Condensed Aromatics. Part XV. Chrysene

B. N. Cyvin[a], P. Klaeboe[b], J. C. Whitmer[c], and S. J. Cyvin[a]

Z. Naturforsch. **37a**, 251—258 (1982); received December 18, 1981

The in-plane and out-of-plane molecular vibrations of chrysene are analysed. Complete sets of independent symmetry coordinates are constructed. The in-plane vibrational frequencies are calculated both by the simple five-parameter approximation and the method of Califano with collaborators. They show a satisfactory agreement with observed values. Calculated frequencies for the out-of-plane vibrations were obtained from a five-parameter approximation. Mean amplitudes of vibration are discussed, and selected values reported. Spectra of chrysene were recorded in Raman and infrared. An almost complete assignment of observed fundamentals was achieved with the aid of the calculated frequencies.

Introduction

Conjugated systems in organic chemistry have been studied by many investigators. In our previous works [1—6], the Hückel molecular orbital theory [7] was combined with theoretical analysis in vibrational spectroscopy [8]. In the present work this theory is applied to chrysene.

Although the electronic spectra of chrysene have been investigated rather extensively [9—11], we have not found any detailed report of the vibrational spectra. In the extensive work of Garrigou-Lagrange et al. [12] twenty-one polycondensed aromatics including chrysene are treated by infrared spectroscopy. However, the investigators were mainly interested in the intensities in limited ranges of the spectrum and their relation to the degree of condensation. The Raman spectrum was recorded by Schrader et al. [13], who used a rudimentary part of the chrysene spectrum for the illustration of Raman laser-micro techniques. Mamantov et al. [14] have reported the matrix isolation Fourier transform infrared spectra of seventeen hydrocarbons. The investigation included chrysene, for which only the four strongest bands are reported.

In the present work complete spectra in Raman, infrared and far infrared were recorded. We also present for the first time an almost complete experimental assignment of the fundamentals along with a complete normal coordinate analysis. Both the in-plane and out-of-plane vibrations are analysed. The mean amplitudes of vibration [15] have also been calculated.

Experimental

Reagent grade chrysene (from BDH) was purified by sublimation in vacuo.

The infrared spectra between 4000 and 200 cm^{-1} were recorded with a Perkin-Elmer model 225 spectrometer equipped with a gold grid polarizer. Far infrared spectra were obtained with an evacuable Fourier transform spectrometer (Bruker model 114 c) using beamsplitters of Mylar (3.5, 6 and 12 μ thickness). The sample was studied as KBr and polyethylene pellets and as a nujol mull on KBr and polyethylene windows. Completely oriented polycrystalline films of chrysene on KBr windows were obtained by slow crystallization of the melt between CsI plates under a temperature gradient. Several sets of dichroism spectra were recorded.

Raman spectra of the solid sample was measured with a Cary 81 spectrometer. The 5145 Å argon line on the 6328 Å helium-neon laser line were used for excitation with 90° or 180° scattering geometry. The best spectra were obtained with the helium-neon laser in the 180° scattering mode.

The solubility of chrysene e.g. in benzene was not sufficient to permit a solution spectrum to be recorded. Attempts were made to record the Raman spectrum of melted chrysene under nitrogen atmosphere. However, strongly fluorescent impurities were formed and no satisfactory Raman spectra were obtained.

---

[a] Division of Physical Chemistry, The University of Trondheim, Norway.

[b] Department of Chemistry, University of Oslo, Norway.

[c] Department of Chemistry, Western Washington University, Wa., USA.

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

0340-4811 / 82 / 0300-0251 $ 01.30/0. — Please order a reprint rather than making your own copy.

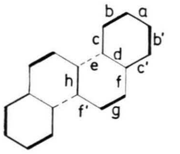


Fig. 1. The carbon skeleton of chrysene. The CC bonds are drawn in accordance with the calculated bond orders.

Molecular Structure

A planar structure with a center of inversion (symmetry C_{2h}) was assumed for the chrysene molecule; see Figure 1. The structural data were taken from the x-ray work of Burns et al. [16] with only small modifications in order to achieve an exactly planar structure. The adopted CC distances are shown as observed data in Table 1. The following distances (in Å) were adopted for the CH bonds [16]: $C_1H = 1.025$, $C_3H = 0.943$, $C_5H = 1.020$, $C_7H = 1.041$, $C_{13}H = 1.035$ and $C_{15}H = 0.972$. For the numbering of atoms, see Figure 2. All bond angles are approximately 120°, none of them deviating more than 2° from this value.

