Iranian Journal of Organic Chemistry Vol. 9, No. 1 (2017) 1981-1993

IranJOC
Iranian Journal of
Organic Chemistry

Theoretical studies on the structural properties, aromaticity and reactivity of 1*H*-phosphole derivatives

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Received: November 2016; Revised: December 2016; Accepted: January 2017

Abstract: In the present research work, we have done a comparative study of 1*H*-phosphole molecule and its derivatives substituted on C2 or C3 atoms with B3LYP/6-311++G(d,p) level of theory. Here, we have done an investigation of their structures, aromaticity, and global and local reactivity of 1*H*-phosphole molecule and its derivatives. The aromaticity property of all compounds was considered by NICS and BIRD indices. Also, we have used frontier orbital HOMO-LUMO energies and relative calculations (global hardness, electronic chemical potential, electronegativity, global softness, nucleophilicity index and electrophilicity index) to explain the stability and reactive nature of 1*H*-phosphole and its derivatives. The reactivity of different atoms in each molecule was studied by Fukui functions.

Keywords: DFT study, 1*H*-phosphole, Aromaticity, Global reactivity, Local reactivity.

Introduction

The 1*H*-phosphole ring is an organic molecule with the chemical formula C_4H_4PH. This heterocyclic compound is the phosphorus analog of the pyrrole molecule. Recently, the organic materials based on the phosphole ring received much attention due to their characteristic optical and electronic properties [1].The phosphole compound has a low-lying lowest unoccupied molecular orbital (LUMO) and low aromaticity [2]. Pentaphenylphosphole is the first phosphole compound that was prepared in 1953 [3]. Hughes and Srivanavit worked on thermal and photochemical ring expansion of some phosphole derivatives. In another work, churchman et.al studied the site of protonation in phosphole derivatives. They found the 1*H*-phospholium salts stabilized by complex transition metal ions [4].

Laszlo Nyulaszi investigated on the substituents effect on the aromatization of phosphole ring in 1995 [5]. Klaus Eichele and his co-workers studied the phosphorus chemical shift tensors of phosphole derivatives by ^{31}P NMR spectroscopy technique of powder samples [6].In 2001, Eric Mattmann et.al.prepared the trivalent 7-phosphanobornenes by enhancing the dienic reactivity of the phosphole materials [7].The de-aromatizing of the phosphole compounds were investigated by Mattmann group. They used the quantum-chemical density functional theory (DFT) computations for study of this property [8]. Jeanne Crassous and Regis Reau synthesized the π-conjugated phosphole derivatives in 2008. They also studied the optoelectronic functions and coordination chemistry of those compounds [9].Some of the phosphole*P*-oxide molecules were reported by Arihiro Saito et.al. in 2009 [10]. The palladium-catalyzed

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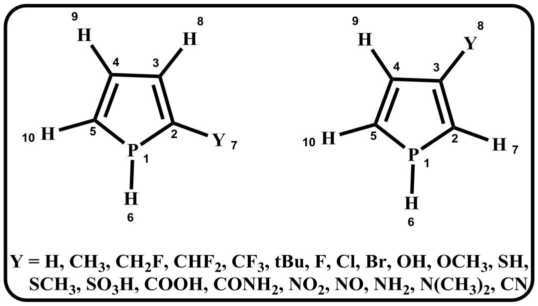
direct synthesis of phosphole derivatives was first reported by the Katsuaki Baba group in 2013 [11].

Recently, the various materials based on this heterocyclic compound were synthesized and studied theoretically [12]. In the present research work, the main aim of my investigations is the study of structural properties, aromaticities and reactivities of various 1*H*-phosphole derivatives containing different substituents on positions 2 or 3.

Results and discussion

The structure of the positions 2 and 3 substituted 1*H*-phospholes is shown in Scheme **1**.



Scheme 1: The studied 1*H*-phosphole derivatives substituted at positions 2 and 3.

The present study is divided into three parts. The first part studies the structural properties of the studied molecules. In second part, aromaticity and stability of the compounds are investigated. Finally, the third part of this research work is related to the study of the global and local reactivity of all molecules.

Bond lengths, bond angles and dihedral angles of the 1*H*-phosphole derivatives

The bond lengths data of the 1H-phosphole derivatives substituted on C2 are collected in Table **1**.

It can be seen from the data, the geometry of the molecules changes depending on the substituent. The P-C2 bond length of 1*H*-phosphole ring containing electron withdrawing substituents on position 2 varies between 1.72 and 1.74 A^{o}. Also, the electron donating groups cause longer distances. We can see the P-C2 distance of phosphole compound containing methyl and t-butyl substituents is 1.737 and 1.842 A^{o}, respectively. Hence, the more electron-donating substituent cause the longer distance of P-C2 bond. The distance of this bond for the molecules containing –CH_2F, -CHF_2 and –CF_3 substituents are 1.736, 1.828 and 1.731 A^{o}, respectively. Exceptionally, the P-C2 bond distance of 1*H*-phosphole substituted by –CHF_2 group is longer than the –CH_2F and –CF_3 groups. Probably, the asymmetric steric bulk distribution of the F atoms of this substituent to hydrogen atom causes the longer distance of P-C2 bond. Also, the –SO_3H substituent polarizes the P-C2 bond. For this reason, the distance of this bond in the molecule containing –SO_3H substituent is 1.824 A^{o}. The P-C5 bond distance of the molecules with electron-withdrawing and electron-donating substituents is in range 1.70-1.73 and 1.81-1.82 A^{o}, respectively. Exceptionally, this bond in 2-(difluoromethyl)-1*H*-phosphole and is 1.815 A^{o}. Also, the P-C5 bond of 1*H*-phosphole-2-sulfonic acid polarized by –SO3H group and is 1.817 A^{o}. The data of the Table **1** shows the range of C2-C3, C3-C4 and C4-C5 bonds lengths of all compounds are 1.35-1.41, 1.40-1.46, 1.35-1.41 and 1.07-1.08 A^{o}, respectively. The P-H6 bond of molecules containing electron-donating substituents is longer than the electron-withdrawing groups.

Table **2** indicates the bond lengths data of the 1H-phosphole compounds substituted on position 3.

The electronegative substituents cause the shorter P-C2 and P-C5 bonds lengths than the electron-donation substituents. These bonds distances are in range 1.71-1.73 and 1.81-1.82 A^{o} for molecules containing electronegative and electron-donating substituents, respectively.The C-C bonds distances vary from 1.35 to 1.45 A^{o}. The short P-H6 bonds are related to the 1*H*-phospholes with electron-withdrawing substituents on position 3. The distance of C-H bonds of all molecules is about 1.08 A^{o}.

It can be seen from the data, the angles order is: C-C-C > C-C-P > C-P-C. The C-C-C angles vary from 113 degree to 117 degree. The range of C-C-P angles of molecules is 105-111 degree. The small and big C-C-P angles relate to the 1*H*-phosphole compounds containing electron-withdrawing and electron-donating substituents, respectively. Also, the C-P-C bond angles are in range 88-99 degree. The molecules with electron-withdrawing substituents on position 2 have bigger C-P-C bond angles than the electron-donating substituents.

Table 1: The bond lengths data of the 1*H*-phosphole derivatives substituted on C2 atom.

