Thione Photochemistry: The *Peri* Cyclization of some Polycyclic Aromatic Thiones^{1,2}

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A number of polycyclic aromatic thiones have been prepared from the corresponding ketones. Several of the thiones in which there is a free *peri* position cyclize, on excitation in the $\pi^* \leftarrow n$ band, to give thiophene derivatives. The structures of these were proven by application of physical methods and by desulfurization to the corresponding benzyl derivatives. The formal hydrogen 1,3 migration involved was, in one case, shown to be intermolecular by the incorporation of deuterium, from deuterium oxide, during the irradiation. In the case of the α -naphthyl derivative, the mechanism of the reaction has been investigated and it has been concluded that the n,π^* singlet is the responsible entity.

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On a préparé un nombre de thiones polycycliques aromatiques à partir des cétones correspondantes. Plusieurs des thiones, ayant une position *péri* libre, cyclisent par excitation de la bande $\pi^* \leftarrow n$ et conduisent ainsi à des dérivés du thiophène. La preuve de la structure de ces dérivés est obtenue par des méthodes physiques et par désulfurisation jusqu'au dérivés benzyliques correspondants. On a démontré, en incorporant un deutérium par l'eau deutériée pendant l'irradiation, que la migration 1,3 impliquée, dans un cas, se fait par un mécanisme intermoléculaire. Le mécanisme de la réaction est étudié sur le dérivé α -naphtyl; on en déduit que l'état singulet, n, π^* est l'entité responsable. [Traduit par le journal]

The literature records extensive preoccupation over the last 50 years with the photochemistry of the carbonyl group. Only much more recently has the thiocarbonyl group attracted attention and then for a very limited selection of environmental situations.⁶

Up to the present, studies of aromatic thiones have been restricted, essentially, to that of thiobenzophenone and, indeed, with the exception of certain substituted thiobenzophenones and of 1-thiobenzoylnapthalene (2), no other simple substituted aryl thiones were known. We have shown that for the former the lowest triplet state was most probably n,π^{*7} and it is this state that has been generally invoked in the photo-

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⁵Laboratoire de Chimie Physique, 33 Talence, France. ⁶For a review, see ref. 1. chemical cycloadditions of most aromatic thiones (4, 5).⁸

We report here the preparation of some polycyclic aromatic thiones and a photocyclization of these substances proceeding through the n,π^* singlet state.

Results and Discussion

The thiones 1b-9b were prepared by benzoylation of the appropriate aromatic hydrocarbon, followed by conversion of the ketone to thione with hydrogen chloride and hydrogen sulfide. The ketones, with the exception of 7a were known substances. The position of the functional group had, however, not been unambiguously established in the cases of 5a and 6a (7, 8) and confirmation was obtained as follows. Compound 5a was prepared by an alternative route from 3-bromofluoranthene by reaction with cuprous cyanide, followed by Grignard reaction with phenylmagnesium bromide. The structure of 3-bromofluoranthene appeared to be assured

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⁷For a discussion of the absorption and emission spectroscopy of thioketones see ref. 3.

⁸An exception is the addition of thiobenzophenone to acrylonitrile (6) which proceeds through an upper singlet.



FIG. 1. Emission from 2-thiobenzoylnaphthalene (EPA) at 77 K. FIG. 2. Emission from 1-thiobenzoylnaphthalene (EPA) at 77 K.

tion of attack in perylene and the co-formation of 3,9-dibenzoylperylene.



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(9, 10). Compound 6a was shown to have the indicated structure by oxidation to the known 2benzoylanthraquinone. Compound 7a was not known and assignment of the position of the benzoyl group rests on the known preferred posiThe salient features of the absorption spectra of the thiones are listed in Table 1. At room temperature all compounds exhibit a relatively weak, structureless, long wavelength absorption which (except for 2b) shows a blue shift with increasing solvent polarity (Table 1). This band is characteristic of aromatic thiocarbonyl compounds and has been assigned to the n,π^* state (11, see also footnote 7). The absorption spectrum of 1b has been previously reported (12).

