Structure Investigations of N-Acylated Imines by Means of UV-Vis Spectroscopy

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Summary. The structures and twist angles about the single C–N bond in some N-acylated imines were determined on the basis of their absorption spectra. The overlapped individual spectral bands are resolved by means of an original computer-based program.

Keywords. N-Acylated imines; Curve fitting; UV-Vis Spectra; Structure; Trans-stilbene.

Strukturelle Untersuchungen von N-Acylierten Iminen mittels UV-Vis-Spektroskopie

Zusammenfassung. Die Strukturen und Torsionswinkel um die C–N-Einfachbindung in einigen N-acylierten Iminen wurden auf Basis der Absorptionsspektren bestimmt. Die überlappenden individuellen Spektralbanden wurden mittels eines Computerprogramms analysiert.

Introduction

The molecules of N-acylated imines **1** and **2** contain a system of directly connected azomethine and carbonyl bonds C=N–C=O, but their chemical [1, 2] and spectral [3, 4] properties are substantially different from the corresponding isoelectronic analogues – 1,3-dienes and 2-enones. While in the 2,3-unsaturated carbonyl compounds **3** and **4** the interaction with nucleophilic reagents proceeds as competitive 1,2- or 1,4-addition, the N-acylated imines in analogous conditions react exclusively through the azomethine bond and in this respect resemble carboyl compounds and arylidene amines (Schiff bases) [5, 6].

The differences observed in the behavior of N-acylated imines could be explained by this assumption, provided the system C=N–C=O is not conjugated. In such a case, due to the electronic configuration of the N-atom [7] and the resulting electronic effects, the molecule of these compounds could be considered non-planar, composed of two parts twisted by a definite angle around the C–N single bond like in benzylidene aniline [8, 9].

In order to test this assumption a number of N-acylated imines and their analogues were studied.
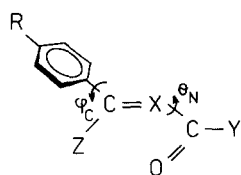
1 X=N,   Y=Ph;   Z=H;   R=H
2 X=N;   Y=Ph;   Z=Ph;   R=H
3 X=CH;   Y=Ph;   Z=H;   R=H
4 X=CH;   Y=Ph;   Z=Ph;   R=H
5 X=N;   Y=Me;   Z=Ph;   R=H
6 X=N;   Y=Me;   Z=OEt; R=H
7 X=N;   Y=Ph;   Z=Ph;   R=OMe
8 X=N;   Y=p-OCH$_3$-C$_6$H$_4$;
   Z=Ph;   R=H
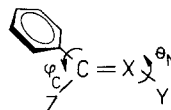
9   X=CH;   Y=Ph;   Z=H
10 X=N;   Y=Ph;   Z=H
11 X=N;   Y=H;   Z=Ph
12 X=CH;   Y=COOH; Z=Ph

Formula 1   **Formula 2**

Results and Discussion

For the purpose of a more general investigation of the relation between the structure of organic compounds and their absorption spectra it was necessary to select a suitable model for evaluation of the non-coplanarity for the separate weakly interacting fragments in N-acylated imines. An ideal system for elucidating the electronic structure as a function of the molecular conformation are *trans*-stilbene (**9**) and its iso-π-electronic analogue – benzylidene aniline (**10**). This pair was used as a model for demonstrating the method developed for compurter-aided resolution of overlapping absorption bands [10]. It allows the determination of all spectral parameters needed, characterizing each individual absorption band. Comparing the molar absorptivities of the corresponding bands it is possible to evaluate quantitatively the twist angle θ around a formally single bond r–s in a conjugated system R–S. At it was shown by Suzuki [11] the dipole strength M^2 or oscillator strength f for an intramolecular charge transfer transition in the system R–S is proportional to $\cos^2\theta_{rs}$. The relation (1), assumed first by Braude [12] for the evaluation of θ was used,

$$\cos^2\theta = \frac{\varepsilon}{\varepsilon_0},\tag{1}$$

where ε is the molar absorptivity of the corresponding absorption band in a sterically hindered molecule and ε_0 is the corresponding value for the planar analogue.

