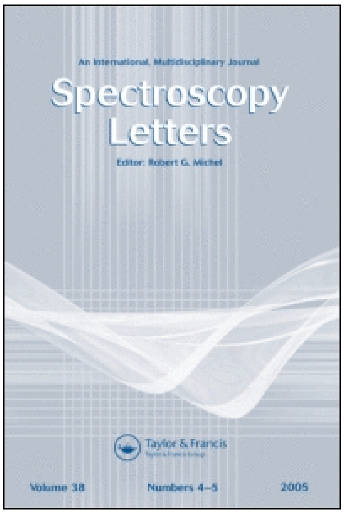

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CONDENSED AROMATICS. PART X
OUT-OF-PLANE VIBRATIONS OF POLYCENES

Keywords: Molecular vibrations, Symmetry coordinates, Polycenes

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ABSTRACT

A method for constructing a complete set of independent symmetry coordinates for the out-of-plane vibrations of any polycene is given. Calculated vibrational frequencies from the previously developed five-parameter approximation are reported for naphthalene, anthracene, naphthacene and pentacene.

In the course of our systematic studies of the molecular vibrations of aromatic hydrocarbons we have developed a five-parameter approximation[1] for the out-of-plane vibrations. Among polycenes naphthalene,[1,2] anthracene,[3] naphthacene[4] and pentacene[4] have been treated according to this method.

In the present work the problem of symmetry coordinates for the out-of-plane vibrations of polycenes is treated in general. The calculated vibrational frequencies for the four polycenes mentioned above are reported.

THE T-MATRIX METHOD

The force-field approximation developed for the condensed aromatics implies an f matrix based on valence coordinates including redundancies. This matrix is converted to a symmetrized F matrix by the T matrix method:[5]

$$F = T' \, f \, T \, , \qquad T = b \, m^{-1} \, B' \, G^{-1}$$

Here the F matrix must be non-singular. It is based on the symmetry coordinates, S. Consequently we need a set of *independent* symmetry coordinates. Such coordinates - without redundancies - are also needed in the computations of vibrational amplitudes (l and K values)[2,6] where the A matrix is an essential part of the analysis;

$$x = A\, S\ , \qquad A = m^{-1}\, B'\, G^{-1}$$

In the following we give a prescription for the construction of an independent, complete set of symmetry coordinates for the out-of-plane vibrations of any polycene. A "method of fragments" is employed in such a way that the symmetry coordinates are obtained successively through the series with 2, 4, 6, ... rings on one hand and 3, 5, 7, ... on the other.

SYMMETRY COORDINATES

The polycenes with an even number of rings may be built up from an ethylene-like fragment shown at the top of Fig. 1. Furthermore is it possible to construct mathematical models without any ring structure. This kind of "opening" of structures has been employed previously, e.g. for perylene[7] and pyrene,[8] and makes it easier to avoid redundancies. The different fragments are built up successively by adding four symmetrically equivalent atoms every time; cf. Fig. 1, where the fragments up to 18 particles are drawn.

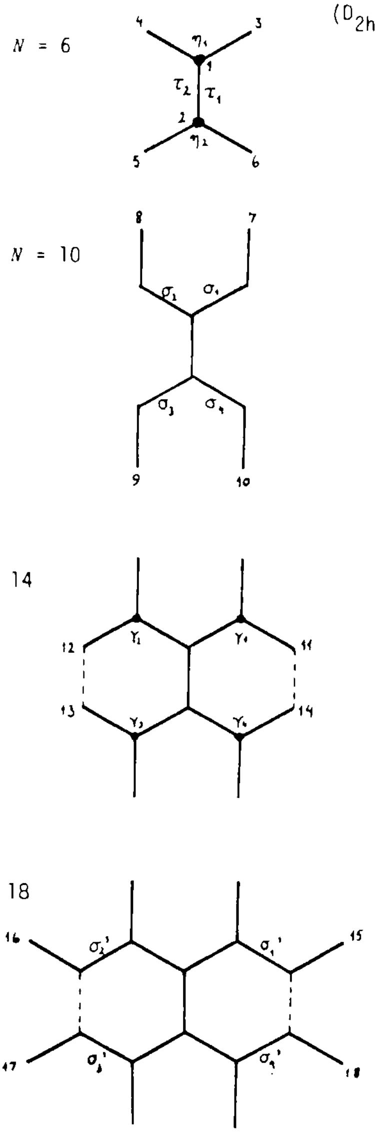
The symmetrical structures for the out-of-plane vibrational modes of the four fragments in question are given in Fig. 1. For every new fragment N (number of particles) increases by 4, and the symmetrical structure is obtained by adding $B_{1g} + B_{2g} + A_u + B_{3u}$ every time. In general it is found

$$\Gamma_{\text{out-of-plane}}(N) = \frac{N-6}{4}\, B_{1g} + \frac{N-2}{4}(B_{2g} + A_u + B_{3u})$$

