Alkyl Derivatives of 3-Amino-5-(2-furyl)-1,2,4-triazole

Part III. A Spectrochemical Study of the Tautomerism

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Tautomerism in alkylated 3-amino-5-(2-furyl)-1,2,4-triazoles has been studied using infrared and ultraviolet spectroscopy. It was found that the compounds existed in the amino form both in the crystalline state and in polar and nonpolar solvents. In 3-alkylamino- and 3-dialkylamino-5-(2-furyl)-1,2,4-triazole, there are three possible positions for the ring hydrogen atom. The IR-spectra of these compounds showed that in the crystalline state, the 2H-3-alkylamino- and the 2H-3-dialkylamino-5-(2-furyl)-1,2,4-triazole, respectively, were the most probable tautomers. This tautomeric form of the dialkylamino compound was also preponderant in chloroform solution. The low solubility of the alkylamino compound did not permit any determination of the tautomerism in this solvent. In tetrahydrofuran solution two or all three tautomeric forms were evident. The UV-spectra indicated that there was also a mixture of tautomeric forms in ethanol and water.

In N-heterocyclic amines, tautomerism is possible between the amino and the imino form. In the earlier literature, many N-heterocyclic amines were assigned the imino form in order to explain their chemical behaviour. Later, it was shown by physical methods that this assumption was incorrect and that the amino form is the most probable. In this paper is presented a study of the tautomerism in alkylated 3-amino-1,2,4-triazoles. A number of alkylated aminotriazoles which could theoretically exist in tautomeric forms were synthesized.*

Substitution of the hydrogen atom of the triazole ring limits the number of possible tautomeric forms and gives compounds, which exhibit only amino-imino tautomerism. In 3-dialkylamino-1,2,4-triazoles the amino structure is fixed but there are three possible positions for the hydrogen atom of the triazole ring.

To study the tautomerism of these compounds, their UV- and IR-spectra were examined and compared. Further comparisons were made with spectra of alkylated 3-amino-1,2,4-triazoles and 3-imino-1,2,4-triazolines, which are incapable of tautomerism.

RING ALKYLATED 3-AMINO-1,2,4-TRIAZoles

In 1-, 2-, and 4-alkylated 3-amino-5-(2-furyl)-1,2,4-triazole the ring hydrogen atom is replaced by an alkyl group. 1- and 4-alkyl-compounds (I and II) may exist in an amino or an imino form, while the 2-alkyl derivative (III) may exist in one amino and two imino forms.

![Chemical Structures](Image)

Infrared spectra. The IR-spectra of compounds I and III in chloroform solution show bands at about 3480 cm⁻¹ and 3395 cm⁻¹ due to the NH₂ asymmetrical and symmetrical stretching, respectively, and a band at 1620 cm⁻¹ which can be assigned to the NH₂ deformation mode \(^{10,11}\) (Figs. 1a and b). The presence of these bands strongly suggests that compounds I and III exist in the amino form in chloroform. A comparison with the spectrum of the 2,4-dimethyl-5-(2-furyl)-3-imino-1,2,4-triazoline, which can only exist in the imino form, further supports the existence of the amino form. This compound has a single band at 3347 cm⁻¹ due to the NH-stretching vibration of the imino group (Fig. 1c). Unfortunately, substance II is not soluble enough in chloroform to give a satisfactory spectrum and therefore cannot be compared with compounds I and III.

The existence of the amino form in chloroform solution does not eliminate the possibility of the existence of other tautomeric forms in the solid state. Differences in the spectra of aminoheterocycles recorded in solution and in solid state have been reported \(^{5,7,9}\) but mostly only the solution spectra have been interpreted.

Fig. 1. IR absorption in CHCl₃ solution.
a. 3-Amino-5-(2-furyl)-1-methyl-1,2,4-triazole (I). b. 3-Amino-5-(2-furyl)-2-methyl-1,2,4-triazole (III). c. 2,4-Dimethyl-5-(2-furyl)-3-imino-1,2,4-triazoline.

