Condensed Aromatics. Part XX. Coronene

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The molecular vibrations of coronene, both in-plane and out-of-plane, are studied. The simple Hückel molecular orbitals are derived and the CC bond orders calculated. The bond orders are used to fix the CC stretching force constants. A complete set of independent symmetry coordinates is constructed. The in-plane vibrational frequencies are calculated by (a) the five-parameter approximation and (b) the Califano-Neto method; those of the out-of-plane vibrations only by the five-parameter approximation. The calculated frequencies are compared with observed values and previous calculations. A few new Raman bands are reported along with the presumably most complete set of infrared frequencies reported so far. A complete assignment of the infrared-active (E_{1u} and A_{2u}) fundamentals is proposed. A majority of the Raman-active frequencies (A_{1g}, E_{1g} and E_{2g}) are also assigned, using Raman, fluorescence and phosphorescence spectra.

Introduction

Conjugated systems in organic chemistry have attracted many investigators. In a previous work [1] the Hückel Molecular Orbital theory [2] was combined with molecular vibration analysis [3]. Calculated bond orders were used to refine stretching force constants for the carbon-carbon bonds. Promising results were obtained for naphthalene, anthracene, biphenylene and perylene. The bending force constants used in this originally proposed simple force field [1] were later revised [4], and a new force field approximation was proposed for the in-plane vibrations. This new "aromatic force field" is still very simple and referred to as the five-parameter approximation. It has been tested by a detailed normal coordinate analysis for pyrene [5], comparing it to the more elaborate aromatic force field due to Califano and Neto with collaborators [6–11]. The five-parameter approximation of the in-plane force fields has been successfully applied to a number of condensed aromatics [12–16]. All these papers [12–16] contain mean amplitudes of vibration [17] calculated from the force field.

Another simple force field approximation, also defined by five parameters, was developed for the out-of-plane vibrations of aromatic molecules, using benzene and naphthalene as the first test molecules [18, 19]. Detailed normal coordinate analyses of anthracene and pyrene [20] using this five-parameter force field were also successful. The force field was used in computations of the perpendicular amplitude coefficients [17] for benzene [14], naphthalene [14] and anthracene [21]. Applications to additional condensed aromatics are also reported [22, 23].

Some recent works contain complete normal coordinate analyses for both in-plane and out-of-plane vibrations of phenanthrene [24], fluoranthene [25], chrysene [26], triphenylene [27], azulene [28] and perylene [29].

In the present work a complete normal coordinate analysis of coronene is reported for the first time. A preliminary communication of some results from this work is included in a previous paper [4].

Although some vibrational spectra of coronene have been reported, no attempts have been made to produce a complete assignment of the vibrational frequencies. A record of the infrared spectrum has recently been reported [30], however no listing of frequencies nor assignments were included. Babkov et al. [31] have investigated the vibrational struc-

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ture of luminescence spectra, assigned the planar vibrations active in Raman ($A_g + E_{2g}$), recorded some supplementary frequencies observed in infrared and Raman, and also included references to numerous works on fluorescence and phosphorescence spectra of coronene. Some of these data are also quoted [31]. In a subsequent short communication by Babkov and Kovner [32] the out-of-plane vibrations of coronene are treated. In the present work a new, extensive list of observed infrared frequencies is given along with a few Raman lines.

In a paper by Zhirnov [33] an argument is presented to show why a part of the spectrum of coronene should be similar to that of benzene.

Experimental

The infrared spectra of coronene were recorded with a grating spectrometer (Perkin-Elmer model 225) in the 4000 – 200 cm^{-1} range and with a fast scan Fourier transform spectrometer (Bruker model 114 C) in the range 4000 – 50 cm^{-1}. The latter instrument is evacuable and was equipped with beam splitters of germanium on KBr and of Mylar with thickness 3.5, 6, 12 and 24 µm. Detectors of TGS were used and a globar and a mercury source employed above and below 150 cm^{-1}, respectively.

We attempted to record a Raman spectrum of polycrystalline coronene with a Cary 81 spectrometer using 90° and 180° excitation. A helium neon laser (6328 Å) and an argon ion laser (5145 Å) were used for excitation. However, the strong fluorescence from coronene covered the Raman spectrum and only a few very intense Raman bands were observed.

The infrared spectra of coronene were recorded with pellets in KBr, polyethylene and adamantane. Moreover, coronene was rapidly melted between CsI plates and cooled under a temperature gradient. Several melting experiments were carried out and a partly oriented polycrystalline film was obtained. The dichroism of the prominent infrared bands were observed in the region 3100 – 200 cm^{-1}.

The Hückel Molecular Orbital (HMO) Model

It may be of interest to give some details of the application of the HMO theory to coronene since this example is not treated in the extensive compilation by Heilbronner et al. [2]. The Hückel molecular orbitals fall into the different symmetry species of the D_{6h} group according to

$$\Gamma_\pi = B_{1g} + 3\,B_{2g} + 4\,E_{1g} + A_{1u} + 3\,A_{2u} + 4\,E_{2u}\,.$$

A complete set of symmetry-adapted linear combinations of the atomic ($2\,p_z$) orbitals is shown in Table 1. The numbering of atoms is shown in Figure 1. The π-energy levels have been obtained and are given in terms of the $x = (\alpha - \varepsilon)/\beta$ values ($x = -2.675$ for the ground state) in Figure 2. Also the

Table 1. Symmetry-adapted combinations (φ') of the $2p_z$ atomic orbitals in the HMO theory. Normalization factors are omitted.

