Condensed Aromatics. Part V

In-Plane Molecular Vibrations of Naphthacene and Mean Amplitudes for Nonbonded CC Distances in General

S. J. Cyvin, J. Brunvoll, and B. N. Cyvin
Division of Physical Chemistry, The University of Trondheim,
Trondheim-NTH, Norway

and

V. S. Mastryukov
Laboratory of Electron Diffraction, Department of Chemistry,
Moscow State University, Moscow, USSR

Z. Naturforsch. **34a**, 1512–1517 (1979); received October 13, 1979

The five-parameter approximation is applied to a normal coordinate analysis of the in-plane molecular vibrations of naphthacene. Vibrational frequencies and mean amplitudes of vibration are reported. The mean amplitudes of vibration for the nonbonded CC distances are studied in particular on the basis of data for benzene, naphthalene, anthracene, pyrene, coronene and naphthacene. The distance types are classified, and characteristic values for the mean amplitudes of the corresponding distances in different molecules are detected.

Introduction

A simple, new aromatic force field for the in-plane vibrations of condensed aromatics was described in previous parts of this series [1, 2] and referred to as five-parameter approximation. This force field was found to be useful in particular for computing reliable mean amplitudes of vibration [3]. Such quantities were computed for benzene and pyrene [2] along with naphthalene, anthracene and coronene [4].

In the present work a normal coordinate analysis according to the five-parameter approximation for naphthacene was performed. The calculated in-plane vibrational frequencies and mean amplitudes of vibration are reported. Furthermore, a systematization of the mean amplitudes for nonbonded CC distances is carried out, based on the computations for benzene [2], naphthalene [4], anthracene [4], pyrene [2], coronene [4] and naphthacene (present work).

This work is a part of a broad program for investigations of condensed aromatics. It contains theoretical analysis, experimental spectroscopical works and gas-phase electron diffraction studies.

Naphthacene

A planar molecular model of symmetry D_{2h} is assumed; see Figure 1. All the benzene rings are assumed to be regular and all interbond angles 120°. For the CC and CH distances the estimated values (produced as averages based on Hückel molecular orbital calculations [5]) of 1.409 Å and 1.084 Å, are adopted. Table 1 shows the CC stretching force constants, which were obtained by means of the bond orders (P) from the simple Hückel molecular orbital theory [5]. These force constants are considered as one parameter in the five-parameter

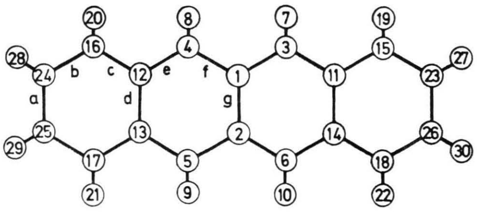


Fig. 1. Numbering of atoms in the naphthacene molecular model; symmetry D_{2h}.

Table 1. Bond orders (P), force constants (f) and mean amplitudes of vibration at 298 K (l) for the CC bonds in naphthacene.

Type *	P	f [mdyne Å^{-1}]	l [Å]
a	0.581	4.564	0.0483
b	0.741	5.127	0.0469
c	0.530	4.397	0.0484
d	0.475	4.217	0.0481
e	0.618	4.693	0.0477
f	0.584	4.577	0.0480
g	0.458	4.163	0.0483

* See Figure 1.

Reprint requests to Prof. S. J. Cyvin, Division of Physical Chemistry, The University of Trondheim, N-7034 Trondheim-NTH, Norwegen.

0340-4811 / 79 / 1200-1512 $ 01.00/0. — Please order a reprint rather than making your own copy.

approximation. The others four are (in mdyne/Å): 5.0 for CH stretchings, 0.7 for CCC bendings where an H atom is attached to the central C, 0.4 for CCC bendings where three CC bonds meet, and 0.35 for the CCH bendings.

The calculated frequencies of the in-plane vibrations are shown in Table 2.