In Fig. 2, spectra of alkyltriazoles in the solid state are presented. No characteristic NH₂-frequencies are observed in the 3400 cm⁻¹ region and the 1620 cm⁻¹ band in chloroform solution is shifted to about 1640 cm⁻¹ in solid state. This may indicate the existence of the imino form of the substances I, II, and III in the solid state. However, the differences can also be explained by strong intermolecular hydrogen bond interaction of the amino group in the solid state. It has been shown that the NH₂ bending vibration is shifted to higher frequencies when the amino group participates in hydrogen bonding.¹²,¹³

To investigate further, which of the two forms that is the most plausible, IR-spectra of the deuterated compounds were recorded. They exhibit absorption bands from ND-vibrations in the 2300—2500 cm⁻¹ region and the band at 1640 cm⁻¹ in the undeuterated compounds disappears. The imino band at 1630 cm⁻¹ of 2,4-dimethyl-5-(2-furyl)-3-imino-1,2,4-triazoline is unaffected by deuteration (Figs. 2g and h). This shows that the band at 1640 cm⁻¹ in the undeuterated alkyltriazoles is due to an internal deformation of an amino group.

Ultraviolet spectra. Further evidence was adduced from the UV-absorption spectra of the three monoalkyltriazoles (I, II, and III) and of some of their derivatives (Table 1). Compounds I, II, and III exhibit an absorption maximum

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Fig. 2. IR absorption in KBr phase. a. 3-Amino-5-(2-furyl)-1-methyl-1,2,4-triazole (I). b. Do. deuterated. c. 3-Amino-5-(2-furyl)-2-methyl-1,2,4-triazole (III). d. Do. deuterated. e. 3-Amino-5-(2-furyl)-4-methyl-1,2,4-triazole (II). f. Do. deuterated. g. 2,4-Dimethyl-5-(2-furyl)-3-imino-1,2,4-triazoline. h. Do deuterated (in CDCl₃ solution).
Table I. The UV absorption spectra in ethanol and 0.01 M hydrochloric acid.

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<tr>
<th>R₁</th>
<th>R₂</th>
<th>R₃</th>
<th>( \lambda_{\text{max}} ) (nm)</th>
<th>( \varepsilon \times 10^{-3} ) (in EtOH)</th>
<th>( \lambda_{\text{max}} ) (nm)</th>
<th>( \varepsilon \times 10^{-3} ) (in 0.01 M HCl)</th>
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<tbody>
<tr>
<td>CH₃</td>
<td>CH₃</td>
<td>CH₃</td>
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<tr>
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<tr>
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<td>H</td>
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<table>
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<th>R₃</th>
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<tbody>
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<td>H</td>
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<td>CH₃</td>
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<td>265</td>
<td>15.1</td>
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</table>

<table>
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<th>R₂</th>
<th>( \lambda_{\text{max}} ) (nm)</th>
<th>( \varepsilon )</th>
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<td>H</td>
<td>H</td>
<td>252*</td>
<td>9.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>278</td>
<td>11.1</td>
</tr>
</tbody>
</table>

* A shoulder.

in chloroform solution at 264—278 nm, whereas 2,4-dimethyl-5-(2-furyl)-3-imino-1,2,4-triazoline absorbs at 301 nm (Fig. 3). The appreciable wavelength shift of the latter band and its low molecular extinction value dismisses the possibility that this band is due to a bathochromic shift of the absorption at 264—278 nm. 3-Dimethylamino-5-(2-furyl)-4-methyl-1,2,4-triazole, which cannot exist in an imino form, has an absorption band at 272 nm. The similarity between this latter spectrum and the spectra of the tautomeric ring alkylated aminotriazoles (Fig. 3 and Table 1) and the difference between the spectra of the latter and the imino compound favours an amino structure for the ring alkylated aminotriazoles.

The UV-spectra of the monoalkyltriazoles (I, II, and III) were practically unchanged when recorded in chloroform, ethanol, and 0.01 M sodium hydroxide showing that there are not tautomeric displacements when the solvent is changed.

Thus the IR- and UV-examination show that the compounds I, II, and III exist in the amino form in the crystalline state and in polar and nonpolar solvents.

AMINO ALKYLATED 1,2,4-TRIAZOLES

The ring hydrogen atom of 3-alkylamino- and 3-dialkylamino-5(2-furyl)-1,2,4-triazole (IX and X) may be situated at either of the three nitrogen atoms thus giving three tautomeric forms (IXa, b, c and Xa, b, c). Besides these tautomeric forms, the 3-alkylamino-derivative (IX) may also exist in two imino forms (IXd, e).

_Ultraviolet spectra._ The UV-spectra of IX and X recorded in water, ethanol, tetrahydrofuran, and ether exhibit a very broad absorption band around 240—270 nm (Figs. 4 and 5) with no distinct peak although several shoulders are visible. The broad absorption band may indicate the presence of several tautomeric forms of IX and X in these solvents. The UV-spectrum of IX and X recorded in cyclohexane shows a more definite band with a maximum at

Fig. 4. UV absorption of 5-(2-furyl)-3-methylamino-1,2,4-triazole (IX) in tetrahydrofuran, ethanol, water, ether solution.

