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CARBAMATE-GROUP CONFORMATION AND IR BAND INTENSITIES

V. L. Furer

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The carbamate group HNCOO appears in many biological compounds and in the polyurethanes, which have many industrial uses [1]. Also, carbamates combine the properties of esters and amides while having some distinctive features. The vibrational spectra of carbamates and polyurethanes have been examined in detail [2—4], and the IR band intensities have been calculated; the force constants and electrooptic parameters have been derived for the simplest carbamates [5].

Those parameters are used here to derive the IR spectra for various conformations of the carbamate group in simple compounds and model polymers. Such calculations are required in order to interpret polyurethane spectra for the various modifications.

Methyl-N-methylcarbamate $CH_3COONHCH_3$ (I) can be made in two crystalline forms, while a liquid specimen is a mixture of the trans and cis conformations for the C—N and O—CH_3 bonds [6]. We have calculated the IR frequencies and intensities for the trans and cis forms of I with an ES-1033 computer and the [7] suite on the basis of the [5] parameters for the carbamate group (Table 1). Those frequencies and intensities differ for the two conformers. Between the trans and cis forms, the amide I band is displaced from 1736 to 1748 cm^{-1}, while the intensity increases. The observed spectra in that region also differ [6]. The IR spectrum for the more stable form has the A band for amide I of simpler shape and lower frequency than that for form B, where it consists of three equal-intensity components. This has been interpreted [6] as due to stronger H bonds in crystalline form A. Our calculations show that the shift in the amide I band to higher frequencies in the observed spectrum for form B is due to the conformation as well as the hydrogen bonds.

The amide II band in the observed spectrum for crystalline form A lies at 1540 cm^{-1}. The band shape alters in crystalline form B on account of a rise in the low-frequency flank. The calculations indicate that the amide II band is shifted to the low-frequency side and reduced in intensity for the cis form.

The amide III band at 1250 cm^{-1} alters little between the conformations; its total intensity in each case is comparable with the observed intensity of I as determined in solution in carbon tetrachloride, where the two conformations are in equilibrium.

The intensity of the 1164 cm^{-1} band calculated for the trans form is almost three times that for the cis form, which is a difference from the observed increase in intensity between crystalline forms A and B.

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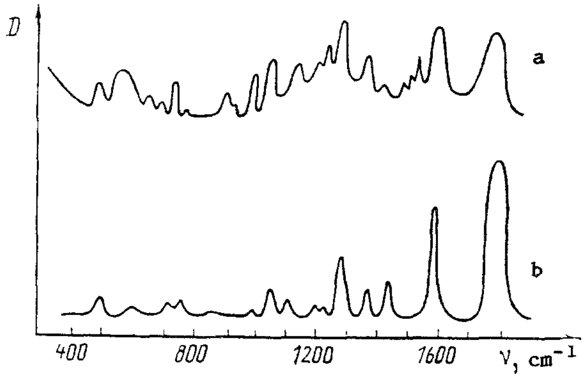

Fig. 1. Observed (a) and theoretical (b) IR spectra for hexamethylene dimethylurethane.

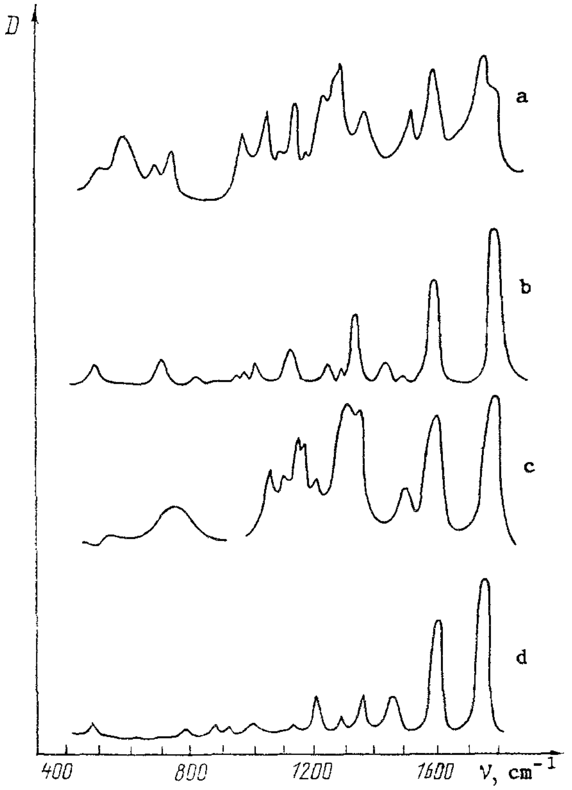

Fig. 2. Observed (a, c) and theoretical (b, d) IR spectra for the α form of 4,6-PU (a) and 2,2-PU (b), and the γ form of 2,6-PU (c) and the γ_2 form of 2,2-PU (d).

