Conformation and Structure of Ethylbenzene in the Vapour Phase

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The molecular structure of ethylbenzene has been studied by gas electron diffraction. Experimental intensities and radial distribution are well reproduced by an average structure with $\tau = 70(3)°$, where τ is the angle between the C—C—C(H_3) plane and the ring plane, mean (r_g) bond lengths $(C—C)_{phenyl} = 139.9(3)$ pm, $C_{phenyl}—C(H_2) = 152.4(9)$ pm, $C(H_2)—C(H_3) = 153.5(12)$ pm, C—H = 109.4(4) pm, and bond angle $C—C—C(H_3) = 111.8(15)°$. (Estimated total errors are parenthesized.) An also acceptable perpendicular model ($\tau = 90°$) is accompanied by very large vibrational amplitudes, while the coplanar conformation ($\tau = 0°$) is excluded. Mixtures of conformers fit the experimental data as well. The barrier to rotation of the phenyl group is estimated from the average structure to be about 7 kJ mol^{-1}. According to CNDO/2 calculations, only the perpendicular form is stable. The results of a geometry optimization are shown.

Introduction

The structure of ethylbenzene, one of the basic derivatives of benzene, has been of interest for some time. It can be regarded as a benzyl compound, $C_6H_5 - CH_2X$ (X: CH_3) or as the simplest of the phenylethyl compounds $C_6H_5 - CH_2 - CH_2Y$ (Y: H), of which the phenethylamines (Y: NH_2) and, with additional ring substitution (*m*-OH, *p*-OH), also the catecholamines are very important biogenic amines and are subjected to extensive X-ray diffraction crystal structure investigations. C_s is the highest possible symmetry for the ethylbenzene molecule, realized either with the *coplanar* conformation, where the phenyl ring lies in the symmetry plane, or with the *perpendicular* conformation, in which the two planes are perpendicular to each other. The conformational behaviour is thought to be responsible for the biological activity of phenethylamines, cf. [1] and references therein.

Even in the earliest works [2] as well as in most assignments of infrared and Raman spectra [3, 4] and force field calculations [5], ethylbenzene was assumed to possess the perpendicular conformation. In addition, the coplanar conformation has been ruled out in low resolution microwave studies of ring substituted ethylbenzene derivatives [6]. According to the far-infrared and Raman studies by Verdonck and van der Kelen [7], ethylbenzene is totally asymmetric in the liquid phase. From an infrared study on liquid ethylbenzene and oriented crystals of two modifications, it was concluded, however, that the coplanar form is favoured energetically in the liquid [8]. X-ray studies have found phenethyl- and catecholamines in most cases in a nearly perpendicular form [9] but p-ethylphenoxyacetic acid seems to exhibit a near to coplanar ethylbenzene moiety in the crystal [10]. Deviations from the perpendicular form were attributed to crystal field effects, hydrogen bonding, etc. [9, 11].

The main purpose of the present electron diffraction investigation was to establish the conformational behaviour of ethylbenzene in the vapour phase.

Experimental

The sample of ethylbenzene, a commercial product, was used after purification [12]. Electron diffraction patterns were taken with an EG-100 A apparatus [13, 14], using the membrane-nozzle system [13] at nozzle temperatures of about 40 °C. The wavelength of the electron beam (60 kV nominal accelerating voltage) was determined from TlCl diffraction patterns [15]. Reduced experimental molecular intensities were obtained in the usual way [16] in ranges $0.0175 \leqq s \leqq 0.1375\ pm^{-1}$ and $0.0825 \leqq s \leqq 0.3525\ pm^{-1}$ ($\Delta s = 0.0025\ pm^{-1}$) for the 499 mm and the 190 mm camera distances (Figure 1).

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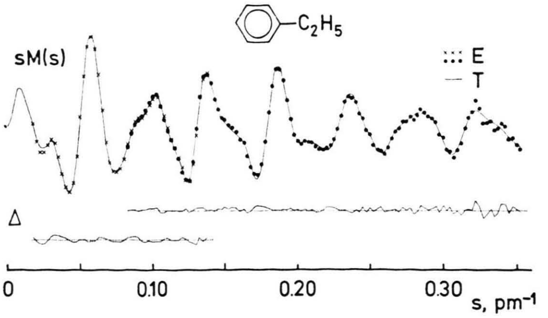

Fig. 1. Experimental (E) molecular intensities of ethylbenzene and theoretical (T) and difference curves (Δ) of model (iii).

