Electronegativity Equalization and Atomic Polar Tensor in Diatomic Molecule

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Among the various methods of studying the structure and electronic properties of polyatomic molecules, infrared spectroscopy is one of the most fundamental ones. In particular, the integrated band intensities, when used in connection with knowledge of the molecular force field, give extremely valuable information on the character of the chemical bonds and on the atomic structure of the molecule[1]. With regard to the latter aspect, the band intensities are interpreted in terms of the so-called atomic polar tensors defined as the set of derivatives of the Cartesian components of the dipole moment with respect to the Cartesian coordinates of each atom in the molecule[2].

The electronegativity is a definite property of the ground state of an atom. According to the Sanderson's principle[3], a unique common electronegativity results when two species of different electronegativities come together to form a third. This process is usually called as the electronegativity equalization[4].

The purpose of this communication is to present the relationship between the electronegativity equalization and the atomic polar tensor for heteronuclear diatomic molecules. Based on the simple bond charge model of diatomic molecules[5], the effects of charge transfer on electronegativity were initially considered. The atomic polar tensors were then predicted from the idea of electronegativity equalization, and these predicted values were compared with those derived from the integrated infrared band intensities.

Consider a diatomic molecule with the equilibrium bond length R_{AB}. In the simple bond charge model, we let $Z_A+\eta$ and $Z_B-\eta$ be the charges on nuclei A and B, where Z_A is the charge on A in the diatomic molecule AA, Z_B the charge on B in BB; η measures the charge transferred[6]. A point charge carrying $-(Z_A+Z_B)$ electrons is located at a distance r_1 from A and r_2 from B, with $r_1+r_2=R_{AB}$; it is assumed that the bond charge in AB is the average of the bond charges in AA and BB. If the bond length in AA is $2r_A$, and in BB is $2r_B$, Pasternak[5] took as a definition of the electronegativity of atom A a formula

$$\chi_A = C(Z_A/r_A), \tag{1}$$

where C depends on bond type.

For the diatomic AB, the natural definition for the electronegativity of atom A, in the final molecule after charge transfer, has the form[7]

$$\chi_A(in\ AB) = C\left(\frac{Z_A+\eta}{r_1}\right), \tag{2}$$

and similarly

$$\chi_B(in\ AB) = C\left(\frac{Z_B-\eta}{r_2}\right). \tag{3}$$

These must be equal to each other and to the molecular electronegativity x_{AB}. Assuming all molecules have the same bond type, this leads to the formula

$$\chi_{AB} = C\left(\frac{Z_A+\eta}{r_1}\right) = C\left(\frac{Z_B-\eta}{r_2}\right) = C\left(\frac{Z_A+Z_B}{R_{AB}}\right)$$
$$= \frac{\chi_A r_A+\chi_B r_B}{r_1+r_2} = \frac{\chi_A R_{AA}+\chi_B R_{BB}}{2R_{AB}}. \tag{4}$$

Then, the electron charge transferred, η, can be denoted as

$$\eta = \frac{r_1 r_2}{r_1+r_2}\left(\frac{r_B}{r_2}\frac{Z_B}{r_B} - \frac{r_A}{r_1}\frac{Z_A}{r_A}\right). \tag{5}$$

Applying the zero-order approximation[5], i.e.

$$r_1 \approx r_A \text{ and } r_2 \approx r_B, \tag{6}$$

to the parenthesized part of Eq. (5), we obtain using Eq. (1),

$$\eta = \frac{r_1 r_2}{CR_{AB}}(\chi_B - \chi_A). \tag{7}$$

We consider now the dipole moment of the diatomic AB. The centroid of positive charge, r, relative to the point defining the centroid of negative charge can be computed from the following relation,

$$-r_1(Z_A+\eta)+r_2(Z_B-\eta) = r(Z_A+Z_B). \tag{8}$$

That is,

$$r = \frac{r_2 Z_B - r_1 Z_A - (r_1+r_2)\eta}{(Z_A+Z_B)}. \tag{9}$$

Accordingly, the dipole moment, μ, is given as

$$\mu = (Z_A+Z_B)r = -(r_1+r_2)\eta + (r_1 Z_B - r_1 Z_A)$$
$$= -R_{AB}\eta + (r_2 Z_B - r_1 Z_A). \tag{10}$$

The dipole moment is defined to direct from the centroid of negative charge to that of positive charge.

