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The Intensity of the n–π^* Absorption Bands of Several Aliphatic Carbonyl Compounds

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The mechanism of the intensity gain of the n–π^* transition has been investigated in several carbonyl compounds; (1) cyclohexane-1,4-dione, (2) *d*-α-bromocamphor, (3) bromonoranisatinone, (4) *d*-α-cyanocamphor, and (5) spiradine A methiodide. The results on the polarized absorption spectra of single crystals at room temperature have revealed that several mechanisms are involved in the appearance of the carbonyl n–π^* band. These mechanisms, (1) the vibronic coupling, (2) the lowering of the symmetry properties of the n and π orbitals by the substituent perturbations, and (3) the charge transfer from the substituents, are discussed theoretically and compared with the experimental results. It is shown that the in-plane components, either parallel or perpendicular to the carbonyl axis, are predominant as the source of the band intensity. The ratio of intensities parallel and perpendicular to the carbonyl axis is estimated by the use of the polarization results.

Since McMurry[1] first discussed the nature of the n–π^* transitions of the carbonyl compounds, there have appeared many experimental and theoretical studies of the mechanism of the intensity gain of the n–π^* electronic transitions.[2] The intensities of the symmetry-forbidden transitions can be observed by vibrational or other kinds of perturbations; the detailed mechanism of these transitions are important in elucidating the origin of the optical activity of the carbonyl compounds.[3] Pople and Sidman[4] studied the vibronic coupling in formaldehyde, considering especially the mixing of the A_2-type n–π^* excited state with the B_1 and B_2-type excited states. Their conclusions were in agreement with those of the classical experimental work of Dieke and Kistiakowsky,[5] who had decided that the transition is allowed along the direction in plane and perpendicular to the carbonyl axis. Cookson and his group[6] noticed the intensification of the n–π^* transition in the β,γ-unsaturated carbonyl compounds; Labhart and Wagniere[7] explained it by the charge-transfer mechanism. Vala and Tanaka[8] have demonstrated that the direction of the n–π^* transition moment of 4,4′-dichlorobenzophenone is parallel to the carbonyl axis and have discussed the mechanism of the intensity gain. In the present paper we will present results on the polarized absorption spectra of several compounds containing carbonyl groups.

The results of the low-temperature spectral studies of cyclohexane-1,4-dione, which are consistent with the present results, will be presented in a separate paper.

The optical activity of the carbonyl compounds have attracted much attention from the organic chemical point of view,[9] and the "octant-rule" has been establisehd[10] and discussed in many papers.[11] The direction of the n–π^* transition moment is definitely important in clarifying the mechanism of the octant rule.[12] The present results will provide fundamental information con-

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1) H. L. McMurry, *J. Chem. Phys.*, **9**, 231, 241 (1941).

2) J. W. Sidman, *Chem. Revs.*, **58**, 689 (1958); V. G. Krishna and L. Goodman, *J. Chem. Phys.*, **36**, 2217 (1962); R. Shimada and L. Goodman, *ibid.*, **43**, 2027 (1965).

3) S. F. Mason, *Quart. Rev.*, **17**, 20 (1963).

4) J. A. Pople and J. Sidman, *J. Chem. Phys.*, **27**, 1270 (1957).

5) C. H. Dieke and G. B. Kistiakowsky, *Phys. Rev.*, **45**, 4 (1934).

6) R. C. Cookson and N. S. Wariyar, *J. Chem. Soc.*, **1956**, 2302.

7) H. Labhart and G. Wagniere, *Helv. Chim. Acta*, **42**, 2219 (1959).

8) M. Vala and J. Tanaka, *J. Chem. Phys.*, **49**, 5222 (1968).

9) C. Djerassi, "Optical Rotatory Dispersion; Application to Organic Chemistry," McGraw-Hill, New York (1960).

10) W. Moffitt, R. B. Woodward, A. Moscowitz, W. Klyne and C. Djerassi, *J. Am. Chem. Soc.*, **83**, 4013 (1961).

11) A. Moscowitz, *Advan. Chem. Phys.*, **4**, 67 (1962); J. A. Schellman and P. Oriel, *J. Chem. Phys.*, **37**, 2114 (1962); G. Wagniere, *J. Am. Chem. Soc.*, **88**, 3937 (1966); O. E. Weigang, Jr., *J. Chem. Phys.*, **43**, 3609 (1963).

12) S. F. Mason, *Mol. Phys.*, **5**, 343 (1963).

