CROATICA CHEMICA ACTA CCACAA 57 (6) 1475—1483 (1984)

CCA-1537

YU ISSN 0011-1643
UDC 541
Original Scientific Paper

Partitioning and Additivity of the Chemical Bond

John B. Moffat

Department of Chemistry and Guelph-Waterloo Centre for Graduate Work in Chemistry, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada

Received April 9, 1984

Changes in the electronic energies of various molecules on substitution of a hydrogen atom by another atom or group can be shown to be similar in magnitude. By considering a variety of recipient molecules, both neutral and cationic, it is shown that the substitution energy for cyano and isocyano groups can be correlated with the charge on the substituent group in the substituted molecule.

INTRODUCTION

One of the oldest and most useful concepts in chemistry is that of the chemical bond. While the current understanding of a chemical bond has become relatively sophisticated, the original representation of a single bond between two atoms by a line and a double bond by two lines, dates from Odling (1860) and Kekulé (1861). Although the theory of the chemical bond has enjoyed considerable development since that time and particularly in the last thirty years, the value of the concept in the hands of the experimentalist does not appear to have diminished.

The development of quantum chemistry with its emphasis on electron densities, atomic and molecular orbitals, and orbital and Hartree-Fock energies, while facilitating both the interpretation of experimental data and the prediction of the results of experiments has at the same time presented the chemist with a significant challenge. How does one incorporate the concept of the chemical bond into quantum chemistry? While in quantum chemistry, the interactions between electrons, between nuclei and each other must be introduced explicitly, the idea of a chemical bond is not introduced in either the formulation of the appropriate fundamental quantum mechanical relationships nor their solution. Indeed, the evidence to this date would suggest that it is not possible to introduce the concept of a bond into the formulations of the requisite quantum theory at the level of the Hamiltonian operator.

On the most fundamental level, there have been a variety of attempts to reconcile the concept of molecular structure with quantum mechanics. Woolley[1,2] has noted that, despite its microscopic nature, the molecule is a classical concept as far as the problem of its spatial structure is concerned, and can be viewed as an example of classical behaviour on a microscopic scale. He argues that a definite molecular structure can only be associated with quantum states that are intrinsically time-dependent and conversely if a molecule is definitely observed in an eigenstate of its associated molecular Schrödinger equation, a molecular structure description is inappropriate. Others[3,4,5] have suggested that the interpretational difficulties inherent in the use of Schrödinger's equation may be circumvented by the development of stochastic electrodynamics as a new fundamental theory for quantum mechanics. Some have attributed the form of molecules to the perturbing effect of the environment[6,7]. Golden[8] interprets molecular structure and bonding in terms of a »boundedness«, criteria for which are generated from fixed linear combinations of the position and conjugate momentum of a particle. In contrast to the contentions of Woolley and Primas, Bader *et al.*[9] view molecular structure as the generic property of the distribution of charge in a total system, and conclude that a molecule has a definite structure in spite of its interactions with the environment, rather than as a consequence of these interactions. Woolley[10] suggests that much can be done without the classical concept of a potential energy surface, and emphasizes the power of wavefunctions possessing the quality of rigidity. Woolley believes that the central question should refer to the qualities of the relevant quantum states in Hilbert space rather than to the structure of the molecule. Trindle[11] has examined the relevance of the Born--Oppenheimer approximation in discussions of molecular structure. In spite of the considerable amount of attention devoted to the concept of the chemical bond, the relationship to quantum mechanics remains a challenge[12,13].

Chemists have also found convenient the assumption that an energy may be associated with each chemical bond. Such a theory has found principal use in assignment of group contributions to thermodynamic functions which in turn has permitted the estimation of reaction heats, entropies and free energies, often for reactions which are not easily accessible experimentally. The earliest methods simply assigned values to each atom present. Later, assignments were made for each bond or group regardless of the molecule in which each was found[14]. More recently Benson and co-workers have developed a 2nd order method which takes into account neighbouring groups in the molecule of interest[15].