The absorption spectro of *trans*-stilbene in cyclohexane and ethanol show three main bands in the near UV-region. According to Suzuki [11] the A-band around 294 nm has a well resolved vibrational fine structure with vibrational sub-bands at about 321, 308, 296 and 284 nm, termed α, β, γ and δ. The calculated parameters of the individual sub-bands of the A-band for *trans*-stilbene in cyclohexane and ethanol are presented in Table 1. The best resolution of the A-band was achieved with five individual vibrational sub-bands [10].

Table 1. Calculated parameters of the individual sub-bands of the A-band for *trans*-stilbene

Solvent	λ_{max} [nm]	ε_{max} [l mol^{-1} cm^{-1}]	$\Delta v^g_{1/2}$ [cm^{-1}]	$I \times 10^{-7}$
Cyclohexane	322.6	10690	976	1.11 α
	311.3	10640	1240	1.40 β
	301.3	11970	2310	2.94 γ
	287.4	14380	3600	5.50 δ
	273.0	8850	5350	5.03 ε
Ethanol	321.8	13920	978	1.44 α
	310.0	18570	1330	2.63 β
	398.4	9590	1590	1.62 γ
	289.7	16500	3290	5.77 δ
	275.0	12240	4890	6.36 ε

Integral intensity $I = \displaystyle\int_0^\infty \varepsilon(v)dv = 1.063\,\varepsilon_{max}\,\Delta v^g_{1/2}$

According to Beale and Roe [13] the positions of the α, β and γ-sub-bands in mixed alcohols at $T = -130\,°C$ are at 326, 311 and 297 nm, which is in very good accordance with the corresponding calculated values. The experimental and simulated spectra of *trans*-stilbene in ethanol along with the resolved individual sub-bands of the A-band are shown in Fig. 1.

The absorption spectra of N-benzylidene aniline (Fig. 2) differs considerably from the iso-π-electronic *trans*-stilbene and *trans*-azobenzene, apparently due to the noncoplanar conformation of **10** [14, 15], where the N-phenyl ring is twisted about the C–N single bond at an angle $\theta_N = 50-60°$ [8, 15, 16]. According to Brocklehurst [14] the structureless band at 315 nm of **10** corresponds to the A-band of **9** and its intensity is reduced due to the twisted conformation of **10**. The value of θ_N could be
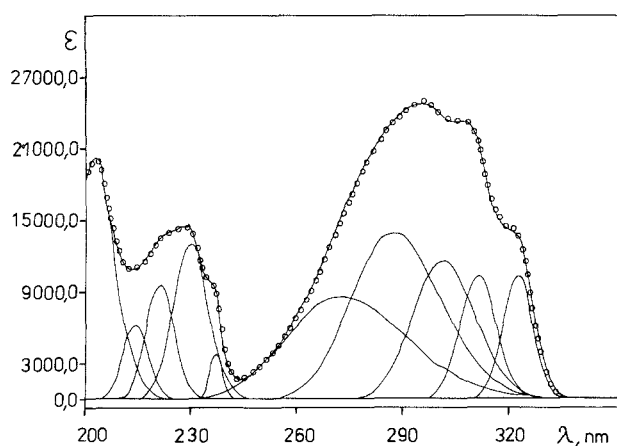

Fig. 1. Absorption spectra of *trans*-stilbene: experimental in cyclohexane (oooo); simulated with the resolved individual bands (——)

estimated using Eq. (1) or the analogue

$$\cos^2\theta = \frac{I}{I_0},$$
(2)

where I and I_0 are the integral intensities of the corresponding absorption bands for the non-coplanar molecule and its planar analogue.

Equation (2) is theoretically more justified since the integral intensity of a band is proportional to the transition probability or to the oscillator strength, respectively. The experimental and simulated absorption spectra of N-benzylidene aniline in ethanol along with the resolved individual bands are given in Fig. 2.

The values of θ_N obtained for **10** using Eqs. (1) and (2) as well as the spectral parameters derived from the resolved overlapped bands are given in Table 2. The results for θ_N are generally in accordance with the published data from the absorption spectra in solution [17–19], X-ray [9, 16] and electron diffraction [8].

