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Semi-empirical Localized MO Calculations of Saturated Carbocyclic and Heterocyclic Compounds

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Localized MO calculations have been carried out by the "energy localization" method of Edmiston and Ruedenberg, based upon the INDO MO's, for 3-, 4-, and 5-membered cycloalkanes and their heterocycles containing one oxygen or nitrogen atom. Furthermore, LMO calculations were performed for the protonated three-membered heterocyclic compounds. The s-nature of the LMO's is discussed and correlated with the bond angle, the bond moment, the bond energy, and the bond polarity. Some LMO density maps are shown.

The usefulness of the localized molecular orbital (LMO) method has been pointed out by many authors.[1-7] Not only has the LMO method an advantage compared with the classical bond concept, but also the results which can be obtained by this method can be correlated directly with some physicochemical concepts or quantities, such as hybridization, the bond angle, and the bond moment.

In this paper, some physical and chemical properties of saturated cyclic compounds are investigated by the LMO method which was presented by Edmiston and Ruedenberg[1] based on the INDO method.[8] The compounds treated are saturated 3-, 4-, and 5-membered cycloalkanes and their heterocycles containing one oxygen or nitrogen atom. The LMO calculation for these compounds has not yet been made except for some LMO studies of three-membered heterocycles and some cycloalkanes.[5-7] Special attention is paid to the correlation between the degree of hybridization (s-nature of LMO's) in these compounds and the experimental quantities to be compared. The results of the bond polarity and the LMO charge maps are given.

Method and Details of Computation

The canonical MO's (CMO's) are obtained by the INDO method of Pople *et al.*,[8] and the LMO's, by the "energy localization" method of Edmiston and Ruedenberg.[1] In a later section, the LMO's total energy will be discussed by using the term "bond energy" presented by Parks and Parr.[2] The outline of the definition of "bond energy" may be briefly given as follows: the total energy by the LMO method, E_{el}, is given as the sum of the i-th LMO's energies, E_i's:[3]

$$E_{\mathrm{el}} = \sum_i E_i$$

$$E_i = \langle i | F + H^{\mathrm{c}} | i \rangle$$

where the summation, i, runs over all the occupied LMO's in the compound and where F and H^{c} denote the Fock and the core operators in the SCF Hamiltonian respectively.

The total energy, E_0, is taken as the sum of the bond energies, B_i's, where B_i belongs to the i-th two - or one-center LMO:

$$E_0 = E_{\mathrm{el}} + E_{\mathrm{n}} = \sum_i B_i$$

where:

$$B_i = E_i + E_{i\leftarrow \mathrm{n}}$$

in which E_{n} is the total core repulsion energy and $E_{i\mathrm{n}}$ is its i-th part.[2]

The geometries of the treated compounds are cited from the literature[9] if they exist. As to ethylene imine, the following values are assumed: C–N 1.488 Å; C–C 1.502 Å; C–H 1.08 Å; N–H 1.00 Å; ∠HCH 112°; as to the protonated ethylene oxide and imine, $\mathrm{O{-}H^+}$ is taken as 0.96 Å and $\mathrm{N{-}H^+}$ is 1.00 Å, and the bond angle between the newly formed $\mathrm{X{-}H^+}$ bond (X=O, N) and the ring plane is assumed to be 56°, the other values remain unchanged. For the sake of simplicity, the rings of all the compounds, with the exception of cyclobutane, are assumed to be planar.

Results and Discussion

As a measure of the degree of localization of each LMO, Table 1 shows the sum of the squared AO-coefficients at the atoms which do not take part in the considered bond or lone pair. The values in Table 1 indicate the achievement of a high degree of localization (more than 90% in almost all LMO's); accordingly, some discussions in later sections based on the assumption of pure localization will be admissible.

