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# Quantum chemical assessment of the possibility of soliton switching

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Bond deformation in the photon-excited state of simplified model systems designed for soliton switching was examined in a quantum chemical manner. It has been concluded that occurrence of the structural change indispensable to the switching function is doubtful.

There has been a growing interest in the molecular-level fabrication of various electronic devices such as the molecular switch, molecular memories, and so on.[1] Under these circumstances Carter[2] has proposed a utilization of the soliton-switching function in a modified *trans*-polyacetylene chain as a "part" for the architecture of electronic switching devices of molecular size. The basic idea of this switching lies in the structural change in the olefin, *trans*-N,N-dimethyl-2-nitroethenamine, by the photon excitation in Fig. 1(a). Therefore, in a *trans*-polyacetylene chain similarly modified, the interchange of single and double bonds accompanied by passage of the soliton controls the possibility of the photon excitation at these modifiers [Fig. 1(b)].

It has been reported from x-ray diffraction measurements that the canonical form *B* in Fig. 1(a) already contributes to the ground-state geometry of this molecule.[3] This tendency has been ascribed to the electron-donating and -accepting properties of amino and nitro groups, respectively, the so-called "push-pull" property. Hence, in the sense of the valence-bond representation, the weight of the canonical form *B* in the excited-state geometry should increase in order to guarantee the desirable structural change.

According to the biradical approach to the bond deformation of $\pi$ electron systems used by Fukui and Tanaka,[4] the bond deformations in the ground and the excited states are essentially determined by the orbital patterns of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), respectively, of the molecular system in its ground state. For instance, this concept was successfully applied to predict the polymer-chain geometry in the excited state of *cis*-polyacetylene,[5] which has been verified experimentally.[6]

In this Rapid Communication, we report the first assessment of the possibility of structural change in the excited state of these compounds by means of this approach.

The molecules *A* and *B* shown in Fig. 2 were employed as model systems for the orbital-pattern analyses. Also, poly (1-amino-2-nitrobutadiene), *C*, was considered as a model for Carter's polymer in Fig. 1(b). Methyl groups connected to the nitrogen atom in Fig. 1 were modeled by hydrogen

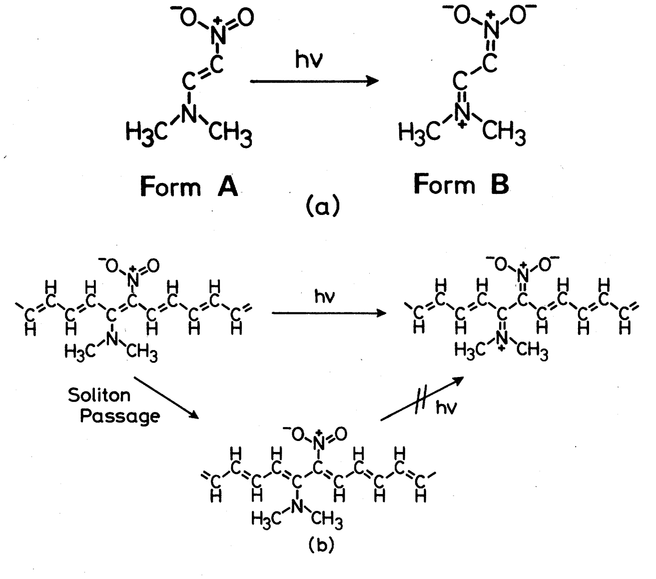

FIG. 1. Basic idea of soliton switching proposed in Ref. 2. (a) Expectation of structural change from the canonical form *A* to *B* in *trans*-N,N-dimethyl-2-nitroethenamine by the photon excitation; (b) mechanism of soliton switching in *trans*-polyacetylene modified with an amino and a nitro group.

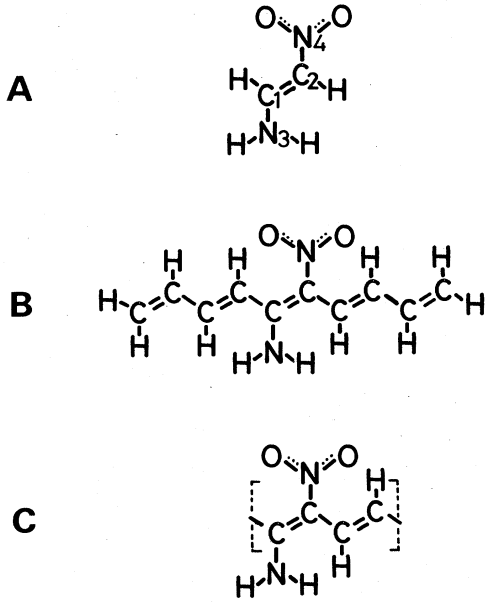

FIG. 2. Model systems employed for the orbital-pattern analyses; 1-amino-2-nitroethene (*A*), 5-amino-6-nitro-1,3,5,7,9-decapentaene (*B*), and poly(1-amino-2-nitrobutadiene) (*C*).

