

## Valence Topological Charge-Transfer Indices for Reflecting Polarity: Correction for Heteromolecules

Francisco Torrens

Institut Universitari de Ciència Molecular, Universitat de València, Dr. Moliner 50, E-46100 Burjassot (València), Spain. <http://www.uv.es/~icmol>. Tel. +34 963 543 182, Fax +34 963 543 156, E-mail [Francisco.Torrens@uv.es](mailto:Francisco.Torrens@uv.es)

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**Abstract:** Valence topological charge-transfer (CT) indices are applied to the calculation of dipole moments  $\mu$ . The  $\mu$  calculated by *algebraic* and *vector semisums* of the CT indices are defined. The model is generalized for molecules with heteroatoms and corrected for  $sp^3$ -heteromolecules. The ability of the indices for the description of the molecular charge distribution is established by comparing them with  $\mu$  of the valence-isoelectronic series of cyclopentadiene, benzene and styrene. Two CT indices,  $\mu_{\text{vec}}$  (vector semisum of vertex-pair  $\mu$ ) and  $\mu_{\text{vec}}^{\text{V}}$  (valence  $\mu_{\text{vec}}$ ) are proposed. The  $\mu_{\text{vec}}^{\text{V}}$  behaviour is intermediate between  $\mu_{\text{vec}}$  and  $\mu_{\text{experiment}}$ . The correction is produced in the correct direction. The best results are obtained for the greatest group. Inclusion of the heteroatom in the  $\pi$ -electron system is beneficial for the description of  $\mu$ , owing to either the role of additional  $p$  and/or  $d$  orbitals provided by the heteroatom or the role of *steric* factors in the  $\pi$ -electron conjugation. The steric effect is almost constant along the series and the dominating effect is electronic. Inclusion of the heteroatom enhances  $\mu$ , which can improve the solubility of the molecule. For heteroatoms in the same group, the ring size and the degree of ring flatterness are inversely proportional to their electronegativity.

**Keywords:** Charge distribution; Dipole moment; Heteroatom; Isoelectronic series; Valence topological charge-transfer index

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### Introduction

Homo and heterocycles were studied as models of fluorescers, organic conducting polymers or nonlinear optical (NLO) materials. New fluorescers contain heteroaromatic components. Some heterocycles recur often in industrial fluorescers. They do not fluoresce themselves, but have a

fluorescence enhancing effect when coupled to conjugated systems. Reiser *et al.* measured the absorption and emission spectra, and fluorescence yields of aromatic benzoxazole derivatives [1]. Lippert *et al.* reviewed the photophysics of internal twisting [2]. Dey and Dogra measured and calculated the solvatochromism and prototropism in 2-(aminophenyl)benzothiazoles [3]. Catalán *et al.* studied the role of the torsion of the phenyl moiety in the mechanism of stimulated ultraviolet light generation in 2-phenylbenzazoles [4]. Levitus *et al.* performed photophysical measurements and semiempirical calculations with 1,4-bis(phenylethynyl)benzene [5]. Organic conducting polymers have a highly anisotropic quasi-one-dimensional (quasi-1D) structure similar to that of charge-transfer (CT) salts [6]. In the conducting state, both materials are ionic. In CT complexes conductivity is greater along the stacking direction, while in conducting polymers conductivity is higher along the chain direction. In these polymers, the chainlike structure leads to strong coupling of the electronic states to conformational excitations peculiar to 1D systems. The relatively weak interchain binding allows diffusion of dopant molecules into the structure, while the strong intrachain C–C bonds maintain the integrity of the polymer. The modulation of the electronic properties of conjugated polymers was studied through design of polymer backbone [7].

The search for NLO organic materials with large values of the second hyperpolarizability ( $\gamma$ ) attracted interest from the experimental and theoretical points of view [8,9]. Morley *et al.* calculated the first hyperpolarizability ( $\beta$ ) of S-heteromolecules [10]. Zhao *et al.* computed  $\gamma$  for modified benzothiazoles, benzoxazoles and benzimidazoles [11]. Meyers *et al.* calculated the geometries and electronic and NLO properties of CT molecules based on the 2-methylene-2H-pyrrole repeating unit [12]. Li *et al.* computed structure–performance characteristics for  $\beta$  and  $\gamma$  of  $\pi$ -conjugated organic chromophores with the Pariser–Parr–Pople model [13]. Yeates *et al.* analyzed (X-ray) and calculated 2-(2-benzothiazolyl)-1-(2-thienyl)ethene as a model for high  $\gamma$  [14]. Gao *et al.* studied the effect of conjugated length on the computed  $\beta$  of organic molecules [15]. Tomonari *et al.* calculated the simplified sum-over-states and missing-orbital analysis on  $\beta$  and  $\gamma$  of benzene derivatives [16]. Glaser and Chen computed asymmetrization effects on structures of dipolar donor–acceptor-substituted molecular organic NLO materials [17]. Raptis *et al.* calculated the polarizability ( $\alpha$ ),  $\beta$  and  $\gamma$  of polysulfanes [18]. Rao and Bhanuprakash computed donor and acceptor organic molecules separated by a saturated C–C  $\sigma$  bond, which show large  $\beta$  [19]. Nakano *et al.* calculated  $\gamma$  of tetrathiapentalene and tetrathiafulvalene [20]. Cheng *et al.* computed  $\alpha$  and  $\beta$  of H-silsesquioxanes [21]. Levitus *et al.* analyzed and calculated the photophysics of 1,4-bis(phenylethynyl)benzene [22] and 1,4-diethynyl-2-fluorobenzene [23] to demarcate the effects of chromophore aggregation and planarization in poly(phenyleneethynylene)s. Öberg *et al.* computed  $\beta$  and  $\gamma$  of organic compounds [24].

