ELSEVIER

Journal of Photochemistry and Photobiology
A: Chemistry 85 (1995) 119–126

Journal of
PHOTOCHEMISTRY
AND
PHOTOBIOLOGY
A: CHEMISTRY

UV–visible spectra of some nitro-substituted porphyrins

M. Karelson[a,*], K. Pihlaja[b], T. Tamm[a], A. Uri[a], M.C. Zerner[c]

[a]*Department of Chemistry, University of Tartu, 2 Jakobi St., Tartu, EE2400, Estonia*
[b]*Department of Physical Chemistry, University of Turku, Turku, SF-20100, Finland*
[c]*Department of Chemistry and Quantum Theory Project, University of Florida, Gainesville, FL 32611, USA*

Received 15 April 1994; accepted 1 June 1994

Abstract

The synthesis and UV spectra of free base 2-nitro-5,10,15,20-tetraphenylporphyrin and copper 2-nitro-5,10,15,20-tetraphenylporphyrin in various solvents are reported. The experimental results are compared with those calculated using the self-consistent field (SCF) configuration interaction (CI) quantum chemical method with INDO/1 parametrization for a series of model compounds. Good agreement is observed between experimental and calculated spectra and predictions for possible solvatochromically sensitive, substituted porphyrins are made.

Keywords: UV/Vis spectra

1. Introduction

Synthetic porphyrins are of considerable interest as clinical agents for the photodynamic therapy of cancer [1–3] and diseases caused by human immunodeficiency viruses [4,5] and as substituent compounds for modelling photosynthetic electron transfer reactions [6]. The accumulation of light energy in these systems occurs through the short-lived singlet excited state of the porphyrin derivative (e.g. chlorophyll) and depends directly on the absorption intensity and spectral width as well as on the rate of subsequent electron transfer reactions. These processes are critically dependent on the structure of the derivative and the environment surrounding the photoactive system. In photodynamic therapy, more emphasis is placed on the generation of singlet molecular oxygen which proceeds via the longer lived triplet state of the porphyrin derivative. Again, the dependence of the photophysical properties of this triplet state on the structure and medium is of paramount importance. Recently, porphyrin derivatives containing electronegative substituents (halogen, nitro group, cyano group) at the 2-position carbons of the porphin ring have been synthesized and studied photochemically [7–10], and it is these systems that we turn our attention to in this paper.

In general, the electronic spectra of porphyrin derivatives are only slightly dependent on the solvent (environment) polarity [11]. However, if the porphin ring is considered to be a superaromatic system, the substitution at the "aromatic" ring atoms should lead to significant solvatochromic shifts due to electron-donating and, particularly, electron-accepting groups. Certainly an asymmetric electron distribution, as in the case of the photosynthetic reaction center, can lead to dramatic effects in the singlet excitation spectra and singlet–triplet transfer energy due to the polarizable environment [12].

In the present work, the synthesis and UV–visible spectra of 2-nitro-5,10,15,20-tetraphenylporphyrin and copper(II) 2-nitro-5,10,15,20-tetraphenylporphyrin in various solvents are reported. The spectra are compared with those modelled quantum chemically for a series of 2-substituted and 2,12-disubstituted porphyrins.

2. Experimental details

Copper(II) 2-nitro-5,10,15,20-tetraphenylporphyrin (**1**) was prepared using the method of Girardeau et al. [13]. After purification by silica column chromatography with toluene elution ($R_f = 0.78$) and crystallization with methanol, the synthesis product was dried under vacuum at 60–70 °C for 3 h. The IR spectrum

---

[*] Corresponding author.

1010-6030/95/$09.50
SSDI 1010-6030(94)03896-3

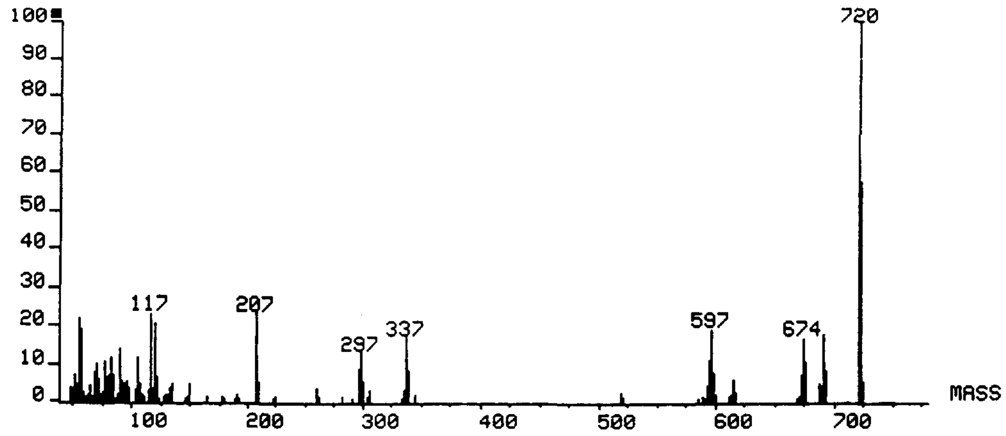


Fig. 1. Mass spectrum (70 eV) of compound 1.

