Theoretical calculation of optical activity of the nonplanar α,β-unsaturated imines

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The nonplanar structures of hypothetical molecule of propenylidenimine simulating rigid geometry of the inherently chiral α,β-unsaturated imine chromophore in heterocyclic compounds have been studied. The rotational strength of the $n\rightarrow\pi^*$ and $\pi\rightarrow\pi^*$ electron transitions has been directly calculated by using the CNDO/S scheme.

Были изучены непланарные структуры гипотетической молекулы пропенилиденимина, которые являются моделью жесткой геометрии ингерентно хирального α,β-ненасыщенного иминового хромофора в гетероциклических соединениях. Был выполнен прямой расчет вращательной силы электронных переходов $n\rightarrow\pi^*$ и $\pi\rightarrow\pi^*$ с использованием схемы CNDO/S.

The quantum chemical calculations of chiroptical properties of molecules are of great use for verification of their spatial structures as well as prediction of the CD spectral characteristics. Satisfactory results are obtained mainly with substances the optical activity of which is due to chiral spatial arrangement of the chromophore group itself (inherently chiral chromophore). The π-electron system of the conjugated α,β-unsaturated imine chromophore is similar to the butadiene arrangement which was thoroughly investigated. The rule of helicity [1, 2] which suggests that an arrangement with a positive angle of torsion about the C-2—C-3 bond should exhibit positive circular dichroism of the long wavelength $\pi\rightarrow\pi^*$ electron transition was theoretically derived for the nonplanar diene system. The optical activity of chiral dienes and enones was studied by the use of quantum chemical calculations [3, 4]. The authors found different signs for the $n\rightarrow\pi^*$ transition in *cis* and *trans* enones and attributed this fact to a change in pseudosymmetrical properties of the molecular orbitals (in contrast to dienes) [3]. The signs of the Cotton effects of these systems were analyzed from the view-point of the qualitative MO theory, too [5, 6]. The conjugated α,β-unsaturated imines built in rigid systems may be also twisted from coplanarity owing to steric stress and nonbonding interactions [7].

The absorption band of alkyl azomethines with the longest wavelength was experimentally found at 250 nm. It corresponds to the $n \rightarrow \pi^*$ electron transition. For optically active cyclic compounds, the sign of its Cotton effect is to be derived from the helicity of the ring [8]. For substances with the conjugated benzylidenimine arrangement, the CD spectra can be interpreted by means of the salicylidenimine rule [9]. Systems of this type were subjected to theoretical calculations [10].

The parameters of optical activity of the nonplanar α,β-unsaturated imine arrangement functioning as an inherently chiral chromophore, have not been quantum chemically studied yet.

Model and method

We used the molecule of propenylidenimine as the simplest model. The both possible geometrical isomers containing the bond of hydrogen to nitrogen were studied. It was *Z* isomer the hydrogen and C-2—C-3 bond of which were positioned on equal side of the reference plane of the N = C double bond and *E* isomer the hydrogen and C-2—C-3 bond of which were positioned on opposite sides [11]. The geometrical arrangement and the bond lengths are given in Fig. 1. All valence angles have the value of 120°. We investigated the change in the calculated parameters of circular dichroism for the rotation of a molecule around the central C-2—C-3 bond in the region $\Phi = 0$—$180°$. A positive angle of torsion Φ represents position of the NH group under the plane of drawing in Fig. 1 while a negative angle of torsion corresponds to position of the NH group over this plane.

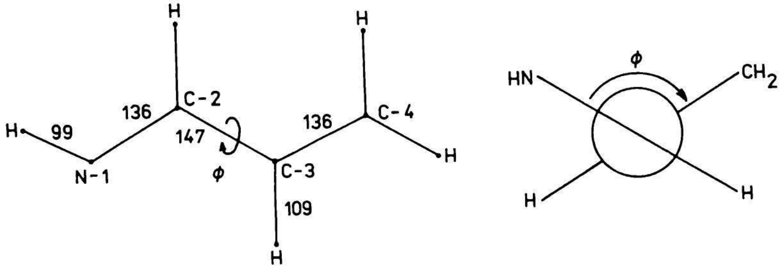

Fig. 1. Molecule of *E* isomer of propenylidenimine in the *trans* conformation ($\Phi = 180°$) with the values of bond lengths (pm). The dextrorotatory sense of rotation ($\Phi > 0°$) is designated in projection.

