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An ab initio quantum chemical investigation of atoms NMR shielding tensors in Adenine-thymine, Adenine-uracil,Guanine-Cytosine & uracil-quartet:comparison between theoretical and experimental results

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ABSTRACT

We have evaluated the NMR shielding tensors for A:T,G:C,A:U in Watson-crick,and U-quartet.we have computed NMR shielding tensors at B3lyp level by using 6-31G(d) basis set.

We have compute anisotropy and asymmetry in A:T,G:C,A:U and U-quartet.The NMR shielding tensors were calculated using the GIAO method.

The natural bonding orbital analysis(NBO)were performed.NBO calculation have been done at B3LYP level.We have evaluated lowest occupancy orbitals,highest energy,donor and acceptor atoms,core and valence orbitals,total lewis,natural population in atoms in NBO calculation.

Keywords: Watson-crick; A:T;G:C;A:U; U quartet;NMRshielding;Choloroform; NBO

INTRODUCTION

Nuclear magnetic resonance (NMR)spectroscopy is a valuable technique for obtaining chemical information.This is because the spectra are very sensitive to changes in the molecular structure.This name sensitivity makes NMR a difficult case for molecular modeling.[1-3]

Computationally predicting couple constants is much easier than predicting chemical shift.NMR chemical shift can be computed using ab-initio methods which actually compute the shielding tensor.

One of the most popular techniques is called GIAO.This originally used for gauge invariant atomic orbitals.More recent version have included ways to relax this condition without loss of accuracy and subsequently the same acronym was renamed gauge including atomic orbitals.The GIAO method is based on perturbation.

NMR spectroscopy is a powerful tool for study the structure dynamics and interaction of biological molecule such as protein and nucleic acids in solution.[4-8]

Information about the structure dynamics and interactions with other RNA molecules, proteins, ions and small ligands can be obtained for RNA and DNA molecules up to 100 nucleotides can be derived from NMR spectroscopic studies.The base-pairing pattern.This includes standard an non standard Watson-crick base pairs and allows verification and prediction of the secondary structure elements of RNA and determination of the base-pair dynamics.[9-14]

Even in the early NMR studies of RNA molecules in the 1970,s it was clear that the region of the imino proton resonances of the guanines and uracils.between 10-15 ppm contained valuable information about base pairing in the RNA molecule. These signals are only observable provided that the imino protons are protected from exchange with the bulk solvent water and are therefore involved in hydrogen bonding. By counting the number of imino proton resonances it is essentially possible to count the number of base pairs.

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The elucidation of base-pairing and more complex hydrogen-bonding patterns in RNA by NMR spectroscopy was the discovery that sizeable scalar coupling across an N-H…N-type hydrogen bond can be observed between the nitrogen atom and proton of the hydrogen bond donor and nitrogen atom of the hydrogen-band acceptor in RNA and DNA through the use of a so-called HNN-COSYexperiment.

The elucidation of hydrogen-bonding pattern involving carbonyl groups as acceptor might benefit from chemical shift analysis.

At the 28 possible base-pairing schemes between the four commen nucleobase guanine(G),adenine(A),cytosine(C) and thymine(T)[or uracil(U)] involving at least two hydrogen bonds nature use relatively.In double stranded DNA pairing between the complementary bases G and C as well as A and T is predeminatly according to the Watson-crick fashion.This pairing scheme allows for antiparallel strand orientation (aps-DNA) in A,B and Z-DNA.The H-bonding patterns between complementary bases are of the reversed Watson-crick (or Donohue) type.[15-18]

Triple-helical DNA was discovered in 1957 not long after the structure of double-stranded DNA had been established.

Four-strand DNA composed of two H bonded DNA duplexes has been implicated in DNA exchange processes.Four stranded DNA structures occur at the ends of chromosomes and consist of cyclic guanine quartets.With four strand RNA,uracil quartet have been stablished.

The structures and interaction energies of guanine and uracil quartets have been determined by B3LYP hybrid density functional calculation.Complexes of metal ion with G-quartets can be classified into different structure type.[19-24] Uracil quartets have not attracted the same interest thus far.An example has been found in an usually stable stable RNA tetraplex formed by parallel strands of r(uG$_4$u).

The u-quartet with N-H…O H bonds has also been investigated at C_{4h}-symmetry.[25 –31]

A recent experiments have shown that difluorotoluen(F) a non polar isoester for thymine T codes efficiently and specifically for adenine(A) in DNA replication.It isunable to form conventional hydrogen bonds with adenine.[32-34]

Ab-initio quantum-chemical calculation with inclusion of electron correlation have recently provided a relatively consistent energies and geometries.

