+ Na]$^+$ ions is about 2, suggesting sodium carceplex ions as the major precursor of fragments. Furthermore, the presence of fragment ions, indicative of rupture of bridging $-O-CH_2-O-$ groups (e.g. m/z 2119.7 $[M - OCH_2O - O]^+$), *which could only derive from the sodium carceplex*, support this interpretation. Obviously loss of all or portions of the pendant ethylphenyl groups, which are also observed (e.g. m/z 1971.6 $[M - PhCH_2CH_2 - O + Na]^+$ and m/z 1997.6 $[M - PhCH_2CH_2 - H + Na]^+$, could occur from either the sodium carcerand or the sodium carceplex precursors. However, taken as a whole, the photodissociation results suggest ring opening to release incarcerated guests is taking place.

Conclusions

Under the laser desorption conditions employed in the present study, carceplexes **1c** with incarcerated dimethylformamide, dimethylacetamide, and dimethyl sulfoxide are sufficiently stable to retain at least some of the guest species in the resulting sodium-attached ions. Furthermore, the degree of guest retention parallels the size order, with the smallest guest being retained most, as expected. It appears that the larger guests lower the barrier to ring opening due to release of steric strain associated with their incarceration. Because of the requirement that the carcerand ring open to permit egress of incarcerated guests, the abundant ions with m/z 2103.7 $[M + Na]^+$ appearing in both the laser desorption and the LD-photodissociation spectra of all three carceplexes must be either ring-opened species or ring-closed species which opened to allow guest departure and subsequently recyclized.

When the doubly-bridged hemicarceplex **1a**–DMA is subjected to the same laser desorption conditions, only free hemicarcerand sodium-attached ions are observed. This behavior parallels that observed upon heating the compound in solution and is not unexpected, due to the relative size of its portals, which permit free egress of guest molecules. Equally important, gas-phase formation of the hemicarceplex also is facile, due to the ease with which neutral solvent can effect entry and the ability of the hemicarceplex interior to serve as a molecular receptor. In fact, under appropriate conditions the hemicarcerand can be converted almost quantitatively to **1a**–DMA. However, a significant amount of the triply-bridged hemicarcerand–α-pyrone host–guest complex derived from **1b** survives laser desorption, and although the parent hemicarcerand also can be shown to form complexes with guests in the gas phase, these reactions appear somewhat less facile than the corresponding reactions of **1a**, consistent with the more restricted access of potential guests to the hemicarcerand's inner phase. Thus, for the triply-bridged hemicarcerand, the more bulky α-pyrone complexes to the extent of about 20%, while DMA complexes with about 78% of the hemicarcerand ions. In summary, the gas-phase chemistry of these substances is consistent with that observed in solution. Finally, the ability to produce and retain substantial amounts of hemicarceplex ions under FTMS trapping conditions raises the intriguing possibility of pursuing gas-phase studies of incarcerated guest chemistry similar to those carried out in solution. This is a prospect we hope to explore.

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The Role of Deuterium in Optical Activity: The CD Spectrum of (*S*,*S*)-Dideuteriooxirane

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Abstract: The circular dichroism of (*S*,*S*)-$[2,3\text{-}^2H_2]$oxirane has been investigated in the gas phase over the 1800–1500-Å region. While the absorption spectrum reveals only two allowed transitions, the CD spectrum shows a third transition which is magnetic dipole allowed and electric dipole forbidden. The CD sign of the first excited state complies with a quadrant rule which was formulated for the oxirane chromophore. This consignate behavior is contrary to the role of deuterium in carbonyl compounds, where an antioctant behavior is observed.

The circular dichroism of the oxirane chromophore has recently been the subject of many experimental[1-5] and theoretical studies.[2,6,7] The interest in oxirane is in part due to its role as a building block for asymmetric synthesis.[8] Optically active oxiranes can be synthesized from naturally occurring chiral compounds.[9,10] Its small size and its rigid skeleton make the oxirane moiety an ideal candidate for ab initio calculations of its rotatory strength.[2,6]

The absorption of oxirane was first reported by Liu and Duncan[11] and by Lowrey and Watanabe.[12] In both of these studies all the sharp features were assigned as members of Rydberg or valence transitions. These assignments were later questioned in an extensive study by Basch et al.[13] They measured the absorption of gaseous oxirane, a solid film of oxirane, and a

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solution of oxirane in hexafluoroacetone. The vibrational structure was completely washed out in the last two techniques, demonstrating the Rydberg character of all the structured bands. The similarity of the vibrational structure of the photoelectron and absorption spectra have further substantiated their assignment.

