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The quantum mechanical study of some of nitrone compounds Using density function theory(DFT , B3LYP/6-31G)

Jaafar .H.Ali and Neda. A . Jassim
Chemistry Dep .,ScienceCollege ,Kerbala Univ.
Kerbala- IRAQ

Abstract

The study involves the application of quantum mechanical calculations using density function theory (DFT) with B3LYP/6-31G on a number of nitrone compounds that containing substitutes (OCH_3 , CH_3, NO_2 , OH , Br , Cl) for the purpose of calculation the equilibrium geometries, energies of HOMO , LUMO orbital , ionization energies , electronic densities , the vibrational modes .

The effect of substitutes on stability of each studied molecule is investigated . The standard thermodynamic functions (U^0 , H^0 , S^0 ,G^0 ,A^0) and Ultraviolet spectra for all substituted nitrone molecules were also investigated.These compounds are compared with the nonsubstituted nitrone compound .

الخلاصة

تضمنت الدراسة تطبيق حسابات ميكانيك الكم باستخدام نظرية دالة الكثافة (DFT) لعدد من مركبات النايترون المشتملة على المعوضات الاتية (OCH_3 , CH_3, NO_2 , OH , Br ,Cl) وذلك لغرض حساب الشكل الهندسي المتوازن ،عزم ثنائي القطب ، طاقات المدارات (HOMO , LUMO)، طاقة التأين ، الشحنات والكثافات الإلكترونية، وكذلك تم حساب الانماط الاهتزازية بالاستناد الى نظرية المجموعة وتم الاستعانة ببرنامج Chemchraft لوصف الحركات الاهتزازية للجزئيات.

فضلا عن ذلك فقد تم دراســة تأثير المجاميع المعوضة على استقراريـه الجزيئة ,وتم حســاب الدوال الثرموداينميكـية (U^0 , H^0 , S^0 ,G^0 ,A^0) ولجميع النايترونات المعوضة كما قورنت مركبات النايترون المعوضة مع مركب النايترون غير المعوض ، كما تم توضيح الاطياف الالكترونية للأشعة الفوق البنفسجية

Introduction

Nitrones have the general chemical formula X-CH=NO-Y. They were first used to trap free radicals in chemical systems and then subsequently in biochemical systems. More recently several nitrones including PBN (α-phenyl-tert-butylnitrone) have been shown to have potent biological activity in many experimental animal models. Many diseases of aging including stroke, cancer development, Parkinson's disease and Alzheimer's disease are known to have enhanced levels of free radicals and oxidative stress[(1)]. Some derivatives of PBN are significantly more potent than PBN and have undergone extensive commercial development in stroke. Recent research has shown that PBN-related nitrones also have anti-cancer activity in several experimental cancer models and have potential as therapeutics in some cancers. Also in recent observations nitrones have been shown to act synergistically in combination with antioxidants in the prevention of acute acoustic noise induced hearing loss[(2)]. The mechanistic basis of the potent biological activity of PBN-related nitrones is not known. Even though PBN-related nitrones do decrease oxidative stress and oxidative damage, their potent biological anti-inflammatory activity and their ability to alter cellular signaling processes cannot readily be explained by conventional notions of free radical trapping biochemistry. This review is focused on our observations and others where the use of selected nitrones as novel therapeutics have been evaluated in experimental models in the context of free radical biochemical and cellular processes considered important in pathologic conditions and age-related diseases.[(3,4)]

The present study was based on density functional theory (DFT) which is a quantum modeling method used in physics and chemistry to investigate the electronic structure(principally the ground state) of many-body systems, in particular atoms, molecules, and the condensed phases. With this theory, the properties of a many-electron system can be determined by using functional,

i.e. functions of another function, which in this case is the spatially dependent electron density. Hence the name density functional theory comes from the use of functional of the electron density. DFT is among the most popular and versatile methods available in condensed-matter physics, computational physics, and computational chemistry. [5,6]

Computational method

Density function theory was developed and applied to the treatment of organic moleculessuch treatment yields the equilibrium geometry and energy values of the molecules in addition to their fundamental vibration frequencies (3N-6) and IR absorption intensities[7,8].

Density function theory method to evaluate the force constants of molecules that are introduced then to the Wilson Secular equation of the following form

$\sum_j L_j (F_{ij} - M_{ij}\lambda) = 0$ ……. (1)

Where , L_j eigen vector coefficients , M atomic mass , F_{ij}force constants ,

Solution of this equation yields vibration frequencies ($\lambda = 4\pi^2 \nu^2 C^2$) and vibration mode eigen vector coefficients, L_j .These coefficients are utilized in evaluating the atomic partial participation values (APP) (the partial contribution of each atom to the molecular vibration), the IR absorption intensities and in doing the graphical representation of each of vibration mode[9]

Sham DFT schemes for open-shell systems, which imply different definitions of the exchange–correlation energy functional and lead to different exact conditions on this functional.

The ground-state electronic energy (E) of a N-electron systemcan be uniquely determined by the electron charge density .[10]

$E = E[\rho(r)]$ .....(2)

$E\,\rho \geq E$……(3)

$$\left[-\frac{1}{2}\nabla^2 + V^{KS}(r)\right]\Phi_i(r) = E_i\Phi(r) \quad \text{…..(2)}$$

$$V^{KS} = V_{ext}(r) + \int \frac{\rho(r^-)}{(r-r^-)} dr^- + V_{xc}(r) \quad \text{……(3)}$$

$$V_{xc}(r) = \frac{\partial E_{xc}[\rho(r)]}{\partial \rho(r)} \quad \text{……...(4)}$$