Species	φ'
B_{1g}	$\varphi_{24} - \varphi_{13} - \varphi_{14} + \varphi_{15} + \varphi_{16} - \varphi_{17} - \varphi_{18} + \varphi_{19} + \varphi_{20} - \varphi_{21} - \varphi_{22} + \varphi_{23}$
B_{2g}	$\varphi_1 - \varphi_2 + \varphi_3 - \varphi_4 + \varphi_5 - \varphi_6$ $\varphi_7 - \varphi_8 + \varphi_9 - \varphi_{10} + \varphi_{11} - \varphi_{12}$ $\varphi_{24} + \varphi_{13} - \varphi_{14} - \varphi_{15} + \varphi_{16} + \varphi_{17} - \varphi_{18} - \varphi_{19} + \varphi_{20} - \varphi_{21} - \varphi_{22} - \varphi_{23}$
E_{1g} (a)	$\varphi_2 + \varphi_3 - \varphi_5 - \varphi_6$ $\varphi_8 + \varphi_9 - \varphi_{11} - \varphi_{12}$ $\varphi_{14} + \varphi_{15} + \varphi_{16} + \varphi_{17} - \varphi_{20} - \varphi_{21} - \varphi_{22} - \varphi_{23}$ $2\varphi_{24} - 2\varphi_{13} + \varphi_{14} - \varphi_{15} - \varphi_{16} + \varphi_{17} - 2\varphi_{18} + 2\varphi_{19} - \varphi_{20} + \varphi_{21} + \varphi_{22} - \varphi_{23}$
E_{1g} (b)	$2\varphi_1 + \varphi_2 - \varphi_3 - 2\varphi_4 - \varphi_5 + \varphi_6$ $2\varphi_7 + \varphi_8 - \varphi_9 - 2\varphi_{10} - \varphi_{11} + \varphi_{12}$ $2\varphi_{24} + 2\varphi_{13} + \varphi_{14} + \varphi_{15} - \varphi_{16} - \varphi_{17} - 2\varphi_{18} - 2\varphi_{19} - \varphi_{20} - \varphi_{21} + \varphi_{22} + \varphi_{23}$ $-\varphi_{14} + \varphi_{15} - \varphi_{16} + \varphi_{17} + \varphi_{20} - \varphi_{21} + \varphi_{22} - \varphi_{23}$
A_{1u}	$\varphi_{24} - \varphi_{13} + \varphi_{14} - \varphi_{15} + \varphi_{16} - \varphi_{17} + \varphi_{18} - \varphi_{19} + \varphi_{20} - \varphi_{21} + \varphi_{22} - \varphi_{23}$
A_{2u}	$\varphi_1 + \varphi_2 + \varphi_3 + \varphi_4 + \varphi_5 + \varphi_6$ $\varphi_7 + \varphi_8 + \varphi_9 + \varphi_{10} + \varphi_{11} + \varphi_{12}$ $\varphi_{24} + \varphi_{13} + \varphi_{14} + \varphi_{15} + \varphi_{16} + \varphi_{17} + \varphi_{18} + \varphi_{19} + \varphi_{20} + \varphi_{21} + \varphi_{22} + \varphi_{23}$
E_{2u} (a)	$-\varphi_2 + \varphi_3 - \varphi_5 + \varphi_6$ $-\varphi_8 + \varphi_9 - \varphi_{11} + \varphi_{12}$ $-\varphi_{14} - \varphi_{15} + \varphi_{16} + \varphi_{17} - \varphi_{20} - \varphi_{21} + \varphi_{22} + \varphi_{23}$ $-2\varphi_{24} + 2\varphi_{13} + \varphi_{14} - \varphi_{15} + \varphi_{16} - \varphi_{17} - 2\varphi_{18} + 2\varphi_{19} + \varphi_{20} - \varphi_{21} + \varphi_{22} - \varphi_{23}$
E_{2u} (b)	$-2\varphi_1 + \varphi_2 + \varphi_3 - 2\varphi_4 + \varphi_5 + \varphi_6$ $-2\varphi_7 + \varphi_8 + \varphi_9 - 2\varphi_{10} + \varphi_{11} + \varphi_{12}$ $-2\varphi_{24} - 2\varphi_{13} + \varphi_{14} + \varphi_{15} + \varphi_{16} + \varphi_{17} - 2\varphi_{18} - 2\varphi_{19} + \varphi_{20} + \varphi_{21} + \varphi_{22} + \varphi_{23}$ $\varphi_{14} - \varphi_{15} - \varphi_{16} + \varphi_{17} + \varphi_{20} - \varphi_{21} - \varphi_{22} + \varphi_{23}$

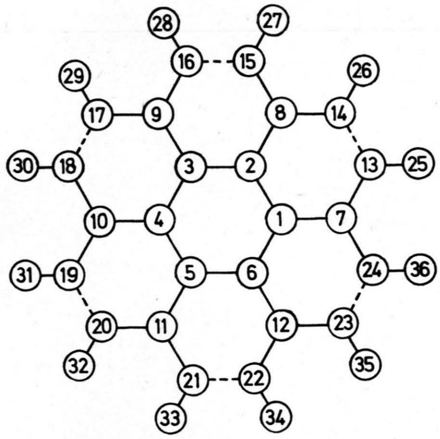

Fig. 1. Numbering of atoms in the coronene molecular model; symmetry D_{6h}.