The rotational strengths were calculated directly in the dipole-velocity formalism on the basis of the CNDO/S wave functions by the use of parametrization according to *Ellis et al.* [12]. The LCI part of calculation involves 36 simply excited configurations including the six highest occupied molecular orbitals and the six lowest nonoccupied molecular orbitals. The program used was described earlier [13]. The calculations were carried out with a computer CDC 3300.

Results and discussion

The course of the values of rotational strength of the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions is depicted in Figs. 2 and 3. The formalism and CNDO/S parameters were optimized for calculating the planar conjugated systems. It is therefore probable that the calculated wave functions of a strained molecule of propenylidenimine better describe the real situation for arrangements near to the planar *cis* or *trans* conformations than for rather nonplanar conformations with an

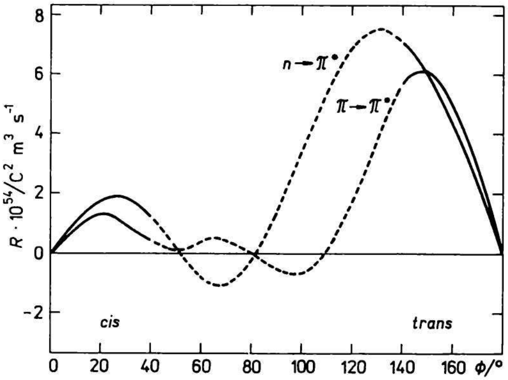

Fig. 2. Dependence of the rotational strength of *E* isomer of propenylidenimine on the angle of torsion Φ.

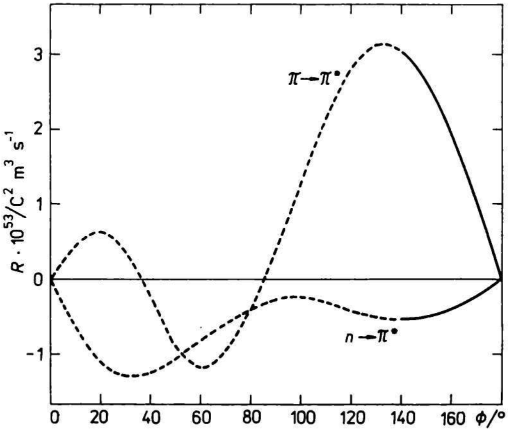

Fig. 3. Dependence of the rotational strength of *Z* isomer of propenylidenimine on the angle of torsion Φ.

angle of torsion near to 90°. If Z isomer of our model is in *cis* conformation, a repulsion between the hydrogen atoms bonded to nitrogen and C-4 carbon is in operation because they get nearer and their distance is smaller than the admissible van der Waals contact distance [14]. The regions encompassed by the full line in Figs. 2 and 3 may really appear in case of heterocyclic compounds (admissible deviation from planarity).

The molecule of propenylidenimine in planar conformation is not active optically because it contains a plane of symmetry. By turning from coplanarity, it loses the symmetry and becomes chiral. If the torsion grows, a hypsochromic shift in the bands corresponding to the energetically lowest $n \rightarrow \pi^*$ transition as well as the $\pi \rightarrow \pi^*$ transition appears (Fig. 4). For the investigated model as well as acrylic aldehyde or butadiene [3], the nodal plane of the π-orbital goes through the C-2—C-3 bond. A decrease in delocalization of the π-electrons due to torsion brings about a decrease in energy of the highest occupied π-orbital that is an asymmetric combination of two π-orbitals (ethylene, azomethine). The lowest anti-bonding orbital π^* which is a symmetric combination of two anti-bonding orbitals displays an increase in energy. In general, that manifests itself by an energy increase of the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ electron transitions. The calculated strengths of oscillators have by decimal order lower values for the $n \rightarrow \pi^*$ transitions ($\sim 10^{-2}$) than for the $\pi \rightarrow \pi^*$ transitions ($\sim 10^{-1}$).

The signs of the rotational strengths in the region of *cis* and *trans* conformers of both isomers (E and Z) are equal for the $\pi \rightarrow \pi^*$ transition. The positive sign calculated for structures with a positive angle is in agreement with the rule of

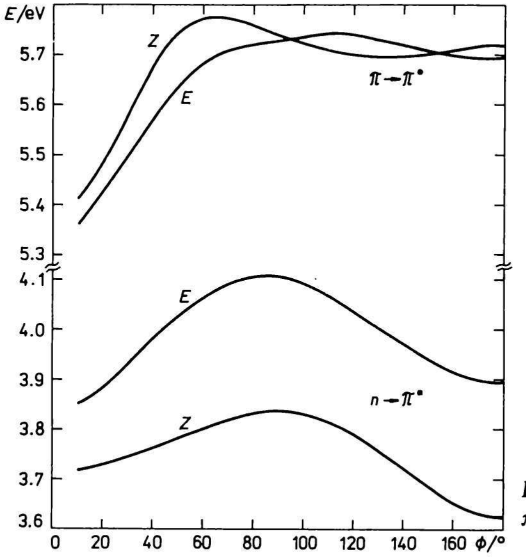

Fig. 4. Dependence of energy of the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ electron transitions on the angle of torsion Φ.

helicity valid for nonplanar dienes or enones (excitation is effectuated by the dextrorotatory helical pathway).