It is possible to evaluate θ_N from the proper model coplanar analogue of **10**, namely 3,3-dimethyl-2-phenyl-3H-indole (**13**). Its long wavelength band [20, 21] is at 309 nm with $\varepsilon_{max} = 16600$. Using Eq. (1) and our spectral data the value of $\theta_N = 49-51°$ is obtained.

The absorption spectra of compounds **1–4** in cyclohexane are presented in Fig. 3. The spectral curves are strongly overlapped. In order to obtain the spectral
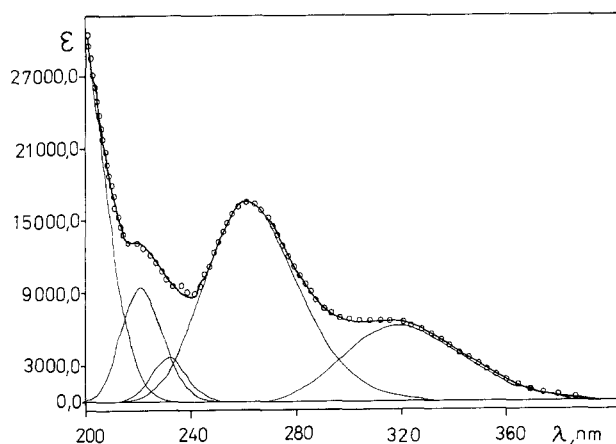

Fig. 2. Absorption spectra of N-benzylidene aniline: experimental in cyclohexane (oooo); simulated with the resolved individual bands (——)

Table 2. Spectral parameters and values of θ_N for N-benzylidene aniline

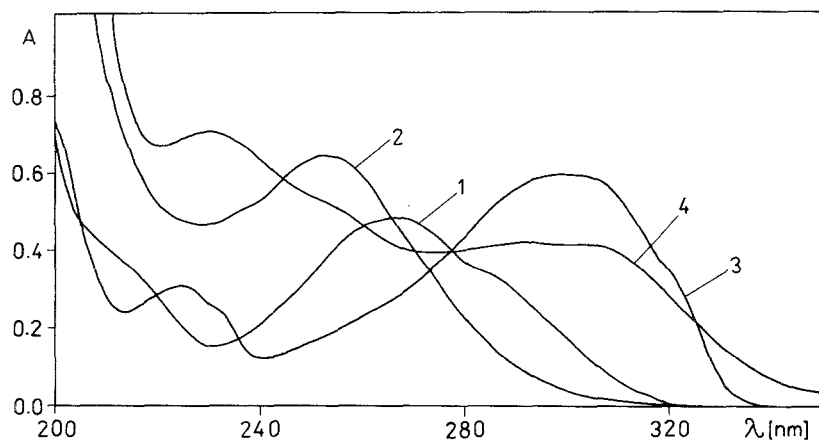| Solvent	λ_{max} [nm]	ε_{max} [l mol^{-1} cm^{-1}]	$\Delta v^g_{1/2}$ [cm^{-1}]	$I \times 10^{-7}$	θ_N Eq. (1)	θ_N Eq. (2)
Cyclohexane	319.4	6430	5170	3.53	59°	62°
	262.0	17000	5960	10.76		
Ethanol	311.9	7090	5160	3.89	59°	62°
	261.1	14330	5820	8.88		
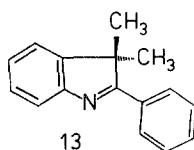
Formula 3

Fig. 3. Absorption spectra of the compounds 1–4 in cyclohexane: 1: $c = 1.58851 \times 10^{-5}$ mol/l; 2: $c = 2.78837 \times 10^{-5}$ mol/l; 3: $c = 2.79544 \times 10^{-5}$ mol/l; 4: $c = 3.85582 \times 10^{-5}$ mol/l; in all cases the path length $l = 1$ cm

parameters for the individual absorption bands needed, it is necessary to use the adapted method for resolution of overlapping absorption bands [10].

In Table 3 the calculated spectral parameters of the individual bands for N-acylated imines and their C-analogues in cyclohexane along with the values of θ_N and φ_C are collected.

