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Photoinduced substitution reaction in halothiophenes. Quantum-mechanical and photochemical studies on nitro- and cyano-derivatives

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2-Iodo-5-nitrothiophene, 2-iodo-5-cyanothiophene, 2-bromo-5-cyanothiophene and 4-iodo-nitrobenzene were studied by steady state and pulsed techniques and by semi-empirical quantum-mechanical calculations. The quantum yields for the direct and sensitized photoarylation of these haloaromatics following the photocleavage of the carbon-halogen bond were measured in benzene. The transient species (triplet states and free radicals) originated by direct and sensitized laser excitation were investigated by nanosecond laser flash photolysis in benzene and methylcyclohexane. The transients were characterized in terms of absorption spectra and decay lifetimes. The triplet states were also characterized by phosphorescence measurements in rigid matrices at low temperature. The quenching rate constants of the triplet states and the quantum yields for singlet oxygen production were determined in methylcyclohexane. The results obtained with sensitizers of different triplet energy indicate that an upper triplet state is involved in the photocleavage of the carbon-halogen bond.

Introduction

The photocleavage of the carbon-halogen bond (C-X) in aliphatic and aromatic halides,¹⁻¹⁰ haloketones¹¹⁻¹³ and halothiophenes^{14–18} has been widely studied over the last decades. In the aryl halides, where the electronic excitation produces a π,π^* excited state, an intersystem crossing (ISC) to a dissociative triplet was proposed.^{3,4,9} Direct evidence for the role of the triplet state in the photodissociation of iodonaphthalene came from experiments with triplet energy sensitizers.¹ Interestingly, for the sensitized dissociation quantum yield a marked temperature effect was observed² as well as a dependence on the triplet energy of the sensitizers.¹ Some experiments^{3,4,9} also gave evidence that the dissociative state is an upper triplet. A clear demonstration of the involvement of an upper triplet in the C-Br bond cleavage was reported by Scaiano et al. for bromonaphthalene and bromophenanthrene by using two lasers-two colors techniques. They found a nice correlation between the photobleaching of the bromo-arene triplets and the increase in the absorption of the benzene-Br complex.10

A photochemical and photophysical study on the photocleavage of the C–X bond in haloderivatives of thiophencarbaldehyde and in 2-acetyl-5-iodothiophene, with formation of the phenylthiophene derivatives in direct and sensitized conditions, was reported by our laboratory.¹⁸ The direct and sensitized photoarylation, following the photocleavage of the corresponding halothiophenes was studied under steady state irradiation. Moreover the triplet states and free radicals formed by excitation were investigated by laser flash photolysis to determine their spectral and kinetic properties together with their formation quantum yields. The results indicated that, for these compounds also, the sensitized photosubstitution takes place in a dissociative upper triplet state mainly localized on the carbon–halogen bond. For the direct photoreaction the main route is probably again the triplet, although a singlet pathway cannot be excluded.

To obtain a more general picture of the behaviour of this class of compounds we extended the photophysical study to halothiophene derivatives containing withdrawing groups (NO₂ and CN) and moreover we undertook semiempirical quantum-mechanical calculations to give information on their excited singlet states.

In the present paper a theoretical description of the singlet excited states of 2-iodo-5-nitrothiophene (INT), 2-iodo-5cyanothiophene (ICNT), 2-bromo-5-cyanothiophene (BCNT) and 4-iodo-nitrobenzene (INB), in terms of nature, energy and transition probability, is presented. For these compounds, photophysical and photochemical studies were performed by steady state and laser flash photolysis techniques. In particular, the quantum yields for the direct and sensitized photoarylation and the spectral and kinetic properties of the triplet states and of non-triplet transients are reported together with the quantum yields of triplet formation (from O₂ ($^{1}\Delta_{g}$) sensitization experiments). Moreover, for the four compounds, phosphorescence spectra and lifetimes were measured in methylcyclohexane/3-methylpentane (MCH/3MP) at 77 K.

