-5-phenyl hydantoin), Nirvanol

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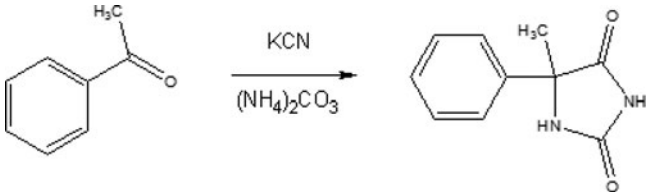


Scheme 1. Synthesis of 5-methyl-5-phenyl hydantoin (I) by the Bucherer method.

(5-ethyl-5-phenylhydantoin), Methetoin (5-ethyl-1-methyl-5-phenyl hydantoin), or Phenytoin (5,5-diphenyl hydantoin), have been found to be valuable precursors of a great variety of heterocyclic systems that are associated with a wide range of biological activities including antiarrytmitc [9], anticonvulsant [10], and antitumoral agents [11]. The best known hydantoin 5,5-diphenylhydantoin, phenytoin, is an anticonvulsant compound having efficacy in the treatment of generalized convulsive and psychomotor epilepsy [12]. Just the anticonvulsant properties of phenytoin are responsible for the synthesis of many hydantoin analogs [13]. Nowadays, phenytoin has found new applications due to the neuro- and cardioprotective properties [14]. In addition, a number of other biological activities of hydantoin derivatives as herbicides and fungicides are known [15,16].

On the other hand, the biocatalitic conversion of 5-subtituted hydantoins to amino acids has received considerable attention for their potential applications in the industrial productions of optically pure amino acids, through an enantioselective enzymatic reaction [17,18]. For these reasons, there has been much interest in the search of new synthetic routes for hydantoin via solution [19], or solid state reactions [20].

The Bucherer–Bergs reaction is the most commonly used method for the synthesis of hydantoins [21]. This multicomponent reaction begins from an aldehyde or a ketone and their ready availability makes this reaction an attractive method for the synthesis of hydantoins [14,22].

Some of the reported studies on hydantoins deal with the determination of their crystal structures [23–26] and the investigation of chirality effects in the solid state [27]. In fact, one chemical family of interest is that of 5-alkyl-5-arylhydantoins [28,29], since an unusual high propensity to crystallize as conglomerates has been reported among these derivatives.

In this paper, the synthesis and structural characterization of the chiral compound 5-methyl-5-phenyl hydantoin (Scheme 1) using X-ray single-crystal diffraction data are described. Also, an supramolecular hydrogen bond patterns analysis is performed in 5,5′-substituted hydantoins searched in the Cambridge Structural Database (CSD, version 5.36, Nov. 2014) [30].

2. Experimental

2.1. *Synthesis*

The title compound was synthesized by the Bucherer-Bergs method [21] (see Scheme 1). 1-phenyl-ethanone (0.20 mmol) was dissolved in 10 mL of ethanol, and then KCN (0.40 mmol) and (NH4)2CO3 (0.80 mmol) were added. This mixture was warmed under a condenser at temperature of 60°C for 15 hr, after which the solution was concentrated to approximately two-thirds of the initial volume and chilled in an ice-bath. The solid was filtered and washed with cool water. Colorless crystals of I suitable for X-ray diffraction analysis were grown by slow evaporation in an ethanol solution. Yield 52%, m.p.: 195–197°C.

2.2. FT-IR and NMR analysis

Melting point was determined on an Electrothermal Model 9100 apparatus. The FT-IR spectrum for the title compound was recorded on a Perkin Elmer 1600 spectrometer employing a KBr disc, in the region from 400 to 4000 cm^{-1}. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker Avance 400 model spectrometer in DMSO-d_6 solution.

FT-IR (KBr) ν cm^{-1}, 3283 cm^{-1} [*t*, N-H], 3207 cm^{-1} [*t*, N-H], 1771 cm^{-1} [*t*, C = O], 1717 cm^{-1} [*t*, C = O], 1494 cm^{-1} [*t*, N-H].

^{1}H NMR (400 MHz, DMSO-d_6) δ = 10.71 (s, H3), 8.59 (s, H1), 7.56 (m, H9-H11), 7.39 (m, H8-H12), 7.28 (m, H10), 1.66 (s, H6).