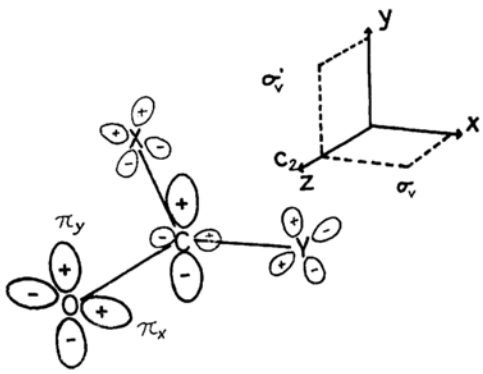

Fig. 1. The perturbing orbitals of all substituents are schematically shown at X and Y. The coordinates for the carbonyl group are shown together, the z is the direction of the carbonyl axis, x is in the plane and perpendicular to the axis, and y is in the direction out of the plane.

cerning the origin of the optical rotatory power of the carbonyl compounds.

Theoretical Considerations

The origin of the electronic transition of formaldehyde is shown to be intensity borrowing by the vibronic interactions. The theory of Pople and and Sidman,[4] confirmed by several experiments,[13] is that the transition moment is along the x axis, as is shown in Fig. 1. However, a little component is found along the carbonyl axis, though it is not big enough to explain the optical activity of the asymmetric ketones.[14] The vibronically-perturbed n–π^* excited states for the C_{2v} symmetry system may be given by:

$$\begin{aligned}\Phi(n\text{–}\pi^*) = {} & \varphi_{A_2}(n\text{–}\pi^*) \\ & + \sum_a \frac{\langle \varphi_{A_2}(n\text{–}\pi^*) \left| \left(\frac{\partial H}{\partial q_a}\right) q_a \right| \varphi_{B_1}(n\text{–}\sigma^*) \rangle}{\varepsilon_{A_2}(n\pi^*) - \varepsilon_{B_1}(n\sigma^*)} \varphi_{B_1}(n\text{–}\sigma^*) \\ & + \sum_b \frac{\langle \varphi_{A_2}(n\text{–}\pi^*) \left| \left(\frac{\partial H}{\partial q_b}\right) q_b \right| \varphi_{B_2}(\sigma\text{–}\pi^*) \rangle}{\varepsilon_{A_2}(n\pi^*) - \varepsilon_{B_2}(\sigma\pi^*)} \varphi_{B_2}(\sigma\text{–}\pi^*) \\ & + \sum_c \frac{\langle \varphi_{A_2}(n\text{–}\pi^*) \left| \left(\frac{\partial H}{\partial q_c}\right) q_c \right| \varphi_{A_1}(\pi\text{–}\pi^*) \rangle}{\varepsilon_{A_2}(n\pi^*) - \varepsilon_{A_1}(\pi\pi^*)} \varphi_{A_1}(\pi\text{–}\pi^*)\end{aligned} \tag{1}$$

where q_a, q_b, and q_c refer to the normal coordinates of the b_1, b_2 and a_1-type vibrational motions. The mixing with higher excited states will allow the n–π^* transition to appear along the x, y, and z axes respectively. A quantitative calculation of these terms is difficult for complex molecules; however, the selection rules can be confirmed by the polarized absorption measurements.

In β,γ-unsaturated ketones the intensity of the n–π^* transition is greatly enhanced, as is shown in Table 1. Labhart and Wagniere[7] suggested that the configurational interaction with the charge-transfer state is the major source of the intensity enhancement. The mixing of the charge transfer in the n–π^* state may be described by:

$$\begin{aligned}\Phi(n\text{–}\pi^*) = {} & \varphi_{A_2}(n\text{–}\pi^*) \\ & + \frac{\langle \varphi_{A_2}(n\text{–}\pi^*) \,|\mathbf{H}|\, \varphi_{CT} \rangle}{\varepsilon_{A_2}(n\pi^*) - \varepsilon_{CT}} \varphi_{CT}\end{aligned} \tag{2}$$

Where φ_{CT} indicates the charge-transfer state from the β,γ-unsaturated bond to the carbonyl group. The other charge-transfer configuration, one which involves the transfer of the nonbonding electron of the carbonyl group to the unsaturated bond, will have a higher energy because of the large ionization potential of the nonbonding electron

Table 1. The energies and intensities of the n–π^* transitions

	Crystal		Solution			
	ν_{max}	ratio $I_x : I_z$	ν_{max}	ε_{max}	$f \times 10^3$	$A(\varepsilon_l - \varepsilon_r)$
Cyclohexane-1,4-dione	35.5	74 : 26	35.0	58	1.50	
d-Camphor			35.1	36	0.80	1.30
d-α-Cyanocamphor	35.0	80 : 20	34.7	42	1.00	0.64
d-α-Bromocamphor	32.0	57 : 43	32.8	107	2.11	1.81
Bromonoranisatinone	32.5	56 : 44				
Dihydrospiradine A			33.3	35	0.65	3.50
Spiradine A			32.8	194	3.18	2.30
Spiradine A methiodide	33.0	0 : 100?				

