

## An Electron Diffraction Investigation of the Molecular Structure of *anti-trans,trans*-2,2'-Dibromobicyclopropyl in the Vapour Phase

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The experimental intensities obtained for the title compound are best reproduced by assuming an equilibrium between an *s-trans* conformer (33 % at 80°C) and a *gauche* conformer with a multiplicity of two.

The following values were found for bond lengths:  $r(\text{C}-\text{Br}) = 1.926(.005)$  Å,  $r(\text{C}-\text{C}, \text{ring}) = 1.527(.004)$  Å,  $r(\text{C}-\text{C}, \text{central}) = 1.490(.013)$  Å, and  $r(\text{C}-\text{H}) = 1.143(.009)$ . Values in parentheses are estimated standard deviations, and bond lengths are  $r_a$ -values.

Bond angles, torsional angles, and mean amplitudes of vibration are found in Table 1.

In a previous paper<sup>1</sup> we reported the structure of *anti-cis,cis*-2,2'-dibromobicyclopropyl investigated by electron diffraction. The subject of the present communication is the study of the geometry and the rotational equilibrium of the isomer *anti-trans,trans*-2,2'-dibromobicyclopropyl.

*Table 1.* Structural parameters of *anti-trans,trans*-2,2'-dibromobicyclopropyl. The values in parentheses are estimated standard deviations. The bond lengths ( $r$ ) are  $r_a$ -values, and  $u$  is the root mean square amplitude of vibration.

	$r$ (Å)	$u$ (Å)
C-Br	1.926 (.005)	0.031 (.008)
C <sub>1</sub> -C <sub>2</sub>	1.527 (.004)	0.038 (.004)
C <sub>1</sub> -C <sub>1</sub> '	1.490 (.013)	0.043 (.005)
C-H	1.143 (.009)	0.048 (.010)
Br <sub>1</sub> ...C <sub>1</sub>	2.975 (.004)	0.068 (.006)
Br <sub>1</sub> ...C <sub>1</sub> '	4.262 (.005)	0.102 (.010)
C <sub>2</sub> ...C <sub>1</sub> '	2.611 (.007)	0.078 (.009)

Table 1. Continued.

$\theta$	55.1 (1.0) $^\circ$	(C <sub>1</sub> 'C <sub>1</sub> C <sub>2</sub> = 119.7 $^\circ$ )
$\alpha$	56.5 (0.5) $^\circ$	(C <sub>1</sub> C <sub>2</sub> Br <sub>1</sub> = 118.6 $^\circ$ )
<i>s-trans</i> conformer:		
$\phi_t$	160.0 (6.0) $^\circ$	
Br <sub>1</sub> ...Br <sub>2</sub>	7.158 (.005)	0.118 (.020)
Mol fraction	0.33 (0.03)	
<i>gauche</i> conformer:		
$\phi_g$	58.8 (5.0) $^\circ$	
Br <sub>1</sub> ...Br <sub>2</sub>	6.462 (.011)	0.261 (.040)

## EXPERIMENTAL AND CALCULATION PROCEDURE

The compound was synthesized and purified as described before.<sup>2</sup> The purity as determined by VLP chromatography was about 96 %. The main impurity probably is the isomer *anti-cis,trans-2,2'*-dibromobicyclopropyl, which has a gas chromatographic retention time very similar to the *anti-trans,trans* isomer. Diffraction photographs were obtained in the usual way with the Oslo apparatus.<sup>3</sup> The nozzle temperature was ap-

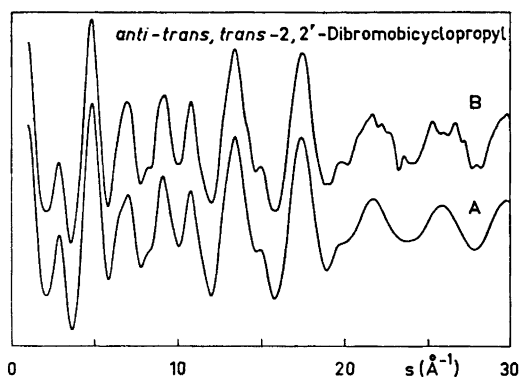


Fig. 1. Reduced molecular intensity curves of *anti-trans,trans-2,2'*-dibromobicyclopropyl. A: Theoretical curve calculated from the parameters in Table 1. B: Experimental curve.

