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AROMATIC STABILITY ENERGY STUDIES ON FIVE-MEMBERED HETEROCYCLIC C_4H_4M ($M = O, S, Se, Te, NH, PH, AsH$ AND SbH): DFT CALCULATIONS

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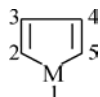
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Energetic, geometric and magnetic criteria were applied to examine the stability and/or aromatic character for the cyclic molecules C_4H_4M ($M = O, S, Se, Te, NH, PH, AsH$ and SbH) at B3LYP/6-311++G** and MP2/6-311++G** levels of theory. The isodesmic reactions and nuclear independent chemical shifts (NICS) calculations were utilized to examine the molecules for energetic and magnetic criteria, respectively. The isodesmic reaction energies reveal that thiophene (C_4H_4S , -23.269 kcal/mol) and pyrrole (C_4H_4NH , -20.804 kcal/mol) have the greatest aromatic stabilization energies and tellurophene (C_4H_4Te , -15.114 kcal/mol) and stibole (C_4H_4SbH , -1.169 kcal/mol) have the lowest aromatic stabilization energies in their corresponding groups at MP2/6-311++G**. The NICS calculations confirmed the results obtained through isodesmic reaction energies.

Keywords: Aromatic character; isodesmic reaction; NICS; five-membered heterocycle; C_4H_4M .

INTRODUCTION

Aromatic character is not a directly measurable or computable quantity. Aromatic character is generally evaluated on the basis of energetic, geometric, and magnetic criteria [1–9]. There is a procedure for the estimation of aromatic stabilization energies (ASE) and/or homo-aromatic stabilization energies (HASE) from various isodesmic reactions [10–14]. Such studies usually require a comparison of non-aromatic model compounds with a corresponding aromatic model compound. Magnetic criterion is estimated through nuclear independent chemical shifts (NICS) calculations [11–14]. As a continuation of our studies [15], the aromatic character is studied in this paper for C_4H_4M molecules ($M = O, S, Se, Te, NH, PH, AsH$ and SbH) with the help of isodesmic reactions, NICS and geometrical parameters calculations (Scheme 1).



Scheme 1. Five-memebered ring C_4H_4M
($M = O, S, Se, Te, NH, PH, AsH$ and SbH)

COMPUTATIONAL METHODS

Full geometry optimizations were carried out for C_4H_4M molecules by DFT and MP2 methods using 6-311++G** basis set [16–18]. All the calculations were carried out with Gaussian-98 program [19]. For DFT calculations, the Becke's hybrid three-parameters functional combined with the Lee-Yang-Parr nonlocal correlation functional (B3LYP) were used. For Te and Sb atoms, the calculations were carried out using LANL2DZ basis set [20]. "Extrabasis" keyword used indicates that additional basis functions are to be added to the basis set specified in the route section. Here 6-311++G**

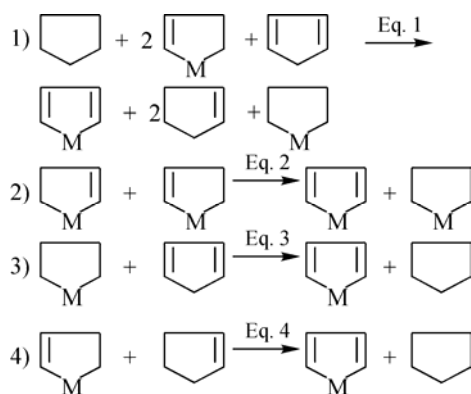
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basis set was used for C and H atoms. "Freq" keyword was used to compute force constants and the resulting vibrational frequencies. Thermodynamic functions obtained through frequency calculations were multiplied by a suitable scaling factor and correction terms.

RESULTS AND DISCUSSION

Here we examine the energetic, geometric and magnetic criteria for the determination of the stability and/or aromatic character of C₄H₄M molecules (Scheme 1). The isodesmic reactions and NICS calculations were applied to examine the molecules for energetic and magnetic criteria, respectively.

Isodesmic reactions were used to estimate the stabilization energies (SE) [11, 12]. Isodesmic reactions energies directly indicate the stabilization energy and indirectly show the aromatic character of a compound. Isodesmic reaction schemes assume only equal numbers of formal single and double bonds in products and reactants. Systems with negative SE are stabilized while systems with positive SE are destabilized. Four isodesmic reactions and relative SE energies were investigated at B3LYP/6-311++G** and MP2/6-311++G** levels (Scheme 2 and Tables 1—4). The first isodesmic reaction (Eq. 1 on Scheme 2) is based on cyclic olefinic and conjugated unsaturated analogues. This isodesmic reaction seems to give the most adequate results and, therefore, it was used. Three other isodesmic reactions (Eqs. 2—4) are simplified versions of the first reaction (Eq. 1).