Here ν_{max} is the frequency of the absorption maximum in the crystalline state and in solutions.
The ratio is that of two components x and z by assuming that the polarization of the transition moment is in the plane of the carbonyl group (see Fig. 1).
ε_{max} is the maximum molar extinction coefficient.

13) J. C. D. Brand, *J. Chem. Soc.*, **1956**, 858.

14) J. Tanaka and K. Ozeki, to be published.

and small matrix elements; therefore, it will be neglected in further discussions. The transition moment induced by the charge-transfer configuration will have the direction inherent in the charge-transfer transition. Although Labhart and Wagniere[7] have not discussed the direction of the induced n–π^* transition, it is along the line connecting the centers of the electron donor and the acceptor groups. Another source of the intensities of the n–π^* transition is the deformation of the nonbonding and π orbitals by the perturbation of the adjacent conjugated systems.

The symmetry properties of the n and π molecular orbitals of the carbonyl group are destroyed when the substituents are located asymmetrically to the plane of the carbonyl group. For instance, the vacant π^* orbital involves not only the $2p\pi_y$ a.o., but also the $2p\pi_x$ a.o. of the carbon and oxygen atoms, because the maximum stabilization of the energy is obtained after the mixing of the orbitals of asymmetric substituents with all the orbitals of the carbonyl group. If we denote the asymmetric substituents by X and Y, as is shown in Fig. 1, the wavefunction of the carbonyl group will be given by:

$$\varphi_n = a_O\pi_x(O) + a_C\pi_x(C) + a_O'\pi_y(O) + a_C'\pi_y(C) + a_X\pi_x(X) + a_Y\pi_x(Y) + a_X'\pi_y(X) + a_Y'\pi_y(Y)$$

$$\varphi_\pi = b_O\pi_y(O) + b_C\pi_y(C) + b_O'\pi_x(O) + b_C'\pi_x(C) + b_X\pi_y(X) + b_Y\pi_y(Y) + b_X'\pi_x(X) + b_Y'\pi_x(Y)$$

$$\varphi_{\pi^*} = c_O\pi_y(O) + c_C\pi_y(C) + c_O'\pi_x(O) + c_C'\pi_x(C) + c_X\pi_y(X) + c_Y\pi_y(Y) + c_X'\pi_x(X) + c_Y'\pi_x(Y)$$

The electronically-allowed component of the n–π^* transition will be given by the transition matrix elements of the type;

$$\langle \sum_I a_I\pi_x(I) | \mathbf{r} | \sum_I c_I'\pi_x(I) \rangle$$

and

$$\langle \sum_I a_I'\pi_y(I) | \mathbf{r} | \sum_I c_I\pi_y(I) \rangle$$

both of which are polarized along the z-axis. The coefficients a_X, b_X,$\cdots$ will be large when the X and Y groups have pronounced substituent effects. However, they will be zero for the strict C_{2v} symmetry system.

A semiquantitative discussion of the mixing of n, π, and π^* orbitals has been presented by Allinger and Tai.[15]

Since the polarization properties of the n–π^* transition produced by these mechanisms are different, it is important to determine the direction of the electronic transition moment with several kinds of carbonyl compounds in order to clarify which mechanism is predominant as the source of the n–π^* intensity.

15) N. L. Allinger and J. C. Tai, *J. Am. Chem. Soc.*, **88**, 2179 (1966).

Experimental

The electronic absorption spectra of the following compounds; (1) cyclohexane-1,4-dione, (2) *d*-α-bromocamphor, (3) bromonoranisatinone, (4) *d*-α-cyanocamphor, and (5) spiradine A methiodide were measured in ethanol or EPA solutions and in the crystalline states. The polarized crystalline absorption spectra were measured by means of an ultraviolet microspectrophotometer described previously.[16] The materials used were recrystallized from ethanol or ligroin. The bromonoranisatinone and spiradine A were gifts from Professor Hirata of our department. The crystalline axes of these crystals were confirmed by the X-ray method before the measurement of the crystalline absorptions.

