Electron Diffraction Study of the Toluene Molecular Geometry

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On the basis of an electron diffraction analysis, the following structural information was obtained on vapour phase toluene molecules: $r_g(\mathrm{C}\cdots\mathrm{C})_{\mathrm{mean}}$ 1.399 ± 0.002 Å, $r_g(\mathrm{C}-\mathrm{C})$ 1.511 ± 0.008 Å, the mean length of the C—H bonds is 1.117 ± 0.005 Å (r_g). The methyl C—H bonds are at least 0.020 Å longer than the phenyl C—H bonds which are not longer than those in benzene.

Toluene has been a favourite reactant in homogeneous gas kinetics due to its role as a powerful free radical scavenger. The assumed mechanism of its action is that toluene can prevent the development of a chain reaction if the energy of the bond broken in the primary act is larger than the C—H bond dissociation energy in the toluene sidechain, or if the lifetime of the radical formed in the primary process is longer than the time which elapses before it reacts with toluene. Thus toluene generally breaks the chains at the first step and the amount of products, especially dibenzyl, yields quantitative information about the relative extent of the chain reaction. The technique is thus based on the relatively weak C—H bond in the sidechain. Several other bond dissociation energy determinations also point to the fact that a phenyl ring weakens the neighbouring bonds although this influence and thus the C—H bond strength is not known accurately. In the light of a recent study on the correlation between the strength and length of bonds by Szabó and Konkoly-Thege[1], it seemed desirable to attempt a determination of the difference between the lengths of the methyl and phenyl C—H bonds[1a].

A sector electron diffraction investigation of toluene by Keidel and Bauer more than 20 years ago[2] yielded

$$r(\mathrm{C}\cdots\mathrm{C}) = 1.39^{2} \pm 0.005\ \text{Å},$$
$$r(\mathrm{C1}-\mathrm{C7}) = 1.51 \pm 0.02\ \text{Å}$$

and the weighted average of the C—H bond lengths 1.11 ± 0.02 Å. The numbering of atoms is given in Figure 1. This analysis, however, did neither contain a least-squares refinement of the parameters nor provided mean amplitudes of vibration.

Recently, Kreiner, Rudolph and Tan[3] have reported the results of a microwave spectroscopic investigation based on the spectra of five further isotopic species of toluene in addition to that of the most abundant species which had been recorded earlier[4]. It was shown that the toluene molecule, disregarding the methyl hydrogens is planar. The substitution coordinates of the carbon and hydrogen atoms adjacent to the ring skeleton were determined. These data, however, did not allow the calculation of any r_s bond distances. Some r_s non-

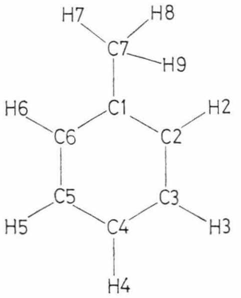

Fig. 1. The numbering of atoms.

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bond distances could be calculated, however. The various r_0 structures which could be obtained, were not considered to be satisfactory by the authors[3].

Experimental

The present electron diffraction data were obtained at room temperature with the Balzers KD-G2 apparatus in Oslo[5]. Four plates (Kodak Electron Image) were chosen from each camera distance of 50 and 25 cm. The wavelength was determined from TlCl patterns and corrected according to benzene data. The procedure of data reduction was as previously described[6]. The reduced molecular intensities and radial distributions are shown in Figures 2 and 3, respectively.

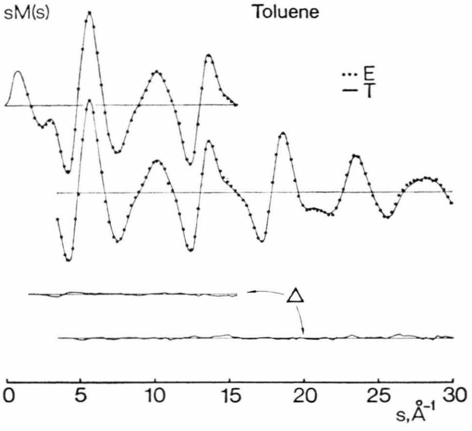

Fig. 2. Molecular intensities, E — experimental, T — theoretical in the two data ranges. The theoretical curves were calculated from the parameters given in Table 1. The difference curves are also shown.

