Optical Activity in βγ-Unsaturated Ketones. Part 1. Effect of the Direction of the Electric Transition Dipole Moment in the Aromatic Group in Benzobicyclo[2.2.2]octen-2-one† Derivatives

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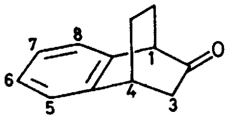
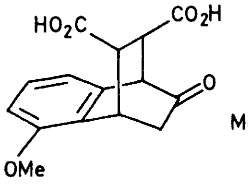
In methoxybenzobicyclo[2.2.2]octen-2-one derivatives, a change in the position of the methoxy-group brings about a change in the direction of the transition dipole moment without much alteration in the σ-electron distribution. We have studied the effects of the change of the direction of the local chromophore on the optical activity and analysed these by application of dynamic and static coupling mechanisms. We have concluded that the optical activity is mainly produced by $\vec{\mu}$–$\vec{m}$ coupling and depends on the direction of the local transition moments.

THE n–π^* transition in βγ-unsaturated ketones produces an unusual intensification in both the absorption [1] and the optical rotatory power.[2-9] The intensification is known to be influenced by the relative position and orientation of the carbonyl group and the unsaturated group.[10-20] In connection with this, we have prepared optically active benzobicyclo[2.2.2]octen-2-one (+)-(1) and its derivatives (+)-(2) to (+)-(5) with the methoxy-group in different positions of the benzene ring and measured the absorption and the c.d. spectra.[21] But we could not give a definite explanation of the origin of the optical rotatory power at that time. In this work, the nature of the Cotton effect is elucidated.



(+)-(1)



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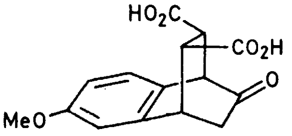
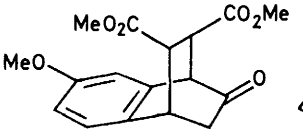


(+)-(3)



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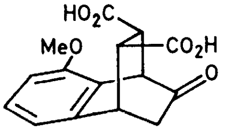

(+)-(5)

The experimental data are summarized in Table 1. A shoulder of the absorption spectra in the longest wavelength region (*ca.* 295 nm) clearly originates from the n–π^* transition of the carbonyl group. The magnitude of the Cotton effect is largest in the 7-methoxy-derivative (+)-(4) and then decreases in the order 6-methoxy (3) > 5-methoxy (2) > 8-methoxy (5) > unsubstituted derivative (1).

The absorption maxima around 280 nm are attributable to the ^1L_b band of the anisole or benzene moiety. The 7-methoxy-derivative apparently exhibits a negative Cotton effect. Other compounds do not show the definite ^1L_b c.d. band owing to overlap with the tail of the large positive n–π^* carbonyl band. But it is reasonable to regard the sign as nearly zero for the 5- and 8-methoxy-compounds and as negative for the 6-methoxy and unsubstituted derivatives from the shape of the curves.

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† Named correctly according to I.U.P.A.C. rules as 3,4-dihydro-1,4-ethanonaphthalen-2(1*H*)-one.

[1] H. Labhart and G. Wagnière, *Helv. Chim. Acta*, 1959, **42**, 2219.

[2] R. C. Cookson and N. S. Wariyar, *J. Chem. Soc.*, 1956, 2302.

[3] R. C. Cookson and J. Hudec, *J. Chem. Soc.*, 1962, 429.

[4] S. F. Mason, *J. Chem. Soc.*, 1962, 3285.

[5] R. E. Ballard, S. F. Mason, and G. W. Vane, *Trans. Faraday Soc.*, 1963, **59**, 775.

[6] R. Grinter, S. F. Mason, and G. W. Vane, *Trans. Faraday Soc.*, 1964, **60**, 285.

[7] A. Moscowitz, *Proc. Chem. Soc.*, 1964, 60.

[8] S. F. Mason, *Proc. Chem. Soc.*, 1964, 61.

[9] K. Mislow, *Ann. New York Acad. Sci.*, 1962, **93**, 459.