Many of the theories proposed for the introduction of the bond concept into quantum chemistry have involved an aposteriori approach, that is, attempts to partition either the wavefunctions or the calculated energies to reflect the behaviour observed with the thermodynamic functions. Allen and Shull[16] appear to have been the first to show by use of the virial theorem that a properly antisymmetrized product function over geminals has both of the properties essential to the bond-energy concept, that the energy of a molecule is the sum of the energies of its individual bonds, and the bond energies are invariant from one molecule to another.

Ruedenberg[17] analyzed the chemical bond by breaking its formation into hypothetical steps. The molecular electron density, pair density and molecular energy are defined for each pair of atoms and for each step. Initially the two atoms which will ultimately form the bond are considered to be in their ground electronic states at infinite separation. A quasiclassical pair density is defined. With the atoms still noninteracting they are elevated to their promotion states. The promoted atoms are then moved together to their equilibrium internuclear separations in the molecules while the promotion state atomic densities and the pair densities are held fixed. By sharing of electrons between atoms and by the transfer of charge from one atom to another the electron density and pair density for the system are converted to the values found in the molecule in its stable configuration. Two types of sharing effects are postulated, namely sharing penetration and sharing interference, the former arising from the change in the electron-electron repulsion due to the change in the average distance between electrons, the latter from the overlap of the atomic wave function.

The validity of this method can be demonstrated by the existence of one or more partitioned terms for a given bond which have similar values in all molecules containing that bond, that is, are characteristic of that bond. The theory has been applied by Moffat and Popkie[18] to the *ab initio* wave functions of a series of nitriles. The sharing interference for the C≡N bond has values of — 16.85 ± 0.05 eV in the neutral nitriles and therefore appears to be characteristic of the CN bond. Further evidence for the use of the sharing interference term as a bond characteristic quantity is found from the existence of a correlation between the experimentally measured bond energy (or bond dissociation energy) and the intrabond interference energy[19].

Fischer and Kollmar[20] have developed a method for partitioning of the energies obtained from the semiempirical CNDO method. Moffat and Tang[21] have applied this approach to a variety of molecules containing CN single, double, and triple bonds. The one-electron two-centre energy term (E^{R}) within this theory is directly related to the interference energy and is found to be characteristic of the bond. This partitioning method has been applied to the isomerization of methyl isocyanide[22], to the reactive dimerization of HCN[23] and the formation of acrylonitrile and propiolonitrile from acetylene and hydrogen cyanide[24]. Kollmar[25] has extended his earlier semi-empirical partitioning method to *ab initio* calculations by inclusion of a term representing the Fock matrix where appropriate.

Ehrenson and Seltzer[26] defined a bond strength index as the sum, over all orbitals between any pair of atoms, of the product of the individual bond order and the corresponding overlap integral. The heat of formation of a molecule can then be expressed as a linear combination of the bond strength index for each of the bonds in the molecule. The bond additivity method of Benson and Buss[51] has been extended to provide data for nitriles[27]. This was employed to calculate the heat of formation of nitriles which in turn was correlated with the bond-strength indices in these molecules[28].

Armstrong, Perkins and Stewart (APS)[29] have, for covalent bonding, provided definitions of valence, degree of bonding and anisotropy and have illustrated their application to semi-empirical wavefunctions. Recently, Natiello and Medrano[30] have employed *ab initio* calculations to demonstrate the relevance of the APS analysis for partitioning the electronic density.

The work of Fliszar, recently emerging in book form[31], is of particular interest and will undoubtedly find increasing application in organic chemistry. Further references relevant to the present discussion may also be found in that work.

Wiberg[32] has very recently proposed a method of group equivalents for converting *ab initio* energies to enthalpies of formation and has demonstrated its applicability to cyclic molecules.

Since the electronic correlation energy is the difference between the exact energy and that calculated by a full Hartree-Fock calculation, it was anticipated, in the same way that bond energies could be assigned, that group contributions to the correlation energy could be obtained. Such a method has been developed and applied to a variety of molecules.[33]

As noted earlier, the concept of bond energy has found application in a wide range of areas in chemistry. While the technique of partitioning[14,15,27] thermodynamic functions into group contributions is well developed, the corresponding process in quantum chemistry has received less attention. Comparison of various sets of molecules, each set containing a common substituent group, with each other and with the corresponding parent molecules has shown that the Born-Oppenheimer electronic energies (including nuclear repulsion) cannot be partitioned into bond energies in an analogous manner to that employed with the thermodynamic functions. However, further examination of the data shows that the change in electronic energy of a given molecule on addition of a substituent group is approximately characteristic of the substituent group for a variety of molecules[34]. Further illustrations of the relative invariance of this substitution energy have been obtained for a number of substituent groups and molecules. However, much of the work from this laboratory has been concerned with molecules containing the cyano and isocyano groups[35].

