A Photophysical Study of Tri-chromophoric Systems Containing Two Naphthalene Moieties: Intramolecular Excimer Fluorescence, Energy Transfer, Phosphorescence, and Delayed Fluorescence

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Photophysical properties of 9,10-di[(1-naphthyl)-methyl]-9,10-dihydro-9,10-phenanthrenediol (**1**), 9,10-di(1-naphthyl)phenanthrene (**2**), 9,10-di(2-naphthyl)phenanthrene (**3**), 10,10-di(1-naphthyl)-9,10-dihydro-9-phenanthrone (**5a**) and 10,10-di(2-naphthyl)-9,10-dihydro-9-phenanthrone (**5b**) have been studied. In contrast to 1,4-di(1-naphthyl)butane compound **1** shows strong (intramolecular) excimer fluorescence in dilute solution at room temperature. As a result of intramolecular triplet-triplet energy transfer the phosphorescence of **2**, **3**, **5a** and **5b** stems from the naphthalene moieties. The increase (compared to naphthalene) of the rate constant of the radiative deactivation of the lowest triplet state is probably due in the case of **2** and **3** to the non-planarity of the molecules, which is expected to increase spin-orbit coupling, while in compounds **5a** and **5b** intramolecular charge-transfer interaction between the carbonyl group and the naphthalene moieties may be responsible for this effect. Delayed fluorescence (from the phenanthrene moiety) of **2** has been observed in fluid solution at room temperature, and an excitation mechanism is proposed.

Investigation of photophysical properties of bi- or tri-chromophoric aromatic compounds is of interest in connection with such important phenomena as e.g., excimer fluorescence, energy transfer, and influence of steric factors on the rate constants of the radiative and non-radiative deactivation of electronically excited states. In this contribution we wish to report on some photophysical properties of compounds **1**–**7**. In **2** and **3** the two naphthalene moieties are electronically isolated from each other and from the phenanthrene moiety for sterical reasons; in the most stable configurations of these compounds the naphthalene moieties are perpendicularly arranged with respect to the phenanthrene moiety. On the other hand, in **1** and **5**–**7** the chromophors (naphthalene, biphenyl and 9,10-dihydro-9-phenanthrone) are separated from each other by sp^3 carbon atoms. This contribution deals with exclusively the photophysical properties of compounds **1**–**7** while the syntheses of **1**–**3** and **5**–**7** will be reported elsewhere [1].

Results and Discussion

Intramolecular Excimer Fluorescence

Dinaphthylalkanes ($C_{10}H_7$-$(CH_2)_n$-$C_{10}H_7$, $n = 1-4$) have first been investigated with regard to the phenomenon of intramolecular excimer fluorescence [2] by Chandross and Dempster [3]. In accordance with the Hirayama $n = 3$ rule [2] strong excimer fluorescence (in fluid solution at room temperature) has been observed with the dinaphthylpropanes only while the dinaphthylmethanes, ethanes, and butanes exhibit exclusively the monomer fluorescence of the naphthalene moieties. In contrast to these findings we have observed that 9,10-di[1-naphthyl)-methyl]-9,10-dihydro-9,10-phenanthrenediol (**1**), where the two naphthyl groups are separated from each other by 4 sp^3 carbon atoms, show strong excimer fluorescence in dilute ($2 \cdot 10^{-4}$ M) fluid solution at room temperature. The observed spectrum (in n-heptane) is depicted in Fig. 1 (curve c). The absorption spectrum (curve a in Fig. 1) as well as the fluorescence excitation spectrum (longest wavelength band at 298 nm) are clearly related to the absorption spectrum of 1-methyl-naphthalene. Thus ground state interaction between the two naphthalene moieties in **1** can be excluded. In

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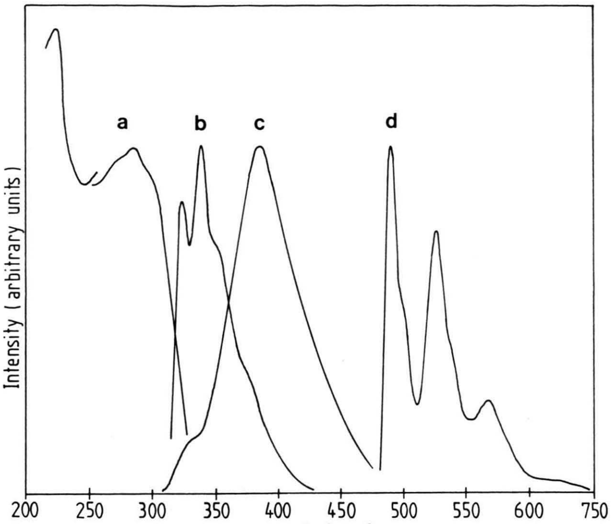