[10] K. Mislow, M. A. W. Glass, A. Moscowitz, and C. Djerassi, *J. Amer. Chem. Soc.*, 1961, **83**, 2771.

[11] A. Moscowitz, K. Mislow, M. A. Glass, and C. Djerassi, *J. Amer. Chem. Soc.*, 1962, **84**, 1945.

[12] E. Bunnenberg, C. Djerassi, K. Mislow, and A. Moscowitz, *J. Amer. Chem. Soc.*, 1962, **84**, 2823.

[13] K. Mislow and J. G. Berger, *J. Amer. Chem. Soc.*, 1962, **84**, 1956.

[14] D. E. Bays, G. W. Cannon, and R. C. Cookson, *J. Chem. Soc.* (*B*), 1966, 885.

[15] D. E. Bays, R. C. Cookson, and S. MacKenzie, *J. Chem. Soc.* (*B*), 1967, 215.

[16] A. Moscowitz, A. E. Hansen, L. S. Forster, and K. Rosenheck, *Biopolymer Symposia*, 1964, **1**, 75.

[17] R. C. Cookson, *Proc. Roy. Soc.*, 1967, **297**, 27.

[18] A. Moscowitz, *Proc. Roy. Soc.*, 1967, **297**, 40.

[19] D. J. Sandman, K. Mislow, W. P. Gidding, J. Dirlam, and G. C. Hanson, *J. Amer. Chem. Soc.*, 1968, **90**, 4877.

[20] D. A. Lightner and W. A. Baevers, *J. Amer. Chem. Soc.*, 1971, **93**, 2677.

[21] K. Takeda, S. Hagishita, M. Sugiura, K. Kitahonoki, I. Ban, S. Miyazaki, and K. Kuriyama, *Tetrahedron*, 1970, **26**, 1435.

An electronic absorption is also observed in the region 230—240 nm, although it is only a shoulder of an absorption in a shorter wavelength region except for the 6-methoxy-derivative. The c.d. spectra show the negative large magnitude of the Cotton effect except for the 7-methoxy-derivative. This absorption may be assigned to the ^1L_a band, although it may be mixed with the charge transfer transition as pointed out by Cookson.[17]

The difference of shape of the c.d. spectra may be caused by a change of the orientation of the local electric transition moments of the aromatic chromophore and/or that of the charge transfer between the aromatic and carbonyl groups, since the transition energy would not vary so much upon changing the position of the methoxy-group.

Labhart and Wagnière[1] attributed the intensification of the n–π^* transition to mixing of the charge transfer transition with the overlap between the oxygen lone pair orbital and the π-orbitals of the olefin group, allowed by the non-planar disposition of the unsaturated groups in the molecule. Further, Mason pointed out the overlap between successive pairs of orbitals on adjacent atoms linking the carbonyl and the vinyl groups.[5] On the other hand, Moscowitz showed that the mixing of the carbonyl n–π^*_{CO} with the olefin π_{CC}–π^*_{CC} transition was due mainly to electrostatic coupling of the two local transitions rather than to charge transfer by use of the Longuet-Higgins–Murrell formalism.[16]

Magnetic dipoles do not couple directly with electric dipoles in the composite system. However, if the transition is of the n–π^* type involving a p–p quantum jump in the atomic orbitals, it is associated with a large quadrupole moment which can interact strongly with the non-homogeneous field of a neighbouring transition dipole. Thus, the coupling takes place by way of the interaction of the electric dipole $\vec{\mu}_1$ with the quadrupole associated with the magnetic dipole $\vec{m}_2$ (the $\vec{\mu}$–$\vec{m}$ coupling mechanism). We can then analyse the c.d. spectra with the Kirkwood approach[22] developed by Höhn and Weigang,[23] Schellman,[24] and Buckingham and Stiles.[25]

Further, since the compounds are conformationally rigid and therefore the p-orbital in both the carbonyl group and benzene ring does not change its position and orientation by altering the position of the methoxy-group, the mixing of other transitions into the n–π^* transition through the σ-bond would not change much. Therefore, these compounds are very suitable for examining the effect caused by a change in the direction of the transition in the perturbers.

