

Photoreaction between 2-Benzoylthiophene and Phenol or Indole

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Laser flash photolysis, density functional theory (DFT) calculations, and product studies have been performed to understand the mechanism of photoreduction of 2-benzoylthiophene (BT) in the presence of phenol or indole. Time-resolved experiments showed that BT ketyl (BTH) and phenoxy (PhO) or indolyl (In) radicals are generated with high rate constants and quantum yields close to 1. However, low conversions (specially in the case of indole) of the starting reagents are obtained upon prolonged lamp irradiation, indicating that recombination within the radical pairs must occur to a large extent, regenerating the starting materials. The solvent-dependence of the quenching rate constants, together with DFT theoretical studies, indicate fundamental differences between the mechanisms of the reaction of BT triplet with phenol and indole. Thus, data for phenol agree with the involvement of a hydrogen-bonded exciplex BT \cdots HOPh, where concerted electron and proton transfer leads to the BTH \cdots Oph radical pair. However, in the case of indole, electron transfer at the BT \cdots HIn stage precedes proton transfer. Finally, C–C cross-coupling products have been isolated and characterized in the preparative irradiation of BT in the presence of phenol and indole. The structures of the products have been confirmed by alternative synthesis.

Introduction

The 2-benzoylthiophene (BT) chromophore is interesting for a number of reasons. Compounds containing BT are used as components of polymerization catalysts,¹ as crystals for generating higher harmonics in Nd:YAG lasers,² as UV absorbers for photographic materials,³ and as photostabilizers of polyolefins.⁴ This chromophore is also present in the nonsteroidal antiinflammatories tiaprofenic acid (TPA) and suprofen (SUP). Both TPA and SUP are known to produce detrimental side-effects on humans upon exposure to sunlight, either after topical or systemic administration.⁵ Such effects involve lipid peroxidation,⁶ photohemolysis,⁷ drug–protein photobinding,⁸ photooxidation of proteins,⁹ and DNA lesions.¹⁰

Despite its relevance to the above-mentioned photobiological and phototechnological applications, very limited information is available in the literature regarding

the photochemical behavior of the benzoylthiophene chromophore.

The lowest lying triplet of BT has a π,π^* configuration involving mainly the thenoyl group and is generated with a quantum yield close to unity.¹¹ BT undergoes [2 + 2] photocycloaddition to olefins through either the C=O or the thiophene C=C bonds. Thus, Arnold et al.¹² have reported formation of oxetanes by photocycloaddition of isobutylene to the carbonyl group of BT using a quartz filter; the resulting products are thermally unstable and eliminate formaldehyde. By contrast, Cantrell has found that Pyrex-filtered irradiation leads to cycloaddition to a thiophene C=C bond.¹³ Furthermore, reaction at the

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[†] Universidad de Valencia.

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(1) Wrzyszczyński, A.; Janota, H. *Polymer* **1996**, *41*, 560.

(2) Vizgert, R. V.; Davydov, B. L.; Kotovshchikov, S. G.; Starodubtseva, M. P. *Kvantovaya Electron* (Moscow) **1982**, *9*, 380. *Chem. Abstr.* **1982**, *96*, 226199r.

(3) Leppard, D. G.; Burdeska, K. Eur. Pat. Appl., 1993. *Chem. Abstr.* **1993**, *119*, 82785x.

(4) Zimin, Y. B.; Levin, P. I.; Matveeva, E. A.; Kozodoi, A. A.; Sotnikova, L. M. *Plast. Massy* **1970**, *20*. *Chem. Abstr.* **1970**, *72*, 101351g.

(5) Boscá, F.; Marín, M. L.; Miranda, M. A. *Photochem. Photobiol.* **2001**, *74*, 637.

(6) Castell, J. V.; Gómez-Lechón, M. J.; Grassa, C.; Martínez, L., A.; Miranda, M. A.; Tarrega, P. *Photochem. Photobiol.* **1994**, *59*, 35.

(7) De Guidi, G.; Chillemi, R.; Costanzo, L. L.; Giufrida, S.; Sortino, S.; Condorelli, G. *J. Photochem. Photobiol. B: Biol.* **1994**, *23*, 125.

(8) Castell, J. V.; Hernández, D.; Gómez-Lechón, M. J.; Lahoz, A.; Miranda, M. A.; Morera, I. M.; Pérez-Prieto, J.; Sarabia, Z. *Photochem. Photobiol.* **1998**, *68*, 660.