Experimental

p-Iodonitrobenzene was a commercial product (Aldrich). INT, ICNT, BCNT were the same as used in previous studies.^{16,17}

Absorption spectra were recorded by a Perkin-Elmer (Lambda 5) double-beam spectrophotometer, while emission was tested by a Spex Fluorolog-2 spectrofluorometer.

The steady-state irradiation of the halothiophene derivatives under direct and sensitized conditions was performed by a high-pressure mercury lamp coupled with interference filters or by the excitation system of the Spex Fluorolog-2 spectrofluorometer using ferrioxalate as an actinometer. The irradiation for the direct photoreaction was performed on deaerated solutions and in total absorption of light. The photosensitized reaction was quantified by irradiating deaerated solutions of the donors acetophenone (A) and phenanthrene (Ph) at 330 nm, benzophenone (B) at 340 nm and chrysene (Ch) at 345 nm; the photosensitizers were Baker products (Photosensitizers and Quencher Kit).

The photoproducts, p-phenylnitrobenzene and phenylderivatives of nitrothiophene and cyanothiophene were identified by spectrophotometry, gas chromatography-mass spectrometry (GC-MS) and high-performance liquid chromatography (HPLC) comparing their characteristics with those of pure samples. The quantum yields (estimated error $\pm 10\%$) for the direct or sensitized photoarylation (ϕ_{PA} and ϕ_{SPA} , respectively) were determined spectrophotometrically (halothiophene concentration ca. 10^{-4} M). To avoid an inner filter effect, the conversion percentage was held below 10% in all the experiments. The ϕ_{SPA} values were determined by taking into account the efficiency of the energy transfer process as calculated by the quenching of the donor lifetime (quenching efficiency = $1 - \tau/\tau_0$, where τ_0 and τ are the lifetimes of the donor in the absence and in the presence of the acceptor, respectively) and the amount of the light transmitted in each experiment.

Phosphorescence spectra and lifetimes were measured in methylcyclohexane/3methylpentane (MCH/3MP, 9:1, v/v) at 77 K with a Spex Fluorolog-2 spectrofluorometer equipped with a 1934D phosphorimeter.

Two excitation wavelengths, $\lambda_{exc} = 347$ nm from the second harmonic of a ruby laser (J.K. Lasers) and $\lambda_{exc} = 355$ nm from the third harmonic of a Nd : YAG laser (Continuum), were used in the nanosecond laser flash photolysis experiments (laser energy <5 mJ and pulse width ≤ 20 ns). Other experimental details are given elsewhere.¹⁹ Laser flash photolysis measurements were carried out in a flow-through cell to avoid sample degradation.

Singlet oxygen quantum yields (ϕ_{Δ} , estimated error $\pm 15\%$) were determined under pulsed conditions by recording the phosphorescence of $O_2({}^1\Delta_g)$ with a germanium diode detector in air-equilibrated solutions.²⁰

The lowest excited singlet state energies, electronic structures and transition probabilities of halothiophenes (HTP) were investigated by semi-empirical computational methods. The geometry of the substrates was optimized at an *ab initio* (Hartree–Fock) level with Gaussian 98²¹ using the set of basis 3-21G. The transition energies and oscillator strengths were calculated by the INDO/1-CI semiempirical model²² (ZINDO program of Cerius² 3.8 package). The configuration interaction (CI) calculations included the singly excited configurations built from the 15 highest occupied (HOMO) and 15 lowest virtual (LUMO) molecular orbitals.

Results

Absorption spectra and quantum-mechanical calculations

To gain a better understanding of the nature of the lowest states in the singlet manifold, quantum-mechanical calculations were performed. The electronic states of nitrobenzene (NB) have been extensively investigated by theoretical methods,²³ but little work has been done on halonitrobenzenes and on nitro- and halonitro-derivatives of thiophene. For NB in the planar form,²³ the lowest excited singlet is n, π^* .

Table 1 summarizes the absorption maxima, oscillator strengths and the nature of the lowest singlet–singlet transitions of halo-aromatics obtained by the quantummechanical calculations.

