Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc

Spectral and cyclic voltammetric studies on some intramolecularly hydrogen bonded arylhydrazones: Crystal and molecular structure of 2-(2-(3-nitrophenyl)hydrazono)-5,5-dimethylcyclohexane-1,3-dione

A. Sethukumar, B. Arul Prakasam*

Department of Chemistry, Annamalai University, Annamalainagar, Chidambaram 608 002, India

ARTICLE INFO

Article history: Received 19 July 2009 Received in revised form 1 November 2009 Accepted 1 November 2009 Available online 4 November 2009

Keywords: Hydrogen bonding Cyclic voltammetry NMR XRD RAHB

ABSTRACT

A series of arylhydrazone derivatives (1–7) were prepared by the coupling of acetylacetone/dimedone with respective aromatic diazonium salts and characterized by IR, ¹H and ¹³C NMR spectra. The IR and NMR spectral data clearly manifests the effective intramolecular hydrogen bonding in all the cases. Cyclic voltammetric studies certainly indicate that in all the cases the reduced center is C=N bond of hydrazonic moiety. The single crystal X-ray structural analysis of 2-(2-(3-nitrophenyl)hydrazono)-5,5-dimethylcy-clohexane-1,3-dione (**6**) is also reported. Single crystal X-ray analysis of **6** evidences the intramolecular hydrogen bonding with the N(2) \cdots O(4) distance of 2.642(15) Å, which can be designated as S(6) according to Etter's graph nomenclature. The cyclohexane ring conformation in the molecule (**6**) can be described as an envelope. RAHB studies suggest that the resonance assistance for hydrogen bonding is significantly reduced for the compound (**6**) due to the non-planarity of the six atoms which are involved in resonant cycle S(6) of Etter's graph. The planarity of the resonant cycle S(6) is very much disturbed by the conformational requirement of the cyclohexane ring and hence RAHB concept is less operative in this case.

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1. Introduction

Hydrogen bonds are the most important intermolecular interactions that determine molecular recognition and aggregation in biology and chemistry are implicated in the structures of many novel materials. Long range, anisotropic interactions and those of electrostatic origin like hydrogen bonds [1] received special interest due to its significance from biological [2] perspective and determination of molecular conformation. In some cases hydrogen bonding acts as an active site for initiation of chemical reaction. Studies of how hydrogen bonding can be used to control molecular association continue to yield exciting discoveries in supramolecular chemistry [3]. Hydrogen bonded networks can also be purposefully designed to create novel liquid materials, including liquid crystals, gels and fluids. The types of hydrogen bonding and their effects in molecular conformation and in packing patterns of organic compounds have been extensively studied by analysing the numerous crystal structure data available from Cambridge Structural Database [4].

Arylhydrazones of mono, di and triketones as well as cyclic 1,3-dione *viz.*, cyclohexane-1,3-dione have been reported in the literature [5–11]. Such compounds have been extensively used as

* Corresponding author. Tel.: +91 9443583619.

E-mail address: arul7777@yahoo.com (B. Arul Prakasam).

precursors of potential antidiabetic drugs [12–14]. The arylhydrazone derivatives of β -diketones are important intermediate in organic synthesis because they can be converted into a diverse array of molecules such as poly functional heteroaromatics. Recently, the single crystal X-ray structural studies of two *para*-substituted phenylhydrazone derivatives of acetylacetone have been reported [15].

Several reports are available in the literature [5-11,15] regarding the synthetic and structural aspects of arylhydrazones of mono, di and triketones. The implications of hydrogen bonding on the spectral, electrochemical and structural properties of the β-diketone derivative have received much attention in recent years after the evolution of resonance assisted hydrogen bonding (RAHB) concept. However, such collective studies are very few in the literature and in view of the importance of arylhydrazone derivatives in medicinal and structural chemistry it was thought worthwhile to synthesize some arylhydrazone derivatives of diketones like acetylacetone and dimedone. In the present study a series of arylhydrazone derivatives of acetylacetone and dimedone has been prepared and analyzed by electronic, IR and NMR spectroscopy. Their IR and NMR (¹H and ¹³C) spectra are discussed in terms of the extent of intramolecular hydrogen bonding. Cyclic voltammetric studies is also carried out along with the single crystal X-ray structural analysis of 2-(2-(3-nitrophenyl)hydrazono)-5,5-dimethylcyclohexane-1,3-dione (6).





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2. Experimental

2.1. General

All the reagents and solvents employed were commercially available analytical grade materials used as supplied, without further purification. UV-vis spectra were recorded on a SHIMADZU UV-1650PC digital spectrophotometer by dissolving the sample in spectral grade methanol. IR spectra were recorded on Avatar Nicholet FT-IR spectrophotometer (range 4000–400 cm⁻¹) as a KBr pellet. Proton NMR spectra were recorded at room temperature (298 K) on Bruker AMX-400 spectrometer operating at 400.23 MHz (SWH, 8223.685 Hz; FIDRES, 0.125483 Hz) using TMS as internal reference. ¹³C NMR spectra were recorded in proton decoupled mode on Bruker AMX-400 spectrometer operating at 100.63 MHz (SWH, 24038.461 Hz; FIDRES, 0.366798 Hz). Cyclic voltammetric studies were carried out using a computerized HCH CHI604C Electrochemical analyzer. A three-electrode configuration was used, comprising of glassy carbon as the working electrode, a platinum wire as the counter electrode and Ag|AgCl as the reference electrode. Experiments were carried out at room temperature in DMF using 0.01 M tetrabutylammonium perchlorate as the supporting electrolyte. The solutions were deaerated by purging with a stream of nitrogen gas for 10 min before recording the currentvoltage curve and then a blanket of nitrogen was maintained throughout the experiment. In order to perform CV studies, the GC was polished with fine grade emery powder followed by polishing alumina (0.5 μm).