Scheme 2. Four isodesmic formal equations for the estimation of the stabilization energies (SE) of C₄H₄M molecules (M = O, S, Se, Te, NH, PH, AsH and SbH)

The isodesmic reactions 1, 2 and 4 (Scheme 1) revealed that the stability of C₄H₄M generally decreases from M = O to M = Te as well as from M = NH to M = SbH. The isodesmic reaction energies (Eq. 1) revealed that thiophene (C₄H₄S, -23.269 kcal/mol) and pyrrole (C₄H₄NH, -20.804 kcal/mol) have the greatest aromatic stabilization, while tellurophene (C₄H₄Te, -15.114 kcal/mol) and stibole (C₄H₄SbH, -1.169 kcal/mol) have the lowest aromatic stabilization in their corresponding groups (MP2/6-311++G** level).

NICS calculations were carried out to determine the aromaticity of C₄H₄M molecules at B3LYP/6-311++G** and MP2/6-311++G** levels (Table 5). Positive and negative signs for NICS indicate the aromatic and anti-aromatic characters of the molecules, respectively. NICS (0.4—0.6) calculations generally give more reliable results. Therefore, NICS (0.6) was selected for the determination of aromatic character.

The NICS (0.6) calculations indicated that the aromaticity of C₄H₄M molecules generally decreases from M = O to M = Te as well as from M = NH to M = SbH. However the aromatic character was the greatest for thiophene (C₄H₄S) and pyrrole (C₄H₄NH) and the lowest for tellurophene (C₄H₄Te) and stibole (C₄H₄SbH) in their corresponding groups at both B3LYP/6-311++G** and MP2/6-311++G** levels. The NICS (0.6) calculations results for aromatic character were in agreement with the isodesmic reactions results. However, these results were inconsistent with the rule that "aromaticity increases with the decrease in the electronegativity difference between a heteroatom and its neighboring atoms".

Table 1

Estimated stabilization energies (SE) for C_4H_4M molecules calculated using isodesmic reaction
1) at B3LYP/6-311++G** and MP2/6-311++G** levels of theory

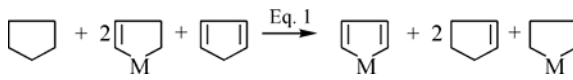
M							SE, (kcal/mol)
B3LYP/6-311++G**							
O	-123286.912	-145077.646	-121775.861	-144336.873	-122529.991	-145833.231	-12.022
S		-347751.557		-347012.240		-348510.382	-16.717
Se		-1604843.614		-1604100.505		-1605603.137	-13.623
Te		-102918.409		-102171.904		-103679.132	-11.428
NH	-123286.912	-132601.631	-121775.861	-131868.629	-122529.991	-133355.283	-17.859
PH		-312456.529		-311703.909		-313214.648	-2.710
AsH		-1501255.901		-1500500.672		-1502014.992	-1.072
SbH		-101626.442		-100869.381		-102386.193	0.100
MP2/6-311++G**							
O	-122968.269	-144712.683	-121447.270	-143971.243	-122206.165	-145474.120	-16.788
S		-347146.786		-346407.948		-347912.100	-23.269
Se		-1603560.160		-1602816.365		-1604324.937	-17.774
Te		-102572.497		-101824.330		-103338.987	-15.114
NH	-122968.269	-132260.063	-121447.270	-131525.082	-122206.165	-133019.055	-20.804
PH		-311868.459		-311112.007		-312631.926	-3.807
AsH		-1499978.759		-1499220.294		-1500742.947	-2.516
SbH		-101303.487		-100542.345		-102069.005	-1.169

Table 2

Estimated stabilization energies (SE) for C_4H_4M molecules calculated using isodesmic reaction
2) at B3LYP/6-311++G** and MP2/6-311++G** levels of theory


M					SE, (kcal/mol)
B3LYP/6-311++G**					
O	-145077.646	-145077.646	-144336.873	-145833.231	-14.812
S	-347751.557	-347751.557	-347012.240	-348510.382	-19.507
Se	-1604843.614	-1604843.614	-1604100.505	-1605603.137	-16.413
Te	-102918.409	-102918.409	-102171.904	-103679.132	-14.218
NH	-132601.631	-132601.631	-131868.629	-133355.283	-20.649
PH	-312456.529	-312456.529	-311703.909	-313214.648	-5.500
AsH	-1501255.901	-1501255.901	-1500500.672	-1502014.992	-3.862
SbH	-101626.442	-101626.442	-100869.381	-102386.193	-2.690
MP2/6-311++G**					
O	-144712.683	-144712.683	-143971.243	-145474.120	-19.996
S	-347146.786	-347146.786	-346407.948	-347912.100	-26.477
Se	-1603560.160	-1603560.160	-1602816.365	-1604324.937	-20.982
Te	-102572.497	-102572.497	-101824.330	-103338.987	-18.322
NH	-132260.063	-132260.063	-131525.082	-133019.055	-24.012
PH	-311868.459	-311868.459	-311112.007	-312631.926	-7.015
AsH	-1499978.759	-1499978.759	-1499220.294	-1500742.947	-5.724
SbH	-101303.487	-101303.487	-100542.345	-102069.005	-4.376

