The Molecular Structure of Allenes and Ketenes. 8.[1] Semiempirical Description of Optical Rotations of Allenes Using Chirality Functions[2]

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Abstract: A comparison between calculated and experimental values for different kinds of allenes demonstrates that the polynomial expression of the corresponding chirality function is able to account for a numerically adequate description of the molar rotations of allenes in the transparent region. Correlations of optical activity data with other physical quantities, such as ^{13}C-chemical shifts, reveal that the parameters used for the calculations of the rotations are numerically well fixed.

(I) Introduction

An essentially algebraic theory applicable to any type of chirality observation[2] χ and any class of molecules[2] has been presented in ref 2. In the form of special expressions characterized by mathematical simplicity, semiempirical methods for the calculation of chirality observations have been proposed. These expressions contain, e.g., formally defined elements, such as ligand-specific parameters $\lambda(R)$, $\mu(R)$, etc., which may be determined experimentally or on the basis of a quantum-mechanical theory. The number of necessary parameters for each ligand R depends upon the symmetry of the molecular skeleton. The quantitative description of a chirality observation by a chirality function naturally guarantees the theoretical determination of the absolute configuration of a molecule.

A preliminary test for the semiempirical description of the molar rotations $[\phi]^{25}\text{D}$ of phenylallenecarboxylic acids using chirality functions has been reported[4] (D being the wavelength of the sodium D line λ 589 nm). For these kinds of "D_{2d} molecules"[4,5] it has been found that one ligand-specific parameter $\lambda(R)$ as the single variable suffices for the numerical calculation of $[\phi]^{25}\text{D}$.

Furthermore, a quantum-mechanical treatment of the molar rotation $[\phi]^{25}\text{D}$ of 1,3-dimethylallene (**1**) (Figure 1) has given the physical interpretation of the parameter $\lambda(CH_3)$ for the σ-inductive donor CH_3.[5] It is the purpose of the present contribution to report further examples for the success of the proposed method[4] to account for a numerically adequate description of the molar rotations of allenes and to investigate solvent effects on the rotations; to extend our treatment of $[\phi]^{25}\text{D}$ to the optical rotatory dispersion (ORD) $[\phi]^{25}\lambda$ in the transparent region ($\lambda \geq 330$ nm); and to give further insights into the physical interpretation of the $\lambda(R)$ parameters and their numerical accuracies.

The discussions are based upon new experimental findings essentially from our laboratories[6-8] and include the allenes **1–24** (Figures 1 and 2) as well as the methyl esters ($COOH \rightarrow COOCH_3$) and the sodium salts ($COOH \rightarrow COONa$) of the corresponding acids **7–9**. The methyl esters are denoted by an appended **e** (e.g., **7e**) and the sodium salts by an appended **s** (e.g., **7s**).

Concerning the molar rotations $[\phi]^{25}\text{D}$ some phenylallenes (**2, 3–9, 12, 13**) have been treated in ref 4.

(II) Theory

Summarizing some aspects of the theory of chirality functions with special emphasis to allenes will facilitate not only the ability to see the relations of this theory to our experimental procedures and discussions but also some relations to a recent proposal[9] relying in part concerning "experimental evidence" on our results for phenylallenecarboxylic acids. For this purpose we make use of the development of the chirality functions in terms of polynomials of the lowest degree in ligand-specific parameters.[2,4]

The chirality observations of interest refer to measurements of pseudoscalar properties of molecules of one kind in an achiral solvent and (equimolar) nonracemic mixtures of constitutional isomers. In order to be different from zero when applied to any possible nonracemic mixture of isomers a chirality function has to be "qualitatively complete".[2,4] The concept of qualitative completeness emerges from the assumption that, apart from accidental cases, no zero chirality observation occurs for an ensemble of chiral molecules, whether it contains only molecules of one kind or is a mixture of nonenantiomeric isomers.

It has turned out that the "qualitatively" complete chirality function" for the allenes as the prototypes of "D_{2d} molecules" is made up additively of two components φ_1 and φ_2 with different structures. Concerning this molecular class with ligand sites at the corners of a tetrahedron of symmetry D_{2d} (Figure 3) the corresponding expression is given by eq 1.

$$\chi(R_1,R_2,R_3,R_4) = \varphi_1(R_1,R_2,R_3,R_4) + \varphi_2(R_1,R_2,R_3,R_4) \tag{1a}$$

$$\begin{aligned}\chi(R_1,R_2,R_3,R_4) = {} & \epsilon_1[\lambda(R_1) - \lambda(R_2)][\lambda(R_3) - \lambda(R_4)] \\ & + \epsilon_2[\mu(R_1) - \mu(R_2)][\mu(R_2) - \mu(R_3)][\mu(R_3) - \mu(R_1)] \\ & [\mu(R_1) - \mu(R_4)][\mu(R_2) - \mu(R_4)][\mu(R_3) - \mu(R_4)]\end{aligned} \tag{1b}$$

The coefficients $\epsilon_i = \pm 1$ ($i = 1, 2$) are sign factors which may be determined experimentally or by a quantum-mechanical theory. From eq 1b one can easily see that the μ term vanishes if two of the ligands are identical, i.e., for molecules of the type (a) in Figure 4. For these kinds of molecules φ_1 represents the qualitatively complete chirality function.