Thus we arrive at the symmetrical structure for the different polycenes; N = 18, 30, 42, ... corresponds to naphthalene, naphthacene, hexacene ..., etc. In general:

$$\Gamma_{\text{out-of-plane}}(Q) = \frac{3Q}{2}\, B_{1g} + \left(\frac{3Q}{2} + 1\right)(B_{2g} + A_u + B_{3u})$$

for the out-of-plane vibrational modes of a Q-cene (polycene with Q rings), where Q = 2, 4, 6, ... Notice that



(D_{2h}) $\Gamma_{\text{out-of-plane}}$

$B_{2g} + A_u + B_{3u}$

$B_{1g} + 2B_{2g} + 2A_u + 2B_{3u}$

$2B_{1g} + 3B_{2g} + 3A_u + 3B_{3u}$

$3B_{1g} + 4B_{2g} + 4A_u + 4B_{3u}$

Fig. 1. The fragments building up polycenes with an even number of rings. Out-of-plane valence coordinates (torsions and out-of-plane bendings) are indicated.

$$N = 6Q + 6$$

We have chosen the following independent symmetry coordinates of the first fragment (cf. Fig. 1).

$$\begin{aligned} S_1(B_{2g}) &\propto \tau_1 - \tau_2 \\ S_1(A_u) &\propto \tau_1 + \tau_2 \\ S_1(B_{3u}) &\propto \eta_1 + \eta_2 \end{aligned}$$

In the building-up process of symmetry coordinates four coordinates should be added for every new group of four symmetrically equivalent atoms. In the next two fragments (see Fig. 1) we may add successively four torsions (σ) and four out-of-plane bendings (γ). The symmetry-adapted combinations of these two types are different. Therefore a full account is given in the following.

$$\begin{aligned} S_1(B_{1g}) &\propto \sigma_1 + \sigma_2 - \sigma_3 - \sigma_4, & S_2(B_{1g}) &\propto \gamma_1 - \gamma_2 - \gamma_3 + \gamma_4 \\ S_2(B_{2g}) &\propto \sigma_1 - \sigma_2 - \sigma_3 + \sigma_4, & S_3(B_{2g}) &\propto \gamma_1 + \gamma_2 - \gamma_3 - \gamma_4 \\ S_2(A_u) &\propto \sigma_1 + \sigma_2 + \sigma_3 + \sigma_4, & S_3(A_u) &\propto \gamma_1 - \gamma_2 + \gamma_3 - \gamma_4 \\ S_2(B_{3u}) &\propto \sigma_1 - \sigma_2 + \sigma_3 - \sigma_4, & S_3(B_{3u}) &\propto \gamma_1 + \gamma_2 + \gamma_3 + \gamma_4 \end{aligned}$$

Normalization and scaling factors are omitted. When the above coordinates are supplemented by the appropriate four combinations of σ' torsions (cf. Fig. 1) we attain at the full set for naphthalene. Hence it contains the following types of symmetry coordinates.

$3B_{1g}$: σ, γ, σ'

$4B_{2g}$: $\tau, \sigma, \gamma, \sigma'$

$4A_u$: $\tau, \sigma, \gamma, \sigma'$

$4B_{3u}$: $\eta, \sigma, \gamma, \sigma'$

This process can be continued to obtain a symmetry coordinate set for any even-number ring polycene.

The polycenes with an odd number of rings may be built up from the eight-atomic fragment shown in Fig. 2. Apart from this single ring at the middle of the molecule we can avoid ring structures in the "opened" molecular model. Starting from this fragment we again add

