ELSEVIER

Journal of Molecular Structure 477 (1999) 209–220

Journal of
MOLECULAR
STRUCTURE

Substituent effects on absorption and fluorescence spectra of carbostyrils

Walter M.F. Fabian*, Karlheinz S. Niederreiter, Georg Uray, Wolfgang Stadlbauer

Institute of Organic Chemistry, Karl-Franzens University Graz, Heinrichstr. 28, A-8010 Graz, Austria

Received 20 July 1998; accepted 3 September 1998

Abstract

Absorption and fluorescence spectra as well as quantum yields of a series of differently substituted carbostyrils (quinolin-2(1H)-ones) are reported. Especially for compounds containing donor substituents in position 6, substantial bathochromic shifts (comparable to analogous coumarins) of both absorption as well as fluorescence transitions are obtained. High absorption intensities and quantum yields are found for 7-donor substituted isomers. Semiempirical molecular orbital calculations (AM1 for structures, ZINDO for electronic transition energies) prove to be a suitable tool for the prediction of absorption and fluorescence properties of these compounds. Ab initio and density functional calculations establish the lactam form as the dominant tautomer of the parent quinolin-2(1H)-one.

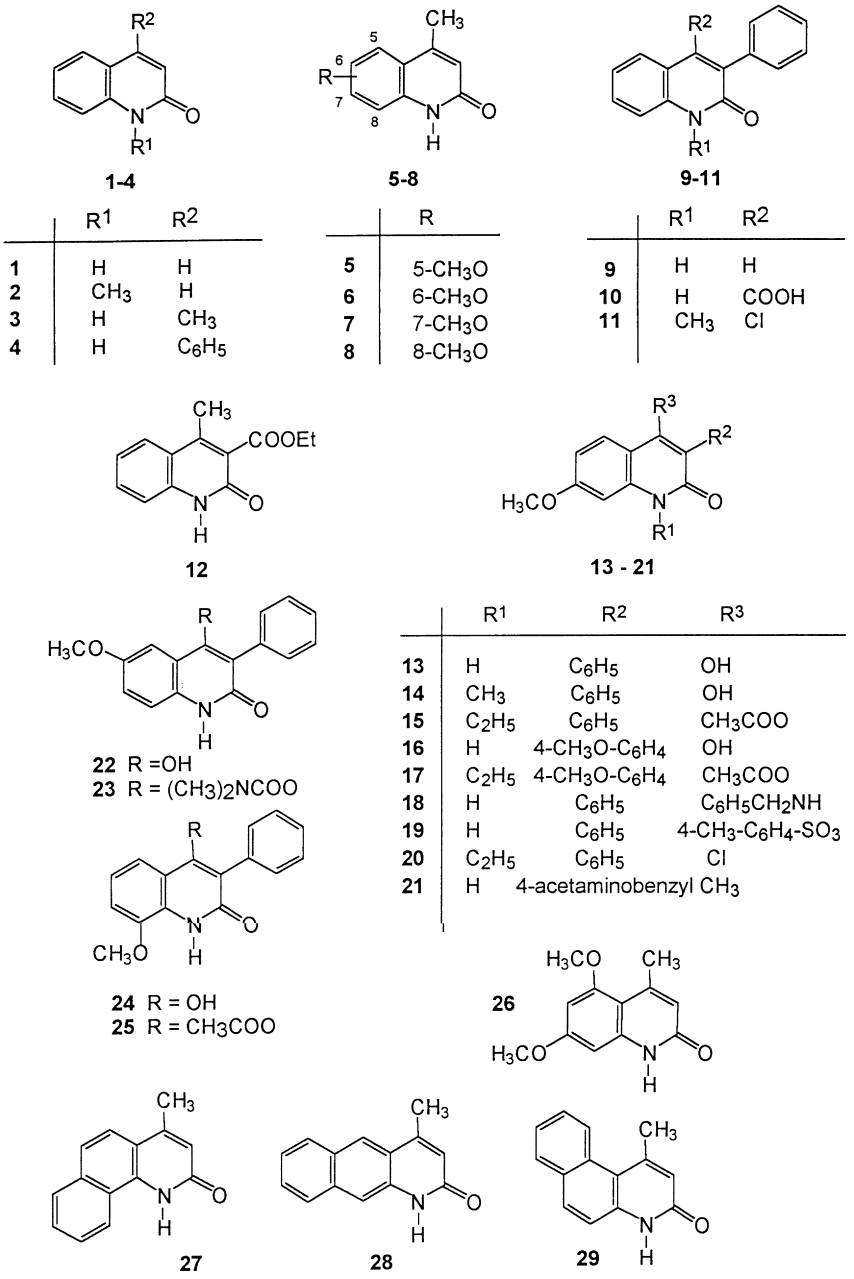
Keywords: Luminescence; Quinolinone; UV spectra

1. Introduction

Coumarins, both naturally occurring as well as synthetic derivatives, have found widespread applications as photosensitizers [1], laser dyes [2–6] or pH-indicators in biochemistry and medicine [7,8]. Consequently, a wealth of experimental and theoretical data on spectral-luminescence characteristics, photophysics and photochemistry of coumarin derivatives is available [1–29]. Considerably less attention was paid to carbostyrils (2(1H)-quinolones) which can be considered as aza-analogues of coumarins [2,11,30–38], possibly because of their comparably shorter absorption and emission wavelength as well as their seemingly diminished sensitivity to substituent effects. Contrarily, carbostyrils offer the advantage of greater chemical and thermal stability. Besides other uses this makes them possible candidates as wave-shifting fluors in high energy particle detection [39]. For this purpose coumarins had turned out to be of insufficient resistance against radiation damage [40]. Recently, interest in luminescent dyes has intensified with emphasis mainly on analytical applications in biological sciences. One of the most promising approaches consists in the use of sensitizing chromophors for lanthanide chelates [41–50] including carbostyrils such as 7-amino-4-methyl-2(1H)-quinolone (carbostyril 124). The long lifetime of lanthanide emissions allows time-resolved fluorescence measurements against background emission and makes these complexes particularly attractive as probes in biological systems. As alternatives to radioactive probes or simple organic fluorophors potential applications comprise biodistribution studies or time-resolved fluoroimmunoassays (e.g., dissociation-enhanced lanthanide fluorescence immunoassay (Delfia®)). As an example for this latter clinical use

* Corresponding author. Tel.: 00 43 316 380 8636; Fax: 00 43 316 380 9840; e-mail: walter.fabian@kfunigraz.ac.at

0022-2860/99/$ - see front matter
PII: S0022-2860(98)00616-4



	R1	R2
1	H	H
2	CH_3	H
3	H	CH_3
4	H	C_6H_5

	R
5	5-CH_3O
6	6-CH_3O
7	7-CH_3O
8	8-CH_3O

	R1	R2
9	H	H
10	H	COOH
11	CH_3	Cl

	R1	R2	R3
13	H	C_6H_5	OH
14	CH_3	C_6H_5	OH
15	C_2H_5	C_6H_5	CH_3COO
16	H	4-CH_3O-C_6H_4	OH
17	C_2H_5	4-CH_3O-C_6H_4	CH_3COO
18	H	C_6H_5	$C_6H_5CH_2NH$
19	H	C_6H_5	4-CH_3-C_6H_4-SO_3
20	C_2H_5	C_6H_5	Cl
21	H	4-acetaminobenzyl	CH_3

Fig. 1. Structures of the investigated compounds.

the determination of lipoprotein (a), a risk factor for coronary heart disease and ischemic cerebrovascular disease [51] might be mentioned. Sensitized lanthanide fluorescence proves also as an attractive alternative to UV detection and other luminescence techniques in the chromatographic separation of drugs and xenobiotics [50]. Fluorescent heterocycles are also valuable enzyme substrates [52,53], e.g. for proteases. Here carbostyril 124 was found to allow a more sensitive determination of enzyme activity than

other fluorophors [52]. Besides the required absorption–emission characteristics for a certain purpose, easy chemical functionalization with predictable effects on the photophysical properties is a necessity.

