Theor Chim Acta (1987) 71: 299-304

Theoretica Chimica Acta

Topological implications of Y-conjugation for electronic transitions of cyanine dyes

Lydie Grajcar[1], Gaston Berthier[2], Jean Faure[1] and Jean-Pierre Fleury[3]

[1] Laboratoire de Physico-Chimie des Rayonnements, UA 75, Université de Paris-Sud, F-91405 Orsay Cedex, France
[2] Laboratoire de Biochimie Théorique, UA 77, Institut de Biologie Physico-Chimique, F-75005 Paris, France
[3] Laboratoire de Synthèse et Photochimie Organiques, UA 135, Ecole Nationale Supérieure de Chimie, F-68093 Mulhouse Cedex, France

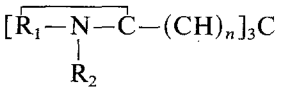
(Received September 18, revised December 1/Accepted December 12, 1986)

To understand connections between electronic transitions of dyes having related conjugated systems, topological arguments from graph theory are often helpful. Using the Chebyshev expansion of the characteristic polynomials of cyanines, it is shown that the two possible structures of tribranched cyanines, i.e., a strongly out-of-plane orientation of one of the conjugated branches or a Y-conjugation of the entire unsaturated system, are both consistent with the similarities between visible absorption of these compounds and of simple chains. To choose between these two structures, evidence from other sources should be added.

Key words: Graph theory — Conjugation — Cyanine spectra

1. Spectroscopic evidence

The properties of tribranched cyanines



$$[\overline{R_1-\underset{\displaystyle R_2}{\underset{|}{N}}-C}-(CH)_n]_3C$$

with one or two N^+ nitrogens in the terminal rings of the dye, are interpreted in two different ways, according as the conjugated system extending between the three nitrogens is more or less planar, or one of the branches strongly deviates from the plane formed by the other two. In the latter case, conjugation of the π electrons does not extend to the out-of-plane branch; and therefore the molecule can be compared to a cyanine dye substituted in the central position, many examples of which are described in the literature. In the former case, the delocalization of the π electrons within the three branches gives rise to those cross-conjugated phenomena [1] which are called Y-conjugation in compounds related to guanidinium ion [2], and the molecule may be assigned to a new family of dyes.

The trinuclear cyanines with three identical branches described by Reichardt et al. are of both types. The [2.2.2] heptamethine cyanine [3] has a visible spectrum in solution, the absorption peaks of which were first assigned assuming a Y-conjugation within an unsaturated system of C_3 symmetry, in agreement with the ^{13}C NMR data for the three branches [4]. Later, however, X-ray analysis of the crystal structure [5] proved that a nitrogen pair N, N^+ is arranged as in an all-trans pentamethine cyanine, whereas the third N^+ belongs to a part which is non coplanar with the preceding chain; this explains an ESCA spectrum with two types of nitrogen. On the other hand, the three branches of the [3.3.3] decamethine cyanine [6] have a slightly skew structure rather close to a plane, allowing a Y-conjugation which gives rise to an ESCA spectrum with three equivalent nitrogens. It should be added that the maxima of the visible absorption spectra for both trinuclear cyanines are close to those of the corresponding penta - or hepta - dinuclear cyanines, irrespective of their geometries and their numbers of neutral and positive nitrogens in the chemical formula, namely one N and two N^+ in a [2.2.2] cyanine or two N and one N^+ in a [3.3.3] cyanine.

The [2.2.4] nonamethine cyanine[1] synthesized by one of us (J-P F) gives an example of a cyanine with three non-identical branches [7]. Whereas this compound has two [2.2] branches like the [2.2.2] cyanine, it also looks like the [3.3.3] one: its visible spectrum consists of two absorption bands, one coinciding with the spectrum of a simple pentamethine cyanine, and the other with that of a heptamethine cyanine. This fact by itself cannot lead to definite conclusions as regards the stereochemistry of the [2.2.4] cyanine, for it can be interpreted in two ways:

(i) any one of the three unsaturated branches strongly deviates from the mean plane of the other two; we are therefore justified in reasoning by analogy with substituted pentamethine and heptamethine cyanines [7].

(ii) an electronic delocalization is still present within the three branches, and we have to consider the corresponding Y-system as a whole; but we are led to look at it as a polymethine cyanine chain as it has already been done for the [3.3.3] cyanine [6].

2. Graph-theory predictions for Y-conjugation

In a first theoretical approach of the cyanine problem, we can neglect the usually big end-groups and perform simple HMO calculations for the remaining conju-

---

[1] Nomenclature of [3]

gated systems, by using the same Coulomb and resonance parameters for C and N atoms, and for CN and CC bonds, in other words, by modelling cyanines upon isoelectronic polymethine anions in which a CH_2 replaces each NR_2 group. It is found that the eigenvalue spectra of the tribranched molecules include a number of levels which are also found, either exactly or very closely, in the energy spectra of the parent chains, in particular as regards their occupied and empty low-energy levels.

