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Photophysical Properties of [N]Phenylenes

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In the present study, photophysical properties of [N]phenylenes were studied by means of stationary and time-resolved absorption and fluorescence spectroscopy (in THF at room temperature). For biphenylene (**1**) and linear [3]phenylene (**2a**), internal conversion (IC) with quantum yields $\Phi_{IC} > 0.99$ is by far the dominant mechanism of S_1 state deactivation. Angular [3]phenylene (**3a**), the zig-zag [4]- and [5]phenylenes (**3b**), (**3c**), and the triangular [4]phenylene (**4**) show fluorescence emission with fluorescence quantum yields and lifetimes between $\Phi_F = 0.07$ for (**3a**) and 0.21 for (**3c**) and $\tau_F = 20$ ns for (**3a**) and 81 ns for (**4**). Also, compounds (**3**) and (**4**) exhibit triplet formation upon photoexcitation with quantum yields as high as $\Phi_{ISC} = 0.45$ for (**3c**). The strong differences in the fluorescence properties and in the triplet formation efficiencies between (**1**) and (**2a**) on one hand and (**3**) and (**4**) on the other are related to the remarkable variation of the internal conversion (IC) rate constants k_{IC} . A tentative classification of (**1**) and (**2a**) as “fast IC compounds”, with $k_{IC} > 10^9$ s⁻¹, and of (**3**) and (**4**) as “slow IC compounds”, with $k_{IC} \approx 10^7$ s⁻¹, is suggested. This classification cannot simply be related to Hückel’s rule-type concepts of aromaticity, because the group of “fast IC compounds” consists of “antiaromatic” (**1**) and “aromatic” (**2a**), and the group of “slow IC compounds” consists of “antiaromatic” (**3b**), (**4**) and “aromatic” (**3a**), (**3c**). The IC in the [N]phenylenes is discussed within the framework of the so-called energy gap law established for non-radiative processes in benzenoid hydrocarbons.

1. Introduction

Characteristic structural features of the [N]phenylenes are alternating fused benzene and cyclobutadiene rings which can be arranged in linear, angular or branched geometries. N signifies the number of benzene units. According to Hückel's rule, the series of [N]phenylenes consists of "antiaromatic" and "aromatic" molecules, the investigation of which is of considerable photophysical and spectroscopic interest. Starting from the parent compound biphenylene (**1**), linear, angular, or branched annelation leads to series of oligomers, namely the linear [N]phenylenes (**2**) and angular annelated compounds including the so-called zig-zag [N]phenylenes (**3**), and, e. g., the branched triangular [4]phenylene (**4**), which has also been named starphenylene (cf. Fig. 1). The synthesis and characterization of larger [N]phenylenes has only been achieved recently (see refs. 1-5 and references therein).

Biphenylene (**1**), first synthesized in 1941,⁶ is a representative alternant, anti-aromatic molecule. Therefore, it has been an object of detailed theoretical and photophysical investigations, and ground and excited state as well as absorption and emission properties are well described.⁷⁻¹⁴ Biphenylene is only weakly fluorescent (in solution, under ambient conditions, fluorescence quantum yields of ca. $\Phi_F = 2 \cdot 10^{-4}$ were reported^{13, 15, 16}), and direct excitation produces only very little triplet state population (with an intersystem crossing quantum yield Φ_{ISC} of less than 10^{-2}).¹⁷⁻²⁰ The charge transfer properties of biphenylene have also found interest, and the structure of its radical cation, as well as inter- and intramolecular electron transfer in biphenylene-containing compounds have been studied.²¹⁻²³ As to the photophysical behaviour of the two [3]phenylenes, Niemeyer has revealed striking differences (in cyclohexane at room temperature): Whereas linear [3]phenylene (**2a**) was found to be non-fluorescent ($\Phi_F < 10^{-5}$), angular [3]phenylene (**3a**) exhibited moderate fluorescence emission ($\Phi_F = 0.047$).²⁴ Larger [N]phenylenes have not yet been subject of detailed spectroscopic studies. To our knowledge the spectroscopic properties of zig-zag [4]- and [5]phenylenes (**3b**), (**3c**), and the triangular [4]phenylene (**4**) are presented for the first time here. The higher oligomers of the linear [N]phenylenes, such as (**2b**) and (**2c**), are not stable under ambient conditions and have not been isolated in unsubstituted form up to now.