The function φ_1, the λ term, satisfies the zero identity 2, regardless of the nature of the ligands R_i.

$$\varphi_1(R_1,R_2,R_3,R_4) + \varphi_1(R_1,R_3,R_4,R_2) + \varphi_1(R_1,R_4,R_2,R_3) = 0 \tag{2}$$

Therefore, it does not contribute to the expression

$$\tfrac{1}{3}[\chi(R_1,R_2,R_3,R_4) + \chi(R_1,R_3,R_4,R_2) + \chi(R_1,R_4,R_2,R_3)] \tag{3}$$

which describes the (nonzero) chirality observation of a nonracemic isomer mixture of the type (b) given in Figure 4. Such a mixture may be built up, e.g., by the compounds **14, 15,** and **16.**

Molecules of the type (a) (Figure 4) or isomer mixtures of

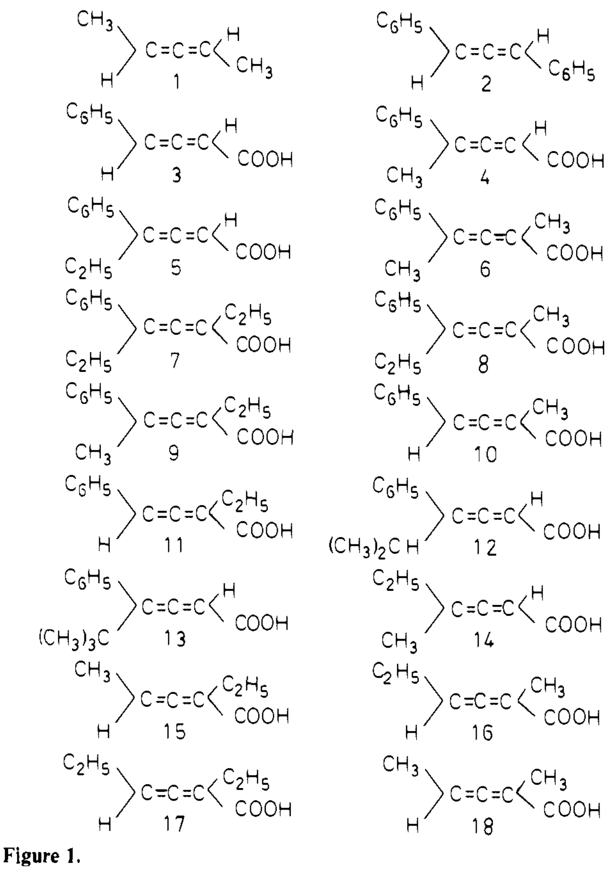


Figure 1.

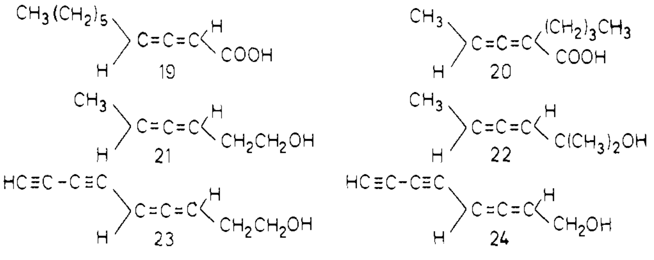


Figure 2.

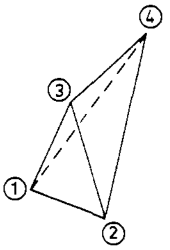


Figure 3.

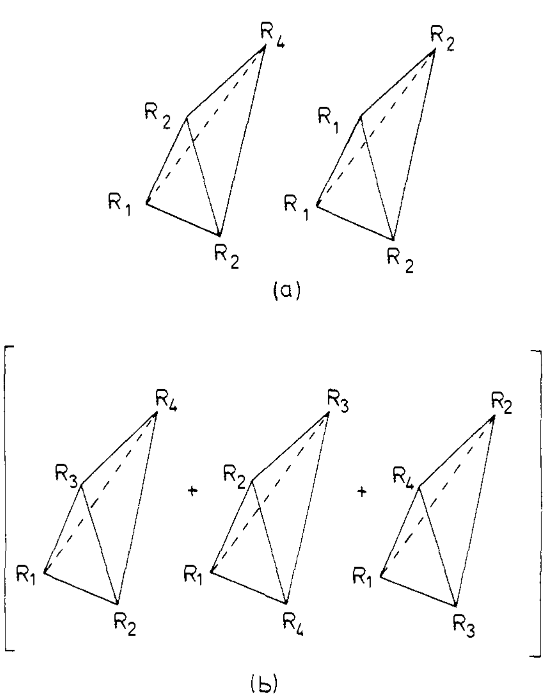
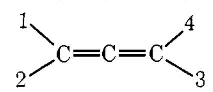


Figure 4.

the type (b) (Figure 4) represent experimental arrangements where an optical activity measurement depends only upon one kind of parameter (λ or μ). In ref 4 it has been shown that the "shortened" approximation (eq 4) ($\epsilon_1 = +1$) is successful in accounting for a numerically satisfying description of the molar rotation $[\phi]^{25}\mathrm{D}(C_2H_5OH)$ of phenylallenecarboxylic acids in ethanol as a "standard" solvent.[4]

$$\chi(R_1, R_2, R_3, R_4) \approx [\lambda(R_1) - \lambda(R_2)]\,[\lambda(R_3) - \lambda(R_4)] \qquad (4)$$



$$\overset{1}{\underset{2}{}}\!>\!C{=}C{=}C\!<\!\overset{4}{\underset{3}{}}$$

The above experimental finding[4] is not unexpected. The μ polynomial represents the (qualitatively complete) chirality function for a molecular class with the skeleton of the regular tetrahedron T_d, whereas eq 1 is the qualitatively complete chirality function of a molecular class with the symmetry D_{2d} of the irregular tetrahedron. Owing to the cumulated double bonds the symmetry situation in allenes differs considerably from the T_d symmetry, and it may be assumed that the λ polynomial describes the relevant part of the phenomenon; i.e., the μ term should be small compared with the λ term and probably be negligible for numerical purposes.

