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Shpol'skii spectroscopy and vibrational analysis of [N]phenylenes

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Vibrationally resolved fluorescence spectra of four angular [N]phenylenes were recorded with laser excited Shpol'skii spectroscopy (LESS) in an *n*-octane matrix at 10 K. In general, the same vibrational frequencies were observed in the fluorescence excitation and emission spectra, indicating that the geometries of ground and electronically excited state are very similar. Because of intensity borrowing from the S₂ state, vibrations of two different symmetries were observed in the fluorescence excitation spectra of angular [3]phenylene and zig-zag [5]phenylene. This finding allowed the location of the S₂ state for these compounds. DFT calculations (RB3LYP/6-31G*) of the ground state vibrational frequencies were made. The calculated vibrational modes were in reasonably good agreement with the experimental data. A new very low-frequency vibration of approximately 100 cm⁻¹ was predicted and experimentally confirmed for all [N]phenylenes investigated. This vibration seems to be unique for [N]phenylenes and is attributed to an in-plane movement of the carbon backbone.

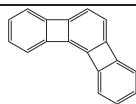
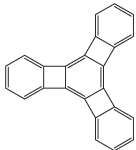
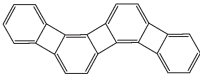
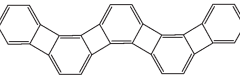
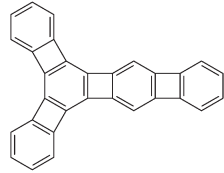
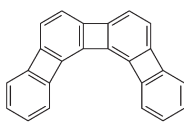
1. Introduction

[N]phenylenes (*N* is the number of benzene units; see Table 1 for structures) are compounds with alternating fused benzene and cyclobutadiene rings. Depending on the arrangement of the rings, a number of topologies can be envisaged, including linear, angular, and branched. Because of the alternating character of aromatic and antiaromatic units according to Hückel's rule, these compounds are of considerable interest from a photophysical and spectroscopic point of view. Depending on the position of the benzene rings, the aromatic character, expressed as the difference in bond length between single and double bonds, and the aromatic ring current, as determined by NICS (nucleus independent chemical shift) calculations,¹ varies. *Ab initio* calculations of the structures of angular [N]phenylenes showed a cyclohexatriene-type bond alternation for the interior benzene rings, which was also confirmed by X-ray structure investigations.²⁻¹¹ In contrast, presumably for reasons of symmetry, bond alternation of the interior benzene rings in linear [N]phenylenes is less pronounced.¹² Interestingly, it was also calculated that angular [N]phenylenes are more stable than linear ones.¹³⁻¹⁶

Recently, photophysical properties of some [N]phenylenes were reported.¹⁷ Using steady-state and time-resolved fluorescence techniques, the fluorescence quantum yields and the rate constants of the radiative and non-radiative deactivation pathways were determined. It was shown that, depending on the geometry of the [N]phenylene, the rate constant of the internal conversion (*k*_{IC}) varied remarkably. Preliminary results showed that the differing behaviour between linear and angular

annelated [N]phenylenes may be related to striking differences in the geometry of the electronic ground and excited states of the former. An exact analysis of ground and excited state vibrations is necessary to obtain an experimental view of the potential energy surfaces of the [N]phenylenes and to verify former theoretical calculations. Unfortunately, the strong spectral overlap of the S₀-S₁ and the S₀-S₂ transitions hampers the analysis of the absorption spectra, especially for the angular [N]phenylenes. Another point of interest is the S₁-S₂ interaction in [N]phenylenes. Theoretical calculations revealed that for the angular [N]phenylenes the S₁-S₂ separation is in the range of only a few hundred cm⁻¹, so that mutual interaction between these two states will be significant. However, the exact 0-0 transition energy of the S₂ state is still unknown for most [N]phenylenes. A detailed fluorescence spectroscopic study could shed light on these phenomena, but, under conventional conditions, the absorption and emission spectra of organic compounds in solution are broad and poorly resolved. Even at ultra-low temperatures, the observed line widths are typically a few hundred wave numbers. However, the line width in optical spectra can be dramatically reduced if the molecules are substitutionally embedded in the lattice of a host crystal.¹⁸ As a result, the observed fluorescence spectrum is no longer broadened by matrix inhomogeneities, and a spectrum with very sharp lines (bandwidths of a few wavenumbers) can be obtained. In Shpol'skii spectroscopy, *n*-alkanes are used as solvents, and for many aromatic organic molecules, such as polycyclic aromatic hydrocarbons (PAHs), a drastic reduction in spectral line width is observed upon cooling to temperatures much below 77 K.^{19,20} It is assumed that the solvent forms

