

Figure 7. Ratio of dipole relaxation time of rigid polar molecules in naphthene solvents to that in other nonpolar solvents as a function of reduced temperature.

present correlation, which makes no explicit reference to viscosity, might have been expected to suppress this "naphthene effect". Even cursory inspection of Figure 6 reveals, however, that solutions in naphthenes exhibit depressed reduced relaxation times in the present correlation as well.

Expressing the naphthene effect as $\tau^*(\text{naphthene})/\tau^*(\text{pure liquid})$, one finds that the effect is primarily a function of the reduced temperature, regardless of the compound involved. A plot of $\tau^*_A(\text{naphthene})/\tau^*_A(\text{pure liquid})$ vs. \bar{T}^* in Figure 7 shows that the effect decreases with decreasing reduced temperature and seems to vanish at $\bar{T}^* = 0.45$. This relation is, of course, a reflection of the molecule size effect noted by Hufnagel. A much larger range in absolute temperature needs to be covered in experiments in order to

obtain better insight into the possible origins of this effect.

Other Work

The importance of the moment of inertia for dipole relaxation had been noted earlier by Powles¹² and by Hill.¹³ However, neither of these authors used his observations as a basis for a systematic correlation of dipole relaxation data.

Conclusions

The present treatment of the dipole relaxation was motivated by the need for methods to predict the rotation and diffusion rates for small molecules and molecule segments in polymeric liquids, where macroscopic viscosity is obviously meaningless as a correlating parameter. The success of the new correlation in handling Nujol solvent augurs well for its applicability in the intended field.

A useful by-product of the work is the definition of a generalized reference system, deviations from which are more easily detected than has been possible before. Already some of these deviations suggested the introduction of a new "roughness" parameter into the consideration of the transport properties of liquids.

A great deal of further work will be necessary to define the barriers to the external rotation of molecules in liquids more accurately. The present assumption that these barriers are proportional to the energy of vaporization is too crude to be satisfactory in the long run. Only after that problem has been solved can one consider the correlation as a safe method to estimate dipole relaxation rates from molecular structure data.

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Isotope Effects in Optical Rotation¹

Norah V. Cohan² and Hendrik F. Hameka³

Contribution from the Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia 4, Pennsylvania. Received June 25, 1965

Abstract: A general theory is derived for the optical rotatory power of molecules which exhibit this property only on account of isotopic substitution. The optical rotatory power is evaluated from the interaction between the nuclei and the radiation field only, and it is concluded that this is a good approximation for infrared light. Detailed calculations are performed for the molecules CHDBrCl , $\text{CCl}^{35}\text{Cl}^{37}\text{BrF}$, and CHDTBr . Various summation rules are derived for the vibrational rotatory strengths.

Recently an attempt was made⁴ to assess the relative magnitudes of electronic and vibrational contributions to molecular optical rotatory power (OR). It was

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found that the vibrational contributions are usually small and that they may be neglected with respect to the

(2) Departamento de Química Inorgánica, Analítica y Fisicoquímica, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Buenos Aires, Argentina.

(3) Alfred P. Sloan Foundation Fellow.

(4) H. F. Hameka, *J. Chem. Phys.*, **41**, 3612 (1964).

electronic contributions when the frequency of the rotated light is well outside of any of the molecular absorption bands and outside the range of normal vibrational frequencies. Under those conditions the OR may be evaluated from the electronic motion only on the assumption that the nuclei are at rest at their equilibrium configuration.

In the present paper we will discuss an interesting example of a situation where the above theoretical description is inadequate, namely, the observed optical rotatory power⁵ of molecules of the type CHDR_1R_2 with R_1 and R_2 arbitrary nonoptically active groups. It may be understood from symmetry considerations that molecules of the type $\text{CH}_2\text{R}_1\text{R}_2$ are not optically active. It is generally agreed upon that the replacement of one of the protons by a deuterium does not change the equilibrium configuration of the nuclei, the electronic wave functions at the equilibrium configuration, and the vibrational force constants. The only effect of the substitution is due to the change in mass in the vibrational motion. We are therefore led to the conclusion that the OR of molecules of the type CHDR_1R_2 is due to the effects of molecular vibrations, either directly through interactions between the nuclei and the radiation field or indirectly through the dependence of the electronic wave functions on the positions of the nuclei.

We should mention an earlier attempt⁶ to derive a theoretical description of the optical activity of the deuterated molecules by means of molecular vibrations. We have some doubts with regard to the consistency of this theory since its derivation starts from Kirkwood's polarizability formulas⁷ which were obtained on the assumption that the nuclei are at rest in their equilibrium positions. We feel therefore that in the subsequent introduction of vibrational motion into Kirkwood's formulas some of the terms should vanish, thus not necessarily leading to correct results.

General Theory

In this section we shall present in greater detail most of our previous analysis.⁴

We start with the theoretical expression for the specific rotation of a gas of identical molecules

$$\phi_0 = -\frac{8\pi N}{3\hbar c} \sum_{(n,v) \neq (0,0)} k_{nv}^2 \Im \times \frac{\langle \psi_{00} | \mathbf{p} | \psi_{nv} \rangle \cdot \langle \psi_{nv} | \mathbf{m} | \psi_{00} \rangle}{k_{nv}^2 - k_\lambda^2} \quad (1)$$

The left-hand side represents the angle of rotation in radians when a beam of linearly polarized light passes through 1 cm of sample. We follow the usual convention that ϕ_0 is positive for dextrorotatory substances. On the right-hand side, N is the number of molecules per unit volume, and c and \hbar have their usual meaning. The letter \Im means "take the imaginary part." The operators are defined as

$$\mathbf{p} = \sum_s e_s \mathbf{r}_s \quad (2)$$

$$\mathbf{m} = \frac{1}{2c} \sum_s \frac{e_s}{m_s} (\mathbf{r}_s \times \mathbf{p}_s) \quad (3)$$

(5) See, for instance, A. Streitwieser, Jr., J. R. Wolfe, and W. D. Shaeffer, *Tetrahedron*, **6**, 338 (1959).

