Gas electron diffraction study of the geometric structure of triallylborane molecule

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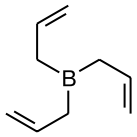
The main structural parameters of the triallylborane molecule having the C_3 symmetry were determined by gas electron diffraction and quantum-chemical calculations at the MP2/6-31G(d,p) and B3LYP/6-31G(d,p) levels. The parameters calculated by the MP2/6-31G(d,p) method are in better agreement with the experimental data than those calculated by the B3LYP/6-31G(d,p) method.

Key words: triallylborane; gas electron diffraction; *ab initio* quantum-chemical calculations; molecular structure; force field.

Triallylborane is the first representative of β,γ-unsaturated boron derivatives. It is extremely chemically reactive and is widely used in organic synthesis.[1—4] Due to the presence of the double bond, the properties of triallylborane differ radically from those of organoboranes of other classes (alkyl, aryl, and vinyl analogs). The specific structural features of the triallylborane molecule are most clearly manifested in its ability to bind to compounds containing the C=O, C=S, C=N, C≡N, C=C, C≡C, or N=O double bonds. This general 2π+2π+2σ-type reaction is called allylboronation.[4] The unique property of triallylborane is its ability to undergo 1,3-sigmatropic shift of boron (permanent allylic rearrangement), whose rate is ~5000 s^{-1} at 100 °C ($\Delta G_{298}^{\neq} = 61.65$ kJ mol^{-1}).[2,5]



Up to now, there has been no experimental data on the main geometric and structural characteristics of this highly symmetrical compound, which are necessary for a deep understanding of its chemical behavior. Structural studies of organoboron compounds present a problem because of their instability in air, due to which all operations are necessary to perform in an inert atmosphere.

In the present study, we investigated the geometric structure and structural parameters of triallylborane by gas electron diffraction and carried out quantum-chemical calculations for this molecule.

Experimental

Triallylborane was prepared by the reaction of sesquiallylaluminum bromide with *n*-butyl borate,[6,7] b.p. 43—45 °C (10 Torr), $n_D^{20} = 1.4500$. The purity of the compound (^{11}B NMR spectroscopic data) was ≥ 99%.

Samples of triallylborane in sealed tubes were used without additional purification. Electron diffraction patterns were obtained on an EG-100M instrument in the following conditions: T = 20 °C, the accelerating voltage was 60 kV, the electron beam current was 0.50 μA, vacuum was $3.5 \cdot 10^{-5}$ Torr, the nozzle—plate distances were 193.94 and 362.28 mm. Simultaneously, electron diffraction patterns of CCl_4 as the standard were measured to determine the electron wavelength. The parameters for CCl_4 were taken from the literature.[8] The films were scanned on a precalibrated UMAX Astra 4500 scanner followed by processing of the electron diffraction data according to a procedure described earlier.[9] The experimental molecular scattering intensity curves were measured in ranges $9.2 \le s \le 29.6$ and $3.4 \le s \le 13.8$ Å^{-1} (Fig. 1).

Quantum-chemical calculations. A conformational search by molecular mechanics methods gave the following two possible nonplanar conformations: an unsymmetrical conformation (one C_{sp^3}—C_{sp^2} bond lies in the plane formed by the boron atom and three carbon atoms, and two other C_{sp^3}—C_{sp^2} bonds deviate from this plane in the opposite directions) and a conformation having the approximate C_3 symmetry. Quantum-chemical calculations by the DFT and MP2 methods with the 6-31G(d,p) and 6-311G(d,p) basis sets confirmed the possibility of existence of these conformations. Calculations at the MP2/6-311G(d,p)

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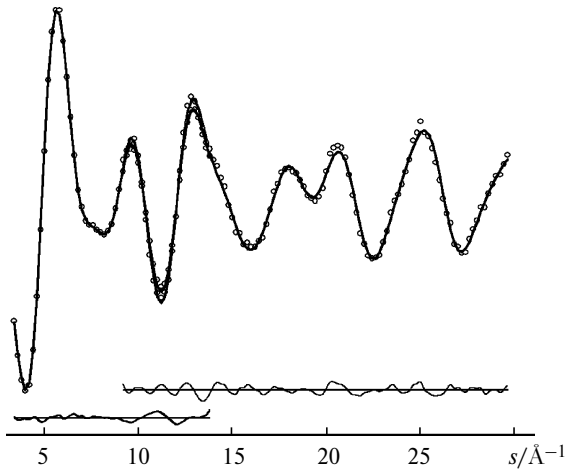

