CALCULATING THE INTENSITIES OF ABSORPTION BANDS OF THE IR SPECTRUM FOR BENZYLIDENE METHYLAMINE AND ITS DEUTEROANALOGS


Key words: benzylidene methylamine, vibrational spectra, intensity, calculation.

Normal vibrations for one of the most elementary Schiff bases (of the type \( R-CH=N-\)R) of benzylidene methylamine (I) and two of its deuteroanalogs — \( H_3-N=CD-C_6H_5 \) (II) and \( CD_3-N=CH-C_6H_5 \) (III) — are calculated in a harmonic approximation in [1, 2]. The obtained force field describes fairly well the experimental frequencies of the IR spectra of these compounds; however, to reliably interpret vibrational spectra, a calculation of band intensities that is brought to the construction of curves for the spectral distribution of the absorption coefficient is needed.

In the present work we calculated the intensities of absorption bands for E and Z isomers of molecules I–III and obtained spectral curves for these compounds. The calculation was performed on an IBM PC according to the complex of programs [3]. The IR spectra were recorded on a PE-180 FIR spectrophotometer. The accuracy of determining the frequencies was \( \pm 1 \text{ cm}^{-1} \). We obtained the absolute intensities for a series of bands of these compounds from the IR spectra of the solutions of these compounds in cyclohexane as in [4].

Figure 1 gives the scheme of molecule I and the notation of the natural coordinates. In a zero approximation, we calculated the band intensities using electrooptical parameters (EOP) of benzene and toluene [5]. However, the subsequent calculation showed that dipole moments of C–C bonds and their derivatives with respect to vibrational coordinates are different from zero. EOP were refined in the successive solution of direct and inverse electrooptical problems for the E and Z isomers.

The set of EOP reflects the electron density distribution in a molecule. Our quantum-chemical calculation [1, 2] showed that the charges on atoms of the E and Z isomer of molecule I are different [2]. Therefore, in a further calculation of the absorption band intensities we used different EOP sets for two structures. The found values of the dipole moments of bonds (D) and derivatives of the dipole moments with respect to vibrational coordinates (D/\( q \)) for the E isomer are given below:

\[
\begin{aligned}
\mu_1 &= 0.239; \\
\mu_2 &= 0.288; \\
\mu_3 &= -0.243; \\
\mu_7 &= 0.113; \\
\mu_8 &= 0.416; \\
\mu_9 &= 0.338; \\
\mu_{10} &= 0.588; \\
\mu_{13} &= 0.087; \\
\mu_{14} &= -1.582; \\
\mu_{15} &= -1.025; \\
\mu_{16} &= 0.244; \\
\mu_{17} &= -0.884; \\
\mu_{10}/\delta q_{10} &= 0.284; \\
\mu_{13}/\delta q_{13} &= 0.350; \\
\mu_{14}/\delta q_{14} &= -1.403; \\
\mu_{16}/\delta q_{16} &= 0.480; \\
\mu_{17}/\delta q_{17} &= 0.570; \\
\mu_{11}/\delta q_{11} &= 0.056; \\
\mu_{7}/\delta q_{7} &= 0.180; \\
\mu_{9}/\delta q_{9} &= 0.182; \\
\delta q_{15} &= 0.621; \\
\delta q_{13} &= 0.373; \\
\delta q_{10} &= 1.065; \\
\delta q_{14} &= 0.875; \\
\delta q_{13}/\delta q_{10} &= 0.209; \\
\delta q_{14}/\delta q_{13} &= -0.497; \\
\delta q_{15}/\delta q_{14} &= 0.515; \\
\delta q_{10}/\delta q_{15} &= -0.561; \\
\delta q_{3}/\delta q_{2} &= -1.103; \\
\delta q_{10}/\delta q_{3} &= 0.163; \\
\delta q_{16}/\delta q_{17} &= 0.200; \\
\delta q_{10}/\delta q_{3,4} &= -1.366; \\
\delta q_{10}/\delta q_{3,9} &= 0.358; \\
\delta q_{10}/\delta q_{10,13} &= 0.115; \\
\delta q_{10}/\delta q_{10,14} &= 1.431; \\
\delta q_{10}/\delta q_{13,14} &= -0.272; \\
\delta q_{15}/\delta q_{13,14} &= -0.306; \\
\delta q_{15}/\delta q_{13,14} &= 0.376; \\
\delta q_{15}/\delta q_{13,14} &= -0.469; \\
\delta q_{15}/\delta q_{15,16} &= 0.100; \\
\delta q_{13}/\delta q_{10,13} &= -0.026; \\
\delta q_{13}/\delta q_{10,14} &= 0.282; \\
\delta q_{13}/\delta q_{13,14} &= 0.755; \\
\delta q_{14}/\delta q_{10,13} &= -0.554; \\
\delta q_{14}/\delta q_{10,14} &= 0.389; \\
\delta q_{14}/\delta q_{13,14} &= -0.012; \\
\delta q_{14}/\delta q_{14,15} &= -0.524; \\
\delta q_{11}/\delta q_{6,7} &= -0.048; \\
\delta q_{11}/\delta q_{18} &= 0.079; \\
\delta q_{16}/\delta q_{15,16} &= -0.564;
\end{aligned}
\]

