

Bastiansen-Morino Shrinkage Effects in Benzene Type Molecules I

S. J. CYVIN

Institutt for teoretisk kjemi, Norges tekniske høgskole, Trondheim, Norway

Bastiansen *et al.* have observed an apparent shrinkage of the long distances in linear chains by their electron-diffraction study of gas molecules. Morino has treated this effect theoretically and shown that the influence of anharmonicity cancel in the spectroscopic calculations of the shrinkage effect.

In the present paper the concept of the shrinkage effect is extended to non-linear conformations of atoms, and applied to the benzene molecular model. The so-called "natural" and "practical" shrinkage effects are introduced. It is found that all the anharmonic terms cancel exactly in the spectroscopic calculations of the practical shrinkage effects in benzene. This is true for the non-linear cases as well as the linear ones.

The Bastiansen-Morino shrinkage effect¹ has been observed in several linear-skeleton molecules by electron-diffraction of gas molecules²⁻⁵. This effect may be computed spectroscopically according to Morino's method⁶ using generalized mean-square amplitudes⁷. Such calculations have been performed for some linear-skeleton molecules⁸ and entirely linear molecules⁹⁻¹¹. The method has also been applied to linear conformations of atoms in a non-linear molecule, *viz.* naphthalene^{12,13}. In the present work the shrinkage effects in benzene are studied, including those for non-linear conformations of atoms.

THEORY

The theory is based on a power-series evaluation of r^e , this being the mean value of an arbitrary internuclear distance in a molecule. To the second-order approximation one has^{7,8,12}

$$r_{ij}^e = \langle r_{ij} \rangle = r_{ij}^e + \langle \Delta z_{ij} \rangle + (\langle \Delta x_{ij}^2 \rangle + \langle \Delta y_{ij}^2 \rangle) / 2r_{ij}^e \quad (1)$$

where r^e is the equilibrium distance, $\langle \Delta z \rangle$ is the so-called anharmonic term, $\langle \Delta x^2 \rangle$ and $\langle \Delta y^2 \rangle$ being the mean-square perpendicular amplitudes. The second-order term will be denoted by K_{ij} , *i.e.*,

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

Hence

$$r_{ij}^g = r_{ij}^e + \langle \Delta z_{ij} \rangle + K_{ij} \quad (3)$$

The r_{ij}^g value for any interatomic distance of a molecule may be obtained by electron-diffraction. The K_{ij} term is obtainable spectroscopically by the standard normal-coordinate analysis of small harmonic vibrations. To be true, the entering r_{ij}^e (see eqn. 2) is not a priori known, but it is assumed that an approximate value will do on this place, since K_{ij} is a correction term.

Considering three atoms of a molecule (Fig. 1) the appropriate shrinkage effect in the linear case is defined by

$$-\delta_{13} = r_{13}^g - (r_{12}^g + r_{23}^g) \quad (4)$$

In the presently studied case of benzene it is desirable to include the non-linear case. The non-linear shrinkage effect (for three atoms) may be defined as

$$-\delta_{13}^N = r_{13}^g - [(r_{12}^g)^2 + (r_{23}^g)^2 - 2r_{12}^g r_{23}^g \cos \varphi_2^e]^{1/2} \quad (5)$$

Here φ_2^e is the equilibrium interbond angle, whose value may be known a priori. The benzene molecule (with all interbond angles of 120°) provides with good examples of this feature. It may be convenient to define another shrinkage effect, *viz.*,

$$-\delta_{13}^P = r_{13}^g - (r_{12}^g \cos \varphi_1^e + r_{23}^g \cos \varphi_3^e) \quad (6)$$

where φ_1^e and φ_3^e are the equilibrium values of the angles indicated on Fig. 1. It should be noticed well that their values may not be known even if φ_2^e is known. The two introduced shrinkage effects defined by eqns. (5) and (6) will be referred to as the "natural" (δ^N) and "practical" (δ^P) shrinkage effects, respectively. These two shrinkage effects would coincide if $r_{12}^g/r_{23}^g = r_{12}^e/r_{23}^e$. Actually it has been found that they are exactly equal to the first order of approximation¹⁴.