Y	P-C2	C2-C3	C3-C4	C4-C5	C5-P	P-H6	C2-Y	C3-H8	C4-H9	C5-H10
H	1.725	1.390	1.420	1.390	1.725	1.391	1.078	1.082	1.082	1.078
CH_3	1.737	1.390	1.422	1.386	1.730	1.392	1.501	1.084	1.083	1.078
CH_2F	1.736	1.388	1.422	1.385	1.729	1.392	1.498	1.081	1.082	1.078
CHF_2	1.828	1.355	1.453	1.354	1.815	1.421	1.483	1.086	1.084	1.082
CF_3	1.731	1.392	1.415	1.391	1.720	1.391	1.483	1.081	1.082	1.078
tBu	1.842	1.357	1.457	1.352	1.814	1.422	1.522	1.084	1.085	1.082
F	1.739	1.375	1.425	1.385	1.733	1.390	1.344	1.081	1.082	1.077
Cl	1.733	1.384	1.421	1.388	1.727	1.391	1.736	1.082	1.082	1.078
Br	1.730	1.385	1.421	1.388	1.727	1.391	1.892	1.082	1.082	1.078
CN	1.736	1.402	1.410	1.394	1.717	1.391	1.409	1.081	1.082	1.078
COOH	1.733	1.400	1.409	1.398	1.715	1.390	1.456	1.081	1.082	1.078
$CONH_2$	1.731	1.399	1.412	1.396	1.717	1.390	1.474	1.083	1.082	1.078
OH	1.834	1.354	1.456	1.353	1.820	1.423	1.358	1.085	1.085	1.081
OCH_3	1.842	1.358	1.457	1.352	1.820	1.423	1.349	1.082	1.085	1.081
SH	1.834	1.356	1.456	1.353	1.820	1.421	1.771	1.084	1.085	1.082
SCH_3	1.839	1.358	1.455	1.353	1.819	1.421	1.768	1.084	1.085	1.082
SO_3H	1.824	1.356	1.451	1.354	1.817	1.421	1.759	1.084	1.084	1.082
NO_2	1.732	1.392	1.408	1.400	1.715	1.390	1.429	1.081	1.082	1.078
NO	1.743	1.406	1.400	1.407	1.708	1.392	1.397	1.081	1.082	1.078
NH_2	1.847	1.361	1.452	1.353	1.819	1.423	1.385	1.085	1.086	1.081
$N(CH_3)_2$	1.855	1.370	1.449	1.354	1.814	1.425	1.378	1.082	1.086	1.081

Table 2: The bond lengths data of the 1*H*-phosphole derivatives substituted on C3 atom.

Y	P-C2	C2-C3	C3-C4	C4-C5	C5-P	P-H6	C2-H7	C3-Y	C4-H9	C5-H10
H	1.725	1.390	1.420	1.390	1.725	1.391	1.078	1.082	1.082	1.078
CH_3	1.813	1.356	1.465	1.352	1.816	1.424	1.082	1.503	1.086	1.082
CH_2F	1.813	1.354	1.463	1.352	1.816	1.423	1.081	1.499	1.086	1.082
CHF_2	1.812	1.354	1.461	1.352	1.814	1.422	1.081	1.499	1.084	1.082
CF_3	1.812	1.353	1.460	1.352	1.814	1.421	1.081	1.498	1.084	1.081
tBu	1.813	1.358	1.470	1.351	1.814	1.424	1.081	1.527	1.085	1.082
F	1.728	1.382	1.411	1.392	1.723	1.390	1.077	1.355	1.081	1.078
Cl	1.726	1.385	1.416	1.390	1.723	1.391	1.077	1.754	1.081	1.078
Br	1.726	1.385	1.417	1.390	1.724	1.391	1.077	1.911	1.081	1.078
CN	1.714	1.401	1.428	1.384	1.727	1.391	1.077	1.423	1.081	1.078
COOH	1.713	1.399	1.426	1.382	1.731	1.392	1.077	1.470	1.082	1.078
$CONH_2$	1.712	1.396	1.427	1.386	1.728	1.392	1.078	1.491	1.083	1.078
OH	1.808	1.354	1.462	1.350	1.820	1.425	1.080	1.365	1.087	1.081
OCH_3	1.803	1.359	1.465	1.352	1.816	1.425	1.080	1.361	1.083	1.082
SH	1.728	1.390	1.423	1.388	1.722	1.391	1.078	1.788	1.082	1.078
SCH_3	1.814	1.359	1.466	1.349	1.817	1.425	1.080	1.769	1.085	1.082
SO_3H	1.814	1.351	1.458	1.351	1.816	1.421	1.081	1.785	1.083	1.082
NO_2	1.711	1..392	1.418	1.383	1.731	1.392	1.077	1.453	1.080	1.078
NO	1.804	1.362	1.461	1.350	1.819	1.421	1.082	1.426	1.082	1.082
NH_2	1.807	1.363	1.466	1.348	1.820	1.427	1.082	1.392	1.086	1.082
$N(CH_3)_2$	1.806	1.369	1.471	1.348	1.819	1.428	1.079	1.395	1.083	1.082

Table **3** collects the bond angles data of the molecules containing various substitutions on position 2.

The bond angles data of the molecules containing different substitutions on position 3 is collected in Table **4**. The order of bond angles of the molecules is: C-C-C (112-117 degree) > C-C-P (105-111 degree) > C-P-C (89-99 degree). From the data, the C-C-P bond angles of 1*H*-phosphole compounds containing electron-donating substituents are bigger than the electron-withdrawing substituents. Also, we can see the molecules with electron-withdrawing and electron-donating substituents have big and small C-P-C bond angles, respectively.

Table 3: The bond angles data of the 1*H*-phosphole derivatives substituted on C2 atom.

Y	P-C2-C3	C2-C3-C4	C3-C4-C5	C4-C5-P	C5-P-C2
H	105.143	115.513	115.513	105.143	98.688
CH_3	103.903	116.577	115.440	104.886	99.194
CH_2F	104.655	115.923	115.637	105.112	98.673
CHF_2	110.056	114.532	113.943	110.842	89.538
CF_3	105.612	115.112	115.511	105.736	98.030
tBu	108.323	115.491	114.625	109.834	90.848
F	107.509	113.676	116.386	105.791	96.638
Cl	106.356	114.426	116.110	105.461	97.647
Br	106.266	114.459	116.076	105.385	97.814
CN	105.240	115.114	115.712	105.766	98.167
COOH	105.504	115.101	115.454	105.886	98.055
$CONH_2$	105.268	115.314	115.365	105.730	98.323
OH	111.247	112.909	115.508	110.391	89.069
OCH_3	111.240	112.667	115.778	110.390	89.101
SH	110.313	113.959	115.067	110.251	89.805
SCH_3	109.943	114.337	114.856	110.420	89.837
SO_3H	111.406	113.450	114.054	111.341	88.597
NO_2	107.449	113.623	115.811	106.448	96.669
NO	105.825	114.499	115.932	106.014	97.729
NH_2	110.015	113.732	115.854	109.949	89.898
$N(CH_3)_2$	109.074	113.906	116.081	109.790	90.224

Table **5** shows the dihedral angles of 1*H*-phosphole compounds substituted on position 2. It can be seen from the data, the molecules with substituents H, CH_3, CH_2F, F, Cl, Br, CN, COOH, $CONH_2$, NO and NO_2 on C2 atom are planar. In other hand, the 1*H*-phosphole compounds containing electron-donating substituents (CHF_2, tBu, OH, OCH_3, SH, SCH_3, NH_2 and NMe_2) and SO_3H group (with polarization of P-C bond) are not planar. The torsion angle range inside the ring of these molecules is 4.5-6.5 degree. Also, the C-C-P-H dihedral angle of these compounds is about 70-77 degree.

The dihedral angles data of 1*H*-phosphole compounds substituted on position 3 is shown in Table **6**.

