IR SPECTRA AND RAMAN SPECTRA OF DI- AND TRISUBSTITUTED ISOCYANURIC ACIDS

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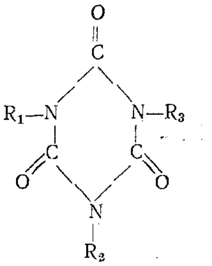
UDC 535.33

The amount of experimental data on the vibrational spectra of substituted isocyanuric acids (I, where R_1, R_2, and R_3 are substituted alkyl groups)



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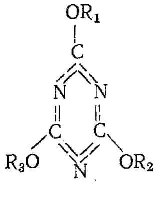

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that is available in the literature is limited [1]. Only data on the IR spectra of triallyl isocyanurates ($R_1 = R_2 = R_3 = CH_2{-}CH{-}CH_2{-}$) are available [2, 3]. There are no data on the Raman spectra.

The IR and Raman spectra of derivatives of isocyanuric acid were measured in the present study in order to refine the assignment of the bands, establish the dependence of the frequencies in the vibrational spectra on the molecular structure, and to expose the diagnostic features.

The IR spectra of the investigated compounds were obtained with a UR-20 spectrophotometer at a scanning rate of 160 cm^{-1}/min with slit program 4. The solids were pressed into KBr pellets, and the liquids were placed between polished KBr plates to record the spectra.

The Raman spectra were obtained with a Coderg PHo spectrophotometer. The spectra were recorded at a scanning rate of 50 cm^{-1}/min and a slit width of 4 cm^{-1}. The intensities of the lines were determined by measurements of the peaks by the base-line method with allowance for the spectral sensitivity of the photomultiplier from the manufacturer's data. The intensity of the maximum band was taken as 10 units.

1,3,5-Triallyl isocyanurate (mp 24.5°C) was synthesized from potassium cyanate and allyl bromide in dimethylformamide at 145-150°; 1,3-diallyl isocyanurate (mp 138-142°) was obtained by acidification of the filtrate from the separation of 1,3,5-triallyl isocyanurate with hydrochloric acid; 1,3,5-tricyanoethyl isocyanurate and 1,3,5-tricarboxyethyl isocyanurate were obtained by previously described methods [4, 5] (the products melted at 223-226°); 1,3-dicyanoethyl isocyanurate (mp 211-212°) was obtained by acidification to pH 1-2 of the filtrate obtained after separation of 1,3-5-tricyanoethyl isocyanurate; 1,3-dicarboxyethyl isocyanurate (mp 287-289°) was obtained by hydrolysis of 1,3-dicyanoethyl isocyanurate in acid medium at 110°; trihydroxyethyl isocyanurate (mp 127-132°) was obtained by the method in [6].

The results of the investigation are presented for trisubstituted ($R_1 = R_2 = R_3$) and disubstituted ($R_1 = R_2$, $R_3 = H$) isocyanuric acids (Tables 1 and 2). We propose the band assignments in Tables 1 and 2 on the basis of a comparison with the spectra of other compounds with similar structural groups, by comparison of the relative intensities in the Raman and IR spectra, and from the results of measurements of the degree of depolarization. The designations of the vibrations were taken from [7].

Translated from Zhurnal Prikladnoi Spektroskopii, Vol. 17, No. 4, pp. 661-665, October, 1972. Original article submitted July 22, 1971.

TABLE 1. IR and Raman Spectra of Trisubstituted Isocyanuric Acids (N—R form of substitution)