$$\rho(r) = \sum_i^N [\Phi_i(r)]^2 \quad \text{……(5)}$$

Kohn-ShamV^{Ks} =Kohn-Sham potential

V_{xc} = exchange – correlation potential

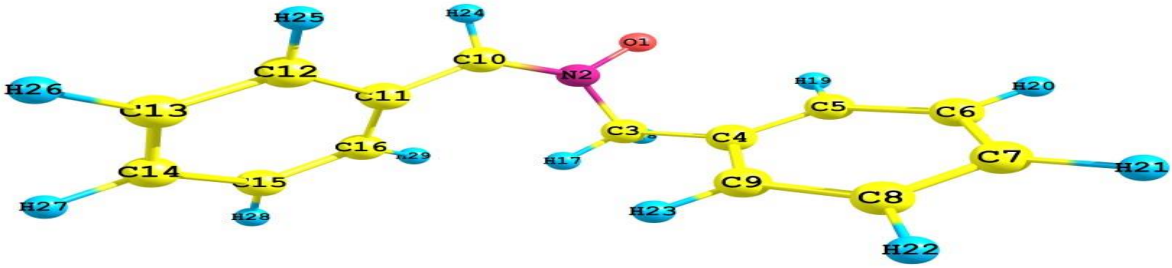
P(r) = electron density

V_{ext}=external potential

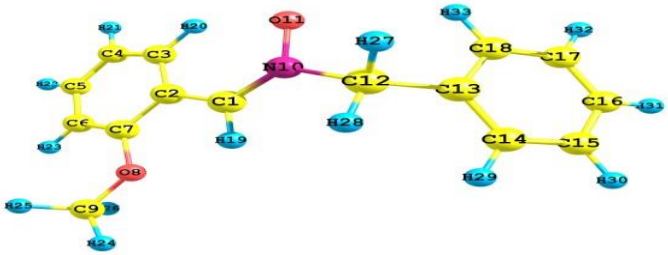
The accurate description of open-shell molecules, in particular of transition metal complexes and clusters, is still an important challenge for quantum chemistry[11]. Although density-functional theory (DFT) is widely applied in this area, the sometimes severe limitations of its currently available approximate realizations often preclude its application as a predictive theory. Here, we review the foundations of DFT applied to open-shell systems, both within the nonrelativistic and the relativistic framework[12].

In particular , we provide an in-depth discussion of the exact theory, with a focus on the role of the spin density and possibilities for targeting specific spin states. It turns out that different options exist for setting up Kohn–Sham DFT schemes for open-shell systems, which imply different definitions of the exchangecorrelation.[13]

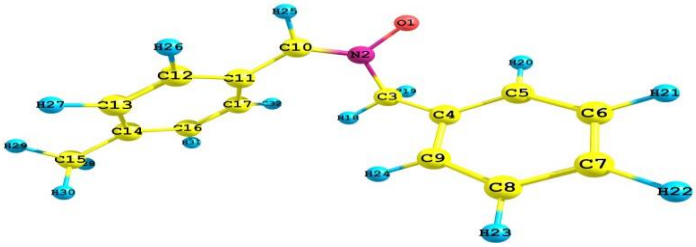
Fig 1 : Structures of studied nitrons usingGaussain O3W and chemchraftbrgram



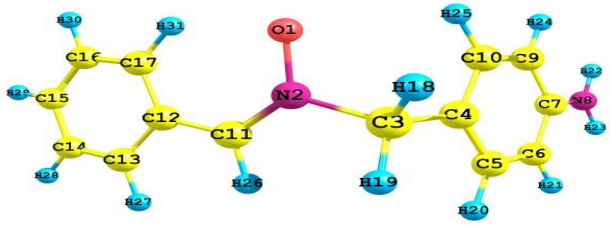
N-benzylidene -1- phenylmethanamine oxide
(1)



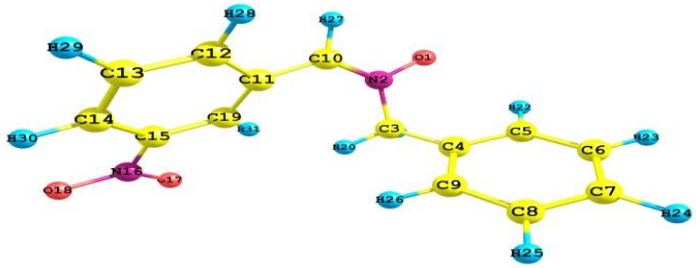
N-(2-methoxybenzylidene)-1- phenylmethanamine oxide
(2)



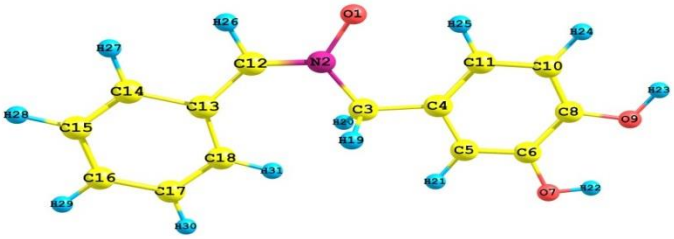
N- (4-methylbenzylidene)-1-phenylmethanamine oxide
(3)



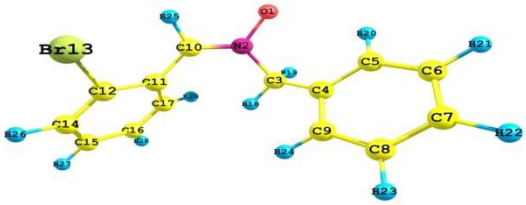
1-(4-aminophenyl)-N-benzylidenemethanamine oxide (4)
(4)



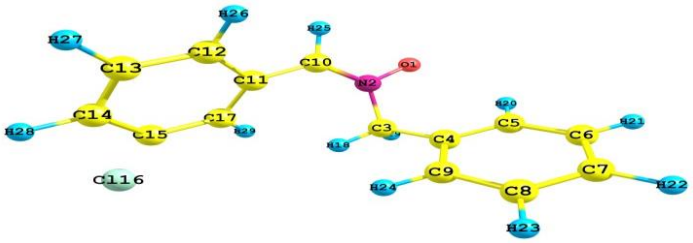
N-(3-nitrobenzylidene)-1phenylmethanamine oxide(5)
(5)



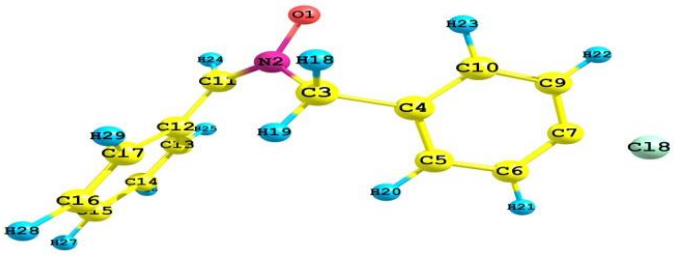
N- benzyliden-1- (3,4 –dihydroxyphenyl)methanamine oxide (6)



N- (2-bromobenzyledene)-1- phenylmethanamine oxide (7)



N- (3-chlorobenzylidene) -1- phenylmethanamine oxide (8)



N- benzylidene -1- (4- chlorophenyl) methanamine oxide (9)

Results and discussion

In this work the DFT (B3LPY /6-31-G) method within the Gaussian O3 software package on a personal computer was applied to calculate the optimized geometries of some nitrone compounds along the calculation of some of their physical properties .

Structural Details

- Bond lengths attached to substitutes are longer than nonsubstitutednitrone compound .this is due to repulsion between the antibonding and bonding electronic paires . (Table 6).
- The adjacent bonds of atoms which carry the electron – with drawing substitutes are shorter compared with the nonsubstitutednitrone. On the other hand , the electron donating groups have the reverse effect. (Table 6).
- The bond angles attached to the electron – with drawing groups are larger compared with nonsubstitutednitrone . On the other hand , the electronedonating groups have the reverse effect (Table 6).

