

Structural and chiroptical properties of rigid system with planar α,β -unsaturated imine group

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The structure of polycyclic compound with a new type of heteroannularly incorporated conjugated imine chromophore has been determined. Measurements of circular dichroism are presented. Disappearance of characteristic couplet of dichroic bands with opposite sign in the region of $\pi \rightarrow \pi^*$ electron transition after protonation is also studied. The origin of optical activity of the $n \rightarrow \pi^*$ transition is approached on the basis of qualitatively derived transition moments $\bar{\mu}$ and \bar{m} .

Была определена структура полициклического соединения с новым типом гетероанулярно включенного сопряженного иминового хромофора. Показаны измерения кругового дихроизма. Исследовано исчезновение характерного каплета дихроических полос противоположного знака в области $\pi \rightarrow \pi^*$ электронного перехода при протонизации. Появление оптической активности $n \rightarrow \pi^*$ перехода показано на основе качественно дедуцированных переходовых моментов $\bar{\mu}$ и \bar{m} .

The reaction of levoglucosenone (*I*) with ammonium carbonate in ethanolic solution did not give expected replacement of the oxygen atom in the pyranose ring by nitrogen atom as it was in the case of some pyrones [1—3]. However, pentacyclic compound containing α,β -unsaturated imine group resulted. On the basis of elemental analysis and spectral data (¹H, ¹³C NMR, mass spectrometry, IR, and UV spectra), this compound was identified as 7,14,15,17-tetraoxa-10-aza-pentacyclo[10.2.1.1.^{2,11}1.^{5,8}0^{3,9}]heptadeca-3,9-dien-2-ol (*II*), with spatial structure shown in Fig. 1 (because of simplification at tabulation of spectral data, the 1,6-anhydro-glucopyranose substructure with carbon—carbon double bond has been numbered with comma). The proposed structure was proved by X-ray structural analysis.

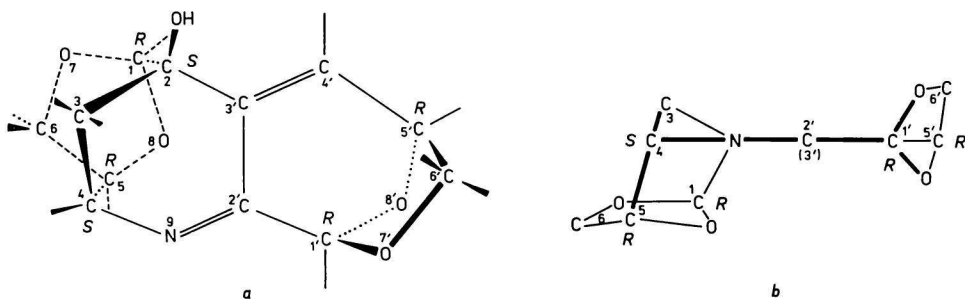


Fig. 1. Spatial structure of the molecule shown in two mutually perpendicular views (*a*, *b*) with depicted absolute configuration (*R/S*) of carbon atoms adjacent to the chromophore.

The compound mentioned above belongs to the rare types of chiral polycyclic compounds containing heteroannularly built in system of conjugated double bonds. Planar α,β -unsaturated imine chromophore is surrounded by the chiral cyclic systems from both sides. It is seen (Fig. 1) that both six-membered rings containing double bonds are in unusual conformation looking like an envelope conformation, known among five-membered rings. This conformation exhibits planar arrangement of five atoms which are linked to the double bonds or which are part of them. Among monocyclic pyranoses, this arrangement is considered to be transitional state (C_s) during change of the chair conformation to the bath conformation [4]. Chiroptical demonstration for compounds of this type was not described so far.

It is known that azometines exhibit $n \rightarrow \pi^*$ electron transition at $\lambda = 250$ nm [5]. The second band, occurring in the region below $\lambda = 200$ nm is attributed to the $\pi \rightarrow \pi^*$ electron transition [6]. The connection into conjugation causes shifting of both bands toward higher wavelengths. Optical activity of inherently chiral structures with nonplanar α,β -unsaturated imine chromophore was theoretically studied by the use of model structure [7]. Cyclic compounds having $C=N$ chromophore were found to show stereochemical correlation between the helicity of ring and the sign of the long wavelength dichroic band [8]. An opinion was expressed that similar correlation with conformation of rings ought to be of use also at heteroannularly incorporated dienes in polycyclic system [9].

