HERBICIDAL HYDROXYLAMINE DERIVATIVES

IX. Determination of the Energy of the Intermolecular Hydrogen Bond of some O-Methylhydroxylamine Derivatives of sym-Triazines in Solution from Their Infrared Absorption Spectra*

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The energies of the intermolecular hydrogen bonds for five amino derivatives of sym-triazines have been obtained. The energies were calculated from the temperature dependence of the equilibrium constants determined from the change on dilution of the "peak" intensities of the stretching vibrations of free N –H groups and those participating in a hydrogen bond. It has been shown that under the action of the hydrogen bond the compounds studied form cyclic dimers in solution similar to those of the carboxylic acids.

The role of the hydrogen bond in the biological activity of organic compounds is universally recognized at the present time (see, for example, [2]). In particular, the point of view appears in the literature in which the action of herbicidal compounds is explained by the blocking of the active centers of biopolymers with the aid of hydrogen bonds [3].

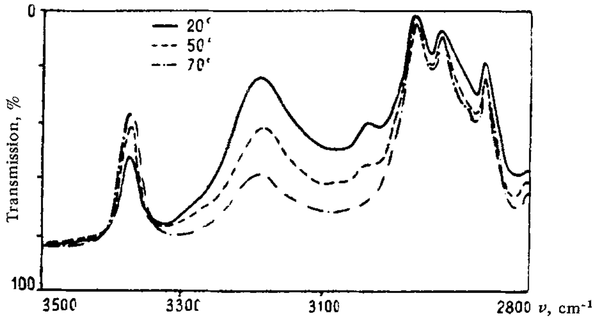

Fig. 1. IR spectra of 2-chloro-4-di-n-propylamino-6-methoxyamino-sym-triazine obtained at various temperatures; concentration 0.0488 mole/l, thickness of the working layer 1.011 mm, solvent hexachlorobutadiene.

sym-Triazine derivatives form a group of widely known herbicides finding considerable application in agriculture, such as prometryne, atrazine, atraton, etc. [4], the mechanism of the action of which is undoubtedly connected with the capacity of their molecules for forming hydrogen bonds with biopolymers. However, there is no information in the literature on the quantitative characteristics of the hydrogen bond for herbicidal compounds of this series. Only comparatively recently has a paper appeared on the qualitative interpretation of the hydrogen bond for sym-triazine derivatives [5].

In the present paper we give data on the energy of the intermolecular [subsequently, for brevity, the word "intermolecular" will be omitted] hydrogen bond of four O-methylhydroxylamine sym-triazine derivatives: 2-chloro-4-diethylamino-6-methoxyamino-sym-triazine (I), 2-chloro-4-di-n-propylamino-6-methoxyamino-sym-triazine (II), 2-methylthio-4-di-n-propylamino-6-methoxyamino-sym-triazine (III) and 2-chloro-4-di-n-butylamino-6-methoxyamino-sym-triazine (IV), synthesized in order to investigate their herbicidal activity [6,7]. For comparison, the energy of the hydrogen bond of the well-known herbicide trietazine or 2-chloro-4-diethylamino-6-ethylamino-sym-triazine (V) [4] was also determined.

In the majority of papers on the determination of the energy of a hydrogen bond using IR spectroscopy, the integral intensities of the X—H bands of the stretching vibrations of monomeric and associated molecules [8] (or those of monomeric molecules alone with the necessary premises and assumptions for this determination taken into account [9]) are measured.

The determination of the integral intensities, particularly in the case of overlapping bands, is always associated with considerably greater errors than the determination of peak intensities. However, it is impossible to use directly the change in the peak intensities with a variation in the temperature to determine the energy of a hydrogen bond because of the possible dependence of the peak intensities on the temperature for the individual compounds (see, for example, [10]).

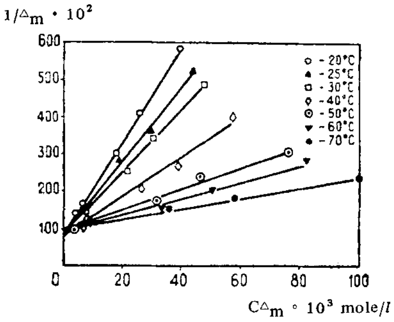

Fig. 2. $1/\Delta_m$ as a function of $C\Delta_m$ for the monomeric band of 2-chloro-4-di-n-propylamino-6-methoxyamino-sym-triazine.

These difficulties can be circumvented if the peak intensities are used to determine the equilibrium constants between the free molecules and those bound by the hydrogen bond, since the absorption coefficients are practically independent of the dilution with a small change in the viscosity of the solution [10].

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*For part VIII, see [1].

