CIRCULAR DICHROISM MEASUREMENTS IN THE VUV*

Aharon GEDANKEN
Department of Chemistry, Bar-Ilan University, Ramat Gan, Israel 52100

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The extension of circular dichroism measurements into the VUV region was motivated by the need to provide supplementary techniques to the absorption studies lacking rotational and vibrational structure. CD as one of these techniques is determined by selection rules which differ from those in absorption and thus enables the assignment of excited electronic states. Another application of VUVCD measurements is the use of correlation between the sign of the CD signal and the absolute configuration to formulate sector rules of chromophores absorbing only in the VUV. In this review we will present results obtained on our home-made instrument capable of measuring CD signal down to ~150 nm. These applications of VUVCD will be demonstrated in systems such as the oxirane chromophore, the methylenecyclohexene chromophore and the amine chromophore. The role of singlet–triplet transitions and their contribution to CD and ORD will also be discussed.

The extension of circular dichroism (CD) measurements to the vacuum ultraviolet region (200 – 100 nm) was motivated by two factors. The first is that many chromophores are transparent in the visible and UV region and absorb only in the VUV region. The second is that for many molecular systems the absorption spectra is broad and structureless and therefore it is impossible to provide an unambiguous assignment for these absorption bands. An impetus exists, therefore, for the use of CD in characterizing these transitions. CD is indeed known as a technique which provides information that supplements absorption studies. In the early seventies, polarizing elements for the VUV region became commercially available and CD instruments were built shortly afterwards[1,2]. The VUVCD work can be divided into two categories: one whose main interest is biological molecules, while the other concentrates on the study of simple and isolated chromophores such as olefins, the benzene ring, oxiranes, etc. In this paper we will review the CD measurements carried out at Bar-Ilan University.

In CD measurements, left and right circularly-polarized light (cpl) is passed through an optically active molecule containing the chromophore of interest, and the difference in absorption of left and right cpl is measured. CD is widely used a) as a spectroscopic tool for identification and characterization of excited states; b) for the determination of the absolute configuration of molecules.

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When CD is used spectroscopically, the basic assumption is that the substituents which create the molecular asymmetry (alkyl radicals, fluorine and hydrogen atoms) only slightly perturb the spectroscopy of the chromophore of interest. This assumption is based on the fact that the excited states of these substituents are higher in energy than the chromophore of interest. The supplementary information that results from CD studies is as follows:

By its ability to measure both positive and negative signals, the CD technique enables one to uncover transitions that are not resolved in normal optical absorption measurements.

The measured quantity in CD is $\Delta\varepsilon = \varepsilon_L - \varepsilon_R$, where ε is the molar extinction coefficient. $\Delta\varepsilon$ is related to the quantum mechanical transition-moment matrix elements via

$$\mathrm{R} \sim \int \Delta\varepsilon/\varepsilon \, \mathrm{d}\nu \sim \mathrm{Im}\langle g|\boldsymbol{\mu}|\, e\rangle \, . \, \langle e|\mathbf{m}|\, g\rangle \, , \qquad (1)$$

where $|g\rangle$ and $|e\rangle$ are the ground and excited electronic states, and where μ and $\mathbf{m}$ are the electronic and magnetic dipole moment operators.

For the absorption extinction coefficient, the analogous expression is

$$\mathrm{D} \sim \int \varepsilon/\nu \mathrm{d}\nu = \langle g|\boldsymbol{\mu}|\, e\rangle \, . \, \langle e|\boldsymbol{\mu}|\, g\rangle \, . \qquad (2)$$

It can be shown that the anisotropy factor $g = \Delta\varepsilon/\varepsilon$ is proportional to $\langle g|\mathbf{m}|\, e\rangle / /\langle g|\boldsymbol{\mu}|\, e\rangle$. Therefore, bands having a large g-value represent magnetic dipole allowed and electro-dipole forbidden transitions, whereas a small g-value indicates the opposite. CD measurements, as a result of the CD selection rules, can provide additional information for the assignment of the magnetic-dipole allowed transitions.

The assignment of an absorption spectrum is always aided by the provision of quantum mechanical calculations of energies and oscillator strengths as a check on a proposed assignment. In the case of CD measurements, spectral assignments can be further substantiated since the sign of the rotational strength (Eq. (*1*)) can be calculated theoretically.

