Dihydronaphthalenone Carboxylates – Spectral Characteristics and Structure

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Z. Naturforsch. **52a,** 457–461 (1997); received December 31, 1996

The absorption and luminescence characteristics of a group of newly synthesized methyl esters of 2-alkyl (*p*-substituted-aryl) – aminomethylene-3,4-dihydro-1(2 H)-naphthalenone-4-carboxylic acids have been investigated. The studied compounds may exist in three tautomeric forms. On the basis of comparison of their electronic spectra to those of similar substances, the observed substituent effect on the position of the UV-VIS absorption bands, the IR spectra and the results of PPP-SCF-CI quantum-chemical calculations it is concluded that the keto tautomer predominates in solution.

Key words: Electronic spectra, Tautomerism, Dihydronaphthalenone carboxylates.

1. Introduction

Enaminones have been intensively studied with respect to their keto-enol tautomerism and E/Z isomerism [1, 2], as well as their use in the synthesis of various compounds via reactions with electrophiles, nucleophiles, etc. [3]. The aim of the present paper is to determine the predominating tautomeric form in solution and the main chromophore of a group of newly synthesized enaminones, namely methyl esters of 2-alkyl (*p*-substituted-aryl) – aminomethylene-3,4-dihydro-1(2 H)-naphthalenone-4-carboxylic acids (further referred to as dihydronaphthalenones), shown in Figure 1. For this purpose, their absorption and luminescence characteristics have been studied. Conclusions are made on the basis of comparison of their electronic spectra to those of similar substances, the observed substituent effect on the position of the UV-VIS absorption bands, the IR spectra and the results of the PPP-SCF-CI quantum-chemical calculations.

2. Results and Discussion

The UV-VIS spectra of the studied compounds in hexane consist of an intensive band in the 24 000–27 000 cm^{-1} region and two bands of lower intensity at shorter wavelengths (see Figure 2). The solvent polarity has an insignificant influence on the position of the absorption bands; upon change of the solvent from hexane to ethanol the longest wavelength maximum suffers a small bathochromic shift of about 500 cm^{-1} (see Table 1). The substituents at position 3 (compare compounds **2** and **3**), as well as these at positions 6 and 7 (compare compounds **4** and **5**) have no effect on the energy of the longest wavelength band, while the R_1 substituent at the nitrogen has a definite influence on it. Change of R_1 from alkyl to phenyl leads to a red shift of the maximum of about 2000 cm^{-1}. A linear dependence is observed between the energy of the absorption maxima of compounds **4, 6–9** and the σ-Hammett constants of the substituent in the aryl group for the whole σ-region, i.e. the absorption maxima monotonously move to the red upon increase of σ, an electron-withdrawing group in para-position of the phenyl substituent leads to a hypochromic shift of the longest wavelength band relative to compound **4**, while an electron donating one has the opposite effect. The observed influence of R_1 on the energy of the lowest absorption transition of the studied substances suggests that the main chromophore of these systems includes the substituent in the enaminone fragment, but not the substituents at positions 3, 6 and 7.

All investigated compounds fluorescence in solution at room temperature; the maxima are in the region 16 000–21 000 cm^{-1}. The bands are broad and structureless. The Stokes shift is of the order of 5000–6000 cm^{-1}. Increase of the solvent polarity results in a red displacement of the emission maxima, the effect