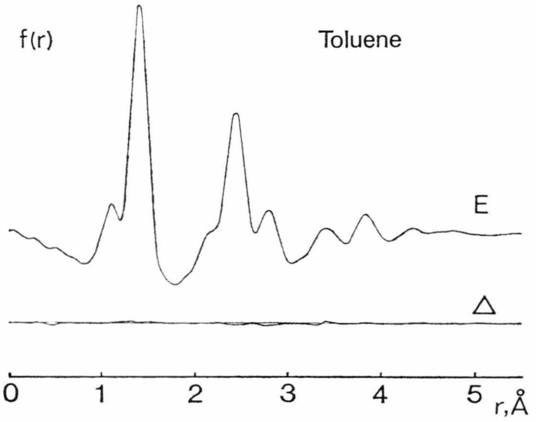

Fig. 3. Experimental radial distribution curve calculated with an artificial damping factor $\exp(-as^2)$, $a = 0.002$ Å^2. The difference curve referring to the distribution calculated from the parameters of Table 1 is also shown.

Analysis, Results, Discussion

The structure refinement was performed under the following assumptions. In the C_6H_5 group the ring has hexagonal symmetry, all C—H bonds adjacent to the ring are of equal length, and all C—C—H angles are 120°. The CH_3 group has C_{3v} symmetry. The least-squares method[6a] was applied to the reduced molecular intensities[6b].

Two schemes were employed for structural refinement. The Budapest scheme used the mean values and differences both for the C—C and C—H bonds and the bond angle C1—C7—H7, as

Table 1. Bond and non-bond distances in toluene from a least squares refinement, using the Budapest scheme. The C1—C7—H7 bond angle was 107.6 (12)° in this refinement. The parenthesized values are the standard deviations obtained ignoring non-diagonal elements of the weight matrix. l^{SP} are the mean amplitudes of vibration calculated[8] from spectroscopic data.

Atomic pairs	Multiplicity	r^a (Å)	l (Å)	l^{SP} (Å)
C1—C2	6	1.3976 (2)	0.051 (1) i	0.046
C1—C7	1	1.509 (2)	0.054 i	0.050
C2—H2	5	1.098 (12)	0.078 (7) ii	0.077
C7—H7	3	1.145 (24)	0.079 ii	0.078
C1 ··· C3	6	2.4207 (3)	0.062 (1) iii	0.054
C1 ··· C4	3	2.7952 (4)	0.068 (2) iv	0.057
C2 ··· C7	2	2.518 (1)	0.074 iii	0.067
C3 ··· C7	2	3.803 (2)	0.072 (3) v	0.067
C4 ··· C7	1	4.304 (2)	0.071 (7) vi	0.065
C1 ··· H2	10	2.166 (2)	0.102 (2) vii	0.099
C1 ··· H3	10	3.416 (2)	0.096 (4) viii	0.096
C1 ··· H4	5	3.893 (3)	0.093 (assumed)	0.093
C1 ··· H7	3	2.153 (12)	0.094 vii	0.109
C2 ··· H7	2	2.804 (9)		0.201
C2 ··· H9	1	3.439 (15)		0.106
C3 ··· H7	2	4.117 (10)		0.176
C3 ··· H9	1	4.574 (12)		0.116
C4 ··· H7	3	4.777 (10)		0.138
C5 ··· H7	2	4.427 (10)		0.161
C5 ··· H9	1	3.954 (12)		0.148
C6 ··· H7	2	3.241 (12)		0.176
C6 ··· H9	1	2.557 (12)		0.147
C7 ··· H2	2	2.725 (1)		0.137
C7 ··· H3	2	4.683 (2)		0.113
C7 ··· H4	1	5.402 (3)		0.097
H2 ··· H3	4	2.496 (3)		0.158
H2 ··· H4	4	4.322 (4)		0.133
H2 ··· H5	2	4.991 (5)		0.118
H2 ··· H7	2	2.743 (8)		0.331
H2 ··· H9	1	3.821 (20)		0.151
H3 ··· H7	2	4.874 (10)		0.235
H3 ··· H9	1	5.553 (12)		0.138
H4 ··· H7	3	5.851 (9)		0.164
H5 ··· H7	2	5.337 (9)		0.212
H5 ··· H9	1	4.626 (15)		0.186
H6 ··· H7	2	3.498 (14)		0.271
H6 ··· H9	1	2.271 (20)		0.201
H7 ··· H8	3	1.891 (46)		0.127

