Molecular Geometry and Nonlinear Optics

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Nonlinear optical phenomena are of major importance because they form the basis for the optical processing and storage of data or images. They are therefore crucial in the development of the future generations of communications systems and computers, and much effort has been devoted to increasing the useful nonlinearity of optical materials. In this issue, Marder *et al.* (*1*) report the synthesis of organic compounds having dramatically enhanced nonlinear properties. It is especially satisfying that their results were achieved through a logical strategy of controlling the molecular geometry of their materials, rather than through the time-honored method of trial and error.

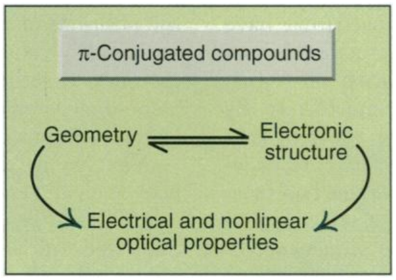


Fig. 1. Geometry and electronic structure of π-conjugated compounds are interconnected. Both feed directly into nonlinear optical properties.

Nonlinearity in the optical response comes from a very strong interaction between light waves and the material in which they propagate; it is directly related, at the microscopic level, to the nonlinear evolution of the induced dipole moment of each unit (μ_{ind}) as a function of the electrical field of the light ($\mathbf{E}$)

$$\mu_{\mathrm{ind}} = \alpha\cdot\mathbf{E} + \beta\cdot\mathbf{EE} + \gamma\cdot\mathbf{EEE} + \ldots$$

The tensors α, β, and γ represent the first-, second-, third-order polarizabilities. The higher order terms can become significant when the external electric field is large enough; in practice, this can be accomplished with the intense fields available in laser light.

At present, nonlinear optical devices are made of ferroelectric inorganic crystals such as $LiNbO_3$, D_2KPO_4, or $BaTiO_3$. In such compounds, the polarization comes from the separation of charges induced by setting the ions in motion through the interaction with the light electric field. The interest now given to organic compounds with extended conjugation, such as those reported in the work of Marder *et al.* (*1*), can therefore be easily understood as follows: In these π-conjugated systems, large charge separation can be obtained through the easy delocalization of the π electron cloud; this means that the nonlinear optical response is not only intrinsically very large but also very fast because it only requires electron motion (the response time can be in the femtosecond regime). In addition, organics present tremendous advantages such as easy processing, in particular through the application of thin-film technology, and the possibility of tailoring a given compound to the precise requirements of a given nonlinear optical effect, namely through substitution.

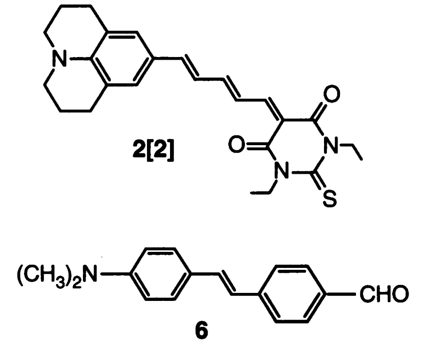
Investigation of the nonlinear optical response of organics started some 20 years ago with the pioneering work of Ducuing and co-workers (*2*). At about the same time, attention began to be paid to the electrical properties of π-conjugated polymers: Interest was tremendously boosted by the 1977 discovery of metallic-like conductivity values in doped (that is, oxidized or reduced) polyacetylene (*3*). Conductivities as large as that of copper at room temperature can now be achieved. More recently, the semiconducting properties of π-conjugated systems have also been exploited, most notably in polymer-based light-emitting diodes (*4*).

The work described by Marder *et al.* (*1*) is of particular importance mainly for two reasons: (i) It reports the highest values of second-order polarizability (β) measured to date and (ii) these unprecedented values were obtained by means of a well-defined strategy based on the control of molecular geometry. In this way, this work bridges the fields of nonlinear optics and electrical conductivity in the case of π-conjugated compounds.

The first point is relevant for actual applications because in electrooptic modulation devices, for instance, higher values mean lower switching voltages and the possibility of relying on shorter waveguide structures. With regard to the second aspect, it has long been suggested that geometry affects the nonlinear optical properties of π-conjugated systems; however, the work of Marder *et al.* (*1*) constitutes the first instance where its influence is investigated in depth and strategically exploited to produce enhanced responses. This emphasizes the strong relation that is present in all π-conjugated organic compounds between geometric structure and electronic structure (Fig. 1).

