INFRARED ABSORPTION SPECTRA OF SOME C-HALOGENATED 1, 2, 4-TRIAZOLE DERIVATIVES

V. Ya. Grinshtein, A. A. Strazdin', and A. K. Grinvalde

Khimiya Geterotsiklicheskikh Soedinenii, Vol. 6, No. 2, pp. 248–258, 1970

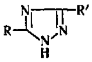
UDC 547.792:543.422.4

The IR absorption spectra of 3(5)-halo and 3, 5-dihalo derivatives of 1, 2, 4-triazoles and of their potassium and silver salts as solids in the 3500–400 cm^{-1} range were studied. The characteristic absorption bands of the triazole ring and the C—H and N—H bonds were established.

In the last ten years numerous investigations have been made of the synthesis and application of various derivatives of the 1, 2, 4-triazoles. There are no specific chemical reactions for distinguishing the triazole ring, and therefore the establishment of characteristic absorption bands in the IR spectra of 1, 2, 4-triazoles could facilitate identification of the compounds.

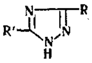
Only a few papers are devoted to the study of the IR spectra of 1, 2, 4-triazoles, however, and those available only contain particular data relating to the absorption bands. In some papers the absorption bands of the amino group in 3- and 4-amino-1, 2, 4-triazoles [1–6], and of the acetyl group in N-acetyl-1, 2, 4-triazole had been studied [3, 4, 7–9]. The data obtained were used to elucidate the tautomeric equilibrium of the aminotriazoles [2, 6]. The stretching vibrations of the N—H bond confirmed that the triazoles are strongly associated in the solid and in solutions [1, 2, 6, 9, 10]. Little is known concerning the assignment of the other absorption bands [1, 9, 11–13].

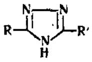
In the present work the absorption bands of 1, 2, 4-triazole and its C-halogenated derivatives, possessing a typical aromatic structure of the triazole ring, were studied. Theoretically it is possible for these compounds to exist in two (for R = R') or in three isomeric forms A—C depending on the position of the proton.

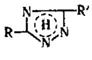

A

I R=R'=H;

IV R=H; R'=Cl


B


C


D

Certain substitution reactions at the ring nitrogen lead to formation of isomers which are derivatives of the basic forms A—C. Therefore, a formula was assumed with an indefinite position of the proton D, which however was not confirmed further.

By investigating the dipole moments of 1, 2, 4-triazole and 3-chloro-1, 2, 4-triazole in dioxane solution the existence was shown of these compounds in the forms I and IV, respectively [14].

Recently in a paper [15] dealing with the tautomeric equilibrium constant the suggestion was put forward that triazole existed as a mixture of isomers with a predominance of form I. Direct proofs of this suggestion have not been obtained as yet.

An ionic structure for triazoles in the crystalline state was proposed [16, 17] on the basis of the presence of the "imino band" $\geq N^{+}$—H in the IR spectrum at 1820 cm^{-1}, but the origin of this weak band has not been substantiated.

It is known that pyrazole exists as a cyclic trimer and a dimer even in dilute carbon tetrachloride solution [18]. A high degree of association of triazoles in the solid state is much more likely than their existence as ion pairs. Investigation of the IR spectra of triazoles in nonpolar solvents is extremely difficult due to their low solubility and low molar coefficients of absorption. Therefore, despite the complications in interpreting the IR absorption bands in the triazole spectra measured on the solids, such investigations are of the most practical application.

No data is available concerning the structure of the potassium and silver salts of 1, 2, 4-triazoles. In the triazole anion the same electronic charges are assumed on the N_1 and N_2 atoms, which possess a higher π-electron density compared with the N_4 atom [1]. This represents a symmetrical structure of the triazole anion.

The scarcity of available data on the fine structure of triazoles in the solid state only allows us to consider in the present work the main correlations between the structure and absorption of C-halogenated 1, 2, 4-triazoles.

