Condensed Aromatics. Part IV. The Five-Parameter Approximation and Mean Amplitudes of Vibration

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Mean amplitudes of vibration from spectroscopic computations for coronene are presented for the first time. Good agreement is found for the results from (a) the simple five-parameter in-plane force field approximation and (b) the more elaborate Califano-Neto force field. Mean amplitudes from the former method (a) for naphthalene and anthracene are also given.

Introduction

In previous parts of this series [1, 2] a new aromatic force field has been developed for the in-plane vibrations of condensed aromatics and referred to as the five-parameter approximation. This force field is considerably simpler than the well-known aromatic force field of Califano and Neto with collaborators [3–5]. The investigation of the mean amplitudes of vibration [6] for pyrene and benzene [2] has shown that very good results for these quantities are obtained from the five-parameter approximation. Furthermore it was tentatively concluded that this method is suitable for producing reliable mean amplitudes for condensed aromatics in general.

In the present paper we give additional support to this statement by reporting the mean amplitudes of vibration for coronene, which have been computed spectroscopically for the first time. Such quantities are supposed to be indispensable in the re-investigation of coronene from modern gas electron diffraction [7, 8], which is in progress. In the earlier gas electron diffraction investigation of naphthalene, anthracene and coronene [9] the mean amplitudes were not considered.

For the sake of completeness we report also the mean amplitudes of vibration for naphthalene and anthracene computed by the five-parameter approximation. The results may be compared with those from previous normal coordinate analyses [10]. We have not found it worth while to reproduce the force field of Neto et al. [3] for naphthalene and anthracene in order to calculate another set of mean amplitudes. It is not believed that this analysis would reveal any unexpected features; the results for mean amplitudes would most probably come close to those from the five-parameter approximation.

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Coronene

The mean amplitudes of vibration [6] were computed for all interatomic distance types (5 bonded and 59 nonbonded) in coronene according to (a) the five-parameter approximation [1, 2] and (b) the Califano-Neto method [3–5]. Values for the temperatures of absolute zero and 298 K were obtained; only the latter ones are discussed in details in the following for the sake of brevity. The normal coordinate analysis with calculated in-plane vibrational frequencies is published previously [1].

For the numbering of atoms it is referred to Figure 1.

The mean amplitudes for the bonded distances are shown in Table 1. The results from the two

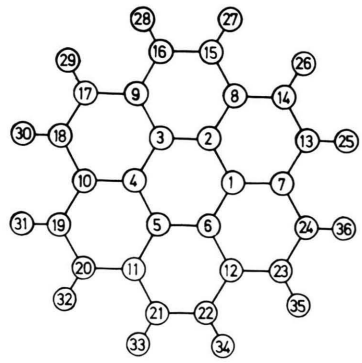

Fig. 1. The numbering of atoms in the coronene molecular model; symmetry D_{6h}.

Table 1. Mean amplitudes of vibration (Å units) for the bonded distances in coronene at 298 K.

	Type		Method	
	i–j *	Distance **	a	b
C—C	1–2	1.438	0.0472	0.0469
	1–7	1.381	0.0474	0.0455
	7–13	1.444	0.0483	0.0477
	13–14	1.362	0.0468	0.0441
C—H	13–25	1.080	0.0774	0.0772

* Numbering of atoms in Figure 1.
** Calculated interatomic distances in Å.
[a] Five-parameter approximation.
[b] Califano-Neto method.

methods are seen to be very close to each other, the largest difference being below 0.002 Å.

Table 2 shows the calculated mean amplitudes for the nonbonded CC distances. They are grouped into 12 main types as illustrated in Figures 2—4.

Table 2. Mean amplitudes of vibration (Å units) for the nonbonded CC distances in coronene at 298 K *.

Type [a]	*i–j*	Distance	a	b
2a	1–3	2.491	0.0565	0.0556
2b	1–8	2.441	0.0567	0.0549
2c	1–13	2.443	0.0571	0.0550
2d	7–14	2.434	0.0563	0.0538
2e	13–24	2.509	0.0640	0.0590
3a	1–4	2.876	0.0606	0.0604
3b	7–8	2.819	0.0612	0.0593
3c	1–14	2.815	0.0603	0.0597
4a	1–9	3.751	0.0617	0.0595
4b	1–15	3.765	0.0624	0.0601
4c	13–15	3.750	0.0663	0.0615
5a	1–10	4.257	0.0647	0.0630
5b	1–16	4.253	0.0639	0.0623
5c	7–15	4.263	0.0674	0.0641
6a	1–17	4.934	0.0663	0.0642
6b	7–9	4.883	0.0665	0.0632
6c	13–16	4.868	0.0676	0.0633
7a	1–18	5.128	0.0674	0.0658
7b	7–16	5.084	0.0681	0.0652
8a	7–10	5.638	0.0684	0.0653
8b	13–22	5.707	0.0731	0.0686
9	7–17	6.173	0.0706	0.0671
10a	7–18	6.476	0.0710	0.0680
10b	13–17	6.496	0.0728	0.0691
11	13–18	7.069	0.0729	0.0700
12	13–20	7.376	0.0738	0.0703
13	13–19	7.501	0.0738	0.0708

