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Molecular Structure of Quadricyclane (Tetracyclo[3.2.0.0^{2,7}.0^{4,6}] heptane) Studied by Gas Electron Diffraction

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The average C-C and C-H bond distances (r_g) and the C_2-C_3-C_4 angle in quadricyclane were determined by gas electron diffraction to be 1.529±0.003 Å, 1.103±0.009 Å and 98.5±2°, respectively. The molecule was found to have C_{2v} symmetry in equilibrium. A number of nonbonded distances were also determined: C_1-C_4=2.43 Å, C_1-C_3=2.50 Å and C_1-C_6=2.18 Å. This structure is compared with those of norbornane and bicyclo[2.1.0]pentane reported in recent publications.

Quadricyclane (tetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane, Fig. 1, QC), which has two cyclopropane rings, one cyclobutane ring and two cyclopentane rings fused together, is a highly strained molecule. The total strain energy measured by the heats of combustion and hydrogenation is reported to be 95.0 kcal/mol.1) Furthermore, two cyclopropane planes are expected to be only about 1.8 Å apart. In spite of these aspects of structural interest, no precise molecular geometry has yet been reported.

The sample prepared by K. Yamamura in Kyoto University2) was vaporized at room temperature, and diffraction photographs were taken3) with 40 kV electrons at the camera lengths of 243.19±0.01 and 107.73±0.01 mm. The molecular intensity and the radial distribution curve (Figs. 2 and 3) were

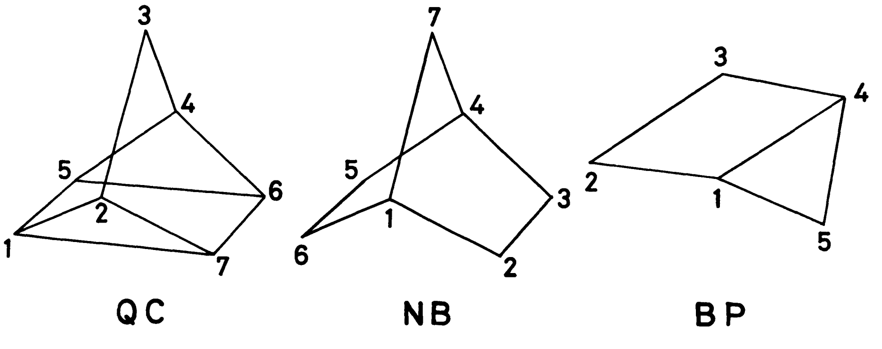

Fig. 1.
Quadricyclane (QC).
Norbornane (NB).
Bicyclo[2.1.0]pentane (BP).

obtained by a standard procedure in the q range of 7 to 120 $Å^{-1}$, and the former was analyzed under the following assumptions:[4)]

1) All the C-H distances are equal.
2) The C-C_i-H angles around each carbon atom C_i (except for C_3) are equal.
3) The H-C_3-H angle is equal to that of norbornane,[5)] 110°.
4) The H-C_3-H plane is perpendicular to the C_2-C_3-C_4 plane, and the angles bisect each other.

The mean amplitudes of vibration were calculated from a set of estimated force constants, mostly taken from the force constants for norbornane (listed in Table 1 of Ref. 5), and were held constant.

A preliminary comparison of the experimental and theoretical molecular intensities made clear that this molecule has C_{2v} symmetry in equilibrium; i.e., the four-membered ring (C_1-C_5-C_6-C_7) is planar. Accordingly, the parameters defining the molecular geometry are five internuclear distances (C_1-C_2, C_2-C_3, C_1-C_5, C_1-C_7 and C-$H_{average}$) plus one skeletal angle (C_2-C_3-C_4). Since the four C-C bond distances are nearly equal, it was difficult to determine the four C-C

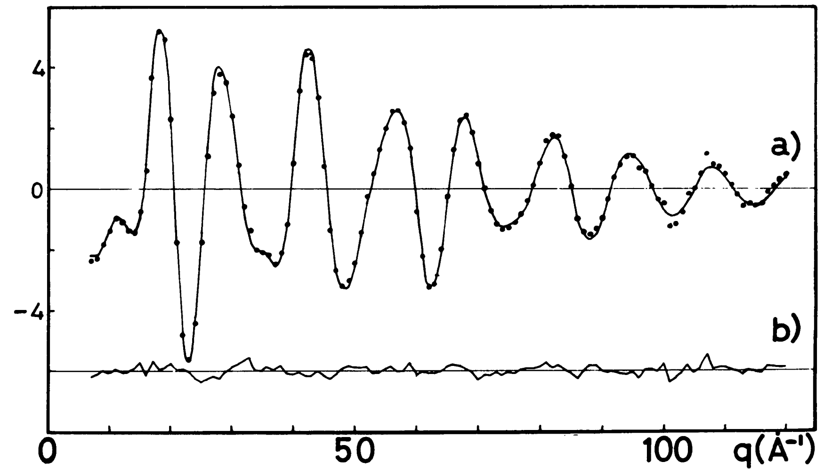

Fig. 2.

