Bastiansen-Morino Shrinkage Effects in Benzene Type Molecules

II. Refinements of Electron-Diffraction Measurements on Benzene Using Spectroscopical Shrinkage Effects

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The theory of Bastiansen-Morino shrinkage effects for the benzene molecular model has been outlined in the previous article of this series. In the present paper, numerical values are given for the shrinkage effects for all types of distances in benzene, as calculated from spectroscopic data. The values are compared with electron-diffraction results.

A least-squares method has been used for refining the observed internuclear distances from electron-diffraction. It was found possible to adjust the measurements within their error limits to fit the non-rigid model based on spectroscopic shrinkage effects. Final results for mean internuclear distances (r^g) obtained from a refined least-squares adjustment, were: CC = 1.4000 Å and CH = 1.0897 Å.

Finally the HH distances in benzene were computed by the different refinements.

The structure of benzene is determined by two parameters when the planar regular hexagonal structure is assumed. By modern gas electron diffraction not less than seven internuclear distances have been observed [1,2]. In situations like this, it has been customary to adjust the observed distance values to the geometry of the model by a least-squares method. This procedure would be correct if the observed distances were true equilibrium values. In the real cases, where only some mean values or values of maximum probability are available, the Bastiansen-Morino shrinkage effects [3-5] should be taken into account. In the first article of this series [6] the theory of the shrinkage effect was outlined and applied to benzene type molecules. In the present work the spectroscopic calculations on shrinkage effects of benzene are reported, and some refinements of electron-diffraction measurements are discussed.

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The ten types of atom pairs in benzene will be identified by Roman figures in the following way:

(i)	$C-C$	bonded atom pair.
(ii)	C_1C_3	non-bonded.
(iii)	C_1C_4	»
(iv)	$C-H$	bonded atom pair.
(v)	C_2H_1	non-bonded.
(vi)	C_3H_1	»
(vii)	C_4H_1	»
(viii)	H_1H_2	»
(ix)	H_1H_3	»
(x)	H_1H_4	»

MEAN-SQUARE PERPENDICULAR AMPLITUDES AND SHRINKAGE EFFECTS FROM SPECTROSCOPIC CALCULATIONS

The spectroscopic shrinkage effects have been computed from the K-values, which are composed of the mean-square perpendicular amplitudes according to eqn. (2) of Paper I [6]:

$$K_{ij} = (\langle \Delta x_{ij}^2 \rangle + \langle \Delta y_{ij}^2 \rangle)/2r_{ij}^e$$

The adopted values of the mean-square perpendicular amplitudes [7] refer to the temperature of 298°K and are quoted in Table 1. It is interesting to compare the magnitudes of the in-plane and out-of-plane amplitude for the same atom pair. In all cases but one, *viz.* (iii), the contributions from out-of plane vibrations are greater, in accord with our expectations. The in-plane contributions, however, are by no means negligible. The resulting K-values are included in Table 1, along with the shrinkage effects as calculated from the evaluated formulae in Paper I [6]. The bond distance values of 1.397 Å and 1.084 Å for $C-C$ and $C-H$, respectively [7], were used in the computations. In benzene the *natural* and *practical* shrinkage effects [5] are coincident for all types of

Table 1. Mean-square perpendicular amplitudes (in Å² units), K-values (Å) and shrinkage effect (Å) for benzene at 298°K from spectroscopic data.

| Atom pair | | Mean-square perpendicular amplitude | | K-value | Shrinkage effect |
		In-plane	Out-of-plane		
CC	i	0.002474	0.005224	0.002755	—
	ii	0.002373	0.004156	0.001349	0.00342
	iii	0.001918	0.001788	0.000663	0.00485
CH	iv	0.014092	0.022644	0.016945	—
	v	0.011858	0.027605	0.009159	0.00734
	vi	0.013876	0.025335	0.005763	0.01479
	vii	0.014308	0.020087	0.004435	0.01802
HH	viii	0.015570	0.046991	0.012608	0.00709
	ix	0.023264	0.045070	0.007951	0.02617
	x	0.025017	0.034308	0.005978	0.03342

Table 2. Internuclear distances and shrinkage effects from two electron-diffraction investigations on benzene. Å units.

