ORGANIC MATERIALS FOR PHOTONICS

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PLAN OF THE PRESENTATION

- WHY PHOTONICS
- DESIGN OF NLO
- MARDER'S PLOT
- ZWITTERIONICS
  and their characterization
  uv, nmr, β, computations
- QUINOID DYES
- FROM MOLECULES TO MATERIALS

- BULK MATERIALS FOR:
  - ⇨ OPTOELECTRONICS
  - ⇨ CAVITY LASING
  - ⇨ LIMITERS

  as
  - ➢ FILMS
  - ➢ GLASSES
  - ➢ POLYMERS

MATERIALS FOR ADVANCED APPLICATIONS

- TRADITIONAL MATERIALS (inorganics, organometallics)

⇩

- ORGANIC **MOLECULAR** MATERIALS (benzene derivatives, classic organic functionalities: OR, NR_2, NO_2)

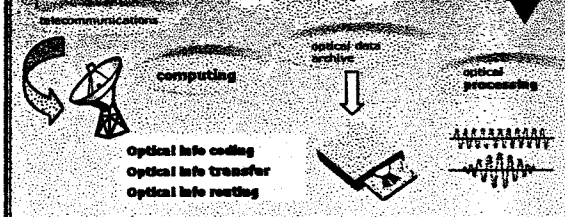
⇩

Our choice

- **ORGANIC MATERIALS FOR PHOTONICS**

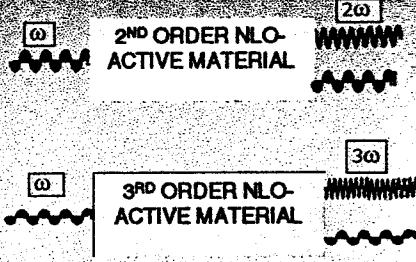
WHY PHOTONICS

- Photonics (interaction with light)
- Optical information processes



Optical info coding
Optical info transfer
Optical info routing

Basics of non-linear optics



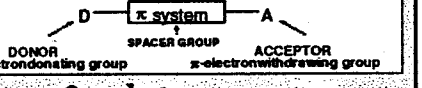
ORGANICS AS PRECURSORS OF MATERIALS FOR NON-LINEAR OPTICS

Molecular polarization

$p_i = \Sigma \alpha_{ij} E_j + \Sigma \beta_{ijk} E_j E_k + \Sigma \gamma_{ijkl} E_j E_k E_l + \ldots$

β = first hyperpolarizability γ = second hyperpolarizability

Push-Pull Molecules



Our choice

π-EXCESSIVE AND π-DEFICIENT HETEROAROMATICS AS D AND A GROUPS

Why heterocycle-based molecular materials?

- non-linear optics, two-photon dyes, optical limiters

π-Electron Donor — Polarizable π-Electron Bridge — π-Electron Acceptor

π-Electron Acceptor — π-Electronrich Bridge — π-Electron Acceptor

- luminescent materials, emitters, LED

Nitrogen ligand — transition metals, lanthanides

MESSAGE

Exploit the unique π-excessive and π-deficient properties of heterocycles as **DONORS** and **ACCEPTORS**

This can be done if....

we quantitatively know the π-electron properties of as many heterocycles as possible and their π-electron distribution site by site

method of choice

- ⇨ Shift / π-Charge Relationships by C-13 and N-15 NMR Spectroscopy
- ⇨ Computational (semiempirical and *ab initio*) methods

From NMR Shift to the π Electron Density

$$\delta^{13}C = 122.8 + \Sigma A_i - 160\,(q^{\pi}_{C} - 1)$$

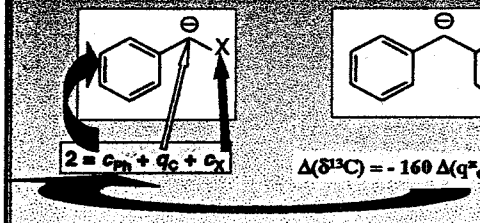
$$\delta^{15}N = 345.4 - 366.3\,(q^{\pi}_{N} - 1)$$

$$\Delta(\delta^{13}C) = -160\,\Delta(q^{\pi}_{C})$$

$$\Delta(\delta^{15}N) = -366.3\,\Delta(q^{\pi}_{N})$$

Bradamante, Pagani, *J. Org. Chem.* **1984**; Bradamante, Pagani *J. Chem. Soc., Perkin Trans 2* **1986**; Barchiesi, Bradamante, Pagani *ibid.* **1987**; Berlin, Bradamante, Ferraccioli *ibid.* **1988**; Abbotto, Alanzo, Bradamante, Pagani *ibid.* **1991**

Charge c_X demands via ^{13}C NMR



Brademante, S.; Pagani, G. A. *J. Org. Chem.* **1984**, *49*, 2863.
Brademante, S.; Pagani, G. *JAI Press* **1996**, 189-263.

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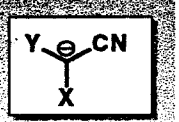
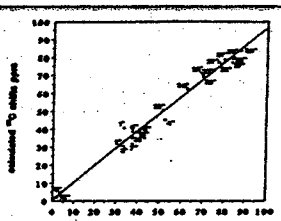
Predictivity Power of chemical shift in di- and tri-substituted carbanionic carbons



X, Y = H, Ph, EWG (COR, CN, ..) azines diazines



$\delta^{13}C_{calc} = (0.958 \pm 0.024)\,\delta^{13}C_{exp} + (0.902 \pm 0.604)(n = 23,\ r = 0.993)$

Ashauer, Brademante, Pagani *J. Org. Chem.* 1993, 58, 449

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Charge Demands of Some Groups

X	c_X
Ph	0.29
CO_2Me	0.40
COMe	0.51
COPh	0.56
CN	0.28
SPh	0.00
Me_3N^+	0.00
2-Pyridyl	0.41
4-Pyridyl	0.41

X	c_X
2-Pyrimidyl	0.43
4-Pyrimidyl	0.50
2-Thiazolyl	0.39
2-Oxazolyl	0.35
2-(*N*-Me)imidazolyl	0.24
2-Benzothiazolyl	0.46
2-Benzoxazolyl	0.44
2-(*N*-Me)benzimidazolyl	0.38

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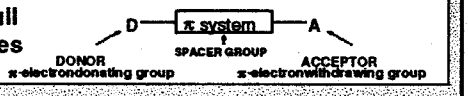
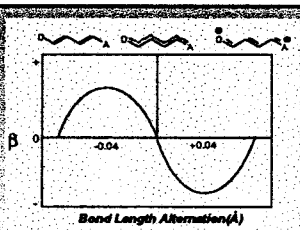


Question

How β is related to D and A ?

CORRELATION BETWEEN β AND ELECTRONIC STRUCTURE (BOND LENGTH ALTERNATION *Marder, 1993)*



- Optimal combination of donor and acceptor substituents for a given π-bridge spacer (specific strength)
- Specific degree with which the two forms contribute to describe the ground state

Contribution of resonance forms to the ground-state structure