There have been various quantum chemical studies on biphenylene and its oligomers, e. g. with emphasis on the "interplay of aromaticity, antiaromaticity, and Baeyer strain".²⁵ Semi-empirical and ab-initio calculations predict that, in comparison to the the linear [N]phenylenes, the zig-zag [N]phenylenes will exhibit much larger HOMO-LUMO separa-

tions, slightly reduced resonance energies, and electronic structures characterized by increased bond localization in the inner benzene rings.²⁵⁻²⁷ ¹H NMR chemical shifts confirm that the aromatic character of the zig-zag [N]phenylenes is reduced due to localisation of the inner benzene rings.²⁸ X-ray structure analysis data show also a strong alternance of the C-C bond length in the central rings of the zig-zag [N]phenylenes.^{5, 29}

In the present work, photophysical investigations of the linear and angular [3]phenylenes (**2a**), (**3a**), the zig-zag [4]- and [5]phenylenes (**3b**), (**3c**), and the triangular [4]phenylene (**4**) were performed (Fig. 1). For comparison, experimental studies of biphenylene (**1**) and quantum chemical calculations were also included.

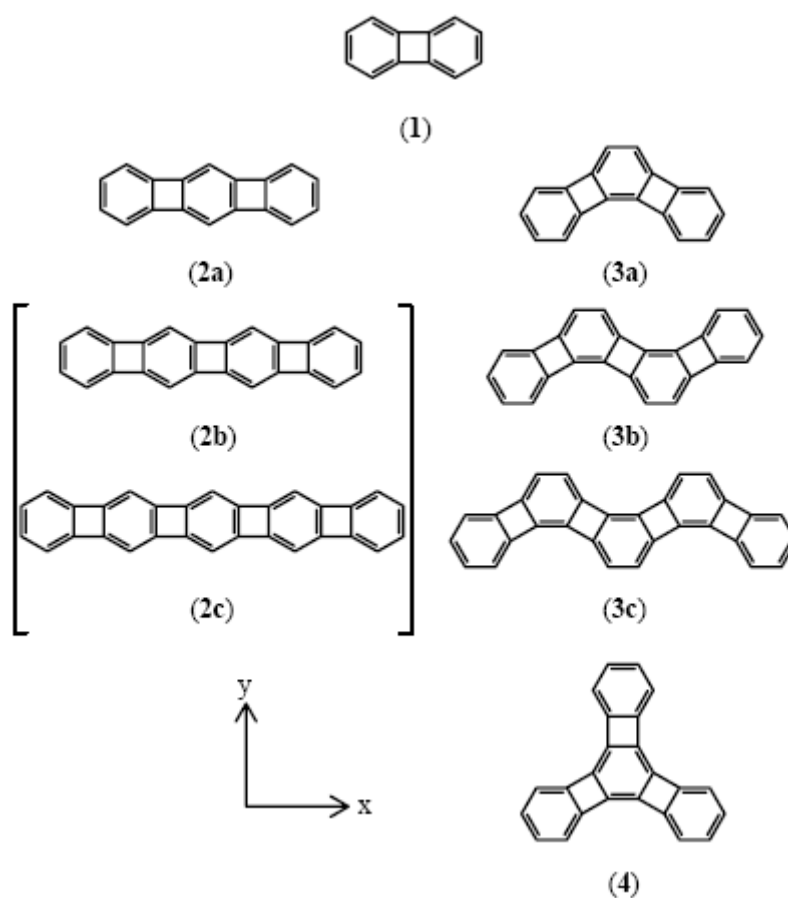


Fig. 1 Structure of [N]phenylenes

2. Experimental details

The [N]phenylenes, except the commercially available biphenylene (**1**), were synthesized and characterized according to the methods described previously.^{3, 5, 29, 30} Biphenylene, tetracene, rubrene and perylene were purchased from Aldrich (Sigma-Aldrich Chemie, Munich, Germany) and used without further purification. The solvents used were HPLC-grade, degassed

by evaporation in an ultrasonic bath and saturated with argon. The samples were prepared under argon and sealed in 10 x 10 mm quartz cells. Sample concentrations were 10^{-6} M to 10^{-4} M for absorption measurements and 10^{-6} M to 10^{-5} M for fluorescence measurements. If not denoted otherwise, all measurements were made at 298 K in tetrahydrofuran (THF).

Absorption spectra were obtained with a Cary 500 UV-VIS-NIR spectrophotometer (Varian Inc., Palo Alto, USA).

Stationary fluorescence measurements were performed with a FL920 fluorimeter (Edinburgh Instruments LTD, Livingston, United Kingdom) using a high pressure xenon lamp or a frequency-doubled titanium sapphire laser (Tsunami 3960; Spectra Physics, Mountain View, USA) as excitation light sources. Fluorescence quantum yields (Φ_F) were determined with perylene ($\Phi_F = 0.98$ in cyclohexane³¹) or angular [3]phenylene in THF as reference compounds. Time-correlated single-photon counting measurements were carried out with the FL920 fluorimeter using a hydrogen flash lamp (nF 900; Edinburgh Instruments) for excitation. The fluorescence lifetime (τ_F) of biphenylene was measured with a gated CCD camera-system (Picostar F; La Vision, Göttingen, Germany; gate width 130 ps). The samples were excited at 355 nm with pulses of ca. 30 ps duration from a mode-locked Nd-YAG-laser (5021 DNS/DPS 10 in ps operation mode; B.M. Industries, Evry, France).