Experimental

Infrared spectra (in KBr pellets; 2.0–3.0 mg of compound per 400 mg KBr) were measured on a Perkin—Elmer 457 instrument. Mass spectra ($U = 70$ eV) were obtained on a JMS-100 D mass spectrometer at an emission of 300 μ A, applying direct sample-introduction technique. ^{13}C NMR (100 MHz) and ^1H NMR (80 MHz) spectra were mea-

sured on a Jeol JNM-FX-100 instrument using DMSO- d_6 as a solvent and TMS as an internal standard. Spectra of circular dichroism were taken on a Dichrograph Mark III (Jobin Yvon, France) instrument. Measurements were performed in 0.1–1.0 cm cells using solutions with $\rho = 0.2$ – 1.0 mg cm^{-3} in 2,2,2-trifluoroethanol, mixture V(ethanol) : V(methanol) = 4 : 1, acetonitrile, and in acetonitrile with HCl. Low-temperature measurements were carried out down to -160°C for solutions in a mixture V(ethanol) : V(methanol) = 4 : 1 using 1 cm cells. Absorption spectra were measured at the same conditions on a Beckman DB-GT instrument. X-Ray structural analysis of monocrystal of compound was performed with a Syntex P2, diffractometer. Basic crystallographic parameters were found out [10]. The structure has been solved on the basis of 800 measured reflections utilizing computing procedures MULTAN [11] and MAGIC [12]. Refinement of the structure [13] by the least-squares method was achieved on $R = 0.041$.

Pentacyclic conjugated imine (II)

To a solution of levoglucosenone (1.26 g; 0.01 mol) in 95 % ethanol (20 cm^3), ammonium carbonate (2.5 g) was added in several portions under reflux. The mixture was refluxed for 4 h. After cooling, the solvent was evaporated *in vacuo* and the obtained compound was recrystallized from ethanol, yielding 1.05 g (83 %) of product having m.p. = 301 – 302°C , $[\alpha]_D^{25} = -139.4^\circ$, $\rho = 10 \text{ g dm}^{-3}$, acetonitrile).

For $\text{C}_{12}\text{H}_{13}\text{NO}_5$ ($M_r = 251.12$) $w_i(\text{calc.})$: 57.39 % C, 5.17 % H, 5.57 % N; $w_i(\text{found})$: 57.50 % C, 5.25 % H, 5.71 % N.

Results and discussion

The structure of the studied compound was determined on the basis of following spectral data.

The IR spectra showed strong absorption bands at $\bar{\nu} = 1640 \text{ cm}^{-1}$ and 1615 cm^{-1} , belonging to the vibration of α,β -unsaturated ketimine group and further bands at $\bar{\nu}/\text{cm}^{-1}$: 3105 ($\nu(\text{OH})$), 1362 ($\delta(\text{OH})$), 1175 ($\nu(\text{C—OH})$), 1110, 1088 ($\nu(\text{C—O—C})$), and 970 ($\delta(\text{C—H})$ in C=C—H). In the mass spectrum, the main peaks were observed at $m/z = 251$ (M^+ , $I_r = 76\%$) and $m/z = 221$ ($M^+ - \text{CH}_2\text{O}$, $I_r = 100\%$). Further fragmentation cannot be unambiguously interpreted, as some fragments can originate by several alternative ways. The data of ^{13}C NMR and ^1H NMR spectra are presented in Tables 1 and 2.