(6) W. Fickett, *J. Am. Chem. Soc.*, **74**, 4204 (1952).

(7) E. B. Wilson, J. C. Decius, and P. C. Cross "Molecular Vibrations," McGraw-Hill Book Co., Inc., New York, N. Y., 1955.

where e_s and m_s are the charge and mass of particle s . \mathbf{r}_s and \mathbf{p}_s are the position and momentum vectors of particle s , referred to a coordinate system that is centered on the center of gravity of the molecule. The functions ψ_{00} and ψ_{nv} are the total molecular eigenfunctions for the ground and excited states of the molecules, respectively, $k_\lambda = \hbar c/\lambda$ is the energy of the incident photons, and the quantities $k_{nv} = \epsilon_{nv} - \epsilon_{00}$ are the molecular excitation energies. In eq 2 and 3 the summations are performed over all particles, electrons and nuclei.

Equation 1 can be rewritten as

$$\phi_0 = -\frac{2\pi e^2 N}{3c^2} \sum_{(nv) \neq (00)} [k_{nv}/k_{nv}^2 - k_\lambda^2] \{ \langle \psi_{nv} | \mathbf{P} | \psi_{00} \rangle \cdot \langle \psi_{00} | \mathbf{M} | \psi_{nv} \rangle + \langle \psi_{00} | \mathbf{P} | \psi_{nv} \rangle \cdot \langle \psi_{nv} | \mathbf{M} | \psi_{00} \rangle \} \quad (4)$$

The operators are now defined as

$$\mathbf{P} = \mathbf{P}_1 - \mathbf{P}_2$$

$$\mathbf{M} = \mathbf{M}_1 - \mathbf{M}_2 \quad (5a)$$

$$\mathbf{P}_1 = \frac{1}{m} \sum_j \mathbf{p}_j$$

$$\mathbf{P}_2 = \sum_\alpha \frac{Z_\alpha}{M_\alpha} \mathbf{P}_\alpha \quad (5b)$$

$$\mathbf{M}_1 = \frac{1}{m} \sum_j [\mathbf{r}_j \times \mathbf{p}_j]$$

$$\mathbf{M}_2 = \sum_\alpha \frac{Z_\alpha}{M_\alpha} [\mathbf{R}_\alpha \times \mathbf{P}_\alpha] \quad (5c)$$

where e and m are the charge and mass of the electron; \mathbf{r}_j and \mathbf{p}_j are the coordinate and momentum of electron j , and \mathbf{R}_α and \mathbf{P}_α are those of nucleus α , all measured again with respect to a coordinate system with the molecular center of gravity as its origin. Z_α is the electric charge of nucleus α in terms of $(-e)$ and M_α , the mass of nucleus α .

Equation 4 can be transformed into a very convenient form by means of several relationships given below. Let us first examine some matrix elements of \mathbf{P}_2 . We can write

$$\langle \psi_{00} | \mathbf{P}_2 | \psi_{nv} \rangle = \frac{i(\epsilon_{nv} - \epsilon_{00})}{\hbar} \sum_\alpha M_\alpha \langle \psi_{00} | \mathbf{R}_\alpha | \psi_{nv} \rangle \quad (6)$$

We make use of the Born-Oppenheimer approximation and write

$$\psi_{00} = F_0(\mathbf{r}, \mathbf{R}) f_0^0(\mathbf{R}) \quad (7a)$$

$$\psi_{nv} = F_n(\mathbf{r}, \mathbf{R}) f_v^n(\mathbf{R}) \quad (7b)$$

where \mathbf{r} denotes symbolically the electronic coordinates and \mathbf{R} the nuclear coordinates. Then

$$\langle \psi_{00} | \mathbf{R}_\alpha | \psi_{nv} \rangle = \langle f_0^0(\mathbf{R}) | \mathbf{R}_\alpha | \langle F_0(\mathbf{r}, \mathbf{R}) | F_n(\mathbf{r}, \mathbf{R}) \rangle_r | f_v^n(\mathbf{R}) \rangle_R \quad (8)$$

where $\langle \dots \rangle_r$ means integration over the electronic coordinates and $\langle \dots \rangle_R$ integration over the nuclear coordinates. Owing to the orthonormality of the electronic wave functions F_0 and F_n

$$\langle \psi_{00} | \mathbf{R}_\alpha | \psi_{nv} \rangle = \delta_{0n} \langle f_0^0(\mathbf{R}) | \mathbf{R}_\alpha | f_v^n(\mathbf{R}) \rangle \quad (9)$$

And replacing (9) in (6) we obtain

$$\langle \psi_{00} | \mathbf{P}_2 | \psi_{nv} \rangle = 0 \text{ for } n \neq 0 \quad (10a)$$

$$\langle \psi_{00} | \mathbf{P}_2 | \psi_{nv} \rangle = \langle f_0^0 | \mathbf{P}_2 | f_v^n \rangle \text{ for } n = 0 \quad (10b)$$

