

Butman et al. [7-11] indicate that these indices are similar for the analogous sodium and potassium systems. One of the possible explanations for this discrepancy may lie in the possible existence of other structures with similar energies, for which the energies of the bonds of the  $\text{Li}^-$  and  $\text{Li}^+$  ions with the  $\text{LiOH}$  molecule differ much less, in addition to the geometrical configurations of  $(\text{Li}_2\text{OH})^-$  and  $(\text{Li}_2\text{OH})^+$  studied.

In conclusion, we express our gratitude to V. G. Solomonik and V. V. Sliznev for a discussion of these results [3].

#### LITERATURE CITED

1. T. P. Pogrebnaya, V. G. Solomonik, and K. S. Krasnov, Abstracts of the Conference on Quantum Chemistry [in Russian], Dnepropetrovsk (1983), p. 57.
2. V. G. Solomonik, V. V. Sliznev, and T. P. Pogrebnaya, *Zh. Strukt. Khim.*, **29**, No. 5, 22-31 (1988).
3. A. V. Nemukhin and N. F. Stepanov, *Zh. Strukt. Khim.*, **28**, No. 1, 25-29 (1987).
4. R. P. Blickensderfer and K. D. Jordan, *Chem. Phys.*, **41**, Nos. 1-2, 193-199 (1979).
5. P. E. M. Siegbahn, J. Almlöf, A. Heiberg, and B. O. Roos, *J. Chem. Phys.*, **74**, No. 4, 2384-2396 (1981).
6. A. V. Nemukhin, N. F. Stepanov, and V. I. Pupyshev, *Chem. Phys. Lett.*, **115**, No. 2, 241-244 (1985).
7. G. G. Brudkovskaya, L. S. Kudin, M. F. Butman, and K. S. Krasnov, *Zh. Neorg. Khim.*, **29**, No. 12, 3020-3023 (1984).
8. M. F. Butman, L. S. Kudin, G. G. Brudkovskaya, and K. S. Krasnov, *Teplofiz. Vysok. Temper.*, **22**, No. 4, 686-691 (1984).
9. M. F. Butman, L. S. Kudin, G. G. Brudkovskaya, and K. S. Krasnov, *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, **27**, No. 8, 904-907 (1984).
10. L. S. Kudin, M. F. Butman, and K. S. Krasnov, *Zh. Strukt. Khim.*, **26**, No. 5, 65-70 (1985).
11. L. S. Kudin, M. F. Butman, and K. S. Krasnov, *Teplofiz. Vysok. Temper.*, **24**, No. 1, 55-61 (1986).

#### CALCULATION OF THE STRUCTURE OF DIACETYLENE AND THE $\pi$ -ELECTRON PARAMETERS FOR COMPOUNDS WITH A $\text{C}\equiv\text{C}$ BOND

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Studies of the electrophysical properties of polymer systems such as carbene [1] and polydiacetylene [2] with an extended conjugation system and calculations for polymers with a  $\text{C}\equiv\text{C}$  bond have led to renewed interest in the parameters of such systems in semiempirical  $\pi$ -electron methods. According to Shustorovich [3], the parameters of conjugated systems with carbon atoms in  $sp$  hybridization differ significantly from the parameters of other conjugated systems containing  $sp^2$ -hybridized carbon. Shustorovich [3] came to this conclusion upon examining the structures of  $\text{HC}\equiv\text{CH}$ ,  $\text{H}_2\text{C}=\text{CH}_2$ , and  $\text{H}_2\text{C}=\text{C}=\text{CH}_2$  and using the method of Salem [4] with the bond length—bond order correlation:

$$R = R_0 - \omega P. \quad (1)$$

Here,  $P$  is the bond order and the constant  $R_0 = 2r_{sp}$  in  $\text{HC}\equiv\text{CH}$  or  $R_0 = 2r_{sp^2}$  in  $\text{H}_2\text{C}=\text{CH}_2$  is given using the  $r_{sp}$  and  $r_{sp^2}$  radii of the carbon atom in the different hybridizations. According to Shustorovich [3],  $\omega = 0.08 \text{ \AA}$ ,  $r_{sp} = 0.675 \text{ \AA}$ , and  $r_{sp^2} = 0.705 \text{ \AA}$ .

The disadvantages of the approach in [3] include the following: 1) in the Salem scheme, relation (1) is an independent hypothesis; 2) the system of equations considered in [3] uses information from only one molecule with a triple bond (acetylene). In order to draw on experimental data on other polyynes, let us consider the diacetylene molecule in the  $\pi$ -electron approximation, as in [5].

