rhenato)boron halide complexes is composed of a rhena-β-diketonate ligand system and a boroxycarbenoid ligand. However, X-ray structural studies indicate that considerably more carbenoid character is present in the Re–C acyl bonds of the (triacylrhenato)boron halide complexes than is present in the corresponding Re–C acyl bonds of rhena-β-diketonate complexes.[10,11] From this structural evidence, the (triacylrhenato)boron halide complexes appear to have a significantly different electronic structure from that of metalla-β-diketonate complexes.

The structural characterization of the η^3-allyl complexes **11**–**14** is essentially unambiguous because of the close correspondence between the ^{1}H NMR spectral data of these complexes and those data of the similar and well-characterized complexes Me_4N-{*cis*-$(OC)_4Re[\eta^3$-$CH_2COCO(Me)BF_2]$} (**15**) and Me_4N{*cis*-$(OC)_4Re[\eta^3$-$CH_2COCO(i\text{-}Pr)BF_2]$} (**16**).[6,15] In complexes **11** and **12**, the methyl substituent on the allyl ligand is required to occupy an anti position. The resonance for this methyl group in **11** and **12** appears at δ ca. 2.00. In complex **15**, the anti methyl resonance occurs at δ 2.13. Similarly, the syn and anti allyl CH_2 proton resonances of **11** and **12** that appear at δ 2.87 and 2.24, respectively, are observed at δ 2.88 and 1.68 in **15**.

For complexes **13** and **14** where the isopropyl group is located predominantly in an allyl anti position the methine proton resonances at δ 1.53 are very close to the chemical shift of δ 1.46 for the methine proton resonance of **16**. Similarly, the isopropyl methyl doublets of **13** and **14** that appear at δ 1.21 and 1.09 are observed in **16** at δ 1.40 and 1.17. The syn- and anti allyl CH_2 proton resonances of **13** and **14** appear at δ ca. 2.92 and 2.20, respectively, and at δ 2.97 and 1.69, respectively, in complex **16**.

From these comparisons, the formation of η^3-allyl ligands in complexes **11**–**14** that possess either an *anti*-methyl or *anti*-isopropyl substituent is apparent. The reason for the slight downfield shift of the allyl anti CH_2 proton resonances in **11**–**14** relative to the corresponding resonances in the model complexes **15** and **16** is not understood, but this may reflect an electronic influence of the unique carbenoid ligand in these new complexes. However, the correspondence between the chemical shifts of the allyl syn CH_2 proton resonances for these two classes of complexes is excellent.

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Registry No. **7**, 73199-27-6; **8**, 73199-28-7; **9**, 88562-90-7; **10**, 88562-91-8; **11**, 88548-43-0; **12**, 88548-45-2; **13**, 88548-47-4; **14**, 88548-49-6.

(10) Lukehart, C. M.; Warfield, L. T. *Inorg. Chim. Acta* **1980**, *41*, 105–110.
(11) Baskar, A. J.; Lukehart, C. M. *J. Organomet. Chem.* **1983**, *254*, 149–157. In [*fac*-$(OC)_3Re(CH_3CO)_3$]BBr, the average Re–C acyl distance is 2.04(3) Å, while in [*cis*-$(OC)_4Re(CH_3CO)_2]_2Cu$,[12] [*cis*-$(OC)_4Re(CH_3CO)_2$]H,[13] and $[PhC(NH_2)_2]$[*cis*-$(OC)_4Re(CH_3CO)_2$][14] the average Re–C acyl distances are 2.152 (5), 2.16 (2), and 2.182 (6) Å, respectively.
(12) Lenhert, P. G.; Lukehart, C. M.; Warfield, L. T. *Inorg. Chem.* **1980**, *19*, 311–315.
(13) Lukehart, C. M.; Zeile, J. V. *J. Am. Chem. Soc.* **1976**, *98*, 2365–2367.
(14) Lenhert, P. G.; Lukehart, C. M.; Sotiropoulos, P. D.; Srinivasan, K. *Inorg. Chem.*, in press.
(15) For general reference to relevant η^3-allyl ^{1}H NMR data see: (a) Green, M. L. H.; Nagy, P. L. I. *J. Chem. Soc.* **1963**, 189–197. (b) Green, M. L. H.; Nagy, P. L. I. *Adv. Organomet. Chem.* **1964**, *2*, 325–363. (c) McClellan, W. R.; Hoehn, H. H.; Cripps, H. N.; Muetterties, E. L.; Howk, B. W. *J. Am. Chem. Soc.* **1961**, *83*, 1601–1607.

Photoinduced Electron Transfer in Polychromophoric Systems. 2.[1] Protonation Directed Switching between Tri- and Bichromophoric Interaction

Ger F. Mes, Hendrik J. van Ramesdonk, and Jan W. Verhoeven*

Contribution from the Laboratory for Organic Chemistry, University of Amsterdam, Nieuwe Achtergracht 129, 1018 WS Amsterdam, The Netherlands. *Received May 17, 1983*

Abstract: The synthesis of a series of molecules D^2–D^1–A is described in which two electron donor chromophores (D^1, a trialkylamino group, and D^2, a (substituted) anilino group) and an electron acceptor chromophore (A, a (cyano)naphthyl group) are linked by a saturated paraffinic skeleton of well-defined conformation, which maintains closest atom–atom distances of 2.4 and 4.7 Å between A and D^1, and D^2, respectively. The fluorescence spectra of the trichromophoric molecules display an intramolecular charge-transfer emission at significantly lower energy than bichromophoric molecules D^1–A lacking the anilino donor. Together with the response of the charge-transfer fluorescence to substituents in the anilino group, this implies that in the emissive excited state a substantial positive charge develops at D^2. Photoinduced electron transfer in bichromophoric molecules D^1–A is effectively canceled upon selective protonation of D^1 in acidified polar media. Under these conditions the trichromophoric systems, however, are found to switch to a mode of electron transport involving direct long-range electron transfer from D^2 to A.