The 1115 cm^{-1} band for vitreous I vanishes on crystallization. The theoretical spectrum for the trans form contains the 1112 cm^{-1} band having intensity $13.6 \cdot 10^{-8}$ cm^2/sec, which corresponds to the 1077 cm^{-1} band with intensity $2.2 \cdot 10^{-8}$ cm^2/sec for the cis form. However, the IR spectra for the two crystalline forms do not have any bands of appreciable intensity in that region.

The 900 cm^{-1} band in the observed spectrum for crystalline B is of higher intensity than that for A, which agrees well with the predicted intensity increase for it for the cis form.

The observed spectra for the two crystalline forms of I are thus closely described by our calculations on the trans and cis conformations for the carbamate group.

TABLE 1. Observed Frequencies and Ones Calculated for Various Conformations ν (in cm^{-1}) together with Band Intensities I (10^{-8} cm^2/sec) for Methyl-N-methylcarbamate

Experiment		Theory				Vibration assignment
		trans form		cis form		
ν	*I*	ν	*I*	ν	*I*	
3474	24	3470	25	3470	25	Amide A
1737	238	1736	257	1748	270	Amide I
1520	132	1510	103	1502	84	Amide II
1465	24	1461	5,4	1462	7,4	(O)CH_3-deformation
		1439	0,2	1435	3,0	(O)CH_3-deformation
1422	12	1436	13	1439	14	(N)CH_3-deformation
1347	14	1381	28	1378	25	(N)CH_3-deformation
1250	124	1290	50	1287	56	Amide III
1196	14	1164	9,0	1162	2,8	C-O stretching
1143	22	1144	2,4	1146	3,4	C-N stretching
1107	18	1112	14	1077	2,2	(O)CH_3 wagging
1003	16	994	3,8	1033	5,2	(N)CH_3 wagging
900	4,0	894	5,6	873	13	C-O stretching
820	20	777	1,8	786	1,8	Amide VI
		664	0,8	633	2,4	Amide IV
465		466	7,6	466	8,0	Amide V
		485	1,2	530	0,2	Skeleton deformation
		309	6,8	325	3,4	Skeleton deformation
		235	1,6	212	0,6	Skeleton deformation
		117	1,6	116	1,2	Amide VII

X-ray diffraction data [1] and IR spectroscopy [8] show that aliphatic polyurethanes based on hexamethylene diisocyanate and ethylene glycol (2,6-polyurethane or 2,6-PU and diethylene glycol or 4,6-PU) will have two crystalline modifications α and γ for 2,6-PU in accordance with the crystallization conditions, which differ in conformation, while 4,6-PU shows only the α modification. Similar structures have been observed for various linear polyurethanes [1]. The spectrum variations in the modifications have been ascribed to differing conformations for the urethane moieties [8]. According to [8], the reduction in the repeat period between the α and γ modifications of 2,6-PU is due to the urethane groups rotating around the adjacent bonds to 40°. Calculations on the repeat period and conformation energy show that the corresponding angle of rotation should be 100° [9].

The author has calculated the IR intensities for polyurethanes in order to define the changes occurring on conformation transformation and on that basis to describe the spectra for linear polyurethanes in the various crystalline forms.

The unit cell in 2,6-PU or 4,6-PU contains numerous atoms and there are hydrogen bonds between the chains, so it is possible to calculate the vibrations only for model compounds, for which the author chose hexamethylene dimethylurethane $CH_3OOCNH(CH_2)_6NHCOOCH_3$ (II) and part of the molecule of a polyurethane containing two methylene and urethane groups, 2,2-PU $[(CH_2)_2OOCNH(CH_2)_2NHCOO]_n$. The IR spectra have been examined and the normal vibrations have been analyzed for the models [10]. Figures 1 and 2 show the observed and theoretical IR spectra for 2,2-PU and II. The match between the calculated and observed frequencies and intensities is satisfactory. The strongest bands for the polyurethanes are associated with vibrations of the urethane group and in-plane vibrations of the CH_2 group, which are highly reproducible. The force and electrooptic parameters for the urethane group may be determined for the low-molecular carbamates and transferred satisfactorily to more complex models for parts of the macromolecules.

