Harmonic Force Fields and Bond Orders for Naphthalene, Anthracene, Biphenylene and Perylene with Mean Amplitudes for Perylene

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Z. Naturforsch. **33a**, 45–54 (1978); received October 25, 1977

Complete normal coordinate analyses were performed for naphthalene, anthracene, biphenylene and perylene, starting from a simple force field with seven adjustable force constants. A relationship between bond orders and carbon-carbon stretching force constants was deduced from: (a) bond distances as a function of bond orders, (b) a version of Badger's rule relating stretching force constants to the bond distances. The relationship was used to modify the initial seven-parameter force field, and the vibrational frequencies calculated from both the initial and modified force fields are discussed. In general the simple force field approximation produces sets of frequencies in remarkably good agreement with experimental assignments. The force field approximation failed badly when applied to benzene. No obvious explanation was found for this unexpected feature, which makes it worth while to continue the investigations. The mean amplitudes of vibration were calculated. For perylene an account of the complete set of mean amplitudes is given for the first time.

Introduction

Conjugated systems in organic chemistry have been studied by many investigators. The Hückel Molecular Orbital (HMO) theory [1] has proved to be a simple, but efficient, tool in these studies. In the present work we attempt to combine the HMO theory with vibrational normal coordinate analysis [2] for some conjugated systems. The main purpose is to correlate bond orders from the simple HMO theory with force constants of carbon-carbon stretchings. In addition we are interested in the calculated mean amplitudes of vibration [3], especially for the carbon-carbon distances.

The four molecules selected for the present investigation are: naphthalene $C_{10}H_8$, anthracene $C_{14}H_{10}$, biphenylene $C_{12}H_8$ and perylene $C_{20}H_{12}$. The structures for all of them have been investigated by gas electron diffraction, and in one case (biphenylene) observed mean amplitudes are reported. In all cases the mean amplitudes calculated from spectroscopic data would be of great help in the interpretation of the electron diffraction experiments. The four molecules have also been investigated spectroscopically, and more or less complete assignments of vibrational frequencies have been proposed. Perylene is a relatively large molecule (thirty-two atoms) for which the calculated mean amplitudes are given here for the first time.

Bond Orders and Interatomic Carbon-Carbon Distances

The bond order (P) for conjugated systems is defined here in the usual way [1] as numbers

$$0 \leqq P \leqq 1 . \tag{1}$$

The definition implies $P = 1.000$ for the "pure" double bond in ethylene. For benzene and graphite the bond orders are 0.667 and 0.525, respectively. Table 1 shows the bond orders calculated here for the four molecules considered. The results for naphthalene, anthracene and biphenylene are identical with those of Heilbronner and Bock [1], while perylene is not included in their compilations. However, also for perylene the bond orders have been calculated by many investigators; the literature is too voluminous to be cited here. Figure 1 shows that the conventional representations of aromatic structures with simple and double bonds are highly misleading when resonance structures are not taken into account.

Many attempts have been done to correlate the bond orders with interatomic CC distances in conjugated systems of organic molecules. One of the most successful approaches is due to Coulson [4] and based on molecular orbital theory. The relatively simple formula

$$r(\text{Å}) = 1.536 - \frac{0.192\,P}{P + 0.765(1 - P)} \tag{2}$$

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reproduces fairly well many experimental CC distances in organic molecules. Here 1.536 Å is the "pure" single bond distance in ethane (corresponding to $P = 0.000$), while 0.192 Å is the difference between the single and double bond distances. Table 1 also includes the calculated CC bond distances according to the Coulson formula (2). They are seen to compare well with the observed distances. The quoted values for naphthalene [5], anthracene [5], biphenylene [6] and perylene [7] are from the cited gas electron diffraction works. The experimental data are in very good agreement with x-ray results for naphthalene [8], anthracene [8] and biphenylene [9]. Most of the differences between the calculated and observed distances are between 0.01 and 0.02 Å. Somewhat more pronounced discrepancies (differences of 0.04—0.05 Å) occur for the weakest bonds in biphenylene and perylene. The high experimental value for distance *e* in biphenylene (see Table 1) is supported by the x-ray result (1.514 Å) [9]. For the distance *e* in perylene (the peri bond) the quoted value (Table 1) falls in-between another electron diffraction result (1.493 Å) [10] and an x-ray value (1.471 Å) [11] published the same year.

