n-π^* *Absorption Spectra of Some Aliphatic Aldehydes*

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Whenever a carbonyl group is in a molecule, a weak absorption appears in a relatively long-wave region. With saturated aldehydes, this absorption appears near 2900 Å and possesses a low intensity which is about the same for all these molecules. The unfailing appearance of this absorption in molecules having a carbonyl group shows that it is due to the CO group and the constancy of its intensity in all these molecules suggests that the corresponding transitions can be given by a common interpretation. The interpretation was first made by Mulliken[1] and McMurry[2]. They say that an electron was thought to be excited from a non-bonding orbital localized on the O atom into an anti-bonding orbital. Such a transition involving the excitation of a non-bonding electron to an anti-bonding π orbital was designated an n-π^* transition by Kasha[3].

In this paper the effects of substituents and of solvents on the 0-0 band frequency of the n-π^* absorption spectra of some aliphatic aldehydes, together with their f-values, are investigated.

Experimental

A Hitachi automatic recording spectrophotometer EPS-2 was used for the measurement of the spectra. A 10 cm. cell was used for vapor, and a 1 cm. cell for solution. The temperature effect was investigated using a 2 cm. cell designed by Ito[4]. The optical density at various concentrations was measured and Beer's law was found to hold for all cases. For the infrared region a Hitachi double-beam recording infrared spectrophotometer EPI-2 was used.

Propionaldehyde, *n*-butyraldehyde and isobutyraldehyde were supplied by Tokyo Kasei Co. Samples were distilled just before the absorption measurement. *n*-Hexane was vigorously shaken with concentrated sulfuric acid, fuming sulfuric acid and nitric acid, then shaken with water, concentrated aqueous solutions of sodium hydroxide and potassium permanganate, dried over calcium chloride, refluxed over phosphorus pentoxide, distilled, passed through a column of freshly activated silica gel and finally distillled. Ethyl alcohol was shaken with ordinary silica gel, refluxed over sodium hydroxide, then finally distilled. Purifications of other solvents were essentially the same as those described in literature*.

Results and Discussion

Position of the n-π^* Absorption.—The n-π^* absorption spectra of aliphatic aldehydes generally appear near 2900 Å. The frequencies of absorption maxima for propionaldehyde, *n*-butyraldehyde and isobutyraldehyde are given in Table I together with values taken from literature for other aliphatic aldehydes. The maxima of the n-π^* absorption of corresponding carboxylic acids are cited in Table II from literature.

TABLE I. ν_{max} OF n-π^* ABSORPTION OF SOME ALDEHYDES IN *n*-HEXANE SOLUTION AND IN VAPOR STATE

Molecule	ν_{max}, cm^{-1}	
	n-hexane	vapor
Formaldehyde	34010[5]	
Acetaldehyde	34500[6]	34591[7]
Propionaldehyde	34119	34143
n-Butyraldehyde	33980	34003
Isobutyraldehyde	33865	33888

TABLE II. ν_{max} OF n-π^* ABSORPTION OF SOME CARBOXYLIC ACIDS IN LIQUID STATE

Molecule	ν_{max}, cm^{-1} liquid[8]
Formic acid	48410
Acetic acid	49003
n-Butyric acid	48764
Palmitic aic	47831

Baba and Nagakura[9] observed for carboxylic acids and ketones that the smaller the ionization potential of the substituent adjacent to the C=O group is, the greater the n-π^* band shifts toward the blue, interpreting the trend in the following way on the basis of the electron migration idea. In the ground state,

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1) R. S. Mulliken, *J. Chem. Phys.*, **3**, 564 (1935).
2) H. L. McMurry, ibid., **9**, 231, 241 (1941).
3) M. Kasha, *Discussions Faraday Soc.*, No. **9**, 14 (1950).
4) M. Ito, *J. Mol. Spectroscopy*, **4**, 106 (1960).

* A. Weissberger, E. S. Proskauer, J. A. Riddick and E. E. Toops, Jr., "Organic Solvents", Interscience Publishers, Inc., New York (1955).

