Structure, Modified Scaled Quantum Mechanical Force Field and *A Priori* Prediction of Vibrational Spectra and Their Assignment and Exponential Scaling of Frequencies of Triphenylene

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Received March 11, 2003

The structure, force field and vibrational spectra of triphenylene are studied by B3LYP/6-31G*(5d) level of theory. The results are compared to those of the related system, phenanthrene. The scale factors in non-redundant local coordinates obtained after fitting the DFT frequencies to the experimental numbers of phenanthrene-d_0 and -d_{10} are transferred to predict the spectra and assignment of triphenylene for in-plane modes. The frequencies based on scaling methodology due to Lee *et al.* are also obtained. These frequencies are compared with the predicted numbers based on scale factors from phenanthrene. Probable assignment for out-of-plane modes is proposed based on simple scaling of Scott and Radom (scale factor 0.9614) as well as by scaling methodology by Lee *et al*.

Key Words : Density functional calculation, Triphenylene, Vibrational spectra

Introduction

Triphenylene is an eighteen π electron planar tetracyclic fused ring system with six membered rings. This system has been attracting much attention very recently. Ionization spectral bands from UV photoelectron measurements have been studied for triphenylene and its radical cation.[1] The NMR properties of triphenylene have also been studied as molecular magnets.[2,3] It is also important in host-guest chemistry as its use has been found in triphenylene scaffold.[4] Unusual phosphorescence spectra of triphenylene are of particular interest both theoretically and experimentally. Polycyclic aromatic hydrocarbons (PAHs) are the largest known class of chemical carcinogens and mutagens.[5] In addition, triphenylene-based discotic (columnar) liquid crystalline materials could be used as device materials. The high charge carrier mobilities, photoconductivity, and photo-physical properties of triphenylene derivatives are of special interest.[6]

Along with these studies, the force field and vibratonal spectra of triphenylene were also studied. The vibrational spectra of several PAHs and their cations and a few anions have been studied in great detail by several authors because of their importance as the origin of infrared emission bands in the emission bands in the interstellar radiation from many galactic sources.[7] Presently the vibrational spectroscopy has become an indispensable tool to study various aspects of isolated molecules and clusters. The specific/complete vibrational analysis was done on various systems e.g. water clusters,[8] sundry weak complexes of benzene and ethene,[9] calix[4]hydroquinone nanotube bundles[10] and many other systems. The nature of inter-ring couplings is also the focus of attention in some of the papers.

The first infrared and Raman spectra of triphenylene in the crystalline state and solution was reported by Schettino.[11] The low temperature high resolution phosphorescence spectrum and fundamentals deduced from the analysis of it was reported by Nishi and co-workers.[12] The matrix-isolated IR spectrum in the range 500-3150 cm^{-1} was reported Hudgins and Sandford.[13] On the theoretical side, the scaled and calculated frequencies were reported by Ling and Lifshitz at the HF level using 3-21G basis set. Some reassignments of the fundamentals of triphenylene were made on the basis of the vibronic activity by QCFF/PI calculation in the phosphorescence spectrum of the disklike moleule.[14] Later Keszthelyi *et al.* reported the structure and vibrational spectra based on HF, B-LYP and B3-LYP methods using 6-31G basis set and revisited the assignment.[15] Langhoff computed the spectra at the B3LYP/4-31G level.[16] He reported the scaled IR active vibrational frequencies (scale factor 0.958). The matrix-isolated IR spectrum in the range 500-3150 cm^{-1} was reported Hudgins and Sandford.[13] Inspite of these studies, there remain some uncertainties in all the empirical assignments. It is to be noted that in the condensed phase, interactions of this PAH with the surrounding medium and with triphnylene molecules leading to clusters can lower the symmetry and affect the force field, thus alter strongly the frequencies and intensities of the vibrational modes. With this view in consideration, the vibrational study on triphenylene of C_{2v} symmetry is relevant. The approach isto simulate the slighly perturbed structure from the global minimum D_{3h} structure so as to reliably assign the experimetal frequencies, thus the calculated frequencies of both the structures will be marginally different.