Electron transport along a chain of redox centers plays a crucial role in the biological energy transformation of the respiratory chain[2,3] and of the photosynthetic system.[4–7] Relatively little is known about the way in which the structure and spatial arrangement of these redox centers direct the rate and the pathway of electron transfer. The study of bichromophoric molecules incorporating an electron donor (D) and acceptor (A) moiety within a single molecule of well-defined conformation has been

(1) For part 1, see: Mes, G. F.; van Ramesdonk H. J.; Verhoeven, J. W. *Recl. Trav. Chim. Pays-Bas* **1983**, *102*, 55–56.
(2) Malmström, B. G. *Annu. Rev. Biochem.* **1982**, *51*, 21–59.
(3) "Tunneling in Biological Systems"; Chance, B., De Vault, D. C., Frauenfelder, H., Marcus, R. A., Schrieffer, J. R., Sutin, N., Eds.; Academic Press: New York, 1979; pp 453–557.
(4) Blankenship, R. E.; Parson, W. W. *Annu. Rev. Biochem.* **1978**, *47*, 635–653.
(5) Jortner, J. *J. Am. Chem. Soc.* **1980**, *102*, 6676–6686.
(6) Chidsey, C. E. D.; Roelofs, M. G.; Boxer, S. G. *Chem. Phys. Lett.* **1980**, *74*, 113–118.
(7) Boxer, S. G.; Chidsey, C. E. D.; Roelofs, M. G. *J. Am. Chem. Soc.* **1982**, *104*, 1452–1454.

0002-7863/84/1506-1335$01.50/0

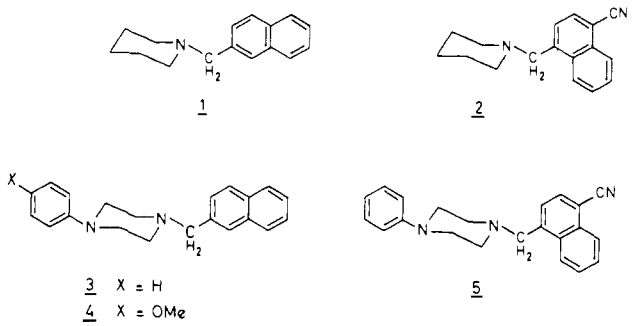


Figure 1. Bi- and trichromophoric systems studied.

shown to reveal many aspects of (photoinduced) electron transfer between two redox centers.[8,9] Trichromophoric molecules constitute the minimum model to study the aspects of consecutive electron transport along a chain of redox centers. Only a few trichromophoric systems have been reported[10-12] till now with the general structure $D^2-(CH_2)_n-D^1-(CH_2)_m-A$. The structure of these molecules, however, allows for a large degree of conformational freedom and the relative importance of the various possible modes of interaction (i.e., D^1/A, D^1/D^2, and D^2/A) in determining the interesting[10-12] photophysical properties of these compounds has not been established quantitatively.

From the studies by Yang et al.[12] it was concluded, however, that in flexible trichromophoric molecules ($n = m = 3$) the relative importance of the various interactions may depend upon the solvent as well as upon the nature of the chromophores. These effects were concluded[12] to result from the occurrence of differently folded excited-state conformations allowing for either D^1/A or $D^2/D^1/A$ interaction, while the relative population of these conformations depends upon solvent as well as upon the molecular structure of the system studied. As a first approach to conformationally more well-defined trichromophoric systems, compounds **3**, **4**, and **5** were synthesized. Their photophysical properties are described below and compared with those of the related bichromophoric molecules **1** and **2** (see Figure 1).

Results and Discussion

Bichromophoric Systems. Inter[13,14] and intramolecular[15-17] electron transfer from tertiary alkylamines and arylamines to photoexcited naphthalene derivatives resulting in quenching of the naphthalene fluorescence and eventual appearance of exciplex-type emission have been documented extensively. As expected the bichromophoric compounds **1** and **2** display these phenomena. In all solvents the naphthalene fluorescence of **1** and **2** is strongly or even completely quenched and a weak broad emission appears at longer wavelength. The charge-transfer (CT) character of the excited state leading to this new emission is evident from the large bathochromic shift[18] upon increasing solvent polarity (cf. Table I). Furthermore the average energy difference between the CT

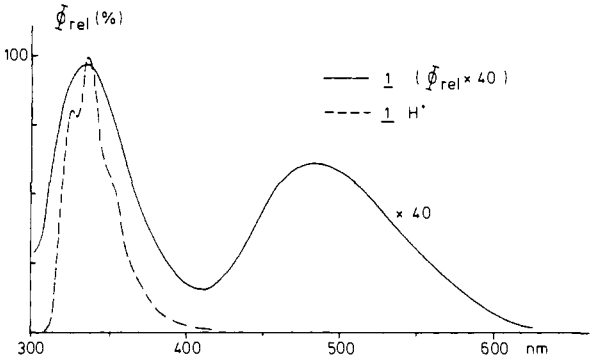


Figure 2. Effect of addition of cyanoacetic acid (0.7 M) on the emission spectrum of **1** (5×10^{-5} M in 2-propanol, excitation at 290 nm).