^{13}C NMR (100.6 MHz, DMSO-d_6) δ = 176.9 (C4), 156.2 (C2), 139.9 (C7), 128.4 (C9-C11, 127.7 (C10), 125.2 (C8-C12), 63.9 (C5), 24.9 (C6).

2.3. X-Ray powder diffraction

X-ray powder diffraction pattern was collected, at room temperature, in a Phillips PW-1250 goniometer using monocromatized CuKα radiation (λ = 1.5418 Å). A small quantity of the hydantoin was ground mechanically in an agate mortar and pestle and mounted on a flat holder covered with a thin layer of grease. The specimen was scanned from 5° to 65° 2θ, with a step size of 0.02° and counting time of 15 s. Silicon was used as an external standard. X-ray powder pattern of 5-phenyl-5-mehtyl hydantoin is show in Fig. 1. The 20 first measured reflections were completely indexed using the program Dicvol04 [31], which gave a unique solution in a monoclinic cell with parameters $\boldsymbol{a}$ = 7.40 Å , $\boldsymbol{b}$ = 6.23 Å , c = 10.90 Å , and β = 108.5°. The systematic absences determined the chiral space group to be P212121, which was confirmed by successful solution and refinement of the crystal structure. In order to confirm the unit cell parameters, a Le Bail refinement [32] was carried out using the Fullprof program [33]. The Fig. 1 shows a very good fit between the observed and calculated patterns.

2.4. X-Ray single-crystal crystallography

Colorless rectangular crystal (0.18, 0.29, and 0.56 mm) was used for data collection. Diffraction data were collected at 296(2) K by ω-scan technique on a Bruker SMART APEX II CCD

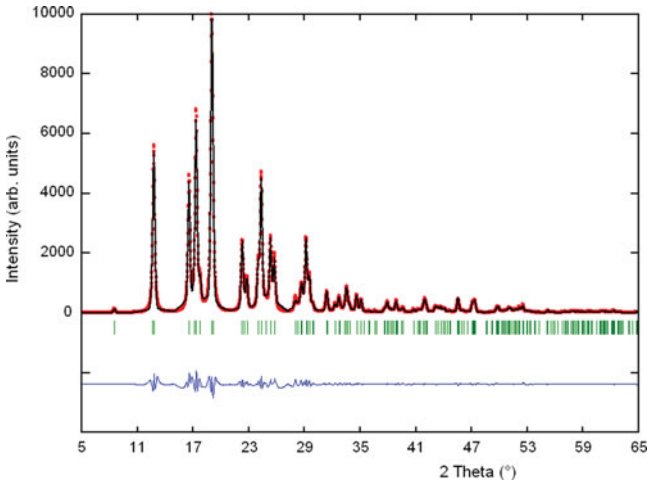


Figure 1. X-ray powder diffraction data for 5-methyl-5-phenyl hydantoin. The powder pattern was refined without structural model to confirm the unit cell parameters.

Table 1. Crystal data, data collection, and structure refinement.

Chemical formula	$C_{10}H_{10}N_2O_2$	CCDC	1008457
Formula weight	190.20	Radiation (MoKα)	$\lambda = 0.71073$ Å
Crystal system	Monoclinic	θ range (°)	2.0–24.3
Space group	P21	*hkl* range	−7, 7; −7, 5; −10, 11
a (Å)	7.398(13)	Reflections	
b (Å)	6.232(12)	Unique	960
c (Å)	10.913(19)	Rint	0.036
β (°)	108.46(4)	With $I > 2\sigma(I)$	587
V (Å 3)	477.3(15)	Refinement method	Full-matrix least-squares on F^2
Z	2	Number of parameters	129
dx (g cm-3)	1.323	$R(F^2)$ [$I > 2\sigma(I)$]	0.1377
F(000)	200	$wR(F^2)$ [$I > 2\sigma(I)$]	0.3905
μ (mm^{-1})	0.094	Goodness of fit on F^2	1.68
Crystal size (mm)	0.18 × 0.29 × 0.56	Max/min $\Delta\rho$ (e Å −3)	0.60/−0.54

diffractometer [34] equipped with MoKα radiation ($\lambda = 0.71073$ Å). The data were corrected for Lorentz-polarization and absorption effects [35]. The structure was solved by direct methods using the SHELXS program [36] and refined by a full-matrix least-squares calculation on *F*2 using SHELXL [37]. All H atoms were placed at calculated positions and treated using the riding model, with C-H distances of 0.97–0.98 A, and N-H distances of 0.86 A. The Uiso(H) parameters were fixed at 1.2Ueq (C, N) and 1.5Ueq (methyl carbon). Table 1 summarizes the crystal data, intensity data collection, and refinement details for the title compound.