Table 1 Geometric properties of the [N]phenylenes

		Molecular symmetry	Symmetry		Polarization measurement	Φ_F
			Vibrations ^a	S ₁ state		
	Angular [3]phenylene (1)	C _{2v}	a ₁ , b ₂	A ₁	Y	0.07 ^b
	Triangular [4]phenylene (2)	D _{3h}	e'	A ₂ '	n.m. ^c	0.15 ^b
	Zig-zag [4]phenylene (3)	C _{2h}	b _u	A _g	Y	0.12 ^b
	Zig-zag [5]phenylene (4)	C _{2v}	a ₁ , b ₂	A ₁	Y	0.21 ^b
	Branched [5]phenylene (5)	C _{2v}			n.m. ^c	~10 ⁻⁵
	Angular [4]phenylene (6)	C _{2v}	a ₁ , b ₂	B ₂	Y	0.06

^a Shpol'skii active. ^b From ref. 17. ^c Not measured.

a lattice in which the PAHs as guest molecules (analytes) can substitute one or more host molecules, resulting in a limited number of possible *sites*. In the ideal case, all analyte molecules occupy identical substitutional sites in the crystalline matrix, and a single-site spectrum is obtained. However, in the case of different possible orientations of the analyte in the host lattice, each subpopulation of analyte molecules will give rise to its own excitation and emission spectrum. A second possible cause for the formation of distinct sites is the formation of different rotational isomers of the solvent molecules, which will also produce slightly different, but well defined microenvironments for the guests. Both effects are thought to be responsible for the *multiplet* structures observed in fluorescence spectra recorded in Shpol'skii matrices. The 0–0 absorption frequencies of these separate sites will be different, but the vibrational frequencies of each site spectrum will be identical. A broad-banded lamp or a short-wavelength laser tuned to a higher electronic transition can be used to excite all guest molecules in all sites simultaneously. Alternatively, with a narrow-bandwidth laser tuned to a sharp S₀–S₁ absorption line, only a single resonant site may be excited selectively (laser excited Shpol'skii spectroscopy, LESS).

In the present work, the suitability of LESS for [N]phenylenes is demonstrated. Excitation and emission spectra of angular [3]phenylene (1), triangular [4]phenylene (2), zig-zag [4]phenylene (3), and zig-zag [5]phenylene (4) were recorded in *n*-octane at 10 K. These spectra will be shown, and their vibronic and multiplet structures will be discussed. For angular [4]phenylene (6) no Shpol'skii spectrum could be obtained because of insufficient embedding in the *n*-alkane matrices; the fluorescence spectral lines were broadened even at temperatures as low as 10 K. For branched [5]phenylene (5) no fluorescence spectrum in solid phase could be observed; its low fluorescence quantum yield is probably related to

the linear part of the molecule. From theoretical calculations and crystal structure analyses it is known that in the linear systems the internal benzene rings are not deformed into a cyclohexatriene type geometry like their angular relatives.^{2–16} Without this stabilizing deformation, radiationless deactivation becomes very effective, due to a strong perturbation of the aromatic perimeter.

2. Experimental section

The [N]phenylenes were synthesized and characterized according to the methods described previously.^{4–6,17} For the low temperature measurements, the compounds were dissolved in *n*-octane (Fluka, Buchs, Switzerland) at a final concentration of 5 × 10⁻⁶ M. The sample solutions were then transferred to an in-lab built sample holder (sample volume 10 μl each), covered with sapphire windows and mounted on a closed-cycle helium refrigerator (Cryodyne Model 21, CTI Cryogenics, Waltham, MA, USA). Four samples could be cooled simultaneously to 10 K. The sample was illuminated at an angle of 30°. The excitation wavelength was varied between 370 nm < λ_{ex} < 485 nm, using a XeCl excimer laser (LPX 110i, Lambda Physik, Göttingen, Germany) pumping a dye laser (LPD 3002, Lambda Physik, Göttingen, Germany). Different dyes had to be employed for the various excitation wavelength regions (370 to 402 nm with QUI; 401 to 418 nm with Exalite 411; 415 to 435 nm with Exalite 428; 432 to 442 nm with Stilbene 420; 440 to 478 nm with Coumarine 47; 465 to 485 nm with Coumarine 102). The laser system was operated at 20 Hz with a pulse width of 10 ns. The [N]phenylene fluorescence was collected by a 3 cm F/1.2 quartz lens and focused on the entrance slit of a 0.6 m triple monochromator (Spex 1877, Edison, NJ, USA) by a 10 cm F/4 quartz lens. For detection of the emission spectra an intensified CCD camera (576T,

