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Solvent Action on Optical Rotatory Power.

II. The Quadrupole Field of the CS₂ Type Molecule*

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The applications of the general expression for the vectorial solvent field in organic liquids are further extended by detailed consideration of quadrupole molecules of the types CS₂. The results of the computation are found satisfying from a theoretical standpoint. The experimental control is undertaken with the aid of a previously developed theory of optical rotatory power in solution. The results are found to be in accord with the existing data.

§1.

IT WAS shown in a previous paper¹ that the average electrostatic field exerted on one molecule (designated as an α -molecule) by a small concentration of other molecules (γ -molecules) in a solution of nonpolar β -molecules, or in a mixed gas of α -, β -, and γ -molecules is given by the expression

$$[F_{(\gamma)\delta}]_{Av}^2 = \frac{n_\gamma}{8\pi^2} \int \partial^2 E_{\alpha\gamma} F_{(\gamma)\delta} d\omega_\gamma,$$

where n_γ is the number of γ -molecules per cc, $E_{\alpha\gamma}$ is the interaction energy of one α -molecule and one γ -molecule, $F_{(\gamma)\delta}$ is the δ -component ($\delta=1, 2, 3$ corresponding to three Cartesian coordinates in the chosen α -molecule) of the field of a γ -molecule at the center of the α -molecule and $d\omega_\gamma$ is the differential element of the 6-space of relative coordinates of the two molecules.

Integrating under the assumptions (i) that both molecules are uniformly polarizable spheres with dipoles at the center, (ii) that the effective radii of the spheres are such that $kT > 5E_{\alpha\gamma}$, and (iii) that the γ -molecules act independently of one another³ gave the result

$$[F_{(\gamma)\delta}]_{Av} = \frac{2\mu_\alpha}{d_{\alpha\gamma}^3} \cdot \frac{4\pi}{3} n_\gamma \left[C + \frac{\mu_\gamma^2}{3kT} \right] (3\delta) \\ = \frac{2\mu_\alpha}{d_{\alpha\gamma}^3} \cdot \frac{n_\gamma}{N} P_\gamma (3\delta), \quad (1)$$

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¹ C. O. Beckmann and K. Cohen, J. Chem. Phys. **4**, 784 (1936).

² $F_{(\gamma)\delta}$ in the notation of the previous paper.

³ These assumptions are unnecessarily restrictive (see reference 1) but no greater generality is required for the present purely illustrative purposes.

where μ_α (parallel to the 3 axis) and μ_γ are the dipole moments of the α - and γ -molecules, respectively, C is the optical polarizability of the γ -molecule, $d_{\alpha\gamma}$ is the minimum distance of approach of the two molecules, N is Avogadro's number, P_γ the molar polarization of γ and (3δ) is the "conversion operator" denoting zero when 3 and δ are different and unity when they are the same. On the further assumptions that the α - and β -molecules also satisfy assumptions (i), (ii), and (iii)³ and that $d_{\alpha\alpha} = d_{\alpha\beta} = d_{\alpha\gamma} = d$, it was found that

$$[F_\delta]_{Av} = [F_{(\alpha)\delta}]_{Av} + [F_{(\beta)\delta}]_{Av} + [F_{(\gamma)\delta}]_{Av} \\ = (2\mu_\alpha/d^3) \cdot [(\epsilon-1)/(\epsilon+2)](3\delta), \quad (2)$$

where ϵ is the dielectric constant of the medium.

This expression is almost identical with that obtained by assuming the solvent to be a continuous medium, namely

$$[F_\delta]_{Av} = (2\mu_\alpha/d^3) \cdot [(\epsilon-1)/(2\epsilon+1)](3\delta). \quad (3)$$

It was pointed out that without assumption (i), this coincidence of form of the equations (2) and (3) would not exist, and that, in general, Eqs. (2) and *a fortiori* (3) are incorrect. On these grounds, it is clear why classifications of solvent action in terms of the macroscopic quantity ϵ are not possible.

In addition to showing at once the necessary limitations of the continuous medium theory and the justification of it within these limitations, this development makes possible the treatment of those classes of molecules for which the continuous medium theory must necessarily—and has empirically—failed.