Table 1Transitions of halo-aromatics calculated by INDO/1-CI(singly excited, 15 occupied and 15 virtual MOs)

Compound	Transition	$\lambda_{\rm max}/{\rm nm}$	f	Nature
	$S_0 \rightarrow S_1$ $S_0 \rightarrow S_2$ $S_0 \rightarrow S_3$ $S_0 \rightarrow S_4$ $S_0 \rightarrow S_5$ $S_0 \rightarrow S_6$	806 544 355 331 299 258	$\begin{array}{c} 0.0000\\ 0.0005\\ 0.011\\ 0.0024\\ 0.060\\ 0.35 \end{array}$	π,π* π,π* π,σ* π,π* π,π* π,π*
I S NO2	$S_0 \rightarrow S_1$ $S_0 \rightarrow S_2$ $S_0 \rightarrow S_3$ $S_0 \rightarrow S_4$ $S_0 \rightarrow S_5$	382 374 330 283 278	0.011 0.0000 0.012 0.31 0.054	π,σ* π,π* π,π* π,π* π,σ*
I S CN	$\begin{split} S_0 &\to S_1 \\ S_0 &\to S_2 \\ S_0 &\to S_3 \\ S_0 &\to S_4 \\ S_0 &\to S_5 \end{split}$	395 288 274 251 247	0.010 0.40 0.012 0.0002 0.0027	π,σ* π,π* π,σ* π,σ* π,σ*
Br	$S_0 \rightarrow S_1$ $S_0 \rightarrow S_2$ $S_0 \rightarrow S_3$ $S_0 \rightarrow S_4$ $S_0 \rightarrow S_5$	430 284 267 265 256	0.0058 0.39 0.032 0.0061 0.0006	π,σ* π,π* π,σ* π,σ* π,σ*

For INB, the lowest excited singlet states S_1 and S_2 are π,π^* in nature, while S_3 is π,σ^* . However, for the three thiophenederivatives (INT, ICNT and BCNT) the lowest state S_1 is π,σ^* and S_2 is π,π^* . On the basis of these results, the reactivity of INT, ICNT and BCNT can involve the S_1 state while for IBN it does not. When the halo-aromatic contains a carbonyl group, as for the molecules investigated previously,¹⁸ the S_1 state becomes n,π^* in nature, with the orbital n localized on the carbonyl group and with low probability of cleavage.

Fig. 1 shows the frontier molecular orbitals involved in the descriptions of the lowest excited states of BrCNT; in particular, the configuration HOMO \rightarrow LUMO mainly describes S₁ (π,σ^*) and the HOMO-1 \rightarrow LUMO + 1 describes S₂ (π,π^*) of INT, ICNT and BCNT.

The maxima of the experimental electronic absorption spectra of INT, ICNT, BCNT and INB in benzene are reported in Table 2 together with the molar absorption coefficients, ε . The ε values, of the order of 10⁴ M⁻¹ cm⁻¹ and comparable with those of the other halothiophenes,¹⁸ give evidence that the absorption band recorded at lowest energies is due to



Fig. 1 Frontier molecular orbitals of BCNT calculated by the ZINDO semi-empirical program (INDO/1 model).

Table 2 Ground state absorption maxima (λ_{max}), direct (ϕ_{PA}) and sensitized (ϕ_{SPA}) photoarylation quantum yields of haloaromatics in benzene at room temperature

				$\phi_{ ext{SPA}}$			
Compound	$\lambda_{\rm max}/{\rm nm}$	$\epsilon/10^4 \ M^{-1} \ cm^{-1}$	$\phi_{\rm PA}$ [$\lambda_{\rm exc}/{\rm nm}$]	A	В	Ph	Ch
	290	1.05	0.008[313]	0.011	≤0.002		
I S NO2	340	1.0	0.20[313]		0.22	0.16	0.07
I S CN	279	1.4	0.34[313]		0.40	0.20	_
Br	276	2.4	0.23[290]		0.28	0.31	_

allowed π,π^* transitions. The energies and the ε values are in good agreement with the computed ones.