Structural Parameters

In the present normal coordinate analysis we adherred to the structural parameters for naphthalene and anthracene used in previous normal coordinate analyses [12, 13]. They include the CC distances from the x-ray investigation of Cruickshank and Sparks [8], which are practically identical to the electron diffraction values quoted in Table 1. The structural data used for biphenylene are from Yokozeki et al. [6], from whom the CC distances are quoted in Table 1. Also for perylene the gas electron diffraction data were adopted. Dallinga et al. [7] have given an over-determined set of structural parameters. We calculated the distance *a* (cf. Fig. 1 and Table 1) from the other CC distances and reported CCC angles and obtained 1.421 Å, which is practically the same as the electron diffraction value contained in Table 1.

A Simple Force Field for Aromatics

Several preliminary calculations were performed in order to obtain a simple approximate force field transferable to many kinds of aromatic molecules.

Table 1. Bond orders with calculated and observed interatomic CC distances.

Distance type[a]	Calculated		Observed[b]
	Bond order	Distance [Å]	Distance [Å]
Naphthalene			
a	0.603	1.408	1.412
b	0.725	1.387	1.371
c	0.555	1.417	1.422
d	0.518	1.424	1.420
Anthracene			
a	0.586	1.411	1.419
b	0.737	1.385	1.390
c	0.535	1.421	1.420
d	0.485	1.430	1.425
e	0.606	1.408	1.404
Biphenylene			
a	0.691	1.393	1.370
b	0.621	1.405	1.428
c	0.683	1.394	1.372
d	0.565	1.415	1.432
e	0.263	1.475	1.524
Perylene			
a	0.629	1.404	1.420
b	0.707	1.390	1.375
b′	0.644	1.401	1.402
c	0.552	1.417	1.412
e′	0.529	1.422	1.429
d	0.526	1.422	1.451
e	0.414	1.444	1.483

[a] See Fig. 1.
[b] From gas electron diffraction [5—7].

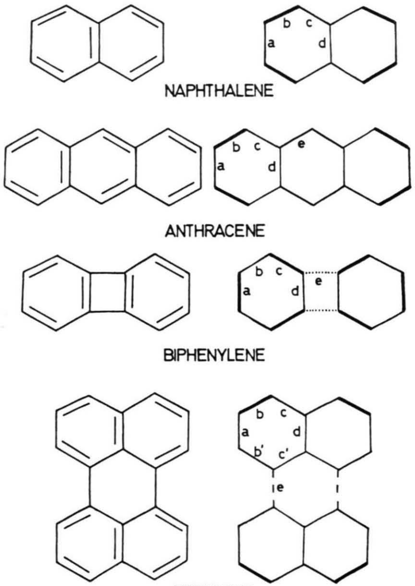

Fig. 1. Naphthalene, anthracene, biphenylene and perylene: Conventional drawings with single and double bonds, and drawings with relevance to calculated bond orders.

A harmonic force field was developed with only seven adjustable parameters. It may be expressed in terms of a diagonal *F* matrix based on valence coordinates including redundancies. Numerical values for these parameters were initially obtained to give good agreement between calculated and observed frequencies in naphthalene. Table 2 shows the seven different types of valence coordinates and the final numerical values of the respective force constants. The angle coordinates (bendings and torsions) were scaled with the appropriate bond distances so that all force constants have the same units (mdyne/Å). The CCC bendings are in typical cases analogous to the ring bendings in benzene; only the inner angles for each ring are included in the more complex aromatics. The torsions introduced are all supposed to be of the CCCC "boat" type as in benzene itself. For the CC out-of-plane bendings (which do not exist in benzene itself) one should tend to include a minimum number of such coordinates. More detailed accounts on the sets of valence coordinates chosen in the different cases are given under the descriptions of the individual molecules.

Table 2. Force constants of the approximate diagonal *F* matrix.

