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π-Conjugated Zwitterions as Paradigm of Donor–Acceptor Building Blocks in Organic-Based Materials

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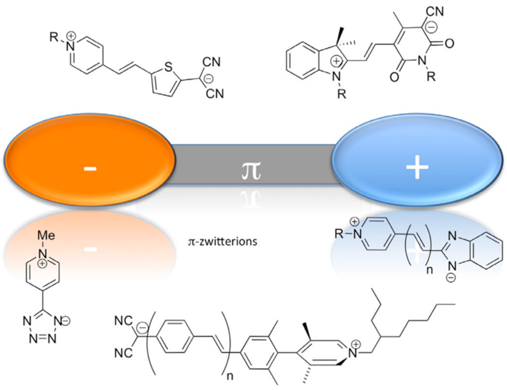

The very peculiar characteristics of zwitterions, as well as a clear and unambiguous definition, have been overlooked in past literature. However, these compounds are particularly important in view of the impact they have had in the recent past and will likely continue to have in the future as components of performing functional organic and hybrid materials. In this Account, we primarily aim to define critically important organic concepts of zwitterions regarding both their design and nomenclature. We will particularly focus on a specific kind of zwitterions we define as π-conjugated zwitterions.

These types of zwitterions are systems pertaining to the class of donor–acceptor (push–pull) molecules. In the ground state, they are preferentially represented in terms of an electron donor moiety bearing a negative net charge, and electron acceptor one bearing a positive net charge connected by a conjugated bridge. As such, they are possibly the most effective example of push–pull structure, possessing relevant features for applications like nonlinear optics, photovoltaics, imaging, and high capacitance dielectrics. In addition, the interaction between these dipolar compounds and the environment is highly specific and can be exploited in the construction of well-organized nanostructures, both in solution and in the solid state. According to the Gold Book of IUPAC for nomenclature, the distinction between zwitterions and the charged molecule called a betaine is subtle. The betaine is a particular class of zwitterion possessing an onium atom not bearing a hydrogen. The two terms are often considered equivalent, thus generating confusion while retrieving literature. In this Account, we define and describe π-conjugated zwitterions systems that are dipolar in the ground state, admitting resonance limiting structures that are neutral and chargeless. For the purpose of this Account and to the benefit of researchers striving to retrieve materials-related zwitterion literature data, we suggest to use the term π-zwitterions instead of the commonly used plain term "zwitterions". We show that this definition enables the clear identification of a class of compounds having unique properties distinct from "dipolar conjugated compounds." We describe the most common donor and acceptor groups in π-zwitterions. In particular, we focus our attention on the special case of the nitrile functionality, which tends to be contiguous to a negative charge. We also address special emphasis to benzenoid components that are substituted by heteroaromatic units in π-zwitterions, because the HOMO–LUMO energetic consequences are specifically involved in these cases. We make reference to the paradigmatic case of π-zwitterions second order nonlinear optical properties. Here, the value of the first hyperpolarizability β versus the alternation in bond length turns out to be a measure of the balance of the chargeless and the dipolar contribution to the description of the zwitterion ground state. We also report literature data, collected both from our group and others, concerning π-zwitterions containing heteroaromatic and/or nitrile groups, those based on the most performing acceptors so far described, and merocyanines. With particular reference to merocyanines, we show how π-zwitterions can play a fundamental role in the fast growing field of organic photovoltaics. Finally, we present π-zwitterions made up of heteroaromatic groups that open new scenarios in heteroaromatic chemistry.

Introduction

Organic π-conjugated compounds have experienced over the last decades a tremendous interest as versatile and highly performing active components in a large variety of devices and applications. Two peculiar characteristics of organic materials are key for their technological exploitation.

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First, most organic conjugated materials can be manufactured by low cost, solution based deposition techniques. Moreover, the intrinsic flexibility of both their electrochemical and optical properties holds promise for custom designed active materials. Among the various design strategies so far exploited to produce performing organic semiconducting materials, the so-called "push–pull" molecules hold a prominent position. By this definition, it is intended the design of a molecule possessing an electron donating (pushing electron density) and an electron withdrawing (pulling electron density) group connected by a conjugated bridge. Push–pull derivatives have been at the core of a tremendous investigation over the last 20 years, mostly for their very relevant nonlinearoptical properties. Also, recent reviews[1–3] show that push–pull derivatives are expected to play a major role in organic photovoltaics and organic electronics.[4,5] The present Account focuses on a very peculiar class of push–pull molecules, so far never clearly addressed with a precise and unambiguous definition, having in common, among other structural features we will describe, a zwitterionic structure. We shall treat π-conjugated zwitterions (or more concisely π-zwitterions) that are dipolar in the ground state but that, thanks to charge delocalization, admit a neutral chargeless structure. On doing this, we primarily aim at defining critically important organic concepts, sometimes previously overlooked, regarding both nomenclature and design of π-zwitterions as new organic materials.

