

## On the Molecular Structure of *cis*-1,4-Ditert.butylcyclohexane

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The electron scattering pattern from gaseous *cis*-1,4-ditert.butylcyclohexane at about 110°C has been recorded from  $s = 1 \text{ \AA}$  to  $45 \text{ \AA}^{-1}$ . The average bond lengths are  $\text{C}-\text{C} = 1.540 \pm 0.002 \text{ \AA}$  and  $\text{C}-\text{H} = 1.107 \pm 0.005 \text{ \AA}$ . The scattering pattern is found to be compatible with both the chair and the boat conformations. But since the best agreement between experimental and theoretical curves is obtained for the boat conformation it is regarded as the most probable.

Since the early work of Sachse<sup>1</sup> great interest has been shown in the conformational problems of the cyclohexanoid system. One of the outstanding features of this system is its ability to exist in two conformations which are known as the boat and chair forms. Electron diffraction investigations of cyclohexane and simple halogen-substituted derivatives by Hassel and co-workers<sup>2</sup> demonstrated that the chair form is predominant.

The chair form is rigid (*i.e.* it has no torsional degree of freedom) and strain-free, whereas the boat form is flexible (*i.e.* it has one torsional degree of freedom) and suffers in its various shapes from varying amounts of Pitzer and van der Waals strain. The chair form of cyclohexane is therefore more stable than the boat by 5.3 to 6.9 kcal/mole.<sup>3,4</sup> At room temperature, therefore, only one cyclohexane molecule in a thousand will be in the flexible form. But if the ring is disturbed, for instance by bulky substituents, the flexible form may become energetically the most favorable, and a number of cyclohexanoid systems in the boat form are known.<sup>5</sup>

It has been estimated that the strain introduced by an axial tert.butyl group is 5.6 kcal/mole greater than that of an equatorial group.<sup>6</sup> This substituent therefore prefers the less strained equatorial position, and in combination with smaller substituents the tert.butyl group has been used as a means for providing conformational homogeneity.<sup>6</sup>

If *cis*-1,4-ditert.butylcyclohexane is to exist in the chair form, one of the substituents must be axial, hence a strain is introduced which is comparable to the chair-boat energy difference.

The present study of gaseous *cis*-1,4-ditert.butylcyclohexane is one of a series of investigations undertaken by different workers in order to determine the molecular conformation.<sup>7</sup>

## EXPERIMENTAL AND CALCULATION METHODS

A sample of *cis*-1,4-ditert.butylcyclohexane was kindly supplied by Professor Wepster, Delft, and used without further purification. The scattering pattern from the gas at about 110°C was recorded on the Oslo apparatus.<sup>8</sup> Exposures were made with three nozzle to photographic plate distances, the three sets of plates thus obtained covered the diffraction ranges  $s = 1$  to  $8 \text{ \AA}^{-1}$ ,  $2$  to  $20 \text{ \AA}^{-1}$  and  $7$  to  $45 \text{ \AA}^{-1}$ . The diffraction parameter  $s = (4 \pi \sin \theta)/\lambda$ , where  $\theta$  is half the diffraction angle and  $\lambda$  the electron wavelength. Four apparently faultless plates from each set were selected for photometering, the traces were read off at  $\Delta s = 0.25 \text{ \AA}^{-1}$  intervals, and the data processed in the usual way.<sup>9</sup> The resulting modified molecular intensity curve extended from  $s = 1.5 \text{ \AA}^{-1}$  to  $42.75 \text{ \AA}^{-1}$ . Fourier inversion yielded the experimental radial distribution (RD) curve shown in Fig. 1.

Theoretical modified molecular intensity curves were calculated from

$$I(s) = \sum_{i \neq j} g_{ij}(s) \exp(-\frac{1}{2}u_{ij}^2 s^2) \sin(R_{ij}s)R_{ij}^{-1}$$

The sum extends over all atom pairs in the molecule,  $R_{ij}$  is the interatomic distance,  $u_{ij}$  is the root mean square amplitude of vibration, and  $g_{ij}(s)$  is a function of the complex atomic scattering factors<sup>9</sup> which were computed by Peacher's method.<sup>10</sup> Theoretical RD curves were obtained by Fourier inversion of theoretical intensity curves.

## STRUCTURE ANALYSIS

An experimental RD curve is shown in Fig. 1. In this curve each interatomic distance  $R_{ij}$  is represented by a peak centered at  $r = R_{ij}$ . The area under the peak is proportional to  $n_{ij}Z_i Z_j / R_{ij}$  where  $n_{ij}$  is the number of times the distance occurs in the molecule. The halfwidth of the peak is determined by the vibrational amplitude  $u_{ij}$ .

