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Extremely Long CC Single Bonds in Stereomers of 6,7,12a,12b-Tetrahydrodipyrido[1,2-a:2',1'-c]pyrazine

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MINDO/3 and MNDO calculations show that the titled compound should exist as two stereomers, dl form being lower in energy than meso form by about 2 kcal/mol. Anomalies in the thermal and photochemical cleavages at a certain CC bond are explained by the properties inherent to the two structures.

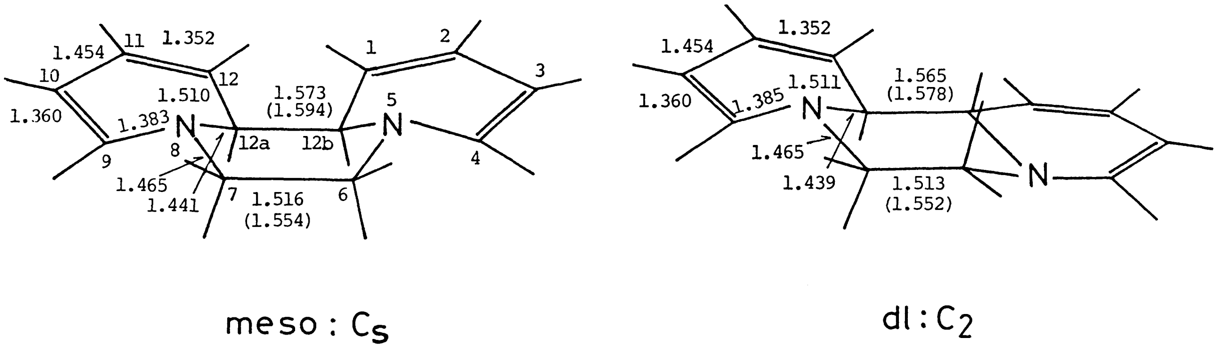
Recently, it has been shown that the reduction of 1,1'-(1,2-ethanediyl)-bis(pyridinium) dibromide with sodium amalgam affords the meso and dl forms of 6,7,12a,12b-tetrahydrodipyrido[1,2-a:2',1'-c]pyrazine (1), i.e., the cyclomers formed by intramolecular cyclization of 1,1'-(1,2-ethanediyl)bis(pyridinyl) diradical.[1,2] Interestingly, the meso form converts thermally to the dl form and, in contrast, light irradiation causes the reverse conversion through the diradical intermediate. Here, the diradical is confirmed by the observation of strong ESR signal due to the triplet transition of a two spin system. From these facts, Muramatsu and his co-workers have arrived at the conclusions that the above conversions would occur through cleavages of the C_{12a}-C_{12b} bonds (Fig. 1).

Our interest is that, of the possible conformations of 1, only two stereomers are isolated and shown to assume the meso and dl forms from the available spectroscopic data. In particular, the ^{1}H and ^{13}C-NMR spectra indicate that the meso form belongs to the symmetry group C_s and the dl form to the symmetry group C_2

because of the magnetic equivalence between two dihydropyridine-like moieties. Under these circumstances, we elucidate here the energetically favourable conformations of 1 by carrying out MINDO/3 and MNDO calculations,[3-5] adopting several conformations as a starting geometrical structure for iterative SCF MO procedures. On the basis of the results, we are concerned with the origins of thermal and photochemical cleavages at a certain CC bond in the two stereomers.

From MINDO/3 MO calculations, it turns out that for the meso form all of the starting C_s conformations suggested by the Dreiding models converge into a unique nuclear arrangement shown in Fig. 1, where the bond lengths (in Å unit) in parentheses refer to those obtained by MNDO. This suggests that no stable conformations should exist other than the equilibrium geometry thus obtained and it should correspond to the minimum point in the ground-state potential energy surface of C_s symmetry. As for the dl form, the situation is just the same as in the above case. Comparison of the total energies shows that the dl structure is more stable than the meso structure by 1.47 kcal/mol in MINDO/3. Similar geometrical parameters are obtained also by MNDO, the energy difference between the two structures being 2.54 kcal/mol.

