Non-linear and Potential Non-linear Optical Materials containing Molybdenum or Tungsten Mononitrosyl Redox Centres. Stilbene Derivatives containing Ferrocenyl, Methoxy or Dimethylamino Donor Groups†

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The compounds $[M(NO)\{HB(dmpz)_3\}X_n\{EC_6H_4(CH{=}CHC_6H_3{-}R,R')\text{-}4\}_{2-n}]$ (dmpz = 3,5-dimethylpyrazolyl, n = 1, E = NH, R = $[(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)]$-4, R′ = H; E = O, R = R′ = H; E = O or NH, R = 4-OMe, R′ = H; R = 4-NMe_2, R′ = H; E = NH, R = 2-OMe, R′ = 4-OMe; R = 3-OMe, R′ = 4-OMe; R = 2-OMe, R′ = 5-OMe; M = Mo, X = Cl or I; M = W, X = Cl; n = 2; E = O, R = R′ = H; E = O or NH, R = 4-OMe or -NMe_2, R′ = H; E = NH, R = 2-OMe, R′ = 4-OMe; R = 3-OMe, R′ = 4-OMe, R = 2-OMe, R′ = 5-OMe; M = Mo) have been synthesised and tested for second-order non-linear optical properties using the Kurtz powder test for second harmonic generation (SHG). The ferrocenyl derivatives have been found to exhibit SHG on irradiation at 1907 nm, whereas all of the derivatives containing NMe_2 or OMe groups are SHG inactive. The crystal structure of $[Mo(NO)\{HB(dmpz)_3\}Cl\{OC_6H_4[CH{=}CHC_6H_4(NMe_2\text{-}4)]\text{-}4\}]$ shows that, although the compound crystallises in a polar space group, the lattice contains pseudo-centrosymmetrically aligned pairs of molecules within each asymmetric unit. This indicates that the differences in second-order non-linear optical properties between the ferrocenyl and other derivatives may be attributed to structural rather than electronic effects.

Molecular materials which exhibit non-linear optical properties are of great interest for potential applications in optical data-processing technology. A wide variety of organic compounds have been shown [1] to exhibit such properties and, more recently, metal–organic compounds have been found to exhibit significant effects.[2–5] In this context the investigation of compounds containing the ferrocenyl moiety as a donor group within dipolar molecules containing nitro or methylpyridinium acceptor groups has proved particularly successful.[2a,3] The demonstration[6] that the mixed-valence compounds $[(NC)_5Ru(\mu\text{-}CN)Ru(NH_3)_5]^-$ and $[(H_3N)_5Ru(\mu\text{-}NC)Ru(\eta^5\text{-}C_5H_5)(PPh_3)_2]^{3+}$ have very high second-order molecular hyperpolarisabilities (β) gives new impetus to the study of metal–organic derivatives, and in particular redox-active homo- or hetero-bimetallic species.

We have been investigating the use of the formally electron-deficient 16-electron $\{M(NO)L\}^{2+}$ [L = tris(3,5-dimethylpyrazol-1-yl)hydroborate, $HB(dmpz)_3$; M = Mo or W] moieties as acceptor groups in the production of non-linear optical materials.[5] We have previously obtained materials which produce significant second harmonic generation (SHG) from 1907 nm by linking $\{Mo(NO)L(X)\}^+$ (X = Cl or I) to ferrocenyl *via* aryl[7] and, with better effect, diarylazo[8,9] groups. In this latter group of compounds the use of donor groups such as NMe_2 or OMe fails to give materials which exhibit SHG and only the use of the ferrocenyl group produces active materials. Since all of these molecules are dipolar donor–acceptor systems which should have significant molecular hyperpolarisabilities, β, this implies an important structural role for the ferrocenyl group in such materials.[8,9] The structures of two complexes which exhibit substantial SHG have been determined and reveal a packing arrangement favourable for phase-matched SHG.[8,9]

In order further to investigate this point, and develop more extensive structure–activity relationships for the non-linear optical properties of materials containing the $\{M(NO)L\}^{2+}$ group, we have extended the range of compounds studied to include bifunctional molecules in which a donor group such as ferrocenyl, OMe or NMe_2 is linked to a $\{M(NO)L(X)\}^{2+}$ acceptor moiety by a stilbene bridge. These new complexes have been fully characterised and subjected to SHG investigation using the Kurtz powder test. The crystal structure of an SHG-inactive compound has been obtained and provides an important complement to the previously reported structures of closely related active materials.[8,9]

Results and Discussion

Synthetic Studies.—The target compounds for non-linear optical evaluation in this study contain the 16-electron $\{M(NO)L(X)_n\}$ (n = 1, M = Mo, X = Cl or I; M = W, X = Cl; n = 0, M = Mo) moiety linked to one or two donor substituted stilbenes. Two basic synthetic approaches have been employed to prepare the stilbenes. The aminostilbene derivatives were readily prepared *via* zinc–ammonium chloride reduction of their nitro precursors which were synthesised by condensation of 4-nitrophenylacetic acid with substituted benzaldehydes according to well established procedures. In this way 4-(dimethylamino)-4′-nitro-,[10] 4-methoxy-4′-nitro-,[11] 2,4-dimethoxy-4′-nitro-,[12] and 3,4-dimethoxy-4′-nitro-stilbene[11] were prepared. These were then reduced giving high yields of the amino derivatives which were characterised by elemental analyses, ^1H NMR spectroscopy and melting-point measurements. 4-amino-2′,5′-dimethoxystilbene (HY^9) was obtained commercially. 4-Amino-4′-(dimethylamino)stilbene (HY^5) has

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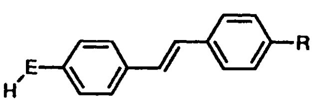
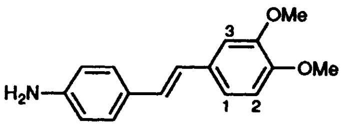
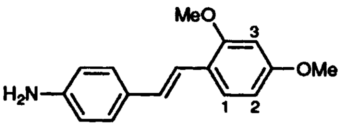
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.



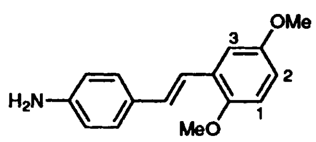
	E	R
HY^1	O	H
HY^2	O	OMe
HY^3	O	NMe_2
HY^4	NH	OMe
HY^5	NH	NMe_2
HY^6	NH	$(C_5H_4)Fe(C_5H_5)$



HY^7



HY^8



HY^9

been prepared previously using a tin chloride–acetic acid reduction of its nitro precursor[13] and 4-amino-4′-methoxystilbene (HY^4) was similarly prepared using a tin chloride–HCl reduction.[14] The use of zinc and ammonium chloride in this study has been found to give slightly improved yields of amine products. Although HY^9 is a known compound,[15] the two other isomers HY^7 and HY^8 are new. These three isomeric dimethoxystilbenes were chosen with a view to increasing the molecular asymmetry of their complexes in the hope of encouraging a non-centrosymmetric crystal packing from which bulk non-linear optical effects might be observed. Such an approach represents a common strategy in the design of purely organic materials for these effects.[1]

4-(Dimethylamino)-4′-hydroxystilbene (HY^3) has previously been prepared using a five-step synthesis,[16] whilst 4-hydroxy-4′-methoxystilbene (HY^2) has been synthesised in two steps.[17] In this work the hydroxystilbenes were prepared in a single step using a chemically simpler McMurry-type reaction[18] between 4-hydroxybenzaldehyde and either 4-dimethylaminobenzaldehyde for HY^3 or 4-methoxybenzaldehyde for HY^2. However, although this route is convenient, very low yields of hydroxystilbenes are produced. It seems likely that the presence of the hydroxyl functionality may hinder the coupling reaction.

Monosubstituted molybdenum derivatives were prepared using established methodology[19,20] involving reaction of either $[Mo(NO)LCl_2]$ or $[Mo(NO)LI_2]$ with a slight excess of the appropriate stilbene in refluxing toluene. The mild tricylic base hexamine (hexamethylenetetramine) favours the formation of monophenoxide complexes from both dihalide precursors. Triethylamine was used in the preparation of monoanilidomolybdenum complexes and all tungsten complexes derived from $[W(NO)LCl_2]$. Molybdenum bis(phenoxide) derivatives were prepared by reaction of $[Mo(NO)LI_2]$ with a little over 2 molar equivalents of the stilbene in the presence of triethylamine. Molybdenum bis(anilide) derivatives were prepared under more forcing conditions by reaction of a monoiodo anilide complex with further stilbene in the presence of the reducing agent sodium dihydronaphthylide $(Na^+C_{10}H_8{}^{\bullet -})$. Displacement of the second iodide occurs readily at room temperature in the co-ordinating solvent tetrahydrofuran (thf), but heating under reflux has been found to give increased yields.[21] Relatively low yields of these bis(anilide) complexes were obtained which is thought to be due, in part at least, to decomposition during column chromatography on silica gel.

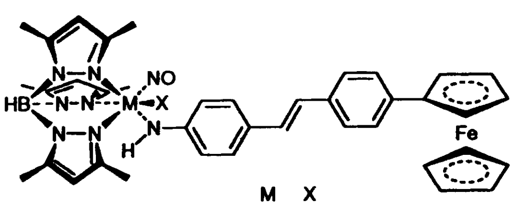
All the new complexes were characterised using IR and ^1H NMR spectroscopy, electron-impact (EI) mass spectrometry, elemental analyses, and cyclic voltammetry (Table 1). The new complexes exhibit $\nu_{max}(BH)$ at *ca.* 2550 cm^{-1} as well as $\nu_{max}(NO)$ at frequencies in accord with their formulations.[19] In addition, the arylamide derivatives exhibit $\nu_{max}(NH)$ at 3300–3260 cm^{-1} due to the amide moiety. The ^1H NMR spectra of the new complexes contain signals attributable to the L ligand and signals from the aryl groups in the stilbene bridges are as expected. The complexes which contain the ferrocenyl group show the usual three ^1H NMR signals (ratio 2:2:5) attributable to the ferrocenyl moiety, whilst those containing NMe_2 or OMe donor groups show singlets from these methyl protons. All of the complexes show molecular-ion envelopes of variable intensity along with varying numbers of fragment envelopes.

Electrochemical Studies.—All of the new complexes show one-electron molybdenum or tungsten reduction waves at potentials which accord with expectations.[22] The ferrocenyl-containing complexes **1**–**3** also exhibit reversible oxidation waves attributable to the ferrocenyl moiety. The electrochemical data for **1**–**3** are shown in Table 2 along with those of their counterparts containing an azo bridge in place of the ethenyl bridge. Data for the remaining complexes **4**–**34** are included in the Experimental section. In most cases one, two, or three completely irreversible oxidation waves are also observed in the region +0.5–1.5 V which are not quoted in Table 2. These may be assigned to either metal-centred oxidations or oxidations of the organic ligands.

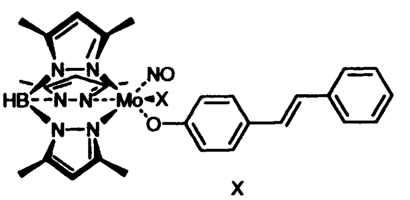
Several general features are apparent in the electrochemical results. The chloromolybdenum-aryloxo complexes **4**, **7** and **11** have reduction potentials in the range −0.29 to −0.33 V while their iodide-containing counterparts **5**, **8** and **12** reduce at slightly more anodic potentials in the range −0.26 to −0.28 V. Their tungsten-containing analogues **10** and **14** reduce at the substantially more cathodic potentials of −0.82 and −0.84 V respectively. These processes are reversible or quasi-reversible with values of ΔE_p in the range 90–130 mV compared to a typical value of 90 mV for ferrocene. The molybdenum bis(aryloxo) complexes **6**, **9** and **13** reduce at potentials in the range −0.62 to −0.63 V with ΔE_p in the range 100–150 mV.

