

An Electron Diffraction Investigation of the Molecular Structure in *anti-cis,cis*-2,2'-Dibromobiscyclopropyl in the Vapour Phase

G. SCHRUMPF and R. STÖLEVIK

Organisch-Chemisches Institut der Universität Göttingen, B.R. Deutschland, and Department of Chemistry, University of Oslo, Blindern, Oslo 3, Norway

The experimental intensities obtained for the title compound are best reproduced by assuming a nearly *s-trans* conformation for the molecule. There is no indication from the experimental data of a second conformer.

The following values were found for the bond lengths: $r(\text{C}-\text{Br}) = 1.926(5)$ Å, $r(\text{C}-\text{C}, \text{ring}) = 1.527(3)$ Å, $r(\text{C}-\text{C}, \text{central}) = 1.470(7)$ Å, and $r(\text{C}-\text{H}) = 1.094(9)$ Å. Values in parentheses are estimated standard deviations, and bond distances are r_a -values.

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

According to well established theoretical interpretations of the nature of bonding in the cyclopropane molecule,^{1,2} the exocyclic carbon orbitals involved in the C-H bonds of cyclopropane are nearly sp^2 hybridized. Those sp^2 hybrid orbitals constitute the σ bond framework of a large variety of organic molecules like conjugated olefins and aromatic compounds. However, extensive conjugation obscures the properties of the pure sp^2-sp^2 bond between carbon atoms. Apart from a small unknown amount of conjugation, the C-C bond between two cyclopropane rings is expected to be a pure σ bond of the sp^2-sp^2 type, and its properties may be studied in these models unaffected by large conjugative interactions.

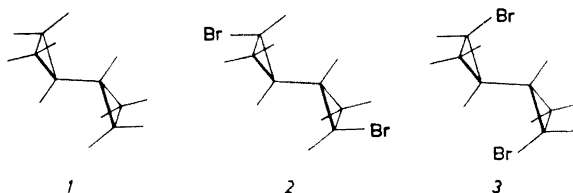


Fig. 1.

In order to investigate the structure and the conformational equilibrium of bicyclopopyl *1* (Fig. 1) an electron diffraction study of this molecule in the vapour phase had been undertaken previously.³ Most of the structural parameters had been obtained. The experimental data indicated the presence of a *trans-gauche* rotational equilibrium, the two conformations being approximately equally populated. However, the equilibrium angle of the *gauche* form and the torsional amplitude of both rotational isomers had not been determined accurately, because the information about the torsion dependent parameters had to be extracted from a region of the radial distribution curve where many distances overlap extensively. In order to overcome this difficulty, the two derivatives *anti-trans,trans*- and the *anti-cis,cis*-2,2'-dibromobiscyclopopyl (*2* and *3*, respectively, Fig. 1) were synthesized.⁴ In both compounds the conformation dependent Br...Br distances are well outside the range of all other distances in the two molecules. Besides, their scattering intensity is a large fraction of the total molecular intensity, a fact that facilitates the quantitative treatment of the conformational problem.

Only one of these dibromobiscyclopopyls can actually be compared to bicyclopopyl, because only in *2* the environments of the central C—C bond are essentially the same as in the hydrocarbon *1*. One may expect that the same potential energy function describes internal rotation in the two molecules *1* and *2*. On the other hand, one may anticipate a completely different conformational behaviour of *3*. The particular spacial relationship between the C—Br bond and the neighbouring cyclopropane ring leads to an extraordinary steric strain in most conformations. This will probably lead to a conformationally pure compound with an *s-trans* structure, because in that rotamer steric repulsion will be a minimum as judged from a molecular model.

In the present paper we report the results of our electron diffraction investigation of the *cis,cis* isomer, whereas our study of the *trans,trans* isomer will be published in a separate paper.⁵

EXPERIMENTAL AND CALCULATION PROCEDURE

The compound was synthesized and purified as described elsewhere.⁴ The purity as determined by VLP chromatography was better than 98 %.

