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Electron-diffraction Study of Gaseous Tricyclo[4.1.0.0^{1,3}]heptane

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The molecular structure of tricyclo[4.1.0.0 ^{1,3}] heptane has been studied by gas-phase electron diffraction. Under the assumption of C_2 symmetry, the electron-diffraction analysis led to the following values for the principal parameters: r_a(C1 – C2) = 1.465(7) Å, r_a(C1 – C3) = 1.519(25) Å, r_a(C2 – C3) = 1.526(10) Å, r_a(C3 – C4) = 1.521(30) Å, r_a(C4 – C5) = 1.572(14) Å, r_a(C – H)$_{av}$ = 1.107(2) Å, ∠C2C1C7 = 162.4(18)°, and the average angle of the five-membered ring ∠(CCC) = 105.1(2)°. The values in parentheses are standard deviations.

Tricyclo[4.1.0.0 ^{1,3}]heptane (TCH) contains highly-strained spiropentane bridged by a dimethylene grouping (see Fig. 1). One can also view the molecule as cyclopentane with two fused cyclopropane rings. The compound was first synthesized by Skattebøl,[1] and its thermal isomerization was investigated by Frey *et al.*[2] The present study was initiated to obtain information concerning the gas-phase structure of TCH in order to gain a better understanding of the strain effects in this molecule.

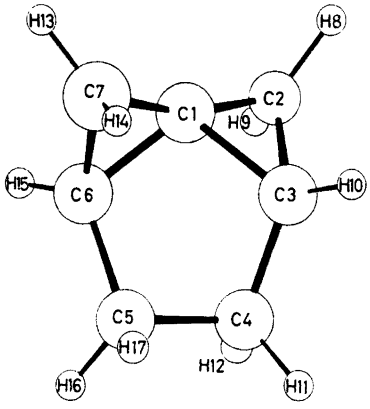

Fig. 1. Tricyclo[4.1.0.0 ^{1,3}]heptane. The numbering of the atoms is indicated.

EXPERIMENT AND DATA PROCESSING

A sample of tricyclo[4.1.0.0 ^{1,3}]heptane was obtained from Prof. L. Skattebøl, University of Oslo. Gas chromatographic analysis (10 % OV 17, a 50 % phenylsilicone, in a glass column at 50 – 150 °C) indicated a maximum of 6.3 % impurity, but it was believed that some thermal rearrangement occurred. The NMR spectrum (Varian HA100) showed a small amount of olefin; integration, based on an assumed 1,2,6-heptatriene structure for the impurity,[1] indicated 3.3 %. It was used without further purification. The diffraction diagrams were recorded with the Oslo apparatus [3] on 24 × 6 cm Scientica 34B50 plates at a nozzle temperature of about 20 °C. Four plates exposed at a camera distance of 480.65 mm and four at 200.65 mm were selected for the structural analysis. The electron wavelength was determined from gold-foil diffraction patterns and adjusted by 0.1 % to 0.06464 Å by calibration with the diffraction patterns of gaseous benzene.

The optical densities were recorded while oscillating the plates, and the experimental intensities were treated in the usual way.[4] They were leveled by using the elastic scattering factors calculated by the partial-wave method,[5] based upon the analytical HF potential for a C-atom [6] and using the best electron density of bonded hydrogen for H.[7] The inelastic scattering factors used were those of Tavard *et al.*[8]

The experimental backgrounds were drawn by hand for each plate, and the average molecular intensities were calculated for each set of plates using the modification function $s/|f_C'|^2$.[4] The final background correction of 20 cm data was made on the modified intensities for each plate. The intensity ranges for the two sets of data were 2.0 – 19.25 and 7.25 – 42.25 Å^{-1} with increments in s of 0.125 and 0.25 Å^{-1}, respec-

