On the Chemistry of Pyrrole Pigments, LXXXVIII [1]: Nonlinear Optical Properties of Linear Oligopyrroles

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Summary. The second order polarizabilities, β_{xxx}, of six linear oligopyrroles of the arylalkylidene-dipyrrinone type (the synthesis of two of them is reported) were estimated from their solvatochromic shifts. A dimethylaminophenylmethylene and a benzodithioleylidenemethylene derivative (**2, 6**) were found to exhibit rather high β_{xxx} values.

Keywords. Nonlinear optical properties; Second order polarizability; Solvatochromic shift; Linear oligopyrroles; Arylalkylidene-dipyrrinones.

Zur Chemie von Pyrrolpigmenten, 88. Mitt. [1]:
**Nicht-lineare optische Eigenschaften von linearen Oligopyrrolen**

Zusammenfassung. Die Polarisierbarkeiten zweiter Ordnung, β_{xxx}, von sechs linearen Oligopyrrolen des Arylalkyliden-pyrrolinon-Typs (die Synthese zweier solcher Derivate wird mitgeteilt) wurden aus ihrem solvatochromen Verhalten abgeschätzt. Ein Dimethylaminophenylmethylen- und ein Benzodithiolylidenmethylen-Derivat (**2, 6**) zeigen bemerkenswert hohe β_{xxx}-Werte.

Introduction

The recent decade has witnessed a strong interest in materials which exhibit nonlinear optical properties. In particular conjugated organic compounds substituted with donor and acceptor residues were synthesized and shown to exhibit quite formidable nonlinear optical responses [2, 3]. Accordingly, they are of great importance to expand the range of applications in laser technology and optical processing of information.

In the search for new organic compounds with potentially interesting nonlinear optical properties we choose to investigate linear oligopyrrolic compounds. Because they are derived as parts from, or are synthesized as models for the natural bile pigments [4], they inherently contain the necessary push pull arrangement of donor and acceptor groups at the ends of a conjugated system as shown in Scheme 1. Moreover, in most cases they also contain a 2 *H*-pyrrolic fragment between these electron donating and accepting moieties. This fragment type was recently shown to enhance nonlinear optical effects [5]. Therefore we centered our investigations

on linear tripyrrolic systems and their aryl (*Ar*) or vinylogous aryl analogs as given by their general formula **I**.
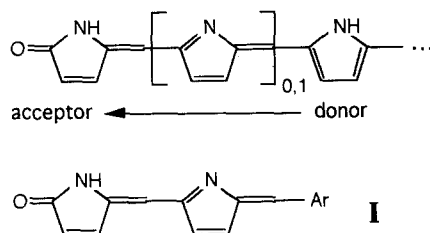
Scheme 1

Material and Methods

Melting points were taken by means of a Kofler hot stage microscope (Reichert, Vienna). ^{1}H-NMR, IR-, UV-VIS-, and M-spectra were recorded using the Bruker AX-200-, Biorad FT-IR-45-, Hitachi U-3210-, and Varian MAT-311-A-instruments. Proton signal and stereochemical assignments were achieved using NOE measurements. Second-order polarizabilities $\beta_{xxx}(2\omega)$ were determined using a recently described method [6]. It is based on the estimation of excited state permanent dipole moments μ_e by means of the solvatochromic shift using the McRae expression

$$(\omega_{eg})_s - \omega_{eg} = A[(n^2-1)/(2n^2+1)] + B[(\varepsilon-1)/(\varepsilon+2) - (n^2-1)/(n^2+2)] \tag{1}$$

$$\text{and } B = (2/4\,\pi\varepsilon_0 hca^3)\mu_g(\mu_e - \mu_g) \tag{2}$$

where $(\omega_{eg})_s$ denotes the frequency of the longest wavelength transition and ω_{eg} is the corresponding frequency in the gaseous state. The dielectricity constant and the refractive index of the solvent is given by ε and n. A and B are constants for a given molecule; a is the radius of a spherical cavity within the solvent which is occupied by the molecule. Thus it is approximated by 0.7 times the maximum length of the molecule [6] in its lowest energy geometry. Standard bond lengths and bonding angles derived from appropriate X-ray data [4] were used to construct molecular models. The speed of light in vacuum is denoted by c, and h is Planck's constant. Ground state permanent dipole moments μ_g were estimated by means of vectorial addition from MNDO+ [7] calculated or known [8] partial moments on the basis of the molecular geometries derived above. As solvents dimethylsulfoxide (*DMSO*) and heptane were chosen to have sufficient data to deduce ω_{eg} and B from (1); μ_e could then be deduced from (2).