The similarities between the $(CH_2(CH)_3)_3C$ or $(CH_2(CH)_4)_3C$ tribranched systems and the $CH_2(CH)_7CH_2$ or $CH_2(CH)_9CH_2$ chains respectively, and those between the less symmetrical [2.2.4] system and the preceding two chains are reflected in their energy levels. To simulate cyanines, the non-bonding level of each of these polymethine compounds must be filled up by one or two additional electrons, in accordance with the number of $N\text{-}R_2$ groups; this yields closed-shell ground states characterized by highest occupied molecular orbitals (HOMO) with the same energy. The next energy levels giving the lowest unoccupied molecular orbitals (LUMO) in tribranched cyanines are equal or close to those of the parent linear chains (i.e., -0.493β and -0.618β for the first two empty orbitals of the [2.2.4] system, vs -0.517β and -0.618β for the LUMO's of the corresponding chains). Similarities between tribranched and simple cyanines also appear for transition moments $\mathfrak{M}$. The values of $\mathfrak{M}$ obtained for tribranched systems and for polymethine chains in mono-cis conformations adapted to the Y-geometries of the former agree in magnitude and direction. Taking the mean distance d between adjacent atoms as the length unit and regular angles of 120° for the molecular geometries, we get $\mathfrak{M}_1 = 1.69$ (long axis) for the first transition and $\mathfrak{M}_2 = 1.18$ (short axis) for the second transition of a [2.2.4] system, as compared to $\mathfrak{M} = 1.82$ and $\mathfrak{M} = 1.49$ respectively for the long and short cis-methine chains included in it.

Similarities of spectra in a series of unsaturated compounds may be understood by theory arguments [8], because of the identity between the adjacency matrix of the graph depicting the β framework and the matrix giving the energies $e = \alpha - x\beta$ of the π MO's in the simplest Hückel approximation [9-11]. The graph of the system of M unsaturated atoms between one nitrogen and the two others in a branched cyanine has the form of a Y-like tree, where the tertiary carbon plays the role of a branching vertex, the total number of vertices being $M = 3m + 1$ with m even for odd symmetrical cyanines and m odd for the even ones.

The characteristic polynomial $P_M(x)$ of a molecular tree can be expressed in powers of x by general methods based on the Coulson-Sachs graphical formulae [12] or by special algorithms adapted to this topology [13, 14]. Instead of writing P_M as an algebraic equation in x, there is an alternative procedure which was used within the framework of the Hückel-London theory of diamagnetism [15] and has been put forward by the recent works of Randic et al. [16]. It consists in expanding P_M in terms of Chebyshev polynomials $T_p(x)$ $(0 \leq p \leq M)$, which are the characteristic polynomials $P_p(x)$ of simple linear graphs. In this way, P_M

is split up into contributions corresponding to elementary molecular graphs, i.e., unsaturated chains. Such a procedure is straightforward for trees, the decomposition of which can be easily achieved by repeated applications of the Heilbronner formula [17].

Modelling cyanines by polymethine anions of the same topology, we immediately observe a great resemblance between the characteristic polynomials of linear and tribranched systems, as is shown in Table 1.

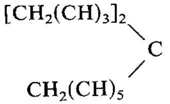
In comparison with a linear graph, the roots of the eigenvalue equation $P_M(x)=0$ obtained for an $M=3m+1$ graph having three identical branches of m vertices are classified as follows:

(i) The solutions of the equation $T_m^2=0$ giving the doubly-degenerate e-levels in a point group with a 3-fold rotation axis. The latter coincide with the single roots found for the antisymmetrical part T_m of the graph T_{2m+1} spanned by two of the branches, choosing the z axis of the appropriate C_{2v} subgroup along the direction of the third one.

(ii) The solutions of the equation $(T_{m+1}-2T_{m-1})=0$ which are roots in principle different from those found for the symmetrical part of the graph T_{2m+1}. There is, however, a strong correlation between the eigenvalues of the two symmetrical subsystems, because the expression $(T_{m+1}-2T_{m-1})$ can be considered as the equation of a pseudo-linear graph resulting from the junction of one branch with the symmetrical combination of the two others (hence, a factor 2 in front of T_{m-1}). Moreover, we can expect that the eigenfunctions of a Y-tree matrix have some relationship with those of the chains, except that the coefficients of the former are distributed among the three branches.