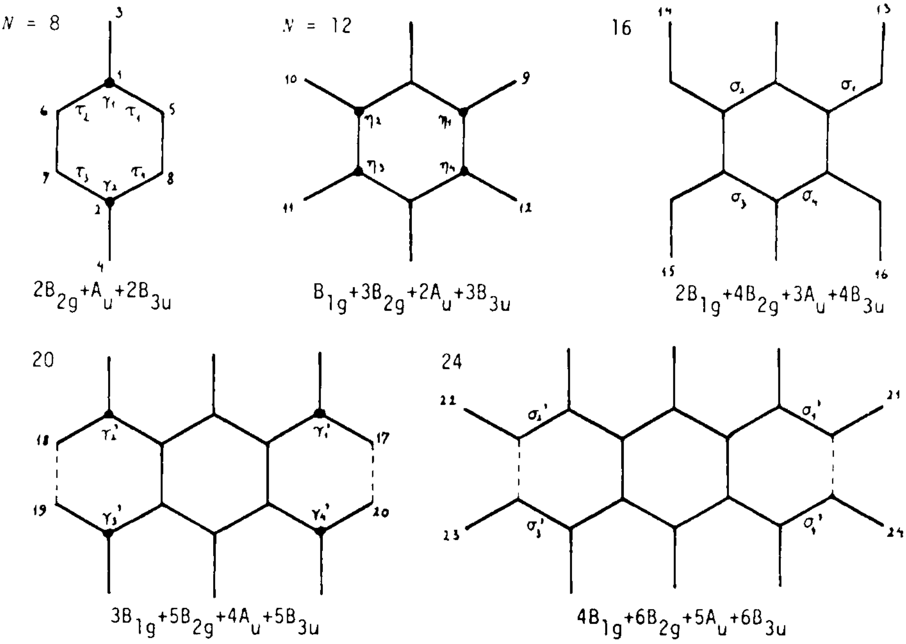


Fig. 2. The fragments building up polycenes with an odd number of rings.

four symmetrically equivalent atoms every time (cf. Fig. 2). The symmetrical structure of the out-of-plane modes again gets an addition of $B_{1g} + B_{2g} + A_u + B_{3u}$ from one fragment to the next. In this case (N = 8, 12, 16, ...) it was found

$$\Gamma_{\text{out-of-plane}}(N) = \left(\frac{N}{4} - 2\right)B_{1g} + \frac{N}{4} B_{2g} + \left(\frac{N}{4} - 1\right)A_u + \frac{N}{4} B_{3u}$$

Here N = 24, 36, 48, ... corresponds to anthracene, pentacene, heptacene, ..., etc. In terms of the number of rings for a Q-cene (Q = 3, 5, 7, ...) one obtains

$$\Gamma_{\text{out-of-plane}}(Q) = \frac{3Q-1}{2} B_{1g} + \frac{3Q+3}{2} B_{2g} + \frac{3Q+1}{2} A_u + \frac{3Q+3}{2} B_{3u}$$

The following set of independent symmetry coordinates for the first fragment of Fig. 2 has been chosen.

$$S_1(B_{2g}) \propto \tau_1 - \tau_2 - \tau_3 + \tau_4, \qquad S_2(B_{2g}) \propto \gamma_1 - \gamma_2$$

$$S_1(A_u) \propto \tau_1 + \tau_2 + \tau_3 + \tau_4$$

$$S_1(B_{3u}) \propto \tau_1 - \tau_2 + \tau_3 - \tau_4, \qquad S_2(B_{3u}) \propto \gamma_1 + \gamma_2$$

The process continues by adding four coordinates for every set of four symmetrically equivalent atoms. The appropriate symmetry-adapted combi-

TABLE 1

Calculated Out-of-Plane Frequencies (cm^{-1}) for Four Polycenes

Species	Naphthalene	Anthracene	Naphthacene.	Pentacene
B_{1g}	941	956	961	961
			909	923
	744	761	761	759
		444	441	445
				427
	400		391	302
		255	160	111
B_{2g}	982	981	983	982
		930	938	941
				904
	889	869	873	870
	745	755	768	771
			683	717
		572	513	542
	476	293	223	371
				179
A_u	976	979	983	982
			913	923
	860	874	872	871
		704	738	752
				665
	596	505	549	521
			342	273
	206	142	110	89
B_{3u}	967	969	968	966
		922	938	946
				900
	772	758	761	759
	432	428	445	450
			414	413
		396	281	390
	196	102		203
			62	42

nations are the same as given above for the case of polycenes with even-number rings.

VIBRATIONAL FREQUENCIES

The frequencies of out-of-plane vibrations calculated according to the five-parameter approximation[2] have been reported for naphthalene,[1] anthracene,[3] naphthacene[4] and pentacene.[4] In these works the calculations are discussed and correlated to observed frequencies. Here the calculated frequencies for the four polycenes are collected in one table (Table 1) in order to show the correlations between them. A number of frequencies are found to be fairly characteristic for all the polycenes studied. (Some unsystematical shifts may probably be explained by an inconsistent assumption of structural parameters; accurate experimental data were adopted for naphthalene and anthracene, while regular hexagonal-ring structures were assumed for naphthacene and pentacene.) In other cases the frequencies are shifted significantly. It is especially found a marked decrease of the lowest frequency in every species when the number of rings increases.

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