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Origin of states connected with twisted intramolecular charge shift in polymethine cations: a simple analytical treatment

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Abstract

Based on the Hueckel method and simple model of long-range interelectron repulsion, the tendency for polymethine cations to form twisted structures in the excited state is elucidated. Changes in energy level positions and populations as well as the intramolecular charge transfer occurring on twisting are simulated in terms of π-decoupling of the corresponding conjugated system. The charge transfer between the fragments formed is shown to depend on the end-group nature and to alternate in direction for rotations of successive bonds in the polymethine chain. It is also reversed on switching from the ground to the excited state. The energy advantage of certain excited-state twistings over the planar form can be understood by taking into account the long-range Coulomb interaction of electrons in a quasi-one-dimensional system. On this basis, electron density transfer from the longer to shorter fragment is preferable and can compensate the general energetic disadvantage of π-decoupling upon twisting. Using the $[Me_2N–(CH)_{13}–NMe_2]^+$ cation as an example, it is inferred that the rotation around the 2–3 bond in the excited state is highly probable for long streptopolymethines, whereas twisting the 1–2 bond is improbable. The reverse predictions are found for boron-containing polymethines. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Hueckel method; Polymethine cations; Twisted structures

1. Introduction

An active research on excited-state energy degradation in polymethine cyanine dyes calls for a better insight into the mechanism of their typical *trans–cis* photoisomerization processes. These processes involve excited-state charge localization and formation of twisted species which can be compared to the twisted intramolecular-charge-transfer (TICT) states [1,2]. A special challenge in this case is to determine the relative tendency for the various bonds in a long polymethine molecule to twist after excitation and to correlate this tendency with the electronic density redistribution over the two mutually perpendicular donor and acceptor moieties. Most informative and illustrative in this respect is a multidimensional potential-energy surface calculated by a suitable quantum-chemical method which can provide a quantitative description of the photochemical conversion (see, e.g. Refs. [3,4]). On the other hand, most pronounced regularities can also be revealed in the framework of qualitative models which are useful in the first stage of a theoretical study. To exemplify, two substantially different types of minima in the S_1 potential surface connected with *trans–cis* photoisomerization of polyenes and polymethine dyes are distinguishable even at the sub-Hueckel level [5], in terms of Dewar's MO perturbation theory [6].

In this paper, we focus on another regularity deducible from similar qualitative MO arguments which concerns the relative probabilities, on the one hand, for different bonds within a polymethine chain of a dye cation to lead to the twisted conformation in the excited state, and on the other hand, for these states with twisted geometry to lose the excitation energy acting as photochemical 'funnels' [7,8].

Barriers are evidently most important to determine which of the bonds is the reactive one. As of now, not only crude models but also sufficiently advanced all-valence methods are not reliable in predicting barrier sizes. In view of this, we chose to adopt the Bell–Evans–Polanyi principle [6] which relates changes in barrier sizes to changes of the relative energies of precursor and successor. A more exothermic product formation is linked with a smaller activation barrier.

For instance, it follows from the data calculated in [9] that the photoexcited cation $[Me_2N–(CH)_{13}–NMe_2]^+$ (Cy(15)) is likely to undergo a twisting around the 2–3 bond in the

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Table 1
Ground state and charge-shift excited state energies of the planar and twisted conformations of the Cy(15) cation calculated by AM1 (ground state energies) and CNDO/S–CI ($S_1 - S_0$ and $S_2 - S_0$ energy differences) [9]

Ground state energy (eV)	0	0.50	0.56	0.61	0.71	0.77	0.85	1.0
Bond rotated by 90°	Planar	1–2	3–4	5–6	7–8	2–3	6–7	4–5
Excited state energy (eV)	2.135	2.06	2.27	2.31	2.32	2.65	3.22	4.18
Bond rotated by 90°	Planar	2–3	4–5	6–7	7–8	5–6	3–4	1–2

excited state, as this structure has an energy advantage over the planar one (see Table 1). The data reported also point to the alternation of the energy differences between twisted and planar forms in successive passing from one bond to the adjacent one along the chain. Upon excitation, the alternation is reversed (see Table 1). In the present paper, these regularities are elucidated using general considerations.

Section 2 is devoted to the simple qualitative arguments which account for the alternation of the magnitude and direction of the charge transferred upon twisting between the mutually perpendicular molecular fragments. This alternation depends on the fragment lengths, the end-group-type, and the electronic states. The relative stability of the excited twisted forms is also considered. The reasoning is illustrated by the results provided by the simple Hueckel method for Cy(15) and its boron-containing analogue.

In Section 3, certain twisted structures are shown to be energetically preferable as compared to the planar form, which is due to the correction for the long-range Coulomb interaction of electron densities transferred between fragments.

Section 4 compares the approach developed and more sophisticated methods, and presents, as a result, a more penetrating insight into the origin of the excited charge-shift states with twisted structure in the quasi-one-dimensional case.

2. Energy spectrum and charge transfer in twisted structures in the Hueckel approximation

Consider a π-conjugated quasi-one-dimensional molecule which absorbs a photon and turns from the all-*trans* planar form into a relatively stable excited state with a twisted structure possessing two mutually perpendicular π-decoupled fragments. Its relative stability results from symmetry factors and hence from the spatial arrangement of electron clouds: the intrafragment de-excitation is prohibited, as there are no vacancies on low-lying MOs, whereas the charge transfer between unconjugated fragments is hindered. The above prerequisites prove to be sufficient for construction of a general qualitative model for an energy spectrum and for the charge transfer direction typical for twisted species.