At 77 K in a rigid matrix of EPA (ether-isopentane-ethanol, 5:5:2), the first absorption band is partially resolved into vibronic bands as has been observed for a number of thicketones and, assuming that the first resolved band is the O-O band, the singlet energies are given in Table 1 together with the spacings between the vibronic bands. In the case of 1b, 2b, and possibly also in 4b, a weak band appeared on the long wavelength side of the (n,π^*) band at 77 K. A similar band had previously been observed for a number of thiocarbonyl compounds (13) and has been tentatively assigned to the singlet \rightarrow triplet transition. Attempts to observe a similar band in the other compounds using more concentrated solutions proved unsuccessful owing to their low solubility.

The luminescent properties of all the compounds have also been measured. These were determined at 77 K in EPA, with the exception of 7b where, due to its low solubility, methyl acetate – ether (2:3) was used as solvent. The emission spectrum of 2b, observed following excitation at 390 or 550 nm, is shown in Fig. 1, (τ 66 µs). The emission from compound 1b is similar to that from 2b (see Fig. 1). Compounds 3b, 4b, and 5b show rather weak luminescence, the shape of which is similar to 1b, but no lifetime measurements were possible. No thione

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			Absorption spectra at 77 K			
Compound	Absorption spectra λ_{max} , nn	OO band	Band	F		
	In cyclohexane	In ethanol ether (1:1)	$E_{\rm s}$ (kJ/mol)	(cm ⁻¹)	(kJ/mol)	
16	618 (2.18), 385 sh (3.43) 371 (3.47), 316 (4.19)	609 (2.21), 375 (3.49) 317 (4.20)	635 (188.4)	1087	164.0	
2 b	610 (2.34), 384 (3.73) 367 (3.82), 318 (4.28)	609 (2.37), 387 sh (3.80) 322 (4.31)	627 (190.8)	1087	172.4	
3 b	622 (2.56), 442 (3.79) 424 (3.79), 383 (3.62) 330 (4.46)	612 (2.62), 436 (3.79) 382 (3.59), 345 sh (4.39) 329 (4.47)	640 (186.9)	959	160.7	
4 b	622 (2.31), 397 (3.64) 327 sh (4.35), 317 (4.38)	610 (2.38), 403 (3.66) 330 sh (4.37), 316 (4.38)	632 (189.3)	928	164.0	
5 b	621 (2.52), 387 (4.10) 318 (4.27)	613 (2.55), 390 (4.09) 340 sh (4.21), 323 <u>(</u> 4.28)	641 (186.6)	1121	159.4	
6 b	614 (2.23), 483 (3.71) 455 (3.66), 428 (3.51) 395 (3.74), 374 (3.94) 345 (4.37)	607 (2.36), 451 (3.79) 457 sh (3.72), 394 (3.79) 374 (4.04), 344 (4.46)	628 (190.5)	970		
7 b (in benzene)	616 (2.74), 471 (4.29) 444 (4.31), 329 (3.77)		_	_		
8 b	612 (2.83), 567 (2.86) 441 (4.27), 324 (4.16)	600 (2.89), 448 (4.23) 325 (4.12)	635 (188.4)	1059		
9 b	615 (2.37), 425 (3.70) 318 (4.00)	590 (2.85), 465 (3.98) 321 (3.98)	620 (192.9)	849		

TABLE 1. Absorption spectra and triplet energies of the thiones

luminescence could be detected from 6b, 7b, and 8b. The spectral position and general similarity to the emission observed from other thioketones⁷ suggests that the emission is phosphorescence from a ${}^{3}(n,\pi^{*})$ state. Assuming this to be true, the triplet energies (E_{T}) are given in Table 1.

All the thiones were excited by irradiation (>520 nm) into the long wavelength (n,π^*) band. Products were found for thiones 1b, 3b, 4b, and 7b, whereas irradiation 5–10 times longer of the others, led only to recovery of starting material. All the reactive compounds had free peri positions, (and were derived from alternant hydrocarbons) and the structures of the products, 1c, 3c, and 4c, indicated that cyclization had occurred at this position; that in 7c is assumed by analogy. The structures of the cyclized products followed from their constitutions, their Raney nickel desulfurization to the corresponding known benzyl derivatives and the observation of a signal for a benzylic proton in their n.m.r. spectra close to 6.2 p.p.m. (14) (except in the case of 7c, which was found too insoluble for n.m.r. spectrum determination). Compound



1c has been obtained by a multistep synthesis previously (15) and the physical data obtained are in agreement with the present observations.