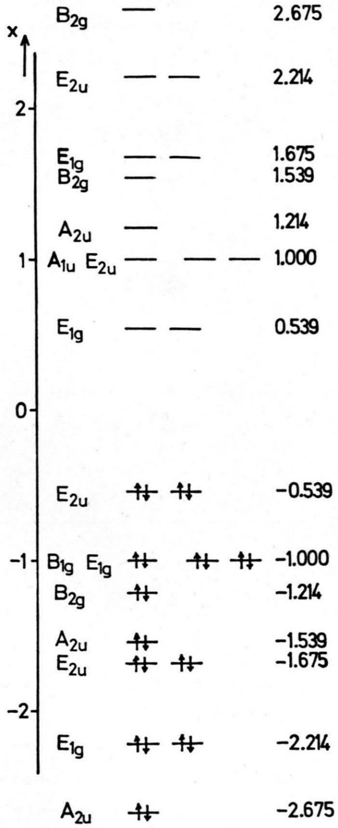

Fig. 2. Hückel molecular orbital energy levels for coronene The electron configuration in the π-ground state is indicated

coefficients combining the Hückel molecular orbitals with the twenty-four atomic orbitals were all determined, although the whole set is too voluminous to be reproduced here. As an example we give the

Table 2. Bond orders with calculated and observed CC bond distances.

CC bond	Bond order	Bond distance, Å				
		Calc.	x-ray [35]	x-ray [36]	E.D. [37]	E. D. [38]
a	0.522	1.423	1.430	1.425	1.438	1.420
b	0.538	1.420	1.430	1.433	1.381	1.418
c	0.538	1.420	1.415	1.415	1.444	1.424
d	0.745	1.384	1.385	1.346	1.362	1.378

ground state HMO:

$$\psi_1 = 0.306 \sum_{i=1}^{6} \varphi_i + 0.207 \sum_{i=7}^{12} \varphi_i + 0.123 \sum_{i=13}^{24} \varphi_i .$$

The set of coefficients belonging to the lower half of the energy levels pertain to the ground state of coronene, as indicated by the electronic configuration in Figure 2. These coefficients were used to calculate the bond orders of the CC distances, *P*, defined in the usual way [2] as numbers between 0 and 1; cf. Table 2.

Molecular Structure

The planar hexagonal structure of D_{6h} symmetry has been established for the coronene molecule. This results in four sets of symmetrically equivalent carbon-carbon bonds. The values for these distances (defined by Fig. 3) are in Table 2, which contains altogether the following data:

(i) bond orders, *P* (see above),

(ii) bond distances calculated from the formula of Coulson [34];

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

(iii) experimental carbon-carbon bond distances from x-ray [35, 36] and electron diffraction data [37, 38].

The agreement between the calculated and observed distances is satisfactory when taking into ac-

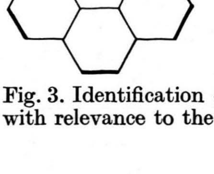

Fig. 3. Identification of the CC bonds in coronene, drawn with relevance to the calculated bond orders.

count the error limits of the experimental data [35 – 38]. In the present analysis we used the most recent gas electron diffraction data [38] for the carbon skeleton of coronene. They are a preliminary refinement produced in 1979. The carbon-hydrogen distance was assumed to be 1.08 Å.

Kekulé Structures

In the Califano-Neto method [6 – 11] for developing in-plane force constants of aromatic molecules the Kekulé structures are needed. In the case of coronene there are twenty Kekulé structures; cf. Figures 4 – 6. They form the basis of a representation of the symmetry group D_{6h}. The distribution over the different irreducible representations was found to be

$$\Gamma_{\text{Kek}} = 6\ A_{1g} + 3\ E_{2g} + 4\ B_{2u} + 2\ E_{1u}\,.$$

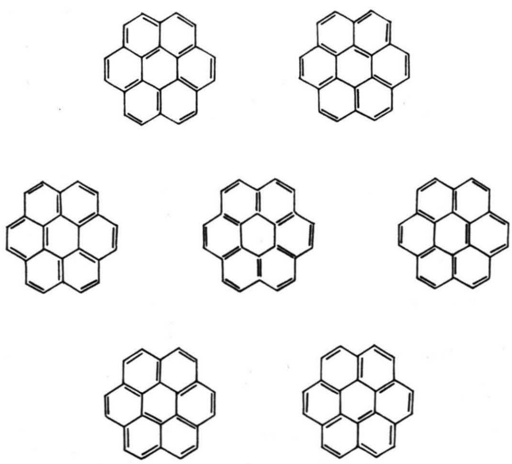

Fig. 4. Kekulé structures of coronene — Part I: The totally symmetrical (A_{1g}) structure in the centre. The outer six structures are symmetrically equivalent and belong to $A_{1g} + E_{2g} + B_{2u} + E_{1u}$.