In order to assist the assignment of the absorption bands of 1, 2, 4-triazoles, a number of the expected normal vibrations for a simplified model of the triazole molecule were determined, and a tentative assignment of the expected absorption bands of the bonds in the frequency range was made. The model of the 1, 2, 4-triazole molecule which we chose had the following limitations. First, the effect of the crystal lattice and molecular association was not taken into consideration. Second, we assumed a planar structure for the triazole molecules which we studied, and also a fixed position for the proton according to formula A. Third, the potassium salts of the triazoles were considered to be completely separated ions possessing the anion structures III and XIV.

The planarity of the ring structure has been established for a number of five-membered aromatic heterocycles and is also normally assumed for 1, 2, 4-triazole.

According to the indicated limitations of the chosen model 1, 2, 4-triazole possesses C_s symmetry and 18 normal vibrations.

III R=R′=H;
XIV R=R′=Br

The anions of 1, 2, 4-triazole and 3, 5-dibromo-1, 2, 4-triazole or their potassium salts according to the formulas III and XIV possess C_{2v} symmetry and 15 vibrations. In Table 1 the assignments are given of the normal vibrations according to bond type and the expected absorption range for 1, 2, 4-triazole and its anion. The indicated ranges are only tentative, since they are chosen in accordance with literature data, for example [19, 20], for the absorption of different azoles.

Table 1. Assignment of the Normal Vibrations of 1, 2, 4-Triazole and Its Anion According to Bond Type and Expected Absorption Interval

Compound	Class and Point Group Symmetry	Stretching Vibrations (ν)			In-plane deformation vibrations (β)			Out-of-plane deformation vibrations (γ)			Total
		ν_{N-H}	ν_{C-H}	ν_{ring}	β_{C-H}	β_{ring}	β_{N-H}	γ_{C-H}	γ_{ring}	γ_{N-H}	
III	C_{2v}										
	A_1		1	2	1	2					6
	B_1		1	2	1	1					5
	B_2							1	1		2
In all			2	4	2	3		1	1		13*
I	C_s										
	A′	1	2	4	2	3	1				13
	A″							2	2	1	5
In all		1	2	4	2	3	1	2	2	1	18
Expected absorption interval, cm^{-1}		3500—3300	3300—3000	1600—1250, 1350—1000 (breathing)	1300—1000	1200—800	1100—700	1000—600	800—500	Below 600	

---

*In addition there are two type A_2 vibrations, which are not active in the IR spectrum (one γ_{C-H} and one γ_{ring})

C—H Stretching vibrations (ν_{C-H}). One or two bands in the 3140–3090 cm^{-1} region. Sometimes masked by the absorption of associated N—H bonds.

N—H Stretching vibrations. 1, 2, 4-Triazole as the solid does not show free N—H absorption. A continuous absorption over a very wide range is observed, about 3200–2400 cm^{-1}, with several maxima. On N-deuteration continuous absorption occurs over a narrower frequency region, about 2400–1900 cm^{-1}, with a maximum evident at 2200 cm^{-1}, and several weak maxima. This indicates the complex nature of the absorption which arises.

C—H In-plane deformation vibrations (β_{C-H}). One or two (usually strong) bands develop in the 1230–1150 cm^{-1} region according to the number of C—H bonds.