Being stronger π donors, the arylamide ligands give rise to substantially more cathodic reduction potentials for the metal nitrosyl centres. Thus the molybdenum halogeno-amido complexes **15**, **16**, **19**, **20**, **23**, **24**, **27**, **28**, **31** and **32** reduce in the range −0.71 to −0.78 V with the iodide-containing complexes once again exhibiting slightly more anodic reduction potentials than their chloride-containing counterparts. Values of ΔE_p are in the range 90–130 mV indicating reversible or quasi-reversible behaviour. The corresponding chlorotungsten-arylamido complexes **18**, **22**, **26**, **30** and **34** again reduce at more cathodic potentials in the range −1.16 to −1.19 V with ΔE_p values in the range 100–150 mV. The molybdenum bis(arylamide) complexes **17**, **21**, **25**, **29** and **33** showed the most cathodic reduction potentials of the compounds reported here with values in the range −1.18 to −1.22 V.[21] These electrode processes were subject to substantial kinetic control with ΔE_p values in the range 130–220 mV.

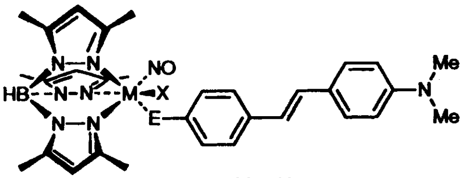
Viewed as a whole the reduction potentials show little sensitivity to changes in the substituents on the aryl ring remote from the $\{M(NO)\}$ centre. However, more substantial differences are apparent if these stilbene complexes are



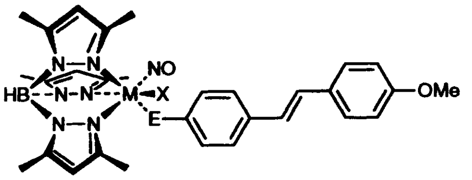
	M	X
1	Mo	Cl
2	Mo	I
3	W	Cl



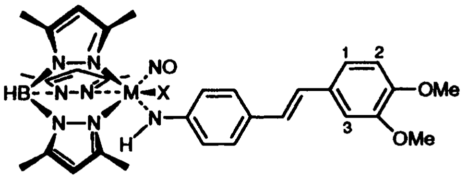
	X
4	Cl
5	I
6	Y^1



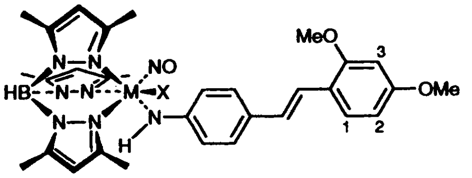
E		M	X
E = O	**7**	Mo	Cl
	8	Mo	I
	9	Mo	Y^3
	10	W	Cl
E = NH	**15**	Mo	Cl
	16	Mo	I
	17	Mo	Y^5
	18	W	Cl



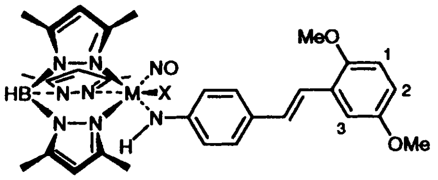
E		M	X
E = O	**11**	Mo	Cl
	12	Mo	I
	13	Mo	Y^2
	14	W	Cl
E = NH	**19**	Mo	Cl
	20	Mo	I
	21	Mo	Y^4
	22	W	Cl



	M	X
23	Mo	Cl
24	Mo	I
25	Mo	Y^7
26	W	Cl



	M	X
27	Mo	Cl
28	Mo	I
29	Mo	Y^8
30	W	Cl



	M	X
31	Mo	Cl
32	Mo	I
33	Mo	Y^9
34	W	Cl

compared with their diarylazo counterparts.[9] The presence of the azo group leads to anodic shifts of 60–70 mV in going from the halogenoaryloxo complexes **7**, **8** and **10** to their counterparts in which the –CH=CH– bridge is replaced by –N=N–. In the case of the bisaryloxo complex **9** this shift is 110 mV. Larger anodic shifts of 120–130 mV are apparent in the reduction potentials when the ethenyl bridge in the arylamido derivatives **15**, **16** and **18** is replaced by an azo bridge.

The electrochemical data for the ferrocenyl-containing complexes are most germane to the study reported here. The oxidation potential of the ferrocenyl moiety is less sensitive to the nature of the bridge between the aryl rings of the ligand than is the metal nitrosyl reduction potential. Thus the reduction potentials of **1** and **3** are shifted anodically by 170 and 190 mV when the ethenyl bridge is replaced by an azo group (Table 2). However, the respective oxidation potentials of the ferrocenyl group experience anodic shifts of only 50 and 30 mV.

Electronic Spectra.—The electronic spectra of several representative complexes were measured in dichloromethane. The results are presented in Table 3 and show that some bands have very high absorption coefficients. Spectra for the ferrocenylstilbene amide and dimethoxystilbene amide chloride complexes were measured in *n*-hexane and in dimethylformamide (dmf) in order to search for any evidence of solvatochromic behaviour. These data are presented in Table 4 and show that only rather small shifts in λ_{max} occur between solutions in dmf and *n*-hexane.

Kurtz Powder Test Results and Structural Studies.—All of the complexes were tested for SHG using modifications of the standard Kurtz powder test on unsized powdered samples. Only the ferrocenyl derivatives **1**–**3** exhibited any detectable SHG (Table 5), complexes **4**–**34** proving to be inactive. All of the complexes have strongly polarisable dipolar molecular structures, and could reasonably be expected to possess large molecular hyperpolarisabilities, β, owing to the strongly electron-donating nature of their organic substituent groups. In particular, the *p*-dimethylamino function should act as a considerably more powerful donor than the organometallic ferrocenyl moiety. Complexes of 4-amino-2′,4′-dimethoxystilbene should also have enhanced hyperpolarisability due to the additive donation effects of the *o*- and *p*-methoxy groups.

Table 1 Elemental analyses, mass spectral molecular ions, ^{1}H NMR spectral and electrochemical data used in compound characterisation

