

**OPTICAL ROTATORY POWER
OF THE FLEXIBLE AROMATIC COMPOUNDS****(S)-(-)-1-PHENYLETHANOL AND (S)-(-)-1-(2-METHYLPHENYL)ETHANOL***O. ČERVINKA^a, M. KRÁL^b and P. MALOŇ^a^a*Department of Organic Chemistry and*^b*Department of Chemical Analysis,**Prague Institute of Chemical Technology, 166 28 Prague 6*

Received December 3rd, 1974

The method allowing to describe the Cotton effects of the compounds with perturbed symmetry of the aromatic chromophore caused by incorporation of the chiral substituent was applied to the model compounds (S)-(-)-1-phenylethanol and (S)-(-)-1-(2-methylphenyl)ethanol. The preferred conformations were located upon using the empirical potential functions. Then the optical rotatory power was computed as a sum of the contributions of one-electron and coupled oscillator mechanisms. It can be derived from the results obtained, that the cause of the opposite signs of the Cotton effect of the 1L_b band at the same absolute configuration of the both compounds is not a change of the preferred conformation but a varying symmetry of the transition. This symmetry change is accompanied by a change of orientation of the transition moments in the both compounds studied.

Recently the development of the semiempirical quantum chemical methods has enabled a rather detailed understanding of the optical activity phenomena¹. However, most of the papers reported deal with the compounds possessing carbonyl chromophore²⁻⁵ and aliphatic compounds respectively, in which the direction of the electric transition moments corresponds to the spatial orientation of σ bonds^{6,7}.

The calculation of the optical rotatory power of aromatic chiral compounds represents the more complicated case because of the necessity to approximate the wavefunctions of their excited states with the aid of several singly excited configurations and due to the lack of information concerning their magnetic transition moments. For these reasons most of the works on the aromatic chromophore were performed within the basis of Kuhn's⁸ and Kirkwood's⁹ theory of coupled oscillators for which the knowledge of electric transition moments of at least two isolated chromophores in the optically active molecule is sufficient¹⁰⁻¹⁵. In the case of a compound which does not belong to the class of rigid molecules a determination of preferred conformations should precede the calculation of the optical rotatory power. This

type of calculation has been reported by Hooker and Schellman¹⁶ on interpreting 1L_b and 1L_a Cotton effects of *o*-, *m*- and *p*-tyrosines.

In our laboratory we are studying the asymmetric reductions of alkyl aryl ketones¹⁷⁻¹⁹ leading to partially optically active alcohols of 1-arylethanol type. The optical purity of the products obtained amounts up to 50 per cent and enables CD measurements at least within the region of 1L_b absorption band of the aromatic nucleus. In this paper we try to interpret the 1L_b Cotton effects of (S)-(-)-1-phenylethanol (*I*) and of (S)-(-)-1-(2-methylphenyl)ethanol (*II*). Both compounds, which are very similar in respect of structure, exhibit inverse Cotton effects at the same absolute configuration in the region under consideration. Thus, it remains to be explained whether this inversion consists in a change of conformational population or in a change of the orientation of transition moments caused by a perturbation of the chromophore with a methyl group.

EXPERIMENTAL

Partially optically active (*R*)-(+)-1-phenylethanol [α_D^{20} 20.40°; optical purity 52.2% and (*R*)-(+)-1-(2-methylphenyl)ethanol [α_D^{20} 10.30°; optical purity 14.4%] were prepared by asymmetric reduction of acetophenone and methyl *o*-tolyl ketone respectively upon using the chiral agent prepared from equimolar amounts of lithium aluminium hydride and (-)-quinine^{17,18}. The absorption spectra and CD curves (recalculated for optically pure compounds) are given in Fig. 1. The (*R*)-(+) absolute configuration was established by Mislow²⁰ for 1-phenylethanol upon applying the chemical correlation to lactic acid and suggested for 1-(2-methylphenyl)ethanol on the basis of qualitative stereochemical analysis of the course of asymmetric reduction¹⁸. The theoretical calculations were executed for (S)-(-) enantiomers of both compounds and consequently the experimental values of rotatory strength were converted in this sense. The CD curve of (S)-(-)-1-phenylethanol (*I*) covering the bands 1L_b and 1L_a was reported previously by Verbit²¹ and for the band 1L_b also by Gillard and Mitchell²². The lastly mentioned authors assigned, however, the (S)-(+) configuration to 1-phenylethanol without any further discussion.

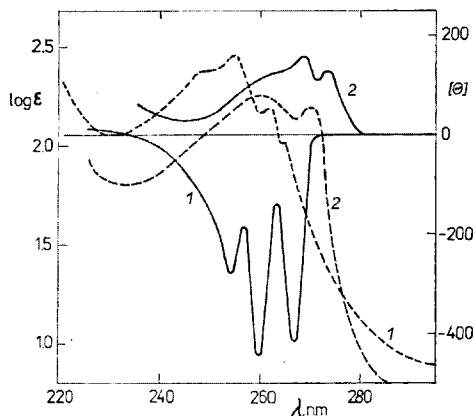
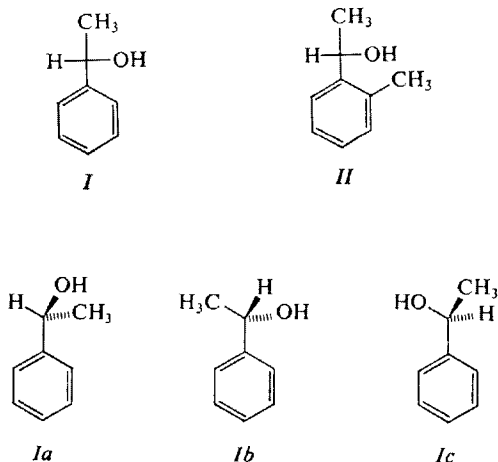


FIG. 1
CD (—) and UV (----) Spectra of
(*R*)-(+)-1-Phenylethanol (*I*) and of (*R*)-(+)-
1-(2-Methylphenyl)ethanol (*II*)

UV spectra were recorded on CF4 Optica Milano and CD curves on Roussel Jouan Dichrographe.

