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Adjacent-DIM-Isoelectronic Molecules and Chemical Similarity II

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Southern Scholars

Senior Project

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ABSTRACT

In a previous paper (I) it was shown that same-period acyclic triatomic molecules which have equal $C_1+2C_2+C_3 \equiv g(C)$, where C_i is the number of valence electrons of atom i and where $i = 2$ is the middle atom, are at least as similar as isoelectronic molecules and are vastly more similar than are molecules chosen at random. In the present paper, $g(C)$ is defined for three tetra-atomic molecular structures, and it is shown that molecules having the same structure and equal $g(C)$ are at least as similar as isoelectronic molecules and are more similar than randomly chosen molecules. These "adjacent Diatomics-in-molecules" series thus join isoelectronic molecules and isovalent molecules as tools to determine chemical similarity. It is suggested again that a theoretical basis for the phenomenon might be constructed using a DIM or similar theory in which non-existent bonds are not replaced with "diatomic molecules."

1. INTRODUCTION

This paper concerns a chemical-similarity diagnostic which may prove to be as useful as comparing isoelectronic and isovalent molecules: series of molecules in which the total numbers of valence electrons associated with adjacent "diatomic molecules" in the molecules are equal. An earlier paper[1] on triatomic adjacent-DIM theory is hereafter referred to as I. The present paper extends this theory to tetra-atomic molecules, presenting statistical analyses of tabulated data for three observables of main-group tetra-atomic molecules with various structures, comparing measures of similarity for isoelectronic and adjacent-DIM series.

2. DEFINITIONS

The period (row) number of atom i of any molecule is R_i; its group number, which tells how many valence electrons are present, is C_i. This paper concerns main-group molecules only, so the domains of R_i and C_i are from 2 to 7 (where i=2 for Li) and from 1 to 7 (1, 2, and 13 to 17 in the IUPAC scheme). All formulae for linear/bent molecules are written so the first and last atomic symbols pertain to the end atoms. For trigonal molecules, the first atomic symbol represents the center atom.

3. THEORY

Because $g(C)$ is based on adjacent-DIM theory, the formula for

$g(C)$ is different for each tetra-atomic molecular structure. If the molecule is linear/bent, then

$$g(C) = C_1+2C_2+2C_3+C_4 \quad , \qquad (1)$$

where 1 and 4 are the atoms at the ends. If it is trigonal, planar or not, then

$$g(C) = 3C_1+C_2+C_3+C_4 \quad , \qquad (2)$$

where 1 is the atom in the center. If its structure is that of a parallelogram or rhomboid, planar or not, or if it is tetrahedroid, then

$$g(C) = C_1+C_2+C_3+C_4 \quad , \qquad (3)$$

independent of the atomic numbering.

4. DATA AND ASSOCIATED ERRORS

This paper depends exclusively on critically analyzed, tabulated data for three observables. Total entropies at 298K (S_{298}) were obtained from the JANAF Tables of 1985.[2] The average of the 95% confidence-limit errors which are given for many of the data is approximately 1%.

$\Delta H_a(Gurvich)$ were taken from the eight-volume USSR thermodynamic tables.[3] The average of the 95% confidence-limit errors associated with individual experimental values is 2.63%. Ionization potentials (IP) were taken from Gurvich *et al.*[4] The average of the 95% confidence-limit errors is 4.23%.

Molecular structures were found in Krasnov[5] and the JANAF tables.[2] There are 124 known-structure molecules for which at

least one datum, for one of the three properties, is known.

5. STATISTICAL ANALYSES

A statistical analysis was performed to test the hypothesis, to 90% confidence, that the variances of adjacent-DIM molecular series are significantly less than the variance of the population (where the population consists of all available data except those in the series being tested). The analysis was also performed for molecules in isoelectronic sequences to provide a comparison for the results of the analysis.

For each property ($\Delta H_a(Gurvich)$, S_{298}, and IP), the majority of the adjacent-DIM molecular series had smaller variance than the population (see Table [1]). However, according to the t test, few of these differences in variance were statistically significant. The results for isoelectronic sequences were similar (Table [1]).

Next, a Chi-squared test was performed on the adjacent-DIM molecular series variances, under the hypothesis that half of the variances should be smaller than the population variance and half should be larger. This null hypothesis is clearly rejected, as shown by the variances in Table [1], for $\Delta H_a(Gurvich)$ and S_{298}; however, it is not rejected for IP. This test led to the conclusion that the number of variances that were smaller than the population variance was statistically significant for $\Delta H_a(Gurvich)$ and S_{298} but for IP.

6. SUMMARY AND DISCUSSION

Comparisons with other molecules from the same isoelectronic and isovalent series are useful tools for the estimation of new data. Now, as a result of the work reported here and in I, comparison with other molecules from the same adjacent-DIM series can be added as a new forecasting tool for some properties of acyclic triatomic molecules containing highly electronegative atoms whose outer atoms come from not-too dissimilar groups. The tool appears to work for heat of atomization and total entropy at 298K for main-group tetra-atomic species. A search for a theoretical basis for this tool would seem to be worthwhile.

ACKNOWLEDGEMENTS

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SOUTHERN SCHOLARS SENIOR PROJECT

Name: Myla Thomas Date: 10-22-98

Major: Physics, Math

Senior Project

A significant scholarly project, involving research, writing, or special performance, appropriate to the major in question, is ordinarily completed the senior year. Ideally, this project will demonstrate an understanding of the relationship between the student's major field and some other discipline. The project is expected to be of sufficiently high quality to warrant a grade of A and to justify public presentation. The completed project, to be turned in in duplicate, must be approved by the Honors Committee in consultation with the student's supervising professor three weeks prior to graduation. The 2-3 hours of credit for this project is done as directed study or in a research class.

Keeping in mind the above senior project description, please describe in as much detail as you can the project you will undertake:

Some previous Physics students worked with Dr. Hefferlin to explore unexpected series of similar acyclic triatomic molecules. They did an elaborate statistical study, with the help of Dr. Brad Davis in California, and established that data for molecules in these series are indeed similar (with statistical significance). Later students saw the same series in various kinds of graphs.

I propose to make a similar statistical analysis for four-atom molecules. This analysis will require finding the structures of the molecules first (linear, trigonal, rhomboidal, etc.). Then it will be necessary to find the averages and standard deviations for all the molecules with each structure for data of each of several properties in the series being investigated.

Expected date of completion 1-20-99

Signature of faculty advisor Ray Hefferlin

Approval to be signed by faculty advisor when project is completed:

This project has been completed as planned: R Hefferlin

This is an "A" project: R Hefferlin

The project is worth 2-3 hours of credit: 2 (counting Research course and Sci Wri)

Advisor's Final Signature R Hefferlin

Chair, Honors Committee _____ Date Approved: _____