Structure analysis

The geometry of molecular models is defined by the independent parameters of Table 1 (cf. Figure 2). Thus C_{3v} symmetry of the methyl group, C_s symmetry and staggered conformation of the ethyl moiety were assumed, and mean aliphatic C – H bond lengths were considered. Distortions of the benzene ring upon substitution were generally ignored; some calculations, however, were specially devised to test their effect. Shrinkage effects were neglected. Some of the parameters e. g. the differences $c - b$ and $e - d$

Table 1. Parameters of the asymmetric (iii) model of ethylbenzene[a].

	r_a, pm	l(ED), pm	l(SP), pm
Independent parameters[b]			
a	139.73 (5)	4.30 (14)	4.64
$(b + c)/2$	152.8 (3)		
$c - b$	1.1 (13)		
$(d + e)/2$	108.8 (3)		
$e - d$	1.0[c]		
∢ C1–C7–C8	111.8 (11)°		
∢ H71–C7–H72	109.5°[c]		
η	125.0°[c]		
∢ C7–C8–H	109.5°[c]		
τ	69.6 (22)°		
Dependent distances			
b	152.2 (6)	4.8 (3)[d]	5.07
c	153.3 (8)	4.8[d]	5.14
d	108.3 (3)	8.2 (3)[e]	7.71
e	109.3 (3)	8.3[e]	7.85
C1 ... C3	242.0 (1)	5.4 (2)	5.51
C1 ... C4	279.5 (1)	5.9 (3)[f]	5.89
C2 ... C7	252.9 (5)	6.5 (4)[g]	7.12
C3 ... C7	381.5 (5)	6.1 (5)[h]	7.04
C4 ... C7	431.7 (6)	6.7 (16)[i]	6.76
C1 ... C8	253.0 (16)	7.2[g]	7.86
C2 ... C8	317.4 (21)	11.7 (16)[j]	11.63
C3 ... C8	445.2 (20)	12.4[i]	12.54
C4 ... C8	508.9 (21)	17.1 (60)[k]	12.14
C5 ... C8	471.4 (27)	18.8 (51)[l]	11.43
C6 ... C8	353.2 (28)	10.5[j]	10.49
C1 ... H2	215.4 (2)	9.6 (4)[m]	9.98
C1 ... H3	340.2 (3)	9.7[j]	9.69
C1 ... H4	387.8 (3)	8.4[h]	9.34
C1 ... H71	214.8 (5)	10.4[m]	10.77
C1 ... H81	347.0 (12)	10.9[j]	10.86
C1 ... H82	276.9 (21)	17.7[f]	17.71
C2 ... H71	341.5 (5)	10.8[j]	10.76
C2 ... H72	275.9 (14)	15.3[f]	15.27
C2 ... H81	415.6 (17)	14.6[i]	14.70
C2 ... H82	352.7 (29)	23.1[j]	23.03
C2 ... H83	289.6 (29)	22.4[f]	22.41
C3 ... H71	456.4 (5)	18.9[l]	11.55
C3 ... H72	409.7 (10)	14.9[i]	14.97
C3 ... H81	548.4 (18)	14.7[c]	14.67
C3 ... H82	460.7 (28)	33.3[l]	25.94
C3 ... H83	414.5 (29)	24.7[i]	24.77
C4 ... H71	479.2 (6)	20.6[l]	13.30
C4 ... H81	613.5 (18)	13.3[c]	13.26
C4 ... H82	502.4 (31)	30.3[k]	25.33
C5 ... H71	398.9 (7)	14.2[h]	15.06
C5 ... H72	446.8 (11)	12.4[i]	12.49
C5 ... H81	569.3 (21)	13.7[c]	13.69
C5 ... H82	452.5 (43)	23.0[i]	23.07
C5 ... H83	495.2 (35)	28.4[k]	23.41
C6 ... H71	259.6 (7)	15.0[f]	15.03
C6 ... H72	328.5 (13)	12.1[j]	12.06
C6 ... H81	442.8 (20)	13.8[i]	13.90
C6 ... H82	341.8 (45)	20.3[j]	20.25
C6 ... H83	396.7 (33)	19.3[h]	20.21
C7 ... H2	272.7 (4)	14.2[f]	14.20
C7 ... H3	468.2 (6)	18.9[l]	11.60
C7 ... H4	540.4 (6)	9.9[c]	9.90
C7 ... H81	216.0 (7)	10.8[m]	11.08
C8 ... H2	309.3 (33)	19.3[j]	19.21
C8 ... H3	518.4 (24)	22.2[k]	17.20
C8 ... H4	613.7 (23)	15.2[c]	15.21
C8 ... H5	558.0 (32)	15.4[c]	15.40
C8 ... H6	371.9 (36)	16.6[h]	17.48
C8 ... H71	214.7 (8)	10.5[m]	10.79
H2 ... H3	248.1 (3)	15.8[c]	15.79
H81 ... H82	178.6 (4)	12.7[c]	12.69