While the substitution energies are reasonably constant for a given substituent, it is anticipated that some second order dependence on the recipient molecule will exist. In the present work such dependence of the substitution energies of the cyano and isocyano groups is studied. For such purpose *ab initio* calculations with a minimal STO-3G basis[36] were carried out on both the recipient molecule and the substituted molecule with geometry optimization of bond lengths and angles to ±0.001 Å and ±0.1°, respectively.

RESULTS AND DISCUSSION

The calculated cyano and isocyano substitution energies with hydrogen cyanide (or isocyanide) and methane as initial recipient molecules are summarized in Tables I and II. A second substitution is performed on both methyl cyanide and isocyanide to provide information on the perturabtion effect of the first substitution on the parent molecule. It may readily be seen, as observed earlier, that the substitution energies are similar, at least to a first order approximation, for a given substituent group. At the same time, the differences between the various values of the substitution energies for a given group appear to reflect a dependence on the recipient molecule. Although this dependence is undoubtedly related to the bond energies of both the hydrogen atom

TABLE I

Cyano Substitution Energies with HCN, HNC, and CH_4

Substitution process	Net charge on substituent group	Substitution energy Hartrees
$HCN \rightarrow NCCN$	0	—90.54426
$HNC \rightarrow NCNC$	—0.088	—90.53712
$CH_4 \rightarrow CH_3CN$	—0.123	—90.54465
$CH_3CN \rightarrow NCCH_2CN$	—0.083	—90.53470
$CH_3CN \rightarrow NCCH_2NC$	—0.082	—90.53561

TABLE II

Isocyano Substitution Energies with HCN, HNC, and CH_4

Substitution process	Net charge on substituent group	Substitution energy Hartrees
HCN → CNCN	—0.088	—90.50635
HNC → CNNC	0.0	—90.46455
CH_4 → CH_3NC	—0.234	—90.50629
CH_3CN → $CNCH_2CN$	—0.196	—90.49725
CH_3CN → $CNCH_2NC$	—0.195	—90.50159

and the donor group with the recipient structure it appears that the substitution energy may most simply be related to the charge on the donor (cyano or isocyano) in the substituted molecule. This is evident from an inspection of columns 2 and 3 in Tables I and II. It may be noted, however, that the data for cyanogen (NCCN) do not follow the correlation. These values are shown in Figures 1 and 2 together with those for substitution on the C_2 and C_3 alkanes (Tables III and IV).

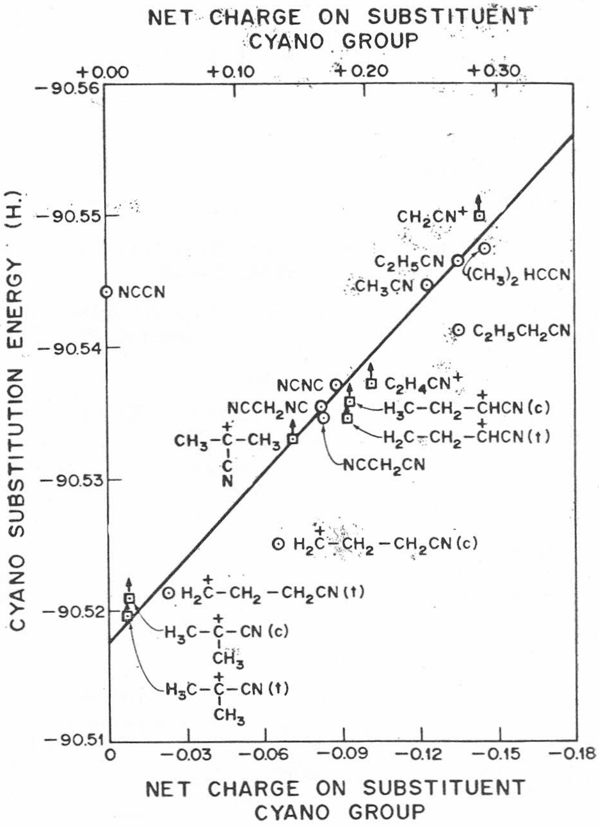


Figure 1. Cyano substitution energy and net charge on substituent cyano group for neutral and positively charged molecules. ○ and □ refer to lower and upper abscissae, respectively. (See text).

