1,17-Heptadecanedioic Acid and 1,19-Nonadecanedioic Acid.—Reduction of the crude keto dibasic acids II and III by the Clemmensen method[9] gave 1,17-heptadecanedioic acid showing m.p. 118–118.5° with sintering at 117.5°[10] in 80.5% yield after two recrystallizations and 1,19-nonadecanedioic acid showing m.p. 118–119°[10] in 63% yield after two recrystallizations. The m.ps. of these acids when mixed with their related keto dibasic acids were lowered markedly; depressions of 6–10° were observed.

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Zero-point Vibrational Contributions to the Optical Rotatory Power of Isotopically Dissymmetric Molcules

BY WILDON FICKETT

RECEIVED FEBRUARY 8, 1952

Recently, several optically active compounds of the type R_1R_2CHD have been prepared.[1,2] The optical rotations, while small, are apparently well established experimentally and are of the order of magnitude to be expected from the isotopic mass dissymmetry. The rotations of such compounds are amenable to theoretical calculation within the framework of Kirkwood's theory of optical rotatory power[3] if the vibrational contributions are explicitly taken into account.

The Born–Oppenheimer approximation[4] may be used to express the molecular wave functions as products of wave functions for the electronic and nuclear motions. For the equilibrium configuration of the nuclei the potential function for the electronic motion possesses a plane of symmetry. The vibrational wave functions, on the other hand, will be sensibly dissymmetric because of the isotopic mass difference.

Kirkwood's theory[3] can be applied to the case of isotopic dissymmetry through explicit representation of the quantities of interest as expectation values over the molecular ground state wave function. We start with Kirkwood's Eq. (32) for $g^{(0)}$

$$g^{(0)} = -\sum_{i \neq h = 1}^{N} ([\overrightarrow{a_3}\alpha^{(i)}\mathrm{T}_{ik}\alpha^{(k)}\overrightarrow{a_2}][\overrightarrow{R_k}\overrightarrow{a_1}])_{\mathrm{Av.}} \qquad (1)$$

in which the sum extends over the N intrinsically inactive groups into which the molecule is divided for the purpose of calculation; α is the group polarizability tensor; and $\overrightarrow{R}$ denotes the position of the group center of mass referred to the molecular center of mass. The unit vectors $\overrightarrow{a}$ define a rectangular coördinate system fixed in space, and the subscript Av. indicates an averaging over all molecular orientations. Expanding $g^{(0)}$ in the normal coördinates of vibration about the equilibrium positions, we obtain

$$g^{(0)} = \sum_{i \neq h = 1} [(\overrightarrow{a_3}\alpha^{(i)}\mathrm{T}_{ik}\alpha^{(k)}\overrightarrow{a_2})(\{\sum_l \left(\frac{\partial \overrightarrow{R_k}}{\partial q_l}\right)_0 q_l\}\overrightarrow{a_1})$$
$$+ (\overrightarrow{R_k}\overrightarrow{a_1})_0(\overrightarrow{a_3}\alpha^{(i)}\{(\sum_l \left(\frac{\partial' \mathrm{T}_{ik}}{\partial q_l}\right)_0 q_l)\alpha^{(k)} + \mathrm{T}_{ik}(\sum_l \left(\frac{\partial \alpha^{(k)}}{\partial q_l}\right) q_l)\} a_2)$$
$$+ (\overrightarrow{R_k}a_1)_0(a_3\alpha^{(i)}\{\sum_l \left(\frac{\partial' \mathrm{T}_{ik}}{\partial q_l}\right)_0 q_l\}\{\sum_n \left(\frac{\partial \alpha^{(k)}}{\partial q_n}\right)_0 q_n\}\overrightarrow{a_2}) + \ldots]_{\mathrm{Av.}}$$

where the q's represent the normal coördinates. We have supposed here that in any one mode of vibration the polarizability of only one group of each pair is appreciably affected by the vibration. The remaining second order terms are neglected for various reasons. The averaging process is carried out as before[3] and for groups with optical symmetry, the result for $\langle g^{(0)} \rangle$, the expectation value of $g^{(0)}$, is analogous to Kirkwood's corrected[5] Eq. (35)

