DENSITY FUNCTIONAL APPROACH TO THE HÜCKEL BETA PARAMETER FOR THE DELOCALIZATION ENERGIES OF ACYCLIC POLYENES

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Abstract
The goal of this study is to use quantum chemistry techniques to quantify the β parameter in Hückel theory as it applies to the stabilization of organic polyenes by conjugation and resonance. The resonance effect on the stability of polyenes is determined through the isodesmic reaction, whereby each polyene is decomposed into localized carbon-carbon single and double bonds. Apart from the resonance effect, the two sides of such a reaction have identical bonding; therefore, the enthalpy of such a reaction is equal to the resonance effect. Isodesmic reaction enthalpies are calculated using density functional theory. The resonance energies of a sequence of polyenes (e.g. 1,3-butadiene) are calculated, and the resulting trends are discussed. Comparison of these resonance energies to the formal Hückel values yields a direct calculation of the β parameter.

Introduction

Hückel theory[1-3] is an early form of molecular orbital theory that has applications[4] to the electronic structure of unsaturated organic molecules. It is a matrix method that depends on two parameters: the Coulomb integral α and the resonance integral β. The method can be applied to the specific problem of stabilization of conjugated systems in which a molecule has extended π-orbitals that allow for long-range delocalization of π-electrons. One particular class of molecules that has this stabilization is the acyclic polyenes: 1,3-butadiene, 1,3,5-hexatriene, and so on. A simple comparison between the Hückel energy of a particular polyene and the combined Hückel energy of an appropriate number of ethylene molecules (the model for the localized double bond) gives a delocalization energy for the polyene as a multiple of resonance integral β. Quantifying the delocalization energy for each polyene leads to a quantitative value of β.

Delocalization energy for the polyenes can be quantified through the use of isodesmic equations.[5] Isodesmic equations are chemical equations in which the reactants and products have the same bonding in addition to the same atoms. If a polyene is taken as one of the reactants, an appropriate number of molecules of ethane and ethylene become the products, modeling the formal double and single bonds of the polyene. Such modeling leads to an overcount of C-H bonds, which is corrected by adding an appropriate quantity of methane molecules to the reactants. Since the two sides of the isodesmic equation have formally identical bonding, the enthalpy of the isodesmic reaction may be taken as the delocalization energy of the polyene.

Computational Methods

Geometry optimizations and vibrational frequency calculations for each molecule were carried out using the PBE1PBE density functional method.[6] Density functional theory is a relatively fast computational method for determining chemical properties. The PBE1PBE functionals were chosen because they gave favorable results in a study[7] relating to their accuracy. All

calculations in this study were carried out using the Dunning cc-pVTZ atomic orbital basis set[8] (4s3p2d1f for carbon and 3s2p1d for hydrogen). Calculations were carried out using the Gaussian16W computational chemistry software[9], and the resulting molecular structures were visualized using the GaussViewW software[10]. Zero-point vibrational energy (ZPE) corrections where ZPE = the sum of (1/2)hν for all vibrations of each molecule were included in the energy of each molecule in this study. Total energy of each molecule is calculated as electronic energy plus ZPE.

Results and Discussion

The isodesmic equations used in this study are shown in Table 1. In each equation, the reactant and products have the same atoms, C-C single bonds, C=C double bonds, and C-H bonds. Therefore, the only difference between the two sides is that one of the reactants is a polyene stabilized by electron delocalization in the π-system. GaussViewW images of the optimized polyenes are shown in Figure 1. Note that GaussViewW renders the formal carbon-carbon single bonds in the solid line / dashed line representation frequently used to show the delocalization of bonds in benzene. This rendering demonstrates the shortening of the single bonds that typically occurs in conjugated π-systems. (Butadiene does not show the dashed line because, while the single bond is shortened, it is still long enough to be outside GaussView's parameters for a benzene-like bond). Because the reactants are stabilized relative to the products, all the reactions listed in Table 1 are endothermic, and the quantity of the endothermicity indicates the degree of π-stabilization in the polyene. The stabilization energies of each polyene are shown in Figure 2.

Since it is delocalization of electrons across the formal single bonds that causes the stabilization, the number of formal single bonds has been chosen as the horizontal axis in Figure 2. The data graphs as a straight line with an excellent fit of $R^2 = 0.9999$. As a theoretical ideal, the linear graph would cross the origin, and the actual equation for the linear fit only misses the origin by about 8 kilojoules per mole. Since the linear fit is of such high quality, the 8 kJ/mole miss of the origin is a consistent underestimate of

the delocalization energy by PBE1PBE, possibly due to basis set incompleteness. The graph predicts that delocalization across

1,3-butadiene

1,3,5-hexatriene

1,3,5,7-octatetraene

1,3,5,7,9-decapentaene

Figure 1. Optimized geometries of polyenes, as rendered by GaussViewW. Carbon atoms are shown in black, hydrogen atoms in gray.

Table 1. Isodesmic reactions of polyenes.