Fig. 5. UV absorption of 3-dimethylamino-5-(2-furyl)-1,2,4-triazole (X) in tetrahydrofuran, ethanol, water, ether, cyclohexane solution.

250 nm indicating that in this solvent one of the tautomers is preponderant. However, owing to the low solubility of IX in cyclohexane it was necessary to use a saturated solution and a 10 cm cell. The concentration of this solution is unknown and therefore the curve is not drawn in Fig. 5.

The UV-spectra of IX and X recorded in nonpolar solvents show an absorption band at 300 nm (Figs. 4 and 5). A comparison with the spectrum of 2,4-dimethyl-3-imino-5-(2-furyl)-1,2,4-triazoline (Fig. 3) would suggest the presence of an imino tautomeric form of IX and X. However, it is evident that X cannot exist in an imino form. Substance IX may exist in an imino form but it is unlikely that this substance behaves differently from the other aminotriazoles examined and that the shoulder at 300 nm in the UV-spectrum of IX is not due to the presence of an imino tautomer.

In polar solvents the long wavelength band at 300 nm of IX and X is shifted to shorter wavelength and is partially concealed by the high intensity.

absorption band. This strong hypsochromic shift in polar solvents is characteristic of a $n \rightarrow \pi^*$ transition.\textsuperscript{14} The intensity of such a band is reported to be very low and molar absorption coefficients between 10 and 1500 are reported.\textsuperscript{14-16} However, it is expected that $n \rightarrow \pi^*$ bands of five-membered ring heterocyclic molecules should be relatively strong.\textsuperscript{17} This has not yet been confirmed, since such bands have not been observed in the spectra of the few five-membered ring heterocycles so far examined. It was assumed that the $n \rightarrow \pi^*$ bands were masked by the more intensive $\pi \rightarrow \pi^*$ bands in these spectra.

The intensity of the long wavelength band of IX and X ($\epsilon_{\text{max}}$ 2000—4000) (Figs. 4 and 5) is higher than expected for $n \rightarrow \pi^*$ transitions. However, the solvent effects observed, the long wavelength absorption and the relatively strong $n \rightarrow \pi^*$ band associated with five-membered ring heterocycles support the assumption that the long wavelength band of IX and X is due to a $n \rightarrow \pi^*$ transition.

Intra- and intermolecular hydrogen bonding may influence the electronic spectra.\textsuperscript{18} An examination of the degree of association of 3-methylamino- and 3-dimethylamino-5-(2-furyl)-1,2,4-triazole (IX and X) in nonpolar solvents was therefore carried out. Fig. 6 shows the spectrum in the 3000—4000 cm\textsuperscript{-1} region of substance X recorded in carbon tetrachloride at different concentrations. The sharp peak at 3460 cm\textsuperscript{-1} is due to a free NH-stretching band and the bands at about 3100 cm\textsuperscript{-1} are due to hydrogen bonded NH-stretching. The solution spectra show that the association increases with rising concentration thus indicating intermolecular hydrogen bonding. At concentrations $4 \times 10^{-4}$ M the bands at 3100 cm\textsuperscript{-1} have almost disappeared and substance X is mainly in an unassociated state. Consequently at the low concentrations ($5 \times 10^{-5}$ M) used when recording the UV-spectra, the association may be negligible. Owing to the low solubility of triazole IX in carbon tetrachloride it was not possible to make any measurements in this solvent but it is expected to behave similarly to the triazole X.

![Fig. 6. NH-stretching absorption bands of 3-dimethylamino-5-(2-furyl)-1,2,4-triazole (X) in carbon tetrachloride.](image)

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Transmission %</th>
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<tbody>
<tr>
<td>$10 \times 10^{-3}$ M</td>
<td>90</td>
</tr>
<tr>
<td>$2 \times 10^{-3}$ M</td>
<td>70</td>
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<tr>
<td>$0.4 \times 10^{-3}$ M</td>
<td>50</td>
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</table>

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ALKYLATED AMINOTRIAZOLES III