An alternative proof of eq 10b is the following

$$\begin{aligned} \langle \psi_{00} | \mathbf{P}_2 | \psi_{0v} \rangle &= -i\hbar \sum_{\alpha} \frac{Z_{\alpha}}{M_{\alpha}} \left\langle \psi_{00} \left| \frac{\partial}{\partial \mathbf{R}_{\alpha}} \right| \psi_{0v} \right\rangle \\ \left\langle \psi_{00} \left| \frac{\partial}{\partial \mathbf{R}_{\alpha}} \right| \psi_{0v} \right\rangle &= \left\langle f_0^0(\mathbf{R}) \left| \left\langle F_0(\mathbf{r}, \mathbf{R}) \right| \times \right. \right. \\ &\quad \left. \left. \frac{\partial F_0(\mathbf{r}, \mathbf{R})}{\partial \mathbf{R}_{\alpha}} \right\rangle_{\mathbf{r}} \left| f_v^0(\mathbf{R}) \right\rangle_{\mathbf{R}} + \right. \\ &\quad \left. \left\langle f_0^0(\mathbf{R}) \left| \left\langle F_0(\mathbf{r}, \mathbf{R}) \left| F_0(\mathbf{r}, \mathbf{R}) \right\rangle_{\mathbf{r}} \right| \frac{\partial f_v^0(\mathbf{R})}{\partial \mathbf{R}_{\alpha}} \right\rangle_{\mathbf{R}} \right. \end{aligned} \quad (11)$$

For $F_0(\mathbf{r}, \mathbf{R})$ real

$$F_0(\mathbf{r}, \mathbf{R}) \frac{\partial F_0(\mathbf{r}, \mathbf{R})}{\partial \mathbf{R}_{\alpha}} = \frac{1}{2} \frac{\partial}{\partial \mathbf{R}_{\alpha}} [F_0(\mathbf{r}, \mathbf{R})]^2$$

and

$$\left\langle F_0 \left| \frac{\partial}{\partial \mathbf{R}_{\alpha}} \right| F_0 \right\rangle_{\mathbf{r}} = \frac{1}{2} \frac{\partial}{\partial \mathbf{R}_{\alpha}} \langle F_0 | F_0 \rangle_{\mathbf{r}} = \frac{1}{2} \frac{\partial}{\partial \mathbf{R}_{\alpha}} \langle 1 \rangle = 0 \quad (12)$$

We can now write

$$\langle \psi_{00} | \mathbf{M}_2 | \psi_{nv} \rangle = \sum_{\alpha} \frac{Z_{\alpha}}{M_{\alpha}} \sum_{pw} \langle \psi_{00} | \mathbf{R}_{\alpha} | \psi_{pw} \rangle \times \langle \psi_{pw} | \mathbf{P}_{\alpha} | \psi_{nv} \rangle \quad (13)$$

and by similar arguments to those given above we see that

$$\langle \psi_{00} | \mathbf{M}_2 | \psi_{nv} \rangle = 0 \text{ for } n \neq 0 \quad (14a)$$

$$\langle \psi_{00} | \mathbf{M}_2 | \psi_{nv} \rangle = \langle f_0^0 | \mathbf{M}_2 | f_v^n \rangle \text{ for } n = 0 \quad (14b)$$

Now let us examine some matrix elements of \mathbf{P}_1 . We can write

$$\langle \psi_{00} | \mathbf{P}_1 | \psi_{0v} \rangle = \langle f_0^0(\mathbf{R}) | \langle F_0(\mathbf{r}, \mathbf{R}) | \mathbf{P}_1 | F_0(\mathbf{r}, \mathbf{R}) \rangle_{\mathbf{r}} | f_v^0(\mathbf{R}) \rangle_{\mathbf{R}} \quad (15)$$

In the absence of an electromagnetic field, the electronic ground-state eigenfunction $F_0(\mathbf{r}, \mathbf{R})$ can always be taken as nondegenerate and real. Therefore

$$\langle F_0(\mathbf{r}, \mathbf{R}) | \mathbf{P}_1 | F_0(\mathbf{r}, \mathbf{R}) \rangle_{\mathbf{r}} = 0 \quad (16)$$

so that

$$\langle \psi_{00} | \mathbf{P}_1 | \psi_{0v} \rangle = 0 \quad (17)$$

By means of a similar argument we find that

$$\langle \psi_{00} | \mathbf{M}_1 | \psi_{0v} \rangle = 0 \quad (18)$$

By making use of eq 10a, 10b, 14a, 14b, 17, and 18, we can finally write eq 4 as

$$\phi_0 = \phi_g + \phi_e \quad (19)$$

where

$$\phi_g = \frac{4\pi e^2 N}{3c^2} \sum_l k_l (k_l^2 - k_{\lambda}^2)^{-1} \langle f_0 | \mathbf{P}_2 | f_l \rangle \cdot \langle f_l | \mathbf{M}_2 | f_0 \rangle \quad (20)$$

and

$$\begin{aligned} \phi_e &= \frac{4\pi e^2 N}{3c^2} \sum_{n \neq 0} k_{nv} (k_{nv}^2 - k_{\lambda}^2)^{-1} \times \\ &\quad \Re \{ \langle \psi_{00} | \mathbf{P}_1 | \psi_{nv} \rangle \cdot \langle \psi_{nv} | \mathbf{M}_1 | \psi_{00} \rangle \} \end{aligned} \quad (21)$$

In eq 20 the subscript 0 labels the vibrational ground state and l labels the excited vibrational states, all of them corresponding to the electronic ground state. ϕ_g represents the contribution due to the direct interactions between the nuclei and the radiation field. It can be evaluated exactly in a straightforward manner if the vibrations are harmonic and if the vibrational normal coordinates are known since it can be reduced to an expression that is independent of the electronic wave functions. This result has some unexpected implications in the theory of infrared intensities, which will be discussed elsewhere.

ϕ_e contains the electronic wave functions of the ground and excited states of the molecule. It can be transformed further by expanding the electronic wave functions in terms of the nuclear displacement coordinates with respect to the equilibrium configuration:

$$\phi_e = \phi_e^{(0)} + \phi_e^{(1)} + \phi_e^{(2)} + \dots \quad (22)$$

It was shown⁴ that $\phi_e^{(0)}$ is the electronic contribution, evaluated on the assumption that the nuclei are at rest and therefore independent of vibrations. The term $\phi_e^{(1)}$, which is linear in the nuclear displacement coordinates, vanishes in the harmonic approximation. The term $\phi_e^{(2)}$ contains the principal contribution of vibrations to ϕ_e . It is practically impossible to obtain reliable theoretical estimates of its magnitude from our present knowledge of electronic wave functions.