Singlet–triplet transition can be observed in regular CD measurements. These transitions are strongly forbidden in absorption measurements and have a molar extinction coefficient of $10^{-4} < \varepsilon < 1$. However, the magnetic-dipole operator which determines the rotational strength is given by

$$\mathbf{m} = \frac{e}{2mc} \sum_i (\mathbf{L}_i + 2\,\mathbf{S}_i) \, ,$$

where $\mathbf{L}_i$ is the orbital angular momentum and $\mathbf{S}_i$ the spin angular momentum of the i-th electron. In magnetic CD it has already been shown that singlet–triplet transition can be detected[3] using a 10 cm cell. This is due to the significant contribution of the spin magnetic moment. It is expected that a similar effect will occur in CD measurement.

A second field in which CD measurement are used is the determination of the absolute configuration of an optically active molecule through chirality rules. These sector rules establish relations between the sign of the CD signal of a specific electronic transition in a chromophore and the absolute configuration of the molecules. Examples of such rules are the octant rules for the $n \rightarrow \pi^*$ in carbonyls[4] and the $\pi \rightarrow \pi^*$ in olefins[5].

In this review we will demonstrate how the spectroscopic and conformational analysis of CD spectroscopy is applied to molecular systems that were studied in the VUV region.

INSTRUMENTATION

The first VUVCD instrument was constructed by Feinleib and Bovey[6]. Their instrument was based on the simultaneous measurement of the absorption for left and right cpl. The small difference was measured by a very accurate bridge circuit. In the early seventies, with the development of phase-sensitive detectors, two more modern instruments based on modulation techniques were successfully operated in the VUV region. In 1978 Johnson reviewed[7] the activity in the VUVCD field and reported six more instruments operating at that time. All these instruments used conventional lamps as light sources. With the development of synchrotron radiation and storage rings, three more groups became involved with CD measurements in the VUV. J. Hormes and his group at Bonn University[8], P. Schnider[9] at the synchrotron radiation center, Stoughton, Wisconsin and J. Sutherland at Brookhaven[10]. There are three advantages to replacing the conventional light source with a Synchrotron, the first being the number of photons obtained from the latter. The synchrotoron source yields a high percentage of linearly polarized light, thus eliminating the introduction of an element (in the conventional systems) which converts the regular light into linearly polarized light. The third advantage is the collimated nature of the Synchrotron beam. In gas phase measurements the study of molecules with a low vapor pressure would require a long pathlength cell (at room temperature). The superiority of a collimated beam for this cell is obvious, while the use of a diverging beam would damage the cpl due to reflections from cell surfaces.

Although the construction of a VUV apparatus has already been reviewed, we will briefly repeat it.

There are two ways of producing linearly polarized light in the VUV either by employing a MgF_2 transmitting prism (Rochon or Wollaston) or a biotite plate[11] from which the reflected light emerges linearly polarized.

Since MgF_2 shows an abrupt change in its birefringence around 135 nm, the extension of VUVCD to higher energies requires the use of the biotite plate[11]. The reflectance of biotite increases towards shorter wavelengths[12] and therefore the wavelength limit is imposed by the transmittance of the next element, the PEM (photoelastic modulator). The PEM (HINDS INT., Hillsboro, Oregon) for VUV measurements is made of CaF_2 and transmits light down to 125 nm. The PEM operates at 50 kHz and converts the linearly polarized light into left and right cpl. The PEM is oriented at 45° to the linearly polarized light. In each cycle the PEM first produces cpl of one rotation and then the other. The modulated beam passes through the sample and is detected by a solar blind photomultiplier (PM). It is recommended that a head-on PM be used in this kind of measurement rather a side-on because of base-line problems. When an optically active compound is placed in the cell the PM will detect an ac signal superimposed on a dc signal. To a good approximation the CD is proportional to the intensity of the ac signal divided by the dc signal. The dc signal is kept constant when the wavelength is scanned by a feed-back mechanism controlling the PM power supply. In this case the intensity of the ac signal measures the CD directly.

Although the CD is measured in the VUV, the calibration of the system is carried out at 290 nm using an aqueous solution of (+)-10-camphorsulfonic acid (CSA). An 0·1% aqueous solution of CSA in a 1 cm cell shows an ellipticity of 0·31 degrees, or a ΔOD of $9{\cdot}4 \,.\, 10^{-3}$.

The detection limit of a CD instrument is determined by the number of photons N reaching the detector. And, since the noise in a CD spectrum is statistical, $\Delta\varepsilon/\varepsilon$ is proportional to $\sqrt{N}/N$. At present the limit of sensitivity in our instrument, with 2 mm slits, is about 10^{-5} in the 330 to 150 nm wavelength range.

