Theoret. chim. Acta (Berl.) 14, 357—362 (1969)

Commentationes

Calculation of the Molecular Parameters of Small-Ring Unsaturated Hydrocarbons by a Refined ω-Technique

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Received April 3, 1969

The electron densities, free valences, bond orders, bond lengths, and localization energies have been calculated for a number of highly-reactive small-ring unsaturated systems by means of a refined ω-technique. The systems considered include fulvene, dimethylenecyclobutene, trimethylenecyclopropane, the dimethylenecyclopropanyl system, methylenecyclopropene and the cyclopropenyl system. In cases where comparison is possible, the calculated bond lengths agree to better than 1% with the experimental values.

Für eine Reihe hochreaktiver, ungesättigter Systeme, die einen kleinen Ring bilden, werden nach einer verbesserten ω-Technik die Elektronendichten, freien Valenzen, Bindungsordnungen, Bindungsabstände und Lokalisierungs-Energien berechnet. Die betrachteten Systeme enthalten Fulven, Dimethylencyclobuten, Trimethylencyclopropan, das Dimethylcyclopropanyl-System, Methylencyclopropen und das Cyclopropenyl-System. Soweit experimentelle Vergleichswerte vorliegen, werden die Bindungslängen mit maximal 1% Abweichung berechnet.

Une technique ω perfectionnée a été utilisée pour calculer les densités électroniques, les valences libres, les indices de liaison, les longueurs de liaison et les énergies de localisation pour des petits cycles non saturés très réactifs. Il s'agit du fulvène, du diméthylènecyclobutène, du triméthylènecyclopropane, du diméthylènecyclopropanyle, du méthylènecyclopropène et du cyclopropényle. Dans les cas où la comparaison est possible, les longueurs de liaison calculées sont en accord avec les longueurs expérimentales à mieux de 1% près.

Introduction

In an attempt to shed some light on the chemical and physical properties of novel, unsaturated small-ring compounds, certain systems were subjected to a refined ω-technique calculation. A computer program was developed which could be used for both alternant and nonalternant hydrocarbons.

It has been recognized for some time that the simple Hückel MO method is not completely adequate in predicting the physical and chemical properties of nonaromatic hydrocarbons. This lack of success is attributed to the presence of a non-self-consistent field which alters the coulomb integral (α), and to the fact that the resonance integral (β) is dependet upon bond distance and also to the neglect of all interactions between non-bonded atoms. Since all coulomb integrals are taken to be equal in HMO, a correction must be made in the case of nonalternants to account for the charges on the atoms. The method of Wheland and Mann [1] was one of the first successful attempts to introduce charge distribution as a perturbation on the coulomb integral. Streitwieser and Nair [2] modified this method slightly through the use of the equation:

$$\alpha_r = \alpha_0 + \omega(1 - q_r)\beta_0 \tag{1}$$

where ω is generally taken to be 1.4 and q_r is the π-electron density on atom r.

In addition to the above modification, it is known that the resonance integral, β_{ij}, is a function of bond distance if atoms i and j are adjacent, like atoms. Both linear [3] and exponential [4] relations have been used to show the variation of β_{ij} with bond distance or mobile bond order. An equation relating the resonance integral of a particular bond to the resonance integral of the ethylene double bond (β_0) can be written in the form:

$$\beta_{ij} = k_{ij}\beta_0 \tag{2}$$

where i and j refer to adjacent atoms and k_{ij} is a constant obtained from either a linear or exponential equation.

This paper reports the results of calculations performed on neutral, free radical, and charged hydrocarbon species in which the charge distribution, bond orders, free valences, and bond distances were obtained by combining the iteration of both α and β to self-consistency. A comparison of the parameters calculated by this technique was made, where possible, with experiment and with the parameters calculated by the SPO method of Dewar and Gleicher [5]. In addition, the localization energies have been calculated in order to determine the sites of greatest reactivity for small-ring systems. The previously demonstrated linear correlation between HMO and SCF Pariser Parr localization energies [6] established the relevance of such simplified calculations.

Details of the Procedures for Calculations

A digital computer program was written in IBM Fortran IV language to calculate the parameters previously discussed.

A symmetric matrix representing the alternant or nonalternant hydrocarbon is read into the computer. This matrix is diagonalized by the Jacobi method. The computer then calculates the mobile π-bond orders, charge densities, and free valences as outlined for the simple HMO theory [7, 8]. From the results of these calculations the resonance integral (bond distance dependent term) is modified by the use of the following equations:

