



QTAIM and NBO Analysis of a New Oxidative Salt of 1,1'-(Ethane-1, 2-diyl) Dipyridinium bisiodate

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ABSTRACT

A theoretical DFT study was employed to investigate the different aspects of electronic structure of the salt of 1,1'-(ethane-1,2-diyl)dipyridiniumbisiodate. The interactions between different molecular orbitals were considered by using DFT method. The results from the quantum mechanical calculations were then used to determine the role of donor- acceptor interactions on the oxidation strength of this salt. Theoretical calculations at the B3LYP/LANL2DZ level of the theory on the molecular entropy and specific heat capacity values over a wide temperature range of 300 to 3000 K confirmed that temperature dependence of vibrational entropy and specific heat capacity is more important than other contributions. Hydrogen bond interactions were analyzed by the quantum theory of atoms in molecules (QTAIM) and natural bond orbital (NBO) analysis. For QTAIM studies, wave functions which were generated by DFT method have been applied to be determined the quantum parameters such as electron density and its Laplacian at the bond critical points. Finally the calculated mean value of $-U/G$ for this salt confirmed a non-covalent nature of O...H bonds.

Key words: EDB; Oxidation strength; Hydrogen bond; QTAIM; NBO.

INTRODUCTION

Iodate is typically used in tropical climates, due to its good resistance to oxidation¹. The iodate anion has the capability to oxidize various functional groups. A diversity of salts with this anion, such as the potassium salt, have been prepared by Singh *et al.*,² Potassium iodate is an oxidizing agent which can cause fires in the presence of the combustible materials or reducing agents.

Potassium iodate is sometimes used for iodization of table salt to prevent the iodine deficiency, because iodide can be oxidized by molecular oxygen to iodine under wet conditions. Iodate salts are also available supported on the commercial anionic resin Amberlyst A26, and also on poly (vinyl pyridine)³.

In this research we attempted to provide further insight into the quantum chemistry aspects

of the electronic structure of this salt using the theoretical methods. A complementary study with the aim of elucidation the molecular properties associated with the oxidation strength is important in order to have a precise idea of the quantum reactivity indices.

Computational details

All calculations were performed with the Gaussian 09 software⁴. As it has been reported that the DFT method by B3LYP function can reproduce good geometrical structures⁵⁻⁸, the structures of the molecules were fully optimized and characterized as true minima by the absence of imaginary frequencies. Using the B3LYP/LANL2DZ level of the theory. Vibrational frequencies were determined to provide an estimation of the zero point vibrational energies (ZPVE).

Natural bond orbital analysis (NBO) which is suggested by Reed *et al.*,⁹⁻¹⁰ as carried out to explore the distribution of electrons into atomic and molecular orbitals. Based on these data, donor-acceptor interactions of EDB salt were fully investigated.

For better analysis of electron density and bond orders evaluation of EDB, quantum theory of atom in molecule was applied. QTAIM is a method that provides a rigorous and unambiguous criterion to determine which atoms are bonded and which are separated in a system¹¹. In this method, the topological properties of the charge density ($\rho(r)$) is of interest and is summarized by its bond critical points (BCPs). These

points refers to some places where the gradient vector field, $\nabla^2\rho(r)$ vanishes. On the other hand, for determining the region in which the electronic charge is locally depleted or concentrated, using the concept of the Laplacian of the electronic charge density $\nabla^2\rho(r)$ is of importance. $\nabla^2\rho(r)$ is positive, then there is a local depletion of charge; the electronic charge density is smaller than the average density in the immediate neighborhood. But wherever $\nabla^2\rho(r)$ is negative, it means that there is a local concentration of charge. Since electron density is concentrated where $\nabla^2\rho(r) < 0$ and it is depleted where $\nabla^2\rho(r) > 0$ the topology of the Laplacian is expressed in terms of $L(r) = -\nabla^2\rho(r)$ ¹².

RESULTS AND DISCUSSION

Structure Analysis

There is one independent crystallographically iodate anions for the salt of 1,1'-(ethane-1,2-diyl) dipyridinium bisiodate (EDB) as shown in figures 1, in which I atoms are in a trigonal-pyramidal environment¹³. Two pyridine rings adopt an anti-conformation with respect to each other; the angle between these two rings is 3.84 degrees and C—H \cdots O weak hydrogen bonds between the cations and anions lead to the formation of layers arranged parallel to the ab plane.