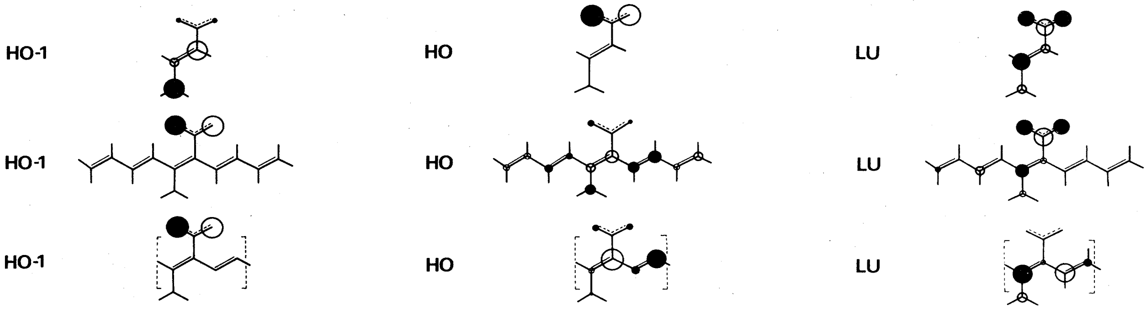

FIG. 3. The patterns of the next HOMO [(HO-1)MO], the HOMO, and the LUMO of the molecules *A* (top) and *B* (middle) along with those of the (HO-1)CO, the HOCO, and the LUCO of the polymer *C* (bottom). The round marks indicate the phase and magnitude of $\pi$ AO's.

atoms for the sake of simplicity, since the function of the amino group will not be very much changed.

The molecular orbitals (MO's) of *A* and *B* were obtained by the *ab initio* [self-consistent-field (SCF), molecular-orbital] method[7] with the Slater-type orbital expanded by 3 Gaussian functions (STO-3G) basis set.[8] The bond distances $C_1$–$C_2$, $C_1$–$N_3$, and $C_2$–$N_4$ in *A* were energetically optimized. Other geometrical parameters in *A*, *B*, and *C* utilized the standard bond lengths and angles obtained for similar molecules.[9,10] The crystal orbital (CO) of *C* was calculated by the tight-binding SCF CO method including all the valence electrons at the level of the complete neglect of differential-overlap approximation as described in Ref. 5. The patterns of the principal MO's and CO's of these are shown in Fig. 3.

The HOMO of *A* represents lone pairs on oxygen atoms in the nitro group, whereas the pattern of the next HOMO [(HO-1)MO] indicates the C=C double bond due to the in-phase overlapping between the carbon $\pi$ atomic orbitals (AO's). For *B* and *C*, the patterns of the HOMO and the highest occupied CO (HOCO), respectively, favor bond alternation in the carbon chains like –C=C–C=C– in the same sense. The level of the lone-pair MO (or CO) of oxygen atoms lies lower in *B* and *C*. These orbital patterns do not favor the $C=NH_2$ double bond due to the out-of-phase overlapping between the carbon $\pi$ and the nitrogen $\pi$ AO's. Note that the contribution from the $\pi$ AO of this nitrogen atom to these orbitals becomes less with the variation from *A* to *C*.

The pattern of the LUMO of *A* indicates that in the excited state of *A* the C=C bond becomes weakened, whereas the $C-NO_2$ bond is strengthened. This feature does not essentially change in *B* and *C*. It should be stressed that there are *no tendencies* to form the $C=NH_2$ double bonds in the excited states of all these molecules because of the out-of-phase overlapping between the carbon and the nitrogen $\pi$ AO's. Furthermore, it is seen that the contribution from the $\pi$ AO of the nitrogen atoms in the $NO_2$ and the $NH_2$ groups to the LUMO or the LUCO becomes diminished in changing from *A* to *C*. As a matter of fact, in *C*, there is almost no participation of the $\pi$ AO's of the $NO_2$ group in the LUCO.

In total, all of these patterns strongly suggest that only the interchange of the C=C bonds with the C–C bonds occurs in the excited state of a long polyene chain irrespective of the existence of a small number of side groups. Therefore, no remarkable structural change could be expected with respect to the bond distances between the main chain and the side groups in the excited state of Carter's polymer. In this respect, we have to be rather skeptical about the occurrence of the soliton-switching function therein.

Finally, it is recommended that this kind of molecular design should utilize quantum chemical assessment as a theoretical screening prior to actual preparation of devices.

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