Compound, m.p. (°C)	Analysis (%),[a] *m*/*z*[b]	IR[c] (cm^{-1})	^{1}H NMR[d] and electrochemical data[e]
HY^6 245 (decomp.)	75.6 (76.0), 5.6 (5.6), 3.4 (3.7); 379	3445m (NH_2) 3350m (NH_2)	7.44 and 7.39 [2 H, d, *J*(HH) 8.6; 2 H, d, *J*(HH) 8.8, $C_6\mathit{H}_4C_5H_4Fe$], 7.35 and 6.68 [2 H, d, *J*(HH) 8.4; 2 H, d, *J*(HH) 8.4, $C_6\mathit{H}_4NH_2$], 7.03 and 6.90 [1 H, d, *J*(HH)$_{trans}$ 15.9; 1 H, d, *J*(HH)$_{trans}$ 16.3, $C\mathit{H}{=}C\mathit{H}$], 4.65 and 4.32 [2 H, t, *J*(HH) 1.9; 2 H, t, *J*(HH) 1.8, C_5H_4], 4.04 (5 H, s, C_5H_5), 3.76 (2 H, br s, NH_2)
HY^8 96.5–98	75.3 (75.3), 6.9 (6.7), 5.3 (5.5)	3460m (NH_2) 3380m (NH_2)	7.47 [1 H, d, *J*(HH) 8.4, $C_6H_3(H^1)$], 7.32 and 6.64 [2 H, d, *J*(HH) 8.6; 2 H, d, *J*(HH) 8.4, C_6H_4], 7.20 and 6.90 [1 H, d, *J*(HH)$_{trans}$ 16.5; 1 H, d, *J*(HH)$_{trans}$ 16.5, $C\mathit{H}{=}C\mathit{H}$], 6.49 [1 H, dd, *J*($H^1H^2$) 8.4 Hz, *J*($H^2H^3$) 2.4, $C_6H_3(H^2)$], 6.45 [1 H, d, *J*(H^2H^3) 2.4, $C_6H_3(H^3)$], 3.84 and 3.81 (3 H, s; 3 H, s, 2 OCH_3), 3.67 (2 H, br s, NH_2)
HY^7 158–160	75.0 (75.3), 6.5 (6.7), 5.2 (5.5)	3460m (NH_2) 3380m (NH_2)	7.32 and 6.67 [2 H, d, *J*(HH) 8.4; 2 H, d, *J*(HH) 8.6, C_6H_4], 7.03 [1 H, d, *J*(H^1H^3) 1.8, $C_6H_3(H^3)$], 7.00 [1 H, dd, *J*(H^1H^2) 8.2, *J*(H^1H^3) 2.0, $C_6H_3(H^1)$], 6.88 (2 H, s, $C\mathit{H}{=}C\mathit{H}$), 6.84 [1 H, d, *J*($H^1H^2$) 8.1, $C_6H_3(H^2)$], 3.93 and 3.89 (3 H, s; 3 H, s, 2 OCH_3), 3.73 (2 H, br s, NH_2)
1[f]	54.9 (54.9), 5.3 (5.0), 13.2 (13.1); 838	1650s (NO) 3240m (NH)	12.59 (1 H, s, NH), 7.58 [2 H, d, *J*(HH) 8.7, C_6H_4], 7.49, 7.46 and 7.46 (4 H, C_6H_4), 7.12 (2 H, s, $C\mathit{H}{=}C\mathit{H}$), 5.87 and 5.80 (2 H, s; 1 H, s, $3Me_2C_3N_2\mathit{H}$), 4.67 and 4.34 [2 H, t, *J*(HH) 1.7; 2 H, t, *J*(HH) 1.7, C_5H_4], 4.05 (5 H, s, C_5H_5), 2.70, 2.42, 2.39, 2.38, 2.37 and 2.04 (3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s, $3\mathit{Me}_2C_3N_2H$)
2	50.1 (50.5), 4.6 (4.6), 12.2 (12.1); 930	1650s (NO) 3240m (NH)	13.03 (1 H, s, NH), 7.63 and 7.53 [2 H, d, *J*(HH) 8.7; 2 H, d, *J*(HH) 8.7, C_6H_4], 7.46 (4 H, C_6H_4), 7.19 and 7.08 [1 H, d, *J*(HH)$_{trans}$ 16.1; 1 H, d, *J*(HH)$_{trans}$ 16.3, $C\mathit{H}{=}C\mathit{H}$], 5.93, 5.86 and 5.78 (1 H, s; 1 H, s; 1 H, s, $3Me_2C_3N_2\mathit{H}$), 4.68 and 4.35 (2 H, s; 2 H, s, C_5H_4), 4.06 (5 H, s, C_5H_5), 2.72, 2.49, 2.46, 2.38, 2.37 and 2.01 (3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s, $3\mathit{Me}_2C_3N_2H$)
3	50.9 (50.7), 4.6 (4.6), 11.9 (12.1); 924	1625s (NO) 3260w (NH)	10.75 (1 H, s, NH), 7.56 and 7.39 [2 H, d, *J*(HH) 8.7; 2 H, d, 8.4, C_6H_4], 7.47 and 7.42 [2 H, d, *J*(HH) 9.0; 2 H, d, *J*(HH) 9.0, C_6H_4], 7.14 and 7.03 [1 H, d, *J*(HH)$_{trans}$ 16.3; 1 H, d, *J*(HH)$_{trans}$ 16.1, $C\mathit{H}{=}C\mathit{H}$], 5.94, 5.88 and 5.83 (1 H, s; 1 H, s; 1 H, s, $3Me_2C_3N_2\mathit{H}$), 4.66 and 4.33 (2 H, s; 2 H, s, C_5H_4), 4.05 (5 H, s, C_5H_5), 2.74, 2.46, 2.42, 2.37, 2.36 and 2.16 (3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s, $3\mathit{Me}_2C_3N_2H$)
4	53.5 (53.3), 5.3 (5.3), 14.8 (15.0); 655	1675s (NO)	7.58 and 7.34 [2 H, d, *J*(HH) 8.6; 2 H, d, *J*(HH) 8.6, C_6H_4], 7.55–7.20 (5 H, c m, C_6H_5), 7.17 and 7.08 [1 H, d, *J*(HH)$_{trans}$ 16.3; 1 H, d, *J*(HH)$_{trans}$ 16.3, $C\mathit{H}{=}C\mathit{H}$], 5.93, 5.90 and 5.77 (1 H, s; 1 H, s; 1 H, s, $3Me_2C_3N_2\mathit{H}$), 2.59, 2.42, 2.42, 2.39, 2.20 and 2.07 (3 H, s; 3 H, s; 3, H, s; 3 H, s; 3 H, s; 3 H, s, $3\mathit{Me}_2C_3N_2H$) −0.29, 100 [90]
5	46.5 (46.7), 4.6 (4.5), 13.3 (13.2); 747	1675s (NO)	7.60–7.20 (9 H, c m, C_6H_4 and C_6H_5), 7.13 (2 H, s, $C\mathit{H}{=}C\mathit{H}$), 5.91 and 5.85 (1 H, s; 2 H, s, $3Me_2C_3N_2\mathit{H}$), 2.58, 2.45, 2.40, 2.38, 2.31 and 2.07 (3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s, $3\mathit{Me}_2C_3N_2H$) −0.26, 100 [90]
6	63.2 (63.5), 5.8 (5.5), 12.3 (12.1); 815	1660s (NO)	7.55–7.10 (18 H, c m, $2C_6H_4$ and $2C_6H_5$), 7.12 and 7.02 [2 H, d, *J*(HH)$_{trans}$ 16.3; 2 H, d, *J*(HH)$_{trans}$ 16.3, $2C\mathit{H}{=}C\mathit{H}$], 5.85 and 5.76 (2 H, s; 1 H, s, $3Me_2C_3N_2\mathit{H}$), 2.41, 2.25 and 2.11 (9 H, s; 6 H, s; 3 H, s, $3\mathit{Me}_2C_3N_2H$) −0.62, 150 [95]
7	53.9 (53.4), 5.5 (5.5), 16.4 (16.1); 698	1690s (NO)	7.53 and 7.32 [2 H, d, *J*(HH) 8.8; 2 H, d, *J*(HH) 8.6, C_6H_4], 7.42 and 6.72 [2 H, d, *J*(HH) 8.8; 2 H, d, *J*(HH) 8.8, C_6H_4], 7.05 and 6.95 [1 H, d, *J*(HH)$_{trans}$ 16.3; 1 H, d, *J*(HH)$_{trans}$ 16.1, $C\mathit{H}{=}C\mathit{H}$], 5.92, 5.88 and 5.76 (1 H, s; 1 H, s; 1 H, s, $3Me_2C_3N_2\mathit{H}$), 2.99 [6 H, s, $N(CH_3)_2$], 2.60, 2.41, 2.39, 2.20 and 2.06 [3 H, s; 6 H, s; 3 H, s; 3 H, s; 3 H, s, $3\mathit{Me}_2C_3N_2H$] −0.33, 100 [90]
8	47.7 (47.2), 4.6 (4.9), 14.3 (14.2); 790	1680s (NO)	7.50 and 7.45 [2 H, d, *J*(HH) 9.2; 2 H, d, *J*(HH) 9.0, C_6H_4], 7.43 and 6.72 [2 H, d, *J*(HH) 8.8; 2 H, d, *J*(HH) 9.0, C_6H_4], 7.09 and 6.92 [1 H, d, *J*(HH)$_{trans}$ 16.3; 1 H, d, *J*(HH)$_{trans}$ 15.9, $C\mathit{H}{=}C\mathit{H}$]; 5.90, 5.84 and 5.83 (1 H, s; 1 H, s; 1 H, s, $3Me_2C_3N_2\mathit{H}$), 2.99 [6 H, s, $N(CH_3)_2$], 2.59, 2.44, 2.39, 2.38, 2.31 and 1.99 (3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s, $3\mathit{Me}_2C_3N_2H$) −0.28, 100 [90]
9	62.4 (62.7), 6.1 (6.1), 14.3 (14.0); 901	1655s (NO)	7.45 and 7.16 [4 H, d, *J*(HH) 8.6; 4 H, d, *J*(HH) 8.6, $2C_6H_4$], 7.40 and 6.72 [4 H, d, *J*(HH) 9.0; 4 H, d, *J*(HH) 8.8, $2C_6H_4$], 6.98 and 6.91 [2 H, d, *J*(HH)$_{trans}$ 16.3; 2 H, d, *J*(HH)$_{trans}$ 15.9, $2C\mathit{H}{=}C\mathit{H}$], 5.84 and 5.76 (2 H, s; 1 H, s, $3Me_2C_3N_2\mathit{H}$), 2.98 [12 H, s, $2N(CH_3)_2$], 2.41, 2.40, 2.25 and 2.12 (3 H, s; 6 H, s; 6 H, s; 3 H, s, $3\mathit{Me}_2C_3N_2H$) −0.63, 100 [90]
10	47.7 (47.4), 4.7 (4.9), 14.2 (14.3); 784	1640s (NO)	7.51 and 7.25 [2 H, d, *J*(HH) 8.7; 2 H, d, *J*(HH) 8.7, C_6H_4], 7.41 and 6.72 [2 H, d, *J*(HH) 8.7; 2 H, d, *J*(HH) 8.9, C_6H_4], 6.99 and 6.93 [1 H, d, *J*(HH)$_{trans}$ 16.6; 1 H, d, *J*(HH)$_{trans}$ 16.6, $C\mathit{H}{=}C\mathit{H}$], 5.93, 5.90 and 5.83 (1 H, s; 1 H, s; 1 H, s, $3Me_2C_3N_2\mathit{H}$), 2.98 [6 H, s, $N(CH_3)_2$], 2.67, 2.40, 2.39, 2.29 and 2.19 (3 H, s; 3 H, s; 6 H, s; 3 H, s; 3 H, s, $3\mathit{Me}_2C_3N_2H$) −0.84, 130 [95]

Table 1 (*continued*)