Princeton Instrument; Trenton, NJ, USA;), with a spectral window of 18 nm was used in the gated mode. The gate served to eliminate contributions from scattered light. The spectral resolution was 0.1 nm. For the excitation spectra, which were recorded at a later stage, the detector was replaced with an intensified CCD camera (DH720-25U-03, Andor Technologies, Belfast, Northern Ireland). The latter was also operated in the gated mode.

The excitation spectra were reconstructed from cross-sections through a time series of emission spectra; for each emission spectrum, the fluorescence resulting from 20 laser pulses was accumulated during a one-second period. The dye laser was set at a constant scan rate of 0.05 nm per second.

Polarisation excitation spectra were obtained with a fluorescence spectrometer (Fluoromax 3, Jobin Yvon, Grasbrunn, Germany), equipped with Wollaston prisms. Samples were prepared by impregnating commercial polyethylene sheets with saturated solutions of [N]phenylenes in *n*-hexane. The polyethylene sheets were stretched up to three times the original length and then cooled to 77 K in a cryostat (Optstat DN1704, Oxford Instruments, Wiesbaden, Germany).

The fundamental vibrations of the [N]phenylenes were also computed. Geometry optimizations and frequency calculations were carried out with density functional theory (DFT) using the B3LYP²¹ method and the 6-31G* basis set,²² as implemented in the Gaussian 98 program.²³ The results were normalized using the scaling factor determined in ref. 24

3. Results and discussion

The four [N]phenylenes 1–4 (see Table 1 for structures) were successfully investigated using Shpol'skii spectroscopy. In preliminary experiments at 77 K, *n*-pentane, *n*-hexane, *n*-heptane, *n*-octane, and *n*-nonane were tested as solvents. The best results were obtained in *n*-octane; the other *n*-alkanes generated only poorly resolved spectra. After cooling the *n*-octane samples to 10 K, highly resolved fluorescence emission and fluorescence excitation spectra could be recorded, except for branched [5]-(5) and angular [4]phenylene (6). For the emission spectra, the samples were excited at 365 nm, which, for all compounds, corresponded to higher excited states, and thus no site selection was applied. A multiple-site structure was found in most of the recorded emission spectra. The origin of this observation may be either the presence of differing conformations of the frozen *n*-octane chains around the analyte or multiple orientations of the target in the *n*-octane lattice.

3.1. Symmetry properties and investigations in stretched polyethylene sheets

The structures and symmetry properties of [N]phenylenes investigated are summarized in Table 1. According to group theoretical considerations, the absorption spectrum of triangular [4]phenylene (D_{3h}) should consist of one strictly forbidden longest wavelength transition ($A_1' \rightarrow A_2'$) and four doubly degenerate symmetry allowed transitions ($A_1' \rightarrow E'$), which is in good agreement with experiment.¹⁷ Thus, the fluorescence of triangular [4]phenylene originates from a $A_2' \rightarrow A_1'$ transition. The S_1 -state symmetries of the other [N]phenylenes under investigation were derived from polarisation excitation spectra in stretched polyethylene sheets. The room-temperature absorption spectra of angular [3]-(1) and the zig-zag [N]phenylenes (3) and (4) show a common structure. The longest wavelength absorption is weakly polarized along the short molecular axis, whereas the other transitions are all strongly polarized along the long molecular axis, as shown for angular [3]phenylene in Fig. 1.