The repulsion between the electronic paires leads to open the apex angle to a larger extent in contrast , the compounds have smallest angle due to higher dipole moment

- The Physical properties:

-Dipole moment of substituted nitrone has higher value compared with nonsubstitutednitrone compound.(Table 1)

- The electronic densities of the carbon atoms attached to the groups CH_3 , NH_2 , OH , OCH_3 , NO_2 lessen compared with nonsubstitutednitrone compound (Table 6) .

while electronic densities of carbon atoms associated to substitutes Br , Cl increase compared with nonsubstitutednitrone . (Table 6)

Some groups increase the negative charge and others decrease the positive charge at the C atom

- HOMO of nitrones attached to the electron donating groups are larger compared with nonsubstitutednitrone , therefore they are lose electrons (oxidation) . On the other hand , the electron – with drawing groups have the reverse effect.This is may be due to the hyperconjunction effect . .(Table 1)
- LUMO of nitrones attached to the electron – with drawing groups are less compared with nonsubstitutednitrone , therefore they are accept electron (Reduction) .While , the electron donating groups have the reverse effect (except OH group) . this is due to the nature of groups attached to C atom..(Table 1)

The high energy of LUMO suggests a high stability and low energy of LUMO suggests a low stability .

- Ionization energies (IP) of nitrones attached to the electron donatinggroups are less compared with nonsubstitutednitrone , so they have ionize easily . however the electron with - drawing groups have the reverse effect..(Table 1)
- Total energy of all substituted nitrones is less compared with nonsubstitutednitronethere bye they are more stable . This is due to increasing in conjugated system . .(Table 1)
-The substituted nitrone with (Br) group has the least energy compared to other substituted nitronecompounds, so it is the most stable.
- Thermodynamic functions (G^o , H^o , U^o , A^o) of nitrones attached to the electron donating groups are larger compared with nonsubstitutednitrone . On the other hand, The electron- with drawing groups have the reverse effect , except NO_2 group . This is due to the nature of substituted groups .(Table 2)
- Entropy function (S^o) of all substituted nitrones compounds is larger compared with nonsubstitutednitronecompound . (Table 2)

* Spectra of IR and UV

I- Vibrational spectra of IR

- Asymmetric stretching frequencies of CH_2 group are larger than symmetric stretching frequencies and for studied nitrones (CH_2 as.st > CH_2 s.st).(Table 4)
- Vibrational stretching frequencies of (NO) are less for OCH_3 , CH_3 , NH_2 , Br substituents and are larger for Cl , OH , substituentsompared with nonsubstitutednitrone.(Table 4)
- Vibrational stretching frequencies of (C=N) of substituted nitrones are larger compared with nonsubstitutednitrone , except NO_2 , OH substituents . This is due to conjugated system effect .
-For all studied nitrone molecules.(Table 4)

CH_2sciss> $\rho\ CH_2$, $\omega\ CH_2 > \tau CH_2$

* Electronic spectra

- Three absorption bands appear for all substituted nitrone compounds .(Table 5)
- The first band due to (N O) group and that is due to electronic transitions π-π^* and n-π^*.
The second band due to electronic transitions in aromatic rings .-
- The third band due to the electronic transitions in aromatic system.
- Wavelength of electronic absorption bands for All substituted nitrones are longer compared with nonsubstitutednitrone. This is due to increasing of conjugated system [14].(Table 5)

When we compare between the experimental and theoretical values , we find a close relation between them , this is support the theoretical study that we have found[15]

Table 1: The calculated standard thermodynamic function at 298.15 K for the (1-9) nitrones

No. of comp.	Point groups	Substituted groups	Dipole moment	E_{HOMO} (a.u)	E_{LUMO} (a.u)	$\Delta(E_{HOMO}-E_{LUMO})$ (a.u)	IP (a.u)	Total energy (a.u)
1	C_1	—	4.022	- 0.204	- 0.053	- 0.151	0.204	- 671.051
2	C_1	$-OCH_3$	4.385	- 0.195	- 0.048	- 0.147	0.195	-785.550
3	C_1	$-CH_3$	4.563	- 0.200	- 0.050	- 0.150	0.200	-710.360
4	C_1	$-NH_2$	4.092	- 0.194	- 0.047	- 0.147	0.194	-726.405
5	C_1	$-NO_2$	4.048	- 0.224	- 0.116	- 0.108	0.224	-875.458
6	C_1	-OH	1.102	- 0.201	- 0.061	- 0.149	0.201	-821.425
7	C_1	-Br	4.777	- 0.210	- 0.061	- 0.149	0.210	-3242.022
8	C_1	3- Cl	3.079	- 0.215	- 0.066	- 0.149	0.215	- 1130.628
9	C_1	4- Cl	5.051	- 0.209	- 0.059	- 0.150	0.211	-1130.627

Table 2 : Calculated total energy (in a.u) ,dipole moments (debye) , orbital energies (HOMO ,LUMO) , (a.u) , the difference between energy of HOMO and LUMO and ionization energies (IPa.u) for the studied compounds

NO. of comp.	Substituted groups	U^0 kJ mol $^{-1}$	H^0 kJ mol $^{-1}$	G^0kJ mol $^{-1}$	A^0 kJ mol $^{-1}$	S^0 kJ mol $^{-1}$
1	—	660 987	663.466	516.478	513.999	0.493
2	$-OCH_3$	754.323	756.802	596.099	593.620	0.539
3	$-CH_3$	738.472	740.951	582.037	579.558	0.533
4	$-NH_2$	709.250	711.729	557.585	555.106	0.517
5	$-NO_2$	672.127	674.606	509.133	506.654	0.555
6	-OH	681.916	683.995	540.585	538.106	0.481
7	-Br	638.307	640.785	481.683	479.095	0.534
8	3- Cl	638.416	640.895	481.683	479.204	0.523
9	4- CI	638.570	641.049	484.818	482.339	0.524

Table 3: Geometric parameters of the studied nitronecompouds R , bond length in angstroms A^0 , and bond angles in degrees . see fig 1 for atom numbring

