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Crystal Structure and Density Functional Calculation of (*E*)-4-Hydroxy-3-methyl-*N*'-(thiophen-2-ylmethylene)-1,4-dihydroquinoxaline-2-carbohydrazide Radical

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The compound (*E*)-4-Hydroxy-3-methyl-*N*'-(thiophen-2-ylmethylene)-1,4-dihydroquinoxaline-2-carbohydrazide ($C_{15}H_{13}N_4O_2S$) is a stable free radical quinoxaline derivative. It was prepared by treatment of an acidified ethanolic solution of 3-methyl-2-(thiophen-2-ylmethylenehydrazinocarbonyl)quinoxaline-4-oxide with a solution of $CuSO_4.5H_2O$. The crystal structure shows that the molecule contains non-planar linking unit between quinoxaline and thiophene rings. Hydrogen bonding (N-H…O), π…π stacking and S…S intermolecular interactions may be effective in the stabilization of the crystal lattice. Density functional theory results agree well with X-ray experimental findings indicating that the free radical is indeed possible and that the stability of this compound might be attributed to the highly electron delocalization of the conjugation system over the whole compound along with the extra stabilization from the intramolecular interactions.

Key Words: Quinoxaline, Crystal structure, Crystal supramolecularity, Density functional theory calculations.

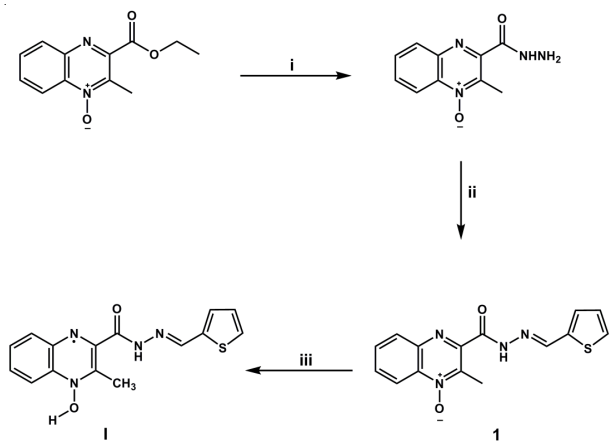
INTRODUCTION

Quinoxalines are of interest because many of their compounds are bioactive with distinct pharmacological profiles, such as being potential antibiotics[1], redox-activated DNA damage agents[2] and seem to have interesting anticancer activity[3]. They are also found to be an efficient agents in redox-activated DNA damage[2]. On the other hand and owing to their electron-withdrawing property, they have been used in electroluminescent devices as electron transporters[4]. As ligands, quinoxalines proven to be useful for metal complexation[5] and their complexes show efficient electroluminescence[6] in organic light-emitting diodes (OLEDs).

In recent years, the synthesis of many quinoxaline derivatives have been reported[7-10]. On the other hand, quinoxaline radicals have frequently been the subject of e.s.r. spectroscopic, as well as theoretical calculation studies[11]. As an extension to our work on quinoxaline system, we have reported the crystal structure of 1,4-dihdroxyquinoxaline-2,3(1H, 4H)-dione[12]. Herein we report the synthesis of a neutral quinoxaline radical *i.e.*, (*E*)-4-Hydroxy-3-methyl-*N*'-(thiophen-2-ylmethylene)-1,4-dihydroquinoxaline-2-carbohydrazide along with its crystal structure and crystal packing analysis.

EXPERIMENTAL

All reagents were used as purchased unless otherwise stated. Compound (*E*)-4-Hydroxy-3-methyl-*N*'-(thiophen-2-ylmethylene)-1,4-dihydroquinoxaline-2-carbohydrazide (**1**) was prepared according to reported method[13], **Scheme-I**.



Scheme-I: Synthesis of **I;** i=$NH_2NH_2{\cdot}H_2O$, stirring for 6 h at room temperature; ii=thiophene-2-carbaldehyde/CH_3COOH, stirring for 20 min at room temperature; iii= $CuSO_4{\cdot}5H_2O/CH_3COOH$, stirring for 16 h at room temperature

Synthesis of compound I: A solution of 3-methyl-2-(thiophen-2-ylmethylenehydrazinocarbonyl)quinoxaline-4-oxide **1** (350 mg, 1.11 mmol) in ethanol (10 mL) acidified with CH_3COOH (1 mL) was treated with a solution of $CuSO_4 \cdot 5H_2O$ (250 mg, 1.00 mmol) dissolved in deionized water (10 mL). The mixture was stirred for 16 h at room temperature. A pale-yellow solid was formed and filtered. Crystallization of the final product from ethanol gave the title quinoxaline radical, **I**, in the form of pale-yellow needle crystals. Yield, 38 %; m.p. 142 ºC decomposition; IR (Kbr, ν_{max}, cm^{-1}): 3366 (w, br), 1681 (s, C=O), 1667 (m, C=N), 1591 (w), 1453 (m), 1370 (m), 1032 (s), 844 (m), 737 (m), 692 (vs).