Table 1. Bond orders, calculated and observed CC bond distances, and CC force constants (*f*).

Distance type[a]	Calculated bond order	Bond distance, Å		*f* mdyne/Å
		Calculated	Observed[b]	
a	0.617	1.406	1.392	4.689
b	0.707	1.390	1.379	5.005
b′	0.712	1.389	1.361	5.023
c	0.583	1.412	1.405	4.573
c′	0.568	1.415	1.427	4.524
d	0.535	1.421	1.406	4.413
e	0.476	1.432	1.465	4.219
f	0.521	1.423	1.418	4.366
f′	0.538	1.420	1.423	4.421
g	0.754	1.382	1.365	5.175
h	0.573	1.414	1.397	4.539

[a] See Figure 1. [b] X-ray data from Ref. [16].

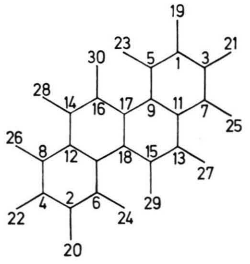


Fig. 2. Numbering of atoms in the chrysene molecular model; symmetry C_{2h}.

$B_g(\psi - \psi')$	$A_u(\psi + \psi')$
2.50	2.17
1.70	1.54
1.29	1.22
0.79	0.88
0.52	− 0.52
− 0.88	− 0.79
− 1.22	− 1.29
− 1.54	− 1.70
− 2.17	− 2.50

Table 2. Hückel energy levels in terms of $x = (\alpha - \varepsilon)/\beta$.

The Hückel Molecular Orbital (HMO) Model

The molecular orbitals according to the HMO model [7] fall into the different species of the C_{2h} group according to

$$\Gamma_\pi = 9\,B_g + 9\,A_u\,.$$

The B_g and A_u types contain respectively the antisymmetrical and symmetrical combinations of the pairs of symmetrically equivalent atomic orbitals. The π-energy levels of the model have been obtained and are given in terms of the x values ($x = -2.50$ for the ground state) in Table 2. Although not reported here, all the coefficients combining the Hückel molecular orbitals with the eighteen atomic orbitals were determined, and used to calculate the bond orders of the CC distances, P, defined in the usual way [7] as numbers

$$0 \leqq P \leqq 1\,.$$

They are given in Table 1 along with theoretical bond distances calculated from the formula of Coulson [17],

$$r(\text{Å}) = 1.536 - 0.192\,P/[P + 0.765(1 - P)]\,.$$

These theoretical distances compare reasonably well with the experimental data included in Table 1. This analysis resembles very much the corresponding studies of Cruickshank et al. [18]. Many modifications of computations along the same lines have been reported; the literature is too voluminous to be reviewed here.

Symmetry Coordinates

The normal modes of vibration are distributed among the symmetry species of the C_{2h} group according to

$$\Gamma_{\text{vib}} = 29\,A_g + 13\,B_g + 14\,A_u + 28\,B_u\,.$$

The A_g and B_u are in-plane modes while B_g and A_u are out-of-plane. The fundamentals of A_g and B_g

are Raman active while those of A_u and B_u are active in the infrared.

In-Plane Coordinates

In order to construct a complete set of *independent* symmetry coordinates we considered an "open" structure as shown in Figure 3. Although this structure has no physical reality, it is useful for identifying redundancies among the coordinates, and does not affect any of the calculated physical properties. Figure 3 shows the valence coordinates used in the construction of in-plane symmetry coordinates. The A_g and B_u species contain the symmetrical and antisymmetrical combinations, respectively, of the pair of coordinates within each symmetrically equivalent set. Thus, for instance,

$$S_1(A_g) = 2^{-1/2}(r_1 + r_1')$$

and

$$S_1(B_u) = 2^{-1/2}(r_1 - r_1').$$

Altogether we have constructed the following in-plane symmetry coordinates, specified in terms of the types of valence coordinates:

(a) $r_1, r_2, \ldots, r_6$,
(b) $d_1, d_2, \ldots, d_8$,
(c) t; the middle bond stretching, occurring only in the A_g species,
(d) $\alpha_1, \alpha_2, \ldots, \alpha_8$,
(e) $\varphi_1, \varphi_2, \ldots, \varphi_6$.