Atom pair		Investigation I r^m	u^2/r^m	$(r^g)^o$	Shrinkage effect
CC	i	1.3975	0.00148	1.3989_8	—
	ii	2.4190	0.00121	2.4202_1	0.0028_9
	iii	2.7964	0.00137	2.7977_7	0.0001_9
CH	iv	1.0850	0.00491	1.0899_1	—
	v	2.1460	0.00412	2.1501_2	0.0108_5
	vi	3.4045	0.00260	3.4071_0	0.0037_1
	vii	3.8737	0.00243	3.8761_3	0.0117_4

Atom pair		Investigation II r^m	u^2/r^m	$(r^g)^o$	Shrinkage effect
CC	i	1.3971	0.00147	1.3985_7	—
	ii	2.4195	0.00121	2.4207_1	0.0016_8
	iii	2.7929	0.00125	2.7941_5	0.0029_9
CH	iv	1.0821	0.00492	1.0870_2	—
	v	2.1515	0.00393	2.1554_3	0.0027_8
	vi	3.4050	0.00222	3.4072_2	0.0001_8
	vii	3.8890	0.00252	3.8915_2	-0.0073_6

CC and HH distances, and for the longest CH distance. In the two remaining cases, *viz.* (v) and (vi), the reported results (Table 1) refer to the *practical* shrinkage effects, and have been calculated according to eqn. (25) and (27) of Paper I *.

INTERNUCLEAR DISTANCES AND SHRINKAGE EFFECTS FROM ELECTRON-DIFFRACTION

Almenningen, Bastiansen and Fernholt [1] have reported two independent electron-diffraction investigations (I and II) on benzene. Their values are quoted in the first column of Table 2, and referred to as r^m, *i.e.* the maximum positions of the radial-distribution curve. These values were transformed to r^g according to the formula [8] **

$$r_{ij}^g = r_{ij}^m + u_{ij}^2/r_{ij}^m$$

using experimental u_{ij}-values (mean amplitudes of vibration) from the same work [1]. The r^g-values along with the corresponding shrinkage effects are included in Table 2. The two types of shrinkage effects identified by (v) and (vi) have been computed as *natural* shrinkage effects, but no substantial differ-

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* With numerical coefficients:
$$\delta_{27} = 0.82742\ K_{17} + 0.90006\ K_{12} - K_{27}$$
$$\delta_{37} = 0.93463\ K_{17} + 1.70993\ K_{12} - K_{37}$$
** A more precise form of this formula reads
$$r_{ij}^g = r_{ij}^f + u_{ij}^2/r_{ij}^e + \ldots.$$
where r_{ij}^f may be replaced by r_{ij}^m for symmetrical peaks.

ences were obtained when the formulae for *practical* shrinkage effects were used tentatively, *viz.*,

(v) $\delta_{27} = 0.82742\ r_{17}{}^{g} + 0.90006\ r_{12}{}^{g} - r_{27}{}^{g}$
(vi) $\delta_{37} = 0.93463\ r_{17}{}^{g} + 1.70993\ r_{12}{}^{g} - r_{37}{}^{g}$

The coincidence of the *natural* and *practical* shrinkage effects is consistent with the theory. It has been shown that the two types of shrinkage effects are identical to a first-order approximation [5].

It is not claimed to give a quantitative significance to the observed shrinkage effects as reported in Table 2. But at least it is a pleasing fact to notice that nine of ten figures came out positive in accord with the theory. It is believed that this did not happen by mere chance.

REFINEMENTS OF THE ELECTRON-DIFFRACTION MEASUREMENTS

A method of least-squares with various modifications was applied for refining the observed electron-diffraction internuclear distances. Since the electron-diffraction measurements are not sufficiently accurate to give significant shrinkage effects, it is hardly justified to perform such delicate refinements of the measurements as has been made in the present work. It was intended, however, to show an application of the derived method, rather than to perform real corrections of the results.

The correction terms ε are given by

$$r_n{}^{g} = (r_n{}^{g})^{\circ} + \varepsilon_n$$

First, for the sake of comparison, the experimental values were adjusted to a model with no shrinkage effects. Two slightly different cases are distinguished, *viz.* the adjustment of the r^{g}-values (case A) on one hand, and r^{m}-values (B) on the other hand.

