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Hydrogen bonded molecular rectangle of *N*,*N*′-bis(3-quinolyl-methylene)diphenylethanedionedihydrazone

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The title compound, *N*,*N*′-bis (3-quinolylmethylene) diphenylethanedionedihydrazone (**I**) (molecular formula, $C_{34}H_{24}N_6$) has been synthesized by the reaction of quinoline 3-carboxaldehyde and diphenylethanedionedihydrazone in 2:1 molar ratio. The molecular structure has been characterized by room-temperature single-crystal X-ray diffraction which reveals that two quinoline moieties are disposed nearly perpendicularly around the central C-C bond giving an 'L' shape to the molecule. This particular geometry gives rise to the hydrogen bonded supramolecular rectangle of two self-complementary molecules. These supramolecular units are further assembled by π-π interaction.

Keywords: Hydrazone, quinoline 3-carboxaldehyde, single-crystal X-ray, π-π stacking interactions, supramolecules

After Jean-Marie Lehn's famous report of supramolecular chemistry[1], the chemistry of molecular assemblies and intermolecular noncovalent binding interactions *i.e*. hydrogen bonding, ionic interactions and π-π stacking interactions have fascinated increasing attention in crystal engineering. In particular, hydrogen bonding π-π stacking interactions which is a powerful organizing force in designing various supramolecules and solid-state architectures[2-4], is extensively used not only for networking numerous organic and organometallic compounds[5,6], but also for generating interesting supramolecular properties, such as electrical, optical and magnetic[7,8] properties. Quinoline groups, with effective sites for coordination to transition metal ions, have been used for the construction of supramolecular coordination compounds[9-12]. In addition, organic imino-quinolyl fragments have proved to be very useful in self-assembly through hydrogen bonding and π-π stacking and the assembled products have relevance to biological systems[13]. Thus, imino-quinolyl ligand like *N*,*N*′-bis(3quinolylmethylene)diphenylethanedionedihydrazone has been designed and synthesized.

Experimental Section

Diphenylethanedionedihydrazone (0.714 g, 3 mmol) was dissolved in anhydrous methanol (25 mL) and in the solution 3-quinoline carboxaldehyde (0.942 g, 6 mmol) was added. The reaction mixture was refluxed under dry atmosphere for about 6 h. Then it was slowly cooled to RT to obtain a yellow crystalline solid of (I) (yield 80%). Elemental analysis for $C_{34}H_{24}N_6$: C 79.05, H 4.68, N 16.27%; found: C 79.15, H 4.63, N 16.29%. [m.p. (uncorrected) > 473 K]. The structure of the compound **I** has been confirmed by, mass spectrometry, ^{1}H and ^{13}C NMR, IR and electronic spectroscopy.

X-ray single crystal data were collected using MoKα (λ = 0.7107 Å) radiation on a BRUKER APEX II[14] diffractometer equipped with CCD area detector. Data collection, data reduction, structure solution/ refinement were carried out using the software package of SMART APEX[15]. The structures were solved by direct methods *SHELXS-97*[16] and standard Fourier techniques, and refined on F^2 using full matrix least squares procedures *SHELXL-97* using the *SHELX-97*[17] package incorporated in *WinGX*[18]. Atoms other than hydrogen atoms were treated anisotropically. Whenever possible, the hydrogen atoms were located on a difference Fourier map and refined. In other cases, the hydrogen atoms were geometrically fixed. The crystallographic details of **I** are summarized in Table I, selected bond lengths and angles of **I** is listed in Table II and selected hydrogen bonding parameters of **I** is shown in Table III.

Table I — Crystal data and Refinement parameters of **I**

Formula	$C_{34}H_{24}N6$
Formula Weight	516.59
Crystal System	Triclinic
Space group	P-1 (No. 2)
a, b, c [Angstrom]	10.885(3) 11.134(3) 12.870(3)
α, β, γ[°]	90.122(6) 114.141(6) 110.277(5)
V [Å^3]	1316.2(6)
Z	2
D(calc) [g/cm**3]	1.304
Mu(MoKa) [/mm]	0.080
F(000)	540
Crystal Size [mm]	0.00 × 0.00 × 0.00
Temperature (K)	293
Radiation [Å]	MoKa 0.71073
Theta Min-Max [°]	1.8, 19.6
Dataset	-10: 10 ; -10: 10 ; -12: 12
Tot., Uniq. Data, R(int)	7310, 2319, 0.053
Observed data [I > 2.0 sigma(I)]	1526
Nref, Npar	2319, 441
R, wR2, S	0.0439, 0.1315, 0.95
Max. and Av. Shift/Error	0.00, 0.00
Min. and Max. Resd. Dens. [e/ Å^3]	-0.19, 0.14

Table II — Bond distance and bond angle table (Å,°)

