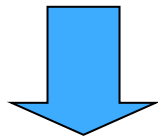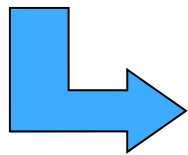# VII. (hyper)polarizability within PT
VII.A. Basic SOS expressions

$$E_i^{(\lambda)} = E_i^{(0)} + \lambda E_i^{(1)} + \lambda^2 E_i^{(2)} + \lambda^3 E_i^{(3)} + \ldots$$
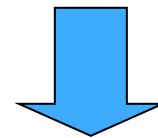
$$H\left(\lambda\right) = H_0 + \lambda W$$

$$E\left(\vec{E}\right) = E\left(\vec{E} = 0\right) - \vec{\mu}_0 . \vec{E} - \frac{1}{2}\vec{\alpha} : \vec{E}\vec{E}$$

$$H = H_0 - \hat{\vec{\mu}} . \vec{E}$$

$$-\frac{1}{6}\vec{\beta} : \vec{E}\vec{E}\vec{E} - \frac{1}{24}\vec{\gamma} : \vec{E}\vec{E}\vec{E}\vec{E} -$$

$$\vec{\mu}_0 = -E_0^{(1)}, \quad \vec{\alpha} = -2E_0^{(2)},$$

$$\vec{\beta} = -6E_0^{(3)}, \quad \vec{\gamma} = -24E_0^{(4)}$$

Using time-independent PT, one gets the static polarizability and hyperpolarizability but the generalization to time-dependent PT enables the calculation of the dynamic responses.

$$\overleftrightarrow{\alpha} = 2 \sum_{j \neq 0} \frac{\left| \left\langle \Psi_j^{(0)} \middle| \vec{\mu} \middle| \Psi_0^{(0)} \right\rangle \right|^2}{\left(E_j^{(0)} - E_0^{(0)} \right)}$$

$$\left\langle \Psi_0^{(0)} \middle| \mu_\varsigma \middle| \Psi_j^{(0)} \right\rangle = \left\langle \Psi_0^{(0)} \middle| - \sum_{i=1}^{N} \varsigma_i + \sum_{A=1}^{M} Z_A \varsigma_A \middle| \Psi_j^{(0)} \right\rangle$$

$$= \left\langle \Psi_0^{(0)} \middle| - \sum_{i=1}^{N} \varsigma_i \middle| \Psi_j^{(0)} \right\rangle$$

$$= \mu_\varsigma^{0j,elec} = \mu_\varsigma^{0j}$$

$$\alpha_{\varsigma\eta} = 2 \sum_{j \neq 0} \frac{\mu_\varsigma^{0j} \mu_\eta^{j0}}{E_j - E_0}$$

$$\vec{\vec{\beta}} = 6 \sum_{j \neq 0} \sum_{k \neq 0} \frac{\left\langle \Psi_0^{(0)} \left| \vec{\mu} \right| \Psi_j^{(0)} \right\rangle \overline{\left\langle \Psi_j^{(0)} \left| \vec{\mu} \right| \Psi_k^{(0)} \right\rangle} \left\langle \Psi_k^{(0)} \left| \vec{\mu} \right| \Psi_0^{(0)} \right\rangle}{\left(E_j^{(0)} - E_0^{(0)} \right) \left(E_k^{(0)} - E_0^{(0)} \right)}$$

$$\overline{\left\langle \Psi_j^{(0)} \left| \vec{\mu} \right| \Psi_k^{(0)} \right\rangle} = \left\langle \Psi_j^{(0)} \left| \vec{\mu} \right| \Psi_k^{(0)} \right\rangle - \left\langle \Psi_0^{(0)} \left| \vec{\mu} \right| \Psi_0^{(0)} \right\rangle \delta_{jk}$$

Two-state approximation for the diagonal elements

$$\alpha_{\zeta\zeta} = 2 \frac{\mu_\zeta^{0j} \mu_\zeta^{j0}}{\Delta E_{j0}}$$

$$\beta_{\zeta\zeta\zeta} = 6 \frac{\mu_\zeta^{0j} \left(\mu_\zeta^{jj} - \mu_\zeta^{00} \right) \mu_\zeta^{j0}}{\Delta E_{j0}^2} = 6 \frac{\mu_\zeta^{0j} \Delta\mu_\zeta^{0j} \mu_\zeta^{j0}}{\Delta E_{j0}^2}$$

VII.B. SOS/CI expressions

$$\alpha_{\zeta\zeta} = 2 \frac{\mu_{\zeta}^{0j}\mu_{\zeta}^{j0}}{\Delta E_{j0}}$$
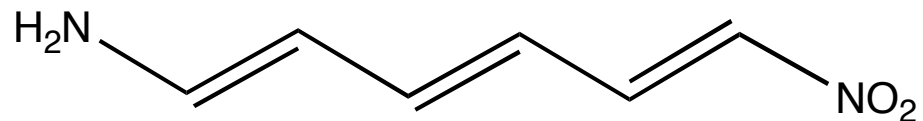
CIS

$\mu^{03} = 2.0723$

$\Delta E_{03} = 5.159$ eV $= 0.1896$ a.u.

α_{zz} (TSA) $= 45.3$ a.u.

CIS(D)

$\Delta E_{03} = 4.453$ eV $= 0.1636$ a.u.

α_{zz} (TSA) $= 52.5$ a.u.

NB: not a good approximation because many states
        contribute to the polarizability

$$\beta_{\zeta\zeta\zeta} = 6\frac{\mu_\zeta^{0j}\left(\mu_\zeta^{jj} - \mu_\zeta^{00}\right)\mu_\zeta^{j0}}{\Delta E_{j0}^2} = 6\frac{\mu_\zeta^{0j}\Delta\mu_\zeta^{0j}\mu_\zeta^{j0}}{\Delta E_{j0}^2}$$

CIS/6-31G

μ^{03} = 2.0723 a.u.

$(\mu^{33} - \mu^{00})$ = 2.024 a.u.

ΔE_{03} = 5.159 eV = 0.1896 a.u.

β_{zzz} (TSA) = 1451 a.u.

CIS(D)/6-31G

ΔE_{03} = 4.453 eV = 0.1636 a.u.

β_{zzz} (TSA) = 1949 a.u.

$$\beta_{\zeta\zeta\zeta} = 6\frac{\mu_\zeta^{03}\left(\mu_\zeta^{33}-\mu_\zeta^{00}\right)\mu_\zeta^{30}}{\Delta E_{30}^2} + 6\frac{\mu_\zeta^{06}\left(\mu_\zeta^{66}-\mu_\zeta^{00}\right)\mu_\zeta^{60}}{\Delta E_{60}^2} + 12\frac{\mu_\zeta^{03}\mu_\zeta^{36}\mu_\zeta^{60}}{\Delta E_{30}\Delta E_{60}}$$

CIS/6-31G

$\mu^{03} = 2.072$ a.u.

$(\mu^{33} - \mu^{00}) = 2.024$ a.u.

$\Delta E_{03} = 5.159$ eV $= 0.1896$ a.u.

$\mu^{06} = 1.198$ a.u.

$(\mu^{66} - \mu^{00}) = 0.574$ a.u.

$\Delta E_{06} = 7.265$ eV $= 0.2670$ a.u.

$\mu^{36} = 1.814$ a.u.

β_{zzz} (Three-SA) = 1451 a.u. + 69 a.u. + 1067 a.u. = 2587 a.u.

VII.C. Variations on the SOS expressions

The general SOS Orr-Ward-Bishop expression of the electronic (dynamic) first hyperpolarizability reads

$$\beta_{\zeta\eta\xi}(-\omega_\sigma;\omega_1,\omega_2) = \sum P_{-\sigma,1,2} \sum_{\substack{n\neq 0 \\ m\neq 0}} \frac{\mu_{0n}^\zeta \bar{\mu}_{nm}^\eta \mu_{m0}^\xi}{\left(E_{n0} - \omega_\sigma\right)\left(E_{m0} - \omega_2\right)}$$

For any diagonal component the OWB expression becomes

$$\beta_{xxx}(-\omega_\sigma;\omega_1,\omega_2) = \sum P_{-\sigma,1,2} \sum_{n}^{\infty}{}' \frac{\mu_{0n}^x \Delta\mu_{n0}^x \mu_{n0}^x}{E_{n0}\left(\omega_\sigma\right) E_{n0}\left(\omega_2\right)} + \sum P_{-\sigma,1,2} \sum_{n}^{\infty}{}' \sum_{m\neq 0}^{\infty}{}' \frac{\mu_{0n}^x \mu_{nm}^x \mu_{m0}^x}{E_{n0}\left(\omega_\sigma\right) E_{m0}\left(\omega_2\right)}$$

dipolar   **octupolar**

Using the Thomas-Kuhn sum rules for m ≠ p,

$$\sum_{m=0}^{\infty}\left(E_{mn}+E_{mp}\right)\mu_{nm}^{x}\mu_{mp}^{x}=0 \qquad\Longrightarrow\qquad \Delta\mu_{n0}^{x}\left|\mu_{0n}^{x}\right|^{2}=-\sum_{m\neq n}^{\infty}{}'\frac{E_{mn}+E_{m0}}{E_{n0}}\mu_{0n}^{x}\mu_{nm}^{x}\mu_{m0}^{x}$$

the dipolar term can be rewritten:

$$\beta_{xxx}\left(-\omega_{\sigma};\omega_{1},\omega_{2}\right)=\sum P_{-\sigma,1,2}\sum_{n}{}'\sum_{m\neq n}^{\infty}{}'\frac{\mu_{0n}^{x}\,\mu_{nm}^{x}\,\mu_{m0}^{x}}{E_{n0}\left(\omega_{\sigma}\right)E_{m0}\left(\omega_{2}\right)}\left[1-\frac{E_{m0}\left(\omega_{2}\right)\left(2E_{m0}-E_{n0}\right)}{E_{n0}E_{n0}\left(\omega_{2}\right)}\right]$$

The OWB and the dipolar-free equations are equivalent provided:

* exact solutions of the Schrödinger equation are used
* the summations (n, m) are carried out up to infinity

This is generally not the case.

M.G. Kuzyk, Phys. Rev. A **72**, 053819 (2005).
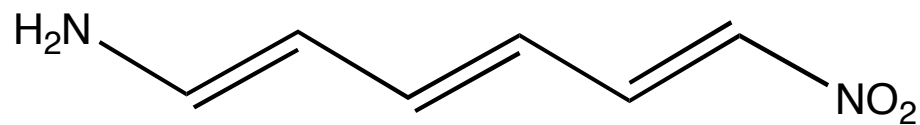
SOS/CIS(D) data
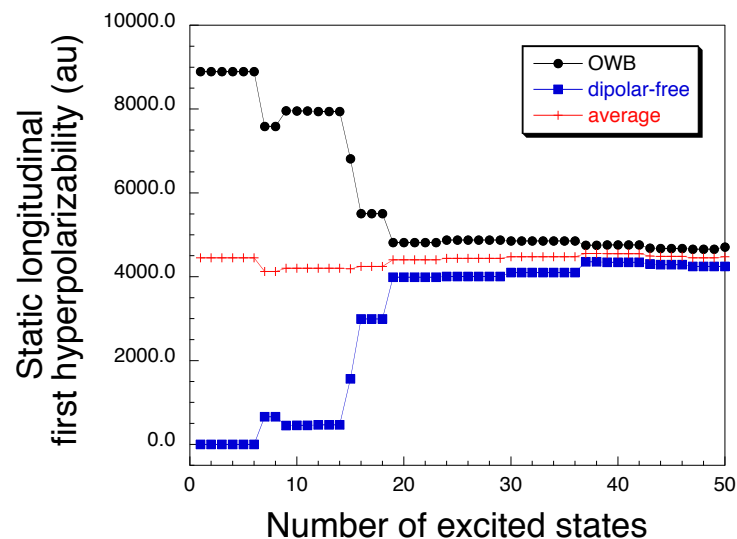
Before ordering (the state ordering is given by the increasing excitation energy)
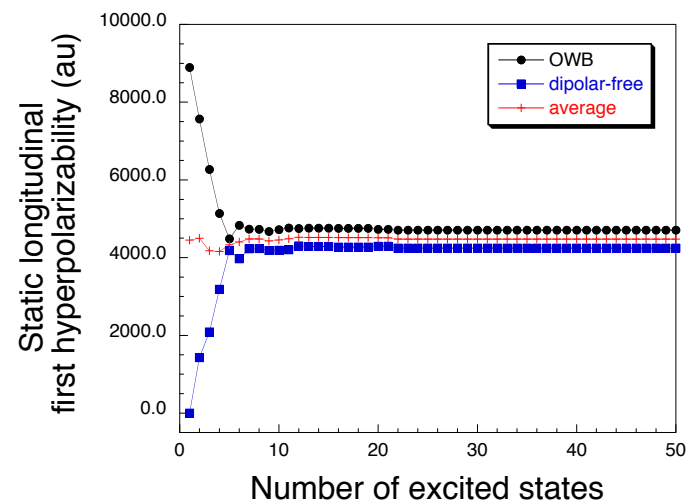
After ordering as a function of the state contribution to β_{zzz}.
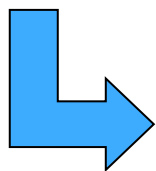
The contributions to the OWB and dipolar-free expressions are essentially of the same magnitude but opposite sign.

B. Champagne and B. Kirtman, J. Chem. Phys. **125**, 024101 (2006).

VIII. Illustrations
VIII.A. shape effects on β

1. Linear "dipolar" molecules

Donor — Conjugated path — Acceptor

β_{zzz}
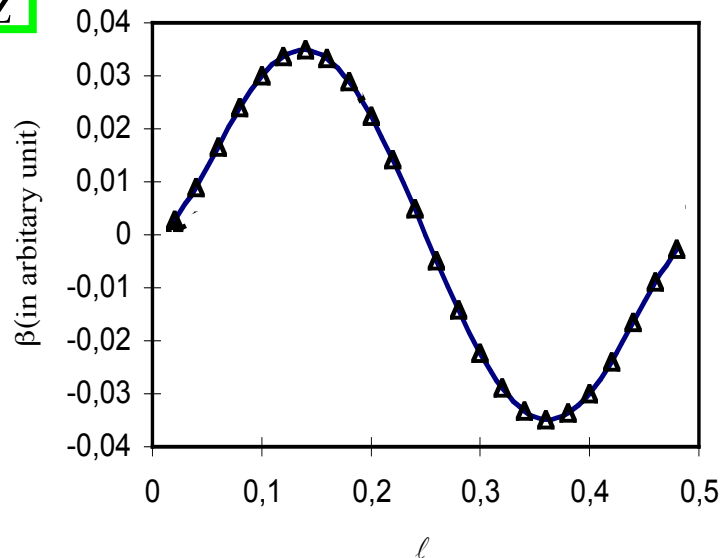
But:

