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Unusual Bonding in the Isomers of 6,7,13a,13b-Tetrahydro-6H-dipyrido[1,2-a:2',1'-c][1,4]diazepine

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MNDO studies on the titled compound reveal that the most stable meso and dl conformers possess an extremely long CC single bond, the latter being lower in energy than the former by 4.9 kJ/mol. Available experimental results are explained by the characteristic molecular properties.

Recently, the meso and dl isomers of 7,8,13a,13b-tetrahydro-6H-dipyrido[1,2-a:2',1'-c][1,4]diazepine (1) have been prepared by Muramatsu et al., and the dynamic behavior of the isomers has been reported together with the spectroscopic data.1) Among other things, of special interest are the interconversion reactions as below. The meso form is converted thermally into the dl form, which reverts photochemically to the meso form, through the diradical intermediate. To understand the unusual isomerizations accompanied with a bond cleavage, it is essential to gain the structural facts of the isomers. In this paper, we undertake MNDO MO calculations2) with the aim of elucidating the energetically most favorable conformations and concomitant properties of 1. Based on the static electronic properties, we are concerned with the possible bond cleavages in the conversion processes.

Since the ^{1}H and ^{13}C NMR spectral data indicate magnetic equivalence between two 1,2-dihydropyridine skeletons of 1, we assume that the meso and dl isomers belong to the molecular-symmetry groups C_s and C_2, respectively. Following the Dreiding models, however, several conformations are possible for each isomer, so that we carry out full geometry optimizations by adopting every possible conformation of 1 with the MNDO MO method.

MNDO calculations reveal that the meso and dl isomers should exist as four and three distinct conformers, respectively. Figure 1 represents the perspective drawings and heats of formation (H_f) of the various equilibrium conformers. It turns out that the most stable dl conformer is lower in energy than the most stable meso one by 4.9 kJ/mol. From the thermochemical conversion, this finding is a matter of great significance. Of the meso conformers, the next stable isomer is close in energy to the most stable one. This is because the two structures differ simply by a spatial arrangement of the methylene groups.

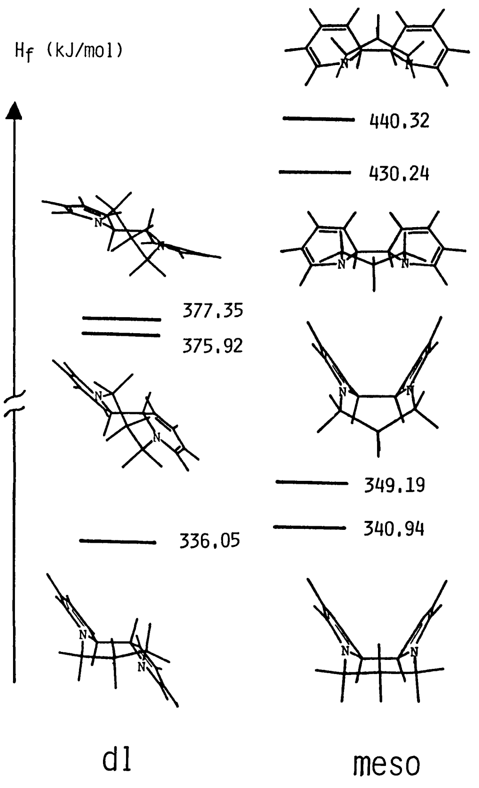

Fig. 1. Relative stability of various conformers of 1.

Figure 2 shows the geometrical parameters of the most stable dl and meso conformers. It is seen that the global features are essentially the same between the two structures, except that the meso conformer takes a cis-form and the dl conformer a trans-form with regard to the orientation of the two 1,2-dihydropyridine rings. As for nitrogen atoms involved in the rings, the fact that the C_4-N and C_{10}-N bonds are shorter than the remaining C-N bonds is suggestive of conjugation with the cis-butadiene-like moieties. Examining of the bond angles around the nitrogen atoms indicates that both nitrogen atoms assume the sp^2 configuration instead of the sp^3 pyramidal configuration. These are found to be intimately related with the result that the 1,2-dihydropyridine rings take nearly planar forms, each possessing the so-called six π-electrons. It is also found that the C_{13a}-C_{13b} bonds are extremely long in comparison with the other CC single bonds as well as the ones in ordinary saturated hydrocarbons.[2)] In the meso and dl structures, the bond lengths are 1.598 and 1.588 Å, respectively. In addition, the bond angles around the C_{13a} and C_{13b} atoms deviate appreciably from those found in ordinary sp^3 hybrid carbon atoms, the deviation amounting to ca. 5°. The occurrence of the long CC bonds is interpreted by means of steric and electronic factors. In the meso structure, the non-bonded interaction arising from H_{13a} and H_{13b} is taken out as the probable factor of steric hindrance, since the atomic distance of 2.18 Å is markedly short even in the equilibrium structure