It should be noted that the values of the integral intensities I and I_0 used in Eq. (2) correspond to the long wavelength bands of 1–4 having common origin [22].

It is obvious from Table 3 that for N-substituted imines 1 and 2 a weak π-electronic interaction between the carbonyl and azomethine groups could be expected resulting in highly disturbed π-electronic conjugation compared to the 2-enones 3 and 4. The calculated values of φ_C (20–30°) for compounds 2 and 4 also prompt the same effect.

Thus, the use of the spectral parameters characterizing each separate individual absorption band allows a quantitative evaluation of the conformational changes of organic molecules [23]. The X-ray data for some N-acylated imines and their analogues, like N-acetyldiphenylketimine (5) and the ethyl ester of N-benzoyl-benzamide (6), confirm our results.

The torsion angles θ_N for 5 and 6 are 73° and 77.6°, while those for φ_C are 38° and 29° and 21.6°, respectively [3, 4], being in very good agreement with the values listed in Table 3.

Table 3. Calculated spectral parameters and values of θ_N and φ_C according to Eq. (2)

Compound	λ_{max} [nm]	ε_{max} [l mol^{-1} cm^{-1}]	$\Delta v^g_{1/2}$ [cm^{-1}]	$I \times 10^{-7}$	θ_N	φ_C
1	266.1	29020	5650	17.43	64°	0°
	294.2	5510	2850	1.67		
2	231.8	15680	9920	16.52		
	257.5	12960	4380	6.04	70°	27°
	279.8	1800	3000	0.57	(74°)[a]	
3	265.1	7560	7160	5.72	–	0°
	286.7	8840	3700	3.48 }[b]		
	299.2	10430	2720	3.01		
	312.2	9960	1870	1.98		
	323.1	4240	960	0.43		
4	229.9	16170	5200	8.94	–	22°
	258.3	10970	5580	6.50		
	282.8	2860	2520	0.77		
	305.6	10110	4360	4.68		(25°)[a]

[a] Calculated from the corresponding spectral parameters in ethanol
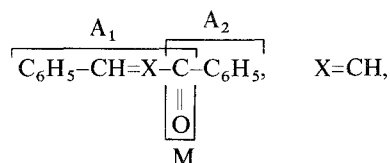[b] Individually resolved long wavelength band

It is interesting to follow the influence of an identical substituent (p-OCH$_3$) in the molecule of **2**, introduced in each weakly interacting fragments $(C_6H_5)_2C=N$ and COC_6H_5.

For this purpose the absorption spectra of **7** and **8** in cyclohexane were analyzed and the results obtained are presented in Table 4. It can be concluded that the electronic effect of the p-OCH$_3$ group in **7** is slightly stronger than in **8**, opposite to the effect observed for the same substituent in **10** and similar to those of planar 1,3-diarylpropen-3-ones [22].

Table 4. Calculated spectral parameters for **7** and **8** in cyclohexane

Compound	λ_{max} [nm]	ε_{max} [l mol^{-1} cm^{-1}]	$\Delta v^g_{1/2}$ [cm^{-1}]	$I \times 10^{-8}$
7	204.5	28580	3700	1.12
	224.6	20310	4760	1.03
	250.3	11500	4240	0.52
	281.8	17510	4650	0.87
8	207.0	38120	4770	1.93
	236.4	10320	4510	0.49
	248.7	9310	2990	0.30
	267.8	21500	5150	1.18

The planar analogues of N-acylated imines **3** and **4** can be considered as a three fragment π-electronic system [22]:

$$\overbrace{C_6H_5-CH=X-C}^{A_1}\overbrace{-C_6H_5,}^{A_2} \qquad X=CH,$$

with the carbonyl group M ($\parallel O$) shown below.

where the carbonyl group (M=CO) is connected on one side with a linear conjugated cinnamoyl fragment A_1, and on the other directly with the phenyl ring, forming the linear conjugated benzoyl system A_2. It was suggested that these "cross-conjugated" fragments A_1 and A_2 behave quasiautonomically [22]. Our results support this approach for N-acylated imines **1** and **2** (X=N), where the interaction between A_1 and A_2 is additionally weakened due to the large values of θ_N. It should be mentioned that such an interaction, however weak, is still existing and could be estimated comparing the absorption spectra of **2** and **11** as well as of **4** and **12**. In the first case the long wavelength maximum of **2** is at about 15 nm bathochromically shifted and more intense relative to that of **11**. In the second one the existence of a phenyl group instead of a hydroxyl one causes a more significant bathochromic effect about 35 nm.