of this metalloporphyrin in $CDCl_3$ showed two intense characteristic peaks adjacent to the nitro group ($\nu = 1327$ cm^{-1} and $\nu = 1527$ cm^{-1}). The mass spectrum of 1 (Fig. 1) shows the molecular ions $C_{44}H_{27}N_5O_2{}^{65}Cu$ and $C_{44}H_{27}N_5O_2{}^{63}Cu$ at *m/z* 722 and 720 in the correct isotopic ratio (corrected) 44.8/100. The other major ions (*m/z* (relative abundance (%), not corrected) are $[M-NO]^{\cdot+}$ at 692 (7.8) and 690 (17.5), $[M-NO_2]^{\cdot+}$ at 676 (10.4) and 674 (16.8), $[M-HNO_2]^{\cdot+}$ at 675 (12.7) and 673 (7.1) and $[M-NO_2-C_6H_5]^+$, $[M-HNO_2-C_6H_5]^+$ and $[M-HNO_2-C_6H_6]^+$ at 599 (7.3), 598 (7.4), 597 (19.0), 596 (4.5) and 595 (11.1). The ion at *m/z* 593 (4.2%) corresponds to a double-charged ion at *m/z* 296.5 (8.8%). A group of double-charged ions is also found at *m/z* 299.5 (2.2), 299 (5.4), 298.5 (13.0), 298 (9.0) and 297.5 (13.0).

2-Nitro-5,10,15,120-tetraphenylporphyrin (2) was obtained by the treatment of the copper salt with sulfuric acid [13]. After crystallization from chloroform–methanol solution, it was dried under vacuum. The ^1H and ^{13}C nuclear magnetic resonance (NMR) spectra of the compound were recorded on a Bruker AC-200 spectrometer in deuterochloroform with tetramethylsilane internal standard at 200 and 50.3 MHz respectively. The ^1H resonance assignments are based on those of Crossley et al. [8]: −2.62 (bs, 2H, NH); 7.70–7.79 (bm, 12H, $H_{m,p}$); 8.16–8.28 (bm, 8H, H_o); 8.71 (bs, 2H, $H_{12,13}$); 8.88–9.03 (bm, 4H, $H_{7,8,17,18}$); 9.05 (s, 1H, H_3). A signal of variable intensity, depending on the method of treatment of the samples and appearing at $\delta = 1.54$ ppm, is most probably caused by minute amounts of water (no respective high-field ^{13}C NMR signal can be detected). In the ^{13}C NMR spectrum of 2-nitro-5,10,15,20-tetraphenylporphyrin (relative to the spectrum of the unsubstituted porphyrin), the characteristic changes due to introduction of the nitro group into the aromatic molecule frame were detected.

The mass spectrum of porphyrin 2 also confirms its structure with the main peaks located at *m/z* 659 ($M^{\cdot+}$, 100), 629 ($[M-NO]^{\cdot+}$, 15.1), 615 (13.5), 614 (44.0), 613 ($[M-NO_2]^{\cdot+}$, 41.7) and double-charged ions at 307.5 (4.0), 307 (27.3) and 306.5 (50.3). The mass spectra of several porphyrin derivatives will be discussed in a future report.

The UV–visible absorption spectra of the two porphyrins 1 and 2 were recorded on a Specord M-40 (Carl Zeiss, Jena) spectrometer using 10 mm and 1 mm quartz cuvettes. Dilute solutions were used for all optical studies corresponding to the linear range of Lambert–Beer plots.

3. Method of calculation

The quantum chemical calculations were performed using INDO/1 parametrization for spectroscopy [14] and configuration interaction singles (CIS) wavefunction. The effect of the dielectric medium on the molecular structure of the chromophore was accounted for by using the reaction field approach [15]. The interaction energy between a dipolar solute molecule and the surrounding medium can be written as

$$E_{\text{int}} = -\frac{1}{2}\frac{2(D-1)}{2D+1}\frac{1}{a^3} = -\frac{1}{2}g(D, a)\mu^2 \qquad (1)$$

where D is the macroscopic dielectric constant of the polarizable medium and a denotes the radius of the spherical cavity of the medium into which the solute molecule with the dipole moment μ is embedded. In a one-electron approximation this leads to the following Schroedinger equation for the solute molecule in the state $|\psi\rangle$ [15]

$$\mathbf{H}|\psi\rangle = (\mathbf{H}_0 - g\langle|\psi|\mu|\psi\rangle\mu)|\psi\rangle = W|\psi\rangle \qquad (2)$$