Fig. 1. Molecular intensity curves of triallylborane (solid and dotted lines represent the calculated and experimental data, respectively) and their differences.

level predicted that the symmetrical conformer is 2.0 kcal mol^{-1} more stable than the unsymmetrical conformer, whereas the energy of the unsymmetrical conformer estimated by the B3LYP/6-31G(d,p) method is 1.2 kcal mol^{-1} lower than that of the symmetrical conformer. It should be noted that the DFT method with geometry optimization using the above basis sets is characterized by a poor convergence regardless of the way of varying of the molecular geometry. Calculations, in which the Cartesian coordinates, parameters of the *z* matrix, or redundant internal coordinates were varied, resulted in poor convergence due to oscillations. The quadratic force field was calculated at the MP2/6-31G(d,p) level, and the rms vibrational amplitudes and vibrational corrections were calculated according to a known procedure.[10] All quantum-chemical calculations were carried out using the Gaussian 03 program package.[11]

Structural analysis. Examination of the two possible conformations allowed us to reject the unsymmetrical conformer. The geometry of the symmetrical conformer (Fig. 2) was described as the *z* matrix. To provide the C_3 symmetry, we used one imaginary atom bound to the boron atom. The structural analysis involved the refinement of the following eight geometric parameters with the simultaneous use of two *sM*(*s*) curves (curves were measured using the long and short nozzle—plate distances): the r_a(B—C), r_a(C—C), and r_a(C=C) distances and the X—B—C, B—C—C, C—C=C, X—B—C—C, and B—C—C=C angles (Table 1). The experimental angles involving the imaginary atom are 81.6(1.5)° (X—B—C) and 144.6(3.8)° (X—B—C—C). The rms vibrational amplitudes calculated according to a standard procedure[10] (using the quantum-chemical MP2/6-311(d,p) force field) and the refined rms vibrational amplitudes are given in Table 2. The agreement factors between the experimental data and the theory for the *sM*(*s*) curves (see Fig. 1) measured using the long and short the nozzle—plate distances were 3.5% and 9.9%, respectively. The total *R* factor was 6.3%.

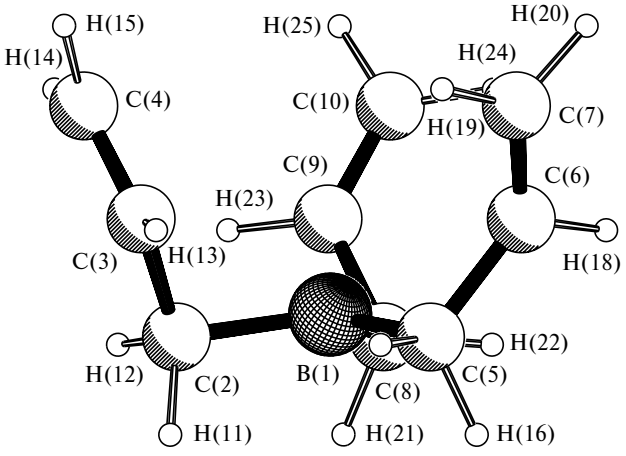

Fig. 2. Model of the triallylborane molecule (C_3 symmetry).