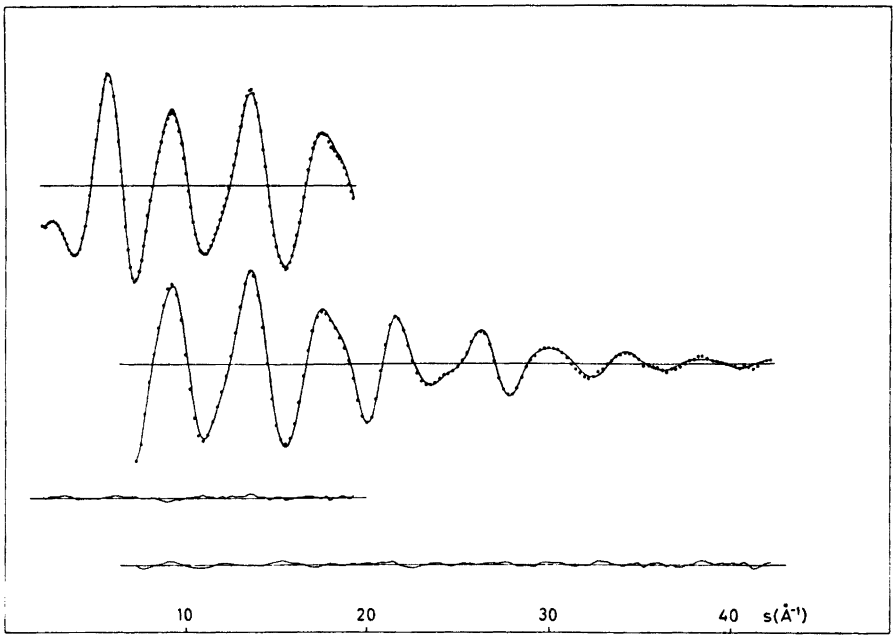

Fig. 2. The experimental intensity data (dots) for tricyclo[4.1.0.0^{1,3}]heptane from the 48 cm and the 20 cm camera distances. The solid line corresponds to the calculated molecular intensities, while the lower curves represent the difference between the experimental and the calculated intensities.

tively (Fig. 2). The radial distribution function calculated by the Fourier transformation of composite molecular intensity [4] is shown in Fig. 3.

ANALYSIS OF DATA

Structural parameters were derived by a least-squares analysis of the molecular intensities under the following assumptions (for numbering of the atoms see Fig. 1):

(1) The molecule has C_2 symmetry.

(2) All C–H bond lengths are equal.

(3) The HC_iH plane is perpendicular to the CC_iC plane and the bisectors of the HC_iH and CC_iC angles are colinear. ($i = 2, 4, 5, 7$).

(4) All the CC_jH angles are equal for $j = 3, 6$.

(5) The vibrational amplitudes, l, and the perpendicular amplitude correction coefficients, K, (see Table 1) were calculated by normal coordinate analysis,[9] using Hildebrandt's program,[10] on the basis of an estimated set of Urey-Bradley force-field parameters. The force constants were derived from those in hydrocarbons such as cyclohexane [11] and are listed in Table 2. The l-values for the C–C bond distances and the C···C non-bonded distances (with the exception of l(C2–C5), which was refined separately) were refined in two groups,[4] keeping the differences within each group at the calculated values. The l-values for the non-bonded C···H and H···H distances were maintained at the calculated values.

Under the above assumptions the structure is described by eleven parameters. The following parameters were used: r(C1–C2), r(C1–C3), $\Delta r = r$(C2–C3) – r(C1–C2), r(C3–C4), r(C4–C5), r(C–H), ∠C6C1C3, ∠HC4H, angle γ (the angle between the C6–C1–C3 and C1–C2–C3 planes), and $\phi 3$ (the dihedral angle C3C4–C5C6).

The interpretation of the main features of the radial distribution curve was straightforward. The peaks at about 1.1 Å and 1.5 Å represent the C–H and C–C bond distances. The shoulder at 2.2 Å is formed by contributions of the C···H non-bonded distances, the