proximately 80°C. Plates from three nozzle-to-plate distances of about 130, 48, and 19 cm were obtained. Four plates from each camera distance were photometered, and the intensity data treated in the usual way.<sup>4</sup> The 130 cm data cover the range 0.625 to 7.25 Å<sup>-1</sup> with  $\Delta s = 0.125$  Å<sup>-1</sup>, the 48 cm data extend from  $s = 1.25$  to 18.0 Å<sup>-1</sup>, and the 19 cm data from  $s = 8.75$  to 45.5 Å<sup>-1</sup>, both in intervals of  $\Delta s = 0.25$  Å<sup>-1</sup>. The modification function was normalized to the C-Br distances.<sup>4</sup> The curves from three different nozzle to plate distances were combined to give the experimental reduced molecular intensity curve (Fig. 1B). The intensity points in the  $s$  range between 0 and 0.625 Å<sup>-1</sup> were calculated. A Fourier transformation of this curve using a damping constant of  $k = 0.0020$  yields the experimental radial distribution curve (RD curve) shown in Fig. 2B. The numbering of the atoms is given in Fig. 3.

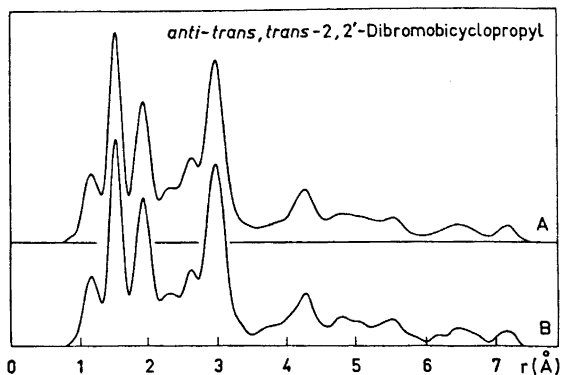


Fig. 2. Radial distribution curves of *anti-trans,trans*-2,2'-dibromobicyclopropyl. A: Theoretical curve. B: Experimental curve. The damping constant for both curves is  $0.0015 \text{ \AA}^2$ .

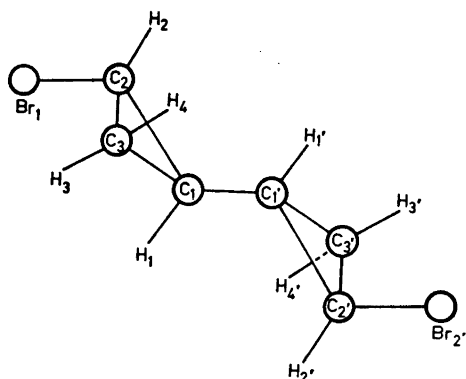


Fig. 3. Numbering of atoms in *anti-trans,trans*-2,2'-dibromobicyclopropyl.

The part from 0 to 3.0 Å is very similar to that of the *cis,cis* isomer,<sup>1</sup> showing the bond distances CH, CC, and CBr at 1.1, 1.5, and 1.9 Å, respectively. In addition, there are the peaks corresponding to distances across one angle, *i.e.* C...H at 2.2 Å, C...C at 2.6 Å, and C...Br at 3.0 Å. The *trans* position of bromine with respect to the neighbouring cyclopropane ring is verified by the shift of the C...Br distance over two angles from 3.3 Å in the *cis,cis* isomer to 4.2 in the *trans,trans* compound. The maxima at 6.5 and 7.2 Å originate from two different Br...Br distances indicating the presence of two rotational isomers, a *s-trans* and a *gauche* conformer. The maximum at 4.2 Å overlaps the various conformation dependent C...C distances. The broad peaks between 4.5 and 5.8 Å correspond to the different C...Br distances. There is extensive overlapping in the RD curve between 3.0 and 5.8 Å making a determination of the geometry from the RD curve difficult. The structure was calculated by the least squares procedure<sup>4</sup> using the molecular intensity. The data are weighted by a function being unity between 5.5 and 25.0 Å<sup>-1</sup> and falling off exponentially beyond these limits ( $w_1 = w_2 = 0.05$ ).<sup>4</sup> Reasonable changes in these limits do not influence the geometry significantly, but have an effect on the  $u$  values.

## BASIC ASSUMPTIONS OF THE STRUCTURAL MODEL

The structure was determined by refining the bond distances and bond angles using a model with the following basic assumptions.

(1) As in the *anti-cis,cis* isomer, the cyclopropane ring was assumed to be an equilateral triangle.

(2) The substituents attached to the three-membered ring are oriented in a plane perpendicular to the ring and containing the bisector of the inner angles of the ring.