From group theoretical considerations, the S_0 - S_1 transition for the homologue series of the zig-zag [N]phenylenes should be $A_1 \rightarrow A_1$ for $N = \text{odd}$ (C_{2v}) and $A_g \rightarrow A_g$ for $N = \text{even}$

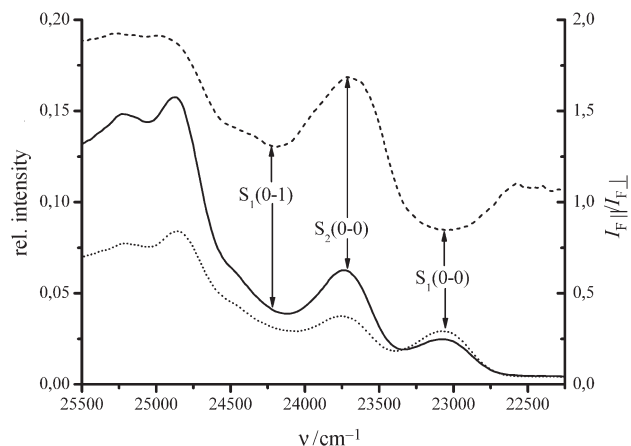


Fig. 1 Fluorescence excitation spectra of (1) ($\lambda_{em} = 480$ nm) in a polyethylene film at 77 K. The measurements were performed with polarization of the excitation light parallel (solid) and perpendicular (dotted) to the direction of stretching. The dashed line corresponds to $I_{||}/I_{\perp}$.

(C_{2h}). The symmetries of the fundamental vibrations which should be observable in the fluorescence spectra can be derived from the appropriate character tables (see Table 1).

3.2. Angular [3]phenylene (1)

In Fig. 2, the fluorescence emission and the site-selective excitation spectra of angular [3]phenylene are shown. In the first, a very regular vibrational pattern was observed which can be attributed either to multiple sites (fortuitously equally spaced in energy), a sequence of fundamental vibrations, or to a combination of fundamental vibrations with a low-frequency vibrational progression. To distinguish between these possible explanations, the excitation spectrum was reconstructed from cross-sections at different emission wave numbers, $\nu_{em} = 22518, 22613$ and 22729 cm^{-1} , respectively. Identical excitation spectra were obtained. This result indicates that the observed vibrational pattern is due to a single site of angular [3]phenylene, otherwise wavelength-shifted excitation spectra would have been expected for the different emission wave numbers. Therefore, the pattern in the emission (excitation) spectrum can either be attributed to a low-frequency progression with a vibrational energy of $\nu \sim 115$ cm^{-1} , showing up at 117 (115), 232 (229), and 346 (340) cm^{-1} , or to a number of

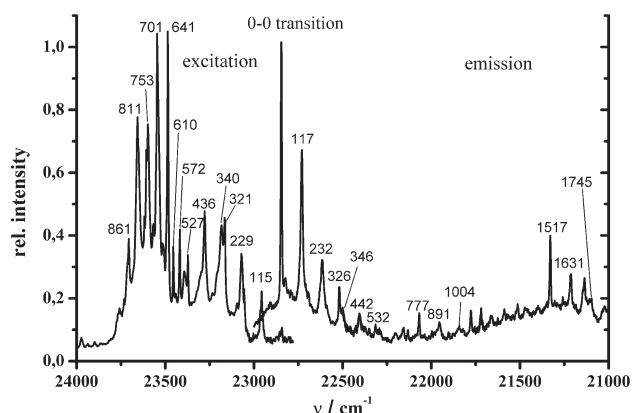


Fig. 2 Fluorescence and fluorescence excitation spectrum of (1) in *n*-octane at 10 K. The numbers are the energy differences (in cm^{-1}) relative to the 0-0 transition. The fluorescence excitation spectrum shown was recorded at $\lambda_{em} = 442$ nm. The emission spectrum was recorded at $\lambda_{ex} = 365$ nm. The intensities in the excitation spectrum are not corrected for the different laser energies.

fundamental vibrations. The former interpretation is tempting, since, in the emission spectrum, the 115 cm⁻¹ progression can also be observed for the 326 cm⁻¹ vibration, the deformation vibration at 777 cm⁻¹, and for the C=C stretching mode at 1517 cm⁻¹ (see Table 3). The same low-frequency progression was also found in the first part of the excitation spectrum.

On the other hand, a theoretical calculation of the fundamental vibrations of angular [3]phenylene also seemed to agree with the experimental observations. According to the C_{2v} character table for angular [3]phenylene, only vibrations of a₁ and b₂ symmetry should be visible (see Table 1). Table 2 shows the calculated fundamental vibrations of angular [3]phenylene up to 1000 cm⁻¹, revealing only small deviations from the measured data. On the basis of these results, it could also be argued that the observed vibrations in the fluorescence emission Shpol'skii spectrum of angular [3]phenylene (and also in the fluorescence excitation spectrum) should be assigned to fundamental vibrations of the molecule.