If we assume that a Vander waals interactions is characterized by distance between the base pairs corresponding to the sum of Vander waals radii the calculated base pair geometries indicate that the interaction cannot be accounted for by a Vander waals interaction alone.

The interaction energy is much smaller than far any other Watson-crick or non-canonical base pair with standartd bases but again larger than expected for a Vander waals interaction alone.

The expression for the nuclear shielding for atom A becomes:

$$\sigma_A = <\psi_0 | p_2^{\sigma} | \psi_0 > + \sum_{i=1}^{\infty} \frac{<\psi_0 | P_1^{pso} | \psi_i><\psi_i | L | \psi_0> + <\psi_0 | L | \psi_i><\psi_i | p_1^{pso} | \psi_0>}{E_0 - E_i}$$

All the cperatores p_2^{σ} and p_1^{σ} are gauge dependent relating to the position of atom A.[35]

The natural bonding orbital analysis (NBO) program the analysis of a many-electron molecular were function in terms of localized electron-pair bonding units.The program carries out the NAO 's , NHO 's ,NBO 's and NLMO 's in the open-shell case the analysis performed inters of different NBO 's for different spin based on distinted density matrices for α and β spin.The second-order perturbative estimate of donor-acceptor interactions in NBO basis.[36-37]

Computational Details:

Molecular geometry was optimized be energy at B3LYP/6-31G(d) in chloroform solvent using the Gaussian 98 set programs.

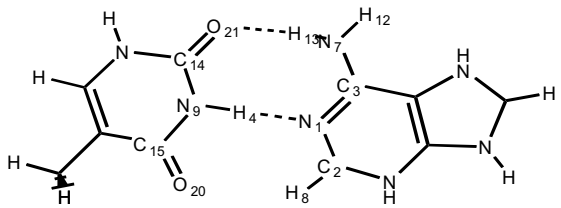

Fig.1. Molecular structure of A:T

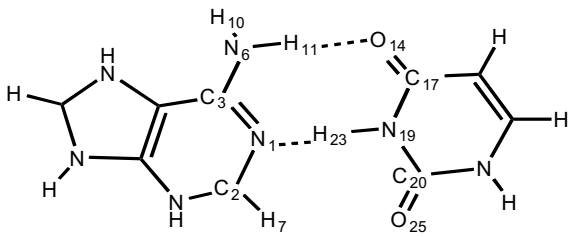

Fig.2. Molecular structure of A:U

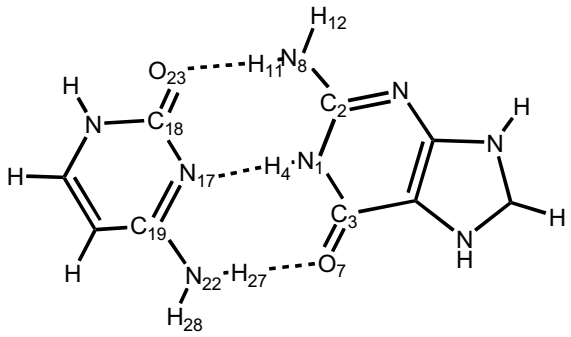

Fig.3. Molecular structure of G:C

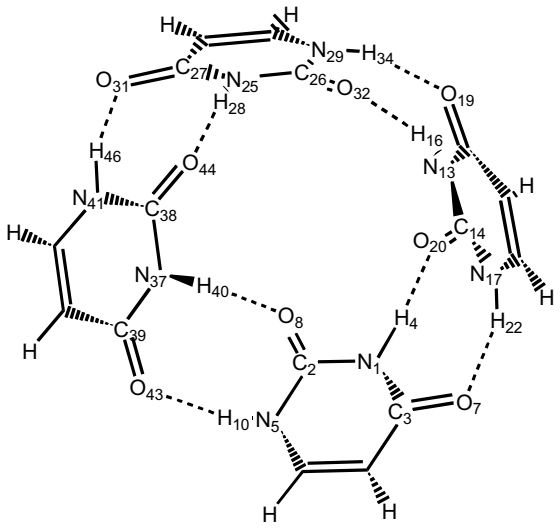

Fig.4. Molecular structure of U quartet.