Strong signals are detected in the CD measurements of alkyl-substituted oxiranes with $\Delta\epsilon/\epsilon$ in the range of $1-4 \times 10^{-3}$.[1-4] The first CD band, peaked at 1730 ± 20 Å, is assigned as the n(O) → 3s Rydberg transition where n(O) represents a nonbonding electron on the oxygen atom. This transition in alkyl-substituted oxirane is only slightly dependent on the nature of the substituent. The sign of the CD of this transition, the n(O) → 3s, for 12 alkyl-substituted oxiranes was found to be related to absolute configuration.[3,4] This correlation is formulated as a $+XY$ quadrant rule, stating that if the alkyl substituent is located in a quadrant having $X > 0$ and $Y > 0$ or $X < 0$ and $Y < 0$, a positive CD will be observed, while a negative CD signal will be observed for the other two quadrants, where X is the out-of-plane axis and Z is the 2-fold axis in the plane. This quadrant rule holds also for epichlorohydrin, where a chloromethyl group is bonded to the ring.[5] We could not find any correlation between the CD sign of the second transition and the absolute configuration of the molecule because the CD of the second transition, n(O) → 3p Rydberg, is always the sum of the three contributions of the 3p manifold to the CD.

Two theoretical approaches toward the explanation of the observed spectrum have been applied. Quantum chemistry ab initio calculation, on the one hand, was able to reproduce the CD sign of the n(O) → 3s and n(O) → 3p Rydberg transitions of (*S*)-2-methyloxirane and (*S*,*S*)-2,3-dimethyloxirane.[2] The semiempirical approach, the coupled oscillator mechanism of Kirkwood[14] and Kuhn,[15] was also applied to the oxirane chromophore and through an independent systems/perturbation approach[7] has successfully been able to account for the sign of the CD signal of all oxiranes studied. The calculated sign matched the observed CD for the n(O) → 3s as well as the n(O) → 3p transition. The contribution of n(O) → $3p_y$ was not included in the calculations because it is electric dipole forbidden.[7]

The role of a deuterium atom in optical activity has been extensively investigated and documented.[16,17] The CD of most of the carbonyl compounds studied showed that deuterium substitution leads to antioctant behavior for the n → π^* transition. This behavior is demonstrated when a deuterium atom is placed in a positive back octant of a carbonyl compound exhibiting a negative CD sign, for the n → π^*, while all other substituents (except an F atom) will show a positive CD signal.[18] Although the dissignate behavior of the deuterium atom appears also in other chromophores,[19] there are also chromophores for which a consignate perturbation of the deuterium atom was observed.[20]

Theoretical attempts to interpret the role of a deuterium substituent and especially the antioctant behavior in carbonyls have changed over the years. The first attempt was to correlate the CD sign and amplitude with differences in electronegativity between H and D,[21] D being assumed to be more electronegative. Using this concept and CNDO/2 calculations, Meyer et al.[21] concluded that D should behave as a dissignate perturber. Other explanations, such as those of Dezentje and Dekkers[22] and Lightner and Bouman,[23] have assumed that a molecule that is made chiral only by isotopic substitution has an equilibrium structure which is achiral, namely, it does not differ from that of the parent compound. However, optical activity is introduced through the unharmonic oscillation of nuclei around their equilibrium positions. The rotatory strength was calculated around the average geometry, in which the molecule is chiral, and not the equilibrium geometry. An assumption was made, therefore, that the only effect that replacement of H by D or ^{16}O by ^{18}O has on the molecular geometry is the shortening of the average bond lengths.[22,23] In all the calculations that have been carried out based on this assumption, the correct sign was predicted.