A closer look at the experimental and calculated frequencies shows that an especially good agreement is found for the vibrations with a₁ symmetry, larger discrepancies appearing for those with b₂ symmetry, which could indicate that the latter are, in fact, progressions of the a₁ fundamental vibrations as indicated in Table 3 (right column).

For angular [3]phenylene the same vibrational frequencies were observed in the fluorescence excitation and emission spectra. This indicates that for angular [3]phenylene the geometries of the ground state S₀ and the first excited singlet state S₁ are very similar. The 0–0 transition was found at 22 846 cm⁻¹ in the emission spectrum. In Table 3, the wave numbers of the vibrations relative to the 0–0 transition found in the excitation and emission spectrum are compared. Especially for the first part (up to about 550 cm⁻¹), a very good agreement between the vibrational patterns in both spectra is evident, indicating only small changes in molecular geometry after electronic excitation. In Fig. 2, in the excitation spectrum (see also Table 3), a

Table 2 Computed (B3LYP/6-31G*) Shpol'skii active vibrational frequencies (in cm⁻¹) of (1)–(4) up to 1000 cm⁻¹

(1)	(2)	(3)	(4)
105 (a ₁)	101 (e')	70 (b _u)	48 (a ₁)
246 (b ₂)	333	269	113 (b ₂)
313 (a ₁)	412	397	150 (a ₁)
410 (b ₂)	548	558	243 (a ₁)
514 (a ₁)	588	587	280 (b ₂)
591 (b ₂)	616	647	359 (b ₂)
592 (a ₁)	697	725	403 (b ₂)
612 (b ₂)	731	808	412 (a ₁)
664 (b ₂)	863	931	513 (a ₁)
677 (a ₁)	984	981	539 (b ₂)
765 (a ₁)	1015	992	587 (b ₂)
848 (b ₂)			592 (a ₁)
934 (a ₁)			594 (a ₁)
			624 (a ₁)
			632 (b ₂)
			643 (b ₂)
			684 (b ₂)
			698 (a ₁)
			752 (a ₁)
			775 (b ₂)
			844 (a ₁)
			914 (b ₂)
			928 (a ₁)
			942 (b ₂)
			972 (a ₁)
			979 (b ₂)
			986 (b ₂)
			986 (a ₁)

Table 3 Experimental vibrations of angular [3]phenylene in *n*-octane at 10 K. The error in the emission wave numbers is ±5 cm⁻¹

	Emission	Excitation	Progression ν ~ 115 cm ⁻¹
0–0 transition/cm ⁻¹	22 846	22 842	0
Δν/cm ⁻¹	117	115	1
	232	229	2
	326	321	1 ^a
	346	340	3
	442	436	2 ^a
	532	527	1 ^b
	553	545	3 ^a
	—	572	
	—	610	
	648	641	(2 ^b)
	691	672	
	715	701	
	777	753	1 ^c
	—	811	
	891	861	2 ^c
	942	917	
	1004	—	3 ^c
	1026	—	
	1068	1059	
	1126	1134	
	1182	1182	
	1221	—	
	1259	1254	
	1333	1296	
	1375	1360	
	—	1413	
	1449	1480	
	1517	—	1 ^d
	1587	1569	
	1631	—	2 ^d
	1658	1650	
	—	1685	
	1710	—	
	1745	—	3 ^d

second group of strong vibrations is present which is not seen in the corresponding emission spectrum. Presumably, these correspond to vibrations with b₂ symmetry, which are under normal circumstances of low intensity. However, due to mixing with the S₂ state (B₂ symmetry) they are increased by intensity borrowing and are therefore observed in the excitation spectrum. This is supported by the polarization spectrum (see Fig. 1), which shows that the S₂ state is located in this region.

On the basis of these considerations, it is concluded that the observed vibrational pattern in the angular [3]phenylene emission spectrum is a combination of fundamental vibrations (a₁ symmetry) and a short progression (see Table 3).

