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ON THE CONFORMATION OF CYCLOHEXANE-1,4-DIONE AND ITS DERIVATIVES—I

INFRARED AND RAMAN SPECTRA OF CYCLOHEXANE 1,4-DIONE AND INFRARED SPECTRUM OF ITS OCTADEUTERO ANALOGUE

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Abstract—Raman spectra of cyclohexane 1,4-dione (I), in chloroform, benzene and water solutions have been recorded. Temperature effect on the spectrum has been studied. The IR spectra of I and its octadeutero analogue in the solid state have also been studied. The spectra have been found on the basis of selection rules applicable for Raman and IR spectra, to be consistent with a single conformer of C_2 symmetry. Plausible causes of conformational preference have been discussed.

INTRODUCTION

THE existence of cyclohexane derivatives normally in the chair conformation in preference to alternative conformations is a widely accepted tenet of conformational analysis.[1–4] It is believed that in this arrangement, the high rotational barriers shelter it from distortion and confer stability and rigidity. Recent work has increasingly brought to light cases where six membered rings do depart from the chair conformation when it is not energetically preferred.[5–7] Nevertheless, in the absence of definite evidence to the contrary, it is customary to take for granted the chair conformation.

It is common practice to infer the conformation of sixmembered rings with triogonal carbon atoms by analogy with cyclohexane.[8–10] Doubts about the relevance of analogy in the case of cyclohexane-1,4-dione (I) came from the work of LeFèvre and LeFèvre, who found that it had a moment of 1·2D.[11] They interpreted their data as

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[1] D. H. R. Barton and R. C. Cookson, *Quart. Revs.* **10**, 44 (1956).

[2] O. Hassel and B. Ottar, *Acta Chem. Scand.* **1**, 929 (1947); O. Hassel, *Quart. Revs.* **7**, 221 (1953).

[3] W. G. Dauben and K. S. Pitzer, *Steric Effects in Organic Chemistry* (Edited by M. S. Newman) p. 1. J. Wiley, New York (1956).

[4] E. L. Eliel, *Stereochemistry* p. 204. McGraw-Hill, New York (1962).

[5] D. H. R. Barton, D. A. Lewis and J. F. McGhie, *J. Chem. Soc.* 2907 (1957).

[6] M. V. Bhatt, *Chem & Ind.* 1452 (1959); M. V. Bhatt, *Proc. Summer School in Organic Chemistry*, Shillong, p. 1. Council of Scientific and Industrial Research, India (1961).

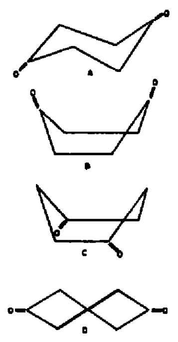
[7] M. Balasubramanian, *Chem. Revs.* **62**, 591 (1962).

[8] D. H. R. Barton, R. C. Cookson, W. Klyne and C. W. Shoppee, *Chem & Ind.* 21 (1954).

[9] P. A. Robins and J. Walker, *J. Chem. Soc.* 3960 (1954); *Ibid.* 1789 (1955); *Chem & Ind.* 727 (1955).

[10] B. J. Armitage, G. W. Kenner and M. J. T. Robinson, *Tetrahedron* **20**, 723, 747 (1964); W. D. Cotterill and M. J. T. Robinson, *Ibid.* **20**, 765 and 777 (1964).

[11] C. G. LeFèvre and R. J. W. LeFèvre, *J. Chem. Soc.* 3549 (1956).



evidence for the existence of 20% boat conformer-C in equilibrium with the predominant chair conformer-A.[12]

The present investigation was started in order to examine whether I exists in a single or in more than one conformation, and also to find out the factors that determine the conformational preference. We restrict ourselves in the present paper to the presentation of spectral data obtained and their interpretation. These data are consistent with a single twist conformation of C_2-symmetry.