A plausible reaction pathway is that indicated in Scheme 1, where the asterisks may represent zero, one, or two electrons.

Along the reaction pathway at some point a

COX	ΕT	AL.:	THIONE	PHOTOCHEMISTRY
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Compound	Concentration ^a (M)	Monitoring λ (nm)	Decay rate ^b	
1 <i>b</i>	8.9×10^{-4}	550	1.41 × 107	
2 b	7.4×10^{-4}	550	5×10^{6}	
3 b	$\begin{cases} 2.5 \times 10^{-5} \\ 6.2 \times 10^{-6} \end{cases}$	No transient	s detected	
4 b	3.2×10^{-5}	450	7.7×10^{6}	
5 b	5.9×10^{-5}	470	6.85×10^{7}	
6 b	2.7×10^{-4}	540	2.5×10^{6}	
7 b	1.18×10^{-4}			
8 b	2.8×10^{-5}	No transionts datastad		
9 b	$\begin{cases} 9.1 \times 10^{-4} \\ 5.7 \times 10^{-4} \end{cases}$	ino transien		

Fable 2 .	Transients	observed	l on flas	sh photolysis
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[•]In cyclohexane. [•]A combination, most probably, of unimolecular and bimolecular rate processes.



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hydrogen atom must be transferred. This could be, in principle, a photochemical 1,3-proton shift (suprafacial) or a two-step intermolecular process. We were able to demonstrate that the transfer could involve a discrete intermediate by showing that the hydrogen transfer could be intermolecular. Irradiation of 1b in acetonitrile containing deuterium oxide led, essentially quantitatively, to the incorporation of one deuteron at the benzylic position. We conclude tentatively that the species represented by the formalism 10 is a singlet and dipolar. This, in itself, does not require that the reaction pathway only include singlets since intersystem crossing along the reaction coordinate, facilitated by the presence of the sulfur atom, is not to be excluded.

The multiplicity of the reaction was then studied. The number of triplet quenchers available having suitable energies, chemical and spectroscopic properties are few: two, of different types, were selected. The quantum yield of the reaction in benzene is 1.2×10^{-3} (excitation ~577 nm). In the presence of $1.2 \times 10^{-2} M$ perylene ($E_{\rm T}$ = 150.5 kJ/mol) a value of 1.29 × 10^{-3} was obtained: identical with the unquenched reaction within experimental error. In the presence of cyclooctatetraene (0.29 M) the quantum yield remained at 1.28×10^{-3} and increase of quencher concentration to 0.59 M produced no change. Now, in the case of quenching by pervlene, assuming the quenching to be diffusion controlled, then it should have been observed with a species of lifetime of the order of 10^{-8} s, or longer. With the same assumption for cyclooctatetraene, quenching should have been observed for a triplet of lifetime $> 10^{-9}$ s. Some doubt is attached to the use of cyclooctatetraene since its triplet energy is not known exactly. It has been shown, however, that it will quench the lowest triplets of thiobenzophenone and Michler's thione at slightly lower than diffusion controlled rates (16).

It was, thus, necessary to show that the triplet of 1b had, indeed, a lifetime which would have permitted quenching.

Several of the compounds were studied by flash photolytic techniques. Using a doubled ruby laser (16) the triplet decay rates determined in cyclohexane at the concentrations used are given in Table 2. A more detailed study was made of compound 1b using a tripled neodymium laser (λ 353 nm).⁹ In benzene solution and using concentrations up to $1.5 \times 10^{-3} M$, a plot was obtained, monitoring the transient at 550 nm, of reciprocal lifetime against concentration. A

⁹The technique used has already been described: see ref. 17.