X-Ray crystallography: Data were collected at 298(2) K using a Bruker SMART instrument equipped with a graphite monochromated (MoK_α radiation, $\lambda = 0.71073$ Å). Cell parameters were retrieved using SMART[14] software and refined using the Bruker SAINT software[14]. Data reduction and correction were performed using the Bruker SAINT software. The data were processed with SAINT[14] and the structure was solved by direct method[14] and refined on F^2 by full-matrix least-squares techniques[15]. Crystallographic details are given in Table-1.

TABLE-1
CRYSTAL DATA AND STRUCTURE REFINEMENT FOR **I**

Empirical formula	$C_{15}H_{13}N_4O_2S$
Formula weight	313.35
Temperature (K)	295(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	
a (Å)	14.2576 (18)
b (Å)	12.0461 (14)
c (Å)	8.4284 (10)
β (º)	104.729 (3)
Volume ($Å^3$)	1400.0 (3)
Z	4
Density (calculated) (Mg/m^3)	1.487
Absorption coefficient (mm^{-1})	0.25
F(000)	652
Crystal size (mm^3)	0.46 × 0.06 × 0.04
Theta range for data collection (º)	1.5 to 27.5
Index ranges	-18<=h<=18, -12<=k<=15, -10<=l<=10
Reflections collected	9694
Independent reflections	1786 [R_{int} = 0.051]
Data / restraints / parameters	3202/0/204
Final R indices [I > 2Σ(I)]	R1 = 0.047, wR2 = 0.125
R indices (all data)	R1 = 0.0986, wR2 = 0.111
Largest diff. peak and hole/ e. $Å^{-3}$	0.24 and –0.31

Density functional theory calculations: The geometry and other properties of the quinoxaline free radical $C_{15}H_{13}N_4O_2S$ have been calculated using the density functional theory (DFT) using the Gaussian 03 program[16]. The spin-unrestricted UB3LYP functional combined with different types of polarization and diffuse basis sets such as 6-31G(d) and 6-31+G(d) were used for the open shell radical compound system. Such basis sets are suitable and flexible to optimize the structure of the quinoxaline free radical compound. HOMO and LUMO molecular orbitals of the optimized geometry were plotted using the CSChem3D ultra program. Note here, that the partial atomic charges and bond order of the quinoxaline free radical compound, **I**, were computed according to the natural bond orbital (NBO) population analysis[17].

RESULTS AND DISCUSSION

The title compound, **I**, has been obtained by the treatment of the ethanolic solution of 3-methyl-2-(thiophen-2-ylmethylenehydrazinocarbonyl)quinoxaline 4-oxide **1** (350 mg, 1.11 mmol), acidified with acetic acid (1 mL) and a solution of $CuSO_4.5H_2O$. The quinoxaline compound **1** resulted from the condensation of the thiophene-2-carbaldehyde with 2-hydrazinocarbonyl-3-methylquinoxaline 4-oxide[18], which was prepared by the nucleophilic substitution of hydrazine monohydrate to the 2-ethoxycarbonyl-3-methyl quinoxaline 1,4-dioxide[19-21], **Scheme-I**. Crystallization of the final product from ethanol gave, the stable free radical quinoxaline derivative that could be identified unambiguously by single crystal X-ray crystallography. The stability of this free radical might be attributed to the highly conjugated π system in this radical. Organic radicals can be long lived if they occur in a conjugated π system, such as the radical derived from α-tocopherol (vitamin E). Many other examples are the thiazyl radicals, which show remarkable kinetic and thermodynamic stability with only a very limited extent of π resonance stabilization[22,23].

Formation of **I** is explained by: First the protonation of the oxygen atom to form N-OH group and leading to a delocalized cationic quinoxaline followed by bonding to Cu(II) ions (*via* the other N in the ring). Upon electron transfer and bond breaking neutral radical quinoxaline and Cu(I) formed. This system and other reactions are under investigation in order to explore all these postulations and to better understanding the chemistry involved.