This paper concerns itself with the evaluation of $[F_{(\gamma)\delta}]_{Av}$ for solvent molecules of one such

class; namely, those molecules with a quadrupole of the CS_2 -type (CO_2 , CSe_2 , C_2N_2). Such compounds, as we can see from the data on CS_2 , are strongly polar but have a zero dipole moment. CS_2 is of particular interest.

§2.

We assume the linear CS_2 molecule to be of such a shape that the surface of nearest approach of the center of a spherical α -molecule is an ellipsoid of revolution with semi-minor axis b and semi-major axis a (Fig. 1). The dipole of one $\text{C} \rightarrow \text{S}$ link, \mathbf{u}_γ , is supposed localized at a point Q whose position vector is \mathbf{q} with center of coordinates at the center of the molecule. Correspondingly, the other dipole is located at $-\mathbf{q}$ and can be denoted by $-\mathbf{u}_\gamma$. The dipole moment of the α -molecule, \mathbf{u}_α , is localized at the center of a spherical molecule. Both the α - and the γ -molecules are considered isotropic with optical polarizabilities A and C , respectively. The external field extending over a molecule is, as before, assumed to be homogeneous.

The equation of the ellipsoid in polar coordinates referred to the center of the carbon atom as origin, with \mathbf{q} taken as the prime directrix is

$$r = b / (1 + e^2 \cos^2 \theta_1)^{1/2}, \quad e^2 = (a^2 - b^2) / a^2.$$

One system of axes (\mathbf{i} , \mathbf{j} , \mathbf{k}) is taken fixed in the CS_2 molecule such that $\mathbf{q} = q\mathbf{k}$ and the other (\mathbf{i}' , \mathbf{j}' , \mathbf{k}') fixed in the α -molecule such that $\mathbf{u}_\alpha = \mu_\alpha \mathbf{k}'$. The position of the α -molecule with respect to the center of the γ -molecule is given by the polar coordinates r , θ_1 , ϕ_1 and the orientation of μ_α is given by the Eulerian coordi-

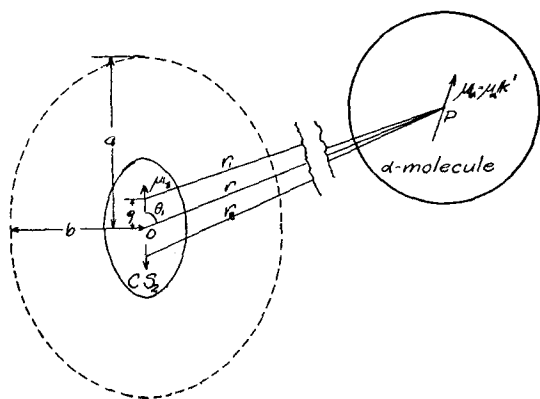


FIG. 1.

nates θ_2 , ϕ_2 , ψ_2 all taken in the conventional manner.⁴

Let \mathbf{r}_1 be the radius vector from the dipole at \mathbf{q} to the center of the α -molecule P , \mathbf{r}_2 the radius vector from the dipole at $-\mathbf{q}$ to P and \mathbf{r} the radius vector from the center of the CS_2 molecule to P . Then \mathbf{r}_1 and \mathbf{r}_2 are given in terms of \mathbf{r} and \mathbf{q} by

$$\mathbf{r}_1 = \mathbf{r} - \mathbf{q}, \quad \mathbf{r}_2 = \mathbf{r} + \mathbf{q}$$

$$\text{or} \quad r_1 = r[1 - 2(q/r) \cos \theta_1 + (q/r)^2]^{1/2},$$

$$r_2 = r[1 + 2(q/r) \cos \theta_1 + (q/r)^2]^{1/2}.$$

Since $q < r$ we may expand r_1 and r_2 in terms of q/r . Reciprocal powers of r_1 and r_2 may be expressed by

$$r_1^{-\nu} = r^{-\nu} \sum_{n=0}^{\infty} (q/r)^n C_n^{\nu/2}(\cos \theta_1), \quad (4)$$

$$r_2^{-\nu} = r^{-\nu} \sum_{n=0}^{\infty} (-q/r)^n C_n^{\nu/2}(\cos \theta_1),$$

where $C_n^{\nu/2}(\cos \theta_1)$ are Gegenbauer functions.⁵ The two used here may be calculated from the Legendre polynomials by the relations