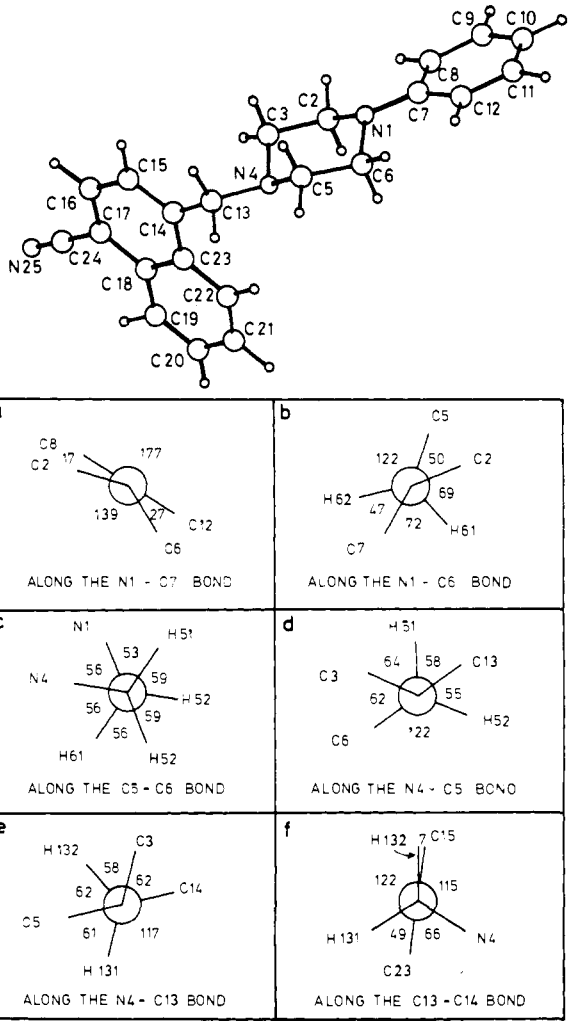


Figure 3. Structure of **5** as determined[23] by single-crystal X-ray diffraction. Newman projection a-f indicate dihedral angles along some relevant bonds.

emission of **1** and **2** of 0.57 eV (4600 cm^{-1}) corresponds nicely to the difference (0.56 V) in reduction potential between naphthalene and 1-cyanonaphthalene (−2.56 V and −2.00 V, respectively in acetonitrile relative to the saturated calomel electrode[19]).

As expected addition of a weak acid such as cyanoacetic acid ($pK_a = 2.45$)[20] readily leads to protonation of the nitrogen atom[21] in **1** and **2**. In the protonated form ($\mathbf{1H^+}$ and $\mathbf{2H^+}$) the possibility

(8) de Schrijver, F. C.; Boens, N.; Put, J. *Adv. Photochem.* **1977**, *10*, 359-465.
(9) Pasman, P.; Rob, F.; Verhoeven, J. W. *J. Am. Chem. Soc.* **1982**, *104*, 5127-5133.
(10) Beecroft, R. A.; Davidson, R. S.; Whelan, T. D. *J. Chem. Soc., Chem. Commun.* **1978**, 911-913.
(11) Beecroft, R. A.; Davidson, R. S. *Chem. Phys. Lett.* **1981**, *77*, 77-81.
(12) Larson, J. R.; Petrich, J. W.; Yang, N. C. *J. Am. Chem. Soc.* **1982**, *104*, 5000-5002.
(13) Beens, H.; Weller, A. In "Organic Molecular Photophysics"; Birks, J. B., Ed.; Wiley: New York, 1975; Vol. 2, pp 159-215.
(14) Meeus, F.; Van der Auweraer, M.; De Schrijver, F. C. *J. Am. Chem. Soc.* **1980**, *102*, 4017-4024.
(15) Chandross, E. A.; Thomas, H. T. *Chem. Phys. Lett.* **1971**, *9*, 393-396.
(16) Davidson, R. S.; Trethewey, K. R. *J. Chem. Soc., Chem. Commun.* **1976**, 827-829.
(17) Meeus, F.; Van der Auweraer, M.; De Schrijver, F. C. *Chem. Phys. Lett.* **1980**, *74*, 218-222.
(18) Plots of the maximum of the CT emission vs. solvent polarity as defined[13,17] by $f - {}^1/_2 f'$, where $f = (\epsilon - 1)/(2\epsilon + 1)$ and $f' = (n^2 - 1)/(2n^2 + 1)$, are linear and have a slope comparable to that observed[13,17] for emission from other highly polar excited states.
(19) Beens, H.; Weller, A. *Acta Phys. Polonica* **1968**, *34*, 593-602.
(20) "Handbook of Chemistry and Physics", 60th ed.; CRC Press Inc.: Boca Raton, FA, **1980**; p D161-166.
(21) Fluorimetric titration of **2** in aqueous medium gave $pK_a = 8 \pm 0.1$, which indicates a slightly decreased basicity as compared to piperazine itself ($pK_a = 9.83$, see ref 20).

Table I. Fluorescence Data of Bi- and Trichromophoric Systems as well as Some Model Compounds in Various Solvent at 20 °C[a]

compd	cyclohexane	di-*n*-butyl ether	diethyl ether	1,2-dimethoxyethane	acetonitrile	2-propanol	2-propanol/0.7 M cyanoacetic acid
2-methylnaphthalene[b]	335 [29.85] 71					335 [29.85] 80	335 [29.85] 80
1[b]	336 [29.76] 2.5	335 [29.85] 1.2	335 [29.85] 0.2	335 [29.85] 0.1	335 [29.85] 7.4	335 [29.85] 2.7	335 [29.85] 100
	370 [27.03] 1.6[d]	400 [25.00] 2.8	415 [24.10] 0.5	470 [21.28] 0.2	500 [20.00] 2.0	490 [20.41] 1.8	
3[b]	340 [29.41] 5.3	345 [28.99] 9.5	340 [29.41] 1.2	350 [28.57] 25.9	350 [28.57] 3.2	345 [28.99] 5.5	340 [29.41] 6.0
	390 [25.64] 3.0	430 [23.26] 7.2	455 [21.98] 0.7	500 [20.00] 1.8	555 [18.02] 0.6	535 [18.69] 1.0	
4[b]	365 [27.40] 26.7	365 [27.40] 11.9	368 [27.17] 6.6	370 [27.03] 2.1	380 [26.31] 5.4	370 [27.03] 8.4	348 [29.87] 1.4
		450 [22.22] 5.3	470 [21.28] 5.1	530 [18.87] 3.2			
4-methyl-1-naphthonitrile[c]	338 [29.59] 116					345 [28.98] 135	345 [28.98] 135
2[c]	440 [22.73] 0.1	500 [20.00] 0.2	540 [18.52] 0.2	570 [17.54] 0.1		345 [28.98] 0.4	355 [28.17] 100
5[c]	495 [20.20] 1.1	555 [18.02] 1.3	580 [17.24] 0.3	345 [28.99] 0.3		345 [28.98] 0.3	360 [27.78] 0.5
N-phenyl-*N'*-methylpiperazine[b]	337 [29.67] 24.5		345 [28.99] 2.8		355 [28.17] 22.6	350 [28.57] 16.2	338 [29.58] 16.2
N-(4-methoxyphenyl)-*N'*-methylpiperazine[b]	365 [27.40] 24.0					375 [26.67] 30.7	360 [27.78] 21.5

[a] The wavelength (λ in nm), wavenumber (ν in $cm^{-1} \times 10^3$), and relative intensity (ϕ_{rel}) of the fluorescence maxima are represented as: λ [ν] [ϕ_{rel}]. All measurements were made at 20 °C for solutions with A (1 cm) between 0.07 and 0.2 at the excitation wavelength (concentrations ~10^{-4}–10^{-5} M). ϕ_{rel} (%) refers to the fluorescence intensity of the bichromophoric molecules (**1** for 290 nm excitation, **2** for 310 nm excitation) in acidified 2-propanol. [b] Excitation at 290 nm. [c] Excitation at 310 nm. [d] Shoulder.