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Concentration $(M \times 10^3)$	Solvent	Quantum yield $(\Phi \times 10^3)$
4.8	Benzene	1.20 ± 0.1
4.4	Benzene-MeOH (4:1)	1.80 ± 0.1
4.3	Benzene-HOAc (4:1)	1.47
4.4	CH ₃ CN	2.61
4.4	$CH_3CN-HOAc (4:1)$	3.0
4.8	Benzene $(1.2 \times 10^{-2} \text{ perylene})$	1.29
4.8	Benzene (0.29 <i>M</i> COT)	1.28
4.8	Benzene (0.588 COT)	1.30

BLE 3.	Quantum	yields	of	cyclization	of	1	b
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unimolecular decay rate of $1.0 \pm 0.1 \times 10^7 \text{ s}^{-1}$ resulted, together with a bimolecular rate constant for quenching of the triplet by ground state thione of $1.8 \pm 1 \times 10^9 M^{-1} \text{ s}^{-1}$. The latter as observed with the triplets of other aromatic thiones (16) and of adamantanethione (18) was close to diffusion controlled. The large error in these determinations is a consequence of the limited concentration range possible.

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The lifetime of $\sim 10^{-7}$ s should have permitted quenching and it was indeed shown that in 10^{-3} M solution in benzene, the transient could be quenched by cyclooctatetraene with a bimolecular rate constant of $2.2 \pm 1 \times 10^9 M^{-1}$ s⁻¹, also close to diffusion controlled. Since no quenching was observed in the quantum yield of cyclization measurements one must conclude that the triplet is not involved in this transformation and that the responsible species is the n,π^* singlet.

The mechanism as formulated involves charge separation and so might be thought to be facilitated by a polar solvent. Small increases were indeed observed (Table 3) but in the most polar system used, which contained the proton donor acetic acid, the quantum yield was rather more than $2\frac{1}{2}$ times that in benzene, yet nevertheless remained very small. The inefficiency of the process may be due to at least two factors. In the first place the intermediate 10 may be formed inefficiently, the greater part of the singlet energy being lost in rapid intersystem crossing. Alternatively, it may be that the intermediate 10 is formed efficiently but reverts almost equally efficiently to the ground state, the overall process being an intramolecular chemical quenching. Under such circumstances the intersystem crossing yield would be low and this would be compatible with the weak emissions observed and in particular with the important difference in intensity of emission between 1b and 2b.

The question arises as to why a similar reaction is not observed for ketones. The explanation may be, aside from geometrical changes caused by changing oxygen for sulfur, that a lowest n,π^* state is required, and that in virtually all polycyclic aromatic ketones in which this might be observed the lowest energy singlet state is π,π^* . The exception is that of the lbenzoylnaphthalene but even here the n,π^* and π,π^* states may be close enough to perturb each other.



To induce the cyclization with a ketone it is required that the aromatic nucleus be separated from the ketone by a saturated carbon to provide both the equivalent of a *peri* position, and to maintain a lowest n,π^* singlet state. Such a process has, in fact, been realized by Sheehan *et al.* (19). In their case, however, that of **11**, the reaction is completely quenchable whilst that of **12** is not. As discussed by the authors this either indicates a change of state, or a lifetime > 10⁻¹⁰ s for a reactive triplet in the second case.

General

Melting points were determined on a Kofler block and are uncorrected. Mass spectra were obtained on a Varian M66 spectrometer.

Experimental Section

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The apparatus used for the recording of emission spectra has been described elsewhere.⁷ For the present work an RCA C31034 photomultiplier was used cooled to -35° . Samples for emission studies or flash photolysis were degassed by the freeze-pump-thaw method to a residual pressure of $< 5 \times 10^{-5}$ Torr.

The apparatus for nanosecond flash photolysis incorporated a pulsed ruby laser, frequency doubler, a model 82-410 Jarrell-Ash monochromator, together with a Xe arc pulsing unit (Northern Precision). The microsecond flash apparatus utilized a Spex monochromator equipped with an EMI 6256B photomultiplier.