- centro-symmetric packing effects which cancel the second-order NLO response

- transparency trade-off

NO₂

NH₂
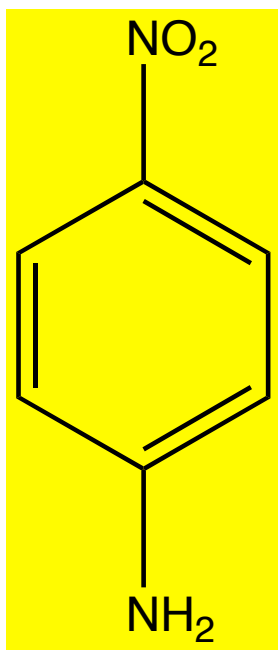
p-nitroaniline
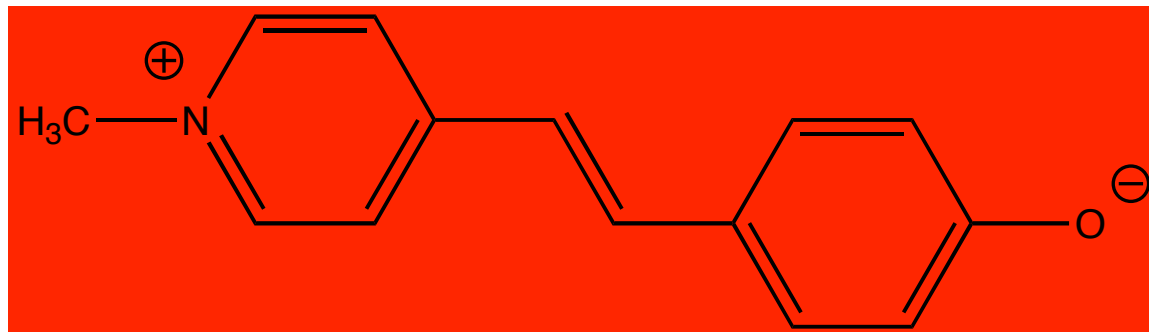
4-[2-(1-methyl-4-pyridinio)ethenyl]phenolate
Merocyanine, Wong, Bosshard, Günter, 1997
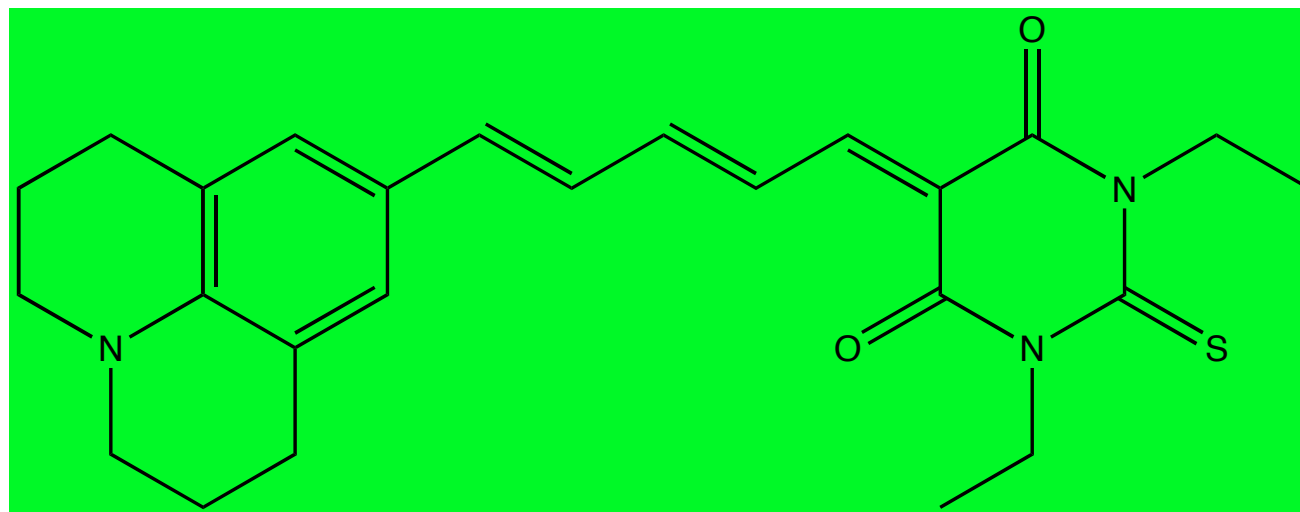
(E,E) 1-(benzeneamine 4-(di-2-propylamino))
pentadieneylidene thiobarbituric, Bourhill *et al*. (1993)

2) Octupolar systems
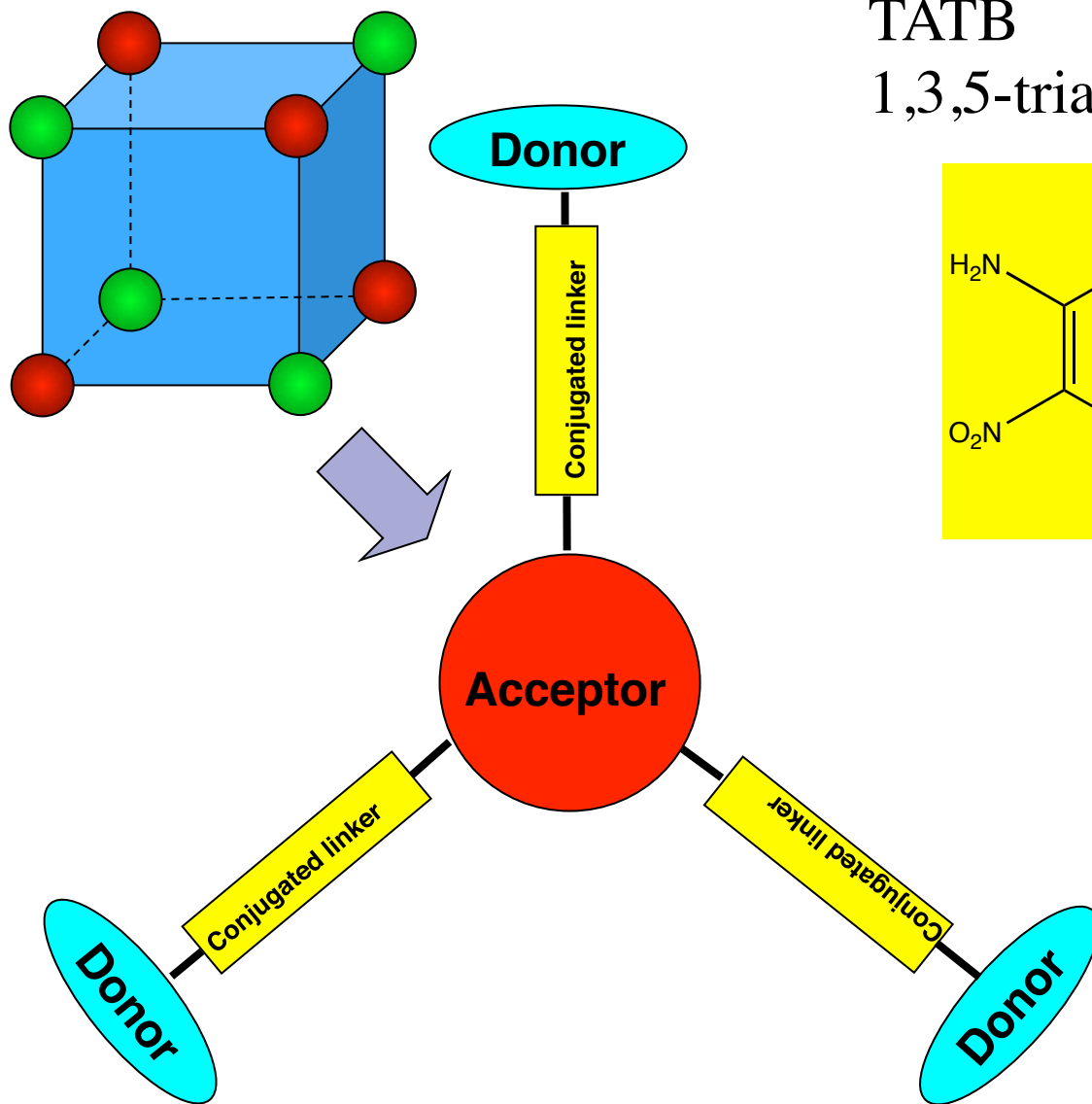
TATB
1,3,5-triamino-2,4,6-trinitrobenzene

Crystal violet

124
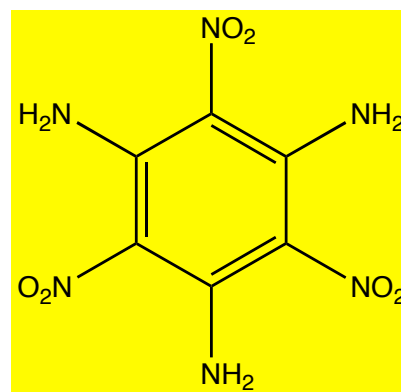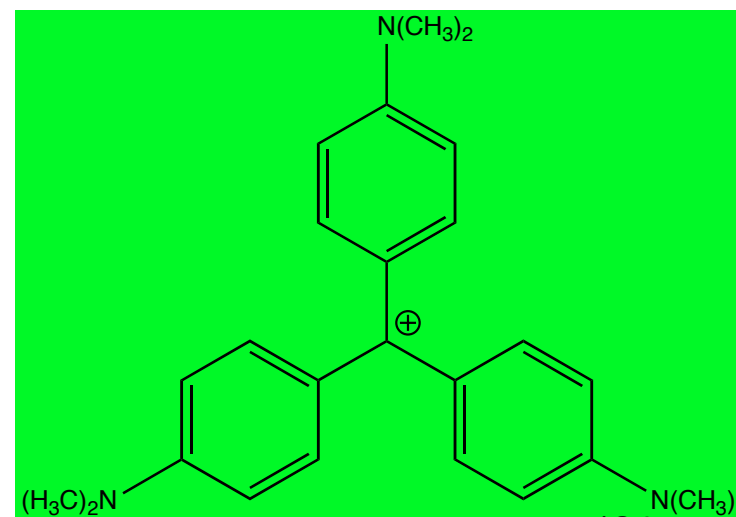
3) Λ- or V-shape systems
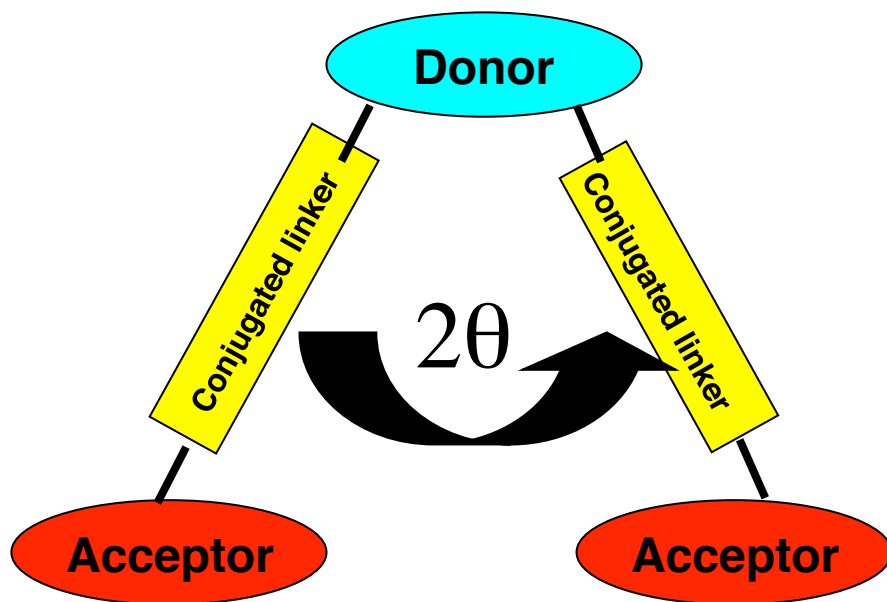
1955-49 dye
of Twieg and collaborators
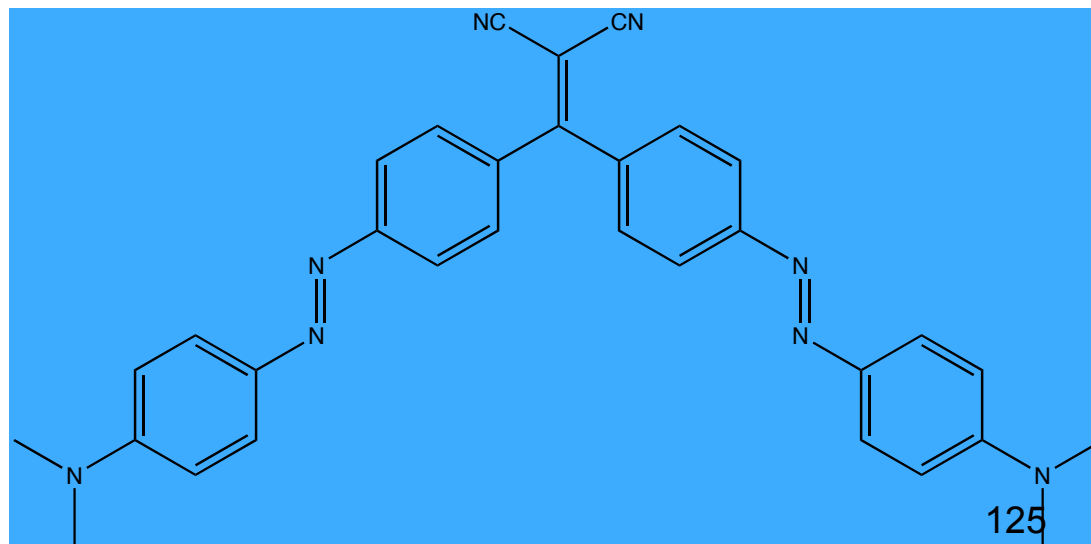
The interest for these systems is mostly due to the presence of two dominant microscopic first hyperpolarizability components (β_{xxz} and β_{zzz}) of which the relative amplitude (η) is governed by the 2θ angle as well as by the charge transfer character (l, determined by the nature of the D/A pair). Using a 3 states (1VB + 2 CT) model, the ratio reads:

amounts to 1/3 (30°) and 3 (60°)

$$\eta = \frac{\beta_{xxz}}{\beta_{zzz}} = \frac{1}{3}\frac{\mathrm{tg}^2\theta}{1-4\ell}\left[2\frac{E_{02}}{E_{01}}+\left(\frac{E_{02}}{E_{01}}\right)^2\right]$$

Generally larger than 1

$l \approx 1/4$, interplay between CT and VB characters, large transfer integrals

2θ = 120°

2θ = 60°

$$\beta_{zzz} = \beta_{zzz}^D = 12\ell\left(1-2\ell\right)\left(1-4\ell\right)\mu^3\left(\frac{1}{E_{02}^2}\right)\cos^3\theta$$
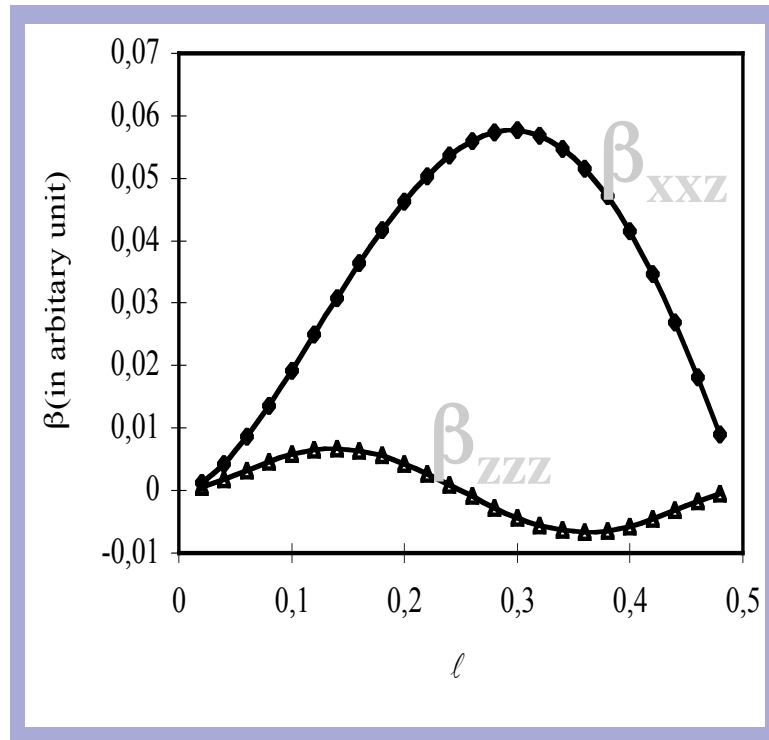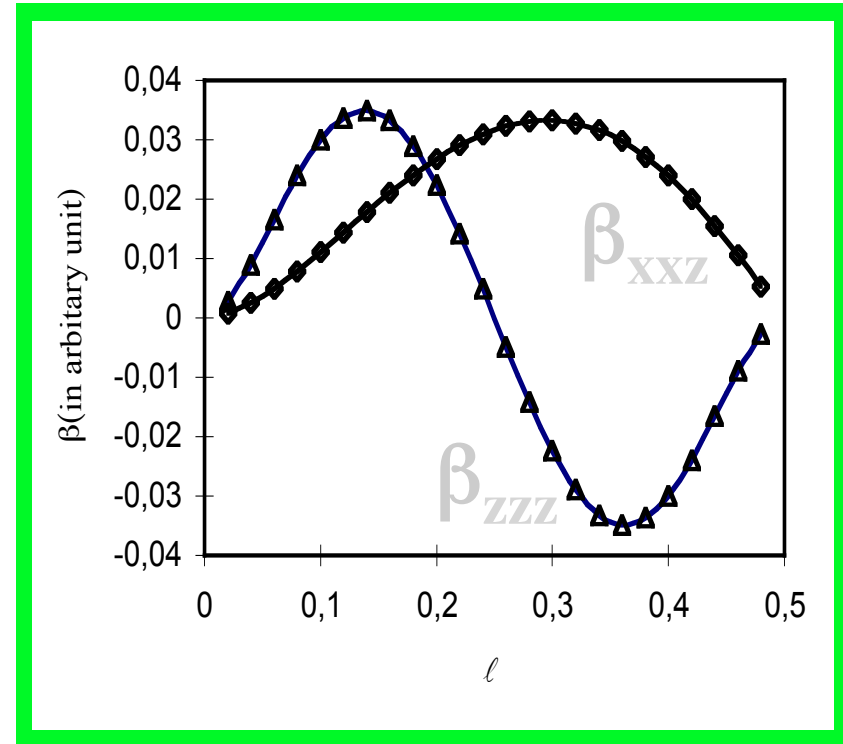
$$\beta_{xxz} = \beta_{xxz}^D + \beta_{xxz}^{TP}$$

