HERBICIDAL HYDROXYLAMINE DERIVATIVES

XL.* ENERGY OF INTERMOLECULAR HYDROGEN BONDING
AND STRUCTURE OF THE ASSOCIATES OF O-METHYLHYDROXYLAMINE
DERIVATIVES OF sym-TRIAZINES

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The energies of intermolecular hydrogen bonding for eight amino derivatives of sym-triazines were obtained from the temperature dependence of the equilibrium constants, which were determined by ebullioscopic and cryoscopic methods. It is shown that the investigated compounds form cyclic, centrosymmetrical dimers under the influence of hydrogen bonds. The nitrogen in the 1 or 5 position of the ring is a proton acceptor.

As previously noted in [2], the most accurate hydrogen bond energies are obtained when the "peak" intensities of the ν_{NH} bands of monomeric and dimeric molecules are used. This method was used to determine the hydrogen bond energy and the difference in the dimer–monomer entropies for 2-chloro-4-n-propylamino-6-methoxy-sym-triazine ($\Delta H = 3.61 \pm 0.07$ kcal/mole, $\Delta S = 15.8 \pm 0.4$ eu).

It is customary to assume that the determination of the integral intensities, particularly in the case of overlapped bands, is always associated with considerably larger errors than the determination of the "peak" intensities. Less accurate hydrogen bond energies should therefore be expected when the integral intensities are used. However, investigations have shown that this does not occur, which makes it possible to calculate the differences in the dimer–monomer enthalpies from the equation

$$\lg K = B - \frac{\Delta H}{2.303\, RT},$$

where $K = A_m^2/A_d$, A_m is the area under the contour of the monomer band, and A_d is the area under the contour of the dimer band; B includes the difference in entropies between the dimer and monomer molecules, the thickness of the operating layer of the cuvettes used, the molar concentration, and the integral absorption coefficients.

Since the areas under the contours of the selected bands were experimentally determined in the spectra of solutions of various concentration at several temperatures, the hydrogen bond energies were calculated as the weighted means of several values. As a rule, the weighted mean energy is in good agreement with the corresponding value determined for one of the concentrations. This method was used to determine the hydrogen bond energy for the following compounds: 2-chloro-4-diethylamino-6-methoxyamino-sym-triazine (I), 2-chloro-4-di-n-propylamino-6-methoxy-sym-triazine (II), 2-methylthio-4-di-n-propyl-amino-6-methoxyamino-sym-triazine (III), 2-chloro-4-di-n-butylamino-6-methoxyamino-sym-triazine (IV), 2-chloro-4-diethylamino-6-ethylamino-sym-triazine (V), 2-chloro-n-propylamino-6-methoxy-sym-triazine (VI), and 2-chloro-4-isopropylamino-6-methylthio-sym-triazine (VII) (Table 1).

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*See [1] for communication XXXIX.

TABLE 1. Hydrogen Bond Energies and Entropies and Their Mean Square Deviations

Com-pound	From the integral intensities of the ν_{NH} bands	From cryoscopic and ebullio-scopic measurements*	
	ΔH, kcal/mole	ΔH, kcal/mole	ΔS, eu
I	3,9±0,4	4,12±0,06	23,2±0,2
II	4,5±0,1	4,10±0,09	22,2±0,3
III	3,0±0,3	—	—
IV	4,0±0,3	2,25±0,09	9,7±0,6
V	4,1±0,2	2,97±0,08	14,9±0,6
VI	3,0±0,1	3,08±0,20	16,6±2,3
VII	2,9±0,2	2,52±0,08	11,7±0,6
VIII	—	4,04±0,04	25,2±1,0
IX	—	3,03±0,12	17,4±1,0

*ΔH is the hydrogen bond energy, and ΔS is the difference in entropies between the dimer and monomer.

