PAPER www.rsc.org/njc | New Journal of Chemistry

The effect of the conformation on the quadratic nonlinear optical response of metal carbonyl based chromophores with one-dimensional charge transfer capabilities: a computational investigation

Jean-François Lamère,[a] Isabelle Sasaki,[a] Pascal G. Lacroix*[a] and Keitaro Nakatani[b]

Received (in Montpellier, France) 27th January 2006, Accepted 23rd March 2006
First published as an Advance Article on the web 10th April 2006
DOI: 10.1039/b601315e

The synthesis and the quadratic nonlinear optical (NLO) properties of (4-(4′-dimethylaminophenyl)pyridine)chromium and tungsten pentacarbonyl are reported. Experimentally, the chromophores exhibit molecular hyperpolarizabilities (β) equal to 15.5 and 21.7×10^{-30} cm^5 esu^{-1}, respectively at 1.064 μm, which arise from a charge transfer capability along the molecular C_2 symmetry axis, in relation to the π-conjugated structure of the ligand. At a more fundamental level, these molecules have been investigated as possible synthetic targets to illustrate the ZINDO prediction that, in chromophores with one-dimensional charge transfer capabilities a specific set of substituents could be found to switch the β direction, on passing from a ground state geometry with co-planar aromatic rings to a conformation in which the rings are perpendicular. Due to the C_2 symmetry requirement, this situation implies that β is necessarily vanishing for a specific conformation. The possibilities to observe experimentally and to use this intriguing effect in a perspective of a molecular switch are critically evaluated.

Introduction

The concept of molecular switches is currently attracting a growing interest from a variety of perspectives,[1,2] and could lead to a family of derivatives with intriguing applications in biology, electronic, and photonic technologies. For instance, molecules with nonlinear optical (NLO) properties have led to a multidisciplinary research area of great importance for the emerging optoelectronics and photonic technologies relevant to all optical computing applications.[3] Furthermore, the inherent tailorability of molecular compounds renders them ideally suited for the creation of materials possessing switchable properties.

Nevertheless, the possibilities for achieving a switch in the quadratic ($\propto E^2$) NLO response has become considered only recently.[4] Most chromophores are built up from three basic components: (i) an electron rich substituent connected, through (ii) a π-electron bridge, to (iii) an electron acceptor counterpart, leading to charge delocalization by resonance. Therefore, switching the NLO response has been achieved either by changing the donating[5] or accepting[6] strength of the substituents or by changing the conjugated capabilities[7] of the bridge. In all instances, the (on → off) switch invariably arises from a reduction of the magnitude of the quadratic hyperpolarizability, defined from the molecular polarization as follows:[8]

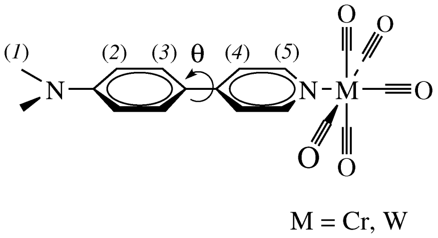
$$\mu_i(E) = \mu_{0i} + \alpha_{ij}E_j + \beta_{ijk}E_jE_k + \ldots \qquad (1)$$

In this equation, μ_0 is the permanent dipole moment, α is the polarizability, and β the quadratic hyperpolarizability, responsible for the NLO properties. Up to now, the most convincing NLO switch seems to be the report by Coe *et al.* that β is 10 to 20 times reduced by oxidation of a ruthenium(II) complex.[5a] Nevertheless, the ultimate molecular NLO switch implies that, in the off-state, a strict cancellation of the β tensor must be achieved on a single entity.

In the present contribution, we wish to report on a computational approach towards this intriguing situation, within the framework of the proven ZINDO/SOS formalism (*vide infra*). In previous studies, we have provided evidences for the possibility of an absolute switch obtained by 90° β rotation achieved upon protonation.[9] However, this idea is based on the assumption that β is a vector in order for the on-state (β parallel to the electric field of the light), to be turned into an off-state after rotation (β orthogonal with respect to the field). In fact, the hyperpolarizability defined in eqn (1) is a third-rank tensor, with 27 components. Except for molecules having pure one-dimensional charge transfer character, in which $\beta \equiv \beta_{zzz}$ along the OZ charge transfer direction, the contribution of off-diagonal tensor components (β_{ijk}) may have to be taken into account, for instance in the case of the promising octupolar geometries (*e.g.* T_d, D_{3h}, D_{2d}).[10] By contrast, we focus here on a situation in which single charge transfer axis and symmetry requirement lead to the assumption that $\beta \equiv \beta_{zzz}$ is valid. The methodology employed for the selection of a suitable chromophore will be presented first. Then, the possibility of perfect β cancellation by mean of intramolecular rotation will be discussed for (4-(4′-aminophenyl)pyridine)chromium pentacarbonyl. To illustrate this computational approach, a chromium and a tungsten analogue will be

---

[a] *Laboratoire de Chimie de Coordination du CNRS (UPR 8241), 205 route de Narbonne, 31077 Toulouse, France. E-mail: pascal@lcc-toulouse.fr; Fax: +33 5 61 55 30 03*
[b] *PPSM, Ecole Normale Supérieure de Cachan (UMR 8531), 61 Avenue du Pdt Wilson, 94235 Cachan, France*



Scheme 1

presented and their NLO properties will be reported (Scheme 1). In the last section, and in a perspective of material science, the possibility to observe a β cancellation in a real molecular device will be critically evaluated.

