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## VIBRATIONAL SPECTRA AND STRUCTURE

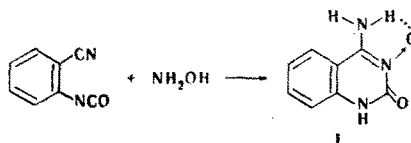
## OF 4-AMINO-1H-QUINAZOLIN-2-ONE 3-OXIDE

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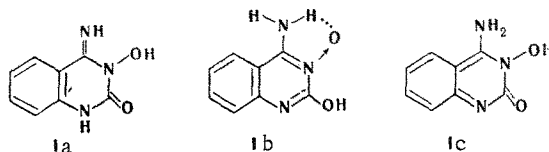
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On the basis of a study of the vibrational spectra in the solid state of the product of the reaction of 2-cyanophenyl isocyanate with hydroxylamine and its isotopic analogs ( $^{15}\text{N} \rightarrow \text{O}$  and  $^{15}\text{NH}_2$ ) it was demonstrated that the compound obtained has the 4-amino-1H-quinazolin-2-one 3-oxide structure.

It has been demonstrated [1] that the reaction of 2-cyanophenyl isocyanate with hydroxylamine leads to I, for which the 4-amino-1H-quinazolin-2-one 3-oxide structure was proposed:



However, one might have assumed that I exists in the various tautomeric forms Ia-c:



To confirm the structure of I we obtained its  $^{15}\text{N}$  isotopic analogs, viz., I with the  $^{15}\text{N}$  isotope in the 3 position of the quinazoline system (I  $^{15}\text{NO}$ ) and I with a  $^{15}\text{N}$ -labeled amino group (I  $^{15}\text{NH}_2$ ), and investigated their vibrational spectra. The IR and Raman spectra of I ( $^{15}\text{NO}$ ) and I ( $^{15}\text{NH}_2$ ) are presented in Table 1.

Compound I is very slightly soluble in ordinary solvents, and this makes it impossible to use NMR spectroscopy to establish the structure and limits the possibilities of IR spectroscopy.

The presence of an intense absorption band in the IR spectrum of I and its isotopic  $^{15}\text{N}$  analogs at  $1730\text{ cm}^{-1}$ , which is absent or very weak in the Raman spectrum, constitutes evidence for the presence of a carbonyl group in the compound and is not in agreement with the Ib form. The band at  $1630\text{ cm}^{-1}$ , the intensity of which is comparable to that of the  $\nu(\text{CO})$  band, which is absent in the Raman spectrum and is shifted to  $1620\text{ cm}^{-1}$  in the spectrum of isotopic analog I ( $^{15}\text{NH}_2$ ), corresponds to the deformation vibrations of the NH

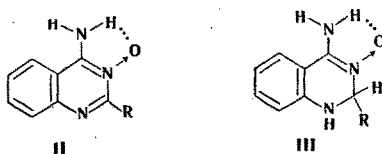
All-Union Scientific-Research Institute of Chemical Agents for the Protection of Plants, Moscow 109088. Translated from *Khimiya Geterotsiklicheskikh Soedinenii*, No. 7, pp. 968-972, July, 1981. Original article submitted September 11, 1980.

TABLE 1. Vibrational Spectra of 4-Amino-1H-quinazolin-2-one and Its Isotopic  $^{15}\text{N}$  Analogs in the Solid State

