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Structural and NBO Studies of Anomeric Effects in Polyoxa, Polyaza and Polycyclics Compounds

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The geometries of four hetrocyclic (polyaza polyoxa polycyclic) compounds have been completely optimized at B3lyp/6-31G** and HF/6-31G* *ab initio* quantum mechanical levels and compared with the X-ray structural data. Natural bond orbital (NBO) analysis has carried out quantitatively to estimate delocalization in O-C-N units. The optimized geometrical parameters agree with the acceptor-donor interaction scheme of NBO analysis. The results show that the structures of considered compounds affected by the anomeric effect.

Key Words: NBO, Anomeric effects, Polyoxa, Polyaza, Polycycles.

INTRODUCTION

The interest in the clinical use of chelating agents as vehicles for delivery of metals to sites in biological systems has led to the study of a large number of many cyclic polyoxa-polyaza ligands. The structure of polycyclic polyoxa polyaza affected mainly by stereoelectronic effects termed as anomeric effect. In this work, a theoretical study of stable structures of four new polycyclic, polyoxa and polyaza and the influence of anomeric effect in their structures have been presented. In addition, the orbital interactions, which cause the anomeric effect, using the natural bond orbital (NBO) analysis is also studied.

The anomeric effect observed more than 45 years ago in carbohydrate derivatives and become an intensively studied and documented topic[1]. Although the bulk information arises from carbohydrates, the anomeric effect is a more general phenomenon. The anomeric effect originally denoted the preference of electronegative substitutes X at the anomeric center of pyranose for the axial configuration. It is also observed in other heterocycles, as well as in acyclic structures, providing a motif C···Y···C···X

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(where Y is a heteroatom with an appropriately oriented unshared pair of electrons and X an electronegative group) is present and many reviews have summarized the phenomenon[2,3]. This is known as the generalized anomeric effect. Although the most common examples of anomeric effect has been observed in cyclic oxygen-containing carbohydrates, there have been recent studies which examine such an effect in phosphorous, sulfur, silicon and nitrogen containing compounds[4].

Theoretically, this behaviour first interpreted in terms of electrostatic interactions (repulsive parallel dipoles) and later on in terms of MO theory. The later interpretation was well endorsed by quantum chemical calculations at various levels and consists in a 2 electrons 2 orbital $n \rightarrow \sigma^*$ stabilizing interaction. The magnitude of which depends on the overlap (*i.e.* relative orientation) of the two orbital and on the energy gap between them.

In terms of valance-bond theory, one may involve equivalently, double bond-no bond resonance or hyperconjugation. These MO arguments account well for the structural characteristics of the anomeric effect, in contrast to the electrostatic rational. We consider the R-O-C-N-R' anomeric unit to be the most interesting, science it incorporates a good donor (N) adjacent to an excellent acceptor (O) and is, thus, capable of exhibiting two unequal anomeric effects: a strong $lp_N \rightarrow \sigma^*_{C\text{-}O}$ interaction and a week $lp_O \rightarrow \sigma^*_{C\text{-}N}$ one[5].

The existence of an anomeric effect in a system is manifest in its structure, *e.g.*, shorter or longer anomeric bonds and larger anomeric bond angles. Hence, in pyranose derivatives electron transfer results in the lengthening of the exocyclic (C—X) bond, in the contraction of the exocyclic C—O bond by increasing its double-bond character and in the opening of the O—C—X angles as compared to its normal tetrahedral value.

A considerable variety of intermolecular stereoelectronic effects and bonding phenomena has subsequently analyzed with NBO technique[6,7]. The NBO method has been shown[8] to be a useful tool for the analysis of the type of interactions involved in the anomeric effect where the delocalization is a lone pair- σ^* density shift.

This work presents a theoretical *ab initio* study of anomeric effect in four following molecules with two O-C-N motifs in five member rings that aim to shed light on the existence and origin of the anomeric effect in these compounds.