Results

1) Cyclohexane-1,4-dione. The crystal structure of cyclohexane-1,4-dione has been determined by Mossel and Romers,[17] and by Groth and Hassel.[18] The crystal is monoclinic, with a space group of $P2_1$ with two molecules in a unit cell. The projection of the molecules in the unit cell on the $(10\bar{1})$ plane, which is the most frequently developed face, is shown in Fig. 2. The crystalline spectra of cyclohexane-1,4-dione at room temperature are shown in Fig. 3. The spectrum in an EPA solution at room temperature is also shown there; its maximum is observed at 35500 cm^{-1}, with a molar extinction coefficient of 60. The crystalline absorption bands were observed

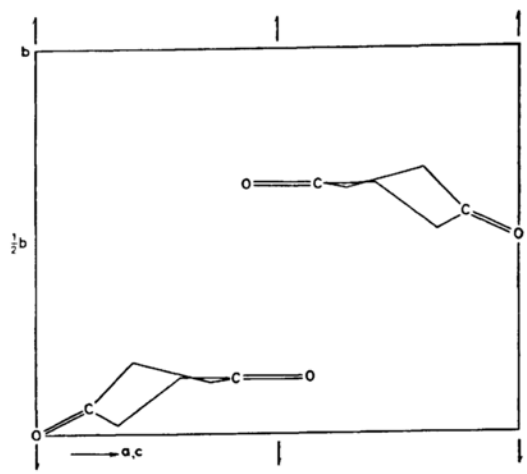

Fig. 2. Projected view of cyclohexane-1,4-dione on to the $(10\bar{1})$ plane according to the X-ray results.

16) J. Tanaka and M. Shibata, This Bulletin, **41**, 34 (1968).

17) A. Mossel and C. Romers, *Acta Cryst.*, **17**, 1217 (1964).

18) P. Groth and O. Hassel, *Acta Chem. Scand.*, **18**, 923 (1964).

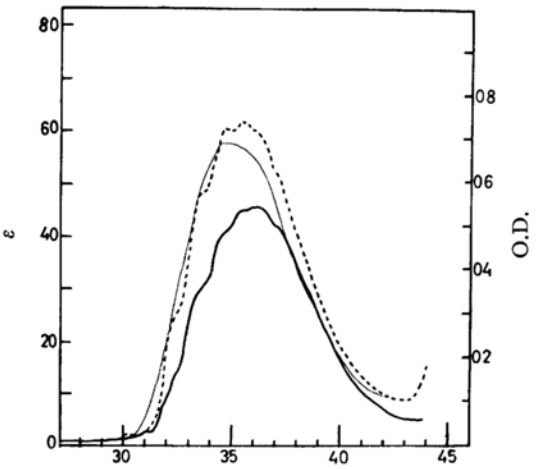

Fig. 3. The spectrum of cyclohexane-1,4-dione in EPA solution at room temperature (fine line) and the absorption of cyclohexane-1,4-dione crystal taken with the $(10\bar{1})$ plane.

—— The light is polarized parallel to the b axis. (bold line).

------ The light is polarized parallel to the $[10\bar{1}]$ axis

Ordinate: left, the molar extinction coefficient for the spectrum of the solution.
right, the optical density for the crystal spectra.

Abscissa: frequency (in 10^3 cm^{-1} unit)

—— in EPA ------ I_{ac} —— I_b

in the same region; they show intervals of 1100 cm^{-1}. The dichroic intensity ratio parallel to and perpendicular to the b axis ($I_b : I_{ac}$) is 1.0 : 1.3. Since the absorption intensities are weak and since the strong transitions are located in the higher-energy region, it is safe to use the oriented gas intensity ratio in discussing the direction of the transition moment. If the transition were allowed along the y axis in Fig. 1, the absorption intensity would be far stronger along the b axis than along the $[10\bar{1}]$ direction. The experimental results are contrary to this presumption; therefore, we may disregard the possibility of the y axis polarization for the n–π^* transition in this compound. Although Brand[19] discovered an out-of-plane component in some α,β-conjugated carbonyls, none of the present results showed any evidence for an out-of-plane component, at least in the saturated ketones. If we restrict the polarization in the plane of the carbonyl group, neither x nor the z axis polarization alone can explain the observed intensity ratio. Therefore, the whole band may be considered to consist of two components, x and z; the ratio of the components has been determined to be $I_x : I_z =$ 0.74 : 0.26. This result indicates that more than two different mechanisms are operative in the present molecule. The low-temperature spectra, which will be presented in the succeeding paper, support this idea by showing the details of the vibrational progressions of this band.

2) *d*-α-Bromocamphor. The crystal structure analysis of *d*-α-bromocamphor and *d*-α-cyanocamphor has been made by Wiebenga and Krom.[20]

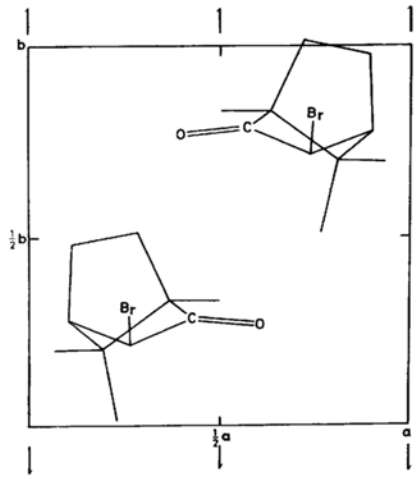

Fig. 4. Projection of the *d*-α-bromocamphor on to the (001) plane by the X-ray results.
The projection of cyanocamphor is nearly the same except that the bromine atom is replaced by the cyano group.