We have performed the second-order magnetic response of Adenine-thymine , Guanine-cytosine , Adenine-uracil.In Watson-crick fashion and u-quartet we use the gauge including atomic orbital (GIAO) method which is implemented in the gaussian 98 program to predict the NMR shielding tensor σ of AT , GC-AU and u-quartet.

We have:

$$\sigma_{iso} = \frac{\sigma_{xx} + \sigma_{yy} + \sigma_{zz}}{3}$$

Where σ_{xx} , σ_{yy} , σ_{zz} are the principle axis value of σ the results calculation by using density functional investingation are summarized in table

We have been obtained anisotropy ($\xi=|\sigma_{33}-\sigma_{iso}|$) and asymmetry ($\eta= |\sigma_{22}-\sigma_{11}|/\xi$) in AT, GC, AU and U-quartet.

We have performed NBO calculation in one bond in A:T, G:C, A:U and U-quartet. We have evaluated hybridation coefficient for bonds ,lowest occupancy orbitals ,donor and acceptor, natural population analysis, percent total lewis orbitals, percent core and valence orbitals.

We performed SCRF=dipole for optimization in chloroform solvent (radious:4Å dielectric constant:4.9).

CONCLUSION AND DISCUSION:

We have optimized A:T, G:C, A:U & U quartet at B3LYP/6-31G(d) in chloroform solvent (Tabels: IV, VI)

We have performed calculation NMR shielding tensors (Tables I, II) .We have evaluated anisotropy, asymmetry and NBO calculation in A:T, G:C, A:U in Watson-crick fashion and u-quartet. (Tabels III,V, VII, VIII).

Table 1. B3LYP/6-31G(d) calculation of isotropy ,σ_{iso} in ppm ,of the nuclear magnetic shielding tensor σ for atomes found by using GIAO method in chloroform

A:T						G:C						A:U					
Atom	σ_{iso}	η	ζ	TMS	exp (ppm)	Atom	σ_{iso}	η	ζ	TMS	exp (ppm)	Atom	σ_{iso}	η	ζ	TMS	exp (ppm)
N1	37.8	0.25	211			N1	109	0.93	62			N1	38	0.24	210		
C2	41.9	0.19	86	137		C2	45	0.73	70	134		C2	42	0.3	85	137	
C3	43.5	0.08	91	136		C3	40.2	0.34	61	139		C3	43	0.06	91	136	
H4	19.8	0.97	12.6	13.4	12.6	H4	21	0.74	13	12.6		N6	147	1.7	22		
N7	179	2.2	21			O7	39	0.29	299			H7	24	0.3	6.4	9.7	8.9
H8	23.5	0.14	6.5	9.8	9	N8	180	43	0.4			H10	27.5	0.4	7.9	5.7	
N9	92.9	0.82	62			H11	23.2	1.4	13	10	9.3	H11	24.4	1.2	10.9	8.9	8.9
H12	27.5	0.3	8	5.7		H12	28.9	1.3	6.3	4.4	12	O14	-25	0.23	342		
H13	24.5	1.3	11	8.8	8	N17	55	0.46	162			C17	33	0.16	70	146	
C14	46.8	0.4	51	132		C18	44	1.5	56	136		N19	91	0.8	64		
C15	35.7	0.65	65	144		C19	34	0.07	97	146		C20	50	1.8	46	129	
O20	64	0.72	272			N22	161	0.3	23			H23	19.5	0.9	13	3.8	13
O21	64	0.04	229			O23	43	0.12	227			O25	30	0.16	226		
						H27	24	1.3	10	9.3	8.5						
						H28	38	0.37	16	5							

Table 2. B3LYP/6-31G(d) calculation of isotropy ,σ_{iso} in ppm ,of the nuclear magnetic shielding tensor σ for atomes found by using GIAO method in chloroform

Atom	σ_{iso}	η	ζ	TMS	Atom	σ_{iso}	η	ζ	TMS
N1	58.97	0.07	5.2		H22	22.2	1.1	6.2	10.4
C2	41.3	2.7	20.2	148	N25	85.9	13.5	5	
C3	27.8	0.78	15.5	162	C26	41.3	2.8	20	148
H4	22	3.1	3.5	10.2	C27	27.8	0.83	15.5	162
N5	112	0.63	19		N29	112	0.63	16	
O7	-23.3	1.7	63.5		O31	-23.6	2.7	63.2	
O8	26.4	0.95	8.7		O32	26	0.9	11	
H10	22.2	1.23	6.3	10.4	N37	86	12.5	5.5	
N13	85.9	12	5.8		C38	41.3	2.8	20.6	148
C14	41.3	2.7	20.7	148	C39	27.8	0.675	16	162
C15	27.8	0.6	16.6	162	H40	22	3.1	3.6	10.2
H16	22	3.14	3.5	10.2	N41	112	0.46	19	
N17	112	0.53	19		O43	-22.9	1.84	62	
O19	-23.3	1.94	61		O44	26	1.6	10.2	
O20	26.1	1.4	8.7		H46	22.2	1.2	6.2	10.4