As mentioned before, in contrast to coumarins only little systematic work concerning the spectral-luminescence characteristics of carbostyrils was done. Photophysical data of a reasonably large number of analytes can be found in work published by Ponomarev [30–34]. However, considering the increasing importance of tailor-made dyes in analytical, medicinal and biochemical applications we found it worthwhile to investigate the prospects of this important class of heterocycles as chromophors or fluorophors in a more systematic manner.

Thus, in the following, absorption and fluorescence spectral characteristics of systematically different substituted (see Fig. 1 for structures) carbostyrils will be presented. The experimental results are complemented by theoretical calculations using semiempirical molecular orbital methods (AM1 [54], ZINDO [55]), which should aid in the design of new and long wavelength absorbing and/or emitting compounds.

2. Experimental

2.1. Molecular orbital calculations

Starting structures of the investigated compounds were created with the aid of the SYBYL molecular modelling package [56]. Semiempirical molecular orbital calculations were done by the MOPAC [57,58] or VAMP [59] program packages. Geometries for ground states were completely optimized (keyword PRECISE) by the semiempirical AM1 [54] Hamiltonian using the eigenvector following routine [60]. Excited states (S_1) structures were obtained either by using the keyword ''EXCITED'' or alternatively, starting form the closed shell determinant by a singles + doubles CI involving up to five occupied and five virtual molecular orbitals. Based on the AM1 optimized structures (S_0 and S_1) electronic transition energies (absorption and fluorescence) were calculated by the ZINDO method [55,61]. Solvent effects were treated with the self-consistent reaction field approximation [62]. For the unsubstituted parent compound carbostyril (2(1H)-quinolone **1**), in addition, ab initio (HF/3-21G, HF/6-31G*) and hybrid HF/density functional (B3LYP/6-31G*) computations [63] using Gaussian 94 [64] were done. Single point calculations (using the B3LYP/6-31G* geometry and zero point energy (ZPE) correction) on **1** and its lactim tautomer (2-hydroxyquinoline) were also performed at the MP2/6-311G** and MP2/6-31 + G** level of theory. For **1** excitation energies were also obtained by ab initio CI-singles (CIS/6-31G*) calculations.

2.2. Synthesis

Chemicals and reagents were purchased form Aldrich or Fluka and used without further purification. Solvents for UV and fluorescence spectra were purified by distillation. Melting points were determined on a Gallenkamp Melting Point Apparatus Mod. MPD-350 in open capillary tubes. IR spectra were recorded on a Perkin-Elmer 298 spectrophotometer in KBr pellets. ^{1}H-NMR spectra were obtained on a Varian XL-200 at 200 MHz in the solvents indicated. Chemical shifts (δ) are expressed in ppm from internal TMS. Microanalyses were performed on a Fisons elemental analyser Model EA 1108.

2(1H)-Quinolinone (carbostyril) (**1**) is commercially available.

N-Methyl-2(1H)-quinolinone (**2**) was obtained from **1** (200 mg, 1.38 mmol) and dimethylsulfate (230 mg, 1.83 mmol) using the procedure described in Ref. [71]; the yield was 50 mg (23%), colorless prisms; m.p. 73°C, lit. m.p. 73°C [78].

4-Methyl-2(1H)-quinolinone (**3**) is commercially available.

4-Phenyl-2(1H)-quinolinone (**4**) was prepared according to Ref. [72].

4-Methyl-6-methoxy-2(1H)-quinolinone (**6**) was obtained from ethyl acetoacetate (8.50 g, 65.3 mmol) and 4-methoxyaniline (2.01 g, 16.3 mmol) using the procedure described in Refs. [73,74]; the yield was 2.91 g (95%), brown prisms, m.p. 258°C–259°C (methanol), lit. m.p. 274°C–275°C [79].

4-Methyl-7-methoxy-2(1H)-quinolinone (**7**) was prepared as described for **6**; the yield was 5.71 g (74%), colorless prisms, m.p. 196°C (ethanol), lit. m.p. 200°C [80].

4-Methyl-8-methoxy-2(1H)-quinolinone (**8**) was prepared as described for **6**; the yield was 1.80 g (59%), brown prisms, m.p. 176°C–178°C (ethanol), lit. m.p. 188°C–190°C [81].

3-Phenyl-2(1H)-quinolinone (**9**) was obtained from phenacetylchloride (1.7 g, 11.0 mmol) and 2-aminobenzaldehyde (1.00 g, 8.25 mmol) using the procedure described in Ref. [75]; the yield was 0.30 g (16%), colorless powder, m.p. 235°C (ethanol), lit. m.p. 235°C–236°C [82].

3-Phenyl-2-oxo-1,2-dihydroquinoline-4-carboxy acid (**10**) was obtained from isatine (1.03 g, 7.00 mmol) and phenylacetylchloride (1.01 g, 6.53 mmol) using the procedure described in Ref. [76]; the yield was 0.57 g (33%), colorless powder, m.p. 265°C (ethanol), lit. m.p. 292°C–294°C [83].

4-Chloro-1-methyl-3-phenyl-2(1H)-quinolinone (**11**) was prepared from 4-hydroxy-1-methyl-2(1H)-quinolone and phosphorylchloride according to Ref. [65].

Ethyl 4-Methyl-2-oxo-1,2-dihydroquinoline-3-carboxylate (**12**) was obtained from diethylmalonate (4.74 g, 29.6 mmol) and 2-aminoacetophenone (1.00 g, 7.40 mmol) using the procedure described in Ref. [77]; the yield was 0.85 g (50%), colorless prisms, m.p. 236°C–237°C (water), lit. m.p. 256°C–258°C [84].

4-Hydroxy-7-methoxy-3-phenyl-2(1H)-quinolinone (**13**) was prepared from panisidine and diethyl phenylmalonate according to Ref. [66].

4-Hydroxy-7-methoxy-1-methyl-3-phenyl-2(1H)-quinolinone (**14**) was prepared from 4-methoxy-N-methylaniline and diethyl phenylmalonate according to Ref. [67].

4-Acetoxy-1-ethyl-7-methoxy-3-phenyl-2(1H)-quinolinone (**15**) was prepared from 1-ethyl-4-hydroxy-7-methoxy-3-phenyl-2(1H)-quinolone and acetanhydride according to Ref. [67].

4-Hydroxy-7-methoxy-3-(4-methoxyphenyl)-2(1H)-quinolinone (**16**) was prepared from diethyl-4-methoxyphenylmalonate and p-anisidine according to Ref. [67]. 4-Acetoxy-1-ethyl-7-methoxy-3-(4-methoxyphenyl)-2(1H)-quinolinone (**17**) was prepared from 1-ethyl-4-hydroxy-7-methoxy-3-(4-methoxyphenyl)-2(1H)-quinolone and acetanhydride according to Ref. [67].