Molecular structure: The asymmetric unit of the title compound, **I**, (Fig. 1) contains one organic moiety. The quinoxaline ring is planar, which can be attributed to a wide range of electron delocalization, with the highest deviation being for C7, 0.070 Å, out the plane. The O_2 attached to N_4 is deviated from the plane by 0.139 Å. The bond lenghts and angles are in normal ranges[24]. The C4-C5, C6-C7 and C8-C15 [1.437, 1.511 and 1.488 Å, respectively] bonds have single bond character compared to multiple bond characters in the delocalized quinoxaline [in the range 1.358-1.405 Å] and thiophene ring [in the range 1.338-1.397 Å]. The N3-C7 [1.317 Å] bond is significantly shorter than others N3-C10 [1.360 Å], N4-C8 [1.347 Å] and N4-C9 [1.391 Å] and all are an intermediate between those typical for the corresponding single and double bonds, suggesting some degree of delocalization. The linking unit between he quinoxaline and thiophene, is not planar. The non-planarity of the chain linking the two aromatic parts of the molecule, C–N–N–C unit, is delocalized, with N2 atom being the largely deviated atom from the plane (0.100 Å out of plane). The angle between quinoxaline and next C–N–N–C unit is 24.73º and the quinoxaline with thiophene ring is 14.06º, while the angle between C–N–N–C unit and thiophene ring is 17.86º.

The C–O bond show the expected full double bond character, while the C–N and N–N bond lengths in the linking unit (Table-2) imply significant electron delocalization. As a result of conjugation, the C=O distance [1.223 Å] are longer than the normal value of 1.20 Å[25] and the C–N bond distances [1.274 and 1.337 Å] are longer than the C=N double bond distance (1.32 Å[25]) and shorter than the C–N single bond distance (1.475 Å[25]). The bond angle sum at each C5, N2 and C6 of about 360º implies sp^2 hybridization for these atoms.

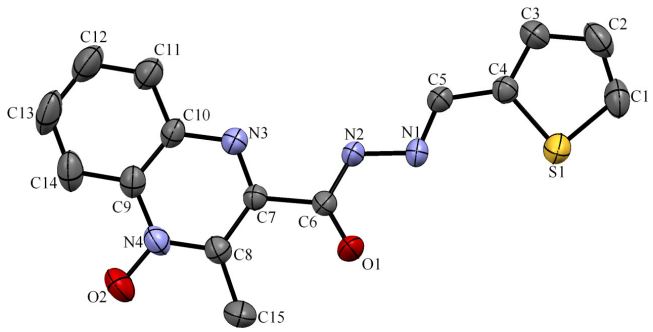


Fig. 1. Molecular structure of **I**, with atom labeling scheme. The thermal probability drawn at the 50 % level

TABLE-2
SELECTED BOND LENGTHS (Å) AND ANGLES RESULTS OF **I**, DETERMINED BY X-RAY DIFFRACTION AND DENSITY FUNCTIONAL THEORY CALCULATIONS

Bond lengths	X-ray	UB3LYP	
		6-31G(d)	6-31+G(d)
S1-C1	1.701(3)	1.730	1.729
C2-C3	1.397(3)	1.424	1.425
N1-N2	1.385(2)	1.353	1.355
N1-C5	1.274(3)	1.290	1.291
C4-C5	1.437(3)	1.463	1.464
N2-C6	1.337(3)	1.383	1.380
N3-C7	1.317(2)	1.351	1.348
N3-C10	1.360(3)	1.369	1.370
N4-O2	1.277(2)	1.403	1.409
O1-C6	1.223(2)	1.225	1.227
C3-C4	1.359(3)	1.382	1.384
N4-C8	1.347(3)	1.390	1.393
N4-C9	1.391(3)	1.400	1.403
C6-C7	1.511(3)	1.506	1.508
C7-C8	1.415(3)	1.389	1.388
C8-C15	1.488(3)	1.498	1.497
C9-C14	1.396(3)	1.395	1.397
C10-C11	1.402(3)	1.411	1.412
C11-C12	1.361(3)	1.389	1.390
Bond angles			
C1-S1-C4	91.56(12)	91.96	91.99
C5-N1-N2	114.56(17)	119.44	119.56
C6-N1-N2	119.49(17)	123.80	122.88
C7-N3-C10	116.66(18)	116.91	116.81
O2-N4-C8	121.82(19)	117.01	116.36
C5-C4-S1	123.07(16)	118.51	118.32
N1-C5-C4	121.99(19)	126.73	126.81
N4-C8-C15	116.44(19)	116.88	117.25
C7-C8-C15	126.40(2)	127.00	126.50
N4-C9-C14	121.00(2)	122.62	122.53
N4-C8-C7	117.20(2)	116.10	116.18
N4-C9-C10	118.11(19)	115.90	116.22
O1-C6-N2	124.43(19)	120.88	120.44
N2-C6-C7	112.88(17)	117.89	117.63

It is worth noting that the intramolecular hydrogen bonding interactions between N2–H2…N3 [2.336 Å] and C15–H15B…O3 [2.287 Å] form 5-membered and 6-memberd rings, respectively, within the molecular geometry.