Bond Distances			
N1 -C1	1.320(6)	C16 -C17	1.411(7)
N1 -C9	1.378(6)	C16 -C21	1.415(8)
N2 -N3	1.425(5)	C17 -C18	1.412(9)
N2 -C10	1.283(6)	C18 -C19	1.361(9)
N3 -C11	1.288(6)	C19 -C20	1.394(8)
N4 -C13	1.327(7)	C20 -C21	1.363(9)
N4 -C17	1.377(7)	C23 -C24	1.395(7)
N5 -N6	1.408(7)	C23 -C28	1.381(8)
N5 -C22	1.280(6)	C23 -C34	1.488(8)
N6 -C34	1.292(6)	C24 -C25	1.389(9)
C1 -C2	1.420(7)	C25 -C26	1.375(10)
C2 -C3	1.360(6)	C26 -C27	1.369(9)
C2 -C10	1.450(7)	C27 -C28	1.375(9)
C3 -C4	1.418(7)	C29 -C30	1.375(8)
C4 -C5	1.416(7)	C30 -C31	1.364(8)
C4 -C9	1.412(7)	C31 -C32	1.373(7)
C5 -C6	1.354(8)	C32 -C33	1.376(8)
C6 -C7	1.391(9)	C1 -H232	0.9300
C7 -C8	1.356(8)	C3 -H16	0.95(4)
C8 -C9	1.391(7)	C5 -H17	0.94(4)
C11 -C12	1.478(7)	C6 -H18	1.00(4)
C11 -C34	1.512(7)	C7 -H19	0.88(5)
C12 -C29	1.379(6)	C8 -H15	0.88(4)
C12 -C33	1.389(7)	C10 -H13	1.08(4)
C13 -C14	1.416(7)	C13 -H5	0.99(4)
C14 -C15	1.382(8)	C15 -H6	0.99(3)
C14 -C22	1.452(8)	C18 -H4	0.88(4)
C15 -C16	1.415(8)	C19 -H3	1.02(5)
C20 -H2	0.96(4)	C28 -H7	0.96(4)
C21 -H231	1.03(3)	C29 -H9	0.91(4)
C22 -H233	1.02(4)	C30 -H10	0.95(4)
C24 -H24	0.9300	C31 -H11	0.91(4)
C25 -H14	1.00(5)	C32 -H32	0.9300
C26 -H8	0.92(6)	C33 -H12	0.94(3)
C27 -H27	0.9300		
Bond Angles			
C1 -N1 -C9	117.6(4)	N4 -C13 -C14	124.5(5)
N3 -N2 -C10	111.1(4)	C13 -C14 -C15	118.1(5)
N2 -N3 -C11	112.7(4)	C13 -C14 -C22	118.9(5)
C13 -N4 -C17	117.2(4)	C15 -C14 -C22	123.0(4)
N6 -N5 -C22	111.8(4)	C14 -C15 -C16	119.6(4)
N5 -N6 -C34	111.5(4)	C15 -C16 -C17	117.9(5)
N1 -C1 -C2	124.4(4)	C15 -C16 -C21	122.9(4)
C1 -C2 -C3	117.5(4)	C17 -C16 -C21	119.2(5)
C1 -C2 -C10	122.0(4)	N4 -C17 -C16	122.8(5)
C3 -C2 -C10	120.5(5)	N4 -C17 -C18	118.5(4)

Results and Discussion

The compound (**I**) was synthesized by condensing diphenylethanedionedihydrazone[19] and quinoline 3-carboxaldehyde in 1:2 molar ratio in anhydrous methanol. It crystallizes in triclinic space group *P*-1 and the asymmetric unit contains a single molecule of (**I**) (Scheme I). Due to the steric crowding between the two phenyl groups substituted on the central C-C bond in (I) the N=C-C=N and C(Ph)- C-C-C(Ph) torsion angles about this bond are −102.25° and −93.55° respectively.

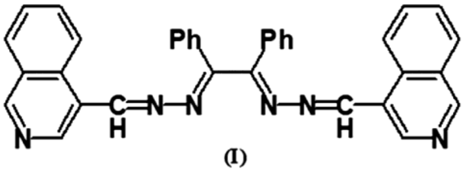
The molecule consists of two identical linear parts connected covalently by a –C-C- bond at the C11 and C34 carbon (Figure 1). Each segment of the molecule is linear and is nearly orthogonally disposed with respect to each other.

This gives rise to the ‘L’ shape of the molecule with two phenyl groups acting as small appendages. Each of the linear segments of the molecule consists of a phenyl and a quinoline group on either side of the central azo group. The molecule is rigid and the plane of the quinoline groups on both branches is perpendicular to each other.

The ‘L’ shape of the molecule is self-complementary for hydrogen bonding. The crystal structure analysis reveals a hydrogen bonded supramolecular rectangle (Figure 2). The quinoline nitrogen atom N1 acts as acceptor for the hydrogen attached to the C13 carbon atom adjacent to the N atom. The hydrogen bonding parameters are given in Table III.