METHODS AND CALCULATIONS

When the dissymmetric molecule is composed from more than one chromophore, the jth total wave function ψ_j can be represented by the linear combination of each local excited state wavefunctions ϕ_i [equation (1) where C_{ij} is

$$\psi_j = \sum_i C_{ij}\phi_{ij} \qquad (1)$$

the mixing coefficient of the jth energy level and the ith local function]. This yields a set of linear equations (2) for

$$\sum_i \sum_j [H_{ij} - S_{ij}(H_{OO} + E)]C_{ij} = 0 \qquad (2)$$

C_{ij} and the secular equation (3) for E where owing to the

$$|H_{ij} - S_{ij}(H_{OO} + E)| = 0 \qquad (3)$$

complete neglect of the electron exchange, $S_{ij} = 1$ if $i = j$ and $S_{ij} = 0$ if $i \neq j$. Regarding the perturbation as small, the Hamiltonian can be separated where H_i is the

$$H = \sum_i H_i + \sum_{i<j} H_{ij} \qquad (4)$$

ith original local Hamiltonian. The second term is equivalent to electrostatic interactions between certain charge distributions.

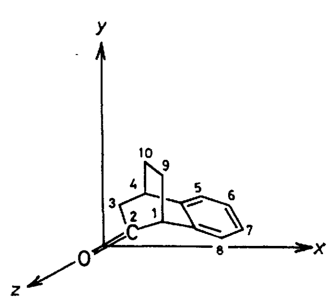

FIGURE 1 Cartesian co-ordinate system used for calculation

The rotational strength R_j of the transition between two stationary states can be calculated by equation (5) by the

$$R_j = \tfrac{1}{2}\left\{\sum_i \sum_k C_{ij}C_{kj}\vec{\mu}_i \cdot \vec{m}_k + \frac{\pi E_j}{hc}\sum_i \sum_k C_{ij}C_{kj}\vec{\mu}_i \cdot (\vec{R}_{ik} \times \vec{\mu}k)\right\} \qquad (5)$$

use of the wave function, $\psi_i = \sum_i C_{ij}\phi_i$ and transition energies, E_j. $\vec{\mu}_i$ and $\vec{m}_k$ are the electric and the magnetic dipole moments of the transition, respectively. $\vec{R}_{ik}$ is the distance vector between two chosen groups i and k.

No attempt was made to determine the correct geometry of this system and we used the idealized one depicted in Figure 1, where the aromatic C–C bond length is 1.392 Å, the single bonds C(1)–C(1a), C(1)–C(2), C(2)–C(3), and C(4)–C(4a) 1.505 Å, and C(3)–C(4) 1.533 Å. The three planes C(1)–C(2)–C(3)–C(4), C(1)–C(1a)–C(4a)–C(4), and C(1)–C(9)–C(10)–C(4) are at 120° to each other.

For a carbonyl group, we take into consideration three kinds of singlet electronic transitions: n–π^*, n–σ^*, and π–π^* transitions. The n–π^* transition is forbidden in an electric dipole moment but allowed in a magnetic dipole moment. In the co-ordinate system employed, the magnetic moment is z-axis polarized and the quadrupole

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[22] J. G. Kirkwood, *J. Chem. Phys.*, 1937, **5**, 479; 1939, **7**, 139.

[23] E. G. Höhn and O. W. Weigang, jun., *J. Chem. Phys.*, 1968, **48**, 1127.

[24] J. A. Schellman, *Accounts Chem. Res.*, 1968, **1**, 144.

[25] A. D. Buckingham and P. J. Stiles, *Accounts Chem. Res.*, 1974, **7**, 258.

moment is only non-zero in the xy element. The n–σ^* transition has an x-axis polarized electric moment and a y-axis polarized magnetic moment and its quadrupole moment is allowed in the xz element. The π–π^* transition has only an allowed electric dipole moment with the z-axis orientation. Aromatic chromophores show the electric transition moments with observable intensity even in the originally forbidden transition.