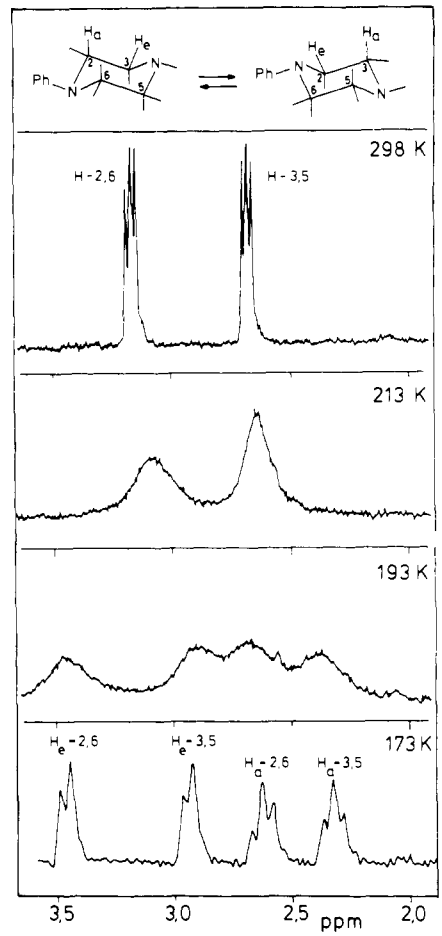


Figure 4. Variation of the piperazine ring proton resonances of **5** with temperature (250 MHz in CD_2Cl_2, chemical shifts relative to Me_4Si). The degenerate conformational interconversion responsible for these phenomena is schematized at the top.

of intramolecular electron transfer is lost with consequent disappearance of the intramolecular CT emission and full restoration of the naphthalene emission (cf. Figure 2 and Table I).

Trichromophoric Systems. The trichromophoric molecules **3**, **4**, and **5** may be considered as extensions of the bichromophoric systems with a second more potent donor site (D^2) in the form of an anilino moiety (**3** and **5**) or a 4-methoxyanilino moiety (**4**).

Conformational Aspects. As we[9] and others[22] have stressed before a proper discussion of the photophysical properties of multichromophoric molecules requires a detailed understanding of the conformational preferences and dynamics of such systems. The trichromophoric molecule **5** presented an excellent opportunity for detailed conformational investigation since crystals suitable for X-ray diffraction were readily obtained by recrystallization from methanol. In the crystal lattice the piperazine ring is found[23] (cf. Figure 3) to adopt a chair conformation with both N-substituents in an equatorial position. The torsional angle of the ring C–C bonds (±56°, see Figure 3c) is close to that found in cyclohexanes. Both ring nitrogen atoms adopt a pyramidal configuration, but that at the anilino nitrogen (N-1) is distinctly more flattened (compare Figures 3a and 3e). This flattening may be attributed to conjugative interaction within the anilino chromophore. The orientation of the phenyl group is such (see Figure 3a) that extensive overlap between its π-system and the N-1 lone pair occurs.[24]

(22) Mauzerall, D.; Ballard, S. G. *Annu. Rev. Phys. Chem.* **1982**, *33*, 377–407.
(23) Abbel, G.; Stam, C. H., to be published.
(24) This contrasts with the strongly twisted orientation and hence minor conjugation recently proposed for the anilino chromophore of *N*-phenylpiperidine in the gas phase by: Rozeboom, M. D.; Houk, K. N.; Searles, S.; Seyedrezai, S. E. *J. Am. Chem. Soc.* **1982**, *104*, 3448–3453.

Variable-temperature ^1H NMR spectroscopy (250 MHz in CD_2Cl_2) provided direct information regarding the preferred conformation and the conformational dynamics of **5** in solution. Geminal protons on the piperazine ring are effectively isochronous at room temperature. This results (cf. Figure 4) in two deceptively simple triplet signals. By comparison with related compounds the low-field signal (δ 3.17) is assigned to the protons at C-2 and C-6, while the high-field signal (δ 2.67) stems from the protons at C-3 and C-5. At low temperature each triplet decoalesces to a broadened doublet and a broadened triplet of equal intensity (see Figure 4). These patterns can unequivocally be assigned to protons occupying respectively equatorial and axial positions. For equatorial protons (H_e) a doublet arises from their strong coupling with the geminal axial proton ($^2J \approx -11$ Hz), while the remaining vicinal coupling constants are too small ($\leq$3 Hz) to be resolved. For axial protons (H_a) the mutual vicinal coupling involves a dihedral angle close to 180° and is therefore of a magnitude comparable to that of the geminal coupling ($^3J_{aa} \approx 11$ Hz), which explains the triplet patterns observed. No decoalescence or significant broadening of other signals is observed at the lowest temperature (173 K) attained. It is therefore concluded that the phenomena depicted in Figure 4 arise from a degenerate conformational interconversion involving ring inversion and simultaneous double nitrogen inversion. This process exchanges the piperazine ring protons between axial and equatorial sites (cf. Figure 4) but leaves the chemical environment of all other nuclei unchanged.