The angle bendings, say φ_{ikj}, were multiplied in the usual way by scaling factors with the dimension of length, viz. $(r_{ik}r_{jk})^{1/2}$.

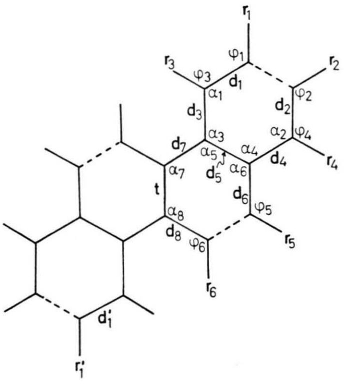


Fig. 3. In-plane valence coordinates of chrysene. The same symbols, marked and unmarked, are used to identify symmetrically equivalent pairs of coordinates; r_1' and d_1' are shown for the sake of illustration.

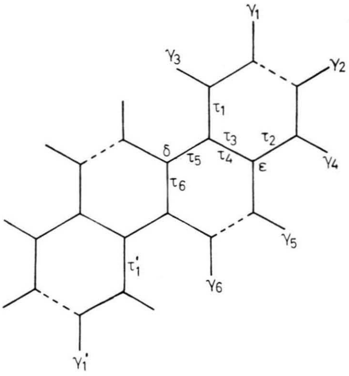


Fig. 4. Out-of-plane valence coordinates of chrysene. For the significance of marked symbols, see legend of Figure 3.

Out-of-Plane Coordinates

Again we considered the "open" structure (see Fig. 4) when choosing the CC torsional coordinates. The CH out-of-plane bendings were included for all of the H atoms even when involving the bonds omitted in the "open" structure. The B_g and A_u species contain the antisymmetrical and symmetrical combinations, respectively, of each pair of symmetrically equivalent coordinates. The complete set of out-of-plane symmetry coordinates is specified below in terms of the types of valence coordinates. The CH out-of-plane bendings are denoted γ; δ and ε are CC out-of-plane bendings, and τ are CC torsions. All the torsions are of the "boat" type within the same benzene ring.

(a) $\gamma_1, \gamma_2, \ldots, \gamma_6$,
(b) $\tau_1, \tau_2, \ldots, \tau_5$,
(c) ε,
(d) τ_6 (for the middle bond),
(e) δ; occurring only in the A_u species.

The torsions, τ_{ijmn}, were multiplied by $(r_{ij}r_{mn})^{1/2}$. The out-of-plane bendings, say γ_{ijkn}, were multiplied by $[(r_{ik}r_{jk})^{1/2}r_{kn}]^{1/2}$ when the anchor atoms are identified by i and j while n is the end atom. These are all conventional scaling factors with the dimension of length.

Normal Coordinate Analysis for the In-Plane Vibrations

Five-Parameter Approximation

The simple five-parameter approximation for the in-plane force field [2, 3, 19] was applied to chrysene.

Table 3. Calculated and observed frequencies (cm^{-1}) assigned to Species A_g.

Frequency No.	Calculated a	Calculated b	Observed Raman[c]
1	3040	3103	3061 w
2	3037	3081	3045 m
3	3035	3068	3038 w
4	3032	3027	3025 w
5	3031	3014	(3025)
6	3030	2995	2997 w, bd
7	1685	1677	1627 m
8	1639	1667	1619 m
9	1596	1651	1603 s
10	1566	1584	1576 vs
11	1550	1524	1560 w
12	1471	1489	1454 w, sh
13	1465	1447	1434 vs
14	1445	1357	1382 vs
15	1348	1329	1364 vs
16	1238	1262	1254 w
17	1178	1238	1230 w
18	1151	1157	1143 m
19	1098	1151	1136 w
20	1064	1115	1087 vw
21	999	1053	1043 w
22	902	1024	1019 vs
23	838	899	880 m
24	737	760	770 s
25	667	675	680 s
26	521	563	570 s
27	408	445	481 w
28	340	353	382 m
29	227	254	293 vs

[a] Five-parameter approximation.
[b] The Califano-Neto method.
[c] Abbrevations: bd broad; m medium; s strong; sh shoulder; v very; w weak.

The derived [2, 19] force constants for the CC bonds (considered as one parameter) are shown in Table 1. The calculated frequencies are given in Table 3 (Species A_g) and Table 4 (Species B_u).