Table III — Hydrogen bonding parameters for **I**

D-H···A	D-H (Å)	H···A(Å)	D···A(Å)	<D-H···A(°)	symmetry
C13-H5···N1	0.99(4)	2.60(4)	3.587(7)	170(3)	1-x,2-y,2-z



(I)

Scheme I — Chemical structure of **I**

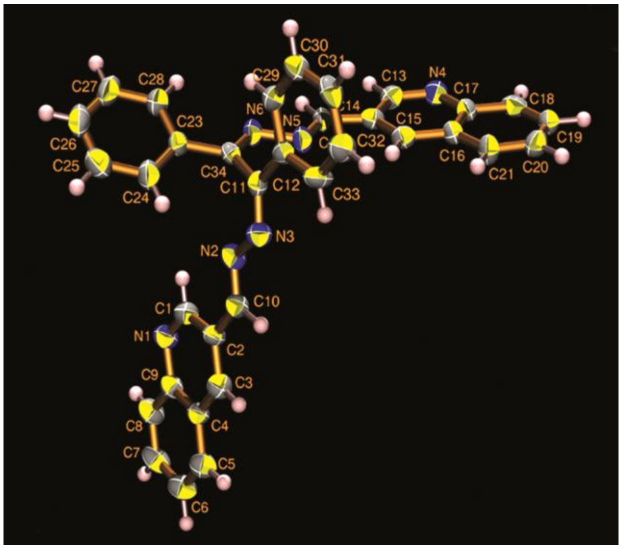


Figure 1 — The ORTEP diagram (30% ellipsoidal probability) of the compound I with atom numbering scheme

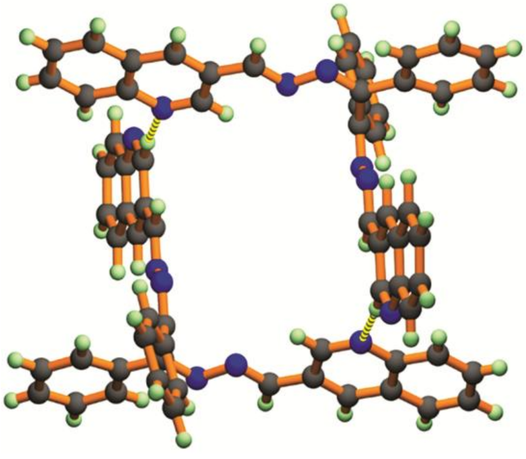


Figure 2 — The self-assembled molecular rectangle through hydrogen bonding in **I**

The size and aromatic nature of the quinoline fragment reveals a high propensity for strong dispersive interaction between the flat molecular surfaces of these rings in the condensed solid phase.

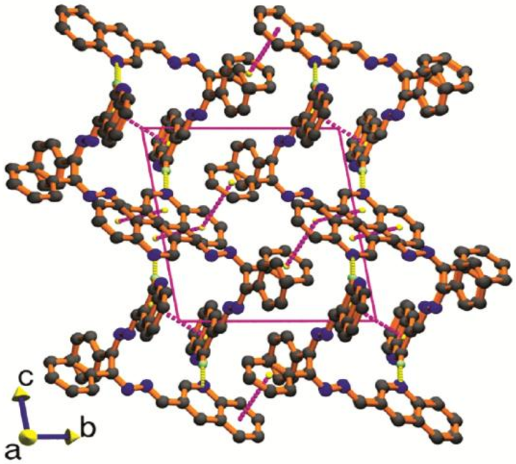


Figure 3 — Theπ-π stacking of hydrogen bonded molecular rectangles in **I**

This spatial as well as enthalpic element is well expressed in the crystal packing arrangement of **(I)**. π-π stacking interactions between the aromatic 3-quinoline rings of neighbouring molecules has been observed in the crystals of (I). Face-to-face overlap between the phenyl substituent of one species and quinoline substituent of another species provides additional stabilizing contribution. Hydrogen bonded molecular rectangles are thus joined at their corners by π-π interaction (Figure 3). In a unit cell four such rectangles are there, center of each is positioned at the cell corners.

In conclusion, we have synthesized a polydentateiminoquinolyl ligand, *N*,*N*′-bis(3-quinolylmethylene) diphenylethanedionedihydrazone and determined its single crystal X-ray structure at room temperature. Interestingly this molecule is predisposed for supramolecular rectangles due to its ‘L’ shaped geometry as well as self-comlimentarity in hydrogen bonding. Generation of molecules or suprmolecules of different well known geometries such as triangle, square, pentagon – in general n-gon is a challenging task in crystal-engineering. In this respect the molecule reported here shows how the design principle, especially ‘L’ shape and suitable positioning of acceptor and donors can give rise to targeted geometry.

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Supplementary Information

Supplementary information is available in the website http://nopr.niscair.res.in/handle/123456789/58776.

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