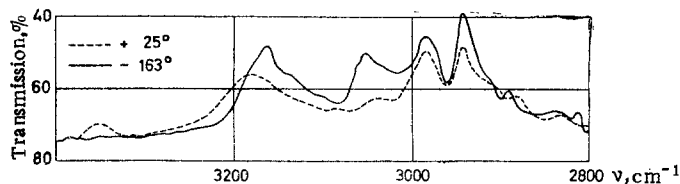Fig. 1   Fig. 2

Fig. 1. IR spectrum of a solution of 2-chloro-4-di-n-propylamino-6-methoxyamino-sym-triazine in hexachlorobutadiene (c 0.01 mole/liter).
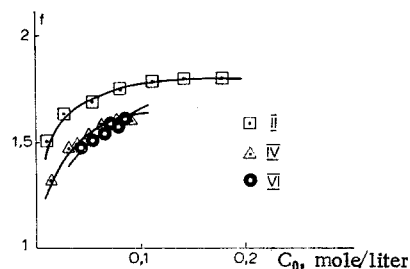
Fig. 2. Dependence of the association factor (f = $\bar{M}/M$, $\bar{M}$ is the measured molecular weight, M is the molecular weight of the monomer molecule) on the molar concentration.

It should be noted that the hydrogen bond energies and their confidence intervals, calculated using the integral intensities, practically coincide with the corresponding values obtained from the "peak" intensities [2].

In addition to the ν_{NH}(free) and ν_{NH}(bond) bands, two other bands are observed at 3000-3100 cm^{-1} for the examined compounds. Iogansen [3] has shown that the presence of these bands can be explained only by Fermi resonance perturbations, which is confirmed by temperature investigations of the complex structure of the ν_{NH}(bond) band (see [2] and Fig. 1). At the same time however, the intensity of the bands of the resonance structure increase as the strength of the hydrogen bond decreases in a number of our compounds, which is not in agreement with Iogansen's premises [3]. In our case, the complex structure of the bands at 3000-3100 cm^{-1} apparently can nevertheless be explained by Fermi resonance perturbations, not of the ν_{NH}(bond) band, but of the ν_{CH} band or a combination of ν_{NH} with the low-frequency vibrations of strictly the hydrogen bond.

The molecular weights of the investigated compounds were measured cryoscopically in CCl_4 solution. As the concentration increases, the average molecular weight asympotitically approaches a doubled value (Fig. 2), which can be explained only by the formation of dimers. It is known [4, 5] that cryoscopic measurements in conjunction with ebullioscopic measurements make it possible to obtain the hydrogen bond energies and the difference in entropies of the dimer—monomer equilibrium. In this case, the equilibrium (dissociation) constants were calculated from the equation

$$K = \frac{2(\mu-1)^2 c_0}{2-\mu}$$

(where μ is the ratio of the molecular weight of the dimer and the average molecular weight, and c_0 is the molar concentration of the substance) and were averaged for three to eight concentrations.

The energies of the hydrogen bonds and the differences in the entropies of the dimer—monomer equilibrium were found for I, II, IV–VII, 2-methoxy-4-di-n-propylamino-6-methoxyamino-sym-triazine (VIII), and 2-methoxy-4-diethylamino-6-ethylamino-sym-triazine (IX) (Table 1).

A comparison of the data on the hydrogen bond energies obtained by different methods demonstrates that the ebullioscopic and cryoscopic measurements give the most accurate values (see Table 2 in [2] and Table 1 in this paper).

We checked the Iogansen intensity rule [6] regarding the proportionality of the hydrogen bond enthalpy to the increase in the square root of the integral intensity of the $\nu_{XH...Y}$ band for our compounds. The average value of the proportionality coefficient proved to be 0.061 ± 0.012, which overlaps statistically with 0.050.

The presence of several proton-acceptor centers in the investigated sym-triazines in [2] made it possible to suggest several possible forms of cyclic dimers for them.

When the nitrogen atom of the amino group in the 4 position participates in the formation of a ring, it is necessary to rotate the substituent attached to the nitrogen atom. However, as our investigations demonstrated, the barrier to internal rotation of the NH_2 group in melamine, calculated by the HMO method using the system of parameters in [7, 8], is 12.5 kcal/mole. The applicability of the selected parameters was checked by calculation of the barrier to internal rotation of the NH_2 group for molecules with known experimental data. Thus the calculated barrier to internal rotation is 11.1 kcal/mole for urea, which is in agreement with 15 ± 3 and 12.7 kcal/mole [9, 10], while that for formamide is 29.5 kcal/mole, which is in agreement with the experimental value 18 ± 3 kcal/mole [11]. Thus the formation of a hydrogen bond, the energy of which is 3–4 kcal/mole for the investigated compounds, does not compensate for the energy outlays necessary for turning of the substituents attached to the nitrogen atom of the amine grouping in the 4 position. In other words, neither "sandwich" nor planar forms of cyclic dimers in which this nitrogen atom particpates as a proton acceptor can be realized.