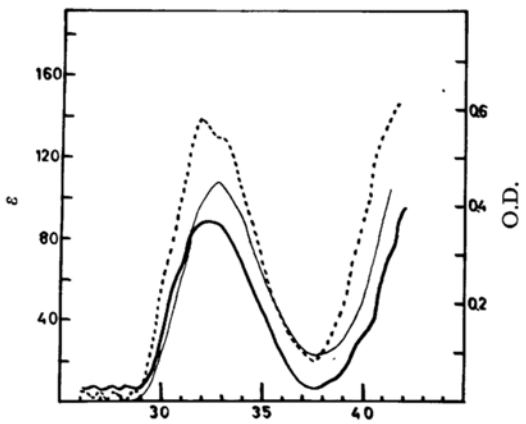

Fig. 5. The spectrum of *d*-α-bromocamphor in the ethanol solution (fine line) and absorption spectra of the crystal.

—— The light is polarized parallel to the b axis (bold line).

------ The light is polarized parallel to the a axis.

Ordinate: left, the molar extinction coefficient for the spectra of the solution.
right, the optical density for the crystal spectra.

Abscissa: frequency (in 10^3 cm^{-1}).

—— in ethanol ------ I_a —— I_b

19) J. C. D. Brand, J. G. Callomon and J. K. G. Watson, *Discussions Faracay Soc.*, **35**, 175 (1963); J. C. D. Brand and G. D. Williamson, *ibid.*, **35**, 184 (1963).

These two compounds are isomorphous. They belong to a monoclinic system, the space group being $P2_1$; two molecules are contained in the unit cell. The crystals develop (001) faces. The projection of the molecules is shown for *d*-α-bromocamphor in Fig. 4, while the spectrum in the ethanol solution is shown in Fig. 5. The maximum of the absorption is shifted about 2300 cm^{-1} to the red and intensity is increased to about three times that of *d*-camphor. This shift was explained by Allinger, Tai and Miller[21] as being due to the effect of the σ^*(C–Br) orbital at the axial position, but the enhancement of the intensity was qualitatively shown and it was not enough to account for the large value observed. The direction of the transition moment was not discussed by these investigators.

The crystalline absorption spectra for the (001) plane are shown in Fig. 5; the dichroic intensity ratio is $I_a : I_b = 1.5 : 1.0$. The out-of-plane component is again neglected with this molecule, since otherwise the *b*-axis spectrum would be much stronger. If the increase in the intensity is produced by the $n\sigma^*$ mixing, the charge-transfer component from the n to σ^* orbital may be expected. Another possible mechanism is the symmetry breakdown of n and π^* orbitals by the axial bromine atom; it would produce the transition along the z axis. The analysis all of the band intensities into the x and z components yielded the value of $I_x : I_z = 0.57 : 0.43$. The direction of the n–σ^* transition nearly coincides with the z axis on this crystalline plane; therefore the increase in the z component may be attributed to either the inherent moment increased along the z axis or to the charge-transfer moment of the n–σ^* type transition. This point will be discussed below.

3) Bromonoranisatinone. Anisatine is a toxic terpenoid separated from seeds of *Illicium Religiosum Siebold et Zuccarini* (Japanese star anise). The crystal structure of bromonoranisatinone was analyzed by Furusaki, Tomiie, Nitta, Sakabe, and Hirata.[22] It has one carbonyl group and two ester groups. The ester groups absorb in the 50000 cm^{-1} region; therefore, we will consider only the carbonyl group in the 33000 cm^{-1} region. The carbonyl is adjacent to the bromine atom at the α position; this conformation can be explained as an intermediate of the axial and equatorial positions. The substituent effect is found to shift the band by just the same order or magnitude as in the case of *d*-α-bromocamphor. The projection of the molecules onto the developed (100) plane is shown in Fig. 6, while the crystalline absorption spectra are shown in Fig. 7. The dichroic ratio was $I_b : I_c = 1.0 : 2.0$. The separation of the band intensities along the x and z components of the carbonyl group showed that the ratio is $I_x : I_z = 0.56 : 0.44$. This finding is very close to that with *d*-α-bromocamphor. The enhancement along the z axis may be originated by a mechanism similar to that of *d*-α-bromocamphor; it will be discussed in the last section.