Low-temperature measurements were performed in methyl-tetrahydrofuran glass at 77 K in an Optistate DN1704 cryostat (Oxford Instruments, Wiesbaden, Germany).

For time-resolved absorption measurements the samples were excited with pulses of ca. 6 ns duration from a Q-switched Nd-YAG-laser (5021 DNS/DPS 10 in ns operation mode) at 355 nm with pulse energies of ca. 600 μ J. The detection of transient absorption signals was performed with a probe beam from a high pressure xenon lamp and the usual combination of monochromator, photomultiplier and digital storage oscilloscope. The triplet extinction coefficients ϵ_T were determined in sensitization experiments with rubrene in THF (T_1 state energy $E(T_1) = 9,300 \text{ cm}^{-1}$, $\epsilon_T = 32,200 \text{ M}^{-1} \text{ cm}^{-1}$ at 485 nm) as triplet acceptor.³² The intersystem crossing quantum yields were measured with the reference excitation method relative to tetracene in hexane ($\epsilon_T = 57,900 \text{ M}^{-1}$ at 465 nm, $\Phi_{ISC} = 0.66$)^{33,34}

Semi-empirical PECE calculations (pair excited configuration interaction) were performed with Vamp 7.0 at the PM3 level.³⁵ Optimized geometries were obtained with Gaussian 98 in the 6-31G* basis at the RB3LYP density functional level.

3. Results and discussion

3.1 Singlet absorption and fluorescence properties

Representative singlet absorption and fluorescence spectra of the compounds under investigation are displayed in Figs. 2 – 4, and their photophysical properties are summarized in Table 1.

Compound Parameter	Biphenylene (1)	Linear [3]phenylene (2a)	Angular [3]phenylene (3a)	Zig-zag [4]phenylene (3b)	Zig-zag [5]phenylene (3c)	Triangular [4]phenylene (4)
$\epsilon_S/10^3 \text{ M}^{-1} \text{ cm}^{-1}$ ($\lambda_{\text{max}}/\text{nm}$) ^a	0.12 ± 0.01 (392)	0.15 ± 0.05 (538)	0.90 ± 0.05 (428)	1.92 ± 0.40 (465)	2.45 ± 0.50 (484)	0.19 ± 0.01 (439)
$E(S_1)/10^3 \text{ cm}^{-1}$ ^b	≈ 24.0 ^c	≈ 17.0 ^d	23.0	21.5	20.7	22.7
Stokes shift/ cm^{-1}	4750	-	750	70	65	150
Φ_F	(2.6 ± 0.3)·10 ⁻⁴	<10 ⁻⁶	0.07 ± 0.01	0.12 ± 0.02	0.21 ± 0.03	0.15 ± 0.02
τ_F/ns	0.23 ± 0.03	≈ 0.03 ^e	20 ± 2	49 ± 2	62 ± 2	81 ± 2
$\tau_{F,0}/\text{ns}$ ^f	900 ± 100	-	290 ± 50	410 ± 70	295 ± 45	540 ± 70
$\epsilon_T/10^3 \text{ M}^{-1} \text{ cm}^{-1}$ ($\lambda_{\text{max}}/\text{nm}$) ^g	10 (339) ^h	-	16 ± 5 (430)	28 ± 5 (585)	75 ± 10 (685)	12 ± 3 (715)
Φ_{ISC}	< 0.01 ^h	< 0.01	0.30 ± 0.10	0.25 ± 0.05	0.45 ± 0.05	0.30 ± 0.10
k_F/s^{-1} ⁱ	1·10 ⁶	> 3·10 ⁵	4·10 ⁶	2·10 ⁶	3·10 ⁶	2·10 ⁶
$k_{\text{ISC}}/\text{s}^{-1}$ ⁱ	< 4·10 ⁷	< 3·10 ⁸	2·10 ⁷	4·10 ⁶	7·10 ⁶	4·10 ⁶
$k_{\text{IC}}/\text{s}^{-1}$ ⁱ	4·10 ⁹	≈ 3·10 ¹⁰ ^e	3·10 ⁷	1·10 ⁷	6·10 ⁶	1·10 ⁷

Table 1 Photophysical properties of [N]phenylenes in THF at room temperature

^a Extinction coefficients of first singlet absorption feature at the wavelengths given in parentheses. ^b S_1 state energy. ^c From vibrational analysis of fluorescence spectrum (ref. 10) or two-photon absorption spectroscopy (ref. 37). ^d From vibrational analysis of absorption spectrum (cf. text). ^e From ref. 24. ^f Calculated radiative lifetimes. ^g Extinction coefficients of triplet absorption at the wavelengths given in parentheses. ^h From refs. 17-20. ⁱ Estimated uncertainties of the rate constants are below ca. ± 30 %.