Table 2. IR Spectra of Substituted 1, 2, 4-triazoles^{a}

1,2,4-triazole (I)	Silver salt of I (II)	Potassium salt of I (III)^{b}	3-Chloro-1,2,4-triazole (IV)	Proposed assignment
3138 (20)	3140 sh		3139 (10)*	ν_{C-H}
3128 (20)	3130 (20) b		3120 (10)*	ν_{C-H}
3200—			3200—	
2400(40—80)			2400 (40—80)	ν_{N-H} assoc.
1900—			1800—	
1750 (10—20)			1650 (5—10)	$2\beta_{N-H}$
1765 (30) b	1765—	1750 (10)	1770 (5) b*	$2\gamma_{C-H}$
	1735 (10)		1750 (3)*	
	1660—			
	1630 (5)			2(825)
1620—			1650—	
1590 sh			1590 sh	β_{N-H} + (683, 718)
1547 inflection	1560—	1530 ?	1540 sh	β_{N-H} + (650, 640) and
1533 (30)	1540 sh	1510 sh	1520 (70)	γ_{C-H} + (683, 663, 684, 640)
1485 (95)	1507 (70)	1490 (100)	1485 (80)	ν_{ring}
1440 sh	1410 sh	1460 sh		
			1430 sh	2(718)
1380 (60)	1340 (100) b	1385 (20)	1385 (70)	ν_{ring}
1360 (20)		1370 sh		2(683, 684)
			1350 (25)	640+718
1330 sh				650+683
1300 (30)				2(650)
1275 (100)	1290 (95)	1280 sh	1290 (100)	ν_{ring}
1258 (80)		1256 (90)	1270—	
1240—	1260—	1250 sh	1250 (90)	
1200 sh	1230 sh			
1185 (55)	1205 (20)	1200 (50)	1190 (60)	β_{C-H}
1153 (90)	1170 (90)	1158 (80)		β_{C-H}
1130 sh	1130 sh		1150 sh	
1110 sh				
1075 sh	1086 (60)	1070 (3)	1088 (60)	
1060 (60)			1065 sh	ν_{ring} (breathing)
1035 sh	1042 (5)	1030 (50)		
988 (95)	995 (60)	998 (40)	1003 (60)	β_{ring}
960 (70)	960 sh	987 sh	980 (50)	β_{ring}
940 inflection		980 (60)	900 sh	
890 (90) b	890 (40)	882 (70)	878 (80) b	γ_{C-H} } β_{N-H}^{d}
	825 (25)			
730 (5) b	720 (5) b			
683 (80)	663 (70) b	684 (40) b	718 (70)	γ_{ring}
650 (70)	635 (10) b		640 (40)	γ_{ring}
640—				
600 sh				
			515—	halogen dependent
			500 (20)	
430—	405 (5) b			
400 (5)				

Table 2 (cont'd)

N-Deutero IV (V)^c	Silver salt of IV (VI)	3-Bromo-1,2 4-triazole (VII)	Silver salt of VII (VIII)	Proposed assignment
3138 (50)*	3142 (10) b*	3130 (10)	3140 sh*	ν_{C-H}
3118 (45)*	3130 sh*		3130 (15) b*	ν_{C-H}
3090 sh		3200—		
3025 (3) b		2700 (40—80)		
2970—		2700—	2700—	
2830 (5—15)		2000 not recorded	2000 not recorded	ν_{N-H} assoc.
2770 (10) b				
2705 (10) b				
2580 (10)				
2400—				
2000 (30—90)				ν_{N-D} assoc.
1980 (20) b				
1880 (10) b				
1780 (5)*				2(898)
1755 (3)*	1750 (2) b		1770—	
			1730 (3)	$2\gamma_{C-H}$
		1740 (10) b		$2\beta_{N-H}$, $2\gamma_{C-H}$
			1700 (5) b	820+890
		1640 (2)	1640 (8) b	2(820)
1540 (3) b		1540 inflection	1525 sh	$\beta_{N-H}+638$,
	1520 sh	1520 (25)	1510 sh	640+898, $\gamma_{C-H}+\gamma_{ring}$
1486 (90)	1488 (95)	1478 (100)	1480 (80)	ν_{ring}
	1430 sh	1425 sh		
1430 (10)	1400 sh	1415 sh		2(718, 697, 708)
	1385 inflection			
1400 (85)	1365 (70)	1365 (70)	1375 (95) b	ν_{ring}
1355 (20)		1340 (40)		640+718, 638+708
1290 (100)	1327 (100)	1287 (55)	1315 (100)	
1270—	1280 (70)	1266 (70)	1282 (95)	ν_{ring}
1260 (80)		1245 (60)		
1227 (90)	1205 (70)	1180 (50)	1196 (50)	β_{C-H}
1190 sh				Impurity IV ?
1150 sh	1150 sh	1150 sh	1146 sh	
	1100 (5)	1120 sh		
1082 (50)	1060 sh	1080 (50)	1085 (10) b	ν_{ring}
1040 (25)	1040 (25) b	1040 sh	1038 (40)	(breathing)
1000 (10)	1005 sh		1010 sh	
972 (70)	990—	1000 (60)	990—	β_{ring}
	940 (3)	975 (15) b	950 (7)	β_{ring}
935 sh		910 (10) b	905 sh	
898 (30)*				γ_{C-H} $\beta_{N-H}{}^{r}$
882 (30)*	875 (20) b	872 (40)	890 (15) b	γ_{C-H}
	825 (8)	830 sh	820 (8)	
770 (3)		770 (5)		
	730 (3)	730 (8) b	730 (10) b	
718 (70)	697 (30)	708 (40)	692 (25)	γ_{ring}
640 (60) b	664 (40)	638 (40)	667 (40)	β_{N-D} and γ_{ring}
510—				
495 (20)	405 (15) b		425—	halogen dependent
			400 (15)	