RESULTS

In this section we will present the CD of some of the chromophores we have recently investigated. The systems were chosen in order to demonstrate the advantages of CD spectroscopy mentioned above.

Oxirane Chromophore

With the extension of CD to the VUV region the oxirane chromophore became amenable to experimental observation. Oxirane absorbs below 180 nm and early absorption measurements have assigned all the observed transitions as Rydberg states[13]. The small size of the oxirane moiety has prompted theoretical *ab initio* calculations that have been essential in our assignment of its excited electronic states[14]. We have carried out these calculations for (−)-*S*-2-methyloxirane (MO) and (−)-(*S*,*S*)-2,3-dimethyloxirane. The calculated sign for the first excited state in these molecules, an $n(\mathrm{o}) \rightarrow 3s$ Rydberg transition, was correctly predicted[14]. This agreement substantiated the identification of this transition as the 3*s* Rydberg. In Fig. 1 we exhibit the gas phase CD and absorption spectra of the MO molecule. Table I presents the calculated and experimental energies, oscillator and rotational strengths of MO. The $n(\mathrm{o}) \rightarrow 3s$ was examined in other monosubstituted oxiranes and appears at almost the same wavelength, namely, 173·5 ± 1·5 nm. Even for disubstituted oxirane only a small red shift is observed. The unambiguous assignment of this transition has led to the next question – whether the sign of the CD signal of this transition is related to the absolute configuration of the molecule. The examination of ten different alkyl (mono, di and tri) substituted oxiranes led to the conclusion that a quadrant rule governs the relation between the CD sign of the $n(\mathrm{o}) \rightarrow 3s$ transition and the absolute configuration of the molecule[15,16]. These planes of symmetry forming the quadrants are presented in Fig. 2. According to this rule an alkyl substituted oxirane having an *S* configuration will show a positive

CD band for the $n(o) \rightarrow 3s$ Rydberg transition whereas an R enantiomer exhibits a negative band for the same transition. For monosubstituted oxiranes this relation is symmetry determined, namely, placing the alkyl group in a certain quadrant determines the CD sign.

The $n(o) \rightarrow 3s$ always shows the strongest CD signal. This is explained by the cancellation effects that the higher Rydberg components show. In Table I we see that the three $n(o) \rightarrow 3p$ components do not show the same sign. This explains why the $n(o) \rightarrow 3s$ is always stronger than the $n(o) \rightarrow 3p$. In one interesting case we observed different behavior. This is demonstrated in the CD and absorption

TABLE I

Summary of calculated and experimental quantities for MO

Transition	Calculated			Experimental		
	E^a	f	rs^b	E^a	f	rs^b
$n(O) \rightarrow R(3s)$	6·4	0·026	+4·92	7·12	0·025	11·8
$n(O) \rightarrow R(3p)$	7·16	0·010	−1·30	7·75	0·062	−10·8
$n(O) \rightarrow R(3p)$	7·34	0·026	+0·42			
$n(O) \rightarrow R(3p)$	7·36	0·006	−0·02			

[a] Excitation energy from the ground state, in eV; [b] rs rotational strength, in 10^{-40} cgs units.

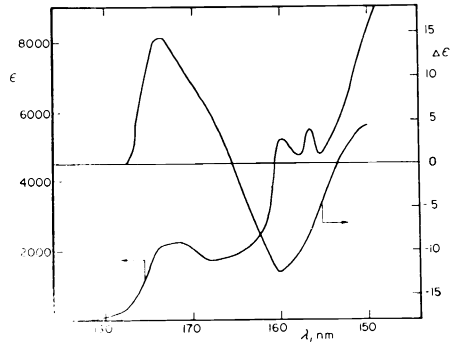

FIG. 1

Absorption and CD spectra (−)-2-methyloxirane. The spectral resolution for both spectra is 1·6 nm

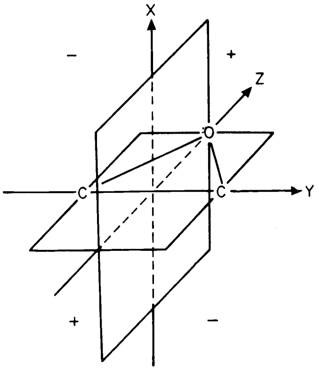

FIG. 2

The planes of symmetry forming the quadrants spectra of (−)-(2*R*, 3*S*)-2-ethyl-3-methyloxirane (Fig. 3). The uniqueness of this molecule is the opposite contribution of the two alkyl groups. This provides us with an opportunity to compare the role of methyl and ethyl groups in inducing optical activity. According to the quadrant rule the two groups have opposite contributions to the CD signal of the $n(\mathrm{o}) \rightarrow 3s$ transition. Thus one would expect a rather small signal due to this cancellation effect. The observed signal is indeed small. The positive signal observed indicates that the contribution of the methyl group outweights that of the ethyl group. The effect of the substituent was correlated with its polarizability[17]. However, this correlation will not hold in our case because the polarizability of the ethyl is larger than that of the methyl.