Fig. 1. Spectra of 9,10-di[1-naphthyl)-methyl]-9,10-dihydro-9,10-phenanthrenediol (**1**). a) Absorption spectrum (chloroform, at wavelengths shorter than 260 nm in n-heptane, room temperature). b) Fluorescence spectrum (methylcyclohexane-n-pentane, 4:1 vol/vol, 77 K). c) Fluorescence spectrum (n-heptane, room temperature). d) Phosphorescence spectrum (methylcyclohexane-n-pentane, 4:1 vol/vol, 77 K).

rigid solution (methylcyclohexane-n-pentane, 4:1, vol/vol) at 77 K **1** exclusively exhibits the monomer fluorescence of the naphthalene moieties (spectrum b in Figure 1). Excimer fluorescence begins to develop above −100 °C and increases steadily with increasing temperature up to ≈0 °C. The excimer fluorescence (387 nm) of **1** is shifted to the red by 4930 cm^{-1} relative to the monomer fluorescence (0, 0 band: 325 nm). Typically the half-width of an excimer band is 15−20% of the frequency of the intensity maximum; in **1** it is 18%. The phosphorescence of **1** in rigid solution at 77 K (spectrum d in Fig. 1) clearly stems from the isolated naphthalene moieties; no indication of excimer phosphorescence [4] has been obtained.

The experimental results lead to the following conclusions: In the most stable configuration of **1** which predominates at low temperature, the two naphthalene moieties are not in the parallel face-to-face (sandwich-type) arrangement, which is a necessary prerequisite for excimer fluorescence. Molecular models show that the most likely ground state cis-configuration of **1** is a staggered one with the two CH_2 groups connected with the naphthyl groups forming a dihedral angle $\theta = 60°$. At room temperature in fluid solution a skewed cis-configuration (half-way between a staggered and eclipsed form, $\theta < 60°$) having the necessary sandwich-type arrangement, becomes stabilized in the electronically excited state through i) intra-annular interaction between the naphthyl groups and ii) a further energy gain due to a conformational change of the biphenyl system present in **1** from a non-planar arrangement (existing in the ground state of **1**) to a planar arrangement (in the electronically excited state of **1**). These two effects are assumed to overcompensate the (destabilizing) larger inter-atomic repulsion in the skewed conformation (compared with the inter-atomic repulsion in the staggered conformation).

Intramolecular Energy Transfer

Compounds **2** and **3** are well appropriate for studying both intramolecular singlet-singlet and triplet-triplet energy transfer because the lowest excited singlet state of phenanthrene ($S_1(P)$) lies lower in energy than the lowest excited singlet state of naphthalene ($S_1(N)$) while the reverse situation holds for the triplet states ($T_1(P) > T_1(N)$). In fact, the phenanthrene-naphthalene pair is one of the classical systems for studying inter- and intramolecular triplet-triplet energy transfer [5].

In accordance with the term scheme of 9,10-di(1-naphthyl)phenanthrene (**2**) and 9,10-di(2-naphthyl)phenanthrene (**3**) the fluorescence of the compounds occurs from the $S_1(P)$ state while the phosphorescence occurs from the $T_1(N)$ state. In Table 1 the position of the 0, 0 bands of fluorescence and phosphorescence (in ethanol at 77 K) as well as the phosphorescence lifetimes of **2** and **3** and for comparison of phenanthrene and naphthalene are given.

Also included in Table 1 are the quantum yields of fluorescence (Y_f) and phosphorescence (Y_p), the quantum yields of triplet formation (Y_T) as well as the rate constants of the radiative deactivation (k_{PT}) and the non-radiative deactivation (k_{GT}) of the lowest triplet state of **2**, **3**, phenanthrene, and naphthalene (all data refer to ethanol solutions at 77 K). As the rate constant of intramolecular triplet-triplet energy transfer (typically 10^{10} sec^{-1} [6]) is much larger than the rate constants of both the radiative and non-radiative transition from the triplet to the ground state, the quantum efficiency of triplet-triplet energy transfer equals ≈1; hence the observed Y_T values refer to the naphthalene moieties in **2** and **3**. The k_{PT} values of **2** and **3** are larger than that of naphthalene, while the

Table 1. Luminescence data of compounds **1**–**7**, naphthalene, phenanthrene and 1,1′-dinaphthylmethane (all data refer to ethanol solutions at 77 K, except where noted): fluorescence 0, 0 band ($\tilde{\nu}_f$), phosphorescence 0, 0 band ($\tilde{\nu}_p$), fluorescence quantum yield (Y_f); phosphorescence quantum yield (Y_p); phosphorescence lifetime (τ_p); quantum yield of triplet formation (Y_T); rate constant of the radiative deactivation (k_{PT}) and the non-radiative deactivation (k_{GT}) of the lowest triplet state.