In this section, the s-nature of the LMO's, the deviation of the bond angle and the bond energy, and so on, will be discussed.

s-Nature. Coulson and Moffitt[10] have pointed out the irregular degree of hybridization of small-membered cycloalkanes. In Table 2 our results are compared with the values of s% and the deviation of bond angle given by Coulson and Moffitt (C–M). The agreement between the two approaches is good. The reliability of the results by the LMO approach has also been examined by comparison between the observed $J_{\mathrm{C^{13}-H}}$ coupling constant,[6,11a-c] and those estimated by means of the empirical formula: $J_{\mathrm{C-H}} = 5 \times (\%\mathrm{s})$ cps.[11a] In Table 3 the agreement is excellent. Hence, this way of estimating the s-nature seems reasonable. The LMO's obtained by means of the INDO and *ab initio* methods have already been

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Table 1. Deviation of localization

(bond A–B: $\sum c^2_{C \neq A \neq B}$; lone pair A: $\sum c^2_{B \neq A}$)

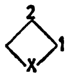
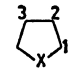
									
bond	X=O	X=NH	X=CH$_2$	X=O	X=NH	X=CH$_2$	X=O	X=NH	X=CH$_2$
X-C	0.022	0.020	—	0.007	0.007	—	0.010	0.006	—
X	0.016	0.019	—	0.013	0.019	—	0.019	0.021	—
C$_1$-C$_2$	0.002	0.004	0.016	0.005	0.005	0.007	0.005	0.005	0.006
C$_2$-C$_3$	—	—	—	—	—	—	0.013	0.011	—

Table 2. s-Nature of cycloalkanes and the deviation of bond angles ($\theta°$)

Molecule	s nature				$\theta°$	
	Coulson-Moffitt [10]		ours		C-M [10]	ours
	C-C	C-H	C-C	C-H		
(CH$_2$)$_3$	19.53	30.49	18.8	32.1	22°	28°55′
(CH$_2$)$_4$	23.59	26.39	24.6	27.8	9°	12°20′
(CH$_2$)$_5$	25.00	25.00	27.3	24.5	0°	2°30′

compared by England and Gordon.[4] Our results in Table 2 are close to that of the *ab initio* LMO calculation of Newton *et al.*, which gives the deviation of the bond angle (C–C–C) as 28.4°, and the 22.9% s character in the CH bond and the 20.8% s character in the CC bond in cyclopropane.[5]

In Table 4, the values of the %s nature of various compounds are collected. From the data, it seems that there is a regular increase in s% in the CC and CX (X=N, O) bonds and the decrease in the CH and NH bonds and lone pairs with the increase in the ring size. The above tendency indicates that the 2s electrons which are highly localized in the CH bonds or the lone pairs of the small-membered ring compounds come to participate in the bonding of the CC or CX bonds with an increase in the ring size.

Table 3. Nmr C-H Coupling (J_{CH}) and s nature

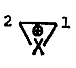
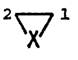
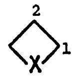
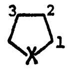
Molecule	$J^{11b,18)}_{CH}$	%s[a]	Calcd %s
(CH$_2$)$_3$	162	32	32.1
(CH$_2$)$_4$	136	27	27.8 (av.)
(CH$_2$)$_5$	131	26	24.5
(CH$_2$)$_2$NH	168	—	33.1 (166)
(CH$_2$)$_2$O	176	—	34.7 (174)

a) $J_{CH} = 5 \times (\%s)$ cps

Since the s AO's energies are generally lower than the p AO's, a high degree of s character leads to a more stable bond. It is commonly known that a bond in the ring plane of small ring compounds is more liable to break than in the normal-size ones, and also that the CH-bond stretching frequencies become smaller with an increase in the ring size,[17] reflecting the decrease in the %s of the bond, as is shown in Table 5.