Table 4: The bond angles data of the 1*H*-phosphole derivatives substituted on C3 atom.

Y	P-C2-C3	C2-C3-C4	C3-C4-C5	C4-C5-P	C5-P-C2
H	105.143	115.513	115.513	105.143	98.688
CH_3	110.987	112.964	115.000	109.965	89.976
CH_2F	110.278	113.967	114.355	110.048	90.216
CHF_2	109.919	114.463	113.943	110.215	90.292
CF_3	109.641	114.888	113.603	110.353	90.296
tBu	111.410	112.293	115.310	109.947	89.297
F	103.961	117.657	114.006	105.679	98.697
Cl	104.407	116.808	114.487	105.566	98.733
Br	104.376	116.848	114.468	105.566	98.743
CN	105.113	115.262	115.218	105.442	98.964
COOH	105.062	115.322	115.487	105.133	98.997
$CONH_2$	105.671	114.650	115.808	104.998	98.872
OH	109.682	114.864	113.767	110.135	90.466
OCH_3	109.963	114.454	113.628	110.355	90.430
SH	105.242	115.372	115.409	105.458	98.519
SCH_3	110.157	114.074	114.142	110.437	90.180
SO_3H	108.692	116.248	112.726	110.583	90.492
NO_2	104.075	117.160	114.164	105.483	99.119
NO	109.425	115.181	113.093	110.629	90.335
NH_2	110.574	113.670	114.304	110.448	90.112
$N(CH_3)_2$	111.089	112.907	114.479	110.723	89.963

Table 5: The dihedral angles data of the 1*H*-phosphole derivatives substituted on C2 atom.

Y	P-C2-C3-C4	C2-C3-C4-C5	C3-C4-C5-P	C4-C5-P-C2	C5-P-C2-C3	C4-C5-P-H6	C3-C2-P-H6
H	0.002	0.006	0.007	0.005	0.002	179.993	179.990
CH_3	0.005	0.008	0.006	0.002	0.001	179.999	179.995
CH_2F	0.005	0.006	0.004	0.001	0.003	179.993	179.997
CHF_2	6.794	0.457	7.562	9.400	9.071	109.858	109.868
CF_3	0.001	0.002	0.003	0.002	0.001	179.999	179.998
tBu	6.059	0.372	6.757	8.445	8.122	108.988	108.807
F	0.019	0.003	0.023	0.029	0.028	179.929	179.934
Cl	0.005	0.004	0.000	0.003	0.005	179.990	179.992
Br	0.003	0.001	0.002	0.004	0.004	179.990	179.991
CN	0.002	0.001	0.003	0.004	0.003	179.991	179.991
COOH	0.004	0.001	0.006	0.007	0.007	179.984	179.984
$CONH_2$	0.004	0.002	0.001	0.003	0.004	179.992	179.993
OH	6.125	0.444	6.811	8.333	8.228	106.025	108.996
OCH_3	5.720	0.717	6.826	8.152	7.898	105.695	108.517
SH	4.988	0.471	5.723	6.997	6.769	104.988	107.394
SCH_3	4.889	0.578	5.816	7.042	6.712	105.009	107.344
SO_3H	7.489	0.090	7.378	9.486	9.561	109.314	109.498
NO_2	0.008	0.002	0.010	0.013	0.012	179.969	179.970
NO	0.004	0.001	0.005	0.006	0.006	179.986	179.986
NH_2	4.507	0.762	5.702	6.724	6.362	103.749	107.127
$N(CH_3)_2$	6.549	0.044	6.664	8.485	8.510	106.206	110.011

Table 6: The dihedral angles data of the 1*H*-phosphole derivatives substituted on C3 atom.

Y	P-C2-C3-C4	C2-C3-C4-C5	C3-C4-C5-P	C4-C5-P-C2	C5-P-C2-C3	C4-C5-P-H6	C3-C2-P-H6
H	0.002	0.006	0.007	0.005	0.002	179.993	179.990
CH_3	7.459	0.273	6.994	9.212	9.498	110.865	110.245
CH_2F	7.507	0.252	7.113	9.386	9.551	111.011	110.500
CHF_2	7.293	0.153	7.525	9.665	9.534	111.020	111.368
CF_3	7.556	0.007	7.572	9.849	9.747	110.883	111.848
tBu	7.332	0.060	7.169	9.278	9.509	110.704	110.445
F	0.001	0.006	0.007	0.005	0.002	179.992	179.990
Cl	0.002	0.006	0.010	0.010	0.007	179.980	179.977
Br	0.003	0.009	0.010	0.007	0.003	179.989	179.985
CN	0.003	0.002	0.005	0.006	0.005	179.986	179.986
COOH	0.002	0.007	0.007	0.005	0.002	179.993	179.990
$CONH_2$	0.002	0.007	0.007	0.005	0.002	179.993	179.989
OH	7.410	0.349	6.869	9.200	9.306	111.605	108.627
OCH_3	7.724	0.407	7.088	9.546	9.690	112.108	109.354
SH	0.001	0.006	0.008	0.006	0.003	179.991	179.988
SCH_3	7.207	0.430	6.571	8.823	9.020	110.557	108.955
SO_3H	7.332	0.412	8.021	10.199	9.697	110.920	112.064
NO_2	0.001	0.001	0.003	0.003	0.003	179.994	179.994
NO	7.902	0.026	7.936	10.387	10.156	111.595	113.629
NH_2	7.232	1.015	5.674	8.083	8.640	110.990	107.162
$N(CH_3)_2$	6.966	0.908	5.552	7.855	8.388	110.759	106.526

From the data, the substituents CH_3, CH_2F, CHF_2, CF_3, tBu, OH, OCH_3, SCH_3, SO_3H, NO, NH_2 and NMe_2 on position 3 of 1H-phosphole heterocyclic compound destroy the planarity of ring. These substituents make the torsion angle in range 7-10 degree inside the ring and the C-C-P-H dihedral angle about 68-72 degree. On other hand, the molecules containing electron-withdrawing substituents on position 3 are plane and have not any torsional and dihedral angles.

Bond orders and aromaticity indices of the 1H-phosphole derivatives:

The aromaticity concept is virtually a tenet of faith to organic chemists yet its quantification is a good parameter to explore the structural properties of the molecules. There are several methods for study of the aromaticitiy property of molecules [13-15]. Here, nucleus independent chemical shift (NICS) and BIRD indices were used for discussion about the aromaticity of the studied compounds.

In 1996, P. Schleyer and his co-workers proposed the NICS index for study of stability and aromaticity in organic rings. They used the absolute magnetic shieldings, computed at ring centers with quantum mechanics computations, as a novel aromaticity/antiaromaticity criterion. The negative and positive NICSs state the aromaticity and antiaromaticity properties, respectively. Also, small nucleus independent chemical shifts denote nonaromaticity [16].

In 1991, Clive Bird reported new index for aromaticity property of five-membered, six-membered, and fused five and six-membered heterocycles [17]. The variation coefficient for the bond orders of a heterocycle compound is given by the expression:

$$V = \frac{100}{\bar{N}} \sqrt{\frac{\Sigma(N - \bar{N})^2}{n}}$$

Where $\bar{N}$ is the arithmetic mean of the various bond orders (N), and n is the number of bonds. The Bird aromaticity index is expressed by following formulas:

$$BIRD\ Index = 100(1 - \frac{V}{V_K})$$

The non-delocalized Kekule variation coefficient (V_K) of bond orders is 35, 33.3 and 35 for a five-membered ring heterocycle, a six-membered ring heterocycle and a five-membered ring fused to the six-membered ring heterocycle, respectively.