It follows from the above discussion that the OR of molecules of the type CHDR_1R_2 is the sum of the contribution ϕ_g , which can be evaluated accurately in some cases, and of the contribution $\phi_e^{(2)}$, which cannot be calculated within any reasonable degree of accuracy. Both contributions depend on the frequency of the rotated light, and this dependence is such that the relative importance of ϕ_g with respect to ϕ_e increases with decreasing frequency. We intend to calculate the contribution to the isotope effect in optical rotatory power due to the term ϕ_g only since we are unable to evaluate $\phi_e^{(2)}$. This calculation should lead to fairly accurate predictions for the optical activity at infrared frequencies and perhaps the low frequency part of the visible light. At higher frequencies we may possibly get a reliable theory for optical activity only by evaluating both ϕ_e and ϕ_g .

Applications of the General Theory

The expression for ϕ_g is given in eq 20, where again $\mathbf{P}_2 = \sum_{\alpha} (Z_{\alpha}/M_{\alpha}) \mathbf{P}_{\alpha}$ and $\mathbf{M}_2 = \sum_{\alpha} (Z_{\alpha}/M_{\alpha}) \mathbf{R}_{\alpha} \times \mathbf{P}_{\alpha}$, and Z_{α} , M_{α} , \mathbf{R}_{α} , and \mathbf{P}_{α} are the charge (in units $-e$), mass, position vector, and momentum, respectively, of nucleus α . The summation is performed over all nuclei in the molecule.

We write \mathbf{R}_{α} as

$$\mathbf{R}_{\alpha} = \mathbf{R}_{0,\alpha} + \delta_{\alpha} \quad (23)$$

where $\mathbf{R}_{0,\alpha}$ is the equilibrium position of nucleus α with respect to a given origin, and δ_{α} is the displacement from equilibrium of nucleus α due to molecular vibrations. We use eq 23 to separate the operator \mathbf{M}_2 of eq 5c into two parts

$$\mathbf{M}_2 = \mathbf{M}_2^{(0)} + \mathbf{M}_2^{(1)} \quad (24)$$

with

$$\begin{aligned} \mathbf{M}_2^{(0)} &= \sum_{\alpha} (\mathbf{Z}_{\alpha}/M_{\alpha}) \mathbf{R}_{0,\alpha} \times \mathbf{P}_{\alpha} \\ \mathbf{M}_2^{(1)} &= \sum_{\alpha} (\mathbf{Z}_{\alpha}/M_{\alpha}) \delta_{\alpha} \times \mathbf{P}_{\alpha} \end{aligned} \quad (25)$$

The contributions of $\mathbf{M}_2^{(0)}$ and $\mathbf{M}_2^{(1)}$ to ϕ_g , according to eq 20, are denoted by $\phi_g^{(0)}$ and $\phi_g^{(1)}$, respectively. In earlier work it was anticipated that $\phi_g^{(1)}$ is much smaller than $\phi_g^{(0)}$ and consequently it was neglected. It will be shown here that $\phi_g^{(1)}$ is exactly zero.

In the harmonic approximation we may define the normal coordinates Q_l , which are related to the Cartesian coordinates δ_{α} by way of

$$Q_l = \sum_{\alpha} \sum_i B_{l,\alpha i} \delta_{\alpha i} = \sum_{\alpha} \mathbf{B}_{l,\alpha} \cdot \delta_{\alpha} \quad (i = x, y, z) \quad (26)$$

where $\delta_{\alpha i}$ and $\mathbf{B}_{l,\alpha i}$ are the x, y, z components of the vectors $\mathbf{B}_{l,\alpha}$ and δ_{α} . The summation over α is to be performed over all N nuclei in the molecule, and l can have the values $1, 2, \dots, (3N - 6)$.

The momentum P_l , which is conjugate to the coordinate Q_l , may be represented by an operator

$$P_l = -i\hbar(\partial/\partial Q_l) \quad (27)$$

in the quantum mechanical description. We have therefore

$$\mathbf{P}_{\alpha} = \sum_l \mathbf{B}_{l,\alpha} \cdot P_l \quad (28)$$

and the operators \mathbf{P}_2 and $\mathbf{M}_2^{(0)}$ may be written as

$$\begin{aligned} \mathbf{P}_2 &= \sum_l \sum_{\alpha} (\mathbf{Z}_{\alpha}/M_{\alpha}) \mathbf{B}_{l,\alpha} \cdot P_l \\ \mathbf{M}_2^{(0)} &= \sum_l \sum_{\alpha} (\mathbf{Z}_{\alpha}/M_{\alpha}) [\mathbf{R}_{0,\alpha} \times \mathbf{B}_{l,\alpha}] \cdot P_l \end{aligned} \quad (29)$$

The vibrational wave function is a product of functions that depend on one coordinate Q_l only; the vibrational ground-state function f_0 is therefore the product of the ground-state functions of all normal modes. It has been shown⁴ that the matrix elements $\langle f_0 | \mathbf{P}_{\alpha} | f_l \rangle$ are nonzero only if the state l represents the situation where one vibrational mode is in its first excited state and all other vibrational modes are in their ground states. If we use the notation f_j for the wave function of the state where the normal mode j is the one that is in its first excited state and where all other modes are in their lowest states we have

$$\langle f_0 | \mathbf{P}_j | f_j \rangle = \delta_{j,j'} i(k_j/2)^{1/2} \quad (30)$$

where k_j is the first excitation energy of mode j . It follows now from eq 20, 25, and 29 that

$$\phi_g^{(0)} = (2\pi e^2 N/3c^2) \sum_j k_j^2 (k_j^2 - k_{\lambda}^2)^{-1} R_j \quad (31)$$

with

$$R_j = \sum_{\alpha} \sum_{\beta} (\mathbf{Z}_{\alpha} \mathbf{Z}_{\beta} / M_{\alpha} M_{\beta}) \mathbf{B}_{j,\alpha} [\mathbf{R}_{0,\beta} \times \mathbf{B}_{j,\beta}] \quad (32)$$

By analogy with the definition of "rotatory strength" for an electronic state, we define R_j as the "vibrational rotatory strength" of vibrational mode j .

