

# The Electronic Structure of Cyclopropane, Cyclopropene and Diazirine An *ab initio* SCF-LCAO-MO Study

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The electronic structure of cyclopropane, cyclopropene and diazirine has been studied within the *ab-initio* SCF-LCAO-MO theoretical framework. The present results lead to a general bonding model for three-membered ring systems. Composition of the MO's, population analyses and electron density distribution diagrams were used to establish the nature of the bonding. The total electron density distributions in cyclopropane and in cyclopropene lead to a "bent bond" + "central hole" bonding model; however the bending angle is only ca. 5° and the central hole is not very deep with respect to the bonding regions (ca. 15% density depression). Special emphasis has been given to the nature of the  $\sigma$  bonds forming the ring system. It has been found that the *ring bonding* in cyclopropane and in cyclopropene is due principally to three MO's: (1) A low lying MO ( $3a_1$ ) composed mainly of C(2s) AO's and contributing electron density principally *inside* the ring triangle. (2) Two MO's ( $6a_1$  and  $3b_2$ ), which are the highest occupied MO's in cyclopropane and lie immediately below the  $\pi$  bond in cyclopropene, composed almost exclusively of C(2p) AO's in the ring plane and leading to electron density maxima *outside* the ring (density bending angle of ca. 20°) and to zero density in the centre of the ring. In the case of diazirine these MO's are appreciably perturbed by the presence of the nitrogen lone pairs. Three MO's contribute mainly to the description of the *lone pairs*, all of which also contribute to some extent to ring bonding. Furthermore, among these three MO's two lie below the  $\pi$  level, one of them being very low in energy. This is quite different from the usual picture. The present bonding picture has been compared to former semi-empirical models (especially the Coulson-Moffitt and the Walsh models). The strain, the " $\pi$ " character and conjugative properties of the three-membered ring are discussed on the basis of its electronic structure. The special bonding features of this system confer on it a *pseudo- $\pi(\psi - \pi)$*  character; the bonds making up the ring may be considered as  $\psi - \pi$  bonds.

Die Elektronenstruktur von Cyclopropan, Cyclopropen und Diazirin wurde im Rahmen einer *ab initio* SCF-LCAO-MO-Methode untersucht. Die Untersuchungen führen zu einem allgemeinen Bindungsmodell für Dreieringe. Der Aufbau der MO's, Populationsanalyse und die Elektronendichte-Verteilungen wurden zur Bestimmung der Bindungsart herangezogen. Die Gesamtelektronendichte-Verteilungen in Cyclopropan und Cyclopropen führen zu einem Bindungsmodell aus „gebogener Bindung“ und „Ringloch“, jedoch ist der Bindungswinkel nur ca. 5° und das Ringloch ist nicht sehr tief (ca. 15% Dichteverringern). Besonderes Augenmerk wurde auf die  $\sigma$ -Bindungen, die das Ring-system bilden gelegt. Dabei wurde festgestellt, daß die Ringbindung in Cyclopropan und Cyclopropen hauptsächlich auf drei MO's beruht: einem niedrig liegenden MO ( $3a_1$ ) das im wesentlichen aus C(2s) AO's besteht und vor allem die Elektronendichte innerhalb des Rings liefert, zwei MO's ( $6a_1$  und  $3b_2$ ), die die höchstens besetzten MO's in Cyclopropan sind und bei Cyclopropen direkt unterhalb der  $\pi$ -Bindung liegt. Sie setzen sich nahezu nur aus C(2p) AO's in der Ringebene zusammen und führen zu einem Dichtemaxima außerhalb des Rings (mit einem Winkel von ca. 20°) und zu einer verschwindenden Dichte im Ringzentrum. Im Fall des Diazirin sind diese MO's durch das einsame Elektronenpaar des Stickstoffs gestört. Drei MO's tragen zu der Beschreibung der einsamen Elektronenpaare bei, die auch alle in gewissem Maß zur Ringbindung beitragen. Darüber hinaus liegen zwei davon unter dem  $\pi$ -Niveau, eines ist energetisch sehr niedrig, im Gegensatz zum üblichen Bild. Das hier diskutierte Bindungsmodell wurde mit früheren semiempirischen Modellen verglichen (ins-

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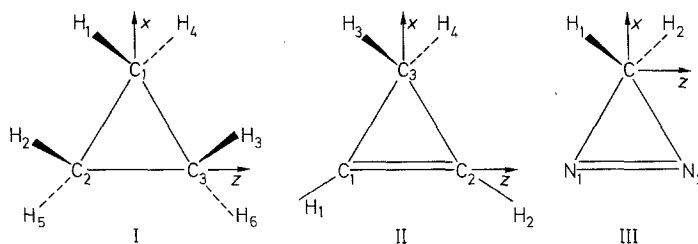
besondere den Modellen von Coulson-Moffitt und von Walsh). Die Spannung, der  $\pi$ -Charakter und die Eigenschaften der Konjugation der Dreieringe werden auf Grund der Elektronenstruktur diskutiert. Die besonderen Bindungseigenschaften sprechen für einen pseudo  $\pi$ -Charakter ( $\psi - \pi$ ), die Ringbindungen können als  $\psi - \pi$ -Bindungen betrachtet werden.

La structure électronique du cyclopropane, du cyclopropène et de la diazirine a été étudiée dans le cadre théorique *ab initio* SCF-LCAO-MO. Les résultats obtenus fournissent un modèle de liaison pour les cycles à trois chaînons. La nature des liaisons a été étudiée à l'aide des OM, des analyses de population et de diagrammes de densité électronique. La distribution des densités électroniques totales conduit à un modèle «liaison courbe» + «cavité centrale»; cependant l'angle de courbure n'est que de  $5^\circ$  et la cavité centrale n'est pas très profonde par rapport aux liaisons (dépression d'environ 15%). La nature des liaisons formant le cycle a été considérée tout spécialement. Trois OM contribuent principalement aux liaisons du cycle: (1) Une OM basse en énergie ( $3a_1$ ), formée principalement d'OA C(2s) et fournissant de la densité électronique principalement à l'intérieur du triangle. (2) Deux OM ( $6a_1$  et  $3b_2$ ), les deux OM de plus haute énergie dans le cyclopropane et celles situées immédiatement en dessous de l'orbitale  $\pi$  dans le cyclopropène, formées presque exclusivement d'OA C(2p) dans le plan du cycle, et présentant leur maximum de densité électronique à l'extérieur du cycle (angle de courbure des densités d'environ  $20^\circ$ ) et une densité nulle au centre du cycle. Dans le cas de la diazirine ces OM sont fortement perturbées par la présence des doublets libres de l'azote. Trois OM contribuent principalement à la description des doublets libres, tout en participant plus ou moins à des liaisons du cycle. Deux de ces OM sont d'énergie inférieure à la liaison  $\pi$ , l'une des deux est tout spécialement basse en énergie. Ce résultat diffère notablement de l'idée que l'on se fait ordinairement de la nature des doublets libres. Le modèle de liaison obtenu dans ce travail est comparé à des modèles semi-empiriques antérieurs (principalement les modèles de Coulson-Moffitt et de Walsh). La tension, le caractère " $\pi$ " et l'aptitude à la conjugaison du cycle à trois chaînons sont discutées à l'aide de sa structure électronique. Les caractères particuliers des liaisons dans ce système lui confèrent un caractère pseudo- $\pi(\psi - \pi)$ , les liaisons du cycle pouvant être considérées comme des liaisons  $\psi - \pi$ .

## 1. Introduction

The chemistry of strained, small ring systems has attracted much interest and a tremendous amount of work has been published and is still going on in this area [1]. The question of the ground state electronic structure of these systems has been subjected to numerous studies of semi-empirical type.

In view of the very broad interest of theoretical studies of small ring molecules we undertook an *ab initio* SCF-LCAO-MO study of three such compounds: cyclopropane I, cyclopropene II, and diazirine III.



The electronic structures of cyclopropane [2-7] and of cyclopropene [8] have been studied within the hybridization scheme using the maximum overlap or the minimum energy criteria [2-8]. The resulting description is based on the "bent-bond" model introduced by Coulson and Moffitt [2]. An alternative model, which can be transformed into the bent-bond one [9], has been proposed by Walsh [10].

Various types of semi-empirical molecular orbital calculations (EHT, CNDO, modified PPP ...) have also been performed on cyclopropane [11–17], cyclopropene [16, 18] and diazirine [19]. The Floating Spherical Gaussian Model (FSGO) has been applied to cyclopropane [20]. Finally *ab initio* SCF-LCAO-MO calculations have recently been performed on cyclopropane [21, 22]. A different basis set has been used in the present calculation of cyclopropane and the computed total energy is nearer to the Hartree-Fock limit than the values previously reported [21, 22]. Furthermore no study of this type has been published on cyclopropene or on diazirine.

## 2. Results

### 2.1. Method of Calculation

The present calculations are of the SCF-LCAO-MO type using a basis set of gaussian functions. The CDC 3600 version of the IBMOL program has been used<sup>1</sup>.