More than two distances (*i.e.* more than three atoms) may be involved in the shrinkage effect. Consider the linear four-atomic conformation 1-2-3-4. In this case the following shrinkage effects may be defined.

$$-\delta_{13} = r_{13}^g - (r_{12}^g + r_{23}^g) \quad (7)$$

$$-\delta_{24} = r_{24}^g - (r_{23}^g + r_{34}^g) \quad (8)$$

$$-\delta_{14} = r_{14}^g - (r_{12}^g + r_{23}^g + r_{34}^g) \quad (9)$$

$$-\delta_{14}' = r_{14}^g - (r_{12}^g + r_{24}^g) \quad (10)$$

$$-\delta_{14}'' = r_{14}^g - (r_{13}^g + r_{34}^g) \quad (11)$$

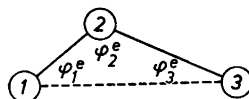
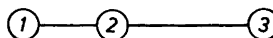


Fig. 1. Equilibrium conformations of three atoms.

Obviously there are only three independent quantities among those given above. The two latter ones may be expressed in terms of the three linearly independent quantities (7)–(9) by the following equations.

$$\delta_{14}' = \delta_{14} - \delta_{24} \quad (12)$$

$$\delta_{14}'' = \delta_{14} - \delta_{13} \quad (13)$$

Eqn. (3) may be applied to the above considered linear shrinkage effects, giving the results

$$-\delta_{13} = K_{13} - (K_{12} + K_{23}) \quad (14)$$

$$-\delta_{24} = K_{24} - (K_{23} + K_{34}) \quad (15)$$

$$-\delta_{14} = K_{14} - (K_{12} + K_{23} + K_{34}) \quad (16)$$

According to these equations the shrinkage effects may be calculated spectroscopically by means of the mean-square perpendicular amplitudes (*cf.* eqn. 2), following Morino's method⁶. Morino was the first one to point out that the anharmonic terms $\langle \Delta z_{ij} \rangle$ (*cf.* eqn. 1) cancel by the computations of this kind in the case of linear chains of atoms^{6,8}. The same feature may occur in the case of non-linear shrinkage effects, as is shown for the first time by the present treatment of the benzene molecule.

TREATMENT OF THE BENZENE MOLECULAR MODEL

In Table 1 a complete list is given of the ten types of interatomic distances in benzene. The equilibrium bond distances are identified by R and D for C–H and C–C, respectively. A further consideration of the anharmonic terms is required. The Δz_{ij} term refers to the cartesian displacements along the equilibrium connecting line of the atom pair in question. Let the directions of the axes of a fixed in-plane cartesian coordinate system be denoted by ξ and η (see Fig. 2). It appears that all of the anharmonic terms $\langle \Delta z_{ij} \rangle$ may be expressed in terms of $\langle \eta_1 \rangle$ and $\langle \eta_7 \rangle$, this being the mean radial displace-

Table 1. Interatomic distances in a benzene type molecule.

Type	Equilibrium value	Mean value
CC	$r_{12}^e = D$ $r_{26}^e = 3^{1/2}D$ $r_{14}^e = 2D$	$r_{12}^g = D + \langle \Delta z_{12} \rangle + K_{12}$ $r_{26}^g = 3^{1/2}D + \langle \Delta z_{26} \rangle + K_{26}$ $r_{14}^g = 2D + \langle \Delta z_{14} \rangle + K_{14}$
CH	$r_{17}^e = R$ $r_{27}^e = (R^2 + D^2 + RD)^{1/2}$ $r_{37}^e = (R^2 + 3D^2 + 3RD)^{1/2}$ $r_{47}^e = R + 2D$	$r_{17}^g = R + \langle \Delta z_{17} \rangle + K_{17}$ $r_{27}^g = r_{27}^e + \langle \Delta z_{27} \rangle + K_{27}$ $r_{37}^g = r_{37}^e + \langle \Delta z_{37} \rangle + K_{37}$ $r_{47}^g = R + 2D + \langle \Delta z_{47} \rangle + K_{47}$
HH	$r_{78}^e = R + D$ $r_{8\ 12}^e = 3^{1/2}(R + D)$ $r_{7\ 10}^e = 2(R + D)$	$r_{78}^g = R + D + \langle \Delta z_{78} \rangle + K_{78}$ $r_{8\ 12}^g = 3^{1/2}(R + D) + \langle \Delta z_{8\ 12} \rangle + K_{8\ 12}$ $r_{7\ 10}^g = 2(R + D) + \langle \Delta z_{7\ 10} \rangle + K_{7\ 10}$

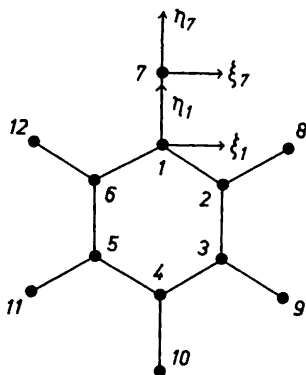


Fig. 2. Benzene molecule model. Numbering of the atoms, and the in-plane cartesian displacement coordinates for atoms 1 and 7.