The quadrant rule for the $n(\mathrm{o}) \rightarrow 3s$ was rationalized on the basis of Schellman's[18] theory emphasizing the symmetry of the molecule. This one electron model which emphasizes the static perturbation of the substituents field affords rules for optical activity. The symmetry of the symmetric oxirane chromophore dictates a quadrant rule according to this theory. This approach was questioned by Rodger[19] pointing out that the $n(\mathrm{o}) \rightarrow 3s$ transition is electric dipole allowed, so the couple oscillator theory of Kirkwood and Kuhn[20] is almost certainly dominant over any other mechanism. By applying the independent systems/perturbation approach to the $n(\mathrm{o}) \rightarrow 3s$ transition, Rodger could reproduce the experimental results[15,16]. According to Rodger[19], the contribution of the alkyl substituents are the results of their position and orientation, unlike the static perturbation theory in which only the position of the substituent is of importance. The calculated contribution of an ethyl group is smaller by about 10% than that of a methyl group. This gives a good explanation of the dominant role of the methyl group in (*S*,*R*)-methylethyloxirane.

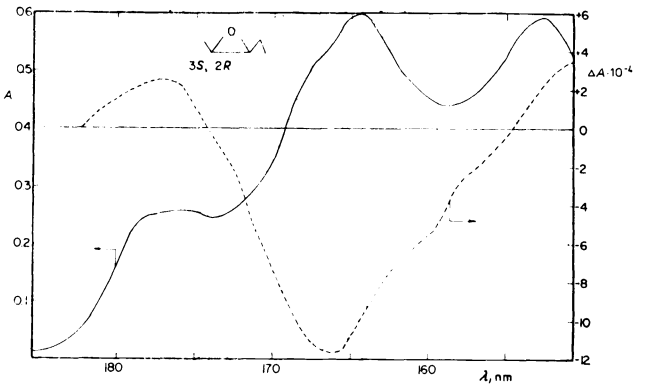

FIG. 3

The absorption (—) and CD (...) spectra of (−)-(2*R*,3*S*)-2-ethyl-3-methyloxirane. The spectral resolution of both spectra is 1·6 nm

The additive nature of two groups positioned in the same quadrant is demonstrated in the experimental results which show that the Δε of (*S*,*S*)-dimethyloxirane is almost twice that of the (*S*)-methyloxirane while their oscillator strength is almost equal. Rodger could reproduce the *n*(o) → 3*p* spectra as well, although the contribution of the magnetic allowed transition *n*(o) → 3*py* was completely neglected. Being a magnetic dipole allowed transition it vanishes in the coupled oscillator mechanism, whereas in the other mechanism it should be much smaller and therefore ignored. The calculations were extended to include the oxetane moeity and again could successfully reproduce the experimental results[16]. It is worth noting that the quadrant rule of the *n*(o) → 3*s* transition holds to three, four, five[21] and six[21] member rings containing oxygen.

Methylenecyclohexane chromophore absorption spectra. The most comprehensive study of chiral olefins was undertaken by Drake and Mason[22]. They successfully assigned the first transition of the olefinic chromophore as the π → 3*s* Rydberg by dissolving the chiral olefin in a variety of solvents whereby the π → 3*s* broadened appreciably and was shifted to higher frequencies. When the solution was cooled, the Rydberg excitation continued to shift to higher energies. Different behaviour was observed for the π → π* transition which was shifted in solution to lower energies. They have also demonstrated that the Scott and Wrixon (+*XYZ*) sector rule can be theoretically obtained by applying either static field or dynamic coupling mechanisms.

The methylenecyclohexane (or more properly, cyclohexylidenemethane) moiety was investigated using our VUVCD machine. This molecular system provided us with a unique opportunity in which the effect of exo vinylic substituents could be isolated and probed. The optically active molecule was (4-methylcyclohexylidene) methane (Fig. 4) in which X and Y were varied.