Table 1 includes the mean amplitudes of vibration [3] at 298 K for the bonded CC distances. $l = 0.0774$ Å was obtained for the three types of bonded CH. For the sake of brevity and uniformity we shall only report the values at room temperature (298 K) also for the nonbonded distances. Nevertheless we are aware of the fact that the gas electron diffraction experiments for higher condensed aromatics must be conducted at higher temperatures, e.g. about 400 °C for coronene. For this particular molecule we have calculated the mean amplitudes at this temperature too in connection with an electron diffraction investigation now being in progress. These values are not given here.

The results for the mean amplitudes of naphthacene at 298 K are summarized in Tables 3, 4 and 5 for the nonbonded CC, CH and HH distances, respectively. In the type notation the first figure (before a classifying decimal point) indicates the minimum number of bonds which connect the atom pair in question. The numbering of atoms (*i–j*) is consistent with Figure 1. The interatomic distances (*r* in Å) are calculated from the adopted structural parameters.

The 38 types of nonbonded CC distances (Table 3) are grouped into 16 main types; the 51 types of nonbonded CH distances (Table 4) are grouped into 26 main types and the 21 HH distances (Table 5) into 17.

Table 2. Calculated in-plane vibrational frequencies for naphthacene.

Species	cm^{-1}	Species	cm^{-1}	Species	cm^{-1}	Species	cm^{-1}
A_g	3036	B_{1u}	3040	B_{3g}	3040	B_{2u}	3036
	3034		3035		3033		3033
	3030		3032		3032		3030
	1609		1649		1688		1604
	1558		1515		1587		1574
	1530		1418		1446		1499
	1449		1306		1291		1478
	1428		1247		1256		1143
	1141		1137		1186		1122
	1100		1016		1051		1096
	890		934		938		887
	720		591		719		718
	657		435		464		659
	634		141		282		484
	251						

Table 3. Mean amplitudes of vibration (*l*) for the nonbonded CC distances in naphthacene at 298 K.

Type	*i–j*	*r* [Å]	*l* [Å]
2.	1–5	2.44	0.0580
	1–11		0.0567
	3–14		0.0578
	11–18		0.0578
	11–23		0.0564
	15–26		0.0565
	3–4		0.0656
	3–15		0.0657
3.1	1–13	2.82	0.0619
	3–6		0.0614
	11–26		0.0609
	15–18		0.0607
3.2	3–5	3.73	0.0639
	3–18		0.0638
	1–15		0.0680
	3–12		0.0677
	3–23		0.0675
4.1	1–17	4.23	0.0684
	3–13		0.0682
	3–26		0.0671
4.2	1–23	4.88	0.0681
	11–12		0.0683
	3–16		0.0830
5.1	1–25	5.08	0.0682
	11–13		0.0687
5.2	3–17	5.63	0.0740
5.3	3–24	6.14	0.0808
	11–16		0.0811
6.1	3–25	6.46	0.0761
	11–17		0.0769
6.2	11–24	7.32	0.0777
	15–16		0.0973
7.2	11–25	7.45	0.0752
7.3	15–17	7.84	0.0832
7.4	15–24	8.57	0.0921
8.1	15–25	8.80	0.0844
8.2	23–24	9.76	0.0862
9.	23–25	9.86	0.0818

Classification of CC Mean Amplitudes

The great number of interatomic distance types in a comparatively large condensed aromatic (e.g. 120 in naphthacene) makes a systematical classification highly warranted. The first obvious classification pertains to the types of atoms and the property of being bonded (CC and CH) or nonbonded (CC, CH and HH). In hydrocarbons the mean amplitudes of CC distances are the most important ones in gas electron diffraction studies [6]. Hence we have concentrated upon the nonbonded CC distances in the present systematization and comparisons of mean amplitudes for several molecules.

Table 4. Mean amplitudes of vibration (*l*) for the nonbonded CH distances in naphthacene at 298 K.