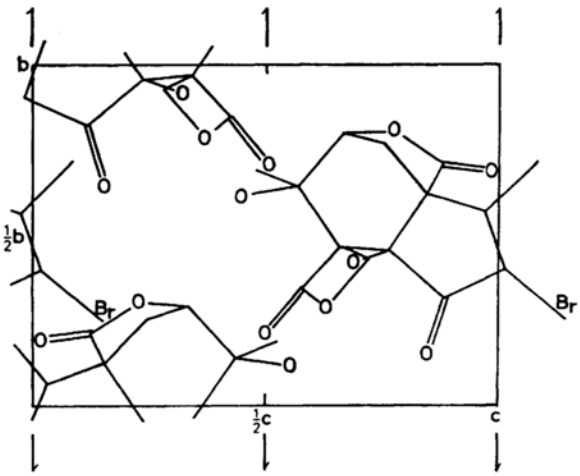

Fig. 6. Projection of bromonoranisatinone on to the (100) plane by the X-ray results.

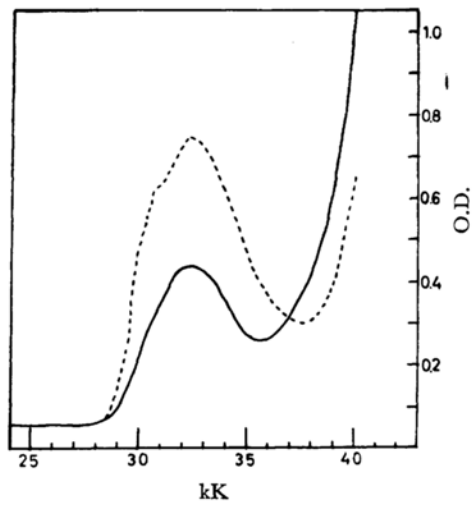

Fig. 7. Absorption spectra of bromonoranisatinone crystal.
—— The light is polarized parallel to the *b* axis (bold line).
------ The light is polarized parallel to the *c* axis.
Ordinate: optical density for the crystal.
Abscissa: frequency (in 10^3 cm^{-1} unit)
—— I_b ------ I_c

4) d-α-Cyanocamphor. The projection of *d*-α-cyanocamphor is almost the same as that of

20) E. H. Wiebenga and C. J. Krom, *Rec. Trav. Chim.*, **65**, 663 (1946).
21) N. L. Allinger, J. C. Tai and M. A. Miller, *J. Am. Chem. Soc.*, **88**, 4495 (1966).
22) N. Sakabe, Y. Hirata, A. Furusaki, Y. Tomiie and I. Nitta, *Tetrahedron Letters*, **52**, 4795 (1965).

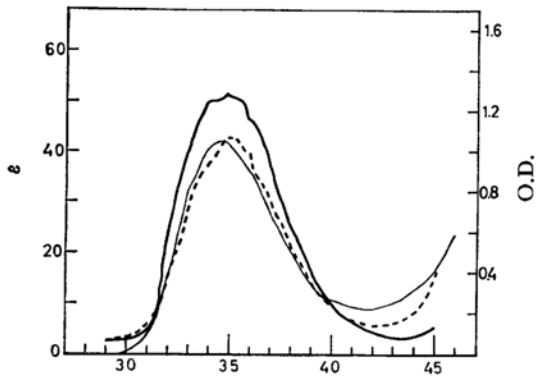

Fig. 8. The spectrum of *d*-α-cyanocamphor in the ethanol solution (fine line) and the absorption spectra of *d*-α-cyanocamphor crystal.
—— The light is polarized parallel to the *b* axis (bold line).
------ The light is polarized parallel to the *a* axis.
Ordinate: left, the molar extinction coefficient for the spectra of the solution.
right, the optical density for the crystal.
Asbcissa: frequency (in 10^3 cm^{-1}).
—— in ethanol ------ I_a —— I_b

d-α-bromocamphor except that the bromine atom is replaced by the cyano group. The spectrum in the ethanol solution is shown in Fig. 8, together with the crystalline spectra. The maximum of the absorption was observed at 33000 cm^{-1}, while the molar extinction coefficient was 42. The integrated intensity ratio for the light polarized parallel to the *b* and *a* axes was $I_b : I_a = 1.0 : 0.74$.

As has been found in the cases of cyclohexane-1,4-dione and *d*-α-bromocamphor, the out-of-plane (*y* aixs) component is negligible; otherwise, the *b*-axis polarized band would be much stronger.