Table 2 (cont'd)

3-Iodo-1,2,4-triazole (IX)	Silver salt of IX (X)	3-Chloro-5-bromo-1,2,4-triazole (XI)	3,5-Dibromo-1,2,4-triazole (XII)	Proposed assignment
3125 (10)	3125 (8) b			ν_{C-H}
3120—		3200—	3200—	
2700(40—80)		2700(40—85)	2390 (20—80)	
			3110 (75) b	
			2960 (75) sh	
			2900 (80) b	ν_{N-H} assoc.
			2800 (70) sh	
2700—			2750 (80) b	
2000 not	2500—	2700—	2500 (50) sh	
recorded	2000 not	2000 not	2410 (30) sh	
	recorded	recorded	2315 (10) b	
			2250 (5) b	
1840—		1660—	1650—	
1770 (40)		1590 (10)	1580 (10)	$2\beta_{N-H}$
1740 inflection				$2\gamma_{C-H}$
	1700 (10)			890+820?
	1660—			
	1610 (5)			2(820)?
		1535 (40) b	1535 sh	β_{N-H} + (638, 712, 708)
1545 (30) b			1518 (30)	γ_{C-H} + (638, 697, 666)
1530 sh	1510 sh			
1468 (80)	1475 (70)	1440 (80)	1425 (80)	ν_{ring}
1440 sh			1410 sh	2(697, 712, 708)
1400 sh		1410 sh	1390 sh	
			1360 (5)	656+708
		1370 sh		657+712
1348 (70)	1375 (90) b	1358 (30)	1340 (30)	ν_{ring}
1335 inflection				638+697
		1320 sh	1310 sh	2(657, 656)
1290 (70)	1340—	1293 (100)	1275 (100)	
1268 inflection	1300 (90)	1268 (80)	1255 (90)	ν_{ring}
1258 (65)	1278 (100)			
1228 (100)				ν_{ring} or β_{C-H}
1200 sh		1190 sh	1200 sh	
1178 (80)	1190 (40)			β_{C-H}
1150 sh	1150 (5)	1145 (25)	1135 (25)	
1072 (50)	1082 (7) b	1085 sh	1080 sh	ν_{ring}
1040 sh		1050 (4)		(breathing)
	1028 (25) b	1029 (90)	1021 (90)	
1000 (95)	1010 sh	1010 sh		β_{ring}
971 (50)		995 (40)	991 (40)	β_{ring}
960 inflection		970 sh	950 sh	
930 inflection				
878 (70)	890 (8) b			γ_{C-H} β_{N-H}^{r}
		850 (30) b	836 (30) b	β_{N-H}
850 sh	820 (5) b			
	768 (2)	750 (1)	730 (5) b	
697 (25)	687 (15)	712 (25)	708 (25)	γ_{ring}
638 (35)	666 (35)	657 (15)	656 (10)	γ_{ring}
		553 (40)		
		407 (30)	467 (40)	halogen dependent

Table 2 (cont'd)