Type	*i–j*	*r* [Å]	*l* [Å]
2.	1–7	2.16	0.101
	7–11		0.100
	11–19		0.101
	15–27		0.100
	19–23		0.100
	23–30		0.101
3.1	3–8	2.67	0.133
	3–19		0.133
	7–15		0.132
3.2	1–9	3.42	0.098
	7–14		0.098
	11–22		0.098
	11–27		0.097
	15–30		0.097
	19–26		0.097
4.1	3–10	3.90	0.095
	11–30		0.095
	15–22		0.095
4.2	1–19	4.07	0.134
	7–12		0.134
	7–23		0.134
4.3	3–9	4.60	0.108
	3–22		0.108
	3–27		0.111
	7–18		0.108
5.1	1–21	4.86	0.124
	7–13		0.124
	7–26		0.123
5.2	3–20	5.00	0.151
	7–16		0.151
5.3	3–30	5.31	0.099
5.4	1–27	5.84	0.107
6.1	1–29	6.14	0.101
6.2	3–21	6.25	0.129
	7–17		0.129
6.3	7–24	6.36	0.149
	11–20		0.150
6.4	3–28	7.04	0.121
7.1	7–25	6.89	0.139
	11–21		0.140
7.2	15–20	7.40	0.165
7.3	3–29	7.52	0.106
7.4	11–28	8.28	0.116
8.1	15–21	8.29	0.143
8.2	11–29	8.49	0.108
8.3	19–24	8.72	0.161
8.4	15–28	9.48	0.131
9.1	19–25	9.12	0.150
9.2	15–29	9.84	0.113
9.3	23–28	10.71	0.124
10.	23–29	10.87	0.114

Table 5. Mean amplitudes of vibration (*l*) for the HH distances (nonbonded) in naphthacene at 298 K.

Type	*i–j*	*r* [Å]	*l* [Å]
3.	19–27	2.49	0.158
	27–30		0.159
4.1	7–8	2.44	0.188
	7–19		0.188
4.2	19–30	4.32	0.133
5.1	7–27	4.76	0.171
5.2	7–10	4.99	0.120
	19–22		0.119
5.3	7–9	5.55	0.133
	7–22		0.133
6.1	7–20	4.88	0.203
6.2	7–30	5.93	0.145
7.1	7–21	6.98	0.158
7.2	7–28	7.15	0.182
8.1	19–20	7.32	0.216
8.2	7–29	7.97	0.157
9.1	19–21	8.86	0.176
9.2	19–28	9.56	0.192
10.1	19–29	10.19	0.166
10.2	27–28	11.64	0.156
11.	27–29	11.90	0.138

A further classification of the interatomic distances is already suggested by the grouping into main types exemplified for naphthacene above. A main group is identified here by a decimal number (cf. Tables 3–5). The first figure refers to the minimal number of bonds separating the atom pair in question. The numbers after the decimal point are ordered according to increasing interatomic distances.

A study of the mean amplitude values makes further distinctions between the distances necessary. As a minimal requirement we have introduced a new concept of "inner" and "outer" CC interatomic distances. For an inner CC distance the connecting straight line between the two C atoms lies completely inside the "body" of the molecule skeleton. For an outer CC distance this connecting line falls in part or completely outside the body. Strictly speaking this distinction is based on the idealized structure with identical, regular benzene rings. Furthermore, a part of the connecting line along the border of the skeleton body is considered as lying inside. Already in naphthalene we find an example of an outer CC for the shortest nonbonded CC distance in addition to the inner "benzene-like" meta-CC.