The total band intensity was divided into the *x* and *z* components; the ratio was then obtained as $I_x : I_z = 0.80 : 0.20$. The effect of the cyano group at the axial β,γ-position is not very prominent, except that the intensity is slightly increased. The donor property of the cyano group is very poor, and the overlapping of cyano π orbitals with the *n* and π orbitals of the carbonyl group is not very large; therefore, few charge transfer effects may be anticipated. Another reason for this may be that the cyano group does not have a strong π–π^* transition in the ultraviolet region; therefore the perturbation is correspondingly small.

5) Spiradine A Methiodide. Spiradine A methiodide, an alkaloid botained from *spiraea japonica*,[23] has an ethylenic bond at the β,γ-position. The absorption intensity for spiradine A in the ethanol solution is $\varepsilon = 194$ at 32800 cm^{-1}, about six times that of the dihydro spiradine A, which has $\varepsilon = 35$ at 33300 cm^{-1}. This increase in the intensity is typical of β,γ-unsaturated ketones. The crystalline structure analysis was made by Sakabe, Sasaki and Hirata,[24] the molecule is projected onto the developed crystalline plane in Fig. 9. The crystalline absorption spectra are presented in Fig. 10. The measurement of the absorption intensities showed that $I_b : I_c = 1.0 : 1.75$. This result may be explained by the direction of the transition moment, which is parallel to either the carbonyl axis or the ethylenic bond. The charge-transfer mechanism produces the moment along the line connecting the donor and acceptor groups the ethylenic and the carbonyl groups. Therefore, the present results show that the charge-transfer contribution is not a major source of the intensity and

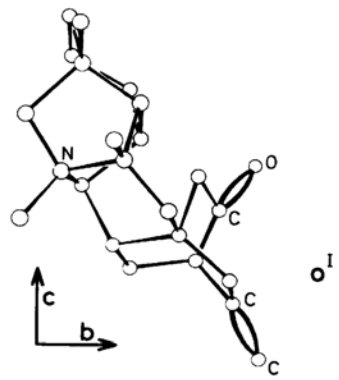

Fig. 9. Projection of spiradine A methiodide onto the (100) plane according to the X-ray results. Eight molecules are contained in a unit cell, but they are related with the two-fold screw axis symmetry operation. (space group $P2_12_12_1$)

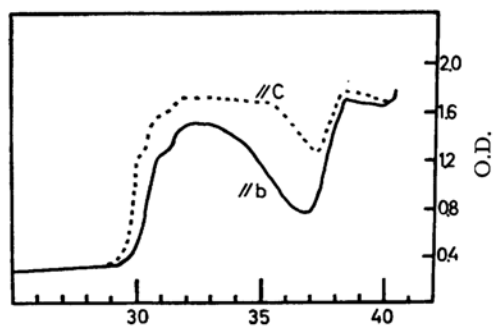

Fig. 10. Absorption spectra of spiradine A methiodide crystal.
—— The light is polarized parallel to the *b* axis (bold line).
------ The light is polarized parallel to the *c* axis.
Ordinate: optical density for the crystal
Abscissa: frequency (in 10^3 cm^{-1} unit)

23) V. I. Frova, A. I. Bankowskii, A. D. Kuzorvkov and M. M. Molodozhnikov, *Med. Prom. S.S.S.R.*, **18**, 19 (1964).

24) G. Goto, K. Sasaki, N. Sakabe and Y. Hirata, *Tetrahedron Letters*, **1968**, 1369.

that the x component also contributes little. Accordingly the origin of the intensity enhancement may be ascribed to either of two reasons; either the symmetry of the carbonyl group is broken by the adjacent double-bond or the ethylenic π–π^* transition moment is mixed in the n–π^* transition of the carbonyl group by the perturbation of the dipole-dipole interaction. The question which of these two alternative mechanisms is predominant can not be answered from the present results only. In addition, the mixing of these two states is not conceivable, since in that case the direction of the transition moment would deviate from the confirmed direction. Further experiments on other β,γ-unsaturated carbonyl compounds are desirable in order to clarify these ambiguities.

Discussion

The findings on spectral data are summarized in Table 1. Cyclohexane-1,4-dione and d-α-cyanocamphor show large x components, 74 and 80%, with the absorption maximam at 35500 and 34700 cm^{-1}, respectively. Pople and Sidman[4] stated that the n–π^* transition induced by the vibrational interaction gives the main component in the x direction in formaldehyde. Although these molecules have heavier atoms attached to the carbonyl group, most of the intensity gain seems to be the same in origin as that of formaldehyde. However, a certain amount of the intensity is found along the z axis; this has significance for the quantitative estimate of the optical activity of asymmetric ketones. This point will be discussed in the succeeding paper.

