

An Electron-Diffraction Investigation of the Molecular Structure of Toluene

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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 toluene¹.

The diffraction patterns were taken in the OSU apparatus under experimental conditions similar to those reported in a recent publication and references cited therein². The sample was purified by distillation before use. The sample-bath temperature was kept at $+7^\circ\text{C}$, 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 method³. Numerical calculations for reduction of data and least-squares analysis were performed using computing programs of the OSU ED library⁴.

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_a -structure⁵. The conversion between r_a and r_g was made by the use of parallel and perpendicular amplitudes of vibration which were taken mostly from the values of benzene⁶. 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 free⁷, 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; $r_g(\text{C}–\text{C})$ $1.399(1)$ Å and $r_g(\text{C}–\text{H})$ $1.101(5)$ Å⁶. The rms amplitudes calculated from the force constants by Lau and Snyder⁸ 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 | $l_{\text{calc}}(295\text{ K})$ |
| 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 ... C ₃ | 0.062(3)} | 0.054 |
| C _M ... C ₂ | 0.070(4)} | 0.066 |
| C ₁ ... C ₄ | 0.068(5)} | 0.060 |
| C _M ... H ₈ | 0.125(7)} | 0.137 |
| C ₃ ... H ₈ | 0.097(9) } | 0.099 |
| C ₁ ... H _M | 0.108(10)} | 0.109 |
| C ₄ ... H ₈ | 0.098(14) | 0.096 |
| C ₅ ... H ₈ | 0.084(9)} | 0.094 |
| C _M ... C ₃ | 0.071(9)} | 0.066 |
| C _M ... C ₄ | 0.070(20) | 0.067 |

^a Distances and rms amplitudes in Å units. Quantities in parentheses are 2σ 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 C₁ through C₆ where C₁ is bonded to the methyl group, C₂, C₆ at the ortho-position, and C₄ at the para-position; H₈ is the hydrogen bonded to C₂; 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 measurements⁹. More detailed structure information may be obtained by a joint analysis of the diffraction and spectroscopic results, which is now under way.

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¹ For a concurrent independent investigation cf. R. Seip, Gy. Schultz, I. Hargittai, and Z. G. Szabó, *Z. Naturforsch.* **32a**, October [1977].

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⁴ L. Hedberg, Fifth Austin Symposium on Gas Phase Molecular Structure, Austin, Texas, March, 1974, p. 37.

⁵ For the definitions of r_α , r_a and r_g , see K. Kuchitsu and S. J. Cyvin, *Molecular Structure and Vibrations*, ed. by S. J. Cyvin, Chapter 12, Elsevier, Amsterdam 1972.

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