Density functional theory calculation results of I: The ground state geometry of the (*E*)-4-hydroxy-3-methyl-*N*'-(thiophen-2-ylmethylene)-1,4-dihydroquinoxaline-2-carbohydrazide radical was optimized at the level of UB3LYP theory using two basis sets, 6-31G(d) and 6-31+G(d), respectively. Selected optimized parameters such as bond lengths and bond angles together with the X-ray data are presented in Table-2. The computed bond lengths and angles are in good agreement with experimental results. On average, the UB3LYP/6-31G(d) results deviate in the range from 0.001 to 0.122 Å for bond lengths and from 0.04º to 4.7º for bond angles. The results obtained using UB3LYP/6-31+G(d) are consistent well with the UB3LYP/6-31G(d) basis set and shows relatively the same deviation in values as compared to experimental X-ray data. As presented in Table-2, a single bond character was obtained for the C4-C5, C6-C7 and C8-C15 bonds [1.463, 1.506 and 1.498 Å respectively] and a multiple bond character was found for all the bonds in the quinoxaline ring [bond distances range from 1.351 to 1.412 Å], as well as the thiophene ring [in the range 1.382 to 1.424 Å]. For the nitrogen atom bears the unpaired electron (N3), the bond lengths with directly bonded atoms (C7 and C10) are relatively shorter than the other ones in the quinoxaline ring as observed experimentally. In addition, the DFT results indicate that the quinoxaline as well as the thiophene rings are still retain planarity since all C-C-C, C-N-C and C-C-N bond angles are closed to 120º. This means that π electrons in the two rings are delocalized in this radical compound. However, the planes of quinoxaline and thiophene rings are not coplanar with an angle of -9.7º, which confirms the experimental findings (14.06º) that mentioned previously. It is noted here that the frequency tests of the optimized geometry using UB3LYP/6-31G(d) and UB3LYP/6-31+G(d) yielded zero imaginary frequencies and hence the optimized geometry of the radical compound is minimum. Fig. 2 shows that the HOMO is mainly localized on the molecular skeleton of the quinoxaline ring, whereas the LUMO is localized on the molecular skeleton of thiophene ring and the bridging unit, therefore this radical compound is expected to exhibit a π→π* transition.

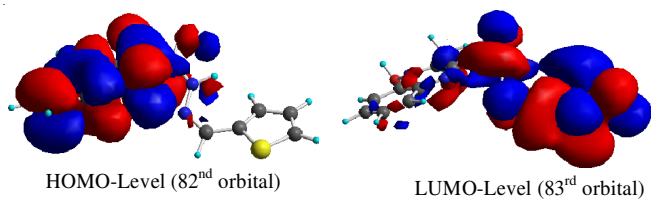


Fig. 2. Schematic diagram of HOMO and LUMO for the free radical compound I, obtained at the UB3LYP/6-31+G(d) level of theory

The natural bond orbital (NBO) population analysis of the quinoxaline ring of **I** shows that the bond orders (BO) of both nitrogen atoms (N3 and N4) are 2.55 and 3.14 respectively. Usually nitrogen atom exhibits a bond orders = 3.0 (plus a lone pair of electrons) in all cases according to its Lewis structure and hence the nitrogen atom (N3) that has a bond

orders = 2.5 is believed to have a single unpaired electron that exists in the anti-bonding orbital. Furthermore, the atomic charge of N3 has the highest positive charge (+0.405) as compared to all atoms in the quinoxaline ring. This might be attributed to the radical nature of N3 in the quinoxaline ring. These results are exactly matched with the bond orders analysis of free nitric oxide (NO radical form) where the N atom was found to exhibit a bond orders = 2.5 using natural bond orbital population analysis technique[26]. The bond orders analysis results of all kinds of nitrogen atoms exist in the free radical compound (Tables 3 and 4) indicate that there are two types of nitrogen atoms, N1, N2 and N4 that exhibit relatively the same bond order of ~3, whereas the nitrogen atom (N3) has a lower bond order by ~0.5.