Interpretation of the ^1H NMR and ^{13}C NMR spectra was based on the fact that the studied compound was produced from two 1,6-anhydro-glucopyranose substructures coming from levoglucosenone (I), where one of them possesses double bond between C-3' and C-4' atoms and C-2' atom is a part of C=N bond (Fig. 1). Then, this substructure can be interpreted as levoglucosenone substituted in the position 3', having C=N bond instead of C=O bond. The second 1,6-anhy-

Table 1

¹³C NMR (100 MHz, DMSO-d₆, internal standard Me₄Si) data of the studied compound

Atom	C-1	C-2	C-3	C-4	C-5	C-6
δ/ppm	101.099	70.691	32.356	56.787	71.471	67.702
Atom	C-1'	C-2'	C-3'	C-4'	C-5'	C-6'
δ/ppm	104.998	162.954	135.795	129.558	73.550	68.482

Table 2

¹H NMR (80 MHz, DMSO-d₆, internal standard Me₄Si) data of the studied compound

Atom	H-1	H-3	H-4	H-5	H _{exo} -6 + 6'
δ/ppm	5.56 s	1.27 d	1.98 dd	4.75 d	3.91 m
Atom	H-1'	O—H	H-4'	H-5'	H _{endo} -6 + 6'
δ/ppm	5.74 s	4.39 s	6.63 d	5.05 t	3.76 m

s — singlet, d — doublet, dd — doublet of doublet, t — triplet, m — multiplet.

dro-glucopyranose substructure with chair conformation of pyranose ring represents actually levoglucosenone possessing reduced double bonds, substituted in the position 2 and 4. The signals were assigned by the comparison of spectral data published for levoglucosenone and reduced levoglucosenone [14—23] taking into account specific substitution in the positions 2, 3', and 4. The supposed structure was supported by this correlation. Likewise, spectral data published recently for dimer of levoglucosenone [24], which contains basic skeletons of the above-mentioned substructures in its structure, are in good agreement with the data found out for our compound.

The results of diffraction analysis [10] approved conclusions derived from interpretation of spectral data and chemical and analytical methods. The solved crystallographic structure of compound is in full accord with the proposed stereospecific structure shown in Fig. 1 with coplanar arrangement of heteroannularly incorporated double bonds.

The parameters of absorption spectra and spectra of circular dichroism for the studied compound were obtained in the protic and aprotic solvents — in acetonitrile and 2,2,2-trifluoroethanol (Figs. 2 and 3). In the absorption spectrum, two bands were observed (Fig. 2). The first band with low intensity belongs to the

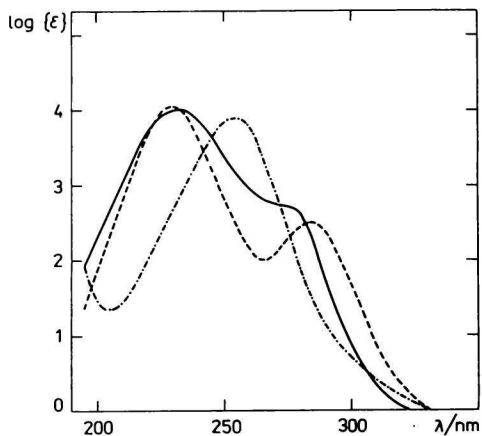


Fig. 2. Absorption spectra of compound in a solution of 2,2,2-trifluoroethanol —, acetonitrile ----, and in acetonitrile with a trace of HCl -.-.-.

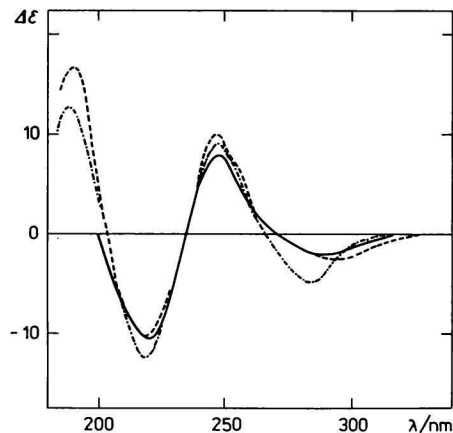


Fig. 3. The CD spectra of compound in a solution of 2,2,2-trifluoroethanol —, acetonitrile ----, and in a mixture of V(ethanol) : V(methanol) = 4 : 1 -.-.-.

$n \rightarrow \pi^*$ transition. The second band at $\lambda = 232$ nm is attributed to the $\pi \rightarrow \pi^*$ transition of conjugated system. The position of this absorption band is similar to *trans* dienes [14].