Type	mdyne/Å
CC stretching	4.7
CH stretching	5.0
CCC bending	0.7
CCH bending	0.3
CCCC torsion	0.1
CH out-of-plane bend	0.2
CC out-of-plane bend	0.15

Naphthalene

The approximate diagonal force field is based on the following valence coordinates: the 11 CC and 8 CH stretchings, 12 CCC and 16 CCH bendings, 12 torsions, 8 CH out-of-plane bendings, and finally 2 symmetrically equivalent CC out-of-plane bendings for the middle bond. The applied numerical values of force constants are shown in Table 2. The calculated frequencies for naphthalene with this approximate seven-parameter force field are found in the left column of Table 3. Considering that the forthy-eight calculated frequencies were obtained from only seven force constant parameters, the over-all agreement with observed frequencies is remarkably good, in spite of the fact that the seven parameters were adjusted with the aid of observed frequency data. The experimental frequencies shown

Table 3. Calculated and observed frequencies (cm^{-1}) for naphthalene.

Species	Calculated		
	Approx.	Refined for CC stretchings	Observed[a]
A_g	3036	3036	3060
	3030	3030	3031
	1564	1559	1577
	1469	1456	1460
	1366	1363	1376
	1057	1062	1145
	868	873	1025
	674	663	758
	426	423	512
B_{1g}	934	934	943
	702	702	717
	312	312	386
B_{2g}	1305	1305	980
	952	952	876
	679	679	846
	379	379	461
B_{3g}	3039	3039	3092
	3031	3031	3060
	1731	1721	1624
	1388	1399	1438
	1244	1244	1239
	1050	1050	1158
	931	945	936
	534	531	506
A_u	1150	1150	970
	776	776	841
	417	417	581
	185	185	195
B_{1u}	3040	3040	3065
	3031	3032	3058
	1489	1509	1595
	1328	1324	1389
	1191	1187	1265
	980	993	1125
	803	795	747
	284	285	359
B_{2u}	3035	3035	3090
	3030	3030	3027
	1548	1560	1509
	1485	1474	1361
	1097	1088	1209
	1042	1043	1138
	844	857	1008
	714	713	618
B_{3u}	999	999	958
	714	714	782
	429	429	476
	139	139	176

[a] References 12 and 14.

in Table 3 are taken from Krainov [14] and also quoted by Hagen and Cyvin [12]. For another complete assignment, see Hollas [15].

Anthracene

The numbers of valence coordinates included in the diagonal F matrix are given in the following: 16 CC and 10 CH stretchings, 18 CCC and 20 CCH bendings, 18 torsions, 10 CH and 4 CC out-of-plane bendings. The calculated frequencies from the seven-parameter force field are given in the left column of Table 4. Those of the in-plane vibrations may be compared with observed values in the right column taken from Neto et al. [16] and also quoted in the previous analysis of Cyvin and Cyvin [13]. Again we are struck by the generally good agreement between the calculated and observed frequencies. This agreement is even more remarkable when keeping in mind that the seven parameter values (Table 2) were adjusted to *naphthalene* frequencies and transferred directly to *anthracene*.

Table 4. Calculated and observed frequencies (cm^{-1}) for anthracene.

Species	Calculated		
	Approx.	Refined for CC stretchings	Observed[a]
A_g	3035	3035	3088
	3033	3033	—
	3030	3030	—
	1570	1559	1561
	1517	1503	1481
	1436	1424	1403
	1111	1101	1261
	1051	1056	1165
	856	866	1007
	741	739	745
	656	639	652
	310	309	—
B_{1g}	967	967	
	711	711	
	401	401	
	186	186	
B_{2g}	1333	1333	
	1094	1094	
	799	799	
	669	669	
	412	412	
	261	261	
B_{3g}	3040	3040	—
	3031	3032	3006
	1767	1757	1631
	1463	1483	1596
	1326	1322	—
	1204	1204	—
	1129	1122	1188
	963	979	—
	902	896	—
	533	533	522
	331	330	400
A_u	1231	1231	
	936	936	
	710	710	
	397	397	
	131	131	
B_{1u}	3040	3040	3100
	3033	3033	3049
	3031	3032	3022
	1667	1660	1620
	1405	1419	1448
	1287	1285	1316
	1216	1211	1274
	1015	1020	1150
	933	944	907
	658	650	651
	181	181	244
B_{2u}	3035	3035	3079
	3030	3030	3048
	1566	1571	1533
	1520	1507	1462
	1454	1427	1398
	1358	1352	1346
	1087	1081	1169
	1052	1054	1225
	863	868	999
	710	697	—
	585	582	615
B_{3u}	1008	1008	
	905	905	
	709	709	
	450	450	
	310	310	
	73	73	

[a] References 13 and 16.