Organic electronic materials are conjugated solids where both optical absorption and charge transport are dominated by partly delocalized  $\pi$  and  $\pi^*$  orbitals [25]. Organic photovoltaic materials differ from inorganic semiconductors in the following important respects. (1) Photogenerated excitations (*excitons*) are strongly bound and do not spontaneously dissociate into charge pairs. This means that carrier generation does not necessarily result for the absorption of light. (2) Charge transport proceeds by *hopping* between localized states, rather than transport within a band, and mobilities are low. (3) The spectral range of optical absorption is relatively narrow compared to the solar spectrum. (4) Absorption coefficients are high so that high optical densities can be achieved, at peak wavelength, with films less than 100nm thick. (5) Many materials are susceptible to degradation in the presence of oxygen or water. (6) As 1D semiconductors, their electronic and optical properties

can be highly anisotropic. These properties impose some constraints on organic photovoltaic devices. (1) A strong driving force such as an electric field should be present to break up the photogenerated excitons. (2) Low charge carrier mobilities limit the useful thickness of devices. (3) Limited light absorption across the solar spectrum limits the photocurrent. (4) Very thin devices mean interference effects can be important. (5) Photocurrent is sensitive to temperature through hopping transport.

In earlier publications,  $\alpha$  of benzothiazole (A)–benzobisthiazole (B) A–B<sub>n</sub>–A ( $n \leq 13$ ) oligomers was calculated and extrapolated to  $n \rightarrow \infty$  [26]. Torsional effects were analyzed [27,28]. CT indices were brought to the calculation of the dipole moment  $\mu$  of hydrocarbons [29]. The model was extended to heteroatoms [30]. An index inspired by plastic evolution improved the results [31,32]. The method was applied to the valence-isoelectronic series of benzene and styrene (2–4 molecules) [33,34]. This study presents a reparametrization of the method for  $sp^3$ -heteromolecules. The next section introduces CT indices. Following that, the correction for  $sp^3$ -heteromolecules is presented. Next, the results are discussed. The last section summarizes the conclusions.

### Topological Charge-Transfer Indices

The most important matrices that delineate the labelled chemical graph are the *adjacency* (**A**) [35] and the *distance* (**D**) matrices, wherein  $D_{ij}=l_{ij}$  if  $i=j$ , “0” otherwise;  $l_{ij}$  is the shortest edge count between vertices  $i$  and  $j$  [36]. In **A**,  $A_{ij}=1$  if vertices  $i$  and  $j$  are adjacent, “0” otherwise. The **D**<sup>[−2]</sup> matrix is the matrix whose elements are the squares of the reciprocal distances  $D_{ij}^{-2}$ . The intermediate matrix **M** is defined as the matrix product of **A** by **D**<sup>[−2]</sup>:

$$\mathbf{M} = \mathbf{A}\mathbf{D}^{[-2]}$$

The *charge-transfer matrix* **C** is defined as  $\mathbf{C} = \mathbf{M} - \mathbf{M}^T$ , where  $\mathbf{M}^T$  is the transpose of **M** [37]. By agreement,  $C_{ii}=M_{ii}$ . For  $i \neq j$ , the  $C_{ij}$  terms represent a measure of the intramolecular *net charge* transferred from atom  $j$  to  $i$ . The *topological CT indices*  $G_k$  are described as the sum, in absolute value, of the  $C_{ij}$  terms defined for the vertices  $i, j$  placed at a topological distance  $D_{ij}$  equal to  $k$

$$G_k = \sum_{i=1}^{N-1} \sum_{j=i+1}^N |C_{ij}| \delta(k, D_{ij}) \quad (1)$$

where  $N$  is the number of vertices in the graph,  $D_{ij}$  are the entries of the **D** matrix, and  $\delta$  is the Kronecker  $\delta$  function, being  $\delta=1$  for  $i=j$  and  $\delta=0$  for  $i \neq j$ .  $G_k$  represents the sum of all the  $C_{ij}$  terms, for every pair of vertices  $i$  and  $j$  at topological distance  $k$ . Other topological CT index,  $J_k$ , I defined as:

$$J_k = \frac{G_k}{N-1} \quad (2)$$

This index represents the mean value of the CT for each edge, since the number of edges for acyclic compounds is  $N-1$ .

