Title: Density functional theory studies on IR spectra of the triphenylene derivatives : a scaled quantum mechanical force field approach

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DENSITY FUNCTIONAL THEORY STUDIES ON IR SPECTRA OF THE TRIPHENYLENE DERIVATIVES. A SCALED QUANTUM MECHANICAL FORCE FIELD APPROACH

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Density functional theory, B3-LYP with the 6-31G* basis set was applied to study the structures and vibrational infrared spectra of triphenylene and the hexasubstituted triphenylene derivatives. The calculated force fields were scaled using the scaled quantum mechanical force field method. The predicted vibrational frequencies were compared with the experimental IR spectra (500–4000 cm^{-1}). The spectra were interpreted and vibrational assignments were reported. This study shows that the scaled density functional force field approach enables, through the transferability of scale factors, good interpretation of vibrational spectra of large molecules.

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1. Introduction

Molecules forming discotic columnar and discotic nematic phases generally consist of a rigid planar core with four to eight flexible aliphatic tails. The structural features associated with both the flexible chain and the rigid core are of the great importance for understanding the mesomorphism of the discotic materials. A number of different methods have been used for studying the structural and orientational order in discotic liquid crystals. These are nuclear magnetic resonance (NMR) [1], X-ray [2] and infrared spectroscopy [3–5]. Despite the fact that vibrational spectroscopy is found to be very sensitive to the structure and orientational ordering of the molecules it is generally not trivial to obtain complete assignment of the fundamental frequencies in the experimental spectra. For large size molecules it is therefore necessary to determine the vibrational frequencies by computational methods and then compare them with the experimental spectra.

In the paper we calculate harmonic vibrational frequencies for triphenylene which is probably the most popular discotic mesogen and for its 2,3,6,7,10,11-alkoxy derivatives (HnT, n = 1, 3, 5, 7). The hybrid B3-LYP functional is used in density

functional theory (DFT) calculations. The experimental IR spectra of the selected compounds have been measured in the solid and the liquid phases and the fundamental frequencies assigned in comparison with the corresponding theoretical spectra.

2. Materials and methods

2.1. Samples description

The molecules used for these studies belong to the triphenylene homologous series. Figure 1 shows the structure of the triphenylene and the hexasubstituted triphenylene derivatives: 2,3,6,7,10,11-hexamethyloxy (H1T) and hexapropyloxy (H3T) triphenylene, and two discotic liquid crystals: 2,3,6,7,10,11-hexapentyloxy (H5T) and hexaheptyloxy (H7T) triphenylene. These liquid crystal (LC) molecules form nematic and columnar discotic phases. The analysis and the comparison of
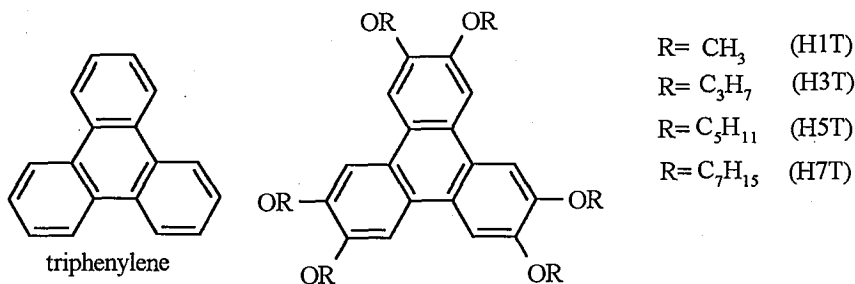

Fig. 1.   Molecular structures of investigated molecules.

the theoretical and experimental spectra for the primary compounds of this homologous series (triphenylene, H1T, and H3T) are helpful in a complete fundamental vibrational assignment and the detailed interpretation of vibrational spectra of large LC molecules (H5T, H7T).

2.2. IR measurement

The experimental spectra for the above compounds were measured in the crystalline phases using BioRad FT-IR 6000 spectrometer. The infrared spectra of triphenylene, the H1T and the H3T in the KBr pellets were measured in the range of 500–4000 cm^{-1} with the spectral resolution of 1 cm^{-1}. Also infrared spectra of the crystalline H5T and the H7T were recorded in the same range for comparison. The LC samples were introduced into the cell by the capillary effect at the temperature a few degrees above the isotropic transition point ($\approx$ 395 K). The thickness of the cell varied from 6 to 11 μm. The IR spectra for both were recorded in the range of 600–4000 cm^{-1}.