Table 1. Total energy components and orbital energies calculated for cyclopropane, cyclopropene and diazirine (in a. u.)<sup>a</sup>

	Cyclopropane		Cyclopropene		Diazirine	
$T$	116.7766		115.6651		147.6529	
$V_{nn}$	74.9756		63.6956		63.8985	
$V_{ne}$	-421.2331		-396.0908		-472.6353	
$V_{ee}$	112.4892		100.9729		113.3859	
$E_{\text{tot}}$	-116.9918		-115.7572		-147.6980	
$\epsilon$	$1a_1$	-11.2515	$1a_1$	-11.2792	$1a_1$	-15.7282
	( $1a'_1$ )					
	$2a_1$	-11.2507	$1b_2$	-11.2771	$1b_2$	-15.7266
	( $1e'$ )					
	$1b_2$	-11.2507	$2a_1$	-11.2669	$2a_1$	-11.3530
	( $1e'$ )					
	$3a_1$	-1.1412	$3a_1$	-1.1906	$3a_1$	-1.5467
	( $2a'_1$ )					
	$4a_1$	-0.8233	$4a_1$	-0.8379	$4a_1$	-0.9521
	( $2e'$ )					
	$2b_2$	-0.8233	$2b_2$	-0.7750	$2b_2$	-0.8744
	( $2e'$ )					
	$1b_1$	-0.6838	$5a_1$	-0.6936	$1b_1$	-0.7112
	( $1a''_2$ )					
	$5a_1$	-0.6139	$1b_1$	-0.6111	$5a_1$	-0.6776
	( $3a'_1$ )					
	$1a_2$	-0.5274	$6a_1$	-0.5029	$6a_1$	-0.5897
	( $1e''$ )					
	$2b_1$	-0.5274	$3b_2$	-0.4354	$2b_1$	-0.5111
	( $1e''$ )					
	$3b_2$	-0.4229	$2b_1$	-0.3701	$3b_2$	-0.4347
	( $3e'$ )					
	$6a_1$	-0.4229				
	( $3e'$ )					

<sup>a</sup> In the case of cyclopropane, the  $D_{3h}$  notation of the MO's is given in parentheses.

<sup>1</sup> Information about this version may be obtained from Dr. A. Veillard, Centre de Calcul, C.R.N., B.P. 20 CR, 67-Strasbourg-3, France.

Table 2. Cyclopropane. a) Atomic population analysis. b) Overlap populations

a) Atomic orbitals	Molecular orbitals										total	Total atomic populations (net charge)		
	1a <sub>1</sub> (1a <sub>1</sub> )	2a <sub>1</sub> (1e')	1b <sub>2</sub> (1e')	3a <sub>1</sub> (2a <sub>1</sub> )	4a <sub>1</sub> (2e')	2b <sub>2</sub> (2e')	1b <sub>1</sub> (1a <sub>2</sub> )	5a <sub>1</sub> (3a <sub>1</sub> )	1a <sub>2</sub> (1e'')	2b <sub>1</sub> (1e'')			3b <sub>2</sub> (3e')	6a <sub>1</sub> (3e')
C <sub>1</sub> 1s+2s	0.667	1.333	0.000	0.486	0.723	0.000	0.000	0.041	0.000	0.000	0.000	0.003	{1.981 (1s) 1.272 (2s)}	C <sub>1</sub> , C <sub>2</sub> , C <sub>3</sub> : 6.438 (-0.438)  H <sub>1</sub> -H <sub>6</sub> : 0.781 (+0.219)
C <sub>2</sub> , C <sub>3</sub> 1s+2s	0.667	0.333	1.000	0.486	0.181	0.543	0.000	0.041	0.000	0.002	0.002	0.001	{1.981 (1s) 1.272 (2s)}	
H <sub>1</sub> , H <sub>4</sub>	0.000	0.000	0.000	0.035	0.191	0.000	0.088	0.092	0.000	0.318	0.000	0.057	0.781	
H <sub>2</sub> , H <sub>3</sub> , H <sub>5</sub> , H <sub>6</sub>	0.000	0.000	0.000	0.035	0.048	0.143	0.088	0.092	0.239	0.079	0.042	0.014	0.781	
C <sub>1</sub> 2p <sub>x</sub>	0.000	0.000	0.000	0.109	0.106	0.000	0.000	0.442	0.000	0.000	0.000	0.295	0.953	
2p <sub>y</sub>	0.000	0.000	0.000	0.000	0.000	0.000	0.490	0.000	0.000	0.697	0.000	0.000	1.187	
2p <sub>z</sub>	0.000	0.000	0.000	0.000	0.000	0.122	0.000	0.000	0.000	0.000	0.922	0.000	1.045	
C <sub>2</sub> , C <sub>3</sub> 2p <sub>x</sub>	0.000	0.000	0.000	0.027	0.118	0.000	0.000	0.110	0.000	0.000	0.428	0.337	1.022	
2p <sub>y</sub>	0.000	0.000	0.000	0.000	0.000	0.000	0.490	0.000	0.523	0.174	0.000	0.000	1.187	
2p <sub>z</sub>	0.000	0.000	0.000	0.082	0.000	0.110	0.000	0.332	0.000	0.000	0.024	0.428	0.976	
b) Bonds	Total overlap populations													
C <sub>1</sub> -C <sub>2</sub>	0.000	0.000	0.000	0.262	-0.090	0.066	0.131	0.061	0.000	-0.1533	0.271	-0.170	0.378	
C <sub>2</sub> -C <sub>3</sub>	0.000	0.000	0.001	0.262	0.144	-0.167	0.131	0.061	-0.230	0.0767	-0.392	0.492	0.378	
C <sub>1</sub> -H <sub>1</sub>	0.000	0.000	0.000	0.031	0.220	0.000	0.086	0.104	0.000	0.3175	0.000	-0.002	0.758	
C <sub>2</sub> -H <sub>2</sub>	0.000	0.000	0.000	0.031	0.055	0.165	0.086	0.104	0.238	0.0794	-0.001	-0.000	0.758	
Total <sup>a</sup>	0.000	0.001	0.001	1.087	0.620	0.620	0.997	0.642	0.489	0.4866	0.124	0.124		

<sup>a</sup> Including overlap populations between non-bonded atoms.

Table 3. Cyclopropene. a) Atomic population analysis. b) Overlap populations

a) Atomic orbitals	Molecular orbitals										total	Total atomic populations (net charge)	
	1a <sub>1</sub>	1b <sub>2</sub>	2a <sub>1</sub>	3a <sub>1</sub>	4a <sub>1</sub>	2b <sub>2</sub>	5a <sub>1</sub>	1b <sub>1</sub>	6a <sub>1</sub>	3b <sub>2</sub>			2b <sub>1</sub>
C <sub>1</sub> , C <sub>2</sub> 1s + 2s	0.999	1.000	0.001	0.479	0.161	0.405	0.100	0.000	-0.001	0.031	0.000	1s 1.981 2s 1.194	C <sub>1</sub> , C <sub>2</sub> : 6.274 (-0.274)
C <sub>3</sub> 1s + 2s	0.003	0.000	1.997	0.368	0.764	0.000	0.094	0.000	-0.003	0.000	0.000	1s 1.981 2s 1.242	C <sub>3</sub> : 6.389 (-0.389)
H <sub>1</sub> , H <sub>2</sub>	0.000	0.000	0.000	0.051	0.057	0.283	0.224	0.000	0.029	0.095	0.000	0.739	
H <sub>3</sub> , H <sub>4</sub>	0.000	0.000	0.000	0.026	0.193	0.000	0.058	0.273	0.089	0.000	0.153	0.793	
C <sub>1</sub> , C <sub>2</sub> 2p <sub>x</sub>	0.000	0.000	0.000	0.042	0.151	0.003	0.110	0.000	0.327	0.397	0.000	1.030	H <sub>1</sub> , H <sub>2</sub> : 0.739 (+0.261)
2p <sub>y</sub>	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.171	0.000	0.000	0.803	0.974	
2p <sub>z</sub>	0.000	0.000	0.000	0.162	0.009	0.253	0.374	0.000	0.296	0.002	0.000	1.096	
C <sub>3</sub> 2p <sub>x</sub>	0.000	0.000	0.000	0.112	0.094	0.000	0.174	0.000	0.523	0.000	0.000	0.904	H <sub>3</sub> , H <sub>4</sub> : 0.793 (+0.207)
2p <sub>y</sub>	0.000	0.000	0.000	0.000	0.000	0.000	0.000	1.110	0.000	0.000	0.000	1.199	
2p <sub>z</sub>	0.000	0.000	0.000	0.000	0.000	0.113	0.000	0.000	0.000	0.949	0.000	1.062	
b) Bonds	Total overlap populations												
C <sub>1</sub> -C <sub>2</sub>	0.001	0.001	0.000	0.410	0.211	0.013	0.010	0.050	0.343	-0.742	0.511	0.807	{σ 0.247 {π 0.560
C <sub>1</sub> -C <sub>3</sub>	0.000	0.000	0.000	0.238	-0.061	0.061	-0.012	0.120	-0.068	0.266	-0.150	0.393	
C <sub>1</sub> -H <sub>1</sub>	0.000	0.000	0.000	0.025	0.060	0.294	0.272	0.000	0.020	0.034	0.000	0.705	
C <sub>3</sub> -H <sub>3</sub>	0.000	0.000	0.000	0.020	0.218	0.000	0.077	0.271	0.069	0.000	0.125	0.781	
Total <sup>a</sup>	0.001	0.001	0.001	1.087	0.661	0.750	0.605	0.858	0.321	-0.139	0.127		

<sup>a</sup> Including overlap populations between non-bonded atoms.