(9) (a) Miranda, M. A.; Castell, J. V.; Hernández, D.; Gómez-Lechón, M. J.; Boscá, F.; Morera, I. M.; Sarabia, Z. *Chem. Res. Toxicol.* **1998**, *11*, 172. (b) Figueiredo, A.; Ribeiro, C. A. F.; Goncalo, M.; Baptista, A. P.; Teixeira, F. J. *Photochem. Photobiol. B: Biol.* **1993**, *18*, 161.

(10) (a) Agapakis-Causse, C.; Boscá, F.; Castell, J. V.; Hernández, D.; Marín, M. L.; Marrot, L.; Miranda, M. L. *Photochem. Photobiol.* **2000**, *71*, 499. (b) Starrs, S. M.; Davies, R. J. H. *Photochem. Photobiol.* **2000**, *72*, 291. (c) Artuso, T.; Bernadou, J.; Meunier, B.; Piette, J.; Pailloux, N. *Photochem. Photobiol.* **1991**, *54*, 205.

(11) (a) Becker, R. S.; Favaro, G.; Poggi, G.; Romani, A. *J. Phys. Chem.* **1995**, *99*, 1410. (b) Arnold, D. R.; Birtwell, R. J. *J. Am. Chem. Soc.* **1973**, *95*, 4599.

(12) Arnold, D. R.; Birtwell, R. J.; Clarke, B. M., Jr. *Can. J. Chem.* **1974**, *52*, 1681.

(13) Cantrell, T. S. *J. Chem. Soc.* **1972**, 155.

carbonyl group also occurs in the [2 + 2] photocycloaddition of BT to 2,5-dimethylthiophene, while methylmaleic anhydrides react with a thiophene C=C bond.¹⁴ Quenching of the BT triplet state by methyl methacrylate (MMA) has been postulated to occur via formation of 1,4-biradicals; however, only formation of uncharacterized polymers (and no oxetanes) has been reported.¹⁵

On the other hand, excited triplet BT is able to abstract hydrogen from suitable donors, though with low efficiency. Traynard and Blanchi have reported quantum yields of 0.17 for the disappearance of BT upon irradiation in 2-propanol, much lower than the value of 1.23 for benzophenone.¹⁶ The reaction products, assumed to be pinacols but not isolated, were only assigned on the basis of UV spectra. By contrast, the pinacols obtained after irradiation of the analogue 2-benzoyl-5-ethylthiophene (Et-BT) in 2-propanol have been isolated and fully characterized.^{17,18} The involved reductive process is mediated by the second excited triplet, of n,π^* character. Temperature dependence experiments agree with the reaction occurring after thermal population of the reactive upper n,π^* ketone triplet.¹⁸

In accordance with the low efficiency of hydrogen abstraction by the benzoylthiophene triplet,¹⁹ its lifetime in neat ¹ButOH ($\tau = 4.5 \mu\text{s}$) is only slightly shorter than in 2,2,2-trifluoroethanol ($5.2 \mu\text{s}$).^{19b} The long lifetime and intensity of BT triplet, as well as the overlap of triplet and ketyl absorptions, have made the clear observation and study of the latter intermediate difficult.

Formal hydrogen abstraction by the BT chromophore can also occur by sequential proton–electron-transfer processes. As a consequence, hydrodimers have been obtained when compounds containing the BT chromophore are irradiated in the presence of electron donors such as *p*-cresol.^{9a,17} In similar cases, the high reactivity of π,π^* triplet ketones toward phenolic hydrogen abstraction has been explained as due to rate-determining electron transfer within the phenol–ketone exciplex, followed by proton transfer.^{20,21} Although phenoxy/ketyl radical pairs are the expected primary intermediates, it is remarkable that up to now C–C cross-coupling products have only been detected and isolated when using a phenol unable to form the hemiketals resulting from C–O coupling, such as the sterically hindered 2,6-di-*tert*-butylphenol.¹⁷ No product studies of this type have been performed with indolic derivatives, although indoles are also able to quench BT-derived triplets.^{9a}

(14) (a) Rivas, C.; Bolívar, R. A.; Gonzalez, R.; Machado, R.; Vargas, F. *Monats. Chem.* **1996**, *127*, 529. (b) Rivas, C.; Bolívar, R. A. *J. Heterocycl. Chem.* **1973**, *10*, 967.

