The Infrared Dichroism of Amides

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The measurement of the infrared dichroism is a useful method of determining the position of hydrogen atoms in molecules. With regard to the structure of amide groups this technique was first applied to urea by Keller[1] and then to acetanilide by Brown and Corbridge.[2] The author suggested in a previous paper[3] that Keller's conclusion was inaccurate and that the correct determination of planarity of urea should be made, using the dichroism of NH stretching vibrations. Recently using the grating spectrometer, Waldron and Badger[4] measured the dichroism of NH stretching vibrations and the planarity of urea molecule was accurately proved. In this paper, the infrared absorption spectra of trichloroacetamide and deuterated monochloroacetamide were measured and the observed vibrational frequencies of amide groups were assigned. With this result together with the measurement of infrared dichroism of benzamide and monochloroacetamide, the position of hydrogen atoms in these molecules is discussed.

Experimental

Infrared spectra of trichloroacetamide and deuterated monochloroacetamide were measured with a Baird spectrophotometer. Infrared dichroism of benzamide and monochloroacetamide were measured with the apparatus described in our previous papers,[5] though we also used a selenium reflexion polarizer (the incident angle about 70°) to provide plane polarized infrared radiation. The direction of the electric vector of the incident radiation was parallel to the entrance slit.

A small amount of the solid was molten between a pair of sylvine plates. The specimens were cooled in such a way as to induce as far as possible the crystallization in oriented linear fashion. Absorption intensities of these specimens were measured with the direction of the orientation of crystals either parallel or perpendicular to the electric vector of the incident plane-polarized radiation.

Materials.—The samples of amide were obtained as follows: benzamide was recrystallized from water (m.p. 127—8°), and monochloroacetamide was prepared from ethyl monochloroacetate and ammonia and then recrystallized from water by Mr. I. Nakagawa (m.p. 120°). Deuterated monochloroacetamide was obtained by repeating the exchange reaction with heavy water, and trichloroacetamide was prepared from ethyl trichloroacetate and ammonia by Mr. T. Sugita (m.p. 140°).

Results

Infrared absorption spectra of deuterated

(1) Keller, *J. Chem. Phys.*, **16**, 1003, (1948).
(2) Brown and Corbridge, *Nature*, **162**, 72 (1948).
(3) Kuratani, *J. Chem. Soc. Japan*, **71**, 22 (1950).
(4) Waldron and Badger, *J. Chem. Phys.*, **18**, 566 (1950).
(5) Shimanouchi, Tsuruta and Mizushima, *Sci. Pap. I. P. C. R.*, **42**, 165 (1945).

monochloroacetamide and trichloroacetamide are given in Fig. 1. and 2.

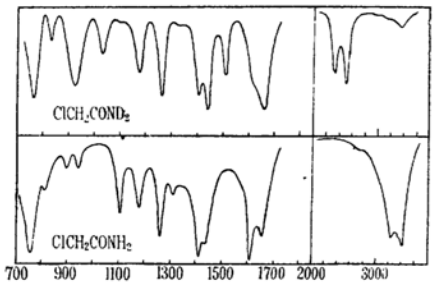

Fig. 1.—Infrared spectra of monochloroacetamide and partially deuterated monochloroacetamide.

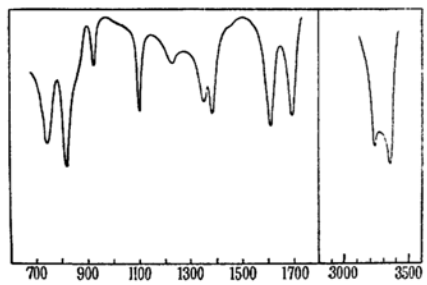

Fig. 2.—Infrared spectrum of trichloroacetamide.

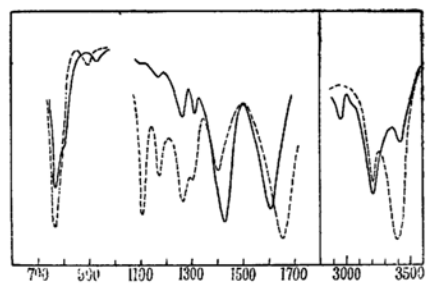

Fig. 3.—Polarized spectra for oriented crystals of monochloroacetamide. Electric vector of the beam is parallel (dotted curve) and perpendicular (full curve) to the direction of the crystal growth.

