Electronic Structures of Methylenecyclopropene and Cyclopropenone

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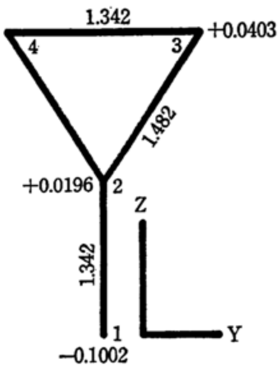
Recently, Saga[1] reported on the dipole moments and pK values of cyclopropenone derivatives. It seemed that it would be very interesting to compare his experimental data with the results of theoretical calculations. This report will describe an application of the semiempirical LCAO SCF MO method, including CI, to the electronic structures of these molecules.

In each iteration process of the SCF procedure, the values of the molecular integrals were recalculated by using the new bond distances, l_{rs}, obtained from the $l_{rs}=1.520-0.186\,p_{rs}$ relation,[2] where p_{rs} is the bond order between the two carbon atoms r and s obtained by the previous iteration process. However, the bond distance of C=O was kept constant throughout the calculation. One- and two-center Coulomb integrals were calculated by the usual approximation proposed by Parr and Pariser[3] and using the values of I_p and A given by Pritchard and Skinner[4] and the value of β obtained by Kon's formula.[5] In the CI calculation only the one-electron excitation configurations were taken into account. The final results may be tabulated as follows:

The calculated dipole moment of cyclopropenone, 4.428 D, seems to be reasonable when it is compared with the observed dipole moment of 3,4-diphenylcyclopropenone, 5.00 D.[1] The bond distances shown in the figures, which were obtained from the SCF p_{rs}'s, may serve to suggest the structures of these molecules. The formal negative charge at the oxygen atom of cyclopropenone seems to be too high to correspond to the pK value, −2.8 (25°C), of 3,4-diphenylcyclopropenone,[1] since the pK value of

(1) Methylenecyclopropene:



a. Dipole moment 1.157 D

b. Molecular orbitals and energies

Symm.	ε_i	C_1	C_2	C_3	C_4
$1b_1$	−14.9557	0.3509	0.5440	0.5390	0.5390
$2b_1$	−11.0664	−0.6535	−0.4408	0.4351	0.4351
$1a_2$	0.4870	0.0000	0.0000	−0.7071	0.7071
$3b_1$	1.2590	0.6707	−0.7140	0.1420	0.1420

c. Transition energies and oscillator strengths (without CI)

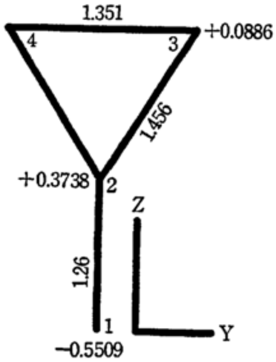
Symm.	Transition	Polarization	Energy (eV)	f
$^1B_2$	3←2	y	5.746	0.17
$^1A_1$	4←2	z	6.792	0.67
$^1A_1$	4←1	z	9.191	0.021
$^1B_2$	3←1	y	9.225	0.42

d. Transition energies and oscillator strengths (after CI)

Symm.	Wave function	Energy (eV)	f
$^1A_1$	$0.9332\Phi_{4\leftarrow2}+0.3594\Phi_{4\leftarrow1}$	5.374	0.41
$^1B_2$	$0.9665\Phi_{3\leftarrow2}+0.2567\Phi_{3\leftarrow1}$	5.483	0.27
$^1B_2$	$0.2567\Phi_{3\leftarrow2}-0.9665\Phi_{3\leftarrow1}$	9.489	0.25
$^1A_1$	$0.3594\Phi_{4\leftarrow2}-0.9332\Phi_{4\leftarrow1}$	9.609	0.23

1) M. Saga, M. S. Thesis submitted to Tohoku Univ., 1964.
2) T. Nakajima and S. Katagiri, *Mol. Phys.*, **6**, 149 (1963).
3) R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 767 (1953).
4) H. A. Skinner and H. O. Pritchard, *Trans. Faraday Soc.*, **49**, 1254 (1953).
5) H. Kon, This Bulletin, **28**, 275 (1955).

(2) Cyclopropenone:



a. Dipole moment 4.428 D

b. Molecular orbitals and energies

Symm.	ε_i	C_1	C_2	C_3	C_4
$1b_1$	−15.8377	0.3855	0.4991	0.5488	0.5488
$2b_1$	−12.3455	−0.7917	−0.2531	0.3932	0.3932
$1a_2$	−0.6787	0.0000	0.0000	−0.7071	0.7071
$3b_1$	0.0798	0.4739	−0.8288	0.2104	0.2104

c. Transition energies and oscillator strengths (without CI).

Symm.	Transition	Polarization	Energy (eV)	f
$^1B_2$	3←2	y	6.066	0.15
$^1A_1$	4←2	z	6.177	0.51
$^1A_1$	4←1	z	8.942	0.007
$^1B_2$	3←1	y	8.997	0.43

d. Transition energies and oscillator strengths (after CI).

Symm.	Wave function	Energy (eV)	f
$^1B_2$	$0.9940\Phi_{3\leftarrow2}+0.1094\Phi_{3\leftarrow1}$	6.030	0.20
$^1A_1$	$0.9925\Phi_{4\leftarrow2}+0.1123\Phi_{4\leftarrow1}$	6.134	0.51
$^1A_1$	$0.1123\Phi_{4\leftarrow2}-0.9925\Phi_{4\leftarrow1}$	8.985	0.0002
$^1B_2$	$0.1094\Phi_{3\leftarrow2}-0.9940\Phi_{3\leftarrow1}$	9.033	0.36
$^3B_2$	$0.5148\Phi_{3\leftarrow2}+0.8573\Phi_{3\leftarrow1}$	2.872	
$^3A_1$	$0.9989\Phi_{4\leftarrow2}-0.0470\Phi_{4\leftarrow1}$	4.204	
$^3A_1$	$0.0470\Phi_{4\leftarrow2}+0.9989\Phi_{4\leftarrow1}$	8.630	
$^3B_2$	$0.8573\Phi_{3\leftarrow2}-0.5148\Phi_{3\leftarrow1}$	8.789	

the tropone molecule has been reported to be −1.02 (20°C) by Hosoya and Nagakura.[6] However, since the correspondence relation between the pK values and π electron densities should be limited within similar molecules, the reason for such a high negative formal charge at the oxygen atom as in cyclopropenone can be attributed to its special structure.

6) H. Hosoya and S. Nagakura, *ibid.*, **39**, 1414 (1966).