CHEMISTRY LETTERS, pp. 1479-1482, 1977. Published by the Chemical Society of Japan

GEOMETRY OPTIMIZATIONS OF 1,3-DIRADICALS: RING-OPENED AZIRIDINE AND ETHYLENE OXIDE

Kizashi YAMAGUCHI, Akinobu NISHIO, Satoshi YABUSHITA, and Takayuki FUENO
Department of Chemistry, Faculty of Engineering Science,
Osaka University, Toyonaka, Osaka 560

The geometry optimization procedure by use of the singlet DODS solution is applied to the ring-opened aziridine and ethylene oxide as examples of the so-called dipolar species. It is found that the trans-bent conformation is the most stable for both species. The diradical character is considerably developed for the optimized geometries inspite of the octet stabilization.

Electronic and geometrical structures of 1,3-dipoles and diradicals have received considerable attention in relation to the mechanisms of 1,3-dipolar addition reactions.$^{1)}$ Houk et al.$^{2)}$ have investigated reasonable geometries of azomethine and carbonyl ylides on the basis of the optimization procedure$^{3)}$ by use of the restricted Hartree-Fock (RHF) solution. However, the RHF solutions of these species are triplet-unstable,$^{4)}$ suggesting the presence of more stable singlet unrestricted HF (^{1}DODS) solutions.$^{5)}$ Thus the azomethine and carbonyl ylides should have the 1,3-diradical property$^{4,5)}$ as well as the zwitterionic property$^{1,2)}$ as shown in Fig. 1. Therefore, the optimized geometries by Houk et al. are insufficient; they require reexamination on the basis of the DODS solutions. In this paper we present the optimized geometries of the ring-opened aziridine (**1**) and ethylene oxide (**2**) which are obtained by the ^{1}DODS optimization procedure.$^{3,6)}$

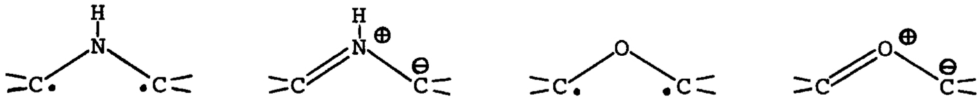
DR(**1**) ZW(**1**) DR(**2**) ZW(**2**)

Figure 1. Diradical (DR) and zwitterionic (ZW) structures of the ring-opened aziridine (**1**) and ethylene oxide (**2**)

The trial geometries of **1** and **2** were obtained by 1,3-bisdehydrogenation of dimethyl amine and ether, respectively.$^{6)}$ These molecules have two methyl groups which are either staggered (S) or eclipsed (E) to the opposite C—X bond (X = NH, O) as in the case of propane. Figure 2 illustrates the staggered-staggered (S,S) conformations of **1** and **2**. Thirteen conformations were obtained from the (S,S)-, (S,E)- and (E,E)-structures in addition to the edge-to-edge conformation.

Computations were conducted in the MINDO/3 approximation.7) Convergence was judged by the same requirement (10^{-4} a.u. in energy) as used previously.6)

Figure 3 illustrates the optimized structures of the four most stable conformations (A-D) of the ring-opened aziridine (**1**). The C-N bond lengths range from 1.32 to 1.34 Å depending on the conformation. Aside from the edge-to-edge structure (C), the HCH angles of therminal methylene groups are about 110°, showing the carbon hybridization intermediate between sp^2 and sp^3. The trans-bent structure (A) is regarded as an (E,E)-like conformation with the C_2-symmetry. The cis-bent structure (B), on the other hand, is one of the (S,S)-like conformations with the C_s-symmetry.

Table 1 summarizes the total and HOMO energies of the optimized conformations of **1**. The trans-bent structure (A) is more stable than the cis-bent structure (B) by 0.122 eV. This energy difference is considerably large, compared with that for the corresponding trimethylene diradicals.6) The C_{2v}-symmetry adapted edge-to-edge (C) and face-to-face (D) conformations are less stable than the bent conformations with lower symmetries (A and B) as in the case of trimethylene diradical.6) The bond indices of the C-N bonds in conformers A, B, and C are about 1.24, indicating a partial double bond character. The C-N bonds of D are essentially single bonds. The spin densities on the terminal carbons are about 0.70, compatible with 1,3-

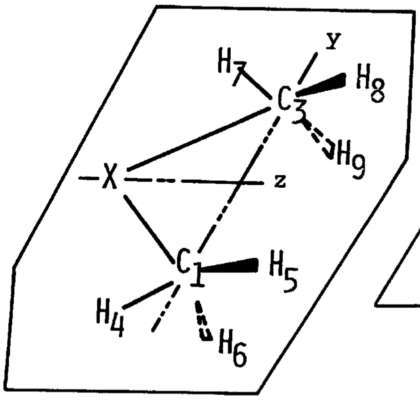

Fig. 2. The staggered-(S,S) conformation of the ring-opened aziridine (X = NH) and ethylene oxide (X = O).