Compound 1							
R(1-2)	1.321	R(12-13)	1.396	A(17-3-18)	109.5	A(11-12-13)	121.0
R(2-3)	1.508	R(12-25)	1.086	A(5-4-9)	119.3	A(11-12-25)	119.1
R(2-10)	1.321	R(13-14)	1.401	A(4-5-6)	120.1	A(11-16-15)	120.8
R(3-4)	1.515	R(13-26)	1.085	A(4-5-19)	119	A(11-16-29)	119.9
R(3-17)	1.087	R(14-15)	1.400	A(4-9-8)	120.5	A(13-12-25)	119.9
R(3-18)	1.093	R(14-27)	1.085	A(4-9-23)	119.7	A(12-13-14)	120.2
R(4-5)	1.406	R(15-16)	1.397	A(6-5-19)	120.9	A(12-13-26)	119.7
R(4-9)	1.404	R(15-28)	1.085	A(5-6-7)	120.4	A(14-13-26)	120.1
R(5-6)	1.398	R(16-29)	1.085	A(5-6-20)	119.6	A(13-14-15)	119.5
R(5-19)	1.083	A(1-2-3)	113.7	A(7-6-20)	120	A(13-14-27)	120.3
R(6-7)	1.401	A(1-2-10)	121.7	A(6-7-8)	119.8	A(15-14-27)	120.2
R(6-20)	1.085	A(3-2-10)	124.4	A(6-7-21)	120.1	A(14-15-16)	120.4
R(7-8)	1.399	A(2-3-4)	111.6	A(8-7-21)	120.1	A(14-15-28)	120.0
R(7-21)	1.086	A(2-3-17)	109.3	A(7-8-9)	119.9	A(16-15-28)	119.5
R(8-9)	1.400	A(2-3-18)	104.4	A(7-8-22)	120.2	A(15-16-29)	119.3
R(8-22)	1.085	A(2-10-11)	128.7	A(9-8-22)	119.8		
R(9-23)	1.087	A(2-10-24)	112.7	A(8-9-23)	119.8		
R(10-11)	1.465	A(4-3-17)	110.2	A(11-10-24)	118.5		
R(10-24)	1.084	A(4-3-18)	111.7	A(10-11-12)	117.8		
R(11-12)	1.413	A(3-4-5)	121.2	A(10-11-16)	124.1		
R(11-16)	1.413	A(3-4-9)	119.6	A(12-11-16)	118.0		

Table 3 contd

Compound 2							
R(1-2)	1.444	R(14-29)	1.087	A(6-5-22)	119.3	A(15-14-29)	119.8
R(1-10)	1.322	R(15-16)	1.399	A(5-6-7)	119.7	A(14-15-16)	119.9
R(1-19)	1.080	R(15-30)	1.086	A(5-6-23)	119.6	A(14-15-30)	119.8
R(2-3)	1.413	R(16-17)	1.401	A(7-6-23)	120.8	A(16-15-30)	120.2
R(2-7)	1.425	R(16-31)	1.086	A(6-7-8)	123.3	A(15-16-17)	119.8
R(3-4)	1.398	R(17-18)	1.398	A(7-8-9)	119.2	A(15-16-31)	120.1
R(3-20)	1.081	R(17-32)	1.086	A(8-9-24)	105.2	A(17-16-31)	120.1
R(4-5)	1.397	R(18-33)	1.084	A(8-9-25)	111.2	A(16-17-18)	120.4
R(4-21)	1.085	A(2-1-10)	126.3	A(8-9-26)	111.2	A(16-17-32)	120.0
R(5-6)	1.402	A(2-1-19)	117.6	A(24-9-25)	109.8	A(18-17-32)	119.6
R(5-22)	1.085	A(1-2-3)	124.5	A(24-9-26)	109.8	A(17-18-33)	120.9
R(6-7)	1.395	A(1-2-7)	117.6	A(25-9-26)	109.7		
R(6-23)	1.083	A(10-1-19)	116.1	A(11-10-12)	114.1		
R(7-8)	1.394	A(1-10-11)	126.0	A(10-12-13)	112.4		
R(8-9)	1.451	A(1-10-12)	119.9	A(10-12-27)	104.2		
R(9-24)	1.089	A(3-2-7)	117.9	A(10-12-28)	108.4		
R(9-25)	1.096	A(2-3-4)	120.9	A(13-12-27)	111.7		
R(9-26)	1.096	A(2-3-20)	117.6	A(13-12-28)	110.9		
R(10-11)	1.326	A(2-7-6)	121.1	A(12-13-14)	120.1		
R(10-12)	1.503	A(2-7-8)	115.6	A(12-13-18)	120.7		
R(12-13)	1.514	A(4-3-20)	121.6	A(27-12-28)	109.0		
R(12-27)	1.093	A(3-4-5)	120.2	A(14-13-18)	119.3		
R(12-28)	1.092	A(3-4-21)	119.6	A(13-14-15)	120.6		
R(13-14)	1.403	A(5-4-21)	120.2	A(13-14-29)	119.7		

Compound 3							
R(1-2)	1.322	R(14-16)	1.405	A(5-6-7)	120.4	A(14-15-29)	111.5
R(2-3)	1.507	R(15-28)	1.095	A(5-6-21)	119.6	A(14-15-30)	111.2
R(2-10)	1.321	R(15-29)	1.096	A(7-6-21)	120.0	A(14-16-17)	121.4
R(3-4)	1.515	R(15-30)	1.099	A(6-7-8)	119.8	A(14-16-31)	119.3
R(3-18)	1.087	R(16-17)	1.397	A(6-7-22)	120.1	A(28-15-29)	108.0
R(3-19)	1.093	R(16-31)	1.086	A(8-7-22)	120.1	A(28-15-30)	107.4
R(4-5)	1.406	R(17-32)	1.085	A(7-8-9)	119.9	A(29-15-30)	107.1
R(4-9)	1.404	A(1-2-3)	113.8	A(7-8-23)	120.2	A(17-16-31)	119.2
R(5-6)	1.398	A(1-2-10)	121.7	A(9-8-23)	119.9	A(16-17-32)	119.0
R(5-20)	1.083	A(3-2-10)	124.4	A(8-9-24)	119.8		
R(6-7)	1.401	A(2-3-4)	111.6	A(11-10-25)	118.5		
R(6-21)	1.085	A(2-3-18)	109.2	A(10-11-12)	117.9		
R(7-8)	1.399	A(2-3-19)	104.6	A(10-11-17)	124.4		
R(7-22)	1.086	A(2-10-11)	128.8	A(12-11-17)	117.5		
R(8-9)	1.400	A(2-10-25)	112.6	A(11-12-13)	121.2		
R(8-23)	1.085	A(4-3-18)	110.1	A(11-12-26)	119.1		
R(9-24)	1.087	A(4-3-19)	111.7	A(11-17-16)	120.9		
R(10-11)	1.464	A(3-4-5)	121.2	A(11-17-32)	120.0		
R(10-25)	1.085	A(3-4-9)	119.5	A(13-12-26)	119.7		
R(11-12)	1.413	A(18-3-19)	109.5	A(12-13-14)	121.2		
R(11-17)	1.412	A(5-4-9)	119.3	A(12-13-27)	119.4		
R(12-13)	1.394	A(4-5-6)	120.1	A(14-13-27)	119.4		
R(12-26)	1.086	A(4-5-20)	119.0	A(13-14-15)	121.0		
R(13-14)	1.407	A(4-9-8)	120.6	A(13-14-16)	117.8		
R(13-27)	1.086	A(4-9-24)	119.6	A(15-14-16)	121.2		
R(14-15)	1.512	R(6-5-20)	120.9	A(14-15-28)	111.4		