(15) Timpe, H. J.; Kronfeld, K. P.; Schiller, M. *J. Photochem. Photobiol. A: Chem.* **1991**, *62*, 245.

(16) Traynard, P.; Blanchi, J. P. *J. Chim. Phys. Physicochim. Biol.* **1972**, *69*, 284.

(17) Miranda, M. A.; Pérez-Prieto, J.; Lahoz, A.; Morera, I. M.; Sarabia, Z.; Martínez-Mañez, R.; Castell, J. V. *Eur. J. Org. Chem.* **1998**, *11*, 172.

(18) Encinas, S.; Miranda, M. A.; Marconi, G.; Monti, S. *Photochem. Photobiol.* **1998**, *67*, 420.

(19) (a) Bosca, F.; Miranda, M. A.; Morera, I. M.; Samadi, A. *J. Photochem. Photobiol. B: Biology* **2000**, *58*, 1. (b) Ortica, F.; Romani, A.; Favaro, G. *J. Phys. Chem.* **1999**, *103*, 1335.

(20) (a) Miranda, M. A.; Lahoz, A.; Boscá, F.; Metni, M. R.; Abdelouahab, F. B.; Castell, J. V.; Pérez-Prieto, J. *Chem. Commun.* **2000**, 2257. (b) Miranda, M. A.; Lahoz, A.; Martínez-Mañez, R.; Boscá, F.; Castell, J. V.; Pérez-Prieto, J. *J. Am. Chem. Soc.* **1999**, *121*, 11569.

(21) (a) Biczók, L.; Bérces, T.; Linschitz, H. *J. Am. Chem. Soc.* **1997**, *119*, 11071. (b) Leigh, W. J.; Lathioir, E. C.; Pierre, M. J. S. T. *J. Am. Chem. Soc.* **1996**, *118*, 12339.

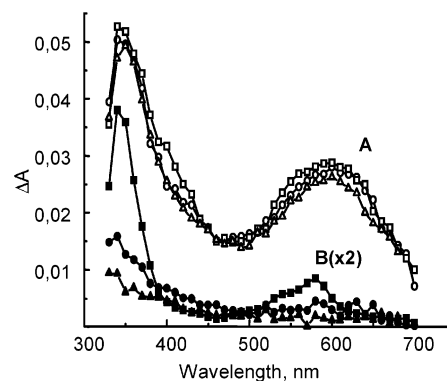


FIGURE 1. A: Transient absorption spectra recorded 50 ns after laser excitation (355 nm) of BT in deaerated methanol (□), acetonitrile (○), or dichloromethane (△) solutions. B: Transient absorption spectra recorded 8 μs after laser excitation (355 nm) of BT in deaerated methanol (■), acetonitrile (●), or dichloromethane (▲) solutions. In part B, absorbances have been multiplied by two.

In this paper, our aim was to perform a detailed study on the photoreactivity of BT toward phenol and indole. Using the laser flash photolysis technique, we have been able to observe clearly the transient absorption spectrum of BT ketyl radical, together with formation of phenoxy and indolyl radicals. Product studies have shown that not only the ketone hydrodimers, but also cross-coupling products can be isolated and characterized in both cases. Furthermore, theoretical studies on the interaction of BT triplet state with phenol and indole have been performed; some interesting differences between ketone/phenol and ketone/indole exciplexes are found.

Results and Discussion

Time-Resolved Studies. Dynamic studies on the reaction of benzoylthiophene with phenol and indole were performed in methanol, acetonitrile, and dichloromethane using 355 nm laser excitation (Nd:YAG).