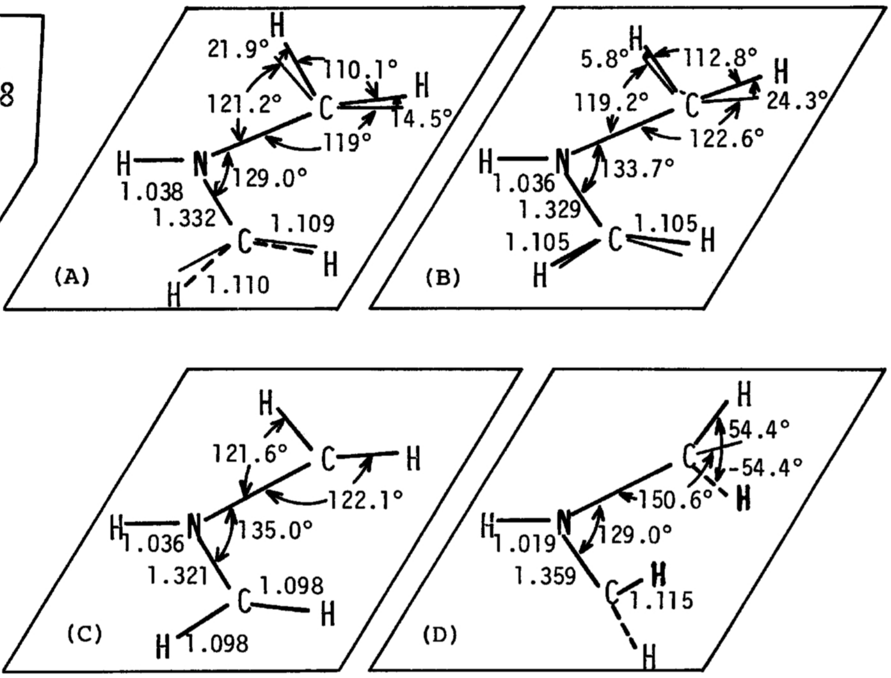

Fig. 3. Optimized geometries of the ring-opened aziridine (**1**). A and B are the trans(C_2)- and cis(C_s)-bent conformations, respectively. C and D are edge-to-edge (C_{2v}) and face-to-face (C_{2v}) conformations, respectively.

Table 1. Total and HOMO energies (eV), bond index (W), and the charge (P) and spin (ρ) densities of ring-opened aziridine

Structure	Trial Geometry	E_{total}	ε_{HOMO}	W_{C-N}	P_C	P_N	ρ_C
A(C_2)	(E-5, E-9)	-518.055	-8.257	1.239	4.137	4.788	0.669
B(C_s)	(S-6, S-9)	-517.933	-8.022	1.235	4.180	4.771	0.710
C(C_{2v})	———	-517.860	-7.564	1.264	4.287	4.690	0.746
D(C_{2v})	(S-4, S-7)	-516.846	-8.501	1.030	3.898	5.123	0.927

diradical property, i.e., DR(1) of Fig. 1. However, the net charges on the N- and C-atoms of the conformation A are 0.212 and -0.137, respectively. This implies a contribution of the zwitterionic structure ZW(1).

Figure 4 shows the optimized structures of the four most stable conformations (A-D) of the ring-opened ethylene oxide (2). The C-O bond lengths are about 1.29 Å, showing a little elongation of the C-O double bonds. The HCH angles of terminal methylene groups of A, B, and D are again about 110°. The trans(A)- and cis(B)-bent structures are the (E,E)- and (S,S)-like conformations, respectively. Thus the geometrical situation is the same as in aziridine.