A. r^{g} *adjusted with no shrinkage.* The observed r^{g}-values were adjusted to fit the geometry of the regular hexagonal model without shrinkage effects. The sum of squares,

$$P = \underset{i}{\Sigma}\ \varepsilon_i^2$$

Table 3. Coefficients of the linear equations $(\underset{k}{\Sigma} c_{nk}\varepsilon_k) - \varepsilon_n = \delta_n$ (theor) $- \delta_n$(expt) $= d_n$

or $\varepsilon_n = c_{n(\mathrm{i})}\varepsilon_{(\mathrm{i})} + c_{n(\mathrm{iv})}\varepsilon_{(\mathrm{iv})} - d_n \cdot k$ refers to the bond distances (i and iv).

n	$c_{n(\mathrm{i})}$	$c_{n(\mathrm{iv})}$	d_n	
(ii)	1.73205	0	0.00053	(0.00174) *
(iii)	2.00000	0	0.00466	(0.00186)
(v)	0.90006	0.82742	−0.00351	(0.00456)
(vi)	1.70993	0.93463	0.01108	(0.01461)
(vii)	2.00000	1.00000	0.00628	(0.02538)

* Figures in parentheses refer to Investigation II of Ref.[1]

was minimized. Here i indicates the distances (i)—(vii) The resulting r^g-values for the bonded C—C and C—H distances (i and iv) are found in Table 6, along with the minimum value of P.

B. r^m *adjusted with no shrinkage*. The observed r^m-values were adjusted by the same procedure as used above for r^g. Next the *refined* r^m-values were transformed to r^g by means of the (u^2/r^m)-values listed in Table 2, and the results for the bond distances are listed in Table 6. Also included is the obtained P-value, where P should have the same significance as before Hence it had to be calculated from the corrections of the r^g-values rather than r^m.

C. *Adjustment with spectroscopic shrinkage effects*. The method of least-squares using spectroscopic shrinkage effects has been described elsewhere [9]. Five linear equations are obtained for the seven correction terms ε_n (see Table 3). The function P was minimized. Hence two additional equations were obtained and made it possible to calculate all the ε's. The results are given in Table 4 and summarized in Table 6, where also the minimum value of P is reported. The P-values give a measure of the fit to the chosen models in the different cases. It is seen that the experimental values fit slightly better the models without shrinkage (A and B) than the presently considered model with spectroscopical shrinkage effects (C). This fact demonstrates again the poor justification for performing real refinements by the present calculations. Nevertheless it is interesting to notice the comparatively great difference between the C—H values obtained by the method C *versus* A and B.

D. *Refined adjustment with spectroscopic shrinkage effects*. The above procedure (C) would be adequate if the same accuracy could be attributed to all the measurements. Here it was tried to take proper account of the different error limits by a modification of the above procedure (C) in the following way. Instead of minimizing the function P, a new polynomial to minimize was produced, *viz.*

$$P' = \sum_i w_i \ \varepsilon_i^2$$

where w_i are some weight factors. In the mentioned electron-diffraction work [1] the absolute magnitudes of 0.003 Å and 0.005 Å are suggested for the error limits of the C—C and C—H bond distance, respectively. Hence it seems reasonable to assume

$$w_{(i)}^{1/2}: w_{(iv)}^{1/2} = 5:3$$

Furthermore, the way of taking the average of the deduced distances, as devised by Almenningen, Bastiansen and Fernholt [1], inspired us to assume

$$w_{(i)} = w_{(ii)} = w_{(iii)}$$

and

$$w_{(iv)}^{1/2}: w_{(v)}^{1/2}: w_{(vi)}^{1/2}: w_{(vii)}^{1/2}$$
$$= \frac{1}{r_{(iv)}} : \frac{1}{r_{(v)}} : \frac{1}{r_{(vi)}} : \frac{1}{r_{(vii)}}$$
$$= (1/1.084):(1/2.1543):(1/3.4019):(1/4.962)$$

The results are given in Table 5 and summarized in Table 6.

Table 4. Correction terms and refined values from adjustment C (Å units).