1) *cis*-2,8-diphenyl-5-hydroxymethyl-1-aza-3,7-dioxabicyclo[3.3.0]octane,
2) 6, 8-di-(2-aminopyridyl)-2,4-dioxa-6,8-diazabicyclo[3.3.0]octane,
3) 4,8-di-(2-aminopyridyl)-2,6-dioxa-4,8-diazabicyclo[3.3.0]octane,
4) 1,3-di(2-aminopyridyl) 4,5-dihydroxy imidazolidine.

EXPERIMENTAL

All the calculations reported here have performed with the GUASSIAN 98 program package[9]. Geometry optimizations were carried out in all molecules at HF/6-31G* level and B3ly/6-31G* and B3ly/6-31G** levels without any symmetry restriction. Analytical vibrational frequencies at all levels have been calculated and used to determine the nature of the located stationary points. Thus, all the founded stationary points were global minima. The natural bond orbital analyses (NBO) were also performed at all computational levels.

Energy stabilizations examined in terms of delocalization of electron density from filled orbital to empty neighboring orbital. The energy associated with the anti-bonds have determined by deleting those orbital from the basis set and recalculating the total energy to evaluate the associated variational energy lowering. In the present work, delocalization with nitrogen and oxygen lone pairs as donors have considered.

RESULTS AND DISCUSSION

cis-2,8-Diphenyl-5-hydroxymethyl-1-aza-3,7,dioxabicyclo[3.3.0]octane

tris(Hydroxymethyl)aminomethane can react with benzaldehyde (1:2 molar ratio) to produce *cis*-2,8-diphenyl-5-hydroxymethyl-1-aza-3,7-dioxabicyclo[3.3.0]octane. The structure of which has been confirmed by NMR spectroscopy and X-ray crystallography[10]. Because of the presence of two consecutive O-C-N motifs, we considered this compound to be a suitable model to study the anomeric effect. It has shown that a 5-membered ring orients polar substituents at the anomeric center in axial or pseudo-axial orientation much stronger than the six-member pyranose ring[11].

Fig. 1 presents the optimized geometry of molecule 1. Selected bond distances, bond angles and torsion angles of X-ray and corresponding computationally optimized values for molecule 1 have given in Table-1. The calculated mean square error (mse) show that the DFT results have better agreement with the X-ray data than the HF calculation, also adding the diffuse functions at the DFT level of calculation do not improve the results. The two-phenyl groups are in a *cis* configuration: pseudo axial for that linked to carbon 3 and pseudo equatorial for that attached to carbon 4. The two five membered rings are significantly puckered in opposite directions.

This molecule has two anomeric motifs (N1-C4-O10, N1-C3-O13). Computed geometry at all levels and X-ray data in Table-1 show that the N1-C3 bond is shorter than both N1-C4 and N1-C2 (even shorter than the usual value of N-C bond length 1.48 Å). N1-C3 is the shortest C-N bond in molecule 1. The C3-O13 is longer than C4-O10 for X-ray and theoretical calculation but the difference for X-ray results is smaller.