* See also footnotes to Table 1. [a] See Figures 2—4.

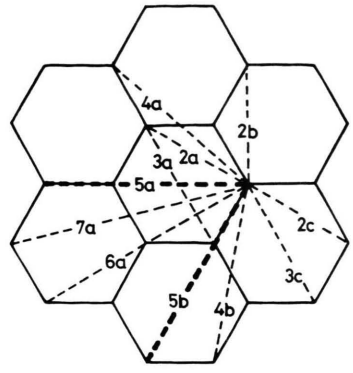

Fig. 2. Classification of the nonbonded CC distances of the 1–*j* types in coronene.

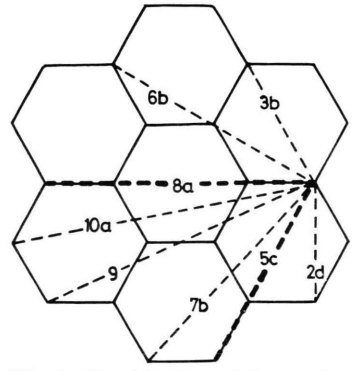

Fig. 3. Classification of the nonbonded CC distances of the 7–*j* types in coronene.

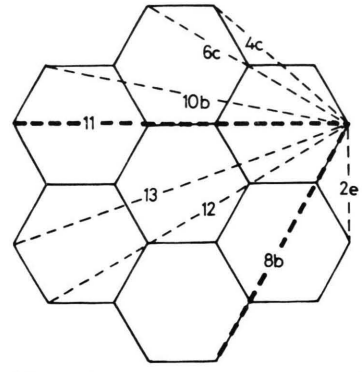

Fig. 4. Classification of the nonbonded CC distances of the 13–*j* types in coronene.

The three figures indicate the distance types of 1–*j*, 7–*j* and 13–*j*, respectively, when referring to the numbering of atoms in Figure 1. A very good agreement is found again between the results from the two methods in question. The differences are about 0.004 Å or less, and only in 2 cases (2e

and 6c) about 0.005 Å. However, the discrepancies were found in general to increase with increasing temperature. For the 2e type distance (13–24), for instance, the differences of 0.003, 0.005 and 0.0085 Å were found at absolute zero, 298 K and 673 K, respectively.

Table 3 shows the mean amplitudes of the nonbonded CH distances grouped into 17 main types;

Table 3. Mean amplitudes of vibration (Å units) for the nonbonded CH distances in coronene at 298 K *.

Type [a]	*i–j*	Distance	a	b
2A	7–25	2.192	0.101	0.101
2B	13–26	2.118	0.100	0.099
3	13–36	2.734	0.131	0.128
4A	1–25	3.416	0.098	0.096
4B	7–26	3.417	0.097	0.095
5	1–26	3.895	0.094	0.094
6	13–27	4.089	0.131	0.128
7A	1–27	4.630	0.108	0.106
7B	13–35	4.624	0.110	0.107
8	7–27	4.894	0.122	0.120
9	1–28	5.333	0.097	0.096
10A	1–29	5.891	0.106	0.104
10B	13–28	5.827	0.107	0.104
11A	1–30	6.182	0.101	0.100
11B	7–28	6.139	0.101	0.099
12	13–34	6.319	0.127	0.124
13	7–29	7.069	0.112	0.110
14	13–29	7.245	0.121	0.119
15A	7–30	7.539	0.103	0.101
15B	13–33	7.560	0.104	0.101
16	13–30	8.149	0.103	0.101
17	13–32	8.330	0.112	0.109
18	13–31	8.527	0.107	0.105

* See also footnotes to Table 1. [a] See Figures 5, 6.

Table 4. Mean amplitudes of vibration (Å units) for the HH distances in coronene at 298 K *.