Calculation of Preferred Conformations

The preferred conformations of the compounds *I* and *II* have not been determined experimentally up to the present. Only Quellette, Marks and Miller²³ effectuated a study of conformations of alkyl aryl methanols by means of NMR spectroscopy of corresponding dimethyl sulphoxidic solutions. Three possible preferred conformations *Ia*, *Ib*, *Ic* of the compound *I* were considered within this study and the conformation *Ia* exhibiting benzylic hydrogen coplanar to aromatic ring was chosen as a starting point. It is probable, that this conformation is energetically the most advantageous one following the analysis of the molecular models.



Moreover, the authors demonstrated the possible existence of a weak hydrogen bond connecting the π -electron system and the hydroxyl group.

The molecular conformation of *I* may be described in terms of three independent torsional angles and in the case of compound *II* even of four ones. For that reason we abstained from a detailed calculation of conformational hypersurfaces with the aid of quantum chemical methods taking into account all valence electrons. These calculations were performed by means of simple empirical potential functions. We applied the method described by Hooker and Schellmann¹⁶ used by them for the interpretation of the preferred conformations of tyrosines. We calculated the contributions of nonbonded pairwise interactions and that of electrostatic interactions using Lennard-Jones 6-12 potential (1) and a function of coulombic type (2) respectively; r_{ij} represents the interatomic distance, $K = 332$ the conversional factor

and ϵ the apparent dielectric constant of solvent. For this constant we have used the value of unity in a same way as did Hooker and Schellmann¹⁶. The values given by Ooi and Scheraga²⁴ were used for the parameters a_{ij} , b_{ij} and the atomic charges q were obtained within the summation of the contributions π and δ calculated by the method HMO and Del Re respectively. In the calculation according to HMO we con-

$$V_{ij}^{nb} = -a_{ij}r_{ij}^{-6} + b_{ij}r_{ij}^{-12} \quad (1)$$

$$V_{ij}^{elst} = Kq_iq_j\epsilon^{-1}r_{ij}^{-1} \quad (2)$$

sidered but the inductive influence of aliphatic groups on the coulomb integral of the corresponding carbon atom ($\delta\alpha$ for methyl group -0.5 ; $\delta\alpha$ for 1-hydroxyethyl group -0.4). A standard set of parameters²⁵ was used for computations of σ -electron distribution by the method of Del Re. We neglected the term describing the barriers to internal rotation (the exchange interaction of electrons localized in orbitals on the atoms connected by a bond), as this term cannot influence qualitatively the results. The computations performed upon using the relations (1) and (2) do not involve the energy of solvation. In addition, the both contributions mentioned above cannot be summed up due to the uncertainty in the chosen value of the apparent dielectric constant¹⁶.

The starting atomic coordinates were calculated from standard bond lengths and bond angles tabulated by Pople and Beveridge²⁶. The initial geometry $\varphi_1 = 0^\circ$ and $\varphi_2 = 0^\circ$ of (S)-(-)-1-phenylethanol (I) is given in Fig. 2. Numerical calculations were tabulated within the range of $0-180^\circ$ (angle φ_1) and $0-360^\circ$ (angle φ_2), the step applied being 15° . The map of nonbonded interactions thus obtained is given in Fig. 3A. The value of φ_2 except of regions of φ_1 about 0° and 180° showing a considerable interaction of hydrogen atoms in the *ortho* positions of the benzene ring with those of the hydroxyl group does not exhibit serious influence on the total

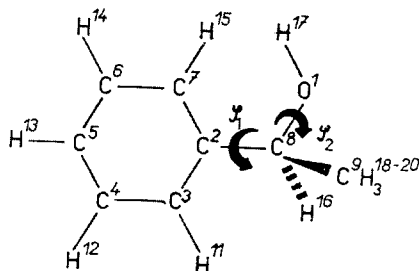


FIG. 2

Starting Geometry of (S)-(-)-1-Phenylethanol (I), $\varphi_1 = 0^\circ$; $\varphi_2 = 0^\circ$

nonbonded energy. Quite the same conclusions can be derived for $\varphi_2 = 0^\circ, 180^\circ$ based on two sections of the conformational map Fig. 3B. The shape of electrostatic interactions Fig. 3C does not show any important geometrical dependence and consequently, it is neglected for the case of *I*. The minimum nonbonded interactions in (*S*)-(-)-1-phenylethanol (*I*) occur at $\varphi_1 \sim 135^\circ$, this position roughly corresponding to the preferred conformation *Ia* with the benzylic hydrogen coplanar to the aromatic nucleus. The computed rotational barrier is about 3 kcal mol^{-1} .