Laser flash photolysis of deaerated BT solutions led to a transient absorbing in the 300–700 nm range, with maxima at 350 ($\epsilon_{\text{max}} = 4800 \text{ M}^{-1} \text{ cm}^{-1}$) and 600 nm ($\epsilon_{\text{max}} = 2900 \text{ M}^{-1} \text{ cm}^{-1}$). In the three solvents, the spectra obtained at short times after the laser pulse matched that previously reported for BT triplet state.^{11a} After longer delay times, a residual absorption peaking at 350 and 580 nm followed triplet disappearance in methanol. This absorption was ascribed to BT ketyl radical formation, due to hydrogen abstraction from the donor solvent (see Figure 1 for a comparison between the absorption spectra obtained in the three solvents at two different times after the laser pulse). Triplet lifetimes were measured in oxygen-free solutions and found to be 1.9 μs in dichloromethane, 1.6 μs in acetonitrile, and 1.4 μs in methanol (a lifetime of 1.4 μs in acetonitrile has been reported in the literature).^{11a}

Quenching of the triplet by phenol and indole was observed in the three solvents at room temperature. The time-evolution of the transient spectra in dichloromethane is shown in Figure 2. Similar spectra were obtained in the other two solvents (not shown). In the presence of phenol the disappearance of the BT triplet was followed by formation of transient(s) with absorption maxima at

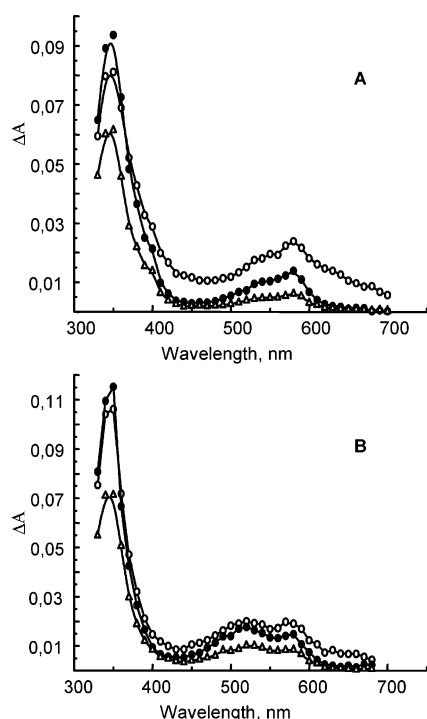


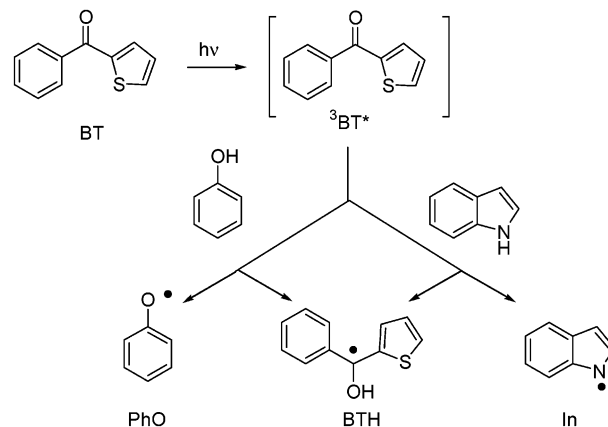
FIGURE 2. A: Transient absorption spectra of a dichloromethane solution of BT (0.9 mM) and phenol (4 mM) at 0.1 μ s (○), 0.5 μ s (●), and 2.0 μ s (△) after the laser pulse. B: Transient absorption spectra of a dichloromethane solution of BT (0.9 mM) and indole (4 mM) at 0.1 μ s (○), 0.5 μ s (●) and 2.0 μ s (△) after the laser pulse.

350 (strong), 390 (shoulder), 540 (shoulder), and 580 nm (medium intensity), and no absorption beyond 625 nm (Figure 2A). Similar spectra were observed when using indole as quencher, but without the shoulder at 390 nm and with an enhanced broad band in the 450–550 nm region (Figure 2B).

It has been reported that the transient BT ketyl radical absorption spectrum possesses two maxima located at 355 and 580 nm.^{19b} The transient absorption spectra for phenoxy and indolyl radicals have also been described. The former displays two maxima at 385–405 nm ($\epsilon_{405} = 3200 \text{ M}^{-1} \text{ cm}^{-1}$)²² and the latter exhibits peaks at 320 ($\epsilon_{320} = 4000 \text{ M}^{-1} \text{ cm}^{-1}$) and 520 nm ($\epsilon_{520} = 2000 \text{ M}^{-1} \text{ cm}^{-1}$).²³ Hence, the spectra obtained at long times after laser irradiation of BT in the presence of phenol and indole might well be the result of an overlap of ketyl (BTH) and phenoxy (PhO) or indolyl (In) radicals absorptions (Scheme 1).