Diffraction photographs were obtained in the usual way with the Oslo apparatus.⁶ The nozzle temperature was approximately 80°C. The electron wave length was determined from a gold foil diffraction pattern. Plates from three different 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.⁷ The 130 cm data cover the *s*-range between 0.500 and 7.375 Å⁻¹ with $\Delta s = 0.125$ Å⁻¹, the 48 cm data extend from *s* = 1.25 to 20.50 Å⁻¹, and the 19 cm data from *s* = 6.75 to 46.50 Å⁻¹ both in intervals of $\Delta s = 0.25$ Å⁻¹. Nonrelativistic atomic scattering factors for 35 kV electrons were computed using the partial wave method.⁸ The calculations for hydrogen and carbon were based on Hartree Fock potentials, those for bromine on a TFD potential.⁹ The resulting average intensity curve modified⁷ by $s/|f_C|/|f_{Br}|$ is shown in Fig. 2, Curve A.

STRUCTURAL ANALYSIS

Preliminary values for the bond distances and bond angles were obtained from the experimental radial distribution curve (Fig. 3, Curve A). The peak at

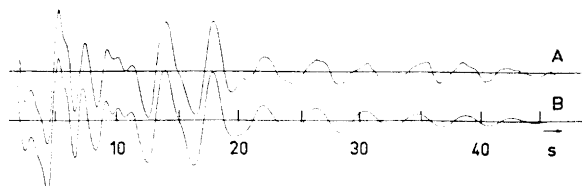


Fig. 2. Reduced molecular intensity curve of *anti-cis,cis-2,2'*-dibromobiscyclopropyl. A. Experimental curve. B. Theoretical curve calculated from the structural parameters listed in Table 1. The inner part of the intensity curves has been omitted.

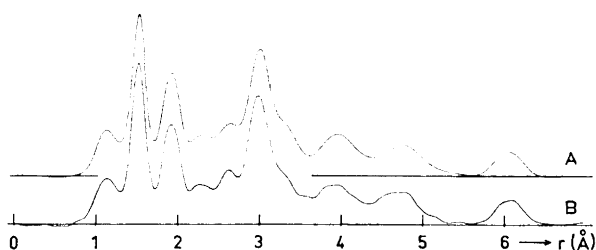


Fig. 3. RD curve of β calculated from the corresponding intensity curve by a Fourier inversion. A. Theoretical curve calculated from the intensity of Fig. 2. B. Experimental curve; damping constant in both calculations, $k = 0.0015 \text{ \AA}^2$.

1.1 Å corresponds to the eight C–H, that at about 1.5 Å to the five C–C, and the maximum at 1.9 Å to the two C–Br bond distances. Nonbonded C...C distances over one angle are found at 2.6 Å. The peak between 2.8 and 3.8 Å contains contributions from the two types of conformation independent nonbonded C...Br distances. The two complex peaks with maxima at about 3.8 and 4.8 Å originate from the various conformation dependent C...Br and C...C distances, and the isolated peak at 6.1 Å corresponds to the Br...Br distance.

A. *Least squares calculations using a rigid s-trans model.* In order to reduce the number of parameters to be refined to a practical limit, the following assumptions about the molecular geometry have been made at the initial stage of the analysis. The numbering of the atoms is shown in Fig. 4.

(1) All C–C bonds in the rings are equal, which implies an equilateral triangle for the cyclopropane ring.

(2) The substituents on each ring, *i.e.* hydrogen, bromine, and the central C–C bond, are oriented in a plane which is perpendicular to the plane of the three-membered ring and which contains the bisector of the inner angles of the three-membered ring. This means that we ignore a possible repulsive interaction between the two substituent atoms Br and C on the same cyclopropane ring.

(3) The position of the hydrogen atoms is the same as determined for the cyclopropane molecule,¹⁰ where $r_{\text{CH}} = 1.089 \text{ \AA}$ and the angle HCH = 115.1°.