Table 2 shows the total and HOMO energies of the optimized conformations of 2. The trans-bent structure is the most stable inspite of its (E,E)-like conformation. This may be attributable to the fact that the MINDO/3 method underestimates the repulsive interactions between the lone pairs of O-atom and terminal CH bonds.[8)]The C_{2v}-symmetry adapted edge-to-edge (C) structure has been calculated to be the

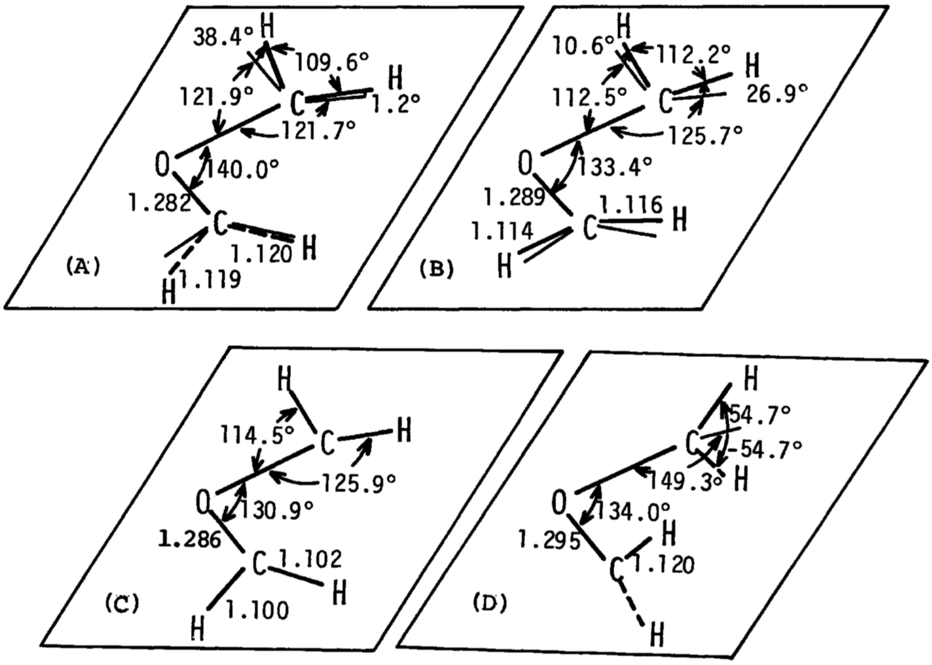

Fig. 4. Optimized geometries of the ring-opened ethylene oxide (2). A and B are the trans(C_2)- and cis(C_s)-bent conformations, respectively. C and D are the edge-to-edge (C_{2v}) and face-to-face (C_{2v}) conformations, respectively.

Table 2. Total and HOMO energies (eV), bond index (W), and the charge (P) and spin (ρ) densities of ring-opened ethylene oxide

Structure	Trial Geometry	E_{total}	ε_{HOMO}	W_{C-O}	P_C	P_O	ρ_C
A(C_2)	(E-5, E-9)	-622.086	-8.896	1.072	3.738	6.262	0.695
B(C_s)	(S-6, S-9)	-621.873	-8.777	1.052	3.773	6.265	0.788
C(C_{2v})	———	-621.511	-8.045	1.071	3.948	6.181	0.969
D(C_{2v})	(S-4, S-7)	-621.735	-8.996	0.991	3.660	6.347	0.713

least stable of the four conformations. The bond indices of the C-O bonds are relatively small for all the conformations. The net charges on the O- and C-atoms of the conformation A are -0.262 and 0.262, respectively. These results indicate that the inductive effect by which σ-electrons of the CH_2 groups are pulled toward the O-atom is a more important contribution than the π-electron delocalization effect which is responsible for the zwitterionic structure ZW(2). Thus the situation is reversed, compared with that of the ring-opened aziridine, for which the contribution of π-electron delocalization, i.e., ZW(1), is of dominant importance except for the structure D.

The present results indicate that the ring-opened aziridine and ethylene oxide exhibit the 1,3-diradical property[4,5] as trimethylene diradical[6] even in the case of the most stable trans-bent conformation. Thus the bond-length alteration and bond-angle deformation cannot effect the disappearance of diradical property of the species in contrast to the case of cyclopentadienyl cation.[6] The conclusions are independent of the approximations employed (CNDO[4], INDO[5] and MINDO/3[6]). Therefore, the electronic structures of the ring-opened aziridine and ethylene oxide should be regarded as the resonance hybrid of the 1,3-diradical and zwitterionic structures (Fig. 1) in contradiction to the conclusions by Huisgen[1] and Houk[2] who propose a complete "1,3-dipole." It should be noted, however, that the diradical property of these species may well disappear in the transition-state region of the 1,3-dipolar additions as a result of the symmetry-allowed orbital interactions with olefins.[9]

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(Received October 24, 1977)