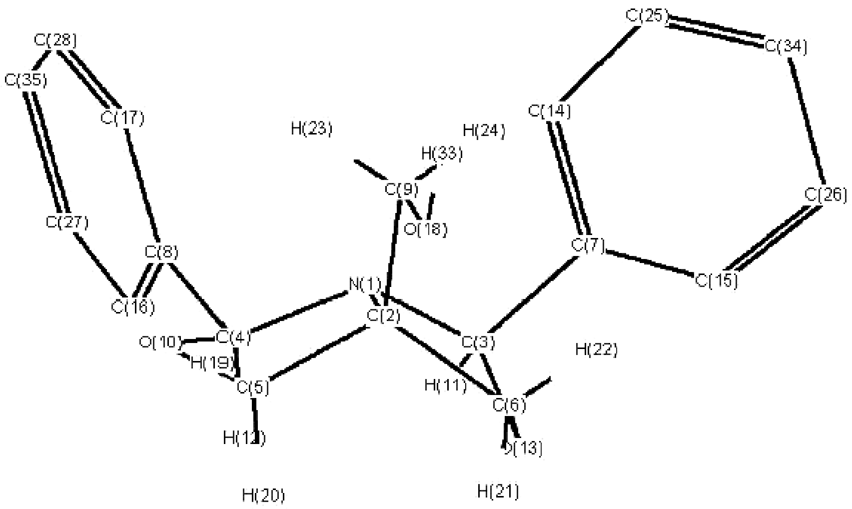

Fig. 1. The optimized geometry of compound **1**. The numbering is shown on the compound structure. The hydrogens of the phenyl group have been omitted for sake of simplicity

TABLE-1
SELECTED STRUCTURAL DATA OF COMPOUND **1**[a]

Structural parameter	X-ray	HF/6-31G*	Blyp/ 6-31G*	B3lyp/ 6-31G**
L				
N1-C2	1.491	1.742	1.490	1.490
N1-C3	1.458	1.450	1.463	1.463
N1-C4	1.477	1.469	1.491	1.491
C3-O13	1.429	1.403	1.432	1.432
C4-O10	1.421	1.390	1.413	1.414
A				
C3-N1-C4	112.90	114.88	114.14	114.15
C3-N1-C2	105.40	106.43	105.87	105.86
C2-N1-C4	105.80	106.94	106.44	106.44
N1-C3-O13	106.00	105.66	106.14	106.15
N1-C4-O10	103.30	104.12	104.23	104.20
D				
O10-C4-N1-C3		142.14	141.72	141.78
O10-C4-N1-C2		24.16	25.31	25.39
N1-C3-O13-C6		-37.86	-39.04	-39.12
N1-C4-O10-C5		-40.49	-41.36	-41.43
mse[b]	0.00	0.64	0.28	0.27

[a]bond length (L, Å), bond, bond angles (Å, °) and dihedral angles (D, °).
[b]mean square error

The conformation of ring A with respect to N1-C3-O13-C6 and lp-N1-C3-O13 torsion angles is *ga* and for ring B is *gg* based on the torsion angles N1-C4-O10-C15 and lp-N1-C4-O10. Oxygen 13 was found noticeably down (0.59 Å for HF, 0.62 Å for DFT calculations and 0.65 Å in X-ray results) the plane, defined by atoms C3-N1-C2 , where as oxygen 10 to be up (0.57 Å for HF, 0.60 Å for DFT calculations) the plane defined by C4-N1-C2. Based on the prescribed positions of O10 and O13, the lone pair of N1 is antiperiplanar to the C3-O13 bond where cannot be antiperiplanar to the C4-O10 bond.

We have used the NBO Fock matrix (HF/6-31G*) to provide an explanation for the anomeric effect in compound 1. The significant donor-acceptor NBO interaction and their second-order perturbation stabilization energies ΔE/(kcal/mol) have shown in Table-2. The lowering of stabilization energies at DFT level of theory than the results at HF level can be attributed to inclusion of electron correlation in the DFT method which results in more delocalization of electrons than the HF method. The NBO results in Table-2 suggest that there are strong interactions in ring A, $lp_{N1} \rightarrow \sigma^*_{C3-O13}$ (8.96 kcal/mol) and $lp_{O13} \rightarrow \sigma^*_{C3-N1}$ (5.64 kcal/mol). In oxazolidine ring B the only noticeable interaction is $lp_{O10} \rightarrow \sigma^*_{C4-N1}$ (7.95 kcal/mol).