TABLE-3
NATURAL BOND ORBITAL POPULATION ANALYSIS OF EACH ATOM IN THE QUINOXALINE RING FRAGMENT CALCULATED AT THE UB3LYP/6-31+G(d) LEVEL OF THEORY

Atom	Charges	Bond order* of N(4)—X (X: N, C and O)	Bond order* of N(3)—X (X: N, C and O)
N(3)	0.405	0.017	-
N(4)	0.173	-	0.017
C(7)	-0.137	0.025	1.211
C(8)	0.345	1.101	0.040
C(9)	0.106	1.056	0.042
C(10)	-0.133	0.011	1.335
C(11)	0.124	0.008	0.039
C(12)	-0.053	0.007	0.015
C(13)	0.158	0.010	0.004
C(14)	0.026	0.035	0.010
O(2)	0.009	0.979	0.002
Other atoms in the whole compound	-	0.044	0.114

*Calculated *via* natural bond orbital population analysis

TABLE-4
NATURAL BOND ORBITAL POPULATION ANALYSIS OF EACH NITROGEN ATOM IN THE FREE RADICAL, **I**, CALCULATED AT THE UB3LYP/6-31+G(d) AND UB3LYP/6-31+G(d) LEVELS OF THEORY

Atom	Charges	Bond order of N(i)—X (X: bonded directly)	Bond order of N(i)—X (X: non-bonded) intra-molecular interaction	Total bond order
N(1)	0.002	2.869	0.249	3.118
N(2)	-0.003	3.021	0.212	3.232
N(3)	0.405	2.546	0.114	2.660
N(4)	0.173	3.136	0.044	3.180

As a conclusion, the DFT calculations agree well with X-ray experimental findings and hence the geometry of the free radical compound with the molecular formula $C_{15}H_{13}N_4O_2S$ is indeed possible. The stability of this compound might be attributed to the highly electron delocalization over the conjugated system along with the intra-molecular interactions between non-bonded atoms (Tables 2 and 3).

Crystal packing and supramolecularity of I: In the crystal structure, intermolecular N-H…O hydrogen bonds [N2-H2N···O1^{i}, 2.15(2) Å and 158(2)Å with N…O 2.950(2) Å; Symmetry code: (i) x, -y+1/2, z+1/2] link the molecules into chains extends parallel to c crystallographic axis (Fig. 3). These chains are further connected to each other *via* π…π offset stacking motif (centroids distances of 4.210 Å) within the of thiophene rings, in b direction, leading to layers running along the ac plane (Fig. 4). The structure also shows other S…S interactions (3.866 Å) between the thiophene molecules which may add extra stability for this lattice.

A part from dipole-dipole and van der Waals interactions, hydrogen bonding, π···π stacking and S…S interactions may be effective in the stabilization of the crystal lattice.

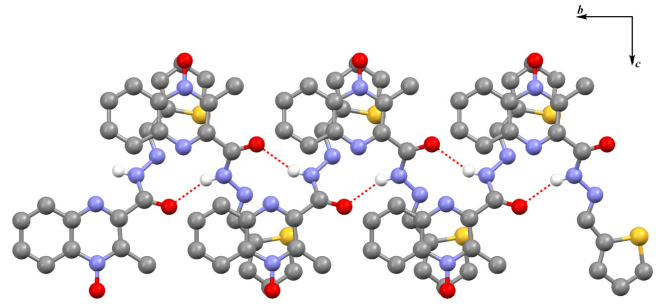


Fig. 3. Partial crystal packing diagram showing the chains of molecules parallel to *c* crystallographic axis. N-H…O hydrogen bonding appear as dotted lines

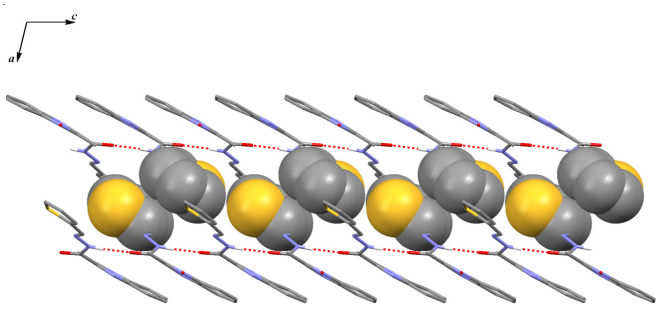


Fig. 4. Crystal packing of the structure showing the N-H…O hydrogen bonding (dotted lines). Thiophene rings involved in aryl…aryl (π…π) stacking interactions are drawn as space-filling representation

Supplementary materials: CCDC 774819 contains the supplementary crystallographic data for this paper. These 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, Cambridge CB2 1EZ, UK; Fax: +44 1223 336033; or e-mail: deposit@ccdc.cam.ac.uk.

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