Table **7** shows the Wibergbond orders data and aromaticity parameters (nucleus independent chemical shift NICS and BIRD indices) of the 1*H*-phosphole derivatives substituted on C2 atom.

Table 7: The bond orders data and aromaticity indices of the 1*H*-phosphole derivatives substituted on C2 atom.

Y	NICS(0)	BIRD Index	$n_{(P1-C2)}$	$n_{(C2-C3)}$	$n_{(C3-C4)}$	$n_{(C4-C5)}$	$n_{(C5-P1)}$
H	-16.227	74.789	1.264	1.534	1.347	1.534	1.264
CH_3	-15.291	71.923	1.225	1.515	1.328	1.550	1.248
CH_2F	-15.411	71.358	1.214	1.514	1.327	1.553	1.251
CHF_2	-4.936	28.019	0.990	1.714	1.162	1.771	1.045
CF_3	-16.125	76.123	1.202	1.472	1.363	1.518	1.299
tBu	-4.186	25.820	1.000	1.744	1.150	1.783	1.031
F	-16.979	68.373	1.212	1.531	1.305	1.568	1.227
Cl	-15.967	71.524	1.199	1.499	1.327	1.546	1.252
Br	-15.733	72.242	1.207	1.502	1.329	1.542	1.256
CN	-16.366	76.703	1.170	1.412	1.390	1.497	1.308
COOH	-15.202	79.130	1.190	1.420	1.401	1.480	1.327
$CONH_2$	-15.333	79.316	1.208	1.439	1.386	1.491	1.314
OH	-4.447	25.940	0.981	1.690	1.147	1.785	1.018
OCH_3	-4.115	26.276	0.981	1.674	1.145	1.787	1.017
SH	-3.944	25.380	0.975	1.704	1.149	1.784	1.021
SCH_3	-3.710	25.456	0.971	1.709	1.152	1.780	1.025
SO_3H	-5.291	28.187	0.976	1.700	1.164	1.765	1.047
NO_2	-15.239	78.360	1.176	1.416	1.400	1.476	1.329
NO	-13.893	78.523	1.162	1.359	1.447	1.432	1.362
NH_2	-3.566	27.682	0.973	1.650	1.161	1.774	1.015
$N(CH_3)_2$	-3.684	29.900	0.974	1.614	1.173	1.761	1.015

From the data, we can see the NICS index of the molecules containing H, CH_3, CH_2F, CF_3, F, Cl, Br, CN, COOH, $CONH_2$, NO_2 and NO substituents on C2 is in minus 16-14 range. The compounds with H, F, Cl, Br, CN, COOH, $CONH_2$, NO_2 and NO substituents indicate the range of 68-80 to BIRD parameter but the molecules containing CH_3, CH_2F and CF_3substituents show 25-30 range. Adversely, the molecules with CHF_2, tBu, OH, OCH_3, SH, SCH_3, SO_3H, NH_2 and NMe_2 substituents show minus 3-5 and 25-30 ranges for NICS and BIRD parameters, respectively.In other hand, for all molecules the C2-C3 and C4-C5 bond orders are greater than the P1-C2, C3-C4 and C5-P1 bond orders. It can be seen from these data, the bonds in all compounds are not equivalent. Also, we can conclude that the NICS and BIRD parameters don't state the aromaticity of the 1*H*-phosphole compounds substituted on C2 atom with electron-withdrawing groups appropriately.

The Wibergbond orders data and aromaticity parameters (NICS and BIRD indices) of the 1*H*-phosphole derivatives substituted on C3 atom are collected in Table **8**.

Table 8: The bond orders data and aromaticity indices of the 1*H*-phosphole derivatives substituted on C3 atom.

Y	NICS(0)	BIRD Index	$n_{(P1-C2)}$	$n_{(C2-C3)}$	$n_{(C3-C4)}$	$n_{(C4-C5)}$	$n_{(C5-P1)}$
H	-16.227	74.789	1.264	1.534	1.347	1.534	1.264
CH_3	-4.931	26.548	1.030	1.736	1.125	1.790	1.033
CH_2F	-5.026	27.284	1.033	1.732	1.128	1.786	1.036
CHF_2	-5.429	28.199	1.042	1.729	1.130	1.784	1.040
CF_3	-5.770	28.414	1.045	1.723	1.127	1.786	1.041
tBu	-4.952	26.083	1.030	1.743	1.121	1.790	1.032
F	-17.807	75.391	1.225	1.505	1.323	1.512	1.281
Cl	-16.641	75.574	1.242	1.500	1.317	1.523	1.274
Br	-16.516	75.307	1.242	1.510	1.324	1.522	1.273
CN	-16.638	75.887	1.313	1.429	1.275	1.562	1.252
COOH	-15.606	74.264	1.325	1.441	1.281	1.577	1.234
$CONH_2$	-15.658	76.230	1.319	1.458	1.297	1.555	1.245
OH	-6.735	28.130	1.020	1.678	1.120	1.783	1.030
OCH_3	-6.832	29.475	1.026	1.670	1.121	1.773	1.035
SH	-15.997	74.277	1.226	1.496	1.306	1.530	1.273
SCH_3	-4.813	26.643	1.007	1.682	1.121	1.796	1.028
SO_3H	-6.486	28.023	1.035	1.729	1.132	1.783	1.041
NO_2	-16.334	75.537	1.326	1.438	1.288	1.567	1.240
NO	-5.340	30.768	1.074	1.625	1.107	1.805	1.030
NH_2	-5.912	27.370	1.017	1.647	1.107	1.800	1.024
$N(CH_3)_2$	-5.447	27.414	1.021	1.638	1.105	1.805	1.022

From the data, the molecules including H, F, Cl, Br, CN, COOH, $CONH_2$, SH and NO_2 substituents show minus 15.5-17.8 and 74.2-76.2 for NICS(0) and BIRD factors, respectively. Adversely, the NICS(0) and BIRD indices of the molecules containing CH_3, CH_2F, CHF_2, CF_3, tBu, OH, OCH_3, SCH_3, SO_3H, NO, NH_2 and NMe_2 groups on C3 atom are in minus 4.8-6.7 and 26-30.8 ranges. In other hand, the C2-C3 and C4-C5 bond orders of all molecules are greatest. We can see the bonds in structures are not equivalent. So, the aromaticity of the structures having electron-withdrawing substituents can't state by NICS and BIRD parameters appropriately. It can be concluded from the bonds order data of the molecules substituted on C2 and or C3 atoms are non-aromatic.

