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New Description of the Substituent Effect on Electronic Spectra by Means of Substituent Constants. V. n-π^* Transition of Aliphatic Carbonyl Groups

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Synopsis. The substituent (X) effect on the carbonyl n-π^* band of CH_3COX is discussed on the basis of a general equation, theoretically derived in order to express the substituent effect on electronic spectra using substituent constants. The results have been successful and are supported by MO calculations.

In this series[1] we have reported a new description of the substituent effect on the electronic spectra by means of substituent constants, since the theoretical background of this kind study has so far been ambiguous.[1] We have used Eqs. 1 and 2 by focusing special attention on the fact that the substituent effect on the electronic ground and excited states is very different:[2]

$$ {}^{1,3}E^{\mathrm{UV}}_{\mathrm{ho}\rightarrow\mathrm{lu}} = aF + bR + c \tag{1}$$

and

$$ {}^{1,3}E^{\mathrm{UV}}_{\mathrm{ho}\rightarrow\mathrm{lu}} = \alpha\sigma_{\mathrm{i}} + \beta\sigma_{\pi}^{+} + \gamma\sigma_{\pi}^{-} + c. \tag{2}$$

Here, F and R are Swain's substituent constants,[3] and σ_{i}, σ_{π}^{+}, and σ_{π}^{-} are Yukawa-Tsuno-Sawada's substituent constants.[4] Singlet or triplet transition energy is expressed by ${}^{1,3}E^{\mathrm{UV}}_{\mathrm{ho}\rightarrow\mathrm{lu}}$, which is mainly contributed from the HOMO→LUMO transition and has the same spectral character in a series of substituents. These equations were derived as an extension of Eq. 3, discussed previously:[5]

$$ (E^{\mathrm{oxd}}_{1/2} - E^{\mathrm{red}}_{1/2}) = k_1 \cdot {}^{1,3}E^{\mathrm{UV}}_{\mathrm{ho}\rightarrow\mathrm{lu}} + k_2. \tag{3}$$

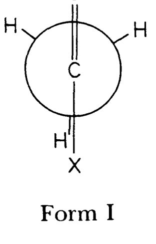
It is noteworthy to point out that the substituent dependence of half-wave oxidation ($E^{\mathrm{oxd}}_{1/2}$) and reduction ($E^{\mathrm{red}}_{1/2}$) potentials is quite different,[1,5] just as a different behaviour is observed for the substituent effect on the electronic ground and excited states.[2] An important condition is that the various kinds of substituent constants (σ_{p}, σ_{m}, σ^{+}, σ^{-}, σ^{*} etc.) reported hitherto can be expressed in the form $[fF+rR+c]$ for aromatic and aliphatic systems, or by $[l\sigma_{\mathrm{i}}+m\sigma_{\pi}^{+}+n\sigma_{\pi}^{-}]$ for π-electron systems. The former and the latter are satisfied by employing the substituent constants proposed by Swain[3] and Yukawa-Tsuno-Sawada,[4] respectively. In addition to our foregoing results that the HOMO→LUMO type π-π^* bands, n-π^* bands of aromatic systems, and charge-transfer spectra of EDA complexes well satisfy Eqs. 1 and 2, we report here that the n-π^* band of aliphatic carbonyl groups of the type CH_3COX is also well described by the application of Eq. 1.

Experimental

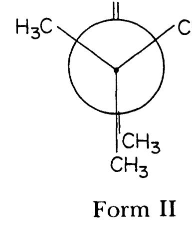
Samples. Here, we have used substances of the type CH_3COX, where X is H, CH_3, C_2H_5, $C(CH_3)_3$, CF_3, Cl, Br, OH, OCH_3, OC_2H_5, $O(CH_2)_2CH_3$, NH_2, $COCH_3$, $COOC_2H_5$. All the samples are commercially available. Special guaranty reagents or spectrograde purity reagents of X=CH_3, C_2H_5, $C(CH_3)_3$, OCH_3, OC_2H_5, $O(CH_2)_2CH_3$ were repeatedly distilled in normal or reduced pressure under a nitrogen atmosphere. Analyzed-grade acetic acid for precise analytical chemistry was used without further treatment. The other samples (X=H, Cl, Br, $COCH_3$, $COOC_2H_5$, CF_3) were all special guaranty reagents and were employed for spectral measurements without further treatment.