Twisting is known to be quite general for polymethine cations possessing conjugated chains that contain an odd number of carbon atoms, two identical heteroatomic end-groups, and an even number of π-electrons. Both planar and twisted forms of the chain should have a closed-shell ground-state structure, i.e. with doubly occupied bonding MOs. If we assume the conjugation between molecular subsystems to be completely broken at the bond rotated by 90°, then both fragments, odd- and even-membered, should possess an integer number of electron pairs, one fragment carrying a positive charge, and the other being uncharged (a 'hole-pair' situation [8,10,11]), depending on the nature of the end-group (see Fig. 1). If we successively vary the rotated bond, i.e. the position of π-decoupling, passing along the chain, it is noticeable that once the fragments change their lengths by an atom, one of them loses and the other gains either a vacant or a doubly occupied electronic level. Thus, the positive charge migrates between them, and their cationic and neutral forms interchange alternatingly for neighbouring bonds, as shown in Fig. 1.

We now turn to the analysis of the excited states of the twisted structures. In principle, the electronic transitions could occur within each of the fragments of the twist-induced chain partitions, but they are hardly possible with regard to the above-mentioned symmetry-based stability condition. Thus, our concern here focuses on the excited states characterized by the absence of vacancies below the singly occupied level in both fragments. As evident, such an excitation is accompanied by a transfer of an electron from the highest doubly occupied MO of one fragment to the other fragment (see Fig. 1) and hence by the change-over between their cationic and neutral form (with switching to a so-called 'dot–dot', i.e., biradicaloid, situation [8,10,11]). In turn, the alternation of charged forms for fragments produced by the successive chain partitions should occur out of phase with respect to the ground state (see Fig. 1).

The above model is consistent with the previously reported [5] qualitative consideration of the polymethine chain terminated by nitrogen atoms; it is represented as an odd-alternant conjugated system π-decoupled at the rotated bond and thus divided into odd-membered polymethinic and even-membered polyenic fragments, each carrying one of the spatially separated frontier molecular orbitals; the positive charge is localized on the even fragments in the ground state and on the odd fragments in the excited state because the transfer of an electron from the polymethinic to the polyenic subsystem occurs upon excitation. This concept proved fruitful in the evaluation of probabilities for various possible twistings occurring on excitations in polymethine molecules with more complex end-groups [12,13]. The