Compound 4							
R(1-2)	1.323	R(14-28)	1.086	A(5-6-21)	120	A(16-15-29)	120.3
R(2-3)	1.509	R(15-16)	1.400	A(7-6-21)	119.6	A(15-16-17)	120.9
R(2-11)	1.321	R(15-29)	1.086	A(6-7-8)	120.9	A(15-16-30)	119.9
R(3-4)	1.509	R(16-17)	1.397	A(6-7-9)	118.3	A(17-16-30)	119.3
R(3-18)	1.093	R(16-30)	1.086	A(8-7-9)	120.7	A(16-17-31)	121.6
R(3-19)	1.093	R(17-31)	1.081	A(7-8-22)	120.9		
R(4-5)	1.403	A(1-2-3)	114.1	A(7-8-23)	121.1		
R(4-10)	1.407	A(1-2-11)	125.7	A(7-9-10)	120.8		
R(5-6)	1.395	A(3-2-11)	120.2	A(7-9-24)	119.4		
R(5-20)	1.087	A(2-3-4)	112.4	A(22-8-23)	118.0		
R(6-7)	1.410	A(2-3-18)	103.7	A(10-9-24)	119.8		
R(6-21)	1.086	A(2-3-19)	108.2	A(9-10-25)	120.1		
R(7-8)	1.384	A(2-11-12)	127.0	A(12-11-26)	117.8		
R(7-9)	1.413	A(2-11-26)	115.2	A(11-12-13)	117.2		
R(8-22)	1.005	A(4-3-18)	112.2	A(11-12-17)	124.2		
R(8-23)	1.005	A(4-3-19)	111.0	A(13-12-17)	118.5		
R(9-10)	1.392	A(3-4-5)	120.8	A(12-13-14)	121		
R(9-24)	1.087	A(3-4-10)	121,0	A(12-13-27)	119.3		
R(10-25)	1.084	A(18-3-19)	109.0	A(12-17-16)	120		
R(11-12)	1.448	A(5-4-10)	118.2	A(12-17-31)	118.5		
R(11-26)	1.083	A(4-5-6)	121.4	A(14-13-27)	119.8		
R(12-13)	1.417	A(4-5-20)	119.7	A(13-14-15)	120		
R(12-17)	1.416	A(4-10-9)	121.0	A(13-14-28)	119.8		
R(13-14)	1.393	A(4-10-25)	119.0	A(15-14-28)	120.1		
R(13-27)	1.087	A(6-5-20)	119.0	A(14-15-16)	119.6		
R(14-15)	1.402	A(5-6-7)	120.4	A(14-15-29)	120.1		

Compound 5							
R(1-2)	1.316	R(14-30)	1.081	A(5-6-23)	119.6	A(16-15-19)	118.4
R(2-3)	1.510	R(15-16)	1.469	A(7-6-23)	120.0	A(15-16-17)	118.1
R(2-10)	1.323	R(15-19)	1.394	A(6-7-8)	119.8	A(15-16-18)	118.0
R(3-4)	1.515	R(16-17)	1.265	A(6-7-24)	120.1	A(15-19-31)	118.4
R(3-20)	1.087	R(16-18)	1.263	A(8-7-24)	120.1	A(17-16-18)	123.9
R(3-21)	1.092	R(19-31)	1.081	A(7-8-9)	119.9		
R(4-5)	1.406	A(1-2-3)	113.6	A(7-8-25)	120.2		
R(4-9)	1.404	A(1-2-10)	121.3	A(9-8-25)	119.8		
R(5-6)	1.398	A(3-2-10)	124.9	A(8-9-26)	119.8		
R(5-22)	1.083	A(2-3-4)	111.4	A(11-10-27)	118.1		
R(6-7)	1.401	A(2-3-20)	109.6	A(10-11-12)	117.6		
R(6-23)	1.085	A(2-3-21)	104.2	A(10-11-19)	124.4		
R(7-8)	1.399	A(2-10-11)	129.2	A(12-11-19)	117.9		
R(7-24)	1.085	A(2-10-27)	112.7	A(11-12-13)	121.5		
R(8-9)	1.399	A(4-3-20)	110.2	A(11-12-28)	118.8		
R(8-25)	1.085	A(4-3-21)	111.9	A(11-19-15)	119.5		
R(9-26)	1.087	A(3-4-5)	121.1	A(11-19-31)	122.0		
R(10-11)	1.462	A(3-4-9)	119.6	A(13-12-28)	119.7		
R(10-27)	1.084	A(20-3-21)	109.3	A(12-13-14)	120.5		
R(11-12)	1.416	A(5-4-9)	119.3	A(12-13-29)	119.8		
R(11-19)	1.409	A(4-5-6)	120.1	A(14-13-29)	119.7		
R(12-13)	1.396	A(4-5-22)	119.1	A(13-14-15)	117.9		
R(12-28)	1.085	A(4-9-8)	120.5	A(13-14-30)	122.2		
R(13-14)	1.397	A(4-9-26)	119.7	A(15-14-30)	119.9		
R(13-29)	1.084	A(6-5-22)	120.8	A(14-15-16)	118.9		
R(14-15)	1.396	A(5-6-7)	120.4	A(14-15-19)	122.8		