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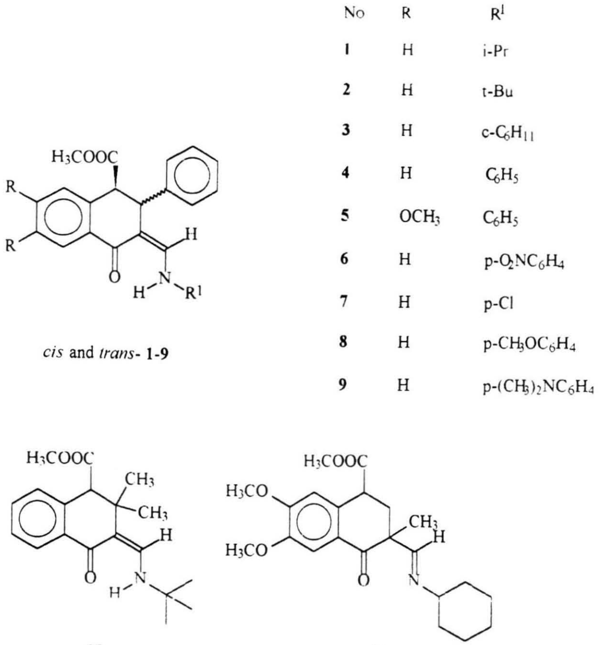

No	R	R^1
1	H	i-Pr
2	H	t-Bu
3	H	c-C_6H_{11}
4	H	C_6H_5
5	OCH_3	C_6H_5
6	H	p-$O_2NC_6H_4$
7	H	p-Cl
8	H	p-$CH_3OC_6H_4$
9	H	p-$(CH_3)_2NC_6H_4$

cis and *trans*- **1-9**

10 **11**

Fig. 1. Compounds investigated.

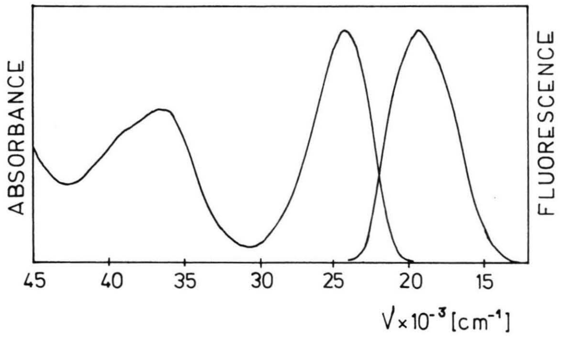

Fig. 2. Absorption and corrected fluorescence spectra of compound **4** in ethanol.

being more pronounced in the case when the substituent in the enaminone fragment R_1 is an aryl group; e.g. passing from hexane to ethanol, the shift is only 50 cm^{-1} for compound **1**, while in the case of **4** it is 2000 cm^{-1}. The substituent effect on the position of the fluorescence maxima resembles that describe above for the absorption ones. The fluorescence quantum yield Q_F in ethanol does not exceed 10^{-2} (see Table 1), the emission intensity in hexane in most cases is even lower, Q_F being less than 10^{-3}.

Table 1. Experimental spectral characteristics of the investigated compounds; ν_{abs}, ν_{fl} energy of the longest wavelength absorption and fluorescence maxima, resp.; Q_F fluorescence quantum yield; $[\nu] = cm^{-1}$; NM – No measurement.

Comp.	Ethanol		Hexane		Ethanol
No.	ν_{abs}	ν_{fl}	ν_{abs}	ν_{fl}	$10^3\ Q_F$
1	27 120	20 520	26 500	20 570	6.6
2	27 100	21 080	26 560	20 530	14.6
3	27 120	20 200	26 450	18 300	1.3
4	25 280	21 280	24 700	19 290	2.2
5	24 960	21 530	24 240	20 210	5.0
6	26 480	20 960	25 700	20 900	<1
7	25 040	20 890	24 640	19 870	4.2
8	24 400	21 520	24 000	18 510	1.3
9	23 920	20 750	22 750	16 040	<1
10	27 100	21 300	27 100	21 100	9.3
11	34 200	28 120	NM	NM	NM

There is practically no difference in the electronic spectra of the *cis* and *trans* isomers of the studied dihydronaphthalenones.

The fixing of the studied compounds by freezing of ethanol solutions at 77 K leads to the well known [4] "blue shift" of the fluorescence Franck-Condon transitions of about 1500 cm^{-1} relative to that at 293 K, and to a considerable enhancement of the fluorescence intensity (more than two orders of magnitude), showing that high-amplitude intramolecular motions probably contribute to the deactivation of the excited states at room temperature. However, the increase of the fluorescence intensity in frozen solution is comparable for the N-alkyl and N-aryl derivatives, indicating that the rotation of the substituent at the nitrogen is not responsible for the poor fluorescence ability of the investigated compounds at 293 K.