Experimental

N-acylated imines (N-benzoylbenzylideneimine [24], N-benzoyldiphenyl-ketimines [25], their 4-OCH$_3$ derivatives [26]) and the corresponding 2-enones, uses as model compounds, were synthesized according to the methods described in the literature. The absorption spectra were recorded on "Specord UV-VIS" and "Lambda 17 Perkin-Elmer" spectrophotometers. The solvents used were of spectral grade. The resolution of the overlapped absorption bands was achieved with an original computer program "CROAB-89" for an IBM-PC/XT/AT computer [10] and is available on request.

References

[1] Zaugg H. E. (1984) Synthesis: 85
[2] Zaugg H. E. (1984) Synthesis: 181
[3] Allmann R., Kupfer R., Nagel M., Wurthwein E.-U. (1984) Chem. Ber. **117**: 1597
[4] Kupfer R., Nagel M., Wurthwein E.-U., Allmann R. (1985) Chem. Ber. **118**: 3089
[5] Dobrev A., Ivanov C., Stanoeva E. (1971) Lieb. Ann. Chem. **752**: 14
[6] Dobrev A., Ivanov C. (1976) Chem. Ber. **104**: 981
[7] Sandorfi C. (1970) The Chemistry of the Carbon–Nitrogen Double Bond. Wiley, New York, p. 8
[8] Traetteberg M., Hilmo I., Abraham R. J., Ljunggren S. (1978) J. Mol. Struct. **48**: 395
[9] Bernstein J. (1972) J. Chem. Soc. Perkin Trans. II **2**: 946
[10] Antonov L., Stoyanov S. (1993) Appl. Spectrosc. **47**: 1030
[11] Suzuki H. (1967) Electronic Absorption Spectra and Geometry of Organic Molecules. Academic Press, New York, p. 261, p. 306
[12] Braude E. A., Sondheimer F. (1955) J. Chem. Soc.: 3754
[13] Beale R. N., Roe E. M. F. (1953) J. Chem. Soc.: 2755
[14] Brocklehurst P. (1962) Tetrahedr. **18**: 299
[15] Haselbach E., Heilbronner E. (1968) Helv. Chim. Acta **51**: 16
[16] Burgi H. B., Dunitz J. D. (1969) Chem. Comm.: 472
[17] Minkin V. I., Zhdanov Yu. A., Medyantzeva E. A., Ostroumov Yu. A. (1967) Tetrahedr. **23**: 3651

[18] Krasovitskii B. M., Bolotin B. M., Nurmukhametov R. N. (1964) Zh. Obsch. Khim. **34**: 3786

[19] Csaszar J. (1986) Acta Phys. et Chem. Szeged **32**: 17

[20] Akava R., Tokumaru K., Kobayashi T. (1980) Bull. Chem. Soc. Japan **53**: 1993

[21] Skrabal P., Steiger J., Zollinger H. (1975) Helv. Chim. Acta **58**: 800

[22] Sukhorukov A. A., Lavrushina O. V., Grif V. H., Dzyuba V. P., Pedchenko N. F., Zadorozhny B. A., Lavrushin B. F. (1978) Zh. Obsch. Khim. **48**: 377

[23] Jaffe H. H., Orchin M. (1960) J. Chem. Soc.: 1078

[24] Kupfer R., Meier S., Wurthwein E.-U. (1984) Synthesis: 688

[25] Banfield J. E., Brown G. M., Davey F. H., Davies W., Ramsey T. N. (1948) Austr. J. Sci. Res. AI: 329

[26] Ivanov C. (1956) Dokl. AN SSSR **109**: 537