The purpose of our study was to determine whether, and in what manner, a substituent lying in the nodal plane of the π orbital contributes to the CD. Deuterium[23,24] and fluorine[25,26] substituents, which are known to exhibit an antioctant effect on the *n* → π* of carbonyls, were of special interest in our system. Other substituents were Cl, Br, CH_3, CD_3 and other alkyl groups. The study included 12 different olefins and was carried out in the gas phase[27].

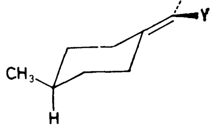

FIG. 4

The molecular configuration of (4-methylcyclohexylidene)methane

In Figs 5 and 6 we present the CD and absorption spectra of (4-methylcyclohexylidene)deuteriomethane and of (4-methylcyclohexylidene)ethane. The assignment of these spectra is given elsewhere[27]. The general trend observed in all the twelve molecules investigated, is that their absorption spectra show a striking similarity to the spectrum of the symmetric methylenecyclohexane which was studied by Robin[28] and also by Demo[29]. The first transition is assigned as the $\pi \rightarrow 3s$ and usually shows one symmetric stretching vibration built on its origin. The second transition is the $\pi \rightarrow \pi^*$ which exhibits a richer vibrational spectrum. The active vibration is also the symmetric stretching and since the absorption maximum usually appears at the $v = 3$ vibration in the progression, it is predicted that the configuration of the molecule in the excited state is stretched compared to the ground state. The $\pi \rightarrow 3s$ and $\pi \rightarrow \pi^*$ always show (in all twelve molecules) opposite sign CD signals. This is in accordance with previous CD studies of chiral olefins[22]. The substitution of

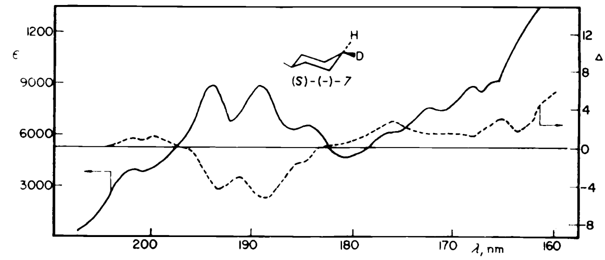

Fig. 5

The absorption (—) and CD (...) spectra of (4-methylcyclohexylidene)ethane. The spectral resolution is 1·6 nm

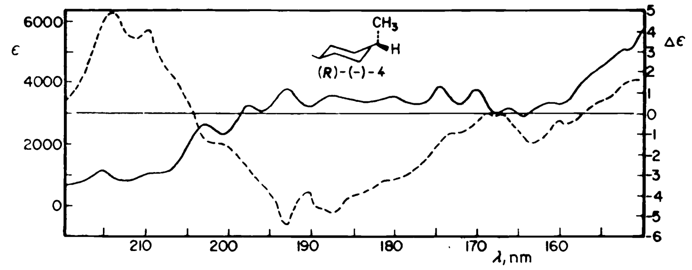

Fig. 6

The absorption (—) and CD (...) spectra of (4-methylcyclohexylidene)ethane. The spectral resolution is 1·6 nm hydrogen by dueterium atoms caused the expected isotope shifts[30]. The introduction of a fluorine atom did not cause any dramatic changes, which is similar to the ethylene case where haloethylenes almost reproduce the ethylene spectrum[31].

CD Spectra and Absolute Configuration

With the CD spectra and absolute configurations of the chiral olefins in hand, it was of interest to ascertain whether a correlation between them could be achieved. The empirical rule formulated by Scott and Wrixon[5] relates the CD sign of the $\pi \rightarrow \pi^*$ state, with the absolute configuration of the chiral olefin. This octant rule works well for many endocyclic compounds but fails for a number of exocyclic olefins.

The Scott–Wrixon rule uses the three intersecting planes of symmetry of the alkene to create the octants. The molecular asymmetry of *I*, the substituted (4-methylcyclohexylidene)methane (Fig. 4), is due solely to having both a substituent other than hydrogen in the 4-position of the cyclohexane ring and that X does not equal Y. Any contribution of allylic axial bonds in *I* would, of course, cancel each other out. In our system the methyl in the 4-position is kept constant and only the substituents X and Y attached to the double bond are varied. It is therefore the nature of the X and Y substituents that will determine the sign of the $\pi \rightarrow \pi^*$ signal. In particular, we were interested in the effect of deuterium and fluorine atoms on the $\pi \rightarrow \pi^*$ transition.