2.2. Preparation of compounds 1-7

Compounds were prepared by the general procedure (Scheme 1) in which anilines (0.5 mmol) were dissolved separately in 1 N HCl (25 cm^3) at 0–5 °C temperature and in each case cooled aqueous solution (10 cm^3) of NaNO₂ (0.40 g) was added drop wise with stirring followed by the addition of acetylacetone (0.50 g, 0.5 mmol)/dimedone (0.70 g, 0.5 mmol) and sodium acetate (5.0 g) dissolved in water (30 cm^3). Corresponding mixtures were further stirred for 4 h at room temperature (~ 25 °C). Solids thus obtained were filtered and washed several times with water followed by ethanol and then dried *in vacuo*. The crude products were recrystallized in ethanol. Compounds **5** and **7** were purified by column chromatography by using benzene as eluent. Yield and melting points of the derived compounds are summarized in Table 1.



Scheme 1.

Table 1

Yield and melting points of the compounds.

Entry	Х	Y	Z	R	Mp (°C)	Yield (%)
1	CH₃	-	CH₃	2-OCH ₃	142	75
2	CH_3	-	CH ₃	3-CI	92	75
3	CH_3	-	CH_3	3-NO ₂	140	78
4	CH ₃	-	CH_3	4-0CH ₃	92	75
5	CH_2	$C(CH_3)_2$	CH_2	$2-OCH_3$	146	73
6	CH_2	$C(CH_3)_2$	CH_2	3-NO ₂	126	75
7	CH_2	$C(CH_3)_2$	CH_2	3-Cl	110	70

All the compounds are recrystallized by using ethanol.

2.3. X-ray crystallography

Details of the crystal data, data collection and refinement parameters for 6 are summarized in Table 2. Crystal was grown by slow evaporation technique using ethanol as solvent. Determination of the unit cell and data collection were performed on a Bruker, 2004 APEX 2 diffractometer using graphite-monochromated Mo K_{α} radiation (λ = 0.71073 Å) at 293 K with crystal size of $0.25 \times 0.20 \times 0.20$ mm. Multi-scan absorption corrections were applied using the SADABS program. The structure was solved by direct methods and successive Fourier difference syntheses (SHELXS-97 [16]) and refined by full matrix least square procedure on F^2 with anisotropic thermal parameters. All non-hydrogen atoms were refined (SHELXL-97 [17]) and placed at chemically acceptable position. Selected bond lengths and bond angles are given in Table 3. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as Supplementary Publications No. CCDC-720911 for 6. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road,

Table 2

Crystal data, data collection and refinement parameters for 6.