The peak at  $1.1 \text{ \AA}$  must correspond to the C—H bond distances, the peak at  $1.5 \text{ \AA}$  to the C—C bond distances, and the peaks at  $2.2 \text{ \AA}$  and  $2.5 \text{ \AA}$  to C...H and C...C distances across a valence angle (e.g. C(1)...C(3)). The peak at  $3.0 \text{ \AA}$  corresponds to C...C distances across two valence angles (e.g. (C1)...C(4), C(2)...C(8), Fig. 2). That the peak is so pronounced shows that a number of

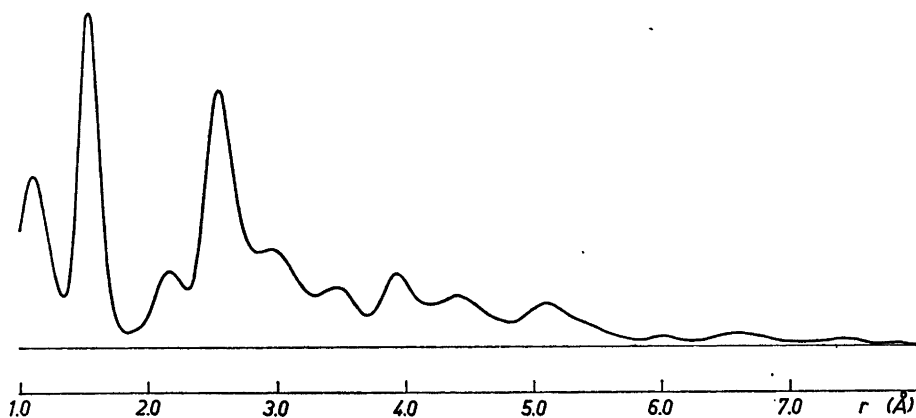


Fig. 1. Experimental radial distribution curve.  $k = 0.0015 \text{ \AA}^2$ .

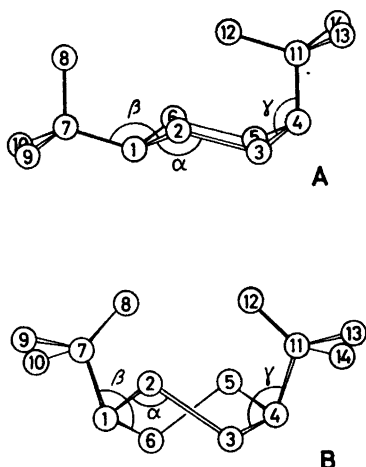


Fig. 2. Molecular models of *cis*-1,4-ditert-butylcyclohexane. A. The chair conformation. B. A boat conformation.

these distances are equal — or nearly equal. This means that the dihedral angles about the C(1)—C(7) and C(4)—C(11) bonds are  $60^\circ$ , that the substituents are in a staggered position.

Beyond  $3.0 \text{ \AA}$  the interpretation of the curve is no longer straightforward; it consists of a maze of unresolved peaks. Only where several C...C distances are equal — or nearly equal — does it rise to a distinct maximum.

Since intramolecular strain is more readily relieved through angle deformation than through stretching of bonds, C—C and C—H bond lengths were refined by least squares calculations on the intensity data under the assumption that they are all equal and have the same vibrational amplitude:

	$r_e(1) (\text{\AA})$	$u (\text{\AA})$
C—C	$1.540 \pm 0.002$	$0.053 \pm 0.002$
C—H	$1.107 \pm 0.005$	$0.089 \pm 0.004$

The standard deviations include the effect of errors in the electron wavelength. To within the error limits these parameter values are the same as those found in the lower normal paraffines.<sup>11</sup>

The carbon framework of the molecule in the chair conformation is sketched in Fig. 2A. The geometry of the molecule is determined by more than hundred unknown parameters, but it is found that the shape of theoretical RD-curves — once the bond lengths and dihedral angles about the C(1)—C(7) and C(4)—C(10) bonds are known — is sensitive only to the magnitude of the CCC valence angles. Only models in which all six CCC valence angles in the ring are equal ( $\alpha$ ), and in which all CCC valence angles within the tert-butyl groups are tetrahedral, were considered. Theoretical RD curves were computed for a series of values of  $\alpha$ ,  $\beta$ , and  $\gamma$ . For each set of values the vibrational amplitudes were varied (within reasonable limits) so as to give the best possible agreement with the experimental curve.