The presence of only two bands in the region of the N—H stretching vibrations (see Fig. 1) gives grounds for speaking of the presence of only one type of associate for the compounds studied*. The linear relationship between the square of the optical density of the free N—H bond (Δ_m^2) and the product of the optical density of the band for N—H participating in a hydrogen bond and the thickness of the working layer ($\Delta_d \cdot l$) and also the linear relationship between the reciprocal of the optical density ($1/\Delta_m$) of the band of the free N—H bond and the product of the optical density of this band and the molar concentration ($C \cdot \Delta_m$, see Fig. 2) permits the statement that the associates are mainly cyclic dimers.

The values of the energy of the hydrogen bond calculated only from the change in the optical density of the band of the monomeric molecules coincides within the 96% confidence limits with the values of the energies obtained by using the bands both of the monomeric and the dimeric molecules, but in the second case the confidence interval is 3 to 6 times smaller. Consequently, only the second scheme of calculation will be considered. In this case, to calculate the equilibrium constants the absorption coefficients of both bands must be borne in mind; these were determined by the extrapolation of the linear relationship between $\Delta_m/C_0 \cdot l$ and $\Delta_d/C_0 \cdot l$ (Fig. 3) to intersect the axes, since

$$\frac{\Delta_m}{\xi_m C_0 l} + \frac{\Delta_d}{\xi_d C_0 l} = 1.$$

The absorption coefficients for the band of the free N—H are given in Table 1.

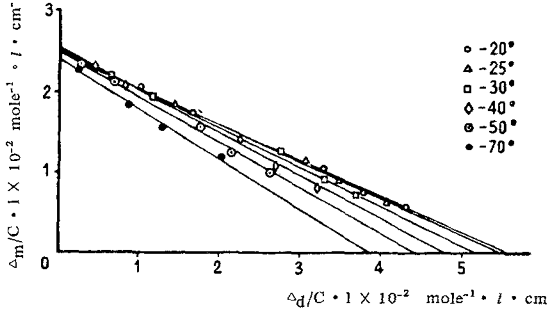

Fig. 3. $\Delta_m/(C_0 \cdot l)$ as a function of $\Delta_d/(C_0 \cdot l)$ for 2-chloro-4-di-n-propylamino-6-methoxyamino-sym-triazine

The values of the equilibrium constants for each temperature were obtained by averaging the constants calculated from the equation

$$K = \frac{\Delta_m^2 \xi_d}{\xi_m^2 \Delta_d l}$$

for 4–5 concentrations.

The energies of the hydrogen bonds and the differences in the entropies between the monomeric and cyclic molecules were calculated from the dependence of the equilibrium constants on the temperature (Table 2).

Table 1

Frequencies and Absorption Coefficients of the Stretching Vibrations of Free N—H

Compound	Frequency ν, cm^{-1}		$\Delta\nu$, cm^{-1}	Absorption coefficient* mole^{-1} · l · cm^{-1}
	free NH	bound NH		
I	3381	3187	194	199—207 (204)
II	3381	3187	194	240—255 (249)
III	3379	3183	196	196—233 (215)
IV	3378	3188	190	239—261 (250)
V	3442	3264	178	296—401 (348)

*The mean absorption coefficients are given in parentheses.

In most papers on the determination of the energy of a hydrogen bond, it is not shown how the error of the energy values given has been calculated. This greatly complicates the evaluation of the reliability of literature data and reduces their value. In the present paper the calculation of the absorption coefficients, the energy of the hydrogen bond, the entropy, and the errors of these magnitudes were carried out by the method of least squares both with the weights of the errors and without them, starting from the assumption of the outline of the monomer band from the dimer band. The values of the energies of the hydrogen bond, the entropy, and their mean-square deviations were practically the same in both cases.

It can be seen from Fig. 3 that in compound II the absorption coefficient of the band of the N—H stretching vibration of the monomeric molecules does not depend on the temperature within the experimental error. This is obviously explained by the very small change in the half-width of the band for the given temperature range. According to Rakov [10], this is possible because the viscosity of the solvent, hexachlorobutadiene, changes little in the given range of temperatures [11].

It can be seen from the data of Table 2 that the replacement of the ethyl radicals of the amino group in position 4 by propyl radicals does not, within the limits of experimental error, lead to a change in the energy of the hydrogen bond, while the replacement of propyl radicals by butyl radicals leads to a considerable decrease in the energy of the hydrogen bond. The replacement of chlorine by a thiomethyl group also leads to a decrease in the energy of the hydrogen bond. In the case of trietazine, there is a marked decrease in the energy of the hydrogen bond as compared with methoxyamino-sym-triazines. This difference can be explained by the influence of the methoxy group; the electronegative oxygen atom increases the displacement of the center of gravity of the electron cloud from the hydrogen atom to the nitrogen atom, which leads to an increase in the donor capacity of the amino group.