Table 4 also shows the s nature in each LMO of the protonated ethylene oxide and imine. The results reveal that the amount of %s increases at the hetero atom in the CX bond, while it decreases at the CX carbon and remains almost unchanged in the other parts, in comparison with the parent compound. Those results indicate that the change in the electronic structure by protonation is limited around the hetero

Table 4. %s Nature of each LMO

								
bond[a]	X=O	X=N	X=O	X=N	X=O	X=N	X=O	X=N
C$_1$-H$_1$[b]	35.5	34.1	34.7	33.1	31.1	29.4	28.6	27.1
C$_1$-H$_2$	34.8	34.1	34.7	33.9	31.1	30.1	28.6	27.8
C$_2$-H$_3$[b]	—	—	—	—	27.0	26.7	25.4	25.0
C$_2$-H$_4$	—	—	—	—	27.0	26.5	25.4	25.0
C$_1$-C$_2$	20.5	19.8	19.3	19.7	26.7	25.5	30.0	28.7
C$_2$-C$_1$	20.5	19.8	19.3	19.7	24.5	25.2	26.8	27.0
C$_2$-C$_3$	—	—	—	—	—	—	26.0	26.8
X-C	19.6	19.6	13.0	16.4	18.1	22.4	20.4	24.5
C-X	13.5	15.2	16.7	17.6	20.1	22.0	23.2	24.7
X(l.p.)	34.2	—	37.3	41.0	32.7	33.9	20.3	31.8
X-H	25.1	28.8	—	27.5	—	22.6	—	20.9

a) The numbers in the table refer to the one of the first atom of the bond. b) C-H bond on the same side of the molecular plane as N-H bond.

Table 5. The values of the highest C-H stretching frequencies[17]

[cm^{-1}]

X	Number of ring atoms 3	4	5
C	3078	2990	2964
O	3010	2996	2975
N	3060	—	2958

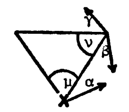
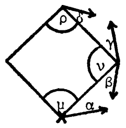
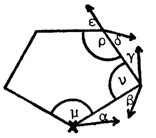
atom directly bonded to the proton.

Some attempts have previously been made to correlate the degree of hybridization to the bond angle.[12–16] We have estimated the bond angle by the vector sum of the coefficients of p AO's; the data are summarized in Table 6. The results are as follows: the bond angles in the ring plane decrease towards the tetrahedral angle with an increase in the ring size, and the deviation becomes smaller in all cases. The decrease in the bond angle is somewhat surprising and in contradiction to previous results. It indicates that there is not always a strict correlation between the hybridization and the bond angle.

Bond Energy. Parks and Parr pointed out that the additivity and the invariance of bond energy, as defined by them, hold under the assumptions that the neutral penetration term is negligible and that the bond is homopolar.[2] Hirao calculated the bond energy of various types of CH bonds with respect to hydrocarbons and pointed out that the bond energy parallels the degree of hybridization[3] and is nearly equal within the bonds of the same degree of hybridization.[19]

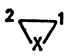
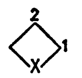
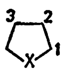
Table 7 lists the values of the bond energy, while their dependence on the ring size is plotted in Fig. 1. The invariance of the bond energy does not hold in these heterocyclic compounds, but the change due to the ring size is parallel to that of the s nature of the bonds or the lone pairs considered. That is, with an increase in the ring size, the energy of the CH bond and that of the lone pair become higher and those of the CC and CX bonds become lower. This tendency is roughly in accord with the values of s% in Table 3. It is interesting that the change in the CC bond energy between the three- and four-membered rings is most remarkable; this result reflects the large change in the degree of hydribization of their carbon atoms and can also be correlated to the stability of the ring.

Table 6. Deviation of bond angle. geometry

						
angle	X=O	X=NH	X=O	X=NH	X=O	X=NH
α	25°40′	28°	5°35′	7°50′	−3°30′	−1°45′
β	23°	25°30′	10°5′	11°45′	0°20′	1°15′
γ	33°10′	31°	12°	13°15′	0°	1°35′
δ	—	—	13°	12°10′	3°10′	2°30′
ε	—	—	—	—	4°	2°40′
l.p.[a]	62°35′	57°30′	59°	54°	57°15′	52°20′
μ	61°40′	59°40′	94°30′	94°30′	111°	111°
ν	59°10′	60°10′	88°40′	87°38′	109°5′	107°15′
ρ	—	—	88°10′	90°15′	105°25′	107°15′
N-H[b]	—	56°	—	56°	—	56°

a) l.p. = angle between lone-pair orbital and ring plane. b) N-H = angle between N-H bond and ring plane.