Califano-Neto Method

The method of Califano, Neto and Schettino with collaborators [20–24] has not been applied to chrysene before. This method is substantially more laborious than the simple approximation reported above. The calculation employed thirty-six different numerical constants in a rather complicated system involving many interaction terms. The derived CC stretching force constants (in mdyne/Å) range from 5.01 to 7.14. Tables 3 and 4 include the in-plane vibrational frequencies calculated from the Califano-Neto force field.

Table 4. Calculated and observed frequencies (cm^{-1}) assigned to Species B_u.

Frequency No.	Calculated a	Calculated b	Observed Infrared[c]
57	3040	3103	3096 s
58	3037	3080	3086 s
59	3036	3068	3067 s
60	3032	3026	3054 vs
61	3031	3014	3014 s
62	3030	2995	2996 m
63	1649	1652	1625 w
64	1616	1569	1595 s
65	1605	1555	1514 w
66	1535	1478	1485 m
67	1513	1469	1434 vs
68	1489	1409	1405 w
69	1468	1359	1360 m
70	1323	1309	1344 w
71	1250	1280	1299 vs
72	1182	1264	1264 vs
73	1153	1260	1259 s
74	1131	1217	1232 m, sh
75	1054	1149	1143 m
76	1030	1086	1080 w
77	903	1047	977 m
78	857	888	869 vs
79	815	844	813 vs
80	687	693	760 vs
81	547	549	532 w
82	469	520	476 m
83	466	474	422 s
84	139	143	189 w

[a–c] See footnotes to Table 3.

The Kekulé structures have to be deduced as a part of the Califano-Neto method. In the case of chrysene there are eight of them as shown in Figure 5. These Kekulé structures are found to have the following symmetrical structure under the symmetry group C_{2h}.

$$\Gamma_{\text{Kek}} = 5\,A_g + 3\,B_u\,.$$

Discussion

The force constants for the CC stretchings from the two methods (see above) are not directly comparable, as was discussed in detail with the analysis of pyrene [3]. In order to compare the two force fields we have transferred both of them to the same basis of independent symmetry coordinates. The complete symmetry force-constant matrices are not reproduced here for the sake of brevity; only the diagonal elements are given in Table 5. In some cases (especially Nos. 16–23 and 71–78) we find very large differences obtained from the two methods. This phenomenon was not observed in

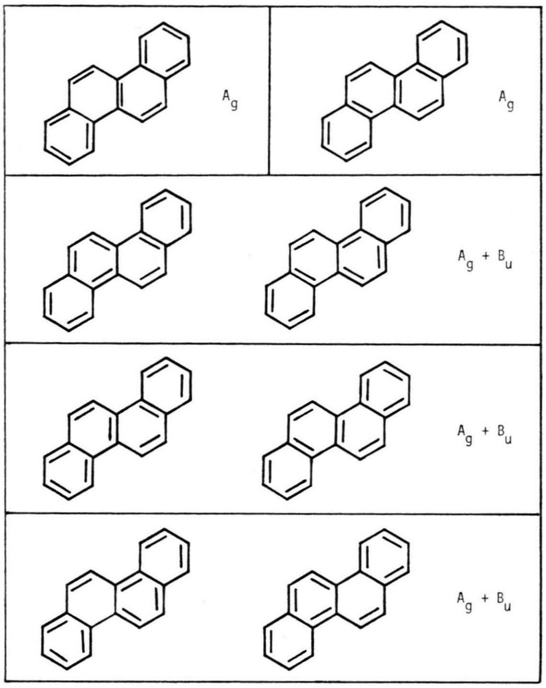


Fig. 5. The eight Kekulé structures of chrysene.

pyrene [3]; a strikingly similar pattern of the force-constant matrices from the two different methods was displayed in that case.

In spite of the large differences in the force-constant matrix elements the calculated frequencies from the two methods (see Tables 3 and 4) are comparable. They demonstrate again in a striking way the practical applicability of the five-parameter approximation [2, 3, 19] in spite of its great simplicity.

Either one of the calculated sets (a and b) of vibrational frequencies (Tables 3 and 4) were found to be useful as an aid in a tentative assignment of present experimental data. The resulting assignments are included in Tables 3 and 4. The agreement between calculated and observed frequencies is better in most of the cases for the set from the Califano-Neto method (b).