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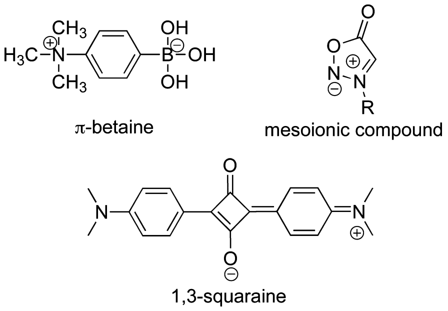

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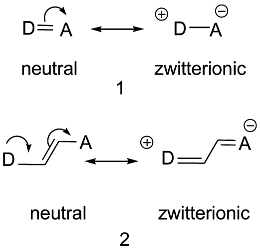

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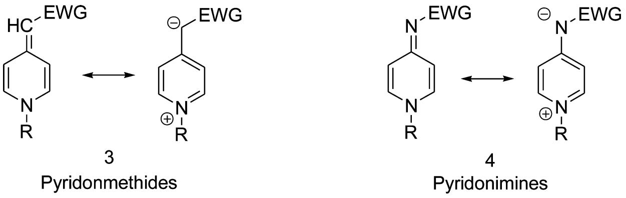

π-Zwitterions: Acceptor and Donor Groups

The name zwitterion has its root in the biological German term "zwitter" that means "hermaphrodite" and that in chemistry indicates, with an adaptation, a compound simultaneously carrying a positive and negative charge. More specifically, the IUPAC Golden Book[6] states that zwitterions are "Neutral compounds having formal unit electrical charges of opposite sign". This definition includes a vast number of compounds like amino acids at the respective isoelectric point, betaines (a subclass of zwitterions where the positive net charge resides on a onium atom bearing no hydrogens), and ylids. Such a broad definition also includes all those peculiar push–pull structures admitting canonical representation like those shown in Scheme 1. [Note that if one of the methyl groups of the π-betaine is replaced by a hydrogen atom, according to IUPAC rules, the structure cannot be considered a betaine anymore but simply a zwitterion (and not a π-zwitterion, according to the present paper).

The admissibility of a neutral canonical resonance structure requires annihilation of the net charges through charge delocalization. For this particular class of compounds, we propose the concise, unambiguous and meaningful definition of π-zwitterions. It should be noted that this definition does not include compounds possessing a positive and a net negative charge but not admitting a chargeless canonical representation, as in the case of what we might call π-betaines like those shown in Scheme 1 as well as mesoionic compounds and squaraines.

There are several examples of compounds pertaining to the π-conjugated systems class, presenting both linear and cyclic net charge bearing end units. Our definition will treat π-conjugated systems where an electron flow from the donor D to the acceptor A originates dipolar general structures such as **1** and **2** that can be written both in an electrically neutral and charge separated general structures (Scheme 2).

The acceptor A is an electron-withdrawing group (EWG) such as $-CHO$, $-CO-R$, $-COOR$, $-CN$, and $-NO_2$, an electron poor heteroaromatic in its azinium or azolium structure and so forth, while the donor D is an electron-rich atom or an

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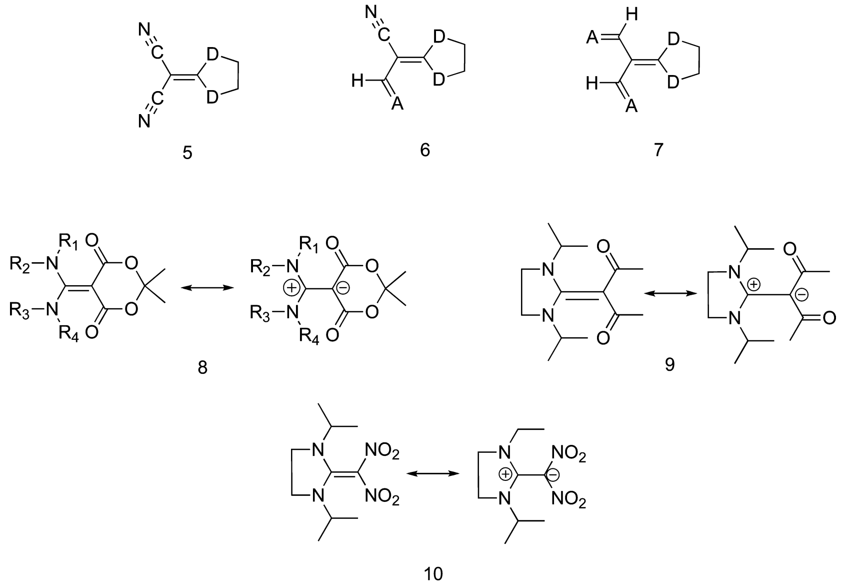

electron pool such as amines, ethers, thioethers, π-excessive heteroaromatics, alkylidene dihydroheteroaromatics admitting upon charge delocalization azinium or azolium resonance structures as in heteroaromatic methides or imines.[7] Indeed, in the neutral structure of pyridonmethides **3** and -imines **4**, and the like for other heteroaromatics, such moieties function as π-donors (Scheme 3).

π-Zwitterion as Simple Donor−Acceptor Ethenes and Polyenes

A number of studies on donor−acceptor ethenes appeared in the literature[8−12] are reported below containing carbonyl, thiocarbonyl, nitro, and cyano groups as EW functionalities in various arrangements where A is usually a carbonyl EW group (Scheme 4).

