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An *ab initio* SCF-MO Calculation of Methylenecyclopropene, Cyclopropenimine, and Cyclopropenone

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An *ab initio* SCF-MO study has been undertaken on the isoelectronic series methylenecyclopropene, cyclopropenimine, and cyclopropenone. A population analysis has been carried out and serves as the basis for a discussion of the chemical properties of the molecules.

The molecular and electronic structure of small, strained ring systems have attracted much interest, and a large amount of theoretical and experimental work has been undertaken in this field. In some previous studies we have investigated the molecular structure and electron distribution in some small ring systems displaying conjugation.[1–3] The methods we used were electron diffraction and semi-empirical molecular orbital calculations, where only the π-electrons were included explicitly. As a continuation of this research program, we have carried through an *ab initio* all electron calculation on the molecules methylenecyclopropene, cyclopropenimine, and cyclopropenone. The main purpose of the study is to obtain information on the electron distribution in the molecules. Of particular interest in this context is the question whether these molecules have pronounced single-bond double-bond structures or a more uniform distribution of the π-electrons.

METHOD OF CALCULATION

The calculations were performed using the computer program REFLECT [4] by which the Roothaan-Hall equations are solved for a Gaussian type basis, making explicit use of the molecular symmetry.

The computations were carried through using (9.5) basis for the carbon, oxygen, and nitrogen atoms. These primitive basis sets were contracted to double zeta basis sets. The orbital exponents and contraction coefficients applied for the heavy atoms were those of Huzinaga.[5] For hydrogen Huzinaga's exponents scaled by the factor 1.25 were used. The assumed geometries used in the calculations are shown in Fig. 1. which also gives the numbering of the

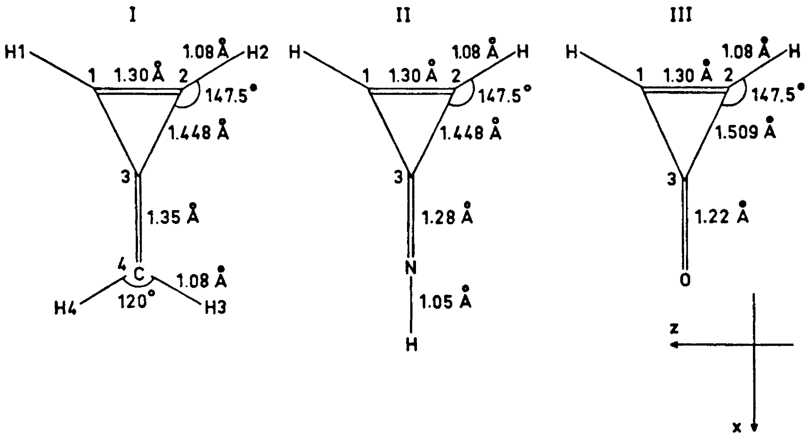

Fig. 1. Numbering of atoms. I Methylenecyclopropene, II cyclopropenimine, III cyclopropenone.

atoms and the coordinate system adopted. For cyclopropenimine, the imino hydrogen atom was assumed to be on the straight line C=N−H. This has been done in order to preserve the symmetry plane orthogonal to the ring plane. We assume that this will be an adequate model for the molecule.

RESULTS AND DISCUSSION

Only the molecular ground states have been considered in this study.

The total molecular energies as well as the orbital energies for all the molecules studied are presented in Table 1, where also the assignments of the molecular orbitals are given.

Table 1. Total energy and orbital energies (a.u.) for methylenecyclopropene, cyclopropenimine, and cyclopropenone.