Laser flash photolysis of aerated solutions could in principle be used to demonstrate the formation of oxygen (phenoxy)- and nitrogen (indolyl)-centered radicals, taking into account their low reactivity toward oxygen compared to that of ketone triplets and ketyl radicals, which are quenched at close to diffusion controlled rates.²⁴ In agreement with expectations, both phenoxy and indolyl absorption spectra were clearly detected at 2 μ s after the laser pulse, in the presence of oxygen

SCHEME 1. Radicals Formed after Quenching of BT Triplet by Phenol or Indole



(Figures 3B and 3C). On the other hand, the BT ketyl radical absorption spectrum was obtained by laser flash photolysis of deaerated methanolic solutions of BT, once the BT triplet had completely disappeared (Figure 3A). It presents maxima at 350 ($\epsilon_{\text{max}} = 9100$), 540 (shoulder), and 580 nm ($\epsilon_{\text{max}} = 2100 \text{ M}^{-1} \text{ cm}^{-1}$). It is remarkable that, while formation of the ketyl radical from benzophenone triplets is associated with a bathochromic shift of ca. 20 nm (from 525 to 545 nm),²⁵ in the case of BT the analogous process leads to a hypsochromic shift of the same magnitude (from $\lambda_{\text{max}} = 600$ to 580 nm).

Molar absorption coefficients of BT triplet and ketyl radical (see above) were determined by a comparative method, using solutions of benzophenone and 2-benzoylthiophene with the same absorbances at the monitoring wavelength. This procedure also allowed us to establish that the efficiencies for the hydrogen transfer from phenol or indole to BT triplet are close to the unity (see Experimental Section).

Quenching of BT triplet by phenol and indole was measured in the three solvents (methanol, acetonitrile, and dichloromethane) by determining the triplet lifetime in the absence and in the presence of several quencher concentrations. The rate constants k_q were obtained from Stern–Volmer plots (Figures 4A and 4B), according to eq 1

$$k_d = 1/\tau_0 + k_q[\text{quencher}] \quad (1)$$

The quenching rate constants for phenol in the different solvents decreased in the order dichloromethane ($2.30 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) > acetonitrile ($0.14 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) > methanol ($0.06 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) (Figure 4A). The values obtained when phenol and indole were used as BT triplet quenchers in dichloromethane were similar ($2.01 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for indole). However, k_q for indole was higher in methanol ($6.00 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) and lower in acetonitrile

(22) (a) Merényi, G.; Lind, J.; Shen, X. *J. Phys. Chem.* **1988**, *92*, 134. (b) Bansal, K. M.; Fessenden, R. W. *Radiat. Res.* **1976**, *67*, 1. (c) Schuler, R. H.; Neta, P.; Zemel, H.; Fessenden, R. W. *J. Am. Chem. Soc.* **1976**, *98*, 3825.

(23) Jovanovic, S. V.; Steenken, S. *J. Phys. Chem.* **1992**, *96*, 6674.

(24) (a) Bejan, E. V.; Font-Sanchis, E.; Scaiano, J. C. *Org. Lett.* **2001**, *3*, 4059. (b) Chattopadhyay, S. K.; Kumar, C. V.; Das, P. K. *J. Photochem.* **1995**, *30*, 81. (c) Smith, R. C.; Reeves, J. C.; Dage, R. C.; Schnettler, R. A. *Biochem. Pharmacol.* **1987**, *36*, 1457. (d) Burton, G. W.; Ingold, K. U. *Acc. Chem. Res.* **1986**, *19*, 194. (e) Wilkinson, F.; Garner, A. *Photochem. Photobiol.* **1978**, *27*, 659.

(25) (a) Bosca, F.; Miranda, M. A. *J. Photochem. Photobiol. B: Biol.* **1998**, *43*, 1. (b) Baral-Tosh, S.; Chattopadhyay, S.; Das, P. K. *J. Phys. Chem.* **1994**, *88*, 1404. (c) Porter, G.; Windsor, M. W. *Proc. R. Soc. London Ser. A* **1958**, *245*, 238.