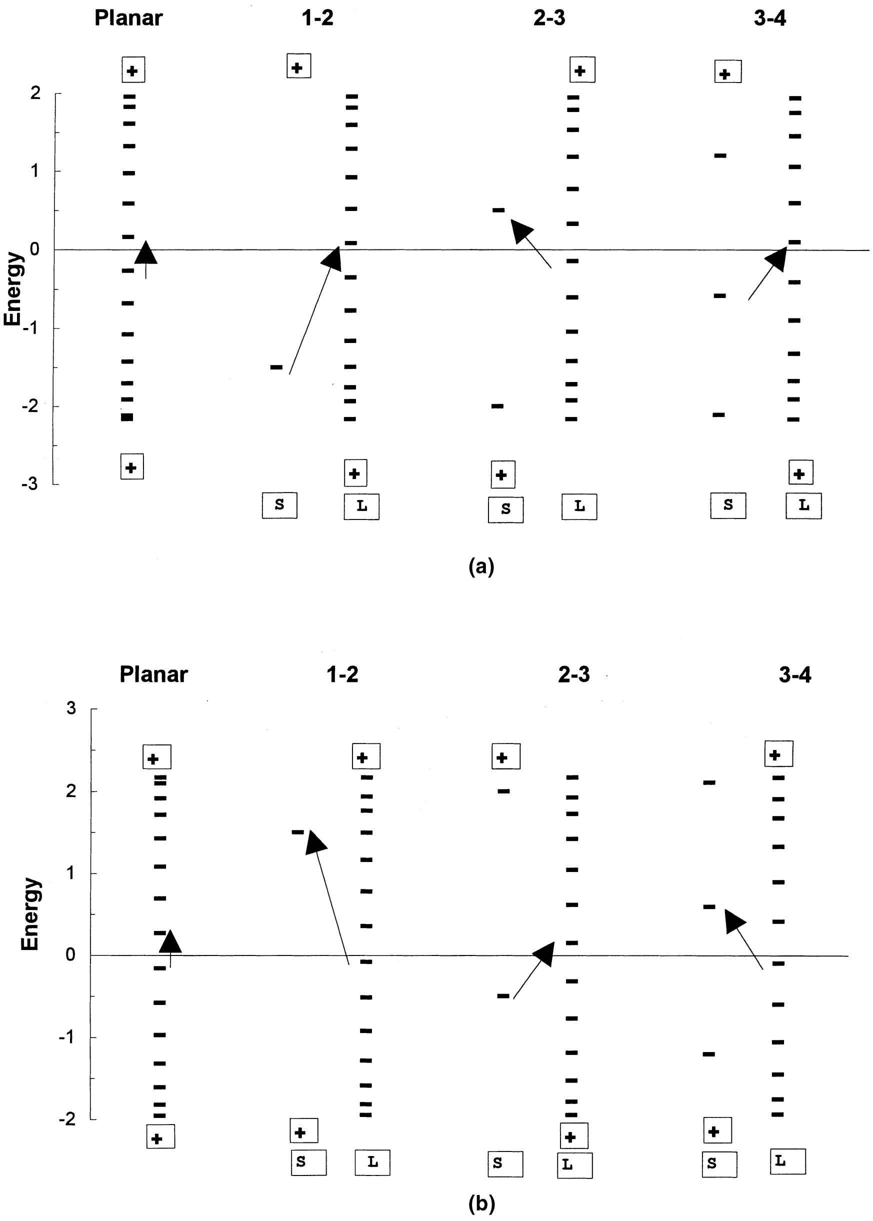

Fig. 1. Energy spectra (in units of $|\beta|$) for planar and twisted structures of the cations $[H_2N–(CH)_{13}–NH_2]^+$ (a) and $[HB–(CH)_{13}BH]^+$ (b). Arrows denote electronic excitations. Cationic charges at fragments in the ground and excited state are indicated at the bottom and top, respectively. Short and long fragments are respectively labeled by 'S' and 'L'. (HMO approximation).

treatment developed in this section produces a more general picture irrespective of a concrete end-group and also elucidates the alternation in the inter-fragment charge transfer for the successive bonds rotated.

As an illustration, we refer to the results provided by the simple Hueckel method for the streptopolymethine cation Cy(15) and its boron-containing analogue. As far as the π-approximation is concerned, hereafter we regard amino groups as terminal groups of Cy(15) without differentiation for alkyl substitution. Fig. 1 is based on the Hueckel calculation of the energy spectra and π-MOs for the corresponding planar forms and some of the possible pairs of the polymethine chain fragments terminated by either a NH_2 or a BH group. As seen from the figure, the positive charge of the planar Cy(15) cation is concentrated on the even fragment in the twisted ground state and transfers to the odd fragment upon excitation of the twisted form. The p-electron level of the boron atom lies above that of the carbon atom, i.e. above the Fermi level, and hence the resulting charge distribution is opposite for the polymethine cation with BH end-groups as compared to NH_2-polymethines. Numerical results are presented only for Cy(15) (see Tables 2 and 3) where the twisted forms were previously calculated by more sophisticated methods [9] (see also Table 1). Tables 2 and 3 list the values of atomic electron densities, the charges transferred between the fragments (for unambiguous under-

Table 2
Atomic π-electron densities and charge transfers, i.e. the changes in total π-density of the smaller fragment, q_0 (in units of the electron charge), and total π-energies, E_g (in units of $|\beta|$) obtained by the Hueckel method for the ground state of the planar and the various twisted forms of the Cy(15) cation

Atom (number), charge		Planar structure	Bond twisted						
			(1–2)	(2–3)	(3–4)	(4–5)	(5–6)	(6–7)	(7–8)
N (1)	+2	1.7621	2	1.6	1.8502	1.681	1.8182	1.7102	1.8052
C (2)	+1	0.7511	0.9123	0.4	0.9066	0.5782	0.8635	0.6414	0.842
C (3)	+1	1.1215	1.0009	1.0565	1.2432	1.0394	1.1903	1.0654	1.1691
C (4)	+1	0.8804	0.9105	0.9991	0.898	0.7014	0.984	0.7729	0.9681
C (5)	+1	1.0674	1.0037	1.0584	1.0014	1.0666	1.1439	1.0111	1.1175
C (6)	+1	0.908	0.9065	0.996	0.8951	0.9985	0.878	0.7991	0.9941
C (7)	+1	1.0528	1.0093	1.0629	1.006	1.0698	1.0024	1.0812	1.1039
C (8)	+1	0.9144	0.8989	0.9897	0.8883	0.9932	0.873	0.9972	0.8482
C (9)	+1	1.0528	1.0196	1.0719	1.0157	1.0778	1.0107	1.0872	1.0046
C (10)	+1	0.908	0.8844	0.9767	0.8743	0.9811	0.8601	0.9869	0.8381
C (11)	+1	1.0674	1.0408	1.0913	1.0365	1.0964	1.0307	1.1042	1.0226
C (12)	+1	0.8804	0.8511	0.9455	0.8414	0.9508	0.8277	0.9579	0.8072
C (13)	+1	1.1215	1.0999	1.148	1.0954	1.1522	1.0891	1.1586	1.08
C (14)	+1	0.7511	0.7171	0.8142	0.7074	0.8204	0.6939	0.8291	0.674
N (15)	+2	1.7621	1.745	1.7898	1.7405	1.7931	1.7344	1.7978	1.7252
q_0		–	0.2379	−0.513	0.3653	−0.515	0.4174	−0.49	0.4566
E_g		−22.84	−22.31	−22.07	−22.17	−22.09	−22.13	−22.1	−22.11

For the nitrogen atom and the nitrogen–carbon bond, the Coulomb integral α_N and resonance integral β_{NC} are respectively, set equal to $\alpha_N = \alpha_C + 1.5\beta$ and $\beta_{NC} = \beta$.

