that was never fully tested, apparently because of the greater attention given to anisotropic group interactions as a result of Kirkwood's theory.[10] The present results suggest that the isotropic atom model has greater validity than is generally supposed. The model is attractive because reasonably good atom polarizabilities are available, the locations of the polarizable points are relatively well defined, and some polarizability is assigned to each atom rather than to a single point in a group of atoms. In regard to the values used here for the atom polarizabilities, it might be argued that these are not necessarily physically meaningful, since they are adjusted to fit $\bar{\alpha}$ values using a somewhat arbitrary model.[2] However, this fact does not guarantee that the same polarizabilities would be successful in accounting for optical rotations, since $\bar{\alpha}$ depends only on the diagonal elements of the $\mathbf{B}_{ij}$'s, while $[m]$ depends only on the off-diagonal elements. Thus, to the extent that the model is successful in predicting optical rotations, it is implied that the treatment of atoms as isotropically polarizable points is not too far from the truth. In the case of the CN group, this model might be doubted in particular because the valence electrons, which are primarily responsible for polarizability, are extensively shared between the atoms. Yet both the present results and those obtained previously on the polarizabilities of nitriles[3] do not suggest that there is any virtue in treating the CN group as a single point instead of two. In fact, there is less ambiguity in the sign of the rotation for the isotropic atom model.

The potential value of a theory such as this is in its use as a tool for determining molecular structures from observed rotations; one might at least hope to determine the absolute configuration from the sign of rotation, and in favorable cases information on conformation might be obtained. Enough atom polarizability data are available[2] to attempt this with a wide variety of molecules, the only additional data required being bond lengths and angles. In most cases care must be taken to test the sensitivity of the calculations to parameters that are not known accurately, as the case of MBCA illustrates.

Acknowledgment. This investigation was supported by a research grant from the National Institute of General Medical Sciences (GM-13684).

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[10] J. G. Kirkwood, *J. Chem. Phys.*, **5**, 479 (1937).

Optical Rotations of Cyclohexanepolyols from Polarizability Theory

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Abstract: The optical rotations of the 22 possible optically active cyclohexanepolyols at 5893 Å have been calculated by the exact (all-order) version of polarizability theory, assigning isotropic polarizabilities to all atoms and, alternatively, single isotropic polarizabilities to the OH groups. Results are obtained for both the *C1* and *1C* chair forms. The signs agree with available experimental data when these are assigned to the chair form having the least axial substitution, but the predicted magnitudes are larger than observed in most cases. Rotations averaged over staggered OH conformations are comparable to those obtained by treatment of the OH group as an isotropic unit. Uncertainties due to propagation of errors in input parameters are mostly in the range 20–50%. The results correlate fairly well with the predictions of Whiffen's empirical rules, but large rotations are predicted in several cases where these rules predict zero rotation.

The optically active cyclohexanepolyols constitute an important class of compounds for testing a theory of optical rotation, since there are 22 possible enantiomorphic pairs in the series (excluding *gem*-diols) and many of these have been characterized experimentally as to absolute configuration and sodium D line (5893 Å) rotation.[1] In addition, the problem of conformational averaging is not insuperable in these compounds. This paper presents a study of the rotations calculated for all members of the series using the isotropic atom version of the polarizability theory.

Recent studies of the isotropic atom model have shown that the model is useful in accounting for polarizabilities of molecules,[2,3] and a few calculated rotations[4,5] have shown that it can give realistic results for this property as well. The present study was carried out as a further test of the model, both to gain insight into the mechanism of optical rotation and to explore the usefulness of the theory as a means of interpreting observed rotations in terms of absolute configurations or conformations.

The primary insight into the origin of optical rotation in the cyclohexanepolyols to date has come from the empirical rules of Whiffen,[6] which find impressive agreement with experiment in ascribing a rotational contribution to each pair of hydroxyls located on adjacent carbon atoms. This suggests that pairwise interactions of nearest neighbor hydroxyls dominate the rotation.[7]

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[1] T. Posternak, "The Cyclitols," Holden-Day, San Francisco, Calif., 1965.