A complete picture was obtained on the spectral effects from the urethane group conformations from calculations on the absorption for the α modification, which corresponds to a planar completely stretched conformation for the chain, and on two modifications in which the urethane groups are turned around the C—O and C—N bonds through 100° in the same sense (γ_1) or in opposite senses (γ_2). The molecular symmetry is reduced from the α form to the γ form, and the number of frequencies observed in the IR spectrum increases. In the calculated spectra for the nonplanar conformations, the frequencies differ little from the corresponding ones for the planar conformation. There are appreciable shifts in the amide I, II, and V bands. The amide III band is at 1323 cm^{-1} for α, 1343 for γ_2, and 1333 for γ_1. The low-frequency shift from γ to α agrees with experiment. The intensity of the amide III band for γ_1 is less than those for α and γ_2. The 1231 and 1257 cm^{-1} bands for α correspond to 1256 and 1297 for γ_1. For γ_2, only the 1269 cm^{-1} band is predicted for this region. The strong 1211 cm^{-1} band for α splits into 1121 and 1189 or 1133 and 1200 cm^{-1} in the calculated spectra for γ_1 and γ_2, correspondingly. Below 800 cm^{-1}, the bands for the out-of-plane C=O and NH vibrations are displaced to the high-frequency side for the nonplanar conformations. Similar changes in the amide V band have been observed for the γ form of 2,6-PU.

We calculated the spectra for the γ forms for angles of rotation around the C—O and C—N bonds between 0 and 180°. The urethane-group bands shift monotonically as the angle increases. The amide I band shifts 30 cm^{-1} downward, while II, III, and V shift upward by 10, 30, and 35 cm^{-1}, correspondingly.

There are thus only quite small shifts and intensity changes in the IR bands for the polyurethane group rotation. In a real polymer those conformation changes are accompanied by H-bond rearrangement, so the observed spectra show more substantial changes.

The calculations on these compounds reproduce the frequencies and intensities for the amide I and II bands at 1700 and 1540 cm^{-1} correctly, but the calculated intensity for amide III is much less than the observed one. The lower calculated intensities for the deformation and wagging vibrations for the CH_2 groups may be due to model imperfections, as the number of methylene groups in the model is less than that in the actual polymer.

The theoretical γ_2 spectrum, where the urethane groups emerge at 100° to the plane of the skeleton, agrees best with the observed spectrum for γ in 2,6-PU; the result also agrees well with the [10] conformation calculations.

Polarized IR spectroscopy gives detailed data on the flexible and rigid parts of the macromolecule as affected by heating and stretching. The measurements have been interpreted from the directions of the transition moments for the urethane group, where it was assumed for the C=O and NH stretching vibrations that the moments were perpendicular to the macromolecular axis. The intensity calculations show that the moments for the amide vibrations have directions dependent on the type of substitution in the carbamate group. The NH and C=O vibration moments lie at 1 and 19° to the C=O line in (I) or 9 and 7° in methyl-N-phenylcarbamate (III). The amide II and III moments lie at 22 and 29° to the C=O direction in (I) or 42 and 17° in (III). The carbamate orientations as determined from the dichroic ratios are thus dependent not only on the segregation but also on the chemical structure, which must be borne in mind in interpreting polarized IR measurements.

The atomic charges have been calculated from the [5] bond dipole moments for carbamates and show that the electronic structure is unusual. The charge on the oxygen atom in the carbonyl group is —0.360 electron units in (I) and is close to the corresponding value in N-methylacetamide $CH_3NHCOCH_3$ —0.378 rather than to the —0.473 for methyl acetate CH_3COOCH_3. The charge on the alkoxyl oxygen atom in a carbamate is —0.476, which is much more than the —0.232 in methyl acetate. The charge on the nitrogen atom in a carbamate at —0.070 is larger than the —0.033 found in an amide. The charges on the carbon atoms in the carbamates, amides, and esters vary widely: 0.436, 0.129, and 0.626 for C=O, —0.140 and —0.173 for (N)CH_3, and 0.063 and —0.098 for (O)CH_3. The charges on the carbamate-group atoms differ appreciably from the values derived by a nonempirical method [11], but the general trends in the charges for the various types of substitution are closely reproduced.

The IR intensity calculations for carbamates enable one to describe the changes in the observed spectra during conformation transformation and to establish the electronic structure for this important class of compound.

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