*To whom correspondence should be addressed.

\[ \frac{\partial \mu_{16}}{\partial \beta_{15,17}} = -0.198; \quad \frac{\partial \mu_{16}}{\partial \alpha_{16,17}} = -0.280; \quad \frac{\partial \mu_{16}}{\partial \alpha_{17,18}} = -0.330; \quad \frac{\partial \mu_{17}}{\partial \beta_{15,16}} = -0.567; \quad \frac{\partial \mu_{17}}{\partial \alpha_{16,17}} = -0.383. \]

EOP for the Z isomer of I differ from the groups CH\textsubscript{3} and -CH=N= \textsuperscript{15}N: \[ \mu_{10} = 0.477; \mu_{13} = 0.030; \mu_{14} = -1.910; \mu_{15} = -0.684; \mu_{16} = 0.282; \mu_{16}/\partial \mu_{15} = -0.920; \mu_{15}/\partial \mu_{10,14} = -0.799; \mu_{15}/\partial \gamma_{14,15} = -0.700; \mu_{16}/\partial \beta_{15,16} = 0.124; \mu_{15}/\partial \beta_{10,13} = -0.010; \mu_{13}/\partial \gamma_{10,14} = 0.336; \mu_{14}/\partial \gamma_{10,14} = 0.617; \mu_{14}/\partial \beta_{13,14} = 0.092; \mu_{14}/\partial \gamma_{14,15} = -0.467; \mu_{16}/\partial \beta_{15,16} = -0.400; \mu_{16}/\partial \beta_{15,17} = -0.534; \mu_{16}/\partial \alpha_{16,17} = -0.250; \mu_{16}/\partial \alpha_{17,18} = -0.420. \]

Table 1 gives the experimental and calculated intensities of a series of absorption bands for three compounds. Figure 2 shows the experimental and calculated IR spectra of molecules I-III. The overall spectral curves are constructed for the E and Z isomers in a ratio of 9:1. As the figure shows the calculated spectra agree fairly well with the experimental ones. However, we emphasize that we observe a doublet band in the experimental spectrum of I in the 1200-cm\textsuperscript{-1} region but, because of a small difference between the calculated frequencies that correspond to this doublet, one wide band results in this region in the theoretical spectrum.

For the E and Z isomers, the charges that are calculated from the found dipole moments of bonds differ for the CH\textsubscript{3} and azomethine groups. The charges on hydrogen atom of the CH\textsubscript{3} are equal to 0.045 and 0.052, and for the azomethine group they are equal to 0.016 and 0.006 for the E and Z isomers respectively.

The values of the total dipole moment of the E and Z isomers for I, calculated from the obtained values of the dipole moments of bonds, are equal respectively to 1.52 and 1.72 D, which is somewhat larger than the experimental value of 1.40 D \[ \textsuperscript{6} \] for I.

In the process of calculation the need emerged for correction of the force field of molecule I obtained in [1]. Some force constants were refined \[ \textsuperscript{2} \] according to the data on displacement of a series of bands in the 1650-1580-cm\textsuperscript{-1} region with \textsuperscript{15}N-substitution \[ \textsuperscript{7, 8} \]. Analysis of the vibration modes showed that the extraplane vibrations of CH\textsubscript{13} and the benzene ring (17a according to Wilson) mix. Calculation the intensities showed that for I and II the extraplane CH\textsubscript{13} vibrations have a larger intensity that the 17a benzene ring vibrations. It is natural to expect the same intensity relation for III. Therefore, we should assign the band at 970 cm\textsuperscript{-1} rather than that at 990 cm\textsuperscript{-1}, as was the case earlier \[ \textsuperscript{1} \], to the extraplane vibration of CH of the azomethine group. In the 1500-cm\textsuperscript{-1} region, where vibrations of the benzene ring 19a manifest themselves, we observed two bands in the experimental spectrum of I, a wide band for III, and one rather narrow band in the spectrum of II. We assigned a