3.3 Zig-zag [5]phenylene (4)

Zig-zag [5]phenylene belongs to the same symmetry group as angular [3]phenylene (C_{2v}), and therefore vibrations with the same symmetry (a₁ and b₂) can be expected (see Tables 1 and 2). The 0–0 transition of the main site is located at 20 670 cm⁻¹. While for angular [3]phenylene a single site structure was observed in the Shpol'skii emission spectrum, for zig-zag [5]phenylene in the fluorescence emission spectrum a multiplet structure was found under non-selective excitation conditions, and the first major fundamental vibration is seen at 252 cm⁻¹ (see Fig. 3). In the excitation spectrum two minor vibrations can be seen at 124 cm⁻¹ and 163 cm⁻¹, which are hidden in the emission spectrum by the site structure of the intense 0–0 transition.

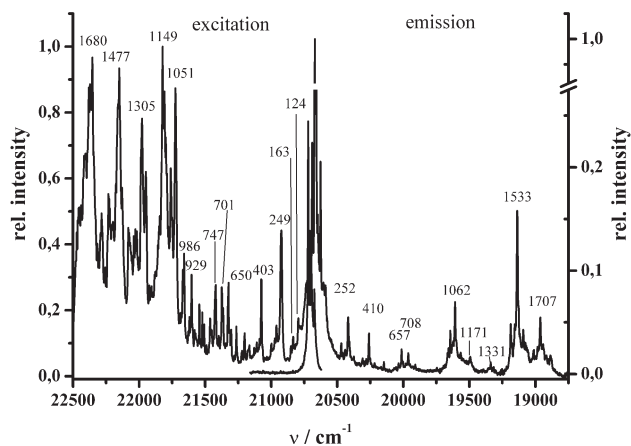


Fig. 3 Comparison of the vibrations in the site-selective fluorescence excitation spectrum ($\lambda_{\text{em}} = 522$ nm) and the fluorescence spectrum ($\lambda_{\text{ex}} = 365$ nm) of (4) in *n*-octane at 10 K. The intensities in the excitation spectrum are not corrected for the different laser energies.

Most likely, the observed pattern originates from fundamental vibrations, which is in good agreement with the theoretical calculations (see Table 2). Similar to what is observed in the case of angular [3]phenylene, it seems that the vibrations with a_1 symmetry are dominant in the emission spectrum and the first part of the excitation spectrum. Again, the observed frequencies of the ground and first electronically excited state are highly similar. Due to intensity borrowing from the S_2 state, the b_2 vibrations become more pronounced in the excitation spectrum (starting around 21 300 cm^{-1}). This finding indicates that the energy difference between the S_1 and S_2 states is larger for the zig-zag [5] compared to angular [3]phenylene. A progression, as found for angular [3]phenylene, was not detected for zig-zag [5]phenylene.

3.4 Triangular [4]phenylene (2)

For triangular [4]phenylene (D_{3h}), a multiplet structure of four different sites was observed, as could be confirmed by spectrally shifted excitation spectra. The spectral analysis was more difficult than for angular [3]phenylene because of overlapping multiplets, especially at higher vibrational frequencies. The 0–0 transition of the strongest emitting site was located at 22 690 cm^{-1} . The vibronic transitions corresponding to this major site were readily identified throughout the emission spectrum and their frequencies were determined (see Fig. 4).

Of the modes indicated by the computational results (numbers given in brackets), only the fundamental vibrations of e' symmetry, e.g., at 102 (101), 341 (333), and 558 (548) cm^{-1} , are observed. No progression, as in the case of angular [3]phenylene, was found in either the emission or the excitation spectrum (see also Table 2). According to the character table, only vibrations of e' symmetry are allowed. A mirror image relationship of the vibronic frequencies is observed, which suggests that there are only small differences in geometry between ground and electronically excited state.

3.5 Zig-zag [4]phenylene (3)

In Fig. 5, the fluorescence emission as well as the excitation spectrum of zig-zag [4]phenylene (C_{2h}) in *n*-octane are shown. The first shows a multiplet of at least five sites when using non-selective excitation. The second was reconstructed for site-selective conditions and shows mostly a single site.