Table 7. Bond energies [eV]

									
bond	X=O	X=N	X=C	X=O	X=N	X=C	X=O	X=N	X=C
C_1-H_1[a]	−68.12	−67.41	−67.68	−67.56	−66.94	−67.19[b]	−66.81	−66.60	−66.74
C_1-H_2	−68.12	−67.66	−67.68	−67.56	−67.10	−67.19	−66.81	−66.74	−66.74
C_2-H_3[a]	−68.12	−67.41	−67.68	−67.79	−67.26	−67.19	−67.64	−67.16	−66.74
C_2-H_4	−68.12	−67.66	−67.68	−67.79	−67.17	−67.19	−67.64	−67.16	−66.74
C_1-C_2	−92.00	−92.64	−92.70	−95.38	−94.84	−94.48	−95.87	−95.59	−96.03
C_2-C_3	—	—	—	−95.38	−94.84	−94.48	−96.65	−96.07	−96.03
X-C	−134.42	−111.01	—	−134.73	−112.49	—	−136.28	−112.98	—
X	−150.18	−106.87	—	−149.31	−106.61	—	−148.84	−106.64	—
X-H	—	−88.19	—	—	−87.83	—	—	−87.35	—

a) C-H bond at the same side of ring plane as N-H. b) average value.

TABLE 8. CHARGE BOND MOMENTS FROM LMO's [D]

								
bond	X=O	X=N	X=O	X=N	X=O	X=N	X=O	X=N
X-C	1.19	0.70	2.60	2.07	1.23	0.68	1.26	0.72
C-C	—	—	—	—	0.11	0.05	0.09	0.07

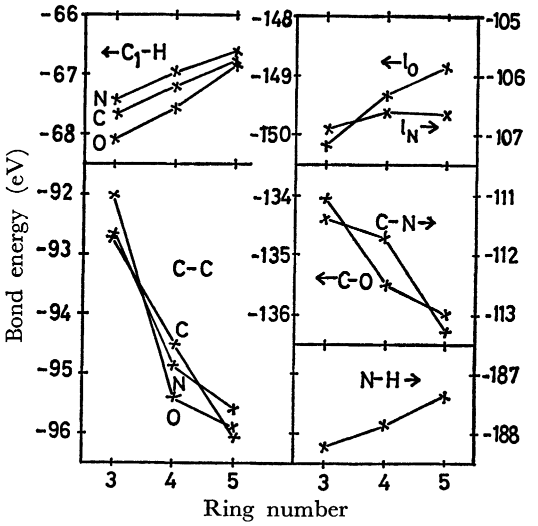


Fig. 1. Various bond energy *vs.* ring number.

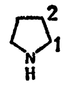
Bond Polarity and Charge-density Contour Maps. The concept of bond polarity can be discussed directly by using the LMO results. Table 8 lists the values of the chargebond moment; μ_{AB}, which have been calculated by the following equation:

$$\mu_{AB} = 4.804\, R_m (Q_{Ai} - Q_{Bi})$$

$$Q_{Ai} = \left(2 \sum_{t}^{\text{on A}} C_{it}(\mathrm{A})^2\right) - 1$$

where R_m is one half of the AB bond distance in units of Å and where the point of origin is the midpoint of the AB bond. Q_{Ai} is the atomic charge of the A atom in the i-th LMO, which is localized in the AB bond. C_{it} is the coefficient of the t-th AO of the A atom in the i-th LMO. The summation, t, runs over all the valence AO's of the atom A. The μ_{AB} value defined above is an approximated one. That is, this value neglects the contribution of atomic dipoles and the moments by the other parts. In spite of this approximation, the μ_{AB} values are well suited for discussing the bond polarity. It may be seen in Table 8 that the moments of the bonds of the same sort are nearly constant, and that the CX moment values are the largest (while being smaller in CN bonds than in CO bonds, as was expected), while the CC bond moments are very small. This result indicates that the polarity in the heterocycles is found only on the CX bond and that the effect of the hetero atom rapidly decreases with the distance. For reference, the AO coefficients of the LMO's in some five-membered rings are listed in Table 9; the values at the corresponding locations are nearly equal. The values of the C_2 atom in the C_1–C_2 and C_2–$C_{2'}$ bonds can be taken as examples. This indicates the same trend as in the results of the bond moments.

