Chem. Ber. **119**, 1683–1688 (1986)

Synthesis and Twisted Intramolecular Charge Transfer(TICT)-Fluorescence of 8,8′-Bi-naphtho[1,2,3,4-*def*]chrysenyl

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Eingegangen am 4. November 1985

Upon irradiation of naphtho[1,2,3,4-*def*]chrysene (**3**) in chlorobenzene a symmetric biaryl, 8,8′-bi-naphtho[1,2,3,4-*def*]chrysenyl (**4**), is formed. Fluorescence studies of **4** reveal that the emission originates from a TICT state.

Synthese und intramolekulare Charge-Transfer(TICT)-Fluoreszenz von 8,8′-Bi-naphtho[1,2,3,4-*def*]chrysenyl

Bei der Belichtung von Naphtho[1,2,3,4-*def*]chrysen (**3**) in Chlorbenzol entsteht ein neues symmetrisches Biaryl, 8,8′-Bi-naphtho[1,2,3,4-*def*]chrysenyl (**4**). Fluoreszenzuntersuchungen an **4** ergaben, daß die Emission aus einem TICT-Zustand erfolgt.

The phenomenon of dual fluorescence of dimethylaminobenzonitrile was discovered in 1962 by *Lippert*[1]. In this system, the longer wavelength fluorescence originates from an excited state in which one electron has been transferred from the dimethylamino (donor, D) to the *p*-cyanophenyl (acceptor, A) group and both parts of the molecule are oriented mutually perpendicular; this has been termed Twisted Intramolecular Charge Transfer (TICT)[2]. Due to the polarity of the TICT state the TICT fluorescence band is shifted to higher wavelengths with increasing solvent polarity.

Even in symmetric polycyclic aromatic compounds like 9,9′-bianthryl (**1**)[3] and 6,6′-bi-benzo[*a*]pyrenyl (**2**)[4], TICT fluorescence has been observed. In these systems, D = A.

In this note we shall describe the preparation and TICT fluorescence properties of the title compound. Upon irradiation of naphtho[1,2,3,4-*def*]chrysene (**3**) in chlorobenzene under argon the as yet unreported compound 8,8′-bi-naphtho-[1,2,3,4-*def*]chrysenyl (**4**) is formed.

The presence of chloride ion and benzene in the irradiated solutions suggests that the solvent acts as a hydrogen acceptor. When the irradiation was carried

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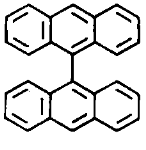
out in the presence of 0.1 M anthracene the formation of **4** was completely suppressed even though under these conditions **3** had still absorbed 96% of the incident light. Since the energy of singlet **3*** is lower than the energy of singlet excited anthracene and, on the other hand, the triplet energy of anthracene is lower than that of **3**[5,6], we conclude that anthracene must have quenched triplet **3*** in this experiment. Hence we conclude that **4** is formed from triplet **3***.



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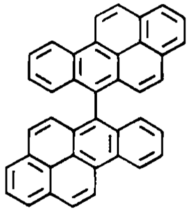

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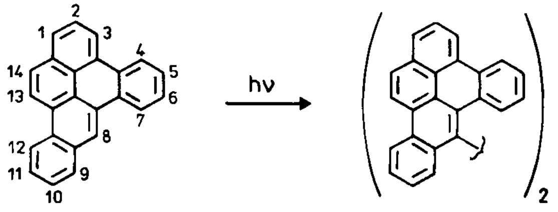
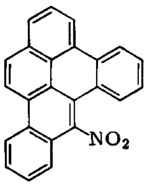


3 **4**



5

To the best of our knowledge, the photochemical formation of a biaryl from an aromatic hydrocarbon has not yet been reported in the literature[7,8].

Interestingly, we find that the same sterically hindered position of **3**, C-8, that enters into photodimerisation, is also active in electronic ground state electrophilic substitution. Bromination and acylation of **3**, to be sure, have been reported to take place at C-1[9]. However, 4-phenyl-1,2,4-triazoline-3,5-dione electrophilically substitutes at C-8[10]. Now, we find that nitration of **3** by nitric acid in acetic anhydride[11], too, leads to 8-nitronaphtho[1,2,3,4-*def*]chrysene (**5**) as the principal product. Compound **5** may open an alternative route to **4** e.g. *via* reduction followed by diazotation, treatment with iodide, and Ullmann reaction.

The molecular structures of **4** and **5** follow unambiguously from their 400 MHz ^1H NMR spectra which in either case show the presence of only one AB, one ABC, and two ABCD systems, with $J_{AB} = J_{BC} = J_{CD} \cong 8$ Hz and the other J values $\leqslant 1.5$ Hz. For the sake of comparison, we have compiled the δ-values of **3**, **4**, and **5** in Table 1; assignments to positions were possible after extensive spin-spin decoupling experiments. The IR spectra of **4** and **5** lack the presence of the γ-CH vibration band of an isolated aromatic H[12], which is present in the IR spectrum of **3**.