Silver salt of **XII (XIII)**	Potassium salt of **XII (XIV)**^{b}	N-Deutero XII (XV)^{c}	Proposed assignment
		3115 (10) b	
		2960 (8) b	
		2915 (10) b	
		2800 sh	ν_{N-H} assoc.
		2780 (10)	
		2750 (8) b	
	2540 (5)	2548 (10)	
		2400—	
		2030 (30—90)	
	2290 (5) b	2315 (70) b	
		2240 (90) b	
		2180 (75) sh	ν_{N-D} assoc.
		2128 sh	
		2110 sh	
		1975 (10)	
		1918 (10)	
1640 (4) b			2(820)
1510 (2) b			697+820
1436 (80)	1423 (90)	1432 (95)	ν_{ring}
	1405 sh	1400 sh	2(710, 708)
1360 (95) b	1335 (60)	1395 (60)	ν_{ring}
		1365 (30)	
		1340 (10)	
1285 (100)	1258 (100) d	1270 (100) b	ν_{ring}
1185 (2)	1190 sh	1180 (4) b	
1150 (2)	1150 sh	1155 (40)	
1085 (4) b	1100 sh	1100 sh	
1039 (35)	1045 (35)	1040 (35)	ν_{ring}
1020 sh	1020 (20)	1020 inflection	(breathing)
	1010 inflection	1010 sh	
	1000 (80)	982 (70)	β_{ring}
	960 sh	950 (70)	
		900 sh	
820 (8) b	750 (10) d	750 (2)	
697 (25)	710 (50)	708 (25)	γ_{ring}
	678 (10)	668 (8)	γ_{ring}
		602 (40) b	β_{N-D}
500 (3) b		465 (45)	halogen dependent
428 (5) b			

<u>Note:</u> (a) In parentheses is given the relative intensity of the band, as percentage intensity of the strongest absorption band of the compound; γ: stretching vibrations; β: deformation vibrations in the plane of the ring; γ: deformation vibrations out of the plane of the ring; b designates broad; sh, shoulder. All frequencies given in cm^{-1}.

(b) Increased background for the potassium salts of III at 3650-2700, 1700-1630, 850-450, and of XIV at 3500-2800, 1680, 800-500 cm^{-1}, which must be due to water impurity in the carbonates.

(c) The compounds were about 90% N-deuterated.

(d) The absorption frequency β_{N-H} is estimated for the following compounds approximately: I: 920-900, IV: 900, VII: 900, IX: 915 cm^{-1}.

*Frequencies by which the presence of the two isomers can be judged.

N—H in-plane deformation vibrations ($\beta_{N—H}$). A characteristic broad band of medium intensity, with both sides mildly sloping, is found in the 950-830 cm^{-1} region. On N-deuteration it appears in the 700-600 cm^{-1} region and has the same characteristic form. The ratio of the frequencies of the N—H and N—D bonds are as follows: 3-chloro-1,2,4-triazole, 1.375; 3,5-dibromo-2,4-triazole, 1.380.

With increase in acidity of the azole the ring nitrogen proton bond is weakened and a reduction in the absorption frequency may be expected. For pyrazole, the acidity of which is far less than the acidity of triazole, the $\beta_{N—H}$ vibration is observed at 1150 cm^{-1} [19]. In a number of 1, 2, 4-triazoles a similar dependence is observed (Table 2); for example, the more acidic compound XII has a lower absorption frequency. This frequency cannot be established accurately for 1, 2, 4-triazole since there are other absorption bands in this region. It is possibly the one at 940–900 cm^{-1}. In the metal salts of 1, 2, 4-triazole this band disappears.

C—H Out-of-plane deformation vibrations ($\gamma_{C—H}$). The presence of a free C—H bond is disclosed by the absorption at about 900–850 cm^{-1}, where there is a band of medium or weak intensity. For N-nonsubstituted triazoles the band is masked by the N—H absorption. For 1, 2, 4-triazole and its metal salts an intense band is observed at ~880 cm^{-1}. A second absorption band for the C—H bond (symmetric vibration) of 1, 2, 4-triazole could not be found. The silver salts of the 3-halo substituted triazoles possess a single broad absorption band at 890–875 cm^{-1}, and the N-deutero-3-chloro-1, 2, 4-triazole (V) has two bands (at 898 and 882 cm^{-1}). All these vibrations have weak overtones, observed also for compound IV. The assumption that these two bands (or broadening of one band) are due to C—H vibrations of two isomeric compounds is confirmed by the presence of two absorption bands in the C—H stretching vibration region.