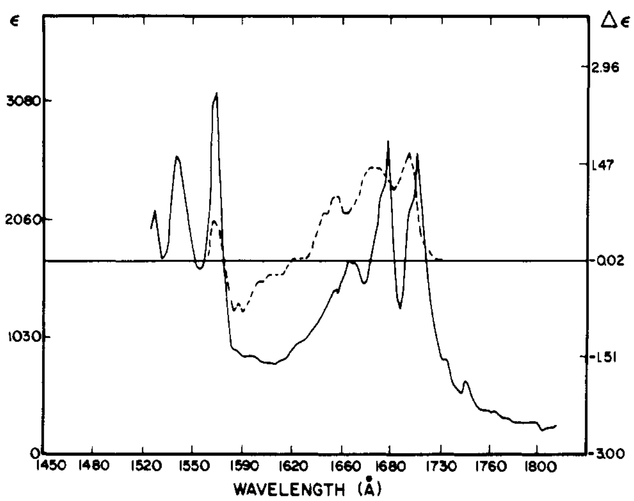

Figure 1. The absorption (—) and CD (- - -) of (*S*,*S*)-dideuteriooxirane in the gas phase. The spectral resolution in the CD measurements is 16 Å, and 4 Å in the absorption. The units of ϵ and $\Delta\epsilon$ are $mol^{-1}\ cm^{-1}\ L$.

The CD and absorption spectra of (*S*,*S*)-dideuteriooxirane are reported in this study. The measurements were carried out in the gas phase. This means that we probe the individual molecules, not molecules surrounded by solvent. This way we also avoid shifts or disappearance of Rydberg transitions which occur when the molecule is embedded in a solution or a solid matrix.[24] The role of the deuterium atom in effecting the optical activity in the oxirane chromophore will be compared with its role in other chromophores, such as the carbonyl moiety.

Experimental Section

The VUVCD instrument used in this study has been described previously.[25] The synthesis of (*S*,*S*)-dideuteriooxirane (DDO) has been reported elsewhere.[26] The DDO sample was subject to freeze and thaw cycles before its introduction in the measurement cell. The vapor pressure was measured using a Wallace and Tiernan absolute pressure gauge. The samples were measured in an 11-cm cell.

Results and Discussion

A. Spectroscopic Results: Optical Spectrum. The absorption and CD spectra are presented in Figure 1. The spectroscopic information that is contained in the absorption data will be outlined first. The absorption spectrum reveals two Rydberg transitions, the lowest being n(O) → 3s, whose origin is peaked at 58 510 ± 30 cm^{-1}, and the n(O) → 3p, whose origin is located at 63 630 ± 30 cm^{-1}. Comparison of the locations of these two origins and the corresponding origins in unlabeled oxirane yields isotopic shifts of 130 cm^{-1} and 30 cm^{-1} for the n(O) → 3s and n(O) → 3p transitions, respectively. These isotopic blue shifts are comparable to those obtained in other molecules.[27]

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The vibrational structure is similar to that seen in the spectrum of unlabeled oxirane, except for a hot band which appears at −1175 cm^{-1} to the red of the n(O) → 3s Rydberg transition. This band is assigned as the $3^0{}_1$ transition. The value of the ν_3 vibration (ring stretching vibration) is between the 1271 cm^{-1} observed for unlabeled oxirane and 1013 cm^{-1} measured for C_2D_4O. The assignment of the various peaks is according to the previous results of Basch et al.[13] and Lowrey and Watanabe.[12] The absence of active nontotally symmetric vibrations and the appearance of only short progression of the totally symmetric vibrations, consisting of one member of ν_3 and ν_5, indicate that the configuration of the molecule is almost unchanged upon excitation to the Rydberg states. This is not surprising since the electron is promoted from a nonbonding orbital and terminates in a nonbonding Rydberg orbital.