The singlet absorption and fluorescence emission spectra of angular [3]phenylene (**3a**) in THF at room temperature are shown in Fig. 2, in which the absorption spectra of biphenylene (**1**) and linear [3]phenylene (**2a**) are also displayed. This is to illustrate the previously already described much stronger red-spectral shift, relative to biphenylene (**1**), found for the linear isomer.³⁰ It is this behaviour, predicted by HOMO/LUMO calculations, that led to the interesting conjecture that infinite linear [N]phenylenes may behave as quasi one-dimensional organic conductors.²⁶

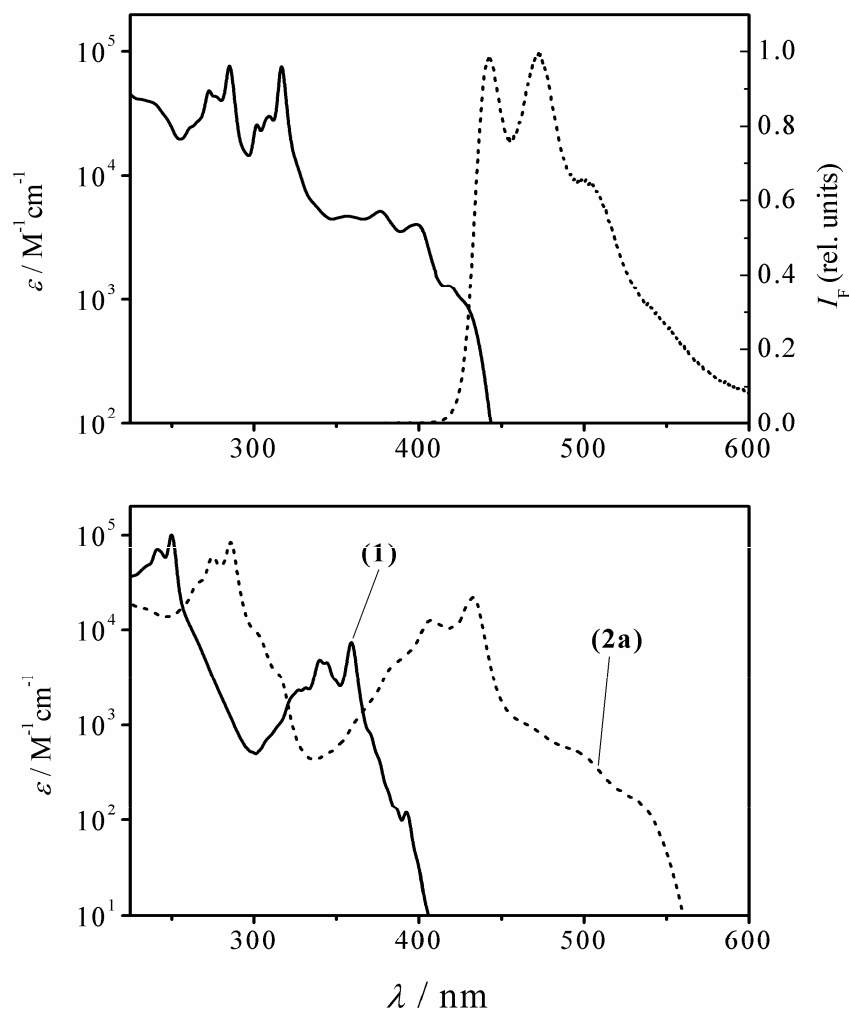


Fig. 2 Logarithmic singlet absorption (solid) and fluorescence emission (dashed) spectra of angular [3]phenylene (**3a**) in THF at room temperature (upper part). For comparison, the logarithmic absorption spectra of biphenylene (**1**) and linear [3]phenylene (**2a**) are also shown (lower part).

The rich spectral features, particularly at low temperatures, in the singlet absorption or fluorescence excitation and fluorescence emission spectra of the zig-zag [4]- and [5]phenylenes (**3b**), (**3c**) and the triangular [4]phenylene (**4**) are illustrated in Figs. 3 - 5. The electronic S_0 - S_1 transition in biphenylene (**1**) is of B_{1g} symmetry and thus one-photon forbidden.³⁶ For the determination of the S_1 state energy, the vibronic 0-0 transition has been located at $E(S_1) \approx 23,900 \text{ cm}^{-1}$, by vibrational analysis of the fluorescence emission spectrum (in rigid glass at 130 K)¹⁰, and at ca. $24,000 \text{ cm}^{-1}$ by two-photon absorption spectroscopy (in cyclohexane solution).³⁷