Compound	$\tilde{\nu}_f$ [cm^{-1}]	$\tilde{\nu}_p$ [cm^{-1}]	Y_f	Y_p	τ_p [sec]	Y_T	k_{PT} [sec^{-1}]	k_{GT} [sec^{-1}]
1	25 840 [a]	–	–	–	–	–	–	–
	30 770 [b]	20 410 [b]	0.25	0.030	2.25	0.75	0.018	0.427
2	28 490	20 660	0.59	0.078	2.40	0.41	0.079	0.337
3	28 250	20 010	0.15	0.17	2.50	0.85	0.080	0.320
4	30 500 [c]	20 920 [c]	0.70 [c]	0.11 [c]	2.60 [c]	0.30	0.141	0.243
Naphthalene	30 770	21 280	0.37 [d]	0.040 [d]	2.60	0.66	0.023	0.361
Phenanthrene	28 820	21 750	0.13 [d]	0.10 [d]	3.30	0.87	0.035	0.268
5a	–	20 620	–	0.49	0.96	1.00	0.510	0.531
5b	–	21 320	–	0.51	1.85	1.00	0.276	0.265
6	30 675	20 530	0.21	0.083	1.85	0.79	0.057	0.484
7a	31 153	20 830	0.26	0.068	2.09	0.74	0.044	0.434
7b	31 250	20 700	0.10	0.060	2.05	0.90	0.032	0.455
1,1′-Dinaphthylmethane	30 860	21 050	0.35	0.030	2.35	0.65	0.020	0.406

[a] In n-heptane at room temperature. – [b] In methylcyclohexane/n-pentane at 77 K. – [c] Ref. [7]. – [d] According to R. Li and E. C. Lim, J. Chem. Phys. **57**, 605 (1972).

k_{GT} values remain approximately unchanged. A similar observation has previously been made with 1,1′-binaphthyl (**4**) [7]. **4** has a larger k_{PT} value than naphthalene (Table 1). This has been explained by the assumption that spin-orbit coupling (SOC) is more effective in the non-planar binaphthyl than in the planar naphthalene molecule. It is theoretically well-established that with increasing deviation from molecular planarity SOC increases [8].

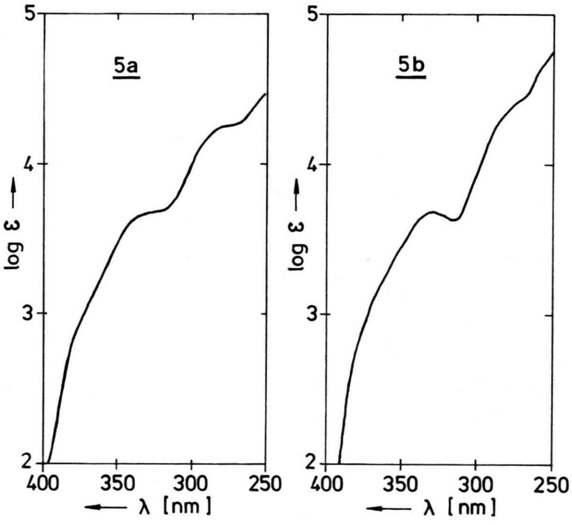


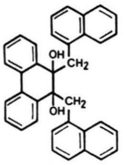
Fig. 2. Absorption spectra (chloroform, room temperature) of 10,10-di(1-naphthyl)-9,10-dihydro-9-phenanthrone (**5a**) and 10,10-di(2-naphthyl)-9,10-dihydro-9-phenanthrone (**5b**).

Influence of Intramolecular Charge-Transfer Interaction on Triplet Deactivation Parameters

In Fig. 2 the absorption spectra (chloroform, room temperature) of the 10,10-dinaphthyl-9,10-dihydro-9-phenanthrones **5a** and **5b** are given. The spectra are very similar, but different from the spectra of naphthalene or dinapthylmethanes. The first broad absorption band in the spectra of **5a** and **5b** appears at longer wavelength than that of naphthalene and obviously stems from the 9,10-dihydro-9-phenanthrone chromophor.