4-Benzylamino-7-methoxy-3-phenyl-2(1H)-quinolinone (**18**) was prepared from **13** and benzylamine according to Ref. [68].

7-Methoxy-4-(4-methylphenyl)-sulfonyloxy-3-phenyl-2(1H)-quinolinone (**19**) was prepared from **13** and p-tosylchloride according to Ref. [68].

4-Chloro-1-ethyl-7-methoxy-3-phenyl-2(1H)-quinolinone (**20**) was prepared from 1-ethyl-4-hydroxy-7-methoxy-3-phenyl-2(1H)-quinolone and phosphorylchloride according to Ref. [69].

3-(4-Acetylamino)-benzyl-7-methoxy-4-methyl-2(1H)-quinolinone (**21**). The preparation consisted of the following steps:

(a) 7-Methoxy-4-methyl-3-(4-nitrobenzyl)-2(1H)-quinolinone: 3-Methoxyaniline (2.46 g, 20 mmol) was added slowly to ethyl acetoacetate (10.41 g, 80 mmol) at 160°C under stirring. The alcohol formed was removed and heating was continued for 30 min. The mixture was concentrated under reduced pressure and the residual oil, representing acetoacetyl-3-methoxyanilide, was used for the next step without further purification. This oil was dissolved in warm ethanol (25 ml) and sodium (0.46 g, 20 mmol) was added in pieces. This mixture was stirred for 3 h at room temperature. Then 4-nitrobenzylbromide (5.18 g, 24 mmol) was added and the mixture gently heated under reflux. After 30 min the formed sodium bromide was filtered and the filtrate concentrated under reduced pressure to a small volume. The brown oil, representing 2-(4-nitrobenzyl)-3-oxopropan-(3-methoxy)-anilide was not isolated and used directly for the following ring closure. It was mixed with 76% sulfuric acid (60 ml) and the mixture heated at 96°C for 45 min. The anilide gradually dissolved, and gave an orange-red solution. The mixture was then cooled to 60°C and poured into water (200 ml). The green precipitate was filtered, taken up in acetone and stirred for 30 min at room temperature until a colorless solid began to precipitate. It was filtered, washed with acetone and dried at 80°C. The yield was 1.84 g (28%), colorless powder, m.p. 280°C (acetone). IR: 2940 m, 2830 m, 1660 s, 1625 m, 1605 m (cm^{-1}), ^1H NMR (DMSO-d_6): $\delta =$ 2.40 (s, 3 H, 4-CH_3), 3.85 (s, 3 H, 7-OCH_3),4.15 (s, 2 H, CH_2),6.82 (d,1 H, $J = 8$ Hz, 6-H), 6.85 (s, 1 H, 8-H), 7.50 (d, 2 H, $J = 8$ Hz, 2-H and 6-H of phenyl), 7.70 (d, 1 H, $J = 8$ Hz, 5-H), 8.15 (d, 2 H, $J = 8$ Hz, 3-H and 5-H of phenyl), 11.70 (s, 1 H, NH). Anal.

Calcd. for $C_{18}H_{16}N_2O_4$: C, 66.66; H, 4.97; N, 8.64. Found: C, 66.41; H, 4.85; N, 8.51.

(b) 3-(4-Aminobenzyl)-7-methoxy-4-methyl-2 (1H)-quinolinone: A solution of 7-methoxy-4-methyl-3-(4-nitrobenzyl)-2(1H)-quinolone (200 mg, 0.6 mmol), glacial acetic acid (10 ml) and conc. hydrochloric acid (3 ml) was heated under reflux and zinc-powder (1.00 g, 15 mmol) was added in small portions. The mixture was cooled to room temperature, diluted with water (15 ml) and brought to pH = 12 by addition of 30% sodium hydroxide solution (35 ml). The precipitate was filtered and washed with water. The yield was 150 mg (83%), colorless prisms, m.p. above 300°C. IR: 3340 m, 2920 m, 1675 s, 1610 s (cm^{-1}), ^{1}H NMR (DMSO-d_6): δ = 2.40 (s, 3 H, 4-CH_3). 3.35 (s, 2 H, NH_2), 3.85 (s, 3 H, 7-OCH_3), 4.80 (s, 2 H, CH_2), 6.45 (d, 2 H, J = 9 Hz, 3-H and 5-H of phenyl), 6.70–6.90 (m, 4 H, 2-H and 6-H of phenyl, 6-H, 8-H), 7.65 (d, 1 H, J = 9 Hz, 5-H), 11.60 (s, 1 H, NH). Anal. Calcd. for $C_{18}H_{18}N_2O_2$: C, 73.45; H, 6.16; N, 9.52. Found: C, 73.35; H, 6.12; N, 9.42.

(c) 3-(4-Acetylamino)-benzyl-7-methoxy-4-methyl-2(1H)-quinolinone: A mixture of 3-(4-aminobenzyl)-7-methoxy-4-methyl-2(1H)-quinolone (50 mg, 0.15 mmol) and acetic anhydride (1.21 g, 11.9 mmol) was stirred at 80°C for 2 h. The mixture was diluted with water and the precipitate was filtered. The solid was washed with water. The yield was 20 mg (40%), colorless prisms, m.p. 237°C. IR: 3300 m, 2910 m, 1665 s, 1605 s (cm^{-1}), ^{1}H NMR (DMSO-d_6): δ = 1.95 (s, 3 H, acetyl-CH_3), 2.35 (s, 3 H, 4-CH_3), 3.80 (s, 3 H, 7-OCH_3), 3.90 (s, 2 H, CH_2), 6.75 (d, 1 H, J = 9 Hz, 6-H), 6.80 (s, 1 H, 8-H), 7.10 (d, 2 H, J = 9 Hz, 3-H and 5-H of phenyl), 7.40 (d, 2 H, J = 9 Hz, 2-H and 6-H of phenyl), 7.60 (d, 1 H, J = 9 Hz, 5-H), 9.80 (s, 1 H, acetylamino-NH), 11.60 (s, 1 H, 1-NH). Anal. Calcd. for $C_{20}H_{20}N_2O_3$: C, 71.41; H, 5.99; N, 8.33. Found: C, 71.52; H, 5.97; N, 8.27.

4-Hydroxy-6-methoxy-3-phenyl-2(1H)-quinolinone (**22**) was prepared from panisidine and diethyl phenylmalonate according to Ref. [66].

4-(N,N-Dimethylcarbamoyloxy)-6-methoxy-3-phenyl-2(1H)-quinolinone (**23**): A solution of **22** (6.0 g, 23 mmol) and N,N-dimethylcarbamoylchloride (5 ml, 47 mmol) in dry pyridine (50 ml) was stirred for 12 h at 20°C. Then the mixture was poured into ice/water (200 ml) and filtered by suction. The yield was 5.0 g (65%), colorless prisms, m.p. 210°C (ethanol). IR: 3100–2980 w, 1750 m, 1730 s, 1665 s, 1640 m, 1605 m, 1580 sh (cm^{-1}); ^{1}H NMR (DMSO-d_6): δ = 2.6 (s, 3 H, N-CH_3), 2.7 (s, 3 H, N-CHO), 3.7 (s, 3 H, O-CH_3) 6.9–7.5 (m, 7 ArH), 8.3 (d, J = 1.5 Hz, 5-H). Anal. Calcd. for $C_{19}H_{18}N_2O_4$: C, 67.45; H, 5.36; N, 8.28. Found: C, 67.57; H, 5.09; N, 7.96.