$$C_{n-1}^{3/2}(z) = (d/dz) P_n(z)$$

$$\text{and} \quad C_{n-2}^{5/2}(z) = \frac{1}{3}(d^2/dz^2) P_n(z).$$

The field of the CS_2 molecule is given by

$$\mathbf{F}_\gamma = -\frac{\mathbf{p}_\gamma}{r^3} + \frac{3\mathbf{r}(\mathbf{r} \cdot \mathbf{p}_\gamma)}{r^5} - \frac{\mathbf{u}_\gamma}{r_1^3} + \frac{3\mathbf{r}_1(\mathbf{r}_1 \cdot \mathbf{u}_\gamma)}{r_1^5} + \frac{\mathbf{u}_\gamma}{r_2^3} - \frac{3\mathbf{r}_2(\mathbf{r}_2 \cdot \mathbf{u}_\gamma)}{r_2^5}. \quad (5)$$

Substituting the values of r_1 and r_2 from (4), expanding and retaining terms of the order $(1/r^3)(q/r)^2$ we obtain

$$\mathbf{F}_\gamma = -\frac{\mathbf{p}_\gamma}{r^3} + \frac{3\mathbf{r}(\mathbf{r} \cdot \mathbf{p}_\gamma)}{r^5} - \frac{12}{r^4} q \mathbf{u}_\gamma \cos \theta_1 + \frac{6\mathbf{r} \mu_\gamma q}{r^5} (5 \cos^2 \theta_1 - 1). \quad (6)$$

⁴ This assignment of coordinates is opposite to that used in the first paper, in which the center of the α -molecule was the main reference point. The subsequent integrations make it obvious that for the present problem the above choice is more convenient.

⁵ E. T. Whittaker and G. N. Watson, *Modern Analysis* (Cambridge University Press, 1935), p. 329.

The field of the α -molecule is given by

$$\mathbf{F}_\alpha = -\frac{\mathbf{p}_\alpha}{r^3} + \frac{3\mathbf{r}(\mathbf{r} \cdot \mathbf{p}_\alpha)}{r^5} - \frac{\mathbf{u}_\alpha}{r^3} + \frac{3\mathbf{r}(\mathbf{r} \cdot \mathbf{u}_\alpha)}{r^5}. \quad (7)$$

The polarizations \mathbf{p}_α and \mathbf{p}_γ may be expressed in terms of the polarizabilities A and C by

$$\mathbf{p}_\alpha = A\mathbf{F}_\gamma \quad \mathbf{p}_\gamma = C\mathbf{F}_\alpha.$$

With the approximations and the procedure given in the previous paper,¹ the interaction energy of the two molecules becomes

$$E_{\alpha\gamma} = (12/r^4)q\mathbf{u}_\alpha \cdot \mathbf{u}_\gamma \cos \theta_1 - (6\mu_\gamma q/r^5)\mathbf{r} \cdot \mathbf{u}_\alpha (5 \cos^2 \theta_1 - 1). \quad (8)$$

Since $[F_{(\gamma)z}]_{Av}$ has no components perpendicular to \mathbf{u}_α , and $F_{(\gamma)z} = \mathbf{F}_\gamma \cdot \mathbf{u}_\alpha / \mu_\alpha$ we have

$$[F_{(\gamma)z}]_{Av} = [F_{(\gamma)z}]_{Av} = 0, \\ [F_{(\gamma)z}]_{Av} = \frac{n_\gamma}{4\pi} \int e^{-E_{\alpha\gamma}/kT} \frac{\mathbf{F}_\gamma \cdot \mathbf{u}_\alpha}{\mu_\alpha} d\tau.$$

Approximating $\exp(-E_{\alpha\gamma}/kT)$ with $(1 - E_{\alpha\gamma}/kT)$, substituting the value of $E_{\alpha\gamma}$ from (8) and evaluating $\mathbf{F}_\gamma \cdot \mathbf{u}_\alpha$ from (6) yields for the average field of a γ -molecule

$$[F_{(\gamma)z}]_{Av} = \frac{n_\gamma}{4\pi} \int \left[1 + \frac{6\mu_\alpha \mu_\gamma q}{kT r^4} \right. \\ \times \{ \cos \epsilon (5 \cos^2 \theta_1 - 1) - 2 \cos \theta_1 \cos \theta_2 \} \\ \times \left[\frac{C\mu_\alpha}{r^6} (1 + 3 \cos^2 \epsilon) + \frac{6\mu_\gamma q}{r^4} \{ \cos \epsilon (5 \cos^2 \theta_1 - 1) \right. \\ \left. \left. - 2 \cos \theta_1 \cos \theta_2 \} \right] r^2 dr d\omega_1 d\omega_2, \quad (9)$$