The *algebraic semisum* CT index  $\mu_{\text{alg}}$  is defined as

$$\mu_{\text{alg}} = \frac{1}{2} \sum_{i=1}^{N-1} \sum_{j=i+1}^N A_{ij} |C_{ij}| = \frac{1}{2} \sum_{e=1}^M |C^e| \quad (3)$$

where  $C^e$  is the  $C_{ij}$  index for vertices  $i$  and  $j$  connected by edge  $e$  [29]. The sum extends for all pairs of adjacent vertices in the molecular graph and  $\mu_{\text{alg}}$  is a graph invariant. An edge-to-edge analysis of  $\mu$  suggests that each edge dipole moment  $\mu^e$  connecting vertices  $i$  and  $j$  can be evaluated from the corresponding edge  $C^e$  index as

$$\mu^e = \frac{1}{2} C^e$$

Each edge dipole can be associated with a vector  $\mu^e$  in space. This vector has magnitude  $|\mu^e|$ , lies in the edge  $e$  connecting vertices  $i$  and  $j$ , and its direction is from  $j$  to  $i$ . The molecular dipole moment vector  $\mu$  results the vector sum of the edge dipole moments as

$$\mu = \sum_{e=1}^m \mu^e = \frac{1}{2} \sum_{e=1}^m C^e$$

summed for all the  $m$  edges in the molecular graph. The *vector semisum CT index*  $\mu_{\text{vec}}$  is defined as the module of  $\mu$ :

$$\mu_{\text{vec}} = N(\mu) = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2} \quad (4)$$

and  $\mu_{\text{vec}}$  is a graph invariant.

When heteroatoms are present, some way of discriminating atoms of different kinds needs to be considered [38]. In valence CT indices terms, the presence of each heteroatom is taken into account by introducing its electronegativity value in the corresponding entry of the main diagonal of the adjacency matrix  $\mathbf{A}$ . For each heteroatom  $X$ , its entry  $A_{ii}$  is redefined as

$$A_{ii}^V = 2.2(\chi_X - \chi_C) \quad (5)$$

to give the *valence adjacency  $\mathbf{A}^V$  matrix* where  $\chi_X$  and  $\chi_C$  are the electronegativities of heteroatom  $X$  and carbon, respectively, in Pauling units. Notice that the subtractive term keeps  $A_{ii}^V=0$  for the C atom (Equation 5). Moreover, the multiplicative factor reproduces  $A_{ii}^V=2.2$  for O, which was taken as standard. From the valence  $\mathbf{A}^V$ ,  $\mathbf{M}^V$  and  $\mathbf{C}^V$  matrices,  $\mu_{\text{alg}}^V$ ,  $\mu_{\text{vec}}^V$  and topological CT indices  $G_k^V$  and  $J_k^V$  can be calculated by following the former procedure with the  $\mathbf{A}^V$  matrix. The  $C_{ii}^V$ ,  $G_k^V$ ,  $J_k^V$ ,  $\mu_{\text{alg}}^V$  and  $\mu_{\text{vec}}^V$  descriptors are graph invariants. The main difference between  $\mu_{\text{vec}}$  and  $\mu_{\text{vec}}^V$  is that  $\mu_{\text{vec}}$  is sensitive only to the *steric* effect of the heteroatoms, while  $\mu_{\text{vec}}^V$  is sensitive to both electronic and steric effects.

### Correction for $sp^3$ -Heteroatom-Containing Compounds

Kubinyi showed that the poor hydrogen-bond-formation capacity of the  $sp^3$ -oxygen atoms that are directly linked to an  $sp^2$ -carbon atom (like in esters, aromatic ethers and furans) is also reflected by a significant decrease of their polarity (MedChem database 1-octanol–water partition coefficient,  $P$ ) in going from aliphatic to araliphatic and to aromatic ethers R–O–R' (Table 1) [39]. Therefore, in this study it is suggested to halve the factor in Equation (5) as