Thus, it is sufficient in these compounds to take into consideration dipole–dipole and dipole–quadrupole interactions. These were calculated by equations (6) and (7),

$$V(\text{dipole–dipole}) = \frac{\vec{\mu}_1 \cdot \vec{\mu}_2}{R^3} - \frac{3(\vec{\mu}_1 \cdot \vec{R})(\vec{\mu}_2 \cdot \vec{R})}{R^5} \qquad (6)$$

$$V(\text{dipole–quadrupole}) = \frac{\vec{R} \cdot \vec{Q}_1 \cdot \vec{\mu}_2}{R^5} - \frac{5}{2}\frac{(\vec{R} \cdot \vec{Q}_1 \cdot \vec{R})(\vec{R} \cdot \vec{\mu}_2)}{R^7} \qquad (7)$$

where $\vec{\mu}_1$ and $\vec{\mu}_2$ are the transition moments in groups 1 and 2, R is the distance between them, $\vec{R}$ is a vector from group 1 to 2 and $\vec{Q}_1$ is the quadrupole tensor.

Table 1 gives the values of transition energies, dipole moments, magnetic moments, and quadrupole moments of local chromophores used for the calculation. Here the n–π^* transition of the carbonyl group was considered to be an electric jump from $2p_x$ to $2p_y$ and n–σ_x from $2p_x$ to an sp hydridized orbital, $1/\sqrt{2}(s\text{-}p_z)$. We used the data for tetralin, 1-methoxytetralin, and 2-methoxytetralin, for the local aromatic chromophores. The direction of the long axis transition dipole moment of 5- and 8-methoxy and unsubstituted derivatives is assumed to be parallel to the line of C(1)–C(4) and that of the short axis one is perpendicular to its line in the benzene plane.

TABLE 1

Energies, electric and magnetic dipole moments, and the quadrupole moments of the transitions of the local chromophores used for calculation

Chromophore	Transition	λ/nm	$10^{20} \times \vec{\mu}$ (c.g.s.)	$10^{20} \times \vec{m}$ (c.g.s.)	$10^{26} \times \vec{\theta}$ (c.g.s.)
O=C<	n–π^*	295		8.1	0.9
	n–σ^*	195[a]	8.57[a]	5.728	0.636
	π–π^*	155[a]	27.5[a]		
Tetralin in heptane	^1L_b	267	6.54		
	^1L_a	213	24.5		
	^1B_b	199	38.2		
	^1B_a	193	39.0		
1-Methoxytetralin in heptane	^1L_b	272	9.62		
	^1L_a	220	28.1		
	^1B_b	203	44.6		
	^1B_a	195	38.9		
2-Methoxytetralin in heptane	^1L_b	282	13.1		
	^1L_a	221	28.5		
	^1B_b	282.5	47.1		
	^1B_a	194	35.2		

[a] I. Absar, C. S. Lin, and K. L. McEwen, *Canad. J. Chem.*, 1972, **50**, 646.

In the 6- and 7-methoxy-derivatives, the direction is calculated by the vector addition of the spectroscopic moments [26] induced by the methoxy-group and the alkyl bridge which makes up the bicyclo[2.2.2]octenone skeleton. The following values were used for calculation: OMe, +31; alkyl bridge, +7.

Further, the transition moment is assumed to be a point dipole, located at the centre of the benzene ring and at the mid-point of the C=O bond.

Knowledge of the direction of the permanent dipole moment is necessary to evaluate the static coupling term [23,25] and was estimated to have an angle of 55° with the C–O direction at the oxygen atom in the 5- and 8-methoxy-derivatives, as the methoxy-group was restricted in free rotation by steric hindrance with the *peri*-hydrogen. But in the 6- and 7-methoxy-derivatives, the direction was assumed to be oriented from the centre of the benzene ring to the oxygen atom.

We calculated the rotational strength of the jth level with equation (5) using the wave functions and transition energies obtained.

RESULT AND DISCUSSION

According to the rotation of the direction of an electric transition dipole moment of the perturber in the benzene ring plane, the perturbation energy V, the simple scalar product, $\vec{\mu} \cdot \vec{m}$, of the local benzene transition moment $\vec{\mu}$ and the local carbonyl magnetic moment $\vec{m}$, and the rotational strength R change gradually. As a preliminary calculation, we plotted these values against the rotation angle θ of the local transition from the line C(5)–C(8) with the hypotheses of constant energy and electric dipole moment of the local transition (Figure 2). With this condition, it is easy to understand that the rotational strength depends on the rotation angle θ of the local transition and reaches a minimum at 63 and a maximum at 153°, but these angles do not coincide with those of the scalar product $\vec{\mu} \cdot \vec{m}$.