Figure 1 shows that the global features are essentially the same between the two structures. As for nitrogen atoms involved, the fact that the C_4-N and C_9-N bonds are shorter than the remaining C-N bonds is suggestive of some conjugation with the cis-butadiene-like moieties. Surprisingly, it is found that the C_{12a}-C_{12b} bonds are extremely long compared with the other CC single bonds as well as the ones in ordinary saturated hydrocarbons.[4,5] We now give probable origins for the occurrence of such long bonds in the two stereomers. In the meso structure,



meso : C_s

dl : C_2

Fig. 1. Geometrical structures of the meso and dl forms of 1 optimized by MINDO/3. Bond lengths in parentheses refer to those optimized by MNDO.

two factors will be taken out, one the non-bonded interaction arising from H_{12a} and H_{12b} and the other the one arising from H_1 and H_{12}, since the associated distances are markedly short even in the equilibrium structure, i.e., 2.08 and 2.39 Å in MINDO/3, respectively. It seems that for relieving the steric interactions the $C_1C_{12b}C_{12a}C_{12}$ skeleton is too rigid to be rotated about the C_{12a}-C_{12b} bond since the moiety is blocked by the remaining groups. Needless to say, the total energy of a system and, hence, the equilibrium geometry consists in a fine balance among several energetic terms. If the CC single bond of question takes a standard length, say 1.52 Å as that of the C_6-C_7 bond, the system will gain an electronic stabilization on the one hand and a repulsive instability on the other hand because of the increasing proximity between the non-bonded hydrogen atoms. It may thus be said, inductively, that a stretch of the CC bond would take place as a most effective way for relaxing the steric repulsions, retaining the symmetry group C_s. In other words, the CC bond is forced to be lengthened so that the associated attractive force should be in competition with the repulsive force arising from the steric interactions in the equilibrium nuclear arrangement. In the dl structure, the H_{12a}-H_{12b} distance (3.08 Å) is markedly long and, accordingly, the steric hindrance between H_1 and H_{12} will be taken out as the probable factor, where the distance is 2.28 Å. In this case, however, such an effect would be slightly small in comparison with in the meso structure (see Fig. 1).

Moreover, we refer to the situation of the C_{12a}-C_{12b} bonds in the electronically excited singlet states of the meso and dl forms arising from a single MO jump from the HOMO to the LUMO. The MINDO/3 results show that the HOMOs as well as the LUMOs of the two forms are essentially the same at the C_{12a}-C_{12b} bond, the former having a bonding character and the latter an anti-bonding one. In Fig. 2 is shown a schematic representation of the HOMO and LUMO at the bond of interest, where valence atomic orbitals whose coefficients are less than 0.10 in absolute value are omitted. It then follows that the

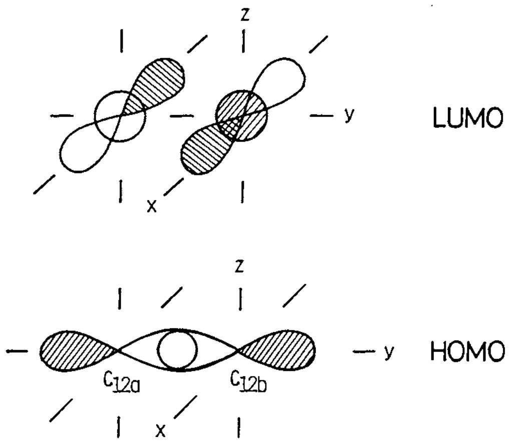


Fig. 2. Representation of the HOMO and LUMO at the C_{12a}-C_{12b} bond of the meso and dl forms obtained by MINDO/3.

CC single bonds would be further lengthened in the excited state compared with in the ground state. It is noted that within the MNDO approximation the LUMO has virtually a non-bonding character at the C_{12a}-C_{12b} bond in the two forms. In any way, the promotion of one electron from the HOMO contributes to weakening of the CC bonds, leading to the result that the CC single bonds should easily cleavage in the electronically excited state.

Finally, we refer to the nature of nitrogen lone-pair interaction6) in the two stereomers briefly. Analyses of orbital properties reveal that in the meso and dl structures through-bond interactions via the C_{12a}-C_{12b} bonds are stronger than through-space interactions and the associated energy splittings between the next HOMO (non-totally symmetry) and the HOMO (totally symmetry) are calculated to be 0.37 (0.34) and 0.39 (0.35) eV by MINDO/3 (MNDO), respectively.

In summary, the thermal bond cleavage in the ground state of the meso form would be attributable to the extremely long CC single bond caused by steric interactions and the photochemical bond cleavages in the excited states of the meso and dl forms to the nature of the HOMO and the LUMO. It is added that, in marked contrast with this work, interesting articles have recently appeared which are concerned with the extremely short CC single bonds,7,8) and further studies on the compounds with such long CC single bonds are now in progress.

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