Global reactivity indices of the 1H-phosphole derivatives:

It is well known that global reactivity indices defined within conceptual DFT is a powerful tool to explain reactivity and the molecular properties [18, 19]. Consequently, we have calculated global hardness (η), electronic chemical potential (μ), electronegativity (χ), global softness (S), nucleophilicity index (N) and electrophilicity index (ω) for all compounds by following formulas [20-22]:

$$\eta\ (\mathrm{eV}) = \frac{(\varepsilon_{\mathrm{LUMO}} - \varepsilon_{\mathrm{HOMO}})}{2}$$

$$\mu\ (\mathrm{eV}) = -\frac{(\varepsilon_{\mathrm{LUMO}} + \varepsilon_{\mathrm{HOMO}})}{2}$$

$$\chi\ (\mathrm{eV}) = -\mu$$

$$S\ (\mathrm{eV}) = \frac{1}{2\eta}$$

$$N\ (\mathrm{eV}) = \varepsilon_{\mathrm{HOMO}} - \varepsilon_{\mathrm{HOMO\,(Tetracyanoethylene)}}$$

$$\omega\ (\mathrm{eV}) = \frac{\mu^2}{2\eta}$$

The data of global reactivity calculations for 1*H*-phosphole derivatives are collected in Tables **9** and **10**. Stability of molecules is relative to the frontier orbitals (HOMO and LUMO) energies of them. The compounds with high HOMO-LUMO energies gap are more stable than the molecules with low HOMO-LUMO energies gap. From the global hardness data, the stability order of the molecules substituted on C2 atom is: H > F >Cl> Br > CH_3> CH_2F > CF_3> CHF_2> CN >tBu> SO_3H > $CONH_2$> OH > OCH_3> COOH > SH > NH_2> SCH_3>$N(CH_3)_2$> NO_2> NO. The stability of the 1*H*-phosphole molecules substituted on C3 atom varies by following order: H > F >$CONH_2$>CN >Cl>CF_3>CH_2F >CHF_2>tBu>CH_3>SO_3H >COOH > Br >SH > OH > OCH_3> NH_2> SCH_3> $N(CH_3)_2$> NO_2> NO. These stability orders indicate the compounds containing SH, OH, OCH_3, NH_2, SCH_3, $N(CH_3)_2$, NO_2 and NOsubstituents on C2 or C3 atoms have less stability than other molecules. Also, the 1*H*-phosphole without any substituent is more stable among all studied molecules. In other hand, the global nucleophilicity and electrophilicity indices of the molecules substituted on C2 atom show the following orders: $N(CH_3)_2$>NH_2>CH_3>OCH_3>SCH_3> H >OH >CH_2F >SH >NO > F >Br >Cl>$CONH_2$>tBu>COOH >CF_3>CN >NO_2> CHF_2>$SO_3H$and NO >NO_2>SO_3H >CHF_2>CN >COOH >SH >SCH_3>$CONH_2$>CF_3>tBu>OH > OCH_3>NH_2>Br >Cl>$N(CH_3)_2$>F >CH_2F >H > CH_3, respectively. We can see from these orders that the molecules containing electron-donating groups have more nucleophilicity among all compounds. In contrast, the electron-withdrawing substituents cause high electrophilicity power of molecules. Figure **1** shows the relationship between global nucleophilicity and electrophilicity indices of the studied 1*H*-phosphole derivatives substituted on C2 atom. It can be deduced that the nucleuphilicity and electrophilicity powers are not related together in these molecules.

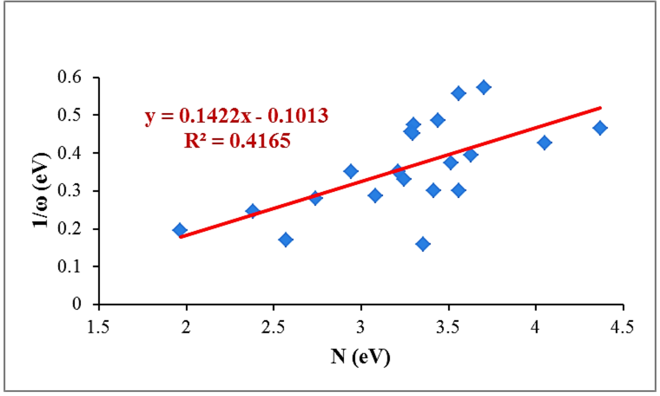


Figure 1: The relationship between global nucleophilicity and electrophilicity indices of the studied 1*H*-phosphole derivatives substituted at positions 2.

The global nucleophilicity of the molecules substituted on C3 atom varies with this order: SH >$N(CH_3)_2$>NH_2>H >SCH_3>OCH_3>F >Br >Cl>OH >$CONH_2$>NO >tBu>CH_3>COOH >CN >CH_2F >NO_2> CHF_2>CF_3>SO_3H. This order shows that the most nucleophilicity power is related to the compounds containing electron-donating substituents.In contrast, the global electrophilicity order of these compounds is: NO >NO_2>SO_3H >CF_3>CHF_2>CH_2F >CN >tBu>OH >SCH_3>COOH >OCH_3 = CH_3>NH_2>$CONH_2$>Br >$N(CH_3)_2$>Cl>F >SH >H. It can be seen from the electrophilicity order, the molecules having electron-withdrawing groups at position 3 are powerful electrophile compounds among all these derivatives.

Figure **2** indicates us the relationship between global nucleophilicity and electrophilicity indices of the studied 1*H*-phosphole derivatives substituted at position 3. It can be concluded that the nucleophilicity and electrophilicity indices are not related together in these molecules.

Local reactivity descriptors of the 1*H*-phosphole derivatives

Fukui function (FF) provides information on the local site reactivity within the molecule and as such it Provides a system for understanding of chemical reactions. These values correspond to the qualitative descriptors of reactivity of different atoms in the molecule.The condensed Fukui functions were computed by taking the finite difference approximations from population analysis of atoms in molecules, depending on the direction of electron transfer, through the following formulas [23]:

$f_k^+ = q_{k(N+1)} - q_{k(N)}$ [for nucleophilic attack]

$f_k^- = q_{k(N)} - q_{k(N-1)}$ [for electrophilic attack]

$$f_k^0 = \frac{[q_{k(N+1)} - q_{k(N-1)}]}{2}$$

[for radical attack]

Where q_k is the gross charge of atom k in the molecule.

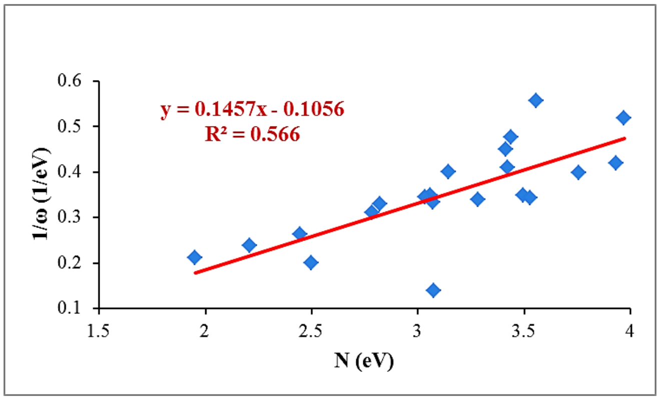


Figure 2: The relationship between global nucleophilicity and electrophilicity indices of the studied 1*H*-phosphole derivatives substituted at positions 3.

Table 9: The global reactivity indices of the 1*H*-phosphole derivatives substituted on C2 atom.

Y	HOMO (a.u.)	LUMO (a.u.)	χ (eV)	μ (eV)	η (eV)	S (1/eV)	N (eV)	ω (eV)
H	-0.21792	-0.01413	3.157	-3.157	2.773	0.361	3.557	1.797
CH_3	-0.21250	-0.01342	3.074	-3.074	2.709	0.369	3.705	1.744
CH_2F	-0.22215	-0.02329	3.339	-3.339	2.706	0.370	3.442	2.060
CHF_2	-0.26118	-0.07407	4.561	-4.561	2.546	0.393	2.380	4.085
CF_3	-0.24040	-0.04550	3.890	-3.890	2.652	0.377	2.945	2.853
tBu	-0.23072	-0.04655	3.772	-3.772	2.506	0.399	3.209	2.839
F	-0.22737	-0.02365	3.415	-3.415	2.772	0.361	3.300	2.104
Cl	-0.22783	-0.02657	3.461	-3.461	2.738	0.365	3.287	2.187
Br	-0.22752	-0.02762	3.471	-3.471	2.720	0.368	3.296	2.215
CN	-0.24794	-0.06291	4.229	-4.229	2.517	0.397	2.740	3.553
COOH	-0.23545	-0.06274	4.057	-4.057	2.350	0.426	3.080	3.502
$CONH_2$	-0.22938	-0.05154	3.822	-3.822	2.420	0.413	3.245	3.018
OH	-0.21942	-0.04368	3.580	-3.580	2.391	0.418	3.516	2.680
OCH_3	-0.21524	-0.04001	3.473	-3.473	2.384	0.419	3.630	2.530
SH	-0.22313	-0.05987	3.850	-3.850	2.221	0.450	3.415	3.337
SCH_3	-0.21785	-0.05989	3.779	-3.779	2.149	0.465	3.559	3.323
SO_3H	-0.27646	-0.09397	5.040	-5.040	2.483	0.403	1.964	5.115
NO_2	-0.25417	-0.10510	4.888	-4.888	2.028	0.493	2.571	5.891
NO	-0.22538	-0.10594	4.508	-4.508	1.625	0.615	3.354	6.253
NH_2	-0.19977	-0.03705	3.222	-3.222	2.214	0.452	4.051	2.344
$N(CH_3)_2$	-0.18815	-0.03297	3.009	-3.009	2.111	0.474	4.367	2.145

