DFT CALCULATIONS ON 1-HETERO-2,5-CYCLOHEXADIENE-1-OXIDE: MOLECULAR STRUCTURE AND STABILITY

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ABSTRACT. Molecular structures of 1-hetero-2,5-cyclohexadiene-1-oxide, X_O, are studied and compared with their corresponding deoxygenated compound, 1-hetero-2,5-cyclohexadiene, X, using DFT at B3LYP/6-311++G** level. The most stable boat conformers are found for O_O, S_O, Se_O, P_O, As_O, S, Se, N, P, As, and the most stable planar conformers are also found for N_O, C_O, Si_O, Ge_O, O, C, Si, Ge. Isodesmic reactions to determine the stabilities of X_O and X are considered. Nuclear independent chemical shifts, NICS, are calculated for the investigation of the homo-aromatic character of X_O and X. The optimised geometries show the bonding in the molecules is explicable in terms of basic chemical concepts. The atomic charges calculated are also reasonable based on the concepts of electronegativity and conjugation.

KEY WORDS: Molecular structure, Stability, 4H-Thiopyran, 4H-Thiopyran-1-oxide, 1-Hetero-2,5-cyclohexadiene-1-oxide, Isodesmic reaction, NICS

INTRODUCTION

1-Hetero-2,5-cyclohexadienes, **X**, specially 4H-thiopyrans are of interest to the chemists due to their corresponding photochromic and photoisomeric characters [1-6]. Therefore, we studied the structure of 1-hetero-2,5-cyclohexadiene, **X**, through DFT calculations [7]. Derivatives of 4H-thiopyran are simply converted to the corresponding 4H-thiopyran-1-oxides and/or 4H-thiopyran-1,1-dioxides [8-10]. The oxidation of organic sulfides to those corresponding sulfoxides and sulfones is a well-understood process for which a large variety of synthetic methods exist [11-19]. The H_2O_2 or trifluoroacetic acid is used for the selective oxidation of sulfides to sulfoxides [20]. Sulfones are produced through the oxidation of sulfides with peracids [21-24]. In this work, the conformational structure and molecular stability of 1-hetero-2,5-cyclohexadiene-1-oxide, **X_O**, are studied and compared with their corresponding deoxygenated 1-hetero-2,5-cyclohexadiene, **X**. Isodesmic formal reactions and homo-aromatic character indicate the molecular stability. The homo-aromatic or aromatic character is not a directly measurable or computable quantity. Aromatic character is generally evaluated on the basis of magnetic, energetic and geometric criteria [25-26]. Magnetic criterion is the important way for the determination of aromatic character. Magnetic criterion is measured through nuclear independent chemical shifts, NICS. The concept of NICS was introduced by Schleyer *et al.* in 1996 as a measure of aromaticity and antiaromaticity (or non-aromaticity) [27]. It is based on a probe with no basis functions (bq) which is placed at or above the geometrical center of a conjugated ring. Its calculated isotropic NMR chemical shift indicates the aromatic properties of the ring, either as an individual moiety in a polycyclic compound or as a molecule. Initially the probe was placed at the geometrical center of the molecules, but after realizing that in some systems the chemical shifts are influenced by the σ system (e.g., cyclopropane) it was placed 0.5 Å above the center (denoted as NICS (0.5)). The method has been used for the assignment of aromatic character in many systems, generally very successfully.

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THEORETICAL METHODS

Full geometric optimizations of 1-hetero-2,5-cyclohexadiene-1-oxide and 1-hetero-2,5-cyclohexadiene were carried out by the density functional theory (DFT) (Scheme 1). Gaussian 98 offers a wide variety of DFT models [28]. B3LYP method is the best method of DFT model. The B3LYP method is formed through a combination of Becke's three parameters hybrid functional and the LYP semilocal correlation function. 6-311++G** basis set is used with the B3LYP method [29-30]. In order to find thermochemical parameters including thermal energy (E), thermal enthalpy (H) and Gibbs free energy (G), keyword "Freq" was used.