Table 4. Diazirine. a) Atomic population analysis. b) Overlap populations

a) Atomic orbitals	Molecular orbitals										total	Total atomic populations (net charge)	
	1a <sub>1</sub>	1b <sub>2</sub>	2a <sub>1</sub>	3a <sub>1</sub>	4a <sub>1</sub>	2b <sub>2</sub>	1b <sub>1</sub>	5a <sub>1</sub>	6a <sub>1</sub>	2b <sub>1</sub>			3b <sub>2</sub>
N <sub>1</sub> , N <sub>2</sub> 1s + 2s	1.000	1.000	0.000	0.687	0.053	0.788	0.000	0.000	0.207	0.000	0.068	1.977 (1s)	N <sub>1</sub> , N <sub>2</sub> 7.163 (-0.163)
C <sub>3</sub> 1s + 2s	0.000	0.000	2.000	0.051	1.019	0.000	0.000	0.116	0.017	0.000	0.000	1.891 (2s) 1.981 (1s) 1.223 (2s)	
H <sub>1</sub> , H <sub>2</sub>	0.000	0.000	0.000	0.015	0.186	0.000	0.171	0.124	0.019	0.227	0.000	0.742	
N <sub>1</sub> , N <sub>2</sub> 2p <sub>x</sub>	0.000	0.000	0.000	0.033	0.209	0.028	0.000	0.458	0.002	0.000	0.471	1.201	H <sub>1</sub> , H <sub>2</sub> : 0.743 (+0.257)
2p <sub>y</sub>	0.000	0.000	0.000	0.000	0.000	0.000	0.343	0.000	0.000	0.633	0.000	0.975	
2p <sub>z</sub>	0.000	0.000	0.000	0.209	0.039	0.079	0.000	0.006	0.717	0.000	0.069	1.119	
C <sub>3</sub> 2p <sub>x</sub>	0.000	0.000	0.000	0.062	0.006	0.000	0.000	0.578	0.092	0.000	0.000	0.738	H <sub>1</sub> , H <sub>2</sub> : 0.743 (+0.257)
2p <sub>y</sub>	0.000	0.000	0.000	0.000	0.000	0.000	0.973	0.000	0.000	0.281	0.000	1.254	
2p <sub>z</sub>	0.000	0.000	0.000	0.000	0.000	0.210	0.000	0.000	0.000	0.000	0.782	0.992	
b) Bonds	Total overlap populations												
N-N	0.000	0.002	0.000	0.659	0.204	-0.800	0.110	0.227	-0.110	0.345	-0.261	0.376	σ -0.079 π 0.455
C-N	0.000	0.000	0.000	0.068	-0.026	0.124	0.160	-0.032	0.038	-0.178	0.045	0.200	
C-H	0.000	0.000	0.000	0.000	0.209	0.000	0.184	0.158	0.011	0.195	0.000	0.758	
Total <sup>a</sup>	0.000	0.002	0.001	0.841	0.594	-0.553	0.822	0.417	-0.020	0.184	-0.171		

<sup>a</sup> Including overlap populations between non-bonded atoms.

Table 5. *Molecular properties of cyclopropane, cyclopropene and diazirine. Calculated and experimental (in brackets [ ]) values*

Properties	Cyclopropane	Cyclopropene	Diazirine
Total molecular energy	-116.9918 a. u. [-117.5760 a. u.] <sup>a</sup>	-115.7572 a. u. [-116.3252 a. u.] <sup>a</sup>	-147.6980 a. u. [-148.3469 a. u.] <sup>a</sup>
Binding energy	0.9403 a. u. [1.2945 a. u.] <sup>a</sup>	0.7043 a. u. [1.0426 a. u.] <sup>a</sup>	0.223 a. u. [0.6719 a. u.] <sup>a</sup>
Dipole moment	0.0 <i>D</i>	0.47 <i>D</i> [0.45 <i>D</i> ] <sup>b</sup>	2.47 <i>D</i> [1.59 <i>D</i> ] <sup>c</sup>
Ionization potentials	11.51(2) eV [9.96 eV] <sup>d</sup> 14.35(2) eV [11.05 eV] 16.70 eV [12.27 eV] 18.60 eV [15.17 eV] 22.40(2) eV [16.52 eV] 31.05 eV [18.8 eV]	10.07 eV [9.95 eV] <sup>e</sup>	11.83 eV [10.18 eV] <sup>f</sup>

<sup>a</sup> See text. - <sup>b</sup> Ref. [27]. - <sup>c</sup> Ref. [28]. - <sup>d</sup> Ref. [33]. For the assignment of the ionization potentials see § 3.1. - <sup>e</sup> Ref. [35]. - <sup>f</sup> Ref. [36].

The gaussian basis set employed consists of 9 *s* and 5 *p* orbitals for carbon and for nitrogen, and of 4 *s* orbitals for hydrogen. The exponents of the gaussian functions are taken from the work of Huzinaga [23]. In this way basis sets of 96, 88 and 80 gaussian functions are obtained for compounds I, II and III respectively. "Contracted" basis functions [24] are then constructed by linear combination of these gaussian functions. The coefficients of the gaussian functions in the contracted functions are also taken from the atomic functions [23]. The basis set of "contracted" functions consists of 4 *s* and 2 *p* functions for carbon and nitrogen and 2 *s* functions for hydrogen. These basis sets have already been described previously [25]. The contracted basis sets thus contain 42, 38 and 34 contracted gaussian for cyclopropane, cyclopropene and diazirine respectively. These contracted gaussian functions are then converted into symmetry-adapted functions. The cyclopropane molecule has been treated as a system of  $C_{2v}$  symmetry like cyclopropene and diazirine. The irreducible representations of the  $D_{3h}$  group to which the MO's would belong are also indicated in Tables 1 and 2.

The bond lengths and bond angles for cyclopropane I [26], cyclopropene II [27] and diazirine III [28] are taken from the literature.

## 2.2. Results of the Computations

Table 2 lists the total energy, the energy components and the orbital energies for the three molecules I-III. Tables 2-4 list the atomic population analyses and the overlap populations for these compounds. Figs. 1-7 represent various electronic distribution diagrams. In all cases, the first three MO's which are strongly localized and nearly pure AO's, have been subtracted so as to clear up the diagrams. Table 5 lists the calculated and the experimental molecular properties (total energy, dipole moment, ionization potentials) for the three compounds<sup>2</sup>.

<sup>2</sup> Additional results, such as expansion coefficients for the MO's, may be obtained from the authors. The electron densities as given in the Figs. 1-7 are in electrons per (a.u.)<sup>3</sup> for mono-electronic orbitals. Total densities for doubly occupied MO's are obtained by multiplying the given numbers by two.

### 3. Discussion

Before discussing our results it seems desirable to consider briefly the significance of these calculations. According to the results obtained for the atoms [23] it would be necessary to use eleven gaussian *s* functions and seven *p* functions for carbon and nitrogen and six *s* functions for hydrogen in order to obtain a wave function which would be very near to the Hartree-Fock limit. The inclusion of polarisation functions (2*p* on hydrogen, 3*d* on carbon and nitrogen) would also be needed. However such large basis sets would require very long computer times. The problem of the contraction of the basis set may also be considered briefly. A detailed study has shown that the contraction *per se* does not seriously affect the quality of the calculation; however the choice of an unbalanced contraction may lead to poor results [29] (see also [24]).

In view of the results discussed below it would seem that the total energies obtained should not be off the Hartree-Fock limit by more than a few tenths of the atomic units. Accordingly the molecular properties calculated should be fairly representative of the real properties of these molecules.

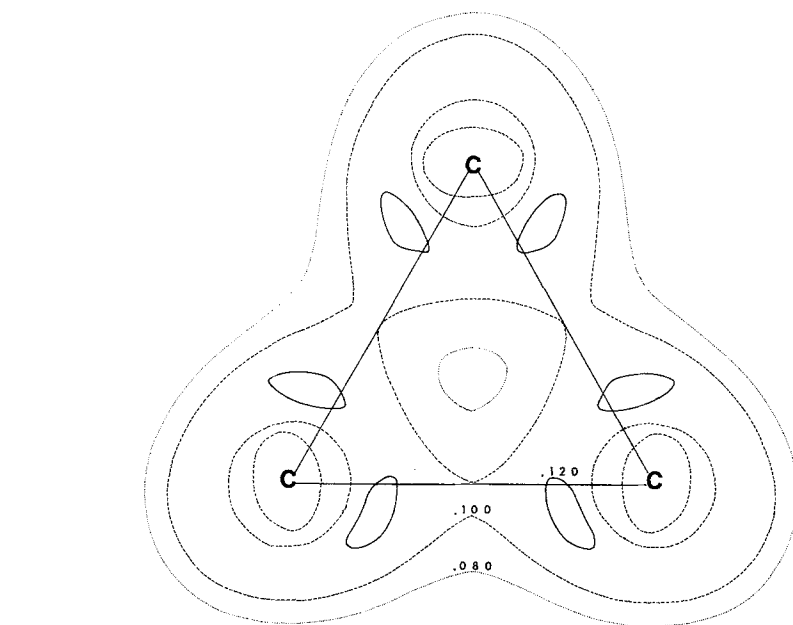
#### 3.1. Cyclopropane. Ground State

The *total molecular energy* obtained for cyclopropane is of  $-116.992$  a. u. This is the lowest value reported so far; previous *ab initio* SCF calculations using gaussian functions [21] or gaussian lobe functions [22] lead to higher total energies. The total experimental energy is of  $-117.576$  a. u.; it has been obtained from the ionisation potentials of the atoms [30], from the dissociation energies into atoms of the elements in their standard state [31] and from the heat formation of cyclopropane from the elements in their standard state [32]<sup>3</sup>. Using the theoretical energy of the separated atoms (calculated with the same basis set [23]) the binding energy is found equal to  $0.94$  a. u. as compared to an experimental values of  $1.29$  a. u. (see Table 5). The monoelectronic *molecular orbital energies* are given in Table 1. There are four pairs of degenerate MO's. The energies obtained are similar to those of Buenker, Peyerimhoff, and Whitten [22].