Steady-state experiments

Direct and sensitized photoarvlation. Direct irradiation of INT, ICNT and BCNT in benzene under steady-state conditions, caused photoinduced substitution of the halogen atom by the phenyl group. The quantum yields for the formation of the phenylderivatives (photoarylation, ϕ_{PA}) are in the range 0.2-0.35 (see Table 2). Iodonitrobenzene irradiated at 313 nm, also gave the corresponding p-nitrobiphenyl (NBP). This photoreaction was proposed by Wolf et al.²⁴ as a synthetic tool even though it has a very low quantum yield ($\sim 1\%$, Table 2). The photoarylation of halothiophenes occurs cleanly and quantitatively as shown by spectrophotometric and HPLC analyses by comparing the photoproduct characteristics with those of pure samples of the phenylthiophene-derivatives. Only long-term irradiation with an unfiltered Hg-lamp caused a slow decrease in the photoproduct absorbance. Spectral changes observed in the UV region under steady state irradiation are reported in Fig. 2 for INT in benzene as an example; the presence of an isosbestic point evidences the cleanliness of the photoreaction. The spectrum 5 of this figure ($\lambda_{max} = 357$ nm) corresponds to the absorption of the photoadduct 2phenyl-5-nitrothiophene. Experiments carried out in other solvents (methylcyclohexane and acetonitrile) did not show considerable changes in the absorption of halothiophenes, even after prolonged irradiation.

Similar behaviour was observed upon irradiation of ICNT in benzene. The absorption of an irradiated solution of ICNT revealed a broadening and a red-shift of the absorption band. The presence of an isosbestic point at 280 nm indicated the formation of one photoproduct, which is 2-phenyl-5 cyanothiophene.

The spectrophotometric analysis of the BCNT in benzene solutions after irradiation showed the appearance of a new absorption band ($\lambda_{max} = 300$ nm), whose intensity increased with the irradiation time. The chromatographic analysis confirmed the formation of only one product, 2-phenyl-5 cyano-thiophene.

In the case of INB, the spectra recorded at increasing irradiation time presented a rise in the intensity and a slight redshift of the UV absorption band. These changes were due to the formation of *p*-nitro-biphenyl (NBP), as was indicated by the chromatographic analysis using a pure sample of NBP. This result was further confirmed by comparing the absorption spectra of the photoproduct and of the commercially available *p*-nitro-biphenyl ($\lambda_{max} = 305$ nm).

The sensitization of the photoreaction by triplet energy (E_T) donors was also investigated. Acetophenone (A, $E_T = 309$ kJ

 mol^{-1}), benzophenone (B, $E_T = 288 \text{ kJ mol}^{-1}$), phenanthrene (Ph, $E_{\rm T} = 259$ kJ mol⁻¹) and chrysene (Ch, $E_{\rm T} = 238$ kJ mol^{-1}) were used as sensitizers. The quantum yields for sensitized photoarylation (ϕ_{SPA}) of the three halothiophenes and INB are reported in Table 2. Except for BCNT, the ϕ_{SPA} values depend on the triplet energy of the sensitizer, in particular, for INT the highest value of ϕ_{SPA} is obtained for B (highest $E_{\rm T}$) and the lowest one pertains to Ch (lowest $E_{\rm T}$) while for ICNT the sensitized arylation quantum yield is halved on going from B to Ph. This behaviour, that reflects a different population of the reactive triplet with the different sensitizers, has already been reported for the photosensitized decomposition of the iodonaphthalene¹ and for other halothiophenes.¹⁸ Unfortunately, it was not possible to follow the sensitization for ICNT and BCNT by Ch because of the lack of triplet quenching even in the presence of a high concentration of acceptor, likely due to the close triplet energies of the two (sensitizer-sensitized) species.

Phosphorescence properties. INT, ICNT and BCNT do not phosphoresce at room temperature, but their emission spectra were recorded in a MCH/3MP matrix at 77 K. The phosphorescence spectra of the three HTPs were similar and presented an unstructured band around 500 nm. In the case of INB, the phosphorescence spectrum obtained under the same experimental conditions has the main maximum at 410 nm. These



Fig. 2 Ground-state absorption spectra of INT in benzene (1) and after 30 (2) 60 (3), 120 (4) and 180 min (5) of irradiation time ($\lambda_{exc} = 313$ nm).

spectra allowed the energy of the emitting triplet (measured at the maximum emission wavelength) in the range 220 and 250 kJ mol⁻¹ to be obtained. For all the samples, the phosphorescence decays follow first-order kinetics with lifetimes in the range 0.5-6 ms, depending on the compound. The emission spectra, lifetimes and triplet energies are very similar to those previously reported for other thiophene derivatives.¹⁸ The characteristics of phosphorescence of INT, ICNT and BCNT are reported in Table 3 together with those of INB for comparison. It is to be noted that the triplet energy of INB is about 50 kJ mol⁻¹ higher than those of the other three compounds.