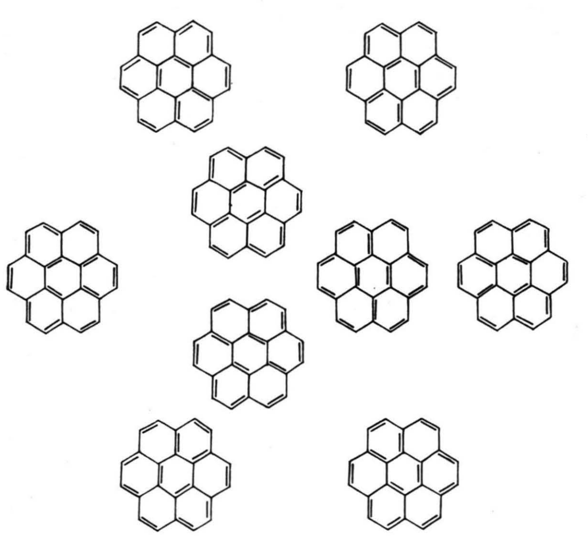

Fig. 5. Kekulé structures of coronene — Part II: Three symmetrically equivalent structures belonging to $A_{1g} + E_{2g}$ (inner part) and six ones (outer part) of $A_{1g} + E_{2g} + B_{2u} + E_{1u}$.

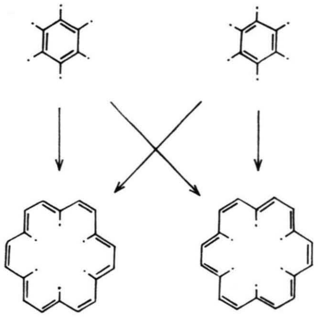

Fig. 6. Kekulé structures of coronene — Part III: Deducing of four structures, which form two symmetrically equivalent pairs, each belonging to $A_{1g} + B_{2u}$.

The general problem of deducing the number and symmetries of Kekulé structures has not been solved. A special solution has been reported [39] for a class of molecules to which chrysene [26] belongs.

Symmetry Coordinates

The normal modes of vibration are distributed among the symmetry species of the D_{6h} group according to

$$\begin{aligned}\Gamma_{\text{vib}} = {} & 6\ A_{1g} + 5\ A_{2g} + 2\ B_{1g} + 4\ B_{2g} + 5\ E_{1g} + 12\ E_{2g} \\ & + 2\ A_{1u} + 3\ A_{2u} + 6\ B_{1u} + 6\ B_{2u} + 11\ E_{1u} \\ & + 6\ E_{2u}\,.\end{aligned}$$

In-Plane Coordinates

In a multi-cyclic planar structure of high symmetry numerous redundancies occur among the symmetrically equivalent sets of internal valence coordinates. In order to construct a complete and independent (no redundancies) set of symmetry coordinates we found it helpful to consider an "open" structure around the central benzene ring as shown in Figure 1. The stretching and bending types used in the construction of symmetry coordinates are indicated on Figure 7. This "open" structure (Fig. 1) has of course no physical reality; on the contrary the omitted bonds are those with the

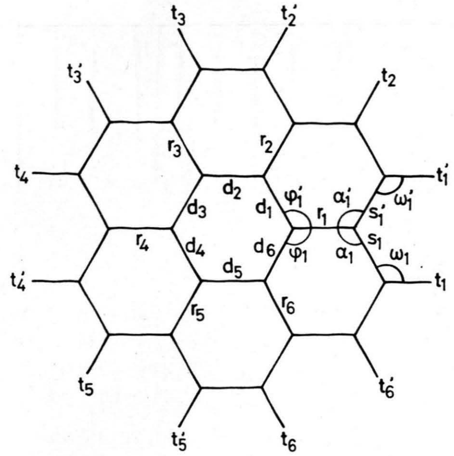

Fig. 7. In-plane valence coordinates used in the construction of the symmetry coordinates. The coordinates s_i, s_i', φ_i, φ_i', α_i, α_i', ω_i and ω_i' ($i = 1, \ldots, 6$) are exemplified only for $i = 1$.

highest bond orders (cf. Table 2). The structure is simply a useful aid for identifying redundancies.

The *d* and *r* stretchings (see Fig. 7) constitute symmetrically equivalent sets of 6 coordinates each. For all the other coordinate types there are 12 coordinates in each symmetrically equivalent set. We have considered the symmetrical and antisymmetrical combinations as $\varphi_i + \varphi_i'$ and $\varphi_i - \varphi_i'$, respectively ($i = 1, 2, \ldots, 6$) and likewise for the *s*, *t*, *α* and *ω* types. Normalization and angle scaling factors are omitted in the present description for the sake of brevity.

Table 3. Types of valence coordinates in the set of in-plane symmetry coordinates.