Table 2. Sample of the least squares results from the Oslo scheme. The parenthesized values are the standard deviations obtained using both diagonal and non-diagonal matrix elements.

	r_a (Å)	l (Å)	r_a (Å)	l (Å)	r_a (Å)	l (Å)
			ϕ(C2−C1−C7−H7) = 0°			
C1−C2	1.3979 (4)	0.0508 (8) i	1.3981 (4)	0.0505 (8) i	1.3986 (5)	0.050 (1) i
C1−C7	1.511 (3)	0.0538 i	1.512 (3)	0.0535 i	1.514 (3)	0.053 i
C2−H2	1.098 (4)	0.084 (3) ii	1.092 (3)	0.082 (3) ii	1.081 (5)	0.069 (9) ii
C7−H7	1.12 (const.)	0.085 ii	1.14 (const.)	0.083 ii	1.183 (21)	0.070 ii
<C1−C7−H7	109.3 (10)°		109.3 (10)°		109.2 (10)°	
R		7.65		7.52		7.46
			ϕ(C2−C1−C7−H7) = 90°			
C1−C2	1.3982 (5)	0.0508 (8) i	1.3983 (4)	0.0507 (8) i	1.3991 (5)	0.049 (1) i
C1−C7	1.513 (3)	0.0538 i	1.514 (3)	0.0537 i	1.516 (3)	0.052 i
C2−H2	1.094 (3)	0.085 (3) ii	1.088	0.082 (3) ii	1.078 (3)	0.062 (8) ii
C7−H7	1.12 (const.)	0.086 ii	1.14 (const.)	0.083 ii	1.197 (14)	0.063 ii
<C1−C7−H7	111.2 (12)°		111.2 (12)°		110.1 (13)°	
R		7.42		7.21		7.00

independent parameters. The Oslo scheme used all four bond distances and the bond angle C1–C7–H7, although the methyl C—H bond length was kept constant at various values in most calculations.

The mean amplitudes of vibration (l values) for the two types of each bond were coupled as well as those for some of the nonbond distances. The initial data were taken from benzene and other systems[7].

A normal coordinate analysis[8] provided calculated mean amplitudes of vibration (and also perpendicular correction terms) using experimental frequencies[9]. This study confirmed our assumption on the differences in the mean amplitudes of vibration both for the two C—C and C—H bonds. The calculated l values are listed in Table 1.

The influence of the assumption on the relative orientation of the methyl group and the ring was also examined. No defined conformation seemed to be preferred and the changes in the other parameters were negligible except for the C1–C7–H7 bond angle.

The other conditions of refinement including the experimental backgrounds have also been changed repeatedly in both schemes. The length of the ring C—C bond and the C—C bond amplitudes proved to be very insensitive to any changes in the refinement conditions. The lengths of the C—C bond adjacent to the ring and the C—H bonds changed a little in the Oslo scheme. When both C—H bond distances were refined simultaneously in the latter, the methyl C—H bond distance became especially large and the C—H l values seemed to be too small. What seems to be most important for our later discussion is, that the C—H bond in phenyl has never been found longer than in benzene or, for that matter, than that determined in the Budapest scheme.

A sample of results from the two schemes obtained in different conditions is given in Tables 1 and 2.