	Compound	2-(2-(3-Nitrophenyl)hydrazono)-5,5-
Empired formula weight 282.9 Crystal dimensions $0.25 \times 0.20 \times 0.20$ (mm) Temperature $293(2)$ K Wavelength 0.71073 Å Crystal system, space Triclinic, $P\overline{1}$ group Unit cell dimensions a $5.8348(10)$ Å b $10.2105(3)$ Å c $12.1654(3)$ Å α $98.353(10)^{\circ}$ β $95.166(10)^{\circ}$ γ $105.45(10)^{\circ}$ Volume $684.84(3)$ Å ³ Z $2Calculated density 1.403 mg/m3Absorption coefficient 0.105 mm-1F(0 \ 0) 304\theta range 1.71-30.87^{\circ}Index ranges -8 \le h \le 8, -14 \le k \le 14, -17 \le l \le 17Reflections collected 17,807Observed reflections 4320Completeness to 99.8\%theta = 30.87Absorption correction Semi-empirical from equivalentsMax. and min. 0.9793 and 0.9743transmissionRefinement method Full-matrix least-squares on F^2Data/restraints/ 4320/0/196parametersFinal R, R_W (obs., data) 0.0446, 0.1336GOOF 1.044$	Empirical formula	C. H. N.O.
Formative regime2052 × 0.20 × 0.20 (mm)Crystal dimensions $0.25 × 0.20 × 0.20$ (mm)Temperature293(2) KWavelength 0.71073 Å Crystal system, space groupTriclinic, $P\overline{1}$ groupUnit cell dimensions a a $5.8348(10) \text{ Å}$ b $10.2105(3) \text{ Å}$ c $12.1654(3) \text{ Å}$ α $98.353(10)^{\circ}$ β $95.166(10)^{\circ}$ γ $105.45(10)^{\circ}$ Volume $684.84(3) \text{ Å}^3$ Z 2 Calculated density 1.403 mg/m^3 Absorption coefficient 0.105 mm^{-1} $\ell(0 \ 0)$ 304 θ range $1.71-30.87^{\circ}$ Index ranges $-8 \le h \le 8, -14 \le k \le 14, -17 \le l \le 17$ Reflections collected $17,807$ Observed reflections 4320 Completeness to 99.8% theta = 30.87 Absorption correctionSemi-empirical from equivalentsMax. and min. 0.9793 and 0.9743 transmissionRefinement methodFull-matrix least-squares on F^2 Data/restraints/ $4320/0/196$ parametersFinal R, R_W (obs., data) $0.0446, 0.1336$ GOOF 1.044	Formula weight	289.29
Crystal unifermineData A 0.20 A 0.20 A 0.20(mm)Data A 0.20 A 0.20 A 0.20(mm)Temperature293(2) KWavelength0.71073 ÅCrystal system, spaceTriclinic, $P\bar{1}$ groupTriclinic, $P\bar{1}$ Unit cell dimensions a a 5.8348(10) Å b 10.2105(3) Å c 12.1654(3) Å α 98.353(10)° β 95.166(10)° γ 105.45(10)°Volume684.84(3) Å ³ Z 2Calculated density1.403 mg/m ³ Absorption coefficient0.105 mm ⁻¹ $l(0 \ 0)$ 304 ϕ range1.71-30.87°Index ranges $-8 \le h \le 8, -14 \le k \le 14, -17 \le l \le 17$ Reflections collected17,807Observed reflections4320Completeness to99.8%theta = 30.87Absorption correctionSemi-empirical from equivalentsMax. and min.0.9793 and 0.9743transmissionRefinement methodFull-matrix least-squares on F^2 Data/restraints/4320/0/196parametersFinal R, R_W (obs., data)0.0446, 0.1336GOOF1.044	Crystal dimensions	$0.25 \times 0.20 \times 0.20$
Temperature293(2) KWavelength0.71073 ÅCrystal system, spaceTriclinic, $P\bar{1}$ groupUnit cell dimensionsa5.8348(10) Åb10.2105(3) Åc12.1654(3) Å α 98.353(10)° β 95.166(10)° γ 105.45(10)°Volume684.84(3) Å ³ Z2Calculated density1.403 mg/m ³ Absorption coefficient0.105 mm ⁻¹ $F(0 0 0)$ 304 θ range1.71-30.87°Index ranges $-8 \le h \le 8, -14 \le k \le 14, -17 \le l \le 17$ Reflections collected17,807Observed reflections4320Completeness to99.8%theta = 30.87Absorption correctionSemi-empirical from equivalentsMax. and min.0.9793 and 0.9743transmissionRefinement methodFull-matrix least-squares on F^2 Data/restraints/4320/0/196parametersFinal R, R_W (obs., data)0.0446, 0.1336GOOF1.044	(mm)	0.23 × 0.20 × 0.20
Wavelength0.71073 ÅCrystal system, space groupTriclinic, $P\bar{1}$ Unit cell dimensions a a 5.8348(10) Å b 10.2105(3) Å c 12.1654(3) Å α 98.353(10)° β 95.166(10)° γ 105.45(10)°Volume684.84(3) Å ³ Z 2Calculated density1.403 mg/m ³ Absorption coefficient0.105 mm ⁻¹ $f(0 \ 0 \ 0)$ 304 ϕ range1.71-30.87°Index ranges $-8 \le h \le 8, -14 \le k \le 14, -17 \le l \le 17$ Reflections collected17,807Observed reflections4320Completeness to theta = 30.87Absorption correctionSemi-empirical from equivalentsMax. and min. transmission.9793 and 0.9743 transmissionRefinement methodFull-matrix least-squares on F^2 Data/restraints/ parameters4320/0/196 tal20/196Final R, R_W (obs., data)0.0446, 0.1336 GOOFGOOF1.044	Temperature	293(2) K