$X = O$ O_O, S S_O, Se Se_O, N N_O, P P_O, As As_O, C C_O, Si Si_O, Ge Ge_O

Scheme 1. The molecular structures of 1-hetero-2,5-cyclohexadiene-1-oxide, X_O, and 1-hetero-2,5-cyclohexadiene, X.

RESULTS AND DISCUSSION

The molecular structures of 1-hetero-2,5-cyclohexadiene-1-oxide (X_O), 4H-pyran-1-oxide (O_O), 4H-thiopyran-1-oxide (S_O), 4H-selenopyran-1-oxide (Se_O), 4H-pyridine-1-oxide (N_O), 4H-phosphinine-1-oxide (P_O), 4H-arsinine-1-oxide (As_O), 2,5-cyclohexadienone (C_O), 4H-siline-1-oxide (Si_O), 4H-germine-1-oxide (Ge_O) are studied and compared with their deoxygenated analogues 1-hetero-2,5-cyclohexadiene (X), 4H-pyran (O), 4H-thiopyran (S), 4H-selenopyran (Se), 4H-pyridine (N), 4H-phosphinine (P), 4H-arsinine (As), 1,4-cyclohexadien (C), 4H-siline (Si), and 4H-germine (Ge) using B3LYP/6-311++G** level (Scheme 1).

Table 1. Bond angle (degree), dihedral angles (degree) and the NBO charge atoms for thiopyran-1-oxide and their analogues at B3LYP/6-311++G** level.
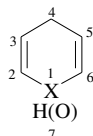
Compound	$A_{2,1,6}$	$D_{2,1,6,5}$	$D_{2,3,4,5}$	$D_{2,1,6,7}$	X_1	C_2	C_3	C_4	$O_7 (H_7)$
X = O$_O$	117.93	4.51	1.57	124.36	-0.259	0.167	-0.229	-0.444	-0.521
X =O	115.99	0.00	0.00	---	-0.532	0.151	-0.269	-0.435	---
X = S$_O$	97.08	20.98	18.07	112.07	1.176	-0.392	-0.163	-0.460	-0.943
X = S	99.61	13.49	21.47	---	0.291	-0.352	-0.203	-0.446	---
X = Se$_O$	94.20	14.74	15.94	107.55	1.319	-0.441	-0.164	-0.461	-0.975
X = Se	96.36	23.00	37.94	---	0.374	-0.396	-0.202	-0.455	---
X = N$_O$	119.00	0.00	0.00	180.00	0.144	-0.062	0.012	-0.238	0.015
X = N	117.95	11.19	10.31	150.74	-0.625	-0.001	-0.254	-0.433	0.384
X = P$_O$	102.57	16.40	13.14	130.50	0.990	-0.296	-0.009	-0.239	-0.323
X = P	98.45	20.55	15.95	100.04	0.569	-0.494	-0.170	-0.456	-0.039
X = As$_O$	98.79	13.66	12.20	118.04	0.858	-0.251	-0.055	-0.234	-0.178
X = As	95.08	18.87	15.41	97.10	0.610	-0.491	-0.177	-0.456	-0.064
X = C$_O$	116.25	0.00	0.00	180.00	0.472	-0.268	-0.111	-0.475	-0.560
X = C	112.92	0.00	0.00	---	-0.450	-0.181	-0.181	-0.450	0.211
X = Si$_O$	105.44	0.00	0.00	180.00	1.895	-0.726	-0.095	-0.483	-1.110
X = Si	103.41	0.01	0.05	---	1.090	-0.633	-0.132	-0.467	-0.175
X = Ge$_O$	103.81	0.00	0.00	180.00	1.759	-0.663	-0.116	-0.478	-1.052
X = Ge	101.45	0.05	0.00	---	0.934	-0.572	-0.150	-0.463	-0.137