3. Results and discussion

The spectroscopic studies confirm the molecular structure of the new chiral hydantoin. The title compound crystallizes in the noncentrosymmetric space group P21 with one molecule in the asymmetric unit, corresponding to a chiral molecule. Figure 2 shows the molecular structure and the atom-labeling scheme of 5-methyl-5-phenyl hydantoin, generated using Diamond program [38]. All geometrical calculations were done using the program Platon [39]. Selected bond distances, bond angles and torsion angles are presented in Table 2.

All bond distances and angles are in agreement with experimental average values found in 136 entries with hydantoin ring fragments, searched in the Cambridge Structural Database (CSD, version 5.35, May. 2014) [29] with N1 and N3 unsubstituted.

The hydantoin ring is essentially plane with a maximal deviations of 0.01 (2) Å in N2 and −0.01 (2) Å in C2. The N1–C2–O2 bond angle 130.0 (2)° is greater than the N3–C2–O2 angle 123.2 (2)°. This difference is also observed in all 136 hydantoins derivative entries including the hydantoin molecule [40], and can be attributed to the fact the N3 atom shares its lone pair between the O2 and O4 atoms, while the N1 atom is involved in a π-resonance with the C2-O2 carbonyl group only [41].

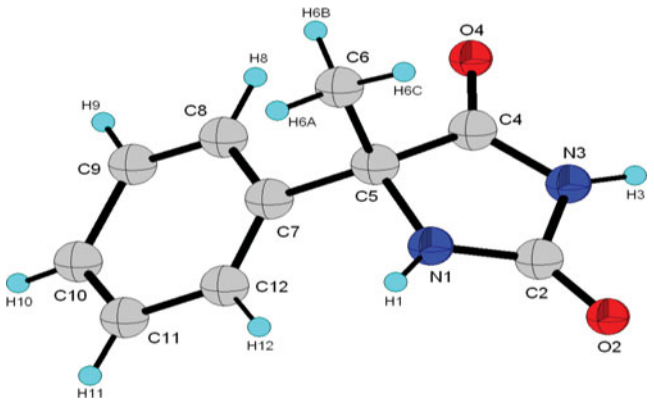


Figure 2. The molecular structure of (I), showing the atomic numbering scheme. Displacement ellipsoids are drawn at 25% probability level. H atoms are shown as spheres of arbitrary radii.

The molecular structure and crystal packing of (I) are stabilized by N–H···O hydrogen bonds. Details of the hydrogen-bonding geometry are given in Table 3.

The structure of (I) is built up from self-assembly of molecules via N–H···O, C–H···O and C–H···N, hydrogen-bonding interactions (Fig. 3 and Table 3). The interactions N1–H1···O4 ($1-x$, $-½+y$, $1-z$) form infinite chains which run along the ***b*** axis with graph-set notation C(5) [42,43] and the interactions N3–H3···O2 ($1-x$, $-½+y$, $1-z$) form infinite zigzag polymeric C(4) chains propagating along the ***a*** axis. Together, these hydrogen-bond patterns produces chains with graph-set C22(8) and created edge-fuse R33(12) rings. The network is reinforced by the weak intermolecular nonconventional hydrogen bonds C1–H1A···O1 and C8—H8···N2. All these interactions are shown in Fig. 3.

Table 2. Selected geometrical parameters (Å , °).

O2-C2	1.24(2)	O4-C4	1.20(3)
N3-C2	1.45(2)	N3-C2	1.38(2)
N1-C5	1.49(2)	N1-C2	1.28(3)
C7-C12	1.39(3)	C7-C8	1.35(3)
C5-C7	1.53(4)	C5-C4	1.52(4)
C2-N3-C4	107.6(2)	N1-C2-O2	130.0(2)
C5-N1-C2	116.3(1)	N3-C2-O2	124.4(2)
C4-N3-C2-O2	− 178.0(2)	C4-N3-C2-N1	− 1.0(2)
C2-N3-C4-O4	177.3(2)	C5-N1-C2-N3	1.0(2)

Table 3. Hydrogen bonds geometry (Å , °). (D, donor; A, acceptor; H, hydrogen).