It is known that the ring nitrogen atoms have the greatest basicity in the melamine molecule [12] and in alkylamino derivatives of sym-triazine [13, 14], while the exocyclic nitrogen atoms even bear a certain positive charge. For this reason, the formation of cyclic dimers with a planar structure in which the exocyclic nitrogen atoms participate should be excluded.

The most favorable conditions for the formation of a hydrogen bond will apparently be found on the ring nitrogen in the 1 position, which leads to the following cyclic, centrosymmetrical dimer with linear hydrogen bonds:
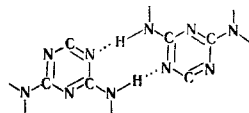
It is not difficult to observe that the formation of cyclic dimers may also occur with the participation of the ring nitrogen in the 5 position. However, an examination of hinged models of the investigated compounds, which contain a dialkylamino group in the 4 position, makes it possible to assume that the formation of hydrogen bonds with the participation of this nitrogen is sterically unfavorable because of overlapping of the van der Waals radii of the dialkylamino carbon atom and the oxygen atom of the methoxyamine grouping.

For VI and VII, in which groupings that do not produce steric hindrance are in the 6 position, the formation of a hydrogen bond is possible with the ring nitrogen in both the 1 position and in the 5 position. In this case, the participation of one or the other nitrogen atom will depend on its basicity.

EXPERIMENTAL

2-Chloro-4-n-propylamino-6-methoxy-sym-triazine (VI). This compound was obtained by the method in [15] and had mp 64–65° (from petroleum ether with bp 40–60°).

2-Chloro-4-isopropylamino-6-methylthio-sym-triazine (VII). A total of 21.3 g (0.36 mole) of isopropylamine was added dropwise to a solution of 58.5 g (0.3 mole) of 2,4-dichloro-6-methylmercapto-sym-triazine in 300 ml of acetone at 10–15°, and a solution of 12 g (0.3 mole) of NaOH in 100 ml of

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water was then added with stirring at the same temperature. The mixture was stirred at 20° for 2 h and at 30-35° for 0.5-1 h to pH 7-8 and cooled. It was then diluted to twice its volume, and the resulting oily layer was extracted with ether. The organic layer was dried with magnesium sulfate and evaporated to give 76.5 g of an oil. Distillation of this oil gave 59.6 g (90%) of VII with bp 127-129° (0.05-0.06 mm). The product crystallized on long standing to give a product with mp 49-49.5° (from n-pentane). Found: S 14.7; Cl 15.7%. $C_7H_{11}ClN_4S$. Calculated: S 14.7; Cl 16.2%.

2-Methoxy-4-di-n-propylamino-6-methoxyamino-sym-triazine. This compound was previously obtained by us in [16] and had mp 98.5-99.5° (from heptane).

2-Methoxy-4-diethylamino-6-ethylamino-sym-triazine (IX). This compound was obtained by the methanolysis of 2-chloro-4-diethylamino-6-ethylamino-sym-triazine according to the method in [17] and had mp 105-106.5° (from n-heptane) (mp 106-108° [18]).

2-Methylthio-4-di-n-propylamino-6-methoxyamino-sym-triazine (III). We previously obtained this compound in [19].

The IR spectra of I-VI were recorded by the method in [2] with an IKS-14 spectrophotometer; the spectrum of VII was recorded with an H-800 spectrophotometer. The half widths of the apparatus function at the frequencies of the absorption maxima were as follows: 7.7 cm^{-1} at $\nu_m \sim 3254$ cm^{-1} for the monomer band, and 7.6 cm^{-1} at $\nu_d \sim 3418$ cm^{-1} for the dimer band.

The integral intensities for the determination of the hydrogen bond energies were calculated as the areas under the optical density contour from the Simpson formula (60-75 cm^{-1} was taken from the maximum of the band of the monomer molecules, and 225-270 cm^{-1} was taken from the maximum of the band of the dimer molecules).

The ebullioscopic measurements were made with a Swientoslawski differential ebulliometer [20], while the cryoscopic measurements were made with a crysostat of the usual construction with a magnetic stirrer. Alcohol and dry ice were used as the cooling mixture. The solvent was analytical grade CCl_4, which was specially purified and repeatedly distilled. The ebullioscopic and cryoscopic constants of the CCl_4 used were 5.1-5.15 and 33.1-33.3, respectively.

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