The geometrical parameters and NBO charge on atoms are calculated *via* B3LYP/6-311++G** level. For X_O and X, the bond angle $A_{2,1,6}$ is decreased from second row to fourth row elements of the table because of increasing the *p* character of heteroatom (Table 1). This is in good agreement with the simple textbook theory that orbital penetration causes a greater energy difference between the *p* and *s* atomic orbitals as one goes down the periodic table. Hence bonding to *sp*-n hybrid orbitals is favoured in the 1st row and bonding to purer *p*-orbitals further down giving a bond angle nearer 90 degrees. The dihedral angles $D_{2,1,6,5}$ and $D_{2,3,4,5}$ indicate that the most stable boat conformer is obtained for O_O, S_O, Se_O, P_O, As_O, **S**, **Se**, **N**, **P**, **As** and the most stable planar conformer is obtained for N_O, C_O, Si_O, Ge_O, **O**, **C**, **Si**, **Ge**. The NBO charge on atoms for 1-hetero-2,5-cyclohexadiene-1-oxide, X_O, and 1-hetero-2,5-cyclohexadiene, X, are presented (Table 1). For X_O, the charge on heteroatom, X_1 is reasonably more than deoxygenated, X, due to attaching to a more electronegative oxygen atom in X_O. Also, the charge on C_3 for X_O is more than that for X due to electron donating resonance of $C_2=C_3$ along with heteroatom, X. For **X** the charge on C_3 is increased from X = O to X = Se as well as from X = N to X = As due to diminishing the electron donating power of Se and As atoms.

It should be noted that for X = N, P, As, N_O and P_O compounds are radicals with an odd number of electrons (Scheme 1).
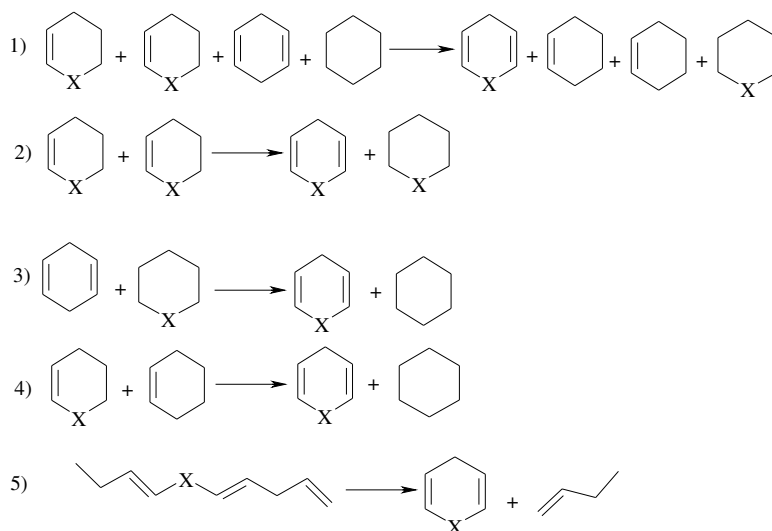
Scheme 2. Five isodesmic reactions for 1-hetero-2,5-cyclohexadiene-1-oxide, X_O and 1-hetero-2,5-cyclohexadiene, **X**.

The compounds X_O and X (except for **C**, C_O, **Si**, Si_O, **Ge** and Ge_O) have 6π-electrons in the ring. It was proposed that the overlap between the lone pair (AO) of heteroatom and the P_z (AOs) of the double-bond carbon atoms (p-π overlap) improve the homo-aromatic character for those compounds. In this work, the homo-aromatic character of those compounds is estimated. Homo-aromatic character is not a directly measurable or computable quantity. Homo-aromaticity is generally evaluated on the basis of energetic, geometric, and magnetic criteria [25-26]. For the energetic criteria, it usually requires the comparison with a non-aromatic model. There are some routes for the estimation of the homo-aromatic stabilization energies (HASE) through various isodesmic reactions [31]. Isodesmic reactions consist of equal numbers