$$\langle g^{(0)} \rangle = \frac{1}{6}\sum_{i \neq k = 1}^{N} \alpha_i\beta_i\Big[\Big(\sum_l \alpha_l^{(k)\prime}\beta_l^{(k)\prime}\langle q_l\rangle\Big)$$
$$(G_{ik} + G'_{ik})(\overrightarrow{R_{ik}}\cdot(\overrightarrow{b_i}\times\overrightarrow{b_k}))$$
$$+ \alpha_i\beta_i(G'_{ik}\overrightarrow{R_{ik}} + G_{ik}\Big(\sum_l \left(\frac{\partial \overrightarrow{R_{ik}}}{\partial q_l}\right)\langle q_l\rangle\Big)))\cdot(\overrightarrow{b_i}\times\overrightarrow{b_k})] \qquad (3)$$

$$\alpha_l^{(k)\prime} = \frac{1}{3}\left\{\left(\frac{\partial \alpha_{11}^{(k)}}{\partial q_l}\right)_0 + 2\left(\frac{\partial \alpha_{22}^{(k)}}{\partial q_l}\right)_0\right\};\ \alpha_l^{(k)\prime}\beta_l^{(k)\prime} =$$
$$\left(\frac{\partial \alpha_{11}^{(k)}}{\partial q_l}\right)_0 - \left(\frac{\partial \alpha_{22}^{(k)}}{\partial q_l}\right)_0$$

$$G'_{ik} = \overrightarrow{b_i'}\left\{\sum_l \left(\frac{\partial \mathrm{T}_{ik}}{\partial q_l}\right)_0 \langle q_l\rangle\right\}\overrightarrow{b_k}$$

where α_{11} and α_{22} are the components of the group polarizability tensor parallel and perpendicular to the optical axis of the group, $\overrightarrow{b}$ is the unit vector along the optical axis, and $\overrightarrow{b'}$ is the corresponding quantity for the derived tensor.

For R_1R_2CHD the principal contributions probably come from C–H and C–D stretching; for this motion the triple vector product in the fourth term of Eq. (3) vanishes, and the third term is found to be small, so that, to a first approximation

$$\langle g^{(0)}\rangle = \frac{1}{6}\sum_i \alpha_i\beta_i[\alpha^{(H)\prime}\beta^{(H)\prime}(G_{i\mathrm{H}} + G'_{i\mathrm{H}})(R_{i\mathrm{H}}\cdot(\overrightarrow{b_i}\times$$
$$\overrightarrow{b_{\mathrm{H}}})\langle X_{\mathrm{H}}\rangle + \alpha^{(\mathrm{D})\prime}\beta^{(\mathrm{D})\prime}(G_{i\mathrm{D}} + G'_{i\mathrm{D}})(\overrightarrow{R_{i\mathrm{D}}}\cdot(b_i\times\overrightarrow{b_{\mathrm{D}}})\langle x_{\mathrm{D}}\rangle] \qquad (4)$$

where x represents the elongation of the bond from its equilibrium distance and the sum extends over all groups other than H and D.

The value of $(\alpha^{(\mathrm{H})\prime}\langle x_{\mathrm{H}}\rangle)$, 0.028 Å.[3] for one C–H bond, has been obtained from the polarizabilities of CH_4 and CD_4.[6] The quantity β' is related to the degree of depolarization of a Raman line in the same way that the quantity β is related to the degree of depolarization of ordinary (Rayleigh) scattered light.[7] It was obtained from the depolarization factor for the ν_1, A_1 line of chloroform.[8] The value $\rho = 0.3$, taken as representative, gives $\beta' = 1.9$. By way of comparison, the value for hydrogen,[6,9] $\rho = 0.14$, gives $\beta' = 1.2$ for the H–H

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(2) E. R. Alexander and A. G. Pinkus, *ibid.*, **71**, 1786 (1949); E. R. Alexander, *ibid.*, **72**, 3796 (1950).

(3) J. G. Kirkwood, *J. Chem. Phys.*, **5**, 479 (1937).

(4) M. Born and J. R. Oppenheimer, *Ann. Phys.*, **84**, 457 (1927).

(5) W. W. Wood, W. Fickett and J. G. Kirkwood, *J. Chem. Phys.*, in press. There is an error of sign in Kirkwood's original paper.