Spectral Measurements. These were performed in the usual manner with a Hitachi spectrophotometer, Model 323, at room temperature. In order to make it possible to record the spectra at shorter wavelengths (as much as possible), the inside air in the spectrometer and the cell compartment was replaced with N_2 gas, and a gas stream was maintained during measurements. Although 10- and 2-mm matched quartz cells were usually used for spectral measurements, in the case of samples having a hydrogen bond formation ability, just like acetic acid, we also used quartz cells with long pass lengths, so that diluted solutions of the samples would be possible for recording the spectra; also, the hydrogen bonding effect on n-π^* bands was diminished, since this kind of effect brings about a blue shift of the bands.[2] Nevertheless, the concentration of acetic acid was about 3×10^{-3} mol dm^{-3}. The dimer formation constant of acetic acid was reported as being 2370 in CCl_4,[6] so that about 67% of 3×10^{-3} mol dm^{-3} was still in the dimer form. We then excluded acetic acid from the present regression study. Also, CH_3CONH_2 was not employed here, since it is not only insoluble in heptane, but its n-π^* band is not clearly recorded in CH_3CN, since that band is hidden in the tail of the strong carbonyl π-π^* band.[7] Solvents used were heptane and acetonitrile of spectrograde purity, which were dried over CaH_2 and then carefully distilled.

Molecular Orbital (MO) Calculation. In order to analyze the character of the n-π^* bands of the carbonyl groups we performed a MO calculation by means of the CNDO/S method proposed by the Jaffé and Duke groups.[8] Such parameter values as the Slater exponent (μ), bonding constant ($-\beta^{0}_{\mathrm{X}}$), one-center repulsion integral (γ_{XX}), ($I^{\mathrm{S}}_{\mathrm{P}}+E^{\mathrm{S}}_{\mathrm{A}}$), and ($I^{\mathrm{P}}_{\mathrm{P}}+E^{\mathrm{P}}_{\mathrm{A}}$) are the same as those employed in our previous papers.[1] The molecular geometries were assumed to be as follows. When X in CH_3COX is alkyl or alkoxyl groups the carbon or oxygen atom in the substituent X, which bonds directly to the C=O group carbon atom, is put in the same plane as that of $(H_3)C$-C=O, where the carbonyl group carbon atom is in sp^2 hybridization (∠120°). The conformation was assumed to be staggerd, as in Form I, and such substitu-



Form I



Form II

ents (X) as *O*-alkyl, $OCOCH_3$, $COCH_3$, $COOC_2H_5$, and alkyl groups are linearly extended in a zig-zag type arrangement, which seems to be in the most reduced steric hindrance. In the case of X=$C(CH_3)_3$ the configuration of Form II was used. All the bond lengths are taken from Ref. 9. The bond angles used are 109°28′, except for the sp^2 carbon atoms with 120°. The substituent effect on n- and π-orbital energies was also checked by ab initio calculations using the 4-31G basis set under the same molecular geometries as mentioned above. CNDO/S calculations were carried out with a FACOM M-382 computer in the Nagoya University Computation Center, the 4-31G ab initio calculations being made with a HITAC M-680 Computer at the Institute for Molecular Science (IMS) using the IMS library program "IMSPACK".

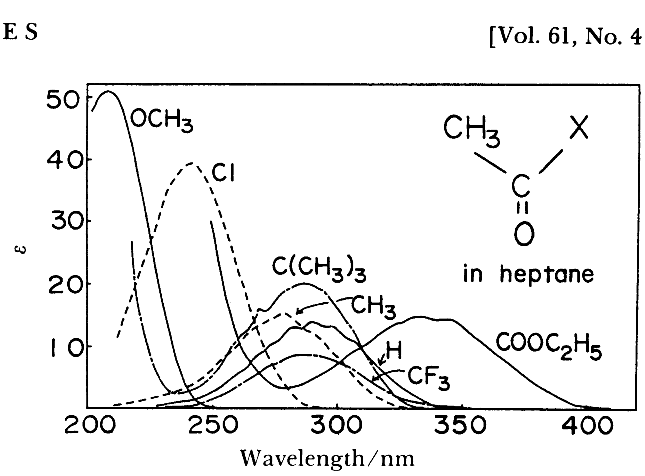


Fig. 1. Absorption spectra of carbonyl n–π* bands of CH_3COX with various substituents X.