of formal single and double bonds in the products and reactants. Systems with negative HASE are homo-aromatic, while those with positive HASE are non-aromatic. Five isodesmic reactions are presented (Scheme 2, Table 2 and 3). Equations 1 and 2 show that **X** does not create a homo-aromatic system and thus it is less stable than **Xo** (Scheme 2). Since sum of energy stabilization of the formal reactants is more than that of the products in equations 1 and 2. The equations 1 and 2 could not give reliable results because of being overlap of double bonds with heteroatom in the reactants of equations 1 and 2. Therefore, the equations 3 and 5 could give reliable results. However, the ring-strain is not considered in the Equation 5. Equations 3 and 5 indicate that the compounds with **X** are more stable than **Xo**. For **X_O** and **X**, stability is generally decreased from second row to fourth row elements of the table according to equation 3. The most stable compounds from isodesmic reaction 3 are found to be **N** (-9.060 kcal/mol) and **O** (-3.525 kcal/mol). This is in agreement with the idea that the 1st row atoms have superior π-bonding abilities to each other compared with heavier atoms. The high stability of **X** with respect to **X_O** may be attributed to dipole moment. Compounds with higher dipole moment possess lower stability. Thus, **X_O** has high dipole moment and low stability.

Table 2.Gibbs free energies, in kcal/mol, for typically isodesmic reactions of 1-hetero-2,5-cyclohexadiene-1-oxide, **X_O** and 1-hetero-2,5-cyclohexadiene, **X**.

Compound	X +	X +	+	⟶	X +	+	+	X
X=O_O	-216853.550	-216853.550	-192911.844	-194419.890	-216091.638	-193665.150	-193665.150	-217616.030
X=O	-169740.233	-169740.233	-146435.515	-147950.157	-168984.012	-147192.078	-147192.078	-170495.129
X=S_O	-419594.837	-419594.837	-192911.844	-194419.890	-418833.079	-193665.150	-193665.150	-420356.927
X=S	-372412.678	-372412.678	-146435.515	-147950.157	-371654.612	-147192.078	-147192.078	-373170.078
X=Se_O	-1676681.176	-1676681.176	-192911.844	-194419.890	-1675919.010	-193665.150	-193665.150	-1677443.928
X=Se	-1629503.267	-1629503.267	-146435.515	-147950.157	-1628744.561	-147192.078	-147192.078	-1630261.730
X=N_O	-204069.463	-204069.463	-192911.844	-194419.890	-203315.009	-193665.150	-193665.150	-204821.588
X=N	-157265.374	-157265.374	-146435.515	-147950.157	-156512.108	-147192.078	-147192.078	-158017.690
X=P_O	-383951.478	-383951.478	-192911.844	-194419.890	-383194.453	-193665.150	-193665.150	-384710.074
X=P	-337115.221	-337115.221	-146435.515	-147950.157	-336358.017	-147192.078	-147192.078	-337874.866
X=As_O	-1572730.083	-1572730.083	-192911.844	-194419.890	-1571970.656	-193665.150	-193665.150	-1573490.290
X=As	-1525913.560	-1525913.560	-146435.515	-147950.157	-1525155.323	-147192.078	-147192.078	-1526673.805
X=C_O	-193665.150	-193665.150	-192911.844	-194419.890	-192911.844	-193665.150	-193665.150	-194419.890
X=C	-147192.078	-147192.078	-146435.515	-147950.157	-146435.515	-147192.078	-147192.078	-147950.157
X=Si_O	-351433.820	-351433.820	-192911.844	-194419.890	-350679.090	-193665.150	-193665.150	-352189.408
X=Si	-304954.702	-304954.702	-146435.515	-147950.157	-304197.680	-147192.078	-147192.078	-305712.622
X=Ge_O	-1473059.492	-1473059.492	-192911.844	-194419.890	-1472303.411	-193665.150	-193665.150	-1473816.356
X=Ge	-216892.988	-216892.988	-192911.844	-194419.890	-1425841.747	-147192.078	-147192.078	-1427358.356

Table 3. Gibbs free energy gaps, in kcal/mol, results of five isodesmic reactions for 1-hetero-2,5-cyclohexadiene-1-oxide, X_O and 1-hetero-2,5-cyclohexadiene, X.