Molecule	Balanced equation
1,3-butadiene	$C_4H_6 + 2\ CH_4 \rightarrow 2\ C_2H_4 + C_2H_6$
1,3,5-hexatriene	$C_6H_8 + 4\ CH_4 \rightarrow 3\ C_2H_4 + 2\ C_2H_6$
1,3,5,7-octatetraene	$C_8H_{10} + 6\ CH_4 \rightarrow 4\ C_2H_4 + 3\ C_2H_6$
1,3,5,7,9-decapentaene	$C_{10}H_{12} + 8\ CH_4 \rightarrow 5\ C_2H_4 + 4\ C_2H_6$

Figure 2. PBE1PBE/cc-pVTZ stabilization energies of polyenes versus the number of formal carbon-carbon single bonds. Energies include zero-point vibrational corrections and are expressed in kJ/mole.

each C-C single bond added to the polyene chain contributes approximately 71 kilojoules per mole to the total π-stabilization of the molecule.
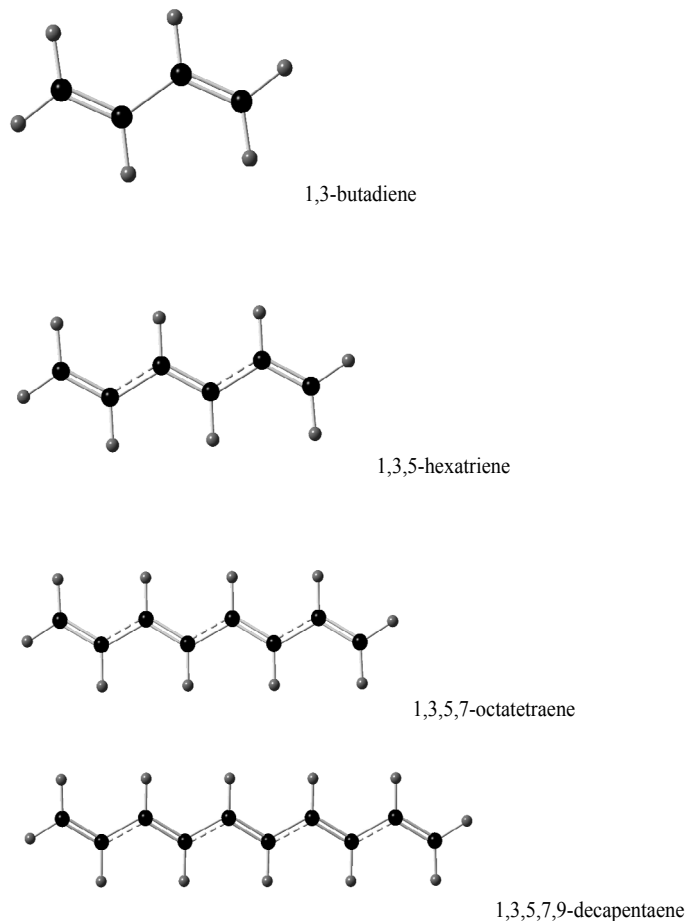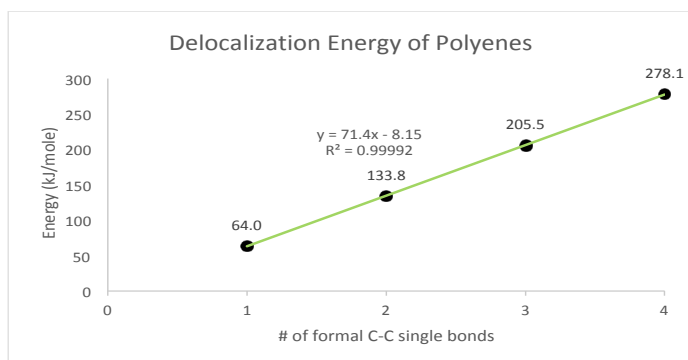
Calculating the Hückel β parameter requires the application of Hückel theory to each polyene in Figure 1. Solving the Hückel matrix[11] for each polyene and allowing 2 π-electrons to occupy each of the lowest-lying (bonding) orbitals leads to a total π-energy in terms of the α and β parameters. The difference between that value and the value $(2\alpha + 2\beta) * x$, where x is the number of formal double bonds in each polyene, is the delocalization energy of each polyene. Table 2 shows the Hückel stabilization energies for each polyene. The table shows that each additional C=C double bond in the polyene confers 0.52β additional delocalization energy. Since the PBE1PBE/cc-pVTZ data from Figure 2 shows that each new bond confers 71.4 kJ/mole of additional π-stabilization, these results indicate that 0.52β = 71.4 kJ/mole. The predicted value of β is therefore 71.4 / 0.52 = 137 kJ/mole. If the strength of the π-bond in a C=C double bond is taken as the difference[12] between single bond enthalpy (348 kJ/mole) and double bond enthalpy (612 kJ/mole), then a π-bond has a strength of 264 kJ/mole. Since Hückel theory indicates that π-bonding stabilizes the ethylene molecule by 2β, an approximate value of β is 132 kJ/mole. The PBE1PBE/cc-pVTZ value of 137 kJ/mole is in good agreement with the value derived from bond enthalpy.

Conclusion

Isodesmic equations can be used to isolate the thermodynamic effects of π-bond delocalization of molecules, including acyclic polyenes. Enthalpies of the isodesmic reactions can be calculated by fast, accurate computational methods, thereby quantifying the stabilizing effects of π-bond delocalization. When these results are combined with the predictions of Hückel theory, the density functional calculations can be used to derive a reasonable value for the Huckel β resonance integral parameter. While these polyenes are well-known molecules, the same computational techniques can be applied to calculate β parameters for other molecules, such as boron nitride or polynitrogen, which may lead to predictions of the stability of novel materials.

Acknowledgments

Table 2. Hückel theory delocalization energies for acyclic polyenes. Since the Hückel-energy for ethylene is 2α+ 2β, the comparison energy is (2α+ 2β)* x, where x is the number of double bonds for each polyene.

Molecule	Hückel π-energy	$(2\alpha + 2\beta) * x$	Difference
C_4H_6	$4\alpha + 4.48\beta$	$4\alpha + 4\beta$	0.48β
C_6H_8	$6\alpha + 7.00\beta$	$6\alpha + 6\beta$	1.00β
C_8H_{10}	$8\alpha + 9.52\beta$	$8\alpha + 8\beta$	1.52β
$C_{10}H_{12}$	$10\alpha + 12.04\beta$	$10\alpha + 10\beta$	2.04β

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