To the best of the knowledge, no study exits on force field, complete vibrational spectra and assignment of this molecule in terms of non-redundant local coordinates. Here the objective is to predict the spectra from a related standard system. The scale factors of the related standard system, phenanthrene with C_{2v} symmetry were transferred to predict

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and assign the spectra of triphenylene with C_{2v} symmetry. The scaled frequencies were compared with the available experimental ones. One of the important aspects of vibrational spectroscopy is to predict accurately the inactive fundamentals $9A2^{//}$ and $5A_1^{//}$. But they were observed due to symmetry lowering in condensed phase though they have very weak intensities. Thus experiments have proven to be difficult in this aspect. Theoretical prediction is of immense value and the predicted values of triphenylene with C_{2v} symmetry will accurately simulate the inactive fundamentals in D_{3h} symmetry. The vibrational frequencies are usually overestimated. Thus there is a need to scale appropriately the frequencies. To this end, a modified scaled quantum mechanical approach (SQM) was used in vibrational analysis for a number of hydrocarbons and heterocycles.[17-19] Here this fitting methodology is also used. Previously, a scaling method for frequencies was developed by Lee *et al.* and this method was successfully applied to s-trans-1,3-butadiene and all-trans-1,3,5,7-octatetraene[20,21]. Here the same scaling approach was used to predict the vibrational spectra. Previously we studied azulene, phenanthrene with a view to evaluating inter-ring couplings and evaluate and analyze the transferability of non-redundant local force constants. In continuation of this work, the results of triphenylene are presented here.

Methodology

The initial geometries of triphenylene and phenanthrene with C_{2v} symmetries were fully optimized using B3LYP/6-31G*(5d) method available in Gaussian94.[22] The vibrational frequencies and cartesian force constants at the optimized geometries were obtained analytically and transformed to local coordinate space following the recommendation of Pulay *et al.*[23] Previously we assigned the fundamentals of phenanthrene and phenanthrene-d_{10} based on HF/4-21G level calculations.[18] Here the DFT frequencies are fitted to the same set of experimental numbers of phenanthrene-d_0 and-d_{10} using the modified SQM procedure. The scale factors were transferred from phenanthrene to triphenylene to predict the in-plane modes. The potential energy distribution (PED) of the in-plane normal modes in local coordinates for triphenylene was computed using force constants after scaling. For out-of-plane modes, a simple scale factor of 0.9614 as recommended by Scott and Radom[25] was used to scale the frequencies. Thus the scaled in-plane force field in non-redundant local coordinates and the assignment were obtained. The scaling methodology of Lee *et al.* is also employed for the present system[20,21] and the results are compared with those of modified SQM.

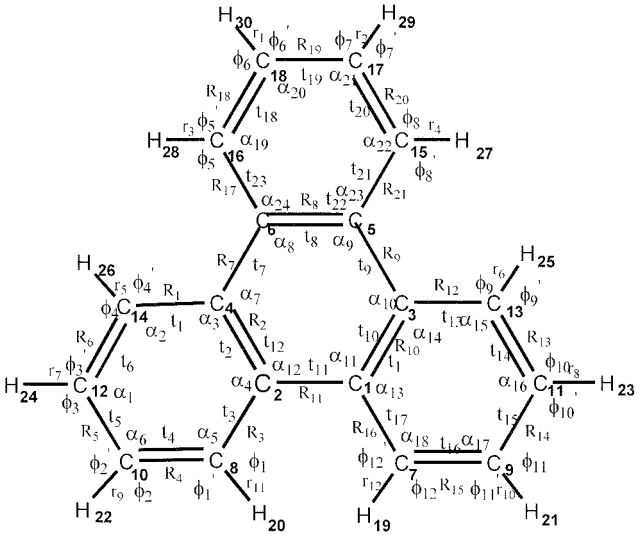

Figure 1. Atom Numberings and Internal Coordinates of Triphenylene.

Results and Discussion

The units of various terms are as follows: The vibrational frequencies in this paper are expressed in cm^{-1}. The stretching and their interaction force constants are in mdyne $Å^{-1}$, bending, wagging, torsions and their interactions are in mdyne Å rad^{-2}. Interactions of stretching force constants with bendings, wags and torsions are in mdyne rad^{-1}. The structure and internal coordinates of triphenylene are shown in Figure 1. The optimized geometrical parameters are presented in Table 1. The DFT frequencies for phenanthrene-d_0 and -d_{10} are fitted to the experimental ones and the fitting reproduces the experimental numbers well with average deviations of 3.1 and 2.5 cm^{-1} with C-H stretches and without C-H stretches respectively. The local and symmetry coordinates are given in Tables 2 and 3, respectively.