In solution, the studied dihydronaphthalenones may exist in the three tautomeric forms (**A, B** and **C**) shown in Figure 3.

As mentioned above, the substituents at positions 3, 6 and 7 have practically no influence on the energy of the absorption transitions, i.e. neither phenyl ring **1** nor phenyl ring **2** participates in the conjugated system. This observation suggests that the enol form **B** is not present in solution, as it involves a conjugation between the substituent in the enaminone fragment and phenyl ring **1**. On the other hand, the electronic spectra of the model compound **11** (see Table 1), which represents the fixed tautomeric form **C**, are quite different in position from those of the studied substances. Consequently, on the basis of the electronic absorption spectra it may be concluded that the tautomeric

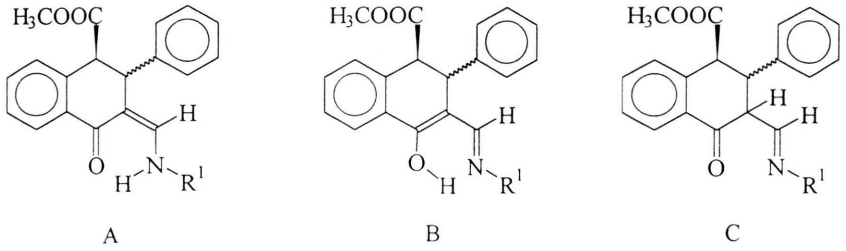

Fig. 3. Tautomeric forms of 3,4-dihydro-1(2H)-naphthalenone-4-carboxylates.

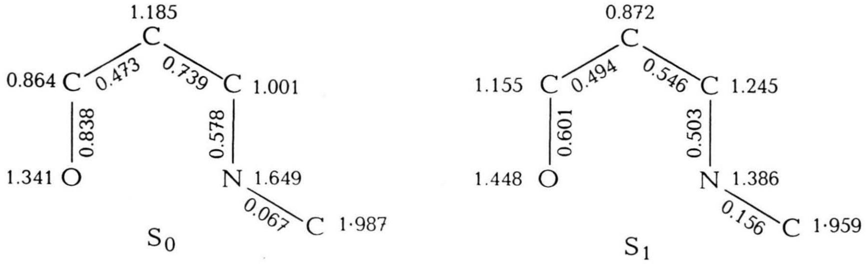

Fig. 4. Computed electron density distribution in the enamnione fragment compound **1**.

form **A** predominates in solution. This assumption is in agreement with the evidence collected during recent years by means of NMR and UV spectroscopy showing that the ground state of enaminone is best characterized by the keto tautomeric form [1, 2]. The ^{1}H-NMR study and the X-ray crystallographic data on the investigated compounds [5] also support this conclusion.

Table 2 shows the results of the performed quantum chemical calculations for compounds **1** and **4**, carried out in π-electronic approximation by the PPP-SCF-CI method [6] with a standard parameterization [7]. It can be seen that the computed energies of the *pp** electronic transitions for both tautomeric forms **A** and **B** are in good agreement with the experimental values (the difference between the calculated and experimentally observed ones in hexane is within the accuracy of the PPP method, 0.2–0.3 eV); the calculated transition energies for **C** do not reproduce the absorption spectra of compounds **1** and **4**, but are in good agreement with that of the model compound **11**. These results support the conclusion drawn above that tautomeric form **C** is not present in solution, but do not allow to distinguish which of the other tautomers predominates.

The IR spectra in dilute chloroform solutions exhibit a band at 3410 cm^{-1}, characteristic of the free NH-group, as well as a band around 3200 cm^{-1}, characteristic of an associated NH-group. The characteristic of the carbonyl group absorption at 1640 cm^{-1} is also observed. These results show that in solution both the intramolecularly hydrogen-bonded and the nonhelated species are present. Similar results, based on IR spectral data, have been reported in the literature for 2-aminomethylene- and 2-phenylaminomethylene-cyclohexanone [1], which is similar in structure to the compounds investigated in the present paper.