[a] l(ED) are from electron diffraction, l(SP) have been averaged and interpolated to $\tau = 70°$ from Brunvoll's spectroscopic calculations [21]. Least-squares standard deviations in parentheses refer to the last digit of the parameter.

[b] Definitions (see Figure 2): a mean C–C length in the ring, b C1–C7, c C7–C8, d mean $(\text{C–H})_{\text{phenyl}}$, e mean $(\text{C–H})_{\text{ethyl}}$, η obtuse angle of bond C1–C7 to plane H71–C7–H72, τ dihedral angle of the C1–C7–C8 plane with the ring plane.

[c] Assumed value.

[d–m] Groups of amplitudes.

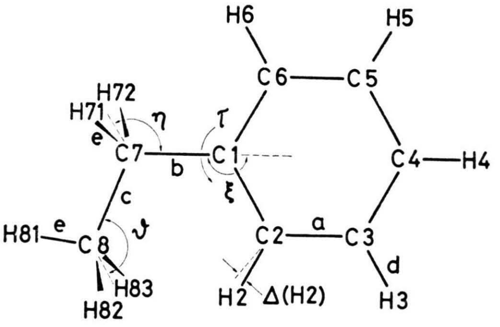

Fig. 2. Geometrical parameters (see Table 1) and numbering of atoms. Δ(H2), ξ, and ϑ are used in the CNDO/2 calculations (see Table 2).

and angles η, H – C7 – H and C7 – C8 – H remained fixed in most of the refinements [17]. Initial values for vibrational amplitudes were calculated by Brunvoll [21] from spectroscopic data; they were either fixed or refined in groups. A modified version of a least-squares refinement program [22] was applied for the structure refinement. The two overlapping ranges of molecular intensities [16] were treated simultaneously as independent data. Coherent and incoherent scattering factors were taken from [23] and [24].

The experimental radial distribution (Fig. 3) offers no direct evidence on the rotational forms of ethylbenzene present in the vapour phase at the temperature of the experiment. Even in the range beyond 230 pm, the largest contributions arise from interatomic distances which are independent of both the dihedral angle τ and the bond angle C – C – C(H_3).

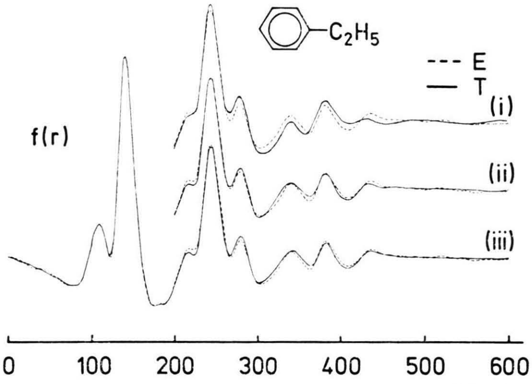

Fig. 3. Experimental (E) and theoretical (T) radial distributions of ethylbenzene. Dihedral angles (τ) and R-factors of models, where

$$R^2 = \sum_s [sM^{\mathrm{E}}(s) - sM^{\mathrm{T}}(s)]^2 / \sum_s [sM^{\mathrm{E}}(s)]^2:$$

(i) Coplanar, $\tau = 0°$, $R = 0.112$;
(ii) Perpendicular, $\tau = 90°$, $R = 0.083$;
(iii) Asymmetric, $\tau = 69.6°$, $R = 0.080$.

The following conformations were considered in the structure analysis:

(i) the coplanar form with symmetry C_s, i. e. $\tau = 0°$,
(ii) the perpendicular form with symmetry C_s, i. e. $\tau = 90°$,
(iii) asymmetric forms with $0 < \tau < 90°$,
(iv) two-component mixtures of such forms.

The perpendicular form resulted in much better agreement with the experimental data than the coplanar form (curves (i) and (ii), Figure 3). In both forms some of the refined amplitudes are much larger than the values calculated from spectroscopic data. When τ was allowed to vary, it converged to about 70° (curve (iii), Fig. 3) from different initial values.