A_{1g}	A_{2g}	E_{2g}	
d	$s - s'$	d	$\varphi + \varphi'$
r	$t - t'$	r	$\varphi - \varphi'$
$s + s'$	$\varphi - \varphi'$	$s + s'$	$\alpha + \alpha'$
$t + t'$	$\alpha - \alpha'$	$s - s'$	$\alpha - \alpha'$
$\alpha + \alpha'$	$\omega - \omega'$	$t + t'$	$\omega + \omega'$
$\omega + \omega'$		$t - t'$	$\omega - \omega'$
B_{1u}	B_{2u}	E_{2u}	
r	$s - s'$	d	$\varphi - \varphi'$
$s + s'$	$t - t'$	r	$\alpha + \alpha'$
$t + t'$	$\varphi - \varphi'$	$s + s'$	$\alpha - \alpha'$
$\varphi + \varphi'$	$\alpha - \alpha'$	$s - s'$	$\omega + \omega'$
$\alpha + \alpha'$	$\omega - \omega'$	$t + t'$	$\omega - \omega'$
$\omega + \omega'$		$t - t'$	

A set of symmetry coordinates for coronene is most easily constructed by analogy with benzene which has the same symmetry. We have employed the pattern of standardized symmetry coordinates given by Cyvin et al. [40]. Table 3 shows the types of valence coordinates in a complete set of independent symmetry coordinates for the in-plane vibrations. The actual normalized linear combinations were found with reference to the benzene model [40] by noticing the following features: (a) the *d* and *r* types in coronene transform like the respective coordinates (*d*, *r*) in benzene, (b) all the symmetrical combinations transform like *r*, and (c) all the antisymmetrical combinations transform like the rocking coordinates, *β*, in the benzene model.

Out-of-Plane Coordinates

Four types of out-of-plane valence coordinates were employed to construct a set of independent out-of-plane symmetry coordinates.

(i) Six torsions δ are defined for the central benzene ring as

$$\delta_1(6-1-2-3), \ldots, \delta_6(5-6-1-2).$$

(ii) Six out-of-plane bendings γ are defined as

$$\gamma_1(2-6-1-7), \ldots, \gamma_6(1-5-6-12).$$

These two types transform like the respective coordinates (δ, γ) in benzene [40], from which the symmetry-adapted combinations have been transferred.

(iii) The twelve torsions of the type ε are defined as

$$\varepsilon_1(6-1-7-13),\ \varepsilon_2(2-1-7-24), \ldots,$$
$$\varepsilon_{11}(5-6-12-23),\ \varepsilon_{12}(1-6-12-22).$$

Table 4 shows the appropriate symmetry-adapted combinations under the different symmetry species. (iv) The CH out-of-plane bendings, say η, are defined as

$$\eta_1(7-23-24-36),\ \eta_2(14-7-13-25), \ldots,$$
$$\eta_{11}(12-21-22-34),\ \eta_{12}(24-12-23-35).$$

These coordinates transform like the set of twelve 2 p_z orbitals φ_{24}, φ_{13}, φ_{14}, ..., φ_{23}. Hence the appropriate symmetry coordinates could be constructed by analogy with the scheme for the symmetry-adapted combinations of atomic orbitals given in Table 1.

Table 4. Out-of-plane symmetry coordinates (S) formed as linear combinations of the ε type torsions. Normalization and scaling factors are omitted.

Species	S
B_{2g}	$\varepsilon_1 - \varepsilon_2 - \varepsilon_3 + \varepsilon_4 + \varepsilon_5 - \varepsilon_6 - \varepsilon_7 + \varepsilon_8 + \varepsilon_9 - \varepsilon_{10} - \varepsilon_{11} + \varepsilon_{12}$
E_{1g} (a)	$\varepsilon_3 - \varepsilon_4 + \varepsilon_5 - \varepsilon_6 - \varepsilon_9 + \varepsilon_{10} - \varepsilon_{11} + \varepsilon_{12}$ $2\varepsilon_1 + 2\varepsilon_2 + \varepsilon_3 + \varepsilon_4 - \varepsilon_5 - \varepsilon_6 - 2\varepsilon_7 - 2\varepsilon_8 - \varepsilon_9 - \varepsilon_{10} + \varepsilon_{11} + \varepsilon_{12}$
E_{1g} (b)	$2\varepsilon_1 - 2\varepsilon_2 + \varepsilon_3 - \varepsilon_4 - \varepsilon_5 + \varepsilon_6 - 2\varepsilon_7 + 2\varepsilon_8 - \varepsilon_9 + \varepsilon_{10} + \varepsilon_{11} - \varepsilon_{12}$ $- \varepsilon_3 - \varepsilon_4 - \varepsilon_5 - \varepsilon_6 + \varepsilon_9 + \varepsilon_{10} + \varepsilon_{11} + \varepsilon_{12}$
A_{1u}	$\varepsilon_1 + \varepsilon_2 + \varepsilon_3 + \varepsilon_4 + \varepsilon_5 + \varepsilon_6 + \varepsilon_7 + \varepsilon_8 + \varepsilon_9 + \varepsilon_{10} + \varepsilon_{11} + \varepsilon_{12}$
A_{2u}	$\varepsilon_1 - \varepsilon_2 + \varepsilon_3 - \varepsilon_4 + \varepsilon_5 - \varepsilon_6 + \varepsilon_7 - \varepsilon_8 + \varepsilon_9 - \varepsilon_{10} + \varepsilon_{11} - \varepsilon_{12}$
E_{2u} (a)	$- \varepsilon_3 + \varepsilon_4 + \varepsilon_5 - \varepsilon_6 - \varepsilon_9 + \varepsilon_{10} + \varepsilon_{11} - \varepsilon_{12}$ $- 2\varepsilon_1 - 2\varepsilon_2 + \varepsilon_3 + \varepsilon_4 + \varepsilon_5 + \varepsilon_6 - 2\varepsilon_7 - 2\varepsilon_8 + \varepsilon_9 + \varepsilon_{10} + \varepsilon_{11} + \varepsilon_{12}$
E_{2u} (b)	$- 2\varepsilon_1 + 2\varepsilon_2 + \varepsilon_3 - \varepsilon_4 + \varepsilon_5 - \varepsilon_6 - 2\varepsilon_7 + 2\varepsilon_8 + \varepsilon_9 - \varepsilon_{10} + \varepsilon_{11} - \varepsilon_{12}$ $\varepsilon_3 + \varepsilon_4 - \varepsilon_5 - \varepsilon_6 + \varepsilon_9 + \varepsilon_{10} - \varepsilon_{11} - \varepsilon_{12}$

