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A Topology–Based Primary Search for Quasi–Linear Conjugated Organics with Large Ground–To–Excited State Change in Dipole Moment

Marina Dekhtyar [1] and Viktor Rozenbaum [2]

[1] Institute of Organic Chemistry, National Academy of Sciences of Ukraine, Murmanskaya Str. 5, 02094, Kiev–94, Ukraine
[2] Institute of Surface Chemistry, National Academy of Sciences of Ukraine, Generala Naumova Str. 17, Kiev, 03164, Ukraine

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A Topology–Based Primary Search for Quasi–Linear Conjugated Organics with Large Ground–To–Excited State Change in Dipole Moment [#]

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Abstract

Motivation. A pronounced change in molecular dipole moment on excitation is the necessary prerequisite for a variety of significant physicochemical phenomena, such as solvatochromism, Stark effect, nonlinear optical response, functioning of biological Brownian motors etc. It is thus challenging to screen vast arrays of structures so as to find the promising selections of the molecules remarkable for their outstandingly large ground–to–excited state changes in dipole moment.

Method. The working model employed is the long–chain approximation of polymethine compounds which represents an analytical approximation of the Hückel molecular orbital method. Computationally, it implies manipulation of inverse adjacency matrices raised to different powers.

Results. An analytical expression derived in terms of the topological long–chain approximation has been used to estimate ground–to–excited state change in dipole moment for conjugated molecules. The theoretical estimates have been benchmarked against available experimental data and a strong correlation, with $R = 0.981$, has been found between them. The relationship between the molecular topological parameters and the change in dipole moment offers the efficient ways to maximize the latter. Based on the regularities revealed, a large–scale search among more than 1000 heterocyclic residues have been carried out so as to find the structures promising sufficiently large differences in dipole moment between the ground and excited state. As a result, about 50 residues were selected as candidate structures for further stages of the relevant molecular design.

Conclusions. The LCA appears to be a convenient tool for estimation of molecular properties at early stages of molecular design; characteristics of the candidate structures selected should be refined by an appropriate higher–level approach.

Keywords. Ground–to–excited state change in dipole moment; long–chain approximation; quasi–linear conjugated systems.

Abbreviations and notations

LCA, long–chain approximation

[#] Dedicated on the occasion of the 65th birthday to Danail Bonchev.

* Correspondence author; E–mail: vrozen@mail.kar.net.

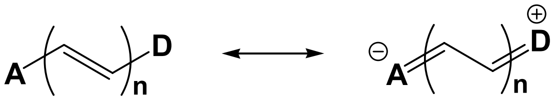
1 INTRODUCTION

It is not surprising that the interest in excitation–induced change in molecular polarity is very old, because it underlies a great diversity of well–observed physicochemical phenomena. First of all, the 1940–50s marked the beginning of considerable research activity on solvatochromic effects [1,2] which have been accorded extensive and profound consideration [3,4]; solvatochromism is pronounced the more, the stronger is a change in dipole moment, $\Delta\mu$, on excitation. As another example, Stark spectroscopy also provides manifestation of the difference in dipole moment between the ground and excited state [5,6]. Further, this characteristic is significant in the nonlinear optical response of molecules: first electronic hyperpolarizability in the two–level approximation is known to be proportional to the magnitude of $\Delta\mu$ [7]. The recent active studies on Brownian motors in biological systems have stimulated renewed attention to the change in charge distribution occurring on molecular excitation [8]: indeed, the flashing dipole moment of a molecule diffusing in an external electric field with an asymmetric potential can induce unidirectional motion. In connection with the above–exemplified manifold importance of molecular dipole moments vastly changing on excitation, it appears desirable to have tools for predicting this characteristic and finding molecules with outstanding $\Delta\mu$ values. At the primary stage of such a search, i.e., in screening vast arrays consisting of thousands of molecules, using all–valence approaches is evidently not optimal because they require a matter of hours or days for computing a medium sized molecule. Preference should be given to sufficiently simple “low–level” approaches which rapidly riddle the massive set of structures like a coarse sieve selecting the most promising structures with outstandingly large $\Delta\mu$. Moreover, methods of this kind enable one to grasp the trends in dipole moment changes, especially if they provide analytical relationships between the structural parameters and the property concerned. On the other hand, simplistic models cannot afford a proper degree of accuracy and it is clear that the preliminary results for a selection of candidate structures, orders of magnitude smaller in number than the initial array, should be verified by high–level computational strategies.