B. CD Spectrum. The CD spectrum in the n(O) → 3s region shows a positive signal which is slightly shifted to the blue, as compared to the absorption spectrum. The typical vibrational structure revealed in the absorption spectrum is repeated in the CD although somewhat less resolved owing to the lower resolution of the CD spectrum. At 1590 Å a negative CD band is observed which does not have a corresponding absorption peak. This peak will be assigned to the n(O) → $3p_y$ Rydberg transition. This transition in the symmetric chromophore has an A_2 symmetry and is therefore electric dipole forbidden and magnetic dipole allowed. A transition having such characteristics should appear in the CD spectrum and not in the absorption. Similar behavior has been observed in olefins[28] and cyclopropane.[29] The n → π^* transition in carbonyls is also magnetic dipole allowed and electric dipole forbidden and indeed appears strongly in CD and weakly ($\epsilon \sim 30$) in the absorption spectrum. This assignment does not agree with Rodger's[7] assumption claiming that the CD of the n(O) → $3p_y$ is very small.

The other two n(O) → 3p transitions, the n(O) → $3p_x$ and n(O) → $3p_z$, are both electric dipole allowed. The positive CD band at 1571 Å overlaps the allowed n(O) → 3p absorption bands. However, from the available data it is impossible to determine whether it is the n(O) → $3p_z$ or the n(O) → $3p_x$.

C. The Role of a Deuterium Substituent. The main motivation for the study of the CD in (*S*,*S*)-dideuteriooxirane was the examination of the deuterium role in the oxirane system. The *S*,*S* enantiomer yields a positive signal for the n(O) → 3s Rydberg transition. Since the deuterium atoms are positioned in a positive quadrant, the results indicate a consignate behavior for the deuterium atom. This result is different from the antioctant behavior observed for carbonyls. A reasonable explanation for this difference would be that the character of the n → π^* transition in carbonyls is a magnetic dipole allowed, electric dipole forbidden transition; the n(O) → 3s transition, on the other hand, is electric dipole allowed. However, the coupling mechanisms applied to the n → π^* in carbonyls[32] show that the isotropic polarizability[33] of a nonpolar and uncharged substituent makes the dominant contribution to the CD. This is also the case for the n(O) → 3s transition in oxiranes.[7] We would therefore have expected that the aforementioned effect of the deuterium atom on the sign of the CD signal would be the same in both systems. In their theoretical study regarding the antioctant behavior of the D atom in carbonyls, Lightner et al.[23] concluded that the C–D bond contributes less than does its mirror image C–H counterpart, due to its lower polarizability. It seems that since exceptions to the oxirane quadrant rule have not been found as yet, our results point out that the C–D bond contributes more than does the C–H bond. Our results rule out correlation of the CD with the difference in polarizabilities of the C–H and C–D bonds, which would also predict the C–H bond as the dominant feature determining the sign.

All the existing models explaining optical activity contain $r_C{}^{-n}$ as one of their common factors, where r_C is the distance between the chromophore and the substituent. Rodger[7] has shown that, for the n(O) → 3s transition in oxirane, the coupled oscillator mechanism, for which $r_C{}^{-2}$ is obtained, is dominant over all mechanisms. It seems that when $r_{C-D}{}^{-2}$ is weighed against $r_{C-H}{}^{-2}$ it predicts a larger contribution for the deuterium atom.

Conclusion

The role of a deuterium atom in creating optical activity in (*S*,*S*)-dideuteriooxirane has been demonstrated in this work. The magnitude of the signal observed ($\Delta\epsilon/\epsilon \simeq 6 \times 10^{-4}$ for the first excited state) is smaller than that of a methyl group,[1,2] but as strong as that of a hydroxyl substitute.[30] For (*S*,*S*)-(−)-2,3-dimethyloxirane, a value of $\Delta\epsilon/\epsilon \simeq 1.25 \times 10^{-3}$ is obtained.[2] In general, when a methyl substituent is compared with a deuterium atom, the ratio between their signals (versus a hydrogen atom) is dependent on the chromophore and the nature of the excited state, and the ratios observed vary between 36[31] to 3.[23] We consider the (2:1) ratio of the CD signals for the n(O) → 3s transitions for methyl and deuterium substituents of the oxirane chromophore to be within the limits of previous observations.[23,27]

The signs of the CD signals of the first excited state for oxiranes with methyl or deuterium substituents located in the same quadrant are the same, in contrast to the antioctant behavior of D in carbonyls.

This leaves the chirality rule formulated for substituted oxiranes without any exceptions.

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