Table 3
Atomic π-electron densities and charge transfers, i.e. the changes in total π-density of the smaller fragment, q_0 (in units of the electron charge), and total π-energies, E_e (in units of $|\beta|$) obtained by the Hueckel method for the excited state of the planar and the various twisted forms of the Cy(15) cation

Atom (number), charge		Planar structure	Bond twisted						
			(1–2)	(2–3)	(3–4)	(4–5)	(5–6)	(6–7)	(7–8)
N (1)	+2	1.7535	1	1.8	1.6115	1.805	1.6819	1.7991	1.7105
C (2)	+1	0.7863	1.0425	1.2	0.7095	0.9673	0.6896	0.894	0.6984
C (3)	+1	1.0584	1.0018	0.9069	0.679	1.0728	0.9165	1.1073	1.0013
C (4)	+1	0.9671	1.0481	0.9958	1.06	1.1549	0.9342	1.0651	0.8957
C (5)	+1	0.959	1.0074	0.9152	1.0029	0.8908	0.7778	1.0219	0.8853
C (6)	+1	1.0313	1.0404	0.9833	1.0541	0.9932	1.0712	1.1127	0.9746
C(7)	+1	0.9188	1.0176	0.9321	1.0119	0.9045	1.0049	0.8682	0.8341
C (8)	+1	1.051	1.0274	0.962	1.0416	0.9726	1.0613	0.9877	1.0874
C (9)	+1	0.9188	1.0342	0.9582	1.0287	0.9321	1.0206	0.8928	1.0094
C (10)	+1	1.0313	1.0059	0.93	1.0192	0.9371	1.0386	0.9506	1.0678
C (11)	+1	0.959	1.0631	0.9981	1.0591	0.9772	1.0525	0.9436	1.0413
C (12)	+1	0.9671	0.9642	0.8773	0.9756	0.878	0.9923	0.8823	1.0188
C (13)	+1	1.0584	1.1312	1.0769	1.1297	1.0632	1.1267	1.0412	1.1208
C (14)	+1	0.7863	0.8206	0.7238	0.8289	0.717	0.841	0.7085	0.8601
N (15)	+2	1.7535	1.7864	1.7404	1.7882	1.7343	1.7909	1.7252	1.7943
q_0		–	−0.754	0.4601	−0.598	0.4346	−0.524	0.4443	−0.475
E_e		−22.41	−20.73	−21.42	−21.48	−21.64	−21.65	−21.7	−21.7

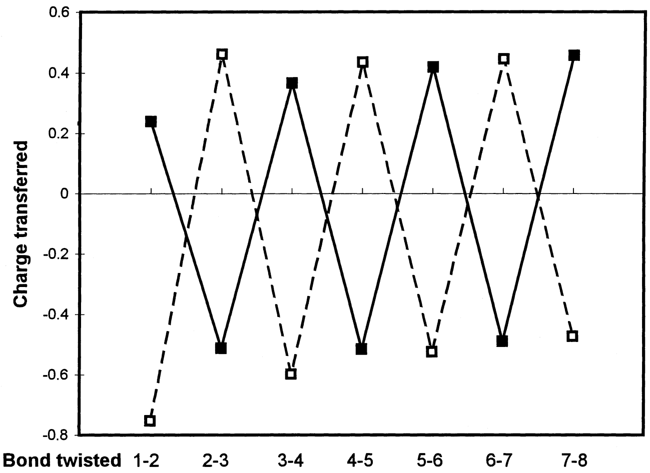

Fig. 2. The relationship between the position of the twisted bond and magnitude of the total π-charge transferred (positive values in units of the electron charge correspond to the electron density transfer from the longer to shorter fragment) in the ground state (solid line) and excited state (dashed line) of the cation Cy(15), with reference to the planar structure (HMO approximation).

standing, they are defined as changes in total π-density of the smaller fragment), q_0, and molecular π-energies (calculated as sums of those for the fragments) in the ground and excited state, E_g and E_e. Relationships between the position of the twisted bond in the chain, on the one hand, and the charge transferred as well as the molecular energy, on the other hand, are demonstrated in Figs. 2 and 3. To estimate the charge transfer associated with a certain twist in the ground and the excited state, we summed changes in atomic electronic densities over the smaller of the two resulting fragments (regarded as separate π-systems), with reference to the corresponding state and moiety of the planar structure.

The magnitudes of the charges transferred upon twisting, q_0, substantially vary only at the end groups and chain ends, whereas in the middle of the chain they approach the value of $0.5e$ (e is the electron charge). Most important is the alternation of q_0 for different bond twistings. This variation of q_0 is the basis for the energetic oscillations as shown below for inclusion of interelectronic repulsion. Ground state energies alternate as bonds in the chain are successively rotated one by one, whereas excited-state energies monotonically decrease (though with alternating rate) as the bond rotated approaches the middle of the chain. Interestingly, the alternation of ground-state energies is in qualitative accord with the data of Table 1, but the magnitude of alternation is much less than that calculated by the AM1 and CNDO/S–CI methods [9] (taking into account that the absolute value of the resonance integral β in the Hueckel approximation is normally taken equal to 4 eV). On the contrary, the trend in the values of excited-state energies (monotonic change) differs essentially from that resulting when more sophisticated techniques are used as in Ref. [9] (alternation). As a consequence, within the simple Hueckel model, the structure twisted around the 2–3 bond in the excited state is calculated to be highly improbable in comparison with alternative twisted conformations, because it is characterized by one of the most high-lying energies. Moreover, all excited-state π-energies of the twisted structures turn out to be higher than that of the planar form by the value of order of $|\beta|$ (due to the π-decoupling of one bond), which practically rules out the occurrence of twisting in the excited state at all, irrespective of the bond position. This suggests that the simple Hueckel method conceptually fails to account for the formation of certain twisted forms of quasi-one-dimensional systems in the excited state. Therefore, to elucidate the origin of the energetically low-lying twisted conformers