The mutual orientation of all the coordinates described above is correct. Table 5 gives a survey of the different types under the appropriate symmetry species for the out-of-plane vibrations.

Spectral Interpretation

The solubility of coronene e. g. in benzene was too low to permit a solution spectrum to be recorded, and we were therefore limited to observe spectra of crystalline samples. Infrared spectra of KBr pellets are shown in Figure 8. The spectra of a partly oriented polycrystalline sample of coronene studied with polarized radiation in two perpendicular directions are shown in Figures 9 and 10. A very strong fluorescence from coronene covered the Raman spectrum regardless of which of the available laser lines were used for excitation. With the 6328 Å He-Ne laser line four Raman bands at 1357, 1340, 480 and 366 cm^{-1} could be detected, apparently being the most intense Raman bands of coronene.

Table 5. Types of valence coordinates in the set of out-of-plane symmetry coordinates.

B_{1g}	B_{2g}	E_{1g}	A_{1u}	A_{2u}	E_{2u}
ε	δ	γ	ε	γ	δ
η	γ	ε	η	ε	γ
	ε	ε		η	ε
	η	η			ε
		η			η
					η

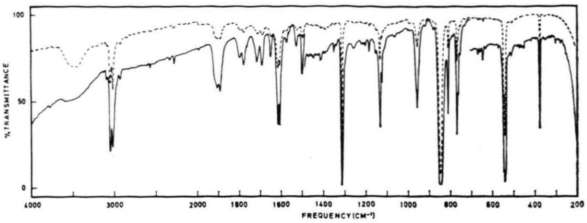

Fig. 8. Infrared spectra of coronene as KBr pellets.

The wave numbers of the infrared bands observed as pellets and as oriented film are listed in Table 6. Arbitrarily, the bands are listed as D (diminished), E (enhanced) and I (invariant) according to the intensity variations in the two polarization directions. As apparent many more bands are observed than the number of the infrared active fundamentals ($11\,E_{1u} + 3\,A_{2u}$) expected. However, nearly all the intense bands (vs, s or m) and a few additional weak lines are interpreted as fundamentals. The

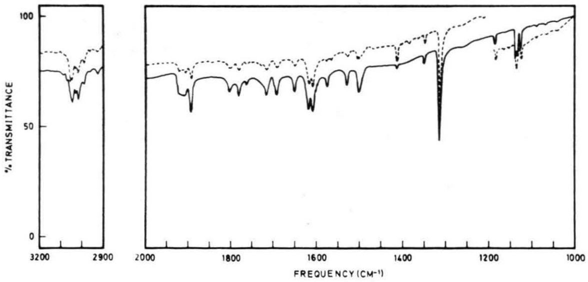

Fig. 9. Infrared spectra of an oriented polycrystalline sample of coronene with polarized radiation. Range 3200 — 1000 cm^{-1}.

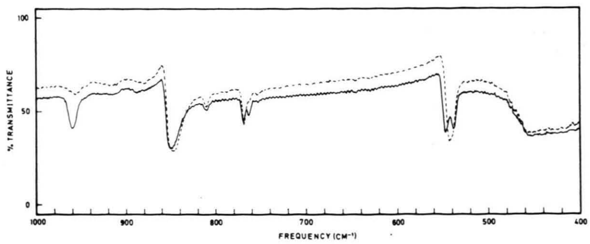

Fig. 10. Infrared spectra of an oriented polycrystalline sample of coronene with polarized radiation. Range: 1000 — 400 cm^{-1}.

remaining bands are either infrared active combinations bands or they are possibly infrared forbidden bands activated in the crystalline state. With the large number of such alternatives no attempts were made to interpret these bands.

Table 6. Infrared spectral data of coronene; frequencies in cm^{-1}.