The absorption spectra of monochloroacetamide with the orientation of crystals parallel or perpendicular to the incident radiation are given in Fig. 3. The experimental results of the absorption spectra of benzamide were in agreement with those of Mann and Thompson.[6] The absorption peaks are summarized in Table 1, in which we have used the term

Table 1

Monochloroacetamide		Benzamide	
Bands	Dichroism	Bands	Dichroism
766 s	∥	768 s	⊥
804 w	⊥ ?	790 s	⊥ ?
890 w	∥ ?	805 s	⊥ ?
924 w	⊥ ?	920 m	?
1100 m	∥	1020 m	?
1180 s	∥	1120 m	∥ ?
1265 s	∥	1140 m	∥
1310 m	∥	1300 m	∥
1410 s	∥	1405 s	⊥
1430 s	⊥	1450 m	?
1610 s	⊥	1575 s	∥
1660 m	∥	1620 s	⊥
2960 m	⊥	1660 s	∥
3200 s	⊥	3200 s	⊥
3400 s	∥	3400 s	∥

"parallel dichroism" to describe larger absorption when the electric vector vibrates parallel to the axis of orientation than when it vibrates in a perpendicular direction, and the term "perpendicular dichroism" which is the reverse. Benzamide has other weaker bands, i. e., 843, 995, 1070, 1175, 1250 and 1495 cm.$^{-1}$, but the dichroism of these bands have not been determined.

Discussion

a) Vibrational Modes of Amide Group.—In the 9 vibrational modes of -$CONH_2$- group, OCN skeletal deformation vibration is not dealt with since this vibration lies beyond the observed frequency region. The remaining 8 modes are indicated in the first column of Table 2.

Table 2

Vibrational Modes	Notations	Assignment
NH_2 symmetric stretching	$\nu(NH_2)_s$	−3400 cm.$^{-1}$
NH_2 antisymmetric stretching	$\nu(NH_2)_a$	−3200
C=O stretching	$\nu(C=O)$	−1660
C−N stretching	$\nu(C-N)$	−1400
NH_2 symmetric deformation	$\delta(NH_2)$	−1600
NH_2 rocking, NH_2 wagging, NH_2 twisting } NH_2 rocking*	$\tau(NH_2)$	−1150, —, —

(* The distinction of these 3 bands is not necessary for the following discussion.)

The characteristic vibrational frequencies of amide groups, i. e., the vibrational frequencies which are commonly found in amide groups are 3400, 3200, 1660, 1600, 1400, and 1150 cm.$^{-1}$.

(6) Mann and Thompson, *Proc. Roy. Soc.* (*London*), **A, 192**, 489 (1948).

These absorption frequencies are also observed in the case of trichloroacetamide which has no C—H bond (see Fig. 2). There is no doubt about the assignment of the first 3 bands and, therefore, only the assignment of the last 3 bands is discussed.

Based on the numerous experimental results, Randall[7] assigns the 1400 cm.$^{-1}$ band to ν(C—N) vibration. This conclusion is also supported by the presence of 1385 cm.$^{-1}$ band in trichloroacetamide (see Fig. 2), since in this case there is no possibility of the presence of $\delta(CH_3)$ vibration. (In general $\delta(CH_3)$ and $\delta(CH_2)$ vibrations are found in 1380—1480cm.$^{-1}$ region.)

The weakness of absorption bands at 1600 and 1100 cm.$^{-1}$ and the appearance of the bands at 830, 925 and 1030 cm.$^{-1}$ in the spectrum of deuterated monochloroacetamide, support the assignments of 1600 and 1100 cm.$^{-1}$ to NH_2 bending vibrations. These assignments are also confirmed by the frequency shift of 1600 and 1150 cm.$^{-1}$ bands in $CO(NH_2)_2$ to 1250 and 990 cm.$^{-1}$ in $CO(ND_2)_2$,[8],[9] and the shift of 1150 cm.$^{-1}$ band in CH_3CONH_2 to lower frequency region in CH_3COND_2.[10] The fact that primary amines have 1600 and 1150 cm.$^{-1}$ bands and secondary amines have only 1150 cm.$^{-1}$ band proves the assignments of 1600 cm.$^{-1}$ band to symmetric deformation vibration, and 1150 cm.$^{-1}$ band to NH_2 or NH rocking vibration. This conclusion is consistent with the assignment of Axford, Janz and Russel[11] on methylhydrazine, and that of Kahovec and Kohlrausch[12] on the Raman lines of various amides. Cleaves and Plyler[13] made the same assignment for 1625 and 1150 cm.$^{-1}$ bands of methylamine measuring the band contours of these bands. These considerations confirm the assignment of vibrational bands of amide groups as indicated in the right column of Table 2.

b) Relation between the Molecular Structure and Infrared Dichroism.—In the first place let us discuss the cofiguration of CNH_2 groups of amide molecules. For CNH_2 group, we may consider 2 configurations, in one of which C—N bond is almost perpendicular to the plane of NH_2 group as in the case of methylamine molecule, and in the other the C—N bond is in the NH_2 plane as in the case of urea molecule.

When the C-N bond is nearly perpendicular to the plane of NH_2 group, the vibrational modes of 1600 and 1150 cm.$^{-1}$ bands become as shown in Fig. 4.[14] In this case the direction of the dipole moment change of ν(C—N)

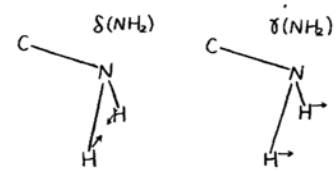

Fig. 4.—Vibrational modes for the nonplanar form.