The presence in the 4,6-diamino-sym-triazines of several proton-accepting centers enables several possible forms of cyclic dimers to be suggested for them. These centers may be either the nitrogen atoms of the triazine ring or the nitrogen atom of the amino group

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*Other bands, of low intensity, are found in the 3100–3000 region which apparently correspond to some other types of associates. Their influence on the accuracy of the determination of the energy differences between the monomer and the (cyclic) dimer is within the limits of the experimental error.

in position 4. The oxygen of the methoxyamino group cannot be a proton-accepting center that would lead to dimers similar to those of the carboxylic acids since trietazine has no methoxy group and the cyclic dimeric form of the associates is retained.

Table 2

Values of the Energy of the Hydrogen Bond and the Entropy*

Compound	ΔS, entropy units	$\sigma_{\Delta S}$, entropy units	ΔH, kcal/mole	$\sigma_{\Delta H}$, kcal/mole
I	18.6	0.7	3.8	0.1
II	20.2	0.5	4.18	0.07
III	17.4	1.1	3.3	0.2
IV	13.0	2.0	3.1	0.3
V	9.9	1.3	2.4	0.2

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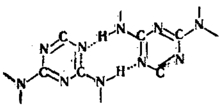
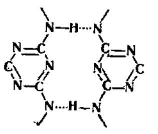
*ΔH is the energyof the hydrogen bond, ΔS is the difference between the entropies of the dimer and the monomer, and σ is the mean-square deviation of the results obtained.

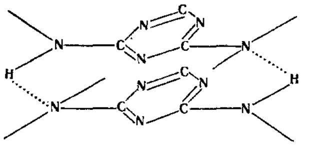
If it is assumed that in trietazine there is a single form of cyclic dimers and in the N-methoxyaminotriazines another form, in the latter case one would expect at least two forms of cyclic dimers, which is contrary to experiment.



In the case of the formation of a hydrogen bond with a nitrogen of the ring, the most favorable conditions will be on the nitrogen atom in position 1, which must lead to a cyclic centrosymmetrical dimer with linear hydrogen bonds.

If hydrogen bonds were formed with the amino group in position 4, in its turn, the existence of two forms of cyclic dimers would be possible: with the rings lying in one plane and with them arranged one under the other (bread-and-butter form of cyclic dimers):





In both the latter cases, it is necessary to develop the substituents on the nitrogen atom forming the hydrogen bond perpendicularly to the plane of the triazine ring, and for this a definite energy is consumed which is connected with the disturbance of the conjugation of the π-electron pair of the nitrogen with the triazine ring [12]. On the other hand, in the first case this must lead to an increase in the proton-accepting capacity of the nitrogen and, consequently, to an increase in the energy of the hydrogen bond so that the two processes may compensate one another from the energy point of view.

In the case of the bread-and-butter form of cyclic dimer, one must expect a gain in energy due to the interaction of the π-electrons in the rings.

EXPERIMENTAL

The spectra of solutions of the compounds studied for calculating the energy of the hydrogen bond were taken in the 3600–2800 cm^{-1} region on an IKS-14 infrared spectrometer with a lithium fluoride prism. Recording scale 1.48 cm^{-1}/mm. The half-widths of the apparatus function at the frequencies of the absorption maxima were: for the monomer band, $\nu_m \sim 3380\ cm^{-1}$, $S = 7.3\ cm^{-1}$; for the dimer band, $\nu_d \sim 3190\ cm^{-1}$, $S = 6.3\ cm^{-1}$. The solvent was hexachlorobutadiene and the thicknesses of the working layers and the concentrations of the compounds studied are given in Table 3. As can be seen (Fig. 1) a wing of the band of the NH group participating in a hydrogen bond is superposed on the absorption band of the free NH group. Consequently, the line of 100% transmission was determined by extrapolating the dimer band to high frequencies. The absorption line of F-1 glass was taken as the line of 0% transmission.

To heat the cells containing the solutions, a cylindrical furnace closed at both ends with lids containing quartz windows was used. The measurement and control of the temperature was carried out with an EPP-09 2M potentiometer with a 10 mV scale, and the sensor was a chromel-constantan thermocouple. The accuracy of the temperature measurements was ±0.05° C and the range of temperatures from +20 to +70° C.

Table 3

Concentration of the Compounds (mole /l) Used for Recording the IR Spectra

Compound	Layer thickness, mm				
	0.212	0.511	1.011	5.007	9.998
I	0.2345	0.0956	0.0488	0.0097	0.0048
II	0.2289	0.1045	0.0524	0.0104	0.0051
III	0.0000	0.0076	0.0397	0.0080	0.0040
IV	0.2260	0.0942	0.0455	0.0094	0.0048
V	0.2367	0.0983	0.0498	0.0125*	0.0046

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*Concentration for a working layer thickness of 4.054 mm.

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