Laser flash photolysis experiments

Direct laser excitation of INT, ICNT and BCNT produces, in general, triplet states and radical species absorbing in the 370-700 nm range. In particular, upon excitation of BCNT in methylcyclohexane a transient signal was detected at the end of the laser pulse whose spectrum presented the main maximum at 430 nm (Fig. 3a) and which decayed with firstorder kinetics having a lifetime of 5.9 µs. The absorption signal recorded at longer wavelengths (450-650 nm) decayed with mixed (first- and second-) order kinetics. These observations indicated the presence of different transient species. In particular, the band at 430 nm was assigned to the $T_1 \rightarrow T_n$ transitions on the basis of the following arguments: (i) it was produced within the laser pulse by a monophotonic process; (ii) it decayed by first-order kinetics; (iii) it was quenched by triplet energy acceptors; (iv) it was quenched by oxygen with a rate constant (k_{ox}) close to the diffusion limit; (v) its location was similar to those observed for the triplets of other halothiophene derivatives previously investigated.¹⁸ On the basis of the kinetic analysis of the signals (mixed first- and secondorder), the absorption in the range 450-650 nm was attributed to the overlap between the triplet and the thienyl radical formed by carbon-halogen cleavage. In fact, as in methylcyclohexane the quantum yield of the photoreaction is negligible, the main decay pathway of radicals is the recombination

Table 3 Phosphorescence properties of haloaromatics in methylcy-clohexane-3-methyl-pentane (9:1) at 77 K $\,$

Compound	$\lambda_{\rm max}/{\rm nm}$	$\tau_{\rm P}/{ m ms}$	$E_{\rm T}/{\rm kJ}~{\rm mol}^{-1}$
	410(sh), 460	0.6	293
NO ₂	525(sh), 560	1.2	226
I S CN	473(sh), 520	0.53	250
Br	496(sh), 535	6.0	242



Fig. 3 Time-resolved absorption spectra of (a) BCNT in MCH recorded at 0.16 (\bigcirc), 1.9 (\triangle), 4.0 (\bigtriangledown) and 7.5 (\diamondsuit) µs; (b) ICNT in MCH recorded at 0.07 (\bigcirc), 0.12 (\triangle), 0.45 (\bigtriangledown) and 1.5 (\diamondsuit) µs; (c) INT in MCH recorded at 0.07 (\bigcirc), 0.15 (\triangle), 0.45 (\bigtriangledown) and 1.5 (\diamondsuit) µs after the laser pulse ($\lambda_{exc} = 355$ nm).

and the related kinetics is second-order. For possible interference on the absorption spectra of the halogen atoms and their complexes with MCH see ref. 18. The direct excitation of INT and ICNT, in MCH also produces the triplet state (absorption 440 nm for both compounds) and thienyl radicals whose contribution to the absorption (450-650 nm) is more evident than for BCNT (Fig. 3b and c). In the region where the triplet absorbs ($\lambda \leq 440$ nm) the signal decayed with firstorder kinetics, while in the range where the radicals also adsorb it is of mixed-order. For the INT and ICNT, the triplet lifetimes (Table 4) were 0.3 and 0.8 µs, respectively; they are considerably shorter than those obtained for the Br-derivative, probably due to the heavy atom effect. In the case of INB in MCH no transient species were detected under direct or sensitized excitation, suggesting that the observation is limited by the time resolution of our set-up. In fact, for nitrobenzene a triplet lifetime on the picosecond timescale was measured.²⁵