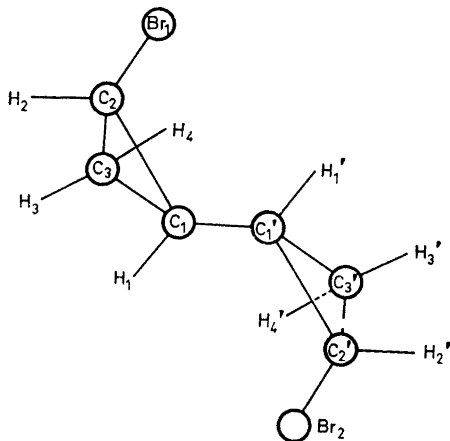


Fig. 4. Numbering of atoms of 3.

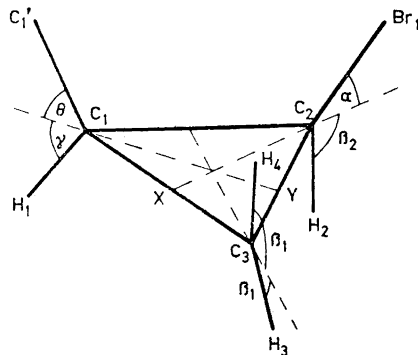


Fig. 5. Definition of angles of the cyclopropane moiety of 3. The bisector of the inner ring angles are indicated by dashed lines.

(4) The molecule exists in a rigid *s-trans* conformation. Rotamers of *gauche* or even *cis* structure are highly improbable and are not considered hereafter.

In order to aid the analysis of the ED data in the initial stage of the investigation, the space group of the crystals was determined by X-ray diffraction to be $P2_1/a$ with two molecules in the unit cell. This is interpreted to mean centrosymmetric molecules, which must, therefore, exist in the *s-trans* conformation in the solid state at room temperature.

Initially the calculations were carried out taking into account the structure of the molecular framework of the heavy atoms carbon and bromine only. The contribution of all distances involving hydrogen atoms to the total intensity was treated as a constant. It was calculated from an assumed model and subtracted from the total intensity. This process was repeated after a series of calculations when a more refined model of the framework had been obtained. Keeping the u -values of the conformation dependent C...C and C...Br distances over the rings constant, the framework parameters refined to reasonable values, but the agreement between the experimental and the theoretical intensity curve was not very satisfactory. In the region between 3.5 and 5.0 Å containing nearly all the distances over the central C—C bond, considerable deviation from the experimental radial distribution curve was observed. Besides, the Br...Br distance calculated from this rigid *s-trans* model is larger than the experimental one as obtained from the RD-curve.

A more refined model was tried by admitting the bromine atoms to leave the bisector plane of the cyclopropane ring. A series of calculations with different values for the angle of deviation from that plane led to improved fit in the region between 3.5 to 5.0 Å, but yielded Br...Br distances too short by 0.2 to 0.5 Å. We therefore dropped this distorted model.

B. *Least squares calculations with a rigid non s-trans model.* Considerable improvement in the fit of the intensity curves could be achieved by varying the angle of torsion ϕ about the central C—C bond. While the *s-trans* conformation possesses C_i symmetry, other rotamers are without any symmetry element. Rotation about the C₁—C₁' bond leads to a splitting of three pairs of heavy atom distances into a longer and a shorter distance C₂...C₃'/C₃...C₂', C₂...Br₂/C₂'...Br₁, and C₃'...Br₁/C₃...Br₂. Although there is no symmetry element in these conformations, it can be shown that rotation about the central C—C bond by an angle of $+\phi$ and $-\phi$, respectively, leads to molecules, which are mirror images of each other. This means that the potential energy as a function of the angle of torsion is symmetric about the *s-trans* form. A converging fit could be obtained by simultaneously varying all distances and u -values involving carbon and bromine. Only the u -values of the two long distance pairs C₂...C₃'/C₃...C₂', and C₂...Br₂/C₂'...Br₁ have been coupled together in the calculation by giving them the same shift in the least squares procedure.

C. *Least squares calculations including hydrogen atom geometry and differences in the C—C bond lengths.* In the next stage of the structural analysis the average length of the C—H bonds as well as their angle of inclination towards the ring plane have been included in the refinement process. Convergence was achieved only when one of these angles was refined at a time. By a mapping procedure, estimates of the three types of angles and the average bond length were obtained.