Nonbonded CC Mean Amplitudes

Systematization of the Data

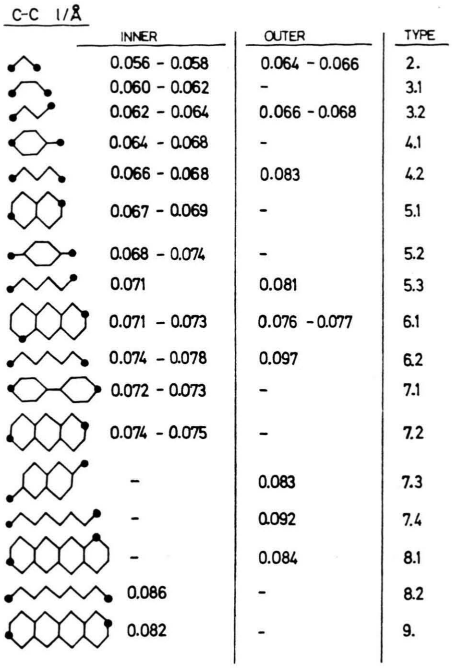
The classification described above makes it convenient to compare the mean amplitudes in different condensed aromatics. For the sake of a unified treatment we have considered the results from the five-parameter approximation only. For the sake of brevity only the results at 298 K are discussed.

The considered molecules, viz. benzene, naphthalene, anthracene, pyrene, coronene and naphthacene, are all "compact" in the sense that an outer CC distance completely outside the skeleton body (not present in benzene) occurs only for the shortest nonbonded distance. The work could be extended to many more types of outer CC distances, e.g. the next-shortest one corresponding to para-CC. This outer CC distance type is present in phenanthrene and condensed aromatics with a "phenanthrene-like" fragment, e.g. triphenylene, chrysene, benzo(c)phenanthrene, benzo(a)anthracene and perylene.

When the mean amplitudes of nonbonded CC distances are classified according to the above system we find characteristic values in the different condensed aromatics, mostly within 0.002 Å. Table 6 shows the different ranges obtained for the inner and outer distance of the shortest type (involving two bonds). The ranges of interatomic distances (r) emerged from the experimental structure parameters actually used in the normal coordinate analyses [2, 4]. The results illustrate the important influence of environments on the mean amplitudes, which has made the distinction between inner and outer distances necessary. A summary of the mean amplitudes of Table 6 is given in one line of Figure 2. All the other types of nonbonded CC distances of the present study have been analysed in the same way. We do not give here the voluminous material corresponding to Table 6 for these other types of distances; only the summarized version is shown in Figure 2. This figure actually gives a comprehensive survey of mean amplitudes based on 2 values for benzene, 11 for naphthalene, 23 for anthracene, 31 for pyrene, 27 for coronene and 38 for naphthacene — altogether 132 values.

Table 6. Ranges of mean amplitudes (l [Å]) for the shortest types of nonbonded CC distances.

Molecule	Inner r [Å] = 2.41–2.49	Outer r [Å] = 2.47–2.51
Benzene	0.0562	—
Naphthalene	0.0564–0.0577	0.0655
Anthracene	0.0565–0.0579	0.0654
Pyrene	0.056 –0.058	0.064
Coronene	0.0563–0.0571	0.0640
Naphthacene	0.0564–0.0580	0.0656–0.0657



C-C l/Å	INNER	OUTER	TYPE
	0.056 - 0.058	0.064 - 0.066	2.
	0.060 - 0.062	-	3.1
	0.062 - 0.064	0.066 - 0.068	3.2
	0.064 - 0.068	-	4.1
	0.066 - 0.068	0.083	4.2
	0.067 - 0.069	-	5.1
	0.068 - 0.074	-	5.2
	0.071	0.081	5.3
	0.071 - 0.073	0.076 - 0.077	6.1
	0.074 - 0.078	0.097	6.2
	0.072 - 0.073	-	7.1
	0.074 - 0.075	-	7.2
	-	0.083	7.3
	-	0.092	7.4
	-	0.084	8.1
	0.086	-	8.2
	0.082	-	9.

Fig. 2. Summary of the nonbonded CC mean amplitudes at 298 K for benzene, naphthalene, anthracene, pyrene, coronene and naphthacene.