In benzene the triplet absorption maxima are again around 440 nm. However, only in the case of BrCNT in benzene did the signal of the triplet absorption decay with first-order kinetics and a triplet lifetime of 10 μ s. In the cases of ICNT and INT the transient spectra are dominated by the non-triplet species (Fig. 4b and c) since the signals decayed with a mixed-order kinetics all over the spectral region investigated. For the mixed first-second-order kinetics $t_{1/2}$ values in the range 1–6 μ s were measured at 500 nm. Attempts were made

 Table 4
 Spectral and kinetic properties of the lowest triplet state produced upon direct excitation of haloaromatics in methylcyclohexane at room temperature together with the singlet oxygen and triplet (lower limit) quantum yields

Compound	$\lambda_{\rm max}/{ m nm}$	$\tau_{\rm T}/\mu s$	$k_{\rm q}/10^9~{ m M}^{-1}~{ m s}^{-1}$	ϕ_{Δ}	$\phi_{\mathrm{T}}^{\mathrm{min}}$
	440, 540	0.3	1.3	0.35	0.70
	440, 540	0.8	1.5	0.66	0.83
Br	430, 530	5.9	0.9	0.75	0.80

to distinguish kinetically between the triplet and thienyl transients but we failed because of the similar lifetimes of the two transients. Furthermore, transient spectra features in benzene are complicated by the presence of additional transients: the halogen atom-benzene complexes (X-benzene, where X stands for I' or Br'). In particular, the halogen atoms produced by photolysis form well-known complexes with solvent molecules which absorb around 500 nm (I'-benzene, $\varepsilon = 2450$ M^{-1} cm⁻¹)^{18,26} and around 550 nm (Br-benzene, $\varepsilon = 2300$ M^{-1} cm⁻¹),¹⁸ depending on the halogen atom. Therefore, in the same range of the radical absorption there is the absorption of the complexes and the tail of the triplet. Moreover, the absorption contribution of thienyl radicals seems higher than that of the X⁻-complexes whose maxima are hardly recognized (in contrast to that observed for similar compounds).¹⁸ Only for BCNT (Fig. 4a) does a secondary maximum due, at least in part, to Br'-benzene complex appear at 550 nm. Unfortunately, under these experimental conditions it was impossible to evaluate the absorption of X-benzene complexes and their concentrations and hence a determination of the formation quantum yields was prevented by the overlap of the transient absorptions.

The energy transfer experiments were performed in benzene to measure the efficiency of the energy transfer process to be used in the determination of $\phi_{\rm SPA}$ using benzophenone (B), phenanthrene (Ph) and chrysene (Ch) as energy donors. The triplet state of B was quenched with rate constant around 1010 $M^{-1} s^{-1} (k_{diff} = 2.7 \times 10^{10} M^{-1} s^{-1})$,²⁷ while the quenching rate constant for Ch was *ca*. 10⁹ $M^{-1} s^{-1}$ for INT and negligible for the other two HTPs. The quenching of the donor triplet was accompanied by the appearance of the $T_1 \rightarrow T_n$ absorption band (440 nm) together with the thienyl band. The determination of the triplet quantum yields (ϕ_{T}) and molar absorption coefficients with the usual energy transfer method (based on the triplet lifetimes and absorption changes measurements)²⁸ was not possible due to the overlap of the absorptions of the various transients in both solvents and to the reactivity of an upper triplet state (see below). Indeed, in the sensitization experiments it was not possible to distinguish between the fraction of the donor, which populated T_1 of the



Fig. 4 Time-resolved absorption spectra of (a) BCNT in benzene recorded at 0.2 (\bigcirc), 1.4 (\triangle), 3.9 (\bigtriangledown) and 10.5 (\diamondsuit) µs; (b) ICNT in benzene recorded at 0.1 (\bigcirc), 0.34 (\triangle), 2.4 (\bigtriangledown) and 7.9 (\diamondsuit) µs; (c) INT in benzene recorded at 0.1 (\bigcirc), 0.34 (\triangle), 0.76 (\bigtriangledown) and 5.0 (\diamondsuit) µs after the laser pulse ($\lambda_{exc} = 347$ nm).