Compound, m.p. (°C)	Analysis (%),[a] *m/z*[b]	IR[c] (cm^{-1})	^{1}H NMR[d] and electrochemical data[e]
11	53.0 (52.7), 5.1 (5.2), 14.2 (14.3); 685	1690s (NO)	7.55 and 7.33 [2 H, d, $J(\mathrm{HH})$ 8.8; 2 H, d, $J(\mathrm{HH})$ 8.6, C_6H_4], 7.46 and 6.91 [2 H, d, $J(\mathrm{HH})$ 8.8; 2 H, d, $J(\mathrm{HH})$ 8.8, C_6H_4], 7.07 and 7.00 [1 H, d, $J(\mathrm{HH})_{trans}$ 16.3; 1 H, d, $J(\mathrm{HH})_{trans}$ 16.3, $\mathrm{C}\mathit{H}{=}\mathrm{C}\mathit{H}$], 5.93, 5.89 and 5.77 (1 H, s; 1 H, s; 1 H, s, $3\mathrm{Me_2C_3N_2}\mathit{H}$), 3.83 (3 H, s, OCH_3), 2.59, 2.42, 2.39, 2.20 and 2.07 (3 H, s; 6 H, s; 3 H, s; 3 H, s; 3 H, s, $3\mathit{Me}_2\mathrm{C_3N_2H}$) −0.31, 110 [90]
12	46.8 (46.5), 4.3 (4.6), 12.4 (12.7); 777	1680s (NO)	7.53–7.43 and 6.91 [6 H, c m; 2 H, d, $J(\mathrm{HH})$ 8.8, $\mathrm{C_6}\mathit{H}_4\mathrm{CH{=}CHC_6}\mathit{H}_4$], 7.10 and 6.98 [1 H, d, $J(\mathrm{HH})_{trans}$ 16.3; 1 H, d, $J(\mathrm{HH})_{trans}$ 16.3, $\mathrm{C}\mathit{H}{=}\mathrm{C}\mathit{H}$], 5.91, 5.85 and 5.84 (1 H, s; 1 H, s; 1 H, s, $3\mathrm{Me_2C_3N_2}\mathit{H}$), 3.83 (3 H, s, OCH_3), 2.58, 2.45, 2.40, 2.38, 2.31 and 1.99 (3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s, $3\mathit{Me}_2\mathrm{C_3N_2H}$) −0.26, 90 [90]
13[g]	60.4 (60.4), 5.2 (5.4), 10.8 (10.9); 875	1660s (NO)	7.47 and 7.16 [4 H, d, $J(\mathrm{HH})$ 9.0; 4 H, d, $J(\mathrm{HH})$ 8.8, $2C_6H_4$], 7.42 and 6.89 [4 H, d, $J(\mathrm{HH})$ 9.0; 4 H, d, $J(\mathrm{HH})$ 8.8, $2C_6H_4$], 6.98 (4 H, s, $2\mathrm{C}\mathit{H}{=}\mathrm{C}\mathit{H}$), 5.84 and 5.76 (2 H, s; 1 H, s, $3\mathrm{Me_2C_3N_2}\mathit{H}$), 3.81 (6 H, s, $2OCH_3$), 2.41, 2.40, 2.25 and 2.12 (3 H, s; 6 H, s; 6 H, s; 3 H, s, $3\mathit{Me}_2\mathrm{C_3N_2H}$) −0.62, 110 [90]
14	47.0 (46.7), 4.6 (4.6), 12.6 (12.7); 771	1630s (NO)	7.52 and 7.26 [2 H, d, $J(\mathrm{HH})$ 8.8; 2 H, d, $J(\mathrm{HH})$ 8.6, C_6H_4], 7.45 and 6.90 [2 H, d, $J(\mathrm{HH})$ 8.8; 2 H, d, $J(\mathrm{HH})$ 8.8, C_6H_4], 7.00 (2 H, s, $\mathrm{C}\mathit{H}{=}\mathrm{C}\mathit{H}$), 5.93, 5.90 and 5.84 (1 H, s; 1 H, s; 1 H, s, $3\mathrm{Me_2C_3N_2}\mathit{H}$), 3.83 (3 H, s, OCH_3), 2.67, 2.40, 2.39, 2.29 and 2.19 (3 H, s; 3 H, s; 6 H, s; 3 H, s; 3 H, s, $3\mathit{Me}_2\mathrm{C_3N_2H}$) −0.82, 110 [95]
15 *ca.* 280	53.8 (53.5), 5.5 (5.7), 18.1 (18.1); 697	1655s (NO) 3290w (NH)	12.61 (1 H, s, NH), 7.55–7.40 and 6.72 [6 H, c m; 2 H, d, $J(\mathrm{HH})$ 8.7, $\mathrm{C_6}\mathit{H}_4\mathrm{CH{=}CHC_6}\mathit{H}_4$], 7.08 and 6.93 [1 H, d, $J(\mathrm{HH})_{trans}$ 16.3; 1 H, d, $J(\mathrm{HH})_{trans}$ 16.3, $\mathrm{C}\mathit{H}{=}\mathrm{C}\mathit{H}$], 5.86 and 5.79 (2 H, s; 1 H, s, $3\mathrm{Me_2C_3N_2}\mathit{H}$), 2.99 [6 H, s, $N(CH_3)_2$], 2.70, 2.42, 2.39, 2.37, 2.36 and 2.03 (3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s, $3\mathit{Me}_2\mathrm{C_3N_2H}$) −0.78, 90 [90]
16 *ca.* 295	47.6 (47.3), 5.0 (5.0), 15.9 (16.0); 787	1660s (NO) 3290w (NH)	13.06 (1 H, s, NH), 7.62–7.40 and 6.72 [6 H, c m; 2 H, d, $J(\mathrm{HH})$ 8.7, $\mathrm{C_6}\mathit{H}_4\mathrm{CH{=}CHC_6}\mathit{H}_4$], 7.14 and 6.89 [1 H, d, $J(\mathrm{HH})_{trans}$ 16.3; 1 H, d, $J(\mathrm{HH})_{trans}$ 16.3, $\mathrm{C}\mathit{H}{=}\mathrm{C}\mathit{H}$], 5.93, 5.86 and 5.77 (1 H, s; 1 H, s; 1 H, s, $3\mathrm{Me_2C_3N_2}\mathit{H}$), 2.99 [6 H, s, $N(CH_3)_2$], 2.72, 2.48, 2.46, 2.37, 2.37 and 2.00 (3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s, $3\mathit{Me}_2\mathrm{C_3N_2H}$) −0.73, 90 [90]
17	63.7 (62.9), 6.2 (6.3), 17.3 (17.2); 899	1635s (NO) 3320w (NH)	8.88 (2 H, s, 2NH), 7.40–7.20 and 6.71 [12 H, c m; 4 H, d, $J(\mathrm{HH})$ 8.8, $2\mathrm{C_6}\mathit{H}_4\mathrm{CH{=}CHC_6}\mathit{H}_4$], 6.94 and 6.87 [2 H, d, $J(\mathrm{HH})_{trans}$ 16.1; 2 H, d, $J(\mathrm{HH})_{trans}$ 16.1, $2\mathrm{C}\mathit{H}{=}\mathrm{C}\mathit{H}$], 5.96 and 5.74 (1 H, s; 2 H, s, $3\mathrm{Me_2C_3N_2}\mathit{H}$), 2.96 [12 H, s, $2\mathrm{N(C}\mathit{H}_3)_2$], 2.47, 2.35 and 2.27 (3 H, s; 9 H, s; 6 H, s, $3\mathrm{Me_2C_3N_2H}$) −1.22, 130 [95]
18	47.8 (47.5), 4.9 (5.0), 15.8 (16.1); 783	1620s (NO) 3280w (NH)	10.77 (1 H, s, NH), 7.51 and 7.36 [2 H, d, $J(\mathrm{HH})$ 8.4; 2 H, d, $J(\mathrm{HH})$ 8.7, C_6H_4], 7.41 and 6.72 [2 H, d, $J(\mathrm{HH})$ 8.9; 2 H, d, $J(\mathrm{HH})$ 8.9, C_6H_4], 7.01 and 6.93 [1 H, d, $J(\mathrm{HH})_{trans}$ 16.3; 1 H, d, $J(\mathrm{HH})_{trans}$ 16.3, $\mathrm{C}\mathit{H}{=}\mathrm{C}\mathit{H}$], 5.94, 5.88 and 5.82 (1 H, s; 1 H, s; 1 H, s, $3\mathrm{Me_2C_3N_2}\mathit{H}$), 2.99 [6 H, s, $\mathrm{N(C}\mathit{H}_3)_2$], 2.73, 2.46, 2.42, 2.37, 2.36 and 2.16 (3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s, $3\mathit{Me}_2\mathrm{C_3N_2H}$) −1.19, 130 [95]
19 *ca.* 270	53.0 (52.8), 5.0 (5.3), 16.2 (16.4); 684	1660s (NO) 3280w (NH)	12.60 (1 H, s, NH), 7.56–7.45 and 6.91 [6 H, c m; 2 H, d, $J(\mathrm{HH})$ 8.6, $\mathrm{C_6}\mathit{H}_4\mathrm{CH{=}CHC_6}\mathit{H}_4$], 7.09 and 6.99 [1 H, d, $J(\mathrm{HH})_{trans}$ 16.3; 1 H, d, $J(\mathrm{HH})_{trans}$ 16.3, $\mathrm{C}\mathit{H}{=}\mathrm{C}\mathit{H}$], 5.87 and 5.79 (2 H, s; 1 H, s, $3\mathrm{Me_2C_3N_2}\mathit{H}$), 3.83 (3 H, s, OCH_3), 2.70, 2.42, 2.39, 2.38, 2.37 and 2.03 (3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s, $3\mathit{Me}_2\mathrm{C_3N_2H}$) −0.77, 120 [90]
20 *ca.* 260	46.7 (46.5), 4.4 (4.7), 14.5 (14.5); 776	1660s (NO) 3280w (NH)	13.06 (1 H, s, NH), 7.61 and 7.50 [2 H, d, $J(\mathrm{HH})$ 8.7; 2 H, d, $J(\mathrm{HH})$ 8.7, C_6H_4], 7.48 and 6.90 [2 H, d, $J(\mathrm{HH})$ 8.9; 2 H, d, $J(\mathrm{HH})$ 8.9, C_6H_4], 7.15 and 6.95 [1 H, d, $J(\mathrm{HH})_{trans}$ 16.3; 1 H, d, $J(\mathrm{HH})_{trans}$ 16.3, $\mathrm{C}\mathit{H}{=}\mathrm{C}\mathit{H}$], 5.93, 5.86 and 5.77 (1 H, s; 1 H, s; 1 H, s, $3\mathrm{Me_2C_3N_2}\mathit{H}$), 3.83 (3 H, s, OCH_3), 2.72, 2.48, 2.46, 2.38, 2.37 and 2.00 (3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s, $3\mathit{Me}_2\mathrm{C_3N_2H}$) −0.73, 100 (90)
21	62.3 (62.0), 5.2 (5.3), 14.2 (14.5); 873	1635s (NO) 3320w (NH)	8.91 (2 H, s, 2NH), 7.42 and 7.27 [4 H, d, $J(\mathrm{HH})$ 8.6; 4 H, d, $J(\mathrm{HH})$ 8.6, $2C_6H_4$], 7.41 and 6.88 [4 H, d, $J(\mathrm{HH})$ 8.8; 4 H, d, $J(\mathrm{HH})$ 8.8, $2C_6H_4$], 6.94 (4 H, s, $2\mathrm{C}\mathit{H}{=}\mathrm{C}\mathit{H}$), 5.96 and 5.75 (1 H, s; 2 H, s, $3\mathrm{Me_2C_3N_2}\mathit{H}$), 3.82 (6 H, s, $2OCH_3$), 2.47, 2.35 and 2.27 (3 H, s; 9 H, s; 6 H, s, $3\mathit{Me}_2\mathrm{C_3N_2H}$) −1.18, 160 [95]
22	46.4 (46.8), 4.7 (4.7), 14.2 (14.5); 771	1620s (NO) 3280w (NH)	10.76 (1 H, s, NH), 7.53 and 7.38 [2 H, d, $J(\mathrm{HH})$ 8.7; 2 H, d, $J(\mathrm{HH})$ 8.4, C_6H_4], 7.45 and 6.90 [2 H, d, $J(\mathrm{HH})$ 8.9; 2 H, d, $J(\mathrm{HH})$ 8.7, C_6H_4], 7.01 (2 H, s, $\mathrm{C}\mathit{H}{=}\mathrm{C}\mathit{H}$), 5.94, 5.88 and 5.82 (1 H, s; 1 H, s; 1 H, s, $3\mathrm{Me_2C_3N_2}\mathit{H}$), 3.83 (3 H, s, OCH_3), 2.73, 2.45, 2.42, 2.37, 2.36 and 2.15 (3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s, $3\mathit{Me}_2\mathrm{C_3N_2H}$) −1.18, 150 [90]

Table 1 (*continued*)