The diagonal force constants at the B3LYP/6-31G* level of theory are listed in Table 4. The fundamental frequencies and their assignments of triphenylene along with their potential energy distribution (PED) given in Tables 5 and 6.

(i) Optimized Geometry: The geometrical parameters in Table 1 are considered up to the third decimal place. At this level of precision the geometry reflects the D_{3h} symmetry. The geometrical parameters (R_{1-6}) of triphenylene (1.414,

Table 1. Optimized geometrical parameters of triphenylene at B3LYP/6-31G*(5d). The bond lengths are in Å and bond angles are in degrees[a]

	Theory	Expt.[b]		Theory	Expt.[b]
R_1	1.414		α_1	119.6	
R_2	1.422		α_2	122.0	
R_3	1.414		α_3	118.4	
R_4	1.383		α_4	118.4	
R_5	1.401		α_5	122.0	
R_6	1.383		α_6	119.6	
R_7	1.467	1.447	α_7	120.0	
R_8	1.422		α_8	120.0	120.0
R_{11}	1.467		α_{19}	122.0	122.0
R_{17}	1.414	1.416	α_{20}	119.6	119.6
R18	1.383	1.378	α_{23}	118.4	118.4
R19	1.401	1.401			

[a]For geometrical parameter, see Fig. 1. [b]Refs. 11, 24.

Table 2. Definition of local coordinates for triphenylene[a]

Coordinate	Description
In-plane	
$l_{1\text{-}21} = R_{1\text{-}21}$	CC stretch
$l_{22\text{-}33} = r_{1\text{-}12}$	CH stretch
$l_{34\text{-}45} = \beta_{1\text{-}12}$	CH rock
$l_{46}\ (\delta_1) = \alpha_1 - \alpha_2 + \alpha_3 - \alpha_4 + \alpha_5 - \alpha_6$	Ring bending
$l_{47}\ (\delta_2) = 2\alpha_1 - \alpha_2 - \alpha_3 + 2\alpha_4 - \alpha_5 - \alpha_6$	Ring bending
$l_{48}\ (\delta_3) = \alpha_2 - \alpha_3 + \alpha_5 - \alpha_6$	Ring bending
$l_{49\text{-}57}\ (\delta_{4\text{-}12})$	Ring bending[2]
Out-of-plane	
$l_{1\text{-}12} = \gamma_{1\text{-}8}$	CH wag
$l13\ (\tau_1) = t_1 - t_2 + t_3 - t_4 + t_5 - t_6$	Ring Torsion
$l_{14}\ (\tau_2) = 2t_1 - t_2 - t_3 + 2t_4 - t_5 - t_6$	Ring Torsion
$l_{15}\ (\tau_3) = t_2 - t_3 + t_5 - t_6$	Ring Torsion
$l_{16\text{-}24}\ (\tau_{4\text{-}9})$	Ring Torsion[3]
$l_{25}\ (\tau_{10}) = t_{16,6,5,3} - t_{4,6,5,15}$	Torsion
$l_{26}\ (\tau_{11}) = t_{1,2,4,14} - t_{8,2,4,6}$	Torsion
$l_{27}\ (\tau_{12}) = t_{7,1,3,5} - t_{2,1,3,13}$	Torsion

[a]See Fig. 1.; the CH rock is defined as, $\beta_i = 2^{-1}(\phi_i - f_i^{/})$. γ_i numberings are same as r_i . [b]$\delta_{4\text{-}6}$, $\delta_{7\text{-}9}$ and $\delta_{10\text{-}12}$ are defined similarly with $\alpha_{7\text{-}12}$, $\alpha_{13\text{-}18}$ and $\alpha_{19\text{-}24}$ respectively. [c]$\tau_{4\text{-}6}$, $\tau_{7\text{-}9}$, $\tau_{10\text{-}12}$ are defined similarly as $\tau_{1\text{-}3}$ with $t_{7\text{-}12}$, $t_{13\text{-}18}$ and $t_{19\text{-}24}$ respectively.