TABLE-2
SIGNIFICANT DONOR-ACCEPTOR NBO INTERACTION AND THEIR SECOND-ORDER ENERGIES ΔE/(kcal/mol) FOR COMPOUND 1

Donor NBO	Acceptor NBO	HF/6-31G*	B3lyp/6-31G*
lp(1)N1	BD* C3-O13	9.26	6.86
lp(1)N1	BD* C9-O18	1.26	0.95
lp(1)O10	BD* N1-C4	2.02	1.32
lp(2)O10	BD* N1-C4	7.58	6.21
lp(1)O13	BD* N1-C3	2.52	1.69
lp(2)O13	BD* N1-C3	5.60	4.55
lp(2)O13	BD* C3-C7	8.94	7.08
lp(1)O18	BD* N1-C2	0.95	0.71
lp(1)O18	BD* C2-C9	1.54	1.02

From above considerations, we have concluded that the conformation of ring A shows cross endo-anomeric effect resulting from delocalization of electrons over the bond sequence N1-C3-O13 and there is a weaker anomeric $lp_{O10} \rightarrow \sigma^*_{C4-N1}$ interaction in ring B.

6, 8-Di-(2-aminopyridyl)2,4-dioxa 6,8-diazabicyclo[3.3.0]octane

Condensation of 2-aminopyridine with glyoxal and formaldehyde in acetonitrile[12] proceed a mixture of two bicyclooctanes compounds **2** and **3**.

The optimized geometry and numbering have shown in Fig. 2. Selected bond distances, bond angles and torsion angles of optimized geometry have shown in Table-3. This molecule has two anomeric O-C-N motifs. The C6-N2 and C7-N3 bond lengths are smaller than C1-N2 and C1-N3 and are all rather smaller than usual value of 1.48Å. The C6-O11 and C7-O10 bond lengths are superior to C18-O11 and C18-O10 bond lengths. The marked sp^2 character of nitrogen atoms, N2 and N3, have presented by significant widening of nitrogen bond angles. Of special interest are the sums of bond angles: 357.7 for N2 and 357.8 for N3 compared with sp^3 standard value 328.5.

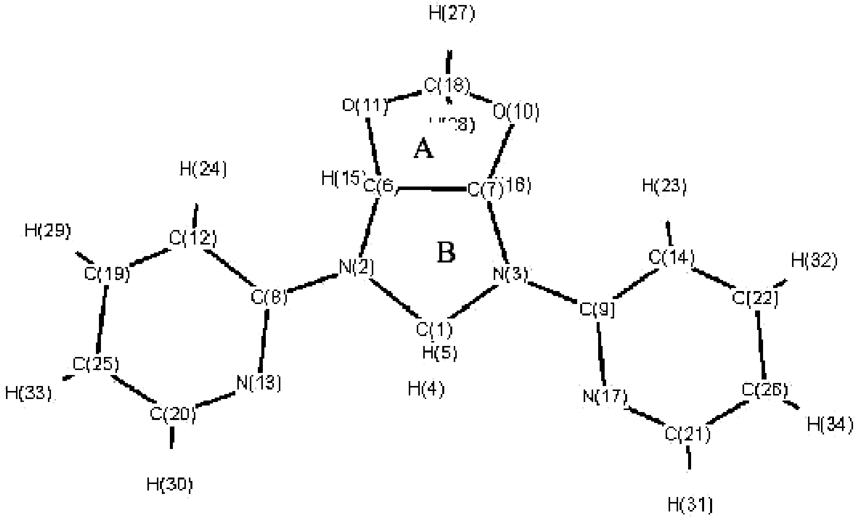

Fig. 2. Optimized geometry of compound **2**. The numbering is shown on the compound structure

The N2-C6-O11 and N3-C7-O10 angles are significantly greater than sp^3 standard value (114.73 in HF computation). It is most noteworthy that both pyridyl rings lie in the plane of the central ring (torsion angle involving the atoms C14-C9-N3-C7 and C12-C8-N2-C6 are 15.15 and 15.1, respectively). The C6-C7-N3-C1 and N3-C7-C6-N2 torsion angles in Table-3, show that the imidazolidine ring (ring A) is essentially planar. In ring A, the C18 atom deviates from the mean plane defined by O10-C7-C6-O11 by 0.51Å.