$$\text{Bond Distance} = -0.206\, p_{ij} + 1.530 \tag{3}$$

$$k_{ij} = -1.54 \ \text{(Bond Distance)} + 3.15 \tag{4}$$

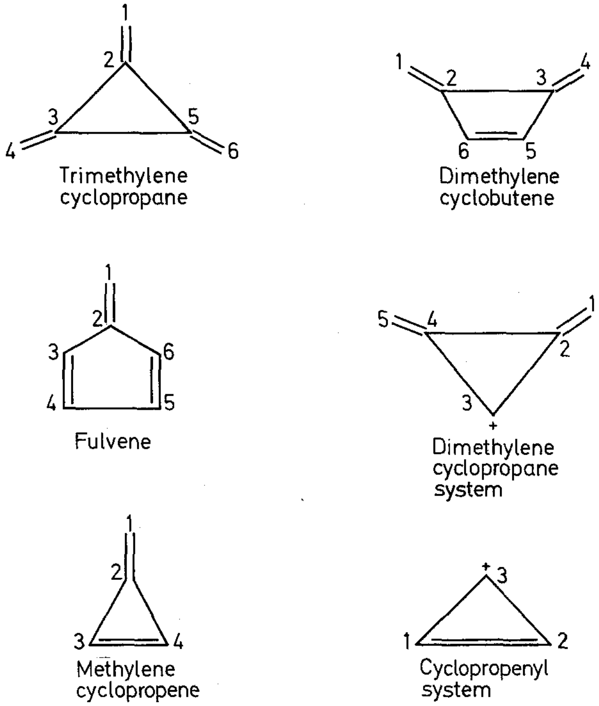
where p_{ij} is the mobile bond order and k_{ij} is the constant of Eq. (2). The process of diagonalizing the matrix is then repeated by the Jacobi method. The resonance integrals are modified only three times by means of Eqs. (3) and (4) since it was found that they change very little with the iteration. Without further modifications of the β_{ij}'s, the coulomb integrals are iterated to a self-consistency of 0.003 on the charge densities by means of the ω-technique. To speed covergence Ettinger's [9] procedure of modifying charge densities as shown in Eq. (5) was used:

$$Q(n)=\frac{Q(n-1)+Q(n)}{2} \tag{5}$$

where n is the number of the iterative step.

Results of the Calculations

The results of the calculations are listed in Table 1. The systems in which numbering of the positions could be ambiguous, are shown in Fig. 1.



Trimethylene cyclopropane

Dimethylene cyclobutene

Fulvene

Dimethylene cyclopropane system

Methylene cyclopropene

Cyclopropenyl system

Fig. 1. Numbering of atom positions on rings

Discussion

The calculated bond lengths for fulvene and for trimethylenecyclopropane agree closely with the parameters calculated by the PPP and SPO methods (see Table 2). In addition, the refined ω-technique calculates bond lengths for trimethylenecyclopropane which vary only in the third decimal place from the experimentally determined distances. A somewhat larger discrepancy occurs between calculated and experimentally-observed bond lengths for butadiene, but even here the difference is less than 1%. These results, in cases where comparison is possible, lead to the conclusion that bond distances calculated for the systems

Table 1. *Molecular parameters calculated by the refined ω-technique*

Atom position	Electron density	Free valence	E_{π^+} [a]	$E_{\pi\cdot}$ [a]	E_{π^-} [a]	Bond	Bond order	Bond distance
Benzene (E_π[b] $= 8.042\,\beta$)								
1	1.000	0.399	1.446	2.487	4.246	1–2	1.667	1.393
Fulvene ($E_\pi = 7.455\,\beta$)								
1	0.840	0.888	1.062	1.642	2.669	1–2	1.844	1.356
2	0.982	0.134	—	—	—	2–3	1.377	1.452
3	1.054	0.518	0.859	1.900	3.659	3–4	1.837	1.358
4	1.035	0.460	1.260	2.116	4.060	4–5	1.435	1.440
Dimethylene cyclobutene ($E_\pi = 7.327\,\beta$)								
1	1.000	0.832	0.979	1.802	0.779	1–2	1.900	1.345
2	1.000	0.220	—	—	—	2–3	1.271	1.474
5	1.000	0.550	1.176	2.033	3.976	2–6	1.342	1.460
						5–6	1.840	1.360
Trimethylene cyclopropane ($E_\pi = 7.432\,\beta$)								
1	1.023	0.861	0.626	1.691	3.490	1–2	1.871	1.351
2	0.977	0.178	1.039	2.719	3.839	2–3	1.342	1.460
Dimethylene cyclopropanyl cation ($E_\pi = 6.805\,\beta$)								
1	0.831	1.013				1–2	1.719	1.382
2	0.875	0.130				2–3	1.587	1.409
3	0.589	0.558				2–4	1.297	1.469
Dimethylene cyclopropanyl radical ($E_\pi = 5.741\,\beta$)								
1	1.083	0.963				1–2	1.769	1.372
2	0.962	0.131				2–3	1.535	1.420
3	0.910	0.661				2–4	1.297	1.469
Dimethylene cyclopropanyl anion ($E_\pi = 3.942\,\beta$)								
1	1.337	0.940				1–2	1.792	1.367
2	1.050	0.148				2–3	1.507	1.426
3	1.227	0.718				2–4	1.285	1.471
Butadiene ($E_\pi = 4.213\,\beta$)								
1	1.000	0.811	1.008	1.833	3.808	1–2	1.921	1.340
2	1.000	0.421	—	—	—	2–3	1.390	1.450
Methylene cyclopropene ($E_\pi = 4.858\,\beta$)								
1	1.233	0.853	−0.097	1.952	4.505	1–2	1.879	1.349
2	0.994	0.178	—	—	—	2–3	1.338	1.460
3	0.887	0.508	1.153	1.928	3.953	3–4	1.887	1.347
Cyclopropenyl cation ($E_\pi = 4.955\,\beta$)								
1	0.667	0.399				1–2	1.667	1.393
Cyclopropenyl radical[c] ($E_\pi = 2.906\,\beta$)								
1	0.863	0.554				1–2	1.862	1.352
3	1.275	1.100				1–3	1.316	1.465
Cyclopropenyl anion[c] ($E_\pi = 0.353\,\beta$)								
1	1.000	0.732				1–2	2.000	1.324
3	2.000	1.732				1–3	1.000	1.530

