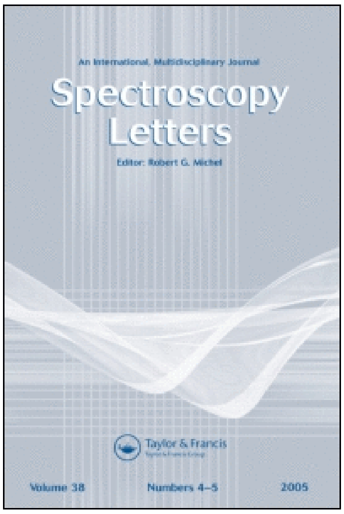

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Condensed Aromatics. Part XIII Triphenylene

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CONDENSED AROMATICS. PART XIII
TRIPHENYLENE

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ABSTRACT

The simple five-parameter force-field approximations were applied to triphenylene. Symmetry coordinates are specified. The frequencies of both in-plane and out-of-plane vibrations were calculated and correlated with observed data from the literature.

Triphenylene, $C_{18}H_{12}$, is a relatively large condensed aromatic molecule. It is supposed to be planar trigonal (symmetry D_{3h}). The 84 normal modes of vibration are distributed among the various symmetry species according to

$$\Gamma_{vib} = 10A_1' + 9A_2' + 19E' + 5A_1'' + 4A_2'' + 9E''$$

In the present work we have performed a normal coordinate analysis of triphenylene according to the simple approximations developed previously. The same approach applied to phenanthrene has been published[1] as the previous part of this paper series. The five-parameter approximation[2,3] developed for the in-plane vibrations is considerably simpler than the well-known aromatic force field of Califano and Neto with collaborators.[4-8] This force field has previously been applied to triphenylene by Schettino.[9] For the out-of-plane vibrations we applied another simple force field with five parameters.[10,11] To our best knowledge is this the first normal coordinale analysis performed for the out-of-plane vibrations of triphenylene.

SYMMETRY COORDINATES

Fig. 1 shows the adopted numbering of atoms in the triphenylene molecular model.

As an aid to avoid redundancies we have considered the "opened" structure obtained when the 13-14 type bonds (indicated with stippled lines in Fig. 1) are omitted. This technique, which has been applied several times previously,[3,11,12] does not imply any physical assumptions about the strength of the bonds.

To avoid redundancies in the construction of the out-of-plane symmetry coordinates is not a trivial task. We applied the "method of fragments"[11] as a systematic approach to this problem.

In-Plane Vibrations

A complete set of independent in-plane symmetry coordinates was chosen in the following way.

(i) Stretchings $d_1(4-5)+d_2(1-6)+d_3(2-3)$ and $t_1(1-2)+t_2(3-4)+t_3(5-6)$ in Species A_1'.

(ii) Symmetry-adapted combinations of the following types in both Species A_1' and A_2': Stretchings 1-7, 7-13, 7-19 and 13-25; bendings

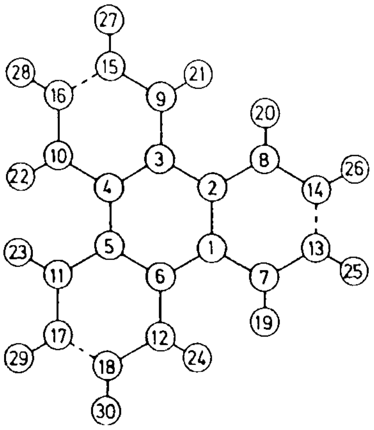

Fig. 1. Numbering of atoms in the triphenylene molecular model (symmetry (D_{3h}).

2-1-7, 1-7-19, 13-7-19 and 7-13-25. Two representative combinations derived from the r_1(1-7) stretching are:

$$(A_1') \qquad r_1+r_2+r_3+r_4+r_5+r_6$$

$$(A_2') \qquad r_1-r_2+r_3-r_4+r_5-r_6$$

Here r_i ($i = 1,\ldots,6$) denotes the i - (i+6) stretching coordinate.

(iii) The appropriate combination of 2-1-6 type bendings in Species A_2' only.

It remains to specify the degenerate E' coordinates.