$$A_{ii}^V = 1.1(\chi_X - \chi_C) \quad (6)$$

for  $sp^3$ -X (–X–), X = O. Table 1 gives the molecular dipole moments  $\mu$  for hydrocarbons and ethers calculated with different charge-transfer indices. The polarity decrease is also reflected by a significant decrease of the differential dipole moment ( $\mu_{\text{ether}} - \mu_{\text{hydrocarbon}}$ ) denoted as  $\Delta(\text{O} - \text{CH}_2)$ . The  $\Delta(\text{O} - \text{CH}_2)$   $\mu_{\text{experiment}}$  decreases with minus  $\Delta(\text{O} - \text{CH}_2) \log P$ . The  $\Delta(\text{O} - \text{CH}_2)$   $\mu_{\text{vec}}$  does not show this diminution, while  $\Delta(\text{O} - \text{CH}_2)$   $\mu_{\text{vec}}^V$  gives very great values. However,  $\Delta(\text{O} - \text{CH}_2)$   $\mu_{\text{vec}}^{V,\text{corrected}}$  is of the same order of magnitude as both  $\mu_{\text{experiment}}$  and  $\mu_{\text{MOPAC-AM1}}$  references. As similar effects were shown for  $sp^3$ -Si, P, Ge, As, Sn, Sb, Pb and Bi heteromolecules [34], Equation (6) is used for all  $sp^3$ -X (–X–), X = O, Si, P, S, Ge, As, Se, Sn, Sb, Te, Pb, Bi, Po.

**Table 1.** Molecular dipole moment (in D) for hydrocarbons and ethers with charge indices.

Method	Compound	X = -CH <sub>2</sub> -	X = -O-	$\Delta(\text{O} - \text{CH}_2)$	$\Delta(\text{O}-\text{CH}_2) \log P^a$
Vector semisum	Et-X-Et	0.407	0.436	0.029	-
	Phe-X-Et	0.739	0.659	-0.080	-
	Phe-X-Phe	0.427	0.333	-0.094	-
Valence vector semisum	Et-X-Et	0.407	2.854	2.447	-
	Phe-X-Et	0.739	2.621	1.882	-
	Phe-X-Phe	0.427	2.742	2.315	-
Corrected valence vector semisum	Et-X-Et	0.407	1.209	0.802	-
	Phe-X-Et	0.739	1.211	0.472	-
	Phe-X-Phe	0.427	1.204	0.777	-
Experiment <sup>b</sup>	Et-X-Et	0.087 <sup>c</sup>	1.170	1.083	-2.50
	Phe-X-Et	0.350	1.410	1.060	-1.21
	Phe-X-Phe	0.260	1.150	0.890	0.07
AM1	Et-X-Et	0.006	1.246	1.240	-
	Phe-X-Et	0.257	1.264	1.007	-
	Phe-X-Phe	0.080	1.252	1.172	-

<sup>a</sup> P is the 1-octanol-water partition coefficient.

<sup>b</sup> Reference 40.

<sup>c</sup> Gaussian-2 composite *ab initio* method calculation taken from Reference 41.

## Calculation Results and Discussion

The molecular CT indices  $G_k$ ,  $J_k$ ,  $G_k^V$  and  $J_k^V$  (with  $k < 6$ ) are listed in Table 2 for the valence-isoelectronic series of benzene (C<sub>6</sub>H<sub>6</sub>). As one might have expected, all the molecules show the same set of  $G_k$  (and, consequently,  $J_k$ ) values. For instance,  $G_1$  is related to the degree of branching and  $G_2$  is related to the number of saturations in the molecule, which are constant throughout the series. On the other hand,  $G_k^V$ , which also depends on the electronegativity of the heteroatom through Equations (5–6), is influenced, in general, by the substitution.

In particular,  $G_1^V$  is related to the absolute differential electronegativity of the heteroatom  $|\chi_X - \chi_C|$  in the molecule. However, an exception occurs:  $G_2^V$  (and, as a result,  $J_2^V$ ) is equal throughout the series. C<sub>5</sub>H<sub>6</sub>Si, C<sub>5</sub>H<sub>6</sub>Ge, C<sub>5</sub>H<sub>6</sub>Sn and C<sub>5</sub>H<sub>6</sub>Pb show the same results for all  $G_k^V$  and  $J_k^V$ . This is due to the fact that Si, Ge, Sn and Pb have the same electronegativity ( $\chi_{\text{Si}} = \chi_{\text{Ge}} = \chi_{\text{Sn}} = \chi_{\text{Pb}} = 1.8$ ). The same happens for C<sub>5</sub>H<sub>5</sub>Sb and C<sub>5</sub>H<sub>5</sub>Bi ( $\chi_{\text{Sb}} = \chi_{\text{Bi}} = 1.9$ ). Although in pyridine and C<sub>5</sub>H<sub>5</sub>As, the N and As atoms have the same absolute differential electronegativity  $|\chi_{\text{N}} - \chi_{\text{C}}| = |\chi_{\text{As}} - \chi_{\text{C}}| = 0.5$ , pyridine is calculated by Equation (5) while C<sub>5</sub>H<sub>5</sub>As, by Equation (6), and so  $G_2^V(\text{pyridine}) = 2G_2^V(\text{C}_5\text{H}_5\text{As})$ .