A classical example of linear π-conjugated polyenic dipolar systems is provided by unsaturated π-conjugated ω-dialkylaminoaldehydes (Scheme 5).[13,14]

Carbocyclic Zwitterions

Main examples of such π-conjugated carbocyclic molecules are calicene[15] and sesquifulvalene.[16] Attainment of aromaticity of the cyclopentadienyl anion on one side and of the cyclopropenyl or tropylium cations in calicene and sesquifulvalene thanks to the electron flow from the donors to the cyclopentadienylidene moiety being certainly the driving force for the existence of such molecules as π-zwitterions (Scheme 6). Conversely, azinium or azolium cations may substitute the positively charged carbocycles of cyclopropenylium or tropilium ions.

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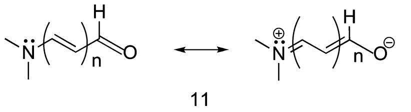

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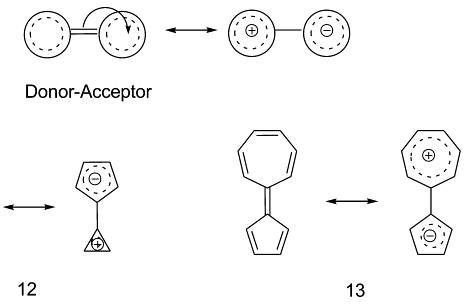

Benzenoid versus Heteroaromatic Building Blocks in π-Zwitterions

The majority of π-donors or acceptors systems are based on aromatics and/or heteroaromatics. Benzenoid systems, with the exception of higher acenes, are constitutionally neither electron-rich nor electron-poor: to become π-donors, they have to be functionalized with electron donor groups (dialkylamino- or diarylamino substituents, alkoxy- and thioether functionalities) and conversely to become π-acceptors, functionalization must take into consideration electronwithdrawing groups EWG (carbonyl-, sulphonyl, cyano substituents, and the like).

On the contrary, heteroaromatics are constitutionally either electron-rich or electron-poor systems. Five membered heteroaromatics like furan, pyrrole, and thiophene are π-excessive systems and thus electron donors while azines (pyridine and corresponding diethero systems, pyrimidine, pyrazine, pyridazine, and the like) are π-deficient systems and therefore electron-withdrawing. Functionalization of these heteroaromatics may finely tune their donating or accepting capacity depending on the nature of the substituent, giving rise to enhancement or reduction of their intrinsic property.

There is a further important advantage presented by heteroaromatics. In a donor–acceptor molecule, charge delocalization converts, at least partially, the aromatic nature of the whole system into a quinoidal system with some loss of the aromatic stabilization energy. This loss is considerably higher in benzenoid systems than in heteroaromatics, notably in furan, pyrrole, and thiophene which are known to have an aromatic stabilization much lower than in benzenoid groups.[17] In molecules containing heteroaromatics, the energy cost of charge delocalization originating quinoidal systems is considerably lower and therefore the delocalized structures are favored. Such peculiar characteristic of π-zwitterions containing heteroaromatics as the charge bearing units has a profound consequence in both optical and nonlinearoptical properties of such molecules. First of all, a lower destabilization associated with the quinoidal form translates into a stabilization of the LUMO, eventually leading to a reduction of the HOMO–LUMO gap with respect to a benzenoid system possessing the same number of π-electrons. Moreover, the polarization of the electronic distribution along the conjugation axis becomes sizably easier.

In this respect, the very relevant work of Marder et al.[18] on the structure property relationships in dipolar molecules for second order nonlinearoptics represents a paradigmatic example of the advantages of the use of heteroaromatics versus benzenoid compounds. Within the framework of the so-called "two level model", the first molecular hyperpolarizability β increases on lowering the HOMO–LUMO gap (eq 1).

$$\beta \propto \frac{{\mu_{eg}}^2 \Delta\mu}{{E_{eg}}^2} \tag{1}$$

where μ_{eg} is the transition moment between ground and excited states (proportional to the extinction coefficient ε), $\Delta\mu$ is the dipole moment difference between ground and excited states, and E_{eg} is the HOMO–LUMO transition (from the absorption spectrum).

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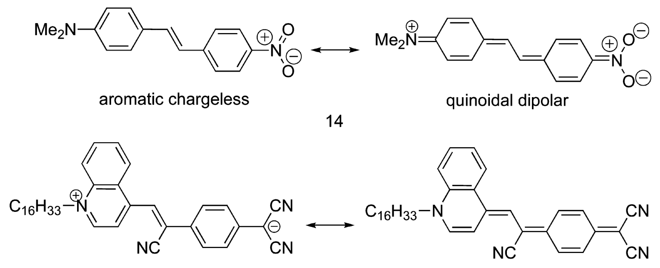


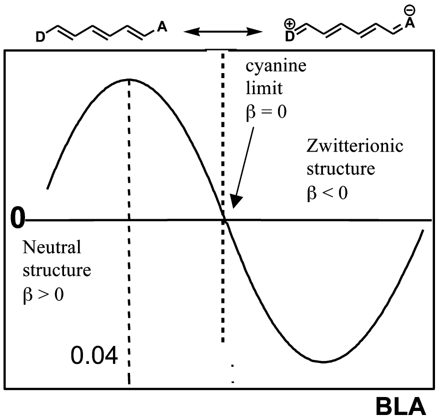


FIGURE 1. Bond length Alternation (BLA) vs molecular hyperpolarizability according to Marder et al.[19] (Adapted from ref 17.)

