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Organometallic complexes for nonlinear optics[☆]

Part 18. Molecular quadratic and cubic hyperpolarizabilities of aryldiazovinylidene complexes

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Dedicated to Professor Martin Bennett, on the occasion of his retirement from the Research School of Chemistry at the Australian National University.

Abstract

The molecular quadratic and cubic optical nonlinearities of a series of aryldiazovinylidene complexes $[Ru(C{=}CPhN{=}NAr)(PPh_3)_2(\eta\text{-}C_5H_5)][X]$ [Ar = Ph (**1**), C_6H_4OMe-*n* (*n* = 2 (**2**), 3 (**3**), 4 (**4**)), $C_6H_4NO_2$-4 (**5**), 3,5-$C_6H_3(NO_2)_2$ (**6**); X = BF_4 (**a**), Cl (**b**), Br (**c**), I (**d**), 4-$MeC_6H_4SO_3$ (**e**), NO_3 (**f**); not all combinations] have been assessed using hyper-Rayleigh scattering and *Z*-scan techniques, respectively. The quadratic optical nonlinearities at 1064 nm are consistent with (i) introduction of polarizing substituents (NO_2, OMe c.f. H); (ii) location of nitro substituent [the conjugated 4-NO_2 c.f. the non-conjugated 3,5-$(NO_2)_2$]; (iii) dipolar composition (the strong donor-electron deficient bridge-strong acceptor composition of **5** and **6** c.f. the strong donor-electron deficient bridge-poor donor composition of **1**–**4**); and (iv) introduction of polyatomic anion (**e**, **f** c.f. **a**–**d**) all making significant contributions to the observed quadratic NLO responses. Absolute values for quadratic nonlinearities are lower than those of related alkynyl complexes. Complex **5d** was assessed across three solvents, with the β_{HRS} data following the trend acetone > dichloromethane > thf, in contrast to the trend in absorption maxima in these solvents. The cubic optical nonlinearities were measured at 800 nm; real components of the nonlinearities are negative, and the imaginary components are significant, consistent with two-photon absorption contributing to the observed responses. The incorporation of nitro substituent in progressing from **1**–**4** to **5** results in a significant increase in both γ_{real} and $|\gamma|$. © 2000 Published by Elsevier Science S.A. All rights reserved.

Keywords: Ruthenium; Vinylidene; Hyperpolarizabilities; Nonlinear optics

1. Introduction

The nonlinear optical (NLO) merit of organometallic complexes has been of significant recent interest [1–5], with the most intensively studied being ferrocenyl and alkynyl complexes. Historically, examination of ferrocenyl complexes preceded evaluation of alkynyl compounds, impetus to development of the latter being given from the suggestion that incorporation of the ligated metal into the plane of the organic π-system should result in complexes with enhanced quadratic NLO merit [6]. The same publication also included the suggestion that metal–carbon multiple bond character should further increase molecular first hyperpolarizability. Alkynyl–metal complexes have some of the largest quadratic optical nonlinearities of organometallic complexes [7–13], but π-bonding in alkynyl–metal complexes is only a minor component of the metal–carbon bonding interaction [14]. It is appropriate therefore to

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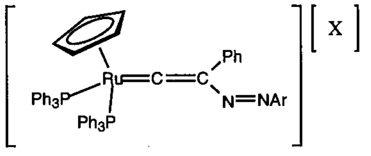
focus attention on molecular complexes with demonstrable metal–carbon multiple bonding.