Compound, m.p. (°C)	Analysis (%),^{a} *m*/*z*^{b}	IR^c (cm^{-1})	^{1}H NMR^d and electrochemical data^e
23	52.3 (52.2), 5.3 (5.4), 15.9 (15.7); 714	1650s (NO) 3270w (NH)	12.60 (1 H, s, NH), 7.55 and 7.46 [2 H, d, *J*(HH) 8.7; 2 H, d, *J*(HH) 8.7, C_6H_4], 7.08 and 7.06 [2 H, s, s, C_6H_3(H^1 and H^3)], 7.09 and 6.99 [1 H, d, *J*(HH)$_{trans}$ 16.3; 1 H, d, *J*(HH)$_{trans}$ 16.3, C*H*=C*H*], 6.87 [1 H, d, *J*(H^{1}H^2) 8.2, C_6H_3(H^2)], 5.87 and 5.80 (2 H, s; 1 H, s, 3Me$_2$C$_3$N$_2$*H*), 3.96 and 3.91 (3 H, s; 3 H, s, 2OCH$_3$), 2.70, 2.42, 2.39, 2.38, 2.37 and 2.03 (3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s, 3*Me*$_2$C$_3$N$_2$H) −0.76, 130 [90]
24	46.4 (46.3), 4.5 (4.8), 14.0 (13.9); 806	1650s (NO) 3270w (NH)	13.06 (1 H, s, NH), 7.62 and 7.50 [2 H, d, *J*(HH) 8.7; 2 H, d, *J*(HH) 8.7, C_6H_4], 7.10 and 7.08 [2 H, d, d, C_6H_3(H^1 and H^3)], 7.15 and 6.95 [1 H, d, *J*(HH)$_{trans}$ 16.3; 1 H, d, *J*(HH)$_{trans}$ 16.3, C*H*=C*H*], 6.87 [1 H, d, *J*(H^{1}H^2) 8.9, C_6H_3(H^2)], 5.93, 5.86 and 5.78 (1 H, s; 1 H, s; 1 H, s, 3Me$_2$C$_3$N$_2$*H*), 3.96 and 3.91 (3 H, s; 3 H, s, 2OCH$_3$), 2.72, 2.49, 2.47, 2.38, 2.37 and 2.00 (3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s, 3*Me*$_2$C$_3$N$_2$H) −0.71, 100 [90]
25	60.8 (60.6), 5.7 (5.4), 13.5 (13.5); 933	1630s (NO) 3300w (NH)	8.92 (2 H, s, 2NH), 7.42 and 7.28 [4 H, d, *J*(HH) 8.4; 4 H, d, *J*(HH) 8.4, 2C_6H_4], 7.04 and 7.00 [4 H, d, d, 2C_6H_3(H^1 and H^3)], 6.94 (4 H, s, 2C*H*=C*H*), 6.84 [2 H, d, *J*(H^{1}H^2) 8.2, 2C_6H_3(H^2)], 5.96 and 5.75 (1 H, s; 2 H, s, 3Me$_2$C$_3$N$_2$*H*), 3.94 and 3.88 (6 H, s; 6 H, s, 4OCH$_3$), 2.47, 2.35 and 2.28 (3 H, s; 9 H, s; 6 H, s, 3*Me*$_2$C$_3$N$_2$H) −1.19, 180 [95]
26	46.8 (46.5), 4.8 (4.8), 13.7 (14.0); 800	1620s (NO) 3270w (NH)	10.76 (1 H, s, NH), 7.53 and 7.38 [2 H, d, *J*(HH) 8.4; 2 H, d, *J*(HH) 8.7, C_6H_4], 7.07 and 7.04 [2 H, s, d, C_6H_3(H^1 and H^3)], 7.00 (2 H, s, C*H*=C*H*), 6.86 [1 H, d, *J*(H^{1}H^2) 8.2, C_6H_3(H^2)], 5.94, 5.88 and 5.83 (1 H, s; 1 H, s; 1 H, s, 3Me$_2$C$_3$N$_2$*H*), 3.96 and 3.90 (3 H, s; 3 H, s, 2OCH$_3$), 2.73, 2.46, 2.42, 2.37, 2.35 and 2.16 (3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s, 3*Me*$_2$C$_3$N$_2$H) −1.17, 110 [90]
27	52.2 (52.2), 5.4 (5.4), 15.9 (15.7); 714	1645s (NO) 3270w (NH)	12.62 (1 H, s, NH), 7.58–7.40 [6 H, c m, C_6H_3(H^1), =CH and C_6H_4], 7.03 [1 H, d, *J*(HH)$_{trans}$ 16.6, =CH), 6.54 and 6.51 [$\frac{1}{2}$ H, d, *J*(H^{2}H^3) 2.5; $\frac{1}{2}$ H, d, *J*(H^{2}H^3) 2.2, *J*(H^{1}H^2) 8.5, C_6H_3(H^2)], 6.48 [1 H, d, *J*(H^{2}H^3) 2.5, C_6H_3(H^3)], 5.87, 5.87 and 5.79 (1 H, s; 1 H, s; 1 H, s, 3Me$_2$C$_3$N$_2$*H*), 3.88 and 3.84 (3 H, s; 3 H, s, 2OCH$_3$), 2.70, 2.42, 2.39, 2.38, 2.37 and 2.03 (3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s, 3*Me*$_2$C$_3$N$_2$H) −0.76, 100 [90]
28	46.6 (46.3), 4.9 (4.8), 14.1 (13.9); 806	1645s (NO) 3270w (NH)	13.07 (1 H, s, NH), 7.62–7.46 [6 H, c m, C_6H_3(H^1), =CH and C_6H_4], 7.03 [1 H, d, *J*(HH)$_{trans}$ 16.6, =CH], 6.54 and 6.51 [$\frac{1}{2}$ H, d, *J*(H^{2}H^3) 2.5; $\frac{1}{2}$ H, d, *J*(H^{2}H^3) 2.5, *J*(H^{1}H^2) 8.7, C_6H_3(H^2)], 6.48 [1 H, d, *J*(H^{2}H^3) 2.2, C_6H_3(H^3)], 5.93, 5.86 and 5.77 (1 H, s; 1 H, s; 1 H, s, 3Me$_2$C$_3$N$_2$*H*), 3.87 and 3.84 (3 H, s; 3 H, s, 2OCH$_3$), 2.72, 2.49, 2.46, 2.37, 2.37 and 2.00 (3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s, 3*Me*$_2$C$_3$N$_2$H) −0.73, 90 [90]
29	60.6 (60.6), 5.7 (5.4), 13.4 (13.5); 933	1630s (NO) 3300w (NH)	8.90 (2 H, s, 2NH), 7.51–7.22 [12 H, c m, 2C_6H_3(H^1), 2=CH and 2C_6H_4], 6.96 [2 H, d, *J*(HH)$_{trans}$ 16.3, 2=CH], 6.52 and 6.49 [1 H, d, *J*(H^{2}H^3) 2.2; 1 H, d, *J*(H^{2}H^3) 2.2, *J*(H^{1}H^2) 8.6, 2C_6H_3(H^2)], 6.45 [2 H, d, *J*(H^{2}H^3) 2.2, 2C_6H_3(H^3)], 5.95 and 5.73 (1 H, s; 2 H, s, 3Me$_2$C$_3$N$_2$*H*), 3.85 and 3.81 (6 H, s; 6 H, s, 4OCH$_3$), 2.46, 2.34 and 2.26 (3 H, s; 9 H, s; 6 H, s, 3*Me*$_2$C$_3$N$_2$H) −1.19, 180 [95]
30	46.7 (46.5), 4.6 (4.8), 14.2 (14.0); 800	1620s (NO) 3270w (NH)	10.78 (1 H, s, NH), 7.56–7.32 [6 H, c m, C_6H_3(H^1), =CH and C_6H_4], 7.02 [1 H, d, *J*(HH)$_{trans}$ 16.3, =CH], 6.54 and 6.51 [$\frac{1}{2}$ H, d, *J*(H^{2}H^3) 2.5; $\frac{1}{2}$ H, d, *J*(H^{2}H^3) 2.2, *J*(H^{1}H^2) 8.6, C_6H_3(H^2)], 6.47 [1 H, d, *J*(H^{2}H^3) 2.2, C_6H_3(H^3)], 5.94, 5.88 and 5.82 (1 H, s; 1 H, s; 1 H, s, 3Me$_2$C$_3$N$_2$*H*), 3.87 and 3.84 (3 H, s; 3 H, s, 2OCH$_3$), 2.73, 2.46, 2.42, 2.36, 2.35 and 2.15 (3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s, 3*Me*$_2$C$_3$N$_2$H) −1.18, 110 [90]
31	52.3 (52.2), 5.3 (5.4), 15.8 (15.7); 714	1655s (NO) 3270w (NH)	12.60 (1 H, s, NH), 7.59 and 7.47 [2 H, d, *J*(HH) 8.4; 2 H, d, *J*(HH) 8.4, C_6H_4], 7.49 and 7.11 [1 H, d, *J*(HH)$_{trans}$ 16.5; 1 H, d, *J*(HH)$_{trans}$ 16.8, C*H*=C*H*], 7.16 [1 H, d, *J*(H^{2}H^3) 2.7, C_6H_3(H^3)], 6.86–6.77 [2 H, c m, C_6H_3(H^1 and H^2)], 5.87 and 5.79 (2 H, s; 1 H, s, 3Me$_2$C$_3$N$_2$*H*), 3.85 and 3.83 (3 H, s; 3 H, s, 2OCH$_3$), 2.69, 2.42, 2.39, 2.38, 2.37 and 2.03 (3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s, 3*Me*$_2$C$_3$N$_2$H) −0.76, 110 [95]
32	46.6 (46.3), 4.9 (4.8), 14.0 (13.9); 806	1655s (NO) 3270w (NH)	13.06 (1 H, s, NH), 7.62 and 7.55 [2 H, d, *J*(HH) 8.7; 2 H, d, *J*(HH) 8.9, C_6H_4], 7.55 and 7.07 [1 H, d, *J*(HH)$_{trans}$ 16.3; 1 H, d, *J*(HH)$_{trans}$ 16.3, C*H*=C*H*], 7.17 [1 H, d, *J*(H^{2}H^3) 2.3, C_6H_3(H^3)], 6.83 [2 H, d, C_6H_3(H^1 and H^2)], 5.93, 5.86 and 5.77 (1 H, s; 1 H, s; 1 H, s, 3Me$_2$C$_3$N$_2$*H*), 3.85 and 3.83 (3 H, s; 3 H, s, 2OCH$_3$), 2.72, 2.49, 2.46, 2.38, 2.37 and 2.00 (3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s, 3*Me*$_2$C$_3$N$_2$H) −0.71, 90 [90]
33	60.5 (60.6), 5.7 (5.4), 13.1 (13.5); 933	1630s (NO) 3300w (NH)	8.92 (2 H, s, 2NH), 7.46 and 7.27 [4 H, d, *J*(HH) 8.2; 4 H, d, *J*(HH) 8.4, 2C_6H_4], 7.34 and 7.05 [2 H, d, *J*(HH)$_{trans}$ 16.5; 2 H, d, *J*(HH)$_{trans}$ 16.7, 2C*H*=C*H*], 7.15 [2 H, d, *J*(H^{2}H^3) 2.8, 2C_6H_3(H^3)], 6.82 [2 H, d, *J*(H^{1}H^2) 9.0, 2C_6H_3(H^1)], 6.75 and 6.72 [1 H, d, *J*(H^{2}H^3) 2.8; 1 H, d, *J*(H^{2}H^3) 2.9; 2C_6H_3(H^2)], 5.96 and 5.75 (1 H, s; 2 H, s, 3Me$_2$C$_3$N$_2$*H*), 3.83 and 3.81 (6 H, s; 6 H, s, 4OCH$_3$), 2.47, 2.35 and 2.27 (3 H, s; 9 H, s; 6 H, s, 3*Me*$_2$C$_3$N$_2$H) −1.16, 220 [95]

Table 1 (*continued*)

Compound, m.p. (°C)	Analysis (%),[a] m/z[b]	IR[c] (cm^{-1})	^{1}H NMR[d] and electrochemical data[e]
34	46.2 (46.5), 4.8 (4.8), 14.2 (14.0); 800	1620s (NO) 3270w (NH)	10.76 (1 H, s, NH), 7.58 and 7.38 [2 H, d, J(HH) 8.7; 2 H, d, J(HH) 8.4, C_6H_4], 7.41 and 7.11 [1 H, d, $J(HH)_{trans}$ 16.3; 1 H, d, $J(HH)_{trans}$ 16.3, C*H*=C*H*], 7.15 [1 H, d, $J(H^2H^3)$ 2.3, $C_6H_3(H^3)$], 6.84 [1 H, d, $J(H^1H^2)$ 8.9, $C_6H_3(H^1)$], 6.79 and 6.76 [$\frac{1}{2}$ H, d, $J(H^2H^3)$ 2.7; $\frac{1}{2}$ H, d, $J(H^2H^3)$ 2.7, $J(H^1H^2)$ 9.1, $C_6H_3(H^2)$], 5.94, 5.88 and 5.83 (1 H, s; 1 H, s; 1 H, s, $3Me_2C_3N_2H$), 3.85 and 3.83 (3 H, s; 3 H, s, $2OCH_3$), 2.73, 2.46, 2.42, 2.37, 2.36 and 2.15 (3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s; 3 H, s, $3Me_2C_3N_2H$) −1.16, 100 [90]

[a] In the order C, H, N with calculated values in parentheses. [b] Position of the ion of highest m/z in the EI mass spectrum. These polyisotopic molecules give ion clusters spread over a range of m/z values so the most intense ion in the cluster is quoted. [c] Obtained from KBr discs. [d] At 25 °C from solutions in $CDCl_3$; data cited as δ_H relative to $SiMe_4$, number of protons, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, c = complex), coupling constant J in Hz and assignment. [e] Electrochemical data given after the NMR data as E_f in V *vs.* SCE, ΔE_p/mV [ΔE_p for ferrocene–ferrocenium (mV)]. [f] Contains 0.25 mol CH_2Cl_2. [g] Contains 0.33 mol CH_2Cl_2.

Table 2 Cyclic voltammetry data for ligands and molybdenum and tungsten ferrocenyl complexes [M(NO)L(X)Y]

M	X	Y	$E_f(M)$[a]/V	ΔE_p/mV	$E_f(Fe)$[a]/V	ΔE_p/mV	ΔE_f/mV
Mo[b]	Cl	*c*	−0.21	100	+0.61	80	820
Mo[b]	I	*c*	−0.15	90	+0.60	80	750
Mo[b]	*c*	*c*	−0.43	140	+0.60	80	1030
Mo[b]	Cl	*d*	−0.57	110	+0.63	90	1200
W[b]	Cl	*d*	−0.97	105	+0.60	100	1570
1 Mo	Cl	Y^6	−0.74	100	+0.58	105	1320
2 Mo	I	Y^6	−0.70	85	+0.57	10	1270
3 W	Cl	Y^6	−1.16	220	+0.57	110	1730

[a] All potentials measured relative to the SCE in dry CH_2Cl_2 using a platinum-bead working electrode, 0.2 mol dm^{-3} $[NBu_4][BF_4]$ as supporting electrolyte and scan rate 200 mV s^{-1}. [b] Values taken from ref. 9. [c] $OC_6H_4N{=}NC_6H_4(C_5H_4)Fe(C_5H_5)$. [d] $HNC_6H_4N{=}NC_6H_4(C_5H_4)Fe(C_5H_5)$.

Table 3 UV/VIS Excitation maxima for selected molybdenum complexes [Mo(NO)L(Cl)Y]

Y	λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})*	
Y^2	564 (9 600)	322 (28 700)
Y^3	610 (8 300)	350 (25 500)
Y^4	509 (12 800)	323 (14 000)
Y^5	560 (18 100)	354 (17 700)

* All spectra recorded in dichloromethane at ambient temperature, concentration *ca.* 10^{-5} mol dm^{-3}.