We found that:

In Adenine-uracil, chemical shift H_{11} is 8.92ppm (exp:7.5-8.5), chemical shift H_7=8.9ppm and chemical shift H_{23} equal 13.04 (exp:13-15ppm).

Chemical shifts are in excellent agreement with experimental data.

ForH_{23} $\Delta\sigma_{iso}=\sigma_{iso\ Au}-\sigma_{isou}$ is 7ppm because H-bond in H_{23} in A:U RN_1-H_{23}=1.836Å(exp:1.82 Å) and R O_{14}-H_{11} equal 1.92 Å (exp:1.93 Å) then distances agreement with experiment data.

NMR shielding tensors in Au summarized in table II.

NBO calculation in Au tabulated in tables III,V.

In Guanine-cytosine:

Chemical shift H_{11} is 9.3ppm (exp:8-9ppm), chemical shift H_4 is 12ppm (exp:12-13ppm) and chemical shift H_{27} equal 8.5ppm (exp:8-9ppm), chemical shift in chloroform in H_4, H_{11} and H_{27} at H-bonding are in excellent agreement with experimental data.

In here $\Delta\sigma_{isoH4}$=6.1ppm (H-bonding), $\Delta\sigma_{isoH11}$ = σ_{isoH11}Gc- σ_{isoH11}G =6.4ppm and $\Delta\sigma_{isoH27}$ = σ_{isoH27} Gc- σ_{isoH27} C =3.8 because H-bonding chemical shift hydrogens in H-bonding larger than Guanine and Cytosine.

In Gc $R_{H4\text{-}N117}$ is1.894Å (exp:1.89Å), $R_{O7\text{-}H27}$ =1.97Å (exp:2.08Å) and $R_{H11\text{-}O23}$ =1.729Å (exp:1.71Å). Distances are agreement with experimental data.

In AT: chemical shift H4 at chloroform solvent is 12.6ppm.In H_8 is9ppm and in H_{13} is8ppm, $\Delta\sigma_{isoH4}$ is 4.2ppm (H-bonding)

$R_{N1\text{-}N9}$ is 2.902Å (exp:2.82Å), $R_{N7\text{-}O21}$ is 2.93Å (exp:2.98Å) and $R_{C2\text{-}O20}$ =3.71Å (exp:3.52Å)

$\Delta\sigma_{isoH4}$ = σ_{isoH4}AT-σ_{isoH4}A = 3.6ppm (Ref:3ppm)

Table 3. NBO calculation in A:T,A:Uand G:C

A:U		A:T		G:C							
atom	Population	atom	population	atom	population	molecule	total lewis	core	valence	LP donor	acceptor
N1	7.6	N1	7.6	N1	7.8	A:U	96.7	36	91.6	O14	N6-H11
C2	5.7	C2	5.7	C2	5.2	A:U				N19	N1
C3	5.5	C3	5.5	C3	5.15	A:U					
N6	7.8	N7	7.8	H4	0.48	G:C	97.1	38	97.5	O25	C2-H7
H7	0.75	H8	0.75	O7	8.8	G:C				O23	C17-H18
H10	0.58	N9	7.7	N8	7.9	G:C				O23	C18-N21
H11	0.53	H12	0.58	H11	0.5	G:C				O23	N8-H11
P14	8.7	H13	0.53	H12	0.57	G:C				N17	N1-H4
C17	5.3	C14	5.15	N17	7.8	G:C				O7	N22-H27
N19	7.7	C15	5.32	C18	4.9	A:T	96.9	38	97.6	O21	N9-C14
C20	5.2	O20	8.6	C19	5.4	A:T				O20	N9-C15
N23	0.53	O21	8.69	N22	7.7	A:T				O20	C2-C8
O25	8.6			O23	7.9	A:T				O21	N7-H13
				H27	0.45	A:T				O21	C14-N18
				H28	0.56	A:T				N1	H4-N9

Table 4. Optimized bond length of A:T,G:C,A:U in the chloroform with 6-31G(d) basis set