Compound 6							
R(1-2)	1.322	R(15-28)	1.085	A(5-6-8)	119.6	A(16-17-18)	121.0
R(2-3)	1.502	R(16-17)	1.398	A(7-6-8)	120.4	A(16-17-30)	119.9
R(2-12)	1.327	R(16-29)	1.085	A(6-7-22)	109.3	A(18-17-30)	119.0
R(3-4)	1.524	R(17-18)	1.398	A(6-8-9)	114.3	A(17-18-31)	117.6
R(3-19)	1.096	R(17-30)	1.085	A(6-8-10)	120.1		
R(3-20)	1.096	R(18-31)	1.079	A(9-8-10)	125.6		
R(4-5)	1.411	A(1-2-3)	118.9	A(8-9-23)	112.5		
R(4-11)	1.402	A(1-2-12)	119.3	A(8-10-11)	120.4		
R(5-6)	1.388	A(3-2-12)	121.8	A(8-10-24)	120.2		
R(5-21)	1.086	A(2-3-4)	120.5	A(11-10-24)	119.5		
R(6-7)	1.386	A(2-3-19)	105.7	A(10-11-25)	120.7		
R(6-8)	1.404	A(2-3-20)	105.7	A(13-12-26)	116.3		
R(7-22)	0.98	A(2-12-13)	132.8	A(12-13-14)	114.4		
R(8-9)	1.401	A(2-12-26)	110.9	A(12-13-18)	128.7		
R(8-10)	1.388	A(4-3-19)	108.5	A(14-13-18)	117		
R(9-23)	0.974	A(4-3-20)	108.5	A(13-14-15)	121.9		
R(10-11)	1.404	A(3-4-5)	113.5	A(13-14-27)	118.7		
R(10-24)	1.087	A(3-4-11)	127.6	A(13-18-17)	120.9		
R(11-25)	1.078	A(19-3-20)	107.3	A(13-18-31)	121.5		
R(12-13)	1.454	A(5-4-11)	118.9	A(15-14-27)	119.5		
R(12-26)	1.083	A(4-5-6)	120.9	A(14-15-16)	120.2		
R(13-14)	1.422	A(4-5-21)	121.4	A(14-15-28)	119.6		
R(13-18)	1.418	A(4-11-10)	120.0	A(16-15-28)	120.2		
R(14-15)	1.391	A(4-11-25)	119.3	A(15-16-17)	119.1		
R(14-27)	1.086	A(6-5-21)	117.6	A(15-16-29)	120.5		
R(15-16)	1.401	A(5-6-7)	120.0	A(17-16-29)	120.4		

Compound 7							
R(1-2)	1.318	R(15-27)	1.085	A(6-7-8)	119.8		
R(2-3)	1.510	R(16-17)	1.395	A(6-7-22)	120.1		
R(2-10)	1.322	R(16-28)	1.085	A(8-7-22)	120.1		
R(3-4)	1.515	R(17-29)	1.084	A(7-8-9)	119.9		
R(3-18)	1.087	A(1-2-3)	113.7	A(7-8-23)	120.2		
R(3-19)	1.093	A(1-2-10)	121.6	A(9-8-23)	119.9		
R(4-5)	1.406	A(3-2-10)	124.5	A(8-9-24)	119.8		
R(4-9)	1.404	A(2-3-4)	111.6	A(11-10-25)	118.6		
R(5-6)	1.398	A(2-3-18)	109.2	A(10-11-12)	119.9		
R(5-20)	1.083	A(2-3-19)	104.5	A(10-11-17)	123.4		
R(6-7)	1.401	A(2-10-11)	128.0	A(12-11-17)	116.5		
R(6-21)	1.085	A(2-10-25)	113.4	A(11-12-13)	119.9		
R(7-8)	1.399	A(4-3-18)	110.2	A(11-12-14)	122.6		
R(7-22)	1.086	A(4-3-19)	111.7	A(11-17-16)	121.5		
R(8-9)	1.399	A(3-4-5)	121.2	A(11-17-29)	119.0		
R(8-23)	1.085	A(3-4-9)	119.5	A(13-12-14)	117.5		
R(9-24)	1.087	A(18-3-19)	109.5	A(12-14-15)	119.5		
R(10-11)	1.461	A(5-4-9)	119.3	A(12-14-26)	119.6		
R(10-25)	1.083	A(4-5-6)	120.1	A(15-14-26)	120.8		
R(11-12)	1.409	A(4-5-20)	119.1	A(14-15-16)	119.6		
R(11-17)	1.416	A(4-9-8)	120.5	A(14-15-27)	119.9		
R(12-13)	1.949	A(4-9-24)	119.7	A(16-15-27)	120.5		
R(12-14)	1.391	A(6-5-20)	120.8	A(15-16-17)	120.2		
R(14-15)	1.398	A(5-6-7)	120.4	A(15-16-28)	120.2		
R(14-26)	1.083	A(5-6-21)	119.6	A(17-16-28)	119.6		
R(15-16)	1.400	A(7-6-21)	120	A(16-17-29)	119.4		

Compound 8							
R(1-2)	1.319	R(14-28)	1.083	A(6-7-8)	119.8		
R(2-3)	1.509	R(15-16)	1.828	A(6-7-22)	120.1		
R(2-10)	1.322	R(15-17)	1.391	A(8-7-22)	120.1		
R(3-4)	1.516	R(17-29)	1.082	A(7-8- 9)	119.9		
R(3-18)	1.087	A(1-2-3)	113.6	A(7-8-23)	120.2		
R(3-19)	1.092	A(1-2-10)	121.5	A(9-8-23)	119.8		
R(4-5)	1.406	A(3-2-10)	124.7	A(8-9-24)	119.8		
R(4-9)	1.404	A(2-3-4)	111.6	A(11-10-25)	118.3		
R(5-6)	1.398	A(2-3-18)	109.5	A(10-11-12)	117.8		
R(5-20)	1.083	A(2-3-19)	104.2	A(10-11-17)	123.8		
R(6-7)	1.401	A(2-10-11)	128.9	A(12-11-17)	118.2		
R(6-21)	1.085	A(2-10-25)	112.8	A(11-12-13)	121.0		
R(7-8)	1.399	A(4-3-18)	110.1	A(11-12-26)	119.1		
R(7-22)	1.086	A(4-3-19)	111.9	A(11-17-15)	119.5		
R(8-9)	1.400	A(3-4-5)	121.2	A(11-17-29)	121.0		
R(8-23)	1.085	A(3-4-9)	119.5	A(13-12-26)	119.9		
R(9-24)	1.087	A(18-3-19)	109.4	A(12-13-14)	120.7		
R(10-11)	1.464	A(5-4-9)	119.3	A(12-13-27)	119.9		
R(10-25)	1.084	A(4-5-6)	120.1	A(14-13-27)	119.5		
R(11-12)	1.413	A(4-5-20)	119.0	A(13-14-15)	118.0		
R(11-17)	1.414	A(4-9-8)	120.5	A(13-14-28)	121.3		
R(12-13)	1.395	A(4-9-24)	119.7	A(15-14-28)	120.7		
R(12-26)	1.085	A(6-5-20)	120.9	A(14-15-17)	122.6		
R(13-14)	1.401	A(5-6-7)	120.4	A(15-17-29)	119.5		
R(13-27)	1.085	A(5-6-21)	119.6				
R(14-15)	1.393	A(7-6-21)	120.0				