Crystal system, space groupTriclinic, $P\bar{1}$ groupUnit cell dimensions a $5.8348(10)$ Å a $10.2105(3)$ Å c $12.1654(3)$ Å α $98.353(10)^{\circ}$ β $95.166(10)^{\circ}$ γ $105.45(10)^{\circ}$ γ $105.45(10)^{\circ}$ Volume $684.84(3)$ Å ³ Z 2 Calculated density 1.403 mg/m ³ Absorption coefficient 0.105 mm ⁻¹ $F(0 0 0)$ 304 θ range $1.71-30.87^{\circ}$ Index ranges $-8 \leq h \leq 8, -14 \leq k \leq 14, -17 \leq l \leq 17$ Reflections collected $17,807$ Observed reflections 4320 Completeness to 99.8% theta = 30.87 Absorption correctionSemi-empirical from equivalentsMax, and min. 0.9793 and 0.9743 transmissionRefinement methodFull-matrix least-squares on F^2 Data/restraints/ parameters $4320/0/196$ parametersFinal R, R_W (obs., data) $0.0446, 0.1336$ GOOF	Wavelength	0.71073 Å
Unit cell dimensions a 5.8348(10) Å b 10.2105(3) Å c 12.1654(3) Å α 98.353(10)° β 95.166(10)° γ 105.45(10)° γ 105.45(10)° γ 105.45(10)° Volume 684.84(3) Å ³ Z 2 Calculated density 1.403 mg/m ³ Absorption coefficient 0.105 mm ⁻¹ $F(0 0 0)$ 304 θ range 1.71–30.87° Index ranges $-8 \le h \le 8, -14 \le k \le 14, -17 \le l \le 17$ Reflections collected 17,807 Observed reflections 4320 Completeness to 99.8% theta = 30.87	Crystal system, space group	Triclinic, <i>P</i> 1
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c 12.1654(3) Å α 98.353(10)° β 95.166(10)° γ 105.45(10)° Volume 684.84(3) ų Z 2 Calculated density 1.403 mg/m³ Absorption coefficient 0.105 mm ⁻¹ $P(0 \ 0)$ 304 θ range 1.71-30.87° Index ranges $-8 \leqslant h \leqslant 8, -14 \leqslant k \leqslant 14, -17 \leqslant l \leqslant 17$ Reflections collected 17,807 Observed reflections 4320 Completeness to 99.8% theta = 30.87 semi-empirical from equivalents Max, and min. 0.9793 and 0.9743 transmission Full-matrix least-squares on F^2 Data/restraints/ 4320/0/196 parameters Final R, R_W (obs., data) 0.0446, 0.1336 GOOF 1.044	b	10.2105(3) Å
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$F(0 \ 0 \ 0)$ 304 θ range $1.71-30.87^{\circ}$ Index ranges $-8 \leqslant h \leqslant 8, -14 \leqslant k \leqslant 14, -17 \leqslant l \leqslant 17$ Reflections collected $17,807$ Observed reflections 4320 Completeness to 99.8% theta = 30.87 Semi-empirical from equivalentsMax. and min. 0.9793 and 0.9743 transmissionFull-matrix least-squares on F^2 Data/restraints/ $4320/0/196$ parametersFinal R, R_W (obs., data)GOOF 1.044	Absorption coefficient	0.105 mm^{-1}
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Observed reflections4320Completeness to99.8%theta = 30.87Semi-empirical from equivalentsAbsorption correctionSemi-empirical from equivalentsMax. and min.0.9793 and 0.9743transmissionRefinement methodFull-matrix least-squares on F^2 Data/restraints/4320/0/196parameters0.0446, 0.1336GOOF1.044	Reflections collected	17,807
Completeness to theta = 30.8799.8%Absorption correction Max. and min.Semi-empirical from equivalents 0.9793 and 0.9743 transmissionRefinement method Data/restraints/ parametersFull-matrix least-squares on F^2 Final R, R_W (obs., data) GOOF0.0446, 0.1336 1.044	Observed reflections	4320
theta = 30.87Absorption correctionSemi-empirical from equivalentsMax. and min.0.9793 and 0.9743transmissionFull-matrix least-squares on F2Data/restraints/4320/0/196parameters0.0446, 0.1336GOOF1.044	Completeness to	99.8%
Absorption correction Semi-empirical from equivalents Max. and min. 0.9793 and 0.9743 transmission Edinement method Refinement method Full-matrix least-squares on F ² Data/restraints/ 4320/0/196 parameters 0.0446, 0.1336 GOOF 1.044	theta = 30.87	
Max. and min. 0.9793 and 0.9743 transmission Full-matrix least-squares on F ² Data/restraints/ 4320/0/196 parameters 0.0446, 0.1336 GOOF 1.044	Absorption correction	Semi-empirical from equivalents
Refinement methodFull-matrix least-squares on F2Data/restraints/4320/0/196parameters0.0446, 0.1336GOOF1.044	Max. and min. transmission	0.9793 and 0.9743
Data/restraints/ 4320/0/196 parameters	Refinement method	Full-matrix least-squares on F^2
parameters Final <i>R</i> , <i>R</i> _W (obs., data) 0.0446, 0.1336 GOOF 1.044	Data/restraints/	4320/0/196
Final <i>R</i> , <i>R</i> _W (obs., data) 0.0446, 0.1336 GOOF 1.044	parameters	
GOOF 1.044	Final R, R _W (obs., data)	0.0446, 0.1336
	GOOF	1.044