N—H Out-of-plane deformation vibration ($\gamma_{N—H}$). We were unable to detect absorption due to this vibration, nor, on N-deuteration, could we observe the appearance or disappearance of any of the bands in the 900–400 cm^{-1} region, except the $\beta_{N—H}$ vibrations. The $\gamma_{N—H}$ absorption band of pyrrole is found at 565 cm^{-1} [19]. It may be assumed that the absorption due to the $\gamma_{N—H}$ vibrations of 1, 2, 4-triazoles when studied as solids is very weak or is found below 400 cm^{-1}.

Ring stretching vibrations (ν_{ring}). For a variety of azoles the ring stretching vibrations give rise to absorption bands in the 1600–1250 cm^{-1} region [19-21]; however, in some cases the absorption due to the ring-stretching vibration is reduced to 1100–900 cm^{-1}. It may be noted that there are also combination frequencies in the 1700–1500 cm^{-1} region which often lead to an erroneous assignment of ring stretching vibrations.

The appearance of four absorption bands may be expected for the ring stretching vibrations of the 1, 2, 4-triazoles (Table 1). Three of these are to be found in the 1520–1240 cm^{-1} region. The frequency of each absorption band regularly changes on passing from one compound to another.

First band (1520–1420 cm^{-1}). The frequency of the absorption bands depends: (a) on the halogen, falling in the series chloro, bromo, iodo derivative; (b) on the symmetry of the substituents in ring positions 3 and 5, nonadditively falling on passing from 3-halo to the 3, 5-dihalo derivative; (c) to a small extent on passing to the triazole metal salts. The band is one of the strongest in the spectrum, its low dependence on external environment (intermolecular association) makes it the most reliable for identifying the triazole ring.

Second band (1410–1340 cm^{-1}). A dependence of the frequency on the halogen in position 3 of the triazole ring is more evident than for the first band. Intermolecular associations and conversion to the triazole metal salts strongly affect the frequency and intensity of the band. The band is usually of medium or high intensity); for the silver salts it is very broad and very strong. For compounds II and XIII there is continuous absorption in the 1420–1300 cm^{-1} region with a single maximum. Compounds VI, VIII and X show continuous absorption at 1440–1300 cm^{-1} with two maxima. The maximum with the lower frequency is now assigned to the third absorption band. Because of the variability in intensity and the presence in this region of combination frequencies the second band is less reliable for identifying the triazole ring.

Third band (1320–1240 cm^{-1}). For N-unsubstituted 1, 2, 4-triazoles and the silver salts of the 3-halo derivatives VI, VIII, X the band is split into 2–3 separate absorption bands. Often this band appears as the strongest in the spectrum, particularly if the splitting is taken into consideration. The potassium salts (III, XIV) show a single absorption band, the frequency coinciding with the lower absorption band of the corresponding N-unsubstitutted triazoles. This suggests assignment of the lower absorption band of N-unsubstituted triazoles to a vibration of the anionic forms. The silver salts absorb at high frequencies, which indicates a reduction in the degree of conjugation between the formal double bonds of the triazole ring. The presence of three bands in this region for 3-halo derivatives of the triazole and two for their silver salts can be explained by the presence of isomers. The third absorption band of the triazole ring depends very little on the nature of the halogen in positions 3 and 3.5, and does not change on N-deuteration. It can be considered reliable for identifying 1 H-1, 2, 4-triazoles, for studying the degree of conjugation in the triazole ring, and for detecting isomers.

Fourth band (1100–1020 cm^{-1}). We assign a set of several absorption bands in this region to the absorption due to ring-stretching vibrations on the basis that the character of the frequency changes in the series of compounds we investigated had a similarity with other absorption bands of the triazole ring. Usually there is a single strong band which often is split into two bands of medium intensity, or into 2–3 bands of medium to weak intensity. It may be noted that a number of the silver salts in the 900–1160 cm^{-1} region always have a single absorption band of medium intensity which could also be assigned to ring deformation vibrations.