$$= 4\ell\left(1-2\ell\right)\mu^3\left(\frac{1}{E_{01}^2} + \frac{2}{E_{01}E_{02}}\right)\sin^2\theta\cos\theta$$
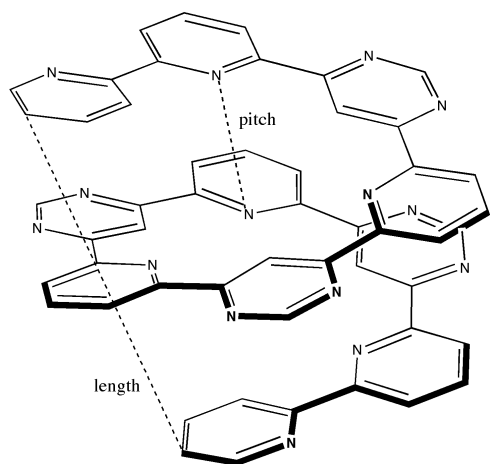
4) Helical
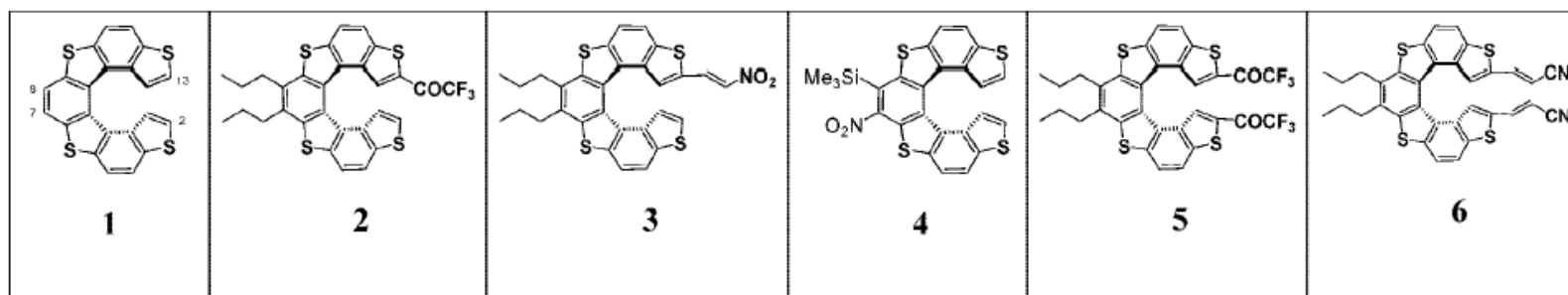
$\mu\beta_{//}$ (10^{-48} esu)

Experiment	/	120	197	130	180	230
Theory	0.1	21	103	52	57	94

- $\mu\beta_{//}$ of **1** is negligible
- $\mu\beta_{//}$ increases when going — from **2** to **3** (stronger acceptor)
  from **5** to **6** (better acceptor)
  from **2** to **5** (mono- versus di-substituted)
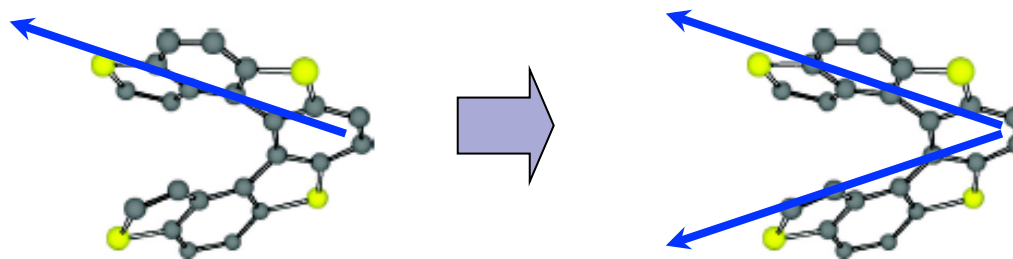
- there is a good qualitative agreement between theory and experiment

Pyridine-pyrimidine strands
TDHF/AM1

	Pitch	torsion angle	length
OPLS-AA	3.76 Å	8.90°	12.59 Å
Exp.	3.63 Å	8.64°	12.65 Å
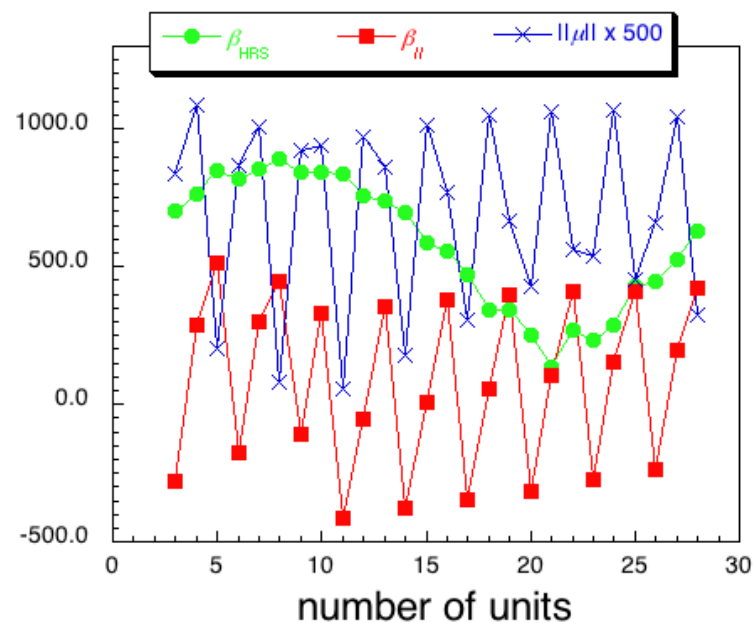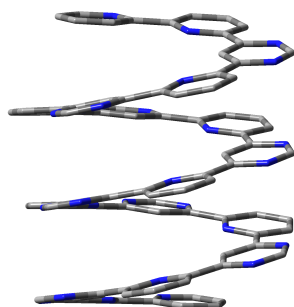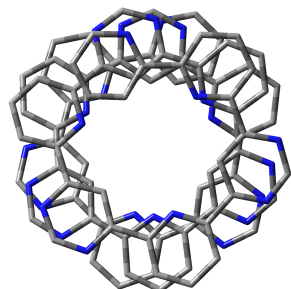
M. Ohkita, J.M. Lehn, G. Bauum, and D. Fenske, Chem. Eur. J. **5**, 3471 (1999).

VIII. Illustrations
VIII.B. Molecular switches

- commute between two or more different forms

- present different properties

- the contrast of properties can be used as a signal revealing the presence of an analyte, a change of the surrounding, …

- often based on a change of color (linear response) but here we concentrate on the second-order NLO response

- the variety of stimuli is broad: pH, P, T, $h\upsilon$, ions, …

B.L. Feringa, *Molecular Switches*, Wiley-VCH, Weinheim, 2001.

indolino[2,1-b]oxazolidines

hυ, OH⁻

hυ, H⁺

open form (OF) coloured

closed form (CF), colourless
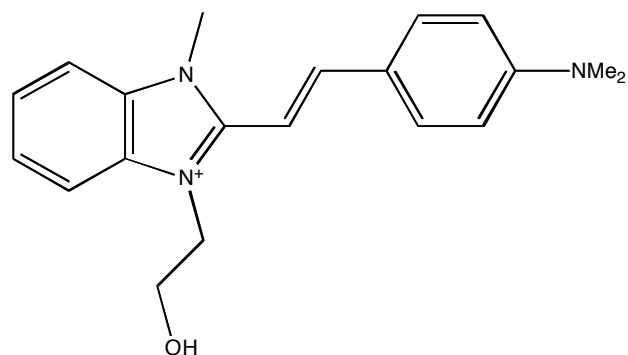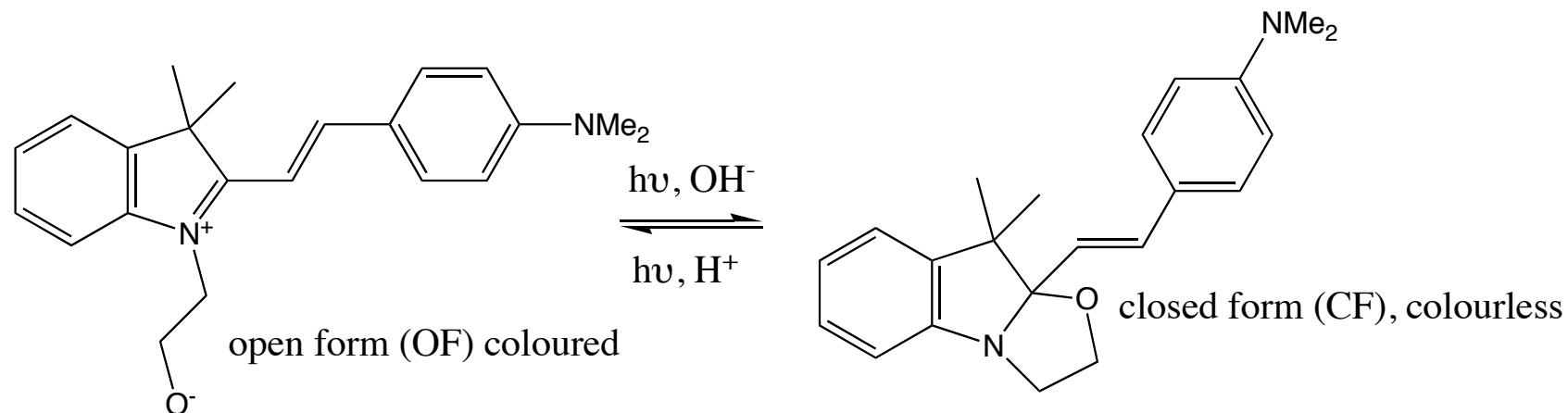
benzimidazolo[2,3-b]oxazolidines

benzothiazolo[2,3-b]oxazolidines

131
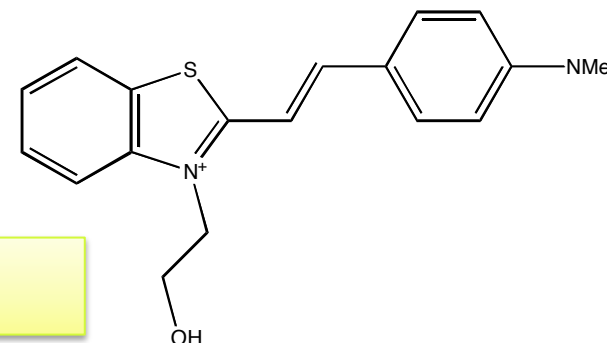
	indolino	benzimidazolo	benzothiazolo
CPHF/6-31G*	2192 (4.30)	1949 (4.53)	2684 (4.48)
TDHF/6-31G* [λ = 1064 nm]	4437 (4.61)	3599 (4.73)	5841 (4.76)
MP2/6-31G*	4112 (4.68)	4412 (4.85)	5479 (4.78)
MP2/6-31G* [λ = 1064 nm] [#]	**8323**	**8147**	**11924**
CPHF/6-311G*	2155 (4.28)	1939 (4.52)	2648 (4.47)
TDHF/6-311G* [λ = 1064 nm]	4383 (4.60)	3623 (4.72)	5801 (4.75)
CPHF/6-31+G*	2296 (4.39)	2058 (4.65)	2811 (4.56)
TDHF/6-31+G* [λ = 1064 nm]	4678 (4.66)	3853 (4.80)	6204 (4.80)

[#] $\beta_{MP2}(-2\omega;\omega,\omega) \approx \beta_{MP2}(0;0,0) \times \dfrac{\beta_{TDHF}(-2\omega;\omega,\omega)}{\beta_{CPHF}(0;0,0)}$

	indolino	benzimidazolo	benzothiazolo
Theory			
β MP2/6-31G* [λ = 1064 nm]	8323	8147	11924
β MP2/6-31G* [λ = ∞, acetonitrile]	**9704**	**7052**	**12107**
Experiment (acetonitrile)			
λ_{max} (nm)	544	401	523
β at λ = 1064 nm	117800	27500	184000
β at λ = ∞ (Γ = 500 cm^{-1}) [#]	**9500**	**10600**	**17200**

$$^{\#}\frac{\beta(-2\omega;\omega,\omega)}{\beta(0;0,0)} = \frac{\omega_{ge}^2\left(\omega_{ge} - i\gamma\right)^2}{\left(\left[\omega_{ge} - i\gamma\right]^2 - 4\omega^2\right)\left(\left[\omega_{ge} - i\gamma\right]^2 - \omega^2\right)}$$

Extracting static β from dynamic β remains a difficult issue.

Extracting static β from dynamic β remains a difficult issue.

Two-state approximation (γ from experimental HWHM)

$$\frac{\beta_{\zeta\zeta\zeta}(-2\omega;\omega,\omega)}{\beta_{\zeta\zeta\zeta}(0;0,0)} = F\left(\omega,\omega_{ge},\gamma\right) = \frac{\omega_{ge}^2\left(\omega_{ge}-i\gamma\right)^2}{\left(\left[\omega_{ge}-i\gamma\right]^2-4\omega^2\right)\left(\left[\omega_{ge}-i\gamma\right]^2-\omega^2\right)}$$

+ inhomogeneous damping (based on the absorption spectrum, through the dispersion factors, which implicitly contains information on the distribution of the transition frequencies)

$$\left|\frac{\beta^{HRS}(-2\omega;\omega,\omega)}{\beta^{HRS}(0;0,0)}\right| = \left\{\int N\left(\omega_{ge}'\right)\left|F\left(\omega,\omega_{ge}',\gamma\right)\right|^2 d\omega_{ge}'\right\}^{1/2}$$

vibronic structure

$$N\left(\omega_{ge}'\right) = \sum_n^{vib.\ levels}\left[\frac{S^n e^{-S}}{n!}\right]e^{-\left[\left(\omega_{ge}'-\omega_n\right)/\gamma_{vib}\right]^2}$$

The parameters are obtained by fitting the UV/visible absorption spectra and are then used to get the static first hyperpolarizability.