4-Hydroxy-8-methoxy-3-phenyl-2(1H)-quinolinone (**24**) was prepared from o-anisidine and diethyl phenylmalonate according to Ref [66].

4-Acetoxy-8-methoxy-3-phenyl-2(1H)-quinolinone (**25**) was prepared from **24** and acetanhydride according to Ref. [70].

5,7-Dimethoxy-4-methyl-2(1H)-quinolinone (**26**) was obtained from ethyl acetoacetate (8.50 g, 65.3 mmol) and 3,5-dimethoxyaniline (2.49 g, 16.3 mmol) using the procedure described in Refs. [73,74]; the yield was 3.30 g (92%), colorless prisms, m.p. 229°C (ethanol). IR: 2930 m, 1670 s, 1630 s, 1610 m (cm^{-1}), ^{1}H NMR (DMSO-d_6): δ = 2.55 (s, 3 H, 4-CH_3), 3.80 (s, 3 H, 5-OCH_3), 3.85 (s, 3 H, 7-OCH_3), 6.05 (s, 1 H, 3-H), 6.30 (s, 1 H, 6-H), 6.45 (s, H, 8-H), 11.40 (s, 1 H, NH). Anal. Calcd. for $C_{12}H_{13}NO_3$: C, 65.74; H, 5.98; N, 6.39. Found: C, 65.52; H, 6.07; N, 6.29.

4-Methyl-2 (1H)-benzo [h] quinolinone (**27**) was obtained from ethyl acetoacetate (8.50 g, 65.3 mmol) and 1-naphthylamine (2.33 g, 16.3 mmol) using the procedure described in Refs. [73,74]; the yield was 1.64 g (89%), yellow prisms, m.p. 279°C–281°C (ethanol), lit. m.p. 293.5°C–294°C [85].

2.3. UV and fluorescence spectra

The UV-Vis spectra were recorded on a Shimadzu UV/Vis scanning spectrophotometer UV-2101PC. The excitation and emission spectra were obtained using a Shimadzu RF-5001PC spectrofluorophotometer. It was fitted with a 150 W xenon lamp operated as a continous wave source, slits selectable in six steps to produce spectral bandwidths of 1.5, 3, 5, 10, 15 and 20 nm, and an R452-01 photomultiplier. Excitation and emission monochromators: ion-blazed holographic concave grating F/2.5.

UV spectra were recorded at a concentration of 10 μg/ml, excitation and emission spectra at a

Table 1
Calculated lactam-lactim tautomerization energies (kcal mol^{-1}) of compound **1**[a]

Method	ΔE	Method	ΔE
B3LYP/6-31G*	−5.3	MP2/6-31G**	−2.0
B3LYP/6-311G**	−4.2	MP2/6-311G**	−1.2
B3LYP/6-31+G**	−4.0	MP2/6-31+G**	−1.6

[a] A negative sign indicates greater stability of the lactam form. All calculations were done at the B3LYP/6-31G* optimized geometries. Zero point energy corrections obtained at the B3LYP/6-31G* level of theory are included in ΔE.

concentration of 1 μg/ml. For the determination of quantum yields emission signals were set in relation to the emission signal of **3** under the same conditions (slit, solvent, temperature and concentration). Compound **3** has quantum yield according to literature [32] of 0.020. Emission spectra are uncorrected.

3. Results

The structures of the investigated compounds are shown in Fig. 1. This set of molecules was chosen to allow assessment of donor or acceptor substituent effects in positions 3 and 4 of the heterocyclic ring as well as positional isomerism of the methoxy group (compounds **5**–**8**). In addition, compounds **26**–**28** serve to describe the effect of increasing the conjugated system by linear or angular benzo-annulation.

3.1. Absorption spectra

According to semiempirical (AM1) molecular orbital calculations the parent carbostyril **1** should almost exclusively (≈ 5 kcal mol^{-1}) exist as the lactam tautomer shown in Fig. 1 [38,86]. In contrast, rather high level ab initio calculations predict a vanishingly small energy difference (≈ 0.1 kcal mol^{-1}) between the two tautomers [87]. Experimental gas phase results appear somewhat contradictory with interpretations ranging from a slight preference of the lactim to the sole existence of the lactam form [88–94]. There seems, however, to be consensus that compared to the 2-hydroxypyridine/2(1H)-pyridone system, in **1** the tautomeric equilibrium is shifted towards the lactam form. Recently, the superiority of density functional methods, especially hybrid HF/DFT approaches over conventional ab initio procedures with respect to geometries of tautomeric species was demonstrated [95–102]. However, tautomerization energies seem to be better predicted by conventional ab initio (e.g. MP2) methods [101,102]. Results for the lactam–lactim tautomerization energy of quinolin-2(1H)-one **1** obtained at various levels of theory are summarized in Table 1. B3LYP/6-31G**ΔE-values are close to previous AM1 results [38,86]. Larger basis sets as the split valence 6-311G** basis or inclusion of diffuse functions result in a slight (≈1 kcal mol^{-1}) lowering of ΔE. Inclusion of electron correlation at the MP2 level of theory – which is regarded to yield more reliable tautomerization energies [101,102] –

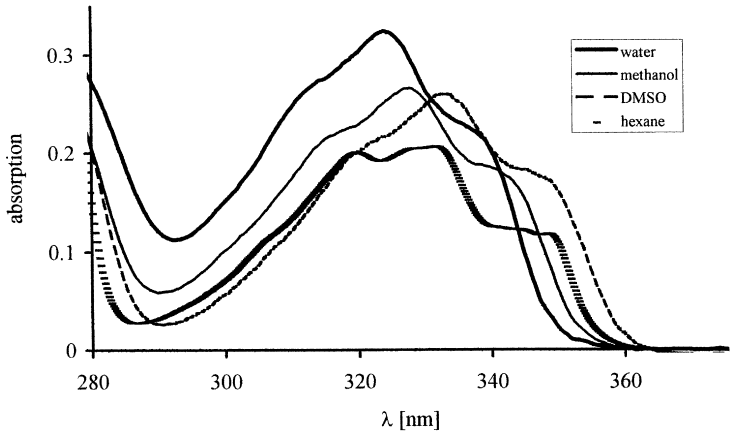


Fig. 2. Absorption spectra of compound **1** in solvents of different polarity.

