CORRELATION OF THE EFFECTIVE ELECTRONEGATIVITY OF MOLECULES WITH VIBRATIONAL FREQUENCIES

M. Arshad A. Beg

Central Laboratories, Pakistan Council of Scientific and Industrial Research, Karachi

The vibrational frequencies of the various bonds are shown to be related to the overall electronic environment of the molecules given by their effective electronegativity. The various aspects of the changes in the electronegativity of molecules are discussed.

In a recent communication the basicity of phosphines was correlated with their effective electronegativity.[1] Since characteristic frequency shifts can also be correlated with the reactivities of the molecules, further support to the idea of the electronegativity of molecules is obtained on making a comparison of these two values. Previous correlations in this respect have been based either on the electronegativity of the central atom[2] or on the sum or product of the electronegativity[3,4] of the substituents. All these correlations are valid to a certain extent. However, since the substituents alter the electron density and the state of hybridization of the central atom resulting in a variation of the properties of the molecule, the electronegativity of the substituent and the central atom both, should be taken into account. This leads to the consideration of the electronegativity of molecules.

Since the frequency shifts are also related to the overall electron density of the molecules which has been shown previously to be a direct consequence of electronegativity,[1] the desirability of a comparison with the electronegativity of the molecules is further indicated. Support for the concept of an overall electronegativity for molecules is also provided by the change in electronegativity with a change in hybridization. Since the withdrawal of *p*-character or of *s*-character would increase or decrease the bond length and bond angles, this would be reflected in the overall electronegativity of the molecules and a measure of this may be seen in the acidity or basicity of the compound.[5] This may also be observed in the shift in a particular characteristic frequency of the molecule. It may be pointed out here that the replacement of one substituent by another shifts the frequencies of all the bonds. For example, in RPOClF the frequencies of P=O, P—F and P—Cl change when R which is an organic substituent is changed. The frequencies of the various bonds of the organic substituent also suffer a calculated shift when such a change is brought about.[4]

The entry of an electronegative group alters the electronic environment of the central atom and there is a redistribution of the electrical charge on the molecule. The overall electronic environment presents a picture in which the whole molecule obtains an effective charge, determined by the substituents and it is under this potential that it would react with another species. The effective electronegativity of the molecules gives the resultant potential on the entire molecule and may be used as a measure of its reactivity towards other species. For example, the poor basicity of amines and phosphines having electron-withdrawing groups on them is a result of the withdrawal of *p*-character which gives rise to an accumulation of *s*-character.[5]

The idea is supported by the following observations:

1. The shifts are observed for every bond including those of the substituents, e.g., the C—H in alkyl or aryl groups as may be seen from Table 1 in reference 6.

2. The higher the electronegativity of the substituent, the higher are the shifts. The mass effect does, however, affect this statement although definite periodicity is maintained for a particular class of compounds. The variation of the phenyl—X frequencies for the various groups of compounds

shown in Fig. 1 is similar to that obtained on the basis of the electronegativity of the central atom.[2] Similarly the very sensitive absorptions like those of the P=O and C=O are known to depend on the electronegativity of the substituents.[7,8] In these cases the correlation with the effective electronegativity of molecules is equally valid.

3. The shift in the frequencies on a change of valence state is also related to the change in the effective electronegativity of the molecule. Thus the P—C antisymmetric stretching frequency and the X-sensitive vibrations are both seen to move to higher frequencies as the valence is changed from three to five.[9] This is because of a change in hybridization.

The lone pair of electrons also contribute to the effective electronegativity. Their participation in the characteristic shifts have recently been demonstrated.[10] The substituents on the other hand substantially alter the electronic environment and hence there is always a positive shift as is the trend when the electronegativity of a molecule rises. Since the effective electronegativity of a molecule is a measure of the electron density or the electronic environment of a molecule, a complete picture would be obtained if the contributions from the π electrons, lone pair electrons and vacant orbitals are all taken into account.
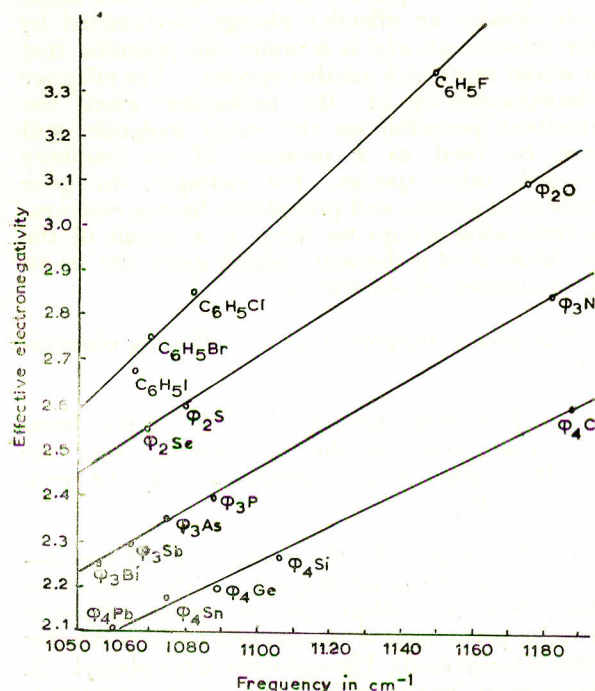
By accounting for the contributions of the substituents at least the shifts in the frequency which have so far been attributed to the inductive effect are explained. The shifts due to the conjugative or mesomeric effect would be explained if the contribution of the π electrons is also added to the overall electronic environment.