(*S*)-(-)-1-(2-methylphenyl)ethanol (*II*), its initial conformation at zero values of the dihedral angles φ_1 and φ_2 being given in Fig. 4 exhibits four degrees of freedom with respect to the possible rotation of the methyl group in the *ortho* position of the aromatic ring. For that reason it seems necessary to organize the calculation in the way to obtain — at a reasonable consumption of the computing time — maximum information of the preferred conformations of this compound. Within the solution of this problem the calculations were executed in the range of $0-360^\circ$ for φ_1 at the

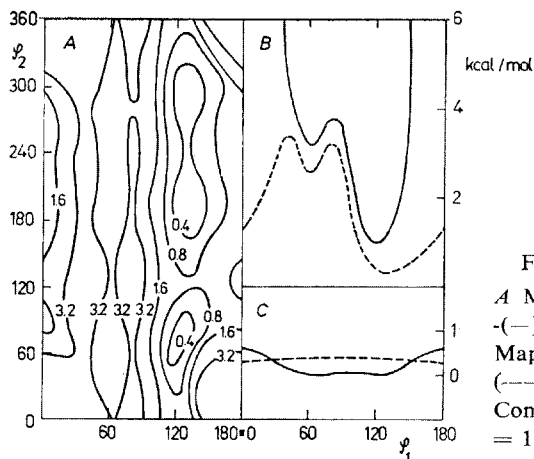


FIG. 3

A Map of Nonbonded Interactions in (*S*)-(-)-1-Phenylethanol (*I*), B Sections of this Map for $\varphi_2 = 0^\circ$ (—) and $\varphi_2 = 180^\circ$ (---), C Electrostatic Interactions in the Compound *I* at $\varphi_2 = 0^\circ$ (—) and $\varphi_2 = 180^\circ$ (---)

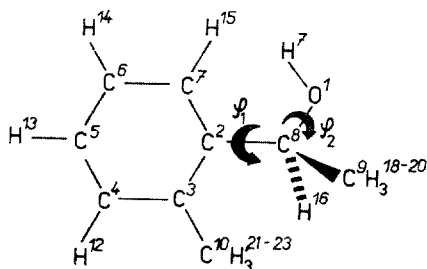
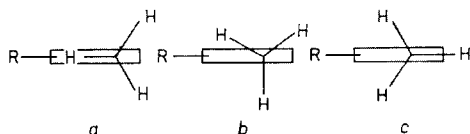


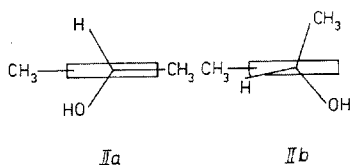
FIG. 4

Starting Geometry of (*S*)-(-)-1-(2-Methylphenyl)ethanol (*II*), $\varphi_1 = 0^\circ$; $\varphi_2 = 0^\circ$

values of 0° , 180° for φ_2 . The process was repeated three times for three different $a-c$ orientations of the methyl group in the *ortho* position. The results obtained are given in Fig. 5-7.



Considering the relations mentioned above and supposing energetically more advantageous b , c orientations of the methyl group, (S)-(-)-1-(2-methylphenyl)ethanol (*II*) exhibits two energetically comparable minima at $\varphi_1 = 240^\circ$ (*IIa*) and $\varphi_1 = 315^\circ$ (*IIb*) respectively on the curves of nonbonded interactions. The conformations *IIa* is, of course, less advantageous due to the proximity of the maximum on the curves of electrostatic interactions. The minimum found within the range of $\varphi_1 \sim 315^\circ$ (*IIb*) corresponds to the preferred conformation *Ia* of (S)-(-)-1-phenylethanol(*I*) conformably with compared Dreiding models of compounds *I* and *II*. The final decision concerning the relative preference of the conformations *IIa* and *IIb* of (S)-(-)-1-(2-methylphenyl)ethanol (*II*) would call for much more detailed calculations using probably more sophisticated method compared with the empirical potential functions here applied. Simple calculations given in this paper favour the conformation *IIb* and indicate the preferred conformations of the both compounds studied to be approximately equal at least at the level of approximation used in this work.



Calculation of Optical Rotatory Strength

The quantity, representing the extent to which the electronic transition from the state *A* to *B* is optically active, is the so-called rotatory strength defined according to Condon²⁷ and Rosenfeld²⁸ by the relation (3)

$$R_{A \rightarrow B} = \text{Im} \{ \langle A | \boldsymbol{\mu} | B \rangle \cdot \langle B | \mathbf{m} | A \rangle \}, \quad (3)$$

where $\boldsymbol{\mu}$ and \mathbf{m} are the operators of electric and magnetic dipole moment respectively and

$$\text{Im} \{ a + ib \} = b. \quad (4)$$

Expressing the operator of electric dipole moment in the dipole velocity representation²⁹ and limiting the calculation to the here important case, in which the wavefunction of the excited state B is composed from two singly excited configurations B_1 and B_2 mixed together to the extent given by LCI coefficients c_{B_1} and c_{B_2} respectively, it is possible to write:

$$R_{A \rightarrow B} = - \frac{e^2 \hbar^2}{4\pi m^2 c^2} \sum_{i,j} c_{B_1} c_{B_2} \frac{\langle A | \nabla | B_i \rangle}{\bar{\nu}_{A \rightarrow B_i}} \langle B_j | \mathbf{r} \times \nabla | A \rangle. \quad (5)$$

In this equation $\bar{\nu}_{A \rightarrow B}$ represents the wavenumber of the transition $A \rightarrow B$ in cm^{-1} , \mathbf{r} is the position vector operator respective for the electron engaged in the transition and the symbols e , \hbar , m , c hold their usual meaning.