Biphenylene

The biphenylene molecule contains a four-membered ring not present in the other aromatics treated here, in addition to the familiar benzene rings. Nevertheless it was attempted to adopt the valence coordinate types specified above and the corresponding force constant values (see Table 2) also to the four-membered ring. Hence a diagonal force constant matrix was constructed on the basis of the following coordinates: 14 CC and 8 CH stretchings, 16 CCC bendings including 4 in the C_4 ring, 16 CCH bendings, 16 torsions including 4 in the C_4 ring, 8 CH out-of-plane bendings, and finally the 4 symmetrically equivalent CC out-of-plane bendings where the atoms of the C_4 ring are taken as the end atoms.

In Table 5 the calculated frequencies from the approximate force field may be compared with observed values. The experimental assignments for all species except B_{3u} are from Girlando and Pecile [17]; that of B_{3u} is from Pecile and Lunelli [18]. The two works give identical assignments for the B_{1u} species; some B_{2u} frequencies from Ref. [18] which deviate from the assignment of Ref. [17] are shown in parentheses in Table 5. The calculated and observed frequenices are seen to be in a qualitative good agreement, which gives additional support to the validity of the very simple approximate force field. The approximate calculations allow a discussion of qualitative features of the assignment such as the differences of the two versions in species B_{2u}. The present results clearly indicate the superiority of the assignment of Ref. [17] *versus* the earlier one of Reference [18]. A substantial discrepancy between the calculated and observed values occurs for the third B_{3u} frequency. The calculations suggest that the experimental assignment is wrong on this point.

Perylene

The following numbers of valence coordinates were used as the basis for the diagonal force constant matrix: 24 CC and 12 CH stretchings, 30 CCC and 24 CCH bendings for the in-plane vibrations; 30 CCCC torsions and 12 CH and 4 CC out-of-plane bendings for the out-of-plane vibrations. The latter type consists of two symmetrically equivalent sets, of which only one (containing 2 coordinates) would be sufficient to include. We have included both sets because of the analogy with naphthalene, where two symmetrically equivalent out-of-plane bendings must be included for the CC middle bond.

The normal modes of vibration are distributed among the symmetry species of the D_{2h} group in the following way.

$$\Gamma = 16\,A_g + 6\,B_{1g} + 8\,B_{2g} + 15\,B_{3g} + 7\,A_u + 15\,B_{1u} + 15\,B_{2u} + 8\,B_{3u}\,.$$

In order to construct a complete set of *independent* symmetry coordinates we considered an "open" structure as shown in Figure 2. This mathematical model with four CC bonds broken up does not affect any physical properties of the calculated

Table 5. Calculated and observed frequencies (cm^{-1}) for biphenylene.

Species	Calculated		
	Approx.	Refined for CC stretchings	Observed[a]
A_g	3035	3035	3074
	3030	3030	3057
	1566	1549	1666
	1530	1533	1462
	1332	1324	1399
	1209	1134	1166
	1055	1055	1105
	852	856	989
	710	707	765
	368	356	395
B_{1g}	1194	1194	—
	928	928	—
	655	655	—
	380	380	—
B_{2g}	992	992	—
	735	735	—
	628	628	—
	175	175	—
B_{3g}	3040	3040	3057
	3032	3032	3010
	1578	1590	1602
	1376	1380	1449
	1216	1219	1288
	1116	1117	1105
	982	982	975
	641	642	600
	474	477	567
A_u	1840	1840	—
	1076	1076	—
	736	736	—
	437	437	—
	339	339	—
B_{1u}	3035	3035	3072
	3030	3030	3030
	1550	1557	1598
	1503	1512	1426
	1381	1379	1260
	1058	1061	1151
	898	905	1019
	800	809	962
	642	644	612
B_{2u}	3040	3040	3072
	3032	3032	3022 (3063)
	1780	1722	1638 (1622)
	1435	1421	1444
	1295	1288	1267
	1111	1116	1128
	973	973	1053 (751)
	729	730	751 (—)
	211	204	212
B_{3u}	1460	1460	915
	755	755	733
	649	649	366
	127	127	120

[a] Parenthesized values and those for species B_{3u} are from Ref. [18]; all others from Ref. [17].