HTPs, and the fraction which produced the radicals through an upper triplet state.

Since it was important to know the triplet yields, we used an indirect method to determine them taking advantage of the ability of the triplets to sensitize singlet oxygen, $O_2({}^1\Delta_a)$. In fact, the halothiophen triplets were efficiently quenched by molecular oxygen with bimolecular rate constants ($k_{\rm ox} \approx 1$ $\times 10^9$ M⁻¹ s⁻¹) close to the diffusional limit. The triplet quenching was accompanied by the appearance of a luminescence in the IR region detected by a Ge-photodiode. This emission was assigned to the $O_2({}^1\Delta_{\sigma})$ phosphorescence for the following reasons: (i) it was produced with the instrumental time resolution; (ii) it decayed by first-order kinetics with lifetimes very close to those already reported for $O_2({}^1\Delta_{\sigma});{}^{29}$ (iii) it was not observed in the absence of the substrate or by bubbling with argon. The emission signal of an air-equilibrated solution extrapolated at "zero time" (I_{Δ}) was proportional to the concentration of $O_2({}^1\Delta_{\rm g}),$ which depends on the quantum yield of the $O_2({}^1\Delta_g)$ production, ϕ_{Δ} , and on the laser energy, $I_{\rm L}$. Therefore, the slopes of the I_{Δ} vs. $I_{\rm L}$ plots, after calibration of the experimental set-up by use of phenalenone as standard $(\phi_{\Delta} = 0.97 \pm 0.03)$ ³⁰ gave ϕ_{Δ} of the thiophene derivatives (Table 4). In air-equilibrated solutions, the quenching efficiency of HTP triplets, defined as the ratio $(\tau^{Ar} - \tau^{air})/\tau^{Ar} =$ $P_{\rm Q}$ where $\tau^{\rm Ar}$ and $\tau^{\rm air}$ correspond to the triplet lifetimes in Ar-saturated and air-equilibrated solutions, respectively, were different for the various HTP and therefore the $\phi_{\rm T}$ values were calculated taking into account the different P_0 values.

Unfortunately, due to the lack of fluorescence it was not possible to measure the singlet lifetimes, however in the presence of heavy atoms they should be short so that it can be assumed that $O_2({}^1\Delta_g)$ is produced only by energy transfer from the lowest triplet state T_1 . Assuming furthermore that the fraction of quenched triplet producing $O_2({}^1\Delta_g)$ is unitary $(S_{\Delta} = 1)$ we determined the lower limits of the ϕ_T values which are reported in Table 4. In general, they are high, as expected for molecules containing heavy atoms such as sulfur and halogens.

Discussion

The dissociation of C-Br and C-I bonds in halobenzene needs energy of 313 ± 5.0 and 286 ± 5.0 kJ mol⁻¹, respectively.³¹ Since it is likely that the energy required for the various halothiophenes is comparable, the dissociation of C-X bonds of these compounds can occur in the lowest excited singlet state. In fact the maximum energy of absorption band at longer wavelengths is around 340 kJ mol⁻¹ for INT and higher for the others. However, the energy of the lowest triplet state of INT, ICNT and BCNT obtained from phosphorescence measurements was 220–250 kJ mol⁻¹ (and 300 kJ mol⁻¹ for INB) and hence should not be sufficient to dissociate the C-X bond as was observed for other HTP's.¹⁸ On the other hand it was stressed that π,π^* triplet⁹ and π,π^* singlet⁴ in haloaromatics are unable to give dissociation because the antibonding π density is placed between carbon atoms. Moreover the flash photolysis experiments of the present work show that the triplets and the radical species were both produced within the laser pulse and this excludes the detected triplet (the lowest, T_1) from being the precursor of the radicals. The decrease in the sensitized photoarylation, paralleling the decrease in the sensitizer energy (Table 1), also gives evidence that the lowest triplet is not reactive (or only slightly reactive). In fact, even though the triplets of benzophenone ($E_{\rm T} = 308 \text{ kJ mol}^{-1}$), phenanthrene ($E_{\rm T} = 259 \text{ kJ mol}^{-1}$) and chrysene ($E_{\rm T} = 238 \text{ kJ}$ mol^{-1}) were efficiently quenched by INT and those of the two former sensitizers by ICNT and BCNT ($k_q \sim 10^{10} \text{ M}^{-1} \text{ s}^{-1}$), the ϕ_{SPA} values of Table 2 show a marked decrease, except for BCNT, on decreasing the energy of the sensitizer (three times for INT). The ICNT and BCNT do not quench the triplet of