The free enthalpy of activation ($\Delta G^\ddagger$) for exchange between two equally populated weakly coupled sites may be approximated[25] from eq 1. In eq 1 R, h, and N denote the gas constant, Planck's

$$\Delta G^\ddagger = RT_c \ln [(RT_c\, 2^{1/2})/(\pi N h \Delta\nu)] \qquad (1)$$

constant, and Avogradro's number, respectively, while $\Delta\nu$ stands for the frequency difference between the exchanging sites—as determined in the low-temperature limit and assumed to be temperature independent—and T_c stands for the temperature at which coalescence of the signals assignable to nuclei residing at these sites occurs. For the protons attached to C-2 and C-6 $\Delta\nu = 208$ Hz (0.83 ppm) with $T_c = 207 \pm 3$ K gives:

$$\Delta G^\ddagger = 39.2 \pm 0.6 \text{ kJ/mol}$$

For the protons attached to C-3 and C-5 $\Delta\nu = 154$ Hz (0.62 ppm) with $T_c = 203 \pm 3$ K gives:

$$\Delta G^\ddagger = 38.9 \pm 0.6 \text{ kJ/mol}$$

The identity of these values once more supports the conclusion that a single conformational rearrangement occurs. Furthermore the magnitude of the barrier is fully comparable with that observed for the coupled ring and nitrogen inversion in simple *N*-alkylated piperidines.[26]

As evident from the effective magnetic C_s symmetry at the piperazine ring and from the isochrony of the protons at C-13 and as might be anticipated on the basis of literature data,[27] no freezing out of the rotations around C-13/C-14 and N-4/C-13 was achieved in the accessible temperature region. Indirect evidence that the rotameric position adopted by these bonds in the crystal lattice (cf. Figure 3) also prevails in solution is obtained from the chemical shift difference between the axial and equatorial protons at C-3 and C-5 detected at low temperature (cf. Figure 4).

Extensive studies on nitrogen compounds[26,27] have shown that this difference stems mainly from shielding of the axial protons under the influence of the axial lone pair on the adjacent nitrogen atom. This typically causes the axial protons to resonate ~1 ppm upfield from the equatorial protons. While such a chemical shift difference (0.83 ppm) is indeed observed for the protons at C-2 and C-6, the chemical shift difference at C-3 and C-5 is markedly

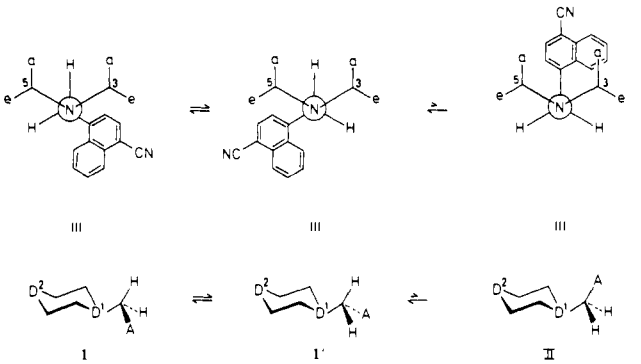


Figure 5. Possible rotamers of **5** around the N4–C13 bond. Axial and equatorial protons are denoted by a and e in the Newman projections. The cyanonaphthyl, tertiary amino and anilino chromophores are indicated by A, D^1, and D^2 in the bottom line.

smaller (0.62 ppm). For the rotameric position of the C-13/N-4 bond adopted in the crystal lattice the naphthyl group is oriented in such a way that significant magnetic shielding of the equatorial proton at C-3 must be expected. In solution rapid interconversion ($\Delta G^\ddagger \sim 20$ kJ/mol) between this rotamer and its enantiomorph (I $\rightleftarrows$ I', cf. Figure 5) is predicted from the data of Bushweller et al.[27] for compounds of the type R_2NCH_2R', whereas a slightly higher barrier probably separates I and I' from the less stable rotamer II in which the naphthyl group is staggered between C-3 and C-5. Preferential population of I and I' leads to shielding of H_e-3 and H_e-5 relative to H_a-3 and H_a-5 and may thus explain the diminished chemical shift difference between axial and equatorial protons at C-3 and C-5 as compared to those at C-2 and C-6.

Photophysical Properties. It seems fair to assume that the conformational aspects discussed above for **5** are characteristic for the other trichromophoric molecules as well. The barrier for the degenerate ring inversion ($\Delta G^\ddagger \approx 39$ kJ/mol) implies that this process occurs with a rate constant $k \approx 10^6$ s^{-1} at room temperature, which is extremely slow as compared to the photophysical processes of electron transfer and fluorescence to be discussed below. The only process which may effectively alter the relative orientation of the chromophores on a time scale compatible with these photophysical processes is provided by the interconversion between the rotamers I/I' and II (see Figure 5). The barriers involved are $\leq$25 kJ/mol which corresponds to a rate constant $k \geq 3 \times 10^8$ s^{-1} at room temperature. The center to center distance between D^2 and A varies from 8.4 Å in I to 7.4 Å in II, with estimated closest atom–atom (N-1–C-14) distances of 5.3 Å and 4.7 Å.

Notwithstanding the relatively remote position thus imposed upon D^2 with respect to both D^1 and A, the emissive properties of **3**, **4**, and **5** are markedly different from those of their bichromophoric counterparts (see Table I). In most solvents **3** and **4** display two distinct emission maxima, analogous to the behavior of **1**. The short wavelength emission of **3** and especially that of **4** is shifted bathochromic relative to that of **1**. This has a rather trivial reason. At the wavelength of excitation (290 nm) not only A but also D^2 absorbs. The short wavelength emission observed for **3** and **4** is therefore composed of the strongly overlapping[28] emissions of these chromophores. The emission of D^2 occurs at slightly longer wavelength than that of A especially in more polar media as evidenced by the data compiled in Table I for the model compounds *N*-phenyl-*N'*-methylpiperazine and *N*-(4-methoxyphenyl)-*N'*-methylpiperazine.