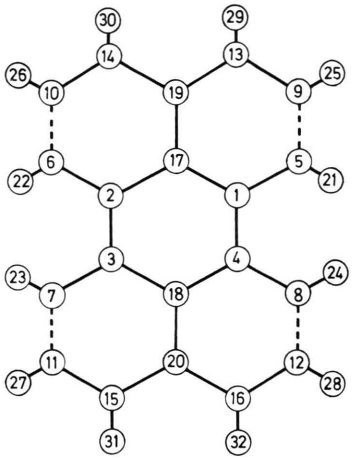

Fig. 2. The perylene molecular model.

results. The peri bond (1–4 and 2–3) stretchings fall into the species A_g and B_{2u}. For the out-of-plane modes we used the appropriate linear combinations of all CH out-of-plane bendings and the torsions of the types 9–13–19–17, 13–19–17–1 and 5–1–17–19 in all the species B_{1g}, B_{2g}, A_u and B_{3u}. In addition we used torsions of the peri bonds in B_{2g} and A_u, out-of-plane CC (17–19 type) bendings in B_{2g} and B_{3u}, and finally 4–1–17–2 type torsions in B_{3u}. For the numbering of atoms; cf. Figure 2.

Table 6 shows the calculated frequencies along with observed values. The latter ones are fluorescence spectra [19, 20] for species A_g and infrared spectra [21] for the other species listed, all values according to the interpretations by Kovner, Babkov and collaborators [22, 23]. The present calculations strongly suggest an interchange of the 850 (B_{1u}) and 535 (B_{2u}) frequencies in the experimental assignment. Otherwise a satisfactory general agreement between the calculated and observed frequencies is found when allowing for the great uncertainties in the experimental assignment. The lowest, unobserved frequencies are very well supported by the calculated frequencies reported in the cited references [22, 23].

Carbon-Carbon Distances and Force Constants (Badger's Rule)

As a first refinement of the approximate valence force field we modified the CC stretching force constants starting from a function in the style of

Table 6. Calculated and observed frequencies (cm^{-1}) for perylene.

Species	Calculated		
	Approx.	Refined for CC stretchings	Observed[a]
A_g	3041	3041	—
	3034	3034	—
	3029	3029	3031
	1793	1752	1581
	1492	1501	1574
	1438	1440	—
	1433	1406	1380
	1282	1275	1369
	1201	1198	1298
	1035	1039	1104
	951	924	—
	881	884	973
	809	801	793
	466	461	550
	422	414	358
	264	259	298
B_{1g}	1115	1115	960
	861	861	900
	719	719	752
	457	457	548
	337	337	430
	198	198	—
B_{2g}	1341	1341	—
	1042	1042	910
	927	927	889
	719	719	791
	596	596	625
	389	389	—
	215	215	249
	136	136	—
B_{3g}	3041	3041	—
	3033	3033	—
	3029	3029	—
	1760	1742	—
	1574	1578	—
	1485	1473	—
	1352	1357	—
	1212	1212	—
	1064	1059	—
	1046	1046	—
	978	978	—
	855	863	—
	727	728	—
	582	579	—
	305	304	—
A_u	1120	1120	960
	876	876	900
	724	724	752
	578	578	658
	388	388	—
	244	244	—
	77	77	—
B_{1u}	3041	3041	3085
	3034	3034	3054
	3029	3029	3052
	1681	1668	1592
	1487	1499	1513
	1462	1448	1382

Table 6 (Continued)

Species	Calculated		Observed[a]
	Approx.	Refined for CC stretchings	
	1398	1394	1367
	1297	1290	1288
	1219	1215	1217
	1035	1040	1151
	906	909	980
	823	817	963
	687	677	850
	556	556	585
	370	368	—
B_{2u}	3040	3041	3051
	3033	3033	3038
	3029	3029	3016
	1714	1697	1605
	1611	1594	—
	1476	1445	1495
	1416	1403	1333
	1314	1306	1281
	1162	1157	1211
	1065	1060	1127
	1021	1025	1085
	854	862	1042
	808	807	535
	559	555	464
	176	171	—
B_{3u}	1282	1282	—
	961	961	967
	914	914	813
	713	713	768
	525	525	544
	390	390	—
	162	162	—
	57	57	—

[a] Quoted in References [22, 23].