Also, the sign of β is a very sensitive gauge of ground state vs excited state polarity. In fact, whenever the ground state dipole moment is higher than the excited state one, the hyperpolarizability assumes negative values. Conversely, when the dipole moment is increased upon optical excitation, the β becomes positive. As such, the measurement of the molecular first hyperpolarizability provides an excellent tool to identify all of the molecules pertaining to the class of the π-zwitterions, excluding all other systems that, even if admitting a limiting resonance structure having zwitterionic character, do not possess a prevalent ground state structure with separated net charges.

There is a considerable structural difference between benzenoid π-zwitterions and heteroaromatic π-zwitterions in which the acceptor is an azinium or azolium moiety. In fact, in the first ones, the chargeless structure is fully aromatic and the dipolar one is quinoidal, while the reverse is true for the second ones. This concept has been taken into consideration by Marder et al.[19] This is shown in the following two examples. Derivative **14**, possessing a positive β value, is not a π-zwitterion (even if the molecule can be represented with a canonical structure having separated charges) (Scheme 7). Conversely, the dipolar quinolinium dicyanomethanido derivative **15** (possessing a negative β value)[4,20] is in its fully aromatic structure and is a real π-zwitterion, since in this case the charge separated canonical structure best represents the molecular ground state electronic structure.

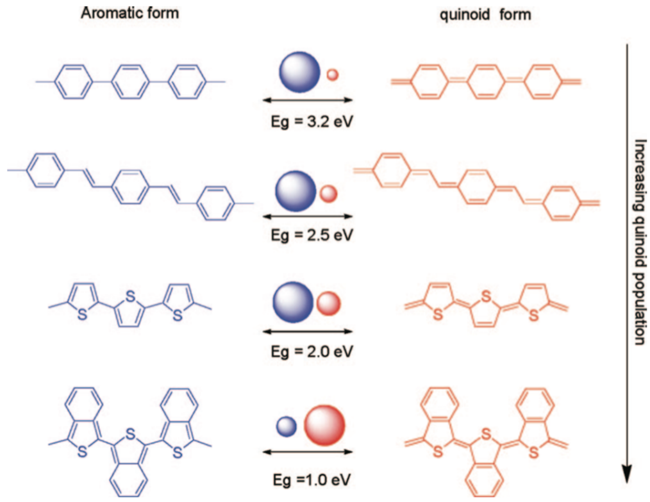


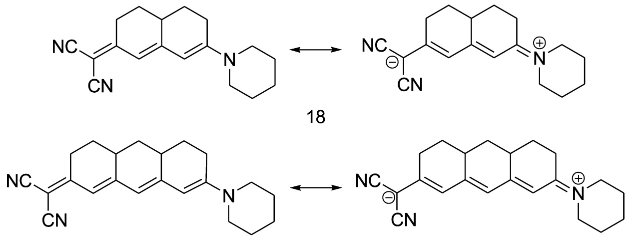
FIGURE 2. Aromatic and quinoid resonance forms of poly(*p*-phenylene), poly(*p*-phenylenevinylene), polythiophene, and polyisothionaphtene. The relative contribution of the mesomeric structures is represented by the size of the colored circles over the arrows. (Reprinted with permission from ref 3. Copyright 2009 American Chemical Society.)

Recently, Cheng et al.[3] reported a quantitative study dealing with the energies changes on going from aromatic and heteroaromatic systems to the quinoidal ones in the case of various π-conjugated bridges (Figure 2).

Second Order Nonlinear Optical Properties as a Tool for the Identification of π-Zwitterions

It can be appreciated from the previous figure that the largest gap is found for the *p*-phenylene derivative, the aromatic system being more stable by 3.2 eV, while for polyisothionaphtene the quinoid system becomes more stable vs the aromatic one by 1 eV. Analogously, the charge transfer capacity from the donor to the acceptor in fully

SCHEME 9



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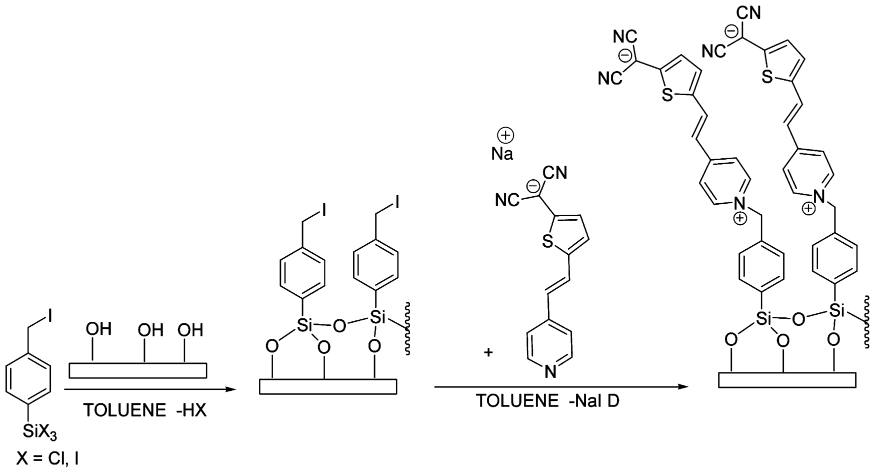

FIGURE 3. Schematic representation of the covalent grafting of zwitterionic chromophoric films by selective alkylation of the chromophore precursor by a surface-bound benzyl iodide monolayer.