Table 2
Solvent dependence of the absorption maxima (in cm^{-1}) of compounds **1**, **2** and **4** (ZINDO-SCRF calculated values are given in parentheses)

Solvent	d.c.[a]	Compound		
		1	**2**	**4**
Gas phase		— (31 700)	— (31 500)	— (31 800)
n-Hexane	1.89	30 100 (31 500)	29 700 (31 300)	29 900 (31 800)
1,4-Dioxane	2.21	30 100 (31 500)	29 900 (31 300)	29 800 (31 800)
Toluene	2.38	30 300 (31 500)	30 000 (31 300)	30 000 (31 800)
Ethyl acetate	6.02	30 200 (31 400)	30 000 (31 300)	29 900 (31 800)
Dichloromethane	9.08	30 400 (31 400)	30 100 (31 300)	30 100 (31 800)
Acetone	20.70	30 400 (31 400)	30 100 (31 300)	30 000 (31 800)
Methanol	32.63	30 500 (31 400)	30 400 (31 300)	30 500 (31 800)
Acetonitrile	35.94	30 400 (31 400)	30 200 (31 300)	30 000 (31 800)
Dimethylsulfoxide	45.00	30 000 (31 300)	29 900 (31 200)	29 700 (31 800)
Water	78.54	30 900 (31 400)	30 700 (31 300)	30 500 (31 800)

[a] Dielectricity constant.

significantly reduces ΔE (see Table 1). Thus, from the data of Table 1 the most likely estimate of the gas phase tautomerization energy of compound **1** is a $\approx$1 kcal mol^{-1} preference for the lactam form. This result is in good agreement with the most experimental findings regarding the 2(1H)-quinolone/2-hydroxyquinoline tautomeric equilibrium [92]. Owing to the larger solvation energy [87,103] of the latter species, in aqueous solution the lactam form by far predominates. In contrast to expectations for a potentially tautomeric system the absorption spectra of **1** are surprisingly insensitive to the solvent polarity (see Fig. 2 and Table 2) and, importantly, similar in the N-CH_3 derivative **2**. Substituents (compare **4** in Table 2) also seem to play only a minor role [32,38]. By IR spectroscopy in $CC1_4$ [104] an enthalpy of association of -8.69 kcal mol^{-1} (to be compared with an AM1 calculated value of -9.44 kcal mol^{-1}) was obtained. In contrast to pyridones [105] in nonpolar solvents (see data for hexane) carbostyril **1** does not show the blue shift expected for hydrogen bonded dimers (ZINDO-SCRF calculations predict a $\sim$300 cm^{-1} increase of the transition energy upon dimerization). Furthermore, even heating up to 122°C does not essentially alter the UV spectrum [94]. The main effect of solvent polarity, thus, appears to be merely a blurring of the vibrational fine structure. Solvents capable of forming hydrogen bonds lead to a notable blue shift attributed to the lower basicity and hence weaker propensity to form hydrogen bonds of carbostyrils in the S_1 state [32]. Also inculded in Table 2 are the results of ZINDO-SCRF calculations regarding the solvent effect. Clearly, the proper treatment of the effect of hydrogen bonds is outside the scope of this approximation. Explicit inclusion of three water molecules in the calculations for **1**, however, does not alter the results significantly (ν_{calc} = 31500 cm^{-1}). From these findings and for reasons of general solubility we choose DMSO as standard solvent whose use should not lead to any special effects.

Generally, even in DMSO as solvent, vibrational fine structure is at least partly resolved (shoulders on either side of the band maximum). The least resolved, barely visible, vibrational structures are found in the spectra of 3-phenyl derivatives (e.g. **13**–**20**) whereas in the benzo-annulated derivative **27** the three peaks are well separated with the first being nearly as intense as the second one. Experimental absorption maxima (wavenumber of the central – normally most intense – peak) and extinction coefficients ϵ measured in DMSO for compounds **1**–**29** are collected in Table 3. Also given in the table are the calculated (ZINDO) transition energies and oscillator strengths *f*.

As can be seen from the data of Table 3 the electronic excitation energy of the carbostyril chromophor is remarkably insensitive to substituents. With few exceptions, e.g. **6**, **22**, **23**, **27**, and – to a lesser extent, for **9**–**11**, **17**, and **25** – the absorption maxima of the investigated compounds are close to $\approx$ 30000 cm^{-1}. Interestingly, in the series of positional isomers of methoxy carbostyrils **5**–**8** the longest wavelength

Table 3
Experimental and calculated (ZINDO) absorption maxima (cm^{-1}), extinction coefficients ϵ ($l\,mol^{-1}\,cm^{-1}$) and oscillator strengths f

Compd	ν_{exp}	ϵ	ν_{calc}	f	Composition[a]
1	30 000	6360	31 300	0.174	82
2	29 900	4250	31 200	0.168	82; 10[b]
3	30 200	6510	31 700	0.154	80; 11[b]
4	29 700	5940	31 800	0.146	68
5	—	—	31 200	0.084	66
6	28 300	6550	28 500	0.158	88
7	29 200[c]	10 000			
	30 500	12 900	31 000	0.358	76
8	29 500	3730	29 900	0.050	77; 10[b]
9	29 000	7850	30 000	0.511	81
10	29 100	6580	30 300	0.432	79
11	29 100	8390	29 800	0.354	85
12	29 800	6660	30 900	0.195	84
13	30 200	14 400	29 100	0.761	87
14	30 000	14 500	29 100	0.704	86
15	29 700	16 900	29 000	0.648	85
16	30 000	17 300	29 100	0.781	86
17	29 300	19 300	28 600	0.677	83
18	30 300	10 800	30 100	0.480	75
19	30 100	23 400	29 600	0.629	84
20	29 500	16 300	29 200	0.611	84
21	29 000[c]	13 000			
	30 300	17 400	30 800	0.396	61
22	28 500	8070	27 800	0.291	78;11[d]
23	27 900	9370	28 400	0.254	83
24	30 200[e]	5750	29 200	0.146	65; 10[d]
25	28 900	5350	29 300	0.153	78; 11[f]
26	30 100[e]	7230			
	31 300	10 200	31 300	0.334	71; 11[g]
	32 700	10 800	31 600	0.162	
27	26 700[h]	6400			
	28 000	7200	28 700	0.170	72
	29 300	4600			
28	—	—	28 100	0.043	55; 18[i]
29	—	—	28 400	0.248	75

[a] Only configurations with contributions $> 1\%$ to S_1 are given; unless otherwise indicated, the quoted value refers to the HOMO → LUMO single excitation.
[b] HOMO − 1 → LUMO + 1 single excitation.
[c] First vibrational band well resolved.
[d] HOMO → LUMO + 2 single excitation.
[e] First and second electronic bands close (**24**) or nearly merged (**26**).
[f] HOMO − 1 → LUMO + 3 single excitation.
[g] HOMO → LUMO + 1 single excitation.
[h] All three vibrational bands of the first electronic transition well resolved.
[i] HOMO − 1 → LUMO single excitation.

absorption is observed for the 6-methoxy derivative (see Fig. 3). In contrast, the largest extinction coefficients are found for 7-methoxy derivatives **7** and **13**–**21** (ϵ between 10 000 and 23 000 compared to values of $\epsilon \approx 7000$ for the 6-methoxycarbostyril **6** and only about 4000 for the 8-methoxy analog **8**, see Table 3).

7,8-Benzo-annulation (**27**) also leads to a significant bathochromic shift of 2000 cm^{-1}, well comparable to a 6-methoxy substituent (**6**), and again only with a modest extinction coefficient of 7200 (calculated oscillator strength $f = 0.170$, described later).- Even the somewhat higher calculated value of $f = 0.248$ for the unavailable 5,6-benzo annulated compound **29** is not promising. Linear annulation (**28**) should lead to an even weaker absorption ($f = 0.043$). Synthesis of this not yet available compound, thus, does not seem to be worthwhile.