The high intensity band in the UV-spectra of alkylated 3-amino-5-(2-furyl)-1,2,4-triazole derivatives (Figs. 3, 4, and 5) is most likely due to a $\pi \rightarrow \pi^*$ transition.\textsuperscript{19}\textsuperscript{31} Alkyl substitution of a ring-nitrogen atom is expected to give a bathochromic shift of the absorption band.\textsuperscript{19}\textsuperscript{30} The ring-alkylated triazoles V, VI, and VII (Table 1) were thus found to absorb at longer wavelengths than alkylamino- and dialkylamino-5-(2-furyl)-1,2,4-triazole IX and X (Figs. 4 and 5). Further the ringalkylated furyltriatoles V and VII, in which the furan ring is in linear conjugation with the two double bonds in the triazole ring, absorb at longer wavelengths than the furyltrimazoles VI in which there is a cross conjugation between the rings (Table 1). Such differences have been reported for other arylheterocycles which may exist as linear and cross conjugated structures.\textsuperscript{19}\textsuperscript{30}

The broad absorption band appearing in the UV-spectra of 3-methylamino- and 3-dimethylamino-5-(2-furyl)-1,2,4-triazole IX and X seems to consist of several bands. Consequently it is not possible from the UV-data to decide which of the tautomeric amino forms of substances IX and X are predominant in the different solvents. The broad absorption band only shows that several tautomers of IX and X exist in the solvents examined with the exception of cyclohexane for which one tautomeric form probably preponderates. Small shifts of the high intensity band in the spectra observed in different solvents may be due both to displacements in the tautomeric equilibrium and to solvent effects.

Spectra of IX and X recorded in alkali and acid solution have distinct peaks (Table 2). In the anionic form of a triazole derivative the charge is not fixed to a particular nitrogen atom but is distributed over the triazole ring, thus accounting for the distinct absorption band. The spectra recorded in acid solution have their absorption maxima in the same region as the spectra of ring alkylated triazoles (Table 1). No information about the tautomeric equilibrium could be adduced from spectra recorded in acid and alkali solution.

Infrared spectra. An IR-spectroscopic examination was performed to gain further understanding of the tautomeric equilibria in alkylamino- and dialkylaminotriazoies IX and X.

A study of the IR-spectra of the ring-alkylated triazole derivatives (Figs. 1, 2, and 7d—f) shows that linear and cross conjugation between the furan and

Table 2. The UV absorption spectra of 3-alkylamino- and 3-dialkylamino-5-(2-furyl)-1,2,4-triazole IX and X in acidic and basic solution.

<table>
<thead>
<tr>
<th>Substituents of the amino group R</th>
<th>$\lambda_{\text{max}}$ (nm) in 0.01 M NaOH</th>
<th>$\varepsilon \times 10^{-3}$</th>
<th>$\lambda_{\text{max}}$ (nm) in 0.01 M HCl</th>
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<tr>
<td>H</td>
<td>271</td>
<td>13.8</td>
<td>265</td>
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<tr>
<td>H</td>
<td>274</td>
<td>11.5</td>
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triazole ring give different ring vibration bands in the 1500—1650 cm\(^{-1}\) region. Substances V and VII with a linear conjugation give one band at 1550—1600 cm\(^{-1}\), while substance VI with a cross conjugation have two bands between 1580 and 1650 cm\(^{-1}\).

The IR-spectra of 3-alkyl- and 3-dialkylaminotriazoles IX and X, recorded in the solid state (Figs. 7a and b), exhibit two absorption bands at 1600—1640 cm\(^{-1}\), which may be assigned to ring vibration bands of a cross conjugated triazole derivative. Consequently the tautomeric forms IXa and Xa, respectively, with a hydrogen atom in 2-position are most probably the main tautomers present in the crystalline state.

The strong absorption bands at 2500—3250 cm\(^{-1}\), due to hydrogen bonded NH-stretching show that the triazole compounds IX and X are associated in solid state. This phenomenon has been reported for 1,2,4-triazole and other heterocycles as imidazole, pyrazole and tetrazole compounds both in solid state and in nonpolar solvents.\(^{32-24}\)

The IR-spectrum of 3-dialkylaminio-5-(2-furyl)-1,2,4-triazole X recorded in a 2 % chloroform solution (Fig. 7c) exhibits two bands at 1600—1640 cm\(^{-1}\) identical with the ring vibration bands observed in the solid state (Fig. 7b). This also shows that in chloroform solution Xa is the most probable tautomeric form. Moreover, the IR-spectrum shows strong absorption bands at 2500—3200 cm\(^{-1}\) due to hydrogen bonded NH-stretching and only a little peak at 3440 cm\(^{-1}\) due to a free NH-stretching indicating that most of substance X is associated in chloroform solution. This agrees with the results obtained in carbon tetrachloride solution as presented in Fig. 6. Unfortunately, 3-alkylamino-5-(2-furyl)-1,2,4-triazole (IX) is not soluble enough in chloroform to give a satisfactory spectrum.