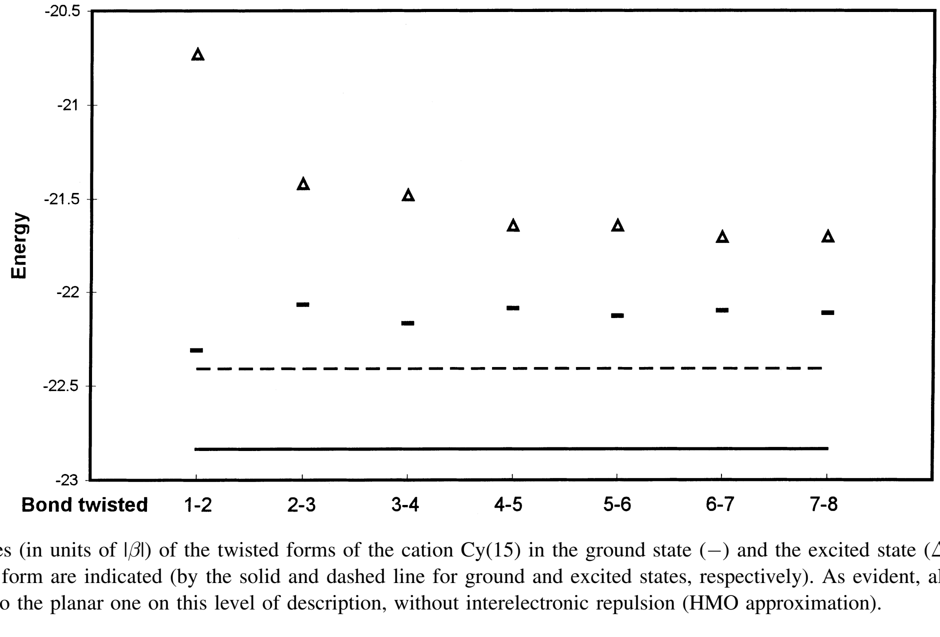

Fig. 3. Total π-energies (in units of $|\beta|$) of the twisted forms of the cation Cy(15) in the ground state (−) and the excited state (Δ). For comparison, the energies of the planar form are indicated (by the solid and dashed line for ground and excited states, respectively). As evident, all twisted structures are unstable with respect to the planar one on this level of description, without interelectronic repulsion (HMO approximation).

in the excited state, we have to include the effects of electron interaction.

3. Contribution of long-range Coulomb repulsion

Present-day powerful computational possibilities in quantum chemistry allows the easy access to any necessary numerical information on the states of even medium-sized molecules, with due regard to the electron–electron interaction up to very high levels [14,15]. Nonetheless, treatment of this kind often has the character of a computer experiment revealing certain trends in molecular parameters but leaving their origin obscure. On the other hand, simple models that involve analytical consideration can be helpful in this respect and heuristically valuable, as far as they provide an insight into the mechanism of the regularities noticed and even enable predictions about new phenomena. We invoke such reasoning here to justify an extremely simplified approach to the description of long-range Coulomb repulsion in quasi-linear systems which is presented below.

Assume that a planar polymethine molecule possesses a uniform electron distribution, whereas a twist induces the intramolecular transfer of the charge q_0 between the π-decoupled molecular fragments formed, each of them being again characterized by the uniform electron distribution. The energy of Coulomb repulsion between electrons uniformly distributed with the density ρ (measured in units of the electron charge e) over a one-dimensional object of the length N (specified by the number of atoms) is given by the product of ρ^2 and some function $f(N)$, determined by the set of two-center Coulomb integrals, γ_{ij}, for all pairs of the ith and jth atoms. Neglecting exchange interactions exponentially decreasing at large distances (their contribution to the total repulsion is at least three times smaller than that from Coulomb interactions even at equilibrium interatomic distances), the function $f(N)$ can be estimated within the continuous approximation (a commonly accepted model implying integration rather than summation of point charges, as for instance, in the treatment of another problem in Ref. [16]):

$$f(N) \approx \int_0^N \mathrm{d}i \int_i^N \mathrm{d}j\, \gamma_{ij} \approx \gamma_{11}\left[N \ln\left(N + \sqrt{N^2+1}\right) - \sqrt{N^2+1}\right]. \tag{1}$$

In deriving this, the approximate expression [6] for γ_{ij} has been used:

$$\gamma_{ij} = \int\int \frac{e^2|\varphi_i(r)|^2|\varphi_j(r')|^2}{|r-r'|}\mathrm{d}r\,\mathrm{d}r' \approx \frac{\kappa}{\sqrt{(i-j)^2+\kappa^2}}\gamma_{11}. \tag{2}$$

Here $\varphi_i(\mathbf{r})$ denotes atomic wave functions, γ_{11} is the one-center integral of electronic repulsion, and $\kappa = e^2/r_{12}\gamma_{11}$ is the ratio of the p-electron-cloud diameter to the average separation between adjacent carbon atoms; κ is assumed equal to unity in the approximation considered [6].