5) V. Henri and S. A. Schou, *Z. Physik.*, **49**, 774 (1928).
6) W. Herold, *Z. physik. Chem.*, **B18**, 265 (1932).
7) P. A. Leighton and F. E. Blacet, *J. Am. Chem. Soc.*, **55**, 1766 (1933).
8) H. Ley and B. Arends, *Z. physik. Chem.*, **B17**, 177 (1932).
9) H. Baba and S. Nagakura, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **72**, 72, 74, 277, 341 (1951).

electron migration from the substituent to the excited π^* orbitals of the C=O group occurs easily, but in the n-π^* excited state, this electron migration becomes difficult since the non-bonding electron then occupies the part of the π^* orbitals. As a result the stabilization energy gained by the molecule due to this electron migration is greater for the ground state than for the n-π^* excited state. So a substituent causes a blue shift for the n-π^* absorption of the unsubstituted compound. Moreover the smaller the ionization potential of the substituent adjacent to the C=O group is, the more easily the electron migration occurs. In other words, the smaller the ionization potential of the substituent is, the larger is the blue shift. The above general view was testified for the case of some aldehydes. No ionization potential data of methyl, ethyl, n-propyl and isopropyl radicals were available, but their order could be estimated from the values for paraffines given in Table III. From these data it can be assumed that the ionization potential decreases in the order of methyl, ethyl, n-propyl and isopropyl radicals. From Baba and Nagakura's theory it is then expected that the n-π^* absorption band of aldehydes would show increasing blue shifts in the order of formaldehyde, acetaldehyde, propionaldehyde, n-butyraldehyde and isobutyraldehyde. However, the actual observation is that while the absorption maxima of acetaldehyde and propionaldehyde lie on the blue side of the formaldehyde maximum, n-butylardehyde and isobytyraldehyde lie on its red side. The situation is about the same as that of the corresponding carboxylic acids, where, acetic and n-butyric acids show blue shifts with respect to formic acid, but palmitic acid shows a red shift of about 580 cm^{-1}. From these observations it seems to be difficult to interpret the effect of the substituent on the absorption frequency solely by the magnitude of ionization potential and to consider only the phenomenon of blue shift as characteristic of the n-π^* transition. In addition to the blue shift caused by the ionizing tendency of the substituent, there seem to be other factors which may counteract the effect causing the blue shift. For such factors hyperconjugation, greater complexity of the molecule and hence steric effects of the alkyl radical may be considered and the general theoretical view of the spectral shift⁹⁾ due to the introduction of a substituent must be supplemented by the consideration of these additional factors.

TABLE III. IONIZATION POTENTIAL OF PARAFFINES

Molecule	Ionization potential, eV.¹⁰⁾
Methane	13.04
Ethane	11.76
Propane	11.21
n-Butane	10.80

Positions of the 0–0 Band. — Absorption spectra were measured at various temperatures

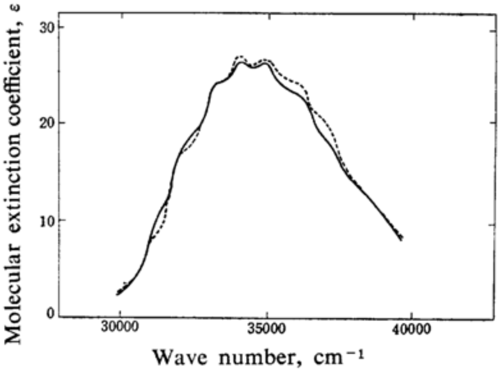

Fig. 1. Effect of temperature on the n-π^* absorption spectrum of propionaldehyde.
——, 9°C; ----, −78°C

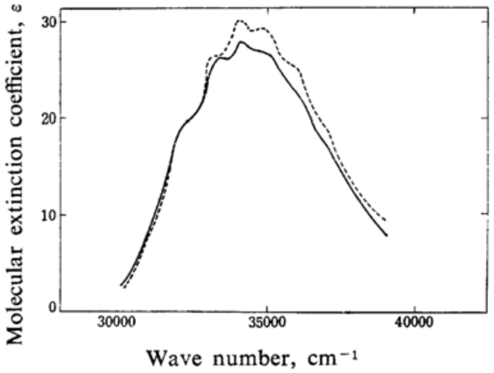

Fig. 2. Fffect of temperature on the n-π^* absorption spectrum of n-butyraldehyde.
——, 9°C; ----, 78°C

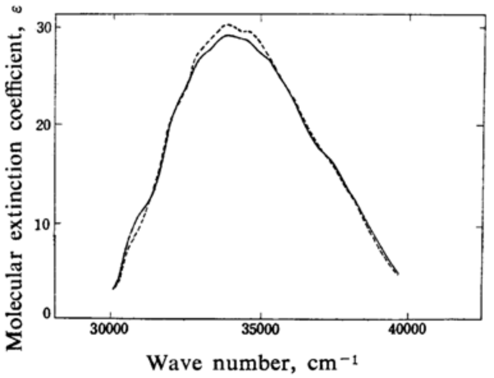

Fig. 3. Effect of temperature on the n-π^* absorption spectrum of isobutyraldehyde.
——, 9°C; ----, −78°C

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10) R. E. Honig, *J. Chem. Phys.*, **16**, 105 (1948).

to facilitate the location of the 0–0 band. The n-π^* absorption spectra of aldehydes in n-hexane solution at 9 and -78°C are shown in Figs. 1, 2 and 3.