Pellet[a]	Oriented film[b]	Earlier work[c]	Interpretation
3053 m[d]	3054 m D[e]		E_{1u}
3045 m	3045 m D		E_{1u}
3017 m	3017 m D		
2990 w, sh	2987 w I		
	2922 vw D		
1918 vw	1922 vw D		
1904 w	1906 w D		
1891 w	1893 w D		
1797 vw	1781 w D		
1777 w			
1713 w	1717 w D		
1685 w	1690 w D		
1647 w	1650 w D		
1614 m	1619 m D	1626	E_{1u}
1606 m	1606 m D		
1598 w, sh	1598 w E		
1575 vw	1574 vw D		
	1563 w E		
1525 w	1538 w D	1531	E_{1u}
1494 w	1500 w D	1476	E_{1u}
1411 vw	1413 vw E		
1340 vw	1348 vw E		
1314 s	1313 s D	1322	E_{1u}
1310 w, sh	1308 w I		
1297 vw, sh			
1184 vw	1183 vw D		
1133 m	1137 w D		E_{1u}
1125 w	1123 w D		E_{1u}
962 w	962 w D		
958 m	957 w D		
849 vs	849 vs E	854	A_{2u}
845 vs	845 vs E		
811 m	811 m E	817	E_{1u}
769 m	768 m E		
764 w	763 w D	773	E_{1u}
753 vw			
646 vw	666 vw E		
549 m	547 m D		
544 s	541 s E	569	A_{2u}
510 vw	511 vw		
379 m	378 m D		E_{1u}
151 m			A_{2u}
135 vw			

[a] KBr pellet (4000 — 300 cm^{-1}), polyethylene pellet (600 — 50 cm^{-1}).
[b] Sample melted between KBr windows and crystallized under a temperature gradient.
[c] Unassigned values from Ref. [31].
[d] Abbreviations used: s, strong; m, medium; w, weak; v, very; sh, shoulder.
[e] Band intensities: D, diminished; E, enhanced and I, invariant for the two polarization directions.

It is apparent from Table 6 that nearly all the bands assigned as E_{1u} and A_{2u} modes are denoted as D and E, respectively. The only exception is the band at 811 cm^{-1} (E) assigned as E_{1u} and possibly the doublet at 549 and 544 cm^{-1} both of which may belong to an A_{2u} mode. Since the crystallographic axes of coronene were not known in our samples, we cannot claim that the dichroic ratios were conclusive to distinguish between the E_{1u} and the A_{2u} modes.

In-Plane Normal Coordinate Analysis

Five-Parameter Approximation

The simple five-parameter approximation [4, 5] was applied to the in-plane vibrations of coronene. The force field is defined in terms of a diagonal force-constant matrix on the basis of valence coordinates including redundancies. The CC stretching force constants are given in Table 7; they are considered as one parameter. The other four parameters are (in mdyne/Å): $f(\mathrm{CH}) = 5.0$ for the CH stretchings; $f(\mathrm{CC_CC}) = 0.4$, pertaining to four types of CCC bendings, where the central C atom is bonded to another C; $f(\mathrm{CC_HC}) = 0.7$ for the symmetrically equivalent CCC bendings where the central C atom is bonded to an H atom; and finally $f(\mathrm{CCH})$ for the CCH bendings.

The calculated frequencies from this approximation are shown in Table 8.

Califano-Neto Method

The force field described by Neto et al. [8] was also adapted to the in-plane vibrations of coronene. Force constant values for CC and CH stretchings were introduced similarly to the approximation described above. The main bending force constants were defined in terms of five numerical parameters. In addition, 342 interaction terms were introduced.

The resulting calculated frequencies are included in Table 8.

Table 7. CC stretching force constants (f in mdyne/Å).

CC bond	f
a	4.37
b	4.42
c	4.42
d	5.14

Table 8. Calculated and observed frequencies (cm^{-1}) for the in-plane vibrations of coronene.

Species	Calculated			Observed	
	a	b	c	d	e
A_{1g}	3060	3034	3054	—	—
	1590	1537	1600	1603/1584	—
	1360	1421	1339	1370/1350	1357/1340
	1250	1083	1161	1250	—
	1084	947	1028	1084	—
	486	380	451	485	480
A_{2g}	—	3035	3048	—	—
	—	1553	1478	—	—
	—	1194	1183	—	—
	—	974	896	—	—
	—	655	602	—	—
E_{2g}	3074	3037	3053	—	—
	3051	3032	3049	—	—
	1633	1669	1555	1631	—
	1441	1561	1439	1434	—
	1405	1457	1393	(1405)	—
	1295	1375	1372	1292	—
	1230	1153	1200	1232	—
	995	1015	1131	993	—
	904	910	991	905	—
	847	653	667	846	—
	596	462	498	(595)	480 ?
	367	306	328	365	366
B_{1u}	—	3038	3050	—	—
	—	1555	1528	—	—
	—	1420	1364	—	—
	—	1170	1114	—	—
	—	562	639	—	—
	—	525	527	—	—
B_{2u}	—	3032	3053	—	—
	—	1648	1499	—	—
	—	1441	1412	—	—
	—	1165	1220	—	—
	—	987	1129	—	—
	—	449	464	—	—
E_{1u}	—	3036	3054	—	3053
	—	3033	3049	—	3045
	—	1615	1587	—	1610
	—	1487	1460	—	1525
	—	1463	1356	—	1494
	—	1286	1275	—	1314
	—	1102	1156	—	1133
	—	1058	1120	—	1125
	—	834	798	—	811
	—	676	787	—	769
	—	325	362	—	379

[a] Ref. [31].
[b] Present; five-parameter approximation.
[c] Present; Califano-Neto method.
[d] Ref. [31]; parenthesized values from fluorescence and/or phosphorescence, the others from Raman. For infrared frequencies from this reference, see Table 6.
[e] Present; Raman for A_{1g} and E_{2g}, infrared for E_{1u}.

