

## Directions of Dipole Moments of Selenophene, Tellurophene and their Tetrahydro Derivatives

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






There has been some controversy regarding the directions of the dipole moments of pyrrole, furan and thiophene (for discussion *cf.* References 1,2). Recently (2) the orientational influence of dipolar solutes on the aromatic solvents, benzene and hexafluorobenzene, as reflected by proton chemical shifts, has been used to settle this question. Mainly based on the upfield shifts on the  $\alpha$  and  $\beta$ -hydrogens (relative to carbon tetrachloride solution) caused by benzene, in contrast to the downfield shifts in pyrrole, it was confirmed that in furan and thiophene as well as in their tetrahydro derivatives the negative end of the dipole is at the heteroatom, opposite to the case in pyrrole. The value and direction of dipole moment of four congener compounds (furan, thiophene, selenophene and tellurophene) and corresponding tetrahydro derivatives are very useful parameters to investigate the influence of the heteroatom on molecular electronic properties and in structure-reactivity correlation studies.

In a previous study (3) the dipole moments of selenophene, tellurophene and their tetrahydro derivatives have been supposed directed from the ring to the heteroatom. This paper gives experimental evidence on the direction of dipole moment of these compounds. The method based on the orientational influence (2) of dipolar solutes on the aromatic solvents has been used in order to have complete and consistent data in the series of five-membered congener heterocycles. The experimental data are reported in Table I together with those for furan, thiophene and their tetrahydro derivatives taken from reference 2.

It can be seen that both selenophene and tellurophene behave similarly to furan and thiophene, giving upfield solvent shifts in hexadeuteriobenzene, while the shifts in hexafluorobenzene show, as previously observed and discussed (2) for furan and thiophene, a more complicated pattern. The tetrahydro derivatives behave as expected by theory, showing solvent shifts of opposite direction in hexadeuteriobenzene and hexafluorobenzene. The nmr data thus show that the dipole moments of selenophene and tellurophene and their tetrahydro derivatives are in the

Table I

Chemical (a) and Solvent (b) Shifts of Congener Five Membered Heterocycles and their Tetrahydro Derivatives (c)

	CCl <sub>4</sub>		C <sub>6</sub> D <sub>6</sub>		C <sub>6</sub> F <sub>6</sub>	
	H $\alpha$	H $\beta$	H $\alpha$	H $\beta$	H $\alpha$	H $\beta$
	7.36	6.29	7.13 -0.23	6.08 -0.21	7.25 -0.11	6.28 -0.01
	3.61	1.79	3.57 -0.04	1.43 -0.36	3.51 -0.10	1.84 +0.05
	7.22	7.06	6.90 -0.32	6.84 -0.22	7.16 -0.06	7.02 -0.04
	2.75	1.91	2.54 -0.21	1.47 -0.44	2.71 -0.04	1.99 +0.08
	7.85	7.22	7.67 -0.18	7.10 -0.12	7.83 -0.02	7.16 -0.06
	2.79	1.96	2.65 -0.14	1.64 -0.32	2.83 +0.04	2.04 +0.08
	8.77	7.70	8.56 -0.21	7.58 -0.12	8.72 -0.05	7.59 -0.11
	3.10	2.03	2.91 -0.19	1.69 -0.34	3.18 +0.08	2.10 +0.07

(a)  $\delta$ -Values relative to TMS as internal standard. (b) Relative to carbon tetrachloride. (c) The values for furan, thiophene and their tetrahydro derivatives are taken from reference 2.

same direction as those of furan and thiophene and their tetrahydro derivatives, with the negative end of the dipole at the heteroatom. Clearly, the direction of the dipole moment in five-membered congener heterocycles cannot be simply related to the electronegativity of the heteroatom but other parameters (geometry of the ring, non bonding electron pair of the heteroatom) must be considered.

## EXPERIMENTAL

Selenophene, tellurophene and their tetrahydro derivatives were prepared as reported in the literature (4-7). The nmr spectra were recorded on a Varian 60 instrument in *ca.* 3% wt/vol solutions.

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