The first long wavelength dichroic band in the spectrum of circular dichroism is situated in the region of the first absorption UV band (Fig. 3). This band can be then attributed unambiguously to the $n \rightarrow \pi^*$ transition. Hypsochromic shift of maximum in both the UV and CD spectra occurs in protic solvent (trifluoroethanol). Following dichroic bands with opposite sign, the positive with maximum at $\lambda = 246$ nm and the negative at $\lambda = 219$ nm, represent couplet belonging to the absorption region of the $\pi \rightarrow \pi^*$ transition. On the long wavelength part of the positive band, there is a shoulder at about $\lambda = 255$ nm, which is the most expressive in acetonitrile. The change of solvent causes only small change with regard to the shape and position of the positive band; the negative band remains unchanged. The measurements at low temperatures down to -160 °C in the mixture V(ethanol) : V(methanol) = 4 : 1 likewise did not show substantial change of dichroic bands. The next registered dichroic band is situated in the region of $\lambda = 190$ nm. This positive Cotton effect is the most intensive in the spectrum. In the absorption spectrum, corresponding absorption band was not registered. It can be supposed that the observed dichroic band is part of another couplet which belongs to the electron transition delocalized on σ bonds and situated in the vacuum ultraviolet region of absorption spectrum.

The shape of the absorption and CD spectra with considerably high values of intensities demonstrates that conjugated chromophoric system is planar and considerably rigid. The origin of the bisignate CD curve in the region of the $\pi \rightarrow \pi^*$ absorption can be due to the presence of a near complete mixing of the electric-dipole $\pi_x \rightarrow \pi_x^*$ and the magnetic-dipole $\pi_x \rightarrow \pi_y^*$ excitations, likewise, as it can be observed in dienes [15] or owing to splitting which is due to the induction of optical activity of electron transition from both sides of the plane of chromophore.

Expressive change of absorption after an addition of a trace of acid is characteristic feature of an azometine group. With steroidal imines, a reversible disappearance of absorption in the region of the $n \rightarrow \pi^*$ transition is observed [5]. The effect due to addition of 0.01 M-HCl to a solution of the studied compound in methanol was followed potentiometrically (the difference between potentials of Sb electrode and saturated calomel electrode) and also in the absorption and CD spectra. The obtained data are presented in Figs. 4 and 5.

In the UV spectra, an increase of absorption of the $n \rightarrow \pi^*$ electron transition and a shift to the higher energies is observed. At fully protonated form, the intensity of the $n \rightarrow \pi^*$ transition increases to such an extent that this merges with

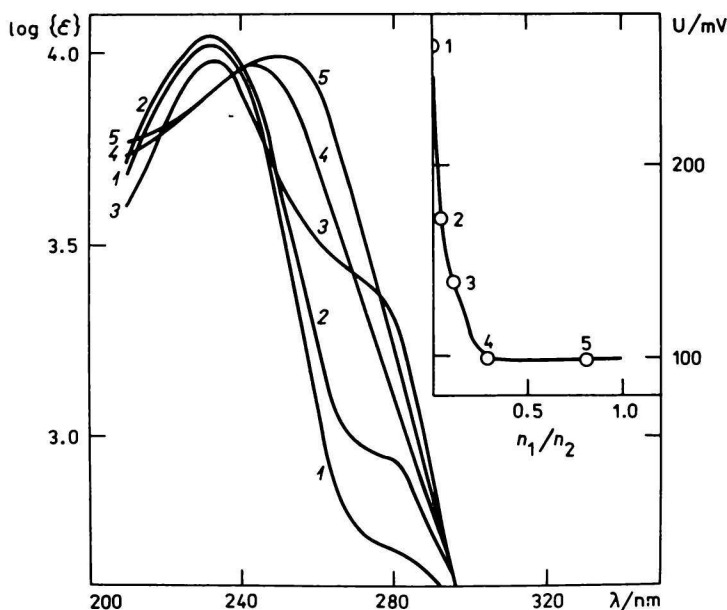
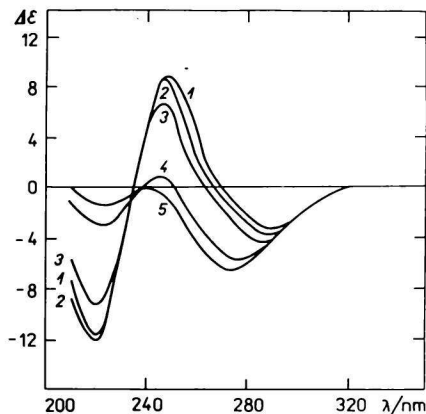


Fig. 4. Absorption spectra of compound in methanol after gradual addition of 0.01 mol dm⁻³ HCl (curves 1–5). Corresponding potentiometric curve is shown in the right corner. The ratio of $n(\text{HCl}) : n(\text{studied compound})$ in the solution is depicted on the coordinate axis (n_1/n_2).