a) Molecular intensities qM(q) of quadricyclane.
dots: experimental solid line: best-fit theoretical

b) Experimental minus theoretical

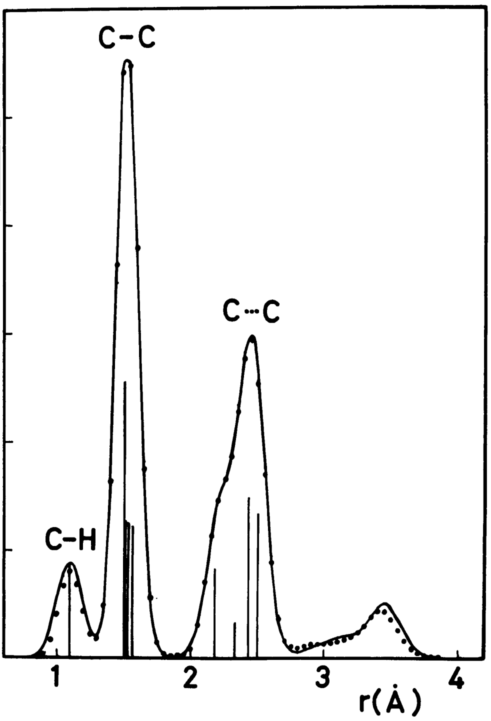

Fig. 3.

Radial distribution curves for quadricyclane with a damping factor of $\exp(-0.00016q^2)$.
dots: experimental solid line: best-fit theoretical

Table 1. Structure of quadricyclane[a)]

$(C-C)_{av}$	1.529 ± 0.003
$(C-H)_{av}$	1.103 ± 0.009
C_1-C_4	2.434 ± 0.004[b,c)]
C_1-C_3	2.498 ± 0.005[b,c)]
C_1-C_6	$2.17_6\pm0.015$[b,c)]
$(C_1-C_5)+(C_1-C_7)$	$3.08\ \pm0.02$[c)]
$\angle C_2-C_3-C_4$	$98.5\ \pm2°$[c)]

a) The r_g distances (in Å) and r_α angle.

b) It was possible to make unambiguous assignments of the radial distribution peaks (Fig. 3) to the nonbonded distances given above.

c) Uncertainties correspond to the constraint in the analysis, $(C_1-C_5)-(C_1-C_2)=0.046\pm0.023$ Å, and include 2.5 times the random errors. The mean amplitudes were held constant at estimated values.

distances separately by the use of the present experimental data alone, although the average C-C and C-H bond distances were determined to within the error limits quoted in Table 1. It was further possible to show, by means of a least-squares analysis with the following additional constraint, that the relations given in Table 1 exist among the skeletal parameters. The difference between the C_1-C_5 and C_1-C_2 distances, Δr, was fixed. Since the r_g(C-C) distances in cyclobutane[6)] and cyclopropane[7)] are 1.558 and 1.512 Å, respectively, Δr was assumed to be 0.046 ± 0.023 Å. With this range of Δr, the analyses gave the parameters and error limits given in Table 1. The sum of the C_1-C_5 and C_1-C_7 distances was estimated from the diagonal distance of the four-membered ring, C_1-C_6.

On the other hand, the C_1-C_2 and C_2-C_3 bonds are expected to resemble those in cyclopropane and norbornane, respectively, according to the known chemical properties.[8)] If one

Table 2. Structure of quadricyclane

	$I^{a,c)}$	$II^{b,c)}$
$(C - C)_{av}$	1.529	1.529
C_1-C_2	1.512(as.)	1.503(4)
C_1-C_5	1.569(7)	1.562(7)
C_1-C_7	1.517(7)	1.518(7)
C_2-C_3	1.537(8)	1.560(as.)
$(C - H)_{av}$	1.103(6)	1.103(6)
$\angle C_2$-C_3-C_4	98.3(5)°	97.5(4)°
$C_1 \cdots C_6$	2.182	2.175
$C_2 \cdots C_4$	2.324	2.346
$C_1 \cdots C_4$	2.433	2.431
$C_1 \cdots C_3$	2.503	2.510
$\angle C_1$-C_2-C_3	110.5°	110.2°
$\angle C_2$-C_1-C_5	104.6°	105.2°
$\theta^{d)}$	62.8°	63.1°
$\phi^{e)}$	106.5°	107.7°

a) The r_g distances (Å) and the r_α angles determined by least-squares analysis. The $r_g(C_1$-$C_2)$ distance was assumed to be equal to that in cyclopropane, 1.512 Å.