A:T		G:C		A:U	
Bond	**Distance (Angstrom)**	**Bond**	**Distance (Angstrom)**	**Bond**	**Distance (Angstrom)**
N9-H4	2.9	N1-H4	1.04	O14-C1	1.23
H13-C14	2.78	N8-O23	2.76	N19-H23	1.04
H8-O20	3.72	N1-N17	2.94	C20-O25	1.22
H13-O21	1.91	H12-O23	3.36	H11-O14	1.92
N1-H4	1.86	O7-H27	1.97	N1-H23	1.84
H8-O20	2.9	C3-H27	2.85	H7-O25	2.86
				N6-O14	2.94
				N1-N19	2.88
				H7-C20	3.56
				N6-H11	1.02

Table 5. Hybridation coefficient of bonds calculated by NBO method

	Bond		**Occupancy**	**Type**
A:T	N1-C2	$0.78SP^{1.82}$ (N) + $0.62SP^{2.02}$(C)	1.99013	σ
	N1-C3	$0.77SP^{2.02}$(N) + $0.63SP^{2.38}$(C)	1.9829	σ
	C2-H8	$0.79SP^{2.1}$(C) + 0.61S (H)	1.97951	σ
	C3-N7	$0.64SP^{2.05}$(C) + $0.76SP^{1.73}$(N)	1.99209	σ
	N7-H13	$0.79SP^{1.75}$(N) + 0.45S (H)	1.9822	σ
	C14-O21	$0.47SP^{1}$(C) + $0.88SP^{1}$(O)	1.99493	π
	N9-C14	$0.78SP^{1.97}$(N) + $0.62SP^{1.78}$(C)	1.98863	σ
	N9-H4	$0.90SP^{2.02}$(N) + 0.43S (H)	1.96675	σ
	N9-C15	$0.79SP^{2.01}$(N) + $0.61SP^{2.49}$(C)	1.98508	σ
	C15-O20	$0.59SP^{2.02}$(N) + $0.80SP^{1.58}$(O)	1.99579	σ
G:C	N1-C2	$0.78SP^{2.03}$(N) + $0.62SP^{2.08}$(C)	1.98698	σ
	N1-C3	$0.79SP^{2.01}$(N) + $0.61SP^{2.28}$(C)	1.9871	σ
	C2-N8	$0.39SP^{1}$(C) + $0.90SP^{1}$(N)	1.99168	π
	C3-O7	$0.59SP^{2.23}$(C) + $0.80SP^{1.95}$(O)	1.99525	σ
	N1-H4	$0.91SP^{1.96}$(N) + 0.41S (H)	1.97219	σ
	N8-H12	$0.84SP^{2.65}$(N) + 0.53S (H)	1.98754	σ
	C18-N17	$0.78SP^{2.2}$(C) + $0.62SP^{1.81}$(N)	1.98755	σ
	C19-N22	$0.64SP^{1}$(C) + $0.87SP^{1}$(N)	1.98608	π
	N22-H27	$0.93SP^{1.63}$(N) + 0.35S (H 0 $0.93SP^{1.63}$(C) + 0.35S (N)	1.97912	σ
A:U	N1-C2	$0.78SP^{1.8}$(N) + $0.62SP^{2.02}$(C)	1.99023	σ
	N1-C3	$0.77SP^{2}$(N) + $0.63SP^{2.42}$(C)	1.98273	σ
	C3-N6	$0.64SP^{2.03}$(C) + $0.70SP^{1.73}$(N)	1.99209	σ
	C2-H7	$0.79SP^{2.1}$(C) + 0.61S (H)	1.979633	σ
	N6-H11	$0.89SP^{1.74}$(N) + 0.44S (H)	1.98099	σ
	C17-O14	$0.87SP^{1}$(C) + $0.47SP^{1}$(O)	1.98569	π
	C17-N19	$0.62SP^{2.18}$(C) + $0.78SP^{1.88}$(N)	1.98940	σ
	N19-C20	$0.78SP^{2.12}$(N) + $0.62SP^{1..95}$(C)	1.98539	σ
	C20-O25	$0.59SP^{1.78}$(C) + $0.80SP^{1.63}$(O)	1.99584	σ
	C20-O25	$0.54SP^{1}$(C) + $0.84SP^{1}$(O)	1.99298	π
	N19-H23	$0.90SP^{2.01}$(N) + 0.42S (H)	1.96597	σ

In NBO ,we found that : in A:T donor is N1 and acceptot is H4-N9 , IN A:U donor is N1 and acceptor is 19, in G:C donor is N17 and acceptor is N1-H4(H-Bonds).

