Spiroconjugated Intramolecular Charge-Transfer Dyes

Przemyslaw Maslak* and Anu Chopra

*Department of Chemistry
The Pennsylvania State University
University Park, Pennsylvania 16802*

Photonics, the optical analogue of electronics, is a new, promising area of technology important in computing and communication. This new field critically depends on preparation of new materials with predictable and tunable optical properties.[1] Organic materials based on charge-transfer (CT) interactions play an important role in this field.[1-3] We describe here a new class of organic charge-transfer dyes wherein the acceptor and donor parts are spiroconjugated.[4,5] This relatively weak "three-dimensional" conjugation allows for the implementation of a modular design of new materials, i.e., the adjustments within donor and acceptor moieties (tunability) may be made independently and lead to materials with expected properties (predictability).

Compounds 1-4 are constructed from an acceptor part (the indandione moiety) and a donor part (substituted diamines). The junction between the parts is of the spiro type. Such an arrangement allows for a spatial penetration of the lone-pair orbitals on the nitrogens and the p orbitals on the carbon atoms of the carbonyl groups. If the symmetry of the LUMO of the acceptor is the same as the symmetry of the HOMO of the donor (antisymmetric versus both molecular planes), then this orbital overlap leads to spiroconjugation.[4,5] The HOMO energy is lowered as compared to the noninteracting donor part, and the LUMO energy is increased as compared to a separate indandione (Figure 1). In addition, both these orbitals "mix in" a little of each other's character, i.e., the HOMO has some electron density on the indandione moiety and the LUMO has non-zero p orbital coefficients on the amine part. The HOMO–LUMO transition should be allowed in these cases and should be of the charge-transfer type.[6]

The spiro compounds were prepared by the condensation of ninhydrin with the corresponding *N,N'*-dimethyl-substituted amines.[7,8] In the control experiments, the concentrated solutions or neat mixtures of 2,2-dimethylindandione and the aromatic diamines showed no evidence of intermolecular charge-transfer formation. Apparently, the orbital overlap is too small and the HOMO–LUMO gap is too large. All spiro compounds showed, however, the presence of new absorption bands in the visible region (Figure 2). The bands followed the Beer–Lambert law over more than a 100-fold change in concentrations, indicating the *intramolecular* nature of the transition.

In **1,** the symmetry of the donor is incorrect.[9] The interaction between the components is very weak and mainly of inductive nature. As the result, the HOMO–LUMO transition is *forbidden*. The charge-transfer band has λ_{max} = 580 nm (benzene) and a low extinction coefficient (ϵ_{580} = 142 M^{-1} cm^{-1}). In the solid state the compound is dark purple.

In contrast, the naphthylamine moiety in **2** has two degenerate HOMO orbitals, and one of them is antisymmetric[9] vs the plane of the dione. This orbital strongly spiroconjugates with the LUMO of the acceptor part. The HOMO's energy is significantly lowered by the spiroconjugation, and the energy of the LUMO is raised correspondingly, increasing the HOMO–LUMO gap. As the result of this orbital "mixing", the CT transition is *allowed* (λ_{max} = 428 nm (benzene), ϵ_{428} = 3.8 × 10^3 M^{-1} cm^{-1}) and significantly shifted to higher energies as compared to **1,** despite the fact that the frontier orbitals of the separate donor and acceptor parts are of nearly equal energy in **1** and **2** (Figure 1). This compound is brown-red in the solid state.

In **3,** the HOMO of the donor has correct symmetry, but it is of lower energy than that in the naphthyl system. Additionally, the seven-membered ring formed may not allow for the perfect overlap between the nitrogen orbitals and the corresponding carbonyl carbon orbitals. The spiroconjugation is thus weaker, and as the result the probability of transition is diminished (λ_{max} = 428 nm (benzene), ϵ_{428} = 1.35 × 10^3 M^{-1} cm^{-1}). This compound is orange-yellow in the solid state.

The HOMO in **4** may be considered as an antisymmetric and symmetric linear combination of the nitrogen lone pair orbitals. The former can interact with the LUMO of the indandione moiety, although the HOMO–LUMO gap is the largest in this case, weakening the interaction even further than that found in **3.** The charge-transfer band has λ_{max} = 428 nm (benzene) and ϵ_{428} = 221 M^{-1} cm^{-1}. In the solid state the compound is red. It is important to note (see below) that despite significant differences in the HOMO's energies of the donor part in **2, 3,** and **4,** the corresponding CT bands are nearly isoenergetic. The strength of the spiroconjugation thus compensates for bringing the donor's HOMO energy closer to that of the acceptor's LUMO.