Absorptions on the longer wave side of the 0–0 band arise from vibrational levels in the ground state and it is expected that the absorption intensity on the red side of the 0–0 band will increase and that on the shorter wave side it will decrease with increasing temperature. If we plot the absorption curves for various temperatures, an intersection point will be obtained near the position of the 0–0 band[13]. The positions of the 0–0 bands determined in this way are given in Table IV. As shown in Fig. 4 the n-π^* absorption spectra of propionaldehyde, n-butyraldehyde and isobutyraldehyde show the progressions of about 940 cm^{-1} interval and ν_{max}'s appear at the respective 0–2 band. The fact that the 0–0 band is weak and the 0–2 band is strong means that the minima of potential curves for the ground and excited states do not lie on top of each other but the minimum of the excited state is shifted so as to correspond to a greater equilibrium C–O distance, or that the force constant of the C=O stretching vibration decreases in the exited state.

Table IV. Position of 0-0 band and f-value of n-π^* absorption of some aldehydes

Molecule	0-0 Band, cm^{-1}	f-Value (29400~43200 cm^{-1})
Propionaldehyde	32250	5.56×10^{-4}
n-Butyraldehyde	32100	5.82×10^{-4}
Isobutyraldehyde	32000	5.58×10^{-4}

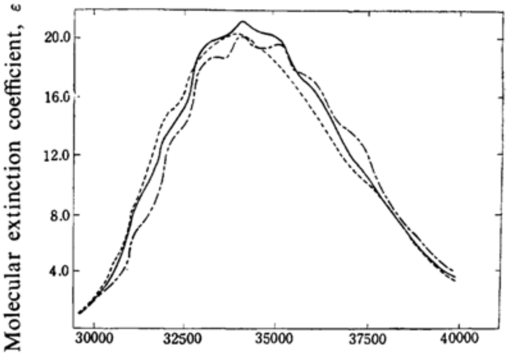

Fig. 4. n-π^* Absorption spectra of propionaldehyde (-·-·), n-butyraldehyde (——) and isobutyraldehyde (-----).

Oscillator Strength.—As the n and π^* orbitals are both formed of the 2p orbitals of different symmetry an n-π^* transition between them is forbidden by local symmetry ("U–A" transition)[14], giving a weak absorption with the f-value of the order of 10^{-4}. f-Values calculated for aldehydes are given in Table IV. They are all of the order of 10^{-4}.

Solvent Effect.—Next we shall discuss the solvent effect on the n-π^* absorption spectra of aldehydes investigated on the basis of a theoretical equation proposed by McRae[15]. We employ McRae's equation in a simplified form after Ito et al.[16] as applied for ketone spectra,

$$\Delta\nu = \text{dispersion term} + B\frac{n_D^2-1}{2n_D^2+1} + C\left[\frac{D-1}{D+2} - \frac{n_D^2-1}{n_D^2+2}\right]$$

$$B = \frac{1}{hc}\,\frac{(M^u{}_{oo})^2-(M^u{}_{ii})^2}{a^3}$$

$$C = \frac{2}{hc}\,\frac{M^u{}_{oo}\{(M^u{}_{oo})-(M^u{}_{ii})\}}{a^3} \qquad (1)$$

Table V. Properties of various solvents

Solvent	Refractive index n_D	Dielectric constant D	$\frac{n_D^2-1}{2n_D^2+1}$	$\frac{D-1}{D+1}$
n-Hexane	1.375	1.89	0.186	
Carbon tetrachloride	1.460	2.238	0.215	
Benzene	1.501	2.284	0.227	
Toluene	1.498		0.226	
Dioxane	1.422	2.209	0.202	
Ethyl ether	1.356	4.335		0.526
Methyl acetate	1.362	6.68		0.654
Acetonitrile	1.344	37.5		0.924
Chloroform	1.449	4.806		0.559
Ethyl alcohol	1.361	24.3		0.809
Isobutyl-alcohol	1.398	17.7		