We will show now that $\phi_g^{(1)}$ is exactly zero. It follows from eq 25, 26, and 28 that $\mathbf{M}_2^{(1)}$ is a linear combination of terms of the type $Q_j P_{j'}$. It is easily verified that

$$\langle f_{j''} | Q_j P_{j'} | f_0 \rangle = 0 \quad (33)$$

and we see that the wave functions f_j , which are the only functions that give nonzero matrix elements for the operator \mathbf{P}_2 , lead to vanishing matrix elements for the operator $\mathbf{M}_2^{(1)}$. Consequently $\phi_g^{(1)}$ is zero.

In order to evaluate the vibrational rotatory strengths R_j numerically, it is convenient to modify eq 32 somewhat. It is customary in the analysis of molecular vibrations⁷ to introduce internal coordinates S_i as a starting point for the theoretical description. The normal coordinates Q_i are then given by

$$\begin{aligned} Q_l &= \sum_m (\mathbf{L}^{-1})_{l,m} S_m = \sum_m (\mathbf{L}^{-1})^+_{m,l} S_m \\ S_m &= \sum_{\alpha} \sum_i s_{m,\alpha i} \delta_{\alpha i} = \sum_m \mathbf{s}_{m,\alpha} \cdot \delta_{\alpha} \end{aligned} \quad (34)$$

Combination of eq 26 and 34 gives

$$\mathbf{B}_{l,\alpha} = \sum_m (\mathbf{L}^{-1})^+_{m,l} \mathbf{s}_{m,\alpha} \quad (35)$$

Hence

$$\begin{aligned} \mathbf{R}_j &= \sum_{\alpha} \sum_{\beta} (\mathbf{Z}_{\alpha} \mathbf{Z}_{\beta} / M_{\alpha} M_{\beta}) \sum_m \sum_n (\mathbf{L}^{-1})^+_{m,j} (\mathbf{L}^{-1})^+_{n,j} \mathbf{s}_{m,\alpha} [\mathbf{R}_{0,\beta} \times \mathbf{s}_{n,\beta}] \end{aligned} \quad (36)$$

which is the expression that we have actually used in our numerical evaluation of the OR.

The following relations have proved to be helpful in our calculations. Let us introduce the matrix $\mathbf{T}^{\alpha\beta}$ whose elements are given by

$$T_{mn}^{\alpha\beta} = (\mathbf{Z}_{\alpha} \mathbf{Z}_{\beta} / M_{\alpha} M_{\beta}) \mathbf{s}_{m,\alpha} \cdot [\mathbf{R}_{0,\beta} \times \mathbf{s}_{n,\beta}] \quad (37)$$

and also the matrix T , which is given by

$$\mathbf{T} = \sum_{\alpha} \sum_{\beta} \mathbf{T}^{\alpha\beta} \quad (38)$$

Equation 36 may now be written as

$$R_j = \{ \mathbf{L}^{-1} \cdot \mathbf{T} \cdot (\mathbf{L}^{-1})^+ \}_{jj} \quad (39)$$

where \mathbf{L}^{-1} is the transformation matrix of eq 34 and $(\mathbf{L}^{-1})^+$ is the transpose of \mathbf{L}^{-1} . It follows from the theory of molecular vibrations⁷ that the matrix \mathbf{L}^{-1} satisfies the relations

$$\begin{aligned} \mathbf{F} \mathbf{G} (\mathbf{L}^{-1})^+ &= (\mathbf{L}^{-1})^+ \mathbf{A} \\ \mathbf{L} + \mathbf{F} \mathbf{L} &= \mathbf{A} \\ \mathbf{L} + \mathbf{G}^{-1} \mathbf{L} &= \mathbf{E} \end{aligned} \quad (40)$$

where \mathbf{F} and \mathbf{G} are the potential and kinetic energy matrices in terms of the internal coordinates S_m , \mathbf{E} is the unit matrix, and \mathbf{A} is a diagonal matrix defined by

$$\Lambda_{j,j'} = (k_j^2 / \hbar^2) \delta_{j,j'} \quad (41)$$

We can now derive a summation rule for the vibrational rotational strengths R_j . It may be recalled that for the contributions to the optical rotatory power from the electronic excited states the sum of the rotatory strengths R_n is equal to zero. It is somewhat surprising that the sum of the vibrational rotatory strengths R_j turns out to be different from zero. From eq 39 it follows immediately that

$$\sum_j R_j = \Gamma \{ \mathbf{L}^{-1} \cdot \mathbf{T} \cdot (\mathbf{L}^{-1})^+ \} \quad (42)$$

where $\Gamma \{ \mathbf{A} \}$ means the trace of the matrix \mathbf{A} . Since the trace of a matrix remains invariant under a similarity

transformation we may derive from eq 40 that

$$\sum_j R_j = \Gamma\{\mathbf{L}^{-1} \cdot \mathbf{T} \cdot \mathbf{G}^{-1} \cdot \mathbf{L}\} = \Gamma\{\mathbf{T} \cdot \mathbf{G}^{-1}\} \quad (43)$$

It should be noticed that the matrices \mathbf{T} and \mathbf{G}^{-1} depend only on the geometry of the molecule and on the charges and masses of the nuclei.