Here we suggest a topological approach that enables consistent, though rough enough, estimation of the difference in dipole moment between the ground and excited state of conjugated organics. It is based on the so–called long–chain approximation (LCA) of polymethine compounds. The LCA developed since the seventies [9–14] is an analytical topological model (within the Hückel molecular orbital method) which is aimed at estimation of the main π–properties of conjugated quasi–linear systems. This model in no way pretends to offer numerically accurate results as far as individual molecules are concerned but it has proved to be adequate and helpful in the qualitative comparative treatment within the series of analogous compounds (see, *e.g.*, Ref. [13] and references therein).

The molecules of the π–conjugated quasi–linear class are constituted by the N–methine chain (N

= $k + 2n$; $k = 0$ or 1, and n is an integer) and two end groups, mostly heterocyclic residues. Initially, the LCA was strictly substantiated for the systems with long chains (large N values) [9,10] but it was shown subsequently that the approximation should also hold good for the molecules containing short chains or even no linear spacer at all ($N = 0$) [12]. In the case that quasi–linear molecules bear no charge (as a rule, at $k = 0$), they are noted for often large [5] and sometimes giant [15] $\Delta\mu$ values. This feature is accounted for in the most straightforward manner by the resonance structures qualitatively describing the electron density distribution in the ground (φ_g) and excited state (φ_e):



φ_g φ_e

It is evident from the scheme that charge separation in the conjugated chain should drastically increase on excitation. In what follows, we mainly focus just on this class of compounds because their large scale of $\Delta\mu$ values is favorable for approximate estimations.

It should be emphasized that the approach involved, although approximate, has at least two advantages over the standard quantum chemical tools in the context of a large–scale screening followed by molecular design: first, the ability to rapidly reduce an initial array of thousands to a selection of tens of structures and, second, analyticity which reveals the regularities of structure–property relationships.

2 THEORETICAL BACKGROUND AND COMPUTATIONAL TECHNIQUE

The method concerned operates on the additive topological parameters of the conjugated end groups of the polymethine chain which are determined only by the end–group structure; they account for the contribution of the end residues to the behavior of frontier molecular levels. In the topological approximation, the structure of an end–group is unambiguously described by its adjacency matrix (a dimensionless counterpart of the topological Hamiltonian) and the additive parameters concerned are determined by the elements of the inverse adjacency matrix (a dimensionless Green's function matrix). To derive the parameters characteristic of two given end groups bound to the polymethine chain through their atoms b_j ($j = 1, 2$), it is sufficient to consider the matrix diagonal element corresponding to the b_j–th atom:

$$g_j(z) = \langle b_j | (z \cdot \hat{\mathbf{I}} - \hat{\mathbf{H}}_j)^{-1} | b_j \rangle \qquad (1)$$

where z is a dimensionless energy variable; $j = 1, 2$ labels two end groups, $\boldsymbol{H}_j$ is an end–group adjacency matrix, b_j denotes the atom of the j–th end group which is bound to the polymethine chain. The generating function for the topological parameters appears as

$$F_j(z) = \pi^{-1}\mathrm{arcctg}\frac{1+\beta_{\mathrm{j}}^2 g_j(z)\cos\theta}{\beta_{\mathrm{j}}^2 g_j(z)\sin\theta}, \quad \theta = \arccos(-z/2) \tag{2}$$

where β is a dimensionless parameter numerically equal to the resonance integral of the bond between the *j*–th end group and the polymethine chain. The first two of the topological parameters are electron donor ability *F* and effective length *L* that determine the end–group–induced perturbation of the position and the width of the molecular energy gap, respectively. These are additive parameters expressed in terms of Green's functions, with the argument *z* assumed to be zero (which corresponds to the energy of the Fermi level):

$$F = \left\{\sum_{j=1}^{2} F_j + (k-1)/2\right\} \; ; \; F_j = \pi^{-1}\mathrm{arcctg}\left[g_j(0)\right]^{-1} \tag{3}$$