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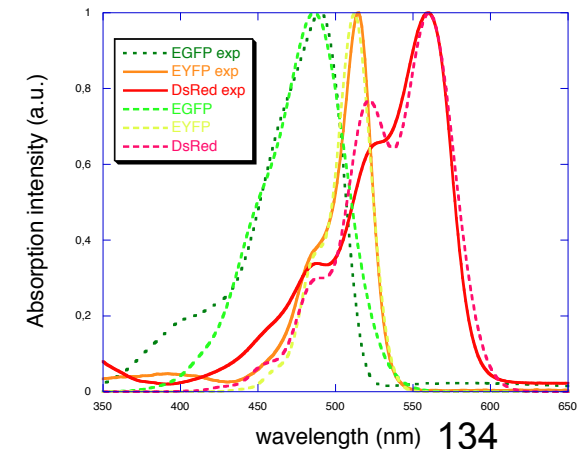
The first diradical was prepared by Thiele and Balhorn in 1904 [In fact, this is not a true diradical but rather a diradicaloïd presenting some diradical character]
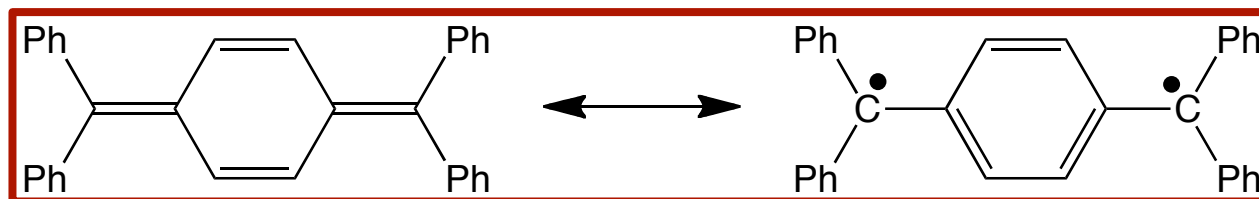
J. Thiele and H. Balhorn, *Ber. Dtsch. Chem. Ges.* **37**, 1463 (1904).

The first stable diradicals were prepared in 1915. They have a specific structure where the substituents bearing the unpaired electrons are in *meta* position.
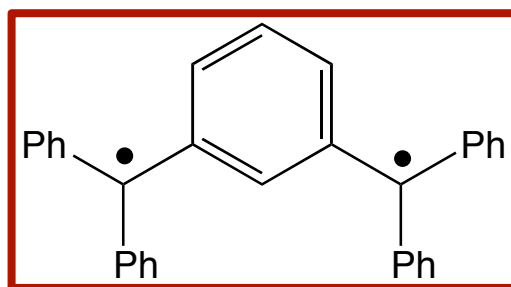
W. Schlenk and M. Brauns, *Ber. Dtsch. Chem. Ges.* **48**, 661 (1915).

Coupling between the unpaired electrons

$$2J = {}^{1}E_{1g} - {}^{3}E_{1u}$$

Singlet
2J < 0

anti-ferromagnetic coupling

Triplet
2J > 0

Ferromagnetic coupling
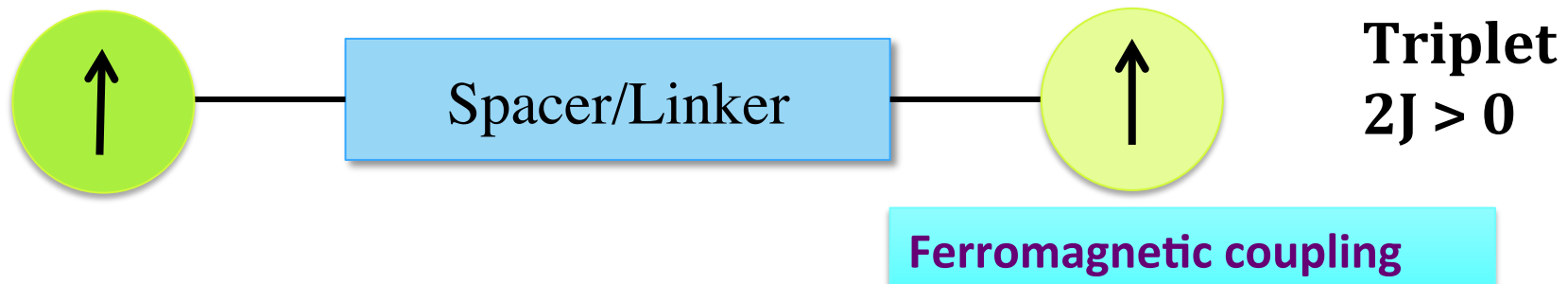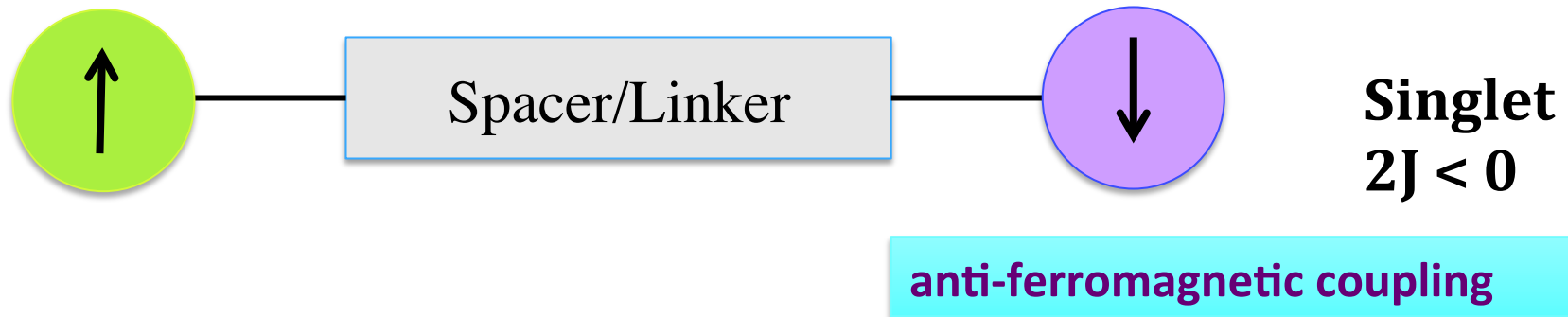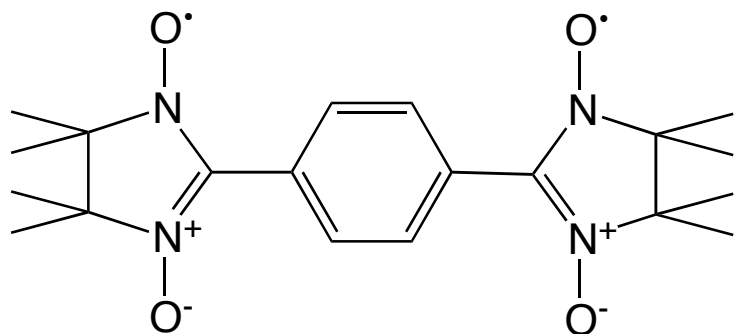
2J/k = -104 K
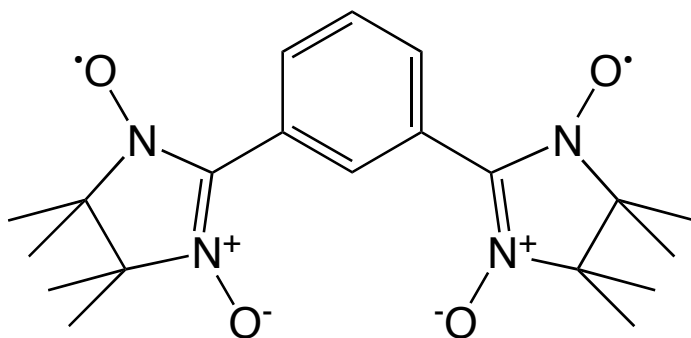
Singlet

2J/k = 36K

Triplet

Small singlet-triplet gap, allowing for spin control and design of molecular switches sensitive to temperature

D.A. Dougherty, *Acc. Chem. Res.* **24**, 88 (1991).

Moreover, compounds with intermediate diradical character can exhibit substantial second hyperpolarizabilities

Diphenalenyl-based compounds (synthesized by T. Kubo *et al.*)
large two-photon absorption : TPA, *Im*[γ(-ω; ω, -ω, ω)]
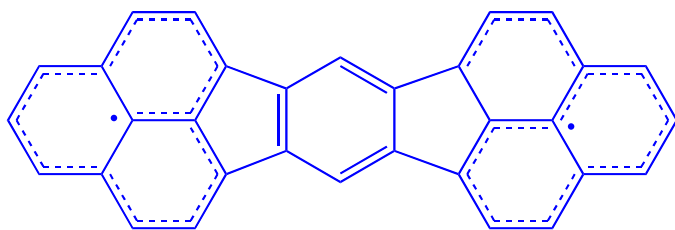
K. Kamada *et al.,* Angew. Chem. Int. Ed. **46**, 3544 (2007).

1,4-bis-(4,5-diphenylimidazol-2-ylidene)-cyclohexa-2,5-diene
large third harmonic generation : THG, γ(-3ω; ω, ω, ω)
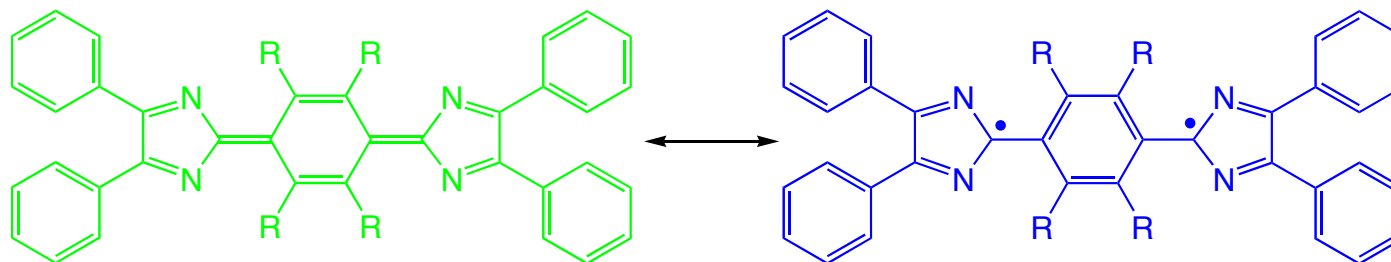
H. Kishida *et al.,* Thin Solid Films **519**, 1028 (2010).

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How to achieve substantial second hyperpolarizabilities (and the corresponding third-order nonlinear susceptibilities) ?

A) increasing the conjugation along the chain (CPHF)
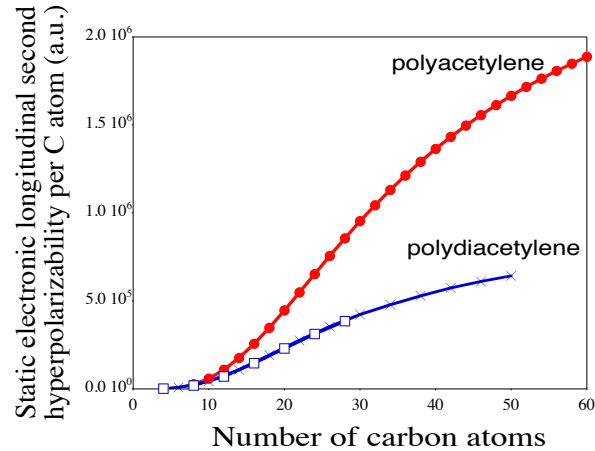
B) placing donor/acceptor substituents at strategic positions (VB-CT model)
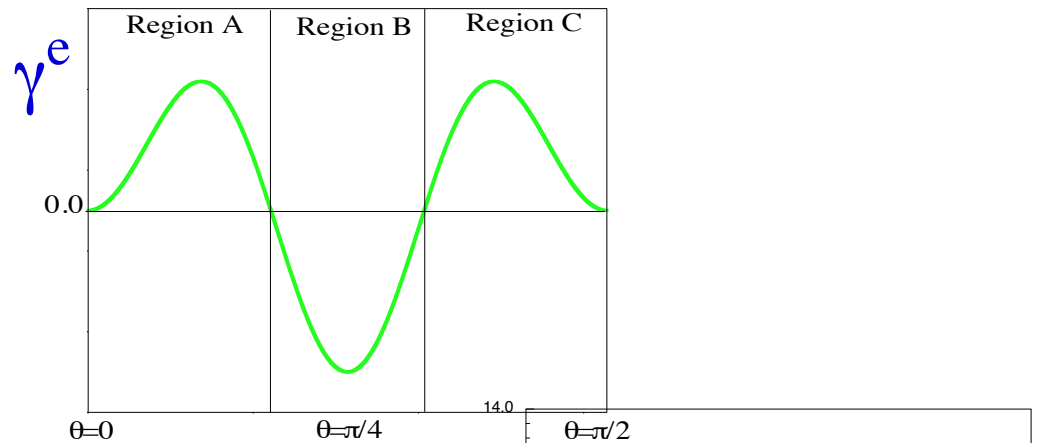
C) charging the system
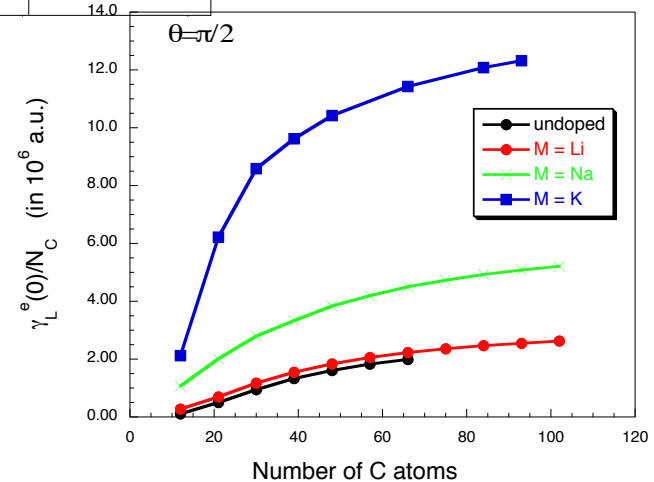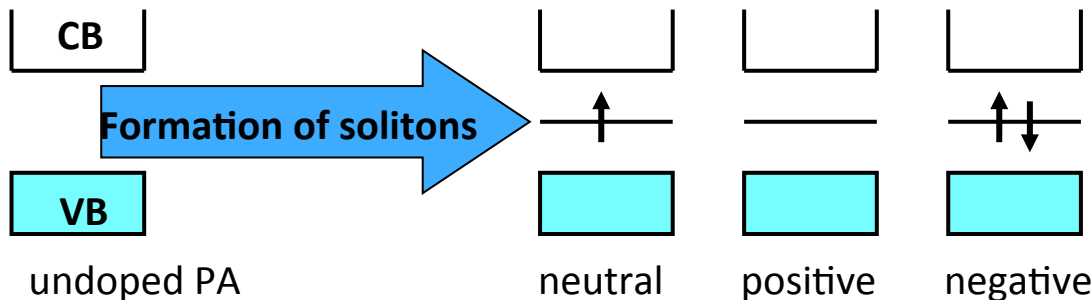
Broader interest of NLO for open-shell systems.