	Investigation I		Investigation II	
	ε	r^g	ε	r^g
i	0.00209	1.4010_7	0.00329	1.4018_6
ii	0.00309	2.4233_0	0.00396	2.4246_7
iii	-0.00048	2.7972_9	0.00472	2.7988_7
iv	0.00131	1.0912_2	0.00802	1.0950_4
v	0.00647	2.1565_9	0.00503	2.1604_6
vi	-0.00628	3.4008_2	-0.00149	3.4057_3
vii	-0.00079	3.8753_4	-0.01079	3.8807_4

Table 5. Correction terms and refined values from adjustment D (Å units).

	Investigation I		Investigation II	
	ε	r^g	ε	r^g
i	0.00132	1.4003_0	0.00103	1.3996_0
ii	0.00175	2.4219_6	0.00005	2.4207_6
iii	-0.00203	2.7957_4	0.00020	2.7943_5
iv	0.00002	1.0899_3	0.00236	1.0893_8
v	0.00471	2.1548_3	-0.00168	2.1537_5
vi	-0.00881	3.3982_9	-0.01064	3.3965_8
vii	-0.00363	3.8725_0	-0.02096	3.8705_7

Table 6. Summarized results from the different refinements of the electron-diffraction measurements *.

	Investigation I		
	$r^g(C-C)$	$r^g(C-H)$	$P(10^{-4}\,\text{Å}^2)$
A	1.3975	1.0849	0.90
B	1.3987	1.0865	0.84
C	1.4011	1.0912	0.98
D	1.4003	1.0899	1.22

	Investigation II		
	$r^g(C-C)$	$r^g(C-H)$	$P(10^{-4}\,\text{Å}^2)$
A	1.3983	1.0887	0.66
B	1.3995	1.0904	1.09
C	1.4019	1.0950	2.57
D	1.3996	1.0894	5.62

* A: r^g adjusted with no shrinkage.
  B: r^m adjusted with no shrinkage.
  C: Adjustment with spectroscopic shrinkage effects.
  D: Refined adjustment with spectroscopic shrinkage effects.

Table 7. Computed r^g-values (in Å) for the HH distances in the cased A—D (see footnote to Table 6).

Distance		A	Investigation I		D
			B	C	
HH	viii	2.4824	2.5018	2.4852	2.4831
	ix	4.2997	4.3098	4.2906	4.2870
	x	4.9648	4.9705	4.9512	4.9470
Distance		A	Investigation II		D
			B	C	
HH	viii	2.4870	2.5065	2.4898	2.4819
	ix	4.3077	4.3179	4.2986	4.2849
	x	4.9741	4.9799	4.9604	4.9445

A brief discussion will be given on the effect of minimizing P' instead of P (*cf.* Tables 4 and 5). By comparing the cases C and D, the absolute magnitudes of ε are found to be smaller in D for the distances i, ii, iv and v, but greater for vi and vii. For the distance iii the investigations I and II gave different results. The absolute magnitudes of the differences between the correction terms ($\varepsilon_{case\ C} - \varepsilon_{case\ D}$) increase in the sequence iv—vii.

FINAL RESULTS

The results of the last refinement (D) for the investigations I and II turned out to come fairly near together. This makes it well justified to take the average. Hence the following final results are obtained:

$$r^g (C—C) = 1.4000 \text{ Å}$$
$$r^g (C—H) = 1.0897 \text{ Å}$$

Because of the reservations already mentioned, it falls outside the scope of this work to try to find any error limits with clear significance.

THE HH DISTANCES

Although the HH distances are very hard to measure by electron-diffraction, it may be of interest to report their values obtained by the four different approaches (A—D). Because of the lack of experimental values of u, the spectroscopic ones [10] were used for transforming r^m-values to r^g (in the case of B). The quantities of u^2/r came out with the figures 0.02303, 0.01637 and 0.01289 for the distances viii, ix and x, respectively. The resulting r^g-values are reported in Table 7.

CONCLUSION

The following conclusion has been drawn from the present study on benzene.

1. The accuracy of the electron-diffraction measurements is not high enough to give quantitative shrinkage effects. Nevertheless there has been observed a trend of positive shrinkage effects in accordance with theory.

2. The electron-diffraction measurements may be adjusted within their error limits to fit accurately the non-rigid model based on spectroscopic shrinkage effects.

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