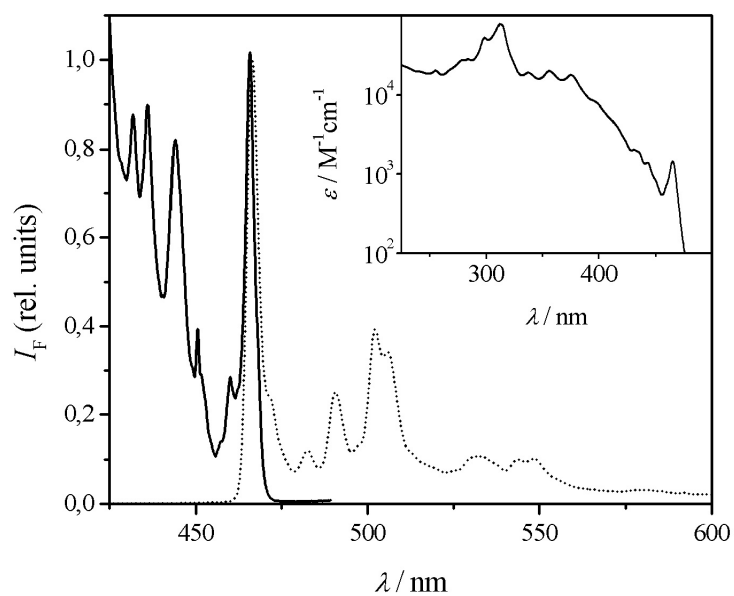


Fig. 3 Fluorescence excitation and emission spectra of zig-zag [4]phenylene (**3b**) in MeTHF at 77 K. Inset: logarithmic singlet absorption spectrum at 298 K in THF.

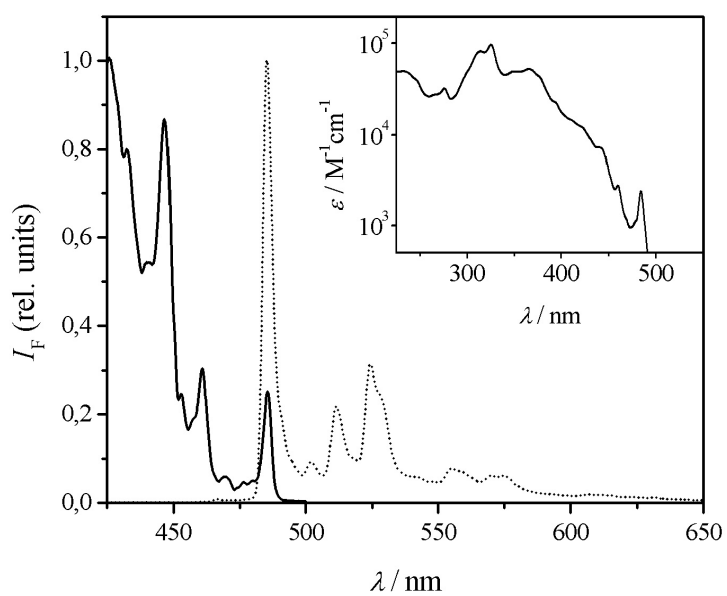


Fig. 4 Fluorescence excitation and emission spectra of zig-zag [5]phenylene (**3c**) in MeTHF at 77 K. Inset: logarithmic singlet absorption spectrum at 298 K in THF.

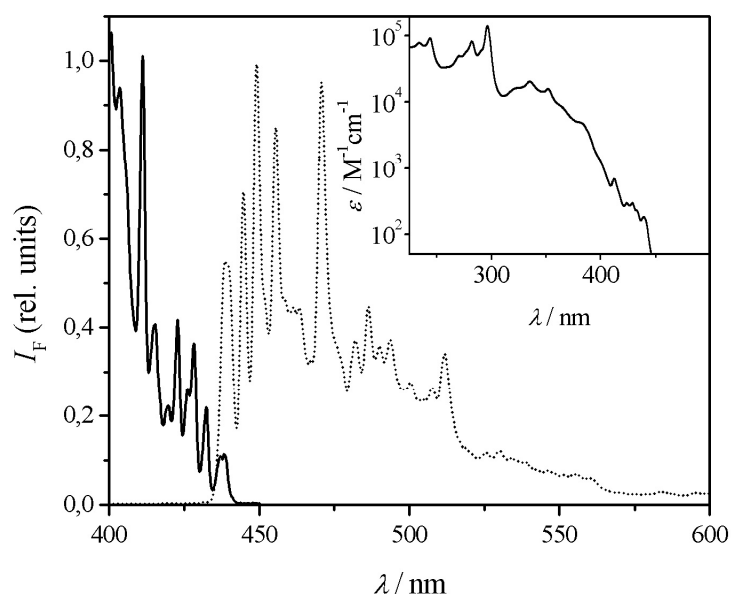


Fig. 5 Fluorescence excitation and emission spectra of triangular [4]phenylene (**4**) in MeTHF at 77 K. Inset: logarithmic singlet absorption spectrum at 298 K in THF.

