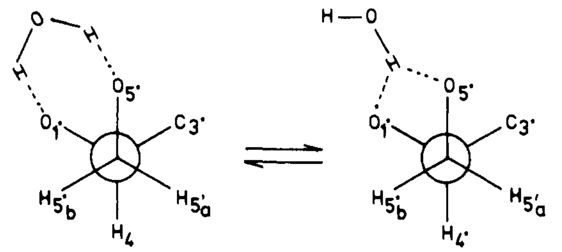

Figure 5. Transformation of intermolecular hydrogen bonding in 5′-AMP (*g,g*).

though we proposed in our previous paper[4] solely the occurrence of a seven-membered ring, the relatively small difference of the interaction enthalpies for the formation of a seven- and five-membered ring, 0.3 kcal/mol (Table I), predicts a dynamic interchange (Figure 5). The occurrence of the latter opens the potentiality for a "through-water" interaction of 5′-AMP and 3′-AMP with enzymic sites.

Polyhydration. The results in Table II show that upon polyhydration the positions between O(1′) and O(5′) as well as those between O(2′) and O(3′), as illustrated in Figure 3, remain important sites, whereas the corresponding location between O(1′) and O(5′) in c-AMP cannot be hydrated in consequence of the large distance between the two oxygen atoms. Upon polyhydration of site O(1′)–O(5′) (with water molecule 1, 5, 7, 9) an interaction enthalpy of −29.9 kcal/mol is obtained. When this value is compared with the enthalpy which is necessary to release four water molecules from bulk water ($4 \times 6.9 = 27.6$ kcal/mol (Table III)), it is clear that upon polyhydration a net enthalpy of hydration of about 2 kcal/mol remains. The same conclusion can also be drawn if less than four water molecules are involved in hydration. So the ab initio results give support to our previous suggestion that the difference in net solvation enthalpy (2–3 kcal/mol[4]) for the hydrolysis of c-AMP with respect to the other phosphate diesters can be mainly attributed to the fact that the location between O(1′) and O(5′) acts as an important hydration site.

The significance of hydrogen bonding as an explanation for the behavior of nucleotides has emerged more lately. Bolton and Kearns[14] offered a model for the intermolecular hydrogen bonding of the 2′-OH group of the ribose ring to the free phosphate oxygen atoms (with the O(2′)–O(7) distance 3.6 Å). They conclude from ^{1}H NMR spectra of cyclic nucleotides in aqueous and mixed solvents that the 2′-OH proton is protected against exchange with bulk water. On the other hand, they could not find any crystallographic evidence for the proposed interaction. Berthod and Pullman[13] showed with ab initio calculations that hydrogen bonding is possible between the O(2′) and O(3′) atom in the free ribose ring via one molecule of water. Our results underline those of Berthod and Pullman for c-AMP and the products of hydrolysis, and furthermore crystallographic evidence is available.[13,16] The distance between the 2′-OH oxygen atom and the nearest phosphate oxygen atom in c-AMP is found to be 5.0 Å.[11] As a corollary to these data, there is unlikely to be an intermolecular hydrogen bonding between the 2′-OH group of the ribose ring and the free phosphate oxygen atom, but rather between the 2′-OH group and the O(3′) phosphate ester oxygen atom. Very recently Bolton and James[15] discussed the local mobility of RNA and DNA also by intramolecular water bridges.

Our study clearly shows that the contribution to the large exothermic enthalpy of hydrolysis of c-AMP arises from solvation and more specifically from the regiospecific hydration in 5′-AMP and 3′-AMP and from the loss in strain of the ribose ring.

Acknowledgment. We gratefully acknowledge Unilever Research, Vlaardingen, The Netherlands, for the financial support of this investigation.

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(14) Bolton, P. H.; Kearns, D. R. *J. Am. Chem. Soc.*, **1979**, *101*, 479–484.

(15) Bolton, P. H.; James, T. L. *J. Am. Chem. Soc.*, **1980**, *102*, 25–31.

(16) In the water dimers the proton donor OH bond was placed along the bissectrix of the water proton acceptor molecule with an O···H distance of 1.9 Å.