**Table 2.** Charge indices up to the fifth order for the valence-isoelectronic series of benzene.<sup>a</sup>

Molecules	<i>N</i>	<i>G</i> <sub>1</sub>	<i>G</i> <sub>2</sub>	<i>J</i> <sub>1</sub>	<i>J</i> <sub>2</sub>
all molecules	6	0.0000	5.3333	0.0000	1.0667

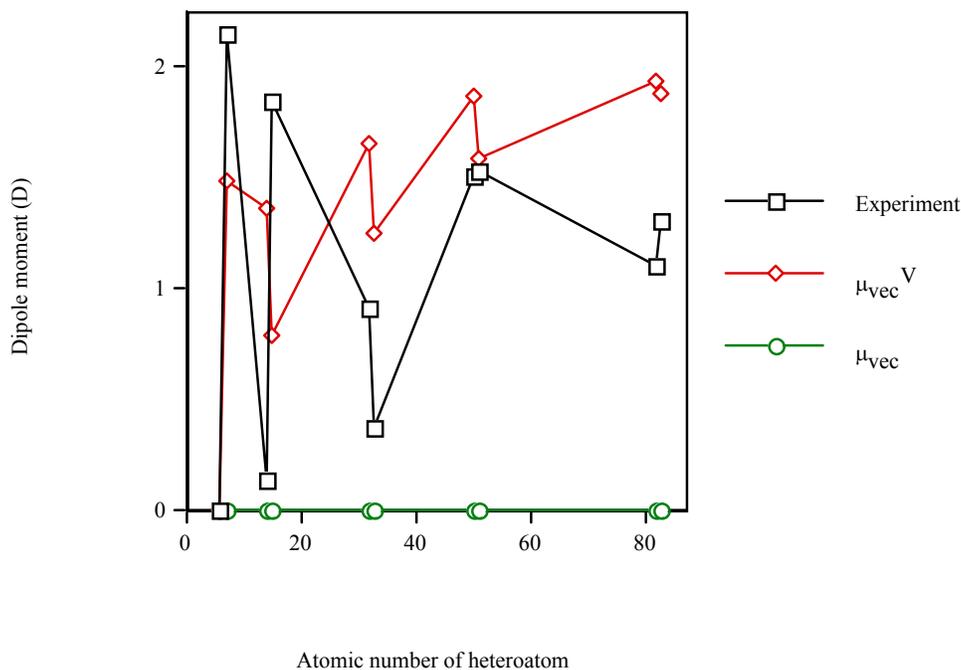
  

Molecules	<i>G</i> <sub>1</sub> <sup>V</sup>	<i>G</i> <sub>3</sub> <sup>V</sup>	<i>J</i> <sub>1</sub> <sup>V</sup>	<i>J</i> <sub>3</sub> <sup>V</sup>
benzene	0.0000	0.0000	0.0000	0.0000
pyridine	2.2000	0.1222	0.4400	0.0244
C <sub>5</sub> SiH <sub>6</sub>	1.5400	0.0856	0.3080	0.0171
C <sub>5</sub> PH <sub>5</sub>	0.8800	0.0489	0.1760	0.0098
C <sub>5</sub> GeH <sub>6</sub>	1.5400	0.0856	0.3080	0.0171
C <sub>5</sub> AsH <sub>5</sub>	1.1000	0.0611	0.2200	0.0122
C <sub>5</sub> SnH <sub>6</sub>	1.5400	0.0856	0.3080	0.0171
C <sub>5</sub> SbH <sub>5</sub>	1.3200	0.0733	0.2640	0.0147
C <sub>5</sub> PbH <sub>6</sub>	1.5400	0.0856	0.3080	0.0171
C <sub>5</sub> BiH <sub>5</sub>	1.3200	0.0733	0.2640	0.0147

<sup>a</sup> *G*<sub>*i*</sub>, *J*<sub>*i*</sub> (*i* > 2), *G*<sub>*i*</sub><sup>V</sup>, *J*<sub>*i*</sub><sup>V</sup> (*i* > 3) are zero for all the entries; *G*<sub>2</sub><sup>V</sup> = 5.3333, *J*<sub>2</sub><sup>V</sup> = 1.0667.

Figure 1 illustrates the increment in the dipole moment of benzene in the presence of the heteroatom. The calculated  $\mu_{\text{vec}}^V$  is of the same order of magnitude as  $\mu_{\text{experiment}}$ , while the calculated  $\mu_{\text{vec}}=0$  remains constant. Since  $\mu_{\text{vec}}$  is sensitive to the steric effect but not to the electronic effect of the heteroatom, it is clear that the electronic effect ( $\mu_{\text{vec}}^V$ ) dominates over the steric one ( $\mu_{\text{vec}}$ ). In particular, the best results are obtained for the fourth long-period (Sn–Sb) and for the group-V heteromolecules.

**Figure 1.** Dipole moment of the valence-isoelectronic series of benzene vs. the atomic number of the heteroatom. Experimental data from Reference 40. Points with *Z* = 14, 15, 32, 33, 50, 51, 82 and 83 are AM1 calculations.