For $k_\lambda \gg k_j$, another useful relation can be derived. In that case we may neglect the term k_j^2 in the denominator of eq 31 and write

$$\phi_g = -(2\pi e^2 N \hbar^2 / 3c^2 k_\lambda^2) \sum_j (k_j^2 / \hbar^2) R_j \quad (44)$$

Using matrix notation and substituting eq 41 gives

$$\sum_j (k_j^2 / \hbar^2) R_j = \Gamma\{\mathbf{A} \cdot \mathbf{L}^{-1} \cdot \mathbf{T} \cdot (\mathbf{L}^{-1})^+\} \quad (45)$$

From eq 40 it follows now that

$$\sum_j (k_j^2 / \hbar^2) R_j = \Gamma\{\mathbf{F} \cdot \mathbf{T}\} \quad (46)$$

It is therefore possible to calculate the contribution ϕ_g to the optical rotatory power of a given molecule from eq 44 and 46 if the frequency of the incident light is significantly larger than the normal vibrational frequencies of the molecule. In this case there is no need to calculate the normal frequencies and normal coordinates, but a knowledge of a reliable set of force constants is required for the determination of \mathbf{F} .

For light with frequencies comparable with the normal frequencies of the molecule, ϕ_g can be calculated only if the complete set of normal frequencies and normal coordinates of the molecule is known. If they are not known but the corresponding quantities for the nonsubstituted molecule are available, then ϕ_g may be calculated with the aid of first-order perturbation theory.⁷ This approach is appropriate only to small changes in mass and it is not suitable for H to D substitution.

We take it that we know the normal frequencies and coordinates for a molecule that is described by the matrices \mathbf{F} and \mathbf{G}_0 . The normal frequencies are given by the set of eigenvalues

$$\mu_j^0 = (k_j^0 / \hbar)^2 \quad (47)$$

and the normal coordinates are determined by the matrix \mathbf{L}_0^{-1} . We seek to determine the corresponding quantities μ_j and \mathbf{L}^{-1} for a molecule that is described by the matrices \mathbf{F} and $\mathbf{G} = \mathbf{G}_0 + \delta\mathbf{G}$. In the approximation of first-order perturbation theory,⁷ which is valid when $\delta\mathbf{G}$ is small, we have

$$\mu_j \approx \mu_j^0 [1 + \{\mathbf{L}_0^{-1} \cdot \delta\mathbf{G} \cdot (\mathbf{L}_0^{-1})^+\}_{jj}] \quad (48)$$

and

$$\begin{aligned} \{\mathbf{L}^{-1}\}_j &\approx \{\mathbf{L}_0^{-1}\}_j + \{\mathbf{L}_1^{-1}\}_j \\ \{\mathbf{L}_1^{-1}\}_j &= \sum_{k \neq j} c_{jk} \{\mathbf{L}_0^{-1}\}_k \end{aligned} \quad (49)$$

where $\{\mathbf{A}\}_k$ stands for the j th column of the matrix \mathbf{A} , and where the coefficients c_{jk} are given by

$$c_{jk} = \mu_k^0 (\mu_j^0 - \mu_k^0)^{-1} \{\mathbf{L}_0^{-1} \cdot \delta\mathbf{G} \cdot (\mathbf{L}_0^{-1})^+\}_{jk} \quad (50)$$

It may be pointed out that the above perturbation treatment is approximate to isotopic substitution, since in that case only the \mathbf{G} matrix and not the \mathbf{F} matrix is affected.

If we substitute the results of eq 48–50 into eq 39 for the R_j we obtain

$$R_j = \sum_{k \neq j} \mu_k^0 (\mu_j^0 - \mu_k^0)^{-1} \times \{\mathbf{L}_0^{-1} \cdot \delta \cdot (\mathbf{L}_0^{-1})^+\}_{jk} \{\mathbf{L}_0^{-1} \cdot \mathbf{T} \cdot (\mathbf{L}_0^{-1})^+\}_{jk} \quad (51)$$

This expression may be useful to calculate the OR due to isotopic substitution of heavy nuclei. In the summation the symbol $k \neq j$ means that k and j should belong to different representations of the unperturbed molecule.

Calculations and Results

A calculation of ϕ_g for a given molecule requires an accurate knowledge of the normal frequencies and particularly of the normal coordinates of the molecule. Even if experimentally determined normal frequencies were available for some of the molecules mentioned in ref 5, still a very reliable knowledge of the normal coordinates would be a prerequisite for a reasonably accurate calculation of ϕ_g . The situation here is similar to what happens in molecular electronic calculations: wave functions that reproduce some of the energies with small errors could lead to very poor results in calculations of other quantities. Therefore, a calculation of ϕ_g should have at its basis a very good set of force constants which not only reproduces the experimental frequencies but which should also be considered reliable from a more general viewpoint.

With these considerations in mind we feel unable at this time to calculate ϕ_g with reasonable accuracy for any of the rather complicated organic molecules for which the OR has been measured. Instead we have selected for our calculations some molecules for which complete and quite accurate sets of force constants are available, namely, CHDBrCl, CCl³⁵Cl³⁷BrF, and CHDTBr, all of which have a tetrahedral arrangement around the carbon atom (see Figure 1). The sets of force constants that we used were obtained from several papers by Cleveland and his co-workers.⁸

A program was written and used, which calculates the normal frequencies, normal coordinates, and the quantities R_j of eq 32 for a molecule from the matrices \mathbf{F} and \mathbf{G} , the ratios Z_α/M_α , and the vectors $\mathbf{R}_{0,\alpha}$ and $\mathbf{s}_{m,\alpha}$. The OR is then easily derived from the output of the computer calculation. Even though ϕ_g is a convenient quantity in theoretical considerations, we decided to transform our results to a more customary form and to express them in terms of the specific rotation $[\alpha]$, which is related to ϕ_g by way of

$$[\alpha] = 1800 \phi_g / \pi \rho \quad (52)$$

where ρ is the density of the pure substance. The specific rotation $[\alpha]$ represents then the angle of rotation in degrees per dm and per g/cm³. To avoid any possible confusion with regard to the configurations of the molecules we calculated, the arrangement of atoms for each of these molecules is shown in Figure 1.