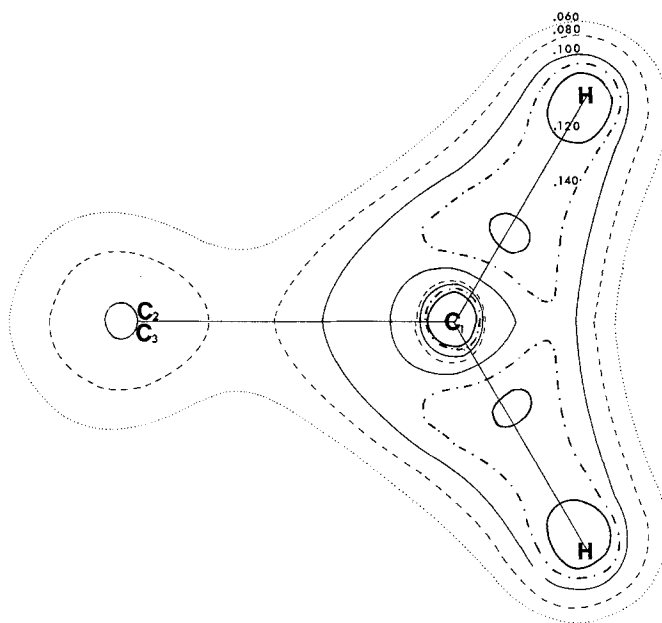
The *dipole moment* is zero by symmetry. The *ionization potentials* present an interesting feature. The ionization potentials from the first two, doubly degenerated, levels differ markedly from the experimental values [33]. However, the two next ones are in very good agreement with the fifth and sixth experimental ionization potentials (see Table 5). One is then tempted to suggest that the two doubly degenerate potentials (i. e. altogether four levels) correspond to the first four experimental potentials. This might mean that the disagreement between calculated and experimental values arises from a splitting of the doubly degenerate levels of the parent molecule each into two levels in the derived radical cation; such a splitting might originate in a Jahn-Teller distortion of the radical cation which removes the degeneracy and leads to four ionization potentials. Further experimental and theoretical results are needed for an interpretation of this phenomenon to be given.

<sup>3</sup> All calculations have been performed for a temperature of  $298^\circ$  K, as the heat of formation of cyclopropane is given for that temperature [32].





a



b

Fig. 1. Total electronic density distributions in cyclopropane I: a) in the plane of the ring ( $xy$ ); b) in the  $xy$  plane perpendicular to the ring. The densities from the  $1a_1$ ,  $2a_1$  and  $1b_2$  MO's have been subtracted

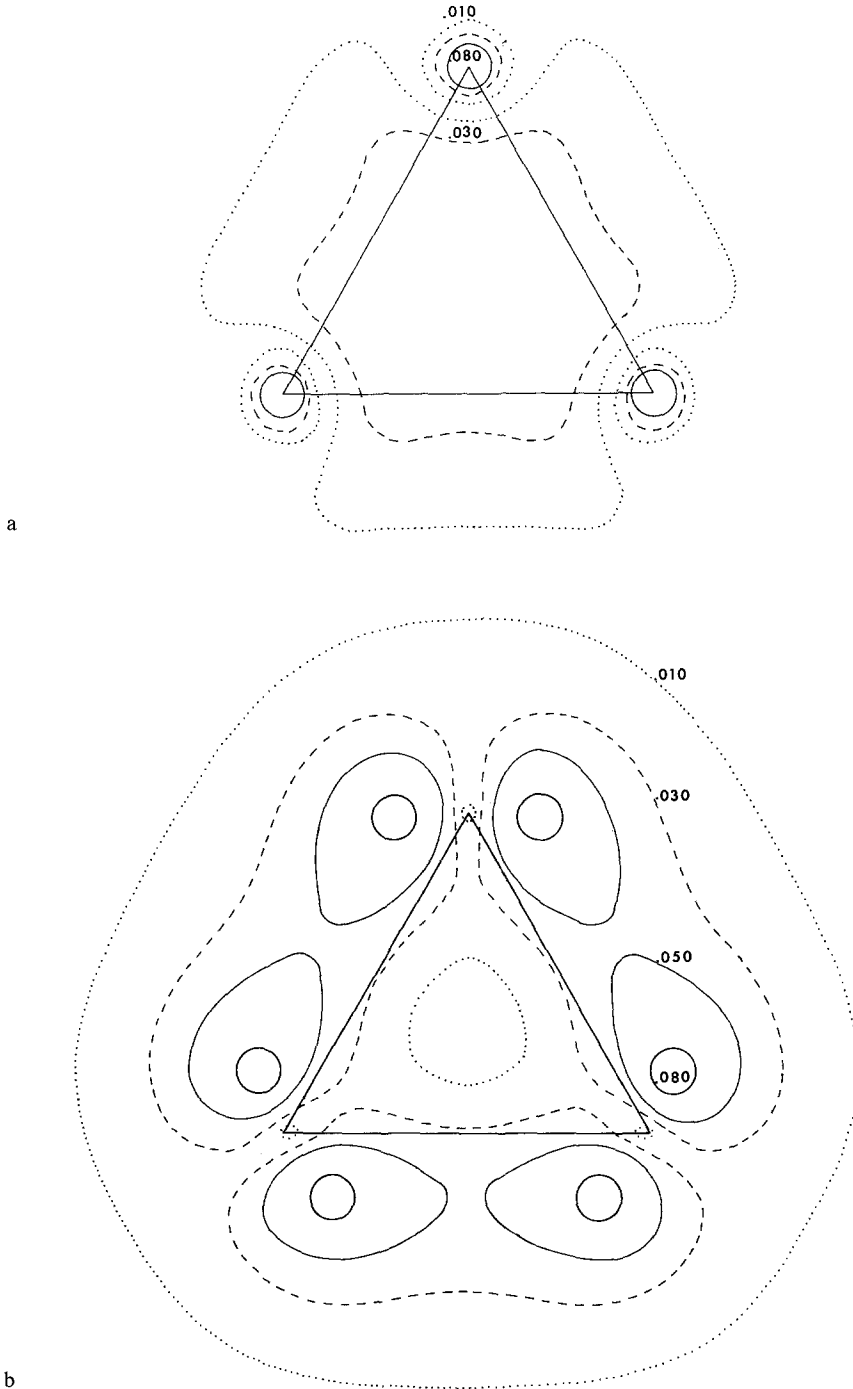
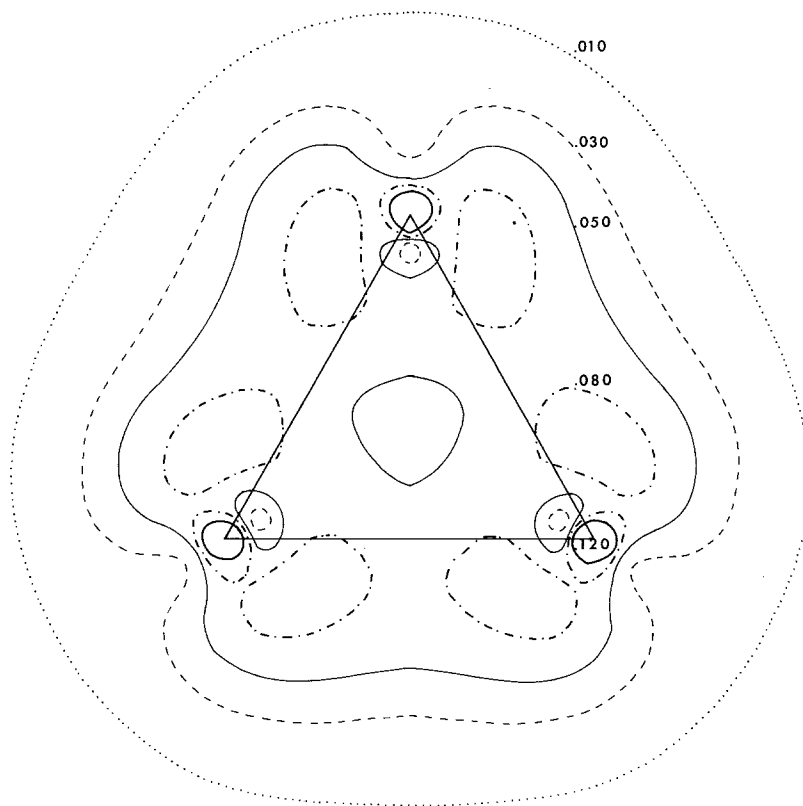
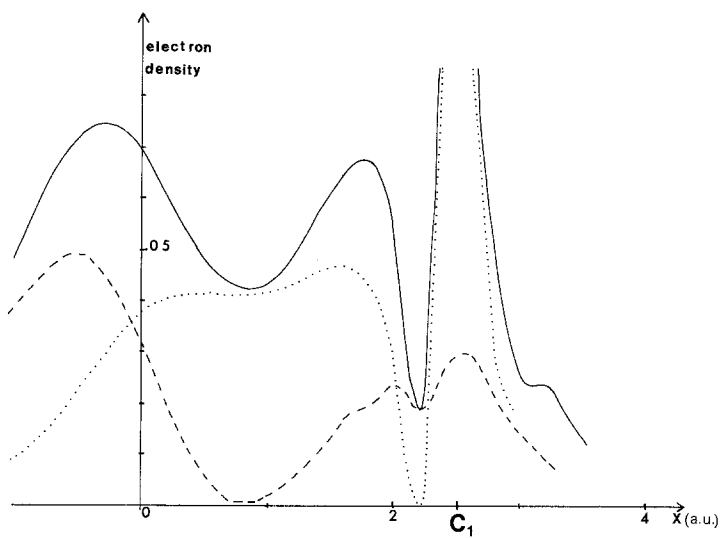


Fig. 2. Electronic density distribution in the ring bond MO's of cyclopropane: a) "internal" MO  $3a_1$  ( $2a_1'$ ); b) "external" MO's  $6a_1 + 3b_2$  ( $3e'$ ); c)  $3a_1 + 6a_1 + 3b_2$ ; d) electron density distribution along x axis for the MO's  $3a_1$  (...),  $6a_1 + 3b_2$  (- - -) and  $3a_1 + 6a_1 + 3b_2$  (—)



c



d

### *Electronic Structure of the Ground State of Cyclopropane*

The nature of the *molecular orbitals* of cyclopropane may be studied by making use of the population analyses given in Table 2 and of the expansion coefficients of the AO's in the MO's. There are three MO's describing mainly the ring C–C bonds:  $3a_1$  ( $2a_1'$ ), low lying MO containing mainly C(2s) AO's (73% s);  $3b_2$  ( $3e'$ ) and  $6a_1$  ( $3e'$ ), the two highest occupied MO's containing mainly C( $2p_x + 2p_y$ ) AO's (91%). Six MO's describe principally the six C–H bonds:  $4a_1$  ( $2e'$ ),  $2b_2$  ( $2e'$ ),  $1b_1$  ( $1a_2''$ ),  $5a_1$  ( $3a_1'$ ),  $1a_2$  ( $1e''$ ) and  $2b_1$  ( $1e''$ ). Adding together the C(s) and C(2p) populations within these two groups of MO's leads to an  $sp^{2.7}$  character for the carbon charge distribution in the orbitals forming the ring and to an  $sp^{2.4}$  character for the carbon charge distribution in the C–H bonds.