Table 10: The global reactivity indices of the 1*H*-phosphole derivatives substituted on C3 atom.

Y	HOMO (a.u.)	LUMO (a.u.)	χ (eV)	μ (eV)	η (eV)	S (1/eV)	N (eV)	ω (eV)
H	-0.21792	-0.01413	3.157	-3.157	2.773	0.361	3.557	1.797
CH_3	-0.23629	-0.04637	3.846	-3.846	2.584	0.387	3.057	2.862
CH_2F	-0.24636	-0.05495	4.100	-4.100	2.604	0.384	2.783	3.228
CHF_2	-0.25888	-0.06793	4.447	-4.447	2.598	0.385	2.443	3.806
CF_3	-0.26759	-0.07565	4.670	-4.670	2.611	0.383	2.206	4.176

tBu	-0.23587	-0.04506	3.945	-3.945	2.596	0.385	3.069	2.998
F	-0.22229	-0.02456	3.359	-3.359	2.690	0.372	3.438	2.097
Cl	-0.22328	-0.02881	3.430	-3.430	2.646	0.378	3.411	2.223
Br	-0.22287	-0.03599	3.522	-3.522	2.543	0.393	3.422	2.439
CN	-0.24493	-0.04993	4.012	-4.012	2.653	0.377	2.822	3.034
COOH	-0.23724	-0.04757	3.875	-3.875	2.581	0.387	3.031	2.909
$CONH_2$	-0.23307	-0.03580	3.658	-3.658	2.684	0.373	3.145	2.493
OH	-0.22803	-0.05000	3.783	-3.783	2.422	0.413	3.282	2.954
OCH_3	-0.22015	-0.04856	3.656	-3.656	2.335	0.428	3.496	2.862
SH	-0.20277	-0.02296	3.071	-3.071	2.446	0.409	3.969	1.928
SCH_3	-0.21911	-0.05013	3.663	-3.663	2.299	0.435	3.525	2.918
SO_3H	-0.27690	-0.08708	4.952	-4.952	2.583	0.387	1.952	4.747
NO_2	-0.25685	-0.09175	4.743	-4.743	2.246	0.445	2.498	5.008
NO	-0.23570	-0.11746	4.805	-4.805	1.609	0.622	3.073	7.175
NH_2	-0.21061	-0.04002	3.410	-3.410	2.321	0.431	3.756	2.505
$N(CH_3)_2$	-0.20410	-0.03749	3.287	-3.287	2.267	0.441	3.933	2.383

Fukui indices indicate the reactive regions as well as the nucleophilic (the site for nucleophilic attack would depend on the values of f_k^+ on the atoms with a positive charge density), electrophilic (the sites for electrophilic attack will be those atoms bearing a negative charge and where the Fukui function f_k^- is a maximum) and radical attack (f_k^0) in the molecule [24]. Table **11** collects the data of the fukui indices of the atoms in the 1*H*-phosphole derivatives substituted on C2 atom. From the data, the compounds show the following affinity for attack in various reactions:

For nucleuphilic attack:
C3: CF3, F, Cl, SO_3H, NO and NH_2
C4: tBu, COOH, $CONH_2$, CH_3, CH_2F, Br, CN,SH, SCH_3, NO_2 and $N(CH_3)_2$
C5:OH, CHF_2 and OCH_3

For electrophilic attack:
C3: CF_3, tBu, Cl, Br, CN, COOH, SH, SCH_3, SO_3H, NO_2, NO, NH_2 and $N(CH_3)_2$
C4: CHF_2, OCH_3, CH3, CH_2F, F and $CONH_2$
C5: OH

For radical attack:
C3:CHF_2,CF3,F,$CONH_2$, OH,SO_3H and OCH_3
C4:CH_2F, CH_3,tBu,Cl,Br, COOH, CN,SH,SCH_3,NO, NH_2 and$N(CH_3)_2$

Table 11: Principal reactivity sitesof 1*H*-phosphole derivatives substituted at position 2 obtained by using Fukui indices.

Y	f_k^+	f_k^-	f_k^0
H	P (0.350), C2 (-0.167), C3 (0.023), C4 (0.023), C5 (-0.0167)	P (-0.303), C2 (-0.046), C3 (-0.065), C4 (-0.065), C5 (-0.046)	P (0.024), C2 (-0.106), C3 (-0.020), C4 (-0.020), C5 (-0.106)
CH_3	P (1.030), C2 (-2.452), C3 (-0.605), C4 (1.789), C5 (-0.498)	P (-0.312), C2 (0.130), C3 (0.535), C4 (-0.707), C5 (-0.074)	P (0.359), C2 (-1.161), C3 (-0.035), C4 (0.541), C5 (-0.311)
CH_2F	P (-0.092), C2 (0.032), C3 (-0.108), C4 (0.090), C5 (-0.121)	P (0.011), C2 (0.017), C3 (-0.006), C4 (-0.147), C5 (-0.142)	P (-0.041), C2 (0.025), C3 (-0.057), C4 (-0.029), C5 (-0.110)
CHF_2	P (0.531), C2 (-0.201), C3 (0.021), C4 (0.019), C5 (0.055)	P (0.067), C2 (-0.106), C3 (0.069), C4 (0.011), C5 (0.126)	P (0.299), C2 (-0.154), C3 (0.045), C4 (0.015), C5 (-0.091)
CF_3	P (-0.336), C2 (0.103), C3 (0.184), C4 (-0.031), C5 (-0.059)	P (-0.317), C2 (0.096), C3 (-0.078), C4 (-0.073), C5 (-0.039)	P (-0.327), C2 (0.100), C3 (0.053), C4 (-0.052), C5 (-0.49)
tBu	P (0.391), C2 (0.471), C3 (-0.587), C4 (0.238), C5 (-0.220)	P (-0.365), C2 (0.441), C3 (-0.619), C4 (-0.038), C5 (-0.057)	P (0.013), C2 (0.456), C3 (-0.653), C4 (0.100), C5 (-0.139)
F	P (-0.291), C2 (-0.214), C3 (0.162), C4 (-0.084), C5 (0.051)	P (-0.241), C2 (-0.034), C3 (-0.068), C4 (-0.095), C5 (-0.064)	P (-0.266), C2 (-0.124), C3 (0.048), C4 (-0.090), C5 (-0.007)
Cl	P (-0.314), C2 (0.018), C3 (0.067), C4 (0.024), C5 (0.032)	P (-0.224), C2 (0.101), C3 (-0.134), C4 (-0.061), C5 (-0.070)	P (-0.270), C2 (0.060), C3 (-0.034), C4 (-0.018), C5 (-0.019)
Br	P (-0.259), C2 (0.039), C3 (-0.070), C4 (0.096), C5 (-0.044)	P (-0.208), C2 (0.027), C3 (-0.075), C4 (-0.071), C5 (-0.064)	P (-0.234), C2 (0.033), C3 (-0.073), C4 (0.013), C5 (-0.054)
CN	P (-0.242), C2 (-0.189), C3 (-0.020), C4 (0.063), C5 (-0.117)	P (-0.282), C2 (0.028), C3 (-0.093), C4 (-0.087), C5 (-0.031)	P (-0.262), C2 (-0.081), C3 (-0.057), C4 (-0.012), C5 (-0.074)
COOH	P (-0.283), C2 (0.032), C3 (0.017), C4 (0.024), C5 (-0.093)	P (-0.271), C2 (0.111), C3 (-0.155), C4 (-0.089), C5 (-0.049)	P (-0.277), C2 (0.072), C3 (-0.437), C4 (-0.033), C5 (-0.071)
$CONH_2$	P (-0.276), C2 (0.093), C3 (-0.056), C4 (0.034), C5 (-0.091)	P (0.0142), C2 (0.239), C3 (0.287), C4 (-0.376), C5 (-0.074)	P (-0.067), C2 (0.166), C3 (0.116), C4 (-0.171), C5 (-0.084)
OH	P (0.583), C2 (0.082), C3 (-0.021), C4 (-0.160), C5 (-0.014)	P (-0.050), C2 (-0.116), C3 (-0.069), C4 (-0.030), C5 (-0.138)	P (0.267), C2 (-0.017), C3 (-0.045), C4 (-0.095), C5 (-0.076)