Results and Discussion

The Nature of n-π* Bands of Aliphatic Carbonyl Substances. Aliphatic carbonyl compounds are typical examples that show clearly weak n-π* bands in a near UV region; thus many studies have been made and reported. Nagakura, Baba, McMurry, Kasha, and McConnell first interpreted the electronic structures and spectra of carbonyl substances by means of molecular orbital theory and discussed the substituent and solvent effects on the n-π* bands.[10] They thus gave a theoretical background regarding the experimental facts that n-π* bands bring about a blue shift by the introduction of electron donating substituents, like OH and NH_2, and also in solvents with a hydrogen bonding ability. Many subsequent investigations have supported these results. We discuss the above substituent effect from the viewpoint of substituent constants. The aliphatic ketones employed here clearly exhibit an n-π* band in the near UV region (200—400 nm) with ε=10—60, some typical spectra in heptane being illustrated in Fig. 1. In Table 1 are listed the spectral data and the orbital energies of the n-HOMO and π*-LUMO calculated by an ab initio 4-31G basis set and the CNDO/S method. The character of the n-π* band of ketones studied was checked by a CNDO/S-CI calculation, which clearly showed that the above-mentioned n-π* bands are strongly (more than 90%) localized in a single configuration contributed from the transition to a π-type LUMO from an n-type HOMO and, thus, having a similar spectral nature. Exceptional compounds are, however, X=$COCH_3$ and $COOC_2H_5$. These have two carbonyl groups in a molecule, so that nonbonding orbitals localized in the two carbonyl group oxygen atoms interact with each other; there therefore occur two n-type occupied MO's, localized mainly at the carbonyl group oxygen atoms. Consequently, the second n-π* configuration is mixed in the first n-π* transition, that is the main configuration, and the longest wavelength n-π* band is quite red shifted.[11] The correlation of the observed n-π* band energies ($E^{\mathrm{obs}}_{\mathrm{n}-\pi^*}$) to the CNDO/S calculated ones ($E^{\mathrm{calcd}}_{\mathrm{n}-\pi^*}$) is however relatively good: $E^{\mathrm{obs}}_{\mathrm{n}-\pi^*}=1.82E^{\mathrm{calcd}}_{\mathrm{n}-\pi^*}-1.50$ in eV unit with a correlation coefficient $r=0.914$ (sample number $n=11$: see Table 1).

Table 1. Observed First n-π* Transition Energies and Calculated n-HOMO and π*-LUMO Energies for Aliphatic Ketones CH_3COX

X	Obseved n-π* band[a)]				Calculated orbital energy/eV			
	in heptane		in CH_3CN		CNDO/S		ab initio 4-31G	
	E/eV	$\varepsilon_{\max}$	*E*/eV	$\varepsilon_{\max}$	n-HOMO	π*-LUMO	n-HOMO	π*-LUMO
H	4.283	14.0	4.343	15.7	−12.221	−0.625	−11.536	3.974
CH_3	4.455	14.6	4.522	15.2	−11.650	−0.305	−11.074	4.163
C_2H_5	4.460	16.8	4.500	18.0	−11.553	−0.279	−11.030	4.160
$C(CH_3)_3$	4.313	20.1	4.353	22.4	−11.241	−0.167	−10.786	4.120
Cl	5.130	39.6	5.205	43.4	−12.569	−1.108	−12.234	3.240
Br	5.134	99.5	—[b)]	—[b)]				
OH	5.939[c)]	43.8[c)]	—[d)]	—[d)]	−12.596	−0.720	−12.268	4.496
OCH_3	5.871	51.3	5.952	56.4	−12.357	−0.559	−12.133	4.622
OC_2H_5	5.848	58.0	5.915	60.3	−12.275	−0.522	−12.041	4.653
$O(CH_2)_2CH_3$	5.868	58.0	5.924	55.7	−12.254	−0.507	−12.004	4.532
CF_3	4.298	8.75	4.360	14.1	−12.444	−1.222	−12.879	2.255
$COOC_2H_5$	3.718	14.8	3.774	19.9				
$COCH_3$	2.959	2.61	2.994	2.45				

a) $\varepsilon_{\max}$ means molar absorption coefficient at the wavenumber of the maximum absorption. b) Acetonitrile solution of acetylbromide is unstable and gradually turns out to be yellow. c) This spectral data are not for the monomer alone, but for the mixture of dimer and monomer of acetic acid. See experimental section in the text. d) The spectra of acetic acid was not recorded because of the end absorption of CH_3CN.