Let us now imagine that the initial molecular system is divided into two fragments including n and $N-n$ atoms, with the respective electron densities ρ_n and ρ_{N-n}. Then the energy U of the Coulomb interaction within such a system can be written as

$$U_{n,N-n}(\rho_n, \rho_{N-n}) = \rho_n^2 f(n) + \rho_{N-n}^2 f(N-n) + \rho_n\rho_{N-n}[f(N) - f(n) - f(N-n)] \tag{3}$$

The first two terms on the right-hand side of this equation account for the contributions from the corresponding fragments and the last one refers to the interaction between them. As can be seen, this last term is constructed so that at $\rho_n = \rho_{N-n} = \rho$, Eq. (3) reduces to the expression for the initial planar system, $\rho^2 f(N)$.

As the object concerned is first characterized by a uniform electron density and upon twisting, the charge q_0 is transferred from one fragment to the other, each of the fragments again obtain uniform electron distribution, then the changes in charge densities of both fragments relative to the initial value ($\Delta\rho_n = \rho_n - \rho$, $\Delta\rho_{N-n} = \rho_{N-n} - \rho$) should meet the condition of charge conservation:

$$n\Delta\rho_n = -(N-n)\Delta\rho_{N-n} = q_0 \tag{4}$$

Provided both n and $N-n$ are large enough and q_0 does not exceed the electron charge, it is evident that the absolute magnitudes of $\Delta\rho_n$ and $\Delta\rho_{N-n}$ should be rather small. Thus the assumption of small $|\Delta\rho_n|$ and $|\Delta\rho_{N-n}|$ compared to ρ holds everywhere, except in the close proximity to the chain ends (see Tables 2 and 3), where the continuous approximation, as such, is inaccurate. With this assumption, the change in the Coulomb interaction energy induced by the transfer of the charge q_0 upon twisting takes the form:

$$\Delta U_{n,N-n} = U_{n,N-n}(\rho + \Delta\rho_n, \rho + \Delta\rho_{N-n}) - U_{n,N-n}(\rho, \rho) \approx \frac{N\rho q_0}{n(N-n)}\left[\frac{N-2n}{N}f(N) + f(n) - f(N-n)\right] \tag{5}$$

It is commonly supposed that the most important part of electron repulsion is given by the interaction with the nearest neighbours which is here referred to as the short-range interaction. It is the part of the interaction included in the long-range interaction model. This nearest-neighbour approximation yields $f(N) = N\gamma_{11} + (N-1)\gamma_{12}$. Substituting this function into Eq. (5) leads to:

$$\Delta U_{n,N-n} \approx -\frac{N-2n}{n(N-n)}\rho q_0 \gamma_{12} \tag{6}$$

For a more accurate calculation, the long-range interaction needs to be taken into account. Then, the explicit form (Eq. (1)) of the $f(N)$ function should be substituted into Eq. (5). We now consider the energy change $\Delta U_{n,N-n}$ associated with the electron density transfer from the longer to the shorter fragment, i.e. at the positive value q_0. With