I		I ( $^{15}\text{NO}$ )		I ( $^{15}\text{NH}_2$ )	
IR	Raman	IR	Raman	IR	Raman
3374 m	—	3374 m	—	3366 m	—
2900 br s	—	2900 br s	—	2900 br s	—
1730 vs	1730 vw	1730 vs	—	1730 vs	—
1630 vs	—	1630 vs	—	1620 vs	—
	1620 m		1620 m		1620 m
	1598 w		1595 w		1595 w
1540 vw	1540 vw	1540 vw	1540 vw	1540 vw	1540 vw
1510 w	1512 m	1510 w	1512 m	1510 w	1512 m
1480 } w	1472 vs	1480 } w	1467 vs	1475 w	1472 vs
1472 } w		1470 } w			
1425 m-w	1425 w	1425 m-w	1425 m	1423 m	1425 w
1350 m	1348 s	1350 m	1350 s	1350 m	1350 s
1295 m	1292 vw	1292 m	1292 vw	1293 m	1295 vw
1268 m	1260 w-m	1265 m		1267 m	1260 w-m
1202 m-s	1200 w	1195 m-s		1200 m-s	1200 vs
1152 s	1150 w	1135 s		1150 s	1150 w
1112 m	1110 vw	1111 m		1110 m	
	1030 m				1030 m
992 w		992 vw		992 vw	
970 vw		970 vw		970 vw	
920 vw		920 vw		915 vw	
890 m		886 m		890 m	
765 sh		765 sh		765 sh	
751 m-s		750 m-s		750 m-s	
725 } m		722 } m		725 } m	
700 } m	700 w	700 } m	700	700 } m	700 w
678 } m		678 } m		678 } m	
665 } m	667 s	663 } m		663 } m	670 s
645 } m	640 w	646 } m		645 } m	
550 w	547 m	555 w		545 w	547 s
530 m		530 m		530 m	
455 m	457 m	455 w			457 m
450 sh	443 w	450 sh		453 m	442 w
380 w	398 w			375 w	397 w
	350 w				350 w
	290 vw				
	203 w				
	180 vw				
	120 vs				117 s

group, the absorption bands of which have high intensities in the case of primary amines and weak intensities in the case of imines [2]. This fact may serve as a confirmation of the presence of an  $\text{NH}_2$  group in I, i.e., it contradicts the Ia structure.

The preparation of a series of compounds that contain a  $\text{H}_2\text{NC}=\text{N} \rightarrow \text{O}$  fragment was described in [3]:



It was demonstrated that the amino group participates in the formation of an intramolecular hydrogen bond with the  $\text{C}=\text{N} \rightarrow \text{O}$  group. However, only the IR spectra of II and III in the region of the stretching vibrations of NH groups have been described. Thus the  $\nu(\text{NH})_{\text{free}}$  band in the spectrum of a dilute solution of II in  $\text{CCl}_4$  is observed at  $3515 \text{ cm}^{-1}$ , while the  $\nu(\text{NH}\dots\text{O})$  band is observed at  $3300 \text{ cm}^{-1}$  [3]. A band at  $3350 \text{ cm}^{-1}$  on the background of broad absorption at  $\sim 3150 \text{ cm}^{-1}$ , which corresponds to vibrations of hydrogen-bonded NH groups, is observed in the IR spectrum of a solid sample (in a KBr pellet) of II in the region of NH stretching vibrations. The certain increase in the  $\nu(\text{NH}\dots\text{O})$  band from  $3300$  to  $3350 \text{ cm}^{-1}$  may be associated with the participation of the oxygen atom of the  $\text{N} \rightarrow \text{O}$  group in the formation of intermolecular bonds, which leads to weakening of the intramolecular  $\text{NH}\dots\text{O}$  bond. A band at  $3374 \text{ cm}^{-1}$ , which can be assigned to the stretching vibration of the NH bond of an amino group intramolecularly bonded with the  $\text{C}=\text{N} \rightarrow \text{O}$  group, is observed in the IR spectrum of a solid sample of I.

In contrast to II, the absorption bands in the IR spectrum of I in the region of the vibrations of the hydrogen bonds are shifted to the lower-frequency region (broad absorption centered at  $\sim 2900\text{ cm}^{-1}$ ); this is evidently due to the formation of complex associates of the molecules through strong hydrogen bonds. The extremely low solubility of I in virtually all solvents may be associated with this.