We assume further that following relation holds,

$$r_2 Z_B - r_1 Z_A \cong 0. \tag{11}$$

Then, from the relation, $r_1+r_2=R_{AB}$ and Eqs.(1) and (11), we get

$$r_1 r_2 = \frac{Z_A Z_B}{(Z_A+Z_B)^2}R_{AB}^2 = \frac{r_A r_B \chi_A \chi_B}{(r_A\chi_A+r_B\chi_B)^2}R_{AB}^2. \tag{12}$$

The dipole moment in Eq. (10) can then be represented as the formula using the relations of Eqs. (9) and (12),

$$\mu = -R_{AB}\eta = -\frac{r_1 r_2}{C}(\chi_B-\chi_A)$$
$$= -\frac{1}{C}\left\{\frac{r_A r_B \chi_A \chi_B}{(r_A\chi_A+r_B\chi_B)^2}\right\}R_{AB}^2(\chi_B-\chi_A). \tag{13}$$

Let's consider a diatomic AB molecule, and assume that A atom is located at the origin and B atom in the positive Cartesian direction. Then, the atomic polar tensors (P_x's) for atoms A and B can be represented as[2]

$$P_X^{(B)} = -P_X^{(A)} = \left(\frac{\partial\mu}{\partial R}\right)_e, \tag{14}$$

Table 1. The Covalent Radius, $r_A = 1/2R_{AA}$, and the Electronegativity, χ_A, of Homonuclear Diatomic Molecule A_2

Molecule(A_2)	r_A(Å)[a]	χ_A(eV)[b]
H_2	0.3707	7.14
F_2	0.7060	10.40
Cl_2	0.9940	8.29
Br_2	1.1405	7.60
I_2	1.3332	6.76
Na_2	1.5394	2.84
Li_2	1.3365	3.00
K_2	1.9526	2.42

[a] Taken from Ref. (8). [b] Mulliken's electronegativities taken from Ref. (9).

where $(\partial\mu/\partial R)_e$ is the dipole moment derivative at geometric equilibrium.

It may be appropriate to mention that the dipole moment represented in Eq. (13) is independent of the location of charges. When A atom in diatomic AB is more electronegative than B atom, the dipole vector will point to the positive axis. On the other hand, the dipole moment will be negative if the value of χ_B is larger than that of χ_A. Hence, we can use Eq. (13) directly to get the atomic polar tensors in Eq. (14).

The simple bond charge formula for the dipole moment under the assumptions of Eqs.(6) and (11) gives the atomic polar tensor of B atom as follows,

$$P_X^{(B)} = \left(\frac{\partial \mu}{\partial R}\right)_e = -\frac{2R_{AB}}{C}\frac{r_A r_B \chi_A \chi_B}{(r_A\chi_A + r_B\chi_B)^2}(\chi_B - \chi_A). \quad (15)$$

It is to be mentioned that Ray *et al.*[7] derived the heteropolar bond length, R_{AB}, in terms of the electronegativities, χ_A and χ_B, and covalent radii, r_A=1/2R_{AA} and r_B=1/2R_{BB}, of the atoms A and B. That is,

$$R_{AB} = r_A + r_B - \frac{r_A r_B (\chi_A^{1/2} - \chi_B^{1/2})^2}{r_A\chi_A + r_B\chi_B}. \quad (16)$$

Hence, we can now predict the atomic polar tensors of a molecule AB solely from the electronegativities and covalent radii of the atoms A and B.

The covalent radii and the Mulliken's electronegativities of some homonuclear diatomic molecules are listed in Table 1. The equilibrium bond distances and the atomic polar tensors for some heteronuclear diatomic molecules calculated from the data in Table 1 using Eqs. (16) and (15), respectively, are shown in Table 2. For comparison, the observed values are also included in Table 2. The value of C in Eq. (15) was assumed to be 6.9696 eV·Å/e as reported by Ray *et al.*[7]

The predicted bond lengths are in fair agreement with the observed values. The largest difference was observed for the FLi molecule. Although the predicted APT's are not exactly consistent with the observed ones, there appears to be good correlation between the two sets. The predicted signs of the atomic polar tensors are in good agreement with the observed ones. Relatively large deviations were observed for the HX (X = halogen) molecules. For other molecules, the values of the predicted atomic polar tensors are relatively in fair agreement with those of the observed ones. The infrared band intensity of the HX molecule is extremely weaker than that of other molecule considered in Table 2. That is, the absolute value of the atomic polar tensor in HX is much smallar than that of other molecule. Then, the difference between

Table 2. Atomic Polar Tensors (APT's) and Equilibrium bond Distances (R_{AB}) of some AB Systems

Molecule(AB)	R_{AB}(Å)		APT(e)[c]	
	Calc.[a]	Obs.[b]	Calc.[d]	Obs.[e]
HF	1.069	0.917	-0.195	-0.317
HCl	1.363	1.275	-0.083	-0.193
HBr	1.511	1.414	-0.036	-0.100
HI	1.704	1.609	0.033	0.011
HLi	1.641	1.596	0.467	0.473
HNa	1.831	1.887	0.531	0.541
ClLi	2.188	2.021	0.731	1.001
ClNa	2.360	2.361	0.836	0.949
ClK	2.684	2.667	1.047	1.074
FLi	1.857	1.564	0.901	0.908
FNa	2.025	1.926	1.028	0.910

[a] Determined from the data in Table 1 using Eq. (13); [b] Taken from Ref. (8); [c] The APT is defined as the dipole moment derivatives, $\partial\mu/\partial$R (see Ref. (2)). The APT's herein correspond to the B atoms in the diatomic AB molecules. The A and B atoms are assumed to be located, respectively, at the origin and in the positive Cartesian coordinate; [d] Calculated from the data in Table 1 using Eq. (12); [e] Taken from Ref. (10).