(iv) Stretchings of the d and t types following the pattern:

$$(E'_a) \quad 2d_1-d_2-d_3 \qquad (E'_b) \quad d_2-d_3$$

(v) Two combinations, (I) and (II), of each of the types which are in common for Species A_1' and A_2'; cf. (ii) above - both as 'a' and 'b' degenerate partners. An actual set of such combinations, which are properly oriented, is given below using the r stretchings as an example.

$$(E'_a \text{ I}) \quad 2r_1+2r_2-r_3-r_4-r_5-r_6 \qquad (E'_b \text{ I}) \quad r_3+r_4-r_5-r_6$$

$$(E'_a \text{ II}) \quad r_3-r_4-r_5+r_6 \qquad (E'_b \text{ II}) \quad -2r_1+2r_2+r_3-r_4+r_5-r_6$$

(vi) One degenerate pair of the 2-1-6 type bendings using the kind of combinations labelled (I) above.

Out-of-Plane Vibrations

It was attained at the following complete set of independent symmetry coordinates.

(i) Torsions $\tau_1(3\text{-}4\text{-}5\text{-}6)+\tau_2(5\text{-}6\text{-}1\text{-}2)+\tau_3(1\text{-}2\text{-}3\text{-}4)$ in Species A_1''.

(ii) Symmetry-adapted combinations of the following types in both A_1'' and A_2'': Torsions 13-7-1-2; out-of-plane bendings 2-6-1-7, 13-1-7-19, 14-7-13-25. Let σ_1(13-7-1-2), σ_2, ..., σ_6 denote the torsions so that σ_i ($i = 1,\ldots,6$) pertains to the torsion of the i - (i+6) bond. Furthermore let γ_1(2-6-1-7), γ_2, ..., γ_6 denote a representative set of out-of-plane bendings so that γ_i has the central atom as number i. Then the symmetry-adapted combinations in the two species in question are different for the torsion and the out-of-plane bendings. The patterns are given below.

$$(A_1'') \qquad \sigma_1+\sigma_2+\sigma_3+\sigma_4+\sigma_5+\sigma_6, \qquad \gamma_1-\gamma_2+\gamma_3-\gamma_4+\gamma_5-\gamma_6$$

(A_2'') $\sigma_1-\sigma_2+\sigma_3-\sigma_4+\sigma_5-\sigma_6$, $\gamma_1+\gamma_2+\gamma_3+\gamma_4+\gamma_5+\gamma_6$

(iii) A degenerate pair of the τ type torsions:

(E''_a) $\tau_2-\tau_3$ (E''_b) $-2\tau_1+\tau_2+\tau_3$

(iv) Two degenerate pairs, (I) and (II), of the same types as under paragraph (ii) above. For the torsions:

$(E''_a\ \mathrm{I})$ $2\sigma_1-2\sigma_2-\sigma_3+\sigma_4-\sigma_5+\sigma_6$ $(E''_b\ \mathrm{I})$ $\sigma_3-\sigma_4-\sigma_5+\sigma_6$

$(E''_a\ \mathrm{II})$ $\sigma_3+\sigma_4-\sigma_5-\sigma_6$ $(E''_b\ \mathrm{II})$ $-2\sigma_1-2\sigma_2+\sigma_3+\sigma_4+\sigma_5+\sigma_6$

For the representative set of out-of-plane bendings:

$(E''_a\ \mathrm{I})$ $2\gamma_1+2\gamma_2-\gamma_3-\gamma_4-\gamma_5-\gamma_6$ $(E''_b\ \mathrm{I})$ $\gamma_1+\gamma_2-\gamma_3-\gamma_4$

$(E''_a\ \mathrm{II})$ $\gamma_1-\gamma_2-\gamma_3+\gamma_4$ $(E''_b\ \mathrm{II})$ $-2\gamma_1+2\gamma_2+\gamma_3-\gamma_4+\gamma_5-\gamma_6$

NORMAL COORDINATE ANALYSIS

Structural Parameters

The bond lengths and interbond angles of the equilibrium structure were taken from crystallographic data.[9,13]

In-Plane Vibrations

The five-parameter approximation applied for the in-plane vibrations is described elsewhere.[2] Table 1 shows the bond orders and force constants for the various types of CC bonds. These force constants are considered as one parameter. The fixed numerical values of the other four parameters are given several places;[2,3,14] see especially the short survey of the approximation in the present journal.[14] Table 1 includes the bond lengths (a) calculated with Coulson's formula,[15] which is quoted elsewhere,[12,14] and (b) observed bond lengths adopted here (see above). The agreement between these two sets (a) and (b) is very satisfactory.