(3) The positions of the hydrogen atoms are those determined for the cyclopropane molecule.<sup>5</sup>

(4) The molecule exists in an *s-trans* conformation, which is in equilibrium with two *gauche* forms of equal structure, the torsional angle of which was to be determined. The concentration ratio of the two rotational isomers was also to be determined.

Some of these assumptions had to be dropped at a later stage of the least squares analysis in order to improve the fit between the experimental and the theoretical curve.

## STRUCTURAL ANALYSIS

Because of the large number of independent parameters to be adjusted, the analysis of the electron diffraction data of this molecule is more complex than that of the *cis,cis* isomer described in the previous communication. Besides the torsional angle of the second rotational isomer and the concentration ratio of the conformers, there are two sets of torsion dependent distances and principally different *u* values. The *u* values of most distances depending on torsion had to be guessed and kept constant during the least squares adjustments. Some of them, in particular those involving only carbon atoms, could be taken from our previous investigation of the *cis,cis* isomer. Mean amplitudes of those distances involving bromine atoms have been estimated with the aid of a very approximate formula.<sup>6</sup> The intensity due to the H...H distances was calculated and subsequently treated as a constant contribution to the total intensity.

Initially, the length of the central CC bond was kept constant and put equal to the length of the bonds within the cyclopropane ring. The angle of the *s-trans* conformation was held constant at 180°. With these restrictions, the bond distances and bond angles refined to reasonable values. The torsional angle of the *gauche* conformer could be refined simultaneously. The RD curve of the model thus obtained deviated from the experimental one in several regions. One important conclusion was drawn from one of these deviations. The theoretical Br...C distance over two angles was found to be too long, when calculated with those bond distances and angles fitting the distances C<sub>2</sub>...C<sub>1</sub>, and Br<sub>1</sub>...C<sub>1</sub> over one angle and equal CC bond lengths. This could not be improved by twisting the two BrCH groups out of the bisector planes. However, there was improved agreement when the length of the central CC bond between the two cyclopropane rings was shortened. A second observation on the RD curve was that the *trans* Br...Br distance computed from the initial

model was always too long compared to the experimental distance by about 0.03 Å. Introducing the torsional angle  $\phi_t$  of the *s-trans* conformation as an additional independent parameter,  $\phi_t$  refines to values less than the exact *s-trans* angle of 180° by 15° to 24° depending on the least squares scheme used. Probably, this result is due to the shrinkage effect originating for the most part from large amplitudes of torsional oscillation of the *s-trans* conformer.

In this investigation, we simulated the shrinkage effect by considering a non-*s-trans* equilibrium structure with an angle of rotation of  $\phi_t$ . Basically, there is a difference between these two models.

An equilibrium angle less than 180° destroys the  $C_i$  symmetry of the molecule and splits up distances which are degenerate in the *s-trans* conformation (cf. the conformational structure of the *cis,cis* isomer<sup>1</sup>). However, a symmetrical torsion about the *s-trans* form with large amplitudes resembles the rigid *s-trans* form on the time average, but introduces a large asymmetric component to the total  $u$  value of conformation dependent distances. We did not differentiate between these two alternatives in the least squares treatment, because the number of parameters becomes too large compared to the usability of the data. We favour the model with a *s-trans* conformation and large amplitudes of torsion.

The  $u$  values of the distances between the heavy atoms, which do not depend on the angle of torsion, could be refined independently. However, this was not possible for all of the  $u$  values of the torsion dependent C...C and C...Br distances of both conformers. There is a strong coupling between the torsional angle of the *gauche* conformation, the relative concentration ratio of the conformers, and the  $u$  values of the heavy atom distances depending on the torsional angle. In later stages of the refinement these  $u$  values had to be varied in groups, *i.e.*, several of them are given the same shift in the least squares iterations. However, only the  $u$  values of the Br...C distances refined to reasonable numbers. The  $u$  values of the Br...H and C...H non bonded distances are difficult to refine. This was possible for the C...H distances over one angle only. All other  $u$  values were guessed or taken from the results of the hydrocarbon bicyclopropyl, which was recently reinvestigated by electron diffraction.<sup>7</sup> In that work, the  $u$  values of the non bonded distances had been calculated from spectroscopic data. We assumed that substitution of hydrogen in *trans* position to the central CC bond in bicyclopropyl by two bromine atoms does not change the overall geometry or the internal rotation very much. Therefore, we used the same  $u$  values for the C...C and C...H non bonded distances as in bicyclopropyl.