The second-order polarizability $\beta_{xxx}(2\omega)$ at a wavelength of 1 907 nm (frequency ω) was estimated using

$$\beta_{xxx}(2\omega) = (3/2\,c^2h^2)\mu_{eg}^2(\mu_e - \mu_g)\omega_{eg}^2/(\omega_{eg}^2 - \omega^2)(\omega_{eg}^2 - 4\omega^2) \tag{3}$$

where μ_{eg} is the transition dipole moment between ground and excited state. It was derived from the absorption band area f (from the molar extinction coefficient ε and band width $\Delta v_{1/2}$ at half band intensity) by means of (4):

$$f = (2\pi\omega_{eg}N_0 nM\mu_{eg}^2)/[3(2.303)\varepsilon_0 ch] \tag{4}$$

with N_0 the Loschmidt number, ε_0 the permittivity of vacuum, and M the molecular mass.

Compounds 1–4 were prepared according to Ref. [9]. 4-Nitroaniline (7) was of commercial origin (Fluka); *DMSO* and heptane were of spectroscopic quality.

(Z,Z)-4-Ethyl-3-methyl-5-[(5-ferrocenyl-2-methylene)-3,4-dimethyl-5 H-pyrrolyl-2-methylene]-3-pyrroline-2-one [5; $C_{25}H_{26}N_2OFe$]

This compound was prepared in analogy to Ref. [9] by condensation of ferrocenecarbaldehyde (Fluka) and the corresponding dipyrrinone [10]; yield 84%, m. p. 220 − 223°C. ^{1}H-NMR (CDCl$_3$, δ, 200 MHz): 10.74 (s, broad, NH), 6.80 (s, CH$_\beta$), 5.85 (s, CH$_\alpha$), 5.00 (m, 2 H, ferrocene), 4.68 (m, 2 H, ferrocene), 4.20 (s, 5 H, ferrocene), 2.52 (q, J = 7.7 Hz, CH$_2$CH$_3$), 2.08 (s, CH$_3$-4′), 2.00 (s, CH$_3$-3′), 1.94 (s, CH$_3$-3), 1.20 (t, J = 7.7 Hz, CH$_2$CH$_3$) ppm. NOE: CH$_2$CH$_3$ → CH$_\alpha$; CH$_3$-3′ → CH$_\alpha$, CH$_3$-4′ → CH$_\beta$. UV-VIS (CHCl$_3$): $\lambda_{max.}$ = 599 (4 600), 431 (17 900), 303 (23 100) nm(ε). IR (KBr): ν = 1 700, 1 630, 1 610 cm^{-1}. MS (70 eV, 100°C): m/e (%) = 426 (20; M^+), 362 (11), 361 (41), 86 (51), 85 (15), 84 (100), 83 (17), 71 (41), 69 (30), 57 (76), 55 (21), 51 (15).

(Z,Z)-4-Ethyl-3-methyl-5-[(5-(1,3-benzodithiolylidenemethylene)-3,4-dimethyl-5 H-pyrrolyl-2-methylene]-3-pyrroline-2-one [6; $C_{23}H_{22}N_2OS_2$]

This compound was prepared in analogy to Ref. [9] by condensation of the appropriate dipyrrinone [10] and 2-formylmethylene-1,3-benzodithiole [11]; yield 57%, m. p. 194 − 195°C. ^{1}H-NMR (CDCl$_3$, δ, 200 MHz): 7.28 (A_2B_2-system), 7.36 (d, J = 12 Hz, CH$_\beta$), 6.65 (d, J = 12 Hz, CH$_\gamma$), 5.87 (s, CH$_\alpha$), 2.50 (q, J = 7.7 Hz, CH$_2$CH$_3$), 2.10 (s, CH$_3$-4′), 2.03 (s, CH$_3$-3′), 1.95 (s, CH$_3$-3), 1.18 (t, J = 7.7 Hz, CH$_2$CH$_3$) ppm. NOE: CH$_2$CH$_3$ → CH$_\alpha$; CH$_3$-3′ → CH$_\alpha$; CH$_3$-4′ → CH$_\beta$. UV-VIS (CHCl$_3$): $\lambda_{max.}$ = 273 (42 800), 343 (18 600), 555 (40 600) nm(ε). IR (KBr): ν = 1 700, 1 650, 1 630 cm^{-1}. MS (70 eV, 100°C): m/e (%) = 406 (85, M^+), 391 (95), 377 (40), 376 (37), 266 (20), 236 (18), 203 (22), 177 (38), 153 (100), 130 (18), 100 (21), 77 (28), 53 (21), 41 (25).