The *atomic population* analysis (Table 2) leads to a negative charge ( $-0.44 e$ ) for the carbon atoms and to a positive charge ( $+0.23 e$ ) for the hydrogens.

C–C *overlap population* analysis (Table 2) is quite low, in agreement [8] with the weakening of these bonds in the strained cyclopropane molecule.

The *electron density distributions* (Figs. 1, 2 and 7) will be discussed below (§ 3.4).

### 3.2. Cyclopropene. Ground State

The *total molecular energy* calculated for cyclopropene amounts to  $-115.757$  a. u. The total experimental energy is of  $-116.325$  a. u. and has been obtained in the same way as for cyclopropane (*vide supra*), using the experimental heat of formation [34]. The calculated binding energy amounts to  $0.704$  a. u. as compared to an experimental value of  $1.043$  a. u. (see Table 5).

The calculated *dipole moment* amounts to  $|0.47| D$ . The direction of the computed moment is from the double bond (positive end) towards the  $\text{CH}_2$  group ( $\mu_x = -0.47 D$ ;  $\mu_y = \mu_z = 0$ ).

The calculated first *ionization potential* is equal to  $10.07$  eV as compared to an experimental value of  $9.95$  eV [35] (Table 5).

### *Electronic Structure of the Ground State of Cyclopropene*

The electronic structure of the cyclopropene ground state may be studied by means of the molecular orbitals, the population analysis and the electron density maps. The nature of the *molecular orbitals* and of the *bonding* may be discussed using the population analyses of Table 3. The MO's of type  $a_1$  (except  $4a_1$ ) and  $b_2$  contribute mainly to the C–C  $\sigma$ -bonds forming the ring system:  $3a_1$  (66% C(2s)),  $6a_1$  (88% C(2p)) and  $3b_2$  (87% C(2p)), and to the vinylic  $\text{C}_1\text{--H}_1$  and  $\text{C}_2\text{--H}_2$   $\sigma$ -bonds ( $2b_2$ ,  $5a_1$ ).

On the other hand, the  $\text{C}_1\text{C}_2$   $\pi$ -bond and the  $\text{C}_3\text{--H}_3$  and  $\text{C}_3\text{--H}_4$   $\sigma$ -bonds are described by the MO's of type  $b_1$  and by  $4a_1$ . It is clearly apparent that the  $\pi$ -bond ( $2b_1$  mainly) is *delocalized* over the two C–H bonds of the methylene group, and conversely one ( $1b_1$ ) of the MO's ( $1b_1$ ,  $4a_1$ ) which give the largest contributions to these C–H bonds is delocalized over the  $\text{C}_1\text{C}_2$   $\pi$ -bond.

The *atomic population* analysis (Table 3) shows that the carbon atoms bear a negative charge and the hydrogens a positive one. The carbon atoms  $C_1$  (or  $C_2$ ) and  $C_3$  have the following charge distributions (Table 3):

$$C_1: 1s^{1.98} 2s^{1.19} 2p\sigma^{2.13} 2p\pi^{0.97}, C_3: 1s^{1.98} 2s^{1.24} 2p\sigma^{1.97} 2p\pi^{1.20}.$$

It is seen that  $C_1$  and  $C_2$  are  $\sigma$  acceptors (0.32 e each) and very weak  $\pi$  donors (0.03 e each); on the other hand  $C_3$  is a  $\sigma$  acceptor (0.21 e) and a  $\pi$ -acceptor (0.20 e).

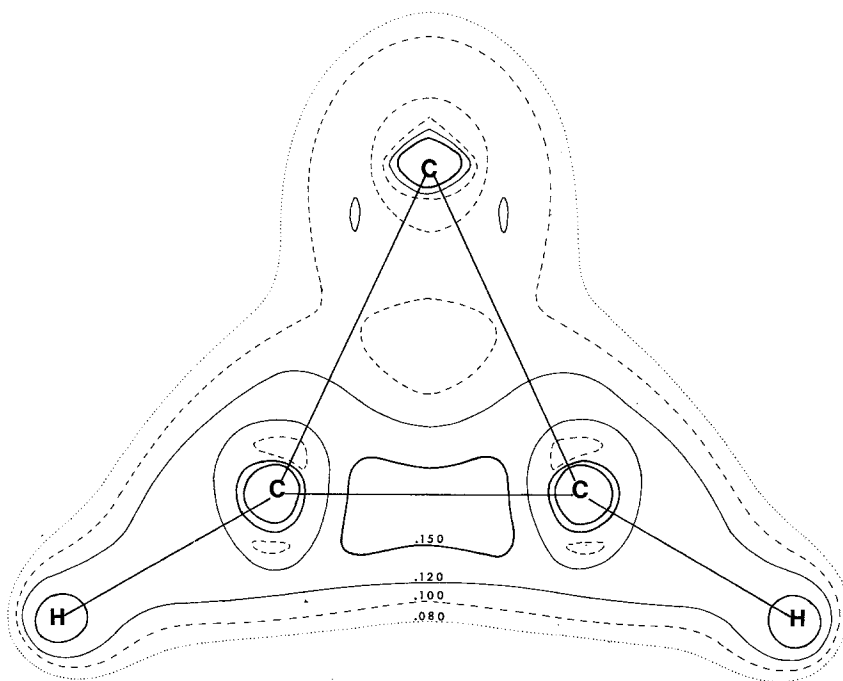


Fig. 3. Total electronic density distribution in the plane ( $xz$ ) of the ring in cyclopropene II ( $1a_1$ ,  $1b_2$  and  $2a_1$  MO's subtracted)

The total *overlap populations* (Table 3) of the C–C bonds are quite low in agreement with the fact that the system is very strained as in the case of cyclopropane. It is interesting to note that the overlap population of the C–C single bonds ( $C_1$ – $C_3$ ) and ( $C_2$ – $C_3$ ) is slightly higher than in cyclopropane (Table 2). The decomposition into  $\sigma$  and  $\pi$  overlap populations shows that the  $C_1=C_2$  double bond is two times more  $\pi$ -bonding than  $\sigma$ -bonding.

The total *electron density* diagrams (Figs. 3, 7b) will be discussed below (§ 3.4). The electronic distributions in the plane  $xy$  perpendicular to the ring (Fig. 4) show clearly the delocalization of the electron density over the  $C_1=C_2$   $\pi$  bond and the C–H bonds of the  $CH_2$  groups.