Table 6. Optimized bond length of A:T,G:C,A:U in the chloroform with 6- 31G(d) basis set

Bond	distance	Bond	distance	Degree
N1-H4	1.031	O7-H22	1.7766	θ 14 20 4=122
C3-O7	1.263	H4-O20	1.845	θ 42 25 48=123
C2-O8	1.260	O8-H40	1.838	
N5-H10	1.034	H10-O43	1.7733	
C15-O19	1.263	O44-H28	1.839	
H16-N13	1.031	N41-H46	1.033	
C14-O20	1.260	H34-O19	1.777	
N14-H22	1.033	H16-O32	1.842	
N29-H34	1.033	O7-N17	2.769	
C26-O32	1.260	O8-N37	2.821	
N25-H28	1.031	N5-O43	2.767	
C27-O31	1.263	N25-O44	2.820	
C38-O44	1.260	O31-N41	2.770	
N37-H40	1.031	O19-N29	2.770	
C39-O43	1.263	N13-O32	2.823	
N41-H46	1.033			

Table 7. Hybridation coefficient of bonds calculated by NBO method

Bond	hybridation coefficient	Bond	hybridation coefficient
N1-C2	$0.79SP^{1.89}$ (N) + $0.61SP^{2.03}$(C)	C26-O32	$0.59SP^{1.87}$(C) + $0.80SP^{1.5}$(O)
N1-C3	$0.79SP^{1.78}$ (N) + $0.60SP^{2.56}$(C)	C26-N29	$0.60SP^{2.14}$(C) + $0.79SP^{1.89}$(N)
N1-H4	$0.85SP^{2.41}$(N) + 0.52S (H)	N29-C33	$0.78SP^{1.79}$(N) + $.61SP^{2.6}$(C)
C2-N5	$0.61SP^{2.14}$(C) + $0.79SP^{1.89}$(N)	C27- N25	$0.79SP^{1.78}$(C) + $0.60SP^{2.56}$(N)
C2-O8	$0.59SP^{1.87}$ (C) + $0.80SP^{1.5}$(O)	N25-H28	$0.83SP^{2.41}$(N) + 0.62S (H)
N5-H10	$0.85SP^{2.48}$(N) + 0.52S (H)	C27-O31	$0.55SP^{2.05}$(C) + $0.83SP^{1.4}$(O)
C14-O20	$0.59SP^{1.87}$(C) + $0.80SP^{1.5}$(O)	C38-O44	$0.59SP^{1.87}$ (C)+ $0.80SP^{1.5}$(O)
C14-N17	$0.61SP^{2.14}$(C) + $0.79SP^{1.89}$(N)	C38-N37	$0.78SP^{1.89}$ (C) + $0.61SP^{2.03}$(N)
N17-H22	$0.85SP^{2.4}$(N) + 0.52S (H)	N41-H46	$0.85SP^{1.82}$ (N)+ 0.62S (H)
C14-N13	$0.79SP^{1.89}$ (C) + $0.61SP^{2.03}$(N)	N37-H40	$0.85SP^{2.48}$(N) + 0.52S (H)
N13-C15	$0.79SP^{1.78}$ (N) + $0.60SP^{2.56}$(C)	C39-O43	$0.59SP^{2.05}$(C) + $0.80SP^{1.4}$(O)
C15-O19	$0.59SP^{2.05}$(C) + $0.80SP^{1.4}$(O)		

Table8. NBO calculation in U quartet

Atom	Natural popu.	Atom	Natural popu.	Lp Donor	Acceptor
N1	7.65	N25	7.650	O31	N25-C27 BD^*
C2	5.211	C26	5.211	O31	C27-C30 BD^*
C3	5.378	C27	5.378	O31	N25-C26 BD^*
H4	0.5138	H28	0.5137	O32	N25-C26 BD^*
N5	7.620	N29	7.620	O32	N25-C27 BD^*
O7	8.650	O31	8.650		
O8	8.642	O32	8.642		
H10	0.5169	C33	5.959		
N13	7.650	N37	7.650		
C14	5.211	C38	5.211		
C15	5.378	H40	0.5137		
H16	0.5138	N41	7.620		
N17	7.620	O43	8.650		
O19	8.650	O44	8.642		
O20	8.642				
H22	0.5171				

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