But experimentally, the energy and electric dipole moment are not constant as shown by the data for 1-methoxy- and 2-methoxy-tetralin (Table 1). Further, the π–π^* transition of the carbonyl group mixes with the n–π^* transition through the static coupling term, since the methoxy-group has a permanent dipole moment. Table 2 gives the experimental and calculated rotational strengths and the transition energies in wavelength units, together with the mixing coefficient of the local transitions to the excited states. The long wavelength band

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[26] J. R. Platt, *J. Chem. Phys.*, 1951, **19**, 263.

arises from an n–π^* transition. The sign of the Cotton effect is, of course, completely consistent with the experimental results. Table 3 gives the degree of the contribution to the rotational strength originating from mainly produced by n–π^* coupling but the local benzene π–π^* transitions and the π–π^* transition of the carbonyl group do not contribute much to the rotational strength. If 1- and 2-methoxytetralin are regarded as local chromophores, their transition energies and magnitude of the electric dipole moment depend little on the position of the methoxy-group, as shown in Table 1. The angle θ of the local transition moment mainly affects the optical activity according to the idealized curve in Figure 2. In fact, the long axis polarization of the benzene transition is predominant in the 5-, 6-, and 8-methoxy-compounds and the short axis one in the 7-methoxy-derivative.

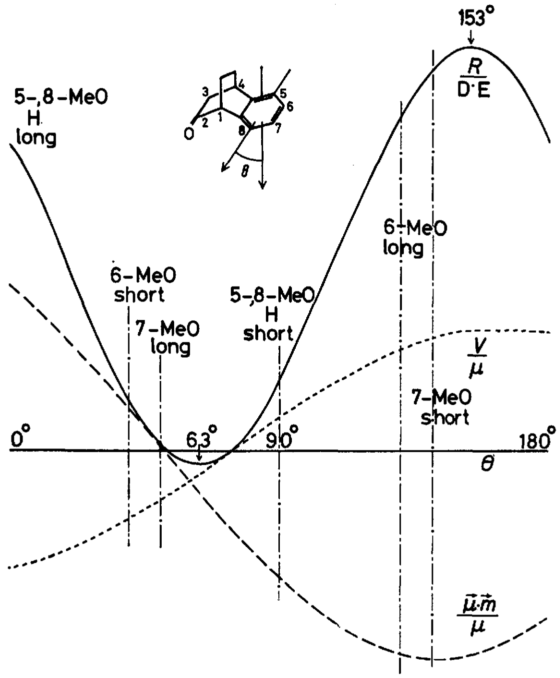

FIGURE 2 Perturbation energy V (– – – –), simple scalar product $\vec{\mu}\cdot\vec{m}$ (— — — —), and rotational strength R (——), as functions of rotational angle θ between the local electric transition moment and the line $\overrightarrow{C(5)\text{–}C(8)}$ with the hypothetical conditions of constant energy and magnitude of the local transition moment

The magnitudes of the rotational strength of the n–π^* transition are in fair agreement with the experimental values for all compounds. The calculated rotational strength decreases in the sequence 7-methoxy > 6-methoxy > 8-methoxy > 5-methoxy > unsubstituted derivatives. On the contrary, the experimental sequence for the 8- and 5-methoxy-derivatives is reversed. However, the contribution of the dicarboxy-groups to the rotational strength is completely neglected in this calculation, although the 5- and 8-methoxy compounds are different in their orientation. It has been reported that the β-axial carboxy and β-*endo*-methoxycarbonyl groups show dissignate[27] behaviour in the rigid adamantane[28] (6) and (7) and bicyclo[2.2.2]-octanone systems[29] (8) and (9) respectively. Since the 5-methoxy-compound has a dissignate and the 8-methoxy-compound a consignate carboxy-group,[27] we might be able to deduce that the additivity of the contributions of the groups is large enough to reverse the sequence of 5- and 8-methoxy-compounds.