From theoretical considerations, only vibrations of b_u symmetry should be evident. On comparing the observed vibrational frequencies in the emission spectrum with those

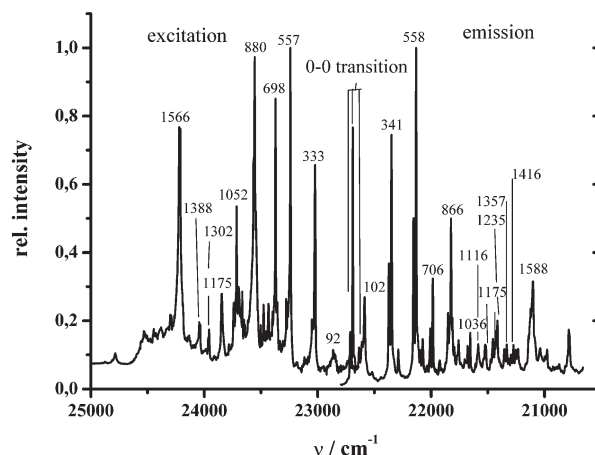


Fig. 4 Fluorescence emission spectrum of (2) in *n*-octane at 10 K ($\lambda_{\text{ex}} = 365$ nm). At least three different sites can be identified. The energy differences given in wave numbers (cm^{-1}) were calculated for the dominant site (0–0 transition at 22 690 cm^{-1}). The fluorescence excitation spectrum was obtained for $\lambda_{\text{em}} = 452$ nm. The intensities in the excitation spectrum are not corrected for the different laser energies.

calculated, including those of the other [*N*]phenylenes investigated (see Table 2), one finds only partial agreement.

In particular, in the site-selective excitation spectrum of zig-zag [4]phenylene in the range between 150 $\text{cm}^{-1} < \Delta\nu < 500$ cm^{-1} , vibrations are detected that are not predicted by computation as fundamental vibrations. Those bands most probably correspond to combinations of low frequency fundamental vibrations of a_u and b_g symmetry, which are predicted by the calculations. In particular, the combinations of the a_u vibration located at 71 cm^{-1} and b_g vibrations at 87 cm^{-1} , 351 cm^{-1} and 460 cm^{-1} are causing the observed bands in the fluorescence excitation spectrum at 151 cm^{-1} , 421 cm^{-1} and 531 cm^{-1} , respectively.

4. Conclusions

The Shpol'skii spectra of the [*N*]phenylenes were also compared with those of related polycyclic aromatic hydrocarbons (PAHs; taken from ref. 19). The main vibrations of organic molecules containing six-membered aromatic rings—namely the C–H in-plane deformation around 1100 cm^{-1} and the C=C stretching modes around 1500 cm^{-1} —are present in the Shpol'skii spectra of both compound classes. However, on

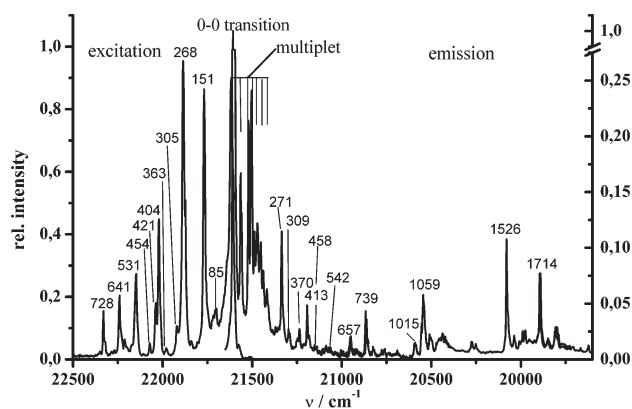


Fig. 5 Comparison of the vibrations in the site-selective fluorescence excitation spectrum ($\lambda_{\text{em}} = 487$ nm) and the fluorescence spectrum ($\lambda_{\text{ex}} = 365$ nm) of (3) in *n*-octane at 10 K. The intensities in the excitation spectrum are not corrected for the different laser energies.

closer inspection, there is only a tentative correspondence between the frequencies of the fundamental vibrations of angular [*N*]phenylenes and those of PAHs. Specifically, PAHs do not exhibit signals in the low frequency region of approx. 100 cm⁻¹. Moreover, for phenanthrene, which could be considered as the PAH analogue of angular [3]phenylene, there is no vibrational progression in the Shpol'skii spectra.¹⁹

For all [*N*]phenylenes investigated, the theoretical calculations were confirmed by the experimental results within an uncertainty of ~20 cm⁻¹ and can therefore be used for assignment of the observed vibrations. The fundamental vibrations of the S₀ state are also present in the S₁ state. As their values do not differ much, at least up to 1000 cm⁻¹, the shapes of the potential energy surfaces of these two states are presumed to be very similar for angular annelated [*N*]phenylenes. In addition, their geometries are very close, as evident from the intensity of the 0–0 transitions in the emission spectra. For such systems, the barrier for thermally induced internal conversion (IC) is usually very high. This would explain the low rate constant of radiationless deactivation *k*_{IC} for these compounds. With respect to the linear [*N*]phenylenes, further investigation are necessary to prove the influence of geometric changes caused by relaxation after electronic transitions on *k*_{IC}.