3.2. Calculated excitation energies and oscillator strengths

As also can be seen from the data presented in Table 3 the agreement between experimental (accurate to about 100 cm^{-1}) and calculated excitation energies is quite good (error $\approx 900\ cm^{-1}$) indicating the predictive power of these calculations. Interestingly, the largest discrepancies between experimental and calculated transition energies are found for the unsubstituted parent compound **1**, its N- and 4-methyl derivatives **2** and **3** and, especially, 4-phenylcarbostyril **4**. To assess a potential effect of the molecular geometry used on the ZINDO calculated excitation energy, for **1** geometries were also computed by ab initio (HF/3-21G, HF/6-31G*) and hybrid HF/DFT (B3LYP/6-31G*, B3LYP/6-311G**) methods yielding absorption maxima of 32500 (HF/3-21G), 32500 (HF/6-31G*), 31300 (B3LYP/6-31G*) and 31 500 cm^{-1} (B3LYP/6-311G**), respectively. Clearly, the lowest difference to the experimental data is obtained when AM1 or B3LYP geometries are used in the ZINDO calculations. Thus we are confident that the use of molecular structures calculated at higher levels of theory will not alter the present results. Not surprisingly, compared to excitation energies, there is less agreement between experimental extinction coefficients ϵ as crude intensity measures and calculated oscillator strenghts f. However, compounds with low ϵ ($\approx 6000\ l\,mol^{-1}cm$) also have low f

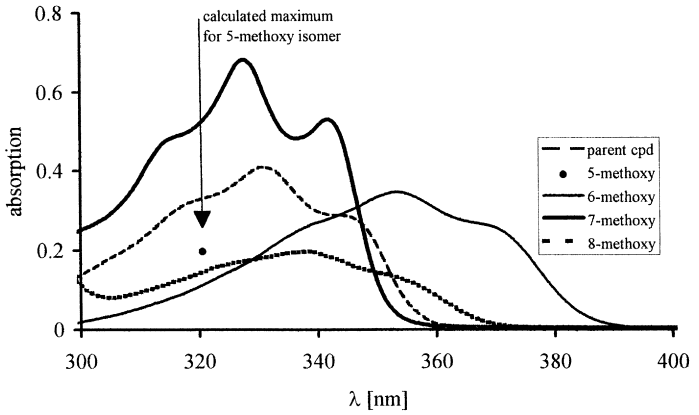


Fig. 3. Absorption spectra of positional isomers of methoxy substituted 4-methylquinolin-2(1H)-ones **6**–**8**.

values (<0.3) whereas those with high ϵ values ($\geq$15 000 l mol^{-1}cm^{-1}) are characterized by $f \geq$ 0.5. As expected, the first excited electronic state is dominated by the HOMO–LUMO single excitation ($\approx$80%) although in a number of cases (e.g. **4**, **5**, **21**, **24**, **28**) rather low coefficients for this configuration are found, usually with no one case exceeding 1% contribution to S_1 (see Table 3). Ab initio CIS/6-31G* calculations on **1** corroborate this finding. However, excitation energies obtained by this procedure are considerably more off ($\approx$10 000 cm^{-1}) than those calculated by ZINDO ($\approx$1000 cm^{-1}).

3.3. Fluorescence spectra

Fluorescence maxima, quantum yields as well as the two differently calculated $S_1 \rightarrow S_0$ transition energies (ν^{EXC} and ν^{C110}, described later) are summarized in Table 4. The fluorescence spectra of the investigated compounds are generally more diffuse than their absorption spectra. However, in several cases clearly resolved vibrational bands are discernible. These are indicated separately in Table 4. As mentioned before, for a number of compounds the contribution of the HOMO $\rightarrow$ LUMO singly excited configuration to S_1 is surprisingly low. Therefore optimization of this state by using the keyword ''EXCITED'' (ν^{EXC} in Table 4) in MOPAC might be questionable. Consequently, excited state calculations are also performed by a single + double CI based on the closed shell RHF determinant (ν^{C110} in Table 4). From previous experience grossly underestimated Stokes shifts can be expected for this procedure. Calculations are also hampered by poor convergence or lack thereof. Additionally in a number of cases the S_1 optimization by either procedure resulted in highly distorted structures. Therefore, calculated $S_1 \rightarrow S_0$ transition energies are to be considered as less reliable than absorption energies.

Substituent effects appear to exert a more pronounced effect on emission than on absorption spectra (see Tables 3 and 4). Within the series of simple isomeric methoxy carbostyrils the longest wavelength fluorescence is found for the 6-methoxy derivative **6**. In line with this result particularly long wavelength emissions are found for the analogous compounds **22** and **23**. Substitution in position 3 with phenyl or ethoxycarbonyl leads also to long wavelength emissions (**9**, **11**, **12**). However, in comparison to these values most additional substituents in position 4 lead rather to a blueshift, even if a 7-methoxy group is present (**13**–**21**). Consequently rather small Stokes shifts are observed for these compounds.

Fluorescence quantum yields are in most cases found in the range between 0.01 and 0.04. Somewhat larger values are found for 7-methoxy derivative **7** (0.052), the simple 3-phenyl derivative **9** (0.061), the 3,4 disubstituted derivative **21** (0.051) and especially for the 4-acetoxy-1-ethyl-6-methoxy-3-phenylcarbostyril **15** (0.105).

Table 4
Experimental and calculated (ν^{EXC} and ν^{CI10})[a] fluorescence maxima (cm^{-1}) and quantum yields Φ_F

Compound	ν_F	Φ_F	ν^{EXC}	ν^{CI10}
1	26 400	0.020	25 900	31 400
2	26 300	0.010	29 000	30 600
3	26 700	0.020	27 500	31 700
4	25 100	0.010	27 500	30 300[b]
	26 500			
5	—	—		30 700
6	24 700	0.033	25 400	27 300
7	27 200	0.052	28 800	30 800
	29 300			
8	25 400	0.009	26 700	29 400
	26 400			
9	24 400	0.061	26 300	—
	25 600			
10	26 100	0.011	23 400	—
	27 300			
11	24 000	0.018	23 100	—
	26 000			
12	23 300	0.010	27 300	29 500
	26 800			
13	26 500	0.009	21 500	28 300
14	26 600	0.008	20 800	—
15	25 500	0.105	24 400	—
16	25 500	0.015	—	—
	26 300			
17	25 100	0.028	21 400	
18	26 200	0.005	—	—
19	26 400	0.009	—	—
20	25 600	0.004	22 200	25 700
21	27 000	0.051	28 200	—
22	24 400	0.040	—	28 100
23	23 500	0.046	—	—
24	25 600	0.007	24 800	29 100[c]
	26 800			
25	23 600	0.022	22 100	—
	25 700			
26	27 000	0.026	29 100	
27	23 600	0.195	26 600	28 600
	24 800			
	26 000			
28	—	—	25 300	27 300
29			26 100	27 200

[a] ν^{EXC}: S_1 geometry optimized using the keyword ''EXCITED''; ν^{CI10}: S_1 geometry optimized using the keyword ''CISD'' = 10.
[b] CISD = 8 values.
[c] CISD = 4 values.