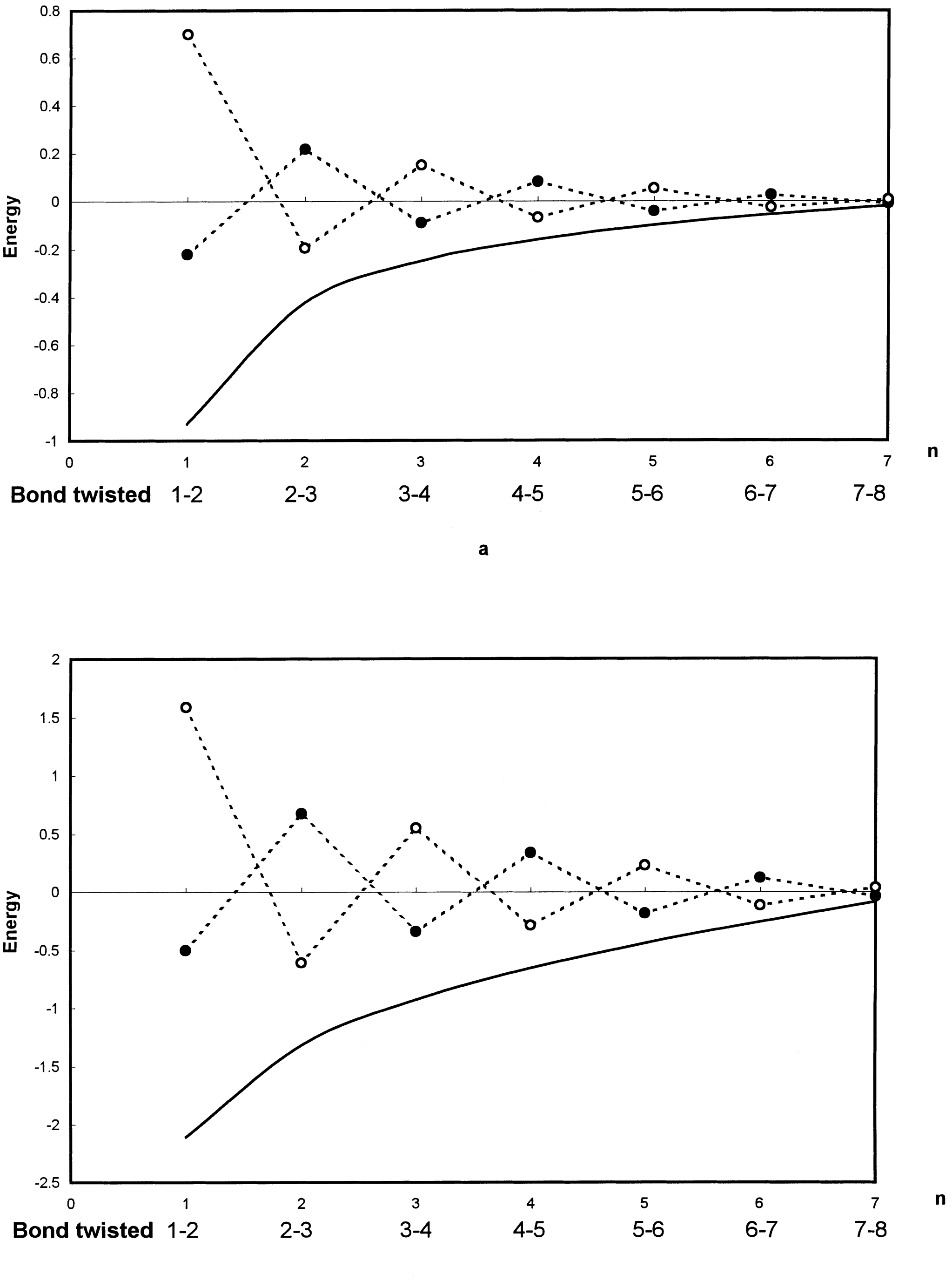

Fig. 4. Twist-induced changes in the energies of the short (a) and long-range (b) interelectron repulsion depending only on fragment lengths n (solid lines) and with the allowance made for charge transfer between two fragments in the HMO approximation (dashed lines with markers). The values of $\Delta U_{n,N-n}$ are measured in the units (a) of $\rho q_0\gamma_{12}$ and (b) of $\rho q_0\gamma_{11}$ (solid lines) and in the units (a) of $\rho\gamma_{12}$ and (b) of $\rho\gamma_{11}$ for the ground state (●) and excited state (○), with reference to the planar structure.

$n < N/2$, the right-hand side of Eq. (6) as well as the bracketed expression in Eq. (5) are negative and hence an electron density transfer from the longer to the shorter fragment is energetically advantageous from the standpoint of Coulomb interactions. Fig. 4(a) and (b) exhibit the respective n-dependences of $\Delta U_{n,N-n}$ for short- and long-range interactions in the units of $\rho q_0\gamma_{12}$ and $\rho q_0\gamma_{11}$, i.e., regardless of the charge transfer magnitude on each specific twisting (see the solid lines). The interrelation of the dependences can be judged taking into account that $\gamma_{12} \approx \gamma_{11}/\sqrt{2}$, in accordance with Eq. (2) at $\kappa = 1$.

The solid curves in Fig. 4(a) and (b) show that in terms of Coulomb repulsion, an energy gain can be connected with localizing a positive charge (twisted system) with reference to the completely delocalized charge (planar system). This gain is small if the twisted moieties are of equal size, i.e. if central bonds are twisted. For small twisted fragments, however, this gain can be sizeable (positive charge localized on the long fragment) with a corresponding strongly disadvantageous situation (positive charge localized on a short fragment). This effect can be understood by the accumulation of Coulomb interaction energy in long moieties, i.e. it is most energetically preferable for a system to place the positive charge (small electronic density) on the longest possible moiety.

In comparing Fig. 4(a) and (b), the changes in energy for twisted structures relative to the planar one which are calculated taking account of the long-range electron interaction notably exceed the values calculated within the nearest-neighbor approximation. This feature can be rationalized in terms of additional logarithmic accumulation of contributions from long-range interactions over chain fragments (see Eq. (1)). The overestimation of long-range interaction effects due to the neglect of screening would be somewhat slighter if the self-consistent values of the charges transferred were calculated. The essential role of long-range interactions is however obvious.

It is shown in the previous section, that the magnitude of the transferred charge q_0 as well as the transfer direction depend on the position of the twisted bond within the chain, i.e. on the length of the cationic and the neutral fragments. With the allowance made for this additional n-dependence of q_0, the twist-induced changes in the energies of short- and long-range Coulomb interactions, $\Delta U_{n,N-n}$, for the ground and excited states in the units of $\rho\gamma_{12}$ and $\rho\gamma_{11}$ are shown in Fig. 4(a) and (b) (see the dashed lines with markers). As seen, the monotonic n-dependences (solid lines) of these energy differences calculated for constant values of charge transfer in the continuous approximation turn into alternating functions (dashed lines) when multiplied by the Hueckel-provided alternating values of the transferred charge q_0. It can be noted that the largest Coulomb energy disadvantage in the ground state and largest advantage in the excited state, with reference to the planar structure, results just from the twist around the 2–3 bond, the effect being most clearly defined for long-range electron interactions.

An important point is that the relative π-energies of Cy(15) twisted structures inversely follow the lengths of the cationic subsystems, i.e. of the even fragments in the ground state and the odd fragments in the excited state. This is consistent with the expected length-dependent weakening of the Coulomb repulsion in the cationic fragments where the electron density is decreased. This regularity is most pronounced when the long-range electron interactions are taken into account, which is evidently due to the additional logarithmic factor in Eq. (1). As a result, the advantage in Coulomb energy is the more significant, the longer is a system with a reduced electron density.

4. Discussion and conclusions

The present paper provides a separate treatment of two contributions to the total π-energy of a conjugated quasi-one-dimensional system which is π-decoupled at a certain bond. One of them represents the energies provided by the Hueckel method which are always higher by approximately $|\beta|$ for twisted structures as compared to the planar one; they show a slight alternation effect in the ground state and monotonically fall in the excited state. The other contribution not contained within the Hueckel model arises from the interelectronic Coulomb repulsion energies which can be lower for certain twisted structures than for the planar case; they alternate both in the ground and the excited state. Addition of the Hueckel and Coulomb contributions can lead to an energy lowering of some twisted structures below the initial planar conformation.