Results and discussion

Selection of candidates

In order to ensure the one-dimensional topology required for the design of chromophores in which β is a pure vector, the investigations have been restricted to molecules built up from the general skeleton **1**, depicted in Scheme 2. In this picture, R_1 and R_2 are donor or acceptor substituents, and θ is the angle between the two aromatic rings. R_1 and R_2 are chosen (*e.g.* $-NO_2$ and $-NH_2$ in compound **2**) in order for the molecule to possess a two-fold symmetry axis in its ground state. This topology is made necessary to ensure that the symmetry axis is maintained for any θ rotation, which leads to the following electronic features: (i) the β magnitude is θ dependent, for a given set of R_1 (donor) and R_2 (acceptor), but (ii) the charge transfer direction (and hence β) stays strictly parallel to the axis whatever the θ value. It can be anticipated that the situation with $\theta = 0°$ will be that allowing the best charge delocalization within the bridge (highest β value), while $\theta = 90°$ will result in a poor orbital overlap (reduced β value). Nevertheless, the overall R_1 to R_2 charge transfer process will stay qualitatively the same, a reverse R_2 to R_1 charge transfer being not possible, owing to the intrinsic electronic capabilities of the substituents. In other words, the β magnitude can change, but not its sign. This situation is exemplified in Fig. 1 for 4-(4′-nitrophenyl)aniline (**2**, Scheme 2), where the calculation indicates a β reduction from 52.8 to 11.6 × 10^{-30} cm^5 esu^{-1}, the sign being not affected by the rotation.

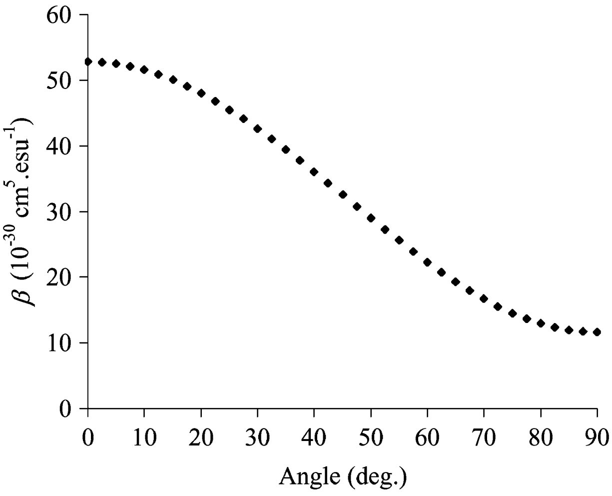
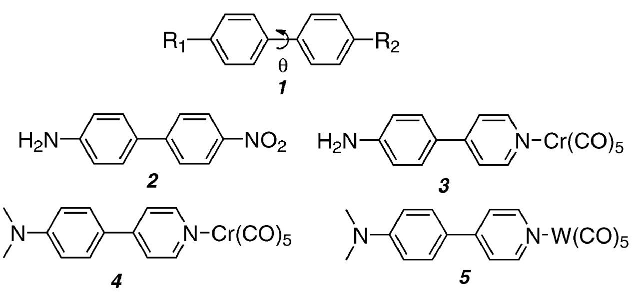


Fig. 1 ZINDO calculated hyperpolarizabilties for compound **2**, as a function of the θ rotation along the molecular C_2 symmetry axis (defined in Scheme 1).



Scheme 2

At this point, it must be emphasized that, if this limitation could be over-passed, changing the β sign between $\theta = 0$ and 90° would necessarily imply that β is strictly vanishing for a specific angular value. However, this situation being hardly expectable within the standard "push–pull" model illustrated by the archetypical structure **2**, we have been screened sets of R_1/R_2 substituents of different natures (organic *vs.* inorganic and organometallic) and non-traditional electronic capabilities. For instance, $(CO)_5Cr-$ or $(H_3N)_5Ru^{II}-$ become intriguing fragments once combined to a pyridine ligand. While electron-rich metal complexes of substituted pyridines have long been reported to possess intense d → π* back-donation transitions,[11] it has also been observed that the weak acceptor pyridine unit has the capability to be turned into a strong one after metal complexation, thus providing the enhancement of a potential intraligand π → π* charge transfer, when a donor substituent is present in *para* position of the pyridine ring.[12–16] These two processes might compete in the overall electronic response of the complex, each of them becoming dominant for different θ ranges, with the outcome of the overall NLO response being gradually tuned from positive to negative values, as a function of the conformation. Finally, and after various computational screenings, the chromium complexes **3** (Scheme 2) was found to be the one having the most intriguing NLO behavior. The origin of its unexpected properties will therefore be thoroughly discussed in the next section, in relation to those of the parent molecular structures **4** and **5** (Scheme 2).

ZINDO investigation of the angular dependence of *β*

The calculated hyperpolarizabilities at $\theta = 0$ and 90° are gathered in Table 1, for molecules **2**, **3** and **4** (the dimethylamino-analogue of molecule **3**). In the ground state ($\theta = 0°$), the β values are positive and equal to 5.8 and 12.8 × 10^{-30} cm^5 esu^{-1}, for **3** and **4**, respectively. This situation indicates that, in **3** and **4**, the overall effect is that of a charge transfer directed from the aniline to the pyridine, contrary to most $(CO)_5Cr-$ and $(CO)_5W-$ based molecules investigated in the literature, in which β is negative (d → π* charge transfer).[13,15]

The most striking result in Table 1 is the negative β value calculated at 90° for compound **3**, which suggests the

Table 1 Quadratic hyperpolarizabilities (β in 10^{-30} cm^5 esu^{-1}) at 1.064 μm, for **2**, **3** and **4**, as calculated by ZINDO for different conformations

	$\theta = 0°$	$\theta = 90°$
2	52.8	11.6
3	5.8	−1.6
4	12.8	1.3

possibility of β cancellation upon θ rotation, as anticipated from the C_2 symmetry. The angular dependence of β is shown more precisely in Fig. 2. As θ increases, the β magnitude is gradually reduced, as previously calculated in **2**. Nevertheless, and in striking contrast *vs.* **2**, the reduction is such in the chromium complex **3** that β is strictly zero at a θ value equal to 63°, then becomes negative.

In order to provide an analysis for the microscopic origin of the NLO response in the present derivatives, it has to be reminded that within the framework of the sum over state (SOS) perturbation theory, β is ultimately related to all electronic transitions of a molecule.[17] Nevertheless, there is a single transition in most cases with low energy (E), large intensity (oscillator strength, f), and large charge transfer capability (dipole moment change, $\Delta\mu$), which significantly contributes to the NLO effect, according to the widely used "two-level" description of β, according to the following relation:[18,19]

$$\beta = \frac{3e^2\hbar f\Delta\mu}{2mE^3}\frac{E^4}{(E^2-(2\hbar\omega)^2)(E^2-(\hbar\omega)^2)} \tag{2}$$

Table 2 ZINDO spectrum calculated at $\theta = 0°$, with absorption maximum ($\lambda_{\max}$), oscillator strengths (f), change in dipole moment upon transitions ($\Delta\mu$ in D), and composition of the dominant excited states involved in the NLO response of **2**

Transition	$\lambda_{\max}$/nm	f	$\Delta\mu$/D	State[a] (%)	Composition of CI expansion[a]
1 → 4	347	0.76	18.0	0.79	$0.910\ \chi_{40\rightarrow41}$
1 → 7	266	0.25	9.3	0.04	$-0.896\ \chi_{40\rightarrow42}$ $+\ 0.344\ \chi_{37\rightarrow41}$

[a] Orbital 40 is the HOMO and 41 the LUMO.