The charge-transfer bands showed pronounced solvatochromic effect.[10] For example, in **2** (the most studied so far) the band shifts from 428 nm in benzene to 400 nm in acetonitrile (Figure

(1) (a) Prasad, P. N.; Williams, D. J. *Introduction to Nonlinear Optical Effects in Molecules and Polymers;* Wiley-Interscience: New York, 1991. (b) Khanarian, G., Ed. *Molecular and Optoelectronic Materials: Fundamentals and Applications;* SPIE: San Diego, CA, 1986. (c) Eaton, D. F. *Science* **1991,** *253,* 281. (d) Glass, A. M. *Science* **1987,** *235,* 1003. (e) Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1984,** *23,* 690. (f) Chemla, D. S.; Zyss, J., Eds. *Nonlinear Optical Properties of Organic Molecules and Crystals;* Academic Press: New York, 1987; Vols. 1 and 2. (g) Flytzanis, C. In *Nonlinear Behavior of Molecules, Atoms and Ions in Electric, Magnetic or Electromagnetic Fields;* Nell, L., Ed.; Elsevier Scientific Publishing Co.: New York, 1979; p 185.

(2) (a) Lalama, S. J.; Garito, A. F. *Phys. Rev.* **1979,** *A20,* 1179. (b) Garito, A. F.; Singer, K. D. *Laser Focus* **1982,** 59. (c) Pugh, D.; Docherty, V. J.; Morley, J. O. *J. Chem. Soc., Faraday Trans. 2* **1985,** *81,* 1179. (d) Pugh, D.; Sherwood, J. N. *Chem. Br.* **1988,** 544. (e) Lyons, M. H., Ed. *Materials for Nonlinear and Electro-optics;* Institute of Physics Conference Series 103; Institute of Physics, Bristol and New York: Cambridge, 1989. (f) Williams, D. J., Ed. *Nonlinear Optical Properties of Organic and Polymeric Materials;* ACS Symposium Series 233; American Chemical Society: Washington DC, 1983.

(3) (a) Wudl, F.; Patil, A. O.; Heeger, A. J. *Chem. Rev.* **1988,** *88,* 183. (b) Prasad, P. N.; Reinhardt, B. A. *Chem. Mater.* **1990,** *2,* 660. (c) Tripathy, S.; Cavicchi, E.; Kumar, J.; Kumar, R. S. *CHEMTECH* **1989,** 620; **1989,** 747. (d) Eaton, D. F. *CHEMTECH,* **1992,** 308. (e) Dupuis, M.; Karna, S. P. *J. Comput. Chem.* **1991,** *12,* 487. (f) Oudar, J. L.; Chemla, D. S. *J. Chem. Phys.* **1977,** *66,* 2664.

(4) (a) Simmons, H. E.; Fukunaga, T. *J. Am. Chem. Soc.* **1967,** *89,* 5208. (b) Hoffmann, R.; Imamura, A.; Zeiss, G. D. *J. Am. Chem. Soc.* **1967,** *89,* 5215.

(5) For a review, see: Durr, H.; Gleiter, R. *Angew. Chem., Int. Ed. Engl.* **1978,** *17,* 559.

(6) (a) Mulliken, R. S.; Pearson, W. B. *Molecular Complexes: A Lecture and Reprint Volume;* Wiley-Interscience: New York, 1969. (b) Foster, R. *Organic Charge-Transfer Complexes;* Academic Press: New York, 1969. (c) Nagakura, S. *Excited States;* Academic Press: New York, 1975; Vol. 2, p 321.

(7) The spiro compounds were prepared by azeotropic removal of water from the benzene solution of ninhydrin and the corresponding secondary amine. The ethylene derivative **4** has been prepared previously.[8] It was found to be unstable under ambient conditions in the solid state.

(8) (a) Schönberg, A.; Singer, E.; Osch, M.; Hoyer, G.-A. *Tetrahedron Lett.* **1975,** 3217. (b) Schönberg, A.; Singer, E.; Eschenhof, B.; Hoyer, G.-A. *Chem. Ber.* **1978,** *111,* 3058. (c) Schönberg, A.; Singer, E.; Eckert, P. *Chem. Ber.* **1980,** *113,* 3094.

(9) The symmetry is used here in a conceptual (i.e., approximate) way and does not strictly reflect the symmetry of the components or spiro compounds. The symmetry of the HOMOs of donor amines was established using the semiempirical MOPAC calculations (Stewart, J. J. P. *J. Comp-Aid. Mol. Des.* **1990,** *4,* 1). The LUMO of the acceptor is antisymmetric vs the amine-containing plane. The critical symmetry element is thus the plane containing the acceptor and perpendicular to the amine plane.

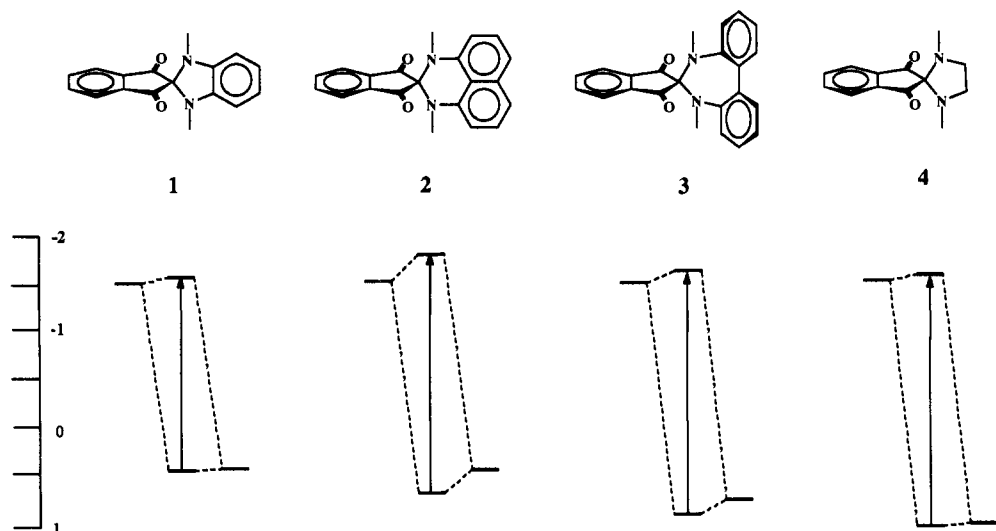(10) Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry;* VCH: Weinheim, 1990.