Substituent Effect on the Fifth Overtone of Aryl C–H Stretching Vibrations

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Abstract: The fifth overtones of aryl C–H stretching vibrations of more than 30 kinds of monosubstituted benzenes in the liquid state have been observed by a thermal-lens technique. The frequency shifts of the overtones from that of benzene, $\Delta\omega$, were found to be proportional to the σ_I values of the substituents, the inductive contribution of the Hammett σ, thus supplying information on the reactivity of the chemical bond. Our experimental results support that a local-mode model is much superior to a normal-mode model for the description of high overtones.

Introduction

The experimental study of highly excited molecular vibration in the ground electronic state provides valuable information on photodissociations, radiationless transitions of molecules, and chemical reactivity of the bond relevant to the observed vibrations. The first application of the thermal-lens technique on the investigation of highly excited C–H stretching vibration in liquids was made by Long, Swofford, and Albrecht[1,2] and the fifth overtones of aryl C–H vibrations of benzene, naphthalene, anthracene, toluene, xylene, and trimethylbenzene were observed. They made measurements of the absorptions in the spectral range of 15 800–17 400 cm^{-1} covered by the CW rhodamine 6G dye laser, and analyzed the spectra on the basis of a local-mode model. Henry and his collaborators have reported that the C–H stretching overtone spectra, $\Delta\nu_{\text{C-H}} = 3$–7 of alkanes and methyl-substituted benzenes observed by using a conventional absorption method,

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(1) M. E. Long, R. L. Swofford, and A. C. Albrecht, *Science*, **191**, 183 (1976).

(2) R. L. Swofford, M. E. Long, and A. C. Albrecht, *J. Chem. Phys.*, *65*, 179 (1976).

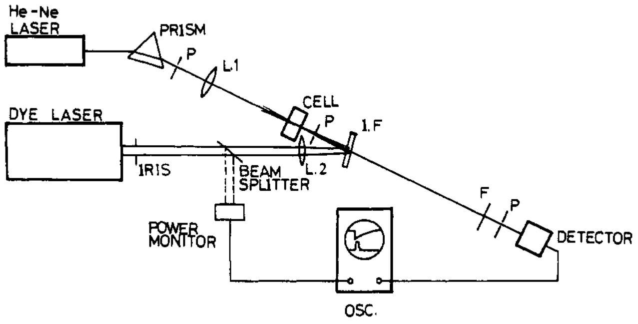

Figure 1. Experimental arrangement: p, pinhole; F, filter; IF, interference filter; L1, lens of f = 240 mm; L2, lens of f = 120 mm.

can be interpreted in terms of the local-mode model.[3,4]

The observation of the hydrogen atom based stretching overtone spectrum has led Henry and Siebrand to contrast the conventional overtone and combination description of excited vibrational states with that obtained through the local-mode model.[5] The experimental and theoretical investigations have demonstrated that the high-overtone spectra of molecular vibrations are well described as corresponding to excitation of localized modes rather than a set of symmetry-allowed combination of anharmonic normal mode.[2,6-8]

In the present article we wish to demonstrate that the observation of the fifth overtones ($\Delta v_{\mathrm{C-H}} = 6$) of the aryl C–H stretching vibrations of more than 30 kinds of monosubstituted benzenes can help to understand the electronic properties of their C–H bonds. The frequency shifts of the fifth overtones from that of benzene were found to be proportional to the σ_{I} values, the inductive contribution of the Hammett σ. Thus, the present experiments supply information on the reactivity of the aromatic C–H bond. Our results indicate that the local-mode picture is more suitable than the normal-mode model.

Experimental Section

Absorption spectroscopy of liquids using the thermal-lens technique offers a method for studying extremely weak transitions. When the molecules in a liquid cell absorb laser light, the density of the sample in the light path generally decreases, giving rise to the change of refractive index. A second much weaker monitoring laser can be directed along the same path through the liquid, and the defocusing of the monitoring beam is produced by the absorption of the primary laser pulse. Figure 1 shows our experimental arrangement used throughout for the present investigation. A flashlamp-pumped dye laser (Chromatix CMX-4) was used for the exciting light source, a He–Ne laser with an average power output of 5 mW operated in the TEM_{00} mode being used for the monitoring light. We can measure the absorption of the exciting laser by observing the decrease in the transmission of the He–Ne laser through a pinhole which is put after the absorption cell. The thermal blooming of the He–Ne laser was observed by means of a photodiode. Samples used were spectrograde or guaranteed reagent grade obtained from Tokyo Kasei Co. Ltd.