4. Conclusions

Compared to coumarins, comparably substituted carbostyrils show much less sensitivity of their absorption–luminescence characteristics on substituent effects. However, as was shown in the present paper, by judiciously choosing the position and nature of substituents, it appears possible to obtain sufficient bathochromic shifts of both UV/Vis as well as fluorescence transition to make these compounds useful for analytical applications. As in coumarins [9] donor substituent (e.g. methoxy) in position 6 has a more pronounced bathochromic effect than in position 7 (compare compounds **6** and **7**, Tables 3 and 4). In contrast, the presence of a 7-methoxy group turns out to significantly enhance absorption intensities. Fluorescence quantum yields of carbostyrils generally are somewhat lower than those of corresponding coumarins [18,32]. Again, an appropriate choice of substituents can lead to sufficiently high values of ϕ_F. Finally, computational methods allow predictions of both absorption and, albeit to a somewhat less degree, fluorescence maxima with reasonable accuracy. Thus, calculations prove a valuable tool in the rational design of dyes with special properties. In addition, the results described in the present paper should provide useful guidelines for the development of carbostyril based dyes with the required spectral-luminescence and photophysical characteristics required for analytical applications in biochemistry and biology. Work along these lines is in progress and results will be presented in due course.

References

[1] R.S. Becker, S. Chakravorti, C.A. Gartner, M. de Graca Miguel, J. Chem. Soc., Faraday Trans. 89 (1993) 1007.
[2] U. Brackmann, Lambdachrome® Laser Dyes, Lambda Physik GmbH, Göttingen, 1986.
[3] B.B. Snavely, in: J.B. Birks (Ed.), Organic Molecular Photophysics, 1, John Wiley and Sons, London, 1973 Chapter 5.
[4] C.V. Shank, A. Dienes, A.M. Trozzolo, J.A. Myer, Appl. Phys. Lett. 16 (1970) 405.
[5] G.A. Reynolds, K.-H. Drexhage, Opt. Commun. 13 (1975) 222.
[6] A.N. Fletcher, D.E. Bliss, J.M. Kauffman, Opt. Commun. 47 (1983) 57.
[7] H.H. Grunhagen, H.T. Witt, Z. Naturforsch. 25b (1970) 373.
[8] R.P. Haughland, in K.D. Larison (Ed.), Handbook of Fluorescent Probes and Research Chemicals, Molecular Probes Inc, Eugene, USA, 1992.
[9] A.G. Gonzalez, J.T. Barroso, Z.D. Jorge, F.R. Luis, Rev. R. Acad. Cienc. Exactas, Fis. Nat. Madrid 75 (1981) 811.
[10] O.S. Wolfbeis, in: S.G. Schulman (Ed.), Molecular

Luminescence Spectroscopy: Methods and Applications, Wiley, New York, 1985 Chapter 3.
[11] R.T. Williams, J. Roy. Inst. Chem. 83 (1959) 611.
[12] G.J. Yakatan, R.J. Juneau, S.G. Schulman, Anal. Chem. 44 (1972) 1044.
[13] P.E. Zinsli, J. Photochem 3 (1974) 55.
[14] R.K. Bauer, A. Kowalczyk, A. Balter, Z. Naturforsch. 32a (1977) 560.
[15] G.S. Beddard, S. Carlin, R.S. Davidson, J. Chem. Soc. Perkin Trans. 2 (1977) 262.
[16] P.-S. Song, W.H. Gordon III, J. Phys. Chem. 74 (1970) 4234.
[17] P.-S. Song, M.L. Harter, T.A. Moore, W.C. Herndon, Photochem. Photobiol. 14 (1971) 521.
[18] W.W. Mantulin, P.-S. Song, J. Am. Chem. Soc. 95 (1973) 5122.
[19] B.S. Kirkiacharian, R. Santus, C. Helene, Photochem. Photobiol. 16 (1972) 455.
[20] T. Lai, B.T. Lim, E.C. Lim, J. Am. Chem. Soc. 104 (1982) 7631.
[21] T.V. Sakhno, G.G. Konoplev, G.A. Valkova, D.N. Shigorin, Zh. Fiz. Khim. 56 (1982) 878.
[22] O.S. Wolfbeis, Z. Naturforsch. 32a (1977) 1065.
[23] O.S. Wolbeis, Z. Phys. Chem. N.F. 125 (1981) 15.
[24] O.S. Wolfbeis, G. Uray, Monatsh. Chem. 109 (1978) 123.
[25] Y. Forster, E. Haas, Anal. Biochem. 209 (1993) 9.
[26] K. Rechthaler, G. Köhler, Chem. Phys. 189 (1994) 99.
[27] S. Sanghi, D. Mohan, Spectrochim. Acta 52A (1996) 1229.
[28] O.A. Ponomarev, E.R. Vasina, S.N. Yarmolenko, V.G. Mitina, Zh. Obshch. Khim. 58 (1988) 438.
[29] O.A. Ponomarev, Yu.F. Pedash, Zh. Fiz. Khim. 63 (1989) 546.
[30] O.A. Ponomarev, E.R. Vasina, A.O. Doromenko, V.G. Mitina, Khim. Fiz 8 (1989) 854.
[31] O.A. Ponomarev, E.R. Vasina, V.G. Mitina, A.A. Sukhorukov, Zh. Fiz. Khim. 64 (1990) 974.
[32] O.A. Ponomarev, E.R. Vasina, S.N. Yarmolenko, V.G. Mitina, N.S. Pivnenko, Zh. Obshch. Khim 60 (1990) 1161.
[33] O.A. Ponomarev, Yu.F. Pedash, O.V. Prezhdo, Zh. Fiz. Khim 65 (1991) 1846.
[34] R. Nakagaki, N. Kitamura, I. Aoyama, H. Ohtsubo, J. Photochem. Photobiol. A 80 (1994) 113.
[35] S.G. Schulman, A.C. Capomacchia, B. Tussey, Photochem. Photobiol. 14 (1971) 733.
[36] O.S. Wolfbeis, E. Lippert, Z. Naturforsch. 33a (1978) 238.
[37] O.A. Ponomarev, E.P. Vasina, A.O. Doroshenko, V.G. Mitina, Zh. Obshch. Khim. 59 (1989) 2072.
[38] G. Saroja, N.B. Sankaran, A. Samanta, Chem. Phys. Lett. 249 (1996) 392.
[39] J.M. Kauffiman, G.S. Bajwa, P.T. Litak, C.J. Kelley, R. Pai, Proceedings of the Conference on Scintillating and Fiber Detectors, 1997, in press.
[40] A. Pla-Dalmau, G.W. Foster, G. Zhang, Nucl. Inst. Meth. A 361 (1995) 192.
[41] M. Li, P.R. Selvin, J. Am. Chem. Soc. 117 (1995) 8132.
[42] P.R. Selvin, J. Jancarik, M. Li, L.-W. Hung, Inorg. Chem. 35 (1996) 700.
[43] M. Li, P.R. Selvin, Bioconjugate Chem. 8 (1997) 127.
[44] E.F.G. Dickson, A. Pollak, E.P. Diamandis, J. Photochem. Photobiol. B 27 (1995) 3.
[45] D. Parker, J.A.G. Willaims, J. Chem. Soc., Perkin Trans. 2 (1996) 1581.
[46] D. Parker, J.A.G. Williams, J. Chem. Soc. Dalton Trans. (1996) 3613.
[47] E. Soini, H. Kojola, Clin. Chem. 29 (1983) 65.
[48] I. Hemmilä, S. Dakubu, T. Lovgren, V.M. Mukkala, H. Siitari, Anal. Biochem. 137 (1984) 335.
[49] I. Hemmilä, Clin. Chem. 31 (1985) 359.
[50] A. Rieutord, P. Prognon, F. Brion, G. Mahuzier, Analyst 122 (1997) 59R.
[51] G. Jürgens, A. Hermann, D. Aktuna, W. Petek, Clin. Chem. 38 (1992) 853.
[52] C. Tzougraki, C. Noula, R. Geiger, G. Kokotos, Liebigs Ann. Chem. (1994) 365.
[53] T. Besson, B. Joseph, P. Moreau, M.-C. Viaud, G. Coudert, G. Guillaumet, Heterocycles 34 (1992) 273.
[54] M.J.S. Dewar, E.G. Zoebisch, E.F. Healy, J.J.P. Stewart, J. Am. Chem. Soc. 107 (1985) 3902.
[55] J.E. Ridley, M.C. Zerner, Theor. Chim. Acta 32 (1973) 111.
[56] SYBYL 6.3, Tripos Associates, St. Louis, MO, USA.
[57] J.J.P. Stewart, J. Comput.-Aided Mol. Des., 4 (1990)1.
[58] MOPAC 6.0, QCPE program no. 455.
[59] T. Clark, VAMP: Erlangen Vectorized Molecular Orbital Package, Version 4.40, Computer-Chemie Centrum University Erlangen-Nürnberg, Germany, 1992.
[60] J. Baker, J. Comput. Chem. 7 (1986) 385.
[61] M.C. Zerner, ZINDO, a comprehensive semiempirical quantum chemistry package, Quantum Theory Project, University of Florida, Gainesville, FL, USA.
[62] M.M. Karelson, M.C. Zerner, J. Phys. Chem. 96 (1992) 6949.
[63] A.D. Becke, J. Chem. Phys. 98 (1993) 5648.
[64] Gaussian 94, Revision B. 3, M.J. Frisch, G.W. Trucks, H.B. Schlegel, P.M.W. Gill, B.G. Johnson, M.A. Robb, J.R. Cheeseman, T. Keith, G.A. Petersson, J. A. Montgomery, K. Raghavachari, M.A. Al-Laham, V.G. Zakrzewski, J.V. Ortiz, J.B. Foresman, C.Y. Peng, P.Y. Ayala, W. Chen, M.W. Wong, J.L. Andres, E.S. Replogle, R. Gomperts, R.L. Martin, D.J. Fox, J.S. Binkley, D.J. Defrees, J. Baker, J.P. Stewart, M. Head-Gordon, C. Gonzalez, J.A. Pople, Gaussian Inc., Pittsburgh PA, 1995.
[65] W. Stadlbauer, Monatsh. Chem. 117 (1986) 1305.
[66] W. Stadlbauer, Th. Kappe, Monatsh. Chem. 116 (1985) 1005.
[67] W. Stadlbauer, R. Laschober, Th. Kappe, Liebigs Ann. Chem. (1990) 531.
[68] W. Stadlbauer, Th. Kappe, Vestn. Slov. Chem. Drus. 33 (1986) 271.
[69] W. Stadlbauer, R. Laschober, Th. Kappe, Monatsh. Chem. 122 (1991) 853.
[70] G. Hojas, diploma thesis, Karl-Franzens-University of Graz, Austria, 1997.
[71] Y. Tagawa, T. Kawaoka, Y. Goto, J. Heterocycl. Chem. 34 (1997) 1677.
[72] S. Chorbadjiev, Synthetic Communications 20 (1990) 3497.
[73] L. Limpach, Ber. Dtsch. Chem. Ges. 64 (1931) 970.