A line of medium intensity at  $1620\text{ cm}^{-1}$  and a weak line at  $1595\text{ cm}^{-1}$  (see Table 1), which are not shifted in the case of isotope substitution of either the nitrogen atom of the N-O group or the nitrogen atom of the amino group, were observed in the Raman spectrum of I at  $1600\text{--}1800\text{ cm}^{-1}$ . In the IR spectrum these bands are overlapped by an intense band of the deformation vibrations of the  $\text{NH}_2$  group at  $1630\text{ cm}^{-1}$ . Similar bands were observed in the IR and Raman spectra of, for example, isatin  $\beta$ -oxime (IV) ( $1618$  and  $1593\text{ cm}^{-1}$ ) and 4-oximino-1H,3H-quinazolin-2-one (V) ( $1618$  and  $1590\text{ cm}^{-1}$ ), which is formed by refluxing I in solution in DMF (the Dimroth rearrangement [4]). The data presented above constitute evidence that these two vibrations are related to the stretching vibrations of the phenyl ring, i.e., I contains a phenyl ring, a fact that is not in agreement with the Ic structure.

The most intense line in the Raman spectrum of I at  $1472\text{ cm}^{-1}$ , which is absent in the Raman spectrum of V, can be assigned with a high degree of probability to the stretching vibration of the C=N bond of the C=N  $\rightarrow$  O group. The rearrangement of I to V is accompanied by conversion of the  $\text{H}_2\text{N-C=N} \rightarrow \text{O}$  fragment to  $\text{HON=C-NH}$  with no alteration of the remainder of the molecule. The disappearance of the intense line at  $1472\text{ cm}^{-1}$  in the Raman spectrum in this case constitutes evidence that it belongs to this fragment of the molecule. Replacement of the nitrogen atom in this group by the  $^{15}\text{N}$  isotope leads to a shift of the frequency to  $1467\text{ cm}^{-1}$ . Replacement of  $^{15}\text{N}$  in the amino group does not affect the frequency of this vibration. The vibration of the C=N bond, which participates in the formation of two rings, is complex. The insignificant shift of its frequency in the case of isotope substitution may be associated with this. The frequency of the stretching vibration of the C=N bond of the nitron group usually shows up at  $1500\text{--}1600\text{ cm}^{-1}$  [5, 6]. In the case of I the lower value of the  $\nu(\text{C=N})$  band is due to conjugation of the C=N bond with the phenyl ring and the carbonyl group, as well as to delocalization of the electron density within the chelate ring.

The band in the IR spectrum at  $1100\text{--}1300\text{ cm}^{-1}$  is related to the stretching vibration of the N $\rightarrow$ O bond [7-9]. The intense band at  $1152\text{ cm}^{-1}$  in the IR spectrum of I, which is shifted most markedly in the case of  $^{15}\text{N-O}$  substitution, corresponds to the stretching vibration of the semipolar N  $\rightarrow$  O bond.

A significant increase in the  $\nu(\text{CO})$  frequency is observed for compounds that contain a CO group adjacent to the strongly electron-acceptor N $\rightarrow$ O group. Thus the  $\nu(\text{CO})$  band in the spectrum of 4-methyl-4-ethyl-2-imidazolinone 1-oxide in the solid state (KBr pellet), in which it may be decreased due to the formation of hydrogen bonds, is observed at  $1800\text{ cm}^{-1}$  [9]. The  $\nu(\text{CO})$  frequency of I at  $1730\text{ cm}^{-1}$  shows up in the lower-frequency region as compared with the preceding example, since the carbonyl group in this case is located in a six-membered ring, while the decrease in the  $\nu(\text{CO})$  band is probably associated with a certain degree of change in the electronic properties of the C=N group due to the formation of intramolecular hydrogen bond, which leads to delocalization of the electron density within the chelate ring. However, the  $\nu(\text{CO})$  band in the spectrum of I nevertheless increases as compared with IV and V, which do not contain a nitron group.

Thus the data presented above constitute evidence that I exists in the 4-amino-1H-quinazolin-2-one 3-oxide form.