[2] J. Applequist, J. R. Carl, and K.-K. Fung, *J. Amer. Chem. Soc.*, **94**, 2952 (1972).

[3] J. Applequist and J. R. Carl, *J. Phys. Chem.*, **77**, 2090 (1973).

[4] J. Applequist, *J. Chem. Phys.*, **58**, 4251 (1973).

[5] J. Applequist, *J. Amer. Chem. Soc.*, **95**, 8255 (1973).

[6] D. H. Whiffen, *Chem. Ind. (London)*, 964 (1956).

[7] See also the discussion by W. Kauzmann, F. B. Clough, and I. Tobias, *Tetrahedron*, **13**, 57 (1967).

Yamana[8,9] has calculated rotations of a number of cyclohexanepolyols using Kirkwood's equation for pairwise interactions applied only to the hydroxyl groups and with the use of arbitrary correction factors has found substantial agreement with experiment and with Whiffen's rules. The present study is based on a more realistic physical model, in that the simultaneous (not pairwise) interactions of all atoms are included and the polarizability parameters have been chosen to fit molecular polarizabilities of related compounds according to the same model. A comparison of the results with the predictions from Whiffen's rules will thus serve as a test for the validity of the simple basis for these rules.

Calculations

The intrinsic molar rotation $[m]$ at vacuum wavelength λ was calculated by means of the equation from polarizability theory[4]

$$[m] = (48\pi^2 N_0/\lambda^2)\sum_{i<j}\mathbf{r}_{ij}\cdot\mathbf{b}_{ij} \qquad (1)$$

where N_0 is Avogadro's number, $\mathbf{r}_{ij}$ is the vector from atom i to atom j, $\mathbf{b}_{ij}$ is the vector related to the relay tensor $\mathbf{B}_{ij}$ by $\mathbf{b}_{ij} = \mathbf{B}_{ij} : \boldsymbol{\varepsilon}$, and the summation is over all pairs of atoms in the molecule such that $i < j$. The $\mathbf{B}_{ij}$ were calculated by the exact (all-order) treatment of point dipole interactions.[2,4] An IBM 360/65 computer was used throughout. Literature values of the specific rotation $[\alpha]$ were converted to $[m]$ by the relation

$$[m] = \frac{3}{n^2 + 2}\frac{M}{100}[\alpha] \qquad (2)$$

where n is the refractive index of the solution (taken as 1.33 for water) and M the molecular weight of the solute.

Atom coordinates were calculated for the chair forms of the cyclohexane ring assuming tetrahedral bond angles (109.471°) at every carbon. The bond lengths were taken to be (in Å): C–H 1.095,[10] C–C 1.540,[10] C–O 1.428,[11] and O–H 0.967.[11] The COH angle was taken as tetrahedral for convenience, although a value of 107.3° has been found for methanol.[11]

The atoms were assigned the isotropic polarizabilities found[2] to fit molecular polarizabilities of a number of simple alkanes and alcohols at wavelength 5893 Å. The rotation calculations are thus confined to this wavelength. The polarizabilities for H, C, and O are (in Å^3) $\alpha_H = 0.135 \pm 0.006$, $\alpha_C = 0.878 \pm 0.014$, and $\alpha_O = 0.465$. The uncertainties for α_H and α_C are standard deviations estimated from the error surface used in optimizing these quantities.[2] The OH groups were treated in the following three ways in order to test alternative means of simplifying the problem of conformational averaging.

Method I. The O and H atoms were assigned the isotropic polarizabilities given above, and each torsion angle θ(H,O,C,H)[12] was allowed to take each of the values −60, 60, and 180°, corresponding to the staggered conformations. The rotation was calculated for each of the 3^n conformations (n = number of OH groups) and the unweighted average found.

Method II. To reduce the number of calculations from 3^n to 1, the OH group was regarded as a single isotropic unit located at the O nucleus. Its polarizability α_{OH} was adjusted to give an optimum fit to the experimental mean polarizabilities of ethanol, 2-propanol, and cyclohexanol, using the methods described elsewhere.[2] The optimum α_{OH} so found is 0.603 ± 0.008 Å^3.