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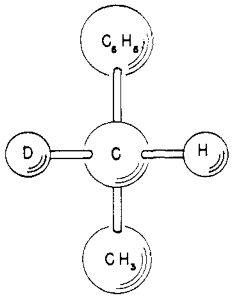
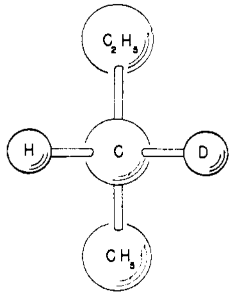
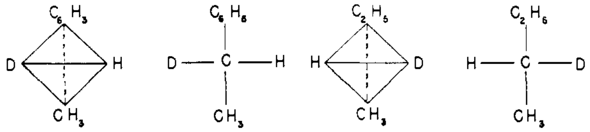
bond. Quantum mechanical calculations[10] assign the positive sign to β' as does a consideration of the known sign of α' and the relative magnitudes of α' and β'.

The optical rotation of the enantiomorph of α-deuteroethylbenzene shown was calculated from Eq. (4). The angle ϕ defining the internal conformation is taken to be zero when the methyl group lies in the plane corresponding to the plane of symmetry of ethylbenzene, and to increase positively as the phenyl group is rotated so as to increase the distance from deuterium to the plane of the ring.







The potential function for the internal conformation can be estimated roughly from the work of Pitzer and Scott on the xylenes.[11] The ethyl group is assumed to have the staggered configuration and to be free to rotate relative to the ring until its hydrogens approach van der Waals contact with those of the ring. The simplified potential function is thus taken to be

$$\begin{array}{lll} V(\phi) = 0 & \text{for} & -30^\circ \leqq \phi \leqq 30^\circ \\ V(\phi) = 0 & \text{for} & 150^\circ \leqq \phi \leqq 210^\circ \\ V(\phi) = \infty & \text{otherwise} & \end{array}$$

The calculated optical rotation is then $[\alpha]^{25}\text{D}$ $+0.41^\circ$ for a medium of refractive index 1.50, corresponding to the pure liquid. The experimental value for the pure liquid enantiomorph prepared by deuteride reduction of (−)-phenylmethylcarbinol is $[\alpha]^{25}\text{D}$ -0.30°. The relative configuration of the carbinol is known.[12] If the deuteride reduction is accompanied by inversion, as is probably the case, then the (−)-α-deuteroethylbenzene has a spatial configuration opposite to that for which the calculations were made, in agreement with the Fischer convention regarding absolute configuration, and consistent with the findings for 2,3-epoxybutane and 1,2-dichloropropane.[5,13]

A calculation for 2-deuterobutane was also carried out, although as far as is known the optically active compound has not been prepared. The problem of internal conformation was treated in terms of three isomers: two "bent" forms of equal energy and one "straight" form, corresponding to the terminology of Szasz, Sheppard and Rank,[14] who determined the equilibrium concentrations of the two forms from the temperature dependence of the infrared spectrum. The calculated optical rotation for the enantiomorph shown is $[\alpha]^{25}\text{D}$ $+1.1^\circ$ for a medium of refractive index 1.33, corresponding to the pure liquid.

The author wishes to thank Professor J. G. Kirkwood for his help and advice throughout this investigation and Professor Verner Schomaker for a helpful discussion of the internal conformation of ethylbenzene.

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Some 10-Substituted Phenothiazines

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RECEIVED MARCH 15, 1952

There is a discrepancy in the literature concerning the melting point of 10-benzylphenothiazine. Desai[1] reported that this compound, m.p. 90.5–91°, was formed by heating a mixture of benzyldiphenylamine and sulfur at 220° for 8 hours. Finzi[2] stated that this particular phenothiazine derivative was obtained by heating phenothiazine and benzyl chloride at 140–145° for 2 hours. However, his product melted at 130°. In connection with the cleavage of some alkoxy heterocycles by compounds containing the imino group, it has been found[3] that the reaction of 2-benzyloxyquinoline with phenothiazine, in refluxing cumene, gave a 90% yield of 2-hydroxyquinoline and a 34% yield of a product melting at 91–92°. The latter compound analyzed for a benzylphenothiazine. A repetition[3] of Finzi's preparation gave a small amount of crystals, m.p. 132–134°. Therefore, the following procedure was attempted in order to prepare the benzyl derivative.[3] A mixture of benzyl chloride and 10-lithiophenothiazine (prepared from phenothiazine and phenyllithium) in a benzene–ether solution and under a nitrogen atmosphere was stirred for one day at room temperature and then one hour at reflux temperature. No pure product has as yet been isolated.

Various 10-(dialkylaminoalkyl)-phenothiazines have been prepared by refluxing in xylene (or similar solvent) a mixture of a dialkylaminoalkyl chloride and phenothiazine in the presence of the

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