**Table 3.** Charge indices up to the fifth order for the valence-isoelectronic series of styrene.

Molecule	$N$	$G_1$	$G_2$	$G_3$	$G_4$	$G_5$
all molecules	8	1.0000	6.8889	0.4375	0.2133	0.0625

Molecule	$J_1$	$J_2$	$J_3$	$J_4$	$J_5$
all molecules	0.1429	0.9841	0.0625	0.0305	0.0089

Molecule	$G_1^V$	$G_2^V$	$G_3^V$	$G_4^V$	$G_5^V$
styrene	1.0000	6.8889	0.4375	0.2133	0.0625
benzaldimine	1.6000	7.1639	0.5569	0.2708	0.0185
benzaldehyde	2.7000	7.4389	0.8014	0.4083	0.0255
C <sub>6</sub> H <sub>5</sub> -CH=SiH <sub>2</sub>	2.5400	6.5039	0.5297	0.3436	0.1241
C <sub>6</sub> H <sub>5</sub> -CH=PH	1.8800	6.6689	0.4375	0.2611	0.0977
thiobenzaldehyde	1.0000	6.8889	0.4375	0.2133	0.0625
C <sub>6</sub> H <sub>5</sub> -CH=GeH <sub>2</sub>	2.5400	6.5039	0.5297	0.3436	0.1241
C <sub>6</sub> H <sub>5</sub> -CH=AsH	2.1000	6.6139	0.4375	0.2886	0.1065
C <sub>6</sub> H <sub>5</sub> -CH=Se	1.2200	6.8339	0.4375	0.2133	0.0713
C <sub>6</sub> H <sub>5</sub> -CH=SnH <sub>2</sub>	2.5400	6.5039	0.5297	0.3436	0.1241
C <sub>6</sub> H <sub>5</sub> -CH=SbH	2.3200	6.5589	0.4808	0.3161	0.1153
C <sub>6</sub> H <sub>5</sub> -CH=Te	1.8800	6.6689	0.4375	0.2611	0.0977
C <sub>6</sub> H <sub>5</sub> -CH=PbH <sub>2</sub>	2.5400	6.5039	0.5297	0.3436	0.1241
C <sub>6</sub> H <sub>5</sub> -CH=BiH	2.3200	6.5589	0.4808	0.3161	0.1153
C <sub>6</sub> H <sub>5</sub> -CH=Po	2.1000	6.6139	0.4375	0.2886	0.1065