Although the coplanar form itself proved to be unsatisfactory, its presence in a mixture of conformers could not be excluded. A typical result of refinements for two-component mixtures (iv) was a ratio of 16 : 84 of the forms with $\tau = 0°$ (fixed) and $\tau \approx 71°$ (refined). Such refinements (iv) involved usually more variable parameters than in the case of single asymmetric conformers (iii), and yet the agreement with experimental diffraction data improved only insignificantly.

The possible effect of ring distortions on the other structural parameters was checked in the following way: The good agreement of electron diffraction [18] and *ab initio* [20] results on the ring distortions in toluene suggested that *ab initio* results on small distortions of the molecular geometry could be adapted for use in an electron diffraction analysis. As such *ab initio* calculations on ethylbenzene are lacking, ring parameters for the model of ethylbenzene were constructed from those in Table 2, assuming that the differences of *ab initio* [20] and our CNDO/2 results on toluene were transferable to our CNDO/2 optimized data on ethylbenzene [25]. Angles in the ring were fixed, since their refinement gave unacceptable structures; the mean aromatic C – C length was refined, other parameters were treated as in previous refinements. Except for $c - b = 5.5$ pm, none of the parameters deviated significantly from those in Table 1, and the agreement of

Table 2. The geometry of ethylbenzene and toluene from quantum chemical calculations[a].

Parameter[b]	Ethylbenzene[c] CNDO/2 this work	Toluene[c] CNDO/2 this work	Toluene[c] *ab initio* Ref. [20]
Distances			
C1–C2	139.59	139.56	138.8
C2–C3	138.35	138.34	138.4
C3–C4	138.42	138.43	138.3
C1–C7	146.55 [151.39]	145.80 [150.61]	151.9
C7–C8	146.60 [151.44]	112.15 [109.12][d]	108.5[d]
C2–H2	111.91 [108.89]	111.89 [108.87]	107.3
C3–H3	111.73 [108.72]	111.72 [108.70]	107.2
C4–H4	111.69 [108.67]	111.71 [108.69]	107.2
C7–H71	112.57 [109.53]	112.01 [108.99]	108.2
C8–H81	112.14 [109.11]		
C8–H82	112.05 [109.02]		
Δ(H2)	0.46	0.18[d]	
Angles			
C6–C1–C2	115.8	116.1	118.6
C1–C2–C3	122.5	122.3	120.8
C2–C3–C4	120.2	120.2	120.2
C3–C4–C5	118.9	119.2	119.5
C1–C7–C8	109.4	110.4[d]	110.6[d]
ξ	178.5	178.9[d]	
C3–C2–H2	118.6	118.6	119.7
C2–C3–H3	119.7	119.8	119.8
H71–C7–H72	104.3	106.5	107.9
η	127.4	132.0	
C7–C8–H81	112.8		
H82-C8-H83	106.6		
ϑ	129.4		

[a] Distances are in pm, angles are in degrees. Values in brackets have been scaled to parameters of related molecules.

[b] See Figure 2 and footnotes to Table 1 for the definition of parameters. Δ(H2) is the deviation of atom H2 from the plane of the ring carbon atoms, ξ is the obtuse angle of bond C1–C7 to the same plane; H2 and C8 are on opposite sides, C7 and C8 on the same side of this plane. ϑ is the obtuse angle of bond C7–C8 to the plane H82–C8–H83.

[c] Perpendicular form.

[d] A hydrogen atom should be substituted for atom C8.

theoretical and experimental radial distributions did not improve appreciably. (Fixing $c - b = 2$ pm led to similar results.)

Results and Discussion

The geometrical parameters (r_a) and mean square amplitudes (l) of the asymmetric (iii) model of ethylbenzene are listed in Table 1. Total errors [16] were estimated from least-squares standard deviations, systematic (scale) errors, and the estimated influence of correlations between experimental data.

The asymmetric conformer ($\tau \approx 70°$) of ethylbenzene, established in this work, may be regarded as an average structure, resulting from large amplitude torsional motions about a perpendicular ($\tau = 90°$) equilibrium conformation [26]. This electron diffraction study has shown that the coplanar form ($\tau = 0°$) is definitely *not* prevailing in the vapour phase, but its presence in a mixture of different conformers cannot be excluded.