According to crystallography structure¹⁴, IO_3^- anions are on the top of the pyridine rings which is in spite of the theoretical data. Theoretical structure shows that IO_3^- anions are around the pyridine rings, according to figure 2.

Table 1: Main geometric parameters in angstrom and degrees at the B3LYP/LANL2DZ level of EDB salt

Parameter	Value	parameter	Value
I1 – O2	1.90	O36 – I33 – O35	102.50
I33 – O34	1.91	O35 – I33 – O35	100.90
C10 – N22	1.50	O34 – I33 – O36	105.36
C15 – N5	1.49	N5 – C15 – C10	111.364
C15 – H 17	1.09	N22 – C10 – C15	109.18
C15 – H16	1.09	N5 – I33 – N22	48.92
C10 – H 12	1.09	N22 – C10 – C15 – N5	165.63
O2 – I 1 – O3	102.73	C10 – N22 – C23 – H24	3.11
O2 – I 1 – O4	104.05	N5 – C6 – O2 – I1	-26.79
O4 – I 1 – O3	100.94	N22 – C23 – O36 – I33	13.22

Table 2: Main vibrational frequencies (cm⁻¹) of EDB salt at B3LYP/LANL2DZ

Description	Frequencies	Description	Frequencies
I1 – O2	255.50	O3 – O4	660.26
I33 – O34	279.39	C10 – C15	1044.81
O35 – O36	635.60	N22 – C10	1188.31
O34 – O35	653.49	C15 – N5	1206.43

Table 3: Selected partial charges of EDB salt from the NBO analysis

Atom	Partial charge	Atom	Partial charge
I1	2.195	N22	-0.364
O2	-1.022	H11	0.277
O3	-1.047	H12	0.266
O4	-1.002	H16	0.257
N5	-0.362	H17	0.240
C10	-0.211	I33	2.178
C15	-0.212	O34	-1.028
O35	-1.012	O36	-1.019

Table 4: Significant natural bond orbital interactions of the EDB salt

Donor	Acceptor	Delocalization Energy(kcal/mol)	Donor	Acceptor	Delocalization Energy(kcal/mol)
Lp O2	σ^* I1 – O3	9.49	Π C13 – C20	Π^* N5 – C8	44.21
Lp O2	σ^* I1 – O4	8.50	Π N22 – C23	Π^* C25 – C29	21.08
Lp O2	σ^* C6 – H7	18.86	Π C27 – C31	Π^* N22 – C23	13.80
Lp O3	σ^* C25 – H26	14.53	Lp O34	σ^* C8 – H9	3.37
Lp O4	σ^* C10 – H11	5.40	Lp O35	σ^* C10 – H12	4.30
Π N5 – C8	Π^* C6 – C18	21.07	Lp O36	σ^* C23 – H24	11.24
Π C6 – C18	Π^* N5 – C8	13.60	Lp O34	σ^* I3 – O35	14.36

Table 5: Laplacian (L2) and charge density (ρ) values of BCP for EDB salt

Bond	Charge density (au)	Laplacian	Bond	Charge density (au)	Laplacian
N22 – C23	0.282	0.121	C23 – H24	0.267	0.246
N22 – C25	0.283	0.118	H26 – O3	0.038	-0.034
H24 – O36	0.037	-0.034	N22 – C10	0.212	0.076
H12 – O36	0.009	-0.008	C10 – C15	0.218	0.104
H17 – O34	0.022	-0.021	N5 – C15	0.218	0.086
H16 – O2	0.019	-0.018	N5 – C8	0.281	0.115
H7 – O4	0.031	-0.021	N5 – C6	0.283	0.120
H9 – O35	0.040	-0.036	C8 – H9	0.264	0.243
C6 – H7	0.269	0.250			

1,1'-(ethane-1,2-diyl) dipyridinium bisiodate salt structure was fully optimized at the B3LYP/LANL2DZ level of the theory. Table 1 shows the optimized geometrical parameters for this salt. According to table 1, OIO bond angles in the range of 100.90° to 105.4°. C—H...O hydrogen bonds

between the cations and anions lead to the formation of layers which have been arranged parallel to the *ab* plane.