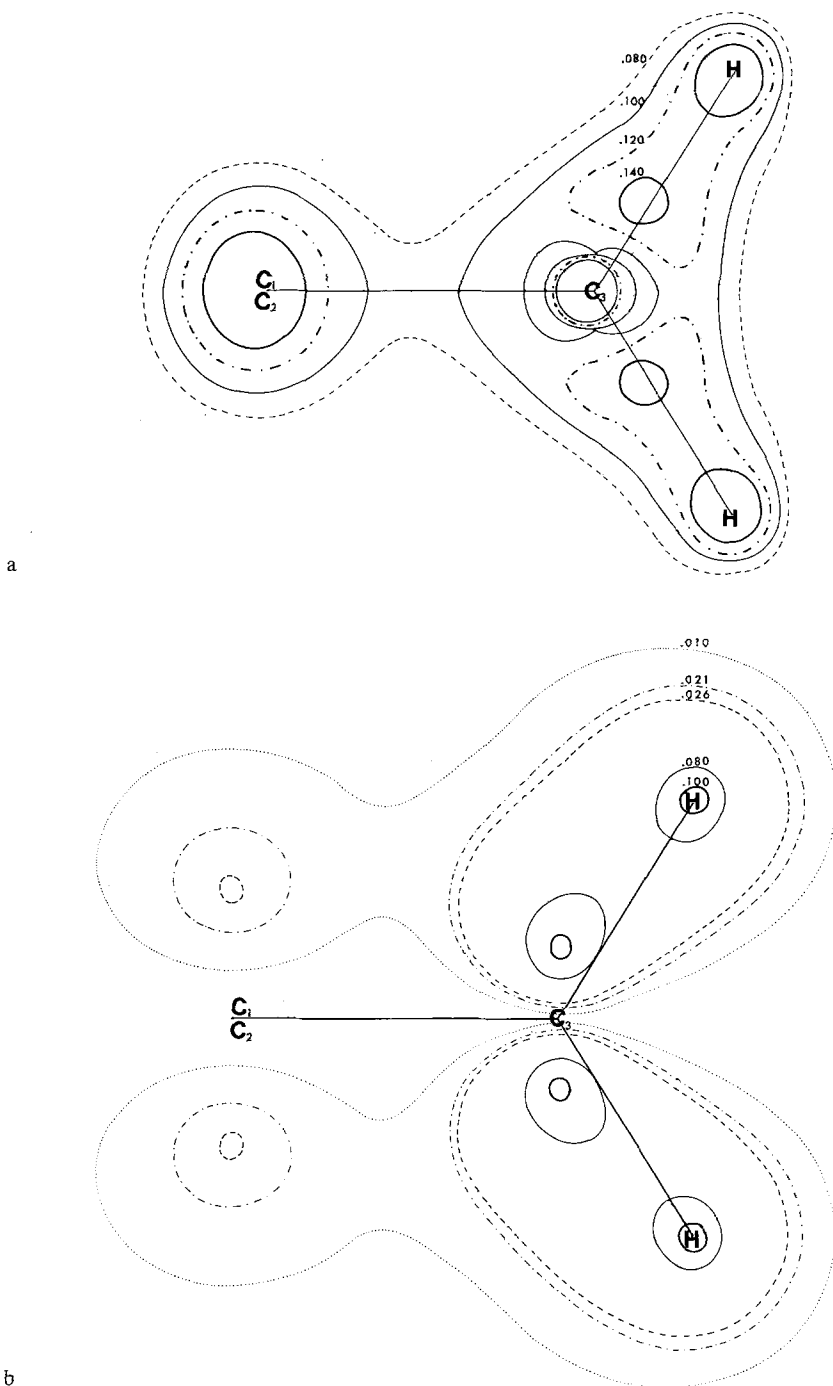


Fig. 4. Electronic density distributions in the xy plane perpendicular to the ring in cyclopropene II: a) total electronic density ( $1a_1$ ,  $1b_2$  and  $2a_1$  MO's subtracted); b) electronic density in the  $\pi$ -type MO's,  $1b_1 + 2b_1$

### 3.3. Diazirine. Ground State

The calculated *total molecular energy* of diazirine amounts to  $-147.698$  a. u., as compared to an experimental energy of  $-148.347$  a. u. obtained in the same way as for cyclopropane (see § 3.1) using the estimated heat of formation [36]. The calculated binding energy is equal to  $0.223$  a. u., the experimental value being  $0.672$  a. u. (see Table 5).

The calculated *dipole moment* ( $2.47 D$ ;  $\mu_x = 2.47 D$ ;  $\mu_y = \mu_z = 0$ ;  $\text{CH}_2(+)$   $\rightarrow$   $\text{N}=\text{N}(-)$ ) and first *ionization potential* ( $11.82$  eV) are quite different from the experimental values ( $1.59 D$  [28] and  $10.18$  eV [36] respectively). The disagreement is especially important in the case of the dipole moment; its origin is not clear but including polarization function into the basis set would probably improve the situation. An ionization potential of  $12.78$  eV has been obtained by an Extended Hückel type calculation [19].

#### *Electronic Structure of the Ground State of Diazirine*

The *nature of the molecular orbitals* of the ground state of diazirine may be discussed using the population analyses (Table 4). It is apparent that all the MO's have been more or less strongly perturbed with respect to cyclopropene by the introduction of the nitrogen atoms. The description of the ring bonds is much less well defined in diazirine than in cyclopropene. This seems to be due to the presence of the *nitrogen lone pairs*. The MO's  $2b_2$ ,  $6a_1$  and  $3b_2$  which are strongly

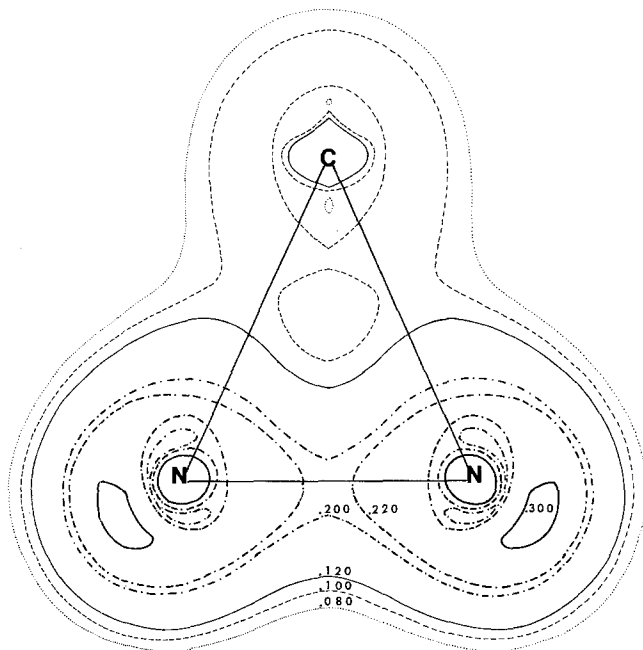


Fig. 5. Total electronic density distribution in the plane ( $xz$ ) of the ring in diazirine III ( $1a_1$ ,  $1b_2$  and  $2a_1$  MO's subtracted)

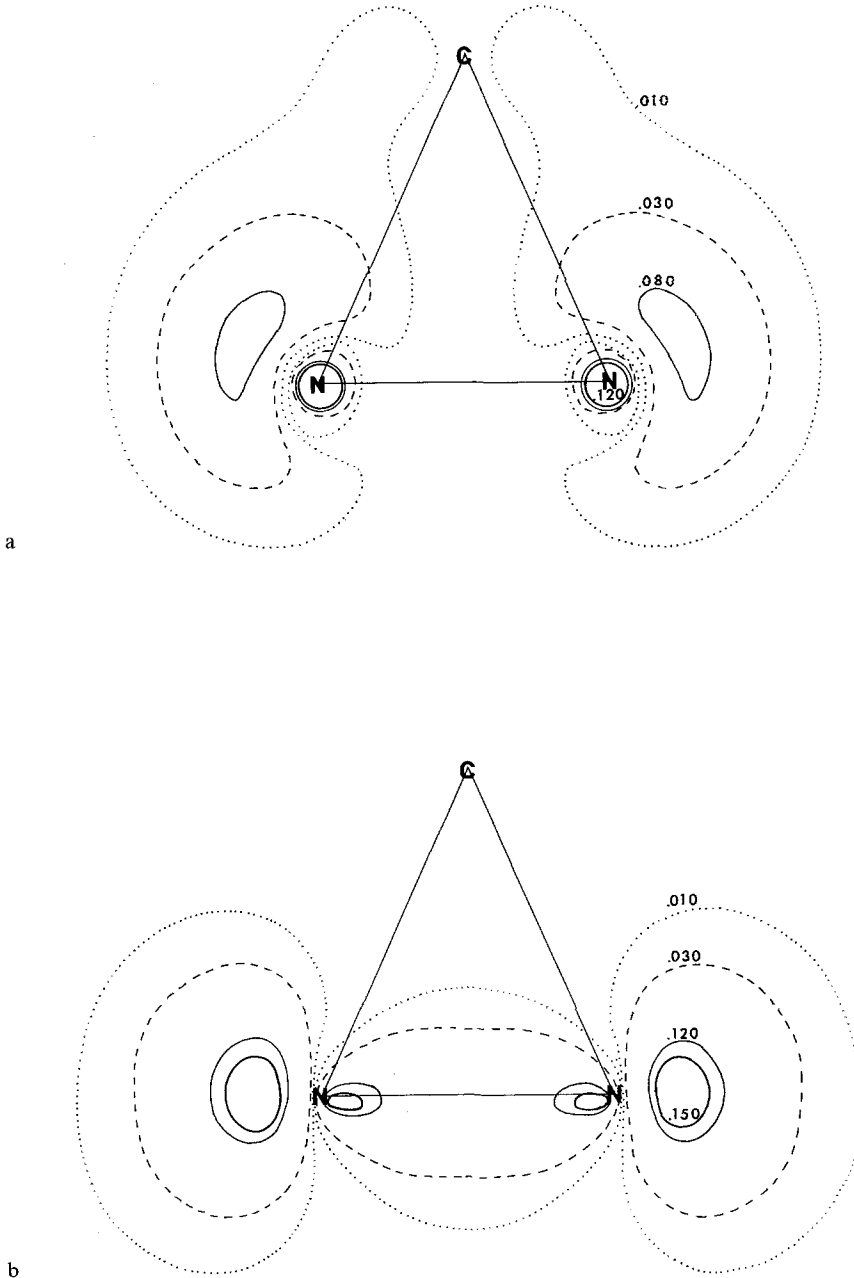
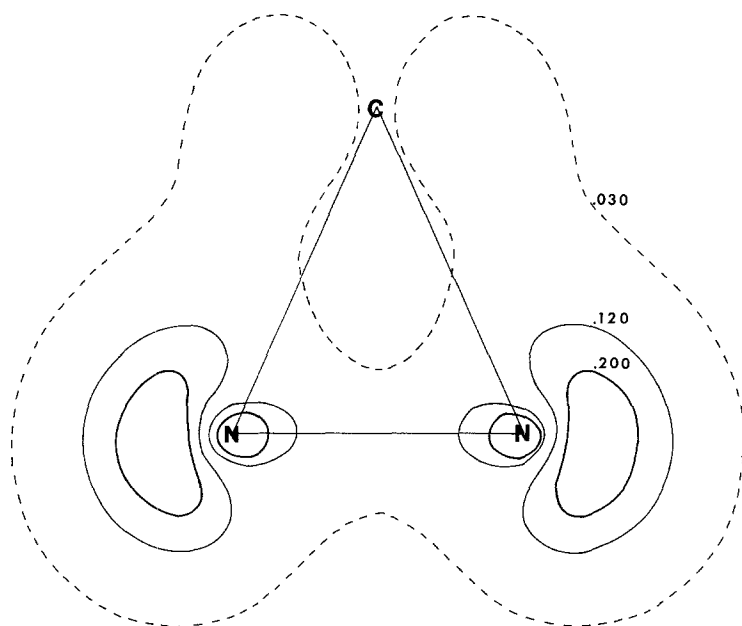
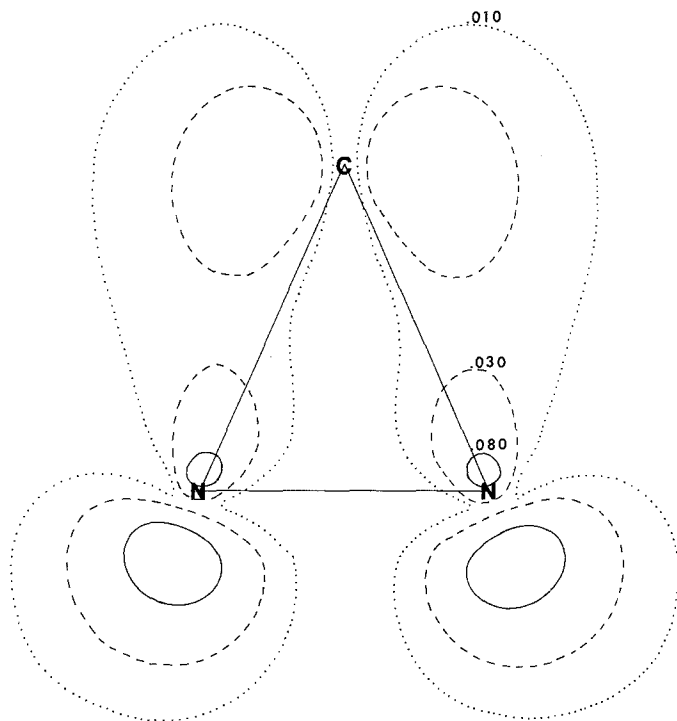


