

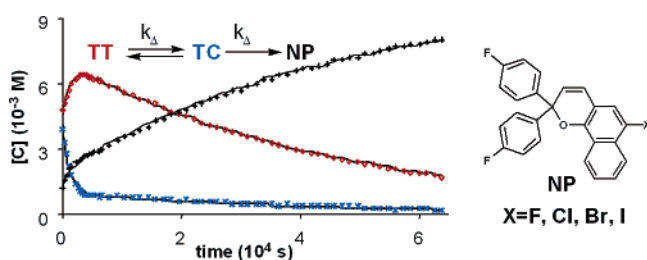
Unexpected Halogen Substituent Effects on the Complex Thermal Relaxation of Naphthopyrans after UV Irradiation

Stephanie Delbaere,* Jean-Claude Micheau,[†]
Michel Frigoli, and Gaston Vermeersch

CNRS UMR 8009, Laboratoire de Physique, Faculté de
Pharmacie, Université de Lille 2, Lille, France

sdelbaer@pharma.univ-lille2.fr

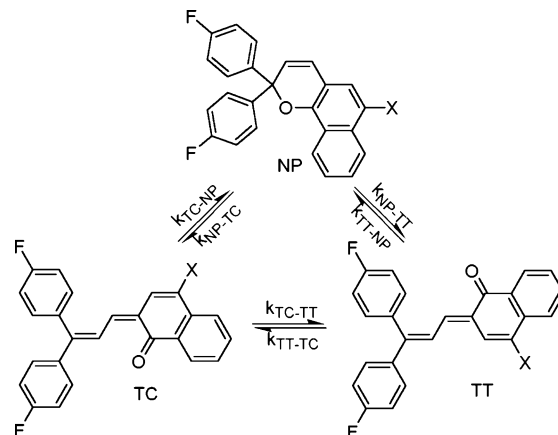
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The kinetics of the thermal fading of four halogenated naphthopyrans (NP) have been analyzed using NMR spectroscopy in CD₃CN. Two photomerocyanines (TT and TC) were detected after UV irradiation. The main relaxation process TC → NP was coupled with TT/TC isomerization. The activation parameters of the various processes were rationalized by considering electronegativity and polarizability of the halogen substituents and their selective solvation by the electronegative nitrogen of acetonitrile.

Organic photochromism finds applications in data storage, optical filters, displays, sensor protection, waveguides, and ophthalmic plastic lenses.^{1–2} Among the most useful and widely investigated photochromic molecules are the 2*H*-naphtho[1,2-*b*]pyrans, which lead, under UV irradiation, to a thermoreversible ring opening. This reaction gives rise to several photoisomers named photomerocyanines. It has been reported that within a given series, the photochromic properties strongly depend on the nature and position of the substituents^{3–5} and solvent environment.^{6–7} Four di(4-fluorophenyl)-2*H*-

SCHEME 1. Complete Model of All of the Possible Isomerization Equilibria between NP, TT, and TC (X = F, Cl, Br, and I)



naphtho[1,2-*b*]pyrans (NP), substituted at the 6-position with a F, Cl, Br, or I atom, were investigated after UV irradiation in order to appreciate the effect of the nature of the halogen on the thermal relaxation. This investigation is of particular interest because the effect of the nature of the halogen substituents was soon noted for its ability to influence hydrogen bond formation,⁸ photochemical reactivity,⁹ and enzymatic dehalogenation reaction.¹⁰ All of the naphthopyran molecules were labeled by two fluorine atoms at the 4 and 4'' positions in order to be detectable by ¹⁹F NMR spectroscopy. For each compound, the two expected photomerocyanine transoid isomers TC (transoid-cis) and TT (transoid-trans) were characterized by variable-temperature (248 < *T* < 288 K) ¹H, ¹³C, and ¹⁹F NMR spectroscopy in acetonitrile solution (Scheme 1), and a kinetic analysis of the complex thermal relaxation was carried out. The activation and thermodynamic parameters of the various thermal isomerization processes were determined and rationalized in regard to the electronegativity and polarizability of the halogenated substituent and their ability to participate in a nonbonded intermolecular interaction^{11,12} with the electronegative nitrogen of CD₃CN.