In linear [3]phenylene (**2a**), the S_0 - S_1 transition is also forbidden, so that the 0-0 transition can also not be observed directly. Probably because of S_1 - S_2 vibronic coupling and intensity borrowing, the singlet absorption spectrum shows a weak vibrational progression (evident only as shoulders in Fig. 2, but clearly resolved in low-temperature spectra, not shown) with ca. 1500 cm^{-1} spacings. If it is assumed that the longest-wavelength (first) absorption feature at ca. 535 – 540 nm belongs to the 0-1 transition, the S_1 state energy can be determined tentatively to be ca. 585 nm ($E(S_1) \approx 17,000\text{ cm}^{-1}$). Polarization measurements and PECI calculations suggest that the prominent absorption band of (**2a**) around 425 nm is due to the allowed long-axis polarized S_0 - S_2 transition and thus corresponds to the band around 360 nm in the biphenylene (**1**) absorption spectrum. As pointed out above, angular [3]phenylene (**3a**) is distinguished by moderate fluorescence with an intense shortest-wavelength (first) emission maximum. From the average wavenumbers of the first absorption and fluorescence features, the S_1 state energy of (**3a**) was determined to be $E(S_1) = 23,000\text{ cm}^{-1}$. It is thus obvious that, relative to biphenylene (**1**), the red-spectral shift of the S_0 - S_1 -absorption band of angular [3]phenylene (**3a**) is only ca. 1000 cm^{-1} which is very small compared to the ca. 7000 cm^{-1} red shift of linear-[3]phenylene (**2a**). The results of the PECI calculations and preliminary polarization measurements suggest that in (**3a**) the S_0 - S_1 transition is of A_1 symmetry, and

that the prominent absorption bands at around 275 and 315 nm are due to B₂ transitions. The zig-zag [4]- and [5]phenylenes (**3b**), (**3c**) and the triangular [4]phenylene (**4**) show also weak S₀-S₁ absorptions, but with well resolved maxima (cf. Figs. 3 – 5). Although the S₀-S₁ absorption bands are markedly superimposed by the much stronger S₀-S₂ transitions, it is obvious from the spectra in Figs. 3 – 5 that the compounds (**3b**), (**3c**), and (**4**) exhibit partial symmetry of the S₀-S₁ absorption and fluorescence spectral features. In addition, these larger [N]phenylenes show only very small Stokes shifts (cf. Table 1), so that their S₀ and S₁ state geometries are probably very similar, in contrast to the situation in biphenylene. The S₁ state energies of (**3b**), (**3c**), and (**4**), given in Table 1, are rather close to E(S₁) of (**3a**).

Our fluorescence quantum yield (Φ_F) and fluorescence lifetime (τ_F) measurements of biphenylene (**1**) and the linear and angular [3]phenylenes (**2a**), (**3a**) confirm earlier investigations: The values determined for (**1**), $\Phi_F = (2.6 \pm 0.3) \cdot 10^{-4}$ and $\tau_F = (230 \pm 30)$ ps, agree well with data reported in the literature [$\Phi_F = (1.8 - 3.3) \cdot 10^{-4}$ and $\tau_F = 240$ -250 ps, in different solvents under ambient conditions].^{13-16, 20, 38} Linear [3]phenylene (**2a**) was found to be non-fluorescent, as also determined earlier.²⁴ The slightly different fluorescence quantum yield and lifetime of angular [3]phenylene (**3a**) determined here, $\Phi_F = (0.07 \pm 0.01)$ and $\tau_F = (20 \pm 2)$ ns, and the data reported by Niemeyer ($\Phi_F = 0.047$ and $\tau_F = 15$ ns; in cyclohexane) may be due to the fact that perhaps in the earlier work the solvent was not completely deoxygenated. The zig-zag [4]- and [5]phenylenes (**3b**), (**3c**) and the triangular [4]phenylene (**4**) are more fluorescent with quantum yields between $\Phi_F = 0.12$ (**3b**) and 0.21 (**3c**). It is interesting to note that the S₁ state lifetimes of the [N]phenylenes under investigation range from ca. 30 ps for linear [3]phenylene (**2a**), as determined by Niemeyer with pump-probe measurements,²⁴ to 81 ns for triangular [4]phenylene (**4**), and thus differ by more three orders of magnitude. The corresponding variation of the fluorescence quantum yields is even larger than five orders of magnitude. From these results, the radiative lifetimes ($\tau_{F,0} = \tau_F / \Phi_F$) of the [N]phenylenes were calculated and found to range from ca. 300 ns for (**3a**), (**3c**) to ca. 900 ns for (**1**). The influence of temperature on τ_F was investigated for angular [3]phenylene (**3a**) and for triangular [4]phenylene (**4**). In comparison to those obtained at room temperature, the fluorescence lifetimes in MeTHF at 77 K approximately doubled to $\tau_F = 40$ ns and 145 ns for (**3a**) and (**4**), respectively. Further low-temperature investigations are under way.