Application of Substituent Constants to the n-π* Band of Aliphatic Ketones. The conditions discussed in the foregoing section necessarily lead to the conclusion that the carbonyl n-π* bands can be explained using Eq. 1, except for diketones. The results of a multiregression analysis for the spectral data in heptane is given in Fig. 2. The agreement between the observed and calculated n-π* band energies is very good. Experimental data in CH_3CN (see Table 1) also gave a regression equation similar to that given in Fig. 2: i. e. ${}^1E^{UV}_{n-\pi^*}=0.960F-0.629R+4.28$ ($n=9$, $r=0.996$). In these regression equations the fact that the contribution of the F term is larger than that of the R term seems to be reasonable (as discussed below). The n and π* orbital energies are listed in Table 1. Regression equations using the F and R constants for 4-31G calculation results are as follows: $\varepsilon_n=-1.941F-0.243R-11.255$ ($n=9$, $r=0.952$) for the n-orbitals, and $\varepsilon_{\pi^*}=-1.206F-0.881R+3.800$ ($n=9$, $r=0.992$) for the π*-LUMO orbitals. It is understood that both the n and π* orbital energies are well described by the two substituent constants, but that the contribution from the F term is extraordinarily large for the ε_n values, showing that the field and inductive effect is predominant for the substituent effect on the nonbonding orbital. The same conclusion as these was also obtained from an analysis utilizing the CNDO/S orbital energies. This is of course reflected in the regression equation in Fig. 2. Kobayashi and Nakamoto[12] discussed in 1949 the substituent effect on aliphatic carbonyl n-π* bands as a function of the charge density at the alpha-atom of >C=O group. Later, Rao et al.[13] studied only the alkyl (X) group substituent effect on the CH_3COX n-π* bands using the Taft σ^* constant. In principle, however, attention was only payed to the substituent effect on the ground state, and the effect on n-π* excited states was explicitly disregarded. Our present treatment makes it possible for the first time to describe the ground and excited states by the same substituent constants; also, the present results applied to the carbonyl n-π* bands are quite good and are compatible with the results from the MO calculations. The correlation equation given in Fig. 2 leads to 6.16 eV (201 nm) for the n-π* band of CH_3CONH_2 in heptane. We think that the accurate singlet n-π* band position of CH_3CONH_2 has still not been reported,[7] and that the data estimated by some authors are contradictory to each other.[7,14–17] Our present estimation shows that the n-π* band is at a shorter wavelength than that (211 nm in heptane) of CH_3COOCH_3; this is in agreement with Nagakura's opinion,[7] who says that the n-π* band of CH_3CONH_2 may occur at a shorter wavelength than 200 nm on the basis of an MO consideration.

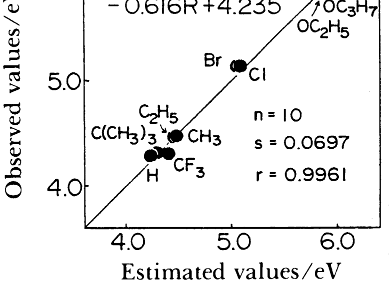


Fig. 2. Linear-least-squares correlation of observed n-π* band energies to the estimated ones using Swain's substituent constants.

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14) For example, Jaffé and Orchin[15] reported 214 nm in water for the n-π* band position of CH_3CONH_2, but Nielsen and Schellman[16] found that no n-π* band appears in the above wavelength region in water and the band may occur at more shorter wavelength. Ab initio CI calculation with double excitations led to 5.85 eV for the n-π* band of $CH_3CONHCH_3$.[17]

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