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Structure and (Hyper)polarizabilities of Five-membered Heterocycles $C_4H_4XH_2$ (X=C, Si, Ge, Sn)†

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Calculated HF/POL and B3LYP/POL linear and quadratic polarizabilities of $C_4H_4XH_2$ (X=C, Si, Ge, Sn) increase remarkably with the atomic number of X.

π-Conjugated heterocyclic polymers containing Si are promising candidates for materials with useful nonlinear optical properties.[1,2] The present work is a theoretical investigation on the structure and linear α and quadratic β dipole polarizabilities of the five-membered monomers $C_4H_4XH_2$ ($X = C$, Si, Ge, Sn) to highlight the role of the heteroatom. The calculations were carried out by conventional *ab initio* and density functional (B3LYP)[3] theories by using Sadlej POL basis sets[4] specifically designed for dipole moments and polarizabilities.

Molecular geometries were optimized at HF and DFT levels under the constraint of C_{2v} symmetry. The obtained structures are true minima in the potential energy curve (no imaginary frequencies). The B3LYP/POL geometries are shown in Fig. 1. They compare well with the available experimental data.[5,6] The C–X bond length and the C–X–C angle steadily increases then decreases, respectively, as the size of the heteroatom increases. This introduces some strain in the ring making the bond angles of the butadienyl moiety to change by as much as 10°. Based on structural parameters, cyclopentadiene seems to be the most strained compound. Increasing ring strain usually moves the C–H stretching band towards higher frequencies.[7] In fact the most intense calculated (B3LYP/POL) A_1-type C–H stretching frequency in cyclopentadiene is $3193\,cm^{-1}$ compared with the corresponding values of 3144, 3140 and $3125\,cm^{-1}$ in the following compounds of the series. Bond length alternation is almost constant through the series, thus significant differential π-electron delocalizations are not expected. The present results agree with recent *ab initio* structures of cyclopentadienes[8–10] and silacyclopentadiene.[10]

Dipole moments μ, and α and β polarizabilities are reported in Table 1. The μ_{exp} of cyclopentadiene ($0.42\,D$)[5] is satisfactorily reproduced by both HF and DFT calculations; μ is directed along the C_2 axis from the ring to the CH_2 group but in the other derivatives it points in the opposite direction. The value of μ steadily decreases down the group, which is consistent with the positive charge density trend on the XH_2 group, as evaluated by atomic polar tensor analysis,[11] which increases with the atomic number of X.

Both the mean dipole polarizability $\langle\alpha\rangle$ and its components increase down the group. $\langle\alpha\rangle$ changes linearly ($r^2 = 0.99$) with the heteroatom polarizability and indicates that the hydrocarbon framework gives an almost constant contribution; [the calculated HF/POL $\langle\alpha\rangle_X$ values are $C(^3P) = 11.61$, $Si(^3P) = 37.92$, $Ge(^3P) = 41.03$, $Sn(^3P) = 58.00$ au). $\langle\alpha\rangle$ is also linearly related ($r^2 = 0.99$) with the mean polarizability of the group 16 chalcogenophenes C_4H_4X ($X = O$, S, Se, Te) obtained at the same level of theory.[12] However, $\langle\alpha\rangle_{14}$ changes more slowly than $\langle\alpha\rangle_{14}$ ($d\langle\alpha\rangle_{16}/d\langle\alpha\rangle_{16} = 0.71$ and 0.76 at the HF/POL and B3LYP/POL levels, respectively) despite the atomic polarizability of the group 14 heteroatom being higher than that of the corresponding group 16 atom (HF/POL $\langle\alpha\rangle_X$ are $O(^3P) = 4.75$, $S(^3P) = 19.00$, $Se(^3P) = 25.16$, $Te(^3P) = 38.80$)[12]. This emphasizes the role of the X–H bond formation and the lack of π-delocalization in the group 14 heterocycles. B3LYP electron correlation enhances $\langle\alpha\rangle$ by 7%. The mean first hyperpolarizability $\langle\beta\rangle$ increases remarkably down the group, showing up the role of the heteroatom. This behaviour parallels that found in the group 16 chalcogenophenes and a linear relation is indeed found between $\langle\beta\rangle_{14}$ and $\langle\beta\rangle_{16}$ (Fig. 2), with a slope of 0.57 (HF) and 0.64 (B3LYP), which again emphasizes the lack of π-delocalization in the neutral ground state of $C_4H_4XH_2$ compounds. This correlation suggests that, as in the group 16 chalcogenophenes, the molecular hardness $\eta = (IP - EA)/2$ could be a determining factor for $\langle\beta\rangle_{14}$. In the absence of experimental IP and EA values of the studied compounds, except for cyclopentadiene ($IP_{exp} = 8.56\,eV^{13}$) we calculated IPs and EAs by ΔSCF procedure using both the Sadlej POL and 3-21 + G* basis sets. The outer electronic configuration of $C_4H_4XH_2$ predicted by both bases is $\ldots a_1, b_2, b_1(\pi), a_2(\pi)$ for all the compounds apart from the Sn derivative where the b_2 orbital lies above the b_1 one. The HOMO a_2 is at constant energy through the series, being localized in the butadienyl framework. The LUMO is predicted to be of $a_1(\sigma^*)$ symmetry by the POL basis and of $b_1(\pi^*)$ symmetry by the 3-21 + G* basis. However, ΔSCF calculations indicated that the lowest energy anionic state is invariably of $^2B_1$ type. The molecular geometries of the cationic and anionic states are available on request. The IP, EA and η estimates are shown in Table 2. It is worth noting the very good agreement among the