TABLE II

Configurations, atomic radii and sign of $\pi \rightarrow \pi^*$ CD of various substituents in *I*

Configuration	Substituent (radii, nm)		CD($\pi \rightarrow \pi^*$)	
	X	Y	predicted	found
(*R*)-(−)-3	Br (0·114)	H (0·037)	(−)	(−)
(*R*)-(−)-4	CH_3 (0·077)	H (0·037)	(−)	(−)
(*R*)-(−)-5	CD_3 (0·077)	H (0·037)	(−)	(−)
(*R*)-(+)-7	D (0·0371)	H (0·037)	(+)	(+)
(*R*)-(−)-8	Cl (0·099)	H (0·037)	(−)	(−)
(*R*)-(−)-9	CH_2CH_3 (0·077)	H (0·037)	(−)	(−)
(*R*)-(−)-6	t-Bu (0·077)	H (0·037)	(−)	(−)
(*R*)-(−)-13	F (0·072)	D (0·0371)	(−)	(−)
(*R*)-(−)-14	F (0·072)	H (0·037)	(−)	(−)
(*R*)-(−)-11	Br (0·114)	F (0·072)	(−)	(−)
(*R*)-(−)-12	F (0·072)	CH_3 (0·077)	(+)	(+)

The ratio of $\Delta\varepsilon/\varepsilon$ for the methyl substituted *I* to the deuterio substituted *I* is just a factor of 4. At first glance we considered it as larger than expected, because the optical activity created by a deuterium substituted compound is usually small. However, a literature survey has shown us that this ratio changes from 36 (ref.[32]) to 3 (ref.[24]) and our number is not exceptionally large. Perhaps, the relatively large number has to do with the proximity of the substituent to the olefinic bond.

In Table II we included the results of the CD sign of the $\pi \rightarrow \pi^*$ transition in all the molecules studied, when the *R* configuration is considered. It can be seen that, with the exception of deuterium, when Y = H a negative CD sign is observed for the $\pi \rightarrow \pi^*$ transition. The alkyl substituents as well as the halogens, including fluorine, exhibit the same consignate effect. Although recognizing the danger inherent in making empirical correlations, we are inclined to suggest that our results can be rationalized in terms of the C–X vs C–Y bond length. The correlation is evident by examining Table II. When the covalent radius of X > Y, then the CD sign of the $\pi \rightarrow \pi^*$ transition will be negative, and when Y > X it will be positive as long as the substituent X or Y does not possess a π delocalized system at the point of attachment to C.

DISCUSSION

As we have previously discussed, the replacement of one of the vinylic hydrogens and one of the hydrogens in the 4-position of the cyclohexane ring by another substituent are both necessary and sufficient conditions to cause molecular chirality in the cyclohexylidenemethane system. This chiral system, *I*, provides one with a unique opportunity to evaluate the contribution to the optical activity of a given perturber X relative to a perturber Y that is located across the symmetry plane of the double bond.

In the analysis of our results certain reasonable assumptions will be made. We will assume that the double bond is planar and that the substituents X and Y lie in the same plane. Although one could argue that this assumption may not apply to certain large substituents, such as tert-butyl, one would agree that it is justified and reasonable for perturbers that are small such as D, H, CH_3, etc. We will also assume that the 4-methyl substituent, common to all the molecules in our study, whatever its contribution is, will be the same for all perturbers X and Y. Therefore, the net effect will be due to these groups.

Of the three leading mechanisms explaining optical activity (static perturbation, dynamic coupling, and the coupled oscillator), two have been applied to the olefin chromophore. The static perturbation mechanism has successfully predicted an octant rule[22] for the sign of the $\pi \rightarrow \pi^*$ signal. However, the substituents that mix the excited states of the symmetry chromophore do not show any dependence on their effective charge or their dipole moment as predicted by theory. This is also obtained for the cyclohexylidenemethane chromophore where again no dependence on the dipole moment is observed.

The dynamic coupling mechanism that has been applied to electric dipole allowed transitions by Weigang[33] contains, except for the geometrical factor, a dependence on the anisotropy of the polarizability of the C—C single bond. This negative value, which has also been used by Scott and Yeh[34], has been questioned by other authors[22]. The geometrical factor, which includes octant as well as conical contributions, would show no contributions since the substituents X and Y in cyclohexylidenemethane *I* lie in the nodal surface. It is also worth noting that Weigang's[33] treatment excludes polar perturbers and would therefore not be applicable to halogen substituents.