According to the relation (3) the optical rotatory strength is given by the dot product of the matrix elements of electric and magnetic dipole operators. It is non-vanishing only in the case of nonzero values of the both matrix elements mentioned above. Only chiral molecules, which do not possess the rotation-reflection axis of symmetry, fulfill this condition. Hence, the wavefunction used in calculating the transition moments must also be a chiral one. Performing the actual calculation it is possible either to start from the wavefunction of the whole chiral molecule (EHT, CNDO) and to compute the optical rotatory strength in the direct process or to utilize the simplified symmetrical wavefunction of the chromophore. In the

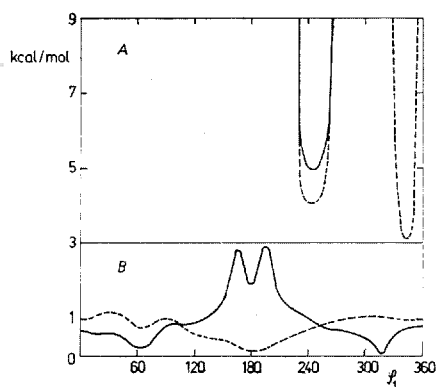


FIG. 5

Nonbonded (A) and Electrostatic (B) Interactions in (S)-(-)-1-(2-Methylphenyl)ethanol (II) at $\varphi_2 = 0^\circ$ (—) and 180° (-----)

The methyl group connected to the aromatic nucleus is in a conformation.

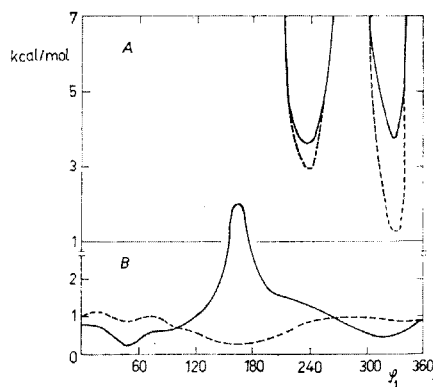


FIG. 6

Nonbonded (A) and Electrostatic (B) Interactions in (S)-(-)-1-(2-Methylphenyl)ethanol (II) at $\varphi_2 = 0^\circ$ (—) and 180° (-----)

The methyl group connected to the aromatic nucleus is in b conformation.

latter case the origin of optical activity is simulated either with the use of the perturbational potential or in coupling the original wavefunction with another chromophore or polarizable group. Direct calculations based on CNDO (ref.^{4,5}) and EHT (ref.³) wavefunctions were successfully applied to the compounds possessing carbonyl chromophore. In the region of aromatic chromophores there is reported only a paper of Bush³⁰ related to the optical rotatory strengths of the both anomers of deoxyadenosine. This paper is based on EHT wavefunctions treated by the method of Gould and Hoffmann³. However this work does not take into account the configurational interaction and consequently the results reported are probably inaccurate. The optical rotatory strength of 1-methylindane was studied upon using the perturbational potential³¹ (one-electron mechanism³²).

The one-electron mechanism, the μ - m mechanism and the coupling with polarizable groups according to Kirkwood⁹ may be considered in the case of compounds of 1-arylethanol type. The lastly mentioned mechanism was successfully applied to CD data of nucleosides by Eyring and coworkers³³⁻³⁵. The μ - m mechanism is not involved in our calculations due to the lack of information related to the magnetic transition moments arising from the aliphatic part of the molecule.

We have calculated the optical rotatory strengths of 1L_b transitions of (S)-(-)-1-phenylethanol (I) and of (S)-(-)-1-(2-methylphenyl)ethanol (II). Within the computation, the optical rotatory strength was divided into contributions presented by the one-electron mechanism³² on the one side and by the Kirkwood mechanism of coupled oscillators⁹ on the other.

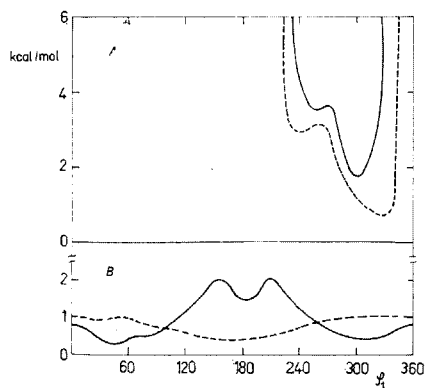


FIG. 7

Nonbonded (A) and Electrostatic (B) Interactions in (S)-(-)-1-(2-Methylphenyl)ethanol (II) at $\phi_2 = 0^\circ$ (—) and 180° (---)

The methyl group connected to the aromatic nucleus is in *c* conformation.

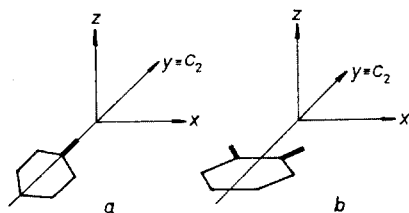


FIG. 8

Orientation of Toluene (a) and *o*-xylenic (b) Chromophore Into the Coordinate System

The necessary information relating to the symmetry and configuration interaction of 1L_b transition of the compounds *I* and *II* was obtained in using PPP π -electron only wavefunctions of toluene and *o*-xylene respectively, supposing the direction of the electric transition moment to be determined predominantly by the nearest surrounding of the chromophore. Further, the C_{2v} local symmetry of the both chromophores was considered. The results of the PPP calculations are given in Table I together with the computational details. The coordinate system used is given in Fig. 8.