OCH_3	P (-0.194), C2 (-0.029), C3 (-0.082), C4 (-0.034), C5 (0.028)	P (-0.303), C2 (-0.175), C3 (0.244), C4 (-0.152), C5 (-0.030)	P (-0.249), C2 (-0.102), C3 (0.081), C4 (-0.093), C5 (-0.001)
SH	P (-0.074), C2 (0.120), C3 (-0.239), C4 (0.069), C5 (0.003)	P (-0.051), C2 (-0.069), C3 (-0.183), C4 (0.052), C5 (-0.145)	P (-0.063), C2 (0.026), C3 (-0.211), C4 (0.061), C5 (-0.071)
SCH_3	P (-0.094), C2 (0.438), C3 (-0.568), C4 (0.100), C5 (-0.023)	P (-0.377), C2 (-0.080), C3 (-0.115), C4 (0.028), C5 (-0.028)	P (-0.237), C2 (0.179), C3 (-0.342), C4 (0.064), C5 (-0.026)
SO_3H	P (-0.018), C2 (-0.050), C3 (0.270), C4 (-0.250), C5 (0.070)	P (-0.048), C2 (0.077), C3 (-0.256), C4 (0.029), C5 (-0.148)	P (-0.033), C2 (0.014), C3 (0.007), C4 (-0.221), C5 (-0.054)
NO_2	P (-0.213), C2 (0.061), C3 (-0.061), C4 (0.000), C5 (-0.028)	P (-0.268), C2 (0.059), C3 (-0.112), C4 (-0.102), C5 (-0.036)	P (-0.241), C2 (0.060), C3 (-0.087), C4 (-0.051), C5 (-0.032)
NO	P (-0.279), C2 (-0.050), C3 (0.111), C4 (-0.064), C5 (-0.025)	P (0.085), C2 (0.225), C3 (-0.372), C4 (0.025), C5 (-0.173)	P (-0.097), C2 (0.088), C3 (-0.131), C4 (-0.020), C5 (-0.099)
NH_2	P (-0.097), C2 (0.803), C3 (0.190), C4 (0.167), C5 (-0.079)	P (-0.019), C2 (-0.109), C3 (-0.153), C4 (0.042), C5 (-0.136)	P (-0.058), C2 (0.347), C3 (0.019), C4 (0.105), C5 (-0.103)
$N(CH_3)_2$	P (0.926), C2 (0.570), C3 (-1.395), C4 (0.633), C5 (-0.325)	P (-0.066), C2 (-0.071), C3 (-0.114), C4 (0.012), C5 (-0.081)	P (0.430), C2 (0.250), C3 (-0.755), C4 (0.323), C5 (-0.203)

C5: NO_2

From the data of the Table **12**, the 1*H*-phosphole derivatives substituted at position 3 indicate the following affinity for attack in various reactions:

For nucleophilic attack:

C2: OH

C4: CHF_2,F, Cl, Br, COOH, $CONH_2$,SH,NO_2, NO and $N(CH_3)_2$

C5: CH_3,CH_2F,CF3,tBu,CN, OCH_3,SCH_3,$SO_3H$and NH_2

For electrophilic attack:

C2: CN, OH andNO_2

C4: CH_2F, CHF_2, CF3, ^{t}Bu, F, Cl, Br, COOH, $CONH_2$, OCH_3,SH,SCH_3,NO and $N(CH_3)_2$

C5: CH_3, $SO_3H$and NH_2

For radical attack:

C2:$CONH_2$, OHand $N(CH_3)_2$

C4: F, Cl, Br, COOH, $NO_2$and NH_2

C5:CH_3,CH_2F,CHF_2,CF3,tBu,CN, OCH_3,SH,SCH_3,SO_3HandNO

Presence of dehydrating agents was the most fascinating method over other reported methods [19-32]. The dehydrating agents used so far for the synthesis of nitriles including *N*-methyl-2-pyrrolidinone [23], $MeSO_2Cl$/alumina [19], silica chloride [21], sodium iodide [22], dichlorophosphate-DBU [24], propyl phosphonic anhydride (T3P) [25], $CuCl_2/NaOMe/O_2$ [26], KF/Al_2O_3,[27] I_2[28], NBS [29] graphite/$MeSO_2Cl$ [30], choline chloride-urea [31] and transition metal catalysts [32]. However, these reported methods suffer from some disadvantages as requirement of drastic reaction conditions [19,22,23,30], limited substrate scope [33], use of expensive and hazardous metallic reagents [34-39]. In addition, some of these methods are not suitable for thermally unstable and enolizable aliphatic aldehydes [24]. Hence, there is still need to develop more efficient and direct methodology for the synthesis of nitrile from aldehyde.

During the past few decades, attention being focused on the development of ultrasound assisted reactions [40]. The application of 'cavitations' as energy source allows organic reactions faster with more selectivity and excellent product yields in shorter reaction time and [41-46]. The utility and applicability of ultrasound promoted reactions have been well documented in literature [47-50].

Table 12: Principal reactivity sitesof 1*H*-phosphole derivatives substituted at position 3 obtained by using Fukui indices.