The ground state molecular orbital taking major part in the electron transition with the longest wavelength has nonbonding character and is localized on the nitrogen atom in the plane of the —C=N—H group. The calculation shows that these optically active $n \rightarrow \pi^*$ electron transitions in both isomers have different signs. The sign is negative for Z isomer and positive for E isomer. By the reason of symmetry, the $n \rightarrow \pi^*$ transition is electrically forbidden. Its nonzero values are obtained by vibronic interaction with energetically higher transitions, in our case mainly because of asymmetric arrangement of adjacent atoms and bonds.

An analysis of the sign of the $n \rightarrow \pi^*$ transition may be performed by the use of the qualitative MO theory [5, 6]. The transition moments $\boldsymbol{\mu}$ and $\boldsymbol{m}$ are to be obtained by formal multiplication of the participating orbitals. According to calculation, the nonbonding orbital stands lower in the order of energies than the highest occupied π orbital. The torsion produces their interaction. The nonbonding orbital (n) is stabilized by symmetrical combination with the π orbital. The $n \rightarrow \pi^*$ electron transition shifts to higher energies. The nonbonding orbital with admixed π orbital ($n + c_1\pi$) and outlined favourable interaction as well as the anti-bonding orbital π^* is represented in Fig. 5. The application of formal multiplication of orbitals [5, 6] with regard to this interaction results in parallel orientation of the transition moments $\boldsymbol{\mu}$ and $\boldsymbol{m}$ (Fig. 5) irrespective of selection of the phases of orbitals. The represented structure of E isomer with a positive angle of torsion is characterized by positive circular dichroism of the $n \rightarrow \pi^*$ transition. As for Z isomer, the positions of lone electron pair and hydrogen bond are interchanged while the above-mentioned favourable interaction requires preservation of the phase of orbital ("hatch"). This change brings about the inverse sense of charge rotation, *i.e.* the opposite orientation of the magnetic transition moment. In this

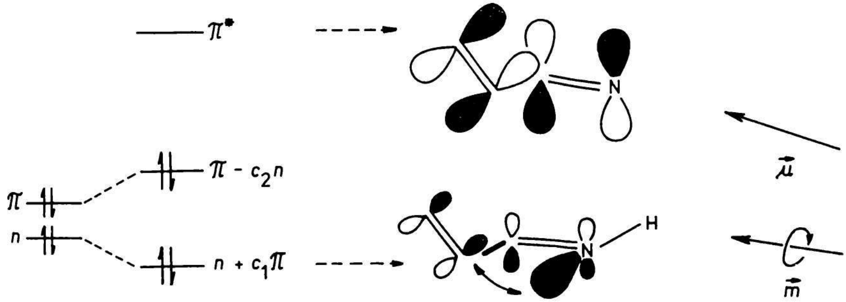

Fig. 5. Molecular orbitals participating in the $n \rightarrow \pi^*$ electron transition and orientations of the $\boldsymbol{\mu}$ and $\boldsymbol{m}$ transition moments for E isomer with a positive angle of torsion Φ.

way, the change in the sign of the Cotton effect may be explained for the $n \rightarrow \pi^*$ transition in geometrical isomers *E* and *Z*.

These results of calculation of rotational strengths of the model structures of propenylidenimine gave these pieces of knowledge:

1. The signs of optical activity of both long wavelengths transitions are equal for the *cis* and *trans* conformation.

2. The sign of the Cotton effect corresponding to the $\pi \rightarrow \pi^*$ electron transition enables us to distinguish the nonplanar structures with a positive angle of torsion from those with a negative one.

3. The identical or opposite sings of both transitions in isomers *E* and *Z* on the $N=C$ bond indicate the orientation of lone electron pair or the orientation of simple bond on the nitrogen atom.

The lack of experimental data does not allow to correlate calculations with experiments yet. As for real molecules, the effect of vicinal substituents will manifest itself in a different degree.

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