In our treatment so far[4] solvent effects (changing ethanol for methanol) have been partly incorporated using the Lorentz factor $((n^2\mathrm{D} + 2)/3)^{10a}$ for the internal field of the solvent cavity, in which the solute molecule is enclosed (nD being the index of refraction). Though this field correction is problematic,[10b] it is small and therefore of minor interest concerning numerical aspects.

(III) Semiempirical Calculations of Optical Rotations of Allenes

(1) Molar Rotations $[\phi]^{25}$D. Following our treatment[4] the (new) parameters $\lambda(COOCH_3)$ and $\lambda(COONa)$ are determined from the rotations of the compounds **7e** and **7s** which are of the type (a) (Figure 4). For completeness and with emphasis to the ORD (subsection III.3) also the parameters which have already been evaluated[4] are summarized in Table I ($\epsilon_1 = +1$, $\lambda(H) = 0$). The second column gives the experimental values of the molar rotations $[\phi]^{25}$D, the third column gives the references for these values, and the fourth column gives the λ(R) parameters determined from $[\phi]^{25}$D.

In Table II experimental and calculated (eq 4) molar rotations are given. For this comparison we have restricted ourselves to molecules where the rotations have been determined under "standard conditions"[4] (ethanol or methanol as the solvent) or where no specific solute–solvent interactions are expected to occur. These compounds are given in Figure 1.

In general, an excellent agreement between calculated and experimental molar rotations is observed. Only four compounds exhibit larger deviations (**1, 11, 15, 17**). In the case of ( )-1,3-dimethylallene (**1**) one cannot be quite sure that the given molar rotation corresponds to that of the optically pure

Table I. Determination of the $\lambda(R)$ Parameters (eq 4) from the Molar Rotations of Allenes having the S Configuration ($\lambda(H) = 0$)

Compd	$[\phi]^{25}D(C_2H_5OH)$, deg	Ref	$\lambda(R)$
2	+1958	4, 11	$\lambda(C_6H_5) = +44.3$
3	+686[a]	4, 12	$\lambda(COOH) = +15.4$
6	+280	4, 13	$\lambda(CH_3) = +7.7$
7	+88.8	4, 13	$\lambda(C_2H_5) = +12.6$
7e	+124	6	$\lambda(COOCH_3) = +16.5$
7s	+211	6	$\lambda(COONa) = +19.3$
12	+422[a]	4, 12	$\lambda((CH_3)_2CH) = +16.9$
13	+390[a]	4, 12	$\lambda((CH_3)_3C) = +18.9$

[a] Values from methanol and corrected using the Lorentz factor: $[\phi]^{25}D(C_2H_5OH) = 1.01[\phi]^{25}D(CH_3OH)$.

compound.[14b] Furthermore, the disagreement may be partly due to the measuring conditions. The measurement has been performed on the neat liquid, so that intermolecular interactions may have some influence. The theory neglects such contributions; i.e., only dilute solutions should be used for the comparisons between experimental and calculated rotations.

The other compounds (**11, 15, 17**), where larger deviations are observed, have two common features: first, there is an ethyl group geminal to the carboxylic functionality; second, all the molecules have only three ligands other than hydrogen.

One might assume that, especially for the alkylallenecarboxylic acids (**15, 17**), the T_d component φ_2 of the (qualitatively complete) chirality function (eq 1b) becomes relevant. However, this is ruled out by the fact that **17** is of type (a) (Figure 4), and therefore, the μ term vanishes ($\varphi_2 = 0$).

Furthermore, it may be that the specific arrangement of ligands (C_2H_5 geminal to COOH) gives rise to ligand interactions which are not incorporated in the theory.[2,4] This assumption is unlikely due to the fact that in most molecules under consideration there are also geminal interactions between the ligands, which obviously have no significant influence on the molar rotations. These ligand interactions have been demonstrated for the allenes using photoelectron,[17] electronic (absorption) spectroscopy,[17] and ^{13}C-NMR spectroscopy.[7b]

Further factors which may have a decisive influence on observed optical rotations and which are ignored by the theory include solvation and conformational effects (special dissymmetric orientations of substituents or different rotamer populations for different substitution patterns). An investigation in how far conformational effects, especially in 1,3-dialkylallenes, determine the optical rotations has failed to give evidence for such a contribution in case of 1,3-dipropylallene.[18b] Therefore, an explanation for the observed deviations for **11, 15,** and **17** in terms of different interactions of the carboxylic group with the solvent owing to the neighboring ethyl substituent is attractive. On the other hand, the largest deviation between experimental and calculated rotations is observed for the allene with two ethyl groups (**17**), i.e., a molecule with the 1,3-dialkylallene subunit generally suspected to exhibit conformational dissymmetry.[18b] Therefore, we cannot preclude that the specific ligand arrangement (ethyl geminal to the carboxylic group and only one substituent in γ position) affects the rotamer populations with respect to the ethyl groups. Furthermore, the rotamer population and not an intrinsic property of the group may be the relevant factor for the solvation of the carboxylic group, so that solvent and conformational effects are operative and, finally, cannot be separated.