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252

Table 3 Selected bond lengths (Å) and bond angles (°) for 6.

Sciected bolid icligation (1) and bolid angles () for w	
C(5)-N(2)	1.4114(14)
C(7)-N(3)	1.3096(13)
C(7)-C(12)	1.4665(15)
C(7)-C(8)	1.4894(15)
C(8)-O(3)	1.2143(14)
C(12)-O(4)	1.2248(13)
N(2)-N(3)	1.3066(13)
N(2)-H(2A)	0.896(18)
$N(2) \cdot \cdot \cdot O(4)$	2.642(15)
$O(4) \cdots H(2A)$	1.993(2)
C(6)-C(5)-N(2)	118.79(10)
C(4)-C(5)-N(2)	120.45(10)
N(3)-C(7)-C(12)	124.97(10)
N(3)-C(7)-C(8)	113.90(9)
C(12)-C(7)-C(8)	120.97(9)
O(3)-C(8)-C(7)	121.81(10)
O(3) - C(8) - C(9)	121.43(10)
C(7)-C(8)-C(9)	116.71(9)
C(9)-C(10)-C(11)	107.12(9)
O(4) - C(12) - C(7)	120.89(10)
O(4)-C(12)-C(11)	121.49(10)
C(7)-C(12)-C(11)	117.58(9)
N(3)-N(2)-C(5)	116.64(9)
N(3)-N(2)-H(2A)	121.1(11)
C(5)-N(2)-H(2A)	121.5(11)
N(2)-N(3)-C(7)	122.01(10)
N(2)−H(2A)···O(4)	128(15)

Cambridge CB2 1EZ, U deposit@ccdc.cam.ac.uk. 1ez, uk. Fax: +44 1223 336 033; or e-mail:

3. Results and discussion

3.1. Electronic spectra

Electronic spectrum of **2** is shown in Fig. 3. The corresponding λ_{max} values are presented in Table 4 together with the IR and NMR spectral data. UV spectra of the compounds showed three absorption maxima at 359–400, 237–257 and 210–215 nm values.



Table 4

UV, IR and NMR spectral data of the compounds.

Compound	UV (λ_{max})	$IR (cm^{-1})^a$			¹ H NMR (ppm) ^b	¹³ C NMR (ppm)	
		v _{C—H}	v_{N-H}	$v_{C=0}$	$v_{C=N}$		
1	396, 257, 214	3006, 2932, 2825	3366	1668	1627	2.50 (s, CH ₃), 2.60(s,CH ₃ '), 3.96 (s, OCH ₃), 6.94–7.74 (aromatic protons), 14.77 (s, NH)	26.6 (CH ₃), 31.5(CH' ₃), 55.9 (OCH ₃), 133.7 (C-3), 111.1–148.5 (aromatic carbons), 197.2 (C-2 and C-4)
2	359, 248, 215	3079, 3003, 2925, 2854	3300	1672	1630	2.49 (s, CH_3), 2.60(s,CH_3'), 7.14–7.45 (aromatic protons), 14.59 (s, NH)	26.5 (CH ₃), 31.6(CH ₃ '), 133.7 (C-3), 114.4–142.7 (aromatic carbons), 196.8 (C-4), 198.2 (C-2)
3	375, 237, 215	3094, 3008, 2923, 2853	3326	1673	1633	2.53 (s, CH ₃), 2.63(s,CH' ₃), 7.56–8.26(aromatic protons), 14.65 (s, NH)	26.6 (CH ₃), 31.7(CH ₃ '), 134.3 (C-3), 110.7–149.3 (aromatic carbons), 196.7 (C-4), 198.5 (C-2)
4	393, 251, 215	3062, 2992, 2923, 2830	3304	1672	1616	2.48 (s, CH ₃), 2.59(s,CH ₃), 3.83 (s, OCH ₃), 6.92–7.38 (aromatic protons), 14.95 (s, NH)	26.5 (CH ₃), 31.4(CH ₃), 55.5 (OCH ₃), 132.7 (C-3), 114.9–158.0 (aromatic carbons), 196.8 (C-4), 197.5 (C-2)
5	400, 256, 210	3021, 2943, 2926, 2855	-	1673	1619	1.13 (s, CH ₃), 2.60 (s, CH ₂), 3.97 (s, OCH ₃), 6.93–7.98 (aromatic protons), 15.48 (s, NH)	28.4 (CH ₃), 30.7 (C-10), 52.3 (C-9), 52.5 (C-11), 55.9 (OCH ₃), 130.6 (C-7), 110.9–149.0 (aromatic carbons), 193.4 (C-8), 196.2 (C-12)
6	376, 247, 212	2975, 2932, 2888	-	1681	1633	$1.15~(s,CH_3),2.64$ and $2.65~(CH_2),7.57{-}8.30$ (aromatic protons), $15.24~(s,NH)$	28.5 (CH ₃), 30.6 (C-10), 52.6 (C-9 and C-11), 131.2 (C-7), 112.1–149. 1 (aromatic carbons), 193.1 (C-8), 197.9 (C-12)
7	380, 251, 210	3076, 2955, 2927	-	1675	1624	1.13 (s, CH ₃), 2.61 (s, CH ₂), 7.19–7.61 (aromatic protons), 15.24 (s, NH)	28.4 (CH ₃), 30.6 (C-10), 52.6 (C-9 and C-11), 130.6 (C-7), 115.5–142. 2 (aromatic carbons), 193.1 (C-8), 197.4 (C-12)

^a For **5–7**, the NH stretching bands were masked by the signals due to residual water. ^b In all the cases the residual solvent signal at 1.5 ppm corresponding to water dissolved in CDCl₃ [21] is ignored.



Fig. 2. Intramolecular hydrogen bonding in dimedone derivatives. (with spectro-scopic numbering).

The lack of absorption bands between 330 and 355 nm [18] and above 400 nm [19] could be attributed to an azo function, together with observation of bands at around 370–400 nm, indicated that compounds are in hydrazone form [14].