Table 2 shows the calculated frequencies along with a previous calculation[9] and the experimental assignment from the same source.[9] The present calculations agree amazingly well with the observed frequencies when taking into account the simplicity of the force field approximation. Only 9 different force constant values are employed in contrast to Schettino's[9] 27.

TABLE 1

Bond Orders, Bond Lengths (Å) and Force Constants (mdyne/Å) for the CC Bonds in Triphenylene

Atom pair	Bond order	Bond length		Force constant
		Calc.	Obs.	
1-2	0.562	1.416	1.416	4.501
1-6	0.428	1.441	1.447	4.067
1-7	0.603	1.408	1.416	4.639
7-13	0.690	1.393	1.378	4.945
13-14	0.637	1.402	1.401	4.756

TABLE 2

Calculated and Observed Frequencies (cm^{-1}) for the In-Plane Vibrations of Triphenylene

Species	Calculated		Obs.	Species	Calculated		Obs.
	Ref.9	Present	Ref.9		Ref.9	Present	Ref.9
A_1'	3089	3035	3055	E'	3089	3041	3085
	3040	3030	3040		3067	3035	3070
	1551	1599	1550		3040	3032	3038
	1462	1530	1458		3032	3030	3024
	1335	1434	1341		1648	1656	1611
	1234	1185	1230		1554	1590	1579
	1158	1106	1180		1495	1535	1500
	1015	876	1062		1424	1492	1434
	680	675	700		1326	1423	1300
	384	332	418		1254	1310	1245
A_2'	3067	3041	3062		1179	1169	1167
	3023	3032	3030		1158	1120	1144
	1585	1601	1560		1080	1005	1110
	1424	1448	1422		1029	945	1052
	1272	1296	1255		1011	879	1003
	1111	1102	1136		789	742	776
	1018	1040	1025		628	649	619
	607	624	607		398	355	410
	549	506	550		195	180	264

Out-of-Plane Vibrations

The five-parameter approximation for the out-of-plane vibrations is described elsewhere.[10] The numerical values of the force constants are also found in previous publications.[10,14,16] It should be noted here that only one type of torsion/torsion interactions has the value 0.02 mdyne/Å, viz. the one pertaining to the 1-2 bond type. The interactions pertaining to the 2-3 bond type have the value 0.07 mdyne/Å although they are of the CCCC/CCCC type. One C-C bond of this type is not common for two benzene rings. This situation was also encountered

TABLE 3

Calculated and Observed Frequencies (cm^{-1}) for the Out-of-Plane Vibrations of Triphenylene

Species	Calculated	Observed^9		
		Infrared	Raman	Luminescence
A_1''	1081			
	978	(980/978)		
	856	861/854		
	595			
	217	(279)		
A_2''	970	949/946		946
	755	741	740	743
	509	422		
	111	152		
E''	992			
	978	980/978		972
	903	936		
	843	851/850		850
	766	711		
	560	570		
	507	532		
	312	279	282	
	141			135

in phenanthrene,[1] where the torsion/torsion interaction for the 1-2 bond (Fig. 1 of Ref. 1) also is 0.07 mdyne/Å.

Table 3 shows the results along with a tentative assignment of observed frequencies from Schettino,[9] who has reported own infrared and Raman data and quoted luminescence data from literature.[17] It is seen to be very well possible to correlate the observed data with our calculations. In Table 3 we have adopted the crystal data[9] of infrared and Raman frequencies. In Species A_2'' we have followed Schettino's[9] assignment. Also in the two other species the assignments are consistent with Schettino, who only has suggested the assignments as E'' *or* A_1''.

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