Table 4 Solvent dependence of UV/VIS excitation maxima for selected complexes [M(NO)L(X)Y]

				λ_{max}[a]/nm			
	M	X	Y	Hexane	CH_2Cl_2	dmf	$\Delta\lambda$[b]/nm
1	Mo	Cl	Y^6	498	519	516	21
				331	335	341	10
2	Mo	I	Y^6	514	536	536	22
				332	340	346	14
3	W	Cl	Y^6	415	430	431	16
				350	325	333	25
23	Mo	Cl	Y^7	317	—	328	11
				492	—	509	17
27	Mo	Cl	Y^8	328	—	336	8
				498	—	517	19
31	Mo	Cl	Y^9	299	—	309	10
				487	—	498	11
26	W	Cl	Y^7	298	—	302	4
				311	—	320	9
				426	—	438	12
30	W	Cl	Y^8	293	—	296	3
				318	—	321	3
				431	—	439	8
34	W	Cl	Y^9	288	—	295	7
				326	—	338	12
				421	—	433	12

[a] All spectra recorded at ambient temperature, concentrations *ca.* 10^{-5} mol dm^{-3}. [b] Difference between highest and lowest λ_{max} values.

Furthermore, the inherent asymmetry of this compound, and also of its 3′,4′ and 2′,5′ isomers, might be expected to encourage the adoption of a non-centrosymmetric crystal packing. However, the absence of any powder SHG is a strong indication that these complexes adopt crystal-packing arrangements in which cancellation of dipoles leads to vanishing $\chi^{(2)}$ values. In order to investigate these structural aspects, a number of attempts were made to obtain single crystals suitable for X-ray diffraction studies but, with one exception, these proved unsuccessful.

Powder X-ray diffraction traces were recorded for complexes **15**, **19** and **27** but no clear patterns were apparent. Such difficulty in obtaining even powder diffraction traces for these complexes shows that they tend to form poorly crystalline solids, unsuited to the observation of bulk non-linear optical effects. This factor seems to be a greater problem with the complexes containing organic donor groups than with those containing ferrocenyl groups. This observation underlines the fact that the ferrocenyl group has a crucial steric as well as electronic role to play in the creation of non-linear-optically active molydenum and tungsten complexes. The X-ray powder diffraction traces from **1**–**3** were very similar to that from the related SHG-active compound $[Mo(NO)L(Cl)(HNC_6H_4\{N{=}NC_6H_4[(C_5H_4)Fe(C_5H_5)\text{-}4]\}\text{-}4)]$[9] suggesting that these compounds all adopt similar packing arrangements. This is unsurprising since the substitution of ethenyl for azo should be an isostructural change. Furthermore, the fact that **1** and **3** show similar relative harmonic intensities for SHG to those of their azo-containing counterparts[9] demonstrates that the electronic differences between the –C=CH– and –N=N– groups have no detectable effect on the non-linear optical activity of these materials. The observation of a more intense SHG signal from the iodo complex **2** than from any of the other {Mo(NO)L} complexes studied so far is noteworthy. This validates the

Table 5 Kurtz powder test results and absorption edges for ferrocenyl complexes [$M(NO)L(X)(NHC_6H_4\{CH{=}CHC_6H_4[(C_5H_4)Fe(C_5H_5)]\text{-}4\}\text{-}4)$]

	M	X	λ^a/nm	SHG^b
1	Mo	Cl	740	35 ± 7
2	Mo	I	760	85 ± 10
3	W	Cl	660	8 ± 2

[a] All spectra recorded at ambient temperature in dichloromethane, concentrations *ca.* 10^{-5} mol dm^{-3}. [b] Relative harmonic intensity for second harmonic generation measured with a 1907 nm laser wavelength using a urea powder standard. [c] Values obtained from 3-acetamido-4-(dimethylamino)nitrobenzene and N-(4-nitrophenyl)-L-pyrrolidine-2-methanol are 35 ± 7 and 150 ± 10.

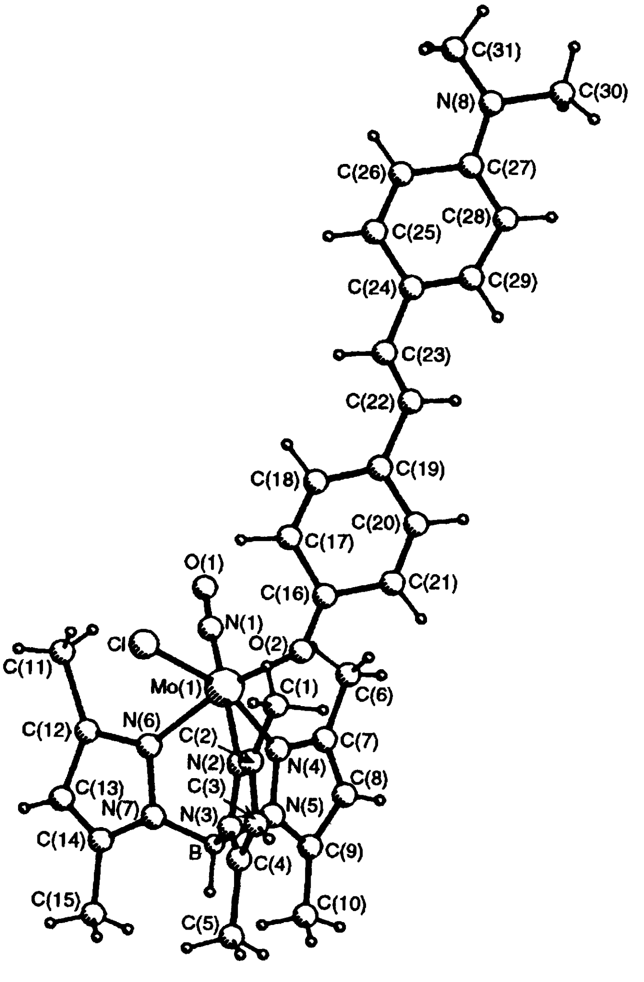


Fig. 1 View of one of the two independent molecules of complex **7** showing the atom numbering

suggestion made in a previous report[9] that the low SHG observed for the complex [$Mo(NO)L(I)(HNC_6H_4\{N{=}NC_6H_4[(C_5H_4)Fe(C_5H_5)]\text{-}4\}\text{-}4)$] is a result of poor sample crystallinity rather than any electronic effects brought about by replacement of chloride by iodide.

Single crystals of the complex [$Mo(NO)\{HB(dmpz)_3\}Cl\{OC_6H_4(CH{=}CHC_6H_4NMe_2\text{-}4)\text{-}4\}$] **7** were obtained and, although not of high quality, these did allow a crystal structure to be determined. The molecular structure is illustrated in Fig. 1, which also shows the atom numbering. There are two independent molecules (**A** and **B**) in the crystal structure and Fig. 1 depicts **A**. The molecules **A** and **B** bear a pseudo-centrosymmetrical relationship to one another, but are otherwise closely similar. The crystal structure also contains two independent molecules of dichloromethane with 0.75 site occupancy. Atomic coordinates are listed in Table 6 and selected bond lengths and angles in Table 7. For reasons outlined in the Experimental section, the accuracy of the determination is not high and detailed discussion of geometrical parameters would not be fruitful.

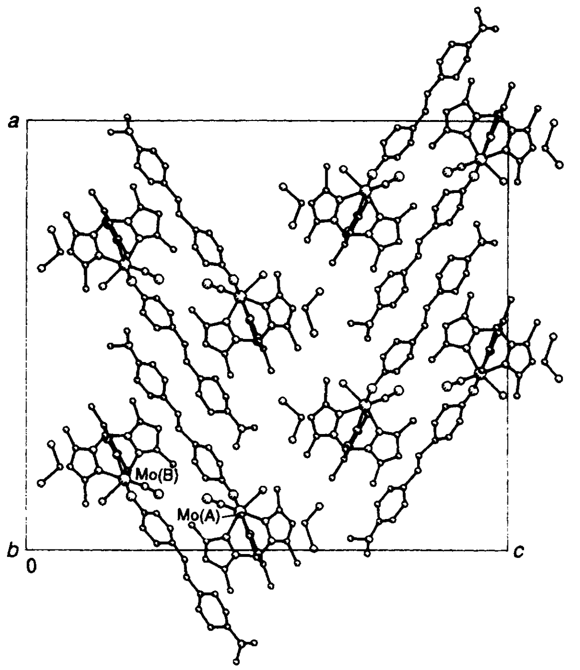


Fig. 2 Crystal packing of complex **7**

The co-ordination about the central molybdenum approximates to octahedral, the maximum angular deviation from ideal octahedral being 16.7° [angle Cl–Mo–N(4) 163.3(6)° in molecule **A**]; mean deviations are 6.5 (molecule **A**) and 5.9° (**B**). Corresponding angles in the two molecules, however, differ only by an average of 1.4°. As is generally found in this class of molybdenum complexes, the Mo–N(nitrosyl) bond is the shortest of the bonds to the ligands, and the bond *trans* to this bond is relatively long [see Mo–N(2) in Table 7]. This *trans* bond-lengthening effect of the nitrosyl group has been noted previously and attributed[23] to the strongly π-accepting nature of the nitrosyl ligand as evidenced by the shortness of the Mo–N (nitrosyl) bonds.

The pyrazolyl rings are essentially planar and make angles within the ranges 105–133 (molecule **A**) and 105–128° (**B**) to one another. The smallest interplanar angle (105° in both molecules) is between the pair of rings encompassing the relatively small nitrosyl ligand, the other dihedral angles being all considerably larger, 122–133°. The geometry of the carbon framework of the 4-dimethylamino-4′-hydroxystilbene ligand may be described in terms of the dihedral angles which the C(16)–C(21) and C(24)–C(29) phenyl rings make with the four-atom C–C=C–C linking residue C(19), C(22)–C(24). These angles, respectively, 11.7 and 10.2 (molecule **A**) and 6.5 and 6.2° (**B**), are quite small and the 14 carbon atoms of the stilbene residue are coplanar to within ±0.14 (molecule **A**) and ±0.13 Å (**B**).