R = OMe   1
R = N(Me)$_2$ 2

X = NH, R = Me   3
X = S, R = H   4

5   6
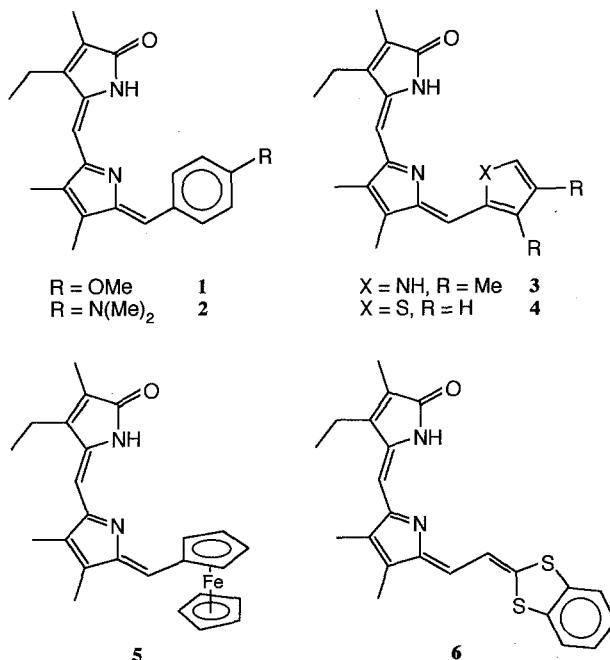
Results and Discussion

The UV-VIS data of compounds 1 − 7 are summarized in Table 1. In addition to the tripyrrinic derivatives 1 − 6, 4-nitroaniline (7), which was extensively studied in the past [2, 6], was included as a reference material.

From the experimental and calculated data of Table 1 the parameters and results of Table 2 were derived by means of equations (1) − (4). Of course, we have to

Table 1. UV-VIS data, ground state permanent dipole moments (μ_g), and cavity radius (a) of 1–7. The molar absorption coefficient ε and $\Delta\nu_{1/2}$ is given for $CHCl_3$ as solvent

Compound	$(\omega_{eg})_{DMSO}$ cm^{-1}	$(\omega_{eg})_{Heptane}$ cm^{-1}	ε	$\Delta\nu_{1/2}$ cm^{-1}	μ_g D	a Å
1	20 635	20 876	18 600	842	1.4	8.2
2	18 080	18 709	27 100	1 642	1.2	8.1
3	18 563	18 650	26 600	1 514	3.7	8.5
4	20 276	20 491	17 100	628	2.5	7.5
5	16 689	16 949	4 600	2 144	2.1	8.6
6	18 051	18 643	40 600	1 438	2.5	10.4
7	25 615	31 446	14 300	2 630	6.1	4.4

Table 2. UV-VIS data derived parameters and results for 1–7

Compound	ω_{eg}, cm^{-1}	μ_e, D	μ_{eg}, D	$-A$, cm^{-1}	$-B$, cm^{-1}	$\beta_{xxx}(1\,907\,nm)$ $\cdot10^{-30}$ esu^{-1} cm^5
1	20 713	18.0	3.9	1 262	424	32
2	18 235	49.8	7.0	3 293	1 106	439
3	18 396	6.2	6.6	455	153	20
4	20 292	8.9	3.3	1 126	378	10
5	16 700	15.9	3.4	1 361	457	41
6	18 008	49.0	8.0	3 099	1 041	578
7	28 571	20.3	5.1	30 529	10 258	21

assume that the geometries of the compounds remain unchanged on proceeding from one solvent to another. However, for common solvents like heptane and dimethylsulfoxide this was demonstrated to be the case for a variety of linear oligopyrroles [4].

From the data of Table 2 it is evident that the chosen way [6] to approximate second order polarizabilities by β_{xxx} and to deduce this value from measurements of solvatochromic shifts yields proper estimates of this nonlinear optical property. Thus the β_{xxx} value for 4-nitroaniline (7) compares favorably with the order of magnitude obtained in previous studies [2, 6]. It turns out that the common arylmethylene-dipyrrinones 1, 3, and 4 are similar in their β_{xxx} values to the reference compound 7. The ferrocene moiety of 5 leads to a doubling of β_{xxx} compared with 7, which underlines the rather minor effect displayed by this residue as observed earlier [3]. Only the strongly electron donating dimethylamino ligand in 2 yields a dramatic increase of β_{xxx}. The donor effect together with the elongated conjugation path in 6 leads to a further increase of β_{xxx}. Accordingly the derivatives 2 and 6 seem to be promising compounds challenging further evaluation of their nonlinear optical properties.

Acknowledgement

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