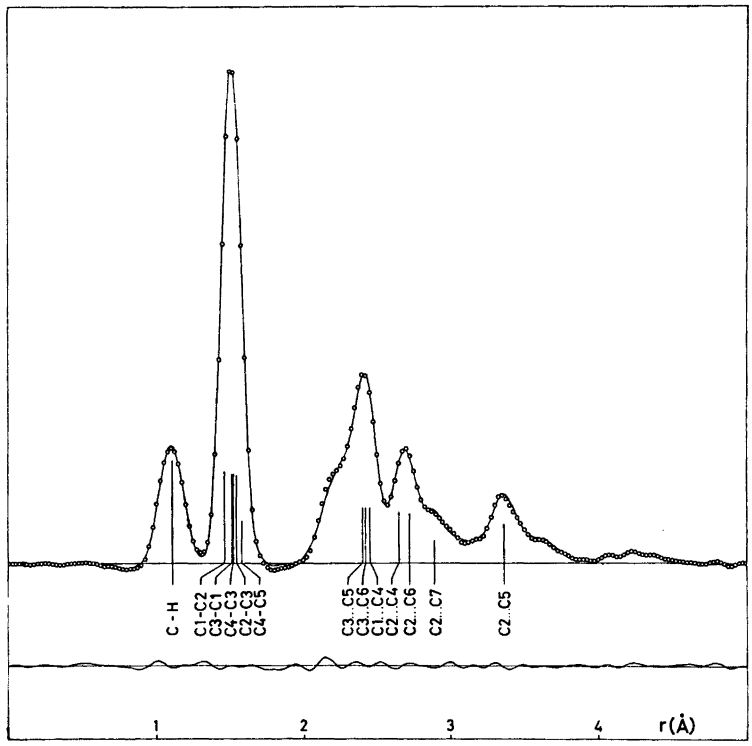

Fig. 3. Experimental (circles) and calculated (solid line) radial distribution curves for tricyclo-[4.1.0.0^{1,3}]heptane. The lower curve represents the difference between the experimental and calculated curves. The position and approximate areas of the most important interatomic distances are indicated. Damping factor exp ($-0.0002\ s^2$) was used.

Table 1. Mean amplitudes of vibration, l, and perpendicular amplitude correction coefficients, K (in Å), calculated from assumed force-field.

Parameter	l	K	Parameter	l	K
C1 – C2	0.051	0.003	C1···H11	0.10	0.006
C1 – C3	0.052	0.002	C1···H12	0.13	0.006
C2 – C3	0.051	0.003	C2···H11	0.11	0.006
C3 – C4	0.052	0.003	C2···H12	0.15	0.007
C4 – C5	0.052	0.003	C4···H8	0.11	0.006
C – H	0.078	0.018	C4···H9	0.14	0.007
C1···C4	0.060	0.001	C5···H8	0.10	0.004
C3···C5	0.065	0.001	C5···H9	0.13	0.005
C3···C6	0.061	0.001	C5···H10	0.13	0.005
C2···C4	0.068	0.002	C6···H8	0.10	0.006
C2···C6	0.066	0.001	C6···H9	0.14	0.006
C2···C7	0.062	0.002	C6···H10	0.12	0.005
C2···C5	0.069	0.001	C6···H11	0.10	0.006
C1···H8	0.10	0.010	C6···H12	0.14	0.006
C3···H8	0.10	0.010	C7···H8	0.12	0.006
C1···H10	0.10	0.009	C7···H9	0.12	0.006
C2···H10	0.10	0.010	C7···H10	0.15	0.005
C4···H10	0.10	0.010	C7···H11	0.12	0.004
C3···H11	0.11	0.010	C7···H12	0.13	0.004
C5···H11	0.11	0.010			

Table 2. Assumed force-field parameters for tricyclo[4.1.0.0^{1,3}]heptane.[a] The number of contributions of each type is given in parentheses.

K(C–C)	2.3(9)	F(C–C–C)	0.34(10)
K(C–H)	4.1(10)	F(H–C–C)	0.53(22)
H(C–C–C)	0.6(16)	F(H–C–H)	0.18(4)
H(H–C–C)	0.3(22)	Y(C–C)	0.11(9)
H(H–C–H)	0.5(4)		

[a] The stretching constants, K, and non-bonded stretching constants, F, are in mdyn Å^{-1}, bending constants, H, and torsional constant, Y, in mdyn Å rad^{-2}.

Table 3. Structural parameters[a] for tricyclo-[4.1.0.0^{1,3}]heptane.

