



CRYSTAL STRUCTURE OF 3,3,6,6-TETRAMETHYL-9-(3-CHLOROPHENYL)-3,4,6,7,9,10-HEXAHYDROACRIDINE-1,8-DIONE-DMF SOLVATE

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The crystal structure of dimethylformamide solvated 3,3,6,6-tetramethyl-9-(3-chlorophenyl)-3,4,6,7,9,10-hexahydroacridine-1,8-dione (C₂₆H₃₃ClN₂O₃) crystallizes in the triclinic space group P-1 with unit cell parameters: $a=9.0814(4)$, $b=11.5650(5)$, $c=12.1354(5)$ Å, $\alpha=91.806(3)^\circ$, $\beta=96.450(3)^\circ$, $\gamma=104.565(4)^\circ$ and $Z=2$. The crystal structure was solved by direct methods and refined by full-matrix least-squares procedures to a final R -value of 0.056 for 2691 observed reflections. The central ring of the acridinedione system adopts a *boat* conformation and the two outer rings adopt *sofa* conformations. The solvent moiety (dimethylformamide) is involved in the existence of intra and intermolecular C-H...O interactions.

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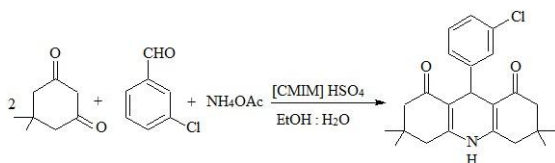
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Introduction

A multicomponent reaction (MCR) provides influential implement for the synthesis of complex molecules by reacting three or more small building blocks. MCRs are economic, selective, minimizing waste, time and power, eco-friendly in organic synthesis.¹⁻³ Acridinediones containing a 1,4-DHP nucleus are used as laser dyes with very high efficiencies of photo initiators.^{4,5} A latest literature review reveals that 1,4-DHP nucleus exhibit Calcium channels blockers and anti-aggregatory activity. Besides this, 1,4-DHP skeleton shows many biological activities such as anti-hypertension, anti-cancer, anti-diabetics, geroprotective, neuroprotactant and anti-HIV.⁶

Synthesis of 1,8-dioxoacridinedione is usually carried out by MCRs of active methylene compound, aldehydes and ammonium acetate or primary amine.⁷⁻⁸ In continuation of our current endeavor on multicomponent reactions, we disclose herein report for the synthesis and structures of 3,3,6,6-tetramethyl-9-(3-chlorophenyl)-3,4,6,7,9,10-hexahydroacridine-1,8-dione (Scheme 1).



Scheme 1. Synthesis of title compound I.

Experimental

All the chemicals were purchased from SD Fine Chem Limited and Thomas Baker, used as received without further purification. Melting point was determined on Labstar melting apparatus. The IR spectra was run on a Perkin-Elmer, FTIR-1600 spectrophotometer and expressed in cm⁻¹ (KBr). ¹H NMR spectra was recorded on Bruker Avance (300 MHz) spectrometer in DMSO-d₆ using TMS as the internal standard. Elemental analysis was performed on a EURO-EA elemental analyzer.

Synthesis

In a 50 ml rounded bottom flask, a mixture of dimedone (2 mmol), 3-chlorobenzaldehyde (1 mmol) and ammonium acetate (1.2 mmol) in mixture of aqueous ethanol (5 ml) was stirred at RT for 5 min. To this [CMIM][HSO₄] (20 mol %) was added and the reaction mixture heated at 85 °C till completion of reaction. The progress of reaction was monitored by TLC. After completion of reaction, the mixture was gradually cool to RT and poured on ice water under stirring, solid were precipitate out. Filter the product and dried. The crude product were recrystallized from ethanol and characterized by IR, ¹H NMR, elemental and single crystal analysis. M.P.: > 300 °C, Yield: 80 %. IR (KBr): 3413, 3269, 2945, 1638, 1602 cm⁻¹. ¹H NMR (300 MHz, DMSO-d₆): δ 0.90(s, 6H, CH₃), 1.02(s, 6H, CH₃), 2.03-2.52(m, 8H, CH₂), 4.85(s, 1H, CH), 7.10-7.31(m, 4H, Ar-H), 9.48(bs, 1H, NH). Analysis: calculated for C₂₃H₂₆ClNO₂ (383.911): C, 71.96 %; H, 6.83 %; N, 3.65 %; found: C, 71.91 %; H, 7.79 %; N, 3.70 %.

Crystal Structure Determination and Refinement

The X-ray intensity data of a well defined crystal (0.30 X 0.20 X 0.10 mm) were collected at room temperature (293 K) by using a CCD area-detector diffractometer (*X'calibur system* – Oxford diffraction, 2010) which is equipped with graphite monochromated MoK α radiation ($\lambda=0.71073$ Å).