Results and Discussion

The fifth overtone frequencies of the aryl C–H vibrations of more than 30 kinds of monosubstituted benzenes observed in the liquid state are listed in Table I, in which the frequency shifts from that of benzene; the widths of the absorption lines (fwhm) and the values of σ_{I}, the inductive contribution of the Hammett σ, of the substituents are also listed. Since the high vibrational overtone is well represented by the local-mode model, its spectrum of the aryl C–H in monosubstituted benzene must have three components, ones for *o*-, *m*-, and *p*-CH bonds, respectively. However, only a single absorption band has been observed for the fifth overtone of the aryl C–H vibration in those molecules as listed in Table I. It is presumably because the frequency differences among the three types of C–H vibrations in these molecules are too small to be observed separately as compared with the absorption line width.

Table I. Fifth Overtone Frequencies of the Aryl C–H Stretching Vibrations of Monosubstituted Benzenes

substituent	freq, cm^{-1}	shift, cm^{-1}	width, cm^{-1}	σ_{I} value[a]
C_2H_5	16 450	−25	260	−0.06
$C(CH_3)_3$	16 460	−15	265	−0.08
CH_3	16 460	−15	275	−0.06
H	16 475	0	235	0.00
$CH{=}CH_2$	16 475	0	280	
NH_2	16 475	0	320	0.11
CH_2CH_2Cl	16 475	0	290	
$CHClCH_3$	16 480	5	300	
CH_2Cl	16 490	15	270	0.11
SH	16 490	15	290	0.28
SCH_3	16 490	15	320	0.22
OH	16 495	20	310	0.28
$C{\equiv}CH$	16 515	40	250	0.20
CH_2CN	16 515	40	280	
OCH_3	16 515	40	270	0.31
$CHCl_2$	16 520	45	285	0.32
CHO	16 525	50	310	0.35
$COCH_3$	16 530	55	320	0.34
OC_6H_5	16 530	55	290	0.38
I	16 530	55	350	0.43
$COOCH_3$	16 535	60	315	0.35
$OCOCH_3$	16 540	65	320	0.40
$COOC_2H_5$	16 545	70	325	0.35
CCl_3	16 555	80	310	0.40
Br	16 565	90	320	0.50
Cl	16 590	115	260	0.51
CN	16 595	120	265	0.61
SO_2NH_2	16 600	125	330	0.53
F	16 620	145	260	0.56
SO_2OCH_3	16 620	145	330	
SO_2Cl	16 630	155	330	

[a] Values of σ_{I} are tabulated for a large number of substituents in R. W. Taft, Jr., "Steric Effects in Organic Chemistry", M. S. Newman, Ed., Wiley, New York, 1956, pp 594–597.

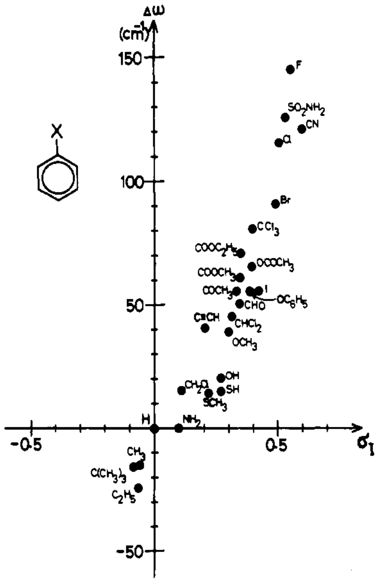

Figure 2. The relation between the frequency shifts of the fifth overtones of the aryl C–H stretching vibrations of monosubstituted benzenes and the σ_{I} values of the substituents.