1.422, 1.414, 1.383, 1.401, 1.383 Å) match well with those of phenanthrene (1.415, 1.427, 1.415, 1.383, 1.408, 1.381 Å). The major differences arise in the case of the sandwitched ring. The values for R_7 , R_8 and R_{11} are 1.467, 1.422 and 1.467 Å for triphenylene, whereas they are 1.435, 1.340 and 1.458 Å for phenanthrene. The calculated geometrical parameters agree well with the experimental values.[11-24]

(ii) Force Field: Triphenylene could be regarded as consisting of a phenanthrene moiety and a benzene ring. Hence we expect similarities between the phenanthrene ring moiety and triphenylene. Based on the diagonal force constants of these two molecules given in Table 4 and some selected interaction force constants, the following inferences could be made regarding the force fields of triphenylene and phenanthrene.

(1) C-H diagonal force constants of triphenylene are larger compared to phenanthrene. Interaction force constants involving C-H (σ bonds) are small and only the first neighbours contribute significantly for all the two systems.

(2) In the case of C-C, the diagonal force conatants of triphenylene are larger than those of phenanthrene although some are similar. The interaction force constants between C-C bonds are much larger compared to phenanthrene and similar to phenanthrene they extend over the entire ring.

(3) Diagonal $f_{\beta\beta}$'s are in general higher for triphenylene than for phenanthrene. C-H-β_i interactions are small and negligible in most cases. C-C-β_i interactions are substantial only for the connecting bonds.

(4) The force constants for ring bendings (δ) are higher for triphenylene compared to phenanthrene.

These conclusions clearly indicate that the force constants of triphenylene are larger than those of phenanthrene although some of them are similar.

Table 3. Definition of symmetry coordinates for in-plane modes of triphenylene in terms of local coordinates[a]

A_1	$S_1 = 2^{-1/2}(R_1 + R_{12})$	B_2	$S_1 = 2^{-1/2}(R_1 - R_{12})$
	$S_2 = 2^{-1/2}(R_2 + R_{10})$		$S_2 = 2^{-1/2}(R_2 - R_{10})$
	$S_3 = 2^{-1/2}(R_3 + R_{16})$		$S_3 = 2^{-1/2}(R_3 - R_{16})$
	$S_4 = 2^{-1/2}(R_4 + R_{15})$		$S_4 = 2^{-1/2}(R_4 - R_{15})$
	$S_5 = 2^{-1/2}(R_5 + R_{14})$		$S_5 = 2^{-1/2}(R_5 - R_{14})$
	$S_6 = 2^{-1/2}(R_6 + R_{13})$		$S_6 = 2^{-1/2}(R_6 - R_{13})$
	$S_7 = 2^{-1/2}(R_7 + R_9)$		$S_7 = 2^{-1/2}(R_7 - R_9)$
	$S_8 = R_8$		$S_8 = 2^{-1/2}(R_{17} - R_{21})$
	$S_9 = R_{11}$		$S_9 = 2^{-1/2}(R_{18} - R_{20})$
	$S_{10} = 2^{-1/2}(R_{17} + R_{21})$		$S_{10} = 2^{-1/2}(r_1 - r_2)$
	$S_{11} = 2^{-1/2}(R_{18} + R_{20})$		$S_{11} = 2^{-1/2}(r_3 - r_4)$
	$S_{12} = R_{19}$		$S_{12} = 2^{-1/2}(r_5 - r_6)$
	$S_{13} = 2^{-1/2}(r_1 + r_2)$		$S_{13} = 2^{-1/2}(r_7 - r_8)$
	$S_{14} = 2^{-1/2}(r_3 + r_4)$		$S_{14} = 2^{-1/2}(r_9 - r_{10})$
	$S_{15} = 2^{-1/2}(r_5 + r_6)$		$S_{15} = 2^{-1/2}(r_{11} - r_{12})$
	$S_{16} = 2^{-1/2}(r_7 + r_8)$		$S_{16} = 2^{-1/2}(\beta_1 + \beta_{12})$
	$S_{17} = 2^{-1/2}(r_9 + r_{10})$		$S_{17} = 2^{-1/2}(\beta_2 + \beta_{11})$
	$S_{18} = 2^{-1/2}(r_{11} + r_{12})$		$S_{18} = 2^{-1/2}(\beta_3 + \beta_{10})$
	$S_{19} = 2^{-1/2}(\beta_1 - \beta_{12})$		$S_{19} = 2^{-1/2}(\beta_4 + \beta_9)$
	$S_{20} = 2^{-1/2}(\beta_2 - \beta_{11})$		$S_{20} = 2^{-1/2}(\beta_5 - \beta_8)$
	$S_{21} = 2^{-1/2}(\beta_3 - \beta_{10})$		$S_{21} = 2^{-1/2}(\beta_6 - \beta_7)$
	$S_{22} = 2^{-1/2}(\beta_4 - \beta_9)$		$S_{22} = 2^{-1/2}(\delta_1 - \delta_7)$
	$S_{23} = 2^{-1/2}(\beta_5 - \beta_8)$		$S_{23} = 2^{-1/2}(\delta_2 + \delta_8)$
	$S_{24} = 2^{-1/2}(\beta_6 - \beta_7)$		$S_{24} = 2^{-1/2}(\delta_3 - \delta_9)$
	$S_{25} = 2^{-1/2}(\delta_1 - \delta_7)$		$S_{25} = \delta_4$
	$S_{26} = 2^{-1/2}(\delta_2 + \delta_8)$		$S_{26} = \delta_6$
	$S_{27} = 2^{-1/2}(\delta_3 - \delta_9)$		$S_{27} = \delta_{10}$
	$S_{28} = \delta_5$		$S_{28} = \delta_{12}$
	$S_{29} = \delta_{11}$		