TABLE 2

Experimental and calculated c.d. spectra and mixing coefficient of the local transitions

	Obs.		Calc.		Mixing coefficients						
Compound	λ/nm	$10^{40}R$ (c.g.s)	λ/nm	$10^{40}R$ (c.g.s.)	n–π^*	n–σ^*	π–π^*	^1L_b	^1L_a	^1B_b	^1B_a
(+)-(1)	296	+31.1	296.1	+23.0	0.995 8	0.008 6	−0.000 8	0.015 9	−0.057 3	0.020 8	−0.066 6
	265	−1.1	267.0	−0.65	−0.016 0	0.008 1	−0.009 1	0.999 8	0.000 6	0.001 0	0.000 6
	220	−16.1	213.5	−16.2	0.061 1	−0.197 8	−0.000 2	0.002 0	0.977 1	−0.032 0	0.037 7
(+)-(2)	294	+33.0	296.3	+26.6	0.994 4	0.009 9	−0.000 3	0.028 6	−0.074 1	0.023 7	−0.065 3
	275[a]	−1.5	272.0	−1.57	−0.028 6	0.011 3	−0.013 2	0.999 4	0.001 7	0.001 4	0.001 3
	227	−16.9	220.4	−18.2	0.076 7	−0.165 0	−0.000 4	0.002 4	0.982 8	−0.022 8	0.020 3
(+)-(3)	297	−35.7	296.6	+29.1	0.986 3	0.008 2	−0.000 4	−0.131 6	0.065 3	−0.048 5	0.056 8
	275[a]	~0 0	281.8	−1.07	0.130 4	0.014 1	−0.010 5	0.991 1	0.012 4	−0.007 2	0.010 0
	239	−40.0	221.7	−35.2	−0.069 1	0.164 5	−0.041 0	−0.006 3	0.982 7	−0.005 3	0.027 3
(+)-(4)	297	+36.1	296.9	+37.6	0.972 7	0.014 6	−0.001 1	0.213 8	−0.031 3	0.079 1	−0.027 3
	280.5	−10.7	281.5	−18.4	−0.213 4	0.028 1	−0.011 7	0.976 3	0.008 4	−0.014 8	0.006 9
	233	+0.80	221.1	+2.16	0.032 7	−0.039 6	−0.041 1	−0.000 7	0.997 8	0.004 0	0.006 2
(+)-(5)	295	+32.0	296.3	+27.7	0.009 9	−0.009 9	−0.004 9	0.029 1	−0.074 0	0.024 2	−0.065 3
	275[a]	−0.45	272.0	−1.58	−0.029 2	0.011 2	−0.012 9	0.999 4	0.001 8	0.001 4	0.001 4
	231	−19.1	220.4	−17.6	0.076 6	−0.164 9	−0.002 5	0.002 3	0.982 9	−0.021 9	0.020 3

[a] Estimated value.

In the region of the benzene ^1L_b transition, we find the interaction between the local carbonyl and benzene transitions and shows that the rotational strength is good agreement between the calculated and experimental results although experimentally the c.d. band

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[27] W. Klyne and D. N. Kirk, *Tetrahedron Letters*, 1973, 1483.

[28] G. Snatzke and G. Eckhardt, *Tetrahedron*, 1968, **24**, 4543.

[29] P. Crabbé, L. H. Zalkow, and N. N. Girotra, *J. Org. Chem.*, 1965, **30**, 1678.

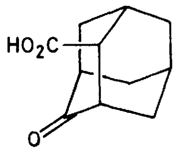
cannot be detected precisely in the 5-, 6-, and 8-methoxy-derivatives. The origin of the optical rotatory power is found to be mainly the $\vec{\mu}$–$\vec{m}$ coupling of the electric moment $\vec{\mu}$ of the ^1L_b transition with the magnetic moment $\vec{m}$ of the n–π^* transition, as shown in Table 3 and the direction of the ^1L_b transition plays an important role. But we cannot neglect the contribution of the $\vec{\mu}$–$\vec{\mu}$ coupling of the ^1L_b transition with the n–σ^* transition.