Assignment	Trihydroxyethyl isocyanurate, R = —CH_2CH_2OH			Tricyanoethyl isocyanurate, R = CH_2CH_2CN			Tricarboxyethyl isocyanurate, R = —CH_2CH_2COOH		Triallyl isocyanurate, R = —$CH_2CH=CH_2$		
	I	II	Raman spectrum of P—P in H_2O_2	ρ	I	II	I	II	I	II	ρ
			190(2)	0		206(1)					
						215(2)					
$\gamma_{C=C-C}$						231(1,3)		245(0,3)			
		288(1,2)				326(0,5)		305(0,4)		295(—0,35)	0,32
γ_{OCC}						342(0,5)		340(0,3)			
						362(0,2)		355(0,7)		360(0,3)	0
$\gamma_{NC=C}$						372(1,8)					
						381(0)					
γ_{CNC}	410m	410(0,4)			403m	406(2)	405w	410(0,4)	413m	415(0,4)	0,37
	425m	420(0,8)									
		430(0,6)									
		440(1,6)									
E', $\gamma_{C-C=O}$	443w	445(0,4)			447s	450(0,5)	447s	445(1,3)	457w	467(—0,8)	0,75
		462(0,8)	465(0,5)	0,49							
γ_{NCN}	545w	474(1,7)	477(0,7)	0,59	488m	490(0,6)	498m	490(0,6)	497w		
γ_{CNC}	560m	567(0,6)			573w	546(2)—	547vw		550m	545(0,6)	0,38
		600(0,6)	595(1,4)	0	600w	600(4,6)	610vw	612(2,3)			
	625m	628(cp4)	645(0,5)	0	675w	690(7,3)	683w	680(1)	665m	677(7,5)	0,15
		702(5)	700(5,5)	0,15			730w	727(2)			
Q_{C-C}	733w		750(0,3)	0	755w	755(0,5)	725vw		745w		
A_2'', ring	775s		777(0,4)	0	781s		767s		775vs		
ρ_{CH_2}, ρ_{CCH}	803vw					815(1,3)	810vw	812(1)			
					840w	837(0,7)		835(0,8)			
Q_{C-N}, ρ_{OCH}		855(2,1)			850w	850(1,2)					
	870vw		865(0,4)	0	860w						
Q_{C-O}, β_{NCN}	897m	900(0,1)	880(0,6)	0,4	882w				890vw	880(0,2)	0,45
A_1', ring	915w	915(0,9)			925w	922(0,9)	920m	925(3,6)	940s	935(1,7)	0,2
	960vw	1038(1)	1030(0,8)		980m				1000s	993(0,7)	0,55
	1005w	1059(0,4)	1060(0,4)	0,48	1000w						
	1041s	1075(0,2)	1075(0,5)	0,65	1020w	1020(1,3)	1025w				
	1062s	1105(1,8)			1060w	1048(1,4)	1045w	1060(0,7)	1075w		
		1129(0,1)					1070w	1070(0,6)	1110w	1110(0,2)	0,48
β_{CH_2}, E'	1160m	1150(0,2)	1170(0,5)		1160w	1160(1,3)	1175s	1165(0,6)	1162w	1195(0,4)	0,68
	1260sh	1250(1,6)			1230vw	1225(0,9)	1220s				
	1280w	1260(0,4)	1265(0,8)	0,4	1240	1240(0,8)	1248	1265(0,8)		1240(0,4)	0,45
	1320sh	1320(1,6)			1270w		1290w		1290m	1285(6)	0,34
					1300s	1305(1,6)	1325w		1320s	1326(0,6)	0,7
	1335w	1337(0,4)	1330(0,8)	0,61	1340vw	1345(0)	1340w	1335(0,8)	1345m	1350(0,6)	0,37
	1365s	1365(0,2)			1350w	1355(1,6)					
	1380sh	1385(0,3)			1363s	1375(2,5)			1360vw		
		1415(0,6)			1420vw	1415(1,2)		1412(1)	1415m	1410(3,4)	0,63
		1436(0,9)	1427(1,5)	0,55		1435(1,6)			1430vw		
		1477(0,8)	1465(1,3)	0,57	1450vw	1442(1,6)		1450(1,9)		1445(3,6)	0,75
E', ring	1475vs				1475vs		1485s		1460vs		
$Q_{C=C}$							1655vw	1650(0,5)	1640vw	1640(10)	0,09
E', $\nu_{C=O}$	1695vs				1705s		1700s		1690s		
		1755(4,2)	1757(10)	0,08		1753(9,6)	1765s	1760(10)		1755(5,5)	0,14
A_1', ν_{CO}					2255s	2250(10)					
					2269m	2262(4)					
—C≡N											
		2812(0,8)									
			2900(3,8)								
	2905m	2942(9,5)	2950(1,7)	0,47	2946m	2945(3,2)	2950m	2940(3,5)			
$\bar{q}_{CH_2}$					2962w						
		2975(3,9)	2975(0,7)	0,21	2978m	2975(0,7)					
$\bar{q}_{OCH_2}$	2990m	3000(2,3)			2990w	2985(7,5)		2985(0,6)	2995m	2983(1,5)	0,27
								3007		3012(2,3)	0,29
		3025(0,7)	3025(2,7)	0,75	3036m	3030(3)		3025(0,8)	3025sh		
		3045(1)						3043(0,8)			
q_{OCH_2}		3125(2,1)						3061(0,8)	3090m	3087(2,1)	0,72
		3298(2,9)									
	3290s										
	3400m										
ν_{OH}											
	3505m										

Note: I denotes the IR spectra, while II denotes the Raman spectra.

TABLE 2. IR and Raman Spectra of Disubstituted Isocyanuric Acids (—P form of substitution)