The maximum frequencies of the absorption spectra for d-camphor, d-α-cyanocamphor, and d-α-bromocamphor in the solution of ethanol are at 35100, 34700 and 32800 cm^{-1} respectively. The effects of the substituents are slightly different; there is a little blue shift for the cyano group and a large red shift for the bromine atom. The maximum molar extinction coefficients are 36, 42, and 107, indicating a typical bathochromic effect, particularly in the bromine atom. According to Allinger, Tai and Miller,[21] the interaction between the σ^* orbital of the C–Br bond and the π^* orbital depresses the transition energy of d-α-bromcaomphor. Mixing of this type induces the transition moment along the line connecting the centers of the σ^* and π^* orbitals. Another possibility is the deformation of the n and π^* orbitals, which would give a transition moment parallel to the carbonyl axis. If the direction of the transition moment could be determined exactly, the contribution of these alternative mechanisms would be elucidated.

Both bromonoranisatinone and d-α-bromocamphor have a bromine atom in the α-position relative to the carbonyl group; the former has its in the position intermediate between the equatorial and axial axes, while the latter has its in the axial axis. Bromonoranisatione shows its absorption maximum at 32500 cm^{-1}; the similar red shift indicates the bathochromic effect of the substituent bromine atom, even for the intermediate geometry. In d-α-bromocamphor the direction of the transition moment could not be conclusively determined, for the carbonyl axis and n-to-σ^* orbital directions are nearly parallel on the measured crystalline plane. Bromonoranisatinone shows a crystalline plane in which the directions of the π–π^* and n–σ^* (C–Br) transitions are different; therefore, these different mechanisms could be distinguished by the polarization measurements. The observed results show that the z component is 43%; this value is exactly the same as that of d-α-bromocamphor. This means that the n–σ^* transition moment contributes little to the enhancement of the overall transition moment; the assumed deformation of π, π^*, and n orbitals seems to be more attractive.

In the n–π^* transitions of the carbonyl group, the magnetic transition moment has a component in the z-axis direction, so if there is to be optical activity there must be an electronic transition moment parallel to the z-axis direction. The optical rotational strength of d-α-bromocamphor is three times those of d-camphor and d-α-cyanocamphor. This may mean that the z component of the transition moment is about three or more times larger in d-bromocamphor than in d-camphor and d-α-cyanocamphor. This would agree with the present findings regarding the crystal spectra; the increase in the z component is established in d-α-bromocamphor and bromonoranisatinone.

The absorption spectra of spiradine A (β,γ-unsaturated ketone), dihydro spiradine A and spiradine A methiodide were investigated in an ethanol solution. The maximum wave numbers differ only slightly, but the maximum molar extinction coefficient increases drastically for β,γ-unsaturated ketone. The β, γ double bond has a great effect on the intensification of the n–π^* transition. Although the mixing of the charge-transfer state was suggested by Labhart and Wagniere, the crystal spectrum gives rather negative evidence for the contribution of the CT transition moment.

The wavefunction for the perturbed n–π^* state of β,γ-unsaturated ketone may be given by:

$$\Phi(n\pi^*) = a\varphi_s(n\pi^*) + b\varphi(\pi\pi^*;\ \mathrm{C{=}O}) + c\varphi(\mathrm{CT}) + d\varphi(\pi\pi^*;\ \mathrm{C{=}C}) \qquad (3)$$

$$c = \frac{\langle\varphi_{n\pi}{}^*|\mathbf{H}|\varphi_{\mathrm{CT}}\rangle}{E_{n\pi}{}^* - E_{\mathrm{CT}}}$$

$$d = \frac{\langle\varphi_{n\pi}{}^*|\mathbf{H}|\varphi_{\pi\pi}{}^*;\ \mathrm{C{=}C}\rangle}{E_{n\pi}{}^* - E_{\pi\pi}{}^*;\ \mathrm{C{=}C}}$$

The appearance of the b term is mainly due to the deformation of the π and n orbitals, as has been

discussed previously, or to the second-order perturbations. The first term, which includes the vibronic mechansisms, is not significant for the whole transition moment, the second will give a component along the carbonyl axis, and the last one, one along the unsaturated carbon-carbon bond. The experiment indicates that either the second or the last one is most important for the present system. Conclusive proof on this point must, however, await some more experiments on other crystalline systems. However, recent results by Kearns, Marsh and Schaffner[25] seemingly show that in α,β-unsaturated ketone the 0–0 transition of the $n-\pi^*$ band is allowed electronically. Further effort along these lines is desirable for the elucidation of the source of the $n-\pi^*$ intensity of the unsaturated ketone.

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25) D. R. Kearns, G. Marsh and K. Schaffner, *J. Chem. Phys.*, **49**, 3316 (1968).