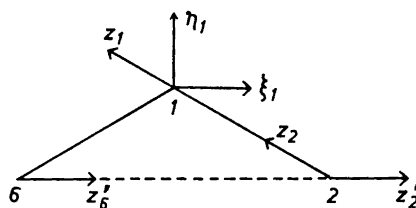


Fig. 3. Part of the benzene molecular model showing the explanation of

$$\Delta z_{12} = z_1 - z_2$$

and

$$\Delta z_{26} = z_2' - z_6'$$

ments of a C and H atom, respectively, while $\langle \xi_1 \rangle = \langle \xi_7 \rangle = 0$ because of symmetry.

Skeleton distances. From geometrical and symmetry considerations it appears that $\langle \Delta z_{12} \rangle = \langle \eta_1 \rangle$, $\langle \Delta z_{26} \rangle = 3^{1/2} \langle \eta_1 \rangle$ and $\langle \Delta z_{14} \rangle = 2 \langle \eta_1 \rangle$. For explanation of the terms Table 1 and Fig. 2 should be consulted. A detailed explanation of Δz_{12} and Δz_{26} is given in Fig. 3. The following set of linearly dependent equations is obtained.

$$r_{12}^g - K_{12} = D + \langle \eta_1 \rangle \quad (17)$$

$$r_{26}^g - K_{26} = 3^{1/2} D + 3^{1/2} \langle \eta_1 \rangle \quad (18)$$

$$r_{14}^g - K_{14} = 2D + 2 \langle \eta_1 \rangle \quad (19)$$

In consequence, the following shrinkage effects may be derived, and they do not contain the anharmonic term.

$$-\delta_{26} = r_{26}^g - 3^{1/2} r_{12}^g = K_{26} - 3^{1/2} K_{12} \quad (20)$$

$$-\delta_{14} = r_{14}^g - 2r_{12}^g = K_{14} - 2K_{12} \quad (21)$$

In the considered case of skeleton distances the natural and practical shrinkage effects are coincident.

CH distances. For the bonded CH distance it has been found

$$r_{17}^g - K_{17} = R - \langle \eta_1 \rangle + \langle \eta_7 \rangle \quad (22)$$

By treating the shortest non-bonded CH distance types, some difficulties occur. From the electron-diffraction point of view it seems natural to consider the shrinkage effect

$$-\delta_{27}^N = r_{27}^g - [(r_{12}^g)^2 + (r_{17}^g)^2 + r_{12}^g r_{17}^g]^{1/2} \quad (23)$$

which is immediately obtainable from observed r^g values. If eqn. (3) were applied to this quantity, however, the result would contain both the equi-

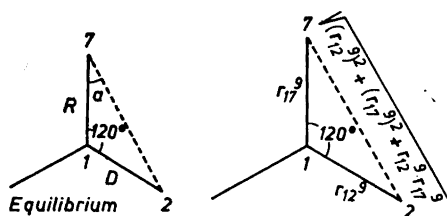


Fig. 4. Consideration of the shortest non-bonded CH distance type, including the definition of α .

Equilibrium distance values and the anharmonicity terms in a complicated way. It was found profitable to introduce the practical shrinkage effect, *viz.*,

$$-\delta_{27}^P = r_{27}^g - r_{17}^g \cos \alpha - r_{12}^g \sin\left(\alpha + \frac{\pi}{6}\right) \quad (24)$$

For the definition of the angle α , see Fig. 4. The application of δ_{27}^P rather than δ_{27}^N made the anharmonicity terms to cancel exactly, leading to the result

$$-\delta_{27}^P = K_{27} - K_{17} \cos \alpha - K_{12} \sin\left(\alpha + \frac{\pi}{6}\right) \quad (25)$$

It should be noticed, however, that the equilibrium distances are not completely eliminated. The angle α depends on their ratio according to

$$R/D = \cos\left(\alpha + \frac{\pi}{6}\right) / \sin \alpha \quad (26)$$

Theoretically this ratio may be determined from electron diffraction and spectroscopic data by means of eqns. (24)–(26). In practice, however, it seems not probable that data of sufficient accuracy required for such computations can be obtained at present. Probably the values of δ^N and δ^P cannot be distinguished in practice.

After a similar treatment of the 3–7 type distances, the following result was obtained.

$$\begin{aligned} -\delta_{37}^P &= r_{37}^g - r_{17}^g \cos b - r_{12}^g \left[\cos b + \sin\left(b + \frac{\pi}{6}\right) \right] \\ &= K_{37} - K_{17} \cos b - K_{12} \left[\cos b + \sin\left(b + \frac{\pi}{6}\right) \right] \end{aligned} \quad (27)$$

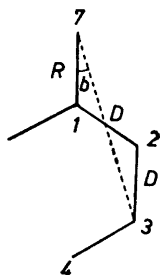


Fig. 5. Definition of the angle b .