When I is allowed to stand in 15% hydrochloric acid, it is converted to the hydrochloride, by neutralization of which at pH 7-8 one can obtain I. The acidification of an aqueous suspension of I to pH 5-6 leads to the production of a substance, which, according to the results of elementary analysis, corresponds to the empirical formula of the dihydrate of I. Heating the hydrate in pure form or a solution of it in DMSO makes it possible to isolate unchanged I. One might have assumed that the dihydrate of I is either a covalent hydrate of I, which is stabilized by a second molecule of water, or simply a dihydrate. The IR and Raman spectra of the isolated hydrate at  $900\text{--}1800\text{ cm}^{-1}$  remain qualitatively unchanged, and one observes only a certain increase ( $1\text{--}10\text{ cm}^{-1}$ ) in most of the vibrational frequencies, which may be associated with a change in the distribution of the electron density in the I molecule due to incorporation of water molecules in polymeric associates. Somewhat more significant changes occur in the low-frequency region of the spectrum, in which the fre-

quencies of the deformation vibrations show up. The absorption in the region of hydrogen bonds in the IR spectrum of the hydrate is shifted to the higher-frequency region (broad absorption with maxima at 3360 and 3170  $\text{cm}^{-1}$ ); this is also probably due to weakening of the hydrogen bonds due to the incorporation of water molecules. These data indicate that a covalent hydrate is not formed and that the hydrate obtained is the dihydrate of I.

#### EXPERIMENTAL

The IR spectra of solid samples of the investigated compounds in KBr pellets were recorded at 250-4000  $\text{cm}^{-1}$  with a Perkin-Elmer 577 spectrometer. The Raman spectra were recorded with a Coderg T-800 spectrometer with excitation by light with wavelength 6328 Å from a helium-neon laser.

4-Amino-1H-quinazolin-2-one 3-Oxide. This compound was obtained as described in [1].

4-Amino-1H-quinazolin-2-one 3-Oxide with  $^{15}\text{N}$  Labeling of the Amino Group in the 4 Position. This compound was obtained from 2-cyanophenyl isocyanate with a  $^{15}\text{N}$ -labeled nitrile group by the method in [1].

4-Amino-1H-quinazolin-2-one 3-Oxide with  $^{15}\text{N}$  Labeling in the 3 Position. This compound was obtained by the reaction of 2-cyanophenyl isocyanate with  $^{15}\text{N}$ -labeled hydroxylamine by the method in [1].

4-Oximino-1H,3H-quinazolin-2-one. A solution of 0.01 mole of I in 50 ml of DMF was refluxed for 4 h, after which it was cooled and poured into a twofold amount of cold water. The resulting precipitate was removed by filtration and washed successively with water and alcohol to give a product with mp 272°C in 95% yield. Found: C 45.4; H 3.8; N 23.7%.  $\text{C}_8\text{H}_7\text{N}_3\text{O}_2$ . Calculated: C 45.2; H 3.9; N 23.7%.

Hydrochloride of I. A 0.01-mole sample of I was allowed to stand in 30 ml of 15-20% hydrochloric acid for one day, after which the precipitate was removed by filtration and recrystallized from methanol to give a product with mp 262-263°C in 92% yield. Found: C 44.8; H 3.8; Cl 16.4; N 19.6%.  $\text{C}_8\text{H}_8\text{ClN}_3\text{O}_2$ . Calculated: C 45.0; H 3.8; Cl 16.6; N 19.7%.

4-Amino-1H-quinazolin-2-one 3-Oxide Dihydrate. A solution of 0.01 mole of the hydrochloride of I in 50 ml of water was made alkaline to pH 5-6 or 8-9 with a 4% solution of potassium hydroxide, and the resulting precipitate was removed by filtration and washed with alcohol to give a product with mp 272°C in 87% yield. Found: C 45.0; H 5.2; N 19.6%.  $\text{C}_8\text{H}_{11}\text{N}_3\text{O}_4$ . Calculated: C 45.1; H 5.0; N 19.7%.

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