In this equation, $\hbar\omega$ is the energy of the incident laser beam. The benchmark reference compound **2** provides a perfect illustration of this model (Table 2), with a calculated spectrum strongly dominated by a single intense low-lying 1 → 4 transition having large charge transfer capability ($\Delta\mu$ = 18.0 D). It is therefore readily assumed that this transition accounts for the qualitative understanding of the NLO response. 83% of the transition (0.910^2 in Table 2) is described as the HOMO (aniline-based) → LUMO (nitrophenyl-based) excitation, which fully agrees with the chemical intuition. The charge transfers associated to this dominant 1 → 4 transition is shown in Fig. 3. In this respect, molecule **2** behaves as a traditional NLO chromophore.

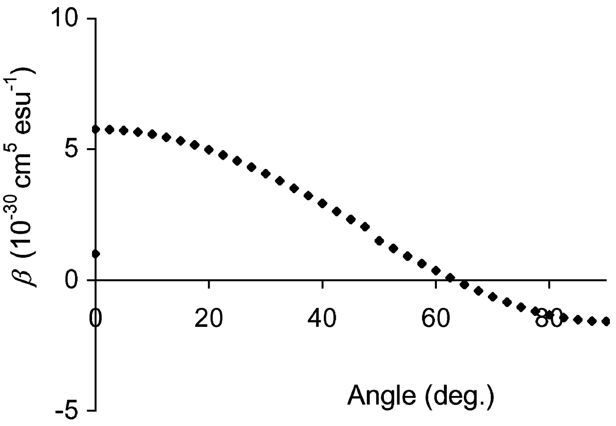


Fig. 2 ZINDO calculated hyperpolarizabilties for **3**, as a function of the θ rotation along the molecular C_2 symmetry axis.

The situation encountered in the chromium complex **3** is more difficult to rationalize. In this case, the calculated spectrum reveals that many transitions exhibit a potential NLO effect ($\propto f\Delta\mu/E^3$), according to eqn. (2). Furthermore, and in striking contrast to **2**, the calculation indicates two types of transitions in complex **3** (Table 3): (i) transitions exhibiting charge transfers from the aniline to the (CO)$_5$Cr–pyridine fragment ($\Delta\mu > 0$), and transitions with charge transfers in the reverse (chromium to aniline, $\Delta\mu < 0$) direction (ii). Owing to the β sign, the first group (i) is dominant, and contains most of the electronic transitions of the molecule. Interestingly, all of them involve charge transfers through the C–C ring connection. The effect of θ rotation is likely to perturbate these charge transfers, and finally to decrease their overall contribution to the optical nonlinearity. The second group (ii) is roughly restricted to the 1 → 5 (HOMO → LUMO based) transition, which involves an intense charge transfer from the chromium atom to the pyridine, with almost no contribution of the aniline fragment, as shown in Fig. 4. In contrast to the previous transitions (i), 1 → 5 is very slightly affected by the θ rotation and its contribution may become dominant at large θ value, thus providing a qualitative illustration for the change occurring in the overall charge transfer properties. Owing to the complexity of the NLO response in metal carbonyl chromophores,[13] the present description may be somewhat over simplified. Nevertheless, it provides a simple and coherent rationale to qualitatively account for the intriguing behavior of complex **3**.

Finally, the NLO behavior of chromium derivative **4** appears to be intermediate between those of **2** and **3**. Although the dimethylamino-fragment is only slightly more donor than the amino-fragment, the calculations indicate a two times enhancement of the β value (from 5.8 to 12.8 × 10^{-30} cm^5 esu^{-1}) between **3** and **4**. The relatively small β value for **3**

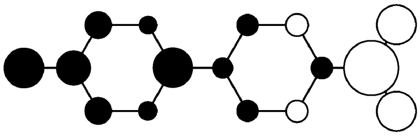


Fig. 3 Difference in electronic population between ground and excited states in the dominant transitions responsible for the NLO effect in chromophore **2**, calculated with θ = 0. The white (black) contribution is indicative of an increase (decrease) in electron density in the charge transfer process.

Table 3 Description of the low-energy (λ_{max}) ZINDO calculated transitions of **4**, with large oscillator strength (*f*), and large charge transfer ($\Delta\mu$) character, in the conformation in which $\theta = 0°$

Transition	λ_{max}/nm	$\Delta\mu$/D	Weight[a]	Composition[b]	Charge transfer character
1 → 5	305	−9.8	1	94% (60 → 61)	$(OC)_5Cr$ → pyridine
1 → 30	195	+6.7	0.4	28% (58 → 64)	$(OC)_5Cr$ → $(OC)_5Cr$
				23% (58 → 67)	$(OC)_5Cr$ → $(OC)_5Cr$
				22% (60 → 63)	Aniline → $(OC)_5Cr$
				21% (60 → 65)	Aniline → $(OC)_5Cr$
1 → 40	180	+30.8	0.25	81% (57 → 65)	Aniline → $(OC)_5Cr$
1 → 36	184	+30.3	0.2	75% (57 → 63)	Aniline → $(OC)_5Cr$
1 → 17	267	+7.4	0.1	86% (57 → 61)	Aniline → pyridine

[a] Calculated with eqn. (2). A reference value of 1 is assigned to transition 1 → 5. [b] Orbital 60 is the HOMO and 61 the LUMO.

suggests that $–NH_2$ and $–Cr(CO)_5$ exhibit rather comparable donating capabilities. The larger difference ($–NMe_2$ *vs.* $–Cr(CO)_5$) encountered in complex **4** is such that the rotation lowers but cannot remove the dominant aniline to pyridine charge transfer effect (Table 1). Along this line, the overall behavior of complex **4** is qualitatively similar to that of the organic chromophore **2**.