b) The $r_g(C_2$-$C_3)$ distance was assumed to be equal to the C_1-C_7 distance in norbornane, 1.560 Å.

c) Uncertainties to be attached to the last significant digits indicate 2.5 times random standard errors.

d) Dihedral angle between the C_2-C_1-C_5-C_4 and C_2-C_7-C_6-C_4 planes.

e) Dihedral angle between the C_1-C_2-C_7 and C_1-C_5-C_6-C_7 planes.

assumes that either the $r_g(C_1$-$C_2)$distance is equal to 1.512 Å or the $r_g(C_2$-$C_3)$ distance is equal to 1.560 Å, then the structures listed in Table 2 are obtained. As a result of a number of other analyses, the parameters and their limits of error listed in Table 3 are estimated. The limits of error include estimates of the uncertainties due to those in the mean amplitudes used. A combination of the yet unknown rotational constants with electron-diffraction data will result in a more complete structure determination.

The structural parameters determined in the present study may be compared with the corresponding parameters of norbornane (Fig. 1, NB) given in Table 3.5) The C_2-C_3-C_4 angle

Table 3. Comparison of structures[a]

Quadricyclane[b]		Norbornane[c]		Bicyclo[2.1.0]pentane[d]	
$(C-C)_{av}$	1.529(3)	$(C-C)_{av}$	$1.548_8(3)$	$(C-C)_{av}$	1.529
C_1-C_2	1.51 (2)	C_1-C_2	$1.53_9(1_2)$	C_1-C_5	1.507(2)
C_1-C_5	$1.56_5(2)$	C_2-C_3	$1.55_7(2_5)$	C_1-C_2	1.528(2)
C_1-C_7	$1.51_5(2)$[e]			C_1-C_4	1.536(1)
C_2-C_3	1.54 (3)	C_1-C_7	$1.56_0(2_4)$		
$(C-H)_{av}$	1.103(9)	$(C-H)_{av}$	$1.125_6(5)$	$(C-H)_{av}$	1.1093
$\angle C_2-C_3-C_4$	$98.5\ (2)^\circ$	$\angle C_1-C_7-C_4$	$93._1(1._7)^\circ$		
C_1-C_6	$2.17_5(2)$	C_2-C_5	2.94_5	C_1-C_3	2.177
C_2-C_4	2.33 (4)	C_1-C_4	2.27		
C_1-C_4	$2.43_4(1)$	C_2-C_4	2.43	C_2-C_5	2.482
C_1-C_3	$2.49_8(2)$	C_2-C_7	2.39		
θ	$63\ (2)^\circ$	θ	$113._1(1._8)^\circ$		
ϕ	$107\ (2)^\circ$			ϕ	$112.74(18)^\circ$

a) See Fig. 1 for numbering.

b) r_g distances and r_α angles. The uncertainties indicate estimated limits of error.

c) r_g distances and r_α angles, Ref. 5. The dihedral angle between the $C_1-C_2-C_3-C_4$ and $C_1-C_6-C_5-C_4$ planes is denoted as θ.

d) r_s structure, Ref. 9. The dihedral angle between the $C_1-C_2-C_3-C_4$ and $C_1-C_5-C_4$ planes is denoted as ϕ.

e) The sum of the C_1-C_5 and C_1-C_7 distances is 3.08±0.02 Å (Table 1).

in QC is larger than the $C_1-C_7-C_4$ angle in NB by about 5°, and the average C-C and C-H bond distances are about 0.02 Å shorter. The dihedral angle between the $C_2-C_1-C_5-C_4$ and the $C_2-C_7-C_6-C_4$ planes in QC is 63°, in contrast to the corresponding angle in NB, 113.1°. The dihedral angle between the two three-membered rings in QC is only about 34°.

The present structure may also be compared with the r_s structure of bicyclo[2.1.0]pentane (Fig. 1, BP) determined recently by Suenram and Harmony by microwave spectroscopy[9] (given in Table 3). The dihedral angle between the $C_1-C_2-C_7$ and $C_1-C_5-C_6-C_7$ planes in QC is smaller than that between the (planar) four-membered ring and the three-membered ring in BP, 112.7°. The C_1-C_2 distance in QC is essentially equal to the analogous distance (C_1-C_5) in BP, whereas the C_1-C_5 and C_1-C_7 bonds in QC seem to be longer and shorter, respectively, than the C_1-C_2 and C_1-C_4 bonds in BP.

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