According to the PPP-SCF-CI calculations (see Table 2), the above species have very close electronic transition energies which may explain why we do not

Table 2. Theoretical (PPP-SCF-CI) and experimental $\pi\pi^*$ transition energies of the possible tautomers of compounds **1** and **4** in cm^{-1}.

Comp.	Trans.	$E_{calc.}/f$				
		A	A(H-bond)	**B**	**C**	E_{exp}
1	$S_0 \rightarrow S_1$	28 820/0.34	28 270/0.37	29 500/0.66	36 470/0.03	27 120
	$S_0 \rightarrow S_2$	49 530/0.16	51 270/0.18	34 740/0.01	41 820/0.47	39 200
	$S_0 \rightarrow S_3$	58 520/0.77	58 370/0.69	40 135/0.02	45 810/0.05	49 100
4	$S_0 \rightarrow S_1$	26 300/0.79	26 040/0.73	25 900/1.12	36 430/0.04	25 280
	$S_0 \rightarrow S_2$	32 250/0.04	33 240/0.04	34 900/0.01	36 500/0.01	38 100
	$S_0 \rightarrow S_3$	38 950/0.19	39 170/0.23	35 390/0.01	37 450/0.74	48 900

observe different maxima for the two forms in the UV-VIS region. On the other hand, the theoretical computations show (see Fig. 4) that upon excitation the electron density on the carbonyl oxygen substantially increases, while that on the nitrogen decreases; at the same time the C=O bond order also diminishes. The above data suggest that the hydrogen bond becomes stronger in the first excited singlet state.

3. Experimental

The absorption spectra are taken on a Specord M-40 (Carl Zeiss, Jena). The fluorescence spectra are recorded on a Perkin Elmer MPF 44 fluorimeter. The fluorescence quantum yields Q_F are measured relative to 3-*p*-methoxyphenylmethylene-1(3H)-isobenzofuranone ($Q_F = 0.12$ in ethanol [8]). The low temperature luminescence measurements are performed at 77 K in the standard phosphorescence accessory to MPF 44 in quartz tubes of 4 mm diameter. The solvents used are of fluorescence grade.

Table 3. Methyl *cis* and *trans*-2-(*p*-substituted anilino)methylene-3-phenyl-1(2H)naphthalenone-4-carboxylates (*cis* and *trans*-**5–9**).

Compound	Yield %	*cis/trans* ratio[a]	Melting points (*cis*) °C[b] Solvent
5	46	48:52	112–113, ethylacetate
6	34	~40:60[c]	214–216, ethylacetate *trans* 185–187, ethylacetate
7	12	37:63	163–165, ethylacetate-light petroleum
8	19	53:47	145–147, ethylacetate-light petroleum
9	31	81:19	75–76, ether

[a] Estimated by ^{1}H-NMR integration of the crude reaction mixture.
[b] Melting points (microhot stage Boetius PHMK 0.5), uncorrected.
[c] Ratio estimated after CC of the reaction mixture.

TLC: Silicagel 60 F 254 on aluminium sheets "Merck"; layer thickness 0.2 mm; solvent systems: ether/hexane 1:1 (1 part) and hexane/ethylacetate/methanol/ammonia 120:100:15:10, upper layer (1 part). Column chromatography (CC): silicagel type 60 "Merck", particle size 0.20–0.063 mm, ethylacetate/hexane 5:95, 10:90. Mass spectra (MS): Jeol JMS D-300, electron impact, 70 eV. IR spectra (cm^{-1}): Specord IR-71 (Carl Zeiss, Jena) in chloroform. ^{1}H-NMR spectra: Bruker Spectrospin WM-250 (250 MHz) in $CDCl_3$ with TMS as internal standard; chemical shifts: in δ ppm, J in Hz.