Fig. 5. The CD spectra of compound in methanol after gradual addition of 0.01 mol dm^{-3} HCl. The numbering of curves corresponds to the ratio n_1/n_2 as in Fig. 4.



formerly the most intensive band of the $\pi \rightarrow \pi^*$ transition. Unusually high intensity of the $n \rightarrow \pi^*$ transition is given by the change of character of wave functions which cancels the so-called symmetrical forbiddance of transition. Dichroic band corresponding to the $n \rightarrow \pi^*$ electron transition is increased and shifted to the lower wavelengths. At fully protonated form, the couplet corresponding to the $\pi \rightarrow \pi^*$ transition disappears. On addition of ammonia, former spectra are obtained. This reversibility confirms that no other processes take part here (cleavage of bonds, etc.) but only protonation of the lone electron pair on the nitrogen atom occurs. During this protonation, mesomeric effect disappears and total polarization of conjugated system is changed. The change in the total electron distribution of chromophore is sensitively reflected by the change of CD spectra also in the region of the $\pi \rightarrow \pi^*$ transition.

Interpretation of the demonstration of optical activity is complicated. It is impossible to carry out a simple correlation of structures as no chiroptical parameters of simpler compounds containing α, β -unsaturated imine chromophore are known. It can be assumed that nodal properties of the highest occupied orbitals will be similar to those of α, β -unsaturated carbonyl chromophore. Optical activity of the long wavelength electron transitions ought to be followed by the sector rule consisting of four nodal planes. However, such application is not effective for the studied compound as in this case it is necessary to take into account an extent of mutual compensation of larger number of contributions.

Optical activity of the studied planar alkylideneimine chromophore is indisputably induced by a complex effect of chirality on four asymmetric carbon atoms C-2(S), C-4(S), C-1'(R), C-5'(R), directly linked to the chromophoric system. According to the second order perturbation theory, molecular orbitals of chirally oriented σ bonds can mix with n respectively π orbitals of the chromophore. This mixing is significant at the energetically nearest situated orbitals. For illustration, resulting n

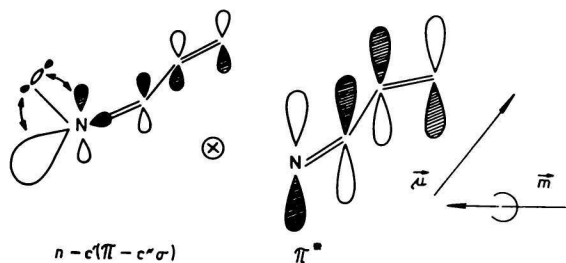


Fig. 6. Molecular orbitals participating in the $n \rightarrow \pi^*$ electron transition and transition moments $\bar{\mu}$ and \bar{m} obtained by their formal multiplication.

orbital with admixed π orbital and one of the nearest σ orbitals (C-3—C-4 bond) is depicted in Fig. 6 on the left. The way of their unfavourable interactions is also drawn. According to *Snatzke's* qualitative MO theory [25], it is possible to determine the orientation of electric ($\bar{\mu}$) and magnetic (\bar{m}) transition moments by the multiplication of orbitals participating in electron transition. The obtained orientation depicted in Fig. 6 results, in accordance with general expression of optical rotational strength $R = (\bar{\mu}) \cdot (\bar{m}) \cdot \cos(\bar{\mu}, \bar{m})$, in the negative sign for $n \rightarrow \pi^*$ electron transition of the above-mentioned system. In addition to the mentioned, probably the most expressive influence of σ bond on the C-4 atom, the other bonds on asymmetric carbon atoms in the proximity of chromophore can also contribute to the optical activity.

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