The time evolution of the concentrations of the three isomers NP, TC, and TT (Figure 1) were deduced from the ¹H and ¹⁹F 1D NMR spectra recorded at regular time intervals during thermal relaxation. Examination of the whole set of kinetics indicates that, whatever the tem-

* Corresponding author. Tel: 333 2096 4023. Fax: 333 2095 9009.
[†] Laboratoire IMRCP, UMR CNRS 5623, Université Paul Sabatier, F-31062 Toulouse, France.

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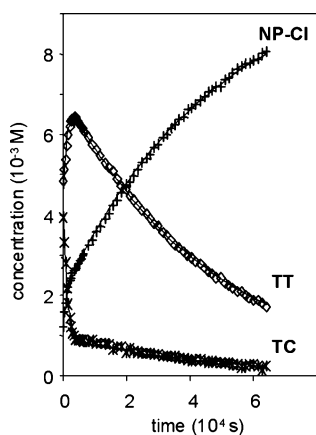


FIGURE 1. Evolution of the concentrations of the three isomers of the NP-Cl compound during thermal relaxation at 273 K of an acetonitrile- d_3 solution after UV irradiation. (Symbols are experimental data; continuous lines correspond to the numerical fitting of the three curves simultaneously.)

perature and the nature of the halogen atom, NP always increases and TC always decreases. On the other hand, TT isomer follows a different evolution exhibiting a more or less intense overshoot or remaining quasiunchanged during the monitoring time (see the Supporting Information). Such a biexponential-like kinetic behavior is in accordance with a three-species system undergoing the six a priori possible connected isomerization processes. To obtain the nature, number, and rate constants of each individual isomerization path, a numerical kinetic analysis of the plots was carried out using this complete model.

Data treatment of each naphthopyran at each temperature demonstrated that, depending on the nature of the halogen substituent, only a limited number of isomerization processes occurred simultaneously. All of the extracted rate constants were then reported on an Eyring plot to check their regular evolution vs temperature variations (Figure 2 and Supporting Information).

Table 1 shows that the investigated naphthopyrans do not exhibit all of the expected pseudo-elementary processes. For instance, for the iodo compound, thermal relaxation is limited to TC \rightarrow NP irreversible isomerization. For the fluoro compound, there are two consecutive irreversible isomerizations: TT \rightarrow TC and NP. Finally, for the chloro and bromo compounds, the situation is slightly more complicated because in addition to these two consecutive reactions there is a reverse TT \leftarrow TC process; hence, there are TT \rightleftharpoons TC \rightarrow NP. The corresponding enthalpy ΔH^\ddagger and entropy ΔS^\ddagger of activation of the various reaction paths have been extracted from the Eyring plots.

For the TT \rightarrow TC reaction, the observed ΔH^\ddagger and ΔS^\ddagger values seem to follow some stereoelectronic substituent parameter: the more electronegative and less bulky substituent (F) giving rise to lower values while the less electronegative and bulkier bromo-substituent, higher values. Although the reverse TT \leftarrow TC process was only detected in chloro- and bromophotomerocyanines, the same trend is observed (i.e., higher activation parameters for the heavier and less electronegative bromo substituent). For the iodo compound, there is an observed lack of TT \rightleftharpoons TC reactivity because the corresponding processes

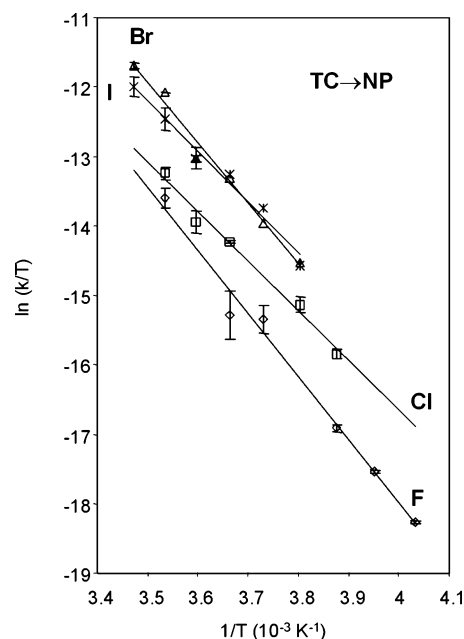


FIGURE 2. Eyring plots of the TC \rightarrow NP relaxation process in the four compounds. Each data point corresponds to an independent determination of the $k_{\text{TC} \rightarrow \text{NP}}$ rate constant by the numerical modeling of the TT, TC, and NP kinetics.