Badger's rule. The function originally given by Badger [24] can be stated as follows:

$$f = 1.86\,(r - d_{ij})^{-3}\,,$$
$$r = d_{ij} + (1.86/f)^{1/3}\,. \tag{3}$$

Here f should be inserted in mdyne/Å units, while r, the interatomic (equilibrium) distance, is in Å. A slightly modified version is given by Herschbach and Laurie [25]:

$$f = [(a_{ij} - d_{ij})/(r - d_{ij})]^3\,,$$
$$r = d_{ij} + (a_{ij} - d_{ij})\,f^{-1/3}\,. \tag{4}$$

For bonds formed from atoms in the first period (such as carbon-carbon) $i = j = 1$, and the following constants have been given in Table I of Reference [25].

$$a_{11} = 1.91, \quad d_{11} = 0.68 \tag{5}$$

resulting in

$$f = 1.861\,(r - 0.68)^{-3} \tag{6}$$

which is essentially identical to the original Badger formula (3).

The definition of the stretching force constant f is clear in the case of diatomic molecules. In polyatomic molecules, especially those with planar rings like the aromatics considered here, the definition of stretching force constants may be rather ambiguous. One should have in mind the lack of invariance properties for force constants [3] (in contrast to compliants). We have therefore modified the numerical factor (1.861) of the Badger's rule in order to make it suit the specific definition of the planar-ring stretching force constant applied here. The constant a_{ij} can be interpreted as a hypothetical bond distance corresponding to a unit force constant. One can then write an expression as

$$f = f'\,[(r' - d_{ij})/(r - d_{ij})]^3 \tag{7}$$

in which f' is some reference force constant and r' the corresponding interatomic distance. The carbon-carbon force constant from the approximate normal coordinate analysis of naphthalene in which all carbon-carbon force constants were adjusted to the same value (4.7 mdyne/Å; cf. Table 2) was used as a reference. The corresponding bond distance was obtained from a weighted average of the calculated carbon-carbon distances in naphthalene (1.4052 Å) according to the Coulson formula (2); cf. Table 1. With this reference Badger's rule takes the following form.

$$f = 1.793\,(r - 0.68)^{-3}\,. \tag{8}$$

The fact that the modified factor has the same order of magnitude as the original value (1.79 *versus* 1.86) indicates that our definition of the stretching force constants in aromatic rings is a reasonable one. The carbon-carbon stretching force constants calculated from Eq. (8) using the interatomic distances according to Eq. (2) — cf. Table 1 — are listed in Table 7.

Bond Orders and Carbon-Carbon Force Constants

Equations (2) and (8) allow us to establish a relationship between the bond orders (P) and the CC stretching force constants (f) in mdyne/Å:

$$f = 1.793\,[(0.235\,P + 0.765)/(0.00916\,P + 0.6548)]^3\,. \tag{9}$$

Figure 3 shows the graphical representation of this function. The points corresponding to the "pure" single and double CC bonds are included, but we have not tested the possible validity of these extrapolations.

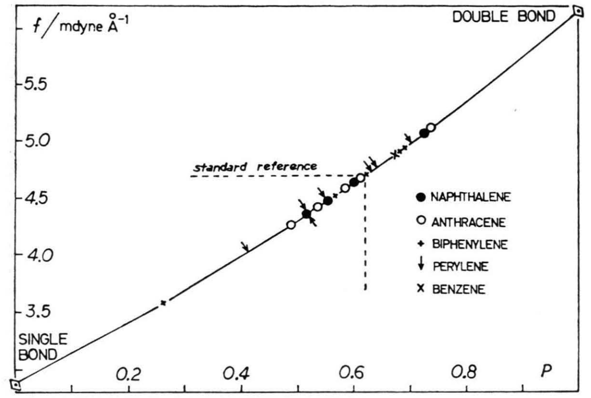

Fig. 3. Carbon-carbon stretching force constant (f) as a function of the bond order (P).

Table 7. Modified force constants for the CC stretchings.