Compound	HASE (eq. 1)	HASE (eq. 2)	HASE (eq. 3)	HASE (eq. 4)	HASE (eq. 5)
$X = O_O$	0.867	-0.568	16.346	7.171	-1.180
$X = O$	2.840	1.325	-3.525	-1.857	-2.222
$X = S_O$	1.103	-0.332	15.802	7.018	4.001
$X = S$	2.182	0.667	0.824	-0.012	-1.146
$X = Se_O$	0.849	-0.586	16.872	7.426	4.297
$X = Se$	1.758	0.243	2.526	0.627	-0.422
$X = N_O$	3.764	2.329	-1.467	-0.286	-1.036
$X = N$	2.463	0.948	-9.060	-4.813	-0.272
$X = P_O$	-0.136	-1.571	7.575	2.285	2.275
$X = P$	-0.926	-2.441	2.207	-0.874	-1.090
$X = As_O$	0.654	-0.781	11.588	4.686	2.073
$X = As$	-0.493	-2.007	3.840	0.159	-1.180
$X = C_O$	0.000	-1.435	0.000	-1.435	-4.003
$X = C$	0.000	-1.515	0.000	-1.515	-0.960
$X = Si_O$	0.576	-0.859	2.272	-0.011	1.039
$X = Si$	0.617	-0.898	0.299	-1.057	0.836
$X = Ge_O$	0.652	-0.782	4.898	1.340	2.050
$X = Ge$	0.808	-0.707	1.966	-0.128	1.373

Table 4A. NICS values, in ppm, of 1-hetero-2,5-cyclohexadiene-1-oxide, X_O, and 1-hetero-2,5-cyclohexadiene, X.
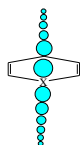
| Compound	NICS (-0.8)	NICS (-0.7)	NICS (-0.6)	NICS (-0.5)	NICS (-0.4)	NICS (-0.3)	NICS (-0.2)	NICS (-0.1)
O_O	-0.33	-0.36	-0.46	-0.68	-1.08	-1.74	-2.68	-3.92
O	1.25	0.98	0.52	-0.14	-0.98	-1.90	-2.74	-3.34
S_O	-1.49	-1.62	-1.82	-2.13	-2.55	-3.10	-3.78	-4.53
S	-1.87	-2.55	-3.34	-4.21	-5.10	-5.92	-6.58	-7.00
Se_O	-1.47	-1.69	-1.98	-2.36	-2.82	-3.37	-3.98	-4.61
Se	-6.50	-7.38	-8.28	-9.15	-9.92	-10.53	-10.92	-11.06
N_O	-0.02	-0.11	-0.20	-0.25	-0.23	-0.15	-0.02	0.09
N	2.38	2.33	2.10	1.66	1.03	0.26	-0.54	-1.23
P_O	-1.34	-1.42	-1.50	-1.57	-1.62	-1.66	-1.68	-1.67
P	-1.28	-1.66	-2.09	-2.55	-3.01	-3.45	-3.83	-4.12
As_O	-1.13	-1.20	-1.25	-1.26	-1.22	-1.12	-0.97	-0.77
As	-2.00	-2.42	-2.87	-3.31	-3.73	-4.09	-4.38	-4.56
C_O	-2.26	-1.82	-1.14	-0.21	0.92	2.13	3.21	3.98
C	-0.85	-1.14	-1.49	-1.89	-2.30	-2.69	-3.01	-3.23
Si_O	-2.03	-1.90	-1.69	-1.40	-1.07	-0.72	-0.42	-0.22
Si	-1.65	-1.73	-1.77	-1.76	-1.72	-1.65	-1.57	-1.51
Ge_O	-1.18	-0.97	-0.70	-0.38	-0.03	0.29	0.56	0.74
Ge	-1.18	-1.33	-1.48	-1.61	-1.73	-1.83	-1.91	-1.95