D–H···A	D–H	H···A	D···A	D–H···A
N1—H1···O4(i)	0.86	2.050	2.89 (2)	167
N3—H3···O2(i)	0.86	2.010	2.82 (2)	158
C1—H1A···O1	0.93	2.560	3.10 (3)	118
C8—H8···N2	0.93	2.410	2.80 (3)	105

Symmetry codes: (i) $1-x, -½+y, 1-z$.

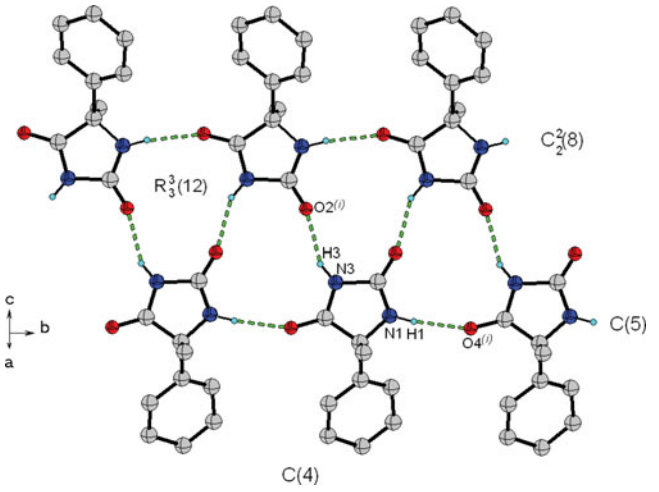


Figure 3. A partial view of the crystal packing shows all hydrogen bonds formed (N–H···O). [symmetry codes: *(i)*1−x, −½+y, 1−z]. H atoms not involved in hydrogen bonding have been omitted for clarity.

In Fig. 4 it can be observed that the hydrogen-bonded molecules form infinite ribbons, parallel to the **b** axis. These ribbons, possessing hydrophilic character, are held together only by means of van der Waals forces between the phenyl groups which are in the vicinity of each other. The union of all interactions generates a three-dimensional network.

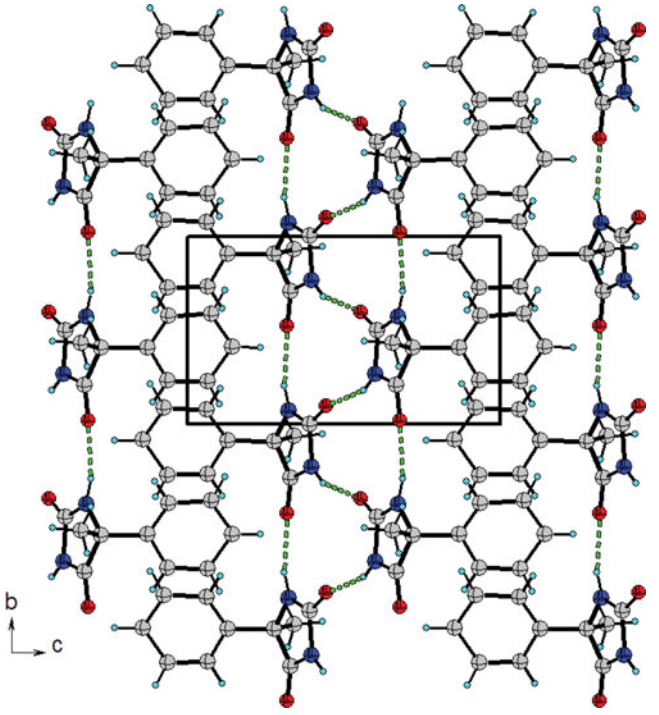


Figure 4. A portion of the crystal packing viewed in the ***bc*** plane. Intermolecular hydrogen bonds, N–H···O are indicated by dashed lines.