Vinylidene complexes form a well-established class of compounds with the metal in the plane of the organic π-system, and crystallographically-verified metal–carbon multiple bonding [15]. Thus far, however, their NLO merit is little explored. We have previously reported the syntheses and characterization (including representative single-crystal X-ray structural studies) of a series of aryldiazovinylidene complexes [16–18]; these complexes are amongst the most stable of vinylidene complexes, and can be stored under ambient conditions for years without decomposition. The bulk susceptibilities of aryldiazovinylidene complexes have been determined by the Kurtz powder technique [18]. Second harmonic generation (SHG) efficiencies of these complexes are low ($\chi^{(2)} \leq 2 \times$ urea, a common standard), but crystal packing in a noncentrosymmetric space group is a necessary requirement for bulk quadratic nonlinearity. A structural study of [Ru(C=CPhN=NC$_6$H$_4$-4-OMe)(PPh$_3$)$_2$(η-C$_5$H$_5$)][BF$_4$] revealed that this complex crystallizes in the centric space group $P\bar{1}$, but is SHG-active with an NLO merit of 1.05 × urea. This surprising result, which has been observed with two other organometallic examples [19–21], has been assigned to a variety of reasons, including SHG by particle surfaces (which must be noncentrosymmetric), crystal defects, decomposition in the laser beam due to the high power of the laser, or fluorescence. If the observed SHG arises from either particle surfaces or crystal defects (a small component of the crystalline material), it suggests that molecular NLO merit is likely to be high. The Kurtz technique employed for these bulk susceptibility measurements is inadequate for developing a molecular level understanding of structure-NLO activity trends. We have therefore utilized hyper-Rayleigh scattering to measure molecular quadratic NLO responses, and report herein the results of these studies, including an assessment of the importance of varying vinylidene complex composition, counter ion, and solvent.



Ar	X	Complex
Ph	BF$_4$	**1a**
C$_6$H$_4$OMe-2	Cl	**2b**
C$_6$H$_4$OMe-3	BF$_4$	**3a**
C$_6$H$_4$OMe-4	Cl	**4b**
C$_6$H$_4$NO$_2$-4	BF$_4$	**5a**
C$_6$H$_4$NO$_2$-4	Cl	**5b**
C$_6$H$_4$NO$_2$-4	Br	**5c**
C$_6$H$_4$NO$_2$-4	I	**5d**
C$_6$H$_4$NO$_2$-4	4-MeC$_6$H$_4$SO$_3$	**5e**
C$_6$H$_4$NO$_2$-4	NO$_3$	**5f**
C$_6$H$_3$(NO$_2$)$_2$-3,5	Cl	**6b**

Fig. 1. Aryldiazovinylidene complex salts examined by hyper-Rayleigh scattering and Z-scan techniques.

The molecular third-order nonlinearities of organometallics have been less well-studied than the second-order NLO merit of these complexes [5], and no third-order NLO data have thus far been reported for vinylidene complexes. We have therefore also probed the cubic NLO performance of the present series of aryldiazovinylidene complexes, and present our results herein.

2. Results and discussion

The aryldiazovinylidene complexes displayed in Fig. 1 were prepared by the literature procedures [17,18], and their identity confirmed by comparison of IR and NMR spectra with previously reported data. The complexes incorporate the electron rich (cyclopentadienyl)bis(triphenylphosphine)ruthenium group; we have previously shown that in dipolar alkynyl complexes with a donor-bridge-acceptor composition, this unit is a superior donor group to classical organic donors (e.g. 4-methoxyphenyl) for quadratic NLO merit [7,9]. The bond distance of the short metal-carbon linkage has been shown crystallographically to correspond to a formal M=C bond [16,18]. The diazovinylidene bridge C=CPhN=N has an electron deficient metal-bound carbon, verified by reaction chemistry at related arylalkynyl complexes (in the absence of competing steric factors, nucleophilic attack occurs at this carbon) and by a pronounced downfield shift of this carbon in the ^{13}C-NMR (ca. 360 ppm). To facilitate structure–activity correlations, the substituents at the azo-bound aryl group encompass the electron donating methoxy at all possible sites (cations **2**–**4**), an electron withdrawing 4-nitro (cation **5**), and a 3,5-bis(nitro) (cation **6**), as well as the 'parent' unsubstituted phenyl group (cation **1**). The counter-ion for these cationic vinylidenes has also been varied, examples with BF$_4$ (**a**), Cl (**b**), Br (**c**), I (**d**), 4-MeC$_6$H$_4$SO$_3$ (**e**) and NO$_3$ (**f**) being examined.