- when elaborating molecular electrochemical switches (at least one of the form is open-shell) [I. Asselberghs *et al.*, Chem. Phys. Lett. **368**, 408 (2003)]
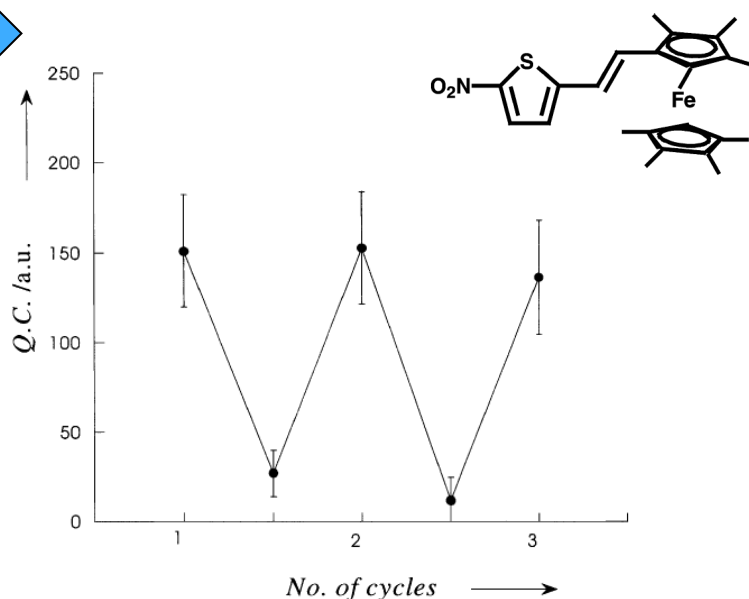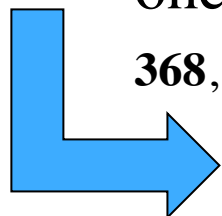
Fig. 5. Electrochemical switching of the HRS response between **1** and [**1**]$^+$ in CH_2Cl_2 (concentration 4.3×10^{-5} M). The solid line represents the HRS response for **1**, and then alternately oxidizing and reducing.

Fig. 1. Plot of hyper-Rayleigh scattering intensity versus the number density of radicals **8** in CH_2Cl_2 at room temperature. The curves in solid line represent the theoretical fit to equation (see text) obtained from the experimental data points.

- experiments have already been carried out for such species [I. Ratera *et al.*, Chem. Phys. Lett. **363**, 245 (2002).]

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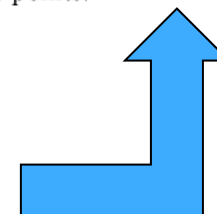
How to calculate the second hyperpolarizabilities of diradicals ?

Model system: *p*-quinodimethane (PQM)

Quinoid ↔ Diradical
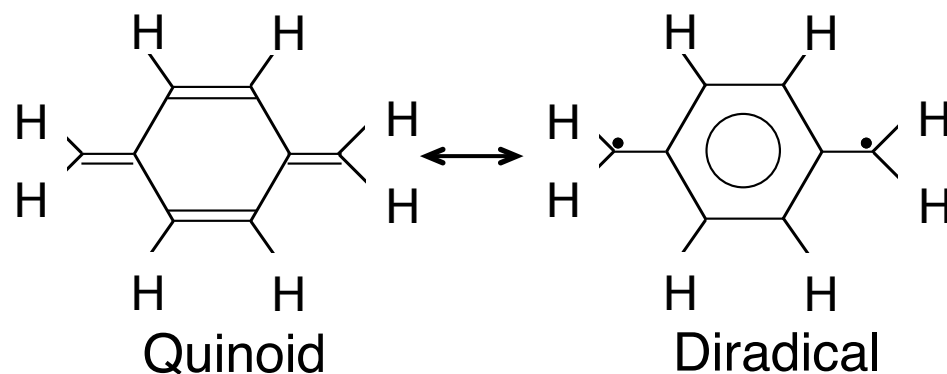
At equilibrium geometry, PQM presents some diradical character.

The external CC bonds are stretched so as to scan the diradical character domain ranging from 0 (closed-shell) to 1 (pure diradical, no interaction).

M. Nakano *et al.*, J. Phys. Chem. A **109**, 885 (2005).

The diradical character value, y, is the weight of the doubly-excited configuration in the MCSCF theory.

It is evaluated using Yamaguchi's expression, *i.e.* within spin-projected UHF theory

$$y_i = 1 - \frac{2T_i}{1 + T_i^2}$$

using the occupation numbers of the corresponding UHF natural orbitals

$$T_i = \frac{\eta_{HOMO-i} - \eta_{LUMO+i}}{2}$$
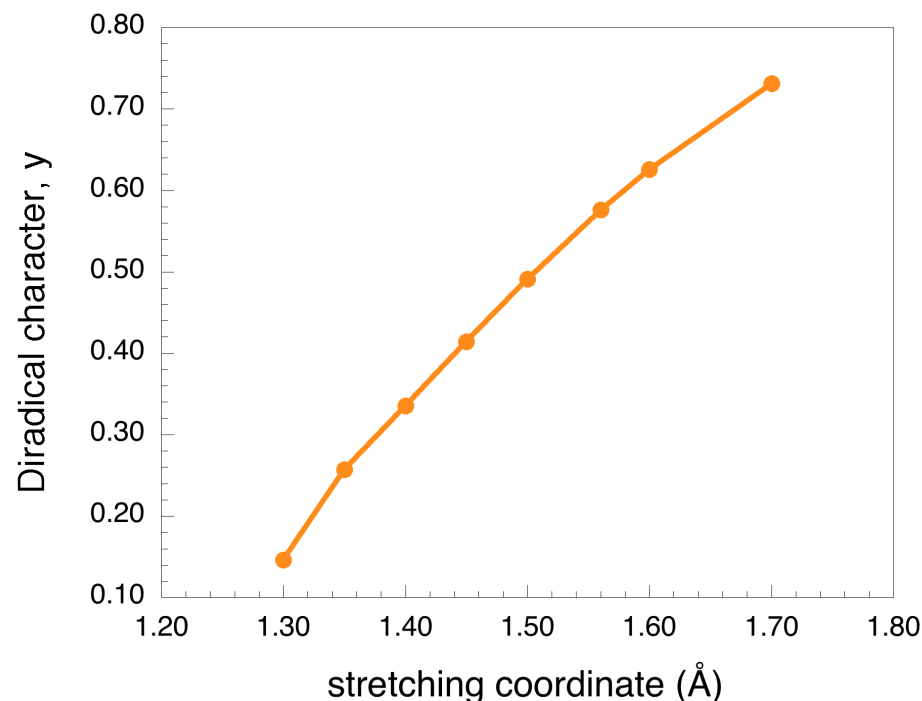
K. Yamaguchi, in Self-Consistent Field Theory and Applications, edited by R. Carbo and M. Klobukowski (Elsevier, 1990) p. 727.

Second hyperpolarizability calculations

- Static

- Finite field method → 4th order numerical derivative of the energy

- electric field amplitudes of the order of 10^{-3} a.u.

- interpreted using hyperpolarizability densities

$$\gamma = -\frac{1}{3!}\int r\rho^{(3)}(\mathbf{r})d^3\mathbf{r} \qquad \rho^{(3)}(\mathbf{r}) = \left.\frac{\partial^3\rho}{\partial F^3}\right|_{\mathbf{F}=0}$$

Reference method: UCCSD(T)
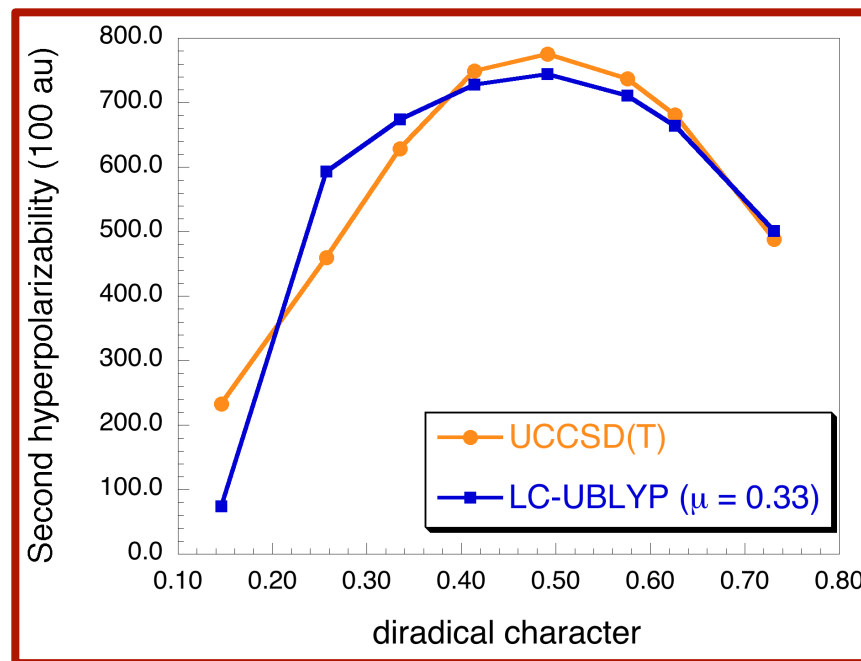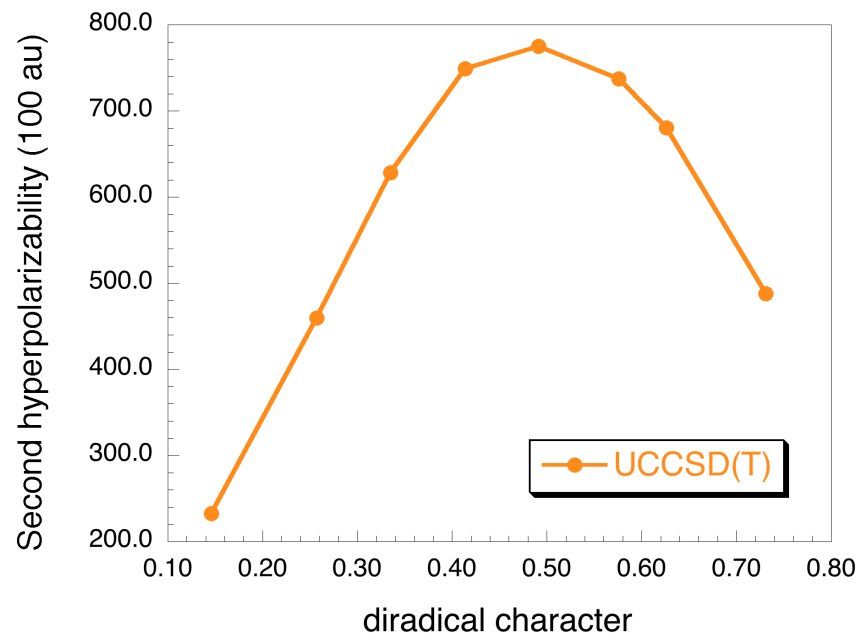**Basis set: 6-31G(d) + p diffuse function**
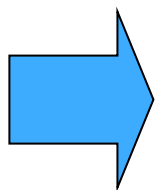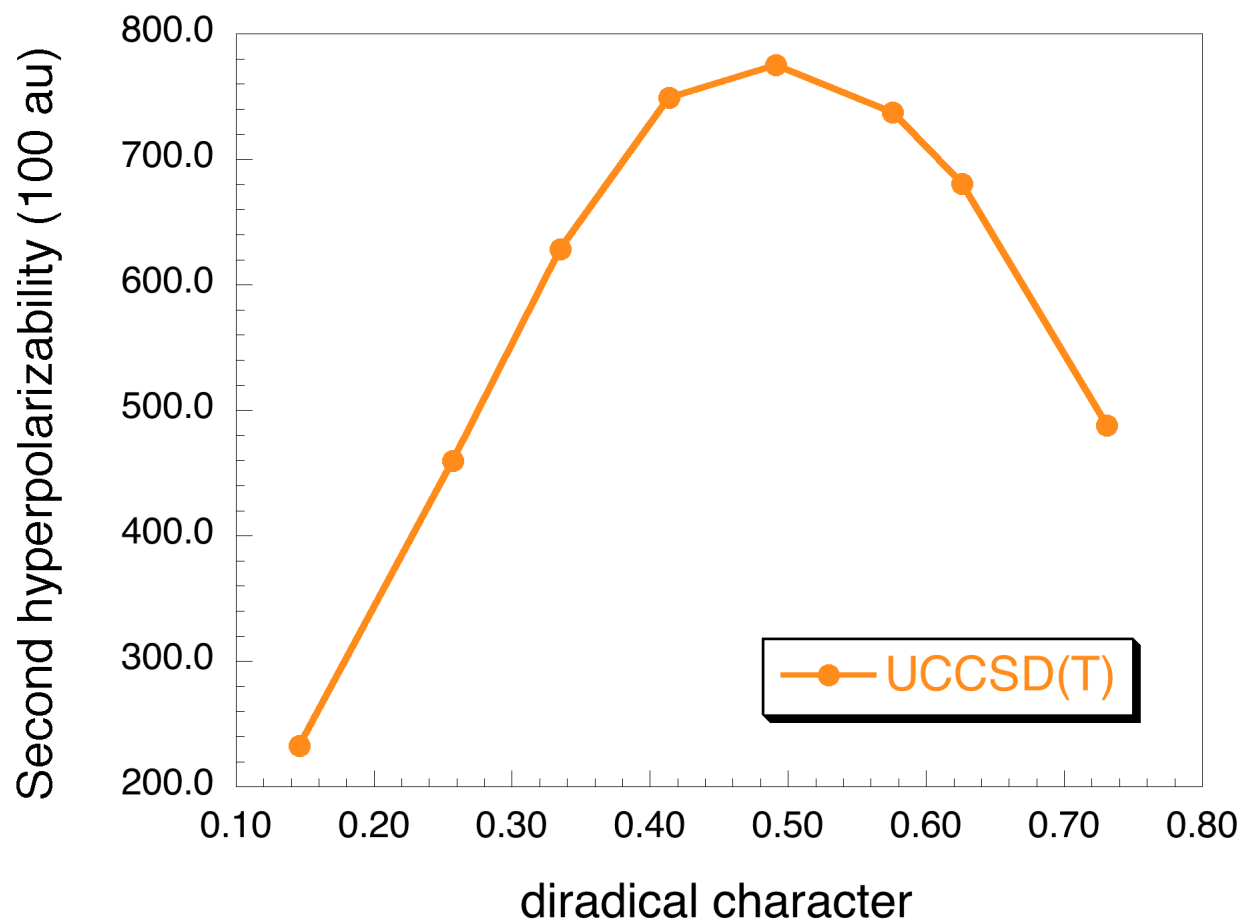
Substantial enhancement in the intermediate y region
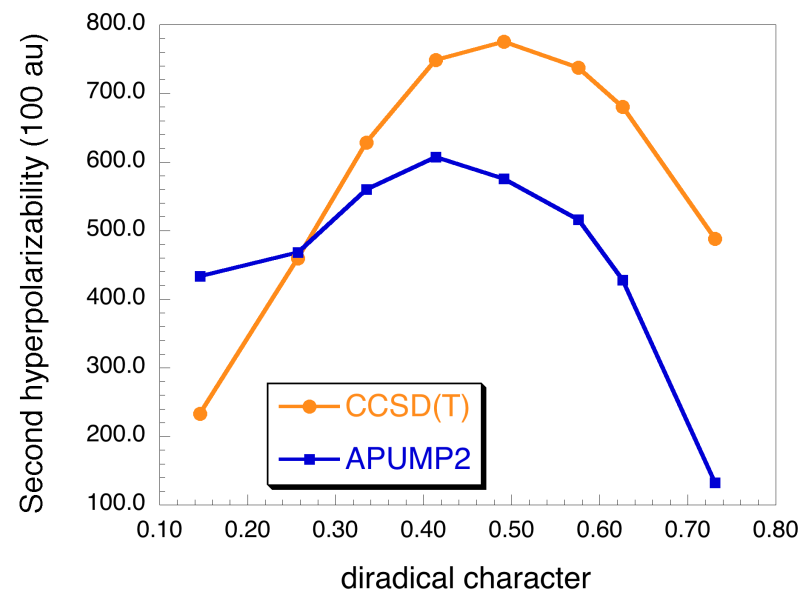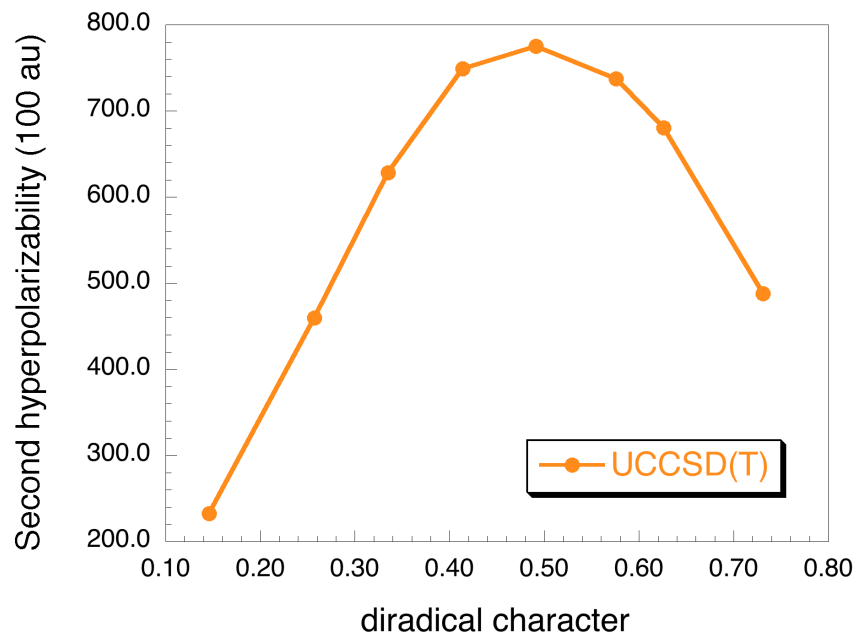
$$^{LS}E_{APUMP2} = {}^{LS}E_{UMP2} + f_{SC}[{}^{LS}E_{UMP2} - {}^{HS}E_{UMP2}]$$

$$f_{SC} = \frac{{}^{LS}\langle S^2 \rangle_{UHF\,X} - s(s+1)}{{}^{HS}\langle S^2 \rangle_{UHF\,X} - {}^{LS}\langle S^2 \rangle_{UHF\,X}}$$