The mean value for the ring C—C bond lengths is very well determined and is strikingly the same as the C—C distance found in benzene[10, 11]. They are compared in terms of different parameters in Table 3. The ring C—C bond distances change very little in other monosubstituted benzene derivatives as well, as seen from the data collected in Table 4. It is important to emphasize that there is no parameter type in which the data for all molecules could be compared. Thus the agreement may be good only to the extent that these parameters with different physical meaning may be compared. However, the ring C—C bond distances are not expected to be strongly influenced by the intramolecular motion. The substitution structures determined by microwave spectroscopy also show relatively little variations in the ring C—C distances within the same molecule which is pleasing in the light of the compelled assumption of putting all ring C—C distances equal in the electron diffraction analysis of toluene.

Table 3. The ring C—C and adjacent to the ring C—H bond lengths in benzene[10] and toluene. The correction terms for interconversion of the toluene distances were taken from Brunvoll et al.[8]

	C—C		C—H	
	benzene	toluene	benzene	toluene
r^a (Å)	1.3971	1.398	1.1018	1.098
r_g (Å)	1.3986	1.399	1.1072	1.104
r_α (Å)	1.395[9]	1.396	1.091	1.087

As the Budapest scheme used the difference Δr(C—H) as independent parameter, it is interesting to quote this result 0.047 (32) Å. Since the standard deviation is very large, it is of importance to examine in more detail the reliability of this result. This can be done by Hamilton's R-factor test[17]. Since the assumptions implied in the test are not necessarily fulfilled by the electron diffraction R-values, however, the results of the test should be used with caution. Applying the test, a series of refinements were performed with fixed values of Δr(C—H) and varying all the other parameters as in the calculation in which Δr(C—H) was determined. According to this test Δr(C—H) is larger than 0.025 Å on a 99% confidence level and larger than 0.020 Å on a 99.5% confidence level. A test for the Oslo refinement scheme provided similar results.

A calculation under the assumption that there is only one type of C—H bond gave 1.111 (3) Å in terms of r_a, and 0.081 (2) as l. It is then interesting to note that the length of the phenyl C—H bond was found to be 1.098 (12) Å, cf. Table 1, or less, cf. Table 2. Note also that this observation is consistent with the structural data on other monosubstituted benzene derivatives showing the C—H bonds adjacent to the ring to be little different from those of benzene. Some relevant data are given in Table 4. Here again allowance must be made for comparing parameters with different physical meaning. It is perhaps a safe estimate that r_s(C—H) is about 0.005 Å smaller than r_z(C—H). Note again that the phenyl C—H bonds in different positions show relatively little variations.

The electron diffraction results on the length of the phenyl C—H bonds of toluene are in complete agreement with the microwave spectroscopic data on other monosubstituted benzene derivatives according to which the C—H bonds depend very little on the nature of the substituent, or, what is especially important for the present discussion, show no considerable lengthening.

There is one more evidende for the relative insensitivity of the positions of the hydrogen atoms in the monosubstituted benzene derivatives as compared with benzene, and that is the close similarity of the substitution distances between hydrogen atoms adjacent to the ring. Fortunately these data are available for toluene as well, and they are compared with data on other molecules in Table 5.

All in all, if the phenyl C—H bonds of toluene are not longer than the C—H bonds of benzene, the reliably determined mean r(C—H) of

Table 4. Ring bond lengths (Å) and the lengths (Å) of the C—H bonds adjacent to the ring in benzene and some of its monosubstituted derivatives.

	Molecules							
	benzene		toluene[c]	benzonitrile[d]	aniline[e]	phenol[f]	fluorobenzene[g]	chlorobenzene[h]
Bonds	r_α^{0a}	$r_z{}^b$	r_α	r_z	r_s	r_0	r_s	r_s
C1—C2				1.396	1.397		1.383	1.402
C2—C3				1.391	1.394		1.395	1.390
C3—C4				1.399	1.396		1.397	1.397
Mean	1.396	1.397	1.396	1.395	1.396	1.398	1.392	1.396
C2—H2				1.088	1.082	1.084	1.081	1.080
C3—H3				1.087	1.083	1.076	1.083	1.081
C4—H4				1.084	1.080	1.082	1.080	1.081
Mean	1.091	1.083	1.087	1.086	1.082	1.081	1.081	1.081

[a] Electron diffraction[10], [b] From high resolution IR spectra[10],
[c] Present work, [d–h] Microwave spectroscopy, Refs. 12—16, respectively.