The effect of a substituent on the central atom and on the overall environment may be visualized from the example of a molecule XYCO in which X is an electronegative element. Since the electronegative potential of an atom is transmitted along a chain or through the central atom, there is a net alteration in the electron population of another atom Y on the other side and there is a resultant change in the frequency of C—Y. The bond angles and bond length are determined by the amount of repulsion which the various bond pairs and lone pairs would exert. Those bonds will be more prone to vibrations which are crowded with lone pairs followed by bond pairs. The increase in mass, however, would make the particular bond rather insensitive to vibration but still there would be a potential effect on the bond because of the repulsions from lone pairs. The vibrational motion is therefore directly connected with the electronic environment and this is given by the electronegativity of the molecule. Because of the change in electron density, there might be a relief in the strain and hence certain vibrations which were previously coupled or were restricted may now be allowed. This may further result in an ease in compression of the bonds, or in the rocking, twisting or wagging mode or in similar vibrations. The total magni-
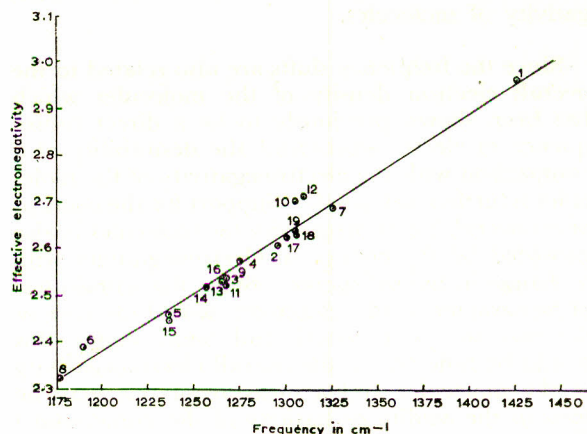

Fig. 1.—Dependence of the X-sensitive vibrational frequency on the effective electronegativity of the IV, V, VI and VII group phenyls.

Fig. 2.—Dependence of the P=O frequency on the effective electronegativity of the phosphoryls. (1. F₃PO, 2 Cl₃PO, 3. Br₃PO, 4. PhCl₂PO, 5. Ph₂ClPO, 6. Ph₃PO, 7. (CF₃)₃PO, 8. Me₃PO, 9. (MeO)₃PO, 10. (MeO)₂FPO, 11. (MeO)₂HPO, 12. (EtO)₂FPO, 13. (EtO)₂HPO, 14. (EtO)₂PhPO, 15.(EtO)PhHPO, 16. (BuO)₂HPO, 17.(PhO)Cl₂PO, 18. (PhO)₂ClPO, 19. (Ph₃O)₃PO.

tude of these effects is given by the effective electronegativity of the molecule which having been altered as seen in XYCO would be exhibited by a small but significant shift in the frequency C=O and of C—X and C—Y.

The dependence of the frequency shifts on the effective electronegativity of molecules may be observed from Fig. 2 which also shows that substances having the same electronegativity have nearly the same P=O absorption. Similar relations have been worked out for bonds like P—C, P—Cl and P—F. The deviations from the linear relationship are noted for compounds having different electronegative substituents on the central atom. It is possible that the resultant electronegativity of the molecule is lower because of a redistribution of electron density and hence the vibrational frequency may be lowered to a certain extent. This clearly indicates the desirability of refinements in this treatment. It is intended to work out the individual contributions of the lone pair and π electrons to obtain better agreement with the observed data. For the present, however, there is sufficient indication that the vibrational frequencies of the various bonds in a mole-

cule can be predicted on the basis of the effective electronegativity.

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