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$$\frac{1}{r_{12}} = \frac{1 - \mathrm{erf}(\mu r_{12})}{r_{12}} + \frac{\mathrm{erf}(\mu r_{12})}{r_{12}}$$

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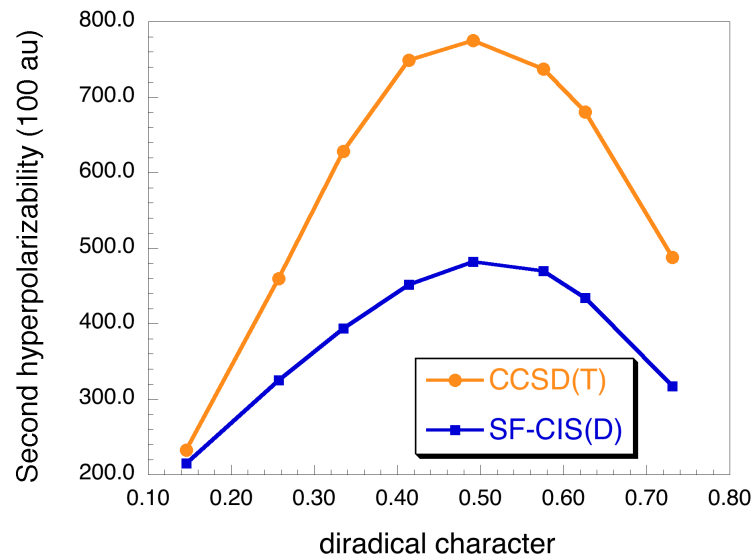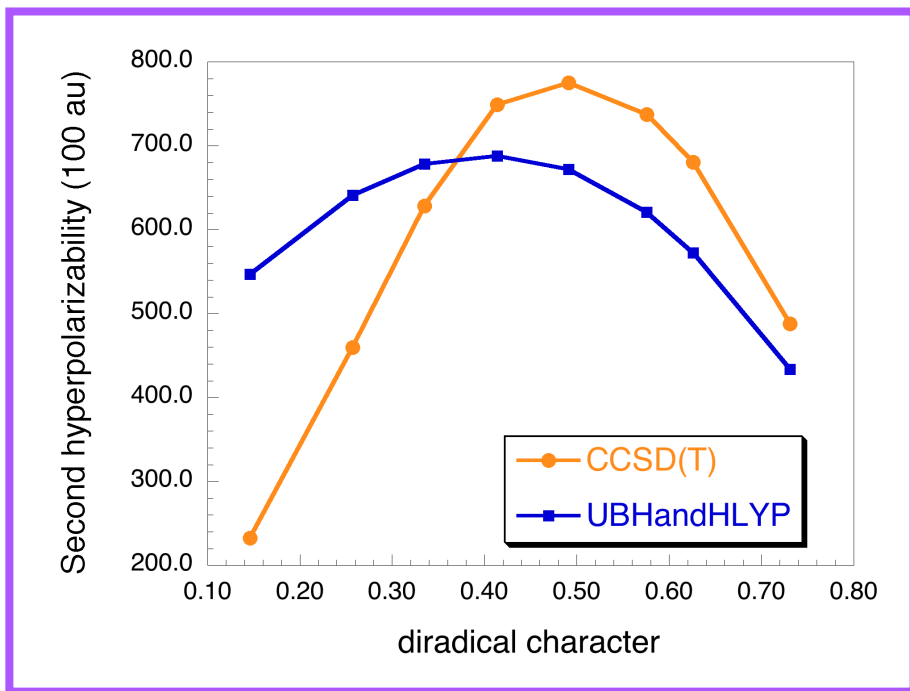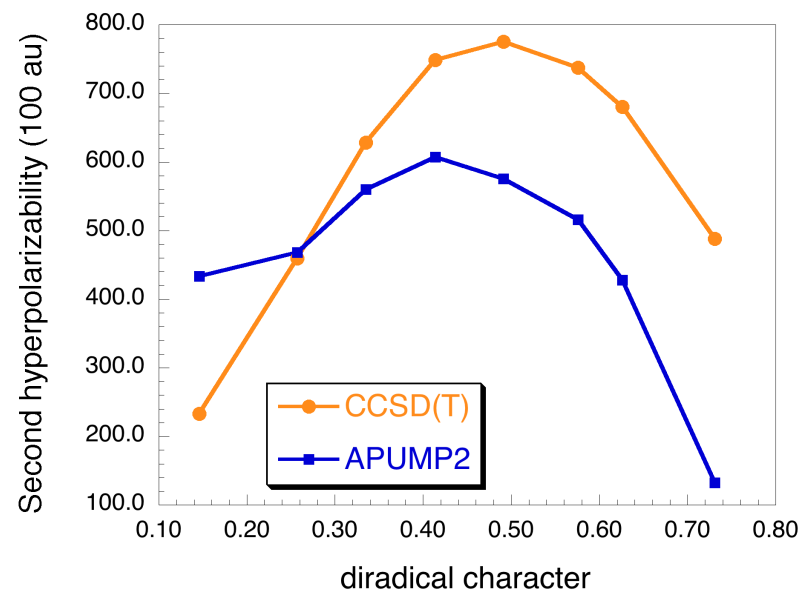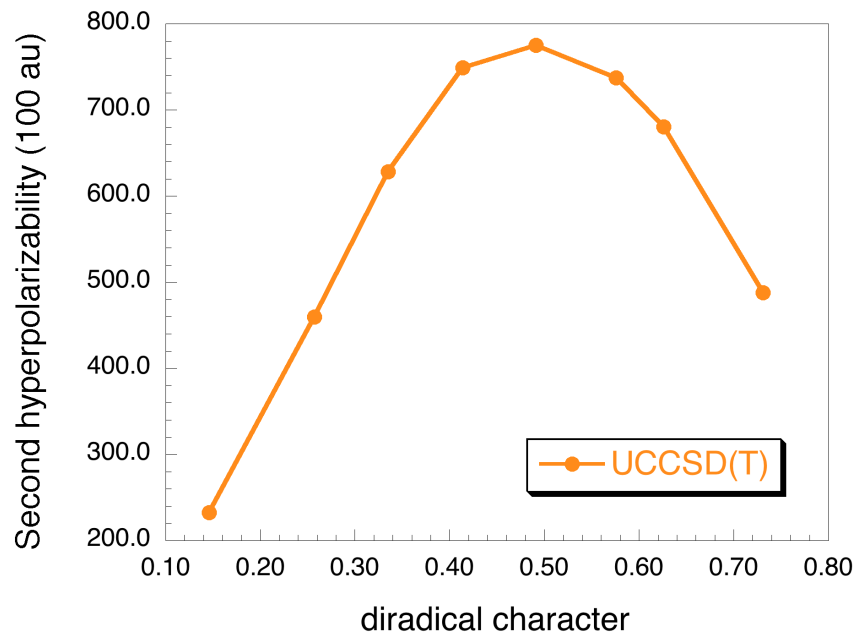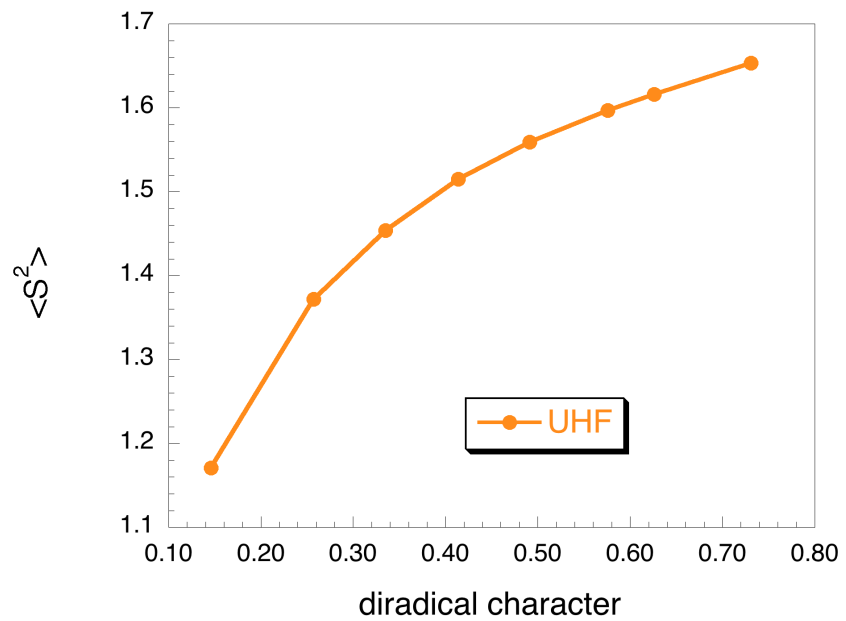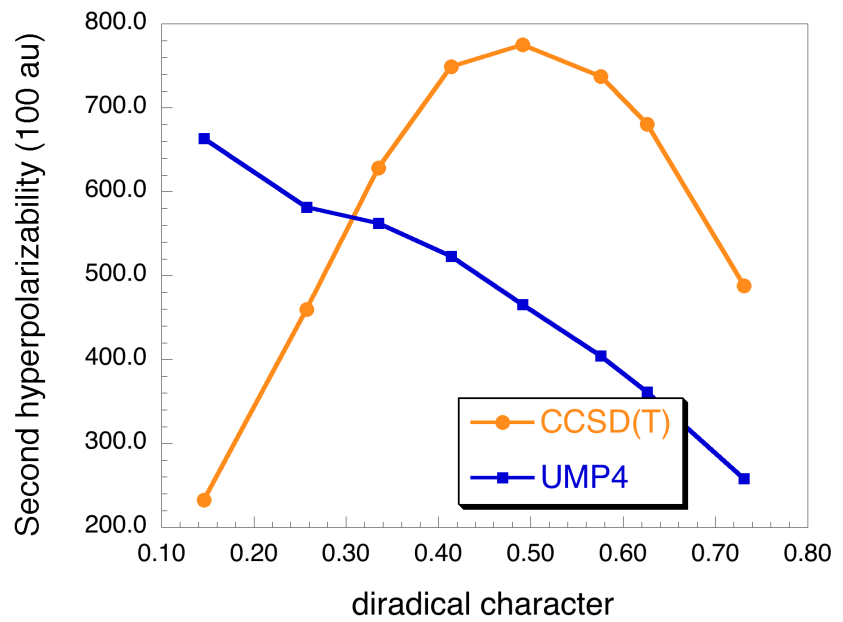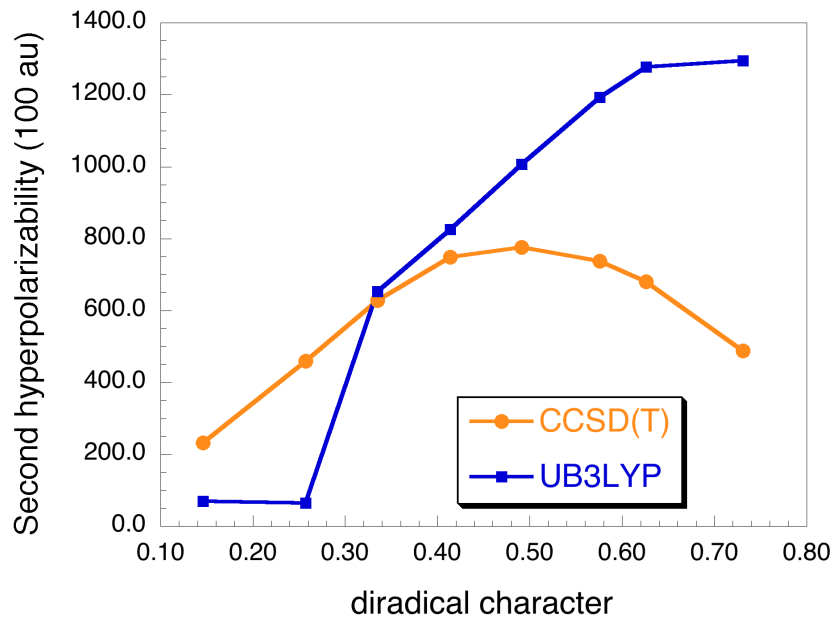