Table II. Experimental and Calculated (eq 4) Molar Rotations of Allenes in Ethanol having the S configuration

Compd	$[\phi]^{25}D(C_2H_5OH)$, deg	Ref	χ, deg
4	+515	6, 12	+564
5	+496	6, 12	+488
8	+253	4, 13	+244
8e	+300	6	+279
8s	+354	6	+368
9	+103	4, 13	+102
9e	+154	6	+143
9s	+249	6	+256
10	+374	6	+342
11	+157	6	+124
15	+34.4	6	+21.6
16	+100	6	+97.0
17	+74.9	6	+35.3
18	+63.5	6	+59.3
1	+51.0[a]	14	+59.3

[a] Measured on the neat liquid ($n^{25}D = 1.425^{16}$) and corrected using the Lorentz factor.

Table III. Experimental and Calculated (eq 4) Molar Rotations of Allenes in Chloroform having the S Configuration

Compd	$[\phi]^{25}D(CHCl_3)$, deg	Ref	χ,[a] deg	$[\phi]^{25}D/\chi$
2	+2117	14	+2020	1.05
5	+566	6	+503	1.13
7	+117	6	+91.6	1.28
8	+259	6	+251	1.03
9	+135	6	+105	1.29
10	+370	6	+352	1.05
11	+159	6	+128	1.24
14	+124	19	+77.7	1.59
14e	+111	19	+83.3	1.33
15	+45.6	6	+22.2	2.06
16	+112	6	+100	1.12
17	+94.5	6	+36.4	2.60
18	+75.6	6	+61.1	1.24

[a] $\chi(CHCl_3) = 1.03\chi(C_2H_5OH)$.

In order to study the solvent effect qualitatively we have measured the molar rotations of some allenes in the very weak protic solvent chloroform $CHCl_3$. $CHCl_3$ is a potential hydrogen bond donor and a common solvent for optical rotation measurements. It is also sufficiently polar to dissolve the acids essentially in monomeric form.

Table III shows the comparison between experimental and calculated molar rotations in chloroform as the solvent. Field effects of $CHCl_3$ are incorporated by the Lorentz factor. The agreement between $[\phi]^{25}D(CHCl_3)$ and $\chi(CHCl_3)$ is not as good as for ethanol. Also in this case the most serious deviations are observed for compounds with substituents geminal to the carboxylic group, whereas the substituents in γ position (ligand site 1 or 2, Figure 3) seem to be of minor importance. The deviations are rather irregular (column 5, Table III) and seem to be not statistically at random. The deviations always point to one direction.

These results suggest that a large part of the deviations between experimental and calculated rotations are due to solvent effects associated with the hydrogen bonding ability of the carboxylic group and the dependency of the interactions of this group with the solvent upon geminal substituents (and their conformations). This assumption is supported by the fact that homologous aliphatic carboxylic acids $R-CH_2-COOH$ (R = H, CH_3, C_2H_5, etc.) have rather irregular dissociation constants,[20] which have been explained by steric hindrance of solvation.[20a] As a further support of our arguments we make use of the rotations of the acid **14** and its methyl ester **14e** (Table III). Usually, the experimental rotations of the esters

Table IV. Experimental and Calculated (eq 4) Molar Rotation of Allenes in Acetonitrile having the S Configuration

Compd	$[\phi]^{25}\mathrm{D}(\mathrm{CH_3CN})$, deg	Ref	χ,[a] deg
5	+504	6	+488
7	+72.0	6	+89.0
8	+237	6	+244
9	+100	6	+102
10	+346	6	+342
11	+117[b]	6	+124
15	+25.7	6	+21.6
17	+70.8	6	+35.3

[a] $\chi(\mathrm{CH_3CH}) = \chi(\mathrm{C_2H_5OH})$. [b] The value for $[\phi]^{25}\mathrm{D}(\mathrm{CH_3CN})$ in ref 6 results from a misprint.

are greater than those of the corresponding acids (cf. Table II) and the rotations of the esters are not much affected in changing a protic solvent for a nonpolar aprotic solvent (cf. $[\phi]^{25}\mathrm{D}$ (**9e**) in ethanol and isooctane).[6] Therefore, the reversal of the sequence of the rotations for **14** and **14e** in chloroform may be associated with the interactions of the protic COOH group and the solvent. This solvent effect of chloroform with the carboxylic group makes it difficult to discuss the test of eq 3 for the compounds **14, 15,** and **16** appropriately. According to the concept of qualitative completeness this mixture of type (b) should give nonzero rotation (eq 5), regardless of the nature of the ligands and the solvent.

$$\tfrac{1}{3}[[\phi]^{25}\mathrm{D}(\mathbf{14}) + [\phi]^{25}\mathrm{D}(\mathbf{15}) - [\phi]^{25}\mathrm{D}(\mathbf{16})] = +19.2^\circ \text{ (for CHCl}_3\text{)} \quad (5)$$

Indeed, eq 5 is different from zero which, however, apart from being a result of experimental errors, may be due to solvent (and conformational) effects in chloroform or may be viewed as a hint that the μ polynomial makes a nonvanishing contribution to the rotations in chloroform or may be both.

In order to be independent at least from hydrogen-bond interactions between the solvent and the carbonyl group of the allenic acids and from the problem of the internal electric field due to the polarization of the solvent molecules we have measured the molar rotations of some allenes in acetonitrile $\mathrm{CH_3CN}$ (Table IV). This solvent is polar and dissolves the acids in monomeric form. Furthermore, acetonitrile has practically the same polarizability as ethanol (i.e., the same index of refraction). Therefore, we can calculate the molar rotations $\chi(\mathrm{CH_3CN})$ directly without any correction with the $\lambda(\mathrm{R})$ parameters from Table I.