2.3. Calculations

All calculations in this study were performed using the 1998 Gaussian suite of program (G98W) [6]. The molecular structures, the harmonic vibrational force constants and absolute IR intensities were calculated by the B3-LYP method (the Becke three-parameter exchange functional in combination with the Lee, Yang and Parr correlation functional) [7, 8] with the 6-31G* basis set [8]. Vibrational force constants were evaluated by analytical calculations of the second derivatives of the molecular potential energy at the corresponding fully optimised geometries. The theoretical DFT force fields were transformed from Cartesian into the local internal co-ordinates using method given by Pulay et al. [9], and then scaled empirically according to the scaled quantum mechanical (SQM) procedure [9–12]:

$$F_{ij}^{\text{scaled}} = (C_i C_j)^{1/2} F_{ij}^{\text{DFT}},$$

where C_i is the scale factor of co-ordinate i, F_{ij}^{DFT} is the B3-LYP/6-31G* force constant in the local internal co-ordinates, and F_{ij}^{scaled} is the scaled force constant. Scaling factors in the SQM method were taken from the set of Rauhut and Pulay [12] (see Table I). The final vibrational frequencies and potential energy distributions (PEDs) were derived by Wilson's GF matrix method [13] from the SQM DFT force fields.

TABLE I

Optimised scaling factors.

Scaling factors	
stretch X–X	0.9254
stretch X–H	0.9182
bend X–X–X	0.9923
bend X–X–H	0.9431
bend H–X–H	0.9171
out-of-plane bends	0.9711
torsion conjugated	0.9389

3. Results and discussion

Experimental and calculated vibrational frequencies for all the molecules are compiled in Table II. In order to improve the visual comparison between experimental and calculated IR spectra, the calculated absorption lines have been replaced by Gaussian functions with a half-width of 5 cm^{-1} (Figs. 2, 3, 4). The theoretical IR intensities were normalised to arbitrary units (100 for the strongest band). The harmonic force constant and frequencies are usually higher than the corresponding experimental quantities (due to the combination of electron correlation effects and limitations of the functional basic set), therefore the scaling procedure is commonly used for the theoretical frequencies set. The calculated

Vibrational frequencies and assignments of triphenylene, H1T, H3T, H5T and H7T.

Triphenylene		H1T		H3T		H5T	H7T	Assignment
obs.[a]	calc.[b]	obs.[a]	calc.[b]	obs.[a]	calc.[b]	obs.[a]	calc.[b]	
ν [cm^{-1}]								
618	630	628	632	670	690	656		$\gamma C_{Ar}-C_{Ar}$
772	768							$\gamma C_{Ar}-H$
779	775	779	776	770	778	768	775	
		834	836	827	823	824	822	$\beta_{as}\, CH_2$
850	854	843	842	840	837	836	837	$\gamma C_{Ar}-H$
				862	867	864	865	νCCC
				892	893	897	913	
994	993	971	972	964	973	980	970	$\beta C_{Ar}-C_{Ar}$
		1021	1038	1035	1027	1031	1043	$\nu_s COC + \nu CCC$
1051	1050	1049	1057	1056	1058	1056	1058	$\beta C_{Ar}-H$
1062	1058	1070	1068	1071	1062	1074	1069	
		1159	1161	1152	1149	1148	1148	$\delta_{as}^- CH_3 + \nu CCC$
		1181	1182	1177	1178	1175	1173	$\gamma_{as} CH_2 + \nu_{as} COC$
1243	1244	1258	1262	1265	1264	1264	1262	$\beta C_{Ar}-H$
				1394	1395	1390	1387	$\gamma_s CH_2$
		1419	1412					$\delta_{as}^+ CH_3$
1433	1436	1435	1438	1440	1444	1440	1439	$\beta C_{Ar}-C_{Ar}$
		1465	1470	1470	1474	1468	1465	$\beta_{as} CH_2$
1503	1501	1521	1520	1521	1521	1517	1516	$\nu C_{Ar}-C_{Ar}$
1603	1610	1620	1615	1620	1615	1618	1616	
				2855	2861	2861	2857	$\nu_s CH_2$
				2938	2943	2936	2928	$\nu_{as} CH_2$
		2904	2894	2877	2897	2874	2874	$\nu_s CH_3$
		2981	3004	2963	2969	2960	2959	$\nu_{as} CH_3$
		3104–3118	3108–3126	3051–3103	3049–3130	3075–3110	3074–3108	$\nu C_{Ar}-H$