Figure 1. Schematic representation of the interaction between the acceptor moiety (modeled by 2,2-dimethylindandione) and the donor component (modeled by N,N'-dimethyldiamine derivatives). The arrows correspond to the CT transitions in spirocompounds 1–4. The scale (in eV vs SCE) approximately reflects the energetics of the system and is based on the redox potentials of the models and the observed maxima of CT transitions.
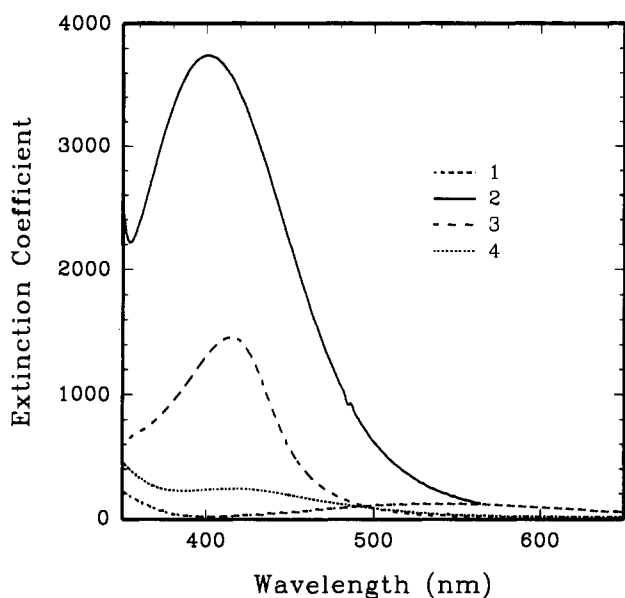

Figure 2. Extinction coefficients (in M^{-1} cm^{-1}) of the charge-transfer bands of 1–4 in acetonitrile. Only the visible part of the spectrum is shown. The indandione and the diamines alone or in mixtures do not have any detectable transitions in this spectral region.

2). Using the solvatochromic data from several solvents[11] and following the McRae formalism,[12] the excited-state dipole moment can be estimated to be ca. 9–13 D in the direction opposite to the ground state dipole. These estimates are qualitatively consistent with the HOMO–LUMO interactions described above, where

the ground state has a dipole along the long axis of the molecule with the dicarbonyl moiety being the electron-deficient end and the excited state resembles an indandione radical anion–amine radical cation pair.[6]

There are at least three special features which make these CT solids of interest. (i) The strength of CT interactions can be easily manipulated by the adjustment of the HOMO and LUMO energy of the donor and acceptor part almost *independently*. Bringing these orbitals closer in energy will make interactions between them stronger, but at the same time the CT transition will move to a higher energy. Thus, (ii) the position of the CT band will only weakly depend on the strength of the donor and acceptor used to construct the spiro compound. These two features are in contrast to the usual situation encountered in "normally" conjugated donor–acceptor systems (such as donor–acceptor-substituted benzenes[2,3]), where independent variations in the HOMO–LUMO gap are impractical, and increasing the donor or acceptor strength unavoidably shifts λ_{max} to longer wavelengths. The third feature involves introduction of conjugating substituents into the donor and acceptor parts (one into each). As a result, (iii) these compounds will be chiral. The chirality of these systems is of the "π type", i.e., the whole π network is chiral. Such a construction should lead to very strong interactions with polarized light.

We are currently investigating the photophysical behavior of these CT materials[13] and preparing new ones according to the design principles described above. We believe that the proposed modular design approach may be useful in generation of new materials[14] with interesting electrical, optical, and magnetic properties.

(11) Paley, M. S.; Harris, J. M.; Looser, H.; Baumert, J. C.; Bjorklund, G. C.; Jundt, D.; Twieg, R. J. *J. Org. Chem.* **1989**, *54*, 3774. The list of solvents used includes benzene, dioxane, THF, pyridine, CH_2Cl_2, acetone, Me_2SO, and CH_3CN.

(12) McRae, E. G. *J. Phys. Chem.* **1957**, *61*, 562.

(13) Preliminary results indicate that the excited states of 2 and 3 are nonfluorescent. Also, a solution of 2 produces visible light in the EFISH experiments when irradiated with the 1064-nm laser light.

(14) Maslak, P.; Augustine, M. P.; Burkey, J. D. *J. Am. Chem. Soc.* **1990**, *112*, 5359.