3.2. IR spectra

IR spectrum of **6** is shown in Fig. 4. In the IR spectra of the compounds, maxima in the region of 1668–1681 cm⁻¹ are observed, which are characteristic carbonyl (C=O) stretching frequencies of α , β -unsaturated ketone. Intramolecular hydrogen bonding is one of the factors which lower the carbonyl stretching frequency by about 50 cm⁻¹ [20]. This lowering is, however, dependent on the strength of the hydrogen bond and hence for the present set of compounds the shift of $\nu_{C=O}$ to lower wave number can be attributed to the intramolecular hydrogen bonding (N–H···O=C). For all the compounds a sharp and less intense band corresponding to N–H stretching frequency are observed at 3304–3366 cm⁻¹ region and the observed shift in values towards the longer wave number region can also be accounted again by the aforementioned possible intramolecular hydrogen bonding.

In addition to the $v_{C=N}$ bands in the region of 1630 cm⁻¹, for all the cases the weak aromatic C—H bands were observed in the region of 3000–3030 cm⁻¹. Similarly aliphatic v_{C-H} bands appear below 3000 cm⁻¹ with moderate intensity. The methylene groups in cyclohexyl ring causes the significant increase in intensity of aliphatic v_{C-H} bands for dimedone derivatives (**5–7**) compared to the arylhydrazones of acetylacetone.

3.3. NMR spectral studies

NMR spectral data of all the synthesized compounds are given in Table 4 along with the splitting patterns. ¹H NMR spectrum of **5** and ¹³C NMR spectrum of **7** are shown in Figs. 5 and 6, respectively.



Fig. 3. UV spectrum of 2 in methanol.

3.3.1. ¹H NMR spectra

PMR spectra of compounds **1–4**, show less intense signal corresponding to >NH proton in the downfield region of 14.59– 14.95 ppm. The observed deshielding can be accounted for by considering the intramolecular hydrogen bonding of >NH proton with the electronegative oxygen. The intramolecular hydrogen bonding results in creation of six-membered pseudo-ring as shown in Fig. 1. The observed two different singlets for two methyl groups with an significant difference of about 1 ppm indicates the restricted rotation about C=N bond and the electronic charge asymmetry due to intramolecular hydrogen bonding. Aromatic protons resonate in the region of 6.92–8.26 ppm with the expected splitting patterns depending on the position of the substituents.

For the dimedone derivatives **5–7**, a low field singlet, δ_{N-H} at around 15 ppm confirm strong intramolecular N-H···O=C hydrogen bonding (Fig. 2) and the maximum dehielding of N–H proton is observed for 5, due to the presence of $-OCH_3$ at ortho position. Methyl substituents associated with the dimedone ring appear as a singlet at around 1.13 ppm as an average from rapidly inter-converting conformers. The methylene signals (2.60-2.65 ppm) also reflect rapid mobility of the dimedone ring at room temperature. For 6, a set of signals were observed for the methylene protons of dimedone ring and it indicates that the chemical shift difference is large enough to appear as a separate signal. However, this difference is not observed for the other two compounds. In all the cases aromatic proton signals appear in the downfield region of 6.93-8.30 ppm with the expected splitting patterns. If a comparison is made between the arylhydrazone derivatives of acetylacetone and dimedone, the NH protons of dimedone derivatives are deshielded to the extent of about 0.5-0.7 ppm. It exemplifies the effective intramolecular hydrogen bonding in dimedone derivatives (in solution) which is well supported by ¹³C NMR spectral studies presented subsequently.







3.3.2. ¹³C NMR spectra

For compounds **1–4**, the two methyl carbons are observed in two different regions [26.5 and 31.5 ppm] with the chemical shift difference of about 5 ppm as a consequence of restricted rotation due to C=N bond as well as the intramolecular H-bonding. The drift of electron density from carbonyl carbon as a result of hydrogen bonding leads to the decrease in electron density on -1^{13} CH'₃ (Fig. 1) and by considering this, the slightly deshielded signal in the range of 31.5 ppm is assigned to -1^{13} CH'₃. The aromatic carbon signals appear in the range of 110.7–158.0 ppm and the observed variations are in line with the substituents at *ortho, meta* and *para* positions. C-3 carbon resonates in the region of 133 ppm with considerably low intensity associated with the sp² carbons. As expected, the 1^{3} C signals for carbonyl carbons are observed in different regions with the small variation in chemical shift values as a consequence of H-bonding.

For compounds **5–7**, retention of a single signal for methyl groups at around 28 ppm denies any conformational preference. C-10, the carbon furthest from carbonyl groups, gives a single line at around 30.6 ppm and the upfield shift of around 20–22 ppm with respect to C-9 and C-11 is observed. Shielding differences

for C-9 and C-11 carbons are observed only for **5** and not for other compounds. This is perhaps, of some subtle geometry or electronic charge asymmetry with in dimedone ring brought about by hydrogen bonding. Coalescence into one signal for C-9 and C-11 for compounds **6** and **7** merely suggests that the chemical shift differences are too small to be detected under the experimental conditions.