Table 3

Estimated stabilization energies (SE) for C₄H₄M molecules calculated using isodesmic reaction 3) at B3LYP/6-311++G** and MP2/6-311++G** levels of theory

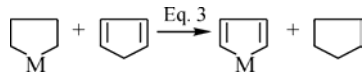
M					SE, (kcal/mol)
B3LYP/6-311++G**					
O	-145833.231	-121775.861	-144336.873	-123286.912	-14.694
S	-348510.382		-347012.240		-12.909
Se	-1605603.137		-1604100.505		-8.420
Te	-103679.132		-102171.904		-3.824
NH	-133355.283	-121775.861	-131868.629	-123286.912	-24.398
PH	-313214.648		-311703.909		-0.313
AsH	-1502014.992		-1500500.672		3.269
SbH	-102386.193		-100869.381		5.761
MP2/6-311++G**					
O	-145474.120	-121447.270	-143971.243	-122968.269	-18.122
S	-347912.100		-346407.948		-16.847
Se	-1604324.937		-1602816.365		-12.426
Te	-103338.987		-101824.330		-6.341
NH	-133019.055	-121447.270	-131525.082	-122968.269	-27.025
PH	-312631.926		-311112.007		-1.079
AsH	-1500742.947		-1499220.294		1.654
SbH	-102069.005		-100542.345		5.662

Table 4

Estimated stabilization energies (SE) for C₄H₄M molecules calculated using isodesmic reaction 4) at B3LYP/6-311++G** and MP2/6-311++G** levels of theory

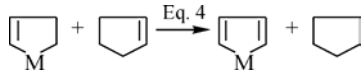
M					SE, (kcal/mol)
B3LYP/6-311++G**					
O	-145077.646	-122529.991	-144336.873	-123286.912	-16.148
S	-347751.557		-347012.240		-17.603
Se	-1604843.614		-1604100.505		-13.812
Te	-102918.409		-102171.904		-10.416
NH	-132601.631	-122529.991	-131868.629	-123286.912	-23.918
PH	-312456.529		-311703.909		-4.301
AsH	-1501255.901		-1500500.672		-1.692
SbH	-101626.442		-100869.381		0.140
MP2/6-311++G**					
O	-144712.683	-122206.165	-143971.243	-122968.269	-20.663
S	-347146.786		-346407.948		-23.266
Se	-1603560.160		-1602816.365		-18.308
Te	-102572.497		-101824.330		-13.936
NH	-132260.063	-122206.165	-131525.082	-122968.269	-27.123
PH	-311868.459		-311112.007		-5.651
AsH	-1499978.759		-1499220.294		-3.639
SbH	-101303.487		-100542.345		-0.961

Table 5

NICS calculations for aromaticities of C_4H_4M molecules at B3LYP/6-311++G** and MP2/6-311++G** levels of theory

M	NICS(0)	NICS(0.2)	NICS(0.4)	NICS(0.6)	NICS(0.8)	NICS(1.0)	NICS(1.2)	NICS(1.4)	NICS(1.6)	NICS(1.8)	NICS(2.0)
B3LYP/6-311++G**											
O	11.8755	11.8881	11.7985	11.3711	10.5278	9.3663	8.0520	6.7370	5.5276	4.4808	3.6140
S	12.8988	12.8738	12.7207	12.2575	11.4119	10.2547	8.9309	7.5891	6.3396	5.2430	4.3173
Se	11.9875	11.9631	11.8133	11.3730	10.5883	9.5332	8.3364	7.1226	5.9847	4.9761	4.1157
Te	11.3105	11.2534	11.0117	10.4778	9.6730	8.7223	7.7458	6.8093	5.9387	5.1449	4.4339
NH	13.5876	13.4755	13.1077	12.4064	11.3672	10.0728	8.6577	7.2605	5.9834	4.8798	3.9624
PH	5.3634	5.3179	5.5640	5.8175	5.8738	5.6635	5.2271	4.6563	4.0431	3.4532	2.9210
AsH	3.8707	3.9023	4.1671	4.4405	4.5619	4.4747	4.2017	3.8052	3.3544	2.9031	2.4835
SbH	2.7238	2.7599	2.8930	2.9769	2.9509	2.8452	2.7026	2.5409	2.3623	2.1680	1.9628
MP2/6-311++G**											
O	12.251	12.183	11.906	11.310	10.388	9.230	7.957	6.688	5.513	4.489	3.636
S	13.375	13.320	13.072	12.493	11.550	10.333	8.982	7.633	6.385	5.292	4.370
Se	12.176	12.134	11.923	11.406	10.558	9.466	8.257	7.046	5.918	4.923	4.077
Te	10.975	10.918	10.666	10.109	9.282	8.331	7.385	6.500	5.689	4.953	4.291
NH	14.713	14.522	13.952	13.031	11.826	10.432	8.961	7.530	6.226	5.100	4.156
PH	5.049	4.930	5.112	5.322	5.370	5.185	4.797	4.287	3.737	3.207	2.728
AsH	8.668	8.357	7.618	6.718	5.840	5.065	4.391	3.792	3.255	2.774	2.348
SbH	2.744	2.760	2.859	2.901	2.839	2.716	2.574	2.424	2.260	2.078	1.881