where

$$\cos \epsilon = \sin \theta_1 \sin \theta_2 \cos(\phi_1 - \phi_2) + \cos \theta_1 \cos \theta_2, \\ d\omega_1 = \sin \theta_1 d\theta_1 d\phi_1 \quad \text{and} \quad d\omega_2 = \sin \theta_2 d\theta_2 d\phi_2.$$

The limits of integration are given by the scheme

$$r \left| \begin{array}{c} \infty \\ b(1-e^2 \cos^2 \theta_1)^{-\frac{1}{2}} \end{array} \right| \theta_1 \left| \begin{array}{c} \pi \\ 0 \end{array} \right| \phi_1 \left| \begin{array}{c} \pi \\ 0 \end{array} \right| \theta_2 \left| \begin{array}{c} 2\pi \\ 0 \end{array} \right| \phi_2 \left| \begin{array}{c} \pi \\ 0 \end{array} \right| \psi_2 \left| \begin{array}{c} 2\pi \\ 0 \end{array} \right|.$$

It is easily shown that

$$\int d\omega_1 d\omega_2 \{ \cos \epsilon (5 \cos^2 \theta_1 - 1) - 2 \cos \theta_1 \cos \theta_2 \} = 0$$

and

$$\int d\omega_1 d\omega_2 \cos^2 \epsilon \{ \cos \epsilon (5 \cos^2 \theta_1 - 1) - 2 \cos \theta_1 \cos \theta_2 \} = 0,$$

thus reducing (9) to

$$[F_{(\gamma)z}]_{Av} = \frac{n_\gamma}{4\pi} \int d\omega_1 d\omega_2 \int r^2 dr \left[\frac{C\mu_\alpha}{r^6} \{ 1 + 3 \cos^2 \epsilon \} \right. \\ \left. + \frac{36\mu_\alpha \mu_\gamma^2 q^2}{kT r^8} \{ \cos \epsilon (5 \cos^2 \theta_1 - 1) - 2 \cos \theta_1 \cos \theta_2 \}^2 \right].$$

In the next step, the integration over r between the limits $r=r_0=b(1-e^2 \cos^2 \theta_1)^{-\frac{1}{2}}$ and $r=\infty$ is carried out. Thus

$$[F_{(\gamma)z}]_{Av} = \frac{n_\gamma}{4\pi} \int \frac{C\mu_\alpha}{3b^3} (1 - e^2 \cos^2 \theta_1)^{3/2} \\ \times (1 + 3 \cos^2 \epsilon) d\omega_1 d\omega_2 + \int \frac{36\mu_\alpha \mu_\gamma^2 q^2}{5kT b^5} (1 - e^2 \cos^2 \theta_1)^{5/2} \\ \times \{ \cos \epsilon (5 \cos^2 \theta_1 - 1) - 2 \cos \theta_1 \cos \theta_2 \}^2 d\omega_1 d\omega_2 \Big].$$

Integrating with respect to ϕ_1 , ϕ_2 and θ_2 we obtain, finally

$$[F_{(\gamma)z}]_{Av} = \frac{2\mu_\alpha}{b^3} \cdot \frac{4\pi}{3} n_\gamma \left[\frac{H}{2} - C + \frac{9}{5} \cdot J \cdot \frac{\mu_\gamma^2}{kT} \cdot \frac{q^2}{b^2} \right], \quad (10)$$

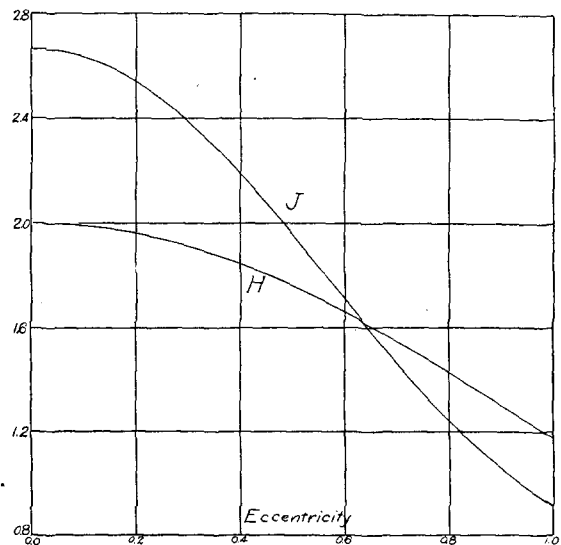


FIG. 2.