All three mechanisms have one factor in common, namely, their dependence on R_{c-x}^{-n}, where R_{c-x} is the distance between the chromophore and a substituent X. This distance dependence is introduced in the matrix element of perturbation. Of the three mechanism, it is the coupled oscillator that exhibits the strongest dependence on $R_{c-x}(R_{c-x}^{-2})$ and therefore, at first glance, appears to be the best candidate to account for our results. We therefore conclude from our data that if, in Fig. 7, $R_{c-x} < R_{c-y}$ and the coordinates of substituent X are such that $X > 0$ and $Y > 0$, then the sign of the CD signal will be positive for the $\pi \rightarrow \pi^*$ transition. If, on the other hand, $R_{c-x} < R_{c-y}$ and its coordinates are $X > 0$, $Y > 0$, then a negative signal will be observed. Our observations dictate that the sign of the CD signal of the $\pi \rightarrow \pi^*$ transition is determined by the position of the substituent closest to the olefinic carbon atoms. Attempts are being made at present to reproduce theoretically[35] the CD of the methylenecyclohexane moeity.

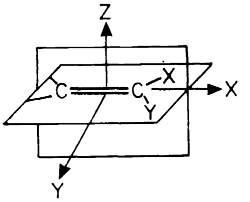

FIG. 7

Sectors defining the sign of $\pi \rightarrow \pi^*$ CD absorption of chiral olefins

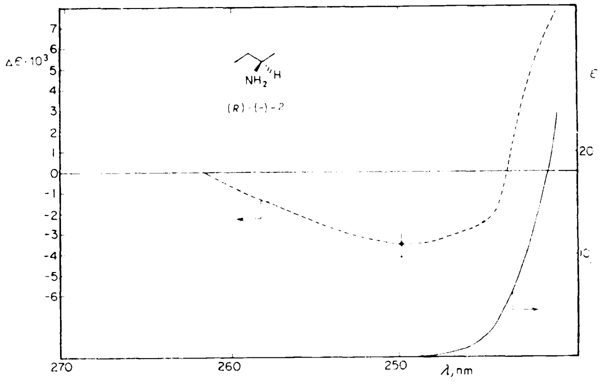

FIG. 8

The absorption (—) and CD (...) spectra of 70 torr of *R*-(—)-2-aminobutane

Singlet–Triplet Transition in CD

We have already mentioned that the magnetic-moment operator contains two contributions: the electronic angular momentum and the spin angular momentum. We therefore expect that singlet–triplet transitions in optically active molecules would be "allowed" and amenable to experimental observation. Indeed, triplet-singlet transitions were observed in emission where the CD of the phosphorescence was measured[36]. These transitions were also detected in magnetic CD in relatively short cells[3]. In absorption CD there are no reports so far for the detection of singlet–triplet transition.

We have measured the CD of $R(-)$-sec-butylamine over the wavelength range of 240 – 150 nm and observed the expected CD for the various Rydberg transitions. The first absorption band of the amine chromophore is assigned as the $n \rightarrow 3s$ Rydberg and its center is located at ~210 nm. It showed a positive CD sign. In many molecules there is a mismatching between the sign of the $[\alpha]_D$, the optical rotation, and the CD sign of the first excited electronic state. This is usually explained as being due to contributions from higher energy transitions of opposite signs which overpower the first excited state and thus determine the sign of the $[\alpha]_D$. In $R(-)$-sec-butylamine we could detect only one weak negative band at higher energies and we therefore looked for CD signals at lower energies, namely, longer than 240 nm, the onset of the $n \rightarrow 3s$ absorption.

In Fig. 8 we present the absorption and CD of $R(-)$-2-aminobutane in the gas phase. The spectrum reveals the tail of the absorption and CD spectra of the $n \rightarrow 3s$ transition. The CD of this transition is positive and it changes sign and peaks at about 250 nm. We attribute this transition to the triplet component of the $n \rightarrow 3s$ Rydberg. We base our assignment on the following arguments:

a) Within the sensitivity of our instrument we could not detect any absorption in the 250 nm region. The measurement is carried out employing the full vapor pressure of the compound (70 torr). This imposes an upper limit for ε of 0·2. Such a small absorption is typical for singlet-triplet absorption.

b) The transition is not part of the $n \rightarrow 3s$ singlet band since a change in sign is observed in the CD of the new band.

c) The singlet $n \rightarrow 3s$ is known as the lowest excited state of the amine chromophore.

d) The minus sign for the triplet state would explain the observed $[\alpha]_D$.

Further measurements are now in progress. The 2-aminobutane molecule is unique, being a very volatile, optically active molecule for which a relatively high concentration of molecules can be obtained in the gas phase.