In the S₁–S₂ overlap region, vibrations of appropriate symmetry are enhanced by intensity borrowing. This effect causes the striking intensity differences between emission and excitation spectra which can be observed especially for angular [3]phenylene and zig-zag [5]phenylene. From these results and the polarization studies of the angular annelated [*N*]phenylenes in polyethylene sheets, the position of the S₂ transition can be estimated with an uncertainty of approx. 100 cm⁻¹. The S₁–S₂ separation for the [*N*]phenylenes investigated is in the range of only a few hundred wave numbers ($\Delta E(S_1-S_2) = 575$ cm⁻¹ for (1), 620 cm⁻¹ for (2), 230 cm⁻¹ for (3) and 700 cm⁻¹ for (4)).

The calculations pinpoint the geometric changes connected to a distinct vibrational mode. The computationally predicted, and for (1)–(4), experimentally verified low frequency vibrations of the angular annelated [*N*]phenylenes are of special interest. Based on the DFT calculations these vibrations can be attributed to an in-plane movement of the carbon backbone, which leads to a widening of the angle α defined by the respective vectors between the centroids of three successive benzene rings (Fig. 6).

Fig. 6 depicts this distortion and the connected change in the molecular geometry of (1). This vibration pattern can be observed for all other angular annelated [*N*]phenylenes. The fixed point moves towards the interior benzene moiety for (2), (3) and (4). The value of α is increased from 120° to 129°. This vibration is a unique feature of angular [*N*]phenylenes and is significant for the understanding of the configurational lability of the recently reported helical [*N*]phenylenes. These

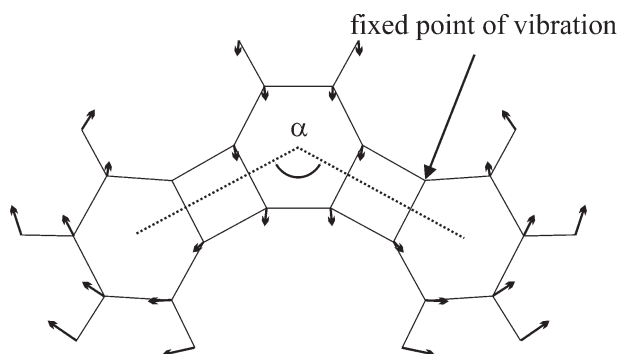


Fig. 6 The calculated in-plane movement of the terminal rings in (1) for the 105 cm⁻¹ vibration. The arrows indicate the atomic movements for one half period. The fixed points of vibration move towards the interior rings for higher oligomers. The deviation of the angle α is $\pm 9^\circ$.

substances, unlike their helical polyarene counterparts, the helicenes, undergo ready enantiomerisation,^{10,11} a property that was attributed to their facile out-of-plane deformability. This deplanarisation of [*N*]phenylenes was already observed in the crystal structures of substituted [*N*]phenylenes,²⁵ and in our calculations we also found the low frequency out-of-plane vibrations ((1): 57 cm⁻¹, (2): 45 cm⁻¹, (3): 30 cm⁻¹ and (4): 19 cm⁻¹), which have been reported previously.¹⁴ The present work adds another rationale and, indeed, both types of distortion may be involved in the transition states for racemisation. The calculations show that similar low frequency in-plane vibrations at ~100 cm⁻¹ are also present in the helical [*N*]phenylenes. An in-plane distortion was already proposed as transition state for the racemisation of helical[6]-phenylene.²⁶ Finally, a deformation along the geometric lines defined by this vibration has been described in the X-ray structure of a “clamped” biphenylene.²⁷

Present work is concerned with the study of deuterated [*N*]phenylenes in order to quantify the influence of the isotopic change on their spectroscopic behavior. In combination with DFT calculations the different observed vibrations can be clearly attributed to certain atom movements.

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