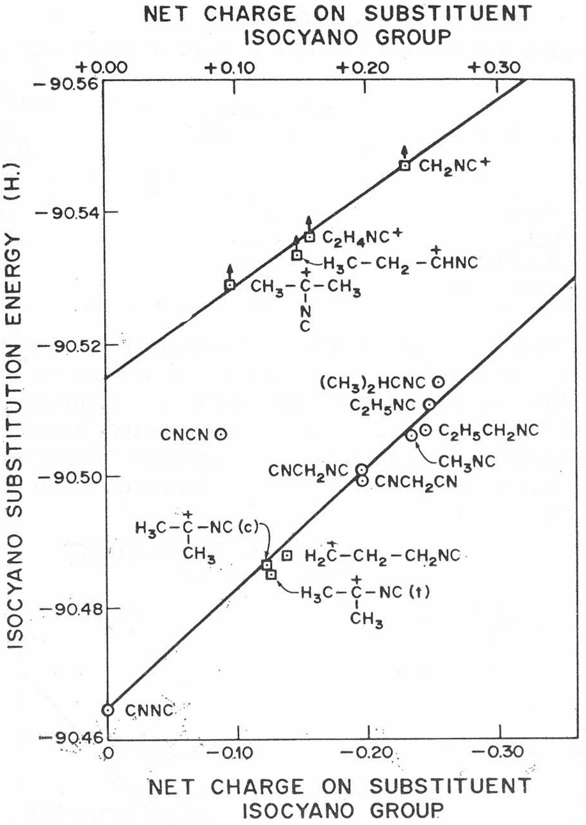


Figure 2. Isocyano substitution energy and net charge on substituent isocyano group for neutral and positively charged molecules. (See text).

TABLE III

Cyano Substitution Energies in Alkanes

Substitution process	Net charge on substituent group	Substitution energy Hartrees
$C_2H_6 \rightarrow C_2H_5CN$	—0.135	—90.54650
$C_3H_8 \rightarrow C_2H_5CH_2CN$	—0.135	—90.54127
$C_3H_8 \rightarrow (CH_3)_2HCCN$	—0.145	—90.54748

TABLE IV

Isocyano Substitution Energies in Alkanes

Substitution process	Net charge on substituent group	Substitution energy Hartrees
$C_2H_6 \rightarrow C_2H_5NC$	—0.247	—90.51100
$C_3H_8 \rightarrow C_2H_5CH_2NC$	—0.244	—90.50590
$C_3H_8 \rightarrow (CH_3)_2HCNC$	—0.254	—90.51433

It is then of interest to examine the effect of altering the charge possessed by the substituent group while maintaining similar structures for the recipient molecules. This may most readily be done by the removal of a hydride ion from a selected neutral molecule, thus producing both a positively charged recipient molecule and a positively charged substituted molecule, both carbenium ions. The substitution energies to generate the cyano- and isocyanocarbenium ions shown in Tables V and VI again are similar to those displayed in Tables I—IV. Although the substituent groups are now positively charged, an approximately linear correlation with substitution energy is again obtained. Since these charged species display, after geometry optimization, structures substantially different from the corresponding neutral species it is not unexpected that the correlations for the neutral and charged molecules do not overlap.

