

INVESTIGATIONS INTO THE CONFORMATION OF NON-AROMATIC RING  
COMPOUNDS XII (1).  
CYCLOHEXANEDIONE 1,4 AND RELATED COMPOUNDS

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Cyclohexanedione 1,4 in solution has a dipole moment that is significantly different from zero; more recent determinations seem to indicate a value of about 1.3 D (2,3,4). Oosterhoff (5) demonstrated by calculations on the basis of rather general assumptions concerning the rotational barriers that this value of the dipole moment is consistent with a conformational equilibrium in which the "stretched" flexible forms predominate (cf. also the discussions by LeFevre and LeFevre (3) and Allinger and Freiberg (4)).

In order to obtain more data on the question of the conformations in which the cyclohexanediones 1,4 occur, a number of compounds containing this system have been synthesized and their dipole moments (Table I) have been determined according to the method of Halverstadt and Kumler (6).

Table I - Dipole moments of some cyclohexanediones 1,4 at 298° K.

compound	$\mu$ (D)	solvent
cyclohexanedione 1,4	1.31	benzene
cis perhydronaphthoquinone 1,4	1.23	"
trans perhydronaphthoquinone 1,4	1.29	"
cis-cis perhydroanthraquinone 9,10	0.95	"
trans-trans perhydroanthraquinone 9,10	1.02	"
cis-trans perhydroanthraquinone 9,10	1.20	"
5,8 endomethyleneperhydronaphthoquinone 1,4	1.47	"
1,4; 5,8 diendomethyleneperhydroanthraquinone 9,10	2.65	"
2,3,5,6 tetrachlorocyclohexanedione 1,4	1.49	dioxane

It would appear that a dipole moment in the order of magnitude of 1 - 1.5 D is a normal feature of this class of compounds. The only exception has been found with the diendomethylene perhydroanthraquinone of which the middle ring could be expected to occur in a boat form on account of the influence of the annealed bicycloheptane rings and for which a dipole moment of 2.7 D has been determined.

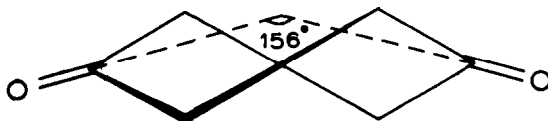
In order to investigate why these cyclohexanediones have a dipole moment of  $\sim 1.3$  D and in order to obtain more definite data on the preferred conformation of these compounds we decided to tackle this problem by X-ray analysis of cyclohexanedione 1,4.

The determination of the crystal structure at  $130^\circ$  K by means of diffraction data with Cu K $\alpha$  radiation gave the following information. The unit cell constants are:  $a = 6.65 \text{ \AA}$ ,  $b = 6.21 \text{ \AA}$ ,  $c = 6.87 \text{ \AA}$ ,  $\beta = 99^\circ 49'$ . The density is 1.28 at  $20^\circ$  C. The unit cell contains two molecules. The only extinctions are reflexions  $0k0$  with  $k$  odd, indicating the space groups  $P2_1$  or  $P2_1/m$ . The latter was rejected because a statistical analysis (7) of the reflexion data clearly favours the former acentric space group which is in accordance with the earlier supposition of Hassel (8).

The structure has been solved by interpretation of sharpened Patterson functions  $P(u,w)$  and  $P(u,v,w)$ . The reliability index  $R(hkl)$  is 15.1% in the present stage of refinement.

It can be concluded that

- .. The molecule does not have the chair conformation.
- !. The two carbonyl bonds are not collinear, the bonds making an angle of  $\sim 156^\circ$  with each other.
- .. The two  $(CH_2)_2C=O$  parts of the molecule are approximately planar.
- .. The molecule does not possess a centre of symmetry but occurs in a twisted cross-over conformation:



It is interesting to note that the lack of symmetry centre in the molecule is in agreement with Kitaigorodskii's rule (9) that centric molecules cannot occupy positions in acentric space groups.

The dipole moment for cyclohexanedione 1,4 of this conformation is calculated to be 1.27 D. This suggests that also in solution a conformation of the type found in the solid state may occur, as is further corroborated by the similarity of the infrared spectra in the solid state and in solution.

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