where $\mathbf{H}_0$ is the solute hamiltonian in the solvent-free phase and μ is the solute dipole moment operator. Full relaxation of the solvent in the field of the solute molecule is assumed by Eq. (2). For spectroscopic excitation of the solute molecule, however, only the electronic relaxation of the solvent is sufficiently fast to be accounted for in the excited state. The rotational–orientational relaxation of the solvent is much slower than the electronic excitation of the solute and therefore the corresponding electric reaction field refers to the ground state of the molecule. In the framework of the CIS theory, the respective electronic excitation energy is presented by the following formula (theory B in Ref. [15])

$$\Delta E = W_{\mathrm{I}} - W_0 = \langle|\psi_{\mathrm{I}}|\mathbf{H}|\psi_{\mathrm{I}}\rangle - \langle|\psi_0|\mathbf{H}|\psi_0\rangle + \tfrac{1}{2}\, g(n_{\mathrm{D}}^2)\langle|\psi_{\mathrm{I}}|\mu|\psi_{\mathrm{I}}\rangle[\langle|\psi_0|\mu|\psi_0\rangle - \langle|\psi_{\mathrm{I}}|\mu|\psi_{\mathrm{I}}\rangle] \qquad (3)$$

where $g(n_{\mathrm{D}}^2)$ denotes the reaction field tensor for the electronic relaxation of the solvent and $|\psi_0\rangle$ and $|\psi_{\mathrm{I}}\rangle$ are the solute molecular total wavefunctions in the ground and Ith excited states respectively. Therefore, in contrast with the classical theory of electronic absorption in liquids, Eq. (3) accounts correctly for the first-order response of the solvent reaction field in the excited states of the chromophore.

Table 1
Absorption maxima and molecular extinction coefficients of the UV–visible spectra of 2-nitro-5,10,15,20-tetraphenylporphyrin in various solvents at 25 °C

Solvent	D[a]	n_{D}[b]	ν (cm^{-1})	ϵ
Heptane	1.92[c]	1.3876	15188	6540
			16680	3980
			18022	4090
			19214	16760
			23704	168400
Toluene	2.38	1.4969	15084	7560
			16586	3700
			17910	4100
			19054	16160
			23375	231100
Ethyl acetate	10.37	1.4448	15180	7700
			16680	3910
			18034	4140
			19172	15880
			23764	244900
Acetone	20.56	1.3587	15152	7750
			16662	3650
			18060sh[d]	3910
			19140	14900
			23780	228200
Acetonitrile	35.94	1.3441	15162	7910
			16674	3700
			18030sh[d]	4000
			19118	14360
			23830	219900

[a] Static dielectric permittivity of pure solvent at 25 °C [16].
[b] Refraction index of pure solvent at 25 °C [16].
[c] At 20 °C.
[d] Shoulder on maxima.

4. Results and discussion

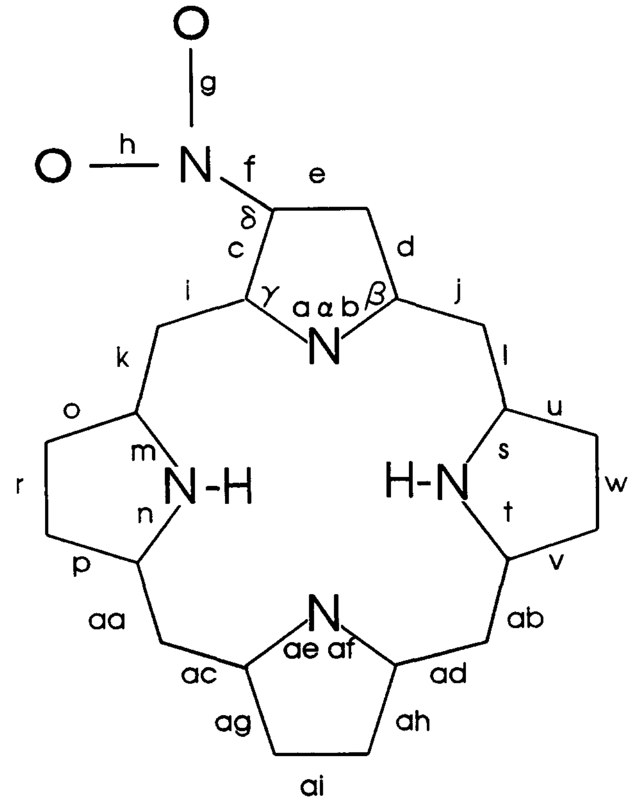
The details of the UV–visible absorption spectra of 2-nitro-5,10,15,20-tetraphenylporphyrin (**2**) and copper(II) 2-nitro-5,10,15,20-tetraphenylporphyrin (**1**) in different solvents are given in Tables 1 and 2 respectively. The choice of solvents was governed by the solubility of the substances and by the intention to study media of widely varying polarity and polarizability. The first of these parameters is described by the static dielectric permittivity D and the second by the refraction index n_{D}. The values of n_{D} and D for the solvents investigated experimentally are given in Tables 1 and 2.

