BARRIERS TO CONFORMATIONAL TRANSFORMATIONS IN SYMMETRICAL LINEAR CONJUGATED SYSTEMS

A. D. Kachkovskii and O. A. Zhukova

A quantum-chemical study has been carried out on conformational transformations in the ground and first excited states of symmetrical polymethine dyes and related \(\alpha,\omega\)-disubstituted polyenes. The magnitude of the trans-cis isomerization barriers depends on the length of the conjugation chain, position of the rotated bond, electron-donor capacity of the terminal groups, and occupancy of the electron shell. The rotation of molecular fragments in the excited state may lead to a change in the nature of the first electronic transition.

Applications of linear conjugated systems (LCS)

\[
G_1 - (CH_2)_m - G_2
\]

are based on their capacity to absorb and emit light in the visible and near-IR spectral regions.

In addition to the common uses of polymethine dyes and related polyenes as sensitizers [1], laser media and quality modulators [2], these systems have recently found use as components of highly sensitive fluorescent labels and readily polarizable systems for nonlinear optics. Hence, a need has arisen for the synthesis of new compounds of this class with useful properties. The fluorescence quantum yield is one of the most important indices. The drop in this index in polymethine dyes and polyenes is related to trans-cis isomerization in the excited state at one of the carbon-carbon bonds in the conjugation chain [3].

In the present work, we carried out a systematic quantum-chemical study of the effects of such factors as molecular topology, occupancy of the electron shell (neutral and charged polyenes), position of the rotated bond, and basicity of the terminal groups on conformational transformations in LCS I. The barriers are determined by the difference in the energies of the initial planar molecule and the conformation, in which two molecular fragments are twisted by 90°. All the excitation energy is presumably spent on the trans-cis isomerization since this process specifically causes a drop in the fluorescence quantum yield. Thus, we used the equilibrium geometry optimized in the ground state density matrix. Only one dihedral angle in the conjugation was altered in the perpendicular conformation.

The decisive factor in selecting a suitable quantum-chemical approximation was accuracy in calculating the excited state energy. As shown in our previous work [4, 5], LCS I is very sensitive to selection of the MO basis for constructing the multiconfigurational function of the excited state, especially upon lengthening of the chain when the molecule absorbs or fluoresces in the near IR. Since, we were interested not in the absolute values of the rotational barriers of the molecular fragments but primarily in their change in homologous series of LCS I, results suitable for analysis were obtained in the AMI approximation using the 25 lowest singly excited configurations.

To a first approximation, the rotational barriers \(B\) are proportional to the extent of \(\pi\)-occupancy of the \(\rho_{\mu\nu}\) bond, at which isomerization occurs such that \(B = (\rho_{\mu\nu} + 0.057)\beta/0.825\) [6], where \(\beta\) is the resonance integral (\(\approx 4\) eV). Since the occupancies of the \(\pi\)-bonds correlate with their length \(R_{\mu\nu} = 1.54 - 0.14\rho_{\mu\nu}\), we have: \(B = aR_{\mu\nu} + b\), where \(a\) and \(b\) are
constants. As shown by calculations for vinylogous series of conjugated compounds I, such a linear dependence between the barrier energies and optimized lengths of C—C bonds is seen only in the very narrow range from 1.34 to 1.39 Å. In the general case, \( B = B(R_{im}) \) is exponential in form.

Symmetrical systems I \((G_1 = G_2)\) with an even number of methine groups in the polymethine chain (PC), \(\alpha,\omega\)-diheterosubstituted polyenes II (HP),

\[
G - (\text{CH}=\text{CH})_m - G,
\]

II

and systems with odd \( m \), polymethine dyes III (PMD)

\[
G - (\text{CH}=\text{CH})_m - \text{CH}=G,
\]

III
differ sharply in the electronic structure [5]. Polyenes II have significant alternation of the occupancy of the adjacent C—C bonds, both in the ground and excited states. Upon excitation, the bond occupancies are significantly altered such that the sequential order of bonds with higher and lower order becomes opposite. On the other hand, levelling-out of the bond occupancies occurs in PMD. Since the magnitude of the rotational barriers is determined by the bond occupancy, the conformational transformations in PMD and HP should differ substantially.