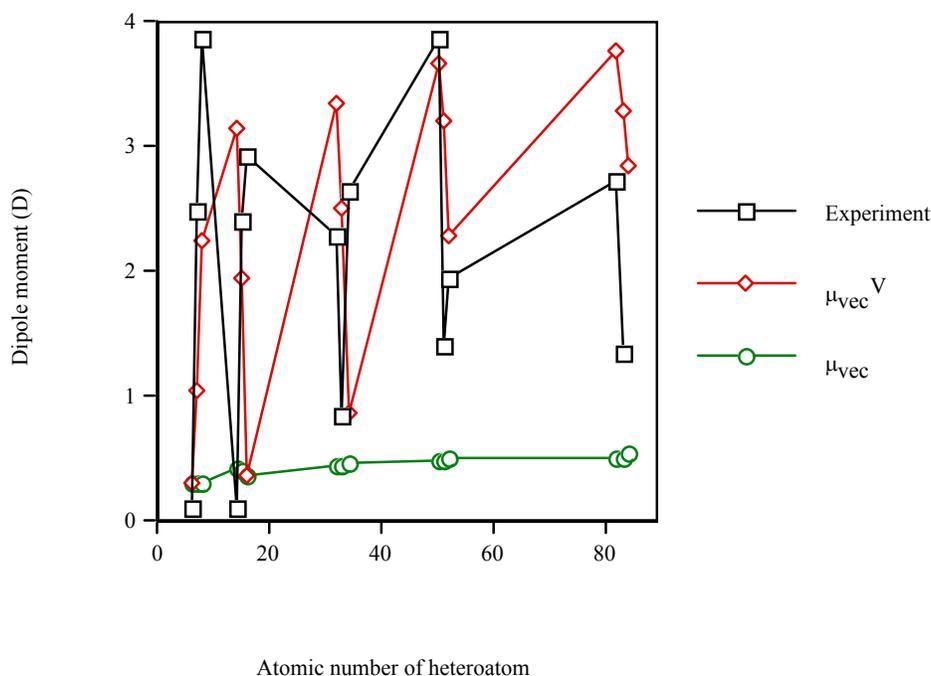
  

Molecule	$J_1^V$	$J_2^V$	$J_3^V$	$J_4^V$	$J_5^V$
styrene	0.1429	0.9841	0.0625	0.0305	0.0089
benzaldimine	0.2286	1.0234	0.0796	0.0387	0.0026
benzaldehyde	0.3857	1.0627	0.1145	0.0583	0.0036
C <sub>6</sub> H <sub>5</sub> -CH=SiH <sub>2</sub>	0.3629	0.9291	0.0757	0.0491	0.0177
C <sub>6</sub> H <sub>5</sub> -CH=PH	0.2686	0.9527	0.0625	0.0373	0.0140
thiobenzaldehyde	0.1429	0.9841	0.0625	0.0305	0.0089
C <sub>6</sub> H <sub>5</sub> -CH=GeH <sub>2</sub>	0.3629	0.9291	0.0757	0.0491	0.0177
C <sub>6</sub> H <sub>5</sub> -CH=AsH	0.3000	0.9448	0.0625	0.0412	0.0152
C <sub>6</sub> H <sub>5</sub> -CH=Se	0.1743	0.9763	0.0625	0.0305	0.0102
C <sub>6</sub> H <sub>5</sub> -CH=SnH <sub>2</sub>	0.3629	0.9291	0.0757	0.0491	0.0177
C <sub>6</sub> H <sub>5</sub> -CH=SbH	0.3314	0.9370	0.0687	0.0452	0.0165
C <sub>6</sub> H <sub>5</sub> -CH=Te	0.2686	0.9527	0.0625	0.0373	0.0140
C <sub>6</sub> H <sub>5</sub> -CH=PbH <sub>2</sub>	0.3629	0.9291	0.0757	0.0491	0.0177
C <sub>6</sub> H <sub>5</sub> -CH=BiH	0.3314	0.9370	0.0687	0.0452	0.0165
C <sub>6</sub> H <sub>5</sub> -CH=Po	0.3000	0.9448	0.0625	0.0412	0.0152

The molecular CT indices  $G_k$ ,  $J_k$ ,  $G_k^V$  and  $G_k^V$  for the valence-isoelectronic series of styrene ( $C_6H_5-CH=CH_2$ ) are collected in Table 3. As expected, all the molecules show the same set of  $G_k$  and  $J_k$  values. However,  $G_k^V$  are influenced by the atomic number of the heteroatom. In particular, the results for thiobenzaldehyde are equal to those for styrene. This is because the electronegativity for the S atom has been taken equal to that of C ( $\chi_S=\chi_C=2.5$ ). The same happens for the Si/Ge/Sn/Pb ( $\chi_{Si}=\chi_{Ge}=\chi_{Sn}=\chi_{Pb}=1.8$ ), P/Te ( $\chi_P=\chi_{Te}=2.1$ ), As/Po ( $\chi_{As}=\chi_{Po}=2.0$ ) and Sb/Bi compounds ( $\chi_{Sb}=\chi_{Bi}=1.9$ ).

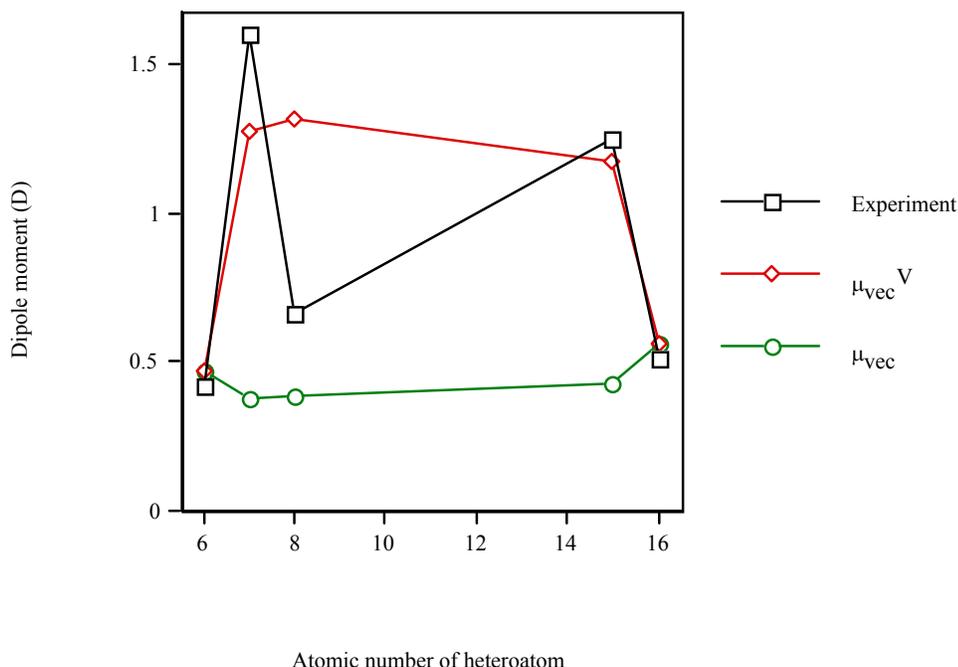
Figure 2 shows the increase in the dipole moment of the valence-isoelectronic series of styrene when the heteroatom is present. Again,  $\mu_{\text{experiment}}$  and  $\mu_{\text{vec}}^V$  vary in a similar fashion, while  $\mu_{\text{vec}}$  remains almost constant ( $\mu_{\text{vec}}\sim 0.43\text{D}$  for the three groups IV–VI). The electronic effect of the heteroatom ( $\mu_{\text{vec}}^V$ ) dominates, in general, over the steric one ( $\mu_{\text{vec}}$ ). In particular, for thiobenzaldehyde ( $Z=16$ ) the result of  $\mu_{\text{vec}}^V = \mu_{\text{vec}}$  (because  $\chi_S=\chi_C$ ) should be taken with care. It is an artefact of the model for S-heteromolecules. Furthermore, the best results are obtained, in general, for the fourth long-period (Sn–Te) and for the group-VI heteromolecules.