TABLE 9. THE AO COEFFICIENTS OF THE ATOMS IN LMO's

	Atom	LMO	s	x	y	z
	O	l. p.±	0.54	0.0	−0.45	±0.70
		$OC_{1,1'}$	0.35	∓0.54	±0.42	0.0
	C_1	C_1O	0.31	−0.46	−0.31	0.0
		C_1C_2	0.38	−0.16	0.57	0.0
		C_1H	0.37	0.31	0.15	±0.47
	C_2	C_2C_1	0.37	0.19	−0.58	0.0
		$C_2C_{2'}$	0.36	−0.60	0.04	0.0
		C_2H	0.35	−0.22	0.29	±0.48
	N	l. p.	0.56	0.0	−0.50	−0.65
		NH	0.33	0.0	−0.35	0.55
		NC_1	0.37	0.52	0.38	0.03
	C_1	C_1N	0.33	−0.47	−0.34	0.01
		C_1C_2	0.38	−0.16	0.57	0.0
		C_1H	0.36	0.32	−0.13	±0.47
	C_2	C_2C_1	0.37	0.20	−0.57	0.0
		$C_2C_{2'}$	0.36	−0.60	0.03	0.0
		C_2H	0.35	0.22	0.29	±0.48
	C_2	$C_2C_{2'}$	0.37	−0.60	0.03	0.0
		C_2H	0.34	0.22	0.29	±0.49

Figures 2(a)–(c) show the LMO density maps for the bonds in the ring plane and the lone pairs of the 3-, 4-, and 5-membered cyclic ethers. The contour lines representing the densities smaller than 1.0 A eÅ^{-3} are omitted. The figures of the LMO-charge maps in the ring bond reveal a shift of the density maxima toward the interatomic lines with an increase in the ring size. Although they indicate a significant polarity of the CO bond, the considerable change in the hybridization (s nature) with a difference in ring size is not demonstrated. This holds true also for the lone pair LMO's. It is worth noticing that the CC bonds always show two maxima, whereas the CO bonds show only one maximum, which is shifted to the oxygen atom. The figures of the cyclic imines are omitted, since they exhibit a shape very similar to that of the cyclic ethers.

Figure 2(d) shows the LMO maps of the CC bond of cyclopropane. It clearly demonstrates that the maximum of the electron density lies outside the CC line. This tendency is reduced in larger ring compounds, as can be seen from the bond-angle data in Table 3.

Figure 2(e) shows the LMO maps of the ring bonds and the lone pair of protonated ethylene oxide. There is no significant change in the shape compared to that of the neutral compound. The change in the CO bond is interesting, since more of the LMO charge