NBO results of stabilization energies in Table-4, show that there are strong interactions $lp_{N2} \rightarrow \sigma^*_{C6-O11}$ and $lp_{N3} \rightarrow \sigma^*_{C7-O11}$ (each 18.47 kcal/mol) and weaker but non-negligible $lp_{O10} \rightarrow \sigma^*_{C7-N3}$ and $lp_{O11} \rightarrow \sigma^*_{N2-C6}$ (each 15.7 kcal/mol) interactions. The above considerations leads to an anticipated anomeric effect in O-C-N moiety due to two cross hyperconjugation. The conformations of C6-O11-C18-O10 and O11-C18-O10-C7 is *gg*. The C18-O11 and C18-O10 bond lengths are equal but. NBO studies show an equal $lp_{O10} \rightarrow \sigma^*_{C18\text{-}O11}$ and $lp_{O11} \rightarrow \sigma^*_{C18\text{-}O10}$ interactions (8 kcal/mol).

TABLE-3
SELECTED STRUCTURAL DATA FOR COMPOUND **2**[a]

Structural parameter	HF/6-31G*	B3lyp/6-31G*	B3lyp/6-31G**
C1-N2	1.449	1.459	1.459
C1-N3	1.449	1.459	1.459
N2-C6	1.426	1.436	1.436
N3-C7	1.426	1.436	1.436
C7-O10	1.397	1.426	1.426
C6-O11	1.397	1.426	1.426
C18-O11	1.392	1.392	1.416
A			
C1-N2-C8	120.8	120.8	120.8
C1-N2-C6	113.8	113.8	114.1
C6-N2-C8	123.3	123.3	123.4
D			
C18-O11-C6-N2	92.10	91.064	88.596
N3-C7-C6-N2	0.02	0.002	0.001

[a]bond length (L, Å), bond, bond angles (Å, °) and dihedral angles (D, °).

TABLE-4
SIGNIFICANT DONOR-ACCEPTOR NBO INTERACTION AND THEIR SECOND-ORDER ENERGIES ΔE/(kcal/mol) FOR COMPOUND **2**

Donor NBO	Acceptor NBO	HF/6-31G*	B3lyp/6-31G*
lp(1)N2	BD* C6-O11	18.47	14.61
lp(1)N2	BD* C8-O13	61.82	47.79
lp(1)O11	BD* O10-C18	2.39	1.11
lp(2)O11	BD* N2-C6	15.70	11.31
lp(2)O11	BD* O10-C18	7.55	6.36
lp(2)O10	BD* N3-C7	15.70	11.31
lp(2)O10	BD* O11-C18	7.55	6.36
lp(1)N3	BD* C7-O10	18.47	14.61

Due to the symmetry and lack of any donor-acceptor, interaction in ring A, we argued that there is not anomeric interaction in N2-C1-N3 unit.

4,8-Di-(2-aminopyridyl)-2,6-dioxa-4,8-diazabicyclo[3.3.0]octane

The optimized geometry of compound **3** has shown in Fig. 3. Selected bond distances, bond angles and torsion angles of optimized geometry have shown in Table-5.

TABLE-5

SELECTED STRUCTURAL DATA OF COMPOUND **3**[a]