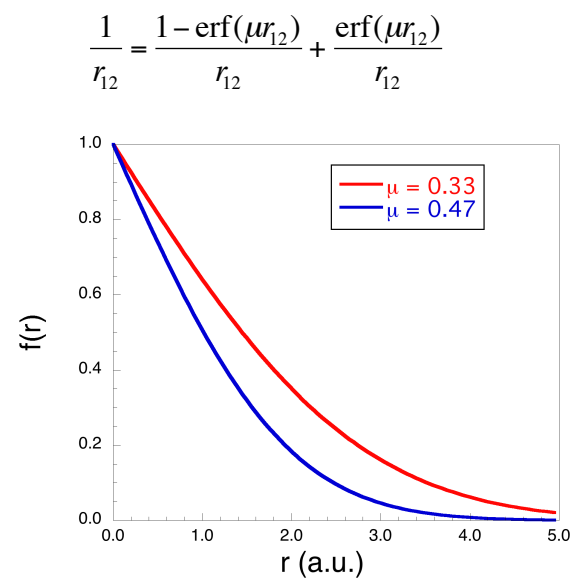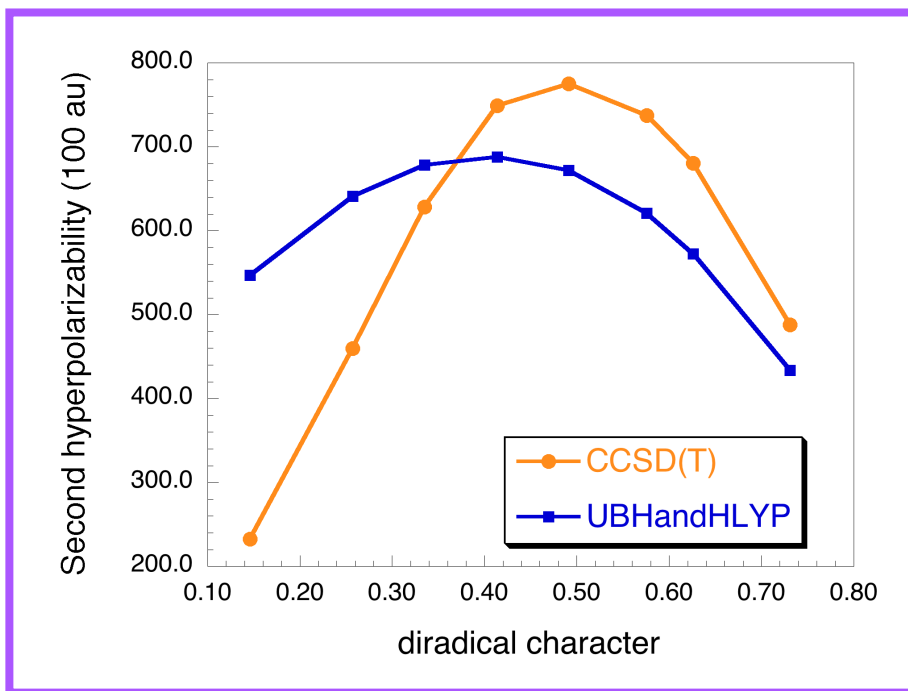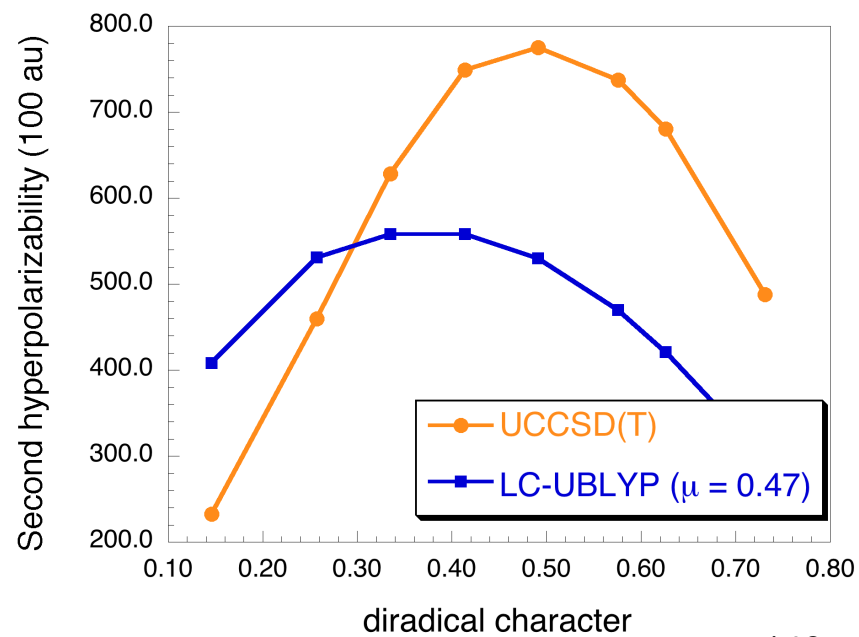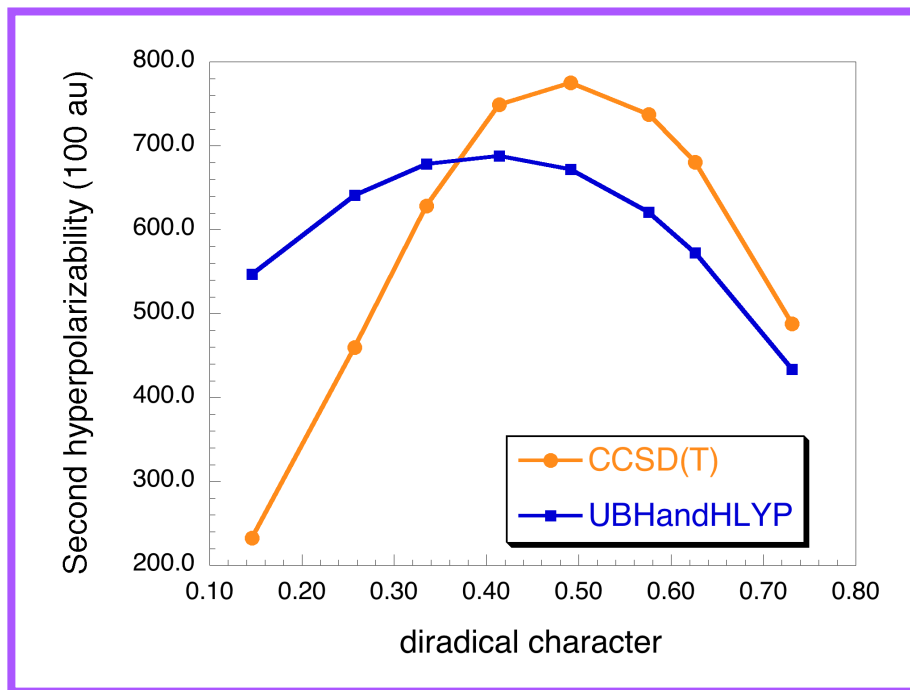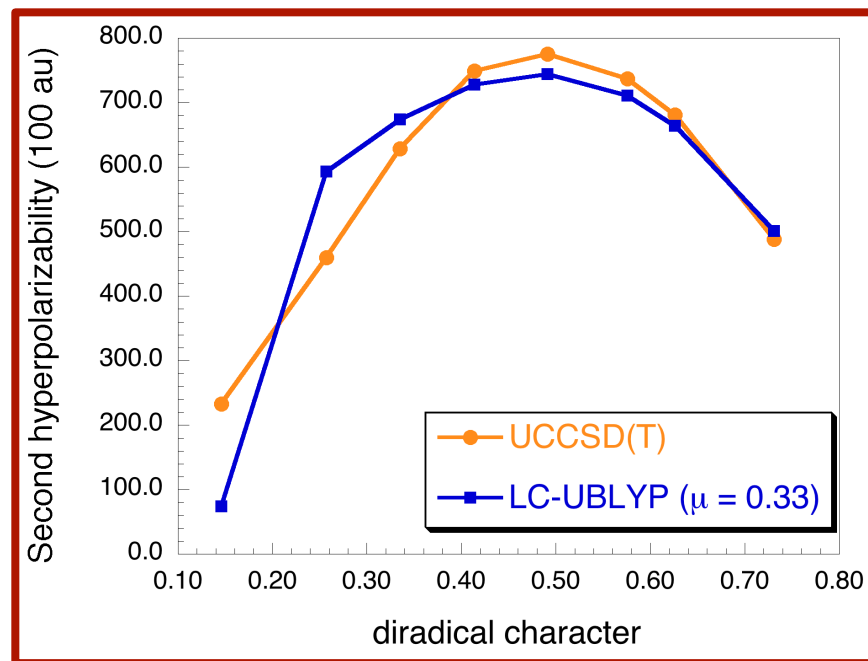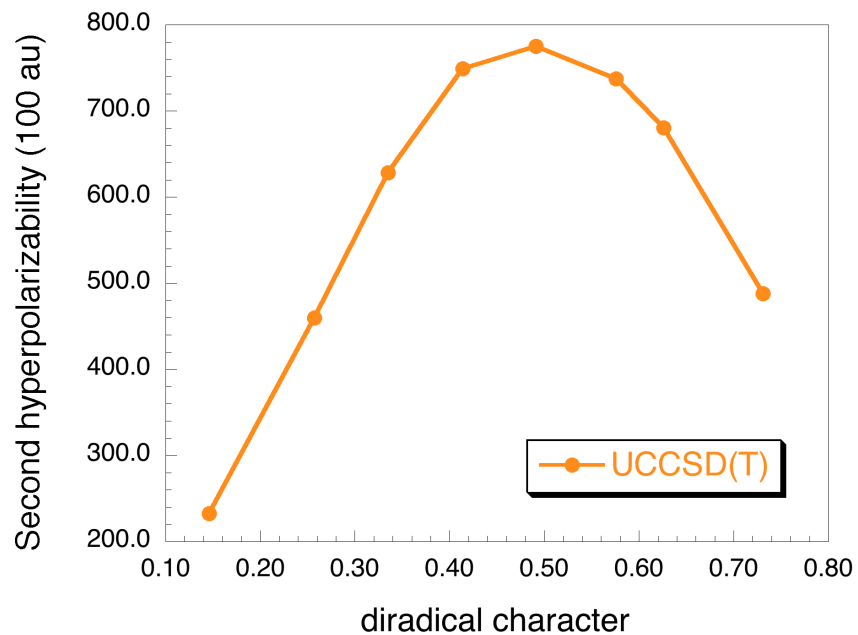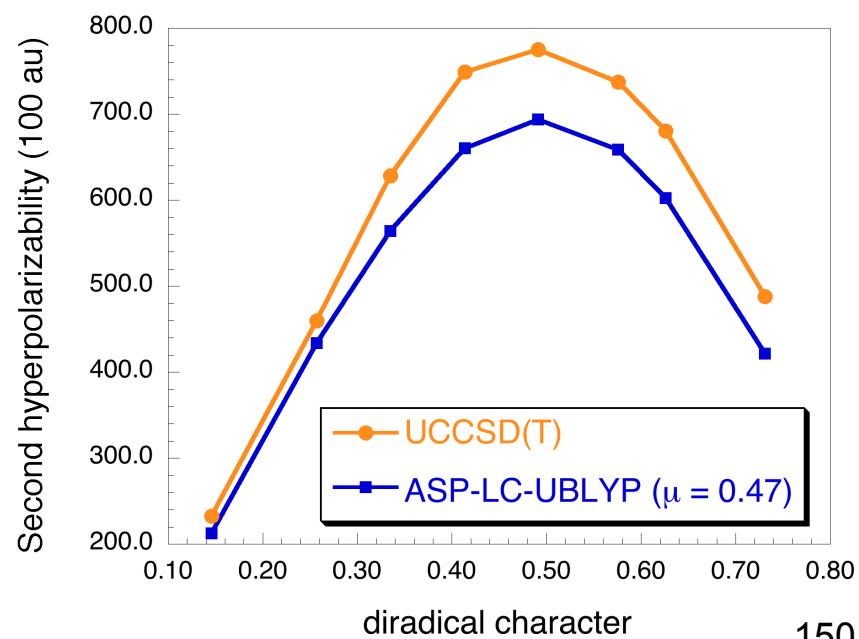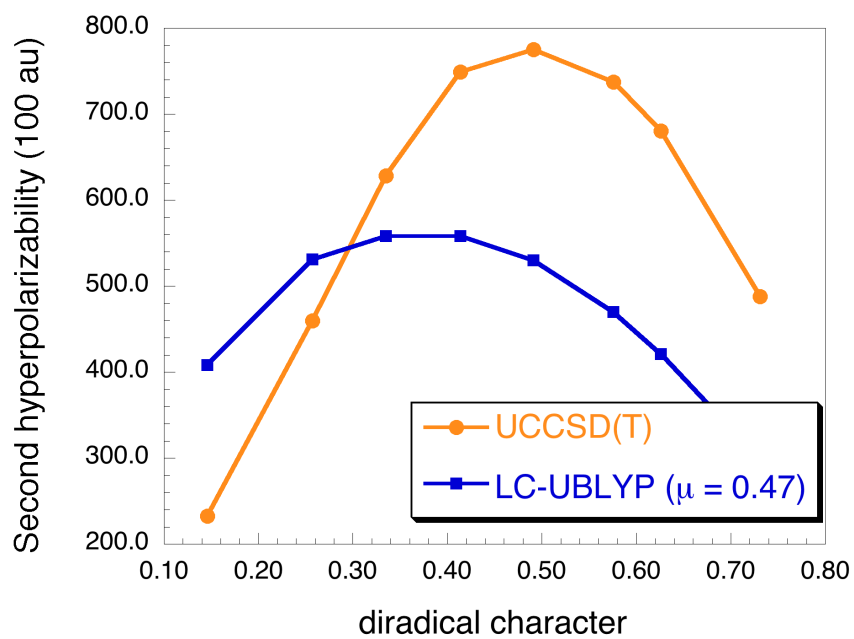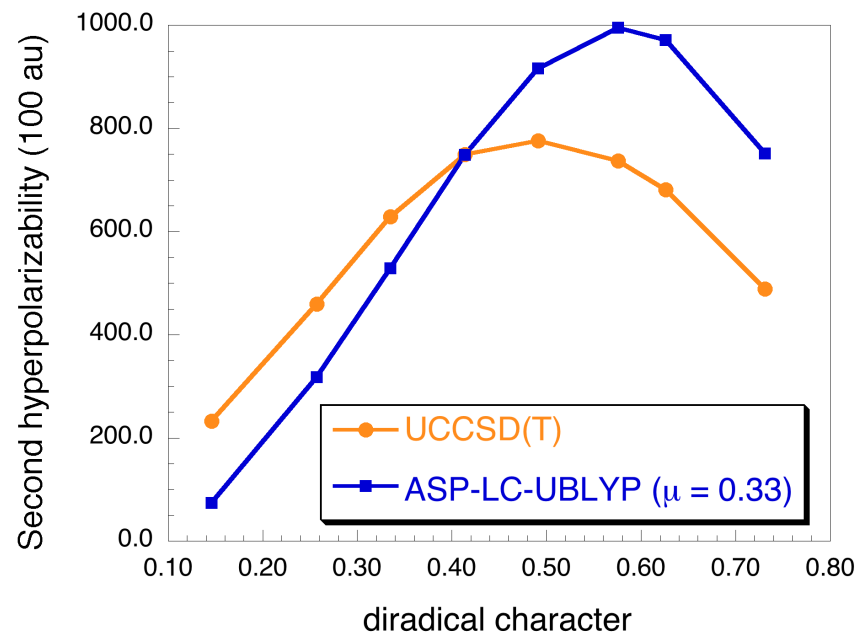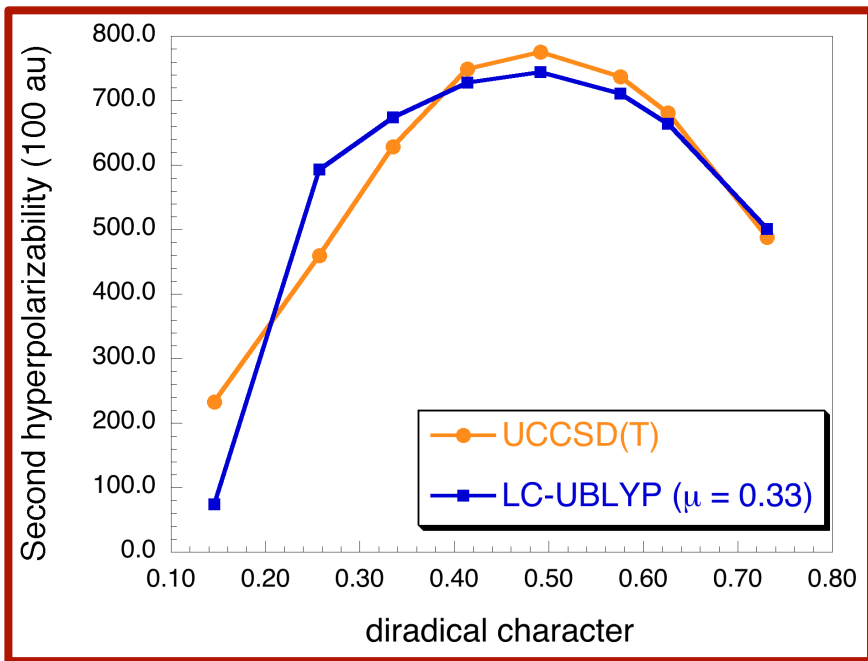
Why is γ so large for intermediate diradical character ?