Fig. 6. Electronic density distribution in the MO's contributing to the nitrogen lone-pairs of diazine: a)  $2b_2$ ; b)  $6a_1$ ; c)  $3b_2$ ; d)  $2b_2 + 6a_1 + 3b_2$





localized on the nitrogens contribute at the same time weakly to the C–N bonds and strongly to the nitrogen lone pairs. It is interesting to note the marked contribution of the low lying  $2b_2$  MO to the description of the lone pairs which are commonly considered as being the highest occupied MO's. The lone pair MO  $6a_1$ , lying below the N=N  $\pi$ -bond MO  $2b_1$ , also shows the same trend. Thus "lone pair" MO's may lie well within other MO's.

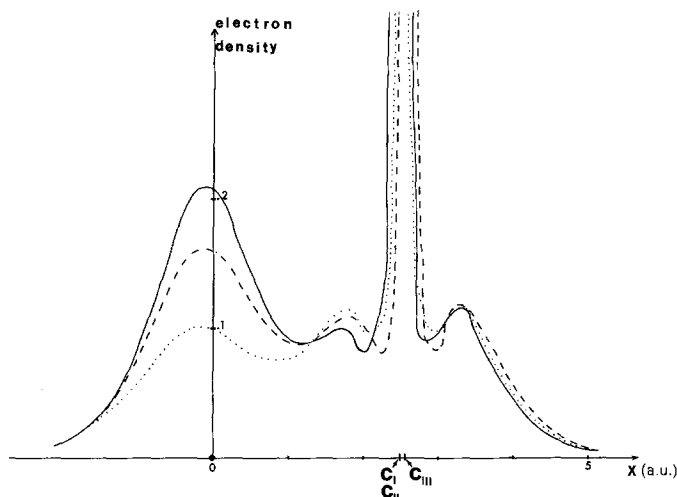


Fig. 7. Total electronic density distribution along the  $x$  axis in cyclopropane (...), cyclopropene (---) and in diazirine (—) ( $1a_1$ ,  $1b_2$  and  $2a_1$  MO's subtracted).  $C_I$ ,  $C_{II}$  and  $C_{III}$  are respectively  $C_1$ ,  $C$  and  $C_3$  in cyclopropane, diazirine and cyclopropene

It is worth noting that the  $6a_1$  and  $3b_2$  MO's bear strong resemblance to the nitrogen lone pair MO's obtained by Clementi [37] for pyrazine (MO's  $10a_1$  and  $11a_1$  in Ref. [37]) and have a similar N( $2s$ ) and N( $2p$ ) composition. However in the case of diazirine the N=N  $\pi$ -orbital ( $2b_1$ ) has an energy between the two lone pair levels (see Table 1 and Fig. 8) whereas for pyrazine all the  $\pi$ -levels were found below the two lone pair MO's [37]. Extended Hückel type calculations [19] gave two highest occupied MO's which resemble to some extent the present  $6a_1$  and  $3b_2$  MO's but are not separated by the  $\pi$  MO. The atomic population analysis (Table 4) shows that the negative charges on the ring are much smaller than in the case of cyclopropene. The C and N atoms have the following charge distributions:

$$C: 1s^{1.98} 2s^{1.22} 2p\sigma^{1.73} 2p\pi^{1.25}, N: 1s^{1.98} 2s^{1.89} 2p\sigma^{2.32} 2p\pi^{0.97}.$$

It is seen that the N atoms are  $\sigma$  acceptors (0.21 e each) and very weak  $\pi$  donors (0.03 e each). C is a  $\pi$ -acceptor but retains its  $\sigma$ -population of the separated atom, whereas in the case of cyclopropene  $C_3$  is found to be both  $\sigma$ - and  $\pi$ -acceptor; the difference may be attributed to the fact that in diazirine the carbon atom is attached to the more electronegative nitrogen atoms.

The total overlap populations (Table 4) lead to some interesting conclusions. The C–N bonds are much weaker than the C–C single bonds in cyclopropene. The N=N bond is weakly  $\sigma$ -antibonding and  $\pi$ -bonding (MO's  $1b_1$  and  $2b_1$ ); the result is a weak N=N double bond.

The *electron density diagrams* (Figs. 5, 6, 7c) provide a closer look at the electronic structure of diazirine. The total electron densities are bent outside the C, N<sub>1</sub>, N<sub>2</sub> triangle (Figs. 5 and 7c); the angle of bending<sup>4</sup> is equal to ca. 5° for the C–N bonds, but is smaller for the N=N double bond (ca. 2–3°). The total electron distribution and the  $1b_1 + 2b_1$  electron distribution in the *xy* plane perpendicular to the ring have much the same shape as in cyclopropene (see Fig. 4). As in the latter case, the delocalization of the electron density over the N=N  $\pi$ -bond and the C–H bonds is clearly apparent. The contour maps for the *nitrogen lone pair orbitals* are given in Fig. 6. The low lying  $2b_2$  MO (Fig. 6a) is clearly the antisymmetric mixing of two nitrogen lone pairs mostly N (2s) character.  $6a_1$  is weakly N–N bonding (Fig. 6b); this result contradicts the overlap population analysis (Table 4b) which give to  $6a_1$  a weakly N–N antibonding character. This seems to arise from the definition of the overlap populations. As a consequence the bonding or antibonding characters deduced from overlap populations should not always be trusted, when these populations are low. In the present case an N–N antibonding character is in addition in contradiction with the  $a_1$  symmetry of the  $6a_1$  MO<sup>5</sup>.  $3b_2$  also contributes to the nitrogen lone pairs as well as to the C–N bonds (Fig. 6c). This MO looks to some extent similar to the  $3b_2$  MO of cyclopropane but is also heavily located at the nitrogen. It may therefore be considered as deriving from one of the upper ring forming MO's (containing almost exclusively  $2p$  AO's; see  $6a_1 + 3b_2$  of cyclopropane, Fig. 2) appreciably mixed with nitrogen lone pairs of  $2p$  character.

There is clearly no *pure* lone pair MO. All MO's contributing to the lone pairs also contribute to some extent to the ring bonds; this may be seen from the total electron distribution map due to the  $2b_2 + 6a_1 + 3b_2$  MO's (Fig. 6d).

### 3.4. *Electronic Structures and the Nature of the Bonding in Cyclopropane, Cyclopropene and Diazirine*

Before discussing the general features of the electronic structures of cyclopropane, cyclopropene and diazirine as they result from the present study, it is important to ascertain which relations they may bear to experimental data and to former theoretical models.

MO composition, atomic and overlap populations have no direct experimental counterpart.

However the electronic distribution may be studied by comparing computed total electron density diagrams with the contour maps obtained from *X*-Rays diffraction studies. The problem is mainly the scarcity of such data in the literature and the very high experimental accuracy required if meaningful results are to be obtained [38].

On the other hand, comparison of the electronic structures resulting from the present all electron SCF-LCAO-MO computations with those obtained from

<sup>4</sup> The bending angle is defined as the angle made by the line joining one of the ring atoms to the point of maximum density (situated on a line perpendicular to a given ring side) with the corresponding ring side (line joining two of the ring atoms).

<sup>5</sup> Further comparisons between electron distribution maps and population analyses are being made in order to delineate the problem.

semi-empirical methods, is rendered difficult by the fact that the concepts (hybridization, interorbital angle, maximum overlap ...) are "eigenvalues" of the language and of the internal structure of the theoretical method employed.

We shall try to specify the general features of the electronic structures of the systems studied here and point out the relations with the semi-empirical models and with the experimental data.