Compound 9							
R(1-2)	1.323	R(15-27)	1.085	A(6-7-9)	122.0		
R(2-3)	1.506	R(16-17)	1.397	A(7-9-10)	118.9		
R(2-11)	1.321	R(16-28)	1.085	A(7-9-22)	120.4		
R(3-4)	1.515	R(17-29)	1.085	A(10-9-22)	120.7		
R(3-18)	1.093	A(1-2-3)	113.6	A(9-10-23)	120.4		
R(3-19)	1.087	A(1-2-11)	121.8	A(12-11-24)	118.6		
R(4-5)	1.403	A(3-2-11)	124.4	A(11-12-13)	117.8		
R(4-10)	1.406	A(2-3-4)	111.4	A(11-12-17)	124.0		
R(5-6)	1.400	A(2-3-18)	104.5	A(13-12-17)	118.1		
R(5-20)	1.086	A(2-3-19)	109.4	A(12-13-14)	121.0		
R(6-7)	1.392	A(2-11-12)	128.6	A(12-13-25)	119.1		
R(6-21)	1.083	A(2-11-24)	112.7	A(12-17-16)	120.7		
R(7-9)	1.394	A(4-3-18)	111.7	A(12-17-29)	119.9		
R(8-7)	1.828	A(4-3-19)	110.2	A(14-13-25)	119.9		
R(9-10)	1.398	A(3-4-5)	119.7	A(13-14-15)	120.2		
R(9-22)	1.083	A(3-4-10)	121.2	A(13-14-26)	119.7		
R(10-23)	1.083	A(18-3-19)	109.4	A(15-14-26)	120.1		
R(11-12)	1.465	A(5-4-10)	119.2	A(14-15-16)	119.5		
R(11-24)	1.085	A(4-5-6)	120.9	A(14-15-27)	120.3		
R(12-13)	1.413	A(4-5-20)	119.9	A(16-15-27)	120.2		
R(12-17)	1.413	A(4-10-9)	120.5	A(15-16-17)	120.4		
R(13-14)	1.396	A(4-10-23)	119.1	A(15-16-28)	120.0		
R(13-25)	1.086	A(6-5-20)	119.2	A(17-16-28)	119.5		
R(14-15)	1.400	A(5-6-7)	118.5	A(16-17-29)	119.3		
R(14-26)	1.085	A(5-6-21)	120.9				
R(15-16)	1.400	A(7-6-21)	120.6				

Table 4: Some vibrational frequencies of the studied nitrone compounds in cm^{-1}

NO. Of COMP.	N—O St.	= C —H ben .	C═N St	CH_2 StS.	CH_2 St.As	= C—H St	C —H Ar. St.
1	1164	1419 866	1620	3109	3201	3226	3186-3246
2	1117	1474 880	1638	3091	3150	3274	3183-3271
3	1149	1418 878	1624	3108	3200	3224	3186-3247
4	1117	1479 846	1639	3087	3145	3227	3176-3271
5	1170	1422 867	1618	3117	3206	3229	3187-3269
6	1174	1445 891	1602	3047	3094	3237	3189-3304
7	1147	1415 847	1622	3108	3194	3245	3186-3246
8	1168	1418 863	1623	3114	3203	3229	3187-3248
9	1166	1417 867	1622	3110	3203	3226	3218-3254

Table 5 :Comparison of theoretical UV transitions energies of the studied molecules

NO. Of Comp.	Substituted groups	First Excited State (nm)	Second Excited State (nm)	Third Excited State (nm)
1	—	244	212	211
2	$-OCH_3$	247	215	209
3	$-CH_3$	235	207	204
4	$-NH_2$	244	213	212
5	$-NO_2$	283	260	236
6	-OH	251	214	210
7	Br	213	211	201
8	3- Cl	251	214	210
9	4- Cl	233	210	206

Table 6 : The charge and electron density . See Fig 1 for atom's numbering
Compound 1

No. of Atom	Charge	electron density	No. of Atom	Charge	electron density
O_1	-0.4304	6.4304	H_{17}	0	1
N_2	-0.1545	5.1545	H_{18}	0	1
C_3	0.1530	3.8470	H_{19}	0	1
C_4	0.0977	3.9023	H_{20}	0	1
C_5	0.0469	3.9531	H_{21}	0	1
C_6	-0.0049	4.0049	H_{22}	0	1
C_7	0.0101	3.9899	H_{23}	0	1
C_8	-0.0031	4.0031	H_{24}	0	1
C_9	-0.0207	4.0207	H_{25}	0	1
C_{10}	0.2332	3.7668	H_{26}	0	1
C_{11}	0.0582	3.9418	H_{27}	0	1
C_{12}	-0.0050	4.0050	H_{28}	0	1
C_{13}	0.0060	3.9940	H_{29}	0	1
C_{14}	0.0153	3.9847			
C_{15}	0.0016	3.9984			
C_{16}	-0.0035	4.0035			

Tabl 6 : contd **Compound 2**

No. of Atom	Charge	electron density	No. of Atom	Charge	electron density
C_1	0.2906	3.7094	C_{18}	0.0393	3.9607
C_2	0.0478	3.9522	C_{19}	0	1
C_3	0.0497	3.9503	H_{20}	0	1
C_4	0.0003	3.9997	H_{21}	0	1
C_5	-4.6005	4.6005	H_{22}	0	1
C_6	-0.0160	4.0160	H_{23}	0	1
C_7	0.2456	3.7544	H_{24}	0	1
O_8	-0.5752	6.5752	H_{25}	0	1
C_9	0.3102	3.6898	H_{26}	0	1
N_{10}	-0.1834	5.1834	H_{27}	0	1
O_{11}	-0.4325	6.4325	H_{28}	0	1
C_{12}	0.1477	3.8523	H_{29}	0	1
C_{13}	0.1021	3.8979	H_{30}	0	1
C_{14}	-0.0295	4.0295	H_{31}	0	1
C_{15}	-0.0028	4.0028	H_{32}	0	1
C_{16}	0.0087	3.9913	H_{33}	0	1
C_{17}	-0.0023	4.0023			

Compound 3

No. of Atom	Charge	electron density	No. of Atom	Charge	electron density
O_1	-0.4329	6.4329	H_{18}	0	1
N_2	-0.1562	5.1562	H_{19}	0	1
C_3	0.1514	3.8486	H_{20}	0	1
C_4	0.0990	3.9010	H_{21}	0	1
C_5	0.0473	3.9527	H_{22}	0	1
C_6	-0.0058	4.0058	H_{23}	0	1
C_7	0.0094	3.9906	H_{24}	0	1
C_8	-0.0039	4.0039	H_{25}	0	1
C_9	-0.0212	4.0212	H_{26}	0	1
C_{10}	0.2317	3.7683	H_{27}	0	1
C_{11}	0.0599	3.9401	H_{28}	0	1
C_{12}	-0.0084	4.0084	H_{29}	0	1
C_{13}	-0.0275	4.0275	$_{30}H$	0	1
C_{14}	0.1175	3.8825	H_{31}	0	1
C_{15}	-0.0211	4.0211	H_{32}	0	1
C_{16}	-0.0343	4.0343			
C_{17}	-0.0048	4.0048			