Table 1. Experimental and theoretical (quantum-chemical) geometric parameters of the triallylborane molecule

Parameter	GE[a]	MP2/6-31G(d,p)	B3LYP/6-31G(d,p)
Bond	r_g/Å	r_e/Å	
B—C	1.583(3)[1]	1.580	1.589
C—C	1.503(3)[1]	1.504	1.510
C=C	1.332(3)[2]	1.338	1.334
$(C—H)_{av}$	1.093[b]	1.086	1.093
Angle		φ/deg	
B—C—C	102.8(0.8)[3]	107.7	111.2
C—C—C	127.4(0.7)[4]	124.5	125.3
B—C—C—C	100.2(3.6)[5]	114.6	116.9
C—B—C—C	72.0[c]	67.6	63.5
C—B—C	117.9(1.5)	120.0	120.0

[a] 1...5 are groups of parameters, the total errors are given in parentheses: 3σ of least-squares + scaling error.
[b] The value is taken from the quantum-chemical calculations.
[c] The dependent parameter.

Results and Discussion

Earlier, the structural parameters of the molecules of two simplest triorganoboranes, *viz.*, trimethylborane[12] and trivinylborane,[13] were determined by gas electron diffraction. Trimethylborane[12] has a planar skeleton with the bond length r_a(B—C) = 1.578(1) Å. Trivinylborane[13] is also planar with the shortened bond r_a(B—C) = 1.558(3) Å and the elongated C=C double bond: r_a(C=C) = 1.370(6) Å (in ethylene, r_a(C=C) = 1.337(2) Å;[12] in propylene, r_a(C=C) = 1.342(2) Å).[12] Using triallylborane as an example, it is of interest to examine the general rule according to which the C—X bond in X—C—C=C systems is opposite the C=C double bond. In this case, the molecular skeleton should be planar (Fig. 3, the φ angle projected onto the C—C bond should be equal to zero), which would, evidently, lead to steric hindrance. However, the C—H bond (instead of the boron atom) can also be oriented toward the C=C bond. The interaction of the π orbitals of the double bonds with the unoccupied p orbital of the boron atom can stabilize the C_3 symmetrical conformation.

Table 2. Experimental and theoretical rms vibrational amplitudes of the triallylborane molecule

Distance	r_e*/Å	Amplitude/Å	
		Experiment**	Calculations***
$(C—H)_{av}$	1.086	0.075	0.075
C=C	1.338	0.056(2)[a]	0.041
C—C	1.504	0.065[a]	0.050
B—C	1.580	0.068[a]	0.053
$(C...H)_{av}$	2.0—2.3	0.115(7)[b]	0.100
$(B...H)_{av}$	2.15—2.30	0.125[b]	0.114
C...C	2.5	0.070(7)[c]	0.064
B...C	2.6	0.115[c]	0.110
C...C	2.7	0.082[c]	0.076
C...H	3.21	0.219(33)[d]	0.132
C...C	3.25	0.256[d]	0.170
C...H	3.35	0.241[d]	0.155
B...C	3.6	0.255[d]	0.168
C...C	3.8	0.272(58)[e]	0.179
C...C	4.1	0.362[e]	0.269
C...C	4.4	0.519(69)[f]	0.365
C...C	4.4	0.391[f]	0.236
C...H	4.6	0.514[f]	0.359
C...C	4.6	0.429[f]	0.274
C...H	4.7	0.564[f]	0.410
C...H	4.9	0.765[f]	0.611
C...H	5.0	0.423[f]	0.269
C...C	5.0	0.525[f]	0.371
C...H	5.0	0.505[f]	0.350
C...H	5.0	0.451[f]	0.297
C...C	5.2	0.642[f]	0.488

* The distance calculated at the MP2/6-31G(d,p) level.
** a,b,c,d,e,f are groups of the least-squares, the total error for the corresponding group is given in parentheses.
*** The parameters were calculated from the theoretical MP2/6-31G(d,p) harmonic force field.

The triallylborane molecule has the C_3 symmetry. The experimental data are in better agreement with the values (except for the C=C bond length) calculated at the MP2/6-31G(d,p) level than with the parameters calculated at the B3LYP/6-31G(d,p) level, because the thermally averaged distances r_g are always longer than the equilibrium distances r_e in the physical sense. One would expect a typical decrease in the bond lengths calculated by quantum-chemical methods as the basis set is extended,

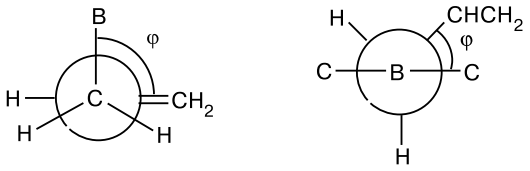

Fig. 3. Newman projections of triallylborane along the C—C (*a*) and B—C (*b*) bonds.