Previously we reported that the frequency shifts of the fifth overtones of the aryl C–H vibrations in $C_6H_5CH_{3-n}Cl_n$ (n = 0, 1, 2, 3) from that of benzene, $\Delta\omega$, are proportional to the value of σ_{I}.[9] The present study shows that almost the same relation

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(3) B. R. Henry, *Acc. Chem. Res.*, *10*, 207 (1977), and references therein.
(4) W. R. A. Greenlay and B. R. Henry, *J. Chem. Phys.*, *69*, 82 (1978).
(5) B. R. Henry and W. Siebrand, *J. Chem. Phys.*, *49*, 5369 (1968).
(6) R. J. Hayward and B. R. Henry, *J. Mol. Spectrosc.*, *57*, 221 (1975).
(7) R. Wallace, *Chem. Phys.*, *11*, 185 (1975).
(8) H. S. Møller and O. S. Mortensen, *Chem. Phys. Lett.*, *66*, 539 (1979).
(9) Y. Mizugai and M. Katayama, *Bull. Chem. Soc. Jpn.*, **53**, 2081 (1980).

holds between the fifth overtone spectra and the values of σ_I of a large number of monosubstituted benzenes as is shown in Figure 2. Schmid and Langenbucher have examined the relationships between the σ_I values of the substituents X and the fundamental C–D stretching vibrations of [4-^{2}H]phenyl-*X* or the fundamental C–H stretching vibrations of [2,4,6-^{2}H]phenyl-*X*.[10] Those are not quite linear as we observed in the relation between the fifth overtone frequencies of molecular vibrations and the σ_I values.

It has been found that the frequencies of the overtone spectra are represented quite adequately by the simple two-parameter equation (1), where v is the vibrational quantum number.

$$G_{v,0} = v(A + vB) \tag{1}$$

If the Morse potential, $U(r - r_e) = D_e[1 - e^{-\beta(r-r_e)}]^2$, is applied for the analysis of the high overtone of the C–H vibration, the vibrational energy is expressed as in eq 2, in which μ is the reduced mass, $(1/m_H + 1/m_C)^{-1}$.

$$G(v) = \beta\sqrt{\frac{D_e h}{2\pi^2 c\mu}}(v + 1/2) - \frac{h\beta^2}{8\pi^2 c\mu}(v + 1/2)^2 = \omega_e(v + 1/2) - \omega_e X_e(v + 1/2)^2 \tag{2}$$

Therefore, the constants A and B are expressed as in eq 3.

$$A = \omega_e - \omega_e X_e \qquad B = -\omega_e X_e \tag{3}$$

The frequencies of a series of the aryl C–H overtone spectra of the transitions between the vibrational levels $v = 0$ and $v = 2$–7, as measured by the thermal-lens technique and a conventional method, can be well expressed by eq 4, respectively, where $G_{v,0}$ is expressed in cm^{-1}.

$$G_{v,0} = 3094v - 59v^2 \text{ for toluene}$$
$$G_{v,0} = 3113v - 58.5v^2 \text{ for } \alpha,\alpha,\alpha\text{-trichlorotoluene}$$
$$G_{v,0} = 3095v - 58.5v^2 \text{ for benzene} \tag{4}$$

The second terms in these equations, i.e., the B constants, are almost the same. If we assume tentatively that the values B for the aryl C–H vibrations of the other monosubstituted benzenes are also constant, each molecule has a different value of A, indicating that the difference in the frequency of the overtone is brought about by the variation of the dissociation energy D_e of the aryl C–H bond. Therefore, the frequency of the higher vibrational overtone gives information on the dissociation energy of the relevant chemical bond. It should be emphasized that the present discussion may be adequate only when the B constants for all of monosubstituted benzenes are the same and the Morse potential can be applied for the analysis of molecular vibrations even in the region of dissociation limit.