In this solvent we have an overall good agreement between calculated and observed rotations with the exception of **7** and **17,** the last compound exhibiting the largest deviations in any solvent. For the allenes **11** and **15** the agreement between calculated and experimental rotations is strikingly improved compared with those in ethanol. Until now we have been unable to give a convincing explanation for the large deviations in case of **7** and **17**. Probably, in acetonitrile, both the ethyl groups in the molecules achieve those preferred conformations which are observed for a single ethyl group in ethylallene,[8] and thus introduce a conformational dissymmetry comparable to that in 1,2-cyclononadiene.[18]

The solvent effects may have an unpredictable influence on the basic model underlying the discussions for chirality observations; e.g., there may be in some solvents the violation of the restricting condition ligand qualities to be independent from neighbor ligands or there may be introduced a conformational dissymmetry. As a consequence, optical activity measurements of allenes which shall be compared with theoretical predictions on the basis of eq 4 should be performed at least in two different solvents, preferentially ethanol (methanol) and acetonitrile. For nonpolar allenic hydrocarbons saturated hydrocarbons as the solvents are also appropriate.

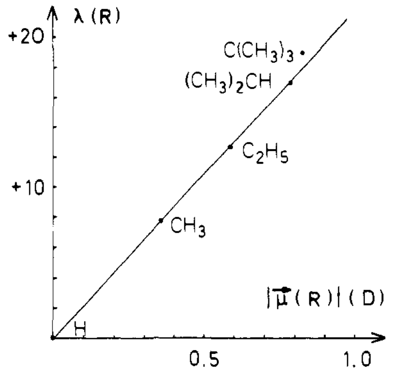


Figure 5. Correlation of the $\lambda(\mathrm{R})$ parameters of inductive substituents and the group moments $|\mu(\mathrm{R})|$.

Owing to the extreme sensitivity of optical activity measurements to solvent and other effects we feel it rather difficult to find well-defined allenic systems for which unambiguous experiments may be performed in order to discuss the concept of qualitative completeness on the basis of eq 3.

(2) Correlations of the $\lambda(\mathrm{R})$ Parameters with Other Substituent Parameters. A quantum-mechanical treatment of the optical rotation $[\phi]^{25}\mathrm{D}$ of (*S*)-1,3-dimethylallene (**1**) has given the physical interpretation of the substituent parameter $\lambda(\mathrm{CH_3})$ of the σ-inductive donor group $\mathrm{CH_3}$.[5] According to the theory the parameter $\lambda(\mathrm{R})$ is related to the difference of the (group) polarizabilities concerning the major axes of the $=\!\mathrm{C{-}R}$ bond, $\Delta\alpha(\mathrm{R}) = \alpha_{rr}(\mathrm{R}) - \alpha_{tt}(\mathrm{R})$, the anisotropy of the polarizability, and a factor $\kappa(\mathrm{R})$, characterizing the variations and reductions of electronic charges in the $\mathrm{C_{sp^2}{-}C_{sp^3}}$ bonding region. The factor $\kappa(\mathrm{R})$ should be viewed as a measure of the polarity of the C-R bond between the allenic terminal carbon atom and the ligand carbon atom.

$$\lambda(\mathrm{R}) = G \cdot \kappa(\mathrm{R}) \cdot \Delta\alpha(\mathrm{R}) \quad (6)$$

In eq 6 G is a geometrical constant depending upon the symmetry of the molecular skeleton.

On the basis of eq 6 the observed large variations of the $\lambda(\mathrm{R})$ parameters for the alkyl groups and the hydrogen atom may be interpreted. For this purpose we consider the extremes $\lambda(\mathrm{CH_3}) = +7.7$ and $\lambda((\mathrm{CH_3})_3\mathrm{C}) = +18.9$. Both the ligands are assumed to be of the (time-averaged) symmetry C_{3v} at least in sterically not hindered allenes. Using an additivity hypothesis for group anisotropic polarizibilities[21] the anisotropies for the polarizabilities of acetonitrile $\mathrm{CH_3{-}CN}$ ($\alpha_\parallel - \alpha_\perp = 1.89$ Å^3)[21] and tertiary butylnitrile $(\mathrm{CH_3})_3\mathrm{C{-}CN}$ ($\alpha_\parallel - \alpha_\perp = 1.68$ Å^3)[21] suggest that also in allenic systems the differences between the group properties $\Delta\alpha(\mathrm{CH_3})$ and $\Delta\alpha((\mathrm{CH_3})_3\mathrm{C})$ are rather small. Then the observed variations of the corresponding $\lambda(\mathrm{R})$ parameters should only be due to the differences in the bonding polarities $\kappa(\mathrm{R})$ of the $\mathrm{C_{sp^2}{-}C_{sp^3}}$ bonds in the alkylallenes. Indeed, an excellent linear correlation (eq 7) (linear correlation coefficient $r = 0.998$) of the parameter $\lambda(\mathrm{R})$ with the group moment $|\mu(\mathrm{R})|$ (Figure 5) is found.

$$\lambda(\mathrm{R}) = 22.11|\mu(\mathrm{R})| - 0.12 \quad (7)$$

The corresponding group moments are identified with the dipole moments of the corresponding phenyl derivatives $\mathrm{C_6H_5{-}R}$[22] which in turn are related to the dipole moments of the allenes $\mathrm{R{-}CH{=}C{=}CH_2}$[8] (in Debye). Furthermore, it has been shown[7b] that the parameters $\lambda(\mathrm{R})$ are linearly related to the parameters $\sigma(\mathrm{R})$ which are used to calculate the $^{13}\mathrm{C}$-chemical shifts of the central carbon atoms of allenes.[7b] Two correlations, eq 8a ($r = 0.981$) and 8b ($r = 0.999$), with nearly

