Molecular Structure of Norbornane and Norbornadiene Studied by Gas Electron Diffraction

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Norbornane (bicyclo[2.2.1]heptane), norbornadiene (bicyclo[2.2.1]hepta-2, 5-diene), and their derivatives have recently been investigated in detail by NMR spectroscopy, X-ray diffraction, and thermochemical methods with particular attention to the effect of intramolecular strain on molecular structure.[1] The purpose of the present study is to obtain more precise information on the gas-phase structures of norbornane and norbornadiene so as to shed light on the strain effect. This paper reports on the striking anomalies observed in their carbon-skeleton structures as compared with ordinary unstrained hydrocarbons.

The samples were kindly provided by Drs. Hiroshi Tanida and Kazuo Tori of Shionogi Research Laboratory. Diffraction photographs were taken at room temperature using 40kV electrons with an apparatus equipped with an r^3-sector.[2] Optical densities were measured by means of a digital microphotometer[3] and were analyzed by a least-squares method, which allowed the experimental reduced molecular intensity for the q values from 15 to 120 to fit to the theoretical expression with a predetermined weight function.[2] The idependent structural parameters listed in Table 1 were taken on the assumption that all the sp^3 C-H distances and H-C-H angles were equal. The mean-square amplitudes of vibration for all the internuclear distances were calculated by the use of a plausible force model, to which the force constants for simpler molecules with analogous geometrical arrangements[4] were transferred. The results were used for the analysis as constants. The most probable values (with their estimated limits of error including possible systematic errors) given in Table 1 refer to the thermal-average atomic positions (the r_a-structure).[2]

TABLE 1. THE r_a-STRUCTURES

	Norbornane	Norbornadiene
C_1–C_2	$1.53_9 \pm 0.01_5$ Å	$1.53_3 \pm 0.005$ Å
C_2–C_3	$1.53_9 \pm 0.02_5$	$1.33_9 \pm 0.005$
C_1–C_7	$1.56_3 \pm 0.01_6$	$1.57_3 \pm 0.010$
$<C_1$–C_7–C_4	$93.2° \pm 1.5°$	$92.0° \pm 0.8°$
$<\theta$	$113.0 \pm 1.5°$	$115.0° \pm 0.8°$
C(sp^3)–H (Av.)	$1.11_4 \pm 0.01_2$	$1.10_0 \pm 0.02_0$
C(sp^2)–H	—	1.098 (ass.)
<H–C–H (Av.)	$110° \pm 3°$	112° (ass.)
<C=C–H	—	$123° \pm 4°$

For norbornane the best-fit structure is found to have the C_{2v} symmetry. The average values of the C-C bond distance, 1.547 ± 0.002 Å, is about 0.01 Å larger than the ordinary sp^3-sp^3 carbon bond distance. A close examination has shown that the C_1–C_7 bridge bond is mainly responsible for this lengthening. This bond appears to be longer than that in cyclobutane,[5] which has one of the longest C-C bonds (about 1.56 Å) ever reported in the literature. The C-C-C angles (the C_1–C_7–C_4 angle in particular) are appreciably smaller than the tetrahedral angle. This finding is in line with the X-ray observations on similar angles in certain derivative molecules in the crystal phase.[1] Therefore, the angle distortions found in crystals should primarily be of intramolecular origin rather than of intermolecular origin.

The frame structure of norbornadiene is quite similar to that of norbornane, except that the C_2=C_3 double bond distance is nearly equal to that in ethylene. The dihedral angle between the $C_1C_2C_3C_4$ and $C_1C_6C_5C_4$ planes, θ, is found to be larger than that observed by Schomaker and Hamilton[6] by about 4°.

Further analysis is now in progress. These molecules are also being studied by gas electron diffraction by Bauer,[7] Dallinga,[8] and Davis.[9] To the authors' knowledge the conclusion of the present paper are consistent with what they have observed so far.

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