Table 4B. NICS values, in ppm, of 1-hetero-2,5-cyclohexadiene-1-oxide, X_O, and 1-hetero-2,5-cyclohexadiene, **X**.
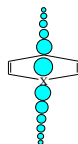
Compound	NICS (0.0)	NICS (0.1)	NICS (0.2)	NICS (0.3)	NICS (0.4)	NICS (0.5)	NICS (0.6)	NICS (0.7)	NICS (0.8)
O_O	-5.37	-6.84	-8.12	-8.98	-9.26	-8.95	-8.16	-7.07	-5.87
O	-3.55	-3.34	-2.74	-1.90	-0.98	-0.14	0.52	0.98	1.25
S_O	-5.33	-6.10	-6.77	-7.29	-7.61	-7.73	-7.66	-7.42	-7.05
S	-7.12	-6.91	-6.40	-5.66	-4.77	-3.82	-2.89	-2.05	-1.33
Se_O	-5.61	-6.07	-6.37	-6.51	-6.47	-6.28	-5.98	-5.59	-5.16
Se	-10.91	-10.50	-9.87	-9.06	-8.16	-7.23	-6.31	-5.45	-4.66
N_O	0.14	0.09	-0.02	-0.15	-0.23	-0.25	-0.20	-0.11	-0.02
N	-1.68	-1.79	-1.55	-1.03	-0.32	0.43	1.12	1.67	2.07
P_O	-1.61	-1.60	-1.60	-1.63	-1.68	-1.76	-1.83	-1.89	-1.91
P	-4.30	-4.35	-4.26	-4.05	-3.75	-3.38	-2.98	-2.57	-2.17
As_O	-0.54	-0.28	-0.06	0.13	0.27	0.34	0.37	0.34	0.28
As	-4.62	-4.40	-4.12	-3.75	-3.33	-2.88	-2.45	-2.04	-1.67
C_O	4.26	3.99	3.22	2.13	0.92	-0.21	-1.14	-1.82	-2.26
C	-3.32	-3.24	-3.02	-2.69	-2.30	-1.89	-1.49	-1.14	-0.85
Si_O	-0.14	-0.22	-0.42	-0.72	-1.07	-1.40	-1.69	-1.90	-2.03
Si	-1.49	-1.51	-1.57	-1.65	-1.72	-1.76	-1.77	-1.73	-1.65
Ge_O	0.81	0.75	0.57	0.29	-0.03	-0.38	-0.70	-0.97	-1.18
Ge	-1.96	-1.94	-1.90	-1.83	-1.73	-1.61	-1.48	-1.33	-1.18

Another accurate method for determining the homo-aromatic character is magnetic criteria. NICS calculations are carried out on X_O and **X** for determination of the aromatic character (Table 4, Figure 1). Negative and positive signs for NICS indicate the aromatic and anti-aromatic characters, respectively. NICS (0.5) calculations generally give reliable results. NICS calculations achieve differential results for non-planar molecules because of two differential electrons current in each surface. Therefore, we have two NICS (+0.5, -0.5) data for non-planar molecules on two surfaces (Table 4 Figure 1). The NICS (+0.5) value is related to the boat region and NICS (-0.5) is related to the opposite region. The NICS (+0.5) calculation generally shows high aromatic character (Figure 1). For **X** compounds, the NICS (+0.5) value as well as aromatic character are increased from **O** to **Se** while NICS (+0.5) for **P** is the highest with respect to those of **As** and **N**. For X_O compounds, the NICS (+0.5) values are decreased from O_O to Se_O while NICS (+0.5) for P_O is the highest with respect to those of As_O and N_O. The calculation of NICS (+0.5) indicates that X_O is the highest among O_O, S_O, Se_O and N_O. This is probably attributed to the carbocationic character of the heteroatom and conjugation of this positive charge with double bonds.