After this investigation was started a good deal of work on cyclohexane-1,4-dione and its derivatives in support of a twist conformation has been published.[13] In a preliminary communication, Allinger and Boyce have found that the Raman spectrum of cyclohexane-1,4-dione (solid) and the IR spectrum (solid and molten state) are not consistent with the chair form A.[14] Furthermore, they suggest that the dipole moment data and the spectral data are consistent with the twist form D. More recently, Groth and Hassel have confirmed this view by a X-ray diffraction study of the mercuric chloride addition compound of cyclohexane-1,4-dione.[15]

EXPERIMENTAL

Cyclohexanone-1,4-dione was prepared from quinol dimethylether by the method of Birch[16] in 45% overall yield, m.p. 74–75°. Recrystallization (EtoAc) gave transparent plates m.p. 78°, lit.[16] m.p. 78°.

Preparation of octadeuterocyclohexane-1,4-dione (II). A solution of cyclohexane-1,4-dione (1·0 g) in 99% D_2O (7 ml), and anhydrous K_2CO_3 (10 mg) were mixed and allowed to stand overnight under N_2. Heavy water was evaporated under red. press. and the residue sublimed between 110–120° at 0·5 mm to yield 370 mg of transparent plates m.p. 78–79°. (Found: C, 60·26, 60·10, D, 13·47, 13·51, Calc. for $C_6D_8O_2$; C, 60·0; D, 13·33%).

The Raman spectra of I was taken using a horizontal helical low press Hg arc as the source, with λ 4358 Å as the exciting radiation. The compound gradually decomposed when violet, or UV radiation was used. The Raman spectra in benzene and $CHCl_3$ solutions were taken at 28°, and that of water solution at 28° and 68°. All the spectra were taken with a Hilger two prism spectrograph which has a reciprocal liner dispersion of about 30 Å/mm in λ 4358 region. Agfa Raman orthochromic

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[12] Recently Chen and LeFèvre have reported that a reinterpretation of their results indicates that I exists in a single twist conformation D. C. Y. Chen and R. J. W. LeFèvre, *Austr. J. Chem.* **16**, 917 (1963).

[13] R. D. Stolow and M. M. Bonaventura *Tetrahedron Letters* No. 2, 95 (1964) and Refs. cited therein.

[14] N. L. Allinger and C. B. Boyce, *J. Amer. Chem. Soc.* **83**, 5028 (1961).

[15] P. Groth and O. Hassel, *Tetrahedron Letters* No. 2, 65 (1964).

[16] A. J. Birch, *J. Chem. Soc.* 102 (1947).

plates were used for recording the spectra. An exposure of one day was found necessary for each spectrum. A filter of $NaNO_2$ was used to cut off the 4047 and 4040 A-radiations.

Attempts to record the Raman spectrum in the molten state failed, because of the decomposition of the compound. IR spectra were recorded on a Perkin-Elmer Model 221 instrument, and on the Perkin-Elmer Infracord Model 137 B. The readings from the Infracord were checked and calibrated against those obtained on the model 221.

All solvents used were purified before use.

TABLE 1. RAMAN FREQUENCIES OF CYCLOHEXANE-1,4-DIONE IN CM^{-1}

	Assignment		Chloroform 28°	Water 28°	Water 68°	Benzene 28°
1.	C—C—	bending	201			
2.	C—C—	bending	224			
3.	C—C—	bending	311			
4.	C—C—	bending	410	423	423	
5.	C—C—	bending	524	528	528	
6.	C—C—	bending	598	597	597	
7.	Ring	breathing	725	728	728	724
8.	C—C—	skeletal	1007	1011	1011	
9.	C—C—	skeletal		1081	1081	
10.	C—C—	skeletal (carbonyl)	1217	1219	1219	1219
11.	C—H	wagging	1310	1304	1304	1304
12.	CH_2	methylene scissoring	1422	1414	1414	
13.	CH_2	asymmetrical bending	1458			
14.	C=O	stretching	1727	1710	1710	1723
15.	C—H	stretching	2902	2907	2907	2902
16.	C—H	stretching	2975	2977	2977	2975

RESULTS AND DISCUSSION

The NMR spectrum of I deuterochloroform solution showed a single signal at 7·28τ (with tetramethylsilane as the standard) indicating the absence of enol and consistent only with a single conformer with all protons equivalent.

The frequency shifts of the Raman lines observed for I in benzene and chloroform taken at 28° and in water solution at 28° and 68°, are given in Table 1. The largest variation was shown by the carbonyl stretching vibrations: νH_2O^{1710}, $\nu CHCl_3^{1727}$, $\nu C_6H_6^{1723}$ cm^{-1}. These variations may be due to hydrogen bonding and changes of solvent polarity. Apart from these minor changss, the position, number and intensity of the Raman lines are not affected significantly by solvent or temperature. (Fig. 3) These results do not therefore reveal the existence of more than one conformer at equilibrium particularly with widely different dipole moments.