3.2 Triplet properties

The triplet-triplet absorption (TTA) spectrum of biphenylene (**1**) has been studied with triplet sensitization experiments, and spectral peaks around 340 nm with an extinction coefficient of $\epsilon_T = 10,000 \text{ M}^{-1} \text{ cm}^{-1}$ and around 370 nm (both in cyclohexane) were reported.^{17, 20} Direct excitation of biphenylene (**1**) or linear [3]phenylene (**2a**) does not lead to the population of the triplet states, so that the quantum yields of inter system crossing (Φ_{ISC}) have already previously been estimated to be below $\Phi_{\text{ISC}} < 0.01$.^{17,18, 20} On the contrary, 355 nm excitation of all other [N]phenylenes investigated here produced transient absorption features that were assigned to the corresponding triplet species. The triplet properties obtained for compounds (**3a**), (**3b**), (**3c**), and (**4**) are also included in Table 1, and some TTA spectra are displayed in Fig. 6. From the results, it is clear that intersystem crossing plays an important role in S_1 state deactivation of angular [3]phenylene (**3a**) ($\Phi_{\text{ISC}} = 0.30$), zig-zag [4]- (**3b**, $\Phi_{\text{ISC}} = 0.25$), and [5]phenylenes (**3c**, $\Phi_{\text{ISC}} = 0.45$). Inspection of the TTA spectra shows, in addition to absorption bands around 450 nm, distinct absorption features in the red spectral region (around 600 - 700 nm). With $\epsilon_T = 75,000 \text{ M}^{-1} \text{ cm}^{-1}$ at 685 nm this band is strongest in the most extended compound, namely zig-zag [5]phenylene (**3c**). At present we have made no attempts to locate the T_1 state energies of the [N]phenylenes under study, for which further triplet sensitization experiments are necessary.

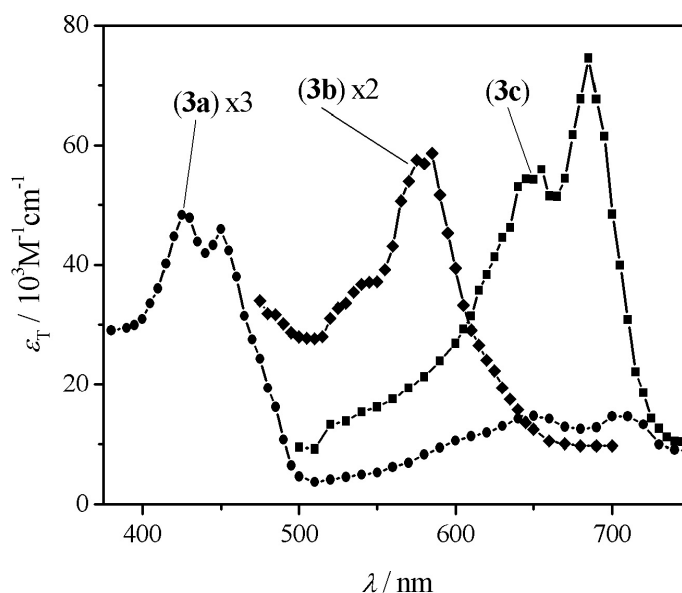


Fig. 6 Triplet absorption spectra of angular [3]phenylene(**3a**), zig-zag [4]phenylene (**3b**) and zig-zag [5]phenylene (**3c**) in THF at 298 K.

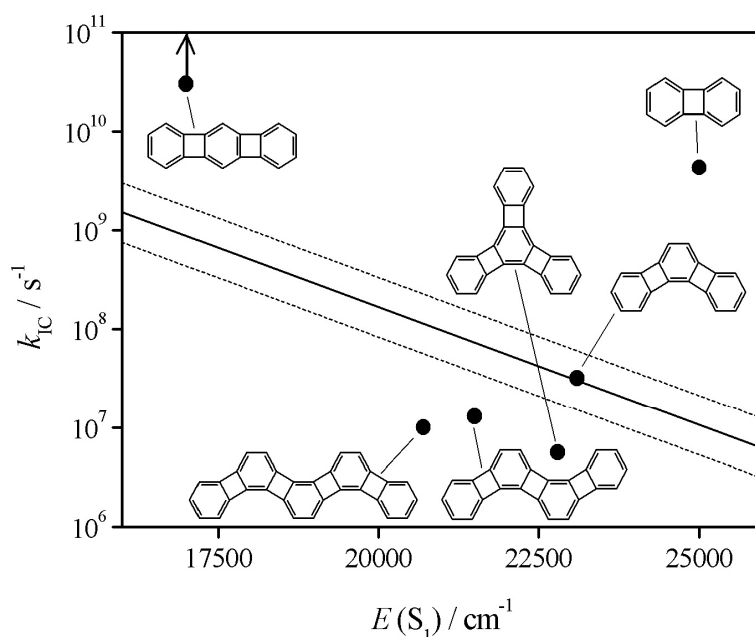


Fig. 7 Logarithmic IC rate constants (k_{IC}) vs. S_1 state energies [$E(S_1)$] of the [N]phenylenes. The solid line depicts the energy gap law for S_1 - S_0 IC in benzenoid hydrocarbons (see text) which predicts k_{IC} values with a reliability approximately within the boundaries given by the dashed lines.