Materials

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1-Benzoylnaphthalene (1a) was prepared as described previously (20), m.p. 75° (lit. (20) m.p. 76°) and shown to be free of the 2-benzoyl derivative by t.l.c. The 2-benzoylnaphthalene (2a) (Pfalz and Bauer) was crystallized from MeOH, m.p. 80° (lit. (21) m.p. 81°). 1-Benzoylpyrene (3a), prepared by a reported method (22) was obtained (from ethanol) in two crystalline forms m.p. 127-128° (lit. (22) m.p. 126°) and 118°. The latter on melting and resolidifying had m.p. 127-128° and the latter form was also obtained on sublimation. 6-Benzoylchrysene (4a) (23) had m.p. 191° (lit. (23) m.p. 192°) from benzenealcohol. 3-Benzoylfluoranthene (5a) (24) was purified by chromatography and crystallized from ethanol, m.p. 128-129° (lit. (24) m.p. 129-130°). 1-Benzoylazulene (8a) (25), 1-amino-4-benzoylnaphthalene (9a) (26), and 1-thiobenzoylnaphthalene (2c) (12) were prepared by reported methods.

3-Cyanofluoranthene

3-Bromofluoranthene (6 g) and CuCN (5 g) in Nmethylpyrrolidone (50 ml) was maintained at 180° for 5 h and the product poured into aqueous ammonia. Isolation with benzene and chromatography on alumina gave the cyanide, m.p. 114° (lit. (24) m.p. 112°).

3-Benzoylfluoranthene

3-Cyanofluoranthene (2 g) in anhydrous benzene (50 ml) was added to the Grignard reagent from bromobenzene (7.9 g) and magnesium turnings (1.2 g) in 100 ml ether. The mixture was refluxed (4 h) and then decomposed with aqueous sulfuric acid (100 ml, 10 N) followed by 5 h further reflux. Isolation with benzene followed by 5 h further reflux. Isolation with benzene followed by chromatography on alumina gave 5a (47%) identical in all respects with that obtained by the previously described procedure.

2-Benzoyl-9,10-dimethylanthracene (8)

This compound (6a) was obtained in two crystalline forms, m.p. $141-142^{\circ}$ and 131° (lit. (8) m.p. 145°) from benzene-ethanol. Oxidation with chromic acid in acetic acid gave the anthraquinone, m.p. 217° (lit. (8) m.p. $216-217^{\circ}$).

3-Benzoylperylene (7a)

Anhydrous aluminum chloride (1 g) was added to a solution of perylene (1.8 g) and benzoyl chloride (1 g) in CS_2 (100 ml) and stirred for 3 h at room temperature. After decomposition with water and chromatography of

the product on alumina, perylene (67%), 7a (20%), and 3,9-dibenzoylperylene (1.5%) (m.p. 291–292°; lit. (27) m.p. 293°) were obtained. The monobenzoyl derivative had m.p. 208°.

Anal. Calcd. for $C_{27}H_{16}O$: C, 90.98; H, 4.53; O, 4.49. Found: C, 90.84; H, 4.57; O, 4.80.

2-Thiobenzoylnaphthalene (2b)

2-Benzoylnaphthalene (1.1 g) was dissolved in 100 ml methanol at -5° (N₂) and HCl and H₂S passed through for 4 h, H₂S passage being continued for a further 4 h. The blue crystals were filtered, dried, and sublimed to give 2b (0.9 g) m.p. 79°, whose i.r. spectrum showed no carbonyl band.

Anal. Calcd. for $C_{17}H_{12}S$: C, 82.24; H, 4.87; S, 12.89. Found: C, 82.01; H, 4.76; S, 12.21.

1-Thiobenzoylpyrene (3b)

1-Benzoylpyrene (2 g) was dissolved in a mixtue of 20 ml benzene and 100 ml alcohol, and HCl-H₂S passed through for $5\frac{1}{2}$ h at 0°. After neutralization (NaHCO₃) the product was chromatographed on Florisil. Elution with CCl₄ – light petroleum gave black crystals (1.46 g), m.p. 141° (methanol).

Anal. Calcd. for $C_{23}H_{14}S$: C, 85.70; H, 4.38; S, 9.93. Found: C, 85.34; H, 4.56; S, 9.99.