Method III. The OH group was regarded as an isotropic unit with $\alpha_{OH} = 0.755$ Å^3, which is the mean polarizability calculated by the dipole interaction theory for an isolated OH group having the bond distance and atom polarizabilities cited above. The C–OH distance was then adjusted to give an optimum fit to the same alcohol data as in method II. The optimum distance so found is 1.57 ± 0.02 Å (*cf.* 1.428 Å in method II).

The mean polarizabilities calculated for four alcohols by each of these methods, using the optimum parameters, are given in Table I. Methanol is included in the table for comparison, although it was not included in the optimization because the experimental value is not as easily fit and tends to produce a less well defined optimum. The data using method I are those reported previously[2] in the determination of atom polarizabilities. It is seen that all three methods give approximately the same fit to the experimental data.

Table I. Mean Polarizabilities (Å^3) of Alcohols at 5893 Å

	Calcd			
Compd	I	II	III	Exptl[a]
Methanol	3.05	3.08	3.05	3.32
Ethanol	5.11	5.10	5.08	5.11
2-Propanol	7.02	7.01	7.02	6.97
Cyclohexanol[b]	11.55	11.53	11.57	11.56

[a] Sources cited in ref 2. [b] Equatorial OH.

The uncertainties σ in the calculated rotations were estimated in methods II and III using the usual theory of small error propagation,[13] which gives the expression

$$\sigma^2 = \mathbf{d}^T\mathbf{V}\mathbf{d} \qquad (3)$$

where $\mathbf{d}$ is a column vector whose elements are the derivatives of $[m]$ with respect to each parameter and $\mathbf{V}$ is a symmetric matrix whose diagonal elements are variances and whose off-diagonal elements are covariances. The required expressions for the derivatives are derived in the Appendix. The variances of all optimized parameters were included in this calculation, namely α_C, α_H, and either α_{OH} (method II) or the C–OH distance (method III). The covariance of α_H and α_C was estimated to be -8.1×10^{-5} Å^6 from the error surface for the optimization of these quantities.[2] Other covariances were set at zero, since no other pairs of quantities were optimized simultaneously.

In addition to the polarizability theory calculations, the rotation was calculated for each structure by Whiffen's rules.[6] For the cyclohexanepolyols the rule is that each pair of OH groups on adjacent carbons is assigned

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[8] S. Yamana, *Bull. Chem. Soc. Jap.*, **33**, 1741 (1960); **34**, 1212 (1961).

[9] S. Yamana, *Experientia*, **21**, 305 (1965).

[10] L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, Chapter 7.

[11] J. D. Swalen, *J. Chem. Phys.*, **23**, 1739 (1955).

[12] Notation of IUPAC-IUB Commission on Biochemical Nomenclature, *Biochemistry*, **9**, 3471 (1970).

[13] See, for example, P. R. Bevington, "Data Reduction and Error Analysis for the Physical Sciences," McGraw-Hill, New York, N. Y., 1969, Chapter 4.

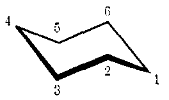
Table II. Intrinsic Molar Rotations (deg cm²/dmol) of 1L-Cyclohexanepolyols at 5893 Å