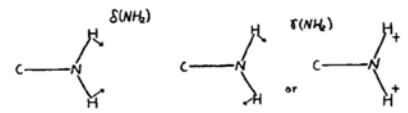

Fig. 5.—Vibrational modes for the planar form.

mode coincides with that of $\gamma(NH_2)$ mode and, therefore, ν(C—N) shows the same dichroism as $\gamma(NH_2)$. However, the direction of the dipole moment change of $\delta(NH_2)$ is perpendicular to that of ν(C—N) and the dichroism of $\delta(NH_2)$ is opposite to that of ν(C—N).

On the other hand, when the 2 hydrogen atoms lie on the same plane with carbon and nitrogen atoms as in the case of urea molecule, the vibrational modes of 1600 and 1150 cm.$^{-1}$ bands become as shown in Fig. 5.[14] In this case ν(C—N) band shows the same dichroism as $\delta(NH_2)$ and the opposite dichroism as $\gamma(NH_2)$. Accordingly the planarity of C—NH_2 group, i. e., whether C—NH_2 group is more similar to methylamine or to urea, is determined from the dichroism of 1600, 1400, and 1150 cm.$^{-1}$ bands. Of course, the accurate angle between C—N bond and NH_2 plane will be determined from the measurement of the pleochroism of these bands, but in the present experiment only the dichroism was measured and only the more favorable form was determined.

Monochloroacetamide.—Since chloroacetyl chloride, bromoacetyl chloride and bromoacetyl bromide[15] have their CH_2 deformation frequencies in the range of 1390—1400 cm.$^{-1}$, the

(7) Randall, Fowler, Fuson and Dangl, "Infrared Determination of Organic Structures" New York (1949).
(8) Kellner, *Proc. Roy. Soc. (London)*, **A. 177**, 456 (1941).
(9) Otvos and Edsall, *J. Chem. Phys.*, **7**, 632 (1939).
(10) Lenormant, *Compt. rend.*, **228**, 1861 (1949).
(11) Axford, Janz and Russel, *J. Chem. Phys.*, **19**, 709 (1951).
(12) Kahovec and Kohlrausch, *Z. phys. Chem.*, **B. 51**, 49 (1942).
(13) Cleaves and Plyler, *J. Chem. Phys.*, **7**, 563 (1939).
(14) Since 1150 cm.$^{-1}$ Raman line of formamide is a polarized one, vibrational modes of this frequency are confined to these figures.
(15) Mizushima and Nakagawa, to be published shortly.

1410 and 1430 cm.$^{-1}$ bands of monochloroacetamide are most reasonably interpreted as being a CH_2 deformation and a C—N stretching vibration, respectively. The propriety of the planar structure as shown in Fig. 5 is deduced from the fact that 1430 and 1610 cm.$^{-1}$ bands have the same dichroism and 1100 cm.$^{-1}$ band has the dichroism opposite to them.

This conclusion is verified by the experiment in the 3 micron region. The same dichroism of ν(C—N) and $\nu(NH_2)_s$, i. e., 1430 and 3200 cm.$^{-1}$ bands, is the excellent evidence of the planarity of C—NH_2 group.

Benzamide.—The opposite dichroism of 1400 and 1140 cm.$^{-1}$ bands assigned, respectively to ν(C—N) and $\gamma(NH_2)$ vibrations of benzamide, prefers the planar structure without the discussion of the dichroism of $\delta(NH_2)$ vibration. The same dichroism of ν(C—N) and $\nu(NH_2)_s$ vibrations confirms this conclusion.

On account of the planarity of carbon, nitrogen and hydrogen atoms, remaining possibilities of amide structure are confined to 2 forms. In one of these, NH_2 group lies on the same plane with C—O—N skeleton (form I), and in the other, CNH_2 plane intersects the plane of C—O—N skeleton at right angles (form II). (Only the more symmetrical forms are considered.)

The depolarization degree of Raman lines assigned to NH_2 stretching vibrations will be useful to distinguish the 2 forms, because in structure I both Raman lines due to NH_2 symmetric and antisymmetric stretching vibrations are polarized, while in structute II, the depolarized Raman line due to NH_2 antisymmetric stretching vibration should be observed. However, the depolarization degree of Raman lines of amides has not yet been measured.

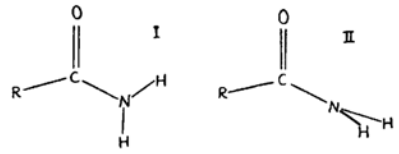

Fig. 6.

The direction of the dipole moment change of $\nu(NH_2)_a$ vibration is parallel to that of ν(C=O) vibration in structure I, and perpendicular in structure II. Therefore from the relation between the dichroism of $\nu(NH_2)_a$ and ν(C=O) (3400 and 1660 cm.$^{-1}$ bands), we can determine whether the structure of amides is consistent with I or II. The experimental result supports structure I for monochloroacetamide and benzamide molecules.

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