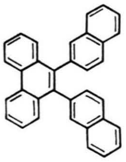
5a and **5b** do not show fluorescence (Table 1). This indicates that n, π* states (localized at the C = O group) lie below the lowest π, π* singlet state of the dihydrophenanthrone chromophor (for the well-understood relationships between the term schemes and luminescence behaviour of carbonyl groups containing aromatic compounds see [9]). The phosphorescence spectra of both **5a** and **5b** resemble closely to the spectrum of naphthalene (0, 0 bands, see Table 1), i.e. intramolecular triplet-triplet energy transfer from the dihydrophenanthrone moiety to the naphthalene moieties takes place.

Although the phosphorescence of **5a** and **5b** stems from the naphthalene moieties the k_{PT} values are significantly higher than that of naphthalene while the k_{GT} values do only slightly change (Table 1). The most likely explanation is based on the assumption that charge-transfer interaction between the C=O group and the naphthalene moieties occurs; it is well established that charge-transfer interaction can strongly enhance SOC in a molecule and hence also the efficiency of spin-forbidden transitions [10]. This explanation of the observed increase of k_{PT} values of **5a** and **5b** compared to that of naphthalene is in accordance with the observation that rate parameters of compounds **6**, **7a**, **7b**, and 1,1′-dinaphthylmethane closely resemble that of naphthalene (Table 1).



1

2



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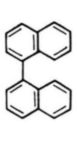

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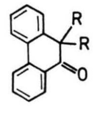
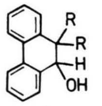
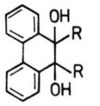


5a : R = 1-naphthyl
5b : R = 2-naphthyl



6
R = 1-naphthyl



7a : R = 1-naphthyl
7b : R = 2-naphthyl

Delayed Fluorescence

Triplet-spectroscopic properties of the dinaphthylphenanthrene **2** have also been studied in fluid solution (cyclohexane and toluene) at room temperature. From the decay rate of triplet-triplet absorption a triplet lifetime of 17 ± 3 μs has been estimated. This value comes close to that observed for naphthalene (≈10 μs [11]) and is very much different from the triplet lifetime of phenanthrene in fluid solution (≈145 μs [12]).

In fluid solution at room temperature **2** exhibits besides the prompt also a delayed fluorescence, the intensity maximum of which lies at 370 nm thus indicating that the delayed fluorescence stems from the phenanthrene moiety. The most likely excitation mechanism involves several steps in the following order: 1. Population of the $S_1(P)$ state of **2**, 2. intersystem crossing from the $S_1(P)$ state to the $T_1(P)$ state, 3. intramolecular triplet-triplet energy transfer from the $T_1(P)$ to the $T_1(N)$ state, 4. intermolecular triplet-triplet annihilation between **2**-molecules being in the $T_1(N)$ state leading to population of the $S_1(N)$ state, 5. intramolecular singlet-singlet energy transfer from the $S_1(N)$ to the lower lying $S_1(P)$ state, 6. radiative deactivation of the $S_1(P)$ state. This kind of excitation mechanism has been previously proposed for the delayed fluorescence of adsorbates of 1-naphthyl-9-carbazyl-methane [13], a compound, which has a similar term scheme as **2** [14].

Experimental

Substances

The synthesis of compounds **1**–**3** and **5**–**7** will be described elsewhere [1]. 1,1′-Dinaphthylmethane was a commercial sample. The purity of the substances was ascertained by standard instrumental analytical methods. The fluorescence and phosphorescence spectra proved to be independent of the excitation wavelength; the phosphorescence decay curves were monoexponential.

Solvents used were of Merck Uvasol quality.

Measurements

Fluorescence and phosphorescence spectra were measured on a Perkin-Elmer MPF 44 E spectrofluorimeter and an Aminco-Keirs spectrophosphorimeter.

Phosphorescence lifetimes were determined using the Aminco-Keirs spectrophosphorimeter equipped with an oscillograph Tektronix 5403.

Quantum yields were derived according to the procedure described in [15] from the quantum corrected spectra measured on the MPF 44 E spectrofluorimeter. Quantum yields of triplet formation were calculated according to: $Y_T = 1 - Y_f$, i.e. on the assumption that S_1–S_0 internal conversion is negligible.

Rate constants were calculated from the experimental data according to

$$k_{PT} = Y_P (Y_T \tau_p)^{-1} \quad [\mathrm{sec}^{-1}],$$

$$k_{GT} = (\tau_p)^{-1} - k_{PT} \quad [\mathrm{sec}^{-1}].$$

Triplet spectroscopic studies of **2** at room temperature were performed as described in [16] in degassed solutions using laser excitation (excimer laser Lambda Physik EMG 500, $\lambda_{Ex} = 308$ nm).

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