[a]From IR spectra crystalline phase (see text).
[b]Frequencies are calculated from the scaled B3-LYP/6-31G* force field.
Key: ν — stretch, νCCC — skeletal, β — in-plane deformation, γ — perpendicular deformation, δ — deformation (δ^--rocking), s, as — symmetric and asymmetric [14].

spectrum was scaled using set of seven scaling factors (see Table I). The most of the fundamentals in the range of 500–2000 cm^{-1} well reproduce vibrations in the experimental spectra. A number of theoretical frequencies are degenerated but they are observed as split peaks in the experimental spectra of the crystalline sample (840, 1210, 1520 cm^{-1} for H1T). There are some frequencies of the neglected intensities in the theoretical spectra, but they are becoming visible in the
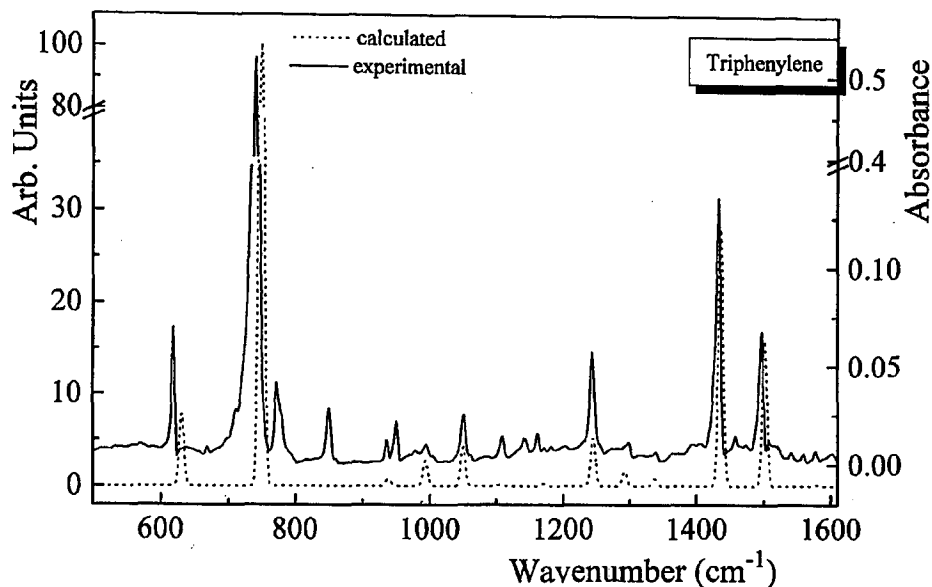
Fig. 2. Experimental and calculated (B3-LYP/6-31G*) infrared spectrum of tripheny-lene.
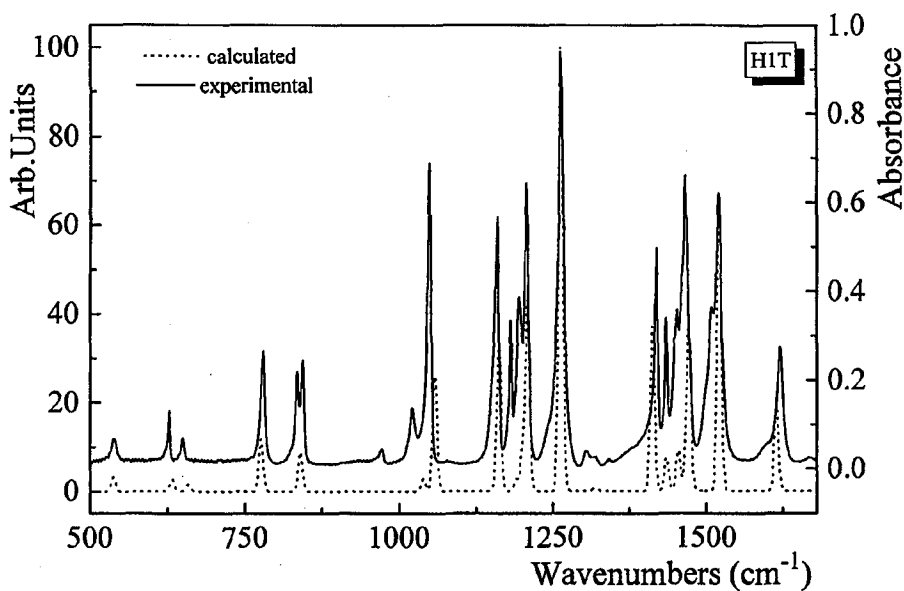