Parameter	r_a(Å)	l(Å)	
C1–C2	1.465(7)	0.054	
C1–C3	1.519(25)	0.055	
C2–C3	1.526(10)	0.054	(4)[b]
C3–C4	1.521(30)	0.055	
C4–C5	1.572(14)	0.055	
C–H	1.107(2)	0.077(2)	
C1···C4	2.45(2)	0.062	
C3···C5	2.41(2)	0.067	
C3···C6	2.42(1)	0.063	
C2···C4	2.66(1)	0.070	(5)
C2···C6	2.72(1)	0.068	
C2···C7	2.89(1)	0.064	
C2···C5	3.363(4)	0.073(3)	
(C–C) average	1.514(2)		
Angles (in degrees)			
∠C2C1C3		61.5(5)	
∠C1C3C2		57.5(7)	
∠C2C1C7		162.4(18)	
γ[c]		50.9(5)	
∠(CCC)[d]		105.1(2)	
∠C6C1C3		105.7(26)	
∠C1C3C4		107.5(13)	
∠C3C4C5		102.3(30)	
ϕ1(C6C1–C3C4)		12.5(5)	
ϕ2(C1C3–C4C5)		31.4(12)	
ϕ3(C3C4–C5C6)		37.9(14)	
∠HC2H		106.3(8)	
∠HC4H		108.4(13)	

[a] For the definition of r_a see Ref. 12. Parenthesized values are estimates of uncertainties, which are the standard deviations. See text for details. The assymmetry constants were (in 10^{-6} Å^3): k (CC)=2.0, k(CH)=10.0, and zero for non-bonded distances. [b] The indicated l-values were refined in groups. [c] Angle between the planes C1–C3–C6 and C1–C2–C3. [d] Average CCC angle in the five-membered ring.

peak at 2.4 Å by the non-bonded C···C distances of the five-membered ring, the peak at 2.7 Å by non-bonded C···C distances of the type C2···C4, and C2···C6, the shoulder at 2.9 Å is mainly formed by the C2···C7 distance and the peak at 3.4 Å by the C2···C5 distance.

There are five different C–C bonds in this molecule, which all contribute to one peak in the radial distribution curve. In order to improve the convergence in the least-squares refinements, it was necessary to apply a correction factor of 0.3 in order to decrease the calculated shift, δx. The applied shift in cycle i, $\delta x_i'$, was given by $\delta x_i' = 0.3\ \delta x_i$ (for more details see Ref. 4). It was determined that the minimum thus found was independent of the input parameters in the least-squares analysis.

The vibrational amplitudes of the C–C bond distances were refined in a group,[4] and values 0.003 Å higher than the calculated ones were obtained. When these vibrational amplitudes were held at the calculated values, the standard deviations of the other parameters decreased by half, and the values of the parameters changed by no more than one standard deviation. The difference in the parameters was insignificant, regardless of whether the calculated shrinkage correction was included in the analysis of the data or not.

The final parameters are shown in Table 3, and the correlation coefficients larger than 0.5 in Table 4. A conventional diagonal weight matrix[4] was used in the least-squares refinements, and the constants for the weighting scheme are shown in Table 5. The standard deviations for the distance parameters and vibrational amplitudes were corrected for data correlation[13] by multiplying the standard deviations, σ_{LS}, obtained from the least-squares refinement by a factor F. (For definition see Ref. 13, eqn. 11.28. For the bond distances listed in Table 3, factor F was about 1.8). $\sigma = [F^2\sigma_{LS}^2 + (0.001r)^2]^{\frac{1}{2}}$. The term involving r provides an estimate of possible systematic error. The standard deviations for the angles were corrected by $\sigma = 1.5\ \sigma_{LS}$.

DISCUSSION

Bicyclo[3.1.0]hexane, which lacks one of the fused cyclopropane rings of TCH, has an "envelope" conformation (C_s symmetry), as

Table 4. Correlation coefficients whose absolute value is greater than 0.5.

