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On the Conformation of 1,4-Cyclohexanedione

Sir:

The outstanding example of a simple six-membered ring which is considered to exist either predominantly,[1,2] or in some part,[3–7] in a boat or polar nonchair conformation is 1,4-cyclohexanedione. The basis for this belief has rested largely on the observation of a dipole moment of *ca.* 1.3 D.[2a,3,5–8] The view that the molecule exists predominantly in a flexible nonchair conformation is a reinterpretation[1] of dipole moment data which were originally interpreted[3,5,6] in terms of an equilibrium between chair and boat in favor of the chair. Recent X-ray structure analyses[2] have also yielded a twist boat structure for which the calculated dipole moment is in good agreement with the value measured in benzene solution. Theoretical studies[1,4,9] support the experimental findings. Infrared, Raman,[1a,b] and nmr spectroscopic[1c,d] studies have been brought to bear on this problem.

We have found that 1,4-cyclohexanedione is a *nonpolar molecule* in the gas phase, using the molecular beam electric deflection method,[10] *i.e.*, the deflection (defocussing) of a beam of this molecule in an inhomogenous electric field (quadrupole focusser). Mass 112 was monitored and no refocussed beam was observed at 293, 374, 396, and 478 °K (Table I).

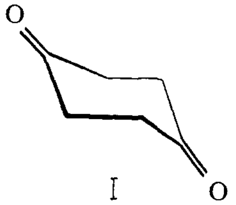
These data are incompatible with the molecule having a 1.3-D dipole moment and indicate that there is a negligible amount of polar molecules present in the temperature range studied. Although X-ray results[2] may result from intermolecular forces in the crystal[11] (reasons for this behavior are probably quite complex), our results are in direct contradiction to the dipole moment measurements in solution and in the gas phase.

Table I. 1,4-Cyclohexanedione Defocussing as a Function of Temperature

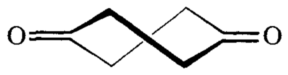
Temp, °K	Sensitivity[a]	Defocussed beam[b]		
		25/0[c]	0/25[d]	25/25[e]
293	0.34	0.06	0.06	0.00
374	0.30	0.08	0.08	0.00
396	0.32	0.08	0.07	0.02
478	0.31	0.12	0.14	0.14

[a] Scattered beam as per cent of straight-through beam. [b] Expressed as per cent of straight-through beam. [c] 25 kV on the A-field focusser. [d] 25 kV on the B field. [e] 25 kV on the A and B fields. Other samples run at room temperature did not show the small increase in signal at this voltage setting.

The experimental results can be interpreted in terms of a nonpolar chair I or fully extended twist boat II.



I



II

Also, complicated tunneling behavior connecting the various polar boat forms could occur. However, refocussing should be observed in the latter case if the potential energy barrier for the motion is not too low (*i.e.*, if the molecule is not completely "flexible"). As an example, ammonia, which has roughly analogous "inversion" behavior, refocusses strongly[12] from the vibrational states below the potential barrier (*i.e.*, the inversion doublets). Thus, it would seem reasonable that our results imply a chair or fully extended twist-boat conformation for the molecule. Our experiments cannot distinguish between these two possibilities. However, the relationship between the carbonyl group and the adjacent methylenes in the chair form is much more like that established for acetaldehyde,[13] which has eclipsed C=O and C—H bonds, than it is in the fully extended twist boat. The chair conformation would thus seem to be the most likely ground state for 1,4-cyclohexanedione in the gas phase.

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(1) (a) N. L. Allinger and L. Frieburg, *J. Amer. Chem. Soc.*, **83**, 5802 (1961); N. L. Allinger, H. M. Blatter, L. A. Frieburg, and F. M. Karkowski, *ibid.*, **88**, 2999 (1966); (b) M. V. Bhatt, G. Srinivasan, and P. Neelakantan, *Tetrahedron*, **21**, 291 (1965); (c) J. B. Lambert, *J. Amer. Chem. Soc.*, **89**, 1836 (1967); (d) C. Y. Chen and R. J. W. LeFevre, *Aust. J. Chem.*, **16**, 917 (1963).

(2) (a) A. Mossel, C. Romers, and E. Havinga, *Tetrahedron Lett.*, 1247 (1963); we are indebted to Professor R. B. Woodward for having pointed out this reference to us; A. Mossel and C. Romers, *Acta Crystallogr.*, **17**, 1217 (1964); the latter reference was kindly pointed out by Professor J. Z. Gougoutas, who also offered helpful discussion of it; (b) P. Groth and O. Hassel, *Proc. Chem. Soc.*, 218 (1963); *Acta Chem. Scand.*, **18**, 923 (1964).

(3) R. J. W. LeFevre and C. G. LeFevre, *J. Chem. Soc.*, 2696 (1935); 3549 (1956).

(4) P. Hazebrook and L. J. Oosterhoff, *Disc. Faraday Soc.*, No. **10**, 87 (1951).

(5) O. Hassel, *Quart. Rev., Chem. Soc.*, **7**, 221 (1953); *Trans. Faraday Soc.*, **30**, 874 (1934).

(6) M. T. Rogers and J. M. Cannon, *J. Phys. Chem.*, **65**, 1417 (1961).

(7) C. W. N. Cumper, G. B. Leton, and A. I. Vogel, *J. Chem. Soc.*, 2067 (1965).

(8) However, the dipole moment and the references cited above should be viewed in the light of the experiments and comments of A. Aihara, K. Chitoku, and K. Higasi (*Bull. Chem. Soc. Jap.*, **35**, 2057 (1962)) who report a dipole moment of 0.43 D for the title compound. See ref 1d for further confirmatory discussion of this illuminating paper.

(9) N. L. Allinger, *J. Amer. Chem. Soc.*, **81**, 5730 (1959).

(10) P. Dowd, T. Dyke, R. Neumann, and W. Klemperer, *ibid.*, **92**, 6325 (1970). See references cited therein for a discussion of the method.

(11) Of particular interest in this connection are the findings of P. Groth and O. Hassel (*Acta Chem. Scand.*, **19**, 1733 (1965); *Tetrahedron Lett.*, 65 (1964)) with respect to the X-ray structures of the diiodoacetylene and mercuric chloride complexes of 1,4-cyclohexanedione. The observation that the angle between the carbonyl groups in the latter case opens up to 175° might indicate some sensitivity of this molecule to its environment in the solid state.

(12) (a) J. P. Gordon, H. J. Zeiger, and C. H. Townes, *Phys. Rev.*, **99**, 1264 (1955); (b) W. E. Falconer, A. Büchler, J. L. Stauffer, and W. Klemperer, *J. Chem. Phys.*, **48**, 317 (1968).

(13) R. W. Kilb, C. C. Lin, and E. B. Wilson, Jr., *ibid.*, **26**, 1695 (1957).

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