Distance type[a]	mdyne/Å
Naphthalene	
a	4.64
b	5.07
c	4.48
d	4.36
Anthracene	
a	4.58
b	5.11
c	4.41
d	4.25
e	4.65
Biphenylene	
a	4.95
b	4.70
c	4.92
d	4.51
e	3.57
Perylene	
a	4.73
b	5.01
b′	4.78
c	4.47
c′	4.39
d	4.38
e	4.02

[a] See Fig. 1.

General Discussion of Calculated Frequencies

The computations of vibrational frequencies from the approximate force field (cf. Table 2) are discussed in the preceding sections. The over-all conclusion gives support to the usefulness of this very simple approximation for making qualitative judgements of the vibrational assignment. Especially it should be noticed (see Tables 3—6) how nicely the orders of magnitude of the lowest frequencies in each species are predicted by the calculations.

Tables 3—6 also include the calculated results with the modified CC stretching force constants (see Table 7) instead of the value 4.7 mdyne/Å. Otherwise all the different types of force constants were maintained on the values shown in Table 2. We believe that this refinement of the force field is a real improvement. However, in many of the cases the differences between calculated and observed frequencies are larger than the differences between the two calculated sets. Only in one extreme case among the molecules treated here we can claim to provide a test of our hypothesis. In biphenylene the stretchings of the weakest CC bonds (type *e*) are found in species A_g and B_{2u}. The most pronounced frequency shift on refining the CC stretching force constants occurs in A_g: 1209 to 1134 cm^{-1} (see Table 5). It seems reasonable to describe the observed frequency 1166 cm^{-1} (A_g) as the symmetrical middle bond stretching. It is seen to agree very well with our calculated value from the modified force field. In species B_{2u} the frequency shifts on refining the force field are not so pronounced. The effect of lowering the stretching force constant for the peri bonds (type *e*) in perylene is more obscure (see Table 6). The corresponding stretching coordinates again fall into the species A_g and B_{2u}. In both of these species it is hard to depict one single frequency as being affected by the force field modification. Applications to additional conjugated hydrocarbons and further experiments would be interesting and might lead to more general conclusions.

Benzene

In order to furnish another test of the approximate force field we calculated the benzene frequencies using (i) the six first force constants from Table 2 and (ii) the same values except for the CC stretching, which was refined to 4.86 mdyne/Å in accord with the bond order (cf. Fig. 3). Surprisingly both calculations failed badly on some crucial points when comparing the frequencies with the well-established experimental assignment [2b]. Table 8 displays substantial disagreements between the calculated and observed frequencies for (a) the lower A_{1g} frequency (Ra-active), (b) both B_{1g} frequencies (inactive), (c) the higher B_{2u} (inactive) and (d) the lowest E_{1u} (ir-active) frequency. From one point of view it is easy to explain the discrepancies, namely as an effect of explicit omissions of important interaction force constants, especially for CC/CC stretchings. But it is not clear why these omissions should be less important in the condensed aromatics. Further investigations in this area seem highly warranted.

In spite of the substantial discrepancies in frequencies the approximate force fields gave reasonable mean amplitudes of vibration. The values of all mean amplitudes, practically identical from (i) and (ii), differed only by few times 0.001 Å on comparison with the accurate values [3] from well-established force fields.

Table 8. Calculated and observed frequencies (cm^{-1}) for benzene.

Species	Calculated		
	Approx.	Refined for CC stretching	Observed[a]
A_{1g}	3030 780	3030 794	3073 993
A_{2g}	1283	1283	1350
B_{1g}	1238 438	1238 438	990 707
E_{1g}	741	741	846
E_{2g}	3037 1556 1044 644	3037 1571 1048 646	3056 1599 1178 606
A_{2u}	686	686	673
B_{1u}	3042 1123	3042 1123	3057 1010
B_{2u}	1501 1073	1520 1078	1309 1146
E_{1u}	3030 1396 881	3031 1402 890	3064 1482 1037
E_{2u}	981 319	981 319	967 398

[a] From Ref. [24].

Mean Amplitudes of Vibration for Perylene

Mean amplitudes of vibration [3] for all types of interatomic distances were computed for all the molecules considered here. For the sake of brevity we shall only report the results from the modified force field calculations for perylene, and only at the temperature of 298 K. Similar results for the other molecules have been given previously; the references are: naphthalene [12, 13], anthracene [13], biphenylene [6, 27]. In perylene, if we are not mistaken, there are 137 different types of interatomic distances. A systematization seems necessary.