The absorption of the next shorter wavelength region is of the benzene ^1L_a transition in nature. The sign and magnitude of the calculated rotational strength agree well with the experimental values. However, the observation that the 7-methoxy-compound (+)-(4), exhibits a c.d. band of opposite sign in its disodium salt and in its dimethyl ester would indicate a contribution from the π–π^* transition of the dicarboxy-groups [30] in this region. But this contribution is considered to be small [30] and can be neglected in the calculation. The origin of the rotatory power is not so simple as in the longer wavelength regions. We find that the contribution of the $\vec{\mu}$–$\vec{m}$ coupling of the ^1L_a transition with the n–π^* transition is about half the total rotational strength and the coupling between the ^1L_a and n–σ^* transitions plays an important role.

TABLE 3

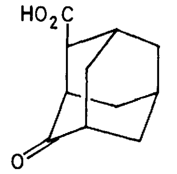
Main configuration and magnitude of the contribution of the local transitions to the rotational strength of the main configuration

Compound	λ/nm	Main configuration	Contributions n–π^*	n–σ^*	π–π^*	^1L_b	^1L_a	^1B_b	^1B_a
(+)-(1)	296.1	n–π^*		0	0.204	0.385	6.777	2.929	12.573
	267.0	^1L_b	−0.395	−0.194	−0.023				
	212.8	^1L_a	−7.155	−7.142	−0.037				
(+)-(2)	296.3	n–π^*		0	0.074	1.032	10.127	3.661	11.786
	272.0	^1L_b	−1.040	−0.403	−0.048				
	220.4	^1L_a	−10.360	−6.660	−0.076				
(+)-(3)	296.9	n–π^*		0	0.095	2.252	11.079	2.710	12.997
	281.5	^1L_b	−2.242	−0.282	−0.558				
	221.1	^1L_a	−11.683	−15.892	−5.702				
(+)-(4)	296.6	n–π^*		0	0.259	16.828	0.216	20.343	0.253
	281.8	^1L_b	−16.858	−1.184	−0.682				
	221.7	^1L_a	−0.230	−1.774	−4.974				
(+)-(5)	296.3	n–π^*		0	0.529	0.047	18.528	0.529	23.177
	272.0	^1L_b	−1.062	−0.397	−0.010				
	220.4	^1L_a	−10.353	−6.659	−0.502				



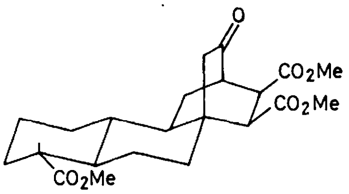
$\Delta\varepsilon_{303}$ + 0.28

(6)



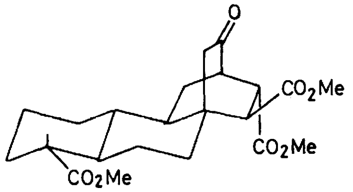
$\Delta\varepsilon_{302.5}$ + 0.47

(7)



$[\phi]_{303}$ -4660

(8)



$[\phi]_{319}$ + 941

(9)

EXPERIMENTAL

U.v. spectra of the tetralin derivatives were measured with a Beckman DK-2A spectrometer in heptane–tetralin $\lambda_{max.}$ 274 (ε 622), 267 (550), 262 (394), 258sh (342), 255sh (249), 218sh (7 650), 213 (8 710), 198 (47 700), and 195 nm (46 700); 1-methoxytetralin $\lambda_{max.}$ 278.5 (ε 1 410), 274 (1 150), 271 (1 230), 230.5sh (5 090), 220.5 (8 240), and 202 nm (46 000); 2-methoxytetralin $\lambda_{max.}$ 288 (ε 2 450), 282.5 (2 240), 279 (2 250), 273sh (1 620), 221 (7 510), and 200.5 nm (42 000).

[7/409 *Received, 7th March,* 1977]

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[30] G. Montaudo and C. G. Overberger, *J. Amer. Chem. Soc.*, 1969, **91**, 753.