The cell dimensions were determined by the least-squares fit of angular settings of 4587 reflections in the θ range 3.52 to 29.01°. A total number of 11110 reflections were collected of which 2691 reflections were treated as observed ($I > 2\sigma(I)$). Data were corrected for Lorentz, polarization and absorption factors.

The structure was solved by direct methods using SHELXS97.⁹ All non-hydrogen atoms of the molecule were located from the E-map. Full-matrix least-squares refinement was carried out by using SHELXL97 software.⁹ The geometry of the molecule is determined by PLATON.¹⁰ All the hydrogen atoms were positioned geometrically and were treated as riding on their parent C/N atoms, with C-H distances of 0.93-0.98 Å and N-H distance of 0.84 Å; and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C/N})$, except for the methyl groups where $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$. The final refinement cycles yielded an *R*-factor of 0.056 ($wR(F^2) = 0.1473$) for the observed data. The residual electron density ranges from -0.355 to 0.185 eÅ⁻³.

Atomic scattering factors were taken from International Tables for X-ray Crystallography (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4). The crystallographic data are summarized in Table 1. CCDC-981749 contains the supplementary crystallographic data for this paper.

Table 1. Crystal data and other experimental details for (1)

CCDC	981749
Crystal description	Yellow block
Crystal size	0.30x0.20x0.10
Empirical Formula	C ₂₆ H ₃₃ ClN ₂ O ₃
Formula weight (g mol ⁻¹)	456.99
Radiation, Wavelength (Å)	Mo K α , 0.71073
Unit cell dimensions	a = 9.0814(4), b = 11.5650(5), c = 12.1354(5) Å, $\alpha = 91.806(3)^\circ$, $\beta = 96.450(3)^\circ$, $\gamma = 104.565(4)^\circ$
Crystal system, Space group	triclinic, P-1
Unit cell volume (Å ³)	1223.40(9)
No. of molecules per unit cell, Z	2
No. of parameters refined	299
Absorption coefficient (mm ⁻¹)	0.185
F(000)	488
θ range for entire data collection (°)	3.53 < θ < 26.00
Limiting indices	-11 ≤ <i>h</i> ≤ 11, -14 ≤ <i>k</i> ≤ 14, -14 ≤ <i>l</i> ≤ 13
Reflections collected/unique	11110 / 4803
Reflections observed ($I > 2\sigma(I)$)	2691
Final <i>R</i> -factor	0.056
$wR(F^2)$	0.1473
Goodness-of-fit	1.024
(Δ / σ) _{max}	0.001
Final residual electron density (eÅ ⁻³)	-0.355 < $\Delta\rho$ < 0.185

Results and discussion

An ORTEP view of the molecule with atomic labeling is shown in Figure 1.¹¹ Its geometry was calculated using the PLATON¹⁰ and PARST¹² software. Bond lengths¹³ and angles have normal values (Table 2) and correspond to those observed in some related structures.^{14,15}

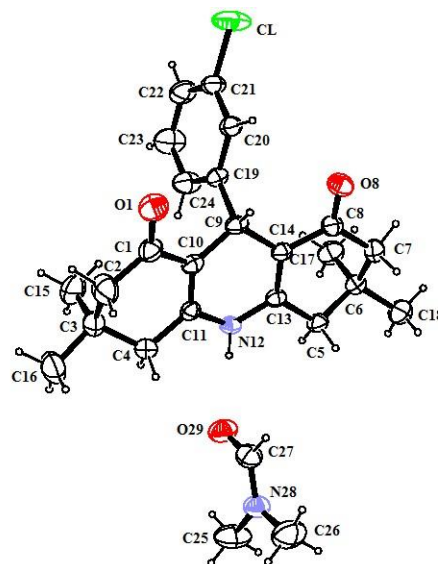


Figure 1. ORTEP view of the molecule with displacement ellipsoids drawn at the 50 % probability level. H atoms are shown as small spheres of arbitrary radii.

The central ring (C9/C10/C11/N12/C13/C14) of the acridinedione moiety adopts a *boat* conformation [$\Delta C_s(\text{C9})=0.66$ & $\Delta C_s(\text{C10-C11})=7.12$] and the four essentially planar atoms (C10/C11/C13/C14) of this ring [maximum deviation 0.1077 (2) Å for C9] form a dihedral angle of 82.06 (8)° with benzene ring. In this ring, N12 and C9 deviate from plane (C10/C11/C13/C14) by 0.0725 (2) and 0.1077 (2) Å, respectively. Both the outer rings adopt *sofa* conformations ($\Delta C_s(\text{C3}) = 0.852$; $\Delta C_s(\text{C6}) = 3.482$).¹⁶ The atoms C3 and C6 deviate from the mean planes defined by (C1, C2, C4, C11, C10) and (C5, C7, C8, C14, C13) by 0.3328 (3) and 0.3345 (2) Å, respectively.