In order to illustrate the present approach, and to test the accuracy of the computational prediction, the model compounds **4** and **5** (tungsten homologue of **4**) have been synthesised, and the NLO response evaluated.

Experimental investigation on the model compounds (4-(4′-dimethylaminophenyl)pyridine)chromium and -tungsten pentacarbonyl

Various $M(CO)_5$ pyridine (M = Cr,[20] Mo[21] and W[22]) derivatives have been reported in the literature. We have selected here a chromium complex, and the tungsten homologue, which are generally closely related derivatives, however with a better stability in the case of tungsten,[23] while chromium carbonyls are potentially explosive compounds and are also carcinogenic.[24] Although ZINDO parameters are not available for tungsten, the computational predictions made on $Cr(CO)_5$-based derivatives might qualitatively be used to describe the electronic features of tungsten analogues as well.[13]

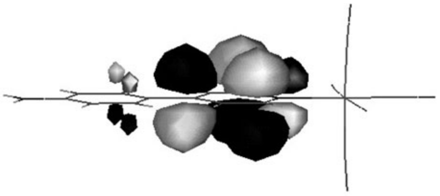
The calculated β value is extremely modest in complex **3** (5.8×10^{-30} cm^5 esu^{-1}), and falls close to the limit range of the detection of the EFISH equipment (*vide infra*). We have therefore tested the quality of the NLO computation on complex **4** (the hyperpolarizability of which is expected to be larger), and on its tungsten homologue **5**. Additionally, the synthesis of 4-(4′-dimethylaminophenyl)pyridine is more simple, compared to that of the aminophenyl homologue, which requires a four-step synthetic procedure and expensive reagents.[25]

The model chromophores were synthesized using conventional photochemical methodology:[15,23,26,27]

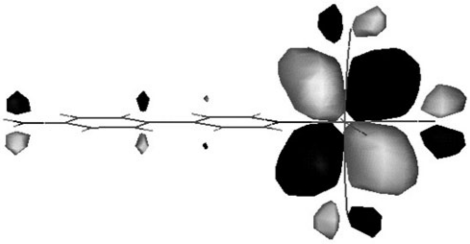
$$M(CO)_6 \xrightarrow[THF]{h\nu} M(CO)_5(THF) + CO \qquad (3)$$

$$M(CO)_5(THF) + L \rightarrow M(CO)_5L + THF \qquad (4)$$

The electronic spectrum of complex **4** is shown in Fig. 5, and compared to the ZINDO calculated data available in Table 4. The experimental spectrum is dominated by an intense and low lying transition having an absorption maximum (λ_{max})



LUMO (61)



HOMO (60)

Fig. 4 Orbitals (HOMO and LUMO) involved in the 1 → 5 transition of complex **3**, which indicates that the aniline fragment is not involved in the charge transfer process.

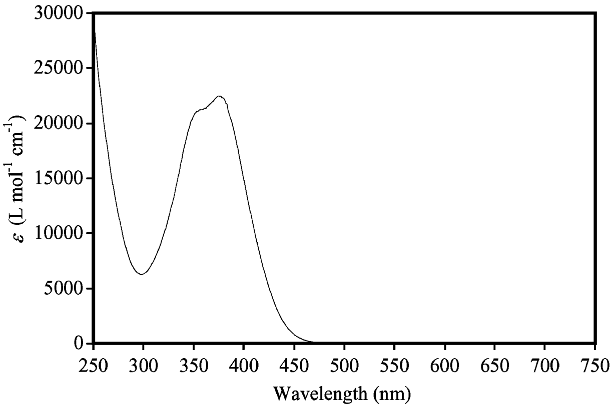


Fig. 5 UV-visible optical absorption spectrum of complex **4**, recorded in dioxane.

Table 4 Comparison of the experimental and ZINDO calculated spectra (λ_{max}, f and ε) of **4**

UV-Vis in dioxane		ZINDO data	
λ_{max}/nm	ε/mol^{-1} L cm^{-1}	λ_{max}/nm	f
374	22 500	305	0.66
~350 (sh)	20 700	267	0.27

located at 374 nm (ε = 22 500 L mol^{-1} cm^{-1}). An additional, but less intense transition is visible as a shoulder around 350 nm. The comparison between experimental and calculated spectra (Table 4) indicates that the experimental UV-visible spectra are slightly red shifted, *vs.* the computational data. Nevertheless, the agreement appears satisfactory and ensure the reliability of the ZINDO analysis for the description of the NLO response of these metal carbonyl derivatives.

Before reporting the experimental NLO properties, the issue of the molecular stability has to be addressed. Although **3** and **4** exhibit modest thermal stabilities (T_d = 135 and 159 °C, respectively), they are stable at room temperature in the solid state, but decompose after only a few minutes in aerobic solution. However, a stability of several days was observed under argon, which was therefore sufficient to envision the measurement of the NLO response by the EFISH technique.

The quadratic hyperpolarizabilities measured under argon atmosphere by the Electric Field Second Harmonic (EFISH) technique[18,28] are shown in Table 5 and compared to the computational values available. First of all, it is observed that all the β values are positive, which confirms that the overall effect is that of a resulting charge transfer from the aniline to the pyridine–M(CO)$_5$ fragments. The data indicates that the agreement is satisfactory between experimental (15.5 × 10^{-30} cm^5 esu^{-1}) and calculated (12.8 × 10^{-30} cm^5 esu^{-1}) β values in the case of **4**, which suggests that the ZINDO prediction is valid for this class of molecules. Interestingly, a larger experimental β value of 21.7 × 10^{-30} cm^5 esu^{-1} is obtained for the tungsten derivative. Although no ZINDO data are available in this case, one may tentatively relate this difference to the well known trend for larger ligand field splitting parameter (Δ) on going down a group (*e.g.* Cr, Mo, W).[29] In the present d^6 configuration, it leads to a reduced donating capability of the tungsten, and finally to a slight enhancement of the overall aniline → pyridine charge transfer effect, in complete agreement with previously reported observations.[13,30]

These sizeable modulations achieved on passing from chromium to tungsten and from amino- to a dimethylamino-substituent may appear somewhat surprising. On the other hand, it seems to indicate that the situation encountered in the chromium derivative **3** is close to balance in terms of relative donor/acceptor electronic capabilities between –NH$_2$ and –Cr(CO)$_5$, in agreement with a calculated β value of 5.8 × 10^{-30} cm^5 esu^{-1} at 1.064 μm, an unusually small value for a molecule of such a large size.[31] Indeed, the donating strengths are probably increased in –NMe$_2$ and reduced in –W(CO)$_5$, thus restoring an observable push–pull character to **5**, and hence an experimental hyperpolarizability of 21.7 × 10^{-30} cm^5 esu^{-1}.