The angle b is defined on Fig. 5, and one has

$$R/D = \left[\cos\left(\frac{\pi}{6} - b\right) / \sin b \right] - 2 \quad (28)$$

For the longest CH type distances it has been found

$$-\delta_{47} = r_{47}^g - r_{17}^g - 2r_{12}^g = K_{47} - K_{17} - 2K_{12} \quad (29)$$

This shrinkage effect involves the atoms 7-1-2-3-4. A linear shrinkage effect may be defined for the atom pair in question, *viz.* 4-7, as shown below.

$$-\delta_{47}^* = r_{47}^g - r_{17}^g - r_{14}^g = K_{47} - K_{17} - K_{14} \quad (30)$$

This quantity may be expressed in terms of the above defined shrinkage effects (see eqns. 21 and 29) as

$$\delta_{47}^* = \delta_{47} - \delta_{14} \quad (31)$$

HH distances. For the HH type distances the following results have been obtained.

$$-\delta_{78} = r_{78}^g - r_{12}^g - r_{17}^g = K_{78} - K_{12} - K_{17} \quad (32)$$

$$-\delta_{8\ 12} = r_{8\ 12}^g - 3\frac{1}{2}r_{12}^g - 3\frac{1}{2}r_{17}^g = K_{8\ 12} - 3\frac{1}{2}K_{12} - 3\frac{1}{2}K_{17} \quad (33)$$

$$-\delta_{7\ 10} = r_{7\ 10}^g - 2r_{12}^g - 2r_{17}^g = K_{7\ 10} - 2K_{12} - 2K_{17} \quad (34)$$

Here again a linear shrinkage effect may be defined:

$$-\delta_{7\ 10}^* = r_{7\ 10}^g - r_{14}^g - 2r_{17}^g = K_{7\ 10} - K_{14} - 2K_{17} \quad (35)$$

This quantity is given in terms of the above defined shrinkage effects (see eqns. 21 and 34) by

$$\delta_{7\ 10}^* = \delta_{7\ 10} - \delta_{14} \quad (36)$$

Utilization of symmetry The method of utilizing symmetry coordinates is an alternative, systematic way of treating the anharmonic terms. Using the notation of previous papers^{15,16} one has $\langle \Delta z_{12} \rangle = \langle d \rangle$, $\langle \Delta z_{26} \rangle = \langle d^* \rangle$, $\langle \Delta z_{14} \rangle = \langle d^{**} \rangle$, etc. for each of the ten types of distances. The coordinates d , d^* , d^{**} , etc., may be expressed linearly in terms of symmetry coordinates, and consequently the anharmonic terms may be expressed in terms of the mean values of symmetry coordinates. One has¹⁴ $\langle S_i \rangle = 0$ for every not totally-symmetric coordinate. Hence the mean values of the two coordinates of species A_{1g} will be the only non-vanishing ones in the case of benzene molecules. With the definition of S_1 and S_2 as given in the mentioned papers^{15,16} one finds

$$\langle \eta_1 \rangle = 6^{-\frac{1}{2}} \langle S_1 \rangle \quad (37)$$

$$\langle \eta_7 \rangle = 6^{-\frac{1}{2}} \langle S_1 \rangle + 6^{-\frac{1}{2}} \langle S_2 \rangle \quad (38)$$

The final results for the shrinkage effects will of course be the same if $\langle S_1 \rangle$ and $\langle S_2 \rangle$ are used instead of $\langle \eta_1 \rangle$ and $\langle \eta_7 \rangle$.

CONCLUSION

Mean amplitudes of vibration from electron-diffraction measurements on benzene were obtained for the first time by Karle¹⁷. More accurate measurements were provided by Bastiansen *et al.*¹⁸ The latter ones were compared with

values from spectroscopic data with satisfactory results¹⁹. The results showed to be in very good correspondence with those recently reported by Kimura and Kubo²⁰.

In view of the existing electron-diffraction data of high accuracy on benzene, it was found desirable to perform further spectroscopic studies on this molecule. As a part of this programme the mean amplitudes of vibration of benzene²¹ and benzene-d₆²² were recalculated, using the method of mean-square amplitude matrices^{15,16}. It is planned to extend these calculations by including the mean-square perpendicular amplitudes, and to apply the presently developed theory of shrinkage effects.

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