It is obvious that the long-wavelength maxima in the UV–visible spectra of both 2-nitro-5,10,15,20-tetraphenylporphyrin and copper(II) 2-nitro-5,10,15,20-tetraphenylporphyrin are rather insensitive to a change in the dielectric properties of the medium. This is quite contrary to the large bathochromic solvatochromic shifts observed in the UV–visible spectra of substituted nitrobenzenes (cf. Ref. [16]), which are the simplest nitro-substituted aromatic systems. This suggests, in turn, that there is no large change in the electron distribution between the ground and the first excited state. One of the major reasons for this apparent inconsistency may be the violation of the coplanarity of the aromatic porphyrin ring and nitro group in molecules **1** and **2** [9,17].

Table 2
Absorption maxima and molecular extinction coefficients of UV–visible spectra of copper(II) 5,10,15,20-tetraphenylporphyrin in various solvents at 25 °C

Solvent	D[a]	n_{D}[b]	ν (cm^{-1})	ϵ
Heptane	1.92[c]	1.3876	17182	6110
			18400	14260
			23854	150900
Toluene	2.38	1.4969	16974	7250
			18214	12880
			23414	187400
Dichloroethane	10.37	1.4488	16962	8130
			18252	12660
			23688	175600
Ethyl acetate	6.02	1.3724	17102	6960
			18358	13340
			23874	212700
Acetone	20.56	1.3587	17052	7310
			18320	12510
			23864	197300
Acetonitrile	35.94	1.3441	17040	7160
			18302	11920
			23904	185200

[a] Static dielectric permittivity of pure solvent at 25 °C [16].
[b] Refraction index of pure solvent at 25 °C [16].
[c] At 20 °C.



Scheme 1.

Table 3
AM1 calculated bond lengths and bond angles of 2-nitroporphyrin in media of varying dielectric permittivity

Parameter[a]	$D=1$	$D=2$	$D=80$
a	1.339	1.339	1.340
b	1.420	1.419	1.417
c	1.472	1.472	1.471
d	1.496	1.496	1.496
e	1.386	1.385	1.384
f	1.453	1.453	1.452
g	1.206	1.206	1.206
h	1.204	1.204	1.204
i	1.368	1.371	1.374
j	1.435	1.435	1.435
k	1.419	1.416	1.412
l	1.361	1.361	1.360
m	1.397	1.398	1.399
n	1.384	1.383	1.383
o	1.435	1.435	1.435
p	1.435	1.435	1.435
r	1.406	1.406	1.407
s	1.400	1.400	1.401
t	1.398	1.398	1.398
u	1.494	1.494	1.493
v	1.493	1.493	1.493
w	1.362	1.364	1.366
aa	1.433	1.434	1.435
ab	1.364	1.364	1.363
ac	1.357	1.357	1.357
ad	1.432	1.432	1.432
ae	1.424	1.424	1.425
af	1.338	1.338	1.338
ag	1.495	1.495	1.495
ah	1.499	1.499	1.500
ai	1.363	1.363	1.362
α	108.2	108.3	108.5
β	109.0	109.0	108.9
γ	109.4	109.4	109.5
δ	127.3	127.4	127.6

[a] Defined in Scheme 1.

In order to obtain information on the dependence of the UV–visible spectrum on the dihedral angle between the porphyrin ring and the nitro group in different solvents, we have performed quantum chemical calculations of the spectra of some model compounds. 2-Nitroporphyrin (**3**) and disubstituted 2-nitro,12-hydroxyporphyrin (**4**) and 2-nitro,12-methoxyporphyrin (**5**) were used. The geometric structures of the molecules were calculated using the semiempirical AM1 model [18,19]. The effect of a polarizable dielectric medium was modelled by self-consistent reaction field (SCRF) theory [20]. The cavity sizes of the solute molecules in solution were calculated automatically proceeding from their mass densities. The macroscopic dielectric constants corresponding to a medium of low dielectric constant ($D=2$) and an aqueous solution at room temperature ($D=80$) were used. The AM1 calculated bond lengths and bond angles for compound **3** are shown in Scheme 1 and Table 3. The effect of the medium on the geometric parameters (bond lengths and bond angles) of the solute molecule is small and thus the optimum geometries of the isolated molecules were used in subsequent spectral calculations based on semiempirical self-consistent field (SCF) configuration interaction (CI) theory using ZINDO [14]. The effect of the dielectric medium was described using SCRF theory [15,21] and assuming the immediate relaxation of electronic polarization during the absorption process. CI calculations were performed following the SCF calculation for the singlet excited states proceeding from single, closed-shell, ground state reference determinants. The active space consisted of the ten highest occupied and ten lowest unoccupied molecular orbitals (MOs). The results of these calculations are given in Tables 4–6.