Bonded Distances

The calculated C—H mean amplitude of 0.0774 Å is consistent with the characteristic value [3] for CH bonds. The C—C mean amplitudes are listed in Table 9 together with the bond orders in the sequence of decreasing magnitudes of P. As expected the mean amplitudes increase slightly (from 0.047 to 0.049 Å), but not exactly uniformly.

Table 9. Bond orders (P) and mean amplitudes (u, Å) at 298 K for bonded CC distances in perylene.

Type[a]	P	u
b	0.707	0.0472
b'	0.644	0.0474
a	0.629	0.0479
c	0.552	0.0482
c'	0.529	0.0475
d	0.526	0.0475
e	0.414	0.0489

[a] See Fig. 1.

Nonbonded CC Distances

The calculated values of all types of carbon-carbon nonbonded distances are surveyed in Figure 4.

Nonbonded CH and HH Distances

Most of the mean amplitudes for the carbon-hydrogen nonbonded distances fall within 0.09 and 0.11_5 Å; in fact it applies to 34 types. A middle range is 0.12—0.13 Å, which pertains to the following 13 types. (1–24), (1–28), (5–23), (5–30), (5–31), (5–32), (9–23), (9–31), (9–32), (13–27), (17–23), (17–27), (19–27). The highest C···H mean amplitudes are found for the following distances (all values in Å): (13–30) 0.138, (9–30) 0.138, (13–23) 0.141, (19–23) 0.144, (13–28) 0.146, (5–28) 0.153, (9–28) 0.159, (13–24) 0.162, (5–24) 0.163, (9–24) 0.171. For the numbering of atoms; see Figure 2.

The H···H mean amplitudes amount from 0.12 to 0.22 Å. The smallest values are found for the

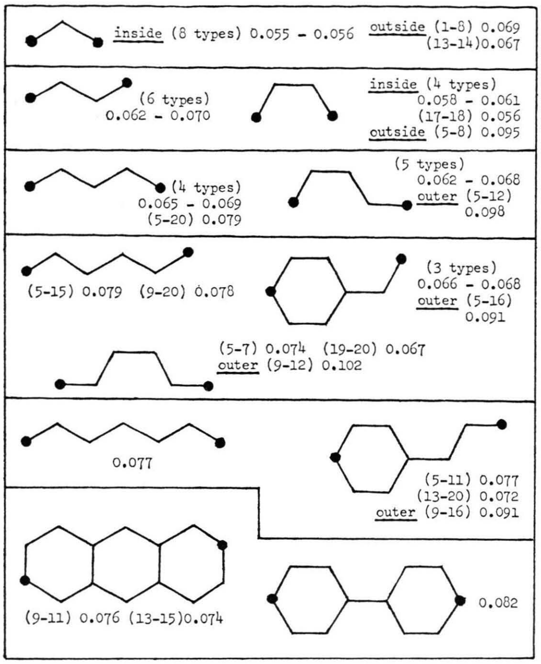

Fig. 4. Survey of mean amplitudes (Å) at 298 K for all types of nonbonded CC distances in perylene.

nearly linear arrangements like (21–22) 0.123 and (21–26) 0.124 (all values in Å). The magnitudes are within reasonable limits even for the extremely long interatomic distances up to 9.7 Å, viz. (29–32) 0.131, (25–27) 0.140, (29–31) 0.132. The highest values of mean amplitudes are found for: (25–28) 0.211, (21–28) 0.215, (21–24) 0.217.

Electron Diffraction Results

Complete sets of calculated mean amplitudes were not available at the time of the electron diffraction investigation of perylene [7, 10] and other condensed aromatics [5] (naphthalene, anthracene and coronene). In the most recent one of these works [7] several models for the structure of perylene were considered during the interpretation of the measurements. In one part of the analysis the efforts to refine the C—C mean amplitudes failed; the obtained value of 0.033 Å was judged as impossibly low. The present calculations (see Table 9) confirm this judgement. The following statement gives additional illustration of the usefulness of calculated mean amplitudes in modern electron diffraction works: The strong correlation between changes in the mean amplitudes (u) and close-lying distances renders it necessary in some cases to *choose* values for the u's [7]. In most of the instances the C—C u values were chosen as 0.046 Å.

Acknowledgement

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

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