The crystal packing is illustrated in Fig. 2. Noteworthy is the arrangement of molecules in (non-crystallographic) centrosymmetric pairs. This leads to cancellation of the molecular dipoles despite the fact that the compound crystallises in a polar space group. This packing arrangement provides further evidence of the important structural role played by the ferrocenyl substituent in the SHG-active compounds reported here and earlier.[9] This bulky group appears to inhibit the pairwise antiparallel packing of molecules found for **7** and, perhaps fortuitously, leads to a favourable molecular orientation for phase matching within crystals of [M(NO)L(Cl)(NH-

Table 6 Fractional atomic coordinates (× 10^4) with estimated standard deviations (e.s.d.s) in parentheses for complex **7**

Atom	*x*	*y*	*z*	*x*	*y*	*z*
Molecule A				Molecule B		
Mo(1)	888(1)	2320(2)	4423	1637(1)	2563(3)	2022(1)
Cl(1)	1396(2)	3748(10)	4899(3)	1130(3)	1102(9)	1559(3)
O(1)	1188(8)	4421(23)	3743(6)	1298(8)	456(24)	2734(7)
O(2)	1280(5)	401(18)	4285(5)	1249(5)	4447(19)	2161(5)
N(1)	1063(6)	3629(20)	4022(7)	1478(7)	1232(21)	2447(6)
N(2)	666(6)	695(2)	4949(6)	1846(6)	4126(23)	1480(6)
N(3)	209(6)	628(20)	5074(6)	2325(7)	4156(22)	1368(7)
N(4)	297(7)	1274(22)	4134(6)	2248(6)	3656(21)	2323(6)
N(5)	−118(6)	935(21)	4334(6)	2645(6)	3932(20)	2087(7)
N(6)	369(7)	4017(23)	4630(7)	2204(6)	785(17)	1854(5)
N(7)	−81(7)	3449(22)	4801(7)	2569(6)	1366(19)	1661(6)
N(8)	4749(8)	82(23)	2106(7)	−2188(7)	4816(24)	4455(8)
C(1)	1409(10)	−778(33)	5190(10)	1068(9)	5124(26)	1215(8)
C(2)	920(8)	−229(23)	5235(6)	1627(12)	4960(33)	1201(10)
C(3)	610(11)	−1031(32)	5507(10)	1927(9)	5645(29)	898(8)
C(4)	195(11)	−331(31)	5390(10)	2356(7)	5069(24)	1009(6)
C(5)	−308(11)	−656(35)	5608(9)	2791(9)	5368(30)	808(8)
C(6)	579(10)	778(32)	3423(9)	1989(10)	3906(35)	3041(9)
C(7)	203(11)	753(30)	3728(9)	2320(7)	4204(24)	2697(6)
C(8)	−220(9)	129(25)	3712(8)	2819(9)	4781(26)	2733(9)
C(9)	−450(7)	270(23)	4104(8)	2975(10)	4455(29)	2347(9)
C(10)	−946(11)	67(35)	4224(11)	3456(8)	4964(27)	2192(9)
C(11)	816(7)	7044(28)	4455(7)	1848(10)	−2051(23)	2080(8)
C(12)	325(13)	5899(35)	4607(13)	2240(6)	−834(19)	1886(6)
C(13)	−183(9)	6235(30)	4761(9)	2611(7)	−1258(23)	1705(7)
C(14)	−333(8)	4757(25)	4900(8)	2886(10)	53(32)	1589(10)
C(15)	−844(10)	4536(27)	5065(10)	3321(8)	308(26)	1330(9)
C(16)	1626(8)	282(26)	4047(8)	862(8)	4596(26)	2437(8)
C(17)	2000(8)	1497(28)	4003(9)	849(9)	5841(30)	2690(9)
C(18)	2371(9)	1249(27)	3779(8)	501(8)	6024(26)	2978(8)
C(19)	2443(7)	−33(24)	3501(7)	170(7)	4919(22)	3020(7)
C(20)	2046(9)	−1126(28)	3486(9)	152(10)	3602(29)	2693(10)
C(21)	1661(8)	−986(24)	3713(8)	515(8)	3528(28)	2397(9)
C(22)	2814(9)	−115(31)	3152(10)	−225(8)	5108(25)	3278(8)
C(23)	3153(9)	733(30)	3140(9)	−634(8)	4025(29)	3317(9)
C(24)	3542(10)	655(28)	2836(8)	−1028(8)	4316(26)	3606(7)
C(25)	3937(7)	1749(26)	2866(8)	−1026(8)	5727(27)	3909(8)
C(26)	4300(10)	1586(32)	2608(9)	−1448(9)	5710(30)	4131(9)
C(27)	4334(7)	152(22)	2322(6)	−1783(12)	4518(37)	4159(12)
C(28)	3938(9)	−843(31)	2279(9)	−1804(10)	3375(30)	3819(9)
C(29)	3576(9)	−519(32)	2567(10)	−1381(11)	3374(31)	3569(11)
C(30)	4730(11)	−1167(36)	1719(9)	−2165(11)	5990(32)	4717(10)
C(31)	5083(11)	1320(34)	2069(12)	−2601(11)	3652(36)	4341(11)
B(1)	−154(10)	1602(29)	4813(7)	2662(11)	3272(32)	1613(9)

Dichloromethane molecules, site occupancy 0.75

Cl(1C)	1543(5)	−56(21)	302(6)	C(1C)	1924(12)	564(37)	689(11)	Cl(2D)	31(4)	4310(27)	5950(5)
Cl(2C)	2448(4)	630(21)	507(4)	Cl(1D)	1017(4)	4903(19)	6068(5)	C(1D)	623(13)	4042(40)	5763(13)

$C_6H_3(Me\text{-}3)\{N{=}NC_6H_3[(C_5H_4)Fe(C_5H_5)]\text{-}4\}\text{-}4)Cl]$ (M = Mo or W)[8,9] and presumably also in **1**.

Conclusion

The results described here provide further evidence for the importance of having bulky substituents at each end of these rod-shaped heterobimetallic complexes in order to produce packing arrangements favourable for SHG. Despite the variety of compounds which have now been examined none of those which lack the bulky ferrocenyl donor function shows any SHG. We have also established that significant changes in ligand structure can be carried out without altering crystal-packing arrangements or bulk non-linear optical activity. However, it should be emphasised that subtle changes in the second-order hyperpolarisability, β, cannot be detected using the Kurtz powder test. In order accurately to assess the effect of electronic changes on β in these novel complexes solution EFISH (electric field induced SHG) measurements will be required.[24]

Experimental

The known compounds 4-(dimethylamino)-4′-nitro-,[10] 4-methoxy-4′-nitro-,[11] 2,4-dimethoxy-4′-nitro-,[12] 3,4-dimethoxy-4′-nitro-[12] and 4-ferrocenyl-4′-nitro-stilbene[25] were prepared using previously described procedures, as were $[M(NO)LX_2]$ (M = Mo, X = Cl or I; M = W, X = Cl).[26] Triethylamine was dried over sodium and stored over activated alumina, and hexamine was recrystallised from absolute ethanol and dried under vacuum. Other reagents were used as supplied, and all reaction solvents were redistilled from drying agents according to standard methods prior to use. All complexation reactions were performed under an atmosphere of dry nitrogen but the products were handled in air. All column chromatography was carried out using silica gel 60 (70–230 mesh) and column dimensions of 40 × 2 cm unless otherwise specified.

Powder tests for SHG were carried out using modifications of the standard Kurtz powder test[27] on unsized powdered samples. Samples were contained in small wells of dimensions 2 × 5 mm formed by fixing a metal washer between a glass microscope slide and glass cover-slip using epoxy resin. The

Table 7 Selected bond lengths (Å) and angles (°)

	Molecule A	Molecule B
Mo(1)–Cl(1)	2.400(8)	2.384(8)
Mo(1)–O(2)	1.947(15)	1.920(15)
Mo(1)–N(1)	1.734(20)	1.792(20)
Mo(1)–N(2)	2.225(19)	2.224(19)
Mo(1)–N(4)	2.102(20)	2.178(18)
Mo(1)–N(6)	2.115(19)	2.219(16)
O(1)–N(1)	1.155(29)	1.225(29)
Cl(1)–Mo(1)–O(2)	99.7(5)	100.1(5)
Cl(1)–Mo(1)–N(1)	91.0(7)	92.0(7)
O(2)–Mo(1)–N(1)	97.9(8)	97.8(8)
Cl(1)–Mo(1)–N(2)	87.8(5)	86.9(5)
O(2)–Mo(1)–N(2)	83.2(7)	84.3(7)
N(1)–Mo(1)–N(2)	178.5(8)	177.7(8)
Cl(1)–Mo(1)–N(4)	163.3(6)	164.0(5)
O(2)–Mo(1)–N(4)	92.9(7)	92.7(7)
N(1)–Mo(1)–N(4)	98.0(8)	95.7(8)
N(2)–Mo(1)–N(4)	83.0(7)	84.9(7)
Cl(1)–Mo(1)–N(6)	85.4(6)	88.9(5)
O(2)–Mo(1)–N(6)	167.8(7)	168.0(6)
N(1)–Mo(1)–N(6)	93.0(8)	89.7(7)
N(2)–Mo(1)–N(6)	86.1(7)	88.3(6)
N(4)–Mo(1)–N(6)	80.1(7)	77.2(6)
Mo(1)–O(2)–C(16)	130.7(14)	131.4(13)
Mo(1)–N(1)–O(1)	176.1(17)	169.2(18)

1064 nm fundamental output of a Nd:YAG laser was passed through a high-pressure hydrogen cell to give a Raman-shifted output at 1907 nm. Pulses (widths 4 ns, repetition rate 1 Hz) were weakly focused onto the sample cells and the second harmonic light at 950 nm measured on an S1 response photomultiplier tube. Boxcar-gate sampling was used to provide data points averaged over ten pulses and the mean of ten of these points provided the final data set.

Infrared spectra were recorded using a Perkin-Elmer 297 spectrometer with samples as KBr discs, 270 MHz ^{1}H NMR spectra from solutions in CDCl$_3$ using a JEOL GX 270 spectrometer. Electron impact mass spectra were recorded using a KRATOS MS 80 RF instrument. Cyclic voltammetric measurements were made using a PAR 174A polarograph. Solutions in CH$_2$Cl$_2$ were *ca.* 10^{-3} mol dm^{-3} in complex and 0.2 mol dm^{-3} in NBu$^n_4$BF$_4$ as base electrolyte. A platinum bead test electrode was used with a scan rate of 200 mV s^{-1}. A saturated calomel electrode (SCE) as reference was used with ferrocene as an internal standard ($E_f = +0.57$ V, $\Delta E_p = 70$ mV). Potentials are quoted relative to the SCE.

4-*Amino*-4′-*ferrocenylstilbene* (HY^6).—A solution of 4-ferrocenyl-4′-nitrostilbene[25] (0.5 g, 1.22 mmol) and ammonium chloride (0.5 g, 9.35 mmol) in acetone (50 cm^3) and water (10 cm^3) was heated to reflux. Zinc powder (0.5 g, 7.65 mmol) was added and the mixture stirred at reflux for 1 h. Further ammonium chloride (0.5 g) and zinc powder (0.5 g) were added and the mixture was stirred at reflux for 22 h. The colour changed from red to orange during this time. The reaction mixture was cooled and the zinc powder filtered off. The acetone was removed *in vacuo* and water (20 cm^3) and dichloromethane (20 cm^3) were added. The orange organic layer was separated and the aqueous layer extracted with further dichloromethane (3 × 10 cm^3). The combined organic extracts were evaporated and the product purified by column chromatography using dichloromethane as eluent. The major orange band yielded upon evaporation 4-amino-4′-ferrocenylstilbene as a pale orange solid (0.43 g, 92%).

4-*Amino*-2′,4′-*dimethoxystilbene* (HY^8).—A solution of 2,4-dimethoxy-4′-nitrostilbene[12] (1.06 g, 3.72 mmol) and ammonium chloride (1.0 g, 18.70 mmol) in acetone (50 cm^3) and water (10 cm^3) was heated to reflux. Zinc powder (0.5 g, 7.65 mmol) was added and the mixture stirred under reflux for 5 h. Further ammonium chloride (0.5 g) and zinc powder (0.5 g) were added, and the mixture was stirred at reflux for 30 min. The colour changed from dark red to yellow-orange during this time. The reaction mixture was cooled and the zinc powder filtered off. The acetone was removed *in vacuo* and water (20 cm^3) and dichloromethane (20 cm^3) were added. The orange organic layer was separated and the aqueous layer extracted with further dichloromethane (3 × 10 cm^3). The combined organic extracts were evaporated and the product obtained as a beige solid which was purified by recrystallisation from ethanol (0.90 g, 95%).

4-*Amino*-3′,4′-*dimethoxystilbene* (HY^7).—This compound was prepared in an identical manner to that of HY^8 using 3,4-dimethoxy-4′-nitrostilbene[11] (1.06 g, 3.72 mmol) in place of 2,4-dimethoxy-4′-nitrostilbene to yield a beige solid (0.89 g, 94%).