For benzyl chloride and bromide electron diffraction gave average dihedral angles of 67.5(45)° and 74.2(13)°, and rotational barriers of 6 kJ mol^{-1} and 8 kJ mol^{-1}, respectively [27], assuming the energy minimum at $\tau = 90°$. Estimations by other methods, based on the same experimental information and assumption, yielded similar numbers [28]. Applying these methods to ethylbenzene we got an estimate of the barrier height of 7 kJ mol^{-1}, whereas CNDO/2 gave 9.3 kJ mol^{-1} for optimized geometries and 12.9 kJ mol^{-1} for standard geometrical models. Rotational barriers from different sources are collected in Table 3. The energy difference of the forms with $\tau = 0°$ and 71°, e. g., was estimated to be about 2.5 kJ mol^{-1} from their ratio of 16 : 84, as obtained in some of our refinements, while -0.8 kJ mol^{-1} (note opposite sign!) was estimated in another work from temperature-dependent infrared band intensities [8].

An ideal cosine-form potential was assumed in most of the cited works. However, the interplay of phenyl and methyl groups is of such a kind that 15° apart from the coplanar conformation the CNDO/2

Table 3. Estimated barrier to rotation (V_2) of the phenyl group in ethylbenzene.

Source	V_2, kJ mol^{-1}	Reference
Thermodynamic functions	5.5	[2]
Thermodynamic functions	4.85	[29]
Average rotational angle	7	this work
STO-3G calculation[a]	19.7	[30]
STO-3G calculation[b]	9.2	[30]
CNDO/2 calculation[a]	12.9	this work
CNDO/2 calculation[c]	9.3	this work

[a] Standard geometrical model [30].

[b] Angle C–C–C(H$_3$) optimized.

[c] Geometry optimized.

potential of internal torsion becomes a maximum. Therefore coplanar ethylbenzene represents a local minimum with respect to a single angle of torsion, while it corresponds to a saddle point on the energy surface concerning the rotation of the phenyl and methyl group simultaneously [1]. In addition, CNDO/2 as well as *ab initio* calculations on phenethyl- and catecholamines (cf. [1, 11] and references therein) and on ethylbenzene itself [30, 31] unequivocally demonstrate that the free molecules have a lower energy in the perpendicular conformation than in the coplanar one.

There are a few experimental data on the geometry and conformation of related free molecules. Two single conformations as well as a mixture of conformers of isopropylbenzene (cumene) seem to be in accord with electron diffraction data [32]. It is instructive to compare ethylbenzene (or, more generally, benzyl compounds, $C_6H_5-CH_2X$) with molecules where the phenyl group is replaced by a vinyl group. Such substituted propylenes, $CH_2=CH-CH_2X$, like allylamine, exist in two forms that are analogous to the coplanar and the "skew" forms of ethylbenzene, respectively: the $C-X$ and $C=C$ bonds can have either *syn* or *gauche* position to each other [33]. Both 1-butene [34] and 2-methyl-1-butene [35] have a *syn* form and a skew form derived from it by a rotation of 120° and 107°. The skew form of 1-butene is energetically preferred [34], as also confirmed by quantum chemical calculations [36]. In 2-methyl-1-butene [35], and also in allylfluoride [37], however, the *syn* form has been found to be more stable.

The average bond lengths and some vibrational amplitudes of ethylbenzene are well established by electron diffraction and agree well with parameters of related molecules and calculated amplitudes [l(SP) in Table 1]. For example, the average ring $C-C$ bond is $r_g = 139.9(2)$ pm in toluene [38] and 140.0(3) pm in *p*-xylene [18]. The $C-C-C(H_3)$ angle and the small differences of $C-C$ and of $C-H$ bond lengths are, on the other hand, strongly correlated with other parameters (rotational angle, amplitudes), and depend on the conditions of refinements and the experimental background used. Information from electron diffraction was not sufficient to determine ring distortions, although a distorted ring geometry transferred from toluene is consistent with the electron diffraction data. The CNDO/2 optimized geometry correctly reflects the succession of magnitudes of ring $C-C$ bond lengths and $C-C-C$ angles, as expected from analogy with toluene (Table 2). The CNDO/2 optimum of angle $C-C-C(H_3)$ in ethylbenzene is 109.4° (Table 2), whereas an *ab initio* optimization of that angle produced 112.0° [30]. In the *syn* and skew conformer of 1-butene 114.8(5)° and 112.1(2)° were obtained by microwave spectroscopy for the $(=)C-C-C(H_3)$ angle [34], whereas 116.0° and 113.0° were found in the corresponding two forms of 2-methyl-1-butene [35].

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