Structural parameter	HF/6-31G*	B3lyp/6-31G*	B3lyp/6-31G**
L			
C1-N3	1.448	1.460	1.460
C1-O2	1.399	1.421	1.422
C15-O9	1.399	1.421	1.422
C15-O10	1.448	1.460	1.460
N3-C7	1.430	1.460	1.441
C7-O9	1.390	1.417	1.417
N10-C6	1.430	1.440	1.441
O2-C6	1.390	1.417	1.417
C1-H4	1.077	1.091	1.091
C1-H5	1.085	1.100	1.100
C15-H22	1.085	1.100	1.100
C15-H21	1.077	1.091	1.091
A			
C1-N3-C8	122.51	122.65	122.64
C8-N3-C7	125.58	124.78	124.70
C1-N3-C7	111.87	111.70	111.70
N3-C7-O9	115.46	115.98	115.95
C6-N10-C19	125.58	124.77	124.70
C6-N10-C15	111.87	111.70	111.70
C19-N10-C15	122.51	122.66	122.64
N3-C1-O2	103.72	104.23	104.20
N10-C15-O9	103.72	104.23	104.20
D			
C11-C8-N3-C7	2.29	10.26	10.26
C26-C19-N10-C6	2.30	1027	10.27
C11-C8-N3-C1	179.96	178.73	178.73
O2-C1-N3-C7	14.68	15.74	15.83

[a]bond length (L, Å), bond, bond angles (Å, º) and dihedral angles (D, º).

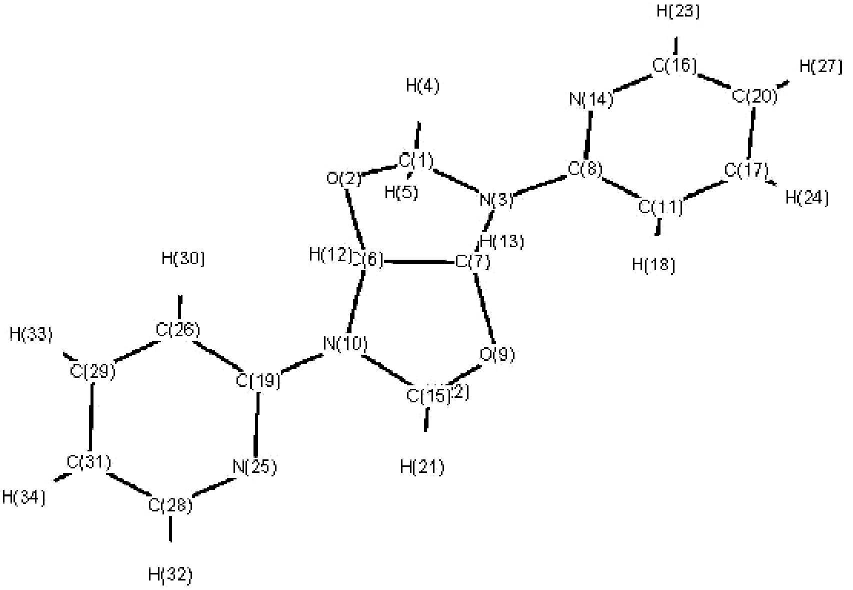

Fig. 3. Optimized geometry of compound **3**. The numbering is shown on the compound structure

There are two types of anomeric O-C-N motifs in this molecule. 1) Inter cyclic 2) intra cyclic. The C7-N3 and C6-N10 bond lengths are smaller than C1-N3 and C15-N10 and are all rather smaller than usual value[1] of 1.48Å. The C6-O2 and C7-O9 bond lengths are partially shorter than C1-O2 and C15-O9 bond lengths. The C1-N3 and C1-O2 bond lengths are shorter than standard values. The marked sp^2 character of nitrogen atoms, N10 and N3, has verified by significant widening of nitrogen bond angles. Of special interest are the sums of bond angles: 359.95 for N10 and 359.96 for N3 compared with sp^3 standard value 328.5. The N10-C6-O2 and N3-C7-O9 angles are significantly greater than sp^3 standard value (115.45 in HF computation). The N3-C1-O2 angle is shorter than sp^3 standard value although it is 1 degree greater than molecule 2. The two pyridyl rings lie in the plane of the oxazolidine rings.