Normal Coordinate Analysis for the Out-of-Plane Vibrations

The previously derived five-parameter approximation for the out-of-plane force field of condensed aromatics [6, 19, 25—27] was applied to chrysene. The calculated frequencies are shown in Table 6. They were used as an aid in a tentative assignment of observed frequencies. The result of this assignment is included in the table.

Spectra Assignments

The infrared spectrum of an oriented polycrystalline sample of chrysene studied with polarized radiation in the region 1700—200 cm^{-1} is shown in Figure 6. A far infrared spectrum of 10 mg and 30 mg chrysene in polyethylene pellets covering the range 500—50 cm^{-1} is given in Figure 7. A complete list of the observed infrared and Raman frequencies has not been given for the sake of brevity. However, nearly all the observed Raman bands and a majority of infrared bands have been assigned as fundamentals and are listed in Tables 3, 4 and 6 together with the calculated values.

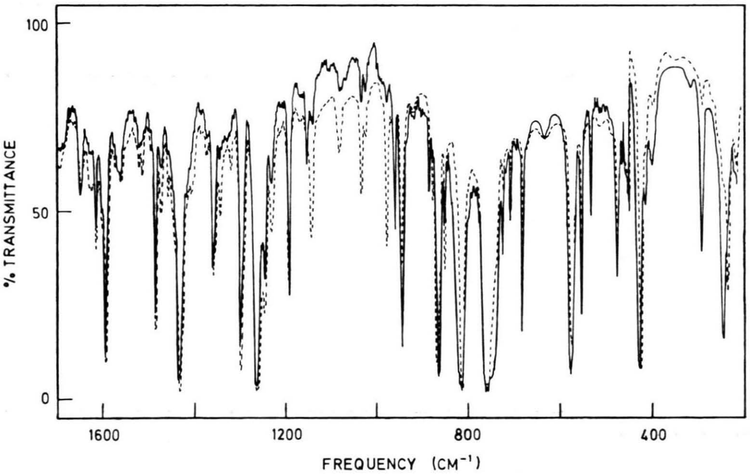


Fig. 6. Infrared spectra of an oriented polycrystalline sample of chrysene with polarized radiation.

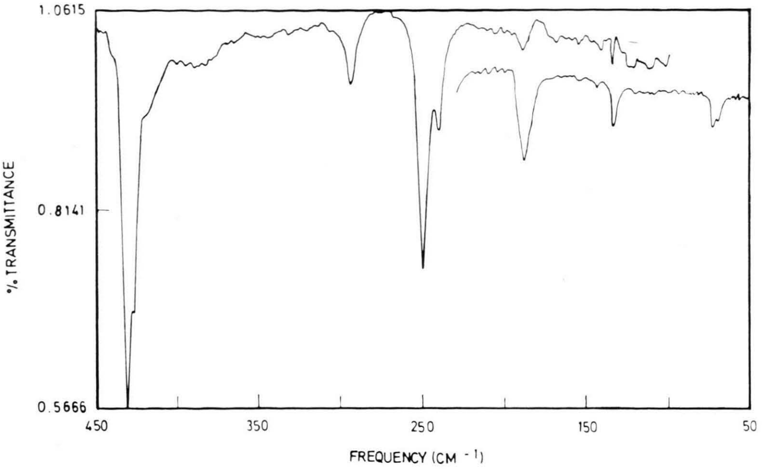


Fig. 7. Far infrared spectra of chrysene in polyethylene pellets, using beamsplitters of 3.5 μ (10 mg sample) and 12 μ thickness (30 mg).

Chrysene crystallizes in the monoclinic space group *I* 2/2 [16] (*B*2/*b* in modern nomenclature) with four molecules in the unit cell. Thus, the vibrations of the free molecule (C_{2h}) and those of the unit cell (C_{2h}) will correlate with retention of the mutual exclusion between the infrared and Raman bands. This is in complete agreement with our results since, apart from typical group frequencies like C–H stretch, there are very few coincidences between the infrared and Raman bands.