It is clear, that the wavefunction of the first excited state is suitable for approximating by two configurations of the same symmetry participating in this transition nearly to the same extent. This result seems to be rather typical in the case of aromatic chromophores. The introduction of the methyl group into the ortho position results in a change of symmetry of the configurations involved and leads finally to a different orientation of the transition moments in the both compounds.

The computation rotatory strength with the use of the one-electron mechanism consists in replacing the wavefunctions of the chiral molecule by the perturbed chromophoric wavefunction obtained upon the action of the electrostatic perturbational potential. The transition moments of this wavefunction fulfill the condition of equation (3) and give rise to a nonzero value of rotatory strength. The non-vanishing components of the both moments can be found upon using standard group-theoretical methods. The calculation was started from the CNDO/2 wavefunctions of toluene and *o*-xylene as model compounds. The C_{2v} local symmetry of both chromophores was considered again. This intentional inaccuracy was used to suppress the influence of hydrogen atoms situated in the methyl groups of model compounds.

TABLE I

PPP Calculation of Toluene and *o*-Xylene

Methyl groups were approximated with the aid of the hyperconjugative model and the following parametrization: C(sp^2): $I = 11.16$ eV, $A = 0.03$ eV; C(H₃): $I = 11.42$ eV, $A = 0.58$ eV; H₃(C): $I = 9.50$ eV, $A = 0.00$ eV; $k_{C-CH_3} = 0.51$; $k_{C-H_3} = 1.25$; $\beta = -2.388$ eV. On the aromatic nucleus the values of bond lengths and bond angles were taken as 1.4 Å and 120° respectively. Bond length C—CH₃ = 1.52 Å; C—H = 1.1 Å.

Compound	$\lambda_{\text{max}} {}^1L_b$, nm	f	CI composition	Symmetry
Toluene	256	0.0003	4-6 0.6993	B_2
			3-5 0.6793	
<i>o</i> -Xylene	260	0.0007	5-7 0.6910	A_1
			4-6 0.6606	

A survey of molecular orbitals and of singly excited configurations of toluene and *o*-xylene used in the calculation is given in Fig. 9 and 10.

The calculations were executed for the conformations *Ia* and *I Ib* of (S)-(-)-1-phenylethanol (*I*) and of (S)-(-)-1-(2-methylphenyl)ethanol (*II*) respectively, supposing the oxygen atom to be the sole origin of the perturbation.

In the case of compound *I*, the wavefunction of the first excited state is approximated by two B_2 configurations contributing to the x -component of the electric transition moment and to the z -component of the magnetic one. Due to the probable affection of 1L_b transition by energetically higher positioned π - π^* transitions, the interactions with the A_1 states contributing to the electric transition moment in the y -direction were also considered. Moreover the π - σ^* states $B_1(\mu_z, m_x)$ and $A_2(m_y)$ were taken into account. The basis determined in this way is able to supply nonzero contributions to the optical rotatory strength along all the three coordinate axes. The terms used in the calculation of the transition moments of both conformations B_2^a and B_2^b were constituted with the use of the first order perturbation theory:

$$\begin{aligned} \langle G|\nabla|B_2^a\rangle &= (G|\nabla|B_2^a) + \sum_{C=A_1^a, A_1^b, B_1^a, B_1^b} \frac{(C|\nabla|B_2^a)}{\Delta E} (G|\nabla|C) = \sqrt{2}(\chi_{18}|\nabla|\chi_{20}) + \\ &+ 2 \cdot \sqrt{2} \left[\frac{(\chi_{19}|V|\chi_{20})}{\Delta E} (\chi_{18}|\nabla|\chi_{19}) + \frac{(\chi_{15}|V|\chi_{18})}{\Delta E} (\chi_{15}|\nabla|\chi_{20}) + \right. \\ &\left. + \frac{(\chi_{21}|V|\chi_{20})}{\Delta E} (\chi_{18}|\nabla|\chi_{21}) + \frac{(\chi_{22}|V|\chi_{20})}{\Delta E} (\chi_{18}|\nabla|\chi_{22}) \right], \end{aligned} \quad (6)$$

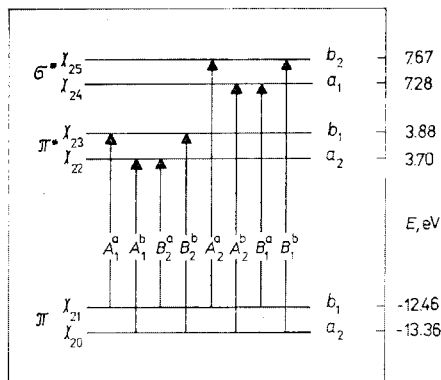
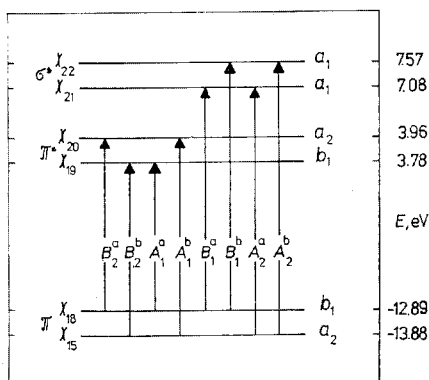