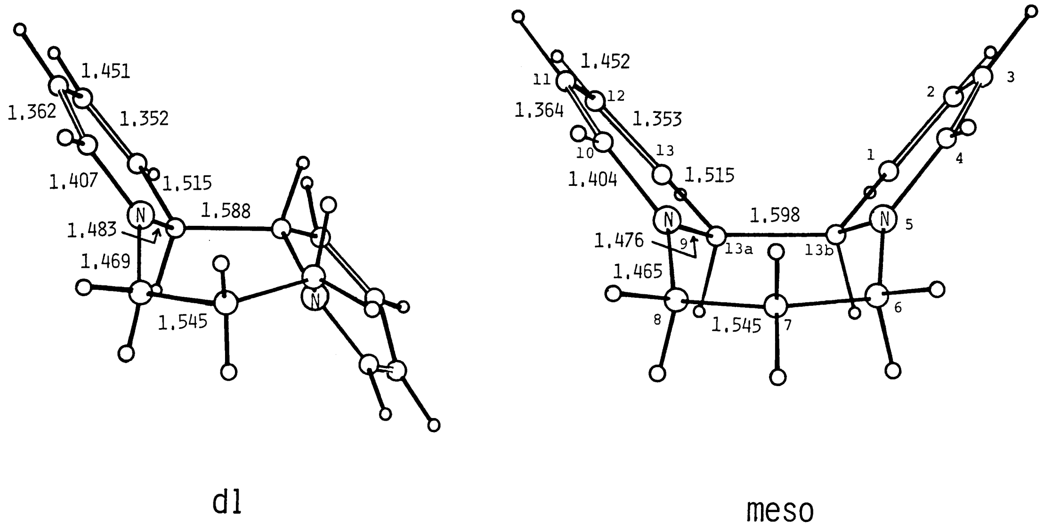

Fig. 2. Bond distances (Å) in the most stable dl and meso forms of 1.

compared with the sum of their van der Waal's radii, 2.40 Å.[3)] In the dl structure, the non-bonded interaction arising from H_1 and H_{13} is taken out as the probable factor because of the proton-proton distance of 2.36 Å being slightly short in comparison with the critical distance. In such cases, lengthening of the CC single bond should take place for relieving the steric interaction. Another probable factor to note is the effect of charge polarization. Evidently, the C_{13a} and C_{13b} atoms are surrounded by the more electronegative nitrogen and sp^2 hybrid carbon atoms, so that the carbon atoms of interest should be charged positively in the ground state. In fact, the inspection of the net atomic charges indicates that the C_{13a} and C_{13b} atoms possess the most positive charges of 0.19 (e) in the two structures. This brings about an extra Coulomb repulsion between the two carbon atoms, leading to an elongation of the CC single bond compared with the ones in usual bonding situations. Accordingly, the origins of the long CC bonds are explained in terms of repulsive forces arising from the steric hindrance and electrostatic interaction.

These characteristic electronic structures of the conformers are substantiated by available spectroscopic information.[1)] The ^1H NMR spectrum of the dl conformer shows that α-methylene protons appear as two distinct sets of multiplets in the regions of 2.75-3.15 ppm and 3.45-3.75 ppm. The pronounced non-equivalence of α-methylene protons can be interpreted by the difference in the spatial arrangements. The dl structure reveals that one of the α-methylene protons points toward the shielding region of the adjacent nitrogen atom and, consequently, the proton NMR signal should appear in the upfield region compared with the remaining proton.[4)] The longest wavelength absorption band of the conformers is observed at the near UV region. Assuming the geometrical structures obtained and using the INDO/S MO CI method,5) the lowest singlet transition energy is calculated to be 3.93 eV for the meso conformer and to be 3.91 eV for the dl conformer, in agreement with the respective experimental values of 3.76 and 3.40 eV. Configuration analysis indicates that the lowest excited singlet state is described mainly by an orbital jump from the HOMO to the LUMO for the meso conformer and from the HOMO to the next LUMO for the dl conformer. Interestingly, the HOMO has a bonding character at the C_{13a}-C_{13b} bond, while the LUMO and the next LUMO possess virtually a nonbonding character in both conformers. It is thus expected that the promotion of one electron from the HOMO contributes to the weakening of the CC bond through decrease in the bonding electrons and increase in the positive charges. As a result, the C_{13a}-C_{13b} bonds in the conformers should be further lengthened in the lowest excited state compared with those in the ground state. This implies that the photodissociation should occur easily in the electronically excited state.

In summary, the thermal conversion of the meso conformer would be responsible for the extremely long CC single bond caused by the steric and electrostatic repulsive effects, in conjunction with the thermodynamic stability of the dl conformer. The photolytic bond cleavages in the meso and dl conformers would be attributable to the bonding nature of the HOMO and the LUMO or the next LUMO, together with the electrostatic interaction. In particular, the effect of Coulomb repulsion in the excited state may be said to play a key role in the occurrence of photochemical bond fission. This will be shown to hold commonly for the homologous members of **1** as well as for the related compounds.6-8) Further studies on the dynamic behavior of the homologues of **1** are in progress.

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