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Ch, probably because of a reversible energy transfer with T_1 and/or an inability to populate the too-high upper triplet. The dependence of ϕ_{SPA} on the E_{T} is explained by the fact that the lowest triplet of halothiophenes (estimated energy 220-250 kJ mol^{-1} , Table 3) is able to quench the triplet of the donors (with the exception already mentioned), but is unable to produce photodissociation. Only the donors, which can populate the upper reactive triplet, are able to sensitize the photoreaction. The same behaviour was observed for halothiophene carbaldehyde and acetyliodothiophene for which the reactive triplet was estimated between 250 and 300 kJ mol^{-1.18} For the compounds studied in the present paper the position of the singlet and triplet states are in the same energy range and likely also that of the reactive triplets. It is to be noted, from the data of Table 2, that on decreasing the sensitizer energy from 308 kJ mol⁻¹ (B) to 238 kJ mol⁻¹ (Ph), the ϕ_{SPA} value for BCNT does not change. This can be an indication that in this compound the energy of the reactive triplet is lower than that of other halothiophenes.

Moreover, Table 2 shows that B does not sensitize the photoarylation of INB and hence this compound should not have a reactive triplet at energies smaller than 300 kJ mol⁻¹. Since the ϕ_{SPA} value became detectable with A as sensitizer (310 kJ mol⁻¹), even though it remains very small (0.01), it is likely that the reactive triplet of this compound is higher than 315 kJ mol⁻¹. This is also in agreement with the finding that INB has the highest E_{T} energy in Table 3.

Assuming that $\phi_{\rm T}$ remains unchanged in benzene, and taking into account the experimental errors on ϕ_{PA} and ϕ_{T} , the sum of the quantum yields for the population of the lowest triplet ($\phi_{\rm T}$) and of the reactive state ($\phi_{\rm PA}$) is close to unity. This means that in the direct photoarylation the photons which do not follow the pathway of ISC to the lowest triplet ($\sim 20\%$) can drive the photocleavage of the C-X bond through a singlet or an upper triplet mechanism. The involvement of π,σ^* singlets in the direct excitation can be hypothesized, particularly taking into account that from semi-empirical calculations the π,σ^* singlets are the lowest for these HTPs (Table 1). The singlet mechanism should be less probable for 5bromo- and 5-iodo-2-thiophencarbaldehyde and 2-acetylthiophene for which, on the basis of semi-empirical calculations (not shown) the lowest singlets are carbonylic n,π^* in nature and the π, σ^* are the upper ones (S₂). If the precursor of dissociation is a triplet state it should be an upper one where an antibonding orbital mainly localized on the C-X bond is half filled. The photoarylation quantum yield of INT sensitized by Ch (Table 1) is the lowest amongst the sensitizers, but is higher than the values previously reported for BTCA, ITCA and AIT.18 Since the sensitized photoreaction quantum yields, for a given donor, should be related to the energy of the reactive upper triplet of the acceptor, it is likely that for INT this triplet is a little lower than those of the HTPs reported previously.¹⁸ However it cannot be excluded that the low $\phi_{\rm SPA}$ of the INT-Ch system is due to a small reactivity of the lowest triplet T_1 .

Perusal of Table 2 shows that ϕ_{PA} and ϕ_{SPA} values are comparable. However for ICNT and BCNT ϕ_{SPA} values with benzophenone are higher than ϕ_{PA} . This behaviour, already observed with high energy sensitizers for thiophene derivatives described earlier,¹⁸ can be due to a difference in the population of the reactive triplet in the direct and sensitized excitation due to an ISC lower than unity or to a difference in reactivity of the states if, in the direct photocleavage, a singlet mechanism is operative.

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