For conjugated systems, an important feature is the existence or not of roots $x_i=0$, corresponding to non-bonding molecular orbitals (NBMO). Since odd Chebyshev polynomials are odd functions of x, the general formulas given in

Table 1. Chebyshev decomposition of polymethine graphs related to the [2.2.4] nonamethine cyanine

Formulas	Characteristic polynomials
Linear chain $(M=2m+1)$	$T_{2m+1}=T_m(T_{m+1}-T_{m-1})$
Tribranched system $(M=3m+1)$	$P_{3m+1}=T_m^2(T_{m+1}-2T_{m-1})$
$CH_2(CH)_7CH_2$	$T_9=T_5T_4-T_4T_3=T_4(T_5-T_3)$
$CH_2(CH)_9CH_2$	$T_{11}=T_7T_4-T_6T_3$
 $[CH_2(CH)_3]_2C\,CH_2(CH)_5$ (for [2.2.4] nonamethine-cyanine[a])	$P_{15}=T_{11}T_4-T_6T_4T_3=T_4(T_7T_4-2T_6T_3)$

[a] Nomenclature of [3]

Table 1 for tribranched systems have roots $x_i = 0$. They are either doubly-degenerate roots of e-symmetry coming from T_m^2 or singly symmetrical roots located in both T_{m+1} and T_{m-1}, according as m is odd or even. To simulate cyanines, one electron per NBMO must be added to the neutral polymethine compounds; thus we have closed-shell systems, the HOMO's of which exchange their symmetry properties together with m. However, it is easy to see that, in connection with the symmetry alternation observed in two successive roots of a Chebyshev polynomial, the LUMO's given by the smallest positive values of x_i change in the opposite direction. Consequently, the parity of m makes no difference as far as (HOMO–LUMO) transitions are concerned.

Similar considerations can be developed for less symmetrical Y-trees, except that we have to consider parent chains of different size. In this way, it is possible to compare the characteristic polynomial P_{15} of the [2.2.4] system with those of the chains T_9 and T_{11} formed by the two short branches and by the long and one of the short branches respectively. If we disregard the exact molecular geometry of each compound, we can classify the roots of P_{15}, T_9 and T_{11} in terms of C_{2v} representations (while noticing that the z axis of the group coincides with the longer branch of the tree for the [2.2.4] system and the 9-center system included in it, but not for the 11-center one). Within this symmetry group, P_{15} and T_9 are split in the same way, giving T_4 as antisymmetrical parts in both cases and rather different symmetrical parts. In fact, the roots of the symmetrical equation $(T_7T_4 - 2T_6T_3) = 0$ are found to be strongly correlated with those of the T_{11} polynomial, using the Heilbronner composition formula adequately. This indicates that the eigenvalue spectrum of a fully conjugated [2.2.4] compound proceeds partly from the long chain, partly from the short chain included in the tree. Taking into account the numerical values of the smallest positive roots of Chebyshev polynomials and using group-theory arguments for transition moments, it is easy to predict a relationship with the heptamethine-cyanine for the first transition of the [2.2.4] nonamethine cyanine, and a relationship with the pentamethine cyanine for the second one.

So, a π-electron delocalization within the three branches of a polymethine system is consistent with the resemblance observed between the visible absorption spectra of tribranched cyanines and corresponding simple cyanines. Clearly, further evidence should be gathered to solve the above-mentioned dilemma.

References

1. See Pullman B, Pullman A (1952) In: Les théories électroniques de la chimie organique, chap VI and VII. Masson, Paris
2. Gund P (1972) J Chem Educ 49:100
3. Reichardt C, Mormann W (1972) Chem Ber 105:1815; (for nomenclature, see this paper, p 1832)
4. Grahn W, Reichardt C (1976) Tetrahedron 32:125; Grahn W (1976) Tetrahedron 32:1931
5. Allmann R, Grahn W, Knecht J, Kucharczyk D, Reichardt C (1985) Chem Ber 118:1295
6. Reichardt C, Knecht J, Mrozek W, Plaas D, Allmann R, Kucharczyk D (1983) Chem Ber 116:1982
7. Niaz Khan M, Fleury JP, Baumlin P, Hubschwerlein C (1985) Tetrahedron 41:5341
8. See Graovac A, Gutman I, Trinajstic N (1977) In: Topological approach to the chemistry of conjugated molecules. Lect Notes Chem 4. Springer, Berlin Heidelberg New York

9. Günthard HH, Primas H (1956) Helv Chim Acta 39:1645
10. Ruedenberg K (1954) J Chem Phys 22:1878
11. Polansky OE, (1975) MATCH 1:183
12. See Trinajstic N (1977) In: Segal GA (ed) Modern theoretical chemistry—Semi-empirical method. Plenum Press, New York
13. Balasubramian K, Randic M (1982) Theor Chim Acta 61:307
14. Balasubramian K (1982) Int J Quantum Chem 21:581; (1984) Theor Chim Acta 65:49
15. Mayot M, Berthier G, Pullman B (1951) J Phys Radium 12:652, 717; (1953) J Chim Phys 50:170, 176
16. Hosoya H, Randic M (1983) Theor Chim Acta 63:473;
    Randic M, Baker B, Kleiner AF (1985) Int J Quantum Chem Symp 19:107
17. Heilbronner E (1953) Helv Chim Acta 36:170