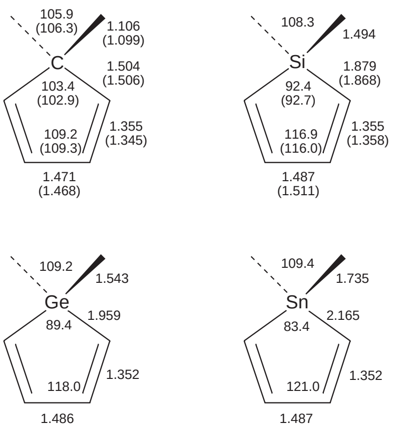

Fig. 1 B3LYP/POL geometries of $C_4H_4XH_2$ ($X = C$, Si, Ge, Sn). Experimental data (in parentheses) are taken from the microwave structure of cyclopentadiene[5] and from the X-ray structure of 1,1-dimethyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene.[6] Distances in Å, angles in degrees.

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† This is a **Short Paper** as defined in the Instructions for Authors, Section 5.0 [see *J. Chem. Research (S)*, 1999, Issue 1]; there is therefore no corresponding material in *J. Chem. Research (M)*.

Table 1 Calculated dipole moments, μ(D), and dipole polarizabilities (au) of $C_4H_4XH_2$ (X = C, Si, Ge, Sn)[a]

	μ_z	α_{xx}	α_{yy}	α_{zz}	$\langle\alpha\rangle$	β_{xxz}	β_{yyz}	β_{zzz}	$\langle\beta\rangle$
$C_4H_4CH_2$									
HF//HF	−0.30	60.01	41.46	65.56	55.68	8.87	−12.26	−30.48	−20.32
B3LYP//B3LYP	−0.47	66.04	42.81	69.10	59.32	18.99	−5.66	−42.94	−17.78
$C_4H_4SiH_2$									
HF//HF	0.67	71.30	52.13	82.53	68.65	1.61	15.35	19.08	21.62
B3LYP//B3LYP	0.55	77.76	54.40	88.84	73.67	14.00	31.80	12.01	20.27
$C_4H_4GeH_2$									
HF//HF	0.42	73.86	55.03	87.66	72.18	6.16	24.71	57.40	52.96
B3LYP//B3LYP	0.33	80.46	57.47	94.38	77.44	19.65	46.56	36.12	61.40
$C_4H_4SnH_2$									
HF//HF	0.14	81.40	62.76	99.66	81.27	9.93	47.87	151.12	125.35
B3LYP//B3LYP	0.14	88.32	65.96	108.22	87.50	35.57	78.06	135.39	149.41

[a]The calculations are performed with the Sadlej POL bases. The molecule is in the *xz* plane. The *z* axis lies along the C_2 axis from the heteroatom to the ring. $\langle\alpha\rangle = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3$; $\langle\beta\rangle = 3/5 \sum_i \beta_{\mu ii} = 3/5(\beta_{zxx} + \beta_{zyy} + \beta_{zzz})$. HF results are from analytic calculations, and B3LYP results are from finite-field calculations using a field strength of 0.0025 au.

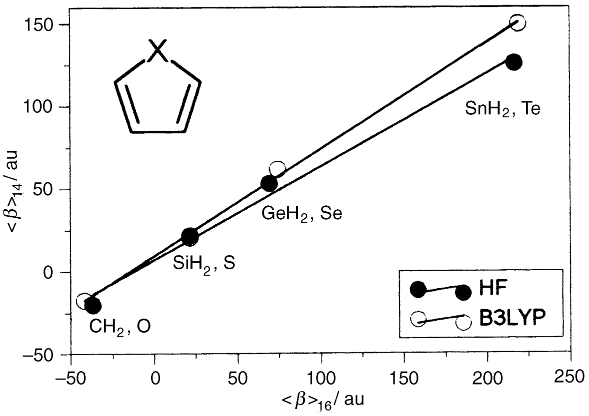

Fig. 2 Relation between the first mean hyperpolarizability of the group 14 and group 16 five-membered heterocycles

Table 2 ΔSCF ionization potentials IP, electron affinities EA and hardness η of $C_4H_4XH_2$ (X=C, Si, Ge, Sn); values in eV; 3-21+G* and Sadlej POL (in parentheses) basis sets results

	IP ($^2A_2$)	EA ($^2B_1$)	$\eta_{\Delta SCF}$
$C_4H_4CH_2$			
HF	7.20 (6.91)	−1.95 (−1.97)	4.57 (4.44)
B3LYP	8.37	−1.06	4.72
$C_4H_4SiH_2$			
HF	7.43 (7.19)	−0.86 (−0.92)	4.15 (4.06)
B3LYP	8.60	0.04	4.28
$C_4H_4GeH_2$			
HF	7.36 (7.12)	−1.04 (−1.00)	4.20 (4.06)
B3LYP	8.52	−0.18	4.35
$C_4H_4SnH_2$			
HF	7.20 (6.98)	−0.95 (−0.91)	4.08 (3.94)
B3LYP	8.37	−0.06	4.22

ΔSCF results obtained by the two basis sets. B3LYP calculations reproduce well the experimental IP of cyclopentadiene. It can be seen that $\langle\beta\rangle$ increases as η decreases, although the correlation is not as good as in group 16 chalcogenophenes.[12] On the assumption that the present IP and EA estimates are sufficiently accurate, this suggests that other factors are important in defining $\langle\beta\rangle$. The B3LYP electron correlation contribution is positive and increases down the group (14–19%), but in silacyclopentadiene it is negative by *ca.* 7%.

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