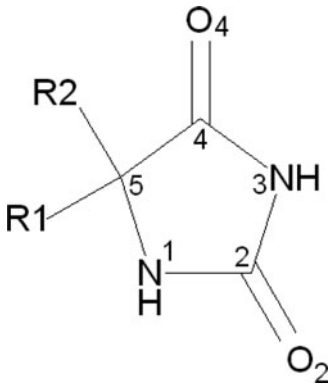
Table 4. Hydrogen bond patterns in 5,5′-substituted hydantoin (nonspiro) retrieved from the CSD [30].

CSD refcode	–*R*1	–*R*2	SG	Supramolecular synthons	Ref.
GODRAS	–C6H5	–NC5H5	P212121	C(4) C(7) C22(12)	[44]
ADUQOF	–CH3	–CH2CH3	P21	C(4) C(4) R22(8)	[45]
BEPNIT	–CH3	–CH3	P212121	C(4) C(4) R22(8)	[46]
BILXUR	–C6H5	–C5NH5	C2/c	C(4) C(4) R22(8)	[47]
ENICUA	–(CH2)2CH3	–(CH2)2CH3	P*nma*	C(4) C(4) R22(8)	[41]
KIDWAX	–C6H5	–C6H9-OCH3	P21	C(4) C(4) R22(8)	[48]
NIWRAN	–CH3	–FC6H4	P*bca*	C(4) C(4) R22(8)	[49]
AHINEK	–CH3	–CH(C6H5)(NH-COCH3)	P21/c	C(7) C(7) R22(8)	[50]
This work **(I)**	–CH3	–C6H5	P21	C(4) C(5) C22(8) R33(12)	**(I)**
AVINID	–CH3	–C6H5-CH2CH3	P212121	C(4) C(5) C22(8) R33(12)	[27]
ENELIT	–CF3	–C6H5	P21	C(4) C(5) C22(8) R33(12)	[51]
LABTIR	–CH2CH3	–C6H5	P212121	C(4) C(5) C22(8) R33(12)	[28]
PHYDAN	–C6H5	–C6H5	Pn21a	C(4) C(5) C22(8) R33(12)	[52]
MUFLOP	–COOCH2CH3	–C6H5	P212121	C(4) C(5) C22(10) R33(14)	[53]
TOTPIB	–CFH2	–CH2SO*p*tol	P21	C(4) C(7) C22(10) R33(14)	[54]
ENIDEL	–(CH2)3CH3	–(CH2)3CH3	P*c*	C(4) C(4) C22(9) R44(17)	[41]

For comparison of supramolecular hydrogen bonding, Table 4 show a search for hydantoin compounds in the CSD database with N1 and N3 unsubstituted and sp3 hybridization at C5, and spiro-fused ring compounds excluded (Scheme 2). A total of 15 structures were found.

Three types of hydrogen-bonding patterns can be observed. In the structure with refcode GODRAS, with substituents phenyl and pyridyl, only single chains can be formed. In the second group, each molecule participle in N–H···O hydrogen bonds, forming a chain of centrosymmetric rings with graph set C(4) C(4)R22(8) except AHINEK with C(7) C(7) R22(8), invariably in centro or noncentrosymmetric space groups. In the third group, the hydantoins can create infinite chains with graph-set along ***a*** and ***b*** axis which generate different chains and edge-fused rings.

The title compound, 5-methyl-5-phenyl hydantoin, belong to the third group were the structures more frequently can generate an infinite chain in graph-set C(4), simultaneously with another C(5), thereby creating C22(8) motif chains and edge-fused R33(12) rings. All this five structures AVINID, ENELIT, LABTIR, PHYDAN, and present compound (I), crystallizes in noncentrosymmetric space groups.



Scheme 2. Structure of 5,5′-substituted hydantoin derivatives.

4. Conclusions

The title compound was synthesized by the Bucherer-Bergs reaction. The structure was unambiguously assigned by X-ray diffraction studies. The FTIR and NMR results were consistent with the structural results. In the crystal structure of 5-methyl-5-phenyl-hydantoin, the molecules are linked by N—H···O hydrogen bonds, forming infinite three-dimensional network described with the graph-set notation C(4) C(5) C22(8) R33(12), in a similar hydrogen-bonding pattern of another chiral 5,5′-substituted hydantoins.

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