Type [a]	*i–j*	Distance	a	b
1	25–26	2.437	0.158	0.158
2	25–36	2.514	0.184	0.181
3	25–27	4.783	0.168	0.165
4	25–28	6.735	0.140	0.137
5	25–34	6.792	0.172	0.169
6	25–29	8.284	0.145	0.143
7	25–30	9.229	0.126	0.124
8	25–32	9.250	0.143	0.141
9	25–31	9.565	0.131	0.129

* See also footnotes to Table 1. [a] See Figure 7.

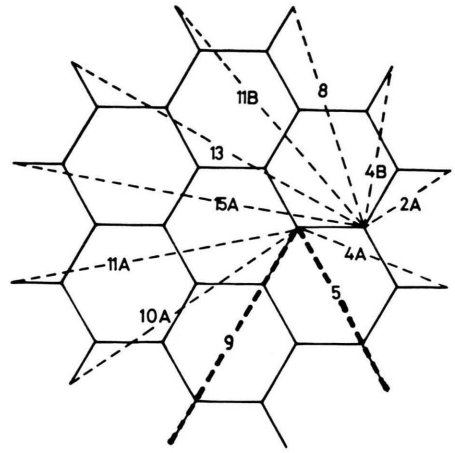

Fig. 5. Classification of the nonbonded CH distances of the types 1–*j* and 7–*j* in coronene.

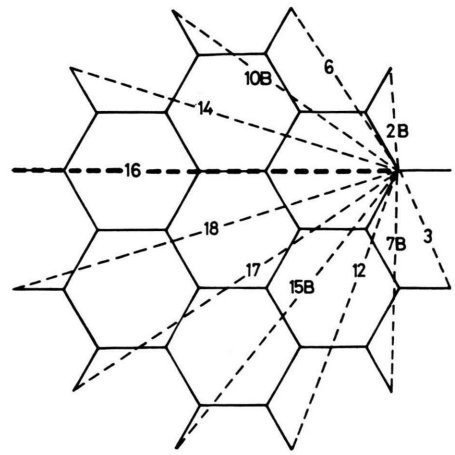

Fig. 6. Classification of the nonbonded CH distances of the 13–*j* types in coronene.

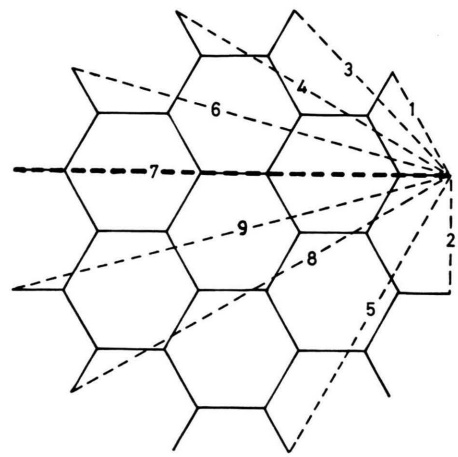

Fig. 7. Classification of the HH distances in coronene.

cf. Figures 5 and 6. All differences between the values obtained by the two methods are about 0.003 Å or less at 298 K. This is also the case for the 9 types of HH distances listed in Table 4. For the identification of these types it is referred to Figure 7.

Naphthalene and Anthracene

For the sake of completeness we have computed the mean amplitudes of vibration for naphthalene and anthracene from the five-parameter approximation of the in-plane force field. A description of the normal coordinate analysis for these molecules was included in a previous paper [1]. Tables 5 and 6

Table 5. Mean amplitudes of vibration, l, for naphthalene at 298 K from the five-parameter approximation.

Type	i–j [a]	Distance [b]	l (Å)
Bonded			
C—C	1–4	1.415	0.0481
C—C	1–5	1.364	0.0471
C—C	5–9	1.421	0.0482
C—C	9–10	1.420	0.0477
C—H	1–11	1.084	0.0774
C—H	5–15	1.084	0.0774
Nonbonded CC			
2a	1–9	2.416	0.0564
2b	1–8	2.414	0.0564
2c	5–10	2.449	0.0577
2d	5–6	2.483	0.0655
3a	1–10	2.801	0.0609
3b	5–8	2.803	0.0605
4a	5–7	3.745	0.0638
4b	1–6	3.722	0.0676
5	1–7	4.221	0.0672
6	1–2	4.831	0.0679
7	1–3	5.034	0.0677
Nonbonded CH			
2A	1–14	2.171	0.101
2B	1–15	2.122	0.100
2C	5–11	2.118	0.100
2D	9–15	2.176	0.101
3	5–16	2.724	0.132
4A	1–18	3.396	0.097
4B	5–14	3.390	0.097
4C	9–11	3.397	0.097
4D	9–17	3.434	0.098
5A	5–18	3.887	0.095
5B	9–13	3.885	0.095
6	1–16	4.081	0.133
7A	5–17	4.621	0.108
7B	5–12	4.598	0.112
8	1–17	4.867	0.123
9	5–13	5.305	0.099
10	1–12	5.795	0.107
11	1–13	6.093	0.101
HH (nonbonded)			
1α	11–14	2.499	0.159
1β	11–15	2.433	0.159
2	15–16	2.516	0.188
—	11–18	4.283	0.134
3	11–16	4.775	0.171
—	15–18	4.971	0.119
—	15–17	5.571	0.133
—	11–17	5.935	0.145
4	11–12	6.708	0.141
—	11–13	7.159	0.125