the atomic polar tensors of the two sets, predicted and observed, in HX may be assumed to indicate the extent of crudeness of the present model. Applying the least-square analysis to all molecules including HX, the two sets are related by the formula,

$$APT(\text{obs}) = 1.052\ APT(\text{calc}) \quad (17)$$

with the standard deviation of 0.104/e. For ClLi, the difference between the predicted atomic polar tensor and the observed one is far beyond the standard deviation. Otherwise, the standard deviation seems to encompass the difference between the two sets for molecules considered in Table 2. This would suggest that the atomic polar tensor of diatomic molecule could be estimated within the above uncertainty range using the relatively simple formula of Eq. (15).

It is remarkable that the integrated infrared intensities may be predicted, with reasonable accuracy, from the electronegativities alone. The difference between the experimental and predicted values of the atomic polar tensors is presumably a measure of the errors introduced by the simple bond charge model. The fair correlation between experiment and theory suggests that it might be possible to correct for those errors empirically, for some classes of systems. Further investigations of this problem seem to be merited.

In summary, the electronegativity equalization that takes place as atoms of different electronegativities come together to form diatomic molecule is shown to encompass the integrated infrared intensity. Within the simple bond charge model predictions are made of the atomic polar tensor and bond length R of a molecule AB, from the electronegativities χ_A and χ_B and covalent radii r_A=1/2R_{AA} and r_B=1/2R_{BB} of the atoms A and B. Although the theoretical values are not exactly consistent with the experimental ones, they seem to be comparable with each other. So far, little information is available about the correlation between infrared intensity and electronegativity. Hence, we believe that this report would provides a basis to understand the more detailed nature regarding the infrared intensity and electronegativity.

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Reduction of Indole-2-Carboxylate and 2-Carboxamide with Magnesium in Methanol†

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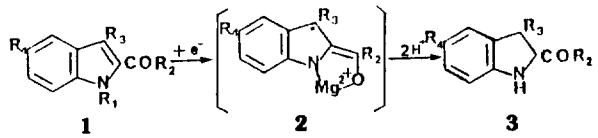
Recently we have reported[1] that magnesium in methanol can be used as a mild and convenient reducing agent for the reduction of α,β-unsaturated esters. To expand our scope for the reduction of indole derivatives[2] where the double bond is fused in aromatic nucleus, we have applied this reagent to various indole carboxylates (1*a-e*) and carboxamides (1*f-g*). Reduction of fused double bond of indole nuclei proceeded smoothly to give corresponding indolines in high yields as summarized in Table 1. Comparing with the known methods[3] for the preparation of indoline carboxylate and carboxamide, it is far more advantageous to use magnesium in methanol in its yields and reaction conditions.



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As with the conjugated esters[1,4], ethyl indole-2-carboxylates (1*b-e*) were reduced along with ester exchange by magnesium methoxide produced during the reduction to give the corresponding methyl indoline-2-carboxylates (3*b-e*). N-acetyl group of 1*d* was cleaved as expected under the reaction condition to give the same product as 1*b*. But the amide group of indole-2-carboxamides (1*f-g*) was inert to magnesium methoxide and gave the corresponding indoline-2-carboxamide (3*f-g*) in high yields. Interestingly 3-position substituted ethyl indole-3-carboxylate (**4**) was not reduced by this reagent. The starting material was completly recovered even after 10 eq. of magnesium was used.

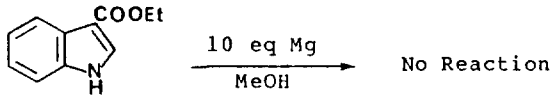

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Table 1. Reduction of 2-substituted indoles to corresponding indolines

Entry	Starting Material(1)				Product[a](3)				Mg(eq)/time(hr)	Yield[b] (%)
	R_1	R_2	R_3	R_4	R_1	R_2	R_3	R_4		
a	H	OCH_3	H	H	H	OCH_3	H	H	3.0/2.0	97
b	H	OC_2H_5	H	H	H	OCH_3	H	H	2.0/2.0	96
c	H	OC_2H_5	CH_3	H	H	OCH_3	CH_3	H	3.5/2.0	98[c]
d	$COCH_3$	OC_2H_5	H	H	H	OCH_3	H	H	3.0/1.5	90
e	H	OC_2H_5	H	Cl	H	OCH_3	H	Cl	3.0/2.5	95[d]
f	H	NH_2	H	H	H	NH_2	H	H	6.0/3.0	90
g	H	$NHCH_3$	H	H	H	$NHCH_3$	H	H	10.0/3.0	94

[a]all compounds have been characterized by ^1H NMR and mass spectroscopy. (see Note). [b]Yield of isolated product. [c]cis and trans mixture (75:25) as determined by g.l.c. and ^1H NMR. [d]Yield of crude product. Compound decomposes.

† Dedicated to Professor Nung Min Yoon on the occasion of his 60th birthday.