Finally differences between the average endocyclic and the central exocyclic C—C bond length were introduced. Because of the strong coupling between these bond distances and their u -values, we were unable to refine them simultaneously. Assuming a u -value of 0.045 Å for the central C—C bond, least squares calculations were performed for several values of this bond differing by an increment of 0.005 Å. The agreement between the experimental and the theoretical intensity curve improved noticeably. This additional degree of freedom allows an adjustment of all distances over the central bond while at the same time keeping the distances within the cyclopropane moiety constant. The best value for the central C—C bond length was found to be 1.470 Å and the average C—C bond length within the ring 1.527 Å. This result does not change much when the u -value of the central C—C bond is increased to 0.050 Å or decreased to 0.040 Å. The computations done during this final stage of the refinement involved strongly damped iterations using 0.5 times the calculated shift of the current iteration cycle and 0.2 times the shift of the previous cycle.

The intensity data show a large noise in the *s*-region above *ca.* 30 Å⁻¹. Therefore, the data between 30 and 46.5 Å⁻¹ have been weighted down in the least squares calculation. The effect of using limited parts of the molecular intensity data for the iterative refinement process was studied by changing the weighting scheme of the experimental intensity. The resulting changes of the geometry are negligibly small, whereas the u -values are more strongly affected.

RESULTS

The intensity curve is best reproduced by assuming an angle of torsion about the central C—C bond of 18° relative to the *s-trans* conformation. This deviation from a rigid *s-trans* form may be interpreted as a real non-*s-trans* equilibrium structure, or it may be an indication of a sizable shrinkage effect.¹¹ There is no indication from the experimental data of the presence of a second conformer.

Table 1. The values in parentheses are estimated standard deviations, and (—) means assumed parameter. The bond lengths (r) are r_a -values, and u is the root mean square amplitude of a distance.

	$r(\text{Å})$	$u(\text{Å})$
C—Br	1.926(5)	0.043(7)
C ₁ —C ₂	1.527(3)	0.045(4)
C ₁ —C ₁ '	1.470(7)	0.045(—)
C—H	1.094(9)	0.083(9)
Br ₁ ...Br ₂	6.063(8)	0.179(8)
Br ₁ ...C ₁	2.991(4)	0.074(5)
Br ₁ ...C ₁ '	3.315(7)	0.127(8)
Br ₁ ...C ₃ '	3.957(20)	0.165(43)
Br ₂ ...C ₃	4.508(20)	0.132(29)
Br ₁ ...C ₂ '	4.798(8)	0.145(16)
Br ₂ ...C ₂	4.783(8)	0.145(16)
C ₂ ...C ₁ '	2.637(6)	0.085(8)
C ₂ ...C ₃	3.609(9)	0.160(—)
C ₃ ...C ₃ '	3.878(9)	0.140(—)
C ₂ '...C ₂ '	4.040(8)	0.184(78)

$$\theta = 50.7 (0.6)^\circ$$

$$\alpha = 55.2 (0.4)^\circ$$

$$\phi = 18.8 (2.0)^\circ$$

$$\gamma = 59.6 (3.0)^\circ$$

$$\beta_1 = 57.9^\circ (-)$$

$$\beta_2 = 53.5^\circ (-)$$

$$C_1'C_1C_2 = 123.3^\circ$$

$$C_1C_2Br_1 = 119.6^\circ$$

The structural parameters are listed in Table 1 together with estimates of their standard deviations. An uncertainty in the wavelength (0.14 %) is included in the standard deviations for distances, and corrections for the effect of correlation¹² between the intensity data are included in all estimates of standard deviations.

The assumption (2) and that of an equilateral triangle for the cyclopropane ring, which were retained in the final model, fit the data well, as indicated by the small standard deviation of the C—C and C—Br bond distances and those over one and two angles. The structural data of the present compound are discussed together with those of the *trans,trans* isomer in the next paper.⁵

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