[a]Abbreviations. SS: Symmetry Species.

Table 4. Scaled(Sc.) force constants of triphenylene and phenanthrene at the B3LYP/6-31G* level

Term	Tri-phenylene Sc.	Phen-anthrene Sc.	Term	Tri-phenylene Sc.	Phen-anthrene Sc.
$R_1\ R_1$	5.484	5.475	$r_{11}\ r_{11}$	5.254	5.205
$R_2\ R_2$	5.993	5.583	$\beta_1\beta_1$	1.099	1.045
$R_3\ R_3$	6.632	6.545	$\beta_2\beta_2$	1.038	1.058
$R_4\ R_4$	7.028	6.968	$\beta_3\beta_3$	1.063	1.024
$R_5\ R_5$	6.480	6.233	$\beta_4\beta_4$	1.098	1.077
$R_6\ R_6$	7.281	7.334	$\beta_5\beta_5$	1.094	
$R_7\ R_7$	6.270	6.126	$\beta_6\beta_6$	1.038	
$R_8\ R_8$	5.714	7.418	$\delta_1\delta_1$	1.644	1.527
$R_{11}\ R_{11}$	6.280		$\delta_2\delta_2$	1.807	1.622
$R_{17}\ R_{17}$	6.622		$\delta_3\delta_3$	1.592	1.453
$R_{18}\ R_{18}$	7.026		$\delta_4\delta_4$	1.736	1.616
$R_{19}\ R_{19}$	6.477		$\delta_5\delta_5$	2.125	1.825
$r_1\ r_1$	5.234		$\delta_6\delta_6$	2.117	1.512
$r_3\ r_3$	5.246		$\delta_{10}\delta_{10}$	1.640	
$r_5\ r_5$	5.246	5.005	$\delta_{11}\delta_{11}$	1.481	
$r_7\ r_7$	5.127	5.128	$\delta_{12}\delta_{12}$	1.902	
$r_9\ r_9$	5.234	5.227			

Table 5. Vibrational Spectra, IR intensities (km/mol) and Assignment for In-plane modes of Triphenylene[a]

