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Description of Quadratic Optical Nonlinearities for Transition-Metal Organometallic Chromophores Using an SCF-LCAO MECI Formalism

David R. Kanis, Mark A. Ratner,* and Tobin J. Marks*

Department of Chemistry and the Materials Research Center
Northwestern University, Evanston, Illinois 60208

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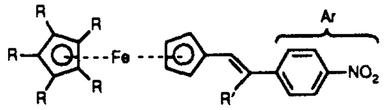
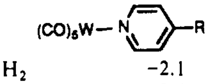
While current activity in molecular and macromolecular nonlinear optical (NLO) materials has focused predominantly on organic π-electron chromophores,[1] recent results suggest that organometallic chromophores may also hold promise.[2,3] In particular, low-lying strongly allowed one-photon metal-to-ligand and ligand-to-metal charge transfer (MLCT, LMCT) transitions[4] could conceivably give rise to large microscopic second-order nonlinearities (β_{ijk}) via a mechanism analogous to the charge-transfer excitations in organic NLO chromophores.[1] The understanding and rational design of organic chromophores has benefitted significantly from efficient, chemically oriented quantum chemical descriptions of π-electron NLO processes.[5-7] We communicate here the first SCF-LCAO approach to describing the second-order NLO characteristics of transition-metal organometallic molecules[8] and report some initial mechanistic observations.

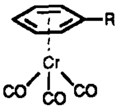
Table I. Comparison of Calculated and Experimental Molecular Quadratic Hyperpolarizability Data in Units of 10^{-30} cm^5 esu^{-1} ($\hbar\omega$ = 0.65 eV)



no.	R	R′	$\beta_{vec}^{exp\,a}$	$\beta_{vec}^{calcd\,b}$	$\beta_{tot}^{calcd\,b}$
1	H	H(cis)	14	29.0	29.1
2	H	H(trans)	34	41.0	41.0
3	H	CN	22	31.9	37.1
4	CH_3	H	40	45.4	45.5
5	CH_3	CN	35	35.3	40.4
6[d]	H	H	21	51.0	56.4
7[e]	H	H	52	73.7	73.8



no.	R	$\beta_{vec}^{exp\,a}$	$\beta_{vec}^{calcd\,b,c}$
8	NH_2	−2.1	−3.60
9	*n*-butyl	−3.4	−5.91
10	H	−4.4	−7.66
11	phenyl	−4.5	−5.28
12	$COCH_3$	−9.3	−16.80



no.	R	$\beta_{vec}^{exp\,a}$	$\beta_{vec}^{calcd\,b}$	$\beta_{tot}^{calcd\,b}$
13	NMe_2	−0.4	−0.51	−3.0
14	NH_2	−0.6	−1.1	−1.9
15	$COOCH_3$	−0.7	−3.1	−4.8
16	H	−0.8	−1.9	−1.9
17	OCH_3	−0.9	−1.5	−1.6
18	*trans*-styryl	−2.2	−4.0	−4.8

[a] Experimental EFISH data of ref 3a. [b] ZINDO-derived parameters defined in footnotes 14, 16, and 17. [c] See footnote 16. [d] Ar = 2,4-dinitro. [e] Ar = 4-(4-nitrophenyl)-*trans*-butadienyl.

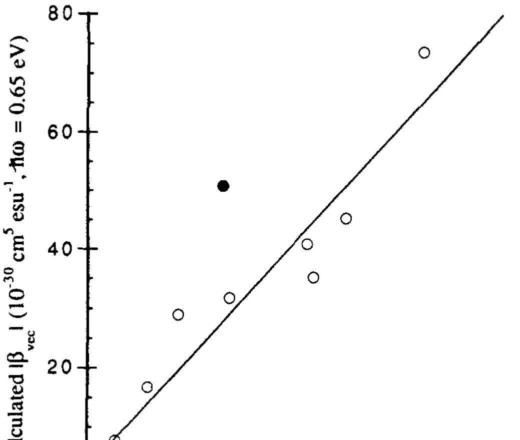


Figure 1. Plot of organometallic chromophore β_{vec} values calculated by the present ZINDO model versus experimental values from ref 3a; $\hbar\omega$ = 0.65 eV. The solid line is a least-squares fit to the data points and is drawn as a guide to the eye. The anomalously small β_{vec}^{exp} noted for chromophore **6** (filled circle) is thought to arise from nonplanarity in the stilbene part of the molecule (see footnote 18).