Prefix[a]	Form[b]	Calcd I	Calcd II	Calcd III	Calcd Whiffen	Exptl
1/2	*C1**	−100	−130 ± 28	−89 ± 25	−36	−43[c]
	1C	−103	−132 ± 48	−84 ± 48	0	
1/3	*C1, 1C*[d]	−46	−68 ± 21	−41 ± 20	0	
1,2/3	*C1*	−27	−35 ± 22	−47 ± 34	−36	
	*1C**	−254	−345 ± 90	−194 ± 63	−72	−74[e]
1,2,4/0	*C1*		+150 ± 43	+67 ± 28	+36	
	*1C**		−154 ± 44	−72 ± 29	−36	
1,2/4	*C1**	+71	+89 ± 25	+31 ± 11	+36	
	1C		−218 ± 64	−105 ± 46	−36	
1/2,4	*C1**		−128 ± 28	−83 ± 23	−36	
	1C		−121 ± 44	−74 ± 42	0	
1,4/2	*C1**		−63 ± 9	−45 ± 22	−36	
	1C		−59 ± 25	−40 ± 25	0	
1,2,3/4	*C1**		−185 ± 44	−117 ± 34	−36	−42[e]
	1C		−175 ± 60	−103 ± 55	0	
1,2/3,4	*C1*[f]		+63 ± 14	−11 ± 21	+72	} −85[e]
	1C		−546 ± 148	−284 ± 101	−108	
1,2,4/3	*C1*		+85 ± 23	+29 ± 10	+36	
	*1C**		−211 ± 60	−108 ± 45	−36	−45[e,g]
1,3/2,4	*C1**		−125 ± 27	−79 ± 22	−36	−34[e]
	1C		−111 ± 40	−65 ± 38	0	
1,2/3,5	*C1*		+37 ± 8	−5 ± 13	+36	
	*1C**		−275 ± 69	−148 ± 44	−72	−72[h]
1,2,5/3	*C1*[f]		+34 ± 7	−4 ± 14	+36	} −10[h]
	1C		−270 ± 67	−146 ± 43	−72	
1,2,4/5	*C1*		+94 ± 21	+29 ± 4	+36	
	*1C**		−215 ± 51	−113 ± 30	−72	
1,4/2,5	*C1, 1C*[d]		−118 ± 31	−81 ± 26	−36	−26[i]
1,2,3,4/5	*C1*		+37 ± 7	0 ± 11	+36	
	*1C**		−265 ± 65	−142 ± 40	−72	
1,2,3/4,5	*C1**		−326 ± 84	−174 ± 55	−72	−81[e]
	1C		−17 ± 16	−34 ± 26	+36	
1,2,3,5/4	*C1**		−57 ± 16	−36 ± 17	0	−7[e]
	1C		−58 ± 18	−31 ± 15	0	
1,2,4/3,5	*C1*		+40 ± 8	−1 ± 11	+36	
	*1C**		−270 ± 67	−144 ± 41	−72	−72[e]
1,2,5/3,4	*C1**		+250 ± 54	+106 ± 25	+108	+63[e]
	1C		−363 ± 87	−170 ± 45	−108	
1,3,4/2,5	*C1**		+96 ± 20	+34 ± 6	+36	+34[e]
	1C		−206 ± 48	−106 ± 28	−72	
1,2,4/3,5,6	*C1*		+302 ± 69	+134 ± 32	+108	
	*1C**		−307 ± 70	−140 ± 33	−108	−93[e]

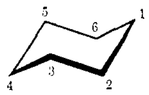
[a] Reference 17. [b] Asterisk designates conformation with least number of axial hydroxyls. [c] N. A. B. Wilson and J. Read, *J. Chem. Soc.*, 1269 (1935); T. Posternak, H. Friedli, and D. Reymond, *Helv. Chim. Acta*, **38**, 205 (1955). [d] The *C1* and *1C* forms are identical. [e] Reference 1, pp 88–125. [f] The *C1* and *1C* forms have the same number of axial hydroxyls. [g] T. Posternak and D. Reymond, *Helv. Chim. Acta*, **38**, 195 (1955). [h] G. E. McCasland, S. Furuta, L. F. Johnson, and J. N. Shoolery, *J. Org. Chem.*, **29**, 2354 (1964). [i] J. D. Ramanathan, J. S. Craigie, J. McLachlan, D. G. Smith, and A. G. McInnes, *Tetrahedron Lett.*, 1527 (1966).

a rotation of ±36 deg cm²/dmol if the torsion angle θ(O,C,C,O) is ±60° (the sign of the rotation being the same as the sign of the angle) and a rotation of zero if the torsion angle is 180°. The total rotation is the sum of the rotations for each pair. The rotation value 36 was obtained by multiplying Whiffen's value 45 by the factor $3/(n^2 + 2)$, taking $n = 1.33$ for water.