It is possible to conceive of four distinct types of conformations for I viz. A, B, C and D. In principle, it is usually possible to decide between these possibilities with the help of selection rules operative for Raman and IR spectra of the different forms.

The number of lines actually observed in 700–1500 cm^{-1} region is 19, in the IR (Fig. 1). In the Raman spectrum there are 14 lines in 200–1500 cm^{-1} region (Table 1), many of which coincide with the IR frequencies (Table 2). Since for model A the mutual exclusion rule should apply, the spectral data suggest that model A is not the predominant one. Also there is no special evidence for favouring model B, which would give rise to a larger number of lines in the Raman than in the IR (Table 3). The spectral data are therefore in better accord with the theoretical predictions for the conformers C and D. Because of the fair degree of correspondence (cf. Tables 1 and 2) between the Raman and IR spectra, we conclude that I exists ordinarily in a conformation C or D in solution (cf. Table 3).

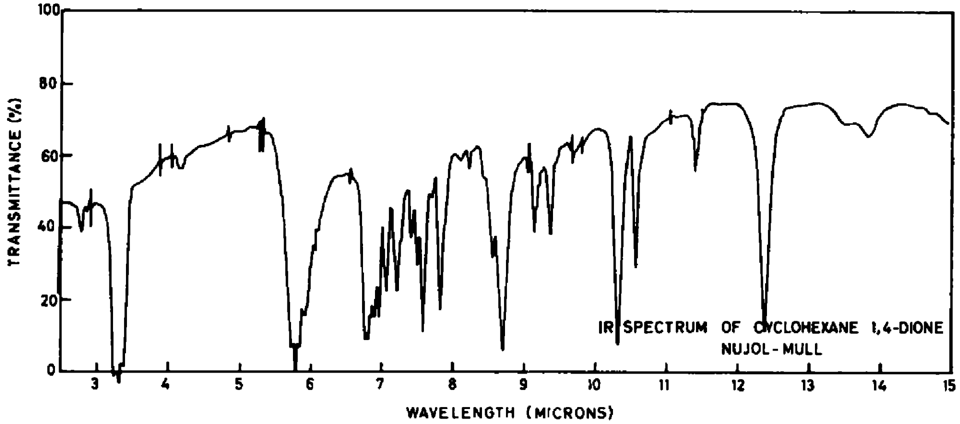

FIG. 1

We have also studied the IR spectrum of octadeuterocyclohexane-1,4-dione (II; Fig. 2). The object of this study was two-fold. Firstly, it enables a study of the influence of smaller effective Van der Waals' radii and reduced non-bonded interactions[17] due to the deuterium atoms on the conformation of I. Secondly, it becomes

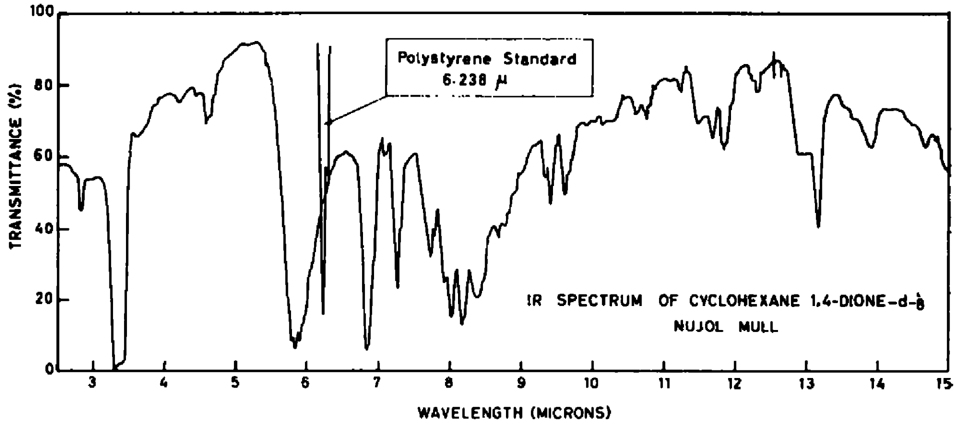

FIG. 2

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[17] L. S. Bartell, *J. Amer. Chem. Soc.* **83**, 3567 (1961), cf. also K. Mislow, R. Greave, A. J. Gordon and G. H. Wahl Jr., *Ibid*, **85**, 1199 (1963) and L. Melander and R. E. Carter, *Ibid*, **86**, 295 (1964).