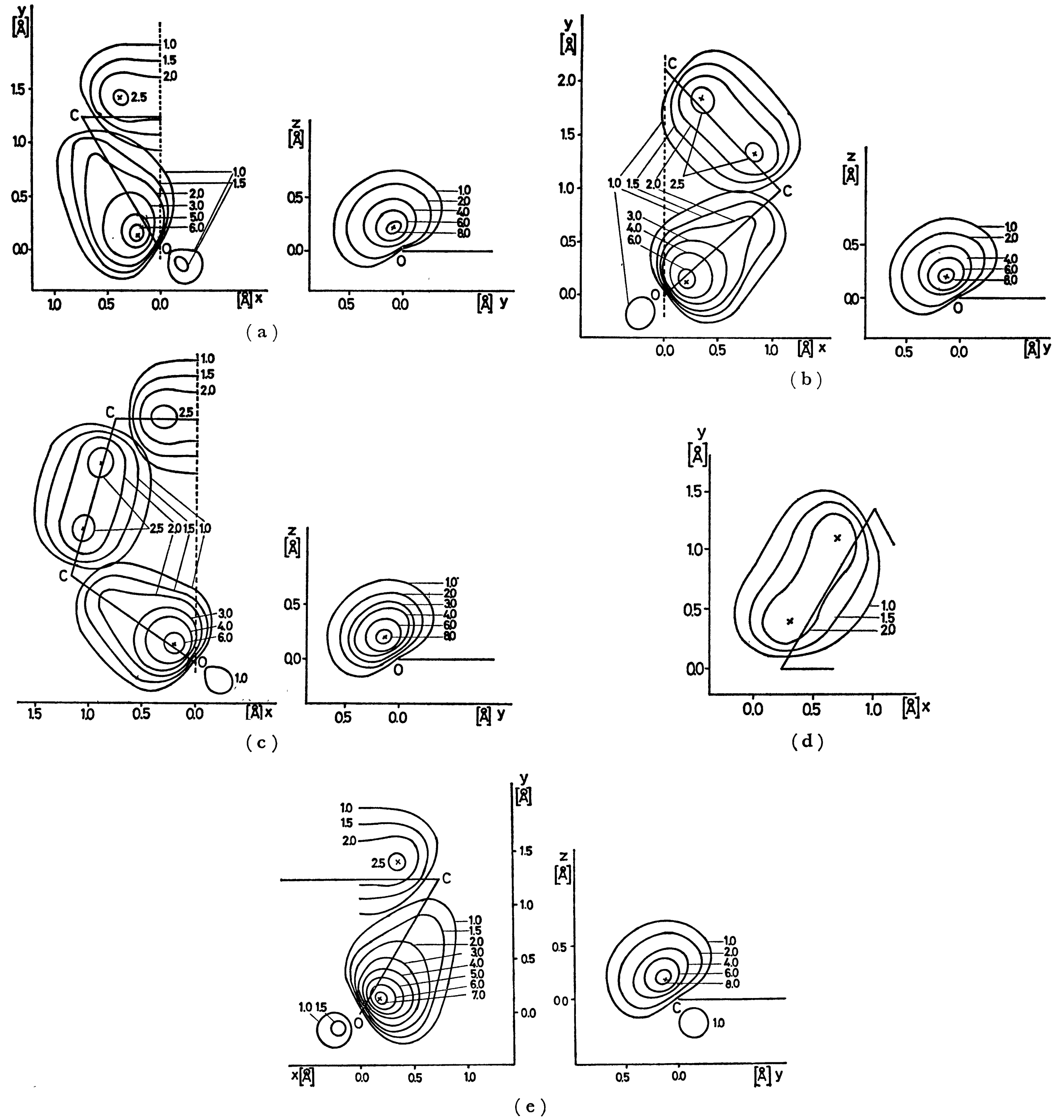


Fig. 2. LMO density maps for the ring bonds and lone pairs of ethylene oxide (a); trimethylene oxide (b); THF (c); C–C bond of cyclopropane (d); ring bonds and lone pair of protonated ethylene oxide (e). Maxima are denoted by a cross. The unit of density is Å^{-3}.

is shifted toward the oxygen atom, and the polarity of the CO bond becomes larger by the protonation. This trend agrees with the results of the charge-bond moment shown in Table 8.

It is interesting to visualize the characteristic features of the LMO's. We show the total-density maps of ethylene oxide and imine in Figures 3(a)–(d). The similarity between the LMO and the total-density pictures is not very clearly demonstrated. The CC bond still holds two maxima outside the ring. As to the CX bond, the maximum near the hetero atom in the LMO map is found to be the tail-off of a broad maximum nearly all around this atom. As going from the LMO picture to the total-electron-density picture, the special characteristics of the single and localized bonds given by the LMO's become more and more diffuse, as is to be expected. The differences between these two maps are produced mainly by the neglect of the overlap effect between the charges of the LMO's.