Frequencies and Thermodynamic Analysis

Fundamental vibrational frequencies of

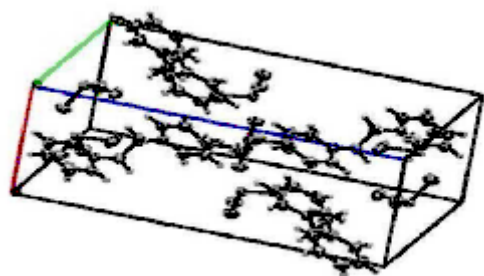


Fig. 1: A fragment of crystal packing of EDB



Fig. 2: Optimized structure of EDB salt

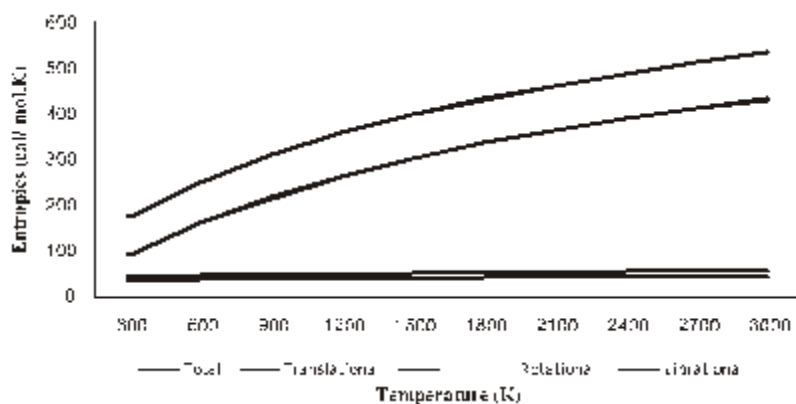


Fig. 3: Entropy behavior of EDB as a function of temperature

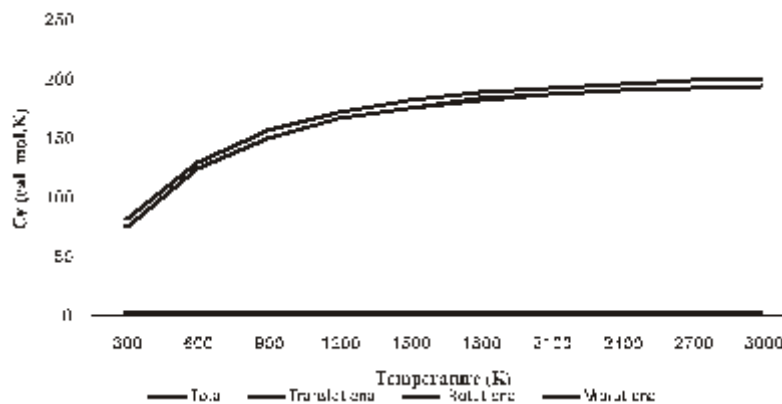


Fig. 4: Specific heat capacity behavior of EDB as a function of temperature

EDB salt which are obtained from the theoretical calculations at the B3LYP/LANL2DZ level, have been assigned and reported in table 2.

Figures 3 and 4 provide the entropy and specific heat capacity values over a wide temperature range of 300 to 3000 K. Translational, rotational, and vibrational contributions to the molecular entropies and molecular specific heat capacity have been considered, and the results have been depicted in figures 3 and 4 respectively. Considering these figures, it has been confirmed that temperature dependent of vibrational entropy and specific heat capacity is more important than other contributions.

NBO Analysis

Charge distributions on EDB salt were calculated by the NBO method. Natural charges on EDB salt indicate that I atoms have positive character, while O and N atoms have negative ones. Negative characters for N and O atoms in the N-C(H) ... O ... I conjunction and positive character for H atom confirms the hydrogen bonding between two (three) molecules. Computed values of the natural charges for N, O and H have been reported in table 3. According to table 3, positive character for H atom induces that to be attracted by O atom, because of the large value of negative charge density on the oxygen atom.