Zig-zag Chains

The discussion may conveniently start with the mean amplitudes pertaining to straight zig-zag chains with varying number of bonds involved. In Fig. 3 the mean amplitudes are plotted *versus* the interatomic distances. The middle values of the different ranges of mean amplitudes in the considered molecules (cf. Fig. 2) are taken. It is found that the mean amplitudes for the inner distances fit one curve fairly closely. Those of the outer distances on the other hand are best fitted to two separate curves pertaining to odd and even number of bonds, respectively. The highest curve (see Fig. 3) is the one pertaining to the even-number bonds. All these features are reasonable, since in the case of odd-number bonds only a part of the line connecting the end atoms lies inside the skeleton body of the molecule.

It may be of interest to compare the curves for mean amplitudes of zig-zag chains in condensed aromatics with the empirical formula of mean

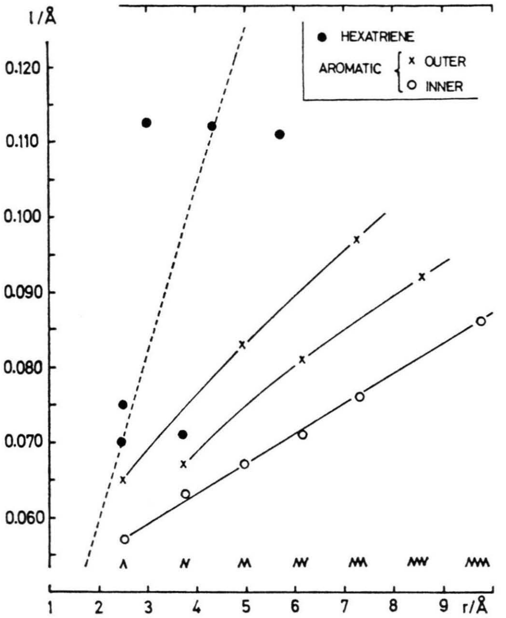


Fig. 3. Mean amplitudes for zig-zag chains in condensed aromatics and cis-1,3,5-hexatriene at 298 K. The stippled curve: $l = 0.013837 + 0.023398\,r - 0.000147\,r^2$; r and l in Å units [7].

amplitudes, $l(\mathrm{CC})/\text{Å}$, for bonded and nonbonded CC distances as a function of the interatomic distance ($r/\text{Å}$):

$$l(\mathrm{CC}) = 0.013837 + 0.023398\,r - 0.000147\,r^2\,.$$

This formula was deduced by Mastryukov and Cyvin [7] on the basis of a great number of electron diffraction data. It is seen (cf. Fig. 3) that the calculated mean amplitudes in condensed aromatics are not at all compatible with the above empirical formula for experimental values, which would predict substantially larger values. It is not difficult to understand the reason. The empirical material does not contain any aromatics apart from benzene, but many molecules with isolated carbon chains and alicyclic structures. It seems intuitively clear that the condensed aromatics are relatively much "stiffer" and hence possess smaller mean amplitudes for distance types of similar interatomic distances.

In Fig. 2 also the nonbonded CC mean amplitudes calculated for trans-1,3,5-hexatriene [8] are plotted. As expected the values are significantly larger than the corresponding ones in condensed aromatics, even those of the outer type. However, the details of the picture are confusing and become even more so when the calculated values for cis-1,3,5-hexatriene [8] and 1,3-butadiene [9] are considered in addition. Especially the butadiene values (0.061 Å for both nonbonded CC distances) are surprisingly low in this context.

General Survey

The calculated mean amplitudes for all the types of nonbonded CC distances, which are listed in Fig. 2, are plotted *versus* the interatomic distances in Figure 4.