Table 5 Experimental (EFISH) and calculated (ZINDO) hyperpolarizabilities (β) for compounds **4** and **5**. The laser wavelength is equal to 1.064 μm

Compound	$10^{30}\beta_{EFISH}$/cm^5 esu^{-1}	$10^{30}\beta_{ZINDO}$/cm^5 esu^{-1}
4	15.5	12.8
5	21.7	N.a.

Critical evaluation for an experimental observation of the β cancellation

In the past two decades, theoretical computational quantum chemistry procedures have profoundly changed the science of chromophore design. In the context of nonlinear optics, the fruitful SOS perturbation theory has successfully been applied to describe the NLO response of many organic and metal organic chromophores. To make progress today, synthetic chemists and experimentalists must apply their chemical intuition in concert with insights provided by computational chemistry to effectively guide synthetic strategies.

Nevertheless, and in a perspective of material science, the issue of how to verify experimentally that the predicted β cancellation by molecular rotation in **3** is real must necessarily be addressed, with the underlying issue of how to monitor the conformational change to tune the NLO response in an operating device. For instance, temperature-dependent β measurements could be performed to test the influence of Boltzmann energy on a population of molecules. In a simplified description, with the assumption that β is restricted to a ground state ($\beta_{//}$) and an excited state ($\beta_{\perp}$) value, the relative averaged β value ($\beta/\beta_{\parallel}$) is expressed as:

$$\frac{\beta}{\beta_{//}} = \frac{1 + \frac{\beta_{\perp}}{\beta_{//}}\exp\left(\frac{-E_g}{0.002T}\right)}{1 + \exp\left(\frac{-E_g}{0.002T}\right)} \quad (5)$$

expression in which E_g is the energy barrier (in kcal) for the θ rotation, the Boltzmann constant being equal to 0.002 kcal mol^{-1} K^{-1}. The possibility for vanishing averaged β value at 300 K would therefore imply the following relation:

$$\beta_{\perp}/\beta_{\parallel} = -\exp(E_g/0.6) \quad (6)$$

This situation is depicted in Fig. 6 as a function of the energy barrier. The energy barrier calculated in **3** is equal to 1.4 kcal, a value which is far too small to lead to a real convincing switch according to the Figure. Nevertheless, this simplified picture suggests that temperature dependent nonlinear optics, which up to now has not attracted much attention, may deserve some interest in the future.

The ultimate and most elegant observation would require the measurements to be performed on a single molecule, pined in a specific conformation. Single-molecule nonlinear optics has occasionally been reported.[32] Nevertheless, although considerable progresses have been achieved, such experiments are restricted to chromophores associated with extremely large β values, and this possibility remains a dream in the present case. A more realistic (but indirect) approach could be envisioned on the basis of single-molecule conductance measurements, following the suggestion by Aviram and Ratner, that a donor–acceptor chromophore should behave as a diode, when placed between two electrodes.[33] These last few years, the

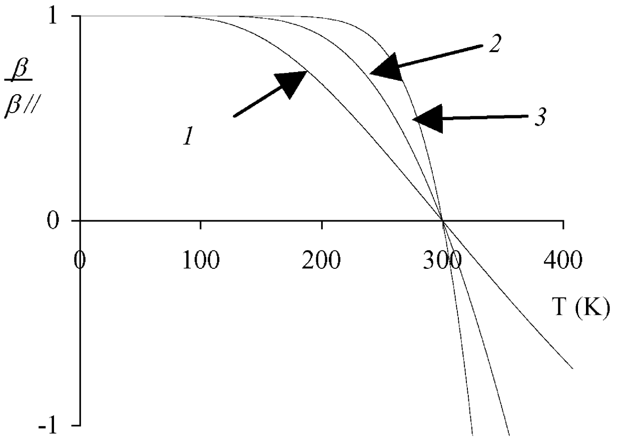


Fig. 6 Temperature dependence of the averaged β value (expressed as $\beta/\beta_{\parallel}$), assuming θ rotation barriers of 1.4 (*1*), 2.8 (*2*) and 5.6 (*3*) kcal mol^{-1}.

study of electron transport within a single molecule has been achieved experimentally using scanning tunneling microscopy (STM).[34] In the case of chromophores such as **3**, one could expect that the linear current–voltage characteristics measured as a function of the θ rotation could indicate the possibility for a reverse overall charge transfer behavior.

The possibility for the control of molecular conformation remains a fundamental issue. By definition, a switch is a device, in which two stable states can be obtained upon an external perturbation. This is not the case in **3**, where the "off" state actually corresponds to an excited conformation rather than a stable state. One might therefore wonder how the θ rotation could be reversibly tuned for a practical use in an operating molecular device. Certainly, using intramolecular motion has become a fascinating issue of contemporary research, for instance in relation to the concept of molecular machines.[35] To make such a device work, various strategies could be considered to supply energy in some way (*via* chemical, photochemical or electrochemical reactions).[36] In the present case, the motion being an oscillation instead of a rotation, no external energy would have to be supplied, but a simple stimulus could be envisioned (*e.g.* an electric field pulse). Reversible controls of these motions would probably be extremely difficult to achieve in an operative device. Nevertheless, Nature has provided many examples of molecular motions occurring in hundreds of different biological molecular machines, each of them specialized for a particular function.[37] This seems not accessible for our generation of scientists, but there is no reason to think that molecular engineering will never be able to reach this goal.