SS	SS (D_{3h})	Expt[b]	sc	unsc	IR int.	ω^{sc}	PED
A_1	A_1'	3117	3107	3243	3.59	3117	$37S_{18} + 21S_{14} + 14S_{15}$
	E'	3098	3105	3241	46.20	3115	$40S_{18} + 22S_{14} + 20S_{13}$
	E'	3091	3094	3222	1.10	3098	$52S_{13} + 40S_{15}$
	A_1'	3085	3086	3206	0.02	3083	$69S_{17} + 21S_{18}$
	E'	3075	3076	3203	46.85	3080	$50S_{14} + 31S_{15}$
	E'	3055	3052	3189	2.44	3067	$86S_{16}$
	E'	1612	1613	1666	0.25	1596	$21S_6 + 16S_3 + 14S_4$
	E'	1579	1567	1634	0.07	1567	$21S_{12}$
	A_1'	1550	1548	1606	0.00	1541	$25S_5$
	E'	1502	1509	1550	11.18	1490	$14S_{23} + 13S_{20}$
	A_1'	1434	1435	1496	0.01	1440	$24S_{21} + 16S_{23} + 15S_{22}$
	E'	1434	1430	1482	20.33	1427	$14S_{22} + 12S_2$
	E'	1341	1340	1383	0.20	1335	$22S_9 + 21S_{19} + 16S_{25}$
	A_1'	1300	1310	1377	0.00	1330	$25S_7 + 22S_2$
	E'	1300*	1284	1337	1.54	1292	$33S_{10} + 18S_{11} + 17S_8$
	E'	1256	1258	1285	3.82	1244	$26S_3 + 18S_{19} + 13S_{22}$
	A_1'	1230	1211	1263	0.00	1223	$24S_1 + 16S_{20} + 12S_3$
	A_1'	1180	1191	1221	0.00	1184	$21S_{21} + 16S_{20}$
	E'	1173	1171	1202	0.27	1166	$49S_{24} + 17S_{23}$
	E'	1106	1106	1142	0.32	1109	$21S_1 + 21S_{25} + 14S_4$
	A_1'	1062	1063	1100	0.00	1069	$51S_5$
	E'	1052	1051	1086	3.69	1057	$40S_{12} + 17S_{23}$
	E'	1003	998	1023	1.58	996	$34S_{25} + 12S_8$
	E'	776	784	789	0.00	773	$40S_{26} + 23S_{25}$
	A_1'	700	700	713	0.00	700	$31S_{27} + 18S_{29} + 13S_2 + 13S_{26}$
	E'	622	633	635	5.59	625	$49S_{29} + 31S_{27}$
	A_1'	418	419	424	0.00	419	$24S_7 + 17S_{27}$
	E'	406	405	410	0.80	406	$59S_{28} + 15S_{26}$
	E'	264	264	265	0.28	263	$41S_{26}$
B_2	E'	3098	3102	3240	50.13	3114	$46S_{11} + 43S_{12}$
	A_2'	3091	3095	3224	0.47	3099	$67S_{14} + 24S_{15}$
	E'	3085	3084	3220	0.23	3095	$44S_{10} + 38S_{12}$
	E'	3075	3075	3203	46.59	3080	$71S_{15} + 22S_{14}$
	E'	3075	3072	3189	2.63	3067	$45S_{10} + 36S_{11}$
	A_2'	3055	3052	3188	0.00	3066	$85S_{13}$
	A_2'	1612	1623	1670	0.00	1601	$29S_9 + 27S_8$
	E'	1612	1616	1665	0.26	1596	$23S_6 + 16S_3$
	E'	1579	1567	1634	0.07	1568	$23S_4 + 20S_5 + 16S_2$
	E'	1501	1501	1550	11.36	1490	$17S_{19} + 13S_7 + 13S_{21}$
	A_2'	1471	1472	1505	0.00	1449	$23S_{18} + 16S_{25} + 13S_3$
	E'	1434	1446	1482	20.19	1427	$24S_{21} + 17S_{16}$
	E'	1341	1341	1383	0.17	1335	$28S_7 + 14S_{20}$
	E'	1300	1294	1336	1.47	1291	$15S_{16} + 14S_3 + 13S_{19} + 12S_{25}$
	A_2'	1256*	1279	1322	0.00	1278	$21S_{20} + 14S_7$
	E'	1245	1239	1285	3.88	1243	$23S_1 + 18S_6 + 14S_2$
	E'	1173	1175	1203	0.27	1166	$31S_{18} + 27S_{17} + 14S_{16}$
	A_2'	1136	1150	1179	0.00	1144	$14S_{17} + 13S_4 + 12S_9 + 12S_{21}$
	E'	1110	1114	1142	0.34	1109	$16S_9 + 14S_8 + 14S_{21} + 13S_2 + 12S_4$
	E'	1052	1054	1087	3.62	1057	$41S_5 + 15S_{16}$
	E'	1005	1015	1023	1.59	997	$60S_{22} + 33S_{27}$
	A_2'	993	993	1015	0.00	989	$26S_{27} + 17S_1 + 13S_{22}$
	E'	776	779	790	0.00	774	$29S_{28} + 14S_{27} + 13S_7$
	E'	622	633	636	5.61	626	$48S_{24} + 27S_{23}$
	A_2'	607	614	617	0.00	607	$40S_{23} + 29S_{28}$
	A_2'	550	560	566	0.00	558	$56S_{25}$
	E'	410	409	411	0.78	406	$64S_{26}$
	E'	264	262	264	0.28	262	$33S_{28} + 17S_7$