The significant results of NBO interactions and their second-order stabilization energies have shown in Table-6. There are two cross hyper conjugation in O9-C7-N3 and O2-C6-N10, $lp_{N10} \rightarrow \sigma^*_{C6\text{-}O2}$ 19.03 kcal mol^{-1} and $lp_{O2} \rightarrow \sigma^*_{C6\text{-}N10}$ 16 kcal mol^{-1} kcal/mol and weaker interactions in O2-C1-N3 and O9-C15-N10, $lp_{O2} \rightarrow \sigma^*_{C1\text{-}N3}$ and $lp_{O9} \rightarrow \sigma^*_{C15\text{-}N10}$ 3.04 kcal mol^{-1} and $lp_{N3} \rightarrow \sigma^*_{C1\text{-}O2}$ and $lp_{N10} \rightarrow \sigma^*_{C9\text{-}O15}$ 1.975 kcal/mol.

TABLE-6
SIGNIFICANT DONOR-ACCEPTOR NBO INTERACTION AND THEIR SECOND-ORDER ENERGIES ΔE/(kcal/mol) FOR COMPOUND 3

Donor NBO	Acceptor NBO	HF/6-31G*	B3lyp/6-31G*
lp(1)N3	BD* C1-O2	1.97	1.44
lp(1)N3	BD* C7-O9	19.03	14.18
lp(1)O2	BD* C1-N3	3.04	2.03
lp(2)O2	BD* C6-N10	16.00	12.53
lp(2)O2	BD* C1-N3	3.41	2.80
lp(1)O9	BD* N10-C15	3.04	2.03
lp(2)O9	BD* N3-C7	16.00	12.53
lp(2)O9	BD* N10-C15	3.41	2.80
lp(1)N10	BD* O2-C6	19.03	14.18
lp(1)N10	BD* O9-C15	1.97	1.44

1,3-Di-(2-aminopyridyl)-4,5-dihydroxy imidazolidine

Condensation of 2-aminopyridine with glyoxal and formaldehyde in water proceed compound[12] **4**. The optimized molecular structure has shown in Fig. 4 and some of the significant bond lengths, bond and torsion angles have presented in the Table-7. From the calculated mean square error it is evident the DFT method is superior than the HF in general.

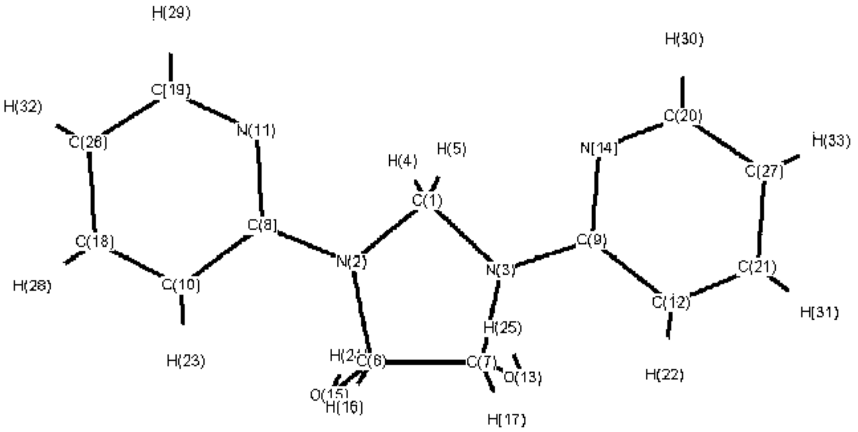

Fig. 4. Optimized geometry of compound **4**. The numbering is shown on the compound