Table V. Determination of $\lambda(R)$ Parameters from Empirical Correlations

Method	Ref	$\lambda(R)$
Eq 10b		$\lambda(CH_3(CH_2)_5) = +12.6$
Eq 11		$\lambda(CH_2CH_2OH) = +12.6$
Eq 9a	35	$\lambda(CH_2OH) = +9.5$
Eq 9b	35, 38	$\lambda(HC{\equiv}CC{\equiv}C) = +37.5$
$[\phi]^{25}D = +(113 \pm 6°)^a$	33	$\lambda(C(CH_3)_2OH) = +14.7$

[a] Measured in methanol and corrected via the Lorentz factor.

Table VI. Experimental and Calculated (eq 4) Molar Rotations of Allenes having the S Configuration

Compd	$[\phi]^{25}D$, deg	Ref	χ, deg
19	$+244^a$	36	+194
21	$+(84 \pm 10)^b$	33	+97.0
23	+475	14, 34	+473
24	$+448^c$	14, 37	$+366^d$

[a] The solvent for the measurement is not given in ref 36. [b] Measured in methanol and corrected via the Lorentz factor. [c] Measured in methylene chloride. [d] Corrected via the Lorentz factor $\chi(CH_2Cl_2) = 1.03\chi(C_2H_5OH)$.

equal slopes have been obtained by a least-squares fit. Equation 8a is valid for (σ-inductive) alkyl groups including hydrogen and eq 8b for mesomeric substituents bonded via a carbon atom to the allenic skeleton.

$$\lambda(R) = -3.47\sigma(R) - 0.85 \quad \text{for inductive groups} \quad (8a)$$

$$\lambda(R) = -3.53\sigma(R) + 33.76 \quad \text{for mesomeric groups} \quad (8b)$$

The ^{13}C-chemical shift parameters $\sigma(R)$ are correlated with the Swain–Lupton[23] resonance parameters $\mathcal{R}$ and Dewar-Grisdale[24] parameters M';[7b] i.e., the $\lambda(R)$ parameters have a common basis with usual substituent constants of linear free energy relationships[25] in physical organic chemistry.

These correlations of the $\lambda(R)$ parameters with other physical quantities show that the $\lambda(R)$ values are numerically well fixed. Consequently, deviations from predicted rotations may provide valuable chemical information concerning solvent effects, ligand interactions, conformational effects, etc.

Concerning the general theory optical rotations[10a,26] $[\phi]^{25}D$ and ^{13}C-chemical shifts[27] δ_C, i.e., differences in magnetic shielding tensor traces, represent second-order properties, because they depend upon ground states $|0\rangle$ and excited states $|i\rangle$ with energies $E_0\ (=h\nu_0)$ and $E_i\ (=h\nu_i)$, respectively. Both involve sums of magnetic transition moment operator matrix elements $\langle 0|\mathbf{m}|i\rangle$.[28]

$$([\phi] \sim \sum_i \nu^2(\nu_{0i}{}^2 - \nu^2)^{-1}\ \mathrm{Im}\langle 0|\mathbf{m}|i\rangle \cdot \langle i|\mu|0\rangle$$

Usually, correlations of the rotations with polarizabilities α are emphasized[26] which involve sums of electric dipole moment operator matrix elements $\langle 0|\mu|i\rangle$.[5,26] Therefore, it is formally interesting that relationships exist between $[\phi]^{25}D$ and δ_C or the substituent effect on these quantities, respectively.

As the parameters $\sigma(R)$ for inductive groups are correlated with the π-electron densities $P_{C_2'}{}^{\pi}$ (CNDO/S),[1] calculated within the CNDO/S approximation, we have a further possibility to obtain $\lambda(R)$ parameters without any reference to optical activity measurements via eq 9a ($r = 0.989$) which has been obtained by a least-squares fit.

$$\lambda(R) = 190.3P_{C_2'}{}^{\pi}(\text{CNDO/S})(RCH{=}C{=}CH_2) - 173.0 \quad \text{for inductive groups} \quad (9a)$$

A corresponding correlation (eq 9b) ($r = 0.998$) involving the π-electron density of the central carbon atom of the allene $R{-}CH{=}C{=}CH_2$ is also valid for mesomeric substituents (C_6H_5, $COOCH_3$, COOH) bonded via carbon to the allenic skeleton (cf. Table V and ref 38).

$$\lambda(R) = 344.0P_{C_2'}{}^{\pi}(\text{CNDO/S})(RCH{=}C{=}CH_2) - 269.3 \quad \text{for mesomeric groups} \quad (9b)$$

From a practical point of view the above empirical correlations are useful for the predictions of new $\lambda(R)$ parameters and consequently the predictions of molar rotations. This shall be demonstrated considering the allenes **19–24**.

From the results embodied in eq 8a three statements concerning inductive substituents emerge.