This can be illustrated by referring to a simple polyene molecule. If one were first to deal exclusively with the σ framework, all the carbon-carbon bonds would turn out to be roughly of equal length (about 1.51 to 1.52 Å). When one adds the π electrons, the molecular wave functions are such that, as a consequence of electron-electron interactions, there occurs a larger π electron density on every other bond, which results in a strong double-bond character with significantly shortened bonds (about 1.34 to 1.35 Å), while the remaining bonds shorten only slightly (about 1.45 Å). This forms the basis for the well-known relation between π bond order and bond length in π-conjugated compounds (*5*). Any π electronic structure modification and geometry relaxation are therefore intimately connected.

This geometric structure–electronic structure coupling is the source of much of the fascinating physics of π-conjugated oligomers and polymers. It is exemplified by the fact that charge storage in doped conjugated polymers takes the form of solitons, polarons, or bipolarons (*6*)—that is, charged defects associated with local geometry relaxations of the polymer chains; in polymer-based light-emitting diodes (*4*), polaron excitons are the species whose efficient recombination leads to emitted light. It is informative to recall that, in the case of a soliton along a polyacetylene (long polyene) chain, for instance, the bond length alternation reverses as one goes from the left to the right of the defect (*6*). This is analogous to the bond alternation reversal experienced by a donor-acceptor polyene



2[2]

6

Fig. 2. Molecules **6** and **2[2]** possess the same number of conjugated carbons between the amino donor and the carbonyl acceptor; however, in going from **6** to **2[2]**, in which the π-conjugated system is judiciously modified, the hyperpolarizability is enhanced 25-fold. Such π-system engineering thus leads to dramatic improvements in nonlinear optical properties.

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in going from the typical polyenic geometry to the charge-separated state geometry (*1*).

Likewise, the geometry relaxations are connected to changes in the electronic structure. For instance, the formation of polarons and bipolarons in a polymer such as polythiophene upon doping provokes the appearance of localized electronic states in the gap (and thus new optical absorptions), which results in effects exploitable in electrochromic displays (polythiophene is red in the neutral state and green-blue in the oxidized state). Polarons and bipolarons can also be formed upon photoexcitation and have been suggested to lead to enhanced third-order nonlinear optical responses in the excited state (*7*). Major efforts are also devoted to the development of π-conjugated polymers that would possess low intrinsic band gaps and thus afford large electrical conductivities without doping. One way to achieve this goal is to control the molecular structure in such a way as to reduce as much as possible the degree of bond length alternation along the backbone; such an approach has been successfully applied to π-conjugated polymers that are based on main chain donor and acceptor moieties and present band gaps as low as 0.5 eV (*8*).

In their work, Marder *et al.* (*1*) show how modifications in molecular geometry can be used to tune and optimize the response (Fig. 2). As is the case for the electrical properties, the optimization of the nonlinear optical response is possible because the geometry evolution is directly connected to an important evolution in the electronic structure (*9*). The magnitude of the effect and its precise control [which may be achievable within supramolecular structures such as proteins (*10*)] makes geometry an essential parameter we must take into account when dealing with the electrical or the second-order, as well as third-order (*11*, *12*), nonlinear optical properties of π-conjugated molecules and macromolecules.

References

1. S. R. Marder, L.-T. Cheng, B. G. Tiemann, A. C. Friedli, M. Blanchard-Desce, *Science* **263**, 511 (1994).
2. J. P. Hermann and J. Ducuing, *J. Appl. Phys.* **45**, 5100 (1974); C. Sauteret *et al.*, *Phys. Rev. Lett.* **36**, 956 (1976).
3. C. K. Chiang *et al.*, *Phys. Rev. Lett.* **39**, 1098 (1977).
4. J. H. Burroughes *et al.*, *Nature* **347**, 539 (1990).
5. L. Salem, *Molecular Orbital Theory of Conjugated Systems* (Benjamin, New York, 1966).
6. A. J. Heeger, S. Kivelson, J. R. Schrieffer, W. P. Su, *Rev. Mod. Phys.* **60**, 781 (1988); J. L. Brédas and G. B. Street, *Acc. Chem. Res.* **18**, 309 (1985).
7. L. Yang *et al.*, *Synth. Met.* **41–43**, 3197 (1991).
8. E. E. Havinga, W. ten Hoeve, H. Wynberg, *ibid.* **55–57**, 299 (1993).
9. F. Meyers *et al.*, in preparation; S. R. Marder, D. N. Beratan, L.-T. Cheng, *Science* **252**, 103 (1991).
10. K. Clays *et al.*, *Science* **262**, 1419 (1993).
11. S. R. Marder *et al.*, *ibid.* **261**, 186 (1993).
12. J. L. Brédas, C. Adant, P. Tackx, A. Persoons, B. M. Pierce, *Chem. Rev.*, in press.