[74] A.L. Searles, R.J. Kelly, J. Am. Chem. Soc. 77 (1955) 6075.
[75] A. Bischler, M. Lang, Ber. Dtsch. Chem. Ges. (1928) 279.
[76] H. Hübner, Ber. Dtsch. Chem. Ges. (1941) 482.
[77] J.A. Robel, Synthesis (1991) 56.
[78] F. Effenberger, W. Hartmann, Chem. Ber. 102 (1969) 3260.
[79] O. Claret, Spectrosc. Lett. 10 (1977) 25.
[80] V.N. Gogte, S.B. Kulkarni, B.D. Tilak, Indian Journal of Chem. Sect. B. 15 (1977) 769.
[81] A.M. Nadzan, K.L. Rinehart Jr., J. Am. Chem. Soc. 99 (1977) 4647.
[82] R.N. Iyer, R. Gopalchari, Indian Journal of Chem. 11 (1973) 234.
[83] C. Kaneko, H. Fujii, S. Kawai, A. Yamamoto, K. Hashiba, Chem. Pharm. Bull. 28 (1980) 1157.
[84] J.C. Powers, I. Ponticello, J. Am. Chem. Soc. 90 (1968) 7102.
[85] Y. Konishi, Nippon Kagaku Kaishi (1973) 118.
[86] W.M.F. Fabian, J. Comput. Chem. 12 (1991) 17.
[87] J. Wang, R.J. Boyd, Chem. Phys. Lett. 259 (1996) 647.
[88] P. Beak, Acc. Chem. Res. 10 (1977) 186.
[89] M.R. Nimlos, D.F. Kelly, E.R. Bernstein, J. Phys. Chem. 91 (1987) 6610.
[90] A. Held, D.F. Plusquellic, J.L. Tomer, D.W. Pratt, J. Phys. Chem. 95 (1991) 2877.
[91] M.A. Baldwin, G.J. Langley, J. Chem. Soc. Perkin Trans. 2 (1988) 347.
[92] A.A. Ahmed, M. Julliard, F. Chanon, M. Chanon, F. Gracian, G. Pfister-Guillouzo, Spectrochim. Acta 53A (1997) 335.
[93] G. Pfister-Guillouzo, C. Guimon, J. Frank, J. Ellison, A.R. Katritzky, Liebigs Ann. Chem. (1981) 366.
[94] J. Mirek, A. Sygula, Z. Naturforsch 37a (1982) 1276.
[95] G. Fogarasi, J. Mol. Struct. 413 (1997) 271.
[96] V. Barone, C. Adamo, J. Phys. Chem. 99 (1995) 15 062.
[97] G. Bakalarski, P. Grochowski, B. Lesyng, J. Leszczynski, Chem. Phys. 204 (1996) 301.
[98] A. Broo, A. Holmen, Chem. Phys. 211 (1996) 147.
[99] B. Hernandez, F.J. Luque, M. Orozco, J. Org. Chem. 61 (1996) 5964.
[100] J.S. Kwiatkowski, J. Leszczynski, Int. J. Quant. Chem. 61 (1997) 453.
[101] J.S. Kwiatkowski, J. Leszczynski, J. Mol. Struct. 376 (1996) 325.
[102] J.S. Kwiatkowski, J. Leszczynski, J. Phys. Chem. 100 (1996) 941.
[103] S.F. Mason, J. Chem. Soc. (1958) 637.
[104] J.C. Petersen, J. Chem. Phys. 75 (1971) 1129.
[105] A. Fujimoto, K. Inuzuka, Spectrochim. Acta 41A (1985) 1471.