TABLE V

Cyano Substitution Energies with a Primary, a Secondary and a Tertiary Carbenium Ion

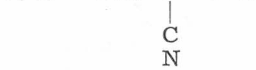
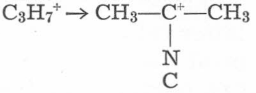
Substitution process	Net charge on substituent group	Substitution energy / Hartrees
$CH_3^+ \rightarrow CH_2CN^+$	+0.286	—90.54491
$C_2H_5^+ \rightarrow C_2H_4CN^+$	+0.204	—90.53718
 $C_3H_7^+ \rightarrow CH_3\text{—}\underset{\underset{N}{\overset{\vert}{C}}}{C^+}\text{—}CH_3$	+0.143	—90.53322

TABLE VI

Isocyano Substitution Energies with a Primary, a Secondary, and a Tertiary Carbenium Ion

Substitution process	Net charge on substituent group	Substitution energy / Hartrees
$CH_3^+ \rightarrow CH_2CN^+$	+0.230	—90.54718
$C_2H_5^+ \rightarrow C_2H_4CN^+$	+0.157	—90.53611
 $C_3H_7^+ \rightarrow CH_3\text{—}\underset{\underset{C}{\overset{\vert}{N}}}{C^+}\text{—}CH_3$	+0.095	—90.52940

Finally it is of interest to select charged species where the separation of the nominal site of the positive charge relative to the substituent group may be adjusted, while maintaining the stoichiometry of the molecule. This may be achieved with the propyl cation where the hydride ion is subtracted from either the α or β position on the propane molecule. The substituent group is then attached to the former cation at either the α or γ position and to the latter at the equivalent α or γ positions. In this way three different substituent-charge separations are obtained. The results are summarized in Tables VII and VIII. It may be noted that, where the nominal site of the positive charge is immediately adjacent to the substituent group, the latter shows a net positive charge. Otherwise the corresponding charge is negative. This reflects the relative ina-

TABLE VII

Cyano Substitution Energies with the Propyl Cation and Three Cyano-Charge Separations

Substitution process	Net charge on substituent group	Substitution energy Hartrees
$C_2H_7^+ \rightarrow H_3C—CH_2—C^+HCN$	+0.186(c) +0.185(t)	—90.53580 —90.53474
$C_3H_7 \rightarrow H_3C—\underset{\underset{CH_3}{\vert}}{C^+}CN$	+0.016(c) +0.014(t)	—90.52108 —90.51971
$C_3H_7^+ \rightarrow H_2C^+—CH_2—CH_2CN$	—0.066(c) —0.023(t)	—90.52514 —90.52142

c-cis t-trans

TABLE VIII

Isocyano Substitution Energies with the Propyl Cation and Three Isocyano-Charge Separations

Substitution process	Net charge on substituent group	Substitution energy Hartrees
$C_3H_7 \rightarrow H_3C—CH_2—C^+HNC$	+0.147(c)	—90.53384
$C_3H_7 \rightarrow H_3C—\underset{\underset{CH_3}{\vert}}{C^+}CN$	—0.122(c) —0.126(t)	—90.48673 --90.48543
$C_3H_7^+ \rightarrow H_2C^+—CH_2—CH_2CN$	—0.138(t)	—90.48802

bility of either the cyano or isocyano group to perturb the structure as the nominal charge site moves away. Interestingly, although the magnitude of the net charges on the substituent groups in these latter cations is considerably smaller than that in either the α-cations or the neutral molecules, nevertheless the substitution energies fall on the linear correlation obtained for the neutral species.

While the present correlations are of a semi-empirical nature, they do provide interesting and potentially useful techniques not only for the assignment of electronic energies to bonds but also a means of estimating the first order perturbational influence of the recipient molecule and substitutional position on such energies.

Acknowledgement. — The financial support of the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged.

REFERENCES

1. R. G. Woolley, *Adv. Phys.* **25** (1976) 27.
2. R. G. Woolley, *Int. J. Quantum. Chem.* **12** (Supp. 1) (1977) 307.
3. P. Claverie and S. Diner, *Int. J. Quantum. Chem.* **12** (Supp. 1) (1977) 41.
4. L. de la Pena-Auerbach and A. M. Cetto, *Int. J. Quantum Chem.* **12** (Supp. 1) (1977) 23.
5. P. Claverie and S. Diner, *Isr. J. Chem.* **19** (1980) 54.
6. R. G. Woolley, *J. Amer. Chem. Soc.* **100** (1978) 1073.
7. H. Primas, *Theor. Chim. Acta* **39** (1975) 127.
8. S. Golden, *Isr. J. Chem.* **19** (1980) 3.