FIG. 9

CNDO/2 Orbitals of Toluene Used in the Calculation of Optical Rotatory Strength

FIG. 10

CNDO/2 Orbitals of *o*-xylene Used in the Calculation of Optical Rotatory Strength

$$\langle B_2^a | \mathbf{r} \times \nabla | G \rangle = (B_2^a | \mathbf{r} \times \nabla | G) + \sum_{C=B_1^a, B_1^b} \frac{(C | \nabla | B_2^a)}{\Delta E} (C | \mathbf{r} \times \nabla | G), \quad (7)$$

$$\langle G | \nabla | B_2^b \rangle = (G | \nabla | B_2^b) + \sum_{C=A_1^a, A_1^b} \frac{(C | \nabla | B_2^b)}{\Delta E} (G | \nabla | C), \quad (8)$$

$$\langle B_2^b | \mathbf{r} \times \nabla | G \rangle = (B_2^b | \mathbf{r} \times \nabla | G) + \sum_{C=A_2^a, A_2^b} \frac{(C | \nabla | B_2^b)}{\Delta E} (C | \mathbf{r} \times \nabla | G). \quad (9)$$

The value of ΔE in the relations (6)–(9) is defined as:

$$\frac{(A | \nabla | B)}{\Delta E} = \frac{(A | \nabla | B)}{E_B - E_A}. \quad (10)$$

Round brackets relate to unperturbed states. The molecular orbitals χ_i can be identified with the aid of Fig. 9. Similar terms were obtained for the compound II, in which the nonvanishing component of the electric dipole moment in the y -direction is supplied by the unperturbed A_1 states. The interaction with the π - π^* states B_2 gives rise to μ_x , m_z and the other components are supplied by the π - σ^* states $B_1(\mu_z, m_x)$ and $A_2(m_y)$. Hence, the transition moments of the A_1^a configuration in the compound II are the following ones:

$$\langle G | \nabla | A_1^a \rangle = (G | \nabla | A_1^a) + \sum_{C=B_2^a, B_2^b, B_1^a} \frac{(C | \nabla | A_1^a)}{\Delta E} (G | \nabla | C), \quad (11)$$

$$\langle A_1^a | \mathbf{r} \times \nabla | G \rangle = \sum_{C=B_2^a, B_2^b, B_1^a, A_2^a} \frac{(C | \nabla | A_1^a)}{\Delta E} (C | \mathbf{r} \times \nabla | G). \quad (12)$$

Similar relations are incorporated in the calculation of the transition moments of the A_1^b configuration.

Numerical calculations of the matrix elements were executed on using atomic functions of carbon in the mono- ξ form³⁶ and a value of ξ_c 1.5679. The sole nonzero integral of the ∇ operator within one-center ones is represented by $\langle 2pz | \nabla | 2s \rangle$. Its value is easily obtainable by analytical computation⁵ and amounts to 0.4526 atomic units. Within two-center integrals it was necessary to compute the values of $\langle 2py | \nabla | 2pz \rangle$, $\langle 2pz | \nabla | 2pz \rangle$, $\langle 2px | \mathbf{r} \times \nabla | 2pz \rangle$, $\langle 2py | \mathbf{r} \times \nabla | 2pz \rangle$. The values of the gradient integrals were determined on using the relations reported in the paper³⁷. The integrals of the $\mathbf{r} \times \nabla$ operator were transformed to overlap integrals. Numerical values of these integrals are given in Table II. The integrals of the magnetic transition moments were expanded according to⁵:

$$\langle A | \mathbf{r} \times \nabla | B \rangle = \mathbf{R} \times \langle A | \nabla | B \rangle + \langle A | \mathbf{r}_A \times \nabla | B \rangle. \quad (13)$$

The particular integrals were first computed in the local coordinates and then transformed into the molecular coordinate system.

The electrostatic perturbational potential can be described by equation

$$V = \sum_k q / |\mathbf{r} - \mathbf{R}_k| \quad (14)$$

in which q represents the charge localized in the centre of the perturbation, \mathbf{r} is the position vector of electron related to this centre and \mathbf{R}_k is the position vector of the atom influenced by the perturbation. The equation (14) can be expanded³⁸ according

TABLE II

Two-center Integrals of the ∇ and $\mathbf{r} \times \nabla$ Operator Represented in Atomic Units

Interatomic distance Å	$\langle 2pz \nabla 2pz \rangle$ $\langle 2py \nabla 2pz \rangle$	$\langle 2px \mathbf{r} \times \nabla 2pz \rangle$ $-\langle 2py \mathbf{r} \times \nabla 2pz \rangle$
1.40	0.2263	0.2694
2.40	0.0448	0.0421
2.78	0.0218	0.0195

TABLE III

Integrals of the $\langle A | V_i | B \rangle$ Type

The values of V_i/q in atomic units are given in the table. The value of q used in the calculation was -0.23 a.u. (the result of the calculation according to Del Re). Carbon atoms of the aromatic nucleus are numbered according to Fig. 11.

i	$\langle 2pz_i V_i 2pz_i \rangle$	$\langle 2pz_i V_i 2px_i \rangle$	$\langle 2pz_i V_i 2py_i \rangle$	$\langle 2pz_i V_i 2s_i \rangle$
2	0.2166	0.0074	0.0147	-0.0186
3	0.1460	0.0056	0.0068	-0.0056
4	0.1111	0.0026	0.0047	-0.0025
5	0.1056	0.0010	0.0048	-0.0021
6	0.1246	-0.0003	0.0066	-0.0034
7	0.1819	-0.0009	0.0127	-0.0110

to the relation (15):

$$|\mathbf{r} - \mathbf{R}_k|^{-1} = \sum_{l=0}^{\infty} A_l(\mathbf{r}, \mathbf{R}_k) P_l(\cos \gamma_k) \quad (15)$$

$$A_l(\mathbf{r}, \mathbf{R}_k) = \begin{cases} r^l/R_k^{l+1} & \text{for } r < R_k \\ R_k^l/r^{l+1} & \text{for } r > R_k \end{cases}$$

