Y. Morino: We have estimated every systematic error for the measurement of the mean amplitudes. For the error due to the finite sample size, which was the most serious, we measured the gas distribution and made a correction to the effect. For the $D-E$ calibration we took photographs below $D=0.5$. The linear relation between D and E in this range had been established by a preliminary experiment.

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Out-of-Plane Molecular Vibrations and "Shrinkage Effects" in Naphthalene Skeleton

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Spectroscopic calculations have been performed for the out-of-plane vibrations of the naphthalene skeleton. The molecule has been treated as a ten-particle, planar regular structure X_2Y_8($X=C$, $Y=CH$). Small harmonic vibrations were assumed. The two linear shrinkage effects have been estimated with the following results referring to 298°K: 0.0073Å for the shorter distance (2-7), and 0.0067Å for the longer distance (1-6). Recent electron-diffraction measurements on naphthalene due to Bastiansen *et al.* are quoted, and certain refinements of their results are discussed.

By the increasing accuracy of electron-diffraction experiments Bastiansen *et al.* have observed a shortening of long interatomic distances in linear chains, referred to as the shrinkage effect[1]. This effect is tentatively explained by considering the molecular vibrations, and may accordingly be calculated spectroscopically by the method of Morino[2], using the generalized mean-square amplitudes[3]. As pointed out by Professor Bastiansen, the same method may be applied to any linear conformation of three atoms in a molecule, e.g. a condensed aromatic. In connection with the recent electron-diffraction investigations of condensed aromatics in the gaseous state[4] even a rough estimate of the shrinkage effects from spectroscopic data would be very useful.

The purpose of the present work was to estimate the order of magnitude of the two different shrinkage effects in naphthalene skeleton, to see if the influence of molecular vibrations could be neglected with confidence. Next it was intended, if possible, to make the first step towards a correction for intramolecular motion of the electron-diffration results on naphthalene. It had been decided to start with the out-of-plane vibrations for two reasons: (i) The theoretical treatment is simpler than that of the in-plane vibrations. (ii) They were believed to give the largest and possibly the main contribution to the shrinkage effects.

Spectroscopic calculations. The spectroscopic computations are based on the usual assumption of small harmonic vibrations[5]. The naphthalene molecule is treated as a ten-particle planar structure X_2Y_8($X=C$, $Y=$ CH) with two regular hexagonal rings in the equilibrium position. For the numbering of

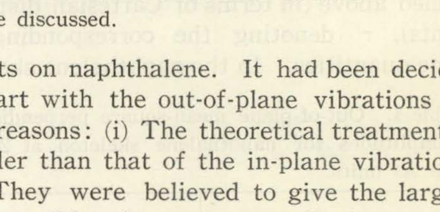

Fig. 1. Numbering of atoms and structural parameters of naphthalene skeleton.

particles, see Fig. 1. When the assigned skeleton frequencies from naphthalene are adapted to this model, it is believed that the computed mean-square amplitude quantities may be identified (as an approximation) with those of the naphthalene skeleton. This method of simplified molecular models has been tried previously for cyclopropane, allene and benzene molecules with satisfactory results[6]. There are 15 types of interatomic distances in the naphthalene skeleton model. The corresponding out-of-plane mean-square perpendicular amplitudes, viz. $\tau_{ij} = \langle (z_i - z_j)^2 \rangle$, have been calculated with the result given in Table I. Details of these computations will be published elsewhere.

For three colinear particles $i-j-k$ the shrinkage effect $\delta_{ij}{}^g$ is given to the first approximation by

$$-\delta_{ik} = (\tau_{ik}+\tau_{ik}')/2r_{ik}^e - (\tau_{ij}+\tau_{ij}')/2r_{ij}^e - (\tau_{jk}+\tau_{jk}')/2r_{jk}^e$$

where r^e represents the appropriate equilibrium distance. The terms τ are the out-of-plane mean-square perpendicular amplitudes defined above (in terms of Cartesian displacements), τ' denoting the corresponding in-plane quantities. In the naphthalene skeleton model there are two different shrinkage effects of the considered type, viz, $\delta_{27}{}^g$ and $\delta_{16}{}^g$. Their orders of magnitude may probably be roughly estimated by neglecting the τ_{ij}' terms in the above formula. The obtained results using the C–C equilibrium bond distance of[7] 1.40 Å are 0.0073Å and 0.0067Å at 298°K for 2 - 7 and 1 - 6, respectively.