$$L = \sum_{j=1}^{2} L_j \; ; \; L_j = -\left[2g'_j(0) + g_j^2(0)\right] / \left[1 + g_j^2(0)\right], \tag{4}$$

where {...} designates taking fractional part of a number. Among a great variety of topological indices used for characterization of molecular structure [16–18], the parameters *F* and *L* are remarkable for their transparent physical meaning. Electron donor ability *F* ranging from 0 to 1 governs molecular redox properties: the closer to 0.5 is its magnitude, the more stable is the corresponding molecule with respect to reducers and oxidizers, whereas it tends to accept electrons at $0 < F < 1/2$ and to donate them at $1/2 < F < 1$. The wavelength of the first electronic transition of the polymethine molecule is proportional to the value $N + 1 + L$. Thus effective length *L* characterizes an effective lengthening of a polymethine chain caused by end groups.

The effects caused by local perturbations of end–group constitution, such as heterosubstitution or introduction of a substituent, can be determined from the derivatives of electron–donor ability and effective length with respect to *z* at $z = 0$:

$$F_j^{'} = -(2\pi)^{-1} L \tag{5}$$

$$L_j^{'} = -\frac{2g''_j(0)}{1+g_j^2(0)} - g_j(0)\frac{8g'_j(0)\left[1-g'_j(0)\right]+g_j^2(0)-1}{2\left[1+g_j^2(0)\right]^2} \tag{6}$$

Computation of the *n*th–order derivative of the Green's function, $\mathbf{g}^{(n)}(z)$, is underlain by the known relationship [12]:

$$\mathbf{g}^{(n)}(z) = (-1)^n n!\,\mathbf{g}^{n+1}(z) \tag{7}$$

In particular, the values $g'_j(0)$ and $g''_j(0)$ are represented, accurate to the sign and the factorial factor, by the diagonal (b_j, b_j) elements of the squared and cubed inverse adjacency matrix, respectively. Thus, the pivot computational procedure was merely finding the inverse adjacency matrix and raising it to the corresponding powers for each compound under study. As an example, calculation of the topological parameters *F*, *L*, and *L'* for all the non–equivalent residues derivable from the pyrrole nucleus is presented in Appendix 1.

3 RESULTS AND DISCUSSION

A simple analytical expression relates the parameters *L* and *L'* to the quantity Δμ of a polymethine compound [19,20]:

$$\Delta\mu = \pi e r_{CC}(N+1)(N+1+L)^{-2}(L_2' - L_1') \tag{8}$$

where *e* is the electronic charge, $r_{CC} \approx 1.247$ Å is the projection of a chain C–C bond onto the long molecular axis. It is seen from the above equation that ground–to–excited state change in dipole moment grows with increasing molecular asymmetry represented by the difference $L_2' - L_1'$ and vanishes for symmetric compounds with $L_2' = L_1'$. Interestingly, the value Δμ changes nonmonotonically with the elongation of the polymethine chain: it grows until the growing (*N*+1) value becomes equal to *L* and decreases thereon. This effect can be rationalized as follows: at short chain lengths, when the end–group contribution to the properties of the conjugated system is notable, the dipole moment increase on excitation regularly grows with the chain length as a result of the growing donor/acceptor separation; with a sufficiently long chain, the conjugated molecule becomes insensitive to the end group influence and, accordingly, to the donor/acceptor strength of the terminal substituent, so that the weakened charge separation overcompensates the increased length of the excited–state dipole and leads Δμ to decrease. Such a trend in Δμ values, *i.e.*, an increase with chain length for short chains and levelling off or even reduction for long chains (due to the decreased interaction between the end groups) was corroborated by the electroabsorption spectroscopic experiments with donor/acceptor–substituted polyenes of varied length [21] and was also pointed out elsewhere [5].