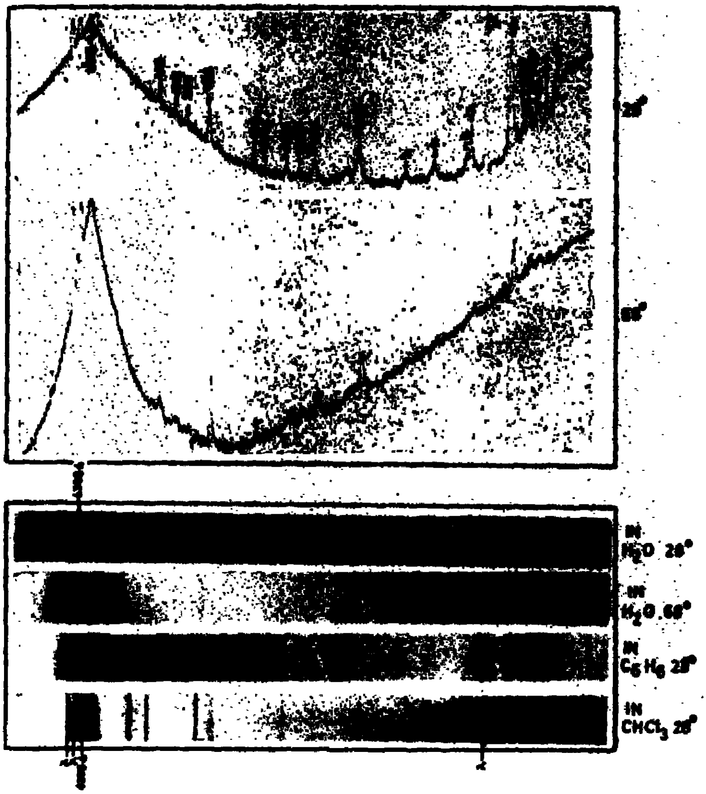

Fig. 3

TABLE 2*. INFRARED FREQUENCIES OF CYCLOHEXANE-1,4-DIONE AND CYCLOHEXANE-1,4-DIONE-d_8 IN CM^{-1}

	Assignment		Cyclohexane 1,4-dione Nujol mull	Cyclohexane 1,4-dione-d_8 Nujol mull	Cyclohexane 1,4-dione Halocarbon mull	Cyclohexane 1,4-dione-d_8 Halocarbon mull
1.	C—C	Skeletal	720	730	740	740 (broad)
			—	755		
			—	773		
2.	C—H	Bending	803	—	802	
			—	843		
			—	855		
3.	C—C—	Skeletal	870	872		
			—	890		
			—	903		
4.	C—C	Skeletal	957	952	955	
5.	C—H	Bending and twisting	968	—		
			—	985		
			—	1043		
6.	C—C	Skeletal	1061	1061	1059	1061
7.	C—H	Bending and twisting	1088	—		
			—	1121		
8.	C—H	Bending and twisting	1144	—		
9.	C—C	Skeletal	1161	1166		
10.	C—C	Skeletal	1212	1203		
11.	C—H	Bending and twisting	1233	—		
			—	1261		
12.	C—H—	Bending and twisting	1274	—		
13.	C—C	Skeletal	1294	1294	1289	
14.	C—H	Wagging	1311	—	1311	
15.	C—H	Wagging and twisting	1328	—	1326	
			1344	—	1341	
16.	C—H	Methylene	1407	—	1403	
		Scissoring	1434	—	1424	
17.	C—H—	Bending	1444	—		
18.	C=O	Stretching	1719	1719	1719	
19.	C—D	Stretching		2179		2193
20.	C—H—	Stretching			2998	
21.	C—H—	Stretching			3072	

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* Peaks due to the medium or due to the instrumental difficulties or due to undeuterated impurity in the deuto compound have not been recorded.