(1) As the ^{13}C-chemical shifts (the $\sigma(R)$ values) for allenes with linear alkyl groups alternate according to the number of their methylene groups,[30] there exist two sets of linear alkyl groups each of them having the same $\lambda(R)$ value for every element of the set.

$$\lambda(CH_3(CH_2)_n) \approx \lambda(CH_3) \quad \text{for } n = 2, 4 \quad (10a)$$

$$\lambda(CH_3(CH_2)_n) \approx \lambda(C_2H_5) \quad \text{for } n = 3, 5 \quad (10b)$$

Equation 10b can be used immediately to estimate the molar rotation of **20**. Unfortunately, only the rotation in chloroform is available,[31] and therefore, "solvent effects" may be expected (subsection III.1). However, as one may assume on the basis of the similar p*K* values of the corresponding aliphatic carboxylic acids[20] the effect of the *n*-butyl group is similar to that of the ethyl group, we would predict $[\phi]^{25}D(\mathbf{20}) \approx [\phi]^{25}D(\mathbf{15})$ in $CHCl_3$. This, indeed, is correct ($[\phi]^{25}D = +45.6$ (Table III) for **15**, and for **20** $[\phi]^{25}D = +47.2$[31] in $CHCl_3$).

(2) Based upon the comparison of $\sigma(CH_3) = -3.2$ ppm[7b] and $\sigma(CH_2SCH_3) = -3.2$ ppm[32] one can expect that a heterosubstituent X has only a small influence, i.e., $\lambda(CR_2X)$ is only slightly changed in comparison to $\lambda(CR_2H)$.

(3) A heterosubstituent X in β position to the allenic skeleton (CR_2CR_2X), exerting a δ effect[29] on the ^{13}C-chemical shift of the central carbon atom of the allene, should have a negligible influence on the parameters σ and λ, i.e.,

$$\lambda(CR_2CR_2X) \approx \lambda(CR_2CR_2H) \quad (11)$$

On the basis of the above statements, the empirical correlations 9a and 9b, or the molar rotations of the corresponding compounds,new $\lambda(R)$ parameters have been determined (Table V). In the first column of Table V the basis for the evaluation of $\lambda(R)$ is given.

Using the $\lambda(R)$ values from Table V the molar rotations of the allenes **19, 21, 23,** and **24** (from Figure 2) have been calculated. The comparison between experimental and calculated rotations for these compounds is given in Table VI.

The agreement is rather satisfying. Therefore, the above $\lambda(R)$ parameters from Table V are also suited for the calculations of molar rotations of allenes. The deviation for **24** probably results from the solvent effect of methylene chloride (similar to the situation in chloroform). Furthermore, the larger deviations for **19** and **24** may be partly due to conformational effects of the long alkyl chains. The possibility that long alkyl chains $(CH_2)_n$-X, especially those with terminal polar groups, such as X = OH and COOH, introduce conformational dissymmetry into allenes becomes more important with increasing *n*.[37] Such effects will surely have a nonnegligible influence on the magnitude of the rotations. Therefore, allenes with such substituents, e.g., some interesting naturally occuring diyne–allene systems,[14,34,37] have not been considered in our investigation.

(3) Optical Rotatory Dispersion in the Transparent Region. The physical interpretation of the $\lambda(R)$ parameters according to eq 6 implies, at least for the inductive groups, the analytical form for the description of the ORD in the transparent region;

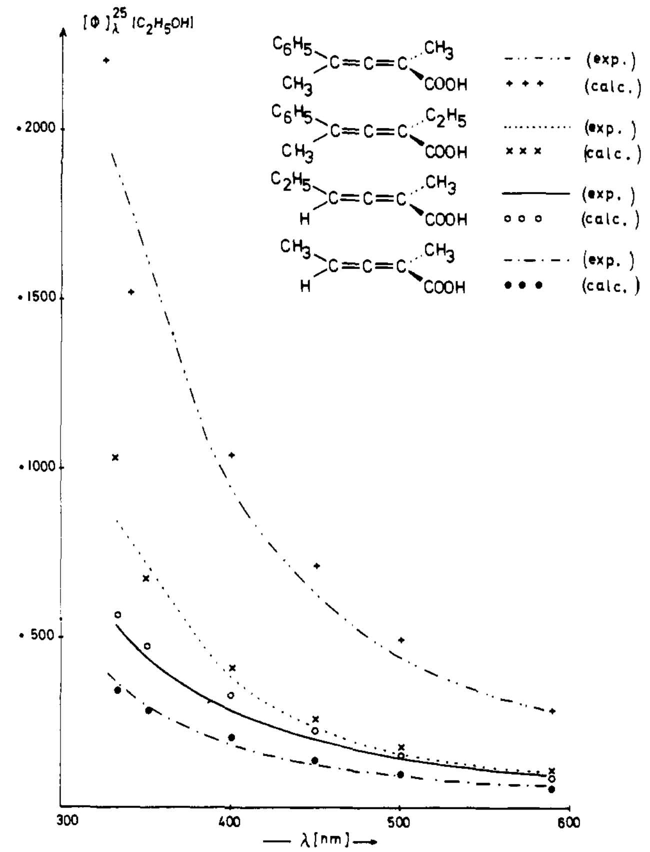


Figure 6. Experimental and calculated optical rotatory dispersion of some allenes in the transparent region.

the wavelength dependency of $[\phi]^{25}\lambda$ is determined via λ(R) by the anisotropy of the polarizability Δα(R). Consequently, the wavelength dependency should involve four constants: C_{rr}, C_{tt}, λ_{rr}, λ_{tt}.[26,41,42]

$$\lambda(R) = \frac{C_{rr}}{\lambda^2 - \lambda_{rr}^2} - \frac{C_{tt}}{\lambda^2 - \lambda_{tt}^2} \qquad (12)$$

However, from a practical point of view it seems to be advantageous to use a simpler relation.

For the discussion of the ORD of allenes we restrict ourselves to the compounds **1–18** (Figure 1), because only for these molecules ORD curves are available;[6,13,18b] i.e., only the λ(R) parameters from Table I are considered.