Table II gives the calculated rotations for the 22 possible optically active cyclohexanepolyols having the 1L configuration. The experimental rotations are given when known and are assigned tentatively to the chair form having the least number of axial hydroxyls (indicated by an asterisk).[14] The *C1* and *1C* chair form designations are those of Reeves,[16] and correspond to the following numbering system.



C1



1C

Substituents "above" and "below" the plane of the ring are separated in the numerical prefixes by slant lines in the recommended manner.[17]

To give an idea of the present computing requirements, each calculation for a molecule with 18 atoms requires 6–20 sec of central processing unit time, depending on the number and type of variables included in the error analysis. For a cyclohexanetriol using method I, the CPU time is 243 sec (cost about $20) without error analysis, due to the factor of 3^n. Thus the cost becomes prohibitive for the higher polyols using method I, and only a few sample calculations were made for comparison with the other methods.

(14) This criterion of least axial substitution is apparently not rigorously followed; electron diffraction studies of the 1/2-diol in the vapor phase have shown that both chair forms are present,[15] in spite of the fact that one form is diaxial and the other diequatorial.

(15) B. Ottar, *Acta Chem. Scand.*, **1**, 521 (1947).

(16) R. E. Reeves, *Advan. Carbohyd. Chem.*, **6**, 107 (1951).

(17) IUPAC–IUB recommended nomenclature, *Biochim. Biophys. Acta*, **165**, 1 (1968).

The rotation of the 1/2-diol (*1C* form) calculated at each OH conformation included in method I is shown in Table III to illustrate the range of values that are included in the average shown in Table II. This large range is typical of most of the compounds to which this method has been applied. The average calculated is clearly strongly dependent on the weights given to the various conformations. The use of equal weights as done here is, of course, arbitrary.

Table III. Calculated $[m]_D$ for 1L-1/2-Cyclohexanediol (*1C* form) as a Function of Hydroxyl Torsion Angles

θ(H,O,C(2),H), deg	θ(H,O,C(1),H) −60°	θ(H,O,C(1),H) 60°	θ(H,O,C(1),H) 180°
−60	+1614	−139	+780
60	−139	−1883	−938
180	+780	−938	−62

The molecular polarizabilities were calculated using the same parameters as for the optical rotation by methods described previously.[2] The mean polarizabilities varied from 12.1 Å^3 for the 1/2-diol to 14.4 Å^3 for the 1,2,4/3,5,6-hexol. Uncertainties estimated by the same methods used for the optical rotations are in the range 0.2–0.3 Å^3. The three methods of treatment of the OH groups give results that agree with each other and with values calculated by summation of additive atom polarizabilities[2] within this range of uncertainty. Further details are omitted here due to the lack of experimental data for comparison.

Discussion

Several points are worth noting in regard to the data in Table II.

1. There is a strong correlation, but not precise agreement, among the various calculations and the experimental rotations. The signs of the calculated rotations are generally correct, but discrepancies with experiment of two- to fourfold are common. The uncertainties are substantial fractions of the rotations (mostly in the range 20–50%), in spite of the fact that these arise from the uncertainties in parameters that are known to within 4% or better. This sensitivity is inherent in optical rotation calculations and may prove impossible to surmount.

2. The agreement between the conformation average (method I) and the isotropic OH treatments (methods II and III) is good enough in the six cases where a comparison is made to justify confidence in the latter methods as reasonable approximations to the unweighted conformation average.

3. The magnitudes calculated by method III are generally in somewhat better agreement with experiment than those from method II. However, in five cases (the *C1* forms of 1,2/3,4, 1,2/3,5, 1,2,5/3, 1,2,3,4/5, and 1,2,4/3,5) the uncertainties calculated in method III are larger than the rotations, so that the sign is ambiguous; no such cases are found by method II. The five ambiguous cases (method III) all happen to be forms which are at least partially unstable by the criterion of least axial substitution; thus a direct experimental sign determination is not likely to be forthcoming.

4. The 1/3-diol is expected to have zero rotation by Whiffen's rules, due to the absence of hydroxyls on neighboring carbons. However, the present calculations indicate that this compound should have a substantial rotation. This is a case which could be tested experimentally.