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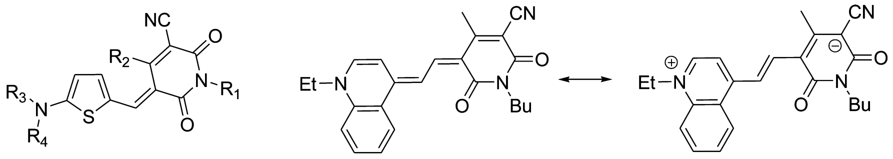

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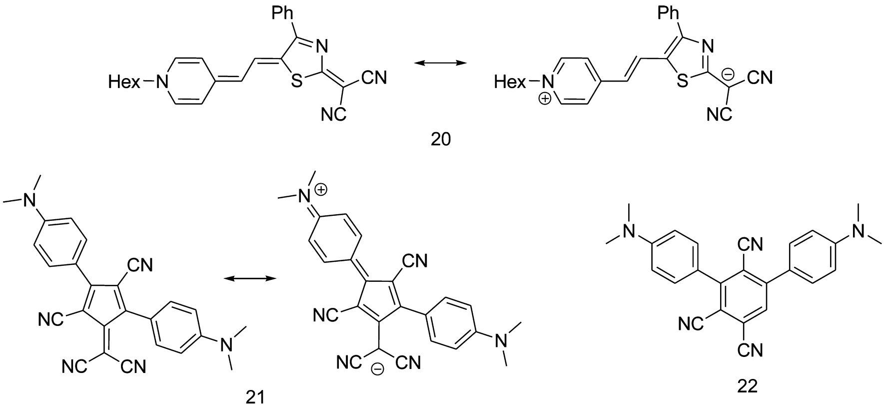

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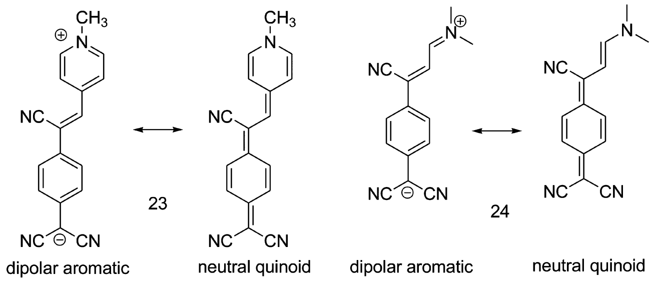

conjugated systems has been evaluated in an outstanding paper by Marder and co-workers[21,22] in terms of the nonlinear property β of the molecule. They defined the BLA (bond length alternation) model that indicates the average bond length difference between double and single bonds in the molecule ground state (Figure 1). A closely related parameter is BOA (π-bond order alternation).[22] The quantity β therefore turns out to be the probe of the relative contributions of the dipolar and neutral chargeless resonance structures of the molecule. In addition, the β value represents a very important parameter in EO material applications. For a given π-bridge, there is an optimal combination of donor and acceptor groups that place the molecule in a certain area of the plot (see Figure 1). If the ground state charge distribution is too asymmetric the β value decreases.[23] At the cyanine limit the molecule is symmetric and β is accordingly zero.

Control of single/double bond length alternation is critical to maintain π electron communication between the donor and acceptor and thus to optimize the molecular hyperpolarizability. Bridges containing aromatic and heteroaromatic groups yield excellent thermal and chemical stability; however, the larger bond length alternation of these species frequently results in poor molecular hyperpolarizability.[24]

The Special Case of the Nitrile Functionality

In nitrile carbanions, the negative charge is firmly held α to the cyano group without extensive charge delocalization onto the nitrogen atoms of the CN group.[25−29] Kleinpeter et al.[30] have studied the dynamic NMR properties of many of these donor−acceptor cyano substituted ethenes (Scheme 8).

Alkylidene malononitriles[31] are accepting groups in the neutral resonance limit structure of zwitterions that shifts to malononitrile carbanions in the delocalized dipolar limiting structure (Scheme 9).

Zwitterions Containing Heteroaromatic and/or Nitrile Functionalities

Würthner and co-workers investigated a number of π-zwitterions containing the above functionalities, and they pointed out dimerization and aggregation as dipolar dyes.[32,33] Diederich et al.[34] described the access to highly functionalized 6,6-dicyanopentafulvene derivatives as π-zwitterions, characterized also by X-ray structure. Since in malononitrile anions the negative charge is firmly held α to the cyano groups, it is thus freely available to be delocalized toward the acceptor groups, to generate polyene chargeless systems. Componds **20**−**30** are examples of real π-zwitterions that exploited such a principle (Schemes 10−13).