Table 5. In-plane symmetry force constants (F_{ii} in mdyne/Å) on the main diagonal of the symmetry F matrix.

i	F_{ii} (Species A_g)		i	F_{ii} (Species B_u)	
	a	b		a	b
1	5.00	5.05	57	5.00	5.05
2	5.00	5.05	58	5.00	5.05
3	5.00	5.05	59	5.00	5.05
4	5.00	5.05	60	5.00	5.05
5	5.00	5.05	61	5.00	5.05
6	5.00	5.05	62	5.00	5.05
7	7.60	8.45	63	7.60	8.45
8	7.62	8.84	64	7.62	8.84
9	7.10	8.61	65	7.10	8.61
10	7.07	8.19	66	7.07	8.19
11	11.81	15.62	67	11.81	15.32
12	7.20	7.60	68	7.20	7.60
13	9.39	12.07	69	9.39	12.32
14	7.23	7.56	70	7.23	7.37
15	10.03	11.73	71	6.76	14.18
16	6.76	14.18	72	6.59	13.86
17	6.59	13.86	73	15.70	40.69
18	15.70	40.69	74	15.37	40.56
19	15.37	40.56	75	16.81	41.54
20	16.81	41.54	76	7.08	14.44
21	7.08	14.44	77	16.78	41.25
22	16.78	41.25	78	7.13	14.90
23	7.13	14.90	79	0.70	1.00
24	0.70	1.00	80	0.71	1.00
25	0.71	1.00	81	0.71	1.00
26	0.71	1.00	82	0.72	1.00
27	0.72	1.00	83	0.69	1.00
28	0.69	1.00	84	0.69	1.00
29	0.69	1.00			

[a,b] See footnotes to Table 3.

No reliable attributions to a_g and b_g modes could be made since we lack Raman polarization values. As apparent from Tables 3 and 6, however, the intense Raman bands were all assigned as a_g fundamentals. The out-of-plane modes (b_g) on the other hand were designated as very weak (only 746 and 166 cm^{-1} were weak). A few additional weak or very weak Raman bands at 2920, 2886, 1184 and 614 cm^{-1} were considered as overtones or combination bands while those at 179, 136, 105 and 49 cm^{-1} were attributed to lattice modes.

Table 6. Calculated and observed frequencies (cm^{-1}) for the out-of-plane vibrations.

Species	No.	Calc.	Raman[a]	Species	No.	Calc.	Infrared[a]
B_g	30	999	989 vw	A_u	43	999	1150 w
	31	987	965 vw		44	990	—
	32	968	948 vw		45	966	943 s
	33	888	861 vw		46	894	884 w
	34	868	831 vw		47	863	852 m
	35	788	805 vw		48	780	820 vs
	36	763	746 w		49	715	744 vs
	37	661	712 vw		50	558	554 m
	38	509	513 vw		51	524	532 w[b]
	39	452	408 vw		52	412	415 w, sh
	40	399	390 w, sh		53	306	292 m
	41	219	197 vw		54	252	246 w, sh
	42	188	179 w		55	123	135 w
					56	70	60 vw

[a] Abbreviations: See footnote to Table 3.
[b] Used twice (also No. 81).

All our infrared dichroism spectra of different samples were similar to the one shown in Fig. 6, suggesting the same crystal orientation relation to the CsI plates for all the samples. The relative orientation of the *a*, *b* and *c*-axes have not been determined by x-ray methods. However, the infrared bands could be divided into three classes: those with a strong component in a preferred direction (x-direction), those with a strong component 90° from the former (y-direction) and a few bands with no preferred direction. All the bands above 1050 cm^{-1} were intense in the x-direction (dotted line in Fig. 6, and additional bands around 3000 cm^{-1}). Below 1000 cm^{-1}, approximately half the bands were more intense in the x-direction, the other half in the y-direction (solid line in Figure 4). The latter class of bands were assigned as the out-of-plane modes a_u of Table 5.

All the bands attributed as b_u modes (Table 4) were without exception intense in the x-direction or without any preferred dichroism. Only for the bands below 200 cm^{-1} (Fig. 7) no polarization data were available.

A number of weaker infrared bands were assigned as combination modes of which 13 belonged to A_u and 18 to B_u.

Mean Amplitudes of Vibration

In chrysene there are 225 types of bonded and nonbonded interatomic distances. The mean amplitudes of vibration, l [15], have been computed for all these distances at different temperatures using the different force fields. For the sake of brevity only an extract of this material is reported in the following. All the mean amplitude values reported here pertain to the temperature of 298 K.

Table 7 shows the results for the bonded CC distances according to the (a) five-parameter approximation and (b) Califano-Neto force field. The differences between the two results are relatively small and similar to deviations found for the other types of distances. Therefore, only the results from one force field, the five-parameter approximation, are treated in the following.