In general, good agreement between the calculated and experimental spectra for compounds **1** and **2** is obtained, giving credence to the predicted calculated values for the model compounds **3**, **4** and **5**. The observed maxima at about 15 000 and 18 000 cm^{-1} correspond to the electronic origin of the Q_x and Q_y transitions respectively [22]. This is confirmed by the frontier MO localization obtained from the INDO/1 SCF calculation. The experimental maxima at about 16 500 and 19 000 cm^{-1} are the $0\rightarrow 1$ vibrational satellites of the Q_x and Q_y transitions respectively. The calculated $0\rightarrow 0$ transition energies are somewhat too high, but the relative

Table 4
INDO/1 CI calculated transition energies and oscillator strengths for 2-nitroporphyrin at different ring–nitro group plane dihedral angles in solvents of different dielectric permittivity

α (°)	Dielectric permittivity of solvent	Transition energy (cm^{-1})	Relative transition energy (cm^{-1})^a	Oscillator strength
0	1	17145	(0)	0.182
	2	16861	−284	0.218
	80	15944	−1201	0.338
	1	19348	(0)	0.031
	2	19313	−35	0.039
	80	18724	−624	0.117
	1	25292	(0)	0.906
	2	24391	−901	0.688
	80	22148	−3144	0.286
	1	26288	(0)	0.870
	2	25763	−525	0.669
	80	23647	−2641	0.277
	1	29053	(0)	0.565
	2	28787	−266	0.675
	80	27710	−1343	0.356
	1	30435	(0)	0.765
	2	29980	−455	0.871
	80	28827	−1608	1.044
	1	31688	(0)	0.381
	2	31369	−319	0.425
	80	30272	−1416	1.117
45	1	17351	(0)	0.155
	2	17114	−237	0.183
	80	16332	−1019	0.286
	1	19335	(0)	0.024
	2	19343	+8	0.023
	80	18974	−361	0.048
	1	25212	(0)	0.593
	2	24126	−1086	0.419
	80	21343	−3869	0.104
	1	26886	(0)	1.123
	2	26514	−372	0.896
	80	24510	−2376	0.306
	1	28864	(0)	0.849
	2	28663	−201	0.967
	80	28001	−863	0.726
	1	30633	(0)	0.720
	2	30011	−622	0.751
	80	28442	−2191	0.878
	1	31450	(0)	0.105
	2	31063	−387	0.232
	80	29994	−1456	0.683
90	1	17598	(0)	0.112
	2	17446	−152	0.126
	80	17037	−561	0.159
	1	19278	(0)	0.026
	2	19325	+47	0.021
	80	19360	+82	0.012
	1	27574	(0)	1.499
	2	27551	−23	1.472
	80	27373	−201	1.330
	1	28198	(0)	1.555
	2	28209	+11	1.575
	80	28178	−20	1.564
	1	31384	(0)	0.425
	2	31219	−165	0.352
	80	30446	−938	0.519
	1	31735	(0)	0.154
	2	31833	+98	0.224
	80	32003	+268	0.194
	1	33599	(0)	0.450
	2	33639	+40	0.456
	80	33947	+348	0.416

^{a}Relative to the isolated molecule.

position of the peaks is described accurately. Within the free electron model, the long-wavelength transitions are forbidden and therefore the corresponding calculated transition oscillator strengths are low, as expected (cf. Table 4). The Soret maxima in the free base compound are calculated to be split by 1000–3000 cm^{-1}, depending on the geometry and solvent. Again the calculated transition energies are overestimated by about 2000 cm^{-1}. The calculations overestimate the Soret splitting. The intensity and splitting of these two Soret components in the free base compound have a long history, and require a more sophisticated computational technique than CIS only [23]. With the exception of the 90° case, the oscillator strength of the Q bands increases and that of the Soret bands decreases dramatically with increasing solvent polarity.

The results of INDO/1 SCRF CI calculations reveal substantial solvatochromic shifts for the nitro-substituted porphyrins. These shifts are apparently dependent on the nitro group and the porphyrin interplanar angle. In the *meso*-tetraphenyl compounds **1** and **2** it is expected that the nitro group will be tilted from the porphyrin cycle plane by nearly 90°. Also, for the *meso*-tetraphenyl-substituted compounds, the effect of the medium used in the model calculations is significantly reduced due to the fact that such molecules are larger than the corresponding *meso*-tetraphenyl-unsubstituted compounds. Therefore the data corresponding to $D=2$ in Tables 4–6 should be closer to the experimental situation even for the media of higher dielectric constant studied experimentally (e.g. acetonitrile). Indeed, the calculations for model compounds **3**–**5** with a 90° interplanar angle between the nitro group and the porphyrin ring show little dependence of the transition energies on the solvent, particularly for media of low dielectric constant.