More significant is the rather large bathochromic shift of the long-wavelength CT-type emission that all trichromophoric molecules display in comparison to the parent bichromophoric systems in both polar and apolar solvents.[29] This bathochromic

(25) Pople, J. A.; Schneider, W. G.; Bernstein, H. J. "High Resolution Nuclear Magnetic Resonance"; McGraw Hill: New York, 1959.
(26) Lambert, J. B.; Featherman, S. I. *Chem. Rev.* **1975**, *75* 611–626.
(27) Bushweller, C. H.; Fleischman, S. H.; Grady, G. L.; McGoff, P.; Rithner, C. D.; Whalon, M. R.; Brennon, J. G.; Marcantonio, R. P.; Domingue, R. P. *J. Am. Chem. Soc.* **1982**, *104*, 6224–6236.
(28) Berlman, I. B. "Handbook of Fluorescence Spectra of Aromatic Molecules"; Academic Press: New York, 1971.
(29) The trichromophoric systems recently reported by Yang et al.[12] seem to display such a bathochromic effect in polar media only.

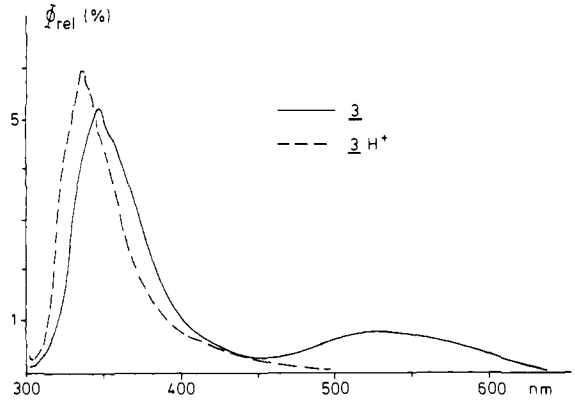


Figure 6. Effect of addition of cyanoacetic acid (0.7 M) on the emission spectrum of **3** (5×10^{-5} M in 2-propanol, excitation at 290 nm).

effect seems characteristic for emissions resulting from both intermolecular[30,31] and intramolecular[1,10-12] trichromophoric DDA interaction. Weller et al.[30] have pointed out that stabilization of the polar excited state in DDA exterplexes relative to that in DA exciplexes may be achieved by delocalization of the positive charge over both donor species. Such a delocalization evidently also occurs in the CT excited state of the present trichromophoric molecules notwithstanding the rather large separation between D^1 and D^2.

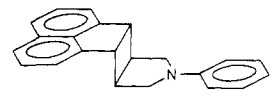
In this connection it seems interesting to note that photoelectron spectroscopic studies[32] of piperazines gave no evidence for through-space or through-bond interaction between the nitrogen centers. Recently, however, Halpern et al.[33] concluded that significant interaction occurs in the excited state from emission studies on *N,N'*-dialkylpiperazines conformationally restricted to a diequatorial chair conformation. That a substantial fraction of the positive charge is indeed transferred to the anilinochromophore in the excited state of the trichromophoric molecules is clear from the observation that introduction of a methoxy group (**3** → **4**) leads to a bathochromic shift of the CT emission by about 0.1 eV, which corresponds to 100% of the reported[12] difference in ionization potential between *N,N*-dimethylaniline (7.13 eV) and *N,N*-dimethyl-*p*-anisidine (7.03 eV)!

Effects of Protonation. The large difference in basicity between the trialkylamino (pK_a = 8–9) and anilino (pK_a = 4–5) nitrogens present in the trichromophoric molecules **3–5** provides the unique opportunity to study the effect of "removal" of the D^1 chromophore via its selective protonation.[1,34] Addition of cyanoacetic acid to an alcoholic solution of **3–5** results in complete quenching of their CT-type emission (cf. Table I) in accordance with the behavior of the bichromophoric systems **1** and **2**. In sharp contrast, however, to the behavior of the bichromophoric systems the emission of the naphthalene chromophore (and eventually also that of the anilino chromophore) remains strongly quenched after protonation of D^1 (cf. Figure 6 and Table I) in all trichromophoric systems. It must thus be concluded that even in the D^1 protonated form rapid intramolecular electron transfer from D^2 to $^1A^*$ (or from $^1D^{2*}$ to A in those molecules where the absorptions of D^2 and A overlap at the wavelength of excitation, i.e., in **3** and especially in **4**) occurs, leading to quenching of the local emission(s) but not to the appearance of a new CT-type emission. An impression of the magnitude of the rate constant (k_{et}) of the long-range electron transfer between D^2 and A can be obtained from the ratio (P) of fluorescence quantum yield of the trichromophoric molecules in acidified solution and that of a suitable model compound (i.e., 2-methylnaphthalene for **3** and **4** or 4-methyl-1-naphthonitrile for **5**) in the same solvent. If it is assumed that k_{et} provides the only additional decay channel in the trichromophoric molecules, than its value may be calculated from eq 2 in which τ represents the fluorescence lifetime of the model compound.

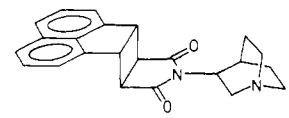
$$k_{et} = (1 - P)/\tau P \qquad (2)$$

For 2-methylnaphthalene τ = 59 ns has been reported.[28] Together with $P = 6/80 = 7.5 \times 10^{-2}$ (cf. Table I) this gives $k_{et} = 2.1 \times 10^8$ s^{-1} for $\mathbf{3H^+}$. A rather similar value ($k_{et} = 9.5 \times 10^8$ s^{-1}) is calculated for $\mathbf{4H^+}$, although in this case spectral overlap with the D^2 chromophore makes the choice of the reference system questionable. In both cases the k_{et} value is of the same order of magnitude estimated above for rotameric interconversions like I ⇄ II (cf. Figure 5). This correspondence, however, seems rather fortuitous since a substantially larger k_{et} value is calculated for $\mathbf{5H^+}$. For the 4-methyl-1-naphthonitrile reference molecule $\tau \approx$ 10 ns has been measured[35] in various solvents. Together with the ϕ_{rel} values given in Table I this leads to $k_{et} \approx 2.7 \times 10^{10}$ s^{-1}, which is much faster than the rate expected for any of the possible conformational interconversions of this molecule.

Anyhow the direct electron transfer from D^2 to A corroborates the rapidly growing body of evidence for the occurrence of fast electron transfer between widely separated donor and acceptor species.[36] Of special relevance in connection with the present results are the data obtained by Chandross,[37] who observed quenching of the naphthalene fluorescence for **6** (but not for **7**) in polar solvents.