Assignment	Diallyl isocyanurate, R = $-CH_2CH=CH_2$	Dicarboxyethyl isocyanurate, R = $-CH_2CH_2COOH$			Dicyanoethyl isocyanurate, R = $-CH_2CH_2CN$	
	I	II	I	II	I	II
$\gamma_{C=C-C}$						222(2)
						343(1)
γ_{OCC}				360(0,6)	403 w	361(2)
γ_{COC}	400 s		430 m		441 m	385(1)
	420 w		443 m	445(3)	454 m	445(2)
γ_{CNC}, $\gamma_{NC=C}$	465 w	465(3)	513 m		483 m	480(1,3)
			538 s	535(0,6)	512 m	505(2)
A_2', γ_{NCN}, γ_{CNC}	560 m	565(1)	585 vw		587 m	
	603 s	600(2)				
	627 w		650 w	650(2)		
A_1', ring	683 w	685(10)	693 w	688(7)	645 m	655(10)
Q_{C-C}	733 w		733 w		724 w	715(0,9)
			775 vs		763 s	
A_2'', ring	765 vs		790 m		820 w	815(2)
	784 s				860 m	
A_1', ring	925 vw	925(1,5)	915 m	922(2)	925 vw	917(0,6)
β_{CH_2}, ρ_{CCH}	945 s				970 m	
Q^{+}_{C-O}, β_{CNH}	990 m		1010 w		988 m	
	1070 w		1060 w	1053(1,4)	1022 w	1015(2)
Q^{-}_{C-O}, β_{NCH}			1135 m	1135(0)	1145 w	1141(0,8)
E', β_{CH_2}	1140 m	1140(0)	1175 w		1160 w	1160(0,7)
			1215			1195(0,6)
			1235 s		1253 w	1241(1)
			1300 m		1303 m	1300(1)
				1343(1)		1347(0,7)
	1317 s	1325(1)				
$\alpha^{+}_{CH_2}$, $\beta_{C=C-H}$	1355 s	1365(1)	1385 w	1390(0,5)	1367 s	1355(0,8)
α_{HCH}	1400 s	1410(4)	1410 s	1415(2)	1412 s	1400(1)
	1450 vs	1430(1)	1432 w	1435(1,5)	1428 s	1448(2)
A_2'', ring	1470 vs		1480 vs		1475 vs	
$Q_{C=C}$	1655 vw	655(4)				
E', ν_{CO}	1690 vs		1688 vs			
A_1', ν_{CO}	1735 vw	1745(10)	1730 vs	1757(10)	1720 vs	1725(1)
						1755(6)
$-C\equiv N$					2257 m	2245(5)
						2265(1)
	2800	2957(6)	2830 vw		2840 vw	2940(2)
	2960 w	2993(4)	2930 vw	2957(7)	2910 w	2975(2)
q_{OCH_2}	3040	3035(5)		2970(6)		3000(0,5)
	3115 m	3090(2)	3130 m	2995(8)	3050 m	3043(2)
	3190 vw			3033(3)	3100 m	3095(1)
ν_{NH}	3245 vs		3250 s		3230 m	3220(4)

The characteristic vibrations of the sym-triazine ring and of the carbonyl groups are diagnostic features of the isocyanuric acid derivatives (N—R substitution). Of the characteristic bands of the sym-triazine ring, the most convenient are the bands at 763-781 cm^{-1} (A_2'') and 1450-1480 cm^{-1} (E'), which are very intense in the IR spectra and of low intensity in the Raman spectra. The corresponding bands of the derivatives of normal cyanuric acid (II) with OR substitution have frequencies of 805-825 and 1555-1585 cm^{-1}. The decrease in the frequencies in the isocyanurates may be associated with a decrease in the multiplicity of the ring C—N bonds, which leads to a corresponding decrease in the force constants and frequencies in the vibrational spectra. The band at 635-683 cm^{-1} (A_1'), which is very intense in the Raman spectra and less intense in the IR spectra, should be assigned to the characteristic bands of substituted isocyanurates.

The valence vibrations of the carbonyl groups appear as two bands. The symmetrical band at 1730-1760 cm^{-1} in the trisubstituted derivatives appears only in the Raman spectra and has a low degree of depolarization. In the disubstituted derivatives, this band is observed not only in the Raman spectra but also in the IR spectra; this indicates a decrease in the symmetry to C_{2v} (diallyl isocyanurate); this band is absent in the IR spectra of the other compounds (dicyanoethyl isocyanurate), which attests to retention of the D_{3h} symmetry of the ring. The high frequency of the symmetrical vibration of the carbonyl groups confirms the previously drawn conclusion regarding the noncharacteristic nature of this vibration with respect to its form because of the participation in it of other coordinates of the $O = C{<}^{N}_{N}$ grouping. The observed correlation [8] between the frequency and multiplicity of the bond is therefore inapplicable here.

Completely unexpected results were obtained in the Raman spectra for the second band of the carbonyl group at 1690-1720 cm^{-1}, which should be assigned to E' symmetry. Despite the fact that it is permitted by the selection rules, it is not observed in the Raman spectra of both tri- and disubstituted compounds.

The characteristic vibrations of the substituting groups ($-OH$, $-CH = CH_2$, COOH, and $-C-N$) appear in the spectra independently of one another without any signs of interaction. The splitting of these bands that is observed in a number of cases ($-OH$ and $-C \equiv N$) is due not to the symmetry properties but to other reasons (intermolecular interaction and Fermi resonance).

In conclusion, the authors sincerely thank A. V. Ioganseen and B. V. Rassadin for placing the PHo spectrometer at our disposal and for their assistance in this research.

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