	∠C6C1C3	ϕ3	γ	∠HC4H	r(C1C3)	r(C1C2)	Δr	r(C3C4)	r(C4C5)
γ	0.88								
∠HC4H	0.55								
∠HC2H			0.52						
r(C1C3)	−0.99		−0.89	−0.58					
r(C1C2)	0.81		0.63	0.72	−0.81				
Δr	−0.66	0.61		−0.65	0.64	−0.89			
r(C3C4)	0.95		0.75	0.61	−0.95	0.87	−0.83		
r(C4C5)	−0.67				0.64	−0.79	0.87	−0.82	
l(C1C3)	0.64			0.63	−0.62	0.89	−0.92	0.77	−0.89
l(C1C4)	0.95		0.89	0.51	−0.95	0.70		0.84	−0.51

Table 5. Constants of the weighting scheme.[4]

Data	48 cm	20 cm
s_1 (in Å^{-1})	4.5	7.5
s_2 (in Å^{-1})	18.5	40.0
w_1	0.25	0.05
w_2	0.05	0.02

shown by microwave spectroscopy [14] and by X-ray diffraction of an *N*-brosylamine derivative.[15] The envelope conformation is much strained in TCH and it is not surprising that this work gives evidence only of the "half-chair" structure shown.

Despite attempting many initial combinations of different C−C distances and CCC angles, only one minimum in the least-squares analysis was found. The high correlation among parameters is reflected in their large standard deviations. The unusual features in the TCH are the very large C2C1C7 angle (162°) compared to spiropentane [16] (137.2°) and the long C4−C5 distance, 1.57 Å.

For comparison, the parameters determined for spiropentane [16] were the following (for numbering of atoms see Fig. 4): r(C1−C3) = 1.469(1) Å, r(C1−C2) = 1.519(3) Å and ∠C1C3C4 = 137.2°. In TCH, r(C1−C2) and r(C2−C3) are found about the same length as in spiropentane. The shortest bonds r(C1−C2) and r(C1−C7) have an included angle of 162°, and must be considered to have almost *sp* hybridization of the central carbon atom. The fact that r(C1−C2) is so short might well be attributed to the large measure of *s*-character.

According to the Suernam and Harmony hypothesis,[17,18] saturated small rings in different polycyclic hydrocarbons "have a certain fixed amount of electron density for C−C bonding which will be distributed around the ring in a manner which is appropriate to achieve the minimum energy configuration". As a consequence the average bond lengths of a given sized ring are fairly constant even though the individual bond lengths in the ring vary. In TCH the average C−C bond lengths (1.503 Å) agree well with cyclopropane, 1.510(2) Å.[19] The agreement is actually better than in spiropentane,[16] for which the average C−C bond length in the 3-membered ring is much shorter, 1.487 Å.

The bond distance r(C4−C5), whose length was found to be 1.57 Å, is significantly longer than the similar bond in cyclopentane,[20] r(C−C) = 1.546(1) Å. A similar trend is found

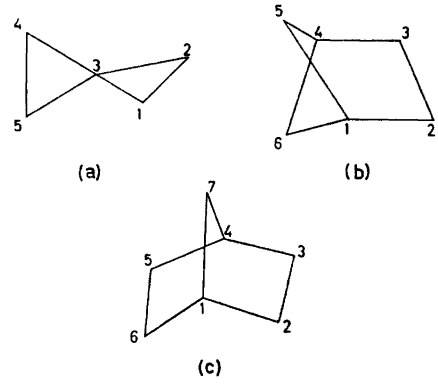

Fig. 4. Numbering of atoms in (a) spiropentane, (b) bicyclo[2.1.1]hexane and (c) norbornane.

in norbornane,[21] where the corresponding distance r(C2 – C3) is 1.557(25) Å. In bicyclo[2.1.1]hexane [22] however, r(C1 – C2) was found to be 1.544(5) Å, and r(C2 – C3) was 1.513(15) Å, which show just the opposite trend. However, other authors [23] report only the average value of these distances, as does Fukuyama *et al.*[24] in 5-thiabicyclo[2.1.1]hexane, because these two parameters are highly correlated in those molecules. In TCH the correlation coefficient between r(C4 – C5) and r(C3 – C4) is –0.82 if the l-values of C – C bond distances are varied; however, if they are not refined, the correlation coefficient of these two distances is only 0.35. The average bond length of the cyclopentane ring in TCH is 1.530(14), in comparison to 1.546(1) in cyclopentane itself.[20]

On the other hand, it is interesting that the average CCC bond angle of the five-membered ring and the torsional angles are quite similar to those in cyclopentane.[20] The average CCC angle in cyclopentane was 104.5° and the torsional angles for conformer with C_2 symmetry were 13.2, 34.3 and 42.3°.

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