To compare the two contributions quantitatively, the values of the parameters β, γ_{11}, and γ_{12} have to be specified. These quantum-chemical constants are not chosen uniquely in various semiempirical methods, as they are adapted independently in each computational technique so as to adequately describe experimental data. Within the Hueckel approximation, it is assumed that $|\beta| \approx 4$ eV, so that the energy disadvantage of the excited state for the structure twisted around the 2–3 bond, in comparison with the planar structure, would amount to $\Delta E_e \approx 0.99\ |\beta| \approx 3.96$ eV (see Table 3). If the interelectronic repulsion is additionally taken into account, the magnitude of β should be somewhat reduced, so as to account for the contribution of this interaction to the characteristics observed in the experiments. For instance, the PPP method involves $|\beta| \approx 2.35$ eV, and $\gamma_{11} \approx 11.13$ eV. Then, the estimation of the Hueckel energy disadvantage yields $\Delta E_e \approx 2.32$ eV. At the same time, the weakening of the interelectronic repulsion caused by the twist of the 2–3 bond gives rise to a decrease in the corresponding Coulomb energy contribution, U_e, so that $\Delta U_e \approx -0.195\gamma_{12} = -1.53$ eV (for $\gamma_{12} = \gamma_{11}/\sqrt{2}$, $\rho = 1$) and $\Delta U_e \approx -0.606\gamma_{11} = -6.75$ eV for short- and long-range Coulomb interactions, respectively. As evident, it is the contribution from long-range interelectronic interactions that is mainly responsible for the relative stability of the excited state for the structure with the 2–3 bond twisted. The results obtained are consistent with those from all-valence methods including electron repulsion (AM1 and CNDO/S–CI in Ref. [9] (see Table 1)) as well as with experimental evidence [17].

Using simple models like that developed above, it is important to clearly define the approximations and their limitations. Regarding the present approach, it should be noted that non-optimized atomic electron densities were included in the calculation of Coulomb corrections to π-energies. Second, instead of the electronic densities obtained by the Hueckel method, the values averaged over the fragments were involved. It is apparent, that the latter assumption is acceptable when both fragments are long enough, but it hardly can hold well for a monoatomic fragment, especially represented by a nitrogen atom whose properties differ notably from those of carbon. It is for this reason that the negative correction to the ground-state Coulomb energy, ΔU_{g}, is overestimated in magnitude for the twist around the 1–2 bond suggesting, in principle, the possibility of a twisted ground state. Allowance for a somewhat larger electron density on the nitrogen atom would evidently lead to the energetic prohibition for this twist in the ground state, in accordance with the results obtained by the all-valence methods [9].

Among the advantages of the approach suggested is its simplicity and the easy access to a deeper insight into the origin of excited-state twisting in quasi-one-dimensional π-conjugated systems. The present model is just intended to be oversimplistic because this creates the possibility to more easily identify the main factors responsible for the preference of certain photoisomers. The Hueckel method enables us to account for the alternation of the charge transferred in successive bond twistings, whereas the correspondingly alternating Hueckel-based corrections to the long-range interelectron repulsion prove to be the governing factor for the formation of energetically preferable excited-state twisted structures. Though the model concerned can hardly pretend to provide a strict quantitative description, it enables sound estimates of competing effects to be obtained in terms of energies. The results obtained are consistent with the results of more accurate methods and can serve as a basis for rather general predictions on the probabilities for excited-state bond twistings. For instance, as the Coulomb repulsive forces make the relative π-energies of twisted structures inversely follow the lengths of cationic subsystems, i.e. of the even fragments in the ground state and the odd fragments in the excited state for nitrogen-terminated polymethine cations and vice versa for their boron-containing analogues, it can be concluded that the 2–3 bond in the polymethine chain with amino or substituted amino end-groups can be generally expected to be the bond most prone to rotations in the excited state. In the case of the boron counterparts, the same is true for the 1–2 bond. It is also notable, that the energy advantage associated with the intramolecular charge transfer increases logarithmically with the fragment length ratio thus contributing to the well-known instability [18] of sufficiently long π-conjugated quasi-one-dimensional systems.

To sum up, the most essential outcomes of the study performed can be formulated:

- A purely topological approach fails to explain relative twisting probabilities in polymethines.
- Separate consideration of Hueckel-based and electron-interaction contributions to polymethine π-energies reveals their role in the arrangement of energy levels for bond twisting in the ground and the excited states.
- An electron interaction model including only π-electrons can reproduce the AM1-based alternation of twisted-structure energies resulting in the prediction that certain bonds should spontaneously twist in the excited states and other should not.
- Nearest-neighbor short-range interactions are insufficient to account for the occurrence of the twist; long-range interelectronic interactions should necessarily be included.
- A simple rule governs twisting probabilities: (a) A twisting is the more advantageous, the longer is the cationic and the shorter is the neutral fragment; (b) in successive bond twisting, the length of cationic and neutral fragments alternates.
- Increased twisting probabilities should be expected in the vicinity of chain ends.
- The model proposed allows symmetric polymethines of arbitrary lengths and with arbitrary end-atoms to be treated from a unified point of view.

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