9. R. F. W. Bader, Y. Jal, S. G. Anderson, and T. T. Nguyen-Dang, *Isr. J. Chem.* **19** (1980) 8.
10. R. G. Woolley, *Isr. J. Chem.* **19** (1980) 30.
11. C. Trindle, *Isr. J. Chem.* **19** (1980) 47.
12. G. Del Re, *Int. J. Quantum Chem.* **19** (1981) 979.
13. G. Berthier, *Int. J. Quantum Chem.* **19** (1981) 985.
14. See, for example, *Estimation of Thermodynamic Properties of Organic Compounds,* G. J. Janz, Academic Press, N. Y., 1958.
15. S. W. Benson, F. R. Cruickshank, D. M. Golden, G. R. Haugen, H. E. O'Neal, A. S. Rodgers, R. Shaw, and R. Walsh, *Chem. Rev.* **69** (1969) 279.
16. T. L. Allen and H. Shull, *J. Chem. Phys.* **35** (1961) 1644.
17. K. Ruedenberg, *Rev. Mod. Phys.* **34** (1962) 326.
18. J. B. Moffat and H. E. Popkie, *Int. J. Quantum Chem.* **11** (1968) 565.
19. J. B. Moffat and H. E. Popkie, *Chem. Phys. Lett.* **5** (1970) 331.
20. H. Fischer and H. Kollmar, *Theor. Chim. Acta* **16** (1970) 163.
21. J. B. Moffat and K. F. Tang, *J. Phys. Chem.* **79** (1975) 654.
22. J. B. Moffat and K. F. Tang, *Theor. Chim. Acta* **32** (1973) 171.
23. J. B. Moffat and K. F. Tang, *J. Theor. Biol.* **58** (1976) 83.
24. J. B. Moffat and K. F. Tang, *Tetrahedron* **29** (1973) 3111.
25. H. Kollmar, *Theor. Chim. Acta* **50** (1978) 235.
26. S. Ehrenson and S. Seltzer, *Theor. Chim. Acta* **20** (1971) 17.
27. J. B. Moffat, *J. Chem. Eng. Data* **13** (1968) 36.
28. J. B. Moffat and K. F. Tang, *J. Mol. Struct.* **15** (1973) 359.
29. D. R. Armstrong, P. G. Perkins, and J. J. P. Stewart, *J. Chem. Soc. Dalton Trans.* (1973) 838.
30. M. A. Natiello and J. A. Medrano, *Chem. Phys. Lett.* **105** (1984) 180.
31. *Charge Distributions and Chemical Effects,* S. Fliszar, Springer-Verlag, New York, 1983.
32. K. B. Wiberg, *J. Comp. Chem.* **5** (1984) 197.
33. J. B. Moffat, *J. Mol. Struct.* **15** (1973) 325.
34. J. B. Moffat, *Chem. Phys. Lett.* **43** (1976) 600.
35. J. B. Moffat, *J. Mol. Struct.* **108** (1984) 93; Chapts. 24 and 27 in: S. Patai and Z. Rappoport (Eds.), *Chemistry of Functional Groups, Supplement C,* Wiley, N. Y. 1983; *J. Mol. Struct.* **88** (1982) 325; *Int. J. Quantum Chem.* **22** (1982) 299; *J. Amer. Chem. Soc.* **104** (1982) 3949; *Tetrahedron Letters* **22** (1981) 1001; *Chem. Phys. Lett.* **76** (1980) 304; *J. Mol. Struct.* **62** (1980) 213, and references therein.
36. W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.* **51** (1969) 2657, QCPE program no. 236.

SAŽETAK

Particija i aditivnost kemijske veze

John B. Moffat

Mnoga molekulska svojstva pokazuju karakterističnu aditivnost. Ona se često može interpretirati particijom odgovarajuće kvantno-mehaničke srednje vrijednosti na doprinose po atomima ili/i vezama. U ovom radu razmotrena je konstantnost energije supstitucije atoma vodika cijano- i izocijano-skupinama. Ustanovljena je korelacija s nabojem supstituenta u supstituiranoj molekuli.