[a]Only contributions to the potential energy distributions (PED) in symmetry coordinates equal to or larger than 10% are included. In-plane and out-of-plane modes are treated separately. When one experimental band has large deviation from the predicted number, the experimental frequency is marked by asterisk. $\omega^{sc} = \omega^{unsc} \exp(-\alpha\, \omega^{unsc})$; For C-H stretches, the scale factor ($\alpha = 1.225 \times 10^{-5}$) from the pair ($\omega^{unsc} = 3243$; $\omega^{sc} = 3117$) was used. For non C-H stretches, the scale factor ($\alpha = 2.548 \times 10^{-5}$) from the pair ($\omega^{unsc} = 758$; $\omega^{sc} = 744$) was used. Abbreviations: sc: scaled; unsc: unscaled; SS: Symmetry Species. [b]From refs. 11, 12, 13.

(iii) Vibrational Spectra: Triphenylene in C_{2v} symmetry has 57 in-plane and 27 out-of-plane normal modes of vibration spanning irreducible representations $29A_1$ (IR,R) + $14A_2$ (R) + $13B_1$ (IR,R) + $28B_2$ (IR,R). The spectral activities are given in parentheses *e.g.* 29 A_1 modes are both IR and Raman active and so on. The vibrational modes of triphenylene in D_{3h} symmetry span the irreducible representations $10A_1^{/}$(R) + $9A_2^{/}$( ) + $19E^{/}$(IR,R) for in-plane and $5A_1^{//}$( ) + $4A_2^{//}$(IR) + $9E^{//}$(R) for out-of-plane motions where the parentheses enclosing no content are both IR and Raman inactive. The B3LYP/6-31G* frequencies obtained for phenanthrene with C_{2v} symmetry from Gaussian94 program are fitted to the experimental ones of phenanthrene-d_0 and -d_{10} for the in-plane fundamentals. The agreement between the fitted and the experimental frequencies is very good for both the isotopomers with an average deviation of 3.1/2.5 cm^{-1} with/without C-H stretches.

Most of the assignments are very straightforward as the frequencies agree with the predicted numbers from very well-studied system, phenanthrene and scaled frequencies by the scaling method of Lee *et al.*[20,21] Some assignments merit some comments. The bands at 1300 and 1341 cm^{-1} (belonging to $E^{/}$ and $A_1^{/}$ respectively) in both the assignments of Schettino[11] and Nishi *et al.*[12] are interchanged. These assignments are in good agreement with the predicted numbers (1340 and 1310 cm^{-1}). Noting that the band at 1300 cm^{-1} has a weak intensity, it is evident that the present assignment is justified.

The bands at 1246 and 1256 cm^{-1} considered as a single fundamental in the work of Hudgins *et al.*[13] are regarded here as two fundamentals. This is also supported by the theoretical predictions. The band at 947 cm^{-1} was reported by Hudgins *et al*. However, in view of the absence of suitable match with the predicted frequencies, the band is uncertain as a fundamental. It is to be noted that the alternative assignment is at 1025 cm^{-1} as reported by Schettino.[11] The bands at 1560 and 1422 cm^{-1} in ref. 11 appear to be doubtful as they are not in agreement with the predicted numbers. This fact was further supported by Keszthelyi *et al.*[15] However, the band at 1180 cm^{-1} suspected by Keszthelyi *et al*. as a fundamental is considered as a fundamental in the present work.