Methylenecyclopropene		Cyclopropenimine		Cyclopropenone	
E_{tot}:	−153.5916	E_{tot}:	−169.5288	E_{tot}:	−189.4122
$1a_1$	−11.3105	$1a_1$	−15.5101	$1a_1$	−20.5793
$1b_1$	−11.3084	$2a_1$	−11.3655	$2a_1$	−11.4262
$2a_1$	−11.3055	$3a_1$	−11.2990	$3a_1$	−11.3419
$3a_1$	−11.2098	$1b_1$	−11.2970	$1b_1$	−11.3399
$4a_1$	−1.2469	$4a_1$	−1.2563	$4a_1$	−1.4156
$5a_1$	−0.9800	$5a_1$	−1.1163	$5a_1$	−1.2450
$2b_1$	−0.8026	$2b_1$	−0.7963	$2b_1$	−0.8255
$6a_1$	−0.7711	$6a_1$	−0.7854	$6a_1$	−0.8063
$7a_1$	−0.6665	$7a_1$	−0.7286	$7a_1$	−0.6950
$3b_1$	−0.5904	$8a_1$	−0.5756	$3b_1$	−0.6152
$8a_1$	−0.5479	$3b_1$	−0.5414	$8a_1$	−0.5944
$1b_2(\pi_1)$	−0.5195	$1b_2(\pi_1)$	−0.5326	$1b_2(\pi_1)$	−0.5885
$4b_1$	−0.4477	$2b_2(\pi_2)$	−0.3483	$2b_2(\pi_2)$	−0.4362
$2b_2(\pi_2)$	−0.3065	$4b_1$	−0.3139	$4b_1$	−0.3931

For computational reasons a decomposing of the total molecular energy providing the necessary data for scaling of the molecular wave function, was not obtained. Hence a reliable estimate of the closeness to the Hartree-Fock limit is rather difficult to make. Huzinaga's calculations on atoms [5] show the need for using eleven *s* type functions and seven *p* type functions for carbon, nitrogen, and oxygen, and six *s* functions for hydrogen. Furthermore, polarization functions would also be needed. The importance of such functions would be enhanced in molecules. For computational reasons we were forced to perform the calculations using smaller basis sets. For one of the molecules, methylenecyclopropene, we have also carried out a calculation using a (7,3) basis for carbon. The total enery in that case was -153.4285 a.u. as compared to -153.5916 a.u. for the (9,5) calculation. We therefore feel that the total energy given by the latter calculation for this molecule should be at most av few tenths of an atomic unit above the Hartree-Fock limit. Furthermore, a comparative study of molecular properties within this series should be reliable also from a quantitative point of view. Admittedly the relative importance of polarization functions and other extensions of the basis is expected to vary from molecule to molecule in this isoelectronic series. For cyclopropenone, the energy of the present calculation compares favourably with that from a work by Clark *et al.*[6] In that work a (5,2) basis was employed, giving a total energy of -187.7254 a.u.

In Table 2 are given the molecular energies and the sum of the atomic ground state energies calculated by the same basis. The difference between the energies should give a somewhat reliable estimate of the total molecular binding energy in each case. We have here neglected the difference between atomic and molecular correlation energy. The differences, also included in the table, indicate that methylenecyclopropene is the most stable of these systems. Cyclopropenone and cyclopropenimine have rather similar binding energies, the latter being somewhat more stable. A point worth noticing is found in comparing the binding energies of the present calculation with those by Lehn

Table 2. Molecular properties for methylenecyclopropene, cyclopropenimine, and cyclopropenone.

Properties	Methylene-cyclopropene	Cyclo-propenimine	Cyclo-propenone
Atomic energy (a.u.)	−152.7376	−168.9488	−188.8543
Calculated molecular energy (a.u.)	−153.5916	−169.5288	−189.4122
Binding energy (a.u.)	0.8540	0.5800	0.5579
(kcal/mol)	536	364	350
Dipole moment (D)	2.11	1.02	4.67
Ionization potentials (eV)	8.34	8.54	10.70
	12.18	9.48	11.87
	14.14	14.49	16.01

Table 3. Gross atomic populations for methylenecyclopropene.