Table I. Out-of-plane mean-square perpendicular amplitudes for naphthalene skeleton at 298°K in Å² units.

Distance (i-j)	Value
2— 3	0.0106
1— 2	0.0100
1— 9	0.0122
9—10	0.0151
1—10	0.0097
1— 3	0.0160
2— 9	0.0200
1— 8	0.0125
1— 4	0.0097
2—10	0.0181
1— 7	0.0148
1— 5	0.0046
1— 6	0.0075
2— 7	0.0092
2— 6	0.0032

Approach to the electron-diffraction refinements. Almenningen, Bastiansen and Dyvik[4] have presented an elaborate electron-diffraction analysis of the C-C distances in naphthalene (and other condensed aromatics). Seven distinct peaks on the radial distribution curve were interpreted as averaged maximum positions of the seven groups of nearly equal C-C distances (see Table II). Hence seven observations were available for determining the five parameters (a, b, c, d, φ) of a general D_{2h} structure, i.e., planar non-regular structure, of the naphthalene skeleton (see Fig. 1). The obtained result (a=1.412, b=1.371, c=1.422, d=1.420, φ=29.42°) was in perfect agreement with refined X-ray data[7].

Table II. Correction terms $\tau_{ij}/2r_{ij}^e$ for naphthalene skeleton. Å units, T=298°K.

Distance (i-j)	Value
2— 3	0.0038
1— 2	0.0036
1— 9	0.0043
9—10	0.0054
1—10	0.0020
1— 3	0.0033
2— 9	0.0041
1— 8	0.0026
1— 4	0.0017
2—10	0.0032
1— 7	0.0020
1— 5	0.0006
1— 6	0.0009
2— 7	0.0010
2— 6	0.0003

The presently calculated shrinkage effects indicate the need of comparatively small, but detectable refinements of the electron-diffraction measurements. Unfortunately the shrinkage effects in naphthalene are not directly observable by electron-diffration because of the overlapping of nearly equal distances.

To estimate the equilibrium distances (r^e) from the observed maximum positions (r^m), the following approximate relations should be used:

$$r_{ij}^g = r_{ij}^m + \langle \Delta\zeta_{ij}^2 \rangle / r_{ij}^e \ ,$$

and

$$r_{ij}^e = r_{ij}^m - \langle \Delta\zeta_{ij} \rangle - (\tau_{ij} + \tau_{ij}')/2r_{ij}^e .$$

Here $\Delta\zeta_{ij}$ is used to denote the interatomic displacements in the direction of the equilibrium connecting line of the atom pair. Hence $\langle \Delta\zeta_{ij}^2 \rangle$ is the mean-square parallel amplitude, $\langle \Delta\zeta_{ij} \rangle$ being referred to as the anharmonic term. It should be noted that the anharmonic terms cancelled in the computations of shrinkage effects.

From the present calculations it is possible to give one part of the above considered refinements, viz. $\tau_{ij}/2_{ij}^e$. These terms are given numerically in Table II for each of the individual distances. In Table III the observed r^m terms are quoted, along with the appropriate correction terms, the latter being average values within each of the seven groups of the figures in Table II.

Table III. Observed maximum positions and calculated corrections. Å units.

r^m(obs.*)	$\tau/2r^e$(calc.)
1.4008	0.0041
2.4349	0.0031
2.8102	0.0027
3.7336	0.0015
4.2191	0.0009
4.8248	0.0010
5.0449	0.0003

* See Ref 4.

The correction terms of Table III should be considered in connection with the other refinements mentioned above. Some simple considerations* indicated that the remaining refinements may be of the same orders of magnitude as the presently enumerated correction terms (Table III). From the given relations it is apparent that a difference between two different corrections is required. To obtain significant final results, it seems therefore probable that calculations of higher precision than the present approximate estimates are needed.

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* Based on assumed mean-square amplitudes $<\Delta\zeta^2>$ and approximate Morse factors.