The starting *N*-[(*p*-substituted)cinnamylidene]anilines used in this study are made by condensation of cinnamaldehyde with the corresponding aniline.

Compounds **1–4**, **10** and **11** are described in [5], while the methyl esters of *cis*- and *trans*-2-alkyl- or 2-(*p*-substituted anilino)methylene-3,4-dihydro-1(2H)-naphthalenone-4-carboxylic acids **5–9** are synthesized for this investigation. Reaction of homophthalic anhydride with the corresponding *N*-(*p*-substituted)cinnamylidene anilines is carried out in dry benzene (20 min reflux), and the resulting acidic mixture is treated with ethereal solution of diazomethane. The diastereoisomers obtained are separated by two successive CC. *Trans*-isomers ar oily substances except for *trans*-6. Some data for compounds **5–9** are listed in Table 3. The elemental analyses for all solid products are satisfactory. Mass spectra show in all cases a molecular ion peak with different relative intensity. The IR spectra exhibit characteristic bands at 1590–1610 cm^{-1} (arom), 1640–1680 cm^{-1} (C=C–C=O), 1720–1735 cm^{-1} (C=O, ester) and 2800–3600 cm^{-1} (NH). Some ^{1}H-NMR spectral data are listed in Table 4.

4. Conclusions

The analysis of the electronic and IR spectra, as well as the available ^{1}H-NMR data [5] indicate that the keto tautomeric form of the studied dihydronaph-

Table 4. Some ^{1}H-NMR spectral data of compounds **5–9**.

Diastereoisomer	$COOCH_3$ (3H, s)	H-4 (1H, d)	H-3 (1H, d)	$J_{3.4}$	$=C\underline{H}-NH-$ (1H, d)	$=CH-N\underline{H}-$ (1H, d)	$J_{=CH\text{-}NH\text{-}}$	arom. H (m)	H-8 (1H, m)
cis-**5–9**	3.55–3.56	4.04–4.13	4.46–4.49	4.9–5.4	6.79–7.09	11.89–12.45	11.7–12.4	6.6–7.7	8.15–8.1
trans-**5–9**	3.62–3.65	4.02–4.15	4.45–4.50	3.4–4.1	6.85–7.09	12.15–12.55	8.5–12.9	6.8–7.6	8.10–8.1

thalenone predominates in solution. The IR spectra additionally show that both the C=O...H-intramolecularly hydrogen bonded and the nonhelated species are present in solution. The results of the PPP-SCF-CI quantum-chemical calculations suggest that the hydrogen bond becomes stronger in the first excited singlet $\pi\pi^*$ state.

Acknowledgements

The authors are grateful to Prof. S. Spassov, Prof. M. Haimova and Prof. B. Jordanov for helpful discussions. S.B. and P.N. also appreciate the financial support provided by the "Scientific Investigations" foundation at the Bulgarian Ministry of Education.

[1] C. A. Grob and H. J. Wilkens, Helv. Chim. Acta **50,** 725 (1967).
[2] M. N. Eberlin, Y. Takahata, and C. Kascheres, J. Mol. Struct. (Theochem) **207,** 143 (1990).
[3] The Chemistry of Functional Groups: The Chemistry of Enamines. Ed., John Z. Rapport Wiley and Sons, 1994.
[4] R. Becker, Theory and Interpretation of Fluorescence and Phosphorescence, Wiley Interscience, New York 1969.
[5] A. Georgieva, E. Stanoeva, S. Spassov, M. Haimova, N. De Kimpe, M. Boelens, M. Keppens, A. Kemme, and A. Mishnev, Tetrahedron **51,** 6099 (1995).
[6] R. G. Parr, Quantum Theory of the Molecular Electronic Structure, Benjamin, New York 1964.
[7] J. Griffiths, Dyes and Pigments **3,** 211 (1982).
[8] P. Nikolov, F. Fratev, and St. Minchev, Z. Naturforsch. **38a,** 200 (1983).