Y	f_k^+	f_k^-	f_k^0
H	P (0.350), C2 (-0.167), C3 (0.023), C4 (0.023), C5 (-0.0167)	P (-0.303), C2 (-0.046), C3 (-0.065), C4 (-0.065), C5 (-0.046)	P (0.024), C2 (-0.106), C3 (-0.020), C4 (-0.020), C5 (-0.106)
CH_3	P (0.535), C2 (-0.689), C3 (0.416), C4 (-0.784), C5 (0.045)	P (-0.409), C2 (-0.084), C3 (-0.010), C4 (0.046), C5 (-0.091)	P (0.063), C2 (-0.387), C3 (0.203), C4 (-0.369), C5 (-0.023)
CH_2F	P (0.093), C2 (-0.372), C3 (0.398), C4 (-0.372), C5 (-0.014)	P (-0.039), C2 (0.014), C3 (0.090), C4 (-0.359), C5 (-0.081)	P (0.027), C2 (-0.179), C3 (0.244), C4 (-0.366), C5 (-0.048)
CHF_2	P (0.050), C2 (-0.451), C3 (0.183), C4 (0.026), C5 (-0.054)	P (-0.046), C2 (-0.064), C3 (0.053), C4 (-0.204), C5 (-0.126)	P (0.002), C2 (-0.257), C3 (0.118), C4 (-0.089), C5 (-0.090)
CF_3	P (0.034), C2 (-0.171), C3 (0.479), C4 (-0.554), C5 (-0.022)	P (-0.518), C2 (-0.141), C3 (0.038), C4 (0.102), C5 (-0.083)	P (-0.242), C2 (-0.156), C3 (0.259), C4 (-0.226), C5 (-0.053)
tBu	P (0.439), C2 (-0.320), C3 (1.041), C4 (-0.719), C5 (-0.065)	P (-0.438), C2 (-0.047), C3 (-0.188), C4 (0.154), C5 (-0.087)	P (0.001), C2 (-0.184), C3 (0.427), C4 (-0.283), C5 (-0.076)
F	P (-0.278), C2 (-0.069), C3 (-0.066),	P (-0.278), C2 (-0.046), C3 (-0.077),	P (-0.278), C2 (-0.058), C3 (-0.072),

	C4 (0.076), C5 (0.000)	C4 (-0.074), C5 (-0.026)	C4 (0.001), C5 (-0.013)
Cl	P (-0.318), C2 (-0.173), C3 (0.023), C4 (0.178), C5 (-0.049)	P (-0.256), C2 (-0.121), C3 (0.167), C4 (-0.162), C5 (-0.014)	P (-0.287), C2 (-0.147), C3 (0.095), C4 (0.008), C5 (-0.032)
Br	P (-0.319), C2 (0.019), C3 (-0.149), C4 (0.224), C5 (-0.054)	P (-0.246), C2 (-0.050), C3 (-0.016), C4 (-0.056), C5 (-0.026)	P (-0.283), C2 (-0.016), C3 (-0.083), C4 (0.084), C5 (-0.040)
CN	P (-0.243), C2 (-0.357), C3 (0.244), C4 (-0.149), C5 (-0.036)	P (-0.259), C2 (-0.073), C3 (-0.080), C4 (-0.007), C5 (-0.034)	P (-0.251), C2 (-0.215), C3 (0.082), C4 (-0.078), C5 (-0.035)
COOH	P (-0.225), C2 (-0.482), C3 (0.262), C4 (0.135), C5 (-0.176)	P (-0.295), C2 (0.095), C3 (0.008), C4 (-0.103), C5 (0.012)	P (-0.260), C2 (-0.194), C3 (0.135), C4 (0.016), C5 (-0.082)
$CONH_2$	P (-0.237), C2 (-0.287), C3 (0.315), C4 (0.046), C5 (-0.103)	P (-0.165), C2 (0.286), C3 (-0.097), C4 (-0.120), C5 (-0.072)	P (-0.201), C2 (-0.001), C3 (0.109), C4 (-0.037), C5 (-0.088)
OH	P (0.261), C2 (0.242), C3 (0.451), C4 (-0.644), C5 (0.166)	P (-0.035), C2 (-0.112), C3 (-0.095), C4 (-0.056), C5 (-0.097)	P (0.113), C2 (0.065), C3 (0.178), C4 (-0.350), C5 (0.035)
OCH_3	P (0.473), C2 (-0.329), C3 (-0.004), C4 (-0.308), C5 (0.313)	P (-0.027), C2 (-0.085), C3 (-0.086), C4 (-0.086), C5 (-0.078)	P (0.223), C2 (-0.207), C3 (-0.045), C4 (-0.197), C5 (0.118)
SH	P (-0.153), C2 (-0.307), C3 (0.048), C4 (0.133), C5 (-0.072)	P (0.106), C2 (0.131), C3 (-0.129), C4 (-0.309), C5 (-0.087)	P (-0.024), C2 (-0.088), C3 (-0.041), C4 (-0.088), C5 (-0.080)
SCH_3	P (0.166), C2 (-0.579), C3 (0.255), C4 (-0.171), C5 (0.039)	P (-0.048), C2 (0.229), C3 (-0.046), C4 (-0.263), C5 (-0.167)	P (0.059), C2 (-0.175), C3 (0.105), C4 (-0.217), C5 (-0.064)
SO_3H	P (-0.108), C2 (-0.553), C3 (0.736), C4 (-0.291), C5 (0.081)	P (-0.051), C2 (-0.010), C3 (-0.174), C4 (-0.088), C5 (-0.143)	P (-0.080), C2 (-0.282), C3 (0.281), C4 (-0.190), C5 (-0.031)
NO_2	P (-0.260), C2 (-0.068), C3 (0.047), C4 (0.097), C5 (-0.121)	P (-0.272), C2 (-0.139), C3 (0.022), C4 (-0.023), C5 (-0.045)	P (-0.266), C2 (-0.104), C3 (0.035), C4 (0.037), C5 (-0.083)
NO	P (-0.015), C2 (-0.338), C3 (0.246), C4 (0.017), C5 (-0.082)	P (-0.312), C2 (-0.091), C3 (0.344), C4 (-0.288), C5 (0.056)	P (-0.164), C2 (-0.215), C3 (0.295), C4 (-0.136), C5 (-0.013)
NH_2	P (-0.138), C2 (-0.055), C3 (-0.242), C4 (0.049), C5 (0.068)	P (-0.051), C2 (-0.060), C3 (-0.133), C4 (-0.035), C5 (-0.100)	P (-0.095), C2 (-0.058), C3 (-0.188), C4 (0.008), C5 (-0.016)
$N(CH_3)_2$	P (-0.018), C2 (-0.161), C3 (-0.189), C4 (0.098), C5 (-0.050)	P (-0.074), C2 (0.127), C3 (-0.091), C4 (-0.239), C5 (-0.046)	P (-0.046), C2 (-0.017), C3 (-0.140), C4 (-0.071), C5 (-0.048)

Computational method

The programs of Gaussian 03 suit [25] can be used in chemistry in order to determine the structural and reactivity properties of various molecules at the atomic level. All molecules were optimized by density functional theory (DFT) computations using the B3LYP exchange-correlation functional with the 6-311++G(d,p) basis set. The computations were done in gas phase. The frequency calculations did not show any imaginary frequency for the molecules. These calculations indicate the accuracy of all computations on the molecules.

Conclusion

In the present study, the structural properties, aromaticity, global reactivity and local reactivity of 1H-phosphole derivatives substituted at positions 2 and 3 were investigated by density functional theory (DFT) method. All compounds were optimized at B3LYP/6-311++G(d,p) level of theory. All computations were done without any structural restrictions at standard conditions (293.15 K and 1 atmosphere). In vibrational computations, no imaginary frequencies were shown for all considered molecules. So, it proves the accuracy of my calculations. The bonds order data and aromaticity studies (NICS and BIRD indices) showed all molecules substituted on C2 and or C3 atoms are non-aromatic. Also, the global reactivity studies showed the molecules containing electron-donating and electron-withdrawing groups have more nucleophilicity and electrophilicity among all compounds, respectively.

Acknowledgement

The corresponding author is grateful to Doctor Mir Babak Bahadori for providing valuable suggestions.

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