The changes of nuclear independent chemical shift, NICS, *vs.* distance of ghost atom are determined (Figure 1). The same groups of the periodic table produce similar dependence curves.

Finally, in comparison of the isodesmic reactions and NICS, we can conclude that the homo-aromatic characters (from NICS) of X_O and **X** do not affect in the stabilities (from isodesmic reactions) of X_O and **X**.
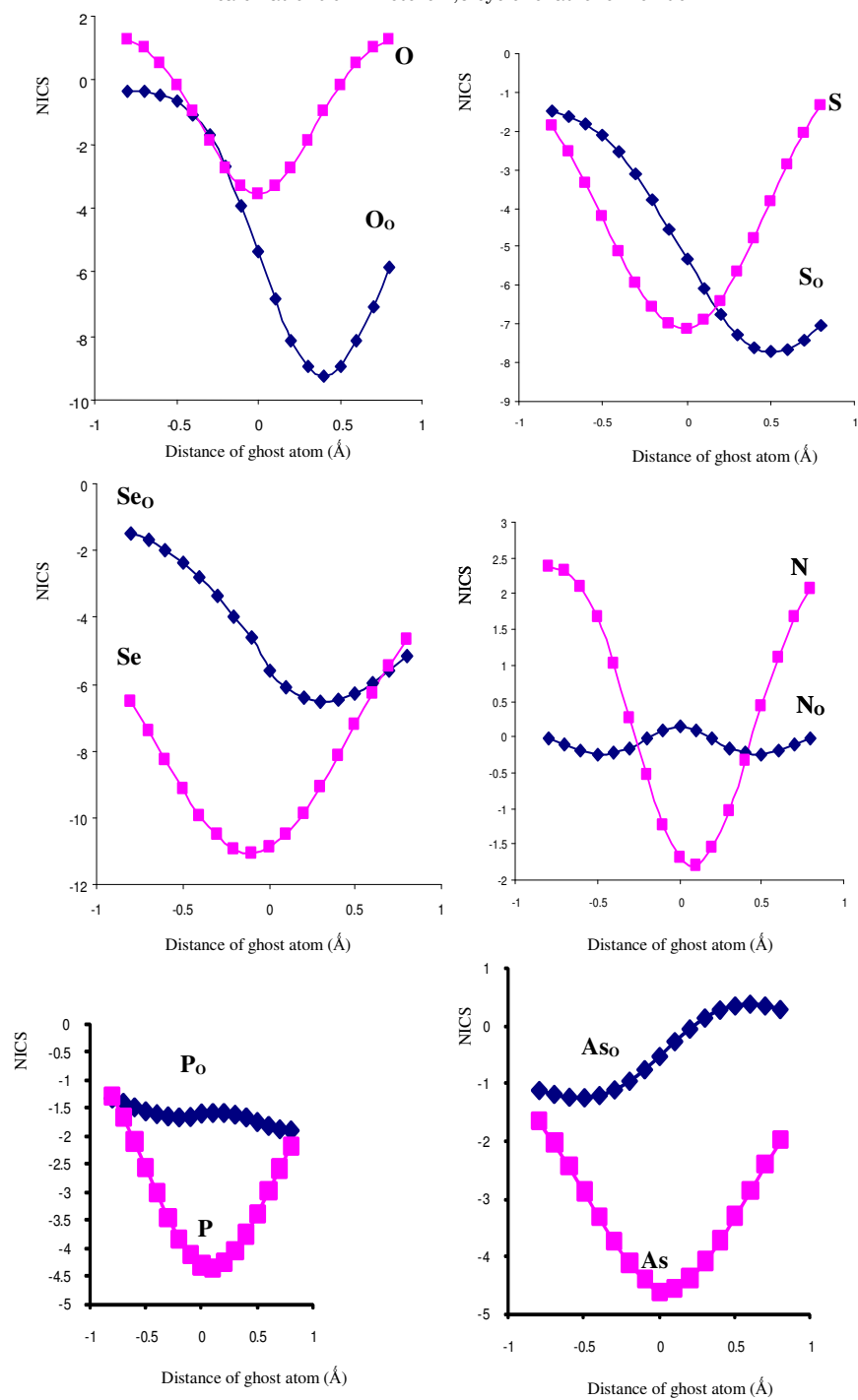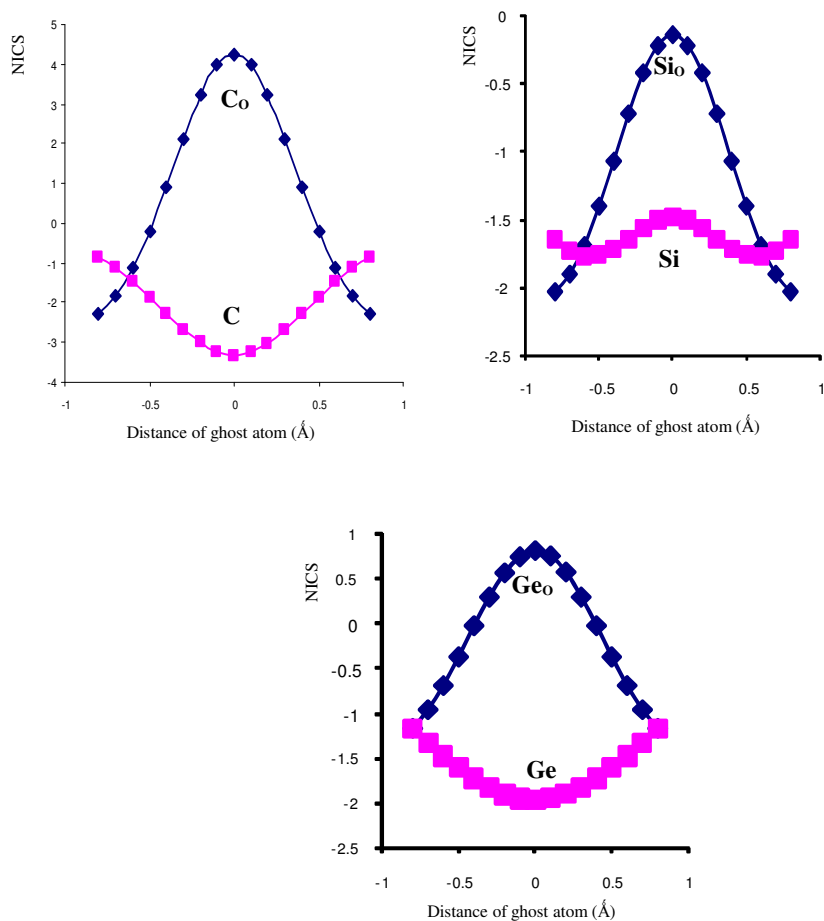
Figure 1. The NICS changes *vs.* distance of the ghost atom for 1-hetero-2,5-cyclohexadiene-1-oxide, X_O, and 1-hetero-2,5-cyclohexadiene, X.

CONCLUSION

The molecular structure of 1-hetero-2,5-cyclohexadiene-1-oxide, X_O, is studied and compared with that of the corresponding deoxygenated compound, 1-hetero-2,5-cyclohexadiene, X, at B3LYP/6-311++G** level. Isodesmic reactions to determine the stabilities of X_O and X are considered. Isodesmic reactions indicate that the compound X is more stable than Xo. For X_O and X, the stability is generally decreased from second row to fourth row elements in the table. Nuclear independent chemical shifts, NICS, are calculated for investigation of the homo-aromatic characters of X_O and X. For X compound, the NICS (+0.5) value as well as the aromatic character are increased from O to Se while NICS (+0.5) for P is the highest with respect to those of As and N.

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