The mean amplitudes of vibration of the Br...H distances were approximated by setting them equal to the  $u$  value of the corresponding C...H distance involving the carbon atom bonded to the bromine atom under consideration.

The least squares refinement yielded an  $R$ -factor of 11.6%. The final theoretical molecular intensity curve is shown in Fig. 1A, its Fourier transform in Fig. 2A. The structural parameters are listed in Table 1 together with estimates of their standard deviations. An uncertainty in the wavelength (0.14%) has been included in the standard deviations for distances. Corrections for the effect of correlation<sup>11</sup> in the experimental intensities are included, too.

## DISCUSSION

The main interest in structural studies within the series of bicyclopropyls originates from the question of how the bonds between two cyclopropane carbon atoms, being largely unaffected by conjugative interaction, determine the properties of these molecules. We concentrated upon two aspects of this problem.

1. *Bond lengths.* One consequence of the constituent  $sp^2$  orbitals which form the central CC bond in bicyclopropyls is a shortening of that bond compared to the CC bond of aliphatic hydrocarbons. This is confirmed by our results yielding 1.49 Å compared to 1.53 Å in aliphatic hydrocarbons.<sup>8</sup> It also holds for the CBr bond which is slightly shortened compared to that in alkyl bromides.<sup>8</sup> The CC and CBr bond lengths of both isomers are the same within the error bounds. The central bond length for both compounds observed in these investigations also compares favourably with the value of 1.487 Å obtained by an X-ray study of solid bicyclopropyl<sup>9</sup> and 1.499 Å for gaseous bicyclopropyl investigated by electron diffraction.<sup>7</sup>

The angles  $\alpha$  and  $\theta$  are a few degrees larger than those of the *cis,cis* isomer *i.e.*, the bond angles  $C_2C_1C_1$  and  $C_1C_2Br_1$  are correspondingly smaller. This opening of the bond angle in the *cis,cis* isomer probably reflects the steric repulsion between the substituents on the ring in *cis* position. The CH bond length appears to be somewhat too long. The  $u$  values are generally smaller than one would expect from general experience and also smaller than those of the *cis,cis* compound.

2. *Rotational isomerism.* The second aspect of the  $sp^2$ - $sp^2$  nature of the central bond in bicyclopropyl is its effect on the internal rotation mode. There are two main questions to be answered by the structural investigations regarding (1) the torsional angle  $\phi_g$  of the *gauche* conformer and (2) the relative amount of both rotational isomers.

In a previous ED study of bicyclopropyl<sup>10</sup> the equilibrium angle of the *gauche* conformation was found to be 35° to 40°. New ED measurements<sup>7</sup> changed this value to  $\phi_g = 48.7^\circ$ . The equilibrium angle of the *gauche* form obtained in the present study is 58.8°. Considering the large standard deviations in this angle of 7° and 5°, respectively, the results of the two measurements are not significantly different. It must be stated, however, that we feel our value to be more reliable than that of the hydrocarbon, if it were not for a real difference between the two molecules brought about by the bromine substitution. In the *trans,trans* derivative, the two rotational isomers exhibit two distinct maxima in the RD curve which are not obscured by overlapping peaks stemming from other distances in the molecule. Their position can be precisely located. Their  $u$  values determined from the least squares treatment of the intensity data do not depend significantly on assumptions as to  $u$  values of other distances or the hydrogen geometry. On the other hand, the region of the RD curve of bicyclopropyl which is significant for determining the *gauche* angle is a broad and quite unstructured area of heavily overlapping peaks.

The concentration of the *s-trans* conformer was obtained by integrating the areas below the two Br...Br peaks. By this method, we obtained 33 % *s-trans* form at 80°C.

If the entropy difference between the two conformers ( $\Delta S = S_g - S_t$ ) is equal to  $R \ln 2$  (originating from the multiplicity of the *gauche* form) then the energy difference is approximately zero. However, we do not know the difference in entropy that might exist between the conformers due to differences in vibrational frequencies. Thus in order to get information about the energy difference between the conformers, a vibrational analysis of the molecule is desirable.

*Acknowledgements.* The authors thank Professor O. Bastiansen for the idea of studying this molecule. We also thank Cand. Real. A. Almenningen for having taken the diffraction photographs. We acknowledge Professor W. Lüttke for his continuing support in connection with this work.

Financial support from *Deutsche Forschungsgemeinschaft* and *Norges almenvitenskapelige forskningsråd* is gratefully acknowledged. The calculations were done at the *Gesellschaft für wissenschaftliche Datenverarbeitung*, Göttingen.

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Received April 2, 1973.