[a] Numbering of atoms in [11].
[b] Calculated interatomic distances in Å.

Table 6. Mean amplitudes of vibration, l, for anthracene at 298 K from the five-parameter approximation.

Type	i–j [a]	Distance [b]	l (Å)
Bonded			
C—C	1–4	1.419	0.0482
C—C	1–5	1.368	0.0470
C—C	5–9	1.436	0.0484
C—C	9–12	1.428	0.0480
C—C	9–13	1.399	0.0478
C—H	1–15	1.080	0.0774
C—H	5–19	1.080	0.0774
C—H	13–23	1.080	0.0774
Nonbonded CC			
2a	1–8	2.423	0.0565
2b	1–9	2.431	0.0565
2c	5–12	2.468	0.0579
2d	9–10	2.434	0.0566
2e	9–14	2.443	0.0578
2f	5–13	2.473	0.0654
3a	1–12	2.817	0.0610
3b	5–8	2.820	0.0606
3c	9–11	2.822	0.0619
3d	13–14	2.807	0.0613
4a	5–14	3.746	0.0639
4b	1–13	3.714	0.0674
4c	5–10	3.756	0.0678
5a	1–14	4.216	0.0672
5b	5–11	4.258	0.0682
6a	1–10	4.866	0.0681
6b	5–6	4.947	0.0828

Table 6 (continued)

Type	i–j[a]	Distance[b]	l (Å)
7	1–11	5.070	0.0682
8	5–7	5.694	0.0739
9	1–6	6.162	0.0807
10	1–7	6.478	0.0761
12	1–2	7.297	0.0775
13	1–3	7.434	0.0749
Nonbonded CH			
2A	1–18	2.162	0.101
2B	1–19	2.123	0.100
2C	5–15	2.125	0.100
2D	9–19	2.186	0.101
2E	9–23	2.148	0.101
3A	5–23	2.696	0.133
3B	13–19	2.719	0.132
4A	1–22	3.402	0.097
4B	5–18	3.389	0.098
4C	9–15	3.414	0.097
4D	9–22	3.448	0.098
4E	9–24	3.421	0.098
5A	5–22	3.900	0.095
5B	9–18	3.897	0.095
5C	13–24	3.887	0.095
6A	1–23	4.057	0.133
6B	9–20	4.113	0.133
7A	5–24	4.613	0.108
7B	13–21	4.623	0.108
7C	13–15	4.594	0.111
8A	1–24	4.848	0.123
8B	9–21	4.902	0.123
—	5–20	5.082	0.151
9	13–17	5.296	0.099
10	9–16	5.832	0.107
11	9–17	6.127	0.101
12	5–21	6.314	0.128
—	1–20	6.394	0.149
—	1–21	6.924	0.139
13	5–16	7.067	0.121

Table 6 (continued)

Type	i–j[a]	Distance[b]	l (Å)
15	5–17	7.544	0.106
17	1–16	8.256	0.116
18	1–17	8.466	0.108
HH (nonbonded)			
1α	15–18	2.473	0.159
1β	15–19	2.444	0.158
2	19–23	2.492	0.187
—	15–22	4.277	0.134
3	15–23	4.758	0.171
—	19–22	4.979	0.119
—	23–24	4.967	0.120
—	19–20	4.985	0.202
—	19–24	5.563	0.133
—	15–24	5.909	0.145
—	19–21	7.046	0.157
—	15–20	7.194	0.181
—	15–21	8.004	0.156
8	15–16	9.182	0.148
9	15–17	9.510	0.131

[a] Numbering of atoms in [10].
[b] Calculated interatomic distances in Å.

show the results at 298 K for naphthalene and anthracene, respectively. The nonbonded distances are grouped into main types according to the same system as used for coronene above. The adopted numbering of atoms is specified in Ref. [11] for naphthalene and Ref. [10] for anthracene.

Acknowledgement

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