Atomic orbitals		$1a_1$	$1b_1$	$2a_1$	$3a_1$	$4a_1$	$5a_1$	$2b_1$	$6a_1$	$7a_1$	$3b_1$	$8a_1$	$1b_2$	$4b_1$	$2b_2$	Total
C_1C_2	$1s+2s$	0.984	1.000	0.067	0	0.459	0.038	0.397	0.212	0.021	−0.001	−0.004	0	0.031	0	3.153
C_3	$1s+2s$	0.0313	0	1.968	0	0.272	0.316	0	0.104	0.231	0	0.013	0	0	0	2.935
C_4	$1s+2s$	0	0	0	2.000	0.070	0.851	0	0.053	0.178	0	0.037	0	0	0	3.189
H_1, H_2		0	0	0	0	0.042	0.007	0.250	0 192	0.055	0.030	0.035	0	0.074	0	0.685
H_3, H_4		0	0	0	0	0.001	0.098	0.001	0.033	0.169	0.265	0.055	0	0.140	0	0.762
C_1,C_2	$2p_x$	0	0	0	0	0.046	0.026	0.002	0.335	0.004	0.082	0.197	0	0.360	0	1.052
	$2p_y$	0	0	0	0	0	0	0	0	0	0	0	0.620	0	0.293	0.913
	$2p_z$	0	0	0	0	0.165	0.014	0.261	0.085	0.253	0.013	0.339	0	0.004	0	1.134
C_3	$2p_x$	0	0	0	0	0.193	0.424	0	0.077	0.045	0	0.425	0	0	0	1.164
	$2p_y$	0	0	0	0	0	0	0	0	0	0	0	0.614	0	0.343	0.957
	$2p_z$	0	0	0	0	0	0	0.173	0	0	0.274	0	0	0.560	0	1.007
C_4	$2p_x$	0	0	0	0	0.039	0.042	0	0.054	0.541	0	0.283	0	0	0	0.959
	$2p_y$	0	0	0	0	0	0	0	0	0	0	0	0.146	0	1.070	1.216
	$2p_z$	0	0	0	0	0	0	0.005	0	0	0.947	0	0	0.222	0	1.174

Table 4. Gross atomic populations for cyclopropenimine.

Atomic orbitals		$1a_1$	$2a_1$	$3a_1$	$1b_1$	$4a_1$	$5a_1$	$2b_1$	$6a_1$	$7a_1$	$8a_1$	$3b_1$	$1b_2$	$2b_2$	$4b_1$	Total
C_1,C_2	$1s+2s$	0	0	1.000	1.000	0.403	0.058	0.413	0.166	0.092	−0.006	0.001	0	0	0.049	3.176
C_3	$1s+2s$	0	2.000	0	0	0.389	0.092	0	0.223	0.027	0.118	0	0	0	0	2.849
N	$1s+2s$	2.000	0	0	0	0.171	1.049	0	0.096	0.079	0.010	0	0	0	0	3.405
H_1,H_2		0	0	0	0	0.036	0.009	0.248	0.116	0.109	0.061	0.080	0	0	0.036	0.695
H_3		0	0	0	0	0.007	0.09	0.048	0.172	0.250	0.045	0	0	0	0	0.564
C_1C_2	$2p_x$	0	0	0	0	0.049	0.006	0.001	0.254	0.081	0.175	0.265	0	0	0.237	1.068
	$2p_y$	0	0	0	0	0	0	0	0	0	0	0	0.492	0.412	0	0.904
	$2p_z$	0	0	0	0	0.145	0.027	0.244	0.012	0.156	0.514	0.024	0	0	−0.007	1.112
C_3	$2p_x$	0	0	0	0	0.119	0.520	0	0.001	0.152	0.238	0	0	0	0	1.030
	$2p_y$	0	0	0	0	0	0	0	0	0	0	0	0.717	0.168	0	0.885
	$2p_z$	0	0	0	0	0	0	0.181	0	0	0	0.774	0	0	0.041	0.996
N	$2p_x$	0	0	0	0	0.045	0.039	0	0.410	0.613	0.100	0	0	0	0	1.207
	$2p_y$	0	0	0	0	0	0	0	0	0	0	0	0.299	1.008	0	1.307
	$2p_z$	0	0	0	0	0	0	0.008	0	0	0	0.483	0	0	1.33	0.821

Table 5. Gross atomic populations for cyclopropenone.