Carbonyl sp² carbon atoms appear as separate signals in the low field region of about 197 and 193 ppm for C-12 and C-8, respectively. Strong intramolecular N—H···O=C hydrogen bonding deshields C-12 with respect to C-8 (Fig. 2) to the extent of *ca.* 4 ppm. Polarization changes of the carbonyl bond through π -conjugation with restricted rotation about N—N bond may well be accompanying factors for the observed deshielding. In general ¹³C=N and *ipso* carbons are identified by their relative low intensities due to longer relaxation times and lower nuclear Overhauser effects.

3.4. Cyclic voltammetric studies

Typical cyclic votammogram of **1** in DMF at 100 mV s^{-1} scan rate is depicted in Fig. 7 and the reduction potentials for the derived compounds (**1–7**) are listed in Table 5. The redox behaviour



Fig. 6. ¹³C NMR spectrum of 7 CDCl₃.

of similar compounds has been reported already [22,23]. From CV studies it was observed that all the compounds undergo two electron reduction processes as reported already [22,23] and the electrode reaction involves the transfer of two electrons per molecule in two successive steps. Keeping in view the feasibility of the different sites of reduction i.e., C=N or C=O it was concluded that the possible reduction site is C=N, since C=O require much higher potential for reduction. Generally, the dimedone derivatives (**5**–**7**) have less negative reduction potentials than the acetylacetone derivatives. Less negative reduction potentials observed for compounds **5**–**7**, indicate the ease of electron addition in the dimedone derivatives (**5**–**7**) and this is because of the weak C=N bond. The



Fig. 7. Cyclic votammogram of 1 in DMF at 100 mV s⁻¹ scan rate.

 Table 5

 Reduction potentials for the compounds 1–7 in DMF.

Compound	$-E_{\rm p}^{\rm c}~({\rm V})$	$-E_{\rm p}^{\rm a}~({ m V})$
1	0.900 1.438	0.750 1.355
2	0.835 1.290	0.453 1.157
3	0.833 1.407	0.479 1.273
4	0.834 1.442	0.535 1.280
5	0.839 1.247	0.365 1.084
6	1.005 1.368	0.400 1.095
7	0.809 1.068	0.342 0.950

observed reduction peak potentials in CV clearly indicate that in all the cases the reduced center is the C=N bond of hydrazonic moiety.

3.5. Single crystal X-ray structural analysis of 6

ORTEP of **6** is given in Fig. 8 and packing diagram is shown in Fig. 9. The unit cell contains two discrete molecules. From the bond lengths it is observed that there is a double bond between C(7) and N(3) with the distance of 1.3096(13) Å. The N(3)—N(2) bond [1.3066(13) Å] is single bond in nature and the conjugation breaks at this point. These values clearly suggest that the molecule is in "enazo" form. There is immediate confirmation of hydrogen bonding between N(2)…O(4) [N(2)—H…O(4)] with the distance of 2.642(15) Å which is shorter than the sum of their covalent radii (2.9 Å). The O(4)…H distance is 1.993(2) Å and the N(2)—H(2A)…O(4) angle is 128(15)°, which manifests the effectiveness of hydrogen bonding. The character of the C=O…H—N intramolecular hydrogen bonding will reflect in the bond parame-



Fig. 8. ORTEP of compound 6.

ters of the pseudo six-membered ring. A relative increase in N(3)–N(2) bond length gives a corresponding decrease in the C(7)–N(3) bond length. The observed variation in bond angles between C(4)–C(5)–N(2) [120.45(10)°] and C(6)–C(5)–N(2) [118.79(10)°] is very small. However, C(12)–C(7)–N(3) angle [124.97(10)°] is greater than that of N(3)–C(7)–C(8) angle [113.90(9)°] to the extent of *ca*. 11°. It is consistent with the realization of an acceptable geometry for maximal hydrogen bond formation between O(4) and N(2).

From the crystal structure it is observed that there is a sixmembered pseudo-ring closed by N-H···O intramolecular hydrogen bonding is created. Generally, six-membered ring intramolecular hydrogen bonds form in preference to intermolecular hydrogen bonds. This type of hydrogen bonding may be designated as S(6) according to Etter's graph nomenclature [24] where, S denotes intramolecular hydrogen bond and the size or degree of the motif is 6. Before considering the conformation of the dimedone ring fragment in compound 6, it is worthwhile to discuss the structural features of dimedone molecule. Single crystal X-ray structural analysis of dimedone [5,5-dimethylcyclohexane-1,3-dione] has been reported already [25]. It was found that the structure of dimedone is enolic nature in the solid state. Also, it is very clear that the effective intermolecular hydrogen bonding (between the hydrogen atom of the enolic –OH and oxygen atom of the carbonyl group) to form infinite chains. The conformation of the dimedone molecule can be best described as an envelope with the carbon which bears the methyl groups is 0.62 Å out of the plane.