The ZINDO (INDO/S) electronic structure formalism[9,10] provides an accurate depiction of *linear* optical phenomena for

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both organic and metal–organic chromophores.[11] Moreover, when implemented within the framework of a sum-over-states perturbation theoretic description of microscopic polarizability,[5-7,12] we recently showed ZINDO to reproduce accurately experimental organic π-electron β parameters ranging over 3 orders of magnitude.[13] The present β_{ijk} calculations focused on several diverse types of transition-metal organometallic molecules for which solution-phase β_{vec}[14] values have been determined by using dc electric field induced second harmonic generation (EFISH) techniques.[3] Metrical parameters were taken from relevant crystal structure data,[2,15] and the basis set of configuration interaction states included 130 monoexcited states (at which point convergence was observed in all cases). Standard ZINDO transition-metal parameters[9a,b,11] were employed,[16] and the sum-over-states MECI (monoexcited configuration interaction) method was used to compute β_{ijk}.[5-7]

ZINDO-derived β_{vec}[14] and β_{tot}[17] values are compiled and compared to experimental data in Table I and Figure 1 for the three classes of organometallic chromophores. Considering experimental uncertainties and the wide diversity of complex molecular structures[18] and substituents involved, as well as the large dispersion in the magnitudes and signs of β_{vec}, the overall agreement with experiment is generally good in terms of orderings, signs, and magnitudes. For molecules **1–7**, we calculate that the ferrocenyl unit behaves as a simple π–donor substituent with β_{vec} in **2** dominated by a single charge-transfer state (MLCT + LLCT) involving the redistribution of 0.4 electrons from the ferrocenyl moiety to the nitro (acceptor) substituent. This transition is calculated to have an oscillator strength of 0.98, a dipole moment change ($\Delta\mu_{ge}$) of 11.0 D, and λ_{max} = 378 nm (observed λ_{max} = 356 nm in dioxane solution[3a]). Metal d–d transitions contribute little to β_{vec}, and the dominant excitation direction closely parallels the dipole moment vector ($\beta_{vec} \approx \beta_{tot}$). Not surprisingly, substituents that enhance the ferrocenyl donor character (**4**, **5**) enhance β_{vec}. In sum, the electronic structural origin of the second-order nonlinearity in **1–7** closely parallels that of the analogous stilbene chromophores.[5a,6c,19]

The ZINDO results for **8–12** reveal that the ground-state dipole moments are antiparallel to those in the excited states which dominate β_{vec}. This convincingly explains the observed negative signs of β_{vec} and arises here because pyridine functions as the strongest σ-donor ligand in the ground state and as the strongest π-acceptor in the relevant excited states. In a simple two-level picture,[1f,20] the modest β_{vec} values observed arise because the dominant states do not involve large $\Delta\mu_{ge}$ values, primarily because tungsten is effectively in an electronically pseudocentrosymmetric environment, surrounded by ligands having unfavorably similar donor/acceptor character. The calculations reveal an analogous situation for **13–18** with the effective electronic pseudocentrosymmetry again leading to undesirable, β-lowering competition between π-acceptors in the various contributing states.

These results indicate that a useful quantum chemical formalism is now available for understanding the quadratic NLO properties of known metal–organic chromophores as well as for aiding in the design of new ones. The richness of mechanisms operative in such chromophores includes both β_{vec}-enhancing charge-transfer processes across the length of the molecule as well as β_{vec}-limiting competition among π-acceptor ligands in coordination spheres having effective electronic centrosymmetry.

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(14) For $i = x, y$, or z,

$$\beta_i = \beta_{iii} + \frac{1}{3}\sum_{j \neq i}(\beta_{jii} + \beta_{iji} + \beta_{iij})$$

$$\beta_{vec}(-2\omega;\omega,\omega) = \sum_{i=1}^{3}\frac{\mu_i\beta_i}{|\mu|}$$

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(17) $\beta_{tot} = (\beta_1^2 + \beta_2^2 + \beta_3^2)^{1/2}$

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Racemization and Geometrical Isomerization of (−)-(*R*,*R*)-Cyclopropane-*1,2*-$^2H_2$

Steven J. Cianciosi, N. Ragunathan, Teresa B. Freedman,*
Laurence A. Nafie,* and John E. Baldwin*

Department of Chemistry, Syracuse University
Syracuse, New York 13244

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Since the thermal interconversion of *cis*- and *trans*-cyclopropane-*1,2*-$^2H_2$ was discovered more than 30 years ago,[1] theoretical and experimental studies have been attracted to different instances of this process.[2] Most of the sophisticated theoretical work has considered only cyclopropane and related trimethylene diradical species,[3] while experimental efforts have been largely directed toward cyclopropanes substituted with various functional

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