Though the estimates provided by the LCA notably (by more than half an order) undervalue excitation–induced dipole moment changes (see Table 1), they demonstrate a strong correlation with the experimental data (see Figure 1). For the sample included in Table 1, the following linear correlation holds: $\Delta\mu_{exp} = 4.8297\ \Delta\mu_{calc} + 0.8314$, with the correlation coefficient *R* = 0.981 and the standard deviation 3.67. In some cases, as, for instance, with the merocyanines described in Refs. [5] and [15], the underestimation is even larger (exceeds an order of magnitude). Such a discrepancy may be attributable to the neglect of the interelectron repulsion thus arising not from the LCA features but from the very nature of the topological model (previously the LCA was shown to reproduce the results of the Hückel method very well [14,22]). This limitation of the approach could be compensated to a certain degree by the appropriately fitted Coulomb and resonance integrals for atoms and bonds.

Table 1. Calculated and experimental values $\Delta\mu$, along with the relevant topological parameters, L and $L'_2 - L'_1$, for a sample of conjugated compounds

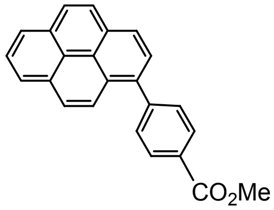
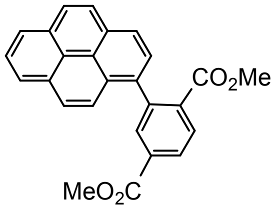
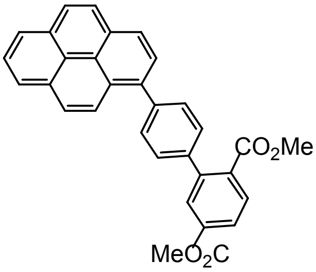
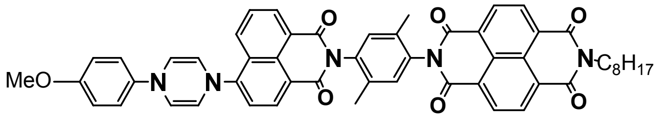
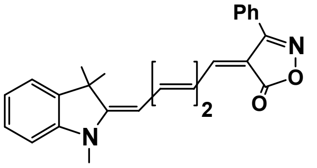
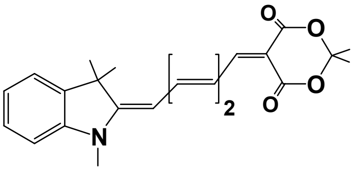
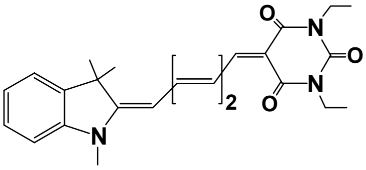
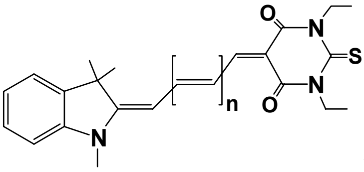
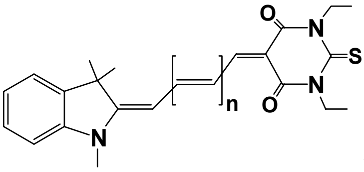
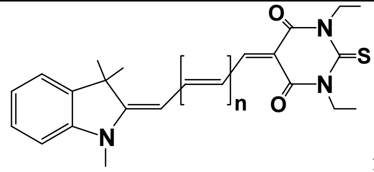
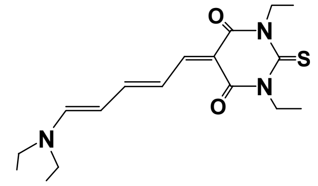
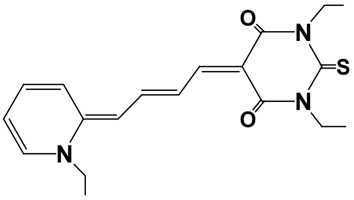
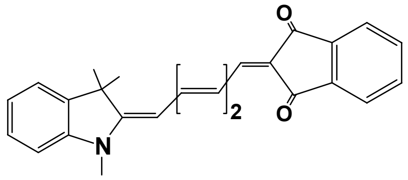
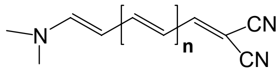
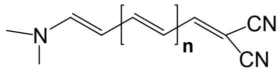
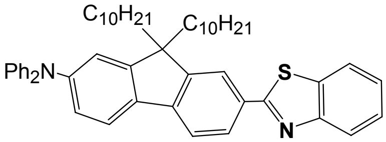
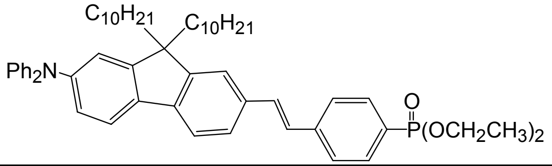
No	Compound	N	L	L'$_1$–L'$_2$	$\Delta\mu_{calc}$, D	$\Delta\mu_{exp}$, D	Ref.
1		0	4.88	4.59	1.76	11.2	[23]
2		0	7.82	23.56	5.70	19.3	[23]
3		0	6.69	23.56	7.49	35.9	[23]
4		0	7.45	55.59	14.64	75	[24]
5		6	4.89	0.94	0.88	6	[5]
6		6	4.60	0.84	0.82	6	[5]
7		6	4.86	1.05	0.98	6	[5]
8	 n = 0	2	5.08	0.48	0.41	2	[5]
9	 n = 1	4	5.08	0.48	0.44	2	[5]