4. Conclusions

The results obtained in this work can give some insight into the photophysical properties of the [N]phenylenes. The data presented in Table 1 show that both the fluorescence and intersystem crossing rate constants, being on the order of $k_F = (1 - 4) \cdot 10^6 \text{ s}^{-1}$ and $k_{ISC} = (4 - 20) \cdot 10^6 \text{ s}^{-1}$, respectively, do not differ very much. It is thus obvious that the strong differences in the fluorescence properties and in the triplet formation efficiencies are related to the remarkable variation of the internal conversion (IC) rate constants k_{IC} . For biphenylene (**1**) and linear [3]phenylene (**2a**), IC is by far the dominant mechanism of S_1 state deactivation. For (**1**), the rate constant $k_{IC} \approx 4 \cdot 10^9 \text{ s}^{-1}$ was previously reported,^{10, 13, 20} and confirmed here. It is clear that IC in (**2a**) is even faster. However, at present the corresponding rate constant is difficult to assess. With the exceedingly low value of Φ_F , and if it is assumed that k_F is on the order of 10^6 s^{-1} also for (**2a**), an order of magnitude estimate of $k_{IC} \approx 10^{12} \text{ s}^{-1}$ is obtained. Hence, the value of $k_{IC} \approx 3 \cdot 10^{10} \text{ s}^{-1}$ in Table 1, which is based on the results of Niemeyer's pump-probe measurements,²⁴ is probably only a lower limit. The fast IC in biphenylene (**1**) has been ascribed to strong vibronic coupling between the S_0 and the S_1 state, which is supposed to be mainly related to geometry changes in the central cyclobutadiene ring (CC vibra-

tions) as a result of photoexcitation.^{11, 13, 24} For the other [N]phenylenes (**3**) and (**4**), the small Stokes shifts and the partial mirror symmetry of the S_0 - S_1 absorption and fluorescence spectra indicate that the geometry changes occurring upon excitation are rather small. It is therefore perhaps not surprising that IC in these compounds is significantly slower than in (**1**) and (**2a**). The data displayed in Fig. 7 suggest a tentative classification of (**1**) and (**2a**) as “fast IC compounds” with $k_{IC} > 10^9 \text{ s}^{-1}$, and of (**3**) and (**4**) as “slow IC compounds” with $k_{IC} \approx 10^7 \text{ s}^{-1}$. Evidently, such a classification cannot simply be related to Hückel’s rule-type concepts of aromaticity because the group of “fast IC compounds” consists of “antiaromatic” (**1**) and “aromatic” (**2a**), and the group of “slow IC compounds” consists of “antiaromatic” (**3b**), (**4**) and “aromatic” (**3a**), (**3c**). In a perturbational approach non-radiative (NR) processes in large organic molecules can be evaluated with Fermi’s Golden Rule under inclusion of the relevant Franck-Condon factors. This leads to an approximate description with the so-called energy gap law which predicts an exponential dependence of the NR rate constant (k_{NR}) on the energy separation (ΔE) of the electronic states involved: $k_{NR} \approx k_0 \exp(-\alpha \Delta E)$, where k_0 and α are constants.³⁹ For S_1 - S_0 IC in benzenoid hydrocarbons, it seems that the Franck-Condon factors are governed by CH (or CD) stretching vibrations, and the constants are approximately given by: $k_0 \approx 10^{13} \text{ s}^{-1}$ and $\alpha \approx 5.5 \cdot 10^{-4} \text{ cm}^{-1}$. The line shown in Fig. 7 was calculated according to the energy gap law with these parameters. For compounds with $\Delta E = E(S_1) - E(S_0) \approx 20,000 - 24,000 \text{ cm}^{-1}$, such as (**3**) and (**4**), a rate constant in the range of $k_{IC} \approx 10^8 - 10^7 \text{ s}^{-1}$ is thus obtained, providing an order of magnitude estimate. This includes the value of $k_{IC} \approx 10^7 \text{ s}^{-1}$ determined from the experimental properties of (**3**) and (**4**). It is therefore possible that the S_1 - S_0 non-radiative transition in the [N]phenylenes classified as “slow IC compounds” is similar to IC in the much better known benzenoid hydrocarbons. However, at present this conjecture is speculative. The synthesis of additional derivatives, especially deuterated systems and structures with larger variations in the S_1 state energies, and associated additional measurements, e. g. direct determination of IC efficiencies, are necessary to improve our understanding on the detailed mechanism of IC in the larger [N]phenylenes.

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