6



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We furthermore wish to stipulate the close resemblance between the conformations I(H^+) and II(H^+) (cf. Figure 5) available to the protonated trichromophoric systems at one hand and fully stretched and partly folded conformations of bichromophoric molecules D–$(CH_2)_4$–A at the other. The present results therefore strongly suggest that in the latter type of compounds intramolecular photoinduced electron transfer is not at all restricted to occur in completely folded conformations. A similar conclusion was reached earlier by Eisenthal et al.[38] for a compound D–$(CH_2)_3$–A in polar solution and by one of us[39] for compounds D–$(CH_2)_n$–A ($n \leq 7$) in both polar and apolar media. It should be stressed that our present conclusions regarding the photophysical properties of the monoprotonated trichromophoric systems refer strictly to the polar solvent media in which selective D^1 protonation can be achieved. Nevertheless this study clearly reveals that the trichromophoric interaction in **3–5** cannot adequately be described by a model involving only nearest neighbor interactions (i.e., D^1/A and D^2/D^1) but that allowance must also be made for direct interaction between the terminal chromophores (D^1/A).

It seems plausible that such direct interaction between the terminal chromophores must also be accounted for in a description

(30) Beens, H.; Weller, A. *Chem. Phys. Lett.* **1968**, *2*, 140–142.
(31) Mimura, T.; Itoh, M. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 1739–1742; *J. Am. Chem. Soc.* **1976**, *98*, 1095–1099.
(32) Nelsen, S. F.; Buschek, J. M. *J. Am. Chem. Soc.* **1974**, *96*, 7930–7934.
(33) Halpern, A. M.; Ramachandran, B. R.; Sharma, S. *J. Phys. Chem.* **1982**, *86*, 2049–2052.
(34) Separate spectrophotometric titration experiments on *N*-phenyl-*N'*-methylpiperazines prove that after protonation of the trialkylamino nitrogen at pH ≈ 8 protonation of the anilino nitrogen cannot be achieved above pH 0. Such a large shift in the aniline pK_a from its normal $pK_a \approx 4.63$ value corresponds with the reported[20] difference between the first and second pK_a of piperazine (9.83 and 5.56).
(35) McCullough, J. J.; Mac Innis, W. L.; Lock, C. J. L.; Faggiani, R. *J. Am Chem. Soc.* **1982**, *104*, 4644–4658.
(36) For recent examples of long-range electron transfer see, e.g.: (a) Norton, K. A.; Hurst, J. K. *J. Am. Chem. Soc.* **1982**, *104*, 5960–5966. (b) Pasman, P.; Koper, N. W.; Verhoeven, J. W. *Recl. Trav. Chim. Pays-Bas* **1982**, *101*, 363–365. (c) Isied, S. S.; Worosila, G.; Atherton, S. J. *J. Am. Chem. Soc.* **1982**, *104*, 7659–7661. (d) Penner, T. L.; Möbius, D. *J. Am. Chem. Soc.* **1982**, *104*, 7407–7413. (e) Calcaterra, L. T.; Closs, G. L.; Miller, J. R. *J. Am. Chem. Soc.* **1983**, *105*, 670–671.
(37) Chandross, E. A., personal communication.
(38) Crawford, M. K.; Wang, Y.; Eisenthal, K. B. *Chem. Phys. Lett.* **1981**, *79*, 529–533.
(39) Borkent, J. H.; de Jong, A. W. J.; Verhoeven, J. W.; de Boer, Th. J. *Chem. Phys. Lett.* **1978**, *57*, 530–534.

of the behavior of other trichromophoric molecules such as those studied by Davidson et al.[10,11] and by Yang et al.[12] Furthermore a simple proton translocation has been shown to divert the pathway of electron transfer. It seems quite feasible that analogous mechanisms are operative in directing the pathway of various biological (photoinduced) electron-transport processes that are known[40,41] to be directly linked to the occurrence of pH gradients.

The preparation of compounds in which D^1 is substituted by a methine group, thus allowing a study of the D^2/A interaction in solvents of widely varying polarity as well as the preparation of other multichromophoric systems with well-defined conformation are actively pursued at the moment.

Experimental Section

Spectra. Electronic absorption and corrected emission spectra were recorded on Cary-17D and SPEX-Fluorolog Instruments respectively. The samples were contained in 1-cm rectangular fused-silica cells. Samples for emission spectroscopy were diluted to A (1 cm) ≤ 0.2 at the wavelength of excitation and were deoxygenated by purging with argon. ^{1}H NMR spectra were recorded on Varian A-60 or XL-100 and Bruker WM-250 instruments.

Materials. Spectrograde solvents were obtained from Merck and used without further purification.

2-Methylnaphthalene was obtained from Aldrich (mp 34–36 °C): UV (cyclohexane) 275 nm (5400 M^{-1} cm^{-1}).

4-Methyl-1-naphthonitrile was prepared as described in ref 35 (mp 53–54 °C): UV (cyclohexane) 297 nm (8800 M^{-1} cm^{-1}).

***N*-(2-Naphthylmethyl)piperidine (1)** was prepared by alkylation of piperidine (Aldrich) with 2-(bromomethyl)naphthalene (Aldrich). A solution of the bromide (4 mmol) in diethyl ether (5 mL) was slowly added to a solution of the amine (8 mmol in 5 mL diethyl ether) and the mixture was stirred for 1 h at room temperature. Piperidine hydrogen bromide, that precipitated from the solution, was removed by filtration. The filtrate was then acidified with HCl (concentrated) and ether was removed in vacuo. The residue was dissolved in warm ethanol (10 mL). From this solution the hydrogen chloride of **1** precipitated upon cooling. Recrystallization was repeated with methanol as a solvent. Finally the free base (**1**) was obtained by addition of potassium hydroxide and extraction with diethyl ether. The free base was purified by recrystallization from methanol: yield, 0.4 mmol (10%); mp 53–54 °C; UV (cyclohexane) 275 nm (5562 M^{-1} cm^{-1}); ^{1}H NMR (100 MHz, $CDCl_3$) δ 8–7.4 (m, 7 H), 3.66 (s, 2 H), 2.45 (t, J = 5 Hz, 4 H), 1.60 (m, 6 H); high-resolution MS, m/z 225.1501; calcd for $C_{16}H_{19}N$, 225.15174.