Table 1. (Continued)

No	Compound	N	L	L'_1–L'_2	$\Delta\mu_{calc}$, D	$\Delta\mu_{exp}$, D	Ref.
10	 n = 2	6	5.08	0.48	0.43	2	[5]
11		5	2.33	0.84	1.36	4	[5]
12		4	3.53	1.07	1.38	12	[5]
13		6	5.05	0.63	0.57	10	[5]
14	 n = 1	5	1.78	0.39	0.73	1.6	[5]
15	 n = 2	7	1.78	0.39	0.62	2.6	[5]
16		0	4.15	5.46	3.88	2.3	[25]
17		2	3.97	4.65	5.41	25	[25]

Note: As in the standard Hückel approximation, only π–centers (atoms donating a p–electron or a lone electron pair to the conjugation system) are included in the calculation. The Coulomb, α_X, and the resonance, $\beta_{XX'}$, integrals for atoms and bonds are defined respectively as $\alpha_C + h_X\beta_{CC}$ and $\eta_{XX'}\beta_{CC}$ with commonly used h_X and $\eta_{XX'}$ values [26,27]: $h_C = 0$, $h_N = 1$, $h_O = 2$, $h_S = 0.7$, $h_P = 0.5$; $\eta_{CC} = \eta_{CN} = 1$, $\eta_{CO} = 0.8$, $\eta_{CS} = \eta_{CP} = 0.4$; for exocyclic oxygen atoms, $h_{\ddot{O}} = 2.3$, $\eta_{CO} = 1$, $\eta_{PO} = 0.4$; for exocyclic sulfur atoms, $h_S = 0.5$, $\eta_{CS} = 0.5$; for cyano groups, $h_N = 2$, $\eta_{CN} = 1.1$.

On the other hand, structural parameters vary in a rather limited range (as a rule, within several tenths for a certain atom/bond) and any dramatic change in the values of *L* and *L'* is only possible if the chosen parameter set causes a singularity in the adjacency matrix concerned. Importantly, undervalued theoretical estimates of a molecular characteristic do not represent a critical obstacle in searching for structures with an outstanding degree of the property concerned. To exemplify, the LCA–provided Δμ values of about 3–5D, *i.e.*, of small to moderate scale, already suggest that large to extra–large dipole moment changes are likely to be observed.