6-Thiobenzoylchrysene (4b)

6-Benzoylchrysene was converted into the thione as described for (2b). The green crystals $(2 g, 94\%; m.p. 184-185^{\circ} (benzene-methanol))$ showed carbonyl stretch in the i.r.

Anal. Calcd. for $C_{25}H_{16}S$: C, 86.18; H, 4.43; S, 9.19. Found: C, 86.21; H, 4.57; S, 9.48.

3-Thiobenzoylfluoranthene (5b)

This was prepared as was 3b in 90% yield and the green crystals had m.p. 142° (benzene-ethanol).

Anal. Calcd. for $C_{23}H_{14}S$: C, 85.70; H, 4.38; S, 9.93. Found: C, 85.85; H, 4.38; S, 10.01.

9,10-Dimethyl-2-thiobenzoylanthracene (6b)

This was prepared as described for 3b. It was obtained as black crystals (methanol), m.p. $144-146^{\circ}$ (86%). The continuing presence of ketone (i.r.) made it impossible to obtain satisfactory analyses for this compound.

3-Thiobenzoylperylene (7b)

The ketone was treated, in methanol-benzene solution, as for 3b. The precipitate which formed (95%) as brown crystals, insoluble in the usual solvents, had m.p. 258°.

Anal. Calcd. for $C_{27}H_{16}S$: C, 81.08; H, 4.33; S, 8.59. Found: C, 81.21; H, 4.43; S, 8.30.

1-Thiobenzoylazulene (8b)

The ketone (560 mg) in 80 ml MeOH was treated at 0° with HCl-H₂S for 4 h (HCl) and 6 h (H₂S). After neutralization (NaHCO₃) and isolation with chloroform the product was chromatographed on Florisil. Light petroleum elution gave **8**b as black crystals (98 mg, 16%), m.p. 68° (light petroleum).

Anal. Calcd. for $C_{17}H_{12}S$: C, 82.24; H, 4.87; S, 12.89. Found: C, 81.60; H, 5.07; S, 12.70.

1-Amino-4-thiobenzoylnaphthalene (9b)

The ketone (3 g) was dissolved in MeOH (100 ml) and HCl and H₂S passed through for 4 and 8 h, respectively, at 0°. The crystalline precipitate was collected, being the hydrochloride (2.8 g).

Anal. Calcd. for $C_{17}H_{14}$ NSCI: C, 68.10; H, 4.66; N, 4.66; S, 10.68; Cl, 11.85. Found: C, 67.78; H, 4.73; N, 4.60; S, 10.72; Cl, 11.95.

The hydrochloride (1.4 g) in MeOH was neutralized with aqueous sodium bicarbonate and, after isolation, the product was crystallized from methanol (0.91 g, 74%) in brown crystals, m.p. 74°.

Anal. Calcd. for $C_{17}H_{13}NS$: C, 77.56; H, 4.94; N, 5.32. Found: C, 77.86; h, 5.22; N, 5.26.

Cyclizations

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These were performed using a 450 W medium pressure lamp in conjunction with a Corning filter C53-68 to absorb wavelengths below 520 nm. Solutions were degassed and irradiated until decolorized.

2-Phenyl-2H-naphtho[1,8bc]thiophene (1c)

The thione (240 mg) in 15 ml benzene was irradiated for 26 h. The product was chromatographed through Florisil to give pale yellow crystals (51%; m.p. 101°; lit. (15c) m.p. 100-101°).

Anal. Calcd. for $C_{17}H_{12}S$: C, 82.24; H, 4.87; S, 12.89. Found: C, 82.25; H, 4.42; S, 12.42.

The same product was obtained using MeCN as solvent (20 ml) containing 1 ml MeOH or water. In the presence of 1 ml D₂O, 2-phenyl-2*D*-naphtho [1,8*bc*] thiophene was obtained. The n.m.r. was identical in all respects with the protium compound except for the complete absence of a singlet at δ 6.18; mol. wt. (mass spectrum) 249.

The possibility of H/D exchange occurring in the final product was excluded by the appropriate control.