Conclusion

In a computational (ZINDO) approach, we have found that metal carbonyl-based chromophores are intriguing molecules, in which a single intramolecular rotation has the potential to lead to a strict β cancellation. This unusual feature likely results from the perfect adjustment of the charge transfer capabilities of the substituents, modulated by the molecular rotation. To illustrate the synthetic feasibility of such systems, and to test the accuracy of the ZINDO prediction, two (chromium and tungsten) derivatives built up from a related ligand have been characterized. A set of experimental and computational data suggests that an adjustment of the donating strength can be achieved between $-NH_2$ and $-Cr(CO)_5$, for a conformation, in which the aromatic rings are twisted by a specific angle, found to be equal to 63° in the semi-empirical analysis.

In a perspective of material science, the chromophores would require additional chemical or physical capabilities, to allow the conformation to be tuned by a suitable stimulus (*e.g.* proton transfer or pulse of electric field). Along this line, complex **3** is certainly not the most promising candidate. Nevertheless, the present investigation suggests that molecules with low NLO responses or modest air- and thermal stabilities might be revisited in some cases, as intriguing chromophores with non-traditional NLO capabilities.

Experimental

Starting materials and equipment

Chromium and tungsten hexacarbonyl (Strem Chemicals) were used as purchased. High-grade solvents (THF, dioxane) were used for the syntheses and EFISH measurements. THF was distilled on Na/benzophenone. Pentane and dichloromethane were distilled prior to use. 4-(4′-Dimethylaminophenyl)pyridine was synthesized following the procedure previously reported.[38] All synthetic operations and measurements involving chromium and tungsten carbonyl derivatives were carried out with exclusion of oxygen, using standard Schlenk techniques. The UV-visible spectra were recorded on a Hewlett Packard 8452A spectrophotometer. ^1H NMR spectra were acquired at 250.13 MHz on a Bruker WM250 spectrometer. The atom labelling used for the assignment is given in Scheme 1. Elemental analyses were carried out at the Laboratoire de Chimie de Coordination in Toulouse, for C, H and N. Thermal measurements were performed by TG/DTA analysis on a Setaram-TGDTA92 thermoanalyser. The experiments were conducted under nitrogen on 5 mg of sample (rate of heating 10 °C min^{-1}). The decomposition temperature (T_d) was assigned as the intercept of the leading edge of the decomposition endotherm with the base line of the DTA scan.

Syntheses

(4-(4′-Dimethylaminophenyl)pyridine)chromium pentacarbonyl. Under a nitrogen atmosphere $Cr(CO)_6$ (220 mg, 10^{-3} mol) was photolyzed for 2 h in 150 mL of freshly distilled THF, using a Pyrex-filtered high-pressure Hg lamp. The resulting yellow $Cr(CO)_5(THF)$ solution was then transferred by cannula to a stirring solution of 4-(4′-dimethylaminophenyl)pyridine (198 mg, 10^{-3} mol) in 100 mL of freshly distilled THF. The resulting solution was stirred at room temperature for 1.5 h, then evaporated to dryness *in vacuo*. The crude product was then purified by chromatography on silica, eluting with 1 : 1 pentane–CH_2Cl_2. Yield: 230 mg (59%) of light yellow material. Anal. Found: C, 55.23; H, 3.38; N, 6.93. Calc. for $C_{18}CrH_{14}N_2O_5$: C, 55.39; H. 3.62; N, 7.19%. T_d = 138 °C. ^1H NMR ($CDCl_3$) for 4-(4′-dimethylaminophenyl)pyridine: δ

3.026 (s, 6H, H(*1*)), 6.784 (d, J = 6.9 Hz, 2H, H(*2*)), 7.497 (d, J = 6.3 Hz, 2H, H(*4*)), 7.586 (d, J = 6.9 Hz, 2H, H(*3*)), 8.541 (d, J = 6.3 Hz, 2H, H(*5*)). For (4-(4′-dimethylaminophenyl)pyridine)chromium pentacarbonyl: 3.035 (s, 6H, H(*1*)), 6.774 (d, J = 8.1 Hz, 2H, H(*2*)), 7.343 (d, J = 4.8 Hz, 2H, H(*4*)), 7.534 (d, J = 8.3 Hz, 2H, H(*3*)), 8.423 (d, J = 5.0 Hz, 2H, H(*5*)).

(4-(4′-Dimethylaminophenyl)pyridine)tungsten pentacarbonyl. The compound was obtained by the same procedure starting from $W(CO)_6$ (352 mg, 10^{-3} mol) instead of $Cr(CO)_6$. Yield: 318 mg (61%) of light yellow material. Anal. Found: C, 41.28; H, 2.40; N, 5.21. Calc. for $C_{18}H_{14}N_2O_5W$: C, 41.40; H. 2.70; N, 5.36%. T_d = 146 °C. ^{1}H NMR ($CDCl_3$): δ 3.052 (s, 6H, H(*1*)), 6.807 (d, J = 8.9 Hz, 2H, H(*2*)), 7.387 (d, J = 6.2 Hz, 2H, H(*4*)), 7.575 (d, J = 8.9 Hz, 2H, H(*3*)), 8.661 (d, J = 6.1 Hz, 2H, H(*5*)).

Computational methods

The molecular geometry used for the calculations of 4-(4′-nitrophenyl)aniline (**2**) was that reported in the literature.[39] For (4-(4′-aminophenyl)pyridine)chromium pentacarbonyl (**3**), the geometry was built up from those of $(CO)_5Cr$–pyridine,[40] and 4-phenylpyridine,[41] for which crystal structures have previously been reported. The bond lengths were fixed at their crystallographic value and the effect of molecular rotation was studied by steps of 2.5°. The all-valence INDO (intermediate neglect of differential overlap) method,[42] was employed for the calculation of the energy of the chromophores in various conformations. The "gas-phase" geometry of **3** was investigated first around the metal atom. The stable conformation was found to be that having two carbonyls eclipsed with respect to the pyridine ring, while the staggered conformation (angle of 45°) was found to be destabilized by about 3.3 kcal mol^{-1}. Although the "solid state" geometry available reveals an apparent trend for the staggered conformation between the pyridine and the CO units, reduced torsion angles (angle $<20°$) are also observed.[43–45] The eclipsed conformation was therefore preferred for the consistency of the INDO method, and any further calculations were performed with this geometry.