Table 1. ^{1}H NMR Chemical Shift values (δ) of **3**, **4** and **5**

pos.	**3** ($CDCl_3$)	**4** (CD_2Cl_2)	**5** ($CDCl_3$)
1	8.21 (bd, 8 Hz)	8.36 (bd, 8 Hz)	8.11 (bd, 8 Hz)
2	7.99 (t, 2 × 8 Hz)	8.09 (t, 2 × 8 Hz)	7.91 (t, 2 × 8 Hz)
3	8.82 (bd, 8 Hz)	8.88 (bd, 8 Hz)	8.71 (bd, 8 Hz)
4	8.74 m	8.70 (bd, 8 Hz)	8.68 (bd, 8 Hz)
5	7.71 m	7.35 (bt, 2 × 8 Hz)	7.72 (bt, 2 × 8 Hz)
6	7.71 m	6.66 (bt, 2 × 8 Hz)	7.59 (bt, 2 × 8 Hz)
7	8.90 m	8.44 (bd, 8 Hz)	8.39 (bd, 8 Hz)
8	9.20 s		
9	8.30 (bd, 8 Hz)	7.14 (bd, 8 Hz)	8.01 m
10	7.80 (m, 2 × 8 Hz)	7.07 (bt, 2 × 8 Hz)	7.82 m
11	7.80 (m, 2 × 8 Hz)	7.64 (bt, 2 × 8 Hz)	7.82 m
12	8.97 (bd, 8 Hz)	9.11 (bd, 8 Hz)	8.89 m
13	9.02 (d, 9 Hz)	9.25 (d, 9 Hz)	8.81 (d, 9 Hz)
14	8.27 (d, 9 Hz)	8.46 (d, 9 Hz)	8.18 (d, 9 Hz)

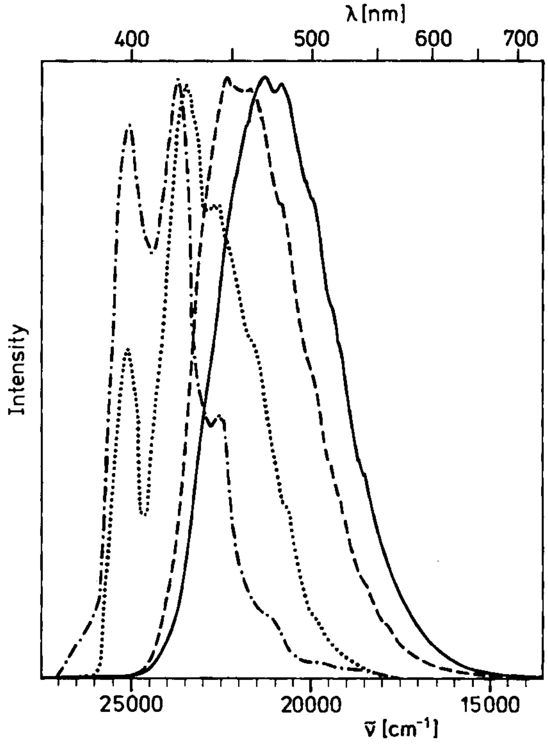


Fig. 1. Emission spectra of **4** in methylcyclohexane (MCH) at 77 K (· · ·), MCH at r.t. (- - -), CH_3CN at r.t. (——), and of **3** in MCH at r.t. (·—·—). Intensities in arbitrary units, normalized to give equal maximum heights

The fluorescence spectra of **4** obtained at room temperature in two solvents of strongly different polarity and in methylcyclohexane (MCH) at 77 K are presented in Fig. 1. The curves in Fig. 1 were found to be reproducible in every detail shown. They are independent of excitation wavelength (295, 307, 395 nm) and of concentration ($c = 1-5 \cdot 10^{-6}$ mol/l).

At 77 K, the emission spectrum of **4** is found to resemble that of **3** which has also been included in Fig. 1. At 77 K, therefore, the emission must occur from a LE (i.e., locally excited) state of **4**. However, in contrast to the emission spectra of **3** which have been found to be virtually independent of medium and temperature, the spectra of **4** strongly depend on these factors as can be seen from Fig. 1. At room temperature, the LE spectrum of **4** has vanished. In its place a new band appears whose strong shift to higher wavelength on increase of the solvent polarity indicates that it must occur from a polar state, i.e., a TICT state. So far, the emission behaviour of **4** resembles that of **2** except for the fact that the LE band of **2** survives up to room temperature; it then appears besides the TICT band[4]. This difference between **2** and **4** may be explained by a more nearly orthogonal spatial arrangement of the two molecule halves in the electronic ground state of **4** as compared to **2**. This would lower the LE → TICT transition barrier in **4** as compared to **2**.