Discussion

Table 8 shows fairly good agreement between the two sets of frequencies calculated in the present work by (a) the five-parameter approximation and (b) the Califano-Neto method. It is noteworthy how the very simple approximation (a) is able to reproduce the qualitative features of the spectra when compared to the results (b) from the considerably more sophisticated method of Califano with collaborators. Quantitative agreement for several frequencies is also achieved. These two sets of calculated frequencies are not directly comparable with the previous calculations [31] reported for the species A_{1g} and E_{2g}; see column a of Table 8. In that analysis [31] observed frequencies for coronene (column d of Table 8) were used in a refinement of the force field; transferred force constants from benzene and naphthalene were used only as a first approximation.

When comparing the calculated frequencies with observed values (columns d and e of Table 8) it should be remembered that most of the fundamentals are spectroscopically inactive; cf. Table 9. Only the A_{1g} and E_{2g} fundamentals are Raman active, while those of E_{1u} are infrared active.

In species A_{1g} and E_{2g} we do not claim that our calculations refute the experimental assignments of Babkov et al. [31] in spite of some significant quantitative differences. The experimental data do not appear to be sufficiently extensive to warrant a more detailed discussion.

In species E_{1u} we have tentatively established a complete assignment (Table 8) of fundamentals from the infrared spectrum (Table 6). The present experimental data seem to be the most extensive infrared frequencies reported so far for coronene. For

Table 9. Symmetrical structure (Γ_{vib}) and activity of the normal frequencies.

Γ_{vib}	in-plane (in-) or out-of-plane (out-)	Activity
6 A_{1g}	in-	Raman
+ 5 A_{2g}	in-	inactive
+ 2 B_{1g}	out-	inactive
+ 4 B_{2g}	out-	inactive
+ 5 E_{1g}	out-	Raman
+12 E_{2g}	in-	Raman
+ 2 A_{1u}	out-	inactive
+ 3 A_{2u}	out-	infrared
+ 6 B_{1u}	in-	inactive
+ 6 B_{2u}	in-	inactive
+11 E_{1u}	in-	infrared
+ 6 E_{2u}	out-	inactive

the sake of comparison Table 6 includes the eight infrared bands from Babkov et al. [31, which were reported without assignments.

Out-of-Plane Normal Coordinate Analysis

Five-Parameter Approximation

The out-of-plane vibrations were analysed here by the five-parameter approximation [19] only. The force-constant matrix in terms of valence coordinates is not entirely diagonal, as some interaction terms between adjacent torsions pertaining to the same CC bond are included. The parameters (in mdyne/Å) are: $f(C_2CC) = 0.15$ for two types of CCCC out-of-plane bendings; $f(C_2CH) = 0.20$ for the symmetrically equivalent CCCH out-of-plane bendings; $f(CCCC) = f(CCCH) = f(HCCH) = 0.05$ for the main terms of all "boat" torsions, two for every CC bond; 0.02 for the twelve CCCC/CCCC torsional interactions; and finally 0.07 for the twelve CCCC/CCCH and six CCCC/HCCH interactions.

The calculated out-of-plane frequencies are shown in Table 10.

Discussion

Concerning the activities of the out-of-plane fundamentals those of E_{1g} are Raman active and A_{2u} infrared active (cf. Table 9). In Table 10 the calculated frequencies from the five-parameter approximation (see above) are compared with the results from a previous analysis [32].

In species A_{2u} our calculation strongly suggests the assignment of infrared fundamentals as shown in column d of Table 10. It conflicts with the assignment proposed by Babkov and Kovner [32] (column c), who apparently did not have access to infrared measurements on coronene as low as 150 cm^{-1}. The 771 s band assigned as an A_{2u} fundamental by Babkov et al. [32] corresponds evidently to our 769 m (Table 6), which we have assigned as an E_{1u} fundamental (cf. Table 8).

In the analysis of Babkov et al. [32] the force constants were adjusted to reproduce the A_{2u} frequencies of their assignment. It is therefore not surprising to find the relatively large disagreements with our calculated frequencies. They are especially pronounced (apart from A_{2u}) in the species B_{2g} and E_{2u}.

Table 10. Calculated and observed frequencies (cm^{-1}) for the out-of-plane vibrations of coronene.

Species	Calculated		Observed	
	a	b	c	d
B_{1g}	792	800	(822)	—
	187	189	(115)	—
B_{2g}	960	1046	—	—
	888	978	—	—
	481	588	—	—
	198	251	225	—
E_{1g}	946	966	930	—
	793	843	—	—
	685	660	(680)	—
	436	469	435	—
	193	281	(225)	—
A_{1u}	943	958	—	—
	536	523	—	—
A_{2u}	850	857	850 vs	847
	771	551	771 s	544
	544	131	544 vs	151
E_{2u}	951	978	—	—
	844	872	—	—
	794	814	—	—
	443	518	—	—
	271	326	—	—
	97	102	—	—

[a] Ref. [32]. [b] Present.

[c] Refs. [31] and [32]; parenthesized values from fluorescence and/or phosphorescence, the others from Raman, except in Species A_{2u}. The latter set are infrared frequencies from [32].

[d] Present; infrared frequencies (Table 9).

In species E_{1g} our calculated frequencies are very compatible with the experimental assignment of Raman, fluorescence and phosphorescence frequencies [31, 32].

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