However, for the conformations corresponding to interplanar angles between the nitro group and the porphyrin ring at 0° and 45° in compounds **3**–**5**, large solvatochromic red shifts were calculated for the Q_x,

Table 5
INDO/1 CI calculated transition energies and oscillator strengths for 2-nitro,12-hydroxyporphyrin at different ring–nitro group plane dihedral angles in solvents of different dielectric permittivity

α (°)	Dielectric permittivity of solvent	Transition energy (cm^{-1})	Relative transition energy (cm^{-1})[a]	Oscillator strength
0	1	17325	(0)	0.186
	2	16938	−387	0.225
	80	15897	−1428	0.352
	1	19542	(0)	0.025
	2	19505	−37	0.032
	80	18724	−818	0.130
	1	25329	(0)	0.894
	2	24386	−943	0.683
	80	22051	−3278	0.285
	1	26247	(0)	0.839
	2	25694	−553	0.654
	80	23501	−2746	0.216
	1	29943	(0)	1.125
	2	29659	−284	1.269
	80	28801	−1142	1.115
	1	30957	(0)	0.565
	2	30495	−462	0.800
	80	29749	−1208	1.469
	1	32614	(0)	0.435
	2	32492	−122	0.432
	80	31392	−1222	0.265
45	1	17441	(0)	0.159
	2	17199	−242	0.189
	80	16327	−1114	0.300
	1	19537	(0)	0.018
	2	19557	+20	0.015
	80	19095	−442	0.048
	1	25263	(0)	0.591
	2	24140	−1123	0.419
	80	21270	−3993	0.132
	1	26756	(0)	0.992
	2	26340	−416	0.790
	80	24226	−2530	0.247
	1	29643	(0)	1.299
	2	29351	−292	1.518
	80	28423	−1220	0.897
	1	31077	(0)	0.353
	2	30391	−686	0.540
	80	29305	−1772	1.573
	1	32140	(0)	0.529
	2	31695	−445	0.582
	80	30323	−1817	0.847
90	1	17688	(0)	0.116
	2	17543	−145	0.130
	80	17084	−604	0.165
	1	19483	(0)	0.021
	2	19555	+72	0.014
	80	19642	+159	0.003
	1	27267	(0)	1.103
	2	27062	−205	0.893
	80	25988	−1279	0.301
	1	28260	(0)	1.396
	2	28234	−26	1.351
	80	28066	−194	1.151
	1	29692	(0)	0.930
	2	29356	−336	1.180
	80	28715	−977	1.834
	1	31691	(0)	0.181
	2	31836	+145	0.152
	80	32740	+1049	0.232
	1	33009	(0)	0.437
	2	33171	+162	0.384
	80	33942	+933	0.642

[a] Relative to the isolated molecule.

Q_y and Soret maxima. The former may exceed 1000 cm^{-1} and the latter 3000 cm^{-1} in media of high dielectric constant. Consequently, 2-nitro-substituted porphyrins, in which the NO_2 group is allowed to participate in polar conjugation with the porphyrin superaromatic ring system, are good candidates for solvation-sensitive photodynamic compounds. The synthesis of analogs of model substances **3**–**5** is in progress.

It is interesting to note that the insertion of a +R group (hydroxy or methoxy group) into the conjugationally active 12-position in the porphyrin ring does not affect greatly the positions of the Q_x, Q_y and Soret maxima. However, the dependence on the change in solvent dielectric constant is somewhat larger for compounds with direct polar conjugation (**4** and **5**). Therefore it would be interesting to search experimentally for solvatochromically active compounds that also allow this type of conjugation between substituents on the porphyrin ring.

In Table 7, the INDO/1 SCF and SCRF calculated molecular energies, solvation energies (E_{sol} and dipole moments (μ) of 2-nitroporphyrin, 2-nitro, 12-hydroxyporphyrin and 2-nitro, 12-methoxyporphyrin are reported at different ring–nitro group place dihedral angles for media of different dielectric permittivity D. Significantly, the dipole moments of the compounds in the ground state are rather dependent on the dielectric constant of the surrounding medium. INDO/1 CI calculations for the dipole moments of the excited states show a similar dependence on D. However, the detailed numerical values of the dipole moment increase are different for different states, and cause, in turn, differences in solvatochromic shifts for different transitions. For the compounds in this study, the dipole moment of the excited state increases more rapidly than that of the ground state with increasing dielectric strength and, consequently, bathochromic (red) solvatochromic shifts are predicted in the UV–visible spectra.

A significant dependence of the calculated dipole moments of the model compounds **3**–**5** on the angle

Table 6

INDO/1 CI calculated transition energies and oscillator strengths for 2-nitro,12-methoxyporphyrin at different ring–nitro group plane dihedral angles in solvents of different dielectric permittivity

