

## INFRARED SPECTRUM OF DICYCLOHEXYL CARBODIIMIDE

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*(Received April 22, 1970)**Introduction*

The study of carbodiimides is of general interest because of their wide applications as condensing agents in peptide synthesis [1, 2]. The antisymmetric  $-\text{N}=\text{C}=\text{N}-$  stretching vibration of carbodiimides was studied by Korana [3] and Meakins and Moss [4]. Korana [3] studied the characteristic bands of  $\text{NHCONH}$  grouping of the ureas and urea derivatives of the corresponding carbodiimides and also the "fingerprint" region of the corresponding areas. However, no complete data of the infrared spectrum of the carbodiimides are available. The infrared spectrum of dicyclohexyl carbodiimide was studied in the  $650\text{--}4000\text{ cm}^{-1}$  region using the KBr disc.

*Experimental*

The infrared spectra were recorded using a Hilger H 800 spectrophotometer with NaCl optics. The dicyclohexyl carbodiimide synthesised by Eastman Organic Chemicals was used in the KBr matrix. The extinction co-efficients were determined in the solution phase, using as solvent carbon tetrachloride.

*Results and discussion*

Dicyclohexyl carbodiimide may be classified as belonging to  $C_i(S_2)$  point group with  $T = 51a_g + 54a_u$  as the representation or as  $C_{2v}$  point group, belonging to the group representation  $T = 36a_1 + 17a_2 + 17b_2$ , according as the angle between  $\text{R}-\text{N}$  and  $\text{N}-\text{R}'$  groups made at the central carbon atom,  $\text{R}$  and  $\text{R}'$  being the cyclohexyl groups in this case. We

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have made use of the conformational studies of cyclohexane derivatives [5-7] and some of the Raman effect data of cyclohexyl and dicyclohexyl compounds [8]. Use is also made of the infrared and Raman effect data [9] of dicyclohexyl carbinol for a comparison of the vibrations of the cyclohexyl groups. The frequencies and vibrational assignments are tabulated. (Table I).

The bands in the CH stretching region corresponding to the cyclohexyl rings were assigned accordingly depending upon the intensity, as belonging to the CH stretching vibration or the combination bands. A very strong band is observed at  $2133\text{ cm}^{-1}$  corresponding

TABLE I  
The infrared spectrum and vibrational assignments of dicyclohexyl carbodiimide

Frequency	Int.	Assignment	Frequency	Int.	Assignment
3338	M	(2857+481)	1178.0	M	C-C skeletal
2929	VS	CH stretching	1140.0	M	CH bending+twisting
2857	S	CH stretching	1134.5	M	
2786	W	(1438+1349)=2787	1115.5	M	CH bending
2659	W	(1622+1036)=2658	1077.5	M	C-N stretching
2133	VS	-N=C=N- stretching	1062.0	M	
1668	W	(835×2)=1670	1036	S	C-C skeletal
1622	S	C=N stretching	1027.5	S	CH bending
1576	M	(1349+227)=1576(?)	1013	S	C-C skeletal
1571	M		1009	S	C-C skeletal
1557	M	(782+773)=1555(?)	1005	M	
1527	W	(1300+227)=1527	995	M	CH bending+twisting
1465	M	CH bending	994	S	C-C skeletal
1443	S	CH <sub>2</sub> Scissoring	920	W	(227+693)
1438	S		883	S	C-C skeletal
1349	S	CH bending	868	W	(434×2)
1338	S	CH wagging+twisting	855	W	(427.5×2)
1305	M	CH wagging	835	M	CH bending
1299.5	S	C-C skeletal	829.5	M	CH bending
1292.0	S	CH bending	807.5	W	
1257.0	M	CH bending+twisting	782	M	CH bending
1248.5	M		773	M	CH bending
1230.0	M	CH bending+twisting	756	M	CH bending

Int. - Intensity; VS - Very strong; S - Strong; M - Medium and W - Weak.

to the antisymmetric  $\text{-N=C=N-}$  valence vibration. The earlier observations of Korana [3] and Meakins and Moss [4] have also shown one band corresponding to the  $2130\text{ cm}^{-1}$  band. The extinction coefficient of the  $2133\text{ cm}^{-1}$  band was determined using the dilute solution phase in carbon tetrachloride for a few concentrations, and was found to be in the range 1400-1450.

According to the assumed symmetry C=N symmetric stretching vibration should be inactive in the infrared. However, band is observed at  $1622\text{ cm}^{-1}$  corresponding to the

C=N valence vibration. Three bands of medium intensity are observed in the range 1550–1580  $\text{cm}^{-1}$ . These may be the bands corresponding to those observed in the case of ureas and urea derivatives. The other weak band is assigned to the combination band, where 227  $\text{cm}^{-1}$  may be assigned to C–C– out of plane bending vibration.

The bands belonging to the other vibrations can be classified as  $\text{CH}_2$  scissoring, CH bending (inplane and out of plane), CH wagging, CH twisting, C–C– skeletal vibrations characteristic of the cyclohexyl ring and C–C– bending vibrations. Two strong bands are observed corresponding to  $\text{CH}_2$  scissoring. The assignments of other vibrations are made on the same line with the compounds containing cyclohexyl groups. The weak bands at 868  $\text{cm}^{-1}$  and 855  $\text{cm}^{-1}$  may be the first overtones of their corresponding vibrations at 434  $\text{cm}^{-1}$  and 427.5  $\text{cm}^{-1}$  and may belong to the C–C– out of plane bending vibrations of the cyclohexyl compounds. On similar grounds the band near 920  $\text{cm}^{-1}$  may also correspond to the combination band, the 693  $\text{cm}^{-1}$  frequency being assigned to the C–C– bending.

The present study of the infrared spectrum of dicyclohexyl carbodiimide, combined with the Raman effect studies will give a clear picture of the structure of the compound, and will be useful in the conformational studies. The Raman effect studies of the Dicyclohexyl carbodiimide is also being undertaken presently. The study of infrared and Raman spectra of a few other carbodiimides are also being undertaken to acquire a complete understanding of the influence of the various groups on the vibrations of the N=C=N group, and the effect of the carbodiimide group over the substituent groups.

One of the authors (V.R) is thankful to the Council of Scientific and Industrial Research, Government of India, New Delhi for the award of a Junior Research Fellowship.

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