5. The *1C* form of the 1/2-diol is expected to have zero rotation by Whiffen's rules due to the coplanarity of the substituents (both are axial). The present calculations do not support this and indicate that the rotation should be comparable to that of the *C1* form. The *1C* forms of the 1/2,4-triol and the 1,3/2,4-tetrol are further examples of this situation; in these cases all of the hydroxyls are axial. The vanishing of the rotation by Whiffen's rules and by Kirkwood's theory (as applied by Yamana[8,9]) for these cases is a result of the pairwise approximation, and the presence of higher order interactions in the present theory should be more realistic. Unfortunately, none of these cases appears amenable to direct experimental test due to the excess of axial substituents.

6. The sign predicted by polarizability theory for the 1,2,3,5/4-pentol is in agreement with experiment, while Whiffen's rules predict zero rotation. This is the only case so far in which polarizability theory has gone beyond Whiffen's rules in accounting for observed signs.

7. In most, but not all, compounds the calculated rotations for the two chair forms differ substantially in magnitude and, in several cases, in sign as well. In six compounds (1,2,4/3, 1,2/3,5, 1,2,4/3,5, 1,2,5/3,4, 1,3,4/2,5, 1,2,4/3,5,6) the uncertainties appear to be small enough to justify an assignment of preferred chair form on the basis of the observed rotation, and in each case this assignment corresponds to that made by the criterion of least axial substitution. This agreement tends to confirm the validity of the latter criterion for these cases, though the rotation data do not rule out the presence of the less preferred chair form as a minor species.

8. The 1,2/3,4- and 1,2,5/3-tetrols are cases in which both chair forms have two axial hydroxyls; thus substantial concentrations of both forms may exist in each compound. Comparison of the observed and calculated rotations supports this possibility. It is clear from the data that the polarizability calculations and Whiffen's rules tend to give rather different estimates of the relative concentrations, though it would be premature to suggest that either method is reliable for this purpose.

9. Whiffen's rules appear to be the more successful means of accounting for most observed rotations. However, it should be borne in mind that the polarizability theory starts with much less information; *i.e.*, it makes no use of parameters obtained from observed rotations or prior knowledge of absolute configurations. Thus the present calculations imply that the polarizability interactions of the atoms are primarily responsible for the optical rotation of these compounds, while Whiffen's rules do not provide information on the mechanism beyond the suggestion that pairwise hydroxyl interactions predominate. The discrepancies between polarizability theory and Whiffen's rules noted above, particularly where the latter predict zero rotation, suggest that the pairwise approximation is not generally valid.

While the above observations indicate that the isotropic atom model is reasonably valid for these compounds, it is worth summarizing here the possible reasons for the failure of the model to give more precise agreement with experiment. (i) The isotropic atom model may be too oversimplified to represent optical behavior accurately. (ii) Deviations of the bond lengths and bond angles from the values assumed here, coupled with the sensitivity of the calculated rotations to structural parameters, are likely to be important sources of error. (iii) The use of an unweighted average over conformations of the OH groups may be unrealistic. (iv) The molecules may exist as mixtures of chair forms, in which case further conformation averaging would be necessary. At present it would not seem possible to say which of these sources of error, if any, is likely to predominate.

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Appendix

Calculation of Derivatives. The derivative of $[m]$ with respect to a quantity q is, from eq 1

$$\frac{\partial[m]}{\partial q} = \frac{48\pi^2 N_0}{\lambda^2}\sum_{i<j}\left(\mathbf{r}_{ij}\cdot\frac{\partial \mathbf{b}_{ij}}{\partial q} + \frac{\partial \mathbf{r}_{ij}}{\partial q}\cdot\mathbf{b}_{ij}\right) \tag{4}$$