The optical spectra of these complexes are of interest and were therefore measured, the results being summarized in Table 1. Incorporation of an electron-donating substituent into the vinylidene ligand in progressing from C=CPhN=NPh in **1** to C=CPhN=NC$_6$H$_4$OMe-n (n = 2, 3, 4) in **2**–**4** leads not surprisingly to a red shift in λ_{max}, with this red shift twice as large for the 'out of conjugation' 3-substituted derivative as for the 'in con-

Table 1
Linear optical and quadratic nonlinear optical response parameters for aryldiazovinylidene complexes [a]

Complex	Acetone (thf) [b]			CH_2Cl_2		
	λ_{max} (nm)	β (10^{-30} esu)	β_0 [c] (10^{-30} esu)	λ_{max} (nm) [ε (10^4 M^{-1} cm^{-1})]	β (10^{-30} esu)	β_0 [c] (10^{-30} esu)
$[Ru(C{=}CPhN{=}NPh)(PPh_3)_2(\eta\text{-}C_5H_5)]BF_4$ (**1a**)	363	14	6.6	363 [2.0]		
$[Ru(C{=}CPhN{=}NC_6H_4OMe\text{-}2)(PPh_3)_2(\eta\text{-}C_5H_5)]Cl$ (**2b**)	373	22	10	377 [1.9]		
$[Ru(C{=}CPhN{=}NC_6H_4OMe\text{-}3)(PPh_3)_2(\eta\text{-}C_5H_5)]BF_4$ (**3a**)	382	23	10	389 [2.0]		
$[Ru(C{=}CPhN{=}NC_6H_4OMe\text{-}4)(PPh_3)_2(\eta\text{-}C_5H_5)]Cl$ (**4b**)	370	26	12	374 [2.1]		
$[Ru(C{=}CPhN{=}NC_6H_4NO_2\text{-}4)(PPh_3)_2(\eta\text{-}C_5H_5)]BF_4$ (**5a**)				413 [2.2]	184	62
$[Ru(C{=}CPhN{=}NC_6H_4NO_2\text{-}4)(PPh_3)_2(\eta\text{-}C_5H_5)]Cl$ (**5b**)				413 [2.1]	137	46
$[Ru(C{=}CPhN{=}NC_6H_4NO_2\text{-}4)(PPh_3)_2(\eta\text{-}C_5H_5)]Br$ (**5c**)				413 [2.2]	136	45
$[Ru(C{=}CPhN{=}NC_6H_4NO_2\text{-}4)(PPh_3)_2(\eta\text{-}C_5H_5)]I$ (**5d**)	417 (415)	150 (101)	48 (33)	413 [2.3]	134	45
$[Ru(C{=}CPhN{=}NC_6H_4NO_2\text{-}4)(PPh_3)_2(\eta\text{-}C_5H_5)][4\text{-}MeC_6H_4SO_3]$ (**5e**)				413 [2.3]	164	55
$[Ru(C{=}CPhN{=}NC_6H_4NO_2\text{-}4)(PPh_3)_2(\eta\text{-}C_5H_5)]NO_3$ (**5f**)				413 [2.4]	181	61
$[Ru\{C{=}CPhN{=}N\text{-}3,5\text{-}C_6H_3(NO_2)_2\}(PPh_3)_2(\eta\text{-}C_5H_5)]Cl$ (**6b**)	395	33	13	402 [1.1]		

[a] All complexes are optically transparent at the fundamental frequency corresponding to the wavelength of 1064 nm. HRS at 1064 nm; values ±10%, using *p*-nitroaniline ($\beta(\text{acetone}) = 25.9 \times 10^{-30}$ esu, $\beta(CH_2Cl_2) = 21.6 \times 10^{-30}$ esu, $\beta(\text{thf}) = 21.4 \times 10^{-30}$ esu) as a reference.