**Figure 2.** Dipole moment of the valence-isoelectronic series of styrene vs. the atomic number of the heteroatom. Point with  $Z = 6$  from Reference 42;  $Z = 7, 14-16, 32-34, 51$  and  $52$  are computed with AM1;  $Z = 8$  from Reference 43;  $Z = 50, 82$  and  $83$  are PM3 calculations.



In order to test the model for other S-containing heterocycle, Figure 3 displays the increase in the dipole moment of the valence-isoelectronic series of cyclopentadiene when the heteroatom is present. Once more,  $\mu_{\text{experiment}}$  and  $\mu_{\text{vec}}^V$  vary in a similar fashion while  $\mu_{\text{vec}}$  remains almost constant ( $\mu_{\text{vec}}\sim 0.45\text{D}$ ). The electronic effect of the heteroatom ( $\mu_{\text{vec}}^V$ ) dominates over the steric one ( $\mu_{\text{vec}}$ ). In particular, for thiophene ( $Z=16$ )  $\mu_{\text{vec}}^V = \mu_{\text{vec}}$  (because  $\chi_S=\chi_C$ ). However, the  $\mu_{\text{vec}}^V$  relative error for thiophene (10%) is even smaller than for cyclopentadiene (12%).

**Figure 3.** Dipole moment of the valence-isoelectronic series of cyclopentadiene vs. the atomic number of the heteroatom. Point with  $Z = 15$  is AM1 calculation.



## Conclusions

The following conclusions can be made from this study:

1. The behaviour of  $\mu_{vec}^V$  is intermediate between  $\mu_{vec}$  and  $\mu_{experiment}$  and so the correction introduced with respect to  $\mu_{vec}$  is produced in the correct direction. The best results are obtained for the greatest group that can be studied.
2. Inclusion of the heteroatom in the  $\pi$ -electron system is beneficial for the description of the dipole moment, owing to either the role of additional  $p$  and/or  $d$  orbitals provided by the heteroatom or the role of steric factors in the  $\pi$ -electron conjugation. The analysis of both electronic and steric factors in  $\mu$  caused by the presence of the heteroatom shows that the electronic factor dominates over the steric one. Work is in progress on the calculation of the dipole moments of a homologous series of 4-alkylanilines, which are percutaneous enhancers of transdermal-delivery drugs.
3. Inclusion of the heteroatom enhances  $\mu$  with the only exception of the insertion of the Si atom in styrene. In turn, the increase in  $\mu$  can improve the solubility of the molecule.
4. For heteroatoms in the same group of the periodic table, the ring size and the degree of ring flatterness are inversely proportional to the electronegativity of the heteroatom, e.g., cyclopentadiene<sub>ring</sub> < C<sub>4</sub>SiH<sub>6 ring</sub> < C<sub>4</sub>GeH<sub>6 ring</sub> < C<sub>4</sub>SnH<sub>6 ring</sub> < C<sub>4</sub>PbH<sub>6 ring</sub> and benzene<sub>ring</sub> < C<sub>5</sub>SiH<sub>6 ring</sub> < C<sub>5</sub>GeH<sub>6 ring</sub> < C<sub>5</sub>SnH<sub>6 ring</sub> < C<sub>5</sub>PbH<sub>6 ring</sub>.
5. Inclusion of the heteroatom increases  $\mu$ , which is smaller for the benzene than for the styrene series. On going from styrene to C<sub>6</sub>H<sub>5</sub>-CH=SnH<sub>2</sub>,  $\mu_{experiment}$  increases by a factor of 41. Although there is a minor steric effect ( $\mu_{vec}$  increases by a factor of 1.6), the major effect is

electronic ( $\mu_{\text{vec}}^V$  augments by a factor of 12). From  $\mu_{\text{vec}}$  to  $\mu_{\text{vec}}^V$  the introduced correction is produced in the correct direction. However, the result for thiobenzaldehyde is uncertain. Work is in progress with the correct parameterization of the method for the S atom. On going from cyclopentadiene to pyrrole,  $\mu_{\text{experiment}}$  increases by a factor of 4. Although there is an antagonistic steric effect (in fact  $\mu_{\text{vec}}$  decreases), the major effect is electronic ( $\mu_{\text{vec}}^V$  is trebled).

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