where

$$H \equiv \int_0^\pi (1 - e^2 \cos^2 \theta_1)^{3/2} \sin \theta_1 d\theta_1,$$

$$J \equiv \int_0^\pi (1 - e^2 \cos^2 \theta_1)^{5/2} \times (1 - 2 \cos^2 \theta_1 + 5 \cos^4 \theta_1) \sin \theta_1 d\theta_1. \quad (11)$$

These may be integrated⁶ to give:

$$H = \frac{1}{4}(2s^3 + 3s + 3e^{-1} \sin^{-1} e),$$

$$J = -s^7 \left(\frac{3}{8e^4} + \frac{1}{2e^2} \right) + \left(s^5 + \frac{5}{4}s^3 + \frac{15}{8}s + \frac{15 \sin^{-1} e}{8e} \right) \left(\frac{1}{3} - \frac{1}{12e^2} + \frac{1}{16e^4} \right),$$

where $s = (1 - e^2)^{1/2}$.

The first term in square brackets of Eq. (10) is the same as that of Eq. (1) multiplied into $H/2$. It is the contribution to $[F_{(\gamma)}]_{Av}$ of the polarizability of the CS_2 molecule. For $e=0$, $H/2=1$ and the two terms become identical. That is, the factor $H/2=H(e)/2$ is the contribution of the ellipticity of the solvent molecule. The ellipticity of the solvent molecules creates, therefore, only a trivial alteration in the form of the field equation. On this account we can understand why the assumption (i) (that the molecules concerned are spherical), used throughout our previous paper,¹ gave formulae in such good agreement with experiment.

The second term in square brackets of (10) is the contribution to the solvent field of the two oppositely directed dipoles of CS_2 . It is this quadrupole which is responsible for the apparently anomalous behavior of CS_2 .

For convenience the integrals H and J have been evaluated and plotted for various values of e between 0 and 1 (Fig. 2). J was evaluated for values of e between 0 and 0.1 by expansion in powers of e . This reduced J to the form

$$J = \frac{8}{3} - \frac{68}{21}e^2 + \frac{37}{21}e^4 - \frac{325}{1386}e^6 + \dots$$

⁶ The authors wish to thank Dr. Irving Kaplan, of these laboratories, for his collaboration in evaluating the integrals.

§3.

The variation of optical rotatory power with solvent, $n_\beta=0$, n_α/n_γ small, is given by the equation¹

$$\Omega = \Omega_1 + \Omega^3 [F_{(\gamma)}]_{Av}, \quad (12)$$

where Ω , the rotivity of the solution, is defined as $[\alpha]/n^2 + 2$, Ω_1 is the rotivity in the absence of an electrostatic field and Ω^3 is the deformability coefficient. To facilitate a comparison with the data on dipole solvents, the coefficient $2\mu_\alpha/b^3$ is removed from the brackets and the expression (10) for $[F_{(\gamma)}]_{Av}$ substituted in (12) to give

$$\Omega = \Omega_1 + \Omega^3 \frac{2\mu_\alpha}{b^3} \left[n_\gamma \left\{ \frac{2\pi}{3} CH + \frac{12\pi}{5} \frac{\mu_\gamma^2}{kT} \left(\frac{q}{b} \right)^2 \cdot J \right\} \right]. \quad (13)$$

While the dipole term in Eq. (1) can be evaluated by an independent measurement, namely, that of dielectric constant, the quadrupole term in (10) and (13) cannot. Values of e , the eccentricity of the ellipsoid, and of q/b must be estimated from other data. Since, however, no method is available for localizing the dipole μ_γ , i.e. fixing the value of q , it was thought desirable to reverse the procedure and calculate q .