The results of the calculations for CHDBrCl are reported in Table I. We also calculated $[\alpha]$ as a function of the frequency of the incident light, or, as it is usually called, the optical rotatory dispersions curve, by using

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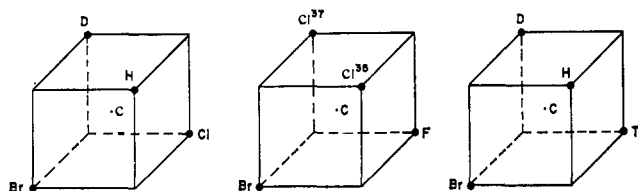


Figure 1. Configuration of optically active molecules considered.

eq 31. This result is shown in Figure 2, where $[\alpha]$ for CHDBrCl is plotted *vs.* the wave number ω_λ in cm^{-1} of the incident light. The specific rotation $[\alpha]_D$ for the D line of sodium is 0.0002° . As a general check on the calculations, we evaluated $\sum_j R_j$ from eq 43 and $\sum_j (k_j^2/\hbar^2)R_j$ from eq 46. The results, namely, -0.0561 and -0.164 , respectively, are in agreement with the values obtained from Table I.

Table I. CHDBrCl

Normal frequencies, ω , cm^{-1}				Vibrational rotatory strength, R , 10^{16} $\text{g}^{-1} \text{cm}$
Observed		Calcd by Cleveland	Present calcn	
Liquid	Gas			
3024	3029	3020	3021	-0.0013
2246	2251	2205	2204	0.0003
1263	1268	1283	1287	-0.0131
1179	1188	1155	1149	-0.0115
866	868	878	879	0.0063
743	746	740	737	-0.0460
707	711	704	706	0.0255
586	591	578	579	0.0255
228	233	227	87	-0.0424

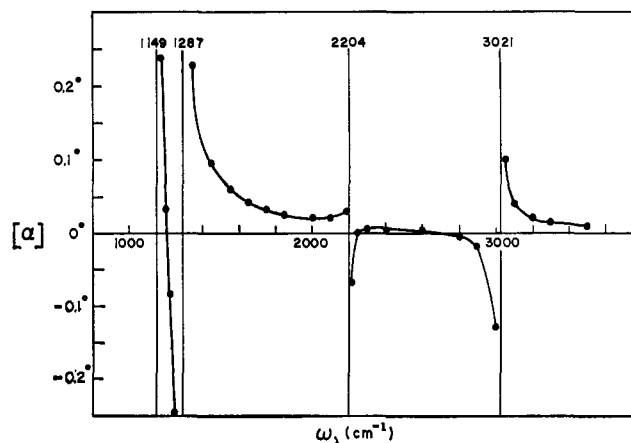
Similar calculations of the R_j were performed for $\text{CCl}^{35}\text{Cl}^{37}\text{BrF}$ and for CHDTBr; the results for both molecules are reported in Table II. We found that $[\alpha]_D \approx 1 \times 10^{-5}$ for $\text{CCl}^{35}\text{Cl}^{37}\text{BrF}$ and $[\alpha]_D = -0.0003^\circ$ for CHDTBr.

Table II

$\text{CCl}^{35}\text{Cl}^{37}\text{BrF}$		CHDTBr	
ω , cm^{-1}	R , 10^{16} $\text{g}^{-1} \text{cm}$	ω , cm^{-1}	R , 10^{16} $\text{g}^{-1} \text{cm}$
1065	0	2047	0.0024
836	-0.0014	2235	-0.0034
783	0.0059	1866	0.0096
499	0.0010	1289	0.0505
386	-0.0210	1204	-0.1165
318	-0.0637	965	0.0298
230	0.0201	773	0.1402
202	0.0715	611	-0.0691
50	-0.0067	237	-0.0099

It may be seen from Table I that we were unable to reproduce the lowest eigenfrequency that was reported by Cleveland, *et al.*,⁸ from Cleveland's force constants. The value that we obtained is different from the experimental value, and we have no explanation for this discrepancy.

We suspect that it might considerably affect the OR for light of frequency comparable to the lower vibra-

Figure 2. Optical rotatory dispersion curve for CHDBrCl: specific rotation *vs.* wavenumber of incident light.

tional absorption frequencies of the molecule. It will probably affect $[\alpha]$ for light of about 1000 cm^{-1} by 10 or 15% and $[\alpha]_D$ by about 1%.

Discussion

Our calculation of ϕ_g contains only two approximations, namely, the harmonic approximation and the assumption that the optical rotation for a liquid or a solution is the same as for a dilute gas. It is generally agreed that these two approximations are permissible and that they cannot lead to significant discrepancies.

From the results in Tables I and II it may be noticed that the vibrational rotatory strengths vary considerably from one fundamental vibration to another, both in sign and in magnitude in what seems to us an unpredictable way. Therefore, all R_j 's should be known for an accurate determination of the OR, and this means that we ought to have an accurate knowledge of the force constants in order to determine the OR.