$P_l(\cos \gamma_k)$ is the Legendre polynomial of the argument

$$P_l(\cos \gamma_k) = \cos \Theta \cos \Theta_k + \sin \Theta \sin \Theta_k \cos(\varphi - \varphi_k) \quad (16)$$

The angles Θ_k and φ_k are given in Fig. 11. The values of the matrix elements given in Table III were computed on using the relation

$$\begin{aligned} & \langle \chi_k(nl_a m_a) | V_k | \chi_k(nl_b m_b) \rangle = \\ & = q \sum_{l=0}^{\infty} U_l(\mathbf{R}_k) (-1)^{m_a} \frac{2\sqrt{\pi}}{2l+1} \sum_{l=|l_a-l_b|}^{l=|l_a+l_b|} \left[\frac{(2l_a+1)(2l_b+1)}{2l+1} \right]^{1/2} \times \\ & \quad \times (l_a l_b - m_a m_b | l_a l_b l m) (l_a l_b 0 0 | l_a l_b l m) Y_l^m(\Theta_k, \varphi_k) \delta_{l l'}. \end{aligned} \quad (17)$$

In this relation $(l_a l_b m_a m_b | l_a l_b l m)$ are the Clebsch-Gordan coefficients,

$$U_l = \int_0^{\infty} A_l(\mathbf{r}, \mathbf{R}_k) R^2(n, l) r^2 dr \quad (18)$$

and $\delta_{l l'}$ is the Kronecker symbol. The method reported above corresponds approximately with the partial point charge model elaborated by Stigter and Schellman³⁹.

The transition moments of the perturbed states thus obtained were used in the calculation of the optical rotatory strength according to equation (5). Starting from

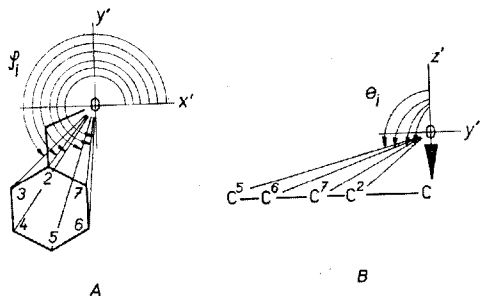


FIG. 11
Definition of the Angles

$A \varphi_i$; $B \theta_i$ necessary for the calculation of the perturbational potential; (in Fig. 11A the oxygen atom is projected into the plane of the aromatic ring).

the electric transition moments the corresponding oscillator strengths were also computed. The resulting values of one-electron rotatory strengths given in Table IV agree in sign with the values obtained experimentally. It may be deduced from the relative magnitudes of the particular contributions to the value of the rotatory strength resulting from the combination of the transition moment components along the directions of the coordinate axes given in Table IV as R_x , R_y , R_z , that the largest contributions to the one-electron rotatory strength are exhibited by the moments acting in the directions y and x for the compounds *I* and *II* respectively. These contributions arise from the A_1 (compound *I*) and A_2 (compound *II*) states. Owing to the possible simulation of higher π - π^* transitions in both compounds with the aid of these states, it is possible to interpret this fact as an influence of higher lying π - π^* transitions on the optical rotatory strength of the 1L_b band.

The perturbed transition moments of both compounds were utilized also in the calculation executed with the aid of coupled oscillators. The optical rotatory strength was calculated on using the modification of the Kirkwood method described by Eyring and coworkers³⁴. The calculation is based on relations

$$R_a = \sum_{b \neq a} \frac{2\pi}{hc} \frac{\nu_a \nu_b \mu_a^2 \mu_b^2}{(\nu_b^2 - \nu_a^2)} GF \quad (19)$$

$$GF = \left[\mathbf{e}_a \cdot \mathbf{e}_b - 3 \frac{(\mathbf{e}_a \cdot \mathbf{R}_{ab})(\mathbf{e}_b \cdot \mathbf{R}_{ab})}{R_{ab}^2} \right] \frac{\mathbf{e}_a \cdot \mathbf{e}_b \cdot \mathbf{R}_{ab}}{R_{ab}^3}, \quad (20)$$

TABLE IV

Oscillator and Optical Rotatory Strength of 1L_b Transitions of (S)-(-)-1-Phenylethanol (*I*) and (S)-(-)-1-(2-Methylphenyl)ethanol (*II*)

The values are given in c.g.s. units.

Compound — conformation		<i>Ia</i>	<i>IIb</i>
$f_{\text{exp.}}$		4.70 10^{-3}	3.19 10^{-3}
$f_{\text{calc.}}$		2.46 10^{-3}	3.60 10^{-3}
R — one-electron	R_x	4.70 10^{-44}	-4.52 10^{-43}
	R_y	2.14 10^{-41}	2.18 10^{-43}
	R_z	7.35 10^{-43}	-1.13 10^{-42}
		2.22 10^{-41}	-5.43 10^{-42}
R — coupled oscillators		7.13 10^{-42}	-2.52 10^{-41}
$R_{\text{calc.}}$		9.35 10^{-41}	-2.57 10^{-41}
$R_{\text{exp.}}$		3.45 10^{-41}	-1.08 10^{-41}

where \mathbf{e}_a is the unit vector in the direction of the electric transition moment, μ_a its magnitude and ν_a the transition frequency; the values of \mathbf{e}_b , μ_b , ν_b are related to the neighbouring polarizable group. R_{ab} represents the distance measured from the chromophore to the group b . The coupling of the transition moments of chromophore and of the moments localized in the bonds C—OH and C—CH₃ was considered. This calculation was executed for the conformations *Ia* and *IIb* too. The values tabulated in the work³⁴ were assigned to the empirical parameters μ_b , ν_b . The results thus obtained are given in Table IV.