From the data on l-menthyl methyl naphthalate,¹ $\Omega - \Omega_1$ and $\Omega^3 \cdot 2\mu_\alpha/b^3$ can be estimated and thus the expression in square brackets of Eq. (13) calculated. This is, in fact, the value (0.71) of the equivalent volume-polarization necessary to put the CS_2 point on the $M\Omega$ volume polarization curve.⁷ The density of l-menthyl methyl naphthalate not being given by Rule,⁸ its molecular volume was estimated as 378.0 cc from the molecular volumes of naphthalic acid, methyl alcohol, menthol and water. Assuming spherical molecules and closest packing the molecular radius was calculated to be 4.80 Å.

The size and shape of the CS_2 molecule were determined by the method of Magat⁹ from the zero point volume of the liquid. This volume was obtained by extrapolating Timmerman's equation for the density of CS_2 ¹⁰ to absolute zero. The volume of the molecule was calculated to be

⁷ Reference 1, p. 796, Fig. 3.

⁸ H. G. Rule, J. Chem. Soc. 669 (1931).

⁹ M. Magat, Zeits. f. physik. Chemie B16, 1 (1932).

¹⁰ Taken from J. W. Mellor, *Comprehensive Treatise on Inorganic Chemistry*, Vol. 6 (Longmans, Green and Co., London, 1925), p. 98.

55.55\AA^3 on the assumption of closely packed spheres. The radius of this sphere bears about the same relationship to radii calculated from gas viscosity and Sutherland's constant, from van der Waals' constant b and from Rankine's collision area that the corresponding radii for the CO_2 molecule¹¹ do to each other. The estimated volume of the CS_2 molecule can be looked upon, therefore, as being very probable. The internuclear C—S distance was taken from the recent data of Cross and Brockway¹² to be 1.54\AA and the effective radius of the C atom from the calculations of Magat to be 1.63\AA . From these data, the effective radius of the S atom was calculated to be 1.87\AA . This model of three overlapping spheres can be closely approximated by an ellipsoid of revolution with a semi-major axis of 3.41\AA and semi-minor axis of 1.97\AA .¹³ The ellipsoid of closest approach is defined, therefore, by the axes $a=8.21\text{\AA}$ and $b=6.77\text{\AA}$, corresponding to an eccentricity of $e=0.566$.

¹¹ H. A. Stuart, *Molekülstruktur* (Julius Springer, Berlin, 1934), p. 36, table 2.

¹² P. C. Cross and L. O. Brockway, *J. Chem. Phys.* 3, 821 (1935).

¹³ It must be recalled that the lower limit of integration of Eq. (9) is not the surface of the CS_2 molecule but the ellipsoid of revolution produced by the center of the spherical α -molecule when rolled over the CS_2 molecule. In this particular case, this ellipsoid differs but slightly from the figures produced by rolling the α -molecule either over the ellipsoidal CS_2 molecule or over the model of three overlapping spheres. Errors due to other approximations are much larger than those due to assuming these three figures equivalent.

From Fig. 2 one can determine the values of the H and J integrals as 1.698 and 1.795, respectively. The polarizability, C , is taken as 87.6×10^{-25} from the compilation of data of Wolf and Fuchs¹⁴ and μ_γ as 3.0 debyes from the estimate of Sidgwick.¹⁵ With $k=1.37 \times 10^{-16}$ and $T=300^\circ\text{K}$, q/b was calculated to be 0.116, giving a value of $q=0.78\text{\AA}$. Our calculated position of the dipole is therefore about halfway between the carbon and sulfur nuclei. The very close agreement between this value of q and one-half the C—S distance, namely 0.77, is to be regarded as fortuitous. Because of the many assumptions made to estimate the size of these molecules, any calculated value of q lying between 0.5 and 1.3\AA would be considered as satisfactory.

The successful treatment of this problem may be looked upon as confirmation of the correctness of the original method. The extension to other types of molecules is limited only by the difficulty in performing certain integrations etc. We note again, with surprise, the good agreement between theory and experiment. This was not foreseen, and its existence indicates the general validity—or perhaps unimportance—of our many auxiliary assumptions.

¹⁴ Article by K. L. Wolf and O. Fuchs in K. Freudenberg, *Stereochemie* (Franz Deuticke, Leipzig and Wien, 1933), p. 233, table 5.

¹⁵ N. V. Sidgwick, *The Covalent Link in Chemistry* (Cornell University Press, 1933), p. 149.