TABLE 1. Activation Parameters ΔH^\ddagger (kJ mol $^{-1}$) and ΔS^\ddagger (J mol $^{-1}$ K $^{-1}$) of the Various Pseudo-elementary Processes Occurring during the Thermal Relaxation of Halogenated NP Molecules^a

	TT \rightarrow TC		TC \rightarrow TT		TC \rightarrow NP	
	ΔH^\ddagger	ΔS^\ddagger	ΔH^\ddagger	ΔS^\ddagger	ΔH^\ddagger	ΔS^\ddagger
F	84 \pm 5	-45 \pm 4	n.d.		76 \pm 4	-42 \pm 2
Cl	85 \pm 4	-10 \pm 1	80 \pm 3	-13 \pm 0.5	53 \pm 4	-120 \pm 10
Br	91 \pm 4	3 \pm 0.5	101 \pm 4	53 \pm 2	73 \pm 4	-43 \pm 2
I	n.d.		n.d.		61 \pm 3	-88 \pm 4

^a n.d.: process too slow to be determined accurately or not detected.

are too slow to be detected in our low-temperature range. For the fluoro compound, the TT \rightarrow TC reaction is still detectable but slow ($\Delta S^\ddagger_{\text{TT} \rightarrow \text{TC}} = -45$ J mol $^{-1}$ K $^{-1}$) while the reverse TT \leftarrow TC is also not detectable.

Examination of the TT \rightleftharpoons TC equilibrium¹³ in chloro- and bromophotomerocyanines shows that in both cases, $\Delta G^\circ = (\Delta H^\ddagger_{\text{TT} \rightarrow \text{TC}} - \Delta H^\ddagger_{\text{TC} \rightarrow \text{TT}}) - T(\Delta S^\ddagger_{\text{TT} \rightarrow \text{TC}} - \Delta S^\ddagger_{\text{TC} \rightarrow \text{TT}})$ is positive (≈ 4 – 5 kJ mol $^{-1}$ at 300 K for chloro- vs bromophotomerocyanines, respectively). TT is more stable than its isomer TC. However, this equilibrium is continuously displaced in the opposite direction by the irreversible TC \rightarrow NP ring closure.

Examination of the relative values of the activation parameters of the TC \rightarrow NP ring closure shows an unexpected order, i.e., Cl < I < (Br \approx F). Light and heavy halogen atoms are mixed. No correlation can be established between the extracted activation parameters and any substituent constant related to the stereoelectronic nature of the halogen substituent. This lack of correlation is the sign that at least two competing effects are

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occurring simultaneously. To find a rational explanation of this unexpected halogen substituent effect on the TC \rightarrow NP thermal relaxation, we have to consider the involvement of some solute–solvent interactions. Indeed, it is well-known¹⁴ that halogens Cl, Br, and I, but not F, are able to form contacts at short interatomic distances with electronegative atoms. As a consequence, I, Br, and Cl compounds but not F compounds can be solvated in acetonitrile solution and the solvation power follows the polarizability scale (I > Br > Cl \gg F). Moreover, to be significant, such a solvation effect must be associated to some structural changes during the course of the reaction. This is the case during the TC \rightarrow NP ring closure reaction, where there is a marked change in the electronic distribution between the open TC and closed NP isomers. Hence, there would be a solvation change between TC and NP. Because the entropies of activation are negative, a degree of freedom is lost when going from the TC-photomerocyanine to a more ordered preclosed activated complex. It is then expected that the closed NP would be tighter (i.e., more solvated) than the open TC and that solvation would decrease the activation parameters.

From these considerations, it appears that electronegativity and polarizability act simultaneously as two opposite factors to determine the relative reactivity of the halogenated naphthopyrans TC \rightarrow NP ring closure. Going from F to I, intramolecular substituent effect gives rise

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to an increase of the activation parameters with bulkiness while intermolecular solvation gives rise to a decrease with polarizability. Hence, the two parameters are operating simultaneously leading to apparently scrambled activation parameter values.¹⁵

Because structural changes are minor during TT \rightleftharpoons TC isomerization, there are only few solvation effects, and the main halogen substituent effects are related to a unique atomic parameter; for instance, activation parameters increase with the size of the halogen.

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Supporting Information Available: Irradiation techniques, NMR details and interpretation of NMR spectra, and kinetic analysis. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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