If q is a polarizability, then $\partial\mathbf{r}_{ij}/\partial q = 0$, while if q is an internal coordinate $\partial\mathbf{r}_{ij}/\partial q$ is defined by the nature of the coordinate. We have also

$$\partial\mathbf{b}_{ij}/\partial q = (\partial\mathbf{B}_{ij}/\partial q):\boldsymbol{\varepsilon} \tag{5}$$

where $\partial\mathbf{B}_{ij}/\partial q$ is a 3×3 block of the matrix[18]

$$\partial\tilde{\mathbf{B}}/\partial q = -\tilde{\mathbf{B}}(\partial\tilde{\mathbf{A}}/\partial q)\tilde{\mathbf{B}} \tag{6}$$

using the notation of previous papers.[2,4] The derivatives may then be calculated from the analytical form of $\tilde{\mathbf{A}}$, which consists of the 3×3 blocks

$$\mathbf{A}_{ii} = \boldsymbol{\alpha}_i^{-1} \tag{7}$$

$$\mathbf{A}_{ij} = r_{ij}^{-3}\mathbf{I} - 3r_{ij}^{-5}\mathbf{r}_{ij}\mathbf{r}_{ij} \qquad (i \neq j) \tag{8}$$

where I is the 3×3 identity matrix. Thus if q is an isotropic atom polarizability α_p, then $\partial\tilde{\mathbf{A}}/\partial\alpha_p$ is a diagonal matrix with diagonal elements zero or $-\alpha_p^{-2}$. If q is an internal coordinate ξ then the diagonal blocks $\partial\mathbf{A}_{ii}/\partial\xi$ vanish and, for $i \neq j$

$$\frac{\partial\mathbf{A}_{ij}}{\partial\xi} = \frac{\mathrm{d}\mathbf{r}_i}{\mathrm{d}\xi}\cdot\boldsymbol{\nabla}_i\mathbf{A}_{ij} + \frac{\mathrm{d}\mathbf{r}_j}{\mathrm{d}\xi}\cdot\boldsymbol{\nabla}_j\mathbf{A}_{ij} = (\mathrm{d}\mathbf{r}_{ij}/\mathrm{d}\xi)\cdot\boldsymbol{\nabla}_j\mathbf{A}_{ij} \tag{9}$$

The last equality holds because $\mathbf{r}_{ij} = \mathbf{r}_j - \mathbf{r}_i$ and $\boldsymbol{\nabla}_i\mathbf{A}_{ij} = -\boldsymbol{\nabla}_j\mathbf{A}_{ij}$, where $\boldsymbol{\nabla}_j = \partial/\partial\mathbf{r}_j$. From eq 8 we find

$$\boldsymbol{\nabla}_j\mathbf{A}_{ij} = 15r_{ij}^{-7}\mathbf{r}_{ij}\mathbf{r}_{ij}\mathbf{r}_{ij} - 3r_{ij}^{-5}(\mathbf{r}_{ij}\mathbf{I} + \mathbf{I}\mathbf{r}_{ij} + \widehat{\mathbf{I}\mathbf{r}}_{ij}) \tag{10}$$

where $\frown$ over the last term indicates that the last two indices of the third order tensor $\mathbf{I}\mathbf{r}_{ij}$ are transposed.

Derivatives of the molecular polarizability tensor $\boldsymbol{\alpha}$ may be calculated in a similar fashion, using

$$\partial\boldsymbol{\alpha}/\partial q = \sum_{i,j}\partial\mathbf{B}_{ij}/\partial q \tag{11}$$

Furthermore, since the components α_n ($n = 1, 2, 3$) of the diagonalized tensor satisfy the relation $|\boldsymbol{\alpha} - \alpha_n\mathbf{I}| = 0$, differentiation of this relation gives

$$\partial\alpha_n/\partial q = \sum_{r,s=1}^{3} C_{rs}(\partial\alpha_{rs}/\partial q)\Big/\sum_{r=1}^{3} C_{rr} \tag{12}$$

where C_{rs} is the cofactor of the (r,s)th element of $\boldsymbol{\alpha} - \alpha_n\mathbf{I}$ and α_{rs} is the (r,s)th element of $\boldsymbol{\alpha}$.

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(18) Equation 6 is derived, for example, in R. A. Frazer, W. J. Duncan, and A. R. Collar, "Elementary Matrices," Cambridge University Press, Cambridge, 1965, p 43.