In a next step, INDO was employed in connection with the sum over state (SOS) formalism[17] for the calculation of the electronic spectra and the molecular hyperpolarizabilities, as a function of the θ rotation between the two aromatic rings (*vide infra*). The energy barrier was found to be equal to 1.4 kcal mol^{-1}, which confirms that this rotation is that to be considered as the basic molecular motion away from the planar ground state conformation. The NLO response of (4-(4′-dimethylaminophenyl)pyridine)chromium pentacarbonyl (**4**) was carried out similarly.

The laser wavelength used for the calculation was 1.064 μm. Details of the computationally efficient INDO-SOS-based method for describing the quadratic molecular optical nonlinearities have been reported elsewhere.[17] In the present approach, the mono-excited configuration interaction (CIS) approximation was employed to describe the excited states. The lowest 100 energy transitions were chosen to undergo CI mixing. All calculations were performed using the INDO/1 Hamiltonian incorporated in the commercially available software package ZINDO.[46] Tungsten being not parametrized by ZINDO, no calculation was performed on compound **5**.

NLO Measurements

The electric field induced second harmonic (EFISH) technique was employed for the β measurements. The principle of the EFISH technique is reported elsewhere.[28] The data were recorded using a nanosecond Nd-YAG pulsed (10 Hz) laser operating at λ = 1.064 μm. The concentrations were around 2×10^{-3} mol L^{-1}. The samples were dissolved under nitrogen in dioxane, using standard Schlenk techniques, and transferred by cannula into the EFISH cell under an inert atmosphere. The centrosymmetry of the solution was broken by dipolar orientation of the chromophores with a high voltage pulse (5 kV) synchronized with the laser pulse. The SHG signal was selected through a suitable interference filter, detected by a photomultiplier, and recorded on an ultrafast Tektronic TDS 620 B oscilloscope. As the NLO response was induced by dipolar orientation of the chromophores, and in order to extract the β values, the dipole moments had to be measured independently by a classic method based on the Guggenheim theory.[47] Further details of the experimental methodology and data analysis are reported elsewhere.[48] Under these experimental conditions, the NLO signal was weak, but sufficient to allow the β determination of **4** and **5**.

The air stability of metal carbonyl derivatives being modest, the EFISH experiments were conducted in an anaerobic argon-purged cell, specially designed for the purpose of the present investigation. The stability of the EFISH signal indicates that the metal carbonyl-based chromophores do not undergo any decomposition during the time of the experiment.

Acknowledgements

The authors thank Dr Rémi Métivier for dipole moment measurements.

References

1 J. M. Lehn, *Supramolecular Chemistry–Concepts and Perspectives*, VCH, Weinheim, 1995.

2 M. D. Ward, *Chem. Soc. Rev.*, 1995, **24**, 121.

3 (*a*) *Molecular Nonlinear Optics: Materials, Physics and Devices*, ed. J. Zyss, Academic Press, Boston, MA, 1994; (*b*) *Nonlinear Optics of Organic Molecules and Polymers*, ed. H. S. Nalwa and S. Miyata, CRC Press, New York, 1997.

4 (*a*) B. J. Coe, *Chem. Eur. J.*, 1999, **5**, 2464; (*b*) I. Asselberghs, K. Clays, A. Persoons, M. D. Ward and J. McCleverty, *J. Mater. Chem.*, 2004, **14**, 2831.

5 See, for example: (*a*) B. J. Coe, S. Houbrechts, I. Asselberghs and A. Persoons, *Angew. Chem., Int. Ed.*, 1999, **38**, 366; (*b*) F. Paul, K. Costuas, I. Ledoux, S. Deveau, J. Zyss, J.-F. Halrt and C. Lapinte, *Organometallics*, 2002, **21**, 5229.

6 See for example: E. Hendrickx, K. Clays, A. Persoons, C. Dehu and J. L. Brédas, *J. Am. Chem. Soc.*, 1995, **117**, 3547.

7 See for example: (*a*) S. L. Gilat, S. H. Kawai and J. M. Lehn, *Chem. Eur. J.*, 1995, **1**, 275; (*b*) K. Nakatani and J. A. Delaire, *Chem. Mater.*, 1997, **9**, 2682; (*c*) J. A. Delaire, I. Fanton-Maltey and K. Nakatani, *Mol. Cryst. Liq. Cryst.*, 2000, **345**, 233; (*d*) M. Sliwa, S. Létard, I. Malfant, M. Nierlich, P. G. Lacroix, T. Asahi, H. Masuhara, P. Yu and K. Nakatani, *Chem. Mater.*, 2005, **17**, 4727.

8 D. J. Williams, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 690.

9 J. P. Costes, J. F. Lamère, C. Lepetit, P. G. Lacroix, F. Dahan and K. Nakatani, *Inorg. Chem.*, 2005, **44**, 1973.

10 (*a*) J. Zyss and I. Ledoux, *Chem. Rev.*, 1994, **94**, 77; (*b*) R. Kannan, G. S. He, T.-C. Lin, P. N. Prasad, R. A. Vaia and L.-S. Tan, *Chem. Mater.*, 2004, **16**, 185; (*c*) J. Brunel, O. Mongin, A. Jutand, I. Ledoux, J. Zyss and M. Blanchard-Desce, *Chem. Mater.*, 2003, **15**, 4139, and references therein.

11 For example: (*a*) P. Ford, F. P. De Rudd, R. Gaunder and H. Taube, *J. Am. Chem. Soc.*, 1968, **90**, 1187; (*b*) A. B. P. Lever, *J. Chem. Educ.*, 1974, **51**, 612.

12 (*a*) D. W. Bruce and A. Thornton, *Mol. Cryst. Liq. Cryst.*, 1993, **231**, 253; (*b*) D. W. Bruce, *Adv. Inorg. Chem.*, 2001, **52**, 151.

13 D. R. Kanis, P. G. Lacroix, M. A. Ratner and T. J. Marks, *J. Am. Chem. Soc.*, 1994, **116**, 10089.

14 (*a*) D. Roberto, R. Ugo, S. Bruni, E. Cariati, F. Cariati, P. Fantucci, I. Invernizzi, S. Quici, I. Ledoux and J. Zyss, *Organometallics*, 2000, **19**, 1775; (*b*) D. Roberto, R. Ugo, F. Tessore, E. Lucenti, S. Quici, S. Vezza, P. Fantucci, I. Invernizzi, S. Bruni, I. Ledoux-Rak and J. Zyss, *Organometallics*, 2002, **21**, 161.