Fig. 3. Experimental and calculated (B3-LYP/6-31G*) infrared spectrum of H1T.

experiment, due to the breaking of symmetry of the molecule in the crystalline phase. The bands in the range of 2900–3100 cm^{-1} are not well reproduced by the
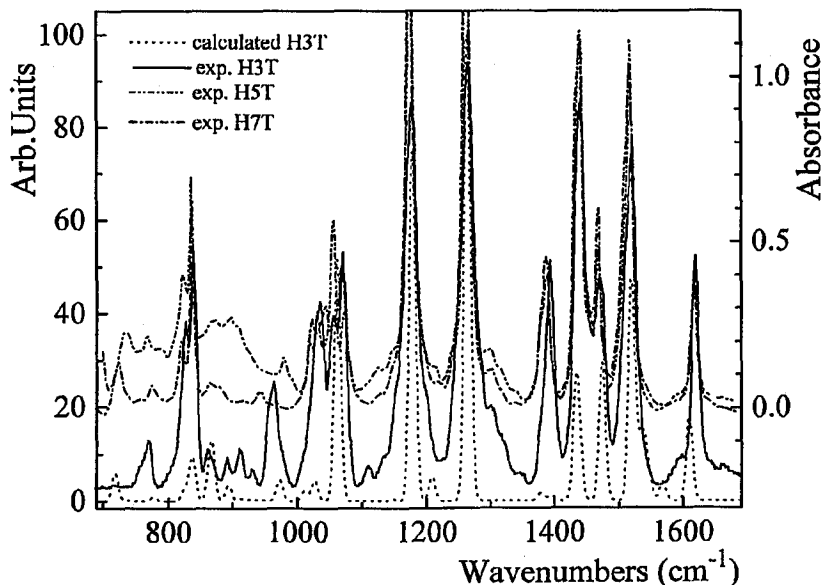
Fig. 4. The comparison of the theoretical (B3-LYP/6-31G*) and experimental spectra
for the H3T, H5T and H7T molecules.

theoretical frequencies. It is due to the strong overlapping of the bands, presence
of the combinational bands and the fact that the C–H stretching frequencies are
largely perturbed by the Fermi resonance effects.

Unfortunately, the H5T and H7T molecules are found to be too large for
ab initio calculations. Therefore only spectra calculated for H3T can be used for
comparison with experimental ones of H3T, H5T and H7T (see Fig. 4). The most
apparent differences are observed in the low frequency range (below 900 cm^{-1}),
which may be affected by manifold of tails conformation and variation of the tail
size. Nevertheless, the theoretical spectra of H3T can practically be applicable in
the band assignment of the whole homologous series starting from $n = 3$.

4. Conclusion

The molecular structure and normal force field have been calculated for
triphenylene and its hexasubstitutes using the B3-LYP/6-31G* method. The usual
scaling procedure of the SQM method was applied to the DFT force field. An
excellent agreement between the theoretical and experimental frequencies has been
observed in the range of 500–2000 cm^{-1}. In contrast, frequencies in the range
of 2900–3100 cm^{-1} are difficult to assign. The results indicate that the density
functional theory is a reliable method of calculation of the fundamentals, and very
useful in obtaining proper assignment of the experimental spectra.

Acknowledgment

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