Table 5. Distances between hydrogen atoms adjacent to the ring in benzene and some of its monosubstituted derivatives.

Atomic pairs	Molecules							
	benzene[a]		toluene[b]	benzonitrile[c]	aniline[d]	phenol[e]	fluorobenzene[f]	chlorobenzene[g]
H2 ··· H3	2.480*	2.487**	2.469	2.483	2.467	2.485	2.504	2.474
H3 ··· H4			2.481	2.477	2.485	2.482	2.478	2.480
H2 ··· H6	4.295*	4.307**	4.283	4.291	4.288	4.281	4.274	4.284
H3 ··· H5			4.290	4.293	4.289	4.290	4.292	4.292

[a] The distances given were calculated from the bond distances, * r_α^0, electron diffraction[10], ** r_z from high resolution IR spectra[10].

[b-g] Microwave spectroscopy, all r_s distances! Refs. 12–16, respectively.

toluene yields that the methyl C—H bonds in toluene are at least 1.126 Å long, in terms of r_a, or 1.131 Å in terms of r_g. The final results[18] of this investigation are summarized in the abstract.

Some further comparison of bond lengths in related systems is of interest. The C1—C7 bond of toluene is of similar length as the C—C bond in propene (r_g 1.506 Å[19]) and is intermediate between the C—C bonds in ethane (r_g 1.533 Å[20]) and biphenyl (central bond 1.489 Å[21]). The methyl C—H bond of toluene is interesting to compare with that in hexamethyl benzene. In the latter r_g(C—H) $= 1.125 \pm 0.003$ Å was found by Karl, Wang and Bauer[22]. Considering the lengthening of the C—H bonds in the side-chains as compared with the C—H bond length in ethane[20], e.g., this effect is expected to be larger in toluene than in hexamethyl benzene.

Finally, we would like to comment upon the possible angular deformations in the ring of toluene. We have calculated the bond angles in the ring using the following data: i) the substitution coordinates of the hydrogen atoms adjacent to the ring from the microwave spectroscopy measurements[3], ii) the electron diffraction $r_\alpha(\text{C}\cdots\text{C})$ parameter which is not expected to be much different from the r_s parameter, and iii) a value of "r_s"(C—H) = 1.082 Å obtained from the electron diffraction r_α(C—H) parameter by subtracting 0.005 Å in order to correct for vibrational effects. Thus we obtained the following angles: C6C1C2 118.6°, C1C2C3 120.9°, C2C3C4 120.0°, and C3C4C5 119.5°. These results suffer, of course, from the assumption of using mean values for the C$\cdots$C and C—H distances, respectively, in addition to the above listed approximations. More reliable values will be produced by microwave spectroscopy when a complete substitution structure will be available. It is comforting, however, that the above angles are in complete agreement with the observations of Domenicano et al.[23] concerning the angular deformations in a large series of monosubstituted benzene derivatives, and also that the above calculations yielded 1.507 Å for the C1—C7 bond which is consistent with our experimental results.

The strength of the C1—C7 bond may be calculated to be 98 kcal · mol^{-1} by the decrement method[1], which is 10 kcal · mol^{-1} more than for ethane. According to the interpolation formula[1] for C—C bonds this corresponds to a 0.025 Å change (shortening) as compared with ethane. The strength of the C—H bond in the side chain of toluene is calculated to be 84 kcal · mol^{-1}. Supposing* that the same interpolation scheme can be applied as for the C—C bonds, the estimated lengthening is 0.048 Å as compared with the C—H bonds adjacent to the benzene ring. Thus there is consistency between the bond energies calculated by the decrement method and the geometrical characterization of the toluene molecule.

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* No interpolation formula has been developed yet for the C—H bonds.

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