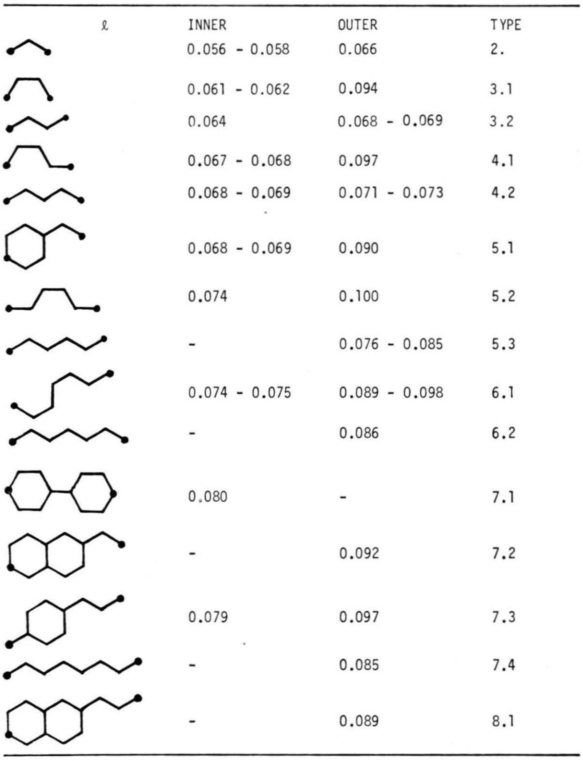
The mean amplitudes for the six types of bonded CH distances at 298 K are all 0.0774 Å.

The nonbonded CC mean amplitudes in numerous condensed aromatics according to the five-parameter approximation have been treated in detail elsewhere [5, 28]. Following the classification of distances developed previously [5, 28] we give a summary of the appropriate ranges of mean amplitudes in Figure 8. These ranges are in general comparable to those of the other condensed aromatics investigated [28]; yet a few comments should be attached to the chrysene values. Within type 5.3 there are three distances, which clearly fall into two basically different categories: (i) 1—10

Table 7. Mean amplitudes (Å units) for the bonded CC distances at 298 K.

Distance type[a]	Five-parameter approximation	Califano-Neto method
a	0.0480	0.0457
b	0.0472	0.0450
b′	0.0472	0.0446
c	0.0480	0.0467
c′	0.0481	0.0472
d	0.0476	0.0456
e	0.0487	0.0487
f	0.0486	0.0465
f′	0.0484	0.0468
g	0.0469	0.0458
h	0.0473	0.0467

[a] See Figure 1.



INNER	OUTER	TYPE
0.056 - 0.058	0.066	2.
0.061 - 0.062	0.094	3.1
0.064	0.068 - 0.069	3.2
0.067 - 0.068	0.097	4.1
0.068 - 0.069	0.071 - 0.073	4.2
0.068 - 0.069	0.090	5.1
0.074	0.100	5.2
-	0.076 - 0.085	5.3
0.074 - 0.075	0.089 - 0.098	6.1
-	0.086	6.2
0.080	-	7.1
-	0.092	7.2
0.079	0.097	7.3
-	0.085	7.4
-	0.089	8.1

Fig. 8. Summary of the nonbonded CC mean amplitudes (l in Å units) for chrysene (see also the text).

and 7—14 ($l=0.076-0.077$ Å), which are comparable with the 9—12 distance in phenanthrene [29], and (ii) the 5—6 distance specific for chrysene ($l=0.085$ Å). Also within type 6.1 the distances 1—12 and 3—14 ($l=0.089$ Å) are comparable with 11—14 in phenanthrene [29], while the 5—8 distance ($l=0.098$ Å) is special for chrysene. Two distances (not included in Fig. 8) are entirely specific for chrysene among the cases studied previously [5, 28, 29], viz. 3—8 ($l=0.085$ Å) and 3—4 ($l=0.083$ Å).

A full report on the 102 types of nonbonded CH mean amplitudes is too voluminous to be given here. Most of these mean amplitudes may be classified according to the types also found in pyrene [3] and were also found to have similar numerical values. Others were found with similar values as the corresponding ones in phenanthrene [29]. The remaining ones, which so far are specific for chrysene, are listed in Table 8.

The 36 types of mean amplitudes for the HH distances range from 0.119 Å (for 23—25) to 0.209 Å (for 23—26) at 298 K. The numerical values are again found to be similar to those in pyrene [3] and phenanthrene [29].

