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Relationes

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Simple Hückel Calculation on Triphenyl Cyclopropenyl Cation

By

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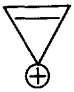
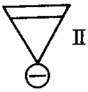
Simple Hückel theory predicts aromaticity for cyclopropenyl cation (I) but not for the anion (II) [4].

The object of the present investigation was to make a complete Hückel calculation on triphenyl cyclopropenyl cation (III) which has been well characterised [1] and see what additional informations may be obtained about these ring systems.



I



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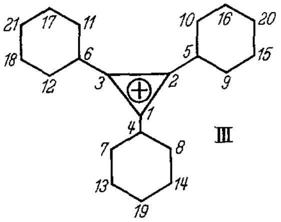

III

The method of calculation is well known. All carbon atoms were taken as equivalent and all C-C bonds were set equal. Overlap was neglected and the Coulomb and resonance integrals were set equal to α and β respectively.

It is sufficient to consider the symmetry group C_{3v}, the representation can be expressed in terms of the irreducible representations of the group as follows

$$\Gamma = 5A_1 + 2A_2 + 7E$$

which enables us to factorise the secular determinant into a fifth, a second and a seventh order determinant.

The basis for representation A_1 is

$$c_1 = c_2 = c_3,\ c_4 = c_5 = c_6,\ c_7 = c_8 = c_9 = c_{10} = c_{11} = c_{12},$$
$$c_{13} = c_{14} = c_{15} = c_{16} = c_{17} = c_{18},\ c_{19} = c_{20} = c_{21}$$

that for A_2 is

$$c_7 = -c_8 = c_9 = -c_{10} = c_{11} = -c_{12},\ c_{13} = -c_{14} = c_{15} = -c_{16} = c_{17} = -c_{18},$$

rest zero

and for E is

$$c_3 = \omega^2 c_1,\ c_6 = \omega^2 c_4,\ c_{11} = \omega^2 c_7,\ c_{17} = \omega^2 c_{13},\ c_{21} = \omega^2 c_{19},\ c_{18} = \omega^2 c_{14},\ c_{12} = \omega^2 c_8$$
$$c_2 = \omega c_1,\ c_5 = \omega c_4,\ c_9 = \omega c_7,\ c_{15} = \omega c_{13},\ c_{20} = \omega c_{19},\ c_{16} = \omega c_{14},\ c_{10} = \omega c_8$$

and either $c_7 = c_8,\ c_{13} = c_{14}$; or $c_7 = -c_8,\ c_{13} = -c_{14}$

where $\omega = e^{2\pi i/3}$ and $\omega^2 = e^{4\pi i/3}$.

The species E appears in doubly degenerate pairs. The AO coefficients of the other degenerate MO are obtained by replacing ω by its complex conjugate ω^* in the above relations. The degenerate MOs with real AO coefficients were then constructed by taking the sum and the difference of the complex MOs. There are twenty electrons in the cation (III) so the ten lowest levels will be occupied. The AO coefficients and energies of the occupied MOs (and the lowest unoccupied MO) of the species A_1, A_2 and E are given in the Tab. 1.

Table 1. MO *energies and* AO *coefficients for triphenyl cyclopropenyl cation*

	Symm.	A_1			A_2	E			
	x	2.609	1.790	0.755	1.000	2.064	1.155	1.000	—0.504
Coeff.	c_1	0.456	0.249	0.221	0.000	0.089	0.148	0.000	0.253
	c_4	0.278	—0.052	—0.276	0.000	0.273	0.321	0.000	0.126
	c_7	0.134	—0.171	—0.215	0.289	0.238	0.110	0.289	0.316
	c_{13}	0.073	—0.254	0.114	0.289	0.216	—0.192	0.289	0.092
	c_{19}	0.055	—0.284	0.300	0.000	0.211	—0.334	0.000	0.074
where x stands for $+ (\varepsilon - \alpha)/\beta$						$c_8 = c_7$ $c_{14} = c_{13}$	$c_8 = c_7$ $c_{14} = c_{13}$	$c_8 = - c_7$ $c_{14} = - c_{13}$	$c_8 = c_7$ $c_{14} = c_{13}$

Charge and Bond Order: From the values of the coefficients given in the Tab. 1 it is possible to calculate the π-electron densities $q_i = 2\Sigma c_i^2$ and bond orders $p_{rs} = 2\Sigma c_r c_s$ over the occupied MOs. The values are given in the Tab. 2.

Table 2. *Electron density and bond order in triphenyl cyclopropenyl cation*

$q_{1, 2, 3}$	= 0,758	$p_{1, 2; 1, 3; 2, 3}$	= 0.577
$q_{4, 5, 6}$	= 1.020	$p_{1, 4; 2, 5; 3, 6}$	= 0.393
$q_{7, 8, 9, 10, 11, 12}$	= 0.961	$p_{7, 13; 8, 14; 9, 15; 10, 16; 11, 17; 12, 18}$	= 0.679
$q_{13, 14, 15, 16, 17, 18}$	= 1.002	$p_{4, 7; 4, 8; 5, 9; 5, 10; 6, 11; 6, 12}$	= 0.611
$q_{19, 20, 21}$	= 0.968	$p_{13, 19; 14, 19; 15, 20; 16, 20; 17, 21; 18, 21}$	= 0.658

It is interesting to note that the π-electron density in the phenyl rings stays close to unity while it is much less than one in the cyclopropane ring. This evidently means that the positive charge is concentrated mainly in the cyclopropane ring. Further the electron densities in the phenyl rings indicate that the nucleophilic substitution reaction should take place at the meta position of the phenyl ring. The calculated bond order values suggest that the exocyclic C-C bonds have high single bond character.