Evaluating the λ(R) parameters for selected wavelengths[6,13] it turns out that, with the exception of the phenyl group, the ratio between the λ(R) values of two different groups R_1 and R_2 is practically independent from the wavelength ($\lambda \geqslant 330$ nm).

$$[\lambda(R_1)/\lambda(R_2)]_\lambda = \text{constant for } \lambda \geqslant 330 \text{ nm} \quad \text{and } R_i \neq C_6H_5 \qquad (13)$$

This is expected for hydrogen and the alkyl groups as the differences between their λ(R) parameters are almost independent from Δα(R) (eq 7). The analytical wavelength dependency of the λ(R) may be approximated in terms of eq 14a and 14b, respectively.

$$[\lambda(R_i)]_\lambda = 0.224\,[\lambda(R_i)]_D \cdot \left(1 + \frac{1.20 \times 10^6}{\lambda^2}\right) \qquad (14a)$$

$$R_i = \text{H, alkyl, COOH, COOCH}_3\text{, COONa}$$

$$[\lambda(C_6H_5)]_\lambda = 0.100[\lambda(C_6H_5)]_D \cdot \left(1 + \frac{3.12 \times 10^6}{\lambda^2}\right) \qquad (14b)$$

These expressions contain only two empirical constants. They are identical concerning the analytical form with the approximation used to describe the wavelength dependency of the average polarizability

$$\bar{\alpha} = \tfrac{1}{3}(\alpha_{11} + \alpha_{22} + \alpha_{33})^{43}$$

In general, ORD curves calculated on the basis of eq 4 and 14 show deviations from the experimental ones by ~10% for $\lambda \geqslant 400$ nm and ~25% for $330 \leq \lambda \leq 400$ nm.

In Figure 6 experimental and calculated ORD curves for some representative allenes (not used for the determination of the eq 14a and 14b) are displayed. For the alkylallenecarboxylic acids (**16**, **18**) the agreement is satisfying on the total interval $\lambda \geqslant 330$ nm, whereas for phenylallenecarboxylic acids (**6**, **8**) the agreement is only sufficient for $\lambda \geqslant 400$ nm. This may be partly due to the different sensitivities of the phenyl group and the other groups toward wavelength. Furthermore, the ORD of the allenes in the transparent region is essentially determined by electronic transitions with energies $\Delta E <$ 50 000 cm^{-1}.[40,44] Phenylallenecarboxylic acids have longer wavelength transitions than alkylallenecarboxylic acids,[40,44] and, within the series of phenyl compounds, the circular dichroisms of the (weak) longest wavelength transitions are partly of different signs.[44] Therefore, the ORD curves for phenylallenes are rather sensitive toward structural changes at the border of the transparent region.

(IV) Summary and Conclusions

As a resumé it has turned out that special expressions of chirality functions involving ligand-specific parameters λ(R) and their quantum-mechanical interpretations form a sound basis for the quantitative description of the optical rotatory dispersion of allenes in the transparent region.

Correlations of the λ(R) parameters with other physical quantities assure the accuracy of the selected numerical values of these parameters which may be buried sometimes by solvent, conformational, and other effects, if experimental and calculated molar rotations of allenes are compared. For practical purposes and problems of (dynamic) stereochemistry[11,18b,45] our treatments offer two application patterns.

(1) From the sign of the (measured) optical rotation in the transparent region ($\lambda \geqslant 330$ nm) the optical purity and the absolute configuration of a given allene may be calculated, provided the allene has substituents whose λ(R) parameters are known.

(2) If for an allene a certain parameter is unknown (cf. ref 45), it may be determined without any reference to optical activity measurements from ^{13}C-chemical shift measurements or semiempirical CNDO/S calculations of π-electron densities via empirical correlations.

The accuracy of our determinations of optical purities is comparable to that achieved with chiral shift reagents using NMR spectroscopy.[33] In case of the allenes purely empirical methods for the determination of absolute configurations ("Lowe's rule"[47]) and the calculations of molar rotations based upon Brewster's classical helix model[48] are covered by our treatment.

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The Microwave Spectrum, Structure, and Dipole Moment of 2-Mercaptoethanol; Evidence for an Intramolecular OH···S Hydrogen Bond

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Abstract: The microwave spectrum of 2-mercaptoethanol has been observed and analyzed in the 18-40-GHz frequency region. Using data from the normal and four additional isotopic species, the structure of the observed rotamer has been shown to be all gauche (GGG). The structural results indicate the presence of an intramolecular hydrogen bond of the type OH···S, with an H···S distance of 2.565 ± 0.003 Å. Dipole moment measurements lead to the values $|\mu_a| = 0.619 \pm 0.015$, $|\mu_b| = 1.478 \pm 0.012$, and $|\mu_c| = 0.965 \pm 0.009$ D, in agreement with expectations for the observed GGG conformation. The present study appears to be the first to present concrete structural evidence for the involvement of sulfur in an intramolecular hydrogen bond in the gas phase. These results have been discussed in relation to other pertinent data.

Rotational isomerism in 1,2-disubstituted ethanes has been studied extensively.[1] The threefold C-C barrier terms lead generally to stable trans or gauche rotamers, the cis forms being sterically unfavored. In the dihaloethanes (except for the difluoro case[2a]) the trans forms are the lowest energy species,[2b] while the situation reverses for the 2-haloethanols, for which the gauche forms are lower in energy.[3-6] This latter phenomenon has been attributed to intramolecular hydrogen bonding, and was carefully investigated by Azrak and Wilson[6] by microwave spectroscopy. These workers found that the stable