Table 6

Calculated bond lengths d (Å), bond angles ω (deg.), bond dihedral angles ω' (deg.) and LUMO-HOMO gaps (eV) for C_4H_4M molecules at B3LYP/6-311++G** and MP2/6-311++G** levels of theory

M	d			ω	ω'	HOMO	LUMO	LUMO-HOMO gap
	X1—C2	C2—C3	C3—C4	C2—X1—C5	C3—C2—X1—C5			
B3LYP/6-311++G**								
O	1.363	1.358	1.435	106.933	0.000	-0.240	-0.006	0.234
S	1.733	1.366	1.428	91.521	0.000	-0.246	-0.026	0.220
Se	1.876	1.362	1.432	87.006	0.000	-0.245	-0.032	0.213
Te	2.075	1.358	1.439	81.409	0.000	-0.241	-0.033	0.208
NH	1.375	1.377	1.425	109.858	0.000	-0.219	-0.012	0.206
PH	1.815	1.354	1.457	90.221	9.375	-0.243	-0.053	0.189
AsH	1.951	1.347	1.464	85.708	7.243	-0.243	-0.055	0.188
SbH	2.154	1.345	1.469	80.27	5.228	-0.240	-0.057	0.183
MP2/6-311++G**								
O	1.360	1.370	1.432	106.961	0.000	-0.319	0.042	0.361
S	1.712	1.382	1.421	92.150	0.000	-0.325	0.042	0.367
Se	1.857	1.380	1.424	87.783	0.000	-0.325	0.041	0.366
Te	2.056	1.378	1.431	81.011	0.000	-0.320	0.040	0.360
NH	1.374	1.388	1.423	110.215	0.000	-0.299	0.068	0.367
PH	1.800	1.368	1.454	90.847	11.558	-0.323	0.041	0.364
AsH	1.935	1.363	1.460	86.423	-9.073	-0.323	0.041	0.364
SbH	2.121	1.354	1.460	80.957	6.957	-0.320	0.039	0.359

In order to confirm their aromatic character, the geometrical parameters of the molecules were calculated. The bond lengths, bond angles and dihedral angles were estimated for C₄H₄M molecules at both B3LYP/6-311++G** and MP2/6-311++G** levels (Table 6). For thiophene (C₄H₄S) and pyrrole (C₄H₄NH), the bond length C₃—C₄ is the closest to the bond length C₂—C₃ in their corresponding groups. Thus, the electron current in the ring and aromatic character was higher for thiophene (C₄H₄S) and pyrrole (C₄H₄NH).

The HOMO-LUMO energy separation has been used as a simple indicator of kinetic stability [21] (Table 6). A large HOMO-LUMO gap implies high kinetic stability and low chemical reactivity. HOMO-LUMO gap decreased from M = O to M = Te as well as from M = NH to M = SbH in the corresponding groups. The HOMO-LUMO energy separations more or less confirmed the stabilization energies obtained by the isodesmic reactions method and NICS calculations.

CONCLUSION

The isodesmic reactions, NICS and geometrical parameters calculations were applied to determine the stability and/or aromatic character of C₄H₄M molecules (M = O, S, Se, Te, NH, PH, AsH and SbH) at both B3LYP/6-311++G** and MP2/6-311++G** levels. The isodesmic reactions and NICS calculations revealed that thiophene (C₄H₄S) and pyrrole (C₄H₄NH) have the greatest aromatic stabilization, while tellurophene (C₄H₄Te) and stibole (C₄H₄SbH) have the lowest aromatic stabilization in their corresponding groups at both B3LYP/6-311++G** and MP2/6-311++G** levels. The calculated geometrical parameters confirmed the aromatic character obtained in the course of isodesmic reactions and NICS calculations.

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