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REFERENCES

1. Schnepp O., Allen S., Pearson E. F.: Rev. Sci. Inst. *41*, 1136 (1970).
2. Johnson W. C.: Rev. Sci. Inst. *42*, 1283 (1971).
3. Lindner R. E., Barth G., Bannenberg E., Djerassi C., Seamans L., Moscowitz A.: Chem. Phys. Lett. *39*, 411 (1976).
4. Moffitt W., Woodward R. B., Moscowitz A., Klyne W., Djerassi C.: J. Am. Chem. Soc. *83*, 4013 (1961).
5. Scott A. I., Wrixon A. D.: Tetrahedron *26*, 3695 (1970).
6. Feinleib S., Bovey F. A.: Chem. Commun. *1968*, 978.
7. Johnson W. C.: Ann. Rev. Phys. Chem. *29*, 93 (1978).
8. Hormes J., Grinter R., Breithaupt B., Kolb D. M.: J. Chem. Phys. *78*, 158 (1983); Gedanken A., Lagier H. D., Schiller J., Klein A., Hormes J.: J. Am. Chem. Soc. *108*, 5342 (1986).
9. Snyder P. A., Rowe E. M.: Nucl. Inst. Methods *172*, 345 (1980).
10. Stevens E. S., Morris E. R., Rees D. A., Sutherland J. C.: J. Am. Chem. Soc. *107*, 2982 (1985).
11. Gedanken A., Levi M.: Rev. Sci. Inst. *48*, 1661 (1977).
12. Robin M. B., Kuebler N. A., Pao Y.: Rev. Sci. Inst. *37*, 922 (1966).
13. Basch H., Robin M. B., Kuebler N. A., Baker C., Turner D. W.: J. Chem. Phys. *51*, 52 (1969).
14. Levi M., Arad-Yellin R., Green B. S., Gedanken A.: Chem. Commun. *1980*, 847; Cohen D., Levi M., Basch H., Gedanken A.: J. Am. Chem. Soc. *105*, 1738 (1983).
15. Gedanken A., Hintzer K., Schurig V.: Chem. Commun. *1984*, 1615.
16. Gedanken A., Schurig V.: J. Phys. Chem. *91*, 1324 (1987).
17. Brewster J. H.: Top. Stereochem. *2*, 31 (1968).
18. Schellman J. A.: J. Chem. Phys. *44*, 55 (1966).
19. Rodger A.: J. Am. Chem. Soc. *110*, 5941 (1988).
20. Kirkwood J. G.: J. Chem. Phys. *5*, 479 (1937); Kuhn W.: Trans. Faraday Soc. *26*, 193 (1960).
21. Bertucci C., Lazzaroni R., Johnson W. C.: Carbohydr. Res. *133*, 152 (1984).
22. Drake A. F., Mason S. F.: Tetrahedron *33*, 937 (1977).
23. Meyer W. L., Loba A. P.: J. Am. Chem. Soc. *83*, 4609 (1961).
24. Lightner D. A., Gawronski J. A., Bouman T. D.: J. Am. Chem. Soc. *102*, 1983 (1980).
25. Barnes C. S., Djerassi C.: J. Am. Chem. Soc. *84*, 1962 (1962).
26. Bauman T. D., Moscowitz A. J.: J. Phys. Chem. *48*, 3115 (1968).
27. Gedanken A., Duraisamy M., Huang J., Rachon J., Walborsky H. M.: J. Am. Chem. Soc. *110*, 4593 (1988).
28. Robin M. B.: *Higher Excited States of Polytomic Molecules*, Vol. 2, pp. 26—27, 30. Academic Press, New York 1976.
29. Demo D. A.: *Thesis*. UCLA 1969.
30. McDiarmid R.: J. Chem. Phys. *84*, 64 (1980).
31. Belanger G., Sandorfy C.: Chem. Phys. Lett. *3*, 361 (1969); J. Phys. Chem. *55*, 2055 (1971).
32. Paquette L. A., Doecke C. W., Kearney F. R., Drake A. F., Mason S. F.: J. Am. Chem. Soc. *102*, 7229 (1980).
33. Weigang O. E.: J. Am. Chem. Soc. *101*, 1965 (1979).
34. Scott A. I., Yeh C. Y.: J. Chem. Soc., Faraday Trans. 2 *71*, 447 (1975).
35. Rodger A.: Private communication.
36. Steinberg N., Gafni A., Steinberg I. Z.: J. Am. Chem. Soc. *103*, 1636 (1981).