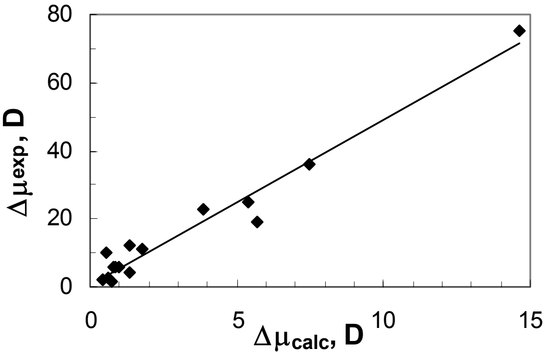
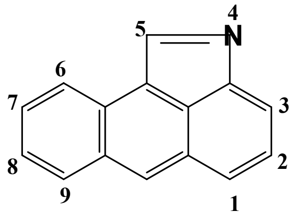
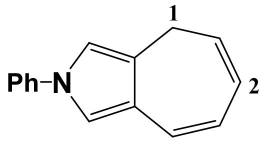
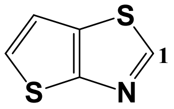
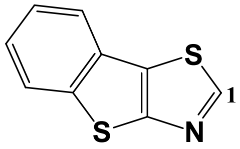
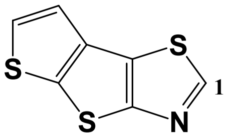
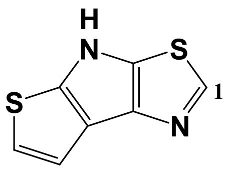
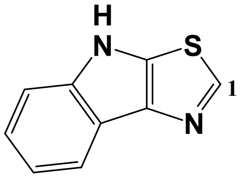


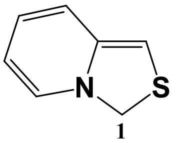
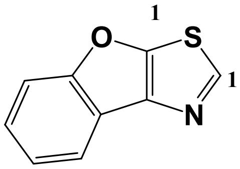
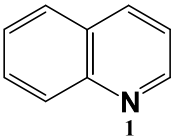
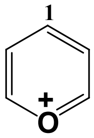
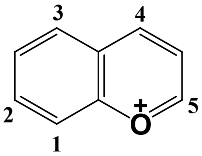
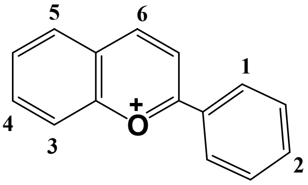
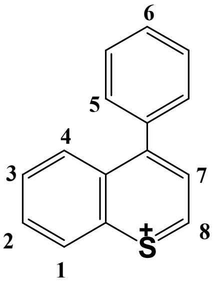
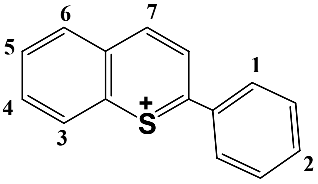
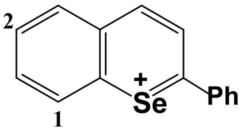
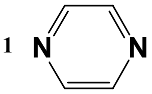
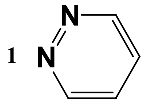
Figure 1. Experimental versus calculated (within the LCA) values Δμ for a sample of 17 conjugated compounds.

Table 2. Topological parameters *F*, *L*, and *L'* for a set of heterocyclic systems promising as end groups of quasi–linear conjugated molecules with large ground–to–excited state changes in dipole moment [a]

No	Heterocycle	Atom bound to the polymethine chain	F	L	L'
18		1	0.75	9.13	40.48
		2	1.00	2.25	11.00
		3	0.75	8.63	43.61
		4	1.00	7.00	91.00
		5	0.75	8.63	40.11
		6	1.00	3.25	19.50
		7	0.85	7.60	71.32
		8	1.00	2.25	9.00
		9	0.85	8.40	70.92
19 [b]		1	0.80	3.80	6.20
		2	0.80	3.80	8.12
20		1	0.87	3.56	–6.05
21		1	0.86	3.41	–5.40
22		1	0.89	3.84	–8.22
23		1	0.91	3.55	–7.19
24		1	0.92	3.87	–8.94

[a] Atom and bond parameters are the same as in Table 1; $h_{Se} = 0.65$, $\eta_{CSe} = 0.35$ [27]

Table 2. (Continued)