Table 2 and Fig. 2 demonstrate the dependence of the solvent-induced shifts on the parameter $\Delta L'$ of the solvent polarity[4]:

$$\Delta L' = \frac{\varepsilon-1}{\varepsilon+2} - \frac{1}{2}\left(\frac{n^2-1}{n^2+2}\right) \quad (\varepsilon = \text{dielectricity constant}, n = \text{index of refraction})$$

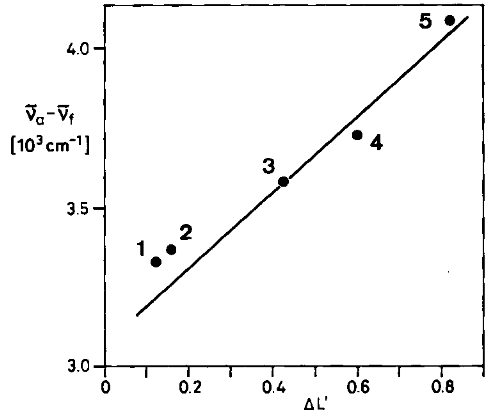


Fig. 2. Differences $\tilde{\nu}_a - \tilde{\nu}_f$ of **4** as a function of $\Delta L'$ ($\tilde{\nu}_a$: longest wavelength absorption maximum, $\tilde{\nu}_f$: center of gravity of the TICT band); correlation coefficient $r = 0.9847$

Band frequencies have been determined according to *Mathias'* rule[13].

Theoretical calculations[14] based on the Microstructural Solvent Interaction Model (MSI)[15] reveal that **4** closely resembles **2** as to dipole moment, Coulomb integral, and MSI-factor (A). The slope predicted from these calculations for the linear relation amounts to $m = 4.5 \cdot 10^3$ cm^{-1}, as compared to the value found experimentally, $m = 1.2 \cdot 10^3$ cm^{-1} (Fig. 2). Thus, in the case of **4**, the effect found experimentally is considerably weaker than predicted. We speculate that this discrepancy may be due to the benzene rings carrying positions 4–7 of **4** which necessarily protrude over the other half molecule thus causing more overlap between the two half molecules than would be present in, say, **1** and **2**. Such overlap, however, is adverse to the TICT effect.

Table 2. Differences between the longest wavelength absorption ($\tilde{\nu}_a$) and emission ($\tilde{\nu}_f$) wavenumbers of **4** in solvents of various polarity. Numbers in the first column refer to the points in Fig. 2

	Solvent	$\Delta L'$	$\tilde{\nu}_a - \tilde{\nu}_f$ [cm^{-1}]
1	Methylcyclohexane	0.125	3236
2	Dioxane	0.160	3278
3	Chloroform	0.426	3528
4	Methylene chloride	0.598	3692
5	Acetonitrile	0.818	4111

The authors wish to thank Dr. *W. Rettig*, Technical University of Berlin, for his valuable contributions to this work.

Experimental Part

UV spectra: Cary 17. – ^{1}H NMR spectra: Bruker AM 400 and Bruker WH 270. – Fluorescence spectra: Fluorolog. – Melting points: Kofler hot stage (Reichert). – Column chromatography: Merck Silica Gel 60 (230–400 mesh), Alumina (Woelm). – Irradiation: Hanau TQ 700, Solidex glass.

8,8'-Bi-naphtho[1,2,3,4-def]chrysenyl (**4**): A solution of 0.63 g (2.09 mmole) of **3** in 700 ml of chlorobenzene was flushed with argon for 1 h and irradiated for 94 h. The solvent was evaporated to 20 ml, a precipitate removed by filtration, and the residue (0.3 g) of the remaining solution separated by column chromatography (silica gel, eluent: hexane, CH_2Cl_2). Yield 11 mg (4.4%), based on unrecovered starting material, m.p. 391–392°C (decomp.). – MS (70 eV): *m/z* = 602 (M^+, 100%). – UV (benzene): λ_{max} (log ε) = 297 (4.70), 309 (4.74), 353 (3.99), 377 (4.17), 398 nm (4.27). – IR (KBr): 830, 820, 755 cm^{-1} (γ-CH).

$C_{48}H_{26}$ (602.7) Calc. C 95.65 H 4.35 Found C 95.45 H 4.50

8-Nitronaphtho[1,2,3,4-def]chrysene (**5**): 1.0 g (3.6 mmole) of **3** was stirred over night at room temperature in 700 ml of acetic anhydride containing 0.6 ml of conc. nitric acid. Unreacted **3** was removed by filtration. After hydrolysis of the acetic anhydride by added water the resulting mixture was extracted with dichloromethane. The combined organic layer was washed with aqueous potassium hydrogen carbonate solution and the solvent was evaporated; the residue was chromatographed with toluene on alumina. Yield 75 mg (40%), based on unrecovered starting material, m.p. 215–217°C. – UV (benzene): λ_{max} (log ε) = 294 (4.39), 307 (4.42), 351 (3.73), 368 (3.85), 386 nm (3.80). – IR (KBr): 1518, 1505, 1355 cm^{-1} (N–O).

$C_{24}H_{13}NO_2$ (347.3) Calc. C 83.00 H 3.74 N 4.03 Found C 83.06 H 3.67 N 4.06

CAS Registry Numbers

3: 192-65-4 / **4**: 99808-65-8 / **5**: 99808-66-9

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