It was shown earlier [5, 7, 8] that the length of the C—C bonds in PC depends on the electron donor capacity of the terminal groups \((TG)\), which is quantitatively characterized by the topological parameter \( \Phi_0 \). An increase in \( \Phi_0 \) corresponds to a shift in electron density from the terminal groups to the polymethine chain. Furthermore, index \( \Phi_0 \) is related to the electron donor capacity of LCS \( \varphi_0 \), which is a qualitative characteristic of the position of the frontier levels relative to the nonbonding \( \pi \)-level of a homogeneous PC [5]. For sufficiently long PMD, \( \varphi_0 = \Phi_0 \). For HP, \( \varphi_0 = \Phi_0 \pm 45^\circ \), i.e., the effects of the same terminal groups in even polyenes and odd polymethines are opposite. This is related to the different arrangements of the frontier MO nodes on bonds or atoms, respectively.

The symmetrical arrangement of the Hückel HOMO and LUMO relative to the nonbonding level \((\varphi_0 = 45^\circ)\) corresponds to the most stable LCS. In this case, the bonds in PMD are most levelled out, while in HP, they maximally alternate in length. As \( \varphi_0 \to 0^\circ \) or \( \varphi_0 \to 90^\circ \), bond alternation appears at the chain ends in PMD, while, on the other hand, the bonds level out in HP.

Calculations with model TG \((-\text{CH}=\text{NH}_2, -\text{CH}=\text{O}, \) and \(-\text{CH}=\text{CH}_2)\) were carried out in this work for LCS I. The topological index increases in this series \((33^\circ, 63^\circ, 90^\circ)\), which is accompanied by an increase in the amplitude of bond alternation at the chain ends in PMD. The calculated rotational barriers for different bonds in the PC in polymethines and the oxidized and reduced forms of polyenes in the ground and excited states are given in Fig. 1.

The magnitude of the rotational barrier in the ground state of PMD reaches both maximal and minimal values at the chain ends. The values of \( B \) for adjacent bonds are levelled out in the middle of the conjugated system and tend to a constant. The barriers are more sensitive to the electron donor capacity of the terminal groups at the chain ends. In previous work [7], we showed that the sequential order of bonds with enhanced and diminished \( \pi \)-occupancy is opposite in polymethines with \( \varphi_0 < 45^\circ \) \((-\text{CH}=\text{NH}_2)\) and \( \varphi_0 > 45^\circ \) \((-\text{CH}=\text{O} \) and \(-\text{CH}=\text{CH}_2)\). The same behavior is observed for the rotational barriers.

The bonds are more levelled out in the excited state of polymethines as reflected in the significant diminution in the amplitude of the rotational barriers. The sign of difference \( B^* \) for neighboring bonds is opposite to the difference \( \Delta B \).

The calculations for neutral polyenes (Fig. 1c, d) in the ground state predict a significantly greater amplitude of alternation of the barriers \( B^0 \) than in polymethines. The sensitivity to the nature of terminal groups is seen mainly in the rotations around the short bonds, where the barriers are significant. However, the difference in the value of \( B^0 \) in the middle of the chain in polyenes with different terminal moieties levels out. On the other hand, the nature of the terminal groups in the excited state has a considerable effect on the conformational transformation such that the introduction of an amino group with low electron donor capacity leads even to a negative value of \( B^* \) for the second bond.

A change in the occupancy of the electron shell (Fig. 1e, f) is accompanied by change in the sequential order of formally single and double bonds. The rotational barriers \( B^0 \) vary in complete accord with this circumstance. Calculations for the excited