The best fit was obtained with  $\alpha = \beta = 115.75^\circ$  and  $\gamma = 116.50^\circ$ . Fig. 3A shows the RD curve computed for this model in the range  $3 \text{ \AA}$  to  $8 \text{ \AA}$ . The

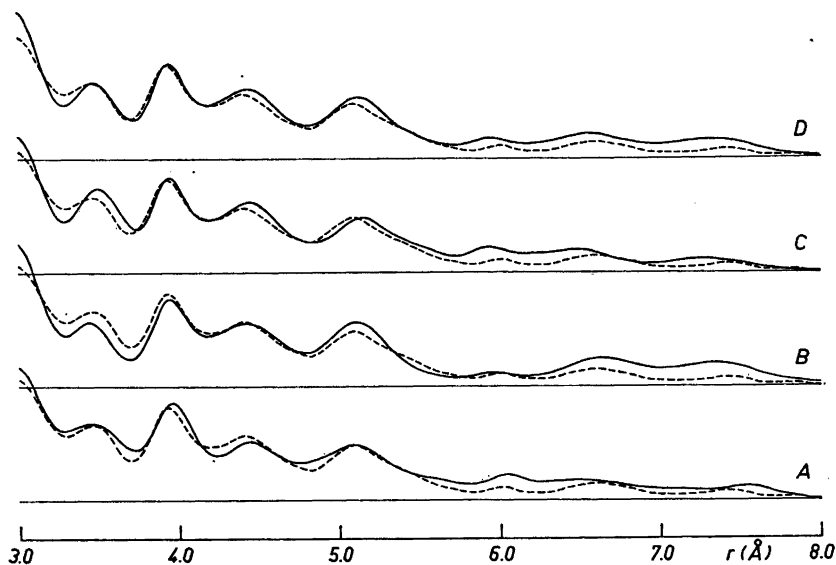


Fig. 3. Theoretical radial distribution curves. A. The chair conformation. B. A boat conformation (see text). C. Another boat conformation (see text). D. A mixture of the two boat conformations. Stipled lines: The experimental curve.  $k = 0.0015 \text{ \AA}^2$ .

agreement with the experimental curve is not very good: in particular the sharp peak at  $4.0 \text{ \AA}$  is nearly  $0.05 \text{ \AA}$  too far to the right, and the peak at  $6.6 \text{ \AA}$  is much less pronounced than in the experimental curve. But, unfortunately, neither is the agreement so poor that the model can be ruled out.

The geometry of the flexible form is determined by the same parameters as the chair and an additional torsional degree of freedom of the  $C_6$  ring. The variation of this torsional parameter has the effect of moving the atoms in the ring on a closed path. Thus different conformations of varying energy are obtained. A minimum energy conformation is obtained when one of the three distances between carbon atoms at opposite sides of the ring (e.g.  $C(1)\cdots C(4)$ ) has taken on its maximum value. The two other distances are then smaller but equal. The energy of this conformation which is called the "skew", "stretched", or "twist" boat, has been estimated to be about  $1.6 \text{ kcal/mole}$  less than that of the true boat.<sup>3,4</sup>

If the  $C_6$  ring of cis-1,4-ditert-butylcyclohexane is in a minimum energy conformation there are two possible conformers: Either the  $C(1)\cdots C(4)$  or the  $C(2)\cdots C(5)$  distance may be the longest. The carbon framework of the molecule with  $C(1)\cdots C(4)$  at its maximum is sketched in Fig. 2B.

Theoretical RD curves were computed for a series of values of the CCC valence angles while the torsional parameter was varied over its entire range. It was found that satisfactory agreement with the experimental curve could be obtained if — and only if — the  $C_6$  ring is in one of its minimum energy conformations.

Fig. 3B shows part of the RD curve computed for the conformer with C(1)···C(4) distance at its maximum,  $\alpha = 114.0^\circ$  and  $\beta = \gamma = 115.0^\circ$ . Fig. 3C shows the curve computed for the conformer with C(2)···C(5) at its maximum and the same valence angles. The agreement with the experimental curve is satisfactory but not very good. Fig. 3D, however, shows an RD curve computed for a 3:1 mixture of the two conformers. The positions and relative magnitude of the peaks are now in close agreement with the experimental curve. That the latter falls below the former between 5.5 and 8 Å is probably due to an error in the envelope and is of no significance. The agreement must therefore be considered very good.

Therefore, even though we have not succeeded in ruling out the chair conformation, we believe that the boat conformation is the *most probable*.

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