For out-of-plane modes, the strategy of scaling due to Scott and Radom[25] employed before to azulene[17] is used here. The frequencies are predicted based on simple scaling recommended by Scott and Radom25 and exponential scaling methodology due to Lee *et al.*[20,21] and compared with the results of Hudgins *et al.*[13]

Table 6. Vibrational Spectra, IR intensities (km/mol) and Assignment of Triphenylene for the out-of-plane modes[a]

SS (C_{2v})	SS (D_{3h})	Expt [13]	sc	unsc	IR int.	ω^{sc}	PED[2]
A_2	$E^{//}$	947	943	981	0.00	957	$22l_1 + 22l_2$
	$A_1^{//}$		934	971	0.00	947	$12l_1 + 12l_2 + 12l_7$
	$E^{//}$		890	926	0.00	904	$14l_9 + 14l_{10} + 13l_5$
	$A_1^{//}$		844	878	0.00	859	$16l_{16} + 12l_{22}$
	$E^{//}$		833	866	0.00	847	$21l_{21} + 21l_{21}$
	$E^{//}$		755	785	0.00	769	$22l_{22}$
	$A_1^{//}$		754	785	0.00	769	$22l_{16} + 11l_{13}$
	$E^{//}$		694	722	0.00	709	$37l_{22}$
	$A_1^{//}$		557	579	0.00	571	$16l_{13} + 16l_{19} +16l_{22}$
	$E^{//}$		536	558	0.00	550	$11l_{22} + 11l_{24}$
	$E^{//}$		421	438	0.00	433	$23l1_4 + 23l_{20} + 16l_{24}$
	$E^{//}$		264	275	0.00	273	$17l_{14} + 20l_{17} + 16l_{15}$
	$A_1^{//}$		106	110	0.00	110	$21l_{16} + 15l_{15} + 15l_{21}$
	$E^{//}$		52	54	0.00	54	$33l_{18} + 15l_{24}$
B_1	$E^{//}$	947	943	981	0.00	957	$18l_9 + 18l_{10} + 15l_7$
	$A_2^{//}$		911	948	1.14	925	$10l_3 + 10l_4$
	$E^{//}$		891	927	0.00	905	$16l_3 + 16l_4 + 12l_1 + 12l_2$
	$E^{//}$		832	865	0.00	846	$20l_5 + 20l_6 + 14l_{11}$
	$E^{//}$		755	785	0.01	770	$14l_{13} + 14l_{19}$
	$A_2^{//}$	741	730	759	142.40	744	$20l_{19}$
	$E^{//}$		694	722	0.01	709	$28l_{13} + 28l_{19}$
	$E^{//}$		536	558	0.00	550	$15l_{25}$
	$E^{//}$		423	440	0.00	435	$20l_{15} + 20l_{21} + 20l_{23}$
	$A_2^{//}$		417	434	2.93	429	$18l_{14} + 18l_{20} + 17l_{23}$
	$E^{//}$		265	276	0.00	274	$31l_{23} + 17l_{20} + 17l_{14}$
	$A_2^{//}$		120	125	1.73	125	$25l_{25} + 25l_{26} + 25l_{27}$
	$E^{//}$		51	53	0.00	53	$32l_{17}$

[a]Only contributions to the potential energy distributions in symmetry coordinates equal to or larger than 10% are included. In-plane and out-of-plane modes are treated separately. $\omega^{sc} = \omega^{unsc} \exp(-\alpha\, \omega^{unsc})$; The scale factor ($\alpha = 2.548 \times 10^{-5}$) was obtained from the pair ($\omega^{unsc} = 758$; $\omega^{sc} = 744$) was used. [b]PEDs of out-of-plane modes are based on unscaled local force field.

Conclusions

The structure, force field and vibrational spectra, and their assignment of triphenylene of C_{2v} symmetry are studied by B3LYP/6-31G* level of density functional theory. The results are compared to the related system, phenanthrene. The force field of triphenylene is higher from its constituent ring system, although some of the force constants are similar. The earlier assignment was confirmed or reassigned for in-plane modes. For in-plane modes, the frequencies scaled by two independent methods match very well, and for out-of-plane modes the agreement is reasonable. The out-of-plane frequencies predicted compare reasonably with the latest assignment obtained from IR spectra.

Acknowledgements. This study was supported by BK21. I thank the anonymous referees for their valuable criticisms/ comments.

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