α (°)	Dielectric permittivity of solvent	Transition energy (cm^{-1})	Relative transition energy (cm^{-1})[a]	Oscillator strength
0	1	17329	(0)	0.189
	2	16923	−406	0.230
	80	15771	−1558	0.370
	1	19652	(0)	0.024
	2	19596	−56	0.032
	80	18625	−1027	0.147
	1	25285	(0)	0.884
	2	24298	−987	0.665
	80	21881	−3404	0.247
	1	26237	(0)	0.827
	2	25636	−601	0.614
	80	23235	−3002	0.194
	1	29911	(0)	1.131
	2	29608	−303	1.280
	80	28669	−1242	1.098
	1	30951	(0)	0.582
	2	30469	−482	0.825
	80	29697	−1254	1.489
	1	32676	(0)	0.416
	2	32528	−148	0.418
	80	31080	−1596	0.200
45	1	17450	(0)	0.161
	2	17187	−263	0.193
	80	16206	−1244	0.319
	1	19646	(0)	0.018
	2	19656	+10	0.015
	80	19014	−632	0.055
	1	25206	(0)	0.581
	2	24020	−1186	0.403
	80	21063	−4143	0.104
	1	26759	(0)	0.581
	2	26298	−461	0.765
	80	23896	−2863	0.210
	1	29609	(0)	1.296
	2	29290	−319	1.525
	80	28261	−1348	0.834
	1	31051	(0)	0.361
	2	30329	−722	0.570
	80	29247	−1804	1.626
	1	32151	(0)	0.527
	2	31662	−489	0.583
	80	30192	−1959	0.864
90	1	17702	(0)	0.117
	2	17543	−159	0.133
	80	17062	−640	0.173
	1	19591	(0)	0.022
	2	19660	+69	0.014
	80	19728	+137	0.002
	1	27286	(0)	1.099
	2	27055	−231	0.874
	80	25928	−1358	0.293
	1	28262	(0)	1.423
	2	28240	−22	1.371
	80	28062	−200	1.208
	1	29706	(0)	0.940
	2	29335	−371	1.236
	80	28685	−1021	1.972
	1	31755	(0)	0.170
	2	31896	+141	0.144
	80	32791	+1036	0.230
	1	33085	(0)	0.421
	2	33253	+168	0.354
	80	34079	+994	0.624

[a] Relative to the isolated molecule

Table 7

INDO/1 SCF calculated molecular energies, solvation energies E_{sol} (kJ mol^{-1}) and dipole moments μ (Debye) of 2-nitroporphyrin (**3**), 2-nitro,12-hydroxyporphyrin (**4**) and 2-nitro,12-methoxyporphyrin (**5**) for different ring–nitro group plane dihedral angles in solvents of different dielectric permittivity D

Compound	Angle (°)	D	SCF energy (hartree)	E_{sol}	μ
3	0	1	−187.020021	(0)	7.95
		2	−187.024350	−11.35	9.73
		80	−187.041716	−56.90	15.27
	45	1	−187.014237	(0)	7.34
		2	−187.017855	−9.05	8.87
		80	−187.030811	−43.47	13.16
	90	1	−187.010205	(0)	6.59
		2	−187.013048	−7.45	7.83
		80	−187.022015	−30.98	10.94
4	0	1	−199.240422	(0)	8.26
		2	−199.245093	−12.26	10.11
		80	−199.264110	−62.13	15.99
	45	1	−199.234645	(0)	7.70
		2	−199.238625	−10.44	9.30
		80	−199.252913	−47.91	13.83
	90	1	−199.230621	(0)	7.02
		2	−199.233855	−8.46	8.34
		80	−199.244811	−37.22	11.65
5	0	1	−206.359835	(0)	8.56
		2	−206.364894	−13.27	10.54
		80	−206.386547	−70.06	17.08
	45	1	−206.354053	(0)	8.00
		2	−206.358374	−11.33	9.70
		80	−206.374503	−53.64	14.71
	90	1	−206.350024	(0)	7.31
		2	−206.353538	−9.21	8.72
		80	−206.364903	−39.02	12.32

between the nitro group and the porphyrin plane also induces a change in their solvation energies. The compounds with small interplanar angles are more favored in media of high dielectric constant, which correspond to physiological conditions, and therefore they are of substantial interest as flexible photoactive agents.

5. Conclusions

The results of quantum chemical calculations indicate that nitro-substituted porphyrins can be good solvatochromically driven photoactive agents. The sensitivity of the position and intensity of the visible transitions and Soret maxima on the solvent dielectric properties is dependent on the angle between the nitro group and porphyrin planes. The coplanar or near-coplanar conformation is favored for larger solvatochromic shifts. Therefore the lack of large shifts in the experimental UV–visible spectra of 2-nitro-5,10,15,20-tetraphenylporphyrin and copper(II) 2-nitro-5,10,15,20-tetraphenylporphyrin, where the NO_2 group is tilted from the ring plane by nearly 90°, is not surprising. A double substitution at the conjugationally active 2,12-positions of the porphyrin ring by $+R$ ($-OH$, $-OCH_3$) and $-R$ ($-NO_2$) groups is predicted to lead to even more sensitive solvatochromic compounds which are therefore of interest as flexible photoactive agents.

Acknowledgements

This work was supported in part through grants from the Estonian Science Foundation and the Office of Naval Research (USA) and by the University of Turku.

References

[1] T.J. Dougherty, Photosensitizers: therapy and detection of malignant tumors, *Photochem. Photobiol., 45* (1987) 879–889.