No	Heterocycle	Atom bound to the polymethine chain	F	L	L'
25 [b]		1	0.99	8.36	–19.17
26		1	0.89	3.17	–5.29
27		1	1.00	2.44	5.98
28		1	0.79	3.00	5.00
29		1	1.00	2.44	7.56
		2	0.89	3.96	18.29
		3	0.89	4.55	19.43
		4	0.70	3.97	5.50
		5	0.70	3.74	5.40
30		1	0.89	4.75	27.63
		2	0.89	4.75	28.87
		3	1.00	2.61	11.15
		4	0.89	4.60	28.01
		5	0.89	5.20	30.12
		6	0.70	4.96	9.95
31		1	1.00	2.61	15.61
		2	0.86	7.54	74.09
		3	1.00	1.94	6.54
		4	0.86	8.08	75.24
		5	0.86	7.81	73.92
		6	0.86	7.81	75.49
		7	1.00	2.44	13.83
		8	0.65	6.09	10.90
32		1	0.86	7.68	71.65
		2	0.86	7.68	73.23
		3	1.00	2.61	15.61
		4	0.86	7.54	72.52
		5	1.00	1.94	6.54
		6	0.86	8.08	73.67
		7	0.65	6.23	9.72
33		1	1.00	2.61	18.93
		2	1.00	1.94	7.93
34		1	0.90	2.90	7.48
35		1	0.90	2.90	5.88

[b] The data refer to the divalent residues resulting from abstracting two hydrogen atoms at the indicated positions

From Eq. (8) it follows that for the value of Δμ to be maximized, the end group structures with the largest possible difference $L_2^{'} - L_1^{'}$ should be chosen, while the chain length $N + 1$ should be possibly close to *L*. With this in mind, we have performed a relatively large–scale screening of heterocyclic end groups (over 100 heterocycles of various classes and, accordingly, over 1000 residues derived from them) and selected 50 structures with large magnitudes of *L*' (the bottom boundary was set equal to 5) – see Table 2.

As seen, the end group collection included in the table is greatly contributed by condensed thiazole nuclei and generally chalcogen–containing heterocycles, which alone gives some idea of systems promising large Δμ values. It can easily be verified that “outstanding” residues from Table 2, when combined with “normal” ones (having *L*' under unity) through a polymethine chain, provide Δμ of at least 3–5 D in terms of the LCA and hence 15–20 D in the realistic scale already at *N* = 0. One would expect an even greater effect if two end groups of a conjugated chain are represented by a couple of structures from Table 2 having *L*' values of different sign. Moreover, an appropriate lengthening of the polymethine chain (up to the length such that *N* + 1 = *L*) affords an auxiliary resource of maximizing the desired difference in dipole moment between the ground and the excited state. To approximately judge the redox stability of a system designed, the values of *F* are also listed in Table 2. At the same time, the results gained by the LCA evidently elucidate only the main trends in Δμ values and can change notably with consideration of interelectron interaction. It is therefore expedient that the candidate structures selected by such a simplistic method should be studied using an appropriate higher–level approach so as to give recommendations for concrete syntheses.

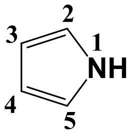
4 CONCLUSIONS

Starting from the topological long–chain approximation, we considered an analytical expression for estimating ground–to–excited state change in dipole moment for conjugated molecules regarded as quasi–linear systems with various end groups. The quantity of interest, Δμ, is related to the topological parameters, effective length *L* and its first derivative *L*' with respect to the energy variable; these are expressed in terms of the end–group Green’s function and its corresponding first and second derivatives. Computationally, the method implies manipulation of squared and cubed inverse topological matrices of end groups. The results provided by the topological approach have been benchmarked against available experimental data and a strong correlation, with *R* = 0.981, has been found between them. At the same time, a dramatic difference (by a factor of about 5) between the calculated and experimental values of Δμ evidently originates from the neglect of the interelectron repulsion and application of generic (not specially fitted) atom and bond constants. A separate challenging task is to study how the values of the Coulomb and resonance integrals for atoms and bonds influence the topological parameters *L* and *L*'.

The standard deviation of the correlation equal to 3.67 suggests that the corresponding linear equation allows for adequate prognostication in the region of sufficiently large Δμ values. The analysis of the expression for Δμ revealed the efficient ways to maximize it, a sufficiently large $L_2^{'} - L_1^{'}$ difference being of most significance. Based on the regularities found, we have carried out a large–scale search (among more than 1000 heterocyclic residues) for the end group structures promising outstanding Δμ values of the resulting conjugated organic compounds. As a result, about 50 residues were selected as candidate structures for studying them with higher–level methods. The LCA appears to be a convenient tool for estimation of molecular properties at early stages of molecular design.