In the absence of  $\pi$ -electrons, let the carbon atoms of diacetylene be located on the  $z$ -axis at points with coordinates,  $-3r_{sp}, -r_{sp}, r_{sp}, 3r_{sp}$ . After the introduction of eight  $\pi$ -electrons, the carbon atom coordinates become equal to  $-3r_{sp} - y, -r_{sp} - x, r_{sp} + x, 3r_{sp} + y$ . The energy of the system becomes:

$$\begin{aligned} E &= E_{\sigma} + E_{\pi}, \\ E_{\sigma} &= E_0 + 2Kx^2 + K(x - y)^2, \\ E_{\pi} &= -2(\beta_1 P_1 + 2\beta_2 P_2), \end{aligned} \quad (2)$$

where  $\beta_1 = \beta_0 - 2\beta'x$ ,  $\beta_2 = \beta_0 + \beta'(x - y)$ ,  $\beta_0$  is the resonance integral of the C—C bond for  $x = y = 0$ ,  $\beta'$  is the derivative of the resonance integral relative to distance,  $K$  is the elasticity constant of the  $\sigma$ -core, and  $P_1$  and  $P_2$  are the orders of the inner and outer bonds in diacetylene, which are expressed through one parameter,  $\varphi$ , determining the coefficients of the occupied molecular orbitals:

$$\begin{aligned} &(\sin \varphi, \cos \varphi, \cos \varphi, \sin \varphi)/\sqrt{2}, \\ &(\cos \varphi, \sin \varphi, -\sin \varphi, -\cos \varphi)/\sqrt{2}. \end{aligned}$$

The equilibrium values of  $x$ ,  $y$ , and  $\varphi$  are determined from the minimum energy condition:

$$\frac{\partial E}{\partial x} = \frac{\partial E}{\partial y} = \frac{\partial E}{\partial \varphi} = 0. \quad (3)$$

Using Eqs. (2) and (3), we obtain a system of equations for  $x$ ,  $y$ , and  $\varphi$ :

$$\begin{aligned} \frac{1}{2} \operatorname{tg} 2\varphi &= (1 + \lambda \sin 2\varphi)/(1 + \lambda \cos 2\varphi), \quad x = -\omega \cos 2\varphi, \\ \xi = y - x &= -2\omega \sin 2\varphi, \quad \lambda = 4\beta'^2/\beta_0 K, \quad \omega = 2\beta'/K. \end{aligned} \quad (4)$$

The difference in bond lengths

$$R_1 - R_2 = -\omega(P_1 - P_2)$$

has the form of the bond length—bond order correlation, which thus is not introduced externally into the model as in the work of Shustorovich [3] and Salem [4] but rather follows from Eq. (4). This latter equation permits us to obtain equations for  $R_1$  and  $R_2$ :

$$R_1 = R_0 - \omega P_1, \quad R_2 = R_0 - \omega P_2. \quad (5)$$

Let us add the equation for the bond length  $R^{ac}$  in acetylene:

$$R^{ac} = R_0 - 2\omega, \quad (6)$$

place  $R_1$ ,  $R_2$ , and  $R^{ac}$  in Eqs. (5) and (6) equal to the experimental values for the bond lengths  $R_1(\text{exp}) = 1.376$ ,  $R_2 = 1.205$  [6], and  $R^{ac} = 1.207$  Å, and obtain three equations for parameters  $\omega$  and  $R_0$ . These equations were solved using the method of least squares together with Eq. (4), in which  $\omega = 2\beta'/K$ , assuming  $K = 48$  eV/Å<sup>2</sup> and  $\beta_0 = \beta(R_0) = 2$  eV. Consistent solutions of system (4) and the least squares problem were obtained for  $R_0 = 1.487$  Å and  $\omega = 0.146 \approx 0.15$  Å. Hence, we estimate  $\beta' = 3.6$  eV/Å.

We note that the value selected for  $K$  is consistent with the calculations for vibrational frequencies in conjugated systems [8], while the value of  $\beta_0$  differs from the value  $\beta = 2.4$  eV in benzene by  $\beta'\Delta R$  (in the vicinity of a double bond,  $\beta' = 4.3$  eV/Å and  $\Delta R = R_0 - R = (1.487 - 1.397)$  Å = 0.09 Å).