Table 3. Comparison of selected experimental data on the geometry of the triallylborane molecule and molecules containing analogous structural fragments (experimental data for the reference molecules are taken from the literature[12,13])

Molecule	r_a/Å			C—C=C angle /deg
	B—C	C—C	C=C	
$B(CH_2—CH=CH_2)_3$	1.580(3)	1.500(3)	1.330(3)	127.4(0.7)
$H_2C=CH_2$	—	—	1.337(2)	—
$CH_3—CH=CH_2$	—	1.506(3)	1.342(2)	124.3(0.4)
$B(CH_3)_3$	1.578(1)	—	—	—
$B(CH=CH_2)_3$	1.558(3)	—	1.370(6)	—

resulting in a better agreement with experimental values. The boron atom is weakly pyramidal. The C—B—C angle is 117.9(1.5)°, and the X—B—C angle is 81.6(1.5)° (90.0° for the planar configuration). The B—C—C angle is 102.8(0.8)°, which is somewhat different from the tetrahedral angle (109.45°). The C—H single bond is projected onto the C=C double bond; the angle φ(H—C—C=C) is 23.5° (see Fig. 3), which approximately confirms the rule of projection of the Y—C bonds in Y—C—C=C systems.

Table 3 gives a comparison of the geometric parameters of the triallylborane molecule with the corresponding parameters of the molecules containing analogous fragments. The C—B bond in the triallylborane molecule is slightly longer than that in the trimethylborane molecule. The C—C single bond length is consistent with the data for the C—C=C systems.[12] The C=C double bond lengths in triallylborane, ethylene, and propylene are somewhat different. The C—C=C bond angle (127.4(7)°) is typical of this fragment.[12]

The Fourier curve (Fig. 4) at 4 Å shows deviations from the theory because of a discrepancy between the calculated rms vibrational amplitudes and experimental values. Variations of the amplitudes in this region do not improve the results (do not decrease the *R* factor) due, apparently, to the fact that the differences in the vibrational amplitudes, which are calculated from the quantum-chemical force field and are not varied, are inconsistent with the experimental values. Nevertheless, this has only a slight effect on the molecular conformation. Yet another possible reason is the presence of impurities of unsymmetrical conformers. The triallylborane molecule has six independent tops (three C—B—C—C and three B—C—C=C) and, hence, can have many additional less stable conformers. This mixture of conformers cannot be adequately simulated in terms of the static model from gas electron diffraction due to low sensitivity of the parameters to the changes in the conformational composition. In the general case, the use of a dynamic model would require a six-dimensional potential function, which is also a complicated problem.

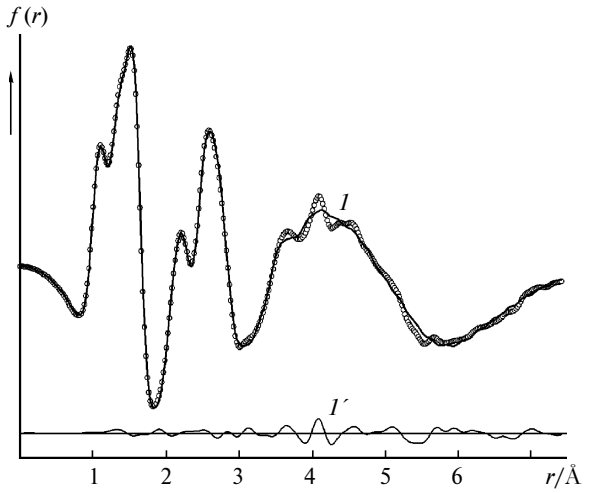

Fig. 4. Radial distribution of atoms in the triallylborane molecule: experimental data are indicated by a dotted line, curves *1* and *1´* represent the calculated data and the difference between the experimental data and the theory.

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