TABLE 3. SYMMETRY CLASSES OF VIBRATIONS OF CONFORMATIONS A, B, C AND D

Type	A C_{2h}					B C_{2v}					C and D C_2			Observed	
	A_g	A_u	B_g	B_u	Total	A_1	A_2	B_1	B_2	Total	A	B	Total	Cyclohexane 1,4-dione	Cyclohexane 1,4-dione-d_8
Skeletal vibration	6	4	3	5	18	6	4	3	5	18	10	8	18	(I) 13	(II)
Raman	+	—	+	—	9	+	+	+	+	18	—	+	18	9	
Activity															
Infrared	—	+	—	+	9	+	—	+	+	14	+	+	18	7	7
Skeletal and C—H vibrations	12	10	9	11	42	12	10	9	11	42	22	20	42	28	
Raman	+	—	+	—	21	+	+	+	+	42	+	+	42	14	
Activity															
Infrared	—	+	—	+	21	+	—	+	+	32	+	+	42	21	18

+ — active — = inactive

possible to sort out the skeletal vibration from C—H vibrations in the IR spectrum of I.

The deutero-compound showed 17 lines in the IR between 700 to 1500 cm^{-1} region. These data confirm our assignment of skeletal vibrations. All the C—H vibrations would be missing in the spectrum of II, and would be replaced by C—D vibrations.

The question that remains is, why the twist conformation is preferred to the more commonly favoured chair form. *A priori*, three factors may be considered: (1) intermolecular forces (2) non-bonded repulsions and (3) entropy considerations. The influence of intermolecular forces in modifying conformational preference is well documented. For example, with 1,2-dibromoethane,[18] the staggered conformer is the exclusive form in the solid state. In passing to the liquid and the vapour states more of the skew form becomes favoured. Similarly, influence of polarity of the medium on the conformational preference has been observed in α-bromocyclohexanones. In passing from a non-polar to polar medium, the proportion of conformer with higher dipole moment increases.[19]

With I, influence of the medium was not perceptible. When the solvent was changed from benzene to water, the Raman spectra did not show significant changes. It seems, therefore, unlikely that the cause of the preference for the twist form may be found in the intermolecular forces.

Because deuterium has a smaller Van der Waals' radius than hydrogen[17] both the ethane barrier and the methylene carbonyl barrier would be reduced, as a consequence, by the substitution of deuterium for hydrogen. We expected, therefore, to find changes in the conformational preference if non-bonded interactions were the determining factor in favouring the twist form. A determination of the dipole moment of the octadeutero compound II showed that its dipole moment of 1·37 D was consistent with a conformation similar to that of I. Furthermore, we found[20] even when the ring is highly substituted as in tetrahalocyclohexane-1,4-diones, it still prefers the

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[18] S. Mizushima, *Structure of Molecules* p. 18. Academic Press, New York (1954).

[19] C. Djerassi, L. E. Geller and E. J. Eisenbraun, *J. Org. Chem.* **25**, 1 (1960).

[20] M. V. Bhatt and G. Srinivasan, unpublished observations.

twist conformation. It is difficult to reconcile these observations with the view that non-bonded interactions are responsible for the preference of the twist conformation in cyclohexane-1,4-dione.

Considering the third possible cause of conformational preference—entropy; a study of models reveals that there is not much difference between the non-bonded interactions in the chair and the twist forms (A and D). There is, however, a difference in the symmetry of the conformations. The chair form belongs to point group C_{2h} having a centre of symmetry. The twist form belongs to point group C_2. It is conceivable that D has higher vibrational and rotational entropy compared to A. In the absence of appreciable difference of enthalpy, the entropy term may control the sign of the free energy difference between A and D, rendering the latter, viz. the twist form, the favoured conformation.[21]

Acknowledgements—We wish to thank Prof. D. K. Banerjee for his interest in this work and Prof. R. S. Krishnan for providing the facilities in his department for the determination of the Raman spectra. We express our appreciation to Dr. Sukh Dev for the NMR data, Dr. P. S. Narayanan for helpful discussions on the interpretation of the Raman spectra and Dr. S. Soundararajan and Mr. V. N. Krishnamurthi for determination of the dipole moments.

[21] We plan to undertake a detailed calculation of the thermodynamic properties of cyclohexane-1,4-dione.