Wang associated the malononitrile anion as a donor with imminium or pyridinium cations as electron acceptors (Scheme 11).[35,36]

Our group took advantage of such a concept and in addition utilized the low E_{ge} energy of five-member heterocycles in the synthesis and characterization of the following systems (Scheme 12).[37,38] Our group used some of the above dicyanomethanidopyridinium zwitterions as building blocks to prepare functional materials having nonlinear optical behavior: (a) Langmuir−Blodgett films with **26**.[39−43]

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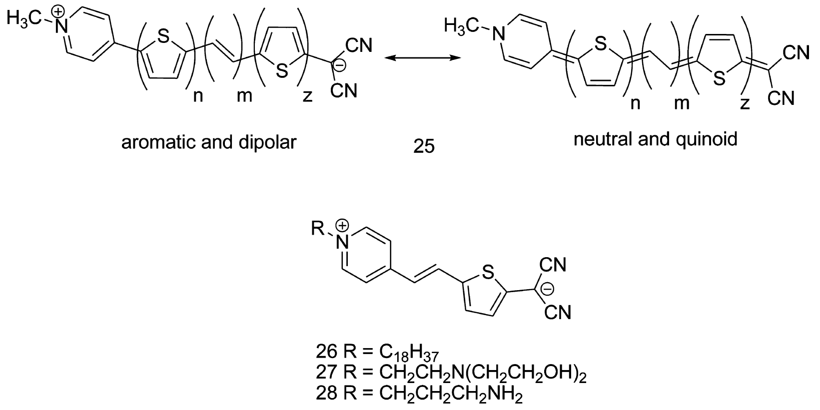

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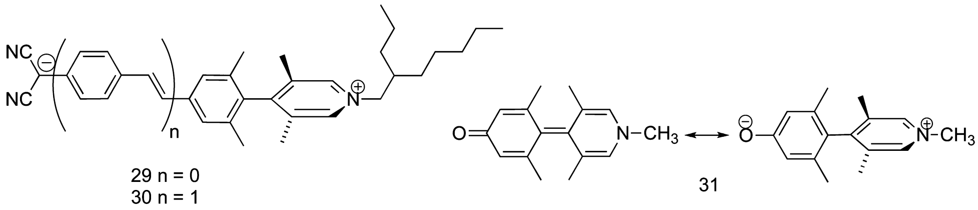

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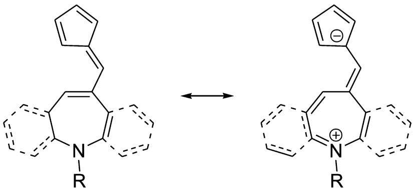


(b) Sol–gel structures with **27**.[44–48] (c) Cross-linked poly(amino-amide) matrixes[49] with **28**.

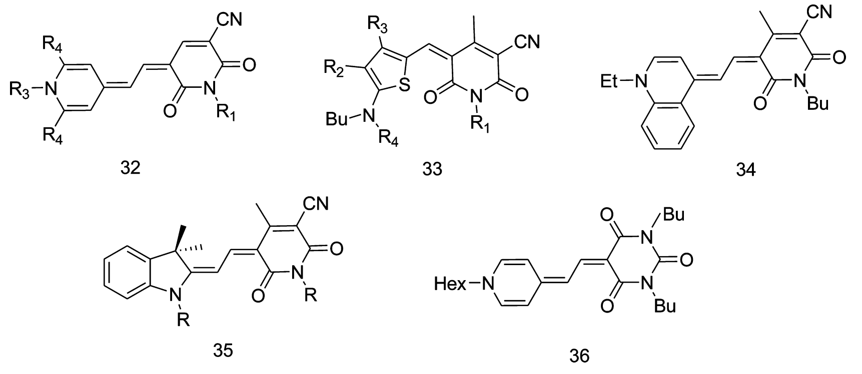
The disclosure by Marks and Yitzchaik of the construction of superlattices into which incorporate π-zwitterions has been definitely the most elegant and innovative application of such systems.[50] From beginning to end, all this led to the design and preparation, starting from the carbanionic precursors of molecules of general structure **25**, of thin films as self-assembled, thiophene spaced siloxane based *N*-benzylpyridinium dicyanomethanido π-zwitterions.[51] To emphasize the importance of thin films devices, other donor–acceptor dyes were subsequently deposited on hydroxylate surfaces: self-assembling occurred in force of hydrogen bonding. As a highly valuable improvement, such films were grown also by physical vapor deposition.[52] Figure 3 shows a schematic representation of the surface grafting process.