Atomic orbitals		Molecular orbitals														
		$1a_1$	$2a_1$	$3a_1$	$1b_1$	$4a_1$	$5a_1$	$2b_1$	$6a_1$	$7a_1$	$3b_1$	$8a_1$	$1b_2$	$2b_2$	$4b_1$	Total
C_1,C_2	$1s+2s$	0	0	1.000	1.000	0.038	0.441	0.416	0.218	0.034	0	−0.01	0	0	0.064	3.201
C_3	$1s+2s$	0	2.000	0	0	0.222	0.169	0	0.229	0.215	0	0.088	0	0	0	2.923
O	$1s+2s$	2.000	0	0	0	1.347	0.076	0	0.055	0.297	0	0.141	0	0	0	3.916
H_1,H_2		0	0	0	0	0.001	0.047	0.241	0.165	0.070	0.055	0.040	0	0	0.055	0.674
C_1,C_2	$2p_x$	0	0	0	0	0.020	0.024	0.002	0.371	−0.001	0.140	0.132	0	0	0.356	1.044
	$2p_y$	0	0	0	0	0	0	0	0	0	0	0	0.277	0.627	0	0.904
	$2p_z$	0	0	0	0	0.007	0.168	0.246	0.041	0.302	0.022	0.343	0	0	−0.012	1.117
C_3	$2p_x$	0	0	0	0	0.153	0.397	0	0.050	0.044	0	0.288	0	0	0	0.932
	$2p_y$	0	0	0	0	0	0	0	0	0	0	0	0.740	0.008	0	0.748
	$2p_z$	0	0	0	0	0	0	0.171	0	0	0.645	0	0	0	0.183	0.999
O	$2p_x$	0	0	0	0	0.148	0	0	0.072	0.636	0	0.472	0	0	0	1.328
	$2p_y$	0	0	0	0	0	0	0	0	0	0	0	0.707	0.737	0	1.444
	$2p_z$	0	0	0	0	0	0	0.018	0	0	0.923	0	0	0	0.889	1.830

Table 6. Total gross atomic charges.

Atoms	Methylene-cyclopropene	Cyclopropen-imine	Cyclo-propenone
C_1, C_2	6.252	6.266	6.266
C_3	6.063	5.769	5.601
C_4	6.538		
O			8.518
N		7.740	
H_1, H_2	0.685	0.696	0.674
H_3		0.564	
H_3, H_4	0.762		

and coworkers [7] for cyclopropane, cyclopropene, and diazirine. Diazirine may be thought of as a cyclopropene molecule where two CH groups have been replaced by two N-atoms. The difference in binding energy between these two species was found to be 0.48 a.u., or 0.24 a.u. for each N atom. In cyclopropenimine, one CH_2 group in methylenecyclopropene, has been replaced by an NH group. The difference in binding energy in this case is 0.27 a.u. Considering the fact that the systems display some discrepancies, the similarities of these magnitudes are of some interest.

Table 1 gives the orbital energies. In the case of all molecules, the first four orbitals are nearly pure a.o.'s and localized to the heavy atom frame of the systems. For cyclopropenone and cyclopropenimine the orbitals with the highest energy describe the lone pairs in nitrogen and oxygen. The two π-orbitals are next to highest in energy. For methylenecyclopropene the highest lying σ-orbital is between the two π-orbirals.

Table 2 also shows the lowest ionization potentials estimated by means of Koopmans' theorem, and the dipole moments of the molecules. By symmetry, the dipole moment components vanish along the y and z axes and the dipole moments for all three molecules coincide with the positive x direction.

The molecular populations have been calculated from a Mulliken type population analysis. The resulting molecular populations are given in Tables 3 – 5. The total σ populations are obtained by adding the $1s$, $2s$, $2px$, and $2pz$ contributions. Table 6 gives the total of these populations. It is seen that all three molecules have practically identical charges on atoms 1 and 2. In cyclopropenimine, the charge on atom C_3 is rather low, and compared to the hydrocarbon there is a net flow of electrons to the external heavy atom.

This effect is even more pronounced for the cyclopropenone molecule, where the very high charge of about 8.5 electrons on the oxygen atom is responsible for the unusual high dipole moment of this molecule. A further study of the electronic distribution is made by investigating the overlap populations given in Tables 7 – 9. It is seen from these tables that the $C=O$ bond in cyclopropenone has a smaller overlap population than the external double bond in the two other molecules. This applies to the σ part as well as the π part of this bond. A remarkable feature is found for the C_1-C_2 bond in cyclopropenimine and cyclopropenone. In these cases the total overlaps are in

Table 7. Overlap populations for methylenecyclopropene.