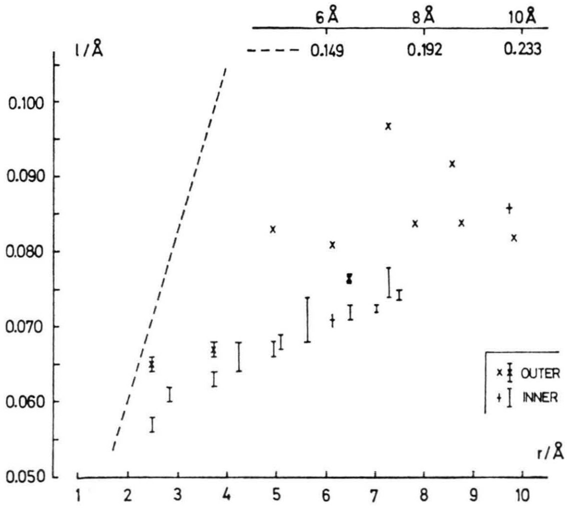


Fig. 4. Mean amplitudes for all types of nonbonded CC distances in condensed aromatics at 298 K (cf. Figure 2). For the significance of the stippled curve, see Fig. 3 and the text.

In three cases, viz. for the types 4.1, 5.2 and 6.2 Figs. 2 and 4 display ranges larger than 0.002 Å. A simple explanation is found when looking at the details of the computations. To take the type 4.1. as an example, the values (in Å) 0.067—0.068 are found for the cases when one of the bonds being a part of the connecting line of the end atoms falls on the border of the skeleton body. These cases may be said to approach the outer types, but are still considered as the inner types according to the present definition. The values (in Å) 0.064—0.065 occur only in pyrene and coronene as the genuine inner types.

Conclusion

The present work shows a convenient way to classify the nonbonded CC distances in condensed aromatics and to systematize the corresponding values of mean amplitudes. Characteristic values for corresponding types in different molecules are detected, and general trends are discussed. The present analysis is not complete; especially some outer types for fairly small interatomic distances (about 2.8—5.7 Å) are lacking. These particular types are all present in phenanthrene and condensed aromatics with a phenanthrene-like fragment.

Similar studies could be done for the CH and HH distances too, although they are less important than the CC distances. The basic data for such studies for the molecules considered here (benzene, naphthalene, anthracene, pyrene, coronene and naphthacene) have actually been published; cf. Tables 4 and 5 of the present work and Refs. [2, 4].

Acknowledgement

Financial support to BNC from The Norwegian Research Council for Science and the Humanities is gratefully acknowledged.

[1] A. Bakke, B. N. Cyvin, J. C. Whitmer, S. J. Cyvin, J. E. Gustavsen, and P. Klaeboe, Z. Naturforsch. **34a**, 579 (1979).

[2] S. J. Cyvin, B. N. Cyvin, J. Brunvoll, J. C. Whitmer, P. Klaeboe, and J. E. Gustavsen, Z. Naturforsch. **34a**, 876 (1979).

[3] S. J. Cyvin, Molecular Vibrations and Mean Square Amplitudes, Universitetsforlaget, Oslo and Elsevier, Amsterdam 1968.

[4] S. J. Cyvin, B. N. Cyvin, and J. Brunvoll, Z. Naturforsch. **34a**, 887 (1979).

[5] E. Heilbronner and H. Bock, Das HMO-Modell und seine Anwendung, Verlag Chemie, Weinheim 1970.

[6] L. V. Vilkov, V. S. Mastryukov, and N. I. Sadova, Opredelenie geometricheskogo stroeniya svobodnykh molekul (Determination of the geometrical structure of free molecules), Khimiya, Leningrad 1978.

[7] V. S. Mastryukov and S. J. Cyvin, J. Mol. Struct. **29**, 15 (1975).

[8] S. J. Cyvin, G. Hagen, and M. Traetteberg, Acta Chem. Scand. **23**, 3285 (1969).

[9] M. Traetteberg, G. Hagen, and S. J. Cyvin, Acta Chem. Scand. **23**, 74 (1969).