The shifts of the frequencies of the fifth overtones of the aryl C–H stretching vibrations from that of benzene are proportional to σ_I, the inductive contribution of the Hammett σ. It should be mentioned, however, that the shift does not depend upon the originally defined Hammett σ, which is related to the free-energy change accompanying the reaction. The σ_I may be regarded as a measure of the free-energy effect of the substituent relative to the H atom resulting from its power to attract or repel electrons through space and σ bonds of the benzene system. Therefore, the frequencies of the aryl C–H stretching vibrations are correlated with the σ_I value, because the C–H bond has mainly the character of a σ bond. The experimental results show that the larger the σ_I value of the substituent, the larger the shift of the overtone frequency; the consequence reveals that the strength of the aryl C–H bond increases when the σ-electron-withdrawing effect of the substituent becomes stronger. However, we are unable to give full explanation to the correlation between the σ_I value and the bond strength. It should be noted that nobody has reported that the increase in the aryl C–H bond strength is brought about by the decrease in the σ-electron density of the carbon atom.

Table II. Inductive Contribution of the Hammett's σ Obtained from the Frequency Shifts of the Fifth Overtone of the Aryl C–H Stretching Vibrations of Monosubstituted Benzenes

substituent	σ_I value	substituent	σ_I value
$CH{=}CH_2$	0.00 ± 0.05	CH_2CN	0.30 ± 0.05
CH_2CH_2Cl	0.00 ± 0.05	SO_2OCH_3	0.70 ± 0.10
$CHClCH_3$	0.05 ± 0.05	SO_2Cl	0.70 ± 0.10

In the present study, we have used the same values of σ_I for *o*-, *m*-, and *p*-CH as was generally assumed. Incidentally, these values must be different, but those are not known exactly; thus we have been unable to estimate the splitting of the spectra. From the observed line width, the separation among the fifth overtone spectra of *o*-, *m*-, and *p*-CH is the order of 50 cm^{-1}. Therefore, if it is possible to observe a more sharp overtone spectrum as is measured in the gas phase, the overtone frequencies of nonequivalent C–H vibrations will be resolved and the values of σ_I will be determined for the individual C–H bond.

The fundamental vibration is well described by the normal mode, which consists of symmetrized linear combination of vibrations of various chemical bonds; its frequency does not correspond directly to the σ_I value of a specific substituent. On the other hand, the hydrogen-assisted overtone of the molecular vibration can be well represented by the local mode. Hence, the frequency of the overtone manifests the nature of the isolated chemical bond, especially its strength or the dissociation energy; this is consistent with our observation that the frequency shifts of the fifth overtones of the aryl C–H stretching vibrations from that of benzene are proportional to the σ_I values as is shown in Figure 2.

Detailed examination of Figure 2 indicates, however, that a slightly different tendency of the relation between the shifts of the overtone frequency $\Delta\omega$ and the value of σ_I is obtained for monohalogenated benzenes. The shifts $\Delta\omega$ and the σ_I values for these compounds are linear, but the straight line connecting the individual points intersects the abscissa at a certain positive σ_I value. For the substituents NH_2 and O–X or S–X, somewhat similar relations as observed in the monohalogenated benzenes are obtained between the σ_I values and the shifts $\Delta\omega$, while the straight line for the other compounds passes through the origin as is shown in Figure 2. For the halogen atoms and the substituent NH_2, O–X, or S–X, not only the inductive contribution on the σ bonds of the benzene system but also the lone pairs of the halogen, N, O, and S atoms in these substituents affect the bond strength of the aryl C–H bond, resulting in the variation of their vibrational frequencies.

Nevertheless, it can be concluded that the frequency shift of the overtone $\Delta\omega$ is almost proportional to the σ_I value. If the σ_I value of the substituent in some monosubstituted benzene is unknown, it can be obtained from the observed frequency shift of the overtone. The σ_I values derived by such a way are listed in Table II.

In conclusion, the present study demonstrates that the frequencies of the fifth overtones of the aryl C–H stretching vibrations of monosubstituted benzenes are well correlated with the inductive contribution of the Hammett σ. The results are attributable to the fact that the high overtone of the molecular vibration can be correctly described by the local-mode model rather than by the normal-mode model.

Acknowledgment. This work was partly supported by a Grant-in-Aid from the Ministry of Education, Science, and Culture of Japan.

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[10] E. D. Schmid and F. Langenbucher, *Spectrochim. Acta*, 22, 1621 (1966).