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[a] E_{π^+}, $E_{\pi\cdot}$, E_{π^-} represent electrophilic, radical and nucleophilic localization energies respectively [10].

[b] π bonding energy.

[c] Self-consistency of 0.003 in charge densities not obtained within 10 iterations.

Table 2. *Experimental and calculated bond distances*

Bond	Bond distance (Å)			
	Experimental	PPP[a]	SPO[a]	Refined – ω
Benzene				
1–2	1.397[b]	1.393	1.393	1.393
Fulvene				
1–2		1.351	1.347	1.356
2–3		1.459	1.466	1.452
3–4		1.354	1.350	1.358
4–5		1.446	1.454	1.440
Trimethylene cyclopropane				
1–2	1.343[c]	1.349	1.346	1.351
2–3	1.453[c]	1.463	1.469	1.460
Butadiene				
1–2	1.344[d]	1.350[e]	1.345[e]	1.340
2–3	1.464[d]	1.456[e]	1.464[e]	1.450

[a] Ref. [5].
[b] Ref. [7], p. 170.
[c] Dorko, E. A., J. L. Henscher, and S. H. Bauer: Tetrahedron **24**, 2425 (1968).
[d] Cole, A. R. H., G. M. Mohay, and G. A. Osborne: Spectrochim. Acta **23**A, 909 (1967).
[e] Isolated single and double bond distances for $sp^2 - sp^2$ overlap.

which have not been determined experimentally represent an accurate calculation of the distances to be expected for them.

The cyclopropenyl radical and anion were the only two systems which did not iterate to self-consistency. In both cases there was an oscillation between two sets of values for bond lengths. In the case of the radical, the bond distances from the two sets of results differed by less than 1%. This fact was not true for the anion however; one set of values was such that the value for the length of the carbon double bond is greater than the value for the single bond. This set of results is obviously trivial and the other set is reported. However, the anomaly for these two species leads to the prediction that the cyclopropenyl radical is capable of only transitory existence *after rehybridization* of the orbital containing the free electron and that the cyclopropenyl anion is not capable of existence *at all in a rehybridized condition.*

The calculation of localization energies was performed in order to determine the sites of small-ring molecules most susceptible to attack. Previous reports have noted the failure of the ω-technique calculations to converge for the allylic and benzylic systems [2]. The present modification over-comes this problem and allows meaningful calculations to be performed. Localization energy has been reported as a positive quantity according to Streitwieser's definition [10]. In order to check the correspondence of the localization energies calculated in this report with those previously calculated by the SCF-PP method [5], the calculated electrophilic and nucleophilic localization energies for a large number of aromatic and non-aromatic systems were compared with the corresponding

SCF-PP energies. The regression equations to measure the correspondence between localization energy for the refined ω-technique and the SCF-PP method have been calculated and show a linear relationship [11].

It is interesting to note that in fulvene the 3 position is most sensitive to electrophilic attack while the 1 position is most sensitive to nucleophilic. The 1 position in dimethylenecyclobutene is most susceptible to all three types of reagents. The calculations for methylenecyclopropene show that electrophilic attack at the 1 position is overwhelmingly favored. This is to be expected since the cyclopropenyl system which forms, obeys the $(4n+2)$ rule. This result implies that the attempted formation of methylenecyclopropene should be carried out by a mechanism that avoids even the transitory existence of the plus charge at the 2 position. Furthermore, the predicted instability of the cyclopropenyl radical and anion suggests that a mechanism which places either a free electron or a negative charge at the 2 position will result in failure to obtain methylenecyclopropene. Greater success is predicted if the 3–4 double bond is introduced into the system after the 1–2 double bond.

The π-bonding energies for fulvene and trimethylenecyclopropane are somewhat high compared to SPO and PPP calculations [5]. Most likely the high values are due to the basic limitation of the HMO method which does not take into account non-bonded interactions. However, in spite of this difficulty it is felt that the localization energy calculations and the bond distance calculations have lead to predictions about small ring compounds which should be of aid in determining the chemical and physical properties of these highly unstable systems.

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