[b] Bracketed data for complex **5d** in thf.

[c] HRS data at 1064 nm corrected for resonance enhancement at 532 nm using the two-level model with $\beta_o = \beta[1-(2\lambda_{max}/1064)^2][1-(\lambda_{max}/1064)^2]$; damping factors not included.

jugation' 2- or 4-substituted examples. Introduction of a nitro group in proceeding from C=CPhN=NPh in **1** to $C{=}CPhN{=}NC_6H_4NO_2$-4 in **5** leads to a significantly larger red shift than is observed on introduction of the electron-donating substituent. A blue shift is observed upon proceeding from $C{=}CPhN{=}NC_6H_4NO_2$-4 in **5** to the bis-nitro ligand $C{=}CPhN{=}N\text{-}3,5\text{-}C_6H_3(NO_2)_2$ in **6**, for which the substituents are 'out of conjugation' with the diazovinylidene unit. The optical absorption maximum for the cation **5** incorporating the $C{=}CPhN{=}NC_6H_4NO_2$-4 ligand is invariant across the series of anions **a**–**f**, consistent either with the absence of ion pairing, or with any ion pairing not modifying the electronic structure of the aryldiazovinylidene chromophore.

Solvatochromism is a useful indicator of the potential for NLO activity, and has even been used (in combination with other measurable parameters) to calculate quadratic optical nonlinearities of organoboron compounds [22]. The optical absorption maxima of selected examples have been measured in solvents of varying polarity. The mononitro complex **5d** experiences a red shift in λ_{max} in proceeding from solvent CH_2Cl_2 to thf and thence to acetone, but the shift observed is very small. In contrast, the dinitro complex **6b** experiences a slight blue shift in proceeding from solvent CH_2Cl_2 to acetone, and the optical absorption maximum for the 'parent' complex **1a** is invariant across this solvent range. The solvatochromism exhibited by **5** and **6** suggests that this class of complex warrants a study of molecular NLO activity.

The molecular quadratic optical nonlinearities of the aryldiazovinylidene complexes were assessed by the hyper-Rayleigh scattering technique, the results from which are collected in Table 1. The aryldiazovinylidene complexes are derivatives of $[Ru(C{\equiv}CPh)(PPh_3)_2(\eta\text{-}C_5H_5)]$, for which $\beta_{HRS} = 16 \times 10^{-30}$ esu ($\beta_0 = 10 \times 10^{-30}$ esu) [7]. The data for the present series of complexes are thus consistent with an increase in the magnitude of the second-order NLO response upon introduction of the functionalized aryldiazo unit for **2**–**5**, but with no increase upon incorporation of the phenyldiazo group (cation **1**). The nonlinearities observed for the vinylidene complexes with electron-withdrawing nitro groups in the present series of complexes (**5**, **6**) are significantly lower than those of alkynyl complexes incorporating the nitro substituent and the same metal and co-ligand combination (e.g. $[Ru(C{\equiv}CC_6H_4\text{-}4\text{-}NO_2)(PPh_3)_2(\eta\text{-}C_5H_5)]$ $\beta_{HRS} = 468 \times 10^{-30}$ esu ($\beta_0 = 96 \times 10^{-30}$ esu) [7]).

The extent of ion pairing in these complexes is unknown, but is likely to be low or negligible in the solvents utilized in the present studies. The contributions of the cation and anion to the observed nonlinearities of these organometallic salts should therefore be largely independent. The anion variation with cation **5** enables an assessment of the contribution of the counter ion. Quadratic optical nonlinearities for the halide salts **5b**, **5c** and **5d** are equivalent within experimental error; the contribution of the halide ligands are therefore equivalent and probably negligible. The anions in the salts **5e** and **5f** are expected to contribute to the observed nonlinearity; not surprisingly, β_{HRS} for these salts are significantly larger than the values for **5b**–**d**. The observed quadratic NLO response for **5e** is consistent with a recent study of $Na[4\text{-}MeC_6H_4SO_3]$ in methanol, for which a β_{HRS} value of 22×10^{-30} esu was found [23], and for which the contribution of the cation Na^+ is likely to be negligible. (Note that measurements quoted in Ref. [23] (a) are in methanol and (b) involve use of the internal reference method (with $\beta_{MeOH} = 0.69 \times 10^{-30}$ esu) at a different laboratory to the present study, so a quantitative comparison with the present data has not been made). Complex **5d** was assessed across three solvents, with the β_{HRS} data following the trend acetone > dichloromethane > thf, in contrast to the trend in absorption maxima.