Table 8. Selected mean amplitudes (l in Å units) for nonbonded CH distances at 298 K.

$i-j$ [a]	R [b]	l
5 — 24	6.475	0.147
5 — 26	6.990	0.155
3 — 24	7.441	0.162
1 — 24	7.503	0.153
5 — 20	8.324	0.120
1 — 26	8.366	0.156
5 — 22	8.443	0.121
7 — 26	8.611	0.128
7 — 20	8.626	0.145
3 — 26	9.086	0.141
7 — 22	9.465	0.112
1 — 20	9.500	0.123
3 — 20	9.627	0.134
1 — 22	9.767	0.119
3 — 22	10.219	0.111

[a] For numbering of atoms, see Figure 2.

[b] Calculated interatomic distance (in Å) from the applied structural parameters.

Acknowledgements

The authors are greatful to Anne Horn, Oslo, who recorded some of the spectra. Financial support to BNC from The Norwegian Research Council for Science and the Humanities is gratefully acknowledged.

[1] J. C. Whitmer, S. J. Cyvin, and B. N. Cyvin, Z. Naturforsch. **33a**, 45 (1978).

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

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

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

[5] S. J. Cyvin, J. Brunvoll, B. N. Cyvin, and V. S. Mastryukov, Z. Naturforsch. **34a**, 1512 (1979).

[6] B. N. Cyvin, G. Neerland, J. Brunvoll, and S. J. Cyvin, Z. Naturforsch. **35a**, 731 (1980).

[7] E. Heilbronner and H. Bock, Das HMO-Modell und seine Anwendung, Verlag Chemie, Weinheim 1970; English translation: The HMO Model and its Application, Wiley-Interscience, London 1976.

[8] E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, Molecular Vibrations, McGraw-Hill, New York 1955.

[9] S. E. Wiberley and R. D. Gonzales, Appl. Spectry. **15**, 174 (1961).

[10] R. L. Hummel and K. Ruedenberg, J. Phys. Chem. **66**, 2334 (1962).

[11] R. S. Becker, I. S. Singh, and E. A. Jackson, J. Chem. Phys. **38**, 2144 (1963).

[12] C. Garrigou-Lagrange, M. F. Ducout, A. Marchand, and M. L. Josien, Bull. Soc. Chim. France **1964**, 63.

[13] B. Schrader and W. Meier, Z. Naturforsch. **21a**, 480 (1966).

[14] G. Mamantov, E. L. Wehry, R. R. Kemmerer, and E. R. Hinton, Anal. Chem. **49**, 86 (1977).

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

[16] D. M. Burns and J. C. Iball, Proc. Roy. Soc. London **A 257**, 491 (1960).

[17] C. Coulson, Proc. Roy. Soc. London **A 169**, 413 (1939).

[18] D. W. J. Cruickshank and R. A. Sparks, Proc. Roy. Soc. London **A 258**, 270 (1960).

[19] S. J. Cyvin, J. Brunvoll, G. Neerland, and B. N. Cyvin, Spectroscopy Letters **13**, 527 (1980).

[20] S. Califano, Ricerca Sci. **A 3**, 461 (1963).

[21] N. Neto, M. Scrocco, and S. Califano, Spectrochim. Acta **22**, 1981 (1966).

[22] V. Schettino, N. Neto, and S. Califano, J. Chem. Phys. **44**, 2724 (1966).

[23] N. Neto and C. di Lauro, Spectrochim. Acta **26A**, 1175 (1970).

[24] V. Schettino, J. Mol. Spectry. **34**, 78 (1970).

[25] S. J. Cyvin, B. N. Cyvin, J. Brunvoll, and G. Neerland, Acta Chem. Scand. **A 34**, 677 (1980).

[26] G. Neerland, B. N. Cyvin, J. Brunvoll, S. J. Cyvin, and P. Klaeboe, Z. Naturforsch. **35a**, 1390 (1980).

[27] S. J. Cyvin, G. Neerland, B. N. Cyvin, and J. Brunvoll, J. Mol. Spectry. **83**, 471 (1980).

[28] S. J. Cyvin and B. N. Cyvin, Spectroscopy Letters **14**, 287 (1981).

[29] S. J. Cyvin, G. Neerland, J. Brunvoll, and B. N. Cyvin, Spectroscopy Letters **14**, 37 (1981).