The fourth band has little dependence on the halogen in the triazole ring, but greater dependence on the symmetry of the substituents in positions 3 and 5. 1, 2, 4-Triazole (I) absorbs at 1060 cm^{-1} and splitting occurs on both sides of the band (at 1075 and 1035 cm^{-1}), the frequencies of which approximately coincide with the intense absorption bands of its potassium and silver salts, as occurs for the third absorption band of the ring. 3-Halo derivatives of I absorb at higher frequencies, 3, 5-dihalo derivatives at lower frequencies.

Ring deformation vibrations (β and γ_{ring}). Of the three deformation vibrations in the plane of the ring two bands are to be found in the 1020–950 cm^{-1} region. For the silver salts they are usually of very low intensity. For the other compounds one or two of the bands have high intensity and because of the constancy of the frequency can serve for identification of the triazole ring.

The out-of-plane deformation vibrations of the triazole ring absorb in the 720–630 cm^{-1} region where there are two bands of medium, more rarely high, intensity. For the potassium salts (III and XIV) only one absorption band may be expected to appear in this region (Table 1) provided the salts are completely separated ions. Compound III does in fact have one absorption band. On passing from XII to XIV the band at 467 cm^{-1} unexpectedly disappears, which, however, is not possible to assign to absorption of the ring γ-vibration. One absorption band of the ring γ-vibration (usually in the 710–680 cm^{-1} region) has a more constant frequency and helps in identification of the triazole ring. A number of triazoles have a weak absorption at ~730 cm^{-1}; the silver salts, in addition, have a weak band at ~830 cm^{-1}. The latter gives an overtone and combination frequency with the $\gamma_{\text{C—H}}$ similar to the ring γ-vibrations, as shown below. Therefore we assume that both these weak absorption bands can be assigned to the ring γ-vibrations of the isomeric structure.

Combination Frequencies and Other Absorption Bands. Absorption in the 600–400 cm^{-1} region can be due to vibrations of the C-halogen bond vibrations, for aliphatic compounds are inapplicable for certain aromatic and heterocyclic compounds [22–26]. Many 3- and 3, 5-halo derivatives of 1, 2, 4-triazoles do not show any absorption bands in this region.

In the 1200–1100 cm^{-1} region, besides the intense absorption bands due to $\beta_{\text{C—H}}$ vibrations there are two weak bands (for the compounds XI, XII, XV one of them is of medium intensity), the assignment of which is not established.

In Table 2 the combination frequencies are indicated, which were verified for all the compounds. The weak (for 1, 2, 4-triazole medium intensity; very broad absorption in the 1900–1750 cm^{-1} region is due to an overtone of the $\beta_{\text{N—H}}$ vibration which as in the fundamental vibration is reduced in frequency with increase in acidity of the triazole. The very broad absorption band of the overtone and fundamental $\beta_{\text{N—H}}$ vibrations is caused by intermolecular association. The overtone of the $\gamma_{\text{C—H}}$ band vibration absorbs in the 1780–1730 cm^{-1} region and is of medium intensity for 1, 2, 4-triazole but very weak for its 3-substituted derivatives. Overtones and a mutual combination frequency were observed for both ring γ-vibrations, which absorb in the same region where there is absorption due to ring-stretching vibrations. In the 1560–1500 cm^{-1} region a weak absorption due to a combination frequency of the $\gamma_{\text{C—H}}$ and γ_{ring} vibrations is noted. Compounds possessing a N—H bond give in this region a broad absorption of medium intensity of the combination frequency between the $\beta_{\text{N—H}}$ and γ_{ring} vibrations. There is no reason to assume that the 1, 2, 4-triazoles which we studied as solids possess absorption bands due to ring stretching vibrations in the region above 1520 cm^{-1}.

EXPERIMENTAL

IR spectra were measured on a UR-10 instrument. The substances were prepared as suspensions in nujol and hexachlorobutadiene.

Compounds IV and VI–X were prepared as described [27, 28]; II and XIII were prepared similarly. Regarding the preparation of compounds XI, XII see [29–31]. Deuterium exchange was carried out by heating at boiling 1 hr with subsequent concentration (compound V), or twice recrystallizing (compound XV), using deuterium oxide (99.9%).