***N*-((1-Cyano-4-naphthyl)methyl)piperidine (2)** was prepared from 4-(bromomethyl)-1-naphthonitrile (prepared according to ref 35) and piperidine by the method described for **1**: yield, 10%; mp 63–65 °C; UV (cyclohexane) 298 nm (8871 M^{-1} cm^{-1}); ^{1}H NMR (100 MHz, $CDCl_3$) δ 8.5–7.0 (m, 6 H), 3.90 (s, 2 H), 2.50 (m, 4 H), 1.50(m, 6 H); high-resolution MS, m/z 250.1464; calcd for $C_{17}H_{19}N_2$, 250.14699.

***N*-Phenyl-*N'*-(2-naphthylmethyl)piperazine (3)** was prepared by alkylation of *N*-phenylpiperazine (Aldrich) with 2-(bromomethyl)-naphthalene in a two-phase system. The piperazine (10 mmol) and the bromide (10 mmol) were stirred for 2 h at room temperature in a two-phase system of dichloromethane (10 mL) and saturated aqueous sodium bicarbonate (10 mL). The organic layer was dried over sodium sulfate and evaporated in vacuo. The crude product was recrystallized from boiling cyclohexane (150 mL): yield, 90%; mp 143–144 °C; UV (cyclohexane) 252 (18 255 M^{-1} cm^{-1}), 275 (6980 M^{-1} cm^{-1}), 285 (sh) nm (5370 M^{-1} cm^{-1}); ^{1}H NMR (100 MHz, $CDCl_3$) δ 8.0–6.8 (m, 12 H), 3.70 (s, 2 H), 3.20 (t, J = 5 Hz, 4 H), 2.70 (t, J = 5 Hz, 4 H); high-resolution MS, m/z 302.1762; calcd for $C_{21}H_{22}N_2$, 302.17829.

***N*-(4-Methoxyphenyl)-*N'*-(2-naphthylmethyl)piperazine (4)** was prepared from *N*-(4-methoxyphenyl)piperazine (Hexachimie) and 2-(bromomethyl)naphthalene via the procedure described for **3**: yield, 90%; mp 123–124 °C; UV (cyclohexane) 248 nm (20 500 M^{-1} cm^{-1}); 275 (sh) (8000 M^{-1} cm^{-1}); 285 (sh) (6250 M^{-1} cm^{-1}); 300 (sh) nm (3400 M^{-1} cm^{-1}); ^{1}H NMR (100 MHz, $CDCl_3$) δ 7.9–7.4 (m, 7 H), 6.9 (br s, 4 H), 3.75 (s, 3 H), 3.72 (s, 2 H), 3.10 (m, 4 H), 2.65 (m, 4 H); high-resolution MS, m/z 332.1840; calcd for $C_{22}H_{24}N_2O$, 332.18885.

***N*-Phenyl-*N'*-((1-cyano-4-naphthyl)methyl)piperazine (5)** was prepared from *N*-phenylpiperazine and 4-(bromomethyl)-1-naphthonitrile via the procedure described for **1**: yield, 10%; mp 142–143 °C; UV (cyclohexane) 298 nm (10 623 M^{-1} cm^{-1}); ^{1}H NMR (100 MHz, $CDCl_3$) δ 8.5–6.8 (m, 11 H), 4.05 (s, 2 H), 3.20 (m, 4 H), 2.70 (m, 4 H); high-resolution MS, m/z 327.1707; calcd for $C_{22}H_{21}N_3$, 327.17354.

***N*-Phenyl-*N'*-methylpiperazine[42]** was prepared by reductive methylation[43] of *N*-phenylpiperazine. To a solution of *N*-phenylpiperazine (10 mmol) in a mixture of acetonitrile (30 mL) and aqueous formaldehyde (37%, 10 mL = 50 mmol) sodium cyanoborohydride (16 mmol) was added. A strong exothermic reaction ensued. The mixture was then stirred for 45 min under gradual addition of acetic acid to maintain neutral pH and finally evaporated in vacuo. The residue was made alkaline by addition of aqueous potassium hydroxide (2 N) and extracted with diethyl ether. The pure product was obtained by fractional distillation of the ether extract: yield, 58%; bp 140 °C (0.01 mmHg); UV (cyclohexane) 252 (13 564 M^{-1} cm^{-1}), 287 nm (1654 M^{-1} cm^{-1}); ^{1}H NMR (60 MHz, $CDCl_3$) δ 7.5–6.8 (m, 5 H), 3.2 (m, 4 H), 2.6 (m, 4 H), 2.3 (s, 3 H).

***N*-(4-methoxyphenyl)-*N'*-methylpiperazine[44]** was prepared by reductive methylation of *N*-(4-methoxyphenyl)piperazine as described above for the N-phenyl derivative: yield, 50%; bp 140 °C (0.01 mmHg); mp 62–64 °C; UV (cyclohexane) 248 (12 246 M^{-1} cm^{-1}); 302 nm (2014 M^{-1} cm^{-1}); ^{1}H NMR (100 MHz, $CDCl_3$) δ 7.0 (s, 4 H), 3.8 (s, 3 H), 3.1 (m, 4 H), 2.6 (m, 4 H), 2.4 (s, 3 H).

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(40) Mitchell, P. *Nature* **1961**, *91*, 144–148.
(41) Lewis, A. In "Frontiers of Biological Energetics"; Dutton, P. L., Leigh, J. S., Scarpa, A., Eds.; Academic Press: New York, 1978; Vol. 1, pp 297–306.
(42) Prelog, V.; Stepan, V. *Collect Czech. Chem. Commun.* **1935**, *7*, 93–102.
(43) Borch, F.; Hassid, A. J. *J. Org. Chem.* **1972**, *37*, 1673–1674.
(44) Davis, W.; Ross, W. C. J. *J. Chem. Soc.* **1949**, *4*, 2831–2835.