Appendix 1

As an illustration of the method involved, we calculate the topological parameters *F*, *L*, and L' for all the non–equivalent residues of the pyrrole nucleus (at positions 1, 2, and 3) starting from the corresponding Green's functions and their relevant derivatives. With the parameters $h_N = \eta_{CN} = 1$ assumed for the nitrogen atom and the nitrogen–carbon bond, the adjacency matrix **H** for the pyrrole molecule is constructed as follows:



$$\mathbf{H} = \begin{pmatrix} 1 & 1 & 0 & 0 & 1 \\ 1 & 0 & 1 & 0 & 0 \\ 0 & 1 & 0 & 1 & 0 \\ 0 & 0 & 1 & 0 & 1 \\ 1 & 0 & 0 & 1 & 0 \end{pmatrix} \tag{A1}$$

The inverse adjacency matrix coincides with the Green's function matrix found at $z = 0$:

$$\mathbf{H}^{-1} = \mathbf{g}(0) = \begin{pmatrix} 0.3333 & 0.3333 & -0.3333 & -0.3333 & 0.3333 \\ 0.3333 & 0.3333 & 0.6667 & -0.3333 & -0.6667 \\ -0.3333 & 0.6667 & 0.3333 & 0.3333 & -0.3333 \\ -0.3333 & -0.3333 & 0.3333 & 0.3333 & 0.6667 \\ 0.3333 & -0.6667 & -0.3333 & 0.6667 & 0.3333 \end{pmatrix} \tag{A2}$$

The squared and cubed inverse adjacency matrices appear as follows:

$$\mathbf{g}^2(0) = \begin{pmatrix} 0.5556 & -0.1111 & -0.2222 & -0.2222 & -0.1111 \\ -0.1111 & 1.2222 & 0.4444 & -0.5556 & -0.7778 \\ -0.2222 & 0.4444 & 0.8889 & -0.1111 & -0.5556 \\ -0.2222 & -0.5556 & -0.1111 & 0.8889 & 0.4444 \\ -0.1111 & -0.7778 & -0.5556 & 0.4444 & 1.2222 \end{pmatrix} \tag{A3}$$

$$\mathbf{g}^3(0) = \begin{pmatrix} 0.2593 & 0.1481 & -0.3704 & -0.3704 & 0.1481 \\ 0.1481 & 1.3704 & 1.0741 & -0.9259 & -1.6296 \\ -0.3704 & 1.0741 & 0.8148 & -0.1852 & -0.9259 \\ -0.3704 & -0.9259 & -0.1852 & 0.8148 & 1.0741 \\ 0.1481 & -1.6296 & -0.9259 & 1.0741 & 1.3704 \end{pmatrix} \tag{A4}$$

Formula (7) implies that $\mathbf{g}'(0) = -\mathbf{g}^2(0)$ and $\mathbf{g}''(0) = 2\mathbf{g}^3(0)$. Thus, the diagonal (*b*, *b*)–elements (*b*=1÷3) of the matrices given in Eqs. (A3) and (A4) provide the first and second derivatives of the Green's functions for the corresponding *b*–pyrrolyl residues. Substituting them into Eqs. (3), (4), and (6) leads to the values of the respective topological parameters *F*, *L*, and L' (see Table A1).

Table A1. Topological parameters *F*, *L*, and L' for three non–equivalent *b*–pyrrolyl residues, along with the relevant diagonal elements of the inverse adjacency matrix raised to the appropriate powers, and the corresponding Green's functions and their derivatives

Atom *b* bound to the polymethine chain.	$\mathbf{g}_{bb}(0)$	$\mathbf{g}^2_{bb}(0)$	$\mathbf{g}^3_{bb}(0)$	$\mathbf{g}'_{bb}(0)$	$\mathbf{g}''_{bb}(0)$	F	L	L'
1	0.3333	0.5556	0.2593	–0.5556	0.5186	0.10	0.90	0.12
2	0.3333	1.2222	1.3704	–1.2222	2.7408	0.10	2.10	–1.88
3	0.3333	0.8889	0.8148	–0.8889	1.6296	0.10	1.50	–1.00

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