Effect of Hetero Substitution in the Phenyl Ring: COULSON and LONGUET-HIGGINS [2] showed that if the Coulomb integral of the atom r is altered by a small amount $\delta\alpha_r$, then the change in energy of any MO involving that atom is given by

$$\delta\varepsilon = c_r^2 \, \delta\alpha_r$$

where c_r is the AO coefficient in the MO under consideration. This relation along with the Tab. 1 enables us to calculate the MO energies of Cyclopropenyl cation in which the phenyl ring is replaced by aza-ring systems like pyridine, taking $\delta\alpha_r = \alpha_N - \alpha_C = 0.2\,\beta$.

The MO energies may be used to calculate two important molecular quantities namely the resonance energy and the longest wave length π-π^* transition energies.

Resonance Energy: The calculated resonance energies of triphenyl cyclopropenyl cation and its aza-derivatives are given in the Tab. 3.

It appears that the triphenyl cyclopropenyl cation is strongly resonance stabilised. The aza-compounds should be more stable except the ortho triaza-compound.

Table 3. *Resonance energies of cyclopropenyl cations*

Compound	Resonance energy (β-units)
Triphenyl cyclopropenyl cation	8.104
19-aza- ,,	9.168
19, 20-diaza- ,,	9.148
19, 20, 21-triaza ,,	9.142
8-aza- ,,	9.168
8, 9-diaza ,,	9.154
8, 9, 12-triaza- ,,	8.060

Longest Wave Length π-π^*-Transition Energies: It is assumed that the longest wave length electronic transition in cyclopropenyl cation arises from transitions involving the π-electrons and not the σ-electrons. The energies of the highest occupied (of species A_1) and the lowest unoccupied (of species E) orbitals were corrected for overlap using the relation [5]

$$\varepsilon_{\text{Hückel}} = \alpha - \varkappa\beta$$

$$\varepsilon_{\text{Corrected}} = \alpha - \varkappa^1\gamma$$

where $\varkappa^1 = \frac{\varkappa}{1-\varkappa S}$ and $\gamma = \beta - S\alpha$,

S being set equal to 0.25. The corrected energy difference between the highest filled and the lowest unfilled MOs obtained in units of γ were converted to cm^{-1} by setting [3] $\gamma = 23{,}000$ cm^{-1}. The results are given in the Tab. 4.

Table 4. *Longest wave length electron transition in cyclopropenyl cation*

Compound	Transition energies calc. [cm^{-1}]	Transition energies exp. [cm^{-1}]
Triphenyl cyclopropenyl cation	27,876	31,545
19-aza- ,,	28,037	—
19, 20-diaza- ,,	27,554	—
19, 20, 21-triaza- ,,	27,414	—
8-aza- ,,	27,414	—
8, 9-diaza- ,,	27,414	—
8, 9, 12-triaza- ,,	27,414	—

In view of the drastic simplifications used the agreement between the calculated and the experimental transition energies for triphenyl cyclopropenyl cation is fair. The calculation predicts that the introduction of nitrogen atoms in the phenyl rings will cause red shift in the longest wave length electron transition except for the 19-aza compound.

Some Comments on the Stability of Triphenyl Cyclopropenyl Anion: If we assume that the triphenyl cyclopropenyl anion differs from the cation in containing two more electrons and none of the molecular parameters are changed, then the present set of calculation will hold for the anion with the only difference that one more MO will be occupied in the anion as compared to the cation. It has been mentioned that the topmost filled MO belongs to the species A_1 and the first empty MO to species E. The two additional electrons in the anion will therefore go to the orbital of symmetry E. But the E-orbitals can accomodate four electrons. Hence the anion will contain an incompletely filled MO and will be a highly unstable biradical.

Concluding remarks: Although a number of interesting correlations have been obtained in this calculation, it should be remembered that Hückel LCAO method makes several simplifying assumptions, one of these, the neglect of electron interaction is particularly serious for ions.

Literature

[*1*] Breslow, J. D., and C. Yuan: J. Amer. chem. Soc. **80**, 5991 (1958).
[*2*] Coulson, C. A., and H. C. Longuet-Higgins: Proc. Roy. Soc. (Lond.) **A 191**, 39 (1947).
[*3*] Platt, J. R.: J. chem. Physics **18**, 1168 (1950).
[*4*] Roberts, J. D., A. Streitwieser, and C. M. Regan: J. Amer. chem. Soc. **74**, 4579 (1952).
[*5*] Wheland, G. W.: J. Amer. chem. Soc. **63**, 2025 (1941).

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