There is some difficulty in comparing our theory with the experimental information⁵ since there are no experimental data available for the molecules we calculated and since the molecules for which measurements have been performed are inaccessible to theoretical studies. Nevertheless, we should note that for the molecules CHDX₂ (with X and Y different halogens) we calculated $[\alpha]_D$ to be of the order of 10^{-4} and that the experimental values of $[\alpha]_D$ are of the order of 0.01 to 1° for molecules of the type CHDR_1R_2 (with R_1 and R_2 organic radicals). This large difference between the two sets of $[\alpha]_D$ values is due to either one of two reasons: (1) the replacement of the halogens by organic radicals causes a sharp increase in $[\alpha]_D$; or (2) the $\phi_e^{(2)}$ contribution of eq 2 is dominant for visible or ultraviolet light. The second possible reason is not attractive from a theoretical point of view since $\phi_e^{(2)}$ cannot be evaluated, but unfortunately it seems the more likely one of the two reasons.

However, it is relatively easy to modify the experimental approach so that it becomes compatible with our theory. It is easily verified that for lower frequencies of the rotated light, $\phi_e^{(2)}$ is proportional with k_λ^2 , and therefore it will rapidly decrease with decreasing k_λ . On the other hand, ϕ_g will become significantly larger if k_λ becomes comparable with the k_j . There-

fore, the importance of $\phi_e^{(2)}$ with respect to ϕ_g will diminish sharply with decreasing k_λ , and at infrared frequencies the OR depends only on ϕ_g and not on $\phi_e^{(2)}$. It may therefore be concluded that our theory

gives an adequate description of the OR of molecules of the type CHDXY for infrared light and that we are not sure whether or not the omission of $\phi_e^{(2)}$ is permissible for visible or ultraviolet light.

Steric Effects on Hydrogen Bonding¹

Surjit Singh and C. N. R. Rao

Contribution from the Department of Chemistry, Indian Institute of Technology, Kanpur, India. Received November 16, 1965

Abstract: Quantitative thermodynamic studies of the hydrogen bonding of sterically hindered alcohols and phenols with donors have been carried out. The enthalpies of hydrogen bonding between hindered hydroxy groups and donors are appreciable and are comparable to those with simple alcohols and phenols. The low equilibrium constants are mainly due to entropy factors. $\Delta\nu_{\text{OH}}$ and ΔH° are not linearly related in the sterically hindered systems. Electrical effects of *para* substituents on the hydrogen bonding of *para*-substituted 2,6-di-*t*-butylphenols with donors have been studied and the results do not show a linear free energy relationship.

It has been known that sterically hindered phenols ("kryptophenols") do not undergo characteristic reactions of simple phenols.² Sterically hindered alcohols and phenols have also been found to be less associated than simple hydroxy compounds^{3,4} and the low equilibrium constants of self-association were found to be due to entropy factors, since the enthalpies were quite large in these systems. Recent studies of Bellamy and co-workers^{5,6} have shown that the relative strengths of hydrogen bonds between donors and mono- or di-*o*-alkylphenols are not greatly affected by the bulk of the alkyl groups except in the case of di-*o*-*t*-butylphenol. These conclusions of Bellamy and co-workers were based on measurements of frequency shifts, $\Delta\nu_{\text{OH}}$, and a few equilibrium constants for the interaction between the hindered phenols with ethers. The hydrogen bonding of several hindered alcohols and phenols with a variety of donors has been reported in the present communication.

Bellamy and co-workers^{5,6} assumed the enthalpy of hydrogen bonding to be proportional to the $\Delta\nu_{\text{OH}}$; thus, on the basis of the low $\Delta\nu_{\text{OH}}$ 2,6-di-*t*-butylphenol was considered to form weak hydrogen bonds with donors. Our recent studies of the self-association of hindered alcohols and phenols⁴ and of hydrogen bonding between various donors and acceptors⁷ indicated to us that a linear $\Delta\nu_{\text{OH}}-\Delta H^\circ$ relation does not hold when one considers hydrogen bonding of a variety of hydroxylic compounds with donors. It was therefore decided to investigate the thermodynamics of

hydrogen bonding of hindered alcohols and phenols with a donor in detail to establish quantitatively the steric effects on the equilibrium constants, the frequency shifts, and the enthalpy of hydrogen bonding. In addition to examining steric effects in hindered phenols, electrical effects of *para* substituents on the hydrogen bonding of sterically hindered phenols have also been studied.

Results and Discussion

Hydrogen bonding data of several mono- and di-*ortho*-substituted phenols with a few donors have been compared with the data on phenol in Table I. It can be clearly seen that in all the cases the equilibrium constants and the $\Delta\nu_{\text{OH}}$ decrease with the increase in the bulk of the *ortho* substituents. Steric effects on equilibrium constants and $\Delta\nu_{\text{OH}}$ are also quite marked in the hindered alcohols (Table II). These results are similar to those of Bellamy and co-workers,^{5,6} but unfortunately the data could not throw any light on the strengths of the hydrogen bonds and the cause for the diminution of equilibrium constants.

Blue shifts of $n-\pi^*$ transitions⁸ of carbonyl and thio-carbonyl groups in the sterically hindered alcohols were also found to be considerably smaller than in simple alcohols. Since $n-\pi^*$ blue shifts are proportional to hydrogen bond energies,^{7,9} this may be taken as evidence of weak hydrogen bonding between the sterically hindered alcohols and donors. However, in the present case, comparison of blue shifts is not valid since there will be little or no self-association of sterically hindered alcohols⁴ when used as solvents while other simple alcohols will be highly associated.¹⁰ Relative comparisons of hydrogen bond energies in terms of blue shifts would be possible only if the magnitude of self-association of alcohols is about the same.

(1) Forms part of the material for the Ph.D. thesis of S. Singh to be submitted to the Indian Institute of Technology, Kanpur, India. All correspondence should be addressed to C. N. R. R.

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