Tabl 6 : contd **Compound 4**

No. of Atom	Charge	electron density	No. of Atom	Charge	electron density
O_1	-0.4280	6.4280	H_{18}	0	1
N_2	-0.1736	5.1736	H_{19}	0	1
C_3	0.1299	3.8701	H_{20}	0	1
C_4	0.1113	3.8887	H_{21}	0	1
C_5	-0.0502	4.0502	H_{22}	0	1
C_6	-0.0373	4.0373	H_{23}	0	1
C_7	0.3339	3.6661	H_{24}	0	1
N_8	-0.1862	5.1862	H_{25}	0	1
C_9	-0.0350	4.0350	H_{26}	0	1
C_{10}	0.0165	3.9835	H_{27}	0	1
C_{11}	0.2283	3.7717	H_{28}	0	1
C_{12}	0.0796	3.9204	H_{30}	0	1
C_{13}	-0.0398	4.0398	H_{31}	0	1
C_{14}	-0.0114	4.0114			
C_{15}	0.0115	3.9885			
C_{16}	-0.0093	4.0093			
C_{17}	0.0597	3.9403			

Compound 5

No. of Atom	Charge	electron density	No. of Atom	Charge	electron density
O_1	-0.4118	6.4118	O_{17}	-0.2893	6.2893
N_2	-0.1533	5.1533	O_{18}	-0.2851	6.2851
C_3	0.1620	3.8380	C_{19}	0.0607	3.9393
C_4	0.0974	3.9026	H_{20}	0	1
C_5	0.0468	3.9532	H_{21}	0	1
C_6	-0.0006	4.0006	H_{22}	0	1
C_7	0.0149	3.9851	H_{23}	0	1
C_8	0.0016	3.9984	H_{24}	0	1
C_9	-0.0201	4.0201	H_{25}	0	1
C_{10}	0.2403	3.7597	H_{26}	0	1
C_{11}	0.0477	3.9523	H_{27}	0	1
C_{12}	0.0359	3.9641	H_{28}	0	1
C_{13}	0.0074	3.9926	H_{29}	0	1
C_{14}	0.0884	3.9116	H_{30}	0	1
C_{15}	0.3024	3.6976	H_{31}	0	1
N_{16}	0.0550	3.9450			

Tabl 6 : contd **Compound 6**

No. of Atom	Charge	electron density	No. of Atom	Charge	electron density
O_1	-0.4224	6.4224	C_{17}	0.0027	3.9973
N_2	-0.2065	5.2065	C_{18}	-0.0142	4.0142
C_3	0.2240	3.7760	H_{19}	0	1
C_4	0.0722	3.9278	H_{20}	0	1
C_5	-0.0278	4.0278	H_{21}	0	1
C_6	0.2601	3.7399	H_{22}	0	1
O_7	-0.2346	6.2346	H_{23}	0	1
C_8	0.2472	3.7528	H_{24}	0	1
O_9	-0.2767	6.2767	H_{25}	0	1
C_{10}	-0.0153	4.0153	H_{26}	0	1
C_{11}	0.0626	3.9374	H_{27}	0	1
C_{12}	0.2225	3.7775	H_{28}	0	1
C_{13}	0.1163	3.8837	H_{29}	0	1
C_{14}	-0.0373	4.0373	H_{30}	0	1
C_{15}	0.0102	3.9898	H_{31}	0	1
C_{16}	0.0169	3.9831			

Compound 7

No. of Atom	Charge	electron density	No. of Atom	Charge	electron density
O_1	-0.4207	6.4207	C_{17}	0.0095	3.9905
N_2	-0.1561	5.1561	H_{18}	0	1
C_3	0.1501	3.8499	H_{19}	0	1
C_4	0.1005	3.8995	H_{20}	0	1
C_5	0.0472	3.9528	H_{21}	0	1
C_6	-0.0035	4.0035	H_{22}	0	1
O_7	0.0119	3.9881	H_{23}	0	1
C_8	-0.0012	4.0012	H_{24}	0	1
C_9	-0.0199	6.0199	H_{25}	0	1
C_{10}	0.2540	3.7460	H_{26}	0	1
C_{11}	0.0978	3.9022	H_{27}	0	1
C_{12}	-0.3378	4.3378	H_{28}	0	1
Br_{13}	0.1615	6.8385	H_{29}	0	1
C_{14}	0.0648	3.9352			
C_{15}	0.0288	3.9712			
C_{16}	0.0130	3.9870			

Tabl 6 : contd **Compound 8**

No. of Atom	Charge	electron density	No. of Atom	Charge	electron density
O_1	-0.4208	6.4208	C_{17}	0.0582	3.9418
N_2	-0.1538	5.1538	H_{18}	0	1
C_3	0.1592	0.8408	H_{19}	0	1
C_4	0.0961	3.9039	H_{20}	0	1
C_5	0.0461	3.9539	H_{21}	0	1
C_6	-0.0025	4.0025	H_{22}	0	1
O_7	0.0125	3.9875	H_{23}	0	1
C_8	-0.0005	4.0005	H_{24}	0	1
C_9	-0.0197	4.0197	H_{25}	0	1
C_{10}	0.2377	3.7623	H_{26}	0	1
C_{11}	0.0605	3.9395	H_{27}	0	1
C_{12}	0.0122	3.9878	H_{28}	0	1
C_{13}	0.0181	3.9819	H_{29}	0	1
C_{14}	0.0735	3.9265			
C_{15}	-0.2478	4.2478			
Cl_{16}	0.0709	6.9291			

Compound 9

No. of Atom	Charge	electron density	No. of Atom	Charge	electron density
O_1	-0.4307	6.4307	C_{17}	-0.0033	4.0033
N_2	-0.1561	5.1561	H_{18}	0	1
C_3	0.1620	3.8380	H_{19}	0	1
C_4	0.1002	3.8998	H_{20}	0	1
C_5	-0.0067	4.0067	H_{21}	0	1
C_6	0.0585	3.9415	H_{22}	0	1
C_7	-0.2279	4.2279	H_{23}	0	1
Cl_8	0.0623	6.9377	H_{24}	0	1
C_9	0.0563	3.9437	H_{25}	0	1
C_{10}	0.0633	3.9367	H_{26}	0	1
C_{11}	0.2390	3.7610	H_{27}	0	1
C_{12}	0.0543	3.9457	H_{28}	0	1
C_{13}	-0.0018	4.0018	H_{29}	0	1
C_{14}	0.0086	3.9911			
C_{15}	0.0183	3.9817			
C_{16}	0.0035	3.9965			

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