

THE ELECTRONIC STRUCTURE OF (3,1,0)-BICYCLOHEXATRIENE

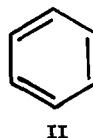
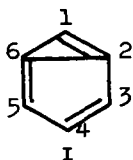
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The perturbation of benzene (II) to (3,1,0)-bicyclohexatriene (I) is a direct analogy to the perturbation of naphthalene to azulene. This latter perturbation



produces a strong red shift in the ${}^1L_b-{}^1A$ transition of naphthalene at 320 $m\mu$ to 680 $m\mu$ in azulene.¹ In addition azulene is a mildly dipolar as predicted from semi-empirical calculations.² Azulene is also one of the few non-alternate hydrocarbons which displays honestly aromatic characteristics. Although attempts to synthesize the bicyclohexatriene I have proved unsuccessful³ we were nevertheless curious as to the effect on the ${}^1L_b-{}^1A$ transition in benzene of perturbing II to I. The only previous calculation on I used on the Huckel method.⁴

The electronic structure of I was estimated using the Pariser-Parr-Pople SCF-CI π -electron approximation. Although not theoretically justifiable, all carbon valence state ionization potentials were assigned a value of 11.22 ev. A value of -2.40 ev was assigned for all C-C bonds. Geometry was computed by assuming all bonds were 1.40 A. The one-centered electron repulsion integral was assigned a value of 10.53 ev and all two-centered

integrals were computed by the approximation of Parr⁵ using a Slater Z value of 3.25. Excited state energies and wave functions were computed using 7 configurations resulting from the single excitation of electrons from occupied orbitals 1, 2, or 3 to unoccupied orbitals 1', 2' or 3', these being number such that the highest occupied orbital in the ground state is 1 and the lowest unoccupied is 1'. Of the 8 possible configurations the transition 3→3' was not included.

The results of the configuration interaction calculations are shown in Table 1 for the 5 lowest computed transitions. The lowest energy transition (3.42 ev) is ${}^1L_b \leftarrow {}^1A$ (${}^1B_1 \leftarrow {}^1A_1$). The ${}^1L_a \leftarrow {}^1A$ lies at 5.36 ev. A much stronger transition lies at 6.74 ev. The corresponding transitions in benzene are computed to lie at 4.60, 5.89 and 6.60 ev and are to be compared with the experimental values of 4.7, 6.0 and 7.0 ev.⁶ The first two of these transitions in benzene (the L_b and L_a) are forbidden and have zero computed oscillator strength before the inclusion of vibronic coupling. Correspondingly the L_b and L_a transitions in I are computed to have weak intensities. This comes from a breakdown of the pairing rule⁷ resulting from the inclusion of the bond between starred atoms. Therefore I is predicted to have a L_b transition at 350 mμ, strongly shifted from the corresponding transition in benzene at 250 mμ with a mild increase in intensity. An additional interesting feature of this calculation is that configuration interaction plays no importance in lowering the calculated SCF excitation energy ($1 \rightarrow 1'$) of 3.52 ev to the 3.42 ev value. The 3.42 ev state is over 97% $1 \rightarrow 1'$ character.

The qualitative or semi-quantitative reasons for the predicted strong red shift of the L_b transition of II on being perturbed to I is found in perturbation theory. Although benzene is computed to have zero π bond order between atoms 2-6 in the ground state the 1L_b and 1L_a excited states have computed bond orders of 0.33 and 0.167, respectively. From the viewpoint of first order perturbation theory these excited states will be stabilized by the product of the bond order and the resonance integral or, using a value of -2.40 ev for latter quantity, -0.79 and -0.40 ev, respectively. From the viewpoint of Moffit⁸, the 2-6 bond represents an even perturbation of the free electron wavefunctions causing a strong red shift in the L_b transition.

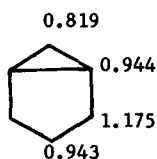
TABLE 1
 Computed Energies of the Excited States and Configurational Wave Functions
 of (3,1,0)-Bicyclohexatriene

Energy (ev)	Oscillator Strength	Symmetry	Weights of Configurations
3.42	0.043	1B_1	$0.988\phi_{1-1}' + 0.040\phi_{2-1}' + 0.149\phi_{1-3}'$
5.36	0.055	1A_1	$0.643\phi_{1-2}' - 0.758\phi_{2-2}' + 0.106\phi_{2-3}' + 0.032\phi_{3-2}'$
6.74	1.090	1A_1	$0.742\phi_{1-2}' + 0.652\phi_{2-2}' + 0.154\phi_{2-3}' + 0.037\phi_{3-2}'$
6.76	0.009	1B_1	$0.049\phi_{1-1}' + 0.834\phi_{2-1}' - 0.550\phi_{1-3}'$
7.67	0.763	1B_1	$0.145\phi_{1-1}' - 0.551\phi_{2-1}' - 0.822\phi_{1-3}'$

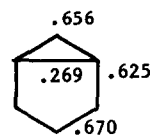
TABLE 2
 Computed Electron Densities of the Ground and 1L_b and 1L_a States

State	Atom	1	2	3	4
Ground		0.819	0.944	1.175	0.943
1L_b		1.330	0.915	0.866	1.108
1L_a		1.022	1.069	1.018	0.804

Although traditionally less reliable (especially in the case of this highly strained molecule), the calculations of the ground state properties of I are interesting. As expected the molecule is predicted to have a dipole moment (2.7 D, the corresponding Huckel moment is 4.7 D) and the electron density and bond orders shown below. The expectation that the three member ring would have a net positive charge and the five member ring a net negative charge is fulfilled.



Electron Densities



Bond Orders

The electron densities in the 1L_b and 1L_a excited states are also given in Table 2.

The total π -energy for I, as computed by the Pople approximation⁹, is -81.9463 ev. The corresponding value for benzene is -81.2208 ev, using the same parameters as with I with the exception that the two centered integral between atoms 1-4 is 4.7850 ev. The computed higher π -electron stability of I over II is primarily due to the extra bond. The computed product, $2 \sum_{\mu < \nu} P_{\mu\nu} \beta_{\mu\nu}$, contributes about -19.20 ev and -20.0 ev to the π -electron energies of II and I, respectively. Conversely, the computed ionization energy of II is 1.10 ev lower than benzene.

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References

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