The potassium salts (compounds III, XIV) were prepared by evaporating to dryness aqueous solutions of compounds I and XII with the equivalent amount of KOH and subsequent treatment with boiling absolute alcohol, ether, and drying in vacuum over P_2O_5 at 100° C.

REFERENCES

1. K. T. Potts, Chem. Rev., **61**, 87, 1961.
2. G. I. Chipen and V. Ya. Grinshtein, Izv. AN LatvSSR, ser. khim., 401, 1962.
3. G. I. Chipen and V. Ya. Grinshtein, Izv. AN LatvSSR, ser. khim., 503, 1962.
4. G. I. Chipen, V. Ya. Grinshtein, and A. K. Grinvalde, Izv. AN LatvSSR, ser. khim., 495, 1962.
5. H. M. Randall, R. G. Flower, N. Fuson, and I. R. Dangl, Infrared Determination of Organic Structures, N. Y., 78, 1959.
6. E. Akerblom and M. Sandberg, Acta Chem. Scand., **19**, 119, 1965.
7. W. Otting, Chem. Ber., **89**, 1940, 1956.
8. H. Staab and G. Seel, Chem. Ber., **92**, 1302, 1959.
9. K. T. Potts, J. Chem. Soc., 3461, 1954.
10. U. Croatto and A. Fava, Ann. Chim., Rome, **54**, 1340, 1964.
11. E. Lieber, D. R. Levering, and L. J. Patterson, Anal. Chem., **23**, 1594, 1951.
12. D. W. Kaiser and G. A. Peters, J. Org. Chem., **18**, 196, 1953.
13. H. G. O. Becker, H. J. Moll, and H. Haufe, Wiss. Z. Tech. Kochsch. Chem. Leuna-Marseburg, 8, 120, 1966.
14. I. B. Mazheika, G. I. Chipen, and S. A. Hiller, KhGS [Chemistry of Heterocyclic Compounds], 776, 1966.
15. C. F. Kröger and W. Freiberg, Chimia, **21**, 161, 1967.
16. W. Otting, Chem. Ber., **89**, 2887, 1956.
17. W. Otting, Angew. Chem., **68**, 417, 1956.
18. D. M. W. Anderson, J. L. Duncan, and F. J. C. Rossotti, J. Chem. Soc., **140**, 1961.
19. A. R. Katritzky, ed., Physical Methods in Heterocyclic Chemistry [Russian translation] Khimiya, Moscow and Leningrad, 504, 532, 1966.
20. E. Borello, A. Zecchina, and A. Appiano, Spectrochim. Acta, **22**, 977, 1966.
21. M. P. W. Mijovič, and J. Walker, J. Chem. Soc., 3381, 1961.
22. J. N. Rai and K. N. Upadhya, Spectrochim. Acta, **22**, 1427, 1966.
23. G. Joshi and N. L. Singh, Spectrochim. Acta, 22, 1501, 1966.
24. V. B. Singh, R. N. Singh, and I. S. Singh, Spectrochim. Acta, **22**, 927, 1966.
25. M. Horak, I. J. Hyams, and E. R. Lippincott, Spectrochim. Acta, **22**, 1355, 1966.
26. V. E. Volkov, V. S. Korobkov, A. V. Korshunov, and M. I. Remarchuk, collection: Application of Molecular Spectroscopy in Chemistry [in Russian], Moscow, Nauka, 50, 1966.
27. J. Thiele and W. Manchot, Ann., **303**, 33, 1898.
28. W. Manchot and R. Noll, Ann., **343**, 1, 1905.
29. C. F. Kröger and H. Frank, Angew. Chem., **77**, 429, 1965.
30. W. Freiberg and C. F. Kröger, Chimia, **21**, 159, 1967.
31. V. Ya. Grinshtein and A. A. Strazdin', KhGS [Chemistry of Heterocyclic Compounds], 1114, 1969.

11 September 1967.

Institute of Organic Synthesis, AS Latvian SSR, Riga