15 L. T. Cheng, W. Tam, G. R. Meredith and S. R. Marder, *Mol. Cryst. Liq. Cryst.*, 1990, **189**, 137.

16 For a review of various NLO properties implying ruthenium(II)-based chromophores, see: H. Le Bozec and T. Renouard, *Eur. J. Inorg. Chem.*, 2000, 229.

17 (*a*) J. F. Ward, *Rev. Mod. Phys.*, 1965, **37**, 1; (*b*) D. R. Kanis, M. A. Ratner and T. J. Marks, *Chem. Rev.*, 1994, **94**, 195.

18 J. L. Oudar, *J. Chem. Phys.*, 1977, **67**, 446.

19 J. L. Oudar and D. S. Chemla, *J. Chem. Phys.*, 1977, **66**, 2664.

20 For recent examples, see: (*a*) M. M. Fares, M. El-Khateeb and K. J. Asali, *J. Inorg. Organomet. Polym.*, 2003, **13**, 143; (*b*) E. Peris, J. A. Mata and V. Moliner, *J. Chem. Soc., Dalton Trans.*, 1999, 3893.

21 For recent examples, see: (*a*) H. A. Cruse and N. E. Leadbeater, *Macromolecules*, 1999, **32**, 4450; (*b*) G. M. Li, J. H. Reibenspies and R. A. Zingaro, *Heteroat. Chem.*, 1998, **9**, 57.

22 For recent examples, see: (*a*) T. W. Stringfield and R. E. Shepherd, *Inorg. Chim. Acta*, 2003, **343**, 156; (*b*) C. J. Aspley, J. R. Lindsay Smith, R. N. Perutz and D. Pursche, *J. Chem. Soc., Dalton Trans.*, 2002, 170; (*c*) H. P. Wu, R. Aumann, R. Frohlich, B. Wibbeling and O. Kataeva, *Chem. Eur. J.*, 2001, **7**, 23.

23 J. M. Kelly and C. J. Long, *J. Organomet. Chem.*, 1982, **235**, 315.

24 R. J. Lewis. Sr., *Sax's Dangerous Properties of Industrial Materials*, Van Nostrand Reinhold, NY, 8th edn, 1992.

25 M. Lamothe, P. J. Pauwels, K. Belliard, P. Schambel and S. Halazy, *J. Med. Chem.*, 1997, **40**, 3542.

26 L. T. Cheng, W. Tam and D. F. Eaton, *Organometallics*, 1990, **9**, 2856.

27 B. S. Creave, C. Long, G. Russel, J. Hamiliton and G. P. Mc Quillan, *Inorg. Chim. Acta*, 1988, **146**, 25.

28 (*a*) B. F. Levine and C. G. Betha, *J. Chem. Phys.*, 1975, **63**, 2666; (*b*) B. F. Levine and C. G. Betha, *J. Chem. Phys.*, 1976, **65**, 1989.

29 D. F. Shriver, P. W. Atkins and C. H. Langford, *Inorganic Chemistry*, Oxford University Press, Oxford, 1994, p. 247.

30 J. Mata, S. Uriel, E. Peris, R. Llusar, S. Houbrechts and A. Persoons, *J. Organomet. Chem.*, 1998, **562**, 197.

31 R. A. Huijts and G. L. J. Hesselink, *Chem. Phys. Lett.*, 1989, **156**, 209.

32 For a review on NLO response in single molecules, see for example: Ph. Tamarat, F. Jelezko, Ch. Brunel, A. Maali, B. Lounis and M. Orrit, *Chem. Phys.*, 1999, **245**, 121.

33 A. Aviram and M. A. Ratner, *Chem. Phys. Lett.*, 1974, **29**, 277.

34 C. Joachim, J. K. Gimzewski and A. Aviram, *Nature*, 2000, **408**, 541.

35 *Molecular Machines*, special issue of *Acc. Chem. Res.*, 2001, **34**(6).

36 R. Ballardini, V. Balzani, A. Credi, M. T. Gandolfi and M. Venturi, *Acc. Chem. Res.*, 2001, **34**, 445.

37 R. D. Vale and R. A. Milligan, *Science*, 2000, **288**, 88.

38 A. N. Kost, A. K. Sheinkman and N. F. Kazarinova, *J. Gen. Chem. USSR*, 1964, **34**, 2059.

39 E. M. Graham, V. M. Miskowski, J. W. Perry, D. R. Coulter, A. E. Stiegman, W. P. Schaefer and R. E. Marsh, *J. Am. Chem. Soc.*, 1989, **111**, 8771.

40 W. Ries, I. Bernal, M. Quast and T. A. Albright, *Inorg. Chim. Acta*, 1984, **83**, 5.

41 A. E. Goeta, S. E. Lawrence, M. M. Meehan, A. O'Dowd and T. R. Spalding, *Polyhedron*, 2002, **21**, 1689.

42 (*a*) M. Zerner, G. Loew, R. Kirchner and U. Mueller-Westerhoff, *J. Am. Chem. Soc.*, 1980, **102**, 589; (*b*) W. P. Anderson, D. Edwards and M. C. Zerner, *Inorg. Chem.*, 1986, **25**, 2728.

43 W. Y. Wong, S. H. Cheung, S. M. Lee and S. Y. Leung, *J. Organomet. Chem.*, 2000, **596**, 36.

44 S. Sakanishi, D. A. Bardwell, S. Couchman, J. C. Jeffery, J. A. Mc Cleverty and M. D. Ward, *J. Organomet. Chem.*, 1997, **528**, 35.

45 U. Klement, *Z. Kristallogr.*, 1993, **208**, 114.

46 *ZINDO, release 9.60, Molecular Simulations Inc.*, Cambridge, UK, 1996.

47 E. A. Guggenheim, *Trans. Faraday Soc.*, 1949, **45**, 714.

48 I. Maltey, J. A. Delaire, K. Nakatani, P. Wang, X. Shi and S. Wu, *Adv. Mater. Opt. Electron.*, 1996, **6**, 233.