Table VI. ν_{max} of n-π^* absorption of some aldehydes in various solvents

Solvent	ν_{max}, cm^{-1}		
	Propionaldehyde	Isobutyraldehyde	n-Butyraldehyde
(Vapor)	34140	33980	34000
n-Hexane	34120	33870	33980
Carbon tetrachloride	34150	33910	34050
Benzene	34330	34040	34150
Toluene	34340	33970	34150
Dioxane	34470	34070	34240
Ethyl ether	34310	33910	34170
Methyl acetate	34470	34040	34270
Acetonitrile	34760	34330	34450
Chloroform	34630	34120	34300
Ethyl alcohol	35050	34260	34470
Isobutyl alcohol	35080		34470

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[13] S. Broderson and A. Langseth, *Danske Mat. Fys. Medd.*, **26**, No. 3 (1951).

[14] J. R. Platt, *J. Chem. Phys.*, **18**, 1168 (1950).

[15] E. G. McRae, *J. Phys. Chem.*, **61**, 562 (1957).

[16] M. Ito, K. Inuzuka and S. Imanishi, *J. Am. Chem. Soc.*, **82**, 1317 (1960).

For the meaning of the symbols appearing in Eq. 1 the paper by Ito et al. is referred to.

Properties of various solvents used are given in Table V and ν_{max} in Table VI.

Solvent Effect of Non-polar Solvents, *n*-Hexane, Carbon Tetrachloride, Benzene, Toluene and Dioxane.—A vibrational fine structure was fairly well observed in the *n*-hexane solution, but in other solvents the stfucture is partially blurred and in dioxane hardly observable at all. This is probably due to the slightly polar nature (0.4 D) of dioxane.

The frequency shift of the solution in non-polar solvents is given as the sum of contributions represented by the first and the second terms of Eq. 1. The contribution from the first term usually gives a red shift, while the contribution from the second term depends on the dipole-polarization force. As the dipole moment of the C=O group in aldehydes decreases during the n-π^* transition, the stabilization by this force is greater in the ground than in the excited state, so that the effect of this force gives a blue shift. If the effect due to the first term is very small compared with that of the second term, a linear relation between ν_{max} and $(n_D^2-1)/(2n_D^2+1)$ should be obtained. However, from the plots of ν_{max} against $(n_D^2-1)/(2n_D^2+1)$ shown in Fig. 5, the linear relation is not observed. It is felt that the contribution from the dipole-polarization effect is greater than the dispersion effect for π-electron containing solvents such as benzene and toluene. For other solvents fairly large red shifts presumably caused by the dispersion effect are observed. The unusually large blue shift in the case of dioxane may be due to the dipole moment of the molecule as mentioned above.

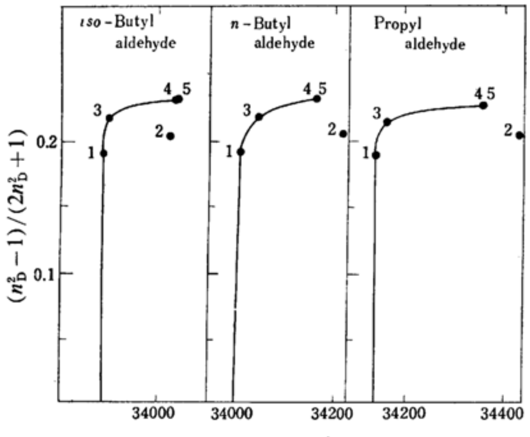

Fig. 5. Relations between ν_{max} and $(n_D^2-1)/(2n_D^2+1.)$
1, *n*-Hexane 2, dioxane 3, carbon tetrachloride 4, toluene 5, benzene.

Solvent Effect of Non-Hydrogen Bonding Polar Solvents, Ethyl Ether, Methyl Acetate and Acetonitrile.—The stabilization energy due to the dipole-dipole force between the solute and solvent molecules becomes smaller after the n-π^* transition. In consequence of the Franck-Condon principle, excited solute molecules will be momentarily surrounded by solvent molecules with sizes and orientations appropriate to their ground state, and as the result of this the excited state energy will become higher, leading to a blue shift. For the case of polar solvents the contribution from the third term in Eq. 1 will be the greatest and the shift depends on D. We assume here that for any of the three polar solvents 1, 2 and 3 the refractive index as well as the dispersion effect of each of them is nearly equal. Then Eqs. 2 and 3 follow from Eq. 1,