α-Helical Coiled Coils: More Facts and Better Predictions

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The α-helical coiled-coil structure is finally in fashion. Previously, only fibrous protein enthusiasts—considered to be the remnants of an *ancien régime*—interested themselves in large, supposedly dull proteins such as keratin, myosin, and fibrinogen that have coiled-coil rod domain structures. Two events changed this situation—the first slowly, the second almost immediately. By the mid-80s, it had become apparent that α-helical coiled coils were far more widespread in protein structures than had been imagined. The presence of a seven–amino acid (heptad) repeat in the sequence of a protein [conventionally referred to as positions *a* to *g*, where *a* and *d* are generally apolar] (*1*) and its implication of a coiled coil–like structure provided a means to recognize tertiary structure from primary structure alone—simply by inspection (albeit with an informed eye). Statistical measures to detect coiled coils in amino acid sequences have strengthened this approach (*2*). Thanks to cDNA technology, many new sequences became available, and the special features of the coiled coil could be recognized in diverse proteins (*3*).

The second event occurred but 2 years ago: This was the determination of the x-ray structure (to 1.8 Å resolution) of the 33-residue leucine zipper portion of the yeast transcription factor GCN4 (*4*). In fact, the discovery of leucine zippers has led to the rediscovery of coiled coils! We can now see in marvelous detail the physical basis for many of the inferences about coiled-coil structure drawn from low-resolution x-ray crystallographic structures (*5*), sequence analysis, and model-building of proteins such as tropomyosin and myosin (*6*). Subsequently other high-resolution structures of coiled-coil proteins—both native and designed—have become available, and these too are enabling us to improve current predictive methods.

Fig. 1. A spectrin repeat. [Adapted from (*12*)]

The first step in predicting coiled coils from sequence is to localize the coiled-coil regions in the sequences—by visual inspection or with the statistical method of Lupas and co-workers (*2*). Various sequence comparison techniques also reveal stretches of coiled coil. The fast Fourier transform technique (*7*) (which determines regularities in the positions of charged or apolar residues) is especially valuable for the long α fibrous proteins. Together, these methods provide a one-dimensional map of the key α-helical features of a protein.

Next, we need to find out where the helices begin and end. Here we can use the fact that Gly and Pro, respectively, often terminate and initiate α helices. The Lupas method (based on a statistical comparison of a sequence with a database of known coiled coils) can be useful if the helices are not too short. Another standard approach to this problem is the use of so-called N- and C-Cap criteria, developed by Richardson and Richardson and Presta and Rose (*8*), which identify residues that tend to be close to the amino and carboxyl termini of an α helix.

The specificity in the packing of α helices (parallel, antiparallel, and the relative axial stagger between them) appears to be governed by ionic interactions, largely between oppositely charged residues in positions *e* and *g* of adjacent α helices (*9*) and not by apolar interactions between residues in the *a* and *d* positions. By maximizing the number of potential interhelix ionic interactions, both the axial staggers between α-helical chains and even the sense of chain connectivity (whether left- or right-handed) in an α-helical bundle may be predicted. Additional information can be obtained from chemical constraints such as the positions of disulfide bonds and from molecular morphology deduced by electron microscopy and nuclear magnetic resonance.

These methods were put to the test recently with the repeat motif of α-spectrin, α-actinin, and dystrophin (*10*). These three proteins are members of the spectrin superfamily: Each contains an α helix–rich rod domain characterized by multiple repeats of a sequence about 110 residues in length. The boundaries of the repeats in α-spectrin were established biochemically, and then a single repeat was expressed that

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