The steric interactions in molecules of alkyl-substituted hydrazones of aldehydes and ketones were calculated. The calculation permitted elucidation of the most probable structures of the indicated molecules. The \( \pi \) electron spectrum was calculated for the structures obtained within the MO LCAO approximation. The results of the calculation permitted an interpretation of the UV spectrum of the molecules.

A large quantity of experimental data on the electronic absorption spectra of mono- and dialkyl hydrazones of saturated and unsaturated aldehydes and ketones was recently obtained [1, 2]. These molecules have the following structure:

\[
\begin{align*}
\text{R}_1' & \quad \text{N}_1 - \text{N}_2 = \text{C}_3 \\
\text{R}_2' & \quad \text{R}_3' & \quad \text{R}_4' & \quad \text{R}_5'
\end{align*}
\]

where \( \text{R}_1 \) is an alkyl radical or a hydrogen atom. The following experimental principles were established in the UV spectra of the compounds examined as a function of the \( \text{R}_1, \text{R}_2, \text{R}_3, \) and \( \text{R}_4 \) substituents: 1) if only one of the indicated substituents is a hydrogen atom (we will subsequently call such compounds A molecules), only one absorption band (\( \lambda = 230-240 \text{ my} \), intensity \( \epsilon \approx 3000-7000 \) for I A molecules; \( \lambda = 260-280 \text{ my} \), \( \epsilon \approx 10,000 \) for II A molecules) \( \pi \rightarrow \pi^* \) transition is observed; 2) if all the substituents are alkyl radicals (B molecules), the band corresponding to the \( \pi \rightarrow \pi^* \) transition is shifted to the short-wave region (\( \lambda \approx 210 \text{ my} \), \( \epsilon \approx 2000-3000 \) for I B molecules; \( \lambda \approx 220 \text{ my} \), \( \epsilon \approx 10,000 \) for II B molecules) and an additional band of the \( n \rightarrow \pi^* \) type appears (\( \lambda \approx 275 \text{ my} \), \( \epsilon \approx 500-700 \) for I B molecules and \( \lambda \approx 320 \text{ my} \), \( \epsilon \approx 2000 \) for II B molecules). In [1, 2], on the basis of analysis of the UV spectra of the compounds under discussion, it is concluded that there is a significant conjugation effect of the unshared electron pair of the \( \text{N}_1 \) atom with the \( \text{N} = \text{C} \) double bond or with the conjugated \( \text{N} = \text{C} = \text{C} \) system in type A molecules. This effect is not observed in type B molecules.

Since the electronic spectra characteristic for class A or B molecules are of the same type within the class limits and depend only slightly on the alkyl substituents (\( \text{R}_1 = \text{CH}_3, \text{C}_2\text{H}_5, \text{C} (\text{CH}_3)_2, \) etc.), one can imagine that the chief difference in the spectra of A and B compounds is associated with the different geometry of such molecules, which is determined to a significant degree by the relationship between the steric interaction of the substituents and the conjugation effect. The goal of the present paper is a quantitative evaluation of the steric effect and the delocalization energy in A and B molecules. The geometry of the molecules was not experimentally determined, and we therefore attempted to find the probable structure of such molecules by calculation. A further problem was the quantum-chemical calculation of the energy levels, frequencies, and intensities of the \( \pi \rightarrow \pi^* \) and \( n \rightarrow \pi^* \) transitions as well as the distribution of electron density in the molecules. This problem is solved in part in this paper within the framework of the Hückel and Pople method. We will present the results of the calculation of I A and I B molecules within the \( \pi \)-\( \sigma \) approximation in our next communication.
a) Calculation of the Steric Interactions

Let us first evaluate the quantitative steric interactions in A and B molecules. These interactions of atoms and groups which are not associated in a valence sense are similar in nature to intermolecular interactions, and they can therefore be estimated by means of the empirical intermolecular interaction potentials proposed in [3-6]. Since the bond lengths and the valence angles of these molecules are not accurately known we have used the standard value [7] and have considered two possible types of hybridization of the N₁ atom, viz., (a) sp² hybridization, and (b) sp³ hybridization.

The arrangement of atoms in a (CH₃)₂N₁-N₂-C(CH₃)R molecule, assuming sp² hybridization of the terminal nitrogen atom for a planar configuration, is shown in Fig. 1. The R substituent may be an alkyl radical (I molecules) or an extension of the conjugation chain (II molecules). The small circles designate the pₓ orbital of the N₁, N₂, and C₁ atoms which make up the conjugation chain. We have calculated the energy of the steric interactions as a function of the angle of rotation φ around the N₁-N₂ bond. In so doing, we assumed that rotation of the C-H bonds of the methyl groups around the N₁-C₁, N₁-C₂, and C₃-C₄ axes could occur, and we selected the optimum orientation of the hydrogen atom of the methyl groups (taking the effect of bond orientation into account) at fixed φ. The calculation showed that the energy of steric repulsion is ca. 110 kcal/mole (4.07 eV) in the case of a planar structure of I B and II B molecules at optimum orientation of the atoms of the C₁H₂H₃H₄ and C₃H₂H₃H₄ radicals. This is due chiefly to the steric interaction of H₁-H₄ and C₁-C₄ atoms (a similar result was obtained in [4] during examination of the n-butane molecule). On rotation of the substituents at a certain angle φ ≠ 0, the energy of the steric interactions decreases sharply (cf. the upper curve in Fig. 3), but this rotation decreases the conjugation of the unshared pair of the N₁ atom with the π-electron system.

Let us now consider A molecules. For this, we have used the same Fig. 1 designating the position of the hydrogen atoms by a dotted line. Calculations show that even when φ = 0 the CH₂...H interaction does not exceed 2 kcal/mole and the energy of steric interactions for A molecules is virtually independent of φ. It hence follows that A molecules have a planar structure as a favorable consequence of conjugation of the unshared pair of the N₁ atom with the π-electron system. The quantitative problem of this conjugation will be examined further.

Let us now consider the steric interaction in the case of sp³ hybridization of the N₁ atom for B molecules. Figure 2 shows the arrangement of atoms in a B molecule at a certain orientation of the N₁-R₁ and N₁-R₂ bonds which we assumed at the outset of the calculation of φ. The unshared pair is shaded and the π orbitals are indicated by small circles. In calculating the steric interactions of the atoms with the unshared pair of nitrogen we used as a model its N-H bond. This model may give a somewhat high value of the steric interactions. Calculations showed that at the indicated bond orientation the energy of steric interaction does not exceed 20 kcal/mole. However, it is not possible in this case even to speak about the partial conjugation of the unshared pair of N₁ with the π-electron system. On rotation of the N₁R₁R₂ group at an angle of −90° the most favorable situation for low conjugation of the unshared pair with the π-electron system develops, but the energy of steric repulsion in this case