$$\nu_1-\nu_2=C\left[\frac{D_1-1}{D_1+2}-\frac{D_2-1}{D_2+2}\right] \tag{2}$$

$$\nu_1-\nu_3=C\left[\frac{D_1-1}{D_1+2}-\frac{D_3-1}{D_3+2}\right] \tag{3}$$

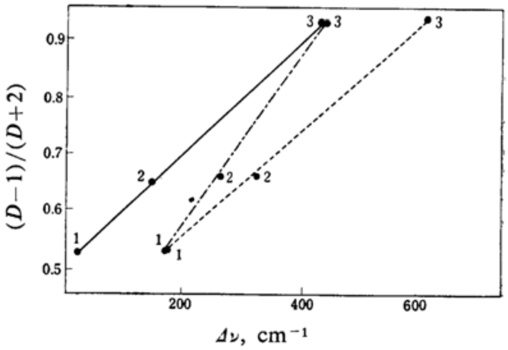

Fig. 6. Relations between frequency difference of n-π^* bands of propionaldehyde (----) *n*-butyraldehyde (-·-·-·) and isobutyraldehyde (——) and $(D-1)/(D+2)$ of various solvents.
Solvent: 1, ethyl ether 2, methyl acetate 3, acetonitrile.

The plots of $\Delta\nu(\nu_{max}-\nu_{max,\,vapor})$ against $(D-1)/(D+2)$ are shown in Fig. 6. A linear relationship is seen for propionaldehydehyde, *n*-butyraldehyde and isobutyraldehyde. From the slopes of the straight lines the values of C in Eq. 1 are obtained. If we know the magnitude of the quantity of a, $M^u{}_{oo}(M^u{}_{oo}-M^u{}_{ii})$ can be calculated, and if moreover the values of $M^u{}_{oo}$ are known, $M^u{}_{ii}$ can be obtained. Diple moment value for the ground state taken from literature and that of the excited state calculated following the above are given in Table VII. If we consider two

TABLE VII. DIPOLE MOMENT AND CONTRIBUTION OF THE C^+-O^- STRUCTURE OF SOME ALDEHYDES CALCULATED FOR $a=3$ Å IN EQUATION 1

Molecule	Dipole moment D		Contribution of the C^+-O^- structure, %	
	Ground state	Excited state	Ground state	Excited state
Propionaldehyde	2.54	1.33	43.3	22.9
n-Butyraldehyde	2.57	1.82	43.8	31.1
Isobutyraldehyde	2.58	1.48	43.9	25.2

resonating structures C=O and C^+-O^- the wave function is given by

$$\Psi = a\psi(C{=}O) + b\psi(C^+{-}O^-)$$

and the dipole moment D can be calculated as

$$D = a^2D'(C{=}O) + b^2D'(C^+{-}O^-)$$

where we take the moments of C=O and C^+-O^- as 0 and $\boldsymbol{er}$, respectively, $\boldsymbol{r}$ being the C–O distance. The calculated results are given in Table VII, showing that the contribution from the structure C^+-O^- is small in the excited state. From this it, is obvious that the electronic configuration of the C=O group is modified greatly in consequence of the *n*-π^* transition.

Effect of Solvents Forming Hydrogen Bonds with Solute Molecules, Chloroform, Ethyl Alcohol and Isobutyl Alcohol. — Frequency shifts are great and ν_{max}'s appear at longer wavelengths than the respective 0–2 band. The reason for these shifts may be attributed to the hydrogen bond formation. As the non-bonding electron localized on the O atom can form hydrogen bonds with solvent molecules the stabilization energy in the ground state will be great. On the other hand, in the excited state one electron is removed from the *n*-orbital and the remaining one electron is not sufficient to form a strong hydrogen bond. Therefore the stabilization energy will be small. In this case a large blue shift will be expected. New bands arise at shorter wavelengths than that of the 0–2 band. The hydrogen bond formation is confirmed by infrared absorption spectra of aldehydes in carbon tetrachloride, ethyl alcohol and isobutyl alcohol solutions. The new bands are distinguished from the C=O stretching vibration bands and are clearly attributable to the hydrogen bond formation.

Summary

The *n*-π^* absorption spectra of propionaldehyde, *n*-butyraldehyde and isobutyraldehyde were measured in various solvents and the effects of substituents and solvents on the *n*-π^* absorption spectra were investigated. For the former effect red shifts instead of blue shifts reported as the characteristic of *n*-π^* transitions were observed. The latter effect was studied using McRae's equation. Hydrogen bonding between solute and solvent molecules is also considered.

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