2-Phenyl-2H-pyreno[1,10bc]thiophene (3c)

This was obtained in 59% yield, after similar irradiation, as pale yellow crystals, m.p. 155° (methanol); $\lambda_{max}(C_6H_{12})$ 386, 367, 361, 349, 292, 230 nm (ε 5400, 1500, 13 800, 15 300, 12 350, 42 500); *m/e* (M⁺) 322; singlet at 6.25 p.p.m. in the n.m.r. spectrum.

Anal. Calcd. for $C_{23}H_{14}S$: C, 85.70; H, 4.38; S, 9.93. Found: C, 86.14; H, 4.42; S, 9.47.

2-Phenyl-2H-chryseno[1,2bc]thiophen (4c)

This was similarly obtained in 58% yield, m.p. 183– 184° (benzene); $\lambda_{max}(C_6H_{12})$ 377, 360, 344, 316, 275, 267 nm (ϵ 5000, 9700, 10 800, 6400, 44 450, 45 000); *m/e* 348 (M⁺); singlet at 6.2 p.p.m. in the n.m.r. spectrum.

Anal. Calcd. for $C_{25}H_{16}S$: C, 86.18; H, 4.63; S, 9.19. Found: C, 86.18; H, 4.95; S, 9.02.

2-Phenyl-2H-peryleno[1,12bc]thiophen (7c)

The thione (28 mg) was suspended in 20 ml benzene and irradiated for 3 h with shaking after which all the material was in solution. After chromatography on silica the product was obtained as brown crystals (60%) m.p. > 350°; $\lambda_{max}(C_6H_{12})$ 473, 445, 422, 357, 338, 240, 228, 218 nm (ε 18 600, 16 200, 10 000, 11 000, 13 800, 5900, 7700, 90 000); *m/e* 372.09823 (M⁺) (calcd. 372.09726).

Desulfurization of the Thiophene Derivatives

A solution of the thiophene in ethanol was refluxed with Raney nickel previously deactivated by heating for 3 h with acetone. The reactions were followed by t.l.c. and interrupted before the appearance of over-reduction compounds. The results are given in Table 4.

Oxidation of 2-Phenyl-2H-naphtho[1,8bc]thiophen

The thiophen (264 mg) *m*-chloroperbenzoic acid (0.48 g) and sodium carbonate (800 mg) were stirred in 10 ml ethylene dichloride for 2 h at room temperature. Isolation of the product after dilution with water and washing gave the corresponding sulfoxide (97%), m.p. 167-168° (lit. 168-169° (15c)).

Quantum Yields

For irradiations ~577 nm the light from a mercury source (HBO 200 W) was passed through a potassium dichromate-copper sulfate filter solution (29). The actinometric solution was Reinecke's salt (30). For the 366 nm line Corning filter CS-52 and CS-7-60 were employed and ferrioxalate actinometry (31). Solutions of 1b were degassed. After irradiation the solution was evaporated under nitrogen and a solution of 100 mg hydroxylamine hydrochloride in 20 ml methanol containing 5 drops of pyridine was added and with the disappearance of the thione color the solvent was evaporated below 40° under nitrogen. The residue was dissolved in benzene and filtered through 20 g silica gel.

A solution of known concentration of fluoranthene was added to the eluent after evaporation and analysis performed by vapor phase chromatography using a glass column packed with 3% SE 30 on Chromasorb W at 180°.

Control experiments indicated that the maximum error introduced by this treatment was $\pm 6\%$. The above sequence was necessary since no means was found of separating the thione and cyclized material by v.p.c.

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TABLE 4. Raney nickel desulfurizations of thiophenes

	Time	Vield of bangul	Recovered thiophene (%)	Melting point (°C)		
Thiophene	(h)	derivative (%)		Experiment	Literature (ref. no.)	
1 <i>c</i>	12	39	45	55–56	55(28)	
3 <i>c</i>	24	37	44	89	89(22)	
4 <i>c</i>	24	60	27	200	200-203(23)	
7c	24	42	36	177	*(present work)	

*Anal. Calcd. for $C_{27}H_{18}$: C, 94.70; H, 5.30. Found: C, 94.66; H, 5.33. This substance was also obtained by refluxing 3-benzoylperylene, 99% hydrazine hydrate and potassium hydroxide in diethylene glycol.

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