The molecular variation within the present series of cations permits correlations of structure with NLO response. The relative magnitude of β_{HRS} for the azo-linked phenyls varies as $C_6H_4NO_2\text{-}4 > 3,5\text{-}C_6H_3(NO_2)_2 > C_6H_4OMe\text{-}n$ ($n = 2,3,4$) > Ph, in parallel with the trend in absorption maxima. The data are therefore consistent with (i) introduction of polarizing substituents (NO_2, OMe c.f. H); (ii) location of nitro substituent (the conjugated $4\text{-}NO_2$ c.f. the non-conjugated $3,5\text{-}(NO_2)_2$) and (iii) dipolar composition (the strong donor-electron deficient bridge-strong acceptor composition of **5** and **6** c.f. the strong donor-electron deficient bridge-poor donor composition of **1**–**4**) all making significant contributions to the observed quadratic NLO responses.

Third-order nonlinearities of **1**–**6** were evaluated by the *Z*-scan technique [24], the results of these measurements being given in Table 2. The real components of the nonlinearities for the aryldiazovinylidenes are negative, and the imaginary components are significant, consistent with two-photon absorption contributing to the observed responses; comment on the effect of structural variation on the magnitude of the hyperpolarizability should therefore be treated with caution, particularly in the light of the large error margins. The incorporation of nitro substituent in progressing from **1**–**4** to **5** results in a significant increase in both γ_{real} and $|\gamma|$. We have noted a similar increase in cubic NLO merit in proceeding from phenylalkynyl complexes to 4-nitrophenylalkynyl complex analogues [10,25,26]. The effect of other modifications (varying the nature of the aryldiazo group, in progressing from Ph to C_6H_4OMe; variation in counter ion for cation **5**) is less clear-cut, and measurements at a different wavelength (one minimizing electronic resonance enhancement) are required to resolve these uncertainties.

3. Experimental

3.1. General considerations

The complexes **1**–**6** were prepared as previously described [16–18], and their identity confirmed by com-

Table 2

Linear optical and cubic nonlinear optical response parameters for aryldiazovinylidene complexes [a]