In doing so it is necessary to compare *comparable* entities (e. g. theoretical electron distributions with experimental ones) and not for instance interorbital angles with experimental or theoretical electron density distributions, as it has sometimes been done.

### *Electronic Structure of the Three-Membered Ring System*

The semi-empirical Coulson-Moffitt [2] and the Walsh [10] models for bonding in cyclopropane have been widely used in organic chemistry for discussing properties and reactivities of small ring systems. They both make use of the hybridization scheme.

The Coulson-Moffitt model [2] leads to the "bent-bond" picture of the bonding in the cyclopropane ring; it has also been applied to cyclopropene [8]. The Walsh model makes use of three carbon  $sp^2$  orbitals (occupied by two electrons) overlapping in the center of the ring and three carbon  $p$  orbitals overlapping at the periphery of the ring [10] for building up the ring bonds.

Because of the widespread use of these models and of the often debated question of which one is the better one, it is worth looking at their relations with the present results.

We shall first discuss the *nature of the MO's* making up the ring bonds. As these are quite well defined in cyclopropane (§ 3.1) and in cyclopropene (§ 3.2) but not in diazirine (§ 3.3) we will only consider the first two systems. Diazirine has been considered in detail above (§ 3.3). In both cyclopropane and cyclopropene the MO's describing the ring C-C  $\sigma$ -bonds are  $3a_1$ ,  $6a_1$  and  $3b_2$ .  $3a_1$  contains ca. 70% C(2s) AO's whereas  $6a_1$  and  $3b_2$  are made up almost exclusively of C(2p) AO's (ca. 90%).

This MO picture is nearer to the Walsh model than to the Coulson-Moffitt one.  $6a_1$  and  $3b_2$  would correspond quite well to overlapping pure  $p$  orbitals, while  $3a_1$  is nevertheless very far from an  $sp^2$  state at each carbon, its composition leading to ca. C( $sp^{0.2}$ ) for cyclopropane and to ca. C( $sp^{0.4}$ ) for cyclopropene.

The present picture is also similar to that resulting from the other molecular orbital calculations [9; 11 b; 22].

The *nature of the bonding* in the ring system may be very well visualized by using the electron density distribution contours. The low lying  $3a_1$  MO of cyclopropane provides electron density *inside* the ring with a plateau of ca. 0.04 e located inside the ring triangle (Fig. 2a and 2d). The two degenerate MO's  $6a_1$  and  $3b_2$  lead to high electron densities *outside* the ring triangle (0.05 e maximum on the  $x$  axis; bending angle of ca.  $20^\circ$ ; Fig. 2d) and to a zero density in the centre of the ring (Fig. 2b and 2d). These two MO's are specially important; they are the highest occupied MO's and as such are the first ones to take part in chemical reactions.

The electron distribution pattern arising from the six electrons in the  $3a_1 + 6a_1 + 3b_2$  MO's (Figs. 2c and 2d) displays a bending angle of ca.  $11^\circ$  and the total electron density contours show only a slight bending of ca.  $5^\circ$ . These results hold also for cyclopropene which shows very similar electron density maps (bending angle of ca.  $5^\circ$  and  $4^\circ$  for the C–C and C=C bonds respectively).

Considering the total density maps one arrives at a “*bent bond*” + “*central hole*” picture of the electron distribution in cyclopropane and cyclopropene (Figs. 1–3, 7), the central hole being however not very deep with respect to the bonding regions (ca. 15% density depression). These special features are much more pronounced (larger bending angle; deeper central hole) when one considers only the two highest occupied MO's ( $6a_1$  and  $3b_2$ ) among those making up the ring  $\sigma$ -bonds ( $3a_1, 6a_1, 3b_2$ ).

EHT calculations on cyclopropane yield an angle of  $7.5 \pm 1^\circ$  between the C–C axis and the point of maximum total electronic density on a line perpendicular to the C–C line [11b]. More pronounced bending has been found using FSGO calculations [20].

Equal electron density contours in the plane of the cyclopropane ring have been given for the six bonding electrons forming the ring C–C bonds in the Coulson-Moffitt model (see [2], p. 16, Fig. 7). These contours are in their overall shape quite similar to those shown in Fig. 2c. This is especially true for the bonding regions outside the C–C axes<sup>6</sup>. No detailed electron density contours are available for the Walsh model, but from what is given in the literature (see [10a], p. 185, Fig. 4) it might seem that detailed electron distribution maps of the Walsh and Coulson-Moffitt models would probably differ *less* than one might expect from the difference in construction of these models.

X-Ray diffraction studies of cyclopropane derivatives [39, 40], especially *cis*-1,2,3-tricyanocyclopropane [40], lead to difference electron density maps which present difference density maxima in the plane of the ring and outside the C–C axes by ca.  $0.3 \text{ \AA}$  (bending angle of ca.  $20^\circ$ ). Difference density maps are of course not directly comparable to *total* density maps, and especially, the position of the maxima is not the same in the two cases, being probably nearer to the C–C axes in the second case. This is also shown by the much larger bending angle (ca.  $20^\circ$ ) obtained for the electron distribution in the highest occupied MO's ( $6a_1 + 3b_2$ ) as compared to the total density distribution.

These results clearly indicate that the electron density maxima in the bonding regions in the plane of the ring lie outside the  $C_3$ -triangle and that there is *comparatively* a “hole” in the center of the ring. Thus theoretical and experimental data both agree and the resulting bonding picture may be described as “*bent bonds*” insofar as this term is employed for describing the electron density patterns and is cut from its original relation with interorbital angles within the hybridization scheme.

As a consequence the debate about the Coulson-Moffitt and the Walsh models loses its interest, their main difference arising from the way they have been build up (see also [9]).

<sup>6</sup> It should be pointed out that the orbital bending angle in the Coulson-Moffitt model (ca.  $20^\circ$ ) is not to be compared to the electron density bending angle; both angles are related but are of different nature.

The bonding picture in aziridine [25] is similar to that obtained for cyclopropane and for cyclopropene.

However oxaziridine [25] displays marked modifications as does diazirine. It finally seems that the *bonding picture* (nature of the MO's making up the ring bonds, electron density distributions) for three-membered ring systems is quite generally based on the present cyclopropane model, more or less marked perturbations of this model being however brought about by the introduction of heteroatoms (especially in diazirine or in oxaziridine [25] where two such atoms are present).

*Nitrogen "lone pairs"*. In view of the debate about the nature of nitrogen "lone pairs" [41] it is worth commenting on diazirine. The nitrogen lone pairs appear in the electron distribution map (Figs. 5 and 6d) as regions with high electron density which are markedly flattened and rounded off as compared to the usual picture of localized lone pairs but are nevertheless clearly visible. When one compares diazirine and cyclopropene one notes that the shape of the contours is very different in the two cases: the "lone pair" extends from the nitrogen, only half as far into space than does the vinylic C-H bond, and is fused into the overall electron distribution, losing much of the directivity associated with a C-H bond. This, together with the easy redistribution of the "lone pair" electron density on changing molecular structure or conformation, points to the danger involved in considering a "lone pair" as a substituent.

### 3.5. Electronic Structure and Properties of Cyclopropane, Cyclopropene and Diazirine

*Ring Strain*. It is well known that the bonds forming strained three-membered rings are less stable and more easily broken than the corresponding bonds in unstrained molecules [16]. As bond energies are proportional to bond overlaps [8], the low overlap populations found in the present study for the ring C-C, C-N and N-N bonds are in agreement with the easier cleavage of three membered rings as compared to less strained ring systems [11, 13].

Furthermore, the  $\sigma$ -component of the C=C double bond in cyclopropene has an appreciably lower overlap population (0.247) than a C-C  $\sigma$ -bond in cyclopropane (0.378) (Tables 2 and 3). One would thus expect that double bond reactions in cyclopropenes are highly exothermic, the opening of the  $\pi$ -bond being accompanied by an increase in the  $\sigma$ -bond strength. This is in agreement with the high reactivity of the double bond in cyclopropenes [1].

" $\pi$ " *character and conjugative properties*. It has been shown above that the two highest ( $6a_1$  and  $3b_2$ ) of the three MO's which give a major contribution to the ring  $\sigma$ -bonds in cyclopropane and in cyclopropene, contain almost exclusively C( $2p$ ) AO's lying in the plane of the ring. Such a picture is clearly reminiscent of an olefinic  $\pi$ -bond giving to these ring systems a *pseudo- $\pi$*  ( $\psi - \pi$ ) character.

Indeed, physical and chemical properties of these small rings (for instance  $C^{13}$ -H nuclear spin-spin coupling constants) place cyclopropane in between aliphatic and olefinic character and cyclopropene in between olefinic and acetylenic character. This  $\psi - \pi$ -character also accounts for the ability of cyclopropane to interact with multiple bonds, empty orbitals (in cations) ... [9, 11 b, 42]. The

resulting  $\pi$ ,  $\psi - \pi$ -“conjugation” leads to characteristic spectral (e. g. in the U. V. range [43, 44]) and chemical (opening reactions, valence tautomerism ... [45, 46]) properties which have in the recent years, given rise to a manifold of very interesting new chemistry. On the basis of the present analysis the optimum geometry for interaction of the upper, almost pure  $p$ , ring MO's with the neighbouring  $p$  AO of the  $\pi$ -bond, is predicted to have the ring plane parallel to the plane of the  $\pi$ -bond. This conclusion is in agreement with the experimental studies (see for instance [43, 44]) and with EHT calculations [42].

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After this manuscript had been completed we received from Dr. M. B. Robin a preprint of his, Dr. D. W. Turner's and their collaborators' work on the optical spectra of three membered ring systems. In this work more accurate experimental results and a discussion of the ionization potentials of cyclopropane may be found. We thank Dr. Robin for sending us the manuscript before publication.

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