One of the authors (G.F.) is indebted to Mr. Tsutomu Minato for making available the computer programs. He also wishes to express his gratitude to the Japanese

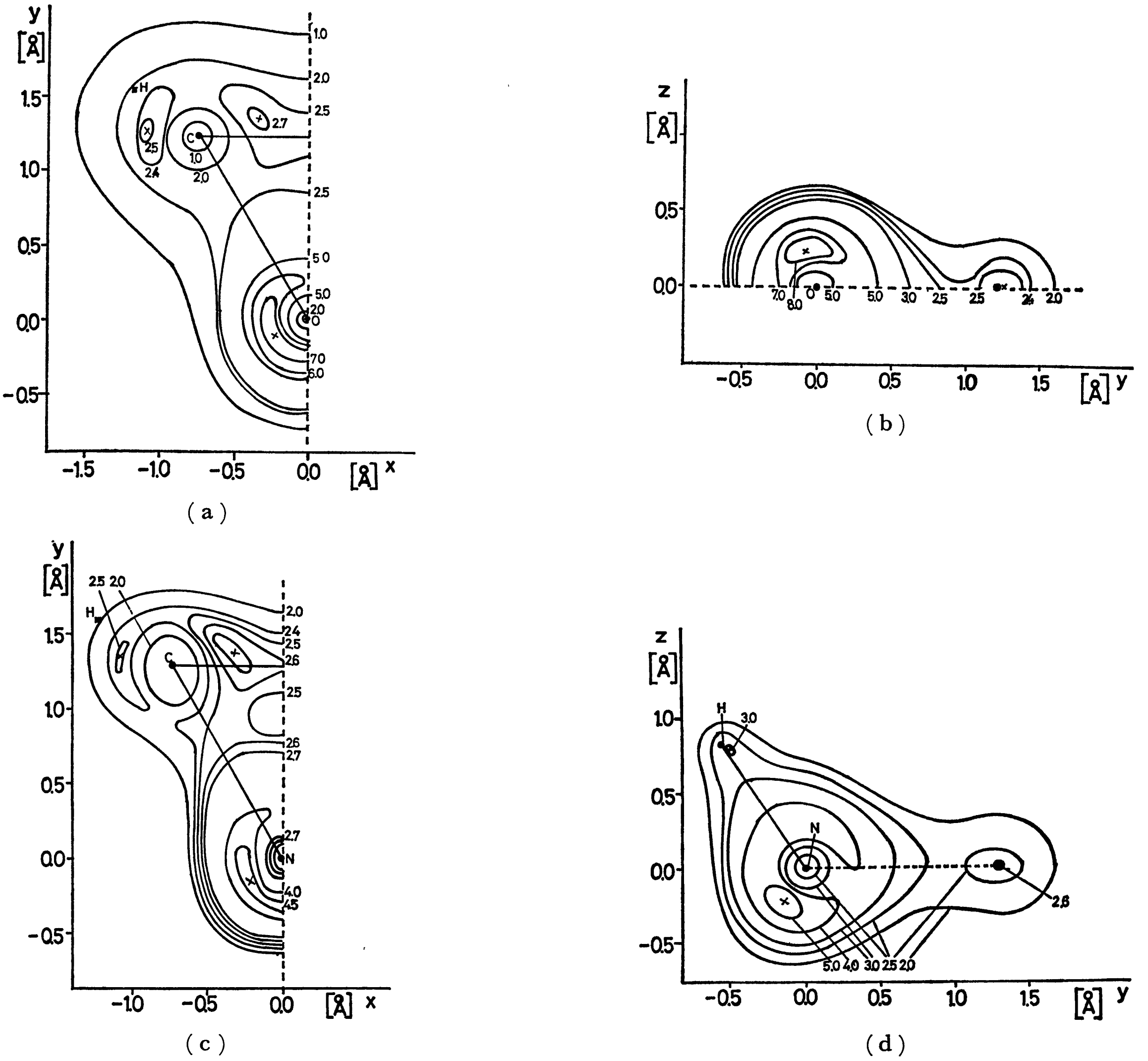


Fig. 3. Total electron density maps in the ring plane (x—y), and perpendicular plane (y—z) crossing the middle of the C–C bond and the heteroatom ethylene oxide (a), (b), and ethylene imine (c), (d); maxima are denoted by a cross (×); the position of the perpendicular C–C bond in the y—z map is denoted by a cross in a circle (⊗); the projected hydrogen position upon the x—y plane is assigned by a square (■); the ring plane in the y—z map is indicated by a dashed line.

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