Excited States of Ethylene Oxide. C.D. Spectrum of (*S*,*S*)-(−)-2,3-Dimethyloxiran

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Summary The circular dichroic and absorption spectra of a substituted ethylene oxide have been measured in the spectral region of 185—150 nm, the former revealing a transition that is not observed in the gas-phase absorption spectrum of ethylene oxide or a derivative.

THE spectroscopy of cyclic ethers has been the object of several theoretical[1,2] and experimental[1,3,4] studies. The sharp bands which appear in the gas phase at 58 380, 63 610, and 69 680 cm^{-1}, and which are not observed in the solid spectrum,[1] could be assigned as Rydberg transitions terminating in 3s, 3p, and 3d orbitals, respectively. Two valence transitions have been observed at 69 500 and 85 000 cm^{-1} with a slight hint of yet another at 63 000 cm^{-1}.[1] These valence bands are not structured and underlie the sharp Rydberg bands in the gas-phase absorption spectrum. The ionization potentials for ethylene oxide and several derivatives have been obtained from photoelectron measurements[1,5] and the c.d. spectra of aliphatic ethers in the gas phase have been measured in the spectral region of 200—140 nm;[6] the main bands being assigned to $n_0 \rightarrow 3s$, $n_0 \rightarrow 3p$, and $n_0 \rightarrow 4s$ transitions.

In the present work we have measured the c.d. and absorption spectra of (*S*,*S*)-(−)-2,3-dimethyloxiran, a compound prepared from (*S*,*S*)-(+)-butane-2,3-diol in a four-step procedure which is described elsewhere.[7,8] The compound was found to contain 98% of the (*S*,*S*) enantiomer $[\alpha]_{6328\,\text{Å}} = -37{\cdot}4°$ (neat). Vapour-phase spectra were obtained at room temperature with a vacuum u.v.-c.d. instrument,[9] using a sample cell of 5 cm in length. The vapour pressure of the sample was measured with a Celesco P7D capacitance manometer.

The c.d. spectrum of the (*S*,*S*)-(−)-dimethyloxiran (Figure) reveals four bands, at least one of which (1665 Å, negative signal) does not have a corresponding peak in the absorption spectrum.

The two positive bands at 1755 and 1602 Å are assigned as the $n_0 \rightarrow 3s$ and $n_0 \rightarrow 3p$ transitions on the following basis. (a) The term values for the 3s and the 3p transitions are 23 500 and 18 800 cm^{-1}, respectively, and agree well with the limit reached by the term values of substituted ethers.[10] (b) The vibrational structure observed for the $n_0 \rightarrow 3s$ band (1100 ± 50 cm^{-1}) is very similar to the spacing observed for the same transition in ethylene oxide;[1] this argument also holds for the $n_0 \rightarrow 3p$ although the vibrational structure is less resolved.

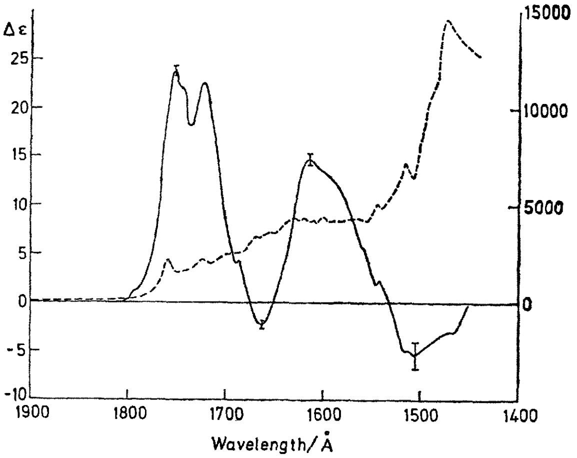

FIGURE. Absorption (- - - -) and c.d. (————) spectra of (*S*,*S*)-(−)-2,3-dimethyloxiran. The spectral resolution of the absorption and of the c.d. spectrum is 16 Å.

The negative c.d. band at 1655 Å is assigned as the $n_0 \rightarrow \sigma^*$ valence transition corresponding to the 63 000 cm^{-1} shoulder in the absorption spectrum of solid ethylene oxide.[1] The theoretical calculations predicted eight valence transitions which fall in the 10·5—13·5 eV region in ethylene oxide[1] the lowest being $2b_2 \rightarrow 7a_1\ \sigma^*$, where the $2b_2$ molecular orbital is an oxygen non-bonding orbital.

The first ionization potential of dimethyloxiran was measured as 9·98 eV.[5] Assuming a term value of 12 500 cm^{-1} for the 3d orbital one would expect the 3d Rydberg band to be observed at 1470 Å. While the c.d. and adsorption spectra show some negative character at this wavelength, the centre of the negative peak is certainly located at lower energies. We therefore suggest that the 1510 Å negative c.d. band should be assigned to a second valence band corresponding to the broad continuous band observed at 1440 Å in solid ethylene oxide.

We are grateful to Prof. V. Schurig and B. Koppenhoffer for helpful advice regarding the preparation of the (*S*,*S*)-(−)-2,3-dimethyloxiran. One of us (A. G.) thanks the Israel Commission for Basic Research for financial support.

(*Received, 6th May* 1980; *Com.* 476.)

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