In view of the NLO response of conformationally tuned chromophores[53–55] and after the efficient synthesis of twisted zwitterionic biaryls became accessible,[56] giant molecular hyperpolarizabilities were obtained. The special stabilization provided by α-cyanocarbanions as donor groups in π-zwitterions such as **29** and **30** was established. Interestingly, all this started from the intuition that twisted merocyanines as **31** could provide a large electron flow, upon optical excitation, from the donor to the acceptor. Results confirmed this hypothesis (Scheme 13).[55] This long exciting research story has been summarized.[57]

Aromaticity and Antiaromaticity in π-Zwitterions

A special case of donor molecules is experienced when a cyclic unsaturated π-system contains a number of π electrons (*n* = 4, 8, etc.) to provide to the molecule a potential antiaromatic character. In addition to obeying such numbers of π electrons, a molecule must be planar to be antiaromatic. The basic innovative concept worth to be followed is this: a planar (or quasi-planar) donor molecule containing 8 π-electrons may move toward aromaticity by donating an electron pair to a conjugated external group. A similar, but not identical, case is found in sesquifulvalene where a nonaromatic group such as the cycloheptatrienyl ring becomes the aromatic tropilium entity by donating an electron pair to the cyclopentadienyl ring. In this case, the net favorable energetic result is that the whole molecule attains

SCHEME 15



aromatic stabilization starting from a nonaromatic set. Once again, heterocyclic chemistry may be useful in suggesting the possible design of antiaromatic systems that upon charge delocalization move toward an aromatic set. Potential examples are the following that make reference to the azepine ring system.[58] Recent literature[59,60] describes the synthesis and properties of boroles as potential systems endowed with high antiaromaticity. Scheme 14 reports possible azepine-related structures whose synthesis is under development.

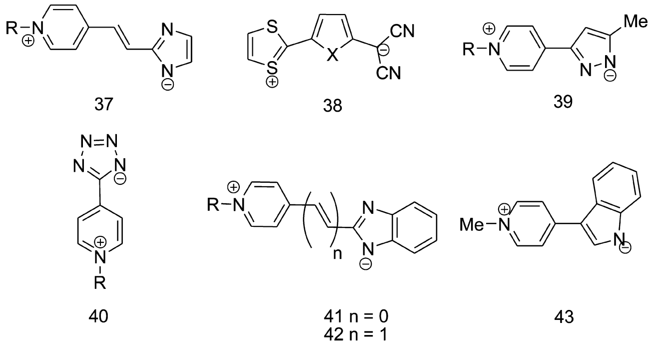
Merocyanines as π-Zwitterions

Würthner drew attention to the aggregation tendency of many zwitterions.[32] Also, he identified the very profitable exploitation of such compounds in bulk heterojunction solar cells.[61] π-Zwitterions are, by their very nature, strongly dipolar. Their aggregation in the solid state normally provides a very high dielectric constant medium. The dissociation of photopromoted excitons in free charges at the donor–acceptor interface of bulk heterojunction solar cells is strongly favored by high dielectric constant media. The exploitation of such a strategy was recently foreseen as one of the key steps toward efficient organic OPVs (Scheme 15).

Entirely Heteroaromatic Zwitterions

Otsubo et al.,[62] Metzger,[4] Alcalde and co-workers,[63−67] and our group[68] were among the first authors to imagine a number of such systems. In the dipolar structure, Otsubo et al. considered 1,3-dithiolium cations as cationic groups, Metzger quinolinium systems, Alcalde and co-workers pyridinium as cationic heteroaromatics and various azolate systems as negatively charged systems, and our group tetrazolate as a negatively charged system. Alcalde and co-workers also considered imidazolate, benzimidazolate, pyrazolate, and indolyl anions as negatively charged donor groups. Scheme 16 shows representative examples of such systems.

SCHEME 16



Solvatochromism of π-Zwitterions

The use of the term "π-zwitterions" under the meaning we defined with all previous examples, thus distinguished from betaines, conveys a precise physicochemical meaning. Explicitly, the optical gap and the balance of the two resonance structures of a π-conjugated zwitterion will always depend upon the polarity of the solvent (solvatochromism) or matrix (solidochromism) in which the π-conjugated zwitterion is present as a guest. A polar medium will better interact, in the solid (or solvate) or in solution, with the charged dipolar structure, while the neutral polyenic structure will not sense the polarity of the medium.

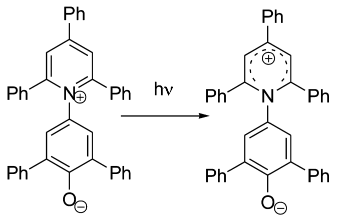
Since betaines cannot be represented by a neutral chargeless conjugated structure, they should not sense the polarity of the medium and should not be solvatochromic. An apparent contradiction to what we have just said for betaines is Reichard's pyridinium *N*-phenolate betaine dye 44 (Scheme 17) which shows the highest negative solvatochromism ever reported. Reichardt correctly assigns the term "betaine" to the ground state of the dye but the term zwitterion to the excited state of the same.[70] Reichardt ascribes this behavior to the different response of the dye to solvent polarity when μ_g is either greater than or less than

μ_e. One might thus say that, in this case, the molecule is indeed a π-zwitterion but only in its excited state.

Our group[68,69] took into consideration for a π-zwitterion the tetrazolate and the pyridinium rings, respectively, as the negatively and positively charged entities. The simplest possible derivative of this class is zwitterion **45**, a remarkably compact structure already possessing sizable, and negative, second order nonlinear optical activity (Scheme 18).