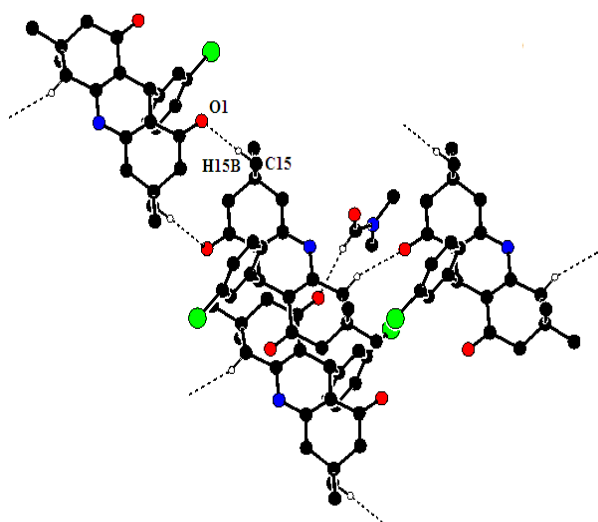
Table 2. Selected bond lengths (Å) and angles (°) for non hydrogen atoms (e.s.d.'s are given in parentheses) for (1)

Bond lengths		Bond angles	
Cl-C21	1.745(2)	C13- N12- C11	121.7(2)
O1- C1	1.228(3)	O1- C1- C10	120.5(2)
O8- C8	1.225(3)	O1- C1- C2	121.5(2)
N12- C13	1.373(3)	O8- C8- C14	121.2(2)
N12- C11	1.377(3)	O8- C8- C7	120.5(2)
C10- C11	1.352(3)	C10- C11- N12	120.3(2)
C13- C14	1.357(3)	N12- C11- C4	116.4(2)
O29- C27	1.215(3)	C14- C13- N12	120.6(2)
N28- C27	1.316(3)	N12- C13- C5	116.0(2)
N28- C25	1.438(3)	C27- N28- C25	120.6(2)
N28- C26	1.450(3)	C27- N28- C26	121.4(2)
		C25- N28- C26	118.0(2)
		O29- C27- N28	126.4(3)

Table 3. Geometry of intra- and inter molecular hydrogen bonds for (1)

D-H...A	D-H (Å)	H...A (Å)	D...A (Å)	∠[D-H...A(°)]	Symmetry code
N12-H12...O29	0.84	2.04	2.873	171	
C25-H25A...O29	0.96	2.37	2.781	105	
C5-H5A...O1	0.97	2.52	3.445	159	x+1,+y,+z
C15-H15B...O1	0.96	2.49	3.393	155	-x,-y+1,-z
C27-H27...O8	0.93	2.32	3.230	165	-x+1,-y+1,-z+1

A part of crystal structure is shown in Figure 2. In (I), molecules are connected to a dimeric formation via C15-H15B...O1 hydrogen bonds generating a R₂²(12) graph-set motif. The DMF solvent takes part in both intra (C25-H25...O29) and inter molecular (C27-H27...O8) interactions (Table 3).

**Figure 2.** A part of crystal structure showing C-H...O intermolecular interactions generating R₂²(12) graph set motif

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References

- Mistry, S. R., Maheria, K.C., *J. Mol. Catal. A*, **2012**, 355, 210.
- Ganguly, C. N., Roy, S., Mondal, P., Saha, R., *Tetrahedron Lett.*, **2012**, 53, 7067.
- Khan, A.T., Das, D. K., *Tetrahedron Lett.*, **2012**, 53, 2345.
- Kumar, S., Singh, K. N., *J. Heterocyclic Chem.*, **2011**, 48, 69.
- Fan, X., Li, Y., Zhang, X., Qu, G., Wang, J., *Heteroatom. Chem.*, **2007**, 18(7), 786.
- Rajacka, A., Yuvaraju, K., Praveen, Murthy, Y. L. N., *J. Mol. Catal. A*, **2010**, 370, 197.
- Kidwai, M., Bhatnagar, D., *Tetrahedron Lett.*, **2010**, 51, 2700.
- Wang, G.-W., Miao, C.-B., *Green Chem.*, **2006**, 8, 1080.
- Sheldrick, G. M., *Acta Cryst.*, **2008**, A64, 112.
- Spek, A. L., *Acta Cryst.*, **2009**, D65, 148.
- Farrugia, L. J., *J. Appl. Cryst.*, **2012**, 45, 849.
- Nardelli, M., *J. Appl. Cryst.*, **1995**, 28, 659.
- Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orphen, A. G., Taylor, R., *J. Chem. Soc. Perkin Trans. 2*, **1987**, S1-S19.
- Kant, R., Gupta, V. K., Kapoor, K., Patil, D. R., Patil, P. P., Deshmukh, M. B., *Acta Cryst.*, **2013a**, E69, o100.
- Kant, R., Gupta, V. K., Kapoor, K., Patil, D. R., Jagdale, S. D., Deshmukh, M. B., *Acta Cryst.*, **2013b**, E69, o101.
- Duax, W. L., Norton, D. A., *Atlas of Steroid Structures*, New York: Plenum Press, **1975**, 1.

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