Our values for parameters  $r_{sp} = 0.744$  Å and  $\omega = 0.15$  Å are less than those for other systems ( $r_{sp} = 0.758$  Å and  $\omega = 0.18$  Å [7]), but these differences are not as significant as in the work of Shustorovich [3]. These results imply that the parameter  $\omega = 2\beta'/K = 0.25$  Å used in the work of Rice et al. [1] is too large and overestimates the effect of the  $\pi$ -electrons on the structure of polymers with conjugated bonds.

The aim of the present work was the evaluation of the interaction constants of  $\pi$ -electrons with nuclear vibrations for conjugated molecules with triple bonds using known structural data. We note that in calculating the electron structure and bond lengths in such molecules as in our previous work [9], we used equations similar to Eqs. (1) and (5) with  $\omega = 0.15$  Å, i.e.,  $\omega$  with approximately the same value as found in this work.

## LITERATURE CITED

1. M. J. Rice, S. R. Phillpot, A. R. Bishop, and D. K. Campbell, *Phys. Rev. B*, **34**, No. 6, 4139-4148 (1986).
2. S. Suhai, *Phys. Rev. B*, **29**, No. 8, 4570-4581 (1984).
3. E. M. Shustorovich, *Zh. Strukt. Khim.*, **5**, No. 2, 325-329 (1964).
4. L. Salem and H. Longuet-Higgins, *Proc. Roy. Soc. A*, **255**, No. 1283, 434-443 (1960).
5. I. A. Misurkin and A. A. Ovchinnikov, *Zh. Strukt. Khim.*, **5**, No. 6, 888-891 (1964).
6. J. H. Callomon and B. P. Stoicheff, *Canad. J. Chem.*, **35**, No. 4, 372-382 (1957).
7. C. Coulson and A. Golebiewski, *Proc. Phys. Soc.*, **78**, No. 506, 1310-1320 (1961).
8. A. A. Ovchinnikov, A. E. Belinskii, I. A. Misurkin, and I. I. Ukrainskii, *Int. J. Quant. Chem.*, **22**, No. 5, 761-774 (1982).
9. T. S. Zhuravleva and I. A. Misurkin, *Zh. Strukt. Khim.*, **5**, No. 4, 656-658 (1964).

## A PROGRAM SET FOR FINDING STRUCTURE-PROPERTY

### CORRELATIONS USING TOPOLOGICAL INDICES

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The relationship of the structure and properties of chemical compounds has long attracted the attention of chemists. However, major advances in this area began to be achieved only about 20 years ago with the introduction of computers, permitting the treatment of extensive data. In this regard, special importance is found for the development of various mathematical models relating structure and property and their programming for various computer classes, including, in particular, personal computers.

In this work, we describe a program set designed for the analysis of the relationship of structure and property in a class of organic compounds using topological indices. Ruvra [1, 2] has reviewed many examples of topological indices and discussed their various applications for the establishing structure-property correlations. An analysis was also given for the abovementioned method. In this approach, the molecular structure is described using a finite set of topological indices  $x_1, \dots, x_k$  (invariants of the "weighted" molecular graphs). Then, a function  $f(x_1, \dots, x_k)$  is selected, such that  $y \approx f(x_1, \dots, x_k)$  for all the compounds of the set studied, where  $y$  is the numerical value of the property. The equation thereby obtained, which relates the structural parameters  $x_1, \dots, x_k$  and a property, is then extrapolated to other compounds of this class.

The following operations are provided in our program set:

- 1) the creation of files for chemical structure and property data;
- 2) the calculation of various topological indices, including indices determined for "weighted" graphs;
- 3) the classification of atoms of various chemical types in the structures of the data file relative to a given classification scheme;
- 4) selection of "weights" for the atoms of different classes using optimization methods with the subsequent distribution of these "weights" over the data file;
- and 5) derivation of correlation equations.

The set has a modular structure, consisting of a lead program and set of slave programs. The lead program permits the selection of the direction of operations 1-5, carries out the loading and filing of other programs, operating in a concrete direction, enters information into the data file or computes it, and organizes the derivation of correlations and the printout of results onto a screen or on a printer. The slave programs include those for computer graphics, calculation of indices, classification, optimization, and distribution of atomic "weights." These programs will be examined in greater detail below.

A special program for graphic input and output of chemical structural information is included for the establishment of a data file in the program set [3]. This program is used for the introduction of structural formulas in the conventional chemical form into the computer by simply drawing them on the display screen. A table of bonds of the corresponding structural formula is automatically constructed using this figure. All the structural and quantitative

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