The total value of optical rotatory strength obtained upon adding the contributions of one-electron and dipole coupling mechanisms (Table IV) exhibits a correct sign for both compounds under study and its order of magnitude agrees with the value obtained experimentally. It can be concluded from the results obtained, that the reversed signs of the Cotton effects of ¹L_b band at equal absolute configuration are not caused by a change of the preferred conformation. The reason for this inversion is the change of the symmetry of the transition combined with the different orientation of the transition moments in both compounds. The remarkable influence of higher π - π^* transitions on the rotatory strength of ¹L_b band is very interesting.

The authors are indebted to professor R. Zahradnik, Dr L. Musil and Dr V. Skála for the necessary CNDO and PPP wavefunctions of the model compounds.

REFERENCES

1. Caldwell D. J., Eyring H.: *The Theory of Optical Activity*. Wiley, New York 1971.
2. Djerassi C.: *Optical Rotatory Dispersion: An Application to Organic Chemistry*. Mc-Graw Hill, New York 1960.
3. Gould R., Hoffmann R.: *J. Amer. Chem. Soc.* 92, 1813 (1970).
4. Pao Y., Santry D. P.: *J. Amer. Chem. Soc.* 88, 4157 (1966).
5. Imamura A., Hirano T., Nagata C., Tsuruta T.: *Bull. Chem. Soc. Jap.* 45, 396 (1972).
6. Brewster J. H.: *Top. Stereochem.* 2, 40 (1964).
7. Brewster J. H.: *Tetrahedron Lett.* 1972, 4356.
8. Kuhn W.: *Trans. Faraday Soc.* 26, 293 (1930).
9. Kirkwood J. G.: *J. Chem. Phys.* 5, 479 (1937).
10. Mason S. F., Vane G. W.: *J. Chem. Soc. B* 1966, 370.
11. Mason S. F., Vane G. W., Schofield K., Wells R. J., Whitehurst J. S.: *J. Chem. Soc. B* 1967, 553.
12. Gottarelli G., Mason S. F., Torre G.: *J. Chem. Soc. B* 1970, 1349.
13. Moscovitz A.: *Thesis*. Harvard University, Cambridge, Mass. 1957.
14. Tinoco I. jr: *Advan. Chem. Phys.* 4, 113 (1962).
15. Teng N. H., Itzkowitz M. S., Tinoco I. jr: *J. Amer. Chem. Soc.* 93, 6257 (1971).
16. Hooker T. M., Schellman J. A.: *Biopolymers* 9, 1319 (1970).
17. Červinka O.: *This Journal* 30, 1684 (1964).
18. Červinka O., Fusek J.: *This Journal* 38, 441 (1973).
19. Červinka O., Bělovský O.: *This Journal* 32, 3897 (1967).
20. Mislow K.: *J. Amer. Chem. Soc.* 73, 3954 (1951).
21. Verbit L.: *J. Amer. Chem. Soc.* 87, 1617 (1965).

22. Gillard R., Mitchell P. R.: *Trans. Faraday Soc.* 65, 2611 (1969).
23. Quelette R. J., Marks D. L., Miller D.: *J. Amer. Chem. Soc.* 89, 913 (1967).
24. Ooi T., Scott R. A., Vanderkooi G., Scheraga H. A.: *J. Chem. Phys.* 46, 4410 (1967).
25. Krugljak J. A.: *Metody Vychislenij v Kvantovoj Khimii*. Naukovaja Dumka, Kiev 1967.
26. Pople J. A., Beveridge D. L.: *Approximate Molecular Orbital Theory*. Mc-Graw-Hill, New York 1970.
27. Condon E. U.: *Rev. Mod. Phys.* 9, 432 (1937).
28. Rosenfeld L.: *Z. Phys.* 52, 161 (1928).
29. Bethe H. A., Salpeter E. E.: *Quantum Mechanics of One and Two Electron Systems*, p. 251. Academic Press, New York 1957.
30. Bush C. A.: *J. Amer. Chem. Soc.* 95, 214 (1973).
31. Caldwell D. J., Eyring H.: *Annu. Rev. Phys. Chem.* 15, 281 (1964).
32. Condon E. U., Altar W., Eyring H.: *J. Chem. Phys.* 5, 753 (1937).
33. Inskeep W. H., Miles D. W., Eyring H.: *J. Amer. Chem. Soc.* 92, 3866 (1970).
34. Miles D. W., Inskeep W. H., Robins M. J., Robins R. K., Winkley M. W., Eyring H.: *J. Amer. Chem. Soc.* 92, 3872 (1970).
35. Miles D. W., Inskeep W. H., Robins M. J., Robins R. K., Eyring H.: *J. Amer. Chem. Soc.* 93, 1600 (1971).
36. Clementi E., Raimondi D. L.: *J. Chem. Phys.* 38, 2686 (1965).
37. Král M.: *This Journal* 35, 1939 (1970).
38. Eyring H., Walter J., Kimball G. E.: *Quantum Chemistry*. Wiley, New York 1944.
39. Stigter D., Schellman J. A.: *J. Chem. Phys.* 51, 3397 (1969).

Translated by P. Maloň.