Complex **1**.—A solution of [Mo(NO){HB(dmpz)$_3$}Cl$_2$] (0.30 g, 0.61 mmol), HY^6 (0.24 g, 0.63 mmol) and triethylamine (0.5 cm^3, 3.7 mmol) in toluene (20 cm^3) was heated under reflux for 3 h. The reaction mixture was then cooled and evaporated to dryness under reduced pressure. The crude product was purified by column chromatography gel using 30% hexane–dichloromethane as the eluent. The major purple band was collected and crystallised from dichloromethane–hexane to give the deep violet product (0.33 g, 65%).

The following complexes were prepared in a similar manner: **2**, using [Mo(NO){HB(dmpz)$_3$}I$_2$]·C$_6$H$_5$Me (0.30 g, 0.39 mmol) and HY^6 (0.16 g, 0.42 mmol), as a deep purple product (0.32 g, 88%); **3**, using [W(NO){HB(dmpz)$_3$}Cl$_2$] (0.30 g, 0.52 mmol) and HY^6 (0.22 g, 0.58 mmol), reaction time 9 h, as a dark orange-brown solid (0.25 g, 52%).

Complex **4**.—This was prepared from [Mo(NO){HB(dmpz)$_3$}Cl$_2$] (0.30 g, 0.61 mmol) and HY^1 (0.14 g, 0.71 mmol) using the procedure described for **1** except that hexamine (0.05 g, 0.36 mmol) was used in place of triethylamine. Column chromatography using 50% hexane–dichloromethane as the eluent afforded the deep purple product (0.34 g, 85%).

The following complexes were prepared similarly: **5**, using [Mo(NO){HB(dmpz)$_3$}I$_2$]·C$_6$H$_5$Me (0.40 g, 0.52 mmol) and HY^1 (0.12 g, 0.61 mmol), as a deep purple solid (0.29 g, 76%); **6**, from [Mo(NO){HB(dmpz)$_3$}I$_2$]·C$_6$H$_5$Me (0.40 g, 0.52 mmol) and HY^1 (0.25 g, 1.27 mmol), with triethylamine (0.5 cm^3, 3.7 mmol) in place of hexamine, as a purple-brown solid (0.23 g, 55%); **7**, using HY^3 (0.17 g, 0.71 mmol) in place of HY^1 and dichloromethane as eluent, as a deep indigo product (0.38 g, 89%).

Complex **8**.—This was prepared in an identical manner to that of complex **5** using HY^3 (0.15 g, 0.63 mmol) in place of HY^1 and dichloromethane as eluent, as a dark green solid (0.33 g, 81%).

Complex **9**.—This was prepared in an identical manner to that of complex **6** using HY^3 (0.30 g, 1.25 mmol) in place of HY^1 and dichloromethane as eluent, as a deep purple solid (0.29 g, 62%).

Complex **10**.—This was prepared in an identical manner to that of complex **7** using [W(NO){HB(dmpz)$_3$}Cl$_2$] (0.40 g, 0.69 mmol), HY^3 (0.18 g, 0.75 mmol), and triethylamine (0.5 cm^3, 3.7 mmol), reaction time 5 h, as a deep pink-purple solid (0.46 g, 85%).

Complex **11** was similarly prepared using [Mo(NO){HB(dmpz)$_3$}Cl$_2$] (0.11 g, 0.22 mmol) and HY^2 (0.052 g, 0.23 mmol) in place of HY^3, as a deep indigo product (0.13 g, 83%).

Complex **12**.—This was prepared in an identical manner to that of complex **8** using [Mo(NO){HB(dmpz)$_3$}I$_2$]$\cdot$C$_6$H$_5$Me (0.16 g, 0.21 mmol) and HY^2 (0.059 g, 0.26 mmol) in place of HY^3, as a deep blue-black solid (0.135 g, 83%).

Complex **13**.—This was prepared in an identical manner to that of complex **6** using HY^2 (0.062 g, 0.27 mmol) in place of HY^1, [Mo(NO){HB(dmpz)$_3$}I$_2$]$\cdot$C$_6$H$_5$Me (0.10 g, 0.13 mmol) and dichloromethane as eluent, as a deep pink-purple solid (0.051 g, 45%).

Complex **14**.—This was prepared in an identical manner to that of complex **10** using [W(NO){HB(dmpz)$_3$}Cl$_2$] (0.13 g, 0.22 mmol) and HY^2 (0.058 g, 0.26 mmol), as a dark orange-brown solid (0.12 g, 71%).

Complex **15**.—This was prepared in a similar manner to that of complex **7** using HY^5 (0.15 g, 0.63 mmol) in place of HY^3 and triethylamine (0.5 cm^3) in place of hexamine, as a deep violet solid (0.35 g, 84%).

Complex **16** was prepared in an identical manner using [Mo(NO){HB(dmpz)$_3$}I$_2$]$\cdot$C$_6$H$_5$Me (0.40 g, 0.52 mmol) and HY^5 (0.15 g, 0.63 mmol), as a deep blue solid (0.31 g, 76%).

Complex **17**.—Sodium (0.1 g, 4.35 mmol) was heated under reflux in dry thf (35 cm^3) for 30 min. Naphthalene (0.1 g, 0.78 mmol) was then added and the mixture stirred for 1 h under reflux during which time the solution became dark green. The mixture was then filtered under nitrogen, to remove excess of sodium, and HY^5 (0.08 g, 0.34 mmol) was added to the filtrate. After stirring the resulting solution for 30 min at room temperature, complex **16** (0.15 g, 0.19 mmol) was added and the mixture stirred under reflux for 2.5 h. The final dark green mixture was filtered in air to give a dark green filtrate from which the solvent was removed *in vacuo*. The product was purified by column chromatography using dichloromethane as eluent, the major green fraction being collected. Further purification was effected by recrystallisation from hexane–dichloromethane to yield a dark green solid (0.10 g, 58%).

Complex **18**.—This was prepared in an identical manner to that of complex **15** using [W(NO){HB(dmpz)$_3$}Cl$_2$] (0.40 g, 0.69 mmol) and HY^5 (0.19 g, 0.78 mmol), reaction time 8 h, as a deep red-brown solid (0.13 g, 24%).

Complex **19**.—This was prepared in a similar manner to that of complex **15** using HY^4 (0.14 g, 0.63 mmol) in place of HY^5, as a deep pink-purple solid (0.33 g, 79%).

Complex **20**.—This was prepared in an identical manner to that of **16** using HY^4 (0.14 g, 0.63 mmol) in place of HY^5, as a deep purple solid (0.33 g, 82%).

Complex **21**.—This was prepared in an identical manner to that of complex **17** using **20** (0.15 g, 0.19 mmol) instead of **16** and HY^4 (0.077 g, 0.34 mmol) instead of HY^5, as a dark green solid (0.062 g, 37%).

Complex **22**.—This was prepared in an identical manner to that of complex **18** using HY^4 (0.18 g, 0.78 mmol) in place of HY^5, as a deep red-brown solid (0.11 g, 21%).

Complex **23**.—This was prepared in a similar manner to that of complex **15** using HY^7 (0.16 g, 0.63 mmol) in place of HY^5, as a deep violet solid (0.32 g, 74%).

Complex **24**.—This was prepared in an identical manner to that of complex **16** using HY^7 (0.15 g, 0.59 mmol) in place of HY^5, as a deep violet solid (0.37 g, 88%).

Complex **25**.—This was prepared in an identical manner to that of complex **17** using **24** (0.15 g, 0.19 mmol) instead of **16** and HY^7 (0.10 g, 0.39 mmol) instead of HY^5. Column chromatography using 5% thf–dichloromethane as eluent followed by recrystallisation afforded a dark green solid (0.058 g, 33%).

Complex **26**.—This was prepared in an identical manner to that of complex **18** using HY^7 (0.20 g, 0.78 mmol) in place of HY^5, as a dark orange-brown solid (0.10 g, 18%).

Complex **27**.—This was prepared in a similar manner to that of complex **15** using HY^8 (0.16 g, 0.63 mmol) in place of HY^5, as a deep violet solid (0.31 g, 72%).

Complex **28**.—This was prepared in an identical manner to that of complex **16** using HY^8 (0.15 g, 0.59 mmol) in place of HY^5, as a deep violet solid (0.35 g, 84%).

Complex **29**.—This was prepared in an identical manner to that of complex **25** using **28** (0.15 g, 0.19 mmol) instead of **24** and HY^8 (0.10 g, 0.39 mmol) instead of HY^7, as a dark green solid (0.063 g, 36%).

Complex **30**.—This was prepared in an identical manner to that of complex **18** using HY^8 (0.20 g, 0.78 mmol) instead of HY^5, as a dark orange-brown solid (0.13 g, 23%).

Complex **31**.—This was prepared in a similar manner to that of complex **15** using HY^9 (0.16 g, 0.63 mmol) in place of HY^5, as a deep violet solid (0.32 g, 74%).

Complex **32**.—This was prepared in an identical manner to that of complex **16** using HY^9 (0.15 g, 0.59 mmol) instead of HY^5, as a deep violet solid (0.32 g, 75%).

Complex **33**.—This was prepared in an identical manner to that of complex **25** using **32** (0.15 g, 0.19 mmol) instead of **24** and HY^9 (0.10 g, 0.39 mmol) instead of HY^7, as a dark green solid (0.032 g, 18%).

Complex **34**.—This was prepared in an identical manner to that of complex **18** using HY^9 (0.20 g, 0.78 mmol) in place of HY^5, as a dark orange-brown solid (0.16 g, 29%).

Crystallography.*—*Crystal data*. [Mo(NO){HB(dmpz)$_3$}Cl{OC$_6$H$_4$(CH=CHC$_6$H$_4$NMe$_2$-4)-4}]$\cdot$0.75CH$_2$Cl$_2$, C$_{31}$H$_{38}$BClMoN$_8$O$_2$$\cdot$0.75CH$_2Cl_2$ **7**, M_r 760.6, orthorhombic, space group $Pca2_1$, a = 28.592(7), b = 7.965(7), c = 32.211(11) Å, U = 7336 Å^3, Z = 8, D_c = 1.377 g cm^{-3}, $F(000)$ = 3132, μ(Mo-Kα) = 0.566 mm^{-1}, λ = 0.710 69 Å.

The crystal (0.7 × 0.4 × 0.4 mm) was mounted on an Enraf-Nonius CAD4 diffractometer; cell dimensions and intensities were measured by ω–2θ scans with graphite-monochromated Mo-Kα radiation. 5359 Unique reflections were scanned in the range $2 < \theta < 23°$, of which 2930 having $I > 2.5\sigma(I)$ were considered observed and used in the analysis. Three standard reflections were remeasured every 2 h to monitor the stability of the system. A slight (< 10%) drop in intensity during the period of data collection was corrected by application of appropriate scaling factors. The structure was determined by direct methods followed by successive rounds of structure-factor and Fourier calculation. The development and refinement of the structure was severely hindered by the paucity of reflection data and by a pseudo-centre of symmetry relating the two independent molecules in the asymmetric unit. Final least-squares refinement using anisotropic thermal parameters for non-hydrogen atoms resulted in R = 0.080, R' = 0.105 for the 2930 observed reflections. Hydrogen atoms were placed in calculated positions riding on their respective bonded atoms with fixed isotropic

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* Contribution from the joint crystallography unit, Universities of Aston and Birmingham.

thermal parameters, $U = 0.1$ Å^2. Weights, $w = 1/[\sigma^2(F) + 0.0035F^2]$, were used in the least-squares refinement. The calculations were terminated when all shift/e.s.d. ratios were < 0.30 and the residual electron density was within the range -0.9 to $+1.7$ e Å^{-3}.

Complex neutral atom scattering factors were employed. Computations were carried out on the University of Birmingham IBM 3090 computer and on the Amdahl 5890 at Manchester Computing Centre with the SHELX 86[28] and 76[29] packages. The molecular diagrams were drawn using PLUTO.[30]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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