There are unusual structural features in the molecule. The C1, C6 and C8 bond lengths to N2 are smaller than usual value[11] of 1.48 Å. The C6-O12 and C7-O13 bond lengths are shortened. The marked sp^2 character of nitrogen atoms, N2 and N3, is nicely illustrated by significant widening of nitrogen bond angles. Of particular interest are the sums of bond angles: 358.75 for N2 and 352.1 for N3 compared with sp^3 standard value 328.5. Short C-O and C-N bonds as well as tightened N2-C6-O12 and N3-C7-O13 (113.7 and 113.3) leads to an anomeric effect in O-C-N moiety due to two cross hyperconjugation from $n_{N2} \rightarrow \sigma^*_{C6\text{-}O11}$ and $n_{O12} \rightarrow \sigma^*_{C6\text{-}N2}$ ($n_{N3} \rightarrow \sigma^*_{C7\text{-}O13}$, $n_{O13} \rightarrow \sigma^*_{C7\text{-}N3}$). Back donation of electrons from N2 and N3, drastically decrease their pyramidality leading to an increase p character of the N2 and N3 lone pairs. The conformations of lp-N3-C7-O13-H21 and lp-N2-C6-O12-H22 are *ga*.

TABLE-7
SELECTED STRUCTURAL DATA OF COMPOUND **4**[a]

Structural parameter	X-ray	HF/6-31G*	B3lyp/ 6-31G*	B3lyp/ 6-31G**
L				
N2-C6	1.436	1.434	1.444	1.444
C6-O12	1.409	1.395	1.420	1.419
C1-N2	1.454	1.455	1.463	1.464
C1-N3	1.454	1.455	1.463	1.464
N3-C7	1.436	1.434	1.444	1.444
C7-O13	1.409	1.395	1.420	1.419
A				
C1-N2-C8	120.9	120.23	120.59	120.58
C8-N2-C6	123.9	124.34	124.72	124.70
C1-N2-C6	114.3	111.42	112.08	112.12
C1-N3-C9	120.9	120.22	120.59	120.58
C1-N3-C7	114.3	111.49	112.08	112.12
C7-N3-C9	123.9	124.33	124.72	124.701
D				
N3-C7-O13-H25	52.80	55.53	55.58	55.65
N2-C6-O12-H24	52.80	55.46	55.58	55.65
C10-C8-N2-C6	1.72	9.55	6.85	6.82
C12-C9-N3-C7	1.72	9.58	6.85	6.81
mse	0.000	0.94	0.58	0.56

[a] bond length (L, Å), bond, bond angles (Å, °) and dihedral angles (D, °).

The NBO interactions and their second-order stabilization energies have shown in Table-8 that there are two cross hyperconjugation in O12-C6-N2 and O13-C7-N3, $lp_{N2} \rightarrow \sigma^*_{C6\text{-}O12}$ 19.66 kcal mol^{-1} and $lp_{O12} \rightarrow \sigma^*_{C6\text{-}N2}$ 9.77 kcal/mol and $lp_{N3} \rightarrow \sigma^*_{C7\text{-}O13}$ 20.42 kcal mol^{-1} and $lp_{O13} \rightarrow \sigma^*_{C7\text{-}N3}$ 14.8 kcal mol^{-1}.

TABLE-8
SIGNIFICANT DONOR-ACCEPTOR NBO INTERACTION AND THEIR SECOND-ORDER ENERGIES ΔE/(kcal/mol) FOR COMPOUND **4**

Donor NBO	Acceptor NBO	HF/6-31G*	B3lyp/6-31G*
lp(1)N3	BD* C7-O13	21.31	15.21
lp(1)N2	BD* C6-O15	21.31	14.02
lp(2)O13	BD* N3-C7	14.04	11.13
lp(2)O15	BD* N2-C6	14.02	11.04

Conclusion

In this study, the anomeric effect of O-C-N units in five membered molecules have investigated. The quantum mechanical calculations confirmed the anomeric effect in these molecules. We utilized the B3lyp/6-31G**, B3lyp/6-31G* and HF/6-31G* levels of computations to identify the completely optimized geometries. The optimized geometries at DFT level of theory agree better with the X-ray data than the HF in the case of compounds **1** and **4**. In these molecules, the anomeric effect has crucial role in stability and conformational geometry. All of the studied molecules have a cross hyperconjugation system. In addition, there exists evidence of $n_O \rightarrow \sigma^*_{C-N}$ interaction in ring B of the compounds **1** and **2**.

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