[2] D. Kessel (ed.), *Methods in Porphyrin Photosensitization,* Plenum, New York, 1985.

[3] B. Roeder, D. Naether, T. Lewald, M. Braune, C. Nowak and W. Freyer, Photophysical properties and photodynamic activity in vivo of some tetrapyrroles, *Biophys. Chem., 35* (1990) 303–312.

[4] R.F. Schinazi, D.W. Dixon and L.G. Mazzili, Porphyrin and phthalocyanine antiviral compositions, PCT Int. Appl. WO 89, 11, 277, 30 November 1989.

[5] H. Toya, Y. Kato, M. Asanaka and T.C. Kurimura, Use of porphyrins and metalloporphyrins in the treatment of diseases caused by human immunodeficiency viruses (HIV-s), European Patent Appl. EP 337, 598, 18 October 1989.

[6] T.A. Moore, D. Gust, S. Hatlevig, A.L. Moore, L.R. Makings, P.J. Pessiki, F.C. De Schryver, M. Van der Auweraer, D. Lexa, R.V. Bensasson and M. Rougée, Photoinitiated electron transfer in carotenoporphyrin–quinone triads: enhanced quantum yields via control of reaction exergonicity, *Isr. J. Chem., 28* (1988) 87–95.

[7] R. Bonnett, A. Harriman and A.N. Kozyrev, Photophysics of halogenated porphyrins, *J. Chem. Soc., Faraday Trans. 1, 88* (1992) 763–769.

[8] M.J. Crossley, M.M. Harding and S. Sternhell, Tautomerism of 2-substituted 5,10,15,20-tetraphenylporphyrins, *J. Am. Chem. Soc., 108* (1986) 3608–3613.

[9] D. Gust, T.A. Moore, D.K. Luttrull, G.R. Seely, E. Bittersmann, R.V. Bensasson, M. Rougée, E.J. Land, F.C. De Schryver and M. Van der Auweraer, Photophysical properties of 2-nitro-5,10,15,20-tetra-*p*-tolylporphyrins, *Photochem. Photobiol., 51* (1990) 419–426.

[10] O.M. Minnetian, I.K. Morris, K.M. Snow and K.M. Smith, New syntheses and reactions of some halogenated porphyrins, *J. Org. Chem., 54* (1989) 5567–5574.

[11] I. Renge, Solvent dependence of the visible absorption maxima of *meso*-tetraphenylporphine, *Chem. Phys. Lett., 185* (1991) 231–236.

[12] M.T. Thompson and M.C. Zerner, The electronic structure and spectroscopy of the photosynthetic center from *Rhodopseudomonas viridis, J. Am. Chem. Soc., 113* (1992) 8210–8216.

[13] A. Girardeau, H.J. Callot, J. Jordan, I. Ezhar and M. Gross, Substituent effects in the electroreduction of porphyrins and metalloporphyrins, *J. Am. Chem. Soc., 101* (1979) 3857–3862.

[14] M.C. Zerner, ZINDO — *A Comprehensive Semi-Empirical SCF/CI Package,* University of Florida, FL 32611, 1990.

[15] M.M. Karelson and M.C. Zerner, A theoretical treatment of solvent effects in spectroscopy, *J. Phys. Chem., 96* (1992) 6949–6957.

[16] Chr. Reichardt, *Solvents and Solvent Effects in Organic Chemistry,* VCH, Weinheim, 2nd edn., 1988.

[17] M.J. Crossley, M.M. Harding and S. Sternhell, Use of NMR spectroscopy to determine bond orders between β- and β'-pyrrolic positions of porphyrins: structural differences between free base porphyrins and metalloporphyrins, *J. Am. Chem. Soc., 114* (1992) 3266–3272.

[18] M.J.S. Dewar, E.G. Zoebisch, E. Healy and J. Stewart, AM1: a new general purpose quantum mechanical molecular model, *J. Am. Chem. Soc., 107* (1985) 3902–3909.

[19] J.J.P. Stewart, MOPAC 6.0, Frank J. Seiler Research Laboratory, United States Air Force Academy, CO 80840, 1990.

[20] M.M. Karelson, T. Tamm, A.R. Katritzky, S. Cato and M.C. Zerner, M.O. calculations applicable to condensed phases: the combination of self-consistent reaction field theory with semi-empirical methods, *Tetrahedron Comp. Methodol., 2* (1989) 295–304.

[21] M. Karelson and M.C. Zerner, On the n–π^* blue shift accompanying solvation, *J. Am. Chem. Soc., 112* (1990) 9405–9406.

[22] M. Gouterman, Spectra of porphyrins, *J. Mol. Spectrosc., 6* (1961) 138–163.

[23] J.D. Baker and M.C. Zerner, Characterization of the random phase approximation with the intermediate neglect of differential overlap hamiltonian in electron spectroscopy. *J. Phys. Chem., 95* (1991) 8614–8619.