Finally, a study of the IR-spectra of IX and X was made in tetrahydrofuran solution. In these spectra a band appeared at 1560—1570 cm\(^{-1}\) in addition to the two bands at 1600—1640 cm\(^{-1}\) (Figs. 8a—c). The new band is most likely due to a ring vibration band of a linear conjugated triazole ring. This may indicate the presence of one or both of the tautomers IXb, IXc and Xb, Xc, respectively, in equilibrium with the tautomeric forms IXa and Xa, respectively. Spectra of some linear conjugated triazole derivatives (Figs. 8d—f) are presented for comparison.

An IR-examination in more polar solvents such as ethanol and water is not practicable, since these solvents exhibit strong absorption in 1500—1700 cm\(^{-1}\) region.

The UV- and IR-spectra have been recorded for methyl, ethyl, and propyl derivatives of IX and X. The spectra of the higher alkyl homologues show the same features as the methyl derivative and hence a similar distribution

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Fig. 7. IR absorption in KBr phase. a. 5-(2-Furyl)-3-methylamino-1,2,4-triazole (IX). b. 3-Dimethylamino-5-(2-furyl)-1,2,4-triazole (X). c. Do. (in chloroform solution). d. 5-(2-Furyl)-2-methyl-3-methylamino-1,2,4-triazole (VI). e. 5-(2-Furyl)-4-methyl-3-methylamino-1,2,4-triazole (V). f. 3-Dimethylamino-5-(2-furyl)-4-methyl-1,2,4-triazole (V).

of tautomers may be inferred for all of them. Therefore only the spectra of the methyl derivatives have been published.

The IR-data show that 3-alkylamino- and 3-dialkylamino-5-(2-furyl)-1,2,4-triazole (IX and X) exist in the solid state mainly in the tautomeric

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forms IXa and Xa, respectively, with the hydrogen atom in 2-position. In chloroform solution, substance X likewise exists in the tautomeric form (Xa). Owing to the low solubility of substance IX it is not possible to obtain a satisfactory spectrum in this solvent. The tautomeric forms IXa and Xa are probably stabilized by the strong intermolecular association within the solutes. In a more polar solvent such as tetrahydrofuran, substances IX and X exist in several tautomeric amino forms.

When comparing the results of the IR- and UV-examination of IX and X, it is important to bear in mind the large difference in the concentration of the solutions used. In the IR-examination, the concentrations used are a thousandfold of the concentrations used in the UV-examination. In a nonpolar solvent, the intermolecular association in the solute is shown to increase with rising concentration. It is found that at the low concentrations used in the UV-measurements, the triazole molecules are unassociated, while when recording IR-spectra the molecules are almost completely associated. Intermolecular association may stabilize one tautomeric form and consequently the tautomeric equilibrium may be displaced by changing the concentration.

UV-spectra of IX and X in ether solution suggest the presence of more than one tautomeric form, while the IR-spectrum of X in chloroform indicates the presence of only one tautomeric form. This difference may be explained by a displacement of the tautomeric equilibrium, caused by the association.

In polar solvents, the solvent molecules form hydrogen bonds with the solute. This may cause displacement of the tautomeric equilibrium of IX and X by stabilizing other tautomeric forms than those present in nonpolar solvents. The IR- and UV-examinations are in concordance with these predictions. Further, in polar solvents a change of the concentration is not expected to cause any significant displacement of the tautomeric equilibrium. The results of the IR- and UV-examinations of IX and X in tetrahydrofuran suggest in both cases the presence of more than one tautomeric form.

EXPERIMENTAL

The infrared spectra are recorded on a Unicam SP. 100 infrared spectrophotometer with sodium chloride optics. Solid state spectra are not quantitatively recorded. In some cases, the measurements were made with nujol suspensions to obviate possible recrystallisation effects which may be introduced during the preparation of KBr discs. 2 % chloroform solutions are used for the solution spectra with a liquid cell thickness of 0.238 mm. The tetrahydrofuran solutions were 1–2 %, depending on the solubilities of the substances.

The ultraviolet spectra are measured with a Unicam SP. 700 recording spectrophotometer. 1 cm quartz cells are used and the concentration of the solutions was $5 \times 10^{-4}$ M. All spectra published here are referred to a linear wavelength scale.

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