Complex	λ_{max} (nm)	γ_{real} (10^{-36} esu)	γ_{imag} (10^{-36} esu)	$\lvert\gamma\rvert$ (10^{-36} esu)
$[Ru(C{=}CPhN{=}NPh)(PPh_3)_2(\eta\text{-}C_5H_5)]BF_4$ (**1a**)	363	-160 ± 60	75 ± 25	180 ± 65
$[Ru(C{=}CPhN{=}NC_6H_4OMe\text{-}2)(PPh_3)_2(\eta\text{-}C_5H_5)]Cl$ (**2b**)	377	-220 ± 150	70 ± 30	230 ± 150
$[Ru(C{=}CPhN{=}NC_6H_4OMe\text{-}3)(PPh_3)_2(\eta\text{-}C_5H_5)]BF_4$ (**3a**)	389	-310 ± 60	90 ± 30	320 ± 65
$[Ru(C{=}CPhN{=}NC_6H_4OMe\text{-}4)(PPh_3)_2(\eta\text{-}C_5H_5)]Cl$ (**4b**)	374	-20 ± 40	80 ± 40	80 ± 50
$[Ru(C{=}CPhN{=}NC_6H_4NO_2\text{-}4)(PPh_3)_2(\eta\text{-}C_5H_5)]BF_4$ (**5a**)	413	-320 ± 100	160 ± 40	360 ± 110
$[Ru(C{=}CPhN{=}NC_6H_4NO_2\text{-}4)(PPh_3)_2(\eta\text{-}C_5H_5)]Cl$ (**5b**)	413	-630 ± 200	160 ± 50	650 ± 210
$[Ru(C{=}CPhN{=}NC_6H_4NO_2\text{-}4)(PPh_3)_2(\eta\text{-}C_5H_5)]Br$ (**5c**)	413	-570 ± 150	150 ± 40	590 ± 160
$[Ru(C{=}CPhN{=}NC_6H_4NO_2\text{-}4)(PPh_3)_2(\eta\text{-}C_5H_5)]I$ (**5d**)	413	-460 ± 50	140 ± 50	480 ± 60
$[Ru(C{=}CPhN{=}NC_6H_4NO_2\text{-}4)(PPh_3)_2(\eta\text{-}C_5H_5)][4\text{-}MeC_6H_4SO_3]$ (**5e**)	413	-580 ± 200	210 ± 50	620 ± 210
$[Ru(C{=}CPhN{=}NC_6H_4NO_2\text{-}4)(PPh_3)_2(\eta\text{-}C_5H_5)]NO_3$ (**5f**)	413	-460 ± 150	200 ± 50	500 ± 160
$[Ru\{C{=}CPhN{=}N\text{-}3,5\text{-}C_6H_3(NO_2)_2\}(PPh_3)_2(\eta\text{-}C_5H_5)]Cl$ (**6b**)	402	[b]	[b]	[b]

[a] All complexes are optically transparent at the fundamental frequency corresponding to the wavelength of 800 nm. *Z*-scan measurements as CH_2Cl_2 solutions. Results are referenced to the nonlinear refractive index of silica $n_2 = 3 \times 10^{-16}$ cm^2 W^{-1}.

[b] Insufficiently soluble.

parison of ^{1}H-NMR and IR spectral data with literature values. UV–vis spectra were recorded using a Cary 5 spectrophotometer as solutions in thf, acetone or CH_2Cl_2 in 1 cm cells.

3.2. Hyper-Rayleigh scattering measurements

The quadratic hyperpolarizabilities were determined via the hyper-Rayleigh scattering (HRS) technique using *p*-nitroaniline as an external reference [27]. HRS measurements were performed at 1064 nm using a Nd:YAG laser (Q-switched Nd:YAG Quanta Ray GCR130-10, 8 ns pulses, 10 Hz) which was focused into a cylindrical cell (7 ml) containing the sample. Solutions of the sample were passed through 0.45 μm filters before use, in order to ensure that any dust was removed. The intensity of the incident beam was varied by rotation of a half-wave plate placed between crossed polarizers. The harmonic scattering and linear scattering were distinguished by appropriate filters; gated integrators were used to obtain intensities of the incident and harmonic scattered light. The experimental procedure has been discussed in detail previously [13].

3.3. Z-scan measurements

Z-scan measurements were performed at 800 nm using 100 fs pulses from a system consisting of a Coherent Mira Ti-sapphire laser pumped with a Coherent Innova or Coherent Verdi cw pump and a Ti-sapphire regenerative amplifier pumped with a frequency-doubled Q-switched pulsed YAG laser (Spectra Physics GCR) at 30 Hz and employing chirped pulse amplification. Tetrahydrofuran solutions were examined in a glass cell with a 0.1 cm path length. The Z-scans were recorded at two concentrations for each compound and the real and imaginary part of the nonlinear phase change determined by numerical fitting using equations given in Ref. [24]. The real and imaginary part of the hyperpolarizability of the solute was then calculated assuming linear concentration dependencies of the nonlinear phase shifts. The nonlinearities and light intensities were calibrated using measurements of a 1 mm thick silica plate for which the nonlinear refractive index $n_2 = 3 \times 10^{-16}$ cm^2 W^{-1} was assumed.

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