VB-VCI approach has recently been used to rationalize the dependence of γ on the diradical character

Two localized natural orbitals a and b, assumed orthogonal.
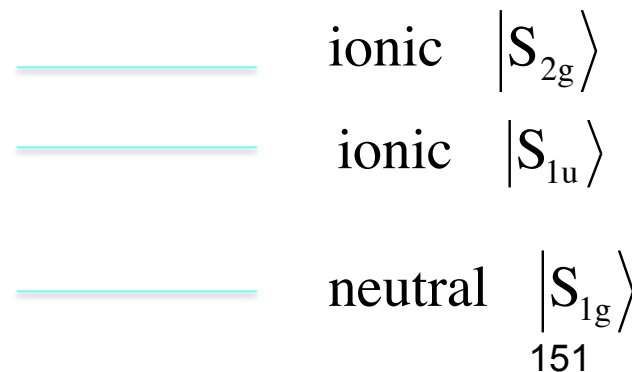The $M_S = 0$ state solutions are obtained by diagonalizing

$$\begin{pmatrix} 0 & K_{ab} & t_{ab} & t_{ab} \\ K_{ab} & 0 & t_{ab} & t_{ab} \\ t_{ab} & t_{ab} & U & K_{ab} \\ t_{ab} & t_{ab} & K_{ab} & U \end{pmatrix}$$

3-(singlet)-state model

$U = U_{aa} - U_{ab}$,

K_{ab} = exchange integral --> $r_K = K_{ab}/U$

t_{ab} = transfer matrix --> $r_t = |t_{ab}|/U$

$$2J = {}^1E_{1g} - {}^3E_{1u} = 2K_{ab} + \frac{U - \sqrt{U^2 + 16t_{ab}^2}}{2} \qquad r_J = 2J/U$$

_____ ionic $\left| S_{2g} \right\rangle$

_____ ionic $\left| S_{1u} \right\rangle$

_____ neutral $\left| S_{1g} \right\rangle$
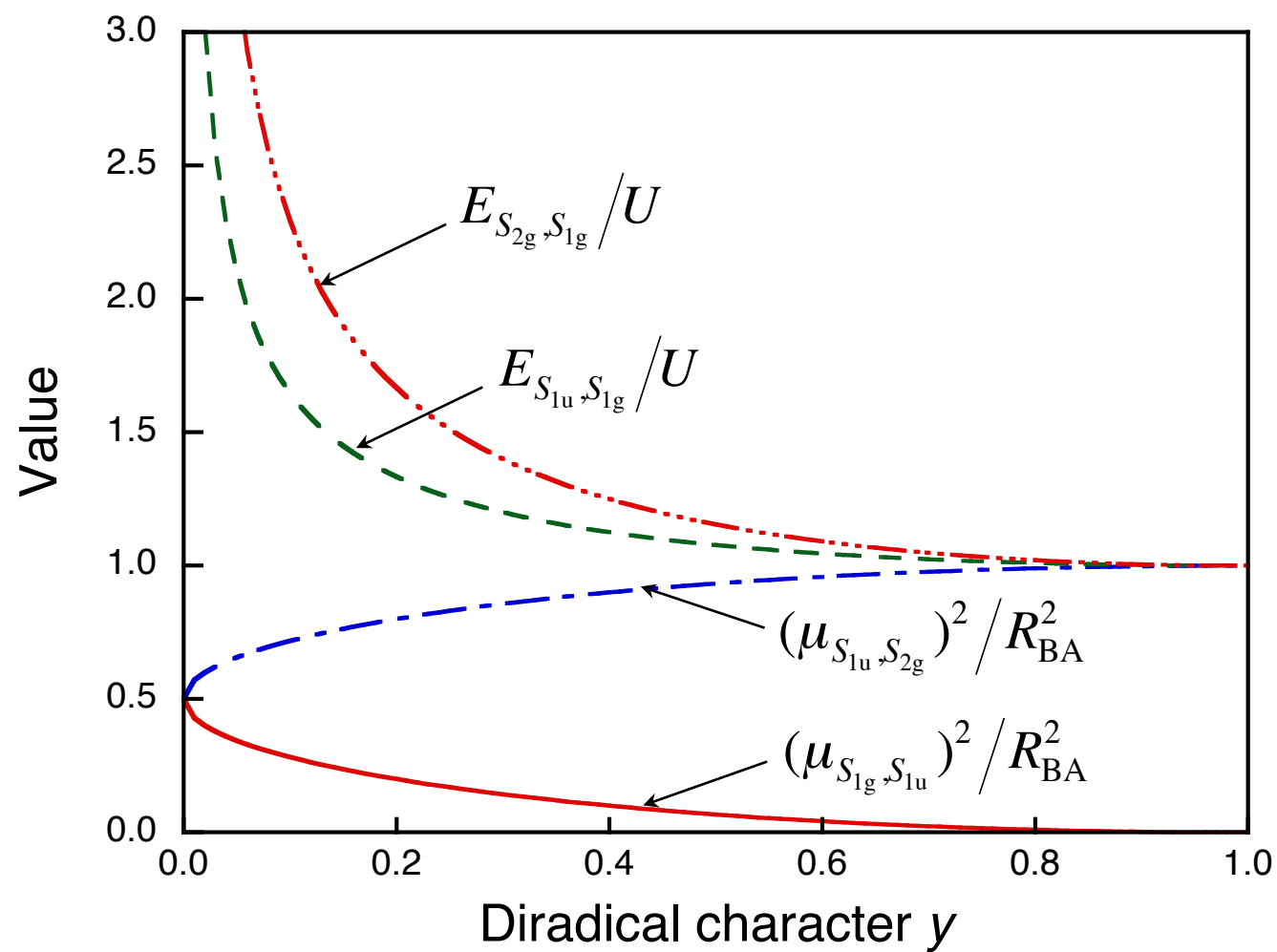
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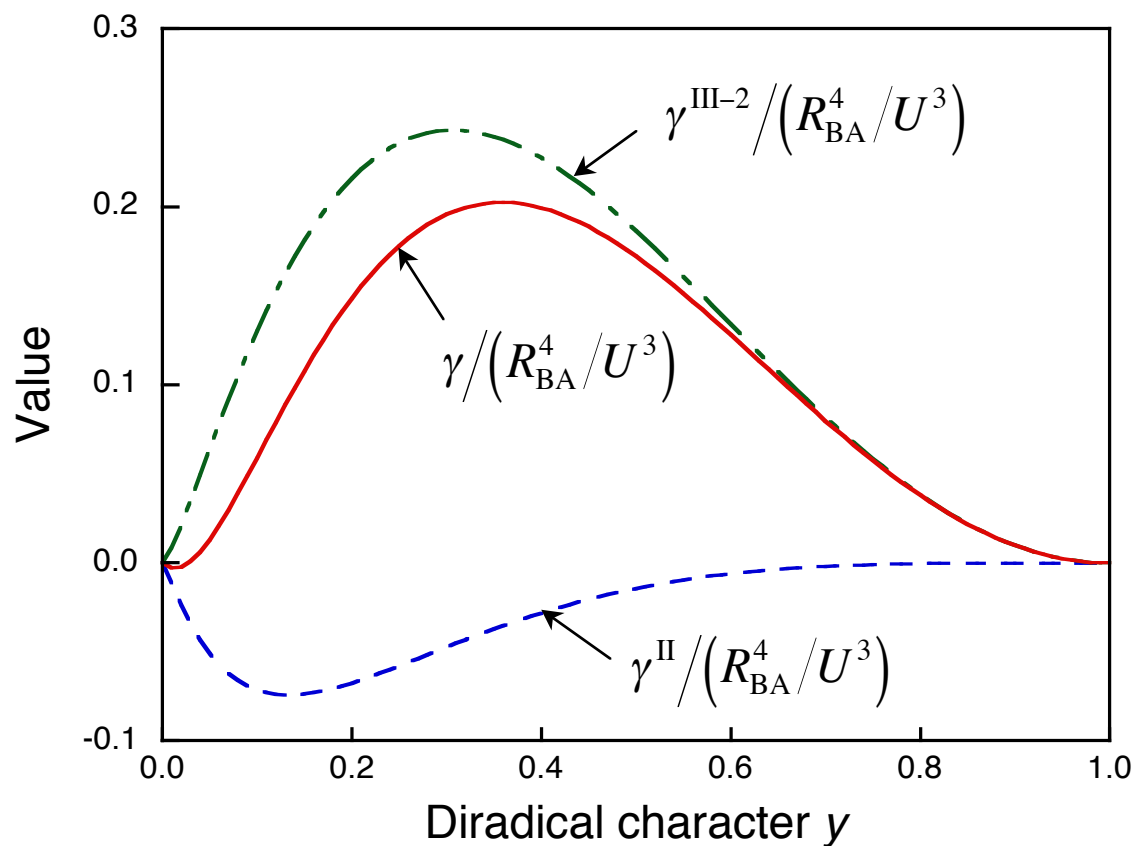$$\left|S_{1g}\right\rangle = \xi\left|g\bar{g}\right\rangle - \zeta\left|u\bar{u}\right\rangle$$

$$y \equiv 2\zeta^2 = 1 - \frac{4r_t}{\sqrt{1 + 16r_t^2}} = 1 - \frac{2\sqrt{(r_K - r_J)(r_K - r_J + 1)}}{1 + 2(r_K - r_J)}$$

$$r_t = |t_{ab}|/U$$

y(0.1) = 0.63
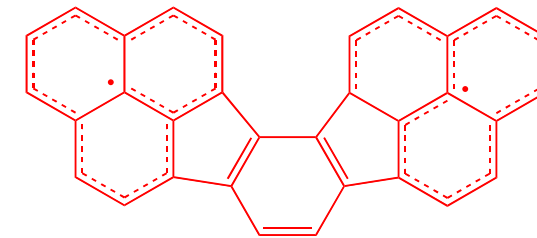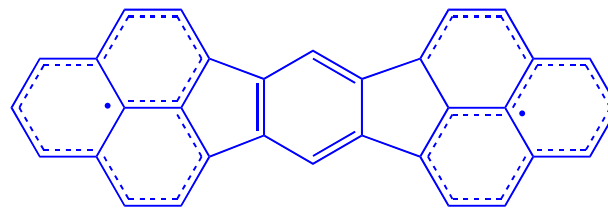y(0.2) = 0.38
y(0.5) = 0.11
y(2.0) = 0.01

y(1.0) = 0.030

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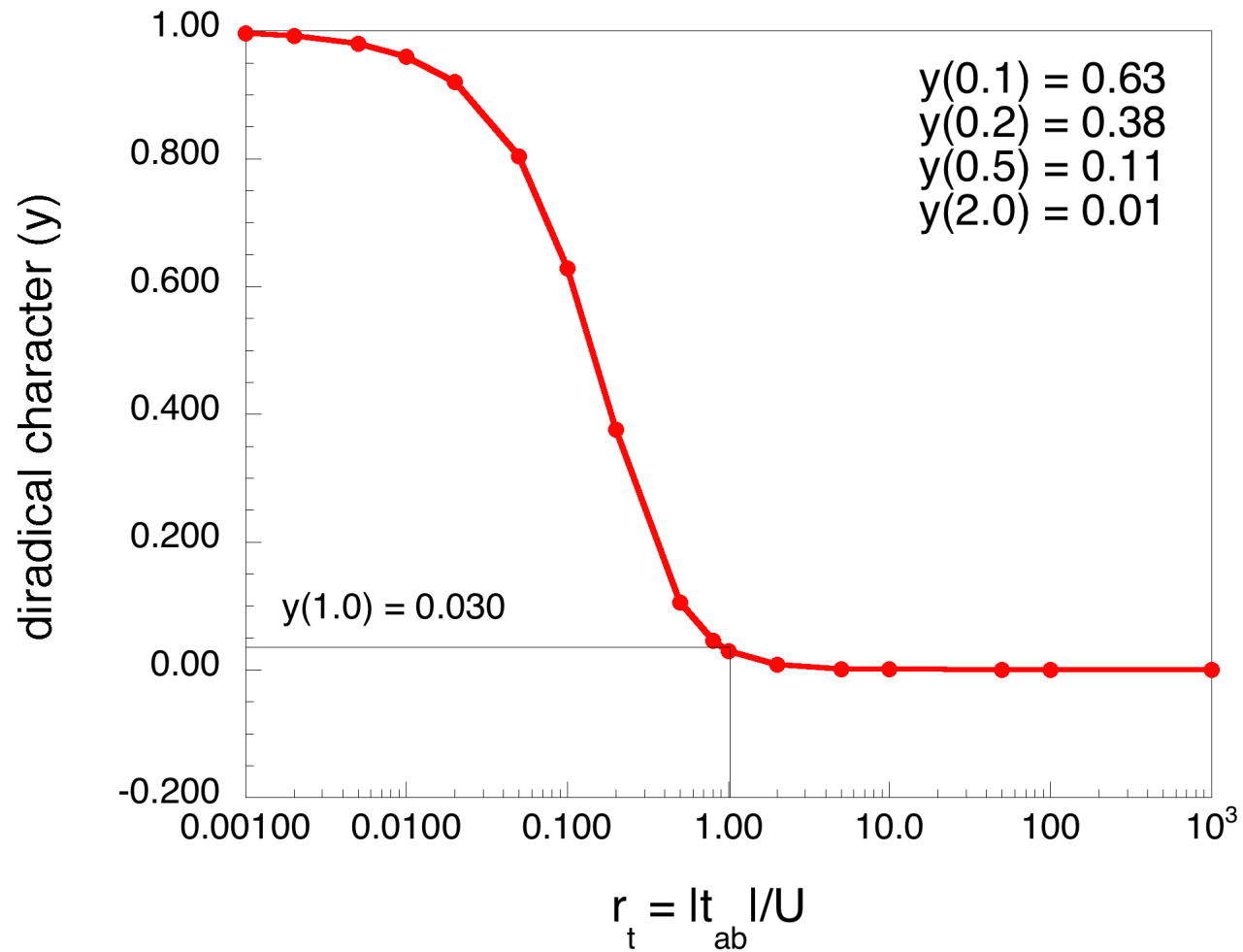
$$\gamma = \gamma^{\mathrm{II}} + \gamma^{\mathrm{III}-2} = -4 \frac{(\mu_{S_{1g},S_{1u}})^4}{(E_{S_{1u},S_{1g}})^3} + 4 \frac{(\mu_{S_{1g},S_{1u}})^2 (\mu_{S_{1u},S_{2g}})^2}{(E_{S_{1u},S_{1g}})^2 E_{S_{2g},S_{1g}}}$$

$$\frac{\gamma}{\left(R_{BA}^4/U^3\right)} = -\frac{8q^4}{\left(1+\sqrt{1-q^2}\right)^2\left(1-2r_K+\frac{1}{\sqrt{1-q^2}}\right)^3} + \frac{4q^2}{\left(1-2r_K+\frac{1}{\sqrt{1-q^2}}\right)^2}\frac{1}{\sqrt{1-q^2}}.$$

$q = 1 - y$

$r_K = 0.0$

M. Nakano *et al.*, Phys. Rev. Lett. **99**, 033001 (2007).

Predictive character of the method starting from optical properties

	y	γ (10⁴ au)	y	γ (10⁴ au)
Full BHandHLYP	0.77	228	0.92	47
VCI parameters from CAS(2,2) calculations	0.54	399	0.83	55

$$2J = {}^1E_{1g} - {}^3E_{1u} = 2K_{ab} + \frac{U - \sqrt{U^2 + 16t_{ab}^2}}{2}$$

$$E_{S_{1u}, S_{1g}} \equiv {}^1E_{1u} - {}^1E_{1g} = U(1 - r_J) = \frac{U}{2}\left(1 - 2r_K + \frac{1}{\sqrt{1 - q^2}}\right),$$

The diradical character can be related to excitation energies

$$y = 1 - \sqrt{1 - \left(\frac{E_{S_{1u},S_{1g}} - E_{T_{1u},S_{1g}}}{E_{S_{2g},S_{1g}}}\right)^2}$$

Diradical Character

$y = 1$

$y = 0$

PhBu-NDPL

Bu-IDPL

TIPS-pentacene

naphthalene

chrysene

anthracene

fluorene

THEORY

EXPERIMENT

S_{2g} ($^1E_{2g}$)

S_{1u} ($^1E_{1u}$)

T_{1u} ($^3E_{1u}$)

S_{1g} ($^1E_{1g}$)

$E_{S_{2g},S_{1g}}$

$E_{S_{1u},S_{1g}}$

$E_{T_{1u},S_{1g}}$

y from UHF NO/6-31G(d,p)

K. Kamada *et al.*, J. Phys. Chem. Lett. **1**, 937 (2010). 156