Bonds	Molecular orbitals $1a_1$	$1b_1$	$2a_1$	$3a_1$	$4a_1$	$5a_1$	$2b_1$	$6a_1$	$7a_1$	$3b_1$	$8a_1$	$1b_2$	$4b_1$	$2b_2$	Total
C_1-C_2	0.000	0.0 0	0.000	0.0 '0	0.192	0.017	0.026	0.062	0.024	−0 040	0.181	0.131	−0.376	0.120	0.388(π= 0.251)
C_1-C_3	0.000	0.000	0.000	0.000	0.125	0.018	0.043	−0.005	−0.008	0.012	−0.121	0.105	0.124	−0.106	0.183(π= −0.001)
C_3-C_4	0.000	0.000	0.000	0.000	0.019	0.273	0.002	0.022	0.020	0.090	−0.014	0.052	−0.113	0.206	0.540(π= 0.258)
C_1-H_1	0.000	0.000	0.000	0.000	0.010	0.002	0.132	0.115	0.035	0.016	0.015	0.000	0.016	0.000	0.341
C_4-H_4	0.000	0.000	0.000	0.000	0.001	0.046	0.000	0.013	0.099	0.127	0.041	0.000	0.072	0.000	0.400

Table 8. Overlap populations for cyclopropenimine.

Bonds	Molecular orbitals $1a_1$	$2a_1$	$3a_1$	$1b_1$	$4a_1$	$5a_1$	$2b_1$	$6a_1$	$7a_1$	$8a_1$	$3b_1$	$1b_2$	$2b_2$	$4b_1$	Total
C_1-C_2	0.000	0.000	0.000	0.000	0.166	0.019	0.008	0.080	−0.002	0.221	−0.162	0.098	0.145	−0.578	−0.003(π=0.243)
C_1-C_3	0.000	0.000	0.000	0.000	0.124	0.027	0.044	−0.019	−0.005	−0.155	0. 62	0.098	−0.090	0.032	0.121(π=0.008)
C_3-N	0.000	0.000	0.000	0.000	0.020	0.260	0.034	0.061	0.028	−0.006	0.126	0.087	0.143	−0.052	0.669(π=0.230)
C_1-H	0.000	0.000	0.000	0.000	0.000	0.000	0.131	0.067	0.070	0.032	0.038	0.000	0.000	−0.031	0.316
$N-H_3$	0.000	0.000	0.000	0.000	0.005	0.048	0.[illegible]00	0.096	0.151	0.026	0.000	0.000	0.000	0.000	0.326

Table 9. Overlap populations for cyclopropenone.

Bonds	Molecular orbitals $1a_1$	$2a_1$	$3a_1$	$1b_1$	$4a_1$	$5a_1$	$2b_1$	$6a_1$	$7a_1$	$3b_1$	$8a_1$	$1b_2$	$2b_2$	$4b_1$	Total
C_1-C_2	0.000	0.000	0.000	0.000	0.019	0.179	0.006	0.091	0.015	−0.050	0.176	0.051	0.186	−0.687	−0.013(π=0.237)
C_1-C_3	0.000	0.000	0.000	0.000	−0.001	0.138	0.039	−0.011	−0.008	0.022	−0.138	0.068	−0.041	0.078	0.146(π=0.027)
C_3-O	0.000	0.000	0.000	0.000	0.218	0.021	0.006	0.024	−0.016	0.163	−0.071	0.144	0.052	−0.104	0.438(π=0.196)
C_1-H_1	0.000	0.000	0.000	0.000	0.000	0.010	0.130	0.099	0.046	0.030	0.017	0.000	0.000	−0.021	0.311

fact negative, indicating the instability of these systems. The differences between the systems are in the σ electrons, the π electron overlaps are nearly identical for all three molecules. Indeed, the systems seem unstable; although the cyclopropenone molecule has been syntesized, it has resisted isolation from solution.[8]

At this point, one must also question the reliability of the Mulliken type population analysis for small strained ring systems.

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