Interestingly, Figure 4 shows that the solvatochromism of **45** is not monotonous, with a transition between a positive and a negative regime for $E_T(30)$ values around 38 kcal mol^{-1}.[70] This result can be rationalized assuming a dominant zwitterionic ground state in polar solvents and a quinoidal structure in very low $E_T(30)$ ones passing through a cyanine-like form for $E_T(30)$ values close to that of THF. According to the BLA model, highest negative β values are expected for molecules possessing an electronic structure intermediate between a localized charge distribution (zwitterionic limit) and the delocalized cyanine limit. Common push–pull molecules can only span limited portions of the BLA plot, and although changes in the sign of the first hyperpolarizabilities as a consequence of solvent effects are known, they are usually limited to small deviations around the cyanine limit.[24] In solution, the contribution of the zwitterionic structure depends upon the specific solvent Reichardt parameter $E_T(30)$. Thus, compound **45** can be (or not be) a π-zwitterion according to local polarity.

SCHEME 17



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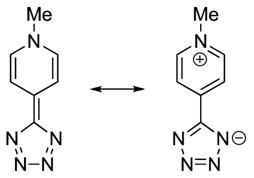
SCHEME 18



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Summary

In conclusion, we have reported a vast number of chemical structures having the common characteristics of being fully conjugated, preferentially represented by a structure having a positive and a negative net charge, admitting a limiting resonance structure having no net charge. We have discussed how all those structures share a number of common features such as a negative molecular hyperpolarizability, a high dipole moment, and a negative solvatochromism. We believe that the direct addressing of all those structure with the common name of π-zwitterions could greatly simplify the retrieval of such structures from chemical databases. Also, π-zwitterions played a major role in optoelectronic materials for second harmonic generation and electro-optic modulators, a field of research among the most active of the last 20 years. Although recently such research is slowing down, π-zwitterions appear to be very promising materials for small molecule organic photovoltaic cells, thus ensuring

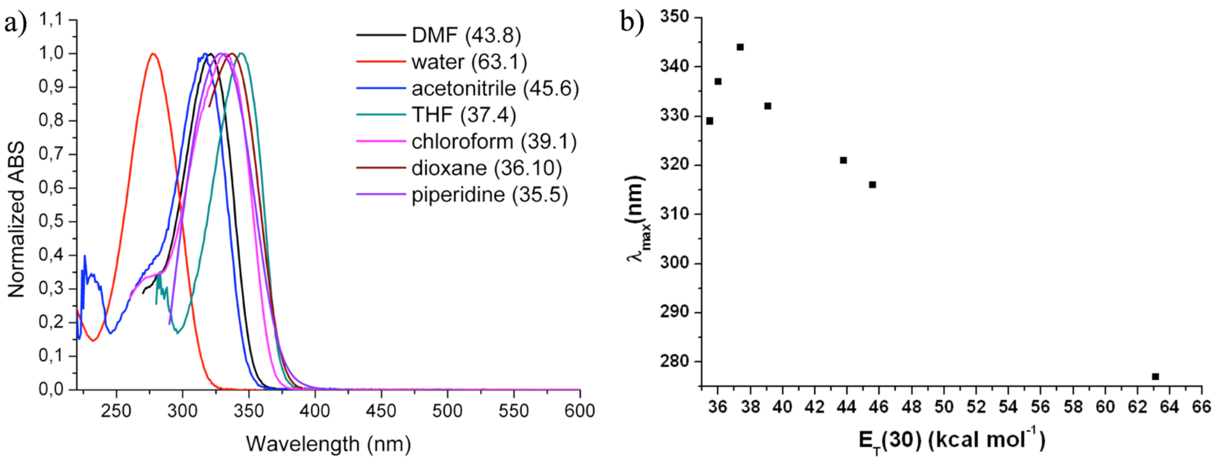

FIGURE 4. (a) Derivative 45 UV–vis absorption spectra in selected solvents. (b) Correlation between λ_{max} and $E_T(30)$ empirical parameter (reported under brackets in (a)) for the employed solvents. (Adapted from ref 67.)

a very bright future, surely deserving a clear and unambiguous definition, for this very peculiar class of compounds.

We wish to thank all the Authors cited in the references that contributed to our papers consenting to proceed toward this Account.

BIOGRAPHICAL INFORMATION

Giorgio A Pagani is presently retired Professor of Organic Chemistry and Material Science. He received his Ph.D. Degree in Industrial Chemistry from the University of Milano in 1963. From 1963 to 1980 he was Chief Researcher at the Italian National Council of Research. In 1972–1973 he was Visiting professor (Associate) at the College of Arts and Sciences of Northwestern University, Evanston, IL. From 1980, he was full Professor in Heterocyclic Chemistry at Milan University, then he joined in 1994 the University of Milano-Bicocca. He is the Italian National Representative at IUPAC (Commission on Physical Organic Chemistry). In 2002, he received the Award of the Italian Chemical Society (Organic Division) for Mechanistic and Theoretical Aspects of Organic Chemistry. His current interests include design, synthesis, and characterization of polar (zwitterionic) organic materials for nonlinear optics and multiphotonics, synthesis of heterocycles and their physical organic chemistry, carbanions and nitranions, synthesis and preparation of conducting polymers from polymerogenic heterocycles, organic nanostructured materials, polymeric and sol–gel materials, self-assembled multilayers for nonlinear optics, frequency-upconverted dye lasers, optical limiters, electrochromic organic materials. He is author or coauthor of ca. 250 papers, many of which relate to Organic Materials.

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FOOTNOTES

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