In **6**, when compared to C(7)—C(8) length [1.4894(15)Å] C(12)—C(7) length [1.4665(15)Å] is slightly decreased. Other structural parameters of dimedone ring are observed as expected. The cyclohexane ring conformation in the present molecule (**6**) can be described as an envelope with the slightly more pronounced puckering of the cyclohexane ring at C(10). The geometric calculations are done by PARST95 [26]. The envelope conformation has been retained with the displacement of C(10) and C(7) to 0.69 and -0.048Å from the plane defined by C(8), C(9), C(11) and C(12). Phenyl ring shows normal bond parameters. Phenyl rings of the adjacent molecules form a pair and are stacked with their tails in opposite directions.

3.6. Resonance assisted hydrogen bonding (RAHB) studies

Strong hydrogen bonding is possible if a suitably polarizable system of π -bonds allows charge flow through covalent bonds from the donor to the acceptor. Such systems are provided, for example, by conjugated double bonds. This cooperativity mechanism is well established for several cases with N–H donors [27]. The concept of RAHB systems is based on the statement that owing the existence of conjugated system where the π electron delocalisation exists which causes the enhancement of the strength of hydrogen bonds. Despite the drawbacks of this concept [28], the π electron delocalisation is observed for RAHBs and that in extreme cases one can observe the equalization of bonds within the pseudoring with the nearly center position of hydrogen atom.

Because of the hydrogen bonding, the C–C [C(12)-C(7)] and the N–N [N(2)-N(3)] bonds gain some double bond character and are shortened, whereas the C=O [C(12)=O(4)] and C=N bonds loose part of their double bond character and are lengthened. To confirm this suggestion, and to quantify the involvement of resonant cycle (Fig. 10) in hydrogen bonding, it is necessary to perform geometrical tests. There are several ways to quantify π -system delocalisation; to make comparison easy, the formalism used by Gilli et al. [27] is used here. It is obvious that in RAHB of increasing strengths, the bond length d_1 reduces and d_4 increases; this means that the difference $q_1 = d_1 - d_4$ is positive and becomes zero or negative with increasing hydrogen bond strength. The difference in the C(12)—C(7) [d_3] and the C=N [d_2] bond lengths, $q_2 = d_3 - d_2$, is also positive and decreases with increasing hydrogen bond strength. In the case of total π -delocalisation at -N=C-C-, q_2 becomes zero. If the arrangement as a whole is a resonant cycle, there must be a correlation between the parameters q_1 and q_2 . Furthermore, the π -delocalisation must increase with reducing hydrogen bond dis-



Fig. 9. Packing diagram of compound 6.



Fig. 10. RAHB in S(6) of Etter's graph.

tance, so that q_1 , q_2 and their sum $Q = q_1 + q_2$ must correlate with $O \cdots N$ (or $H \cdots O$) bond distance.

To check out this concept, we have collected the data of two similar compounds for which the structures have been published recently (compounds (3-(2-(4-methylphenyl)hydrazono)pentane-2,4-dione and 3-(2-(4-chlorophenyl)hydrazono)pentane-2,4-dione [15]) from CCDC and the correlations were made. The results of correlation are not satisfactory and hence the contribution of resonance for the strength of the hydrogen bonding in 6 is not in line with the results obtained for similar compounds [15]. It is also very clear that the O···N bond length is [2.642(15) Å] slightly higher than that of the mean distance of 2.552 Å (derived from about 40 structurally similar compounds [15]). This is a conclusive evidence that the mechanism of resonance assisted hydrogen bonding is significantly reduced for the present compound (6). To have a better RAHB, all the six atoms (in pseudo-ring) of S(6) Etter's group should be in a same plane. Whereas, for compound **6**, the planarity of the six atoms which are involved in resonant cycle (S(6) of Etter's graph - Fig. 10) is very much disturbed by the conformational requirement of the cyclohexane ring (in dimedone fragment) and hence RAHB concept is less operative in this case.

4. Conclusions

Compounds 1-7, were prepared by the coupling of acetylacetone/dimedone with respective aromatic diazonium salts and characterized by IR, ¹H and ¹³C NMR spectra. For compound **6**, single crystal X-ray structure analysis was also performed. The IR and NMR spectral data clearly manifests the effectiveness of the intramolecular hydrogen bonding in all the cases. Cyclic voltammetric studies clearly indicate that in all the cases the reduced center is the C=N bond of hydrazonic moiety and it also evidences the ease of reduction in dimedone derivatives. Single crystal X-ray analysis of 6 indicates that the molecule is in "enazo" form with the effective intramolecular hydrogen bonding [N-H...O]. This type of hydrogen bonding may be designated as S(6) according to Etter's graph nomenclature. The cyclohexane ring conformation in the molecule (6) can be described as an envelope with the slightly more pronounced puckering of the cyclohexane ring at C(10). RAHB studies suggest that the resonance assistance for hydrogen bonding is significantly reduced for the compound **6**. It is also very clear that the planarity of the six atoms which are involved in resonant cycle S(6) of Etter's graph is very much disturbed by the conformational requirement of the cyclohexane ring and hence RAHB concept is less operative in this case. The derived compounds could be used as building blocks for the diverse array of organic compounds with potential biological properties.

Acknowledgement

The authors are extremely thankful to Prof. Dr. K. Ramalingam of Annamalai University for his valuable suggestions regarding the X-ray structural analysis.

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