An Electron-Diffraction Investigation of the Molecular Structure of Toluene

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(Z. Naturforsch. **32 a**, 1063–1064 [1977];
received June 20, 1977)

The structural parameters of toluene have been determined by gas-phase electron diffraction. The bond distances in r_g are as follows: C–C (ring) 1.399 ± 0.002 Å, C–C (methyl) 1.524 ± 0.007 Å, C–H (ring) 1.11 ± 0.01 Å and C–H (methyl) 1.10 ± 0.02 Å.

This note reports results on the molecular structure of toluene [1].

The diffraction patterns were taken in the OSU apparatus under experimental conditions similar to those reported in a recent publication and references cited therein [2]. The sample was purified by distillation before use. The sample-bath temperature was kept at +7 °C, while the nozzle-tip was at room temperature.

Six plates, three at the long camera distance and three at the middle camera distance were selected and the structure refined by the least-squares method [3]. Numerical calculations for reduction of data and least-squares analysis were performed using computing programs of the OSU ED library [4].

A regular hexagonal structure of the ring and the C_{3v} symmetry of the methyl group were assumed. Five geometrical parameters, C–C (ring), C–C (methyl), C–H (ring), C–H (methyl) and HCH (methyl), then determine the structure. All the atomic distances were deduced from these parameters under the geometrical constraint of an r_α-structure [5]. The conversion between r_a and r_α was made by the use of parallel and perpendicular amplitudes of vibration which were taken mostly from the values of benzene [6]. The amplitudes related with the methyl group were assumed as approximate values.

Since the internal rotation of the methyl group is known to be essentially free [7], the contribution of the terms of methyl hydrogen to ring carbon was calculated by superposition of the intensities for three different torsional angles, 0, 15, and 30°, with proper weights. The contribution was nearly negligible, although it was included in the final least-squares refinement. All terms of methyl hydrogen to ring hydrogen were ignored.

The final results for the structure and the rms amplitudes are summarized in Table 1; they are in very good agreement with those of Seip et al. [1]. The HCH angle and the amplitudes not listed in the table were fixed at assumed values. It is seen that the ring structure of toluene is equivalent to that of benzene; r_g(C–C) 1.399(1) Å and r_g(C–H) 1.101(5) Å [6]. The rms amplitudes calculated from the force constants by Lau and Snyder [8] are also listed for comparison.

The rms amplitudes between carbon and hydrogen are mostly in fair agreement with the calculated values within their uncertainties. For those between carbon atoms, however, the experimental values are systematically larger than the calculated ones. This may be due to some unidentified systematic errors in the experimental and analytical procedures. On the other hand, they may be due to a small but significant deviation of the ring from the assumed regular hexagonal shape. Kreiner and coworkers

Table 1. Final results for structure and rms amplitudes of toluene [a, b].

	Geometrical parameters	
	r_a	r_g
C–C	1.3976 (16)	1.399_4
C–C_M	1.5214 (65)	1.523_5
C–H	1.106 (11)	1.112
C_M–H_M	1.097 (16)	1.103
<HCH	109.3° (assumed)	

	rms Amplitudes	
	l	l_{calc} (295 K)
C–C	0.051 (2)	0.046
C–C_M	0.056 (3)	0.049
C–H	0.081 (6)	0.077
C_M–H_M	0.083 (6)	0.079
$C_1 \ldots C_3$	0.062 (3)	0.054
$C_M \ldots C_2$	0.070 (4)	0.066
$C_1 \ldots C_4$	0.068 (5)	0.060
$C_M \ldots H_8$	0.125 (7)	0.137
$C_3 \ldots H_8$	0.097 (9)	0.099
$C_1 \ldots H_M$	0.108 (10)	0.109
$C_4 \ldots H_8$	0.098 (14)	0.096
$C_5 \ldots H_8$	0.084 (9)	0.094
$C_M \ldots C_3$	0.071 (9)	0.066
$C_M \ldots C_4$	0.070 (20)	0.067

[a] Distances and rms amplitudes in Å units. Quantities in parentheses are 2 σ including estimates of correlation and systematic error. The rms amplitudes in curly brackets were refined as groups.

[b] Numbering of atoms is as follows: ring carbons C_1 through C_6 where C_1 is bonded to the methyl group, C_2, C_6 at the ortho-position, and C_4 at the para-position; H_8 is the hydrogen bonded to C_2; C_M and H_M are in the methyl group.

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proposed an equilateral but-non-regular C-hexagon as a reasonable model consistent with their microwave measurements[9]. More detailed structure information may be obtained by a joint analysis of the diffraction and spectroscopic results, which is now under way.

The author wishes to thank Professor Kenneth Hedberg and Mrs. Lise Hedberg for their helpful suggestions in this work. The work was supported by the National Science Foundation under Grant CHE-74-13527.

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