Delocalization of electron density between occupied Lewis-type (bonds or lone pairs) NBO

orbitals and formally unoccupied (anti-bonds and Rydberg's) non-Lewis NBO orbitals corresponds to a stabilizing donor-acceptor interactions. The energy of these interactions has been computed by the second-order perturbation theory according to equation (1)¹⁵.

$$E(2) = \Delta E_{ij} = q_i \{ F^2(i, j) / (E_j - E_i) \} \quad \dots(1)$$

Where q_i is the donor orbital occupancy; E_j and E_i are diagonal elements and (i, j) are off-diagonal elements associated with NBO Fock matrix¹⁶. Table 4 shows the energies of donor-acceptor interactions for EDB salt.

According to table 4 the most important stabilizing effect is due to the strong orbital interactions of $\pi_{C13-C20}$ to π^*_{N5-C8} and $\pi_{N22-C23}$ to $\pi^*_{C25-C29}$. While the transmission between the LP_{O34} to π^*_{C8-H9} and LP_{O35} to $\pi^*_{C10-H12}$ possesses the minimum stabilizing effects. Therefore during the oxidation process, it can be expected that the Π to Π^* donor-acceptor interactions vary sharply.

QTAIM Analysis

QTAIM-based analysis of electron density at different characteristic points, particularly at the bond critical points (BCP), is a powerful tool for investigation of different chemical or physical phenomena¹⁷⁻²². It is well proved that the magnitude of the electron density function estimated at the BCP can reflect the strength of a given bond. The results of the topological analysis (Figure 5) for the

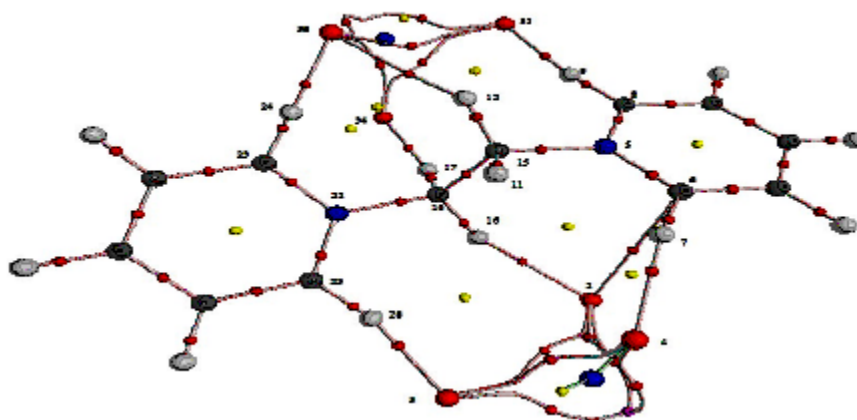


Fig. 5: Molecular graph for the EDB salt using the QTAIM method

electronic charge density of the EDB salt, including the values of the electron density, $\rho(r)$, and the Laplacian, $L(r)$, have been reported in table 5. Considering table 5, negative values of H-O bond laplacian such as H24-O36, H12-O36, H17-O34 represent an interaction between the nucleus and concentration of electron density in these regions. Small values of laplacian are accordance to weak hydrogen bond at this critical bond points. Positive values of laplacian confirm the polar covalent bond nature of C-N and C-H bonds.

In the theoretical charge density studies we have calculated the local potential energy density $U(r_{BCP})$ and kinetic energy density $G(r_{BCP})$ at BCPs essentially to represent a quantity proportional to the non-covalence bond energy. The average value of 0.93 for $-G/U$ quantity, can reveal the hydrogen bond interactions, which previously confirmed by NBO analysis.

CONCLUSION

The molecular properties of the 1,1'-

(Ethane-1,2-diyl) dipyridinium bis(iodate) salt have been investigated using the B3LYP method with LANL2DZ basis set. Obtained result by using the quantum chemical calculations show the hydrogen bond formation in this salt. Vibrational frequencies have been investigated and the behavior of the entropies and the specific heat capacity of this salt in temperature range of 300 to 3000 K have been evaluated. For better understanding of the hydrogen bond importance during the salt formation NBO and QTAIM analysis were applied. Calculated interaction energies, $E(2)$ by NBO method is accordance to $(-U/G)$ values which have been obtained by AIM methods. Considering the NBO and QTAIM results, it is expected that during the oxidation process, π to π^* donor-acceptor interactions have the most important contribution.

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