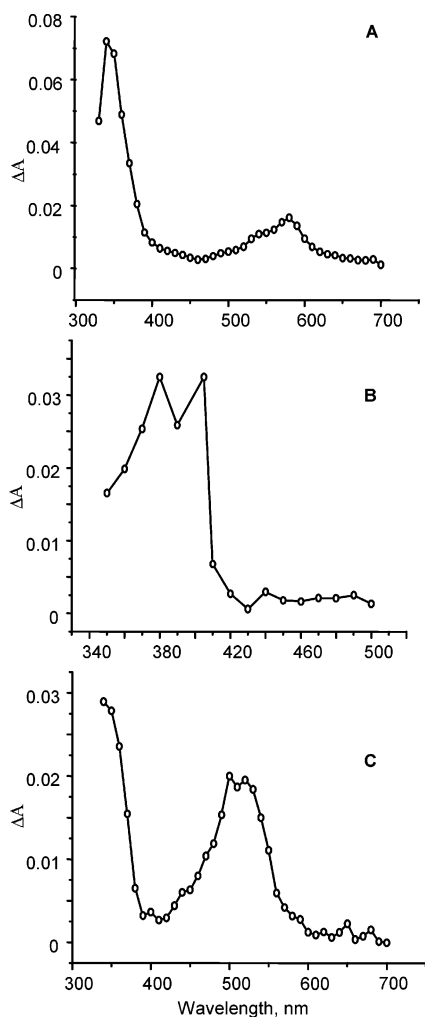


FIGURE 3. A: Transient absorption spectra of a deaerated methanol solution of BT (0.9 mM) obtained 8 μ s after the laser pulse. B: Transient absorption spectra of an aerated dichloromethane solution of BT (0.9 mM) and phenol (4 mM) 2 μ s after the laser pulse. C: Transient absorption spectra of an aerated dichloromethane solution of BT (0.9 mM) and indole (4 mM) 2 μ s after the laser pulse.

($0.60 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) (Figure 4B). The different trends observed for BT triplet quenching in the three solvents could indicate that there are some differences in the mechanisms operating in the reaction of BT triplet with phenol as compared to indole.

In this context, the influence of the solvent on the kinetics of electron-transfer processes has received considerable attention. The Taft model for the solvent-dependent term in the Marcus theory provides a useful approach for prediction of the electron-transfer kinetics.²⁶ This model recognizes the importance of solvent–solute interactions in the development and evolution of the transition state. Thus, there is partial reorientation of the solvent molecules surrounding the reacting species, to form the transition state and the products; these steps depend on the acidities and basicities of the solvent molecules, reactants, and solutes. However, when the

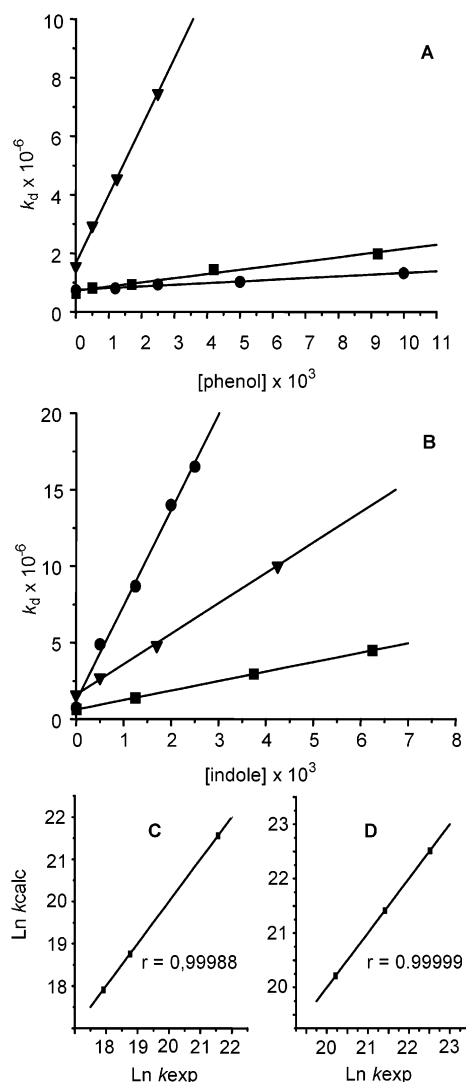


FIGURE 4. A and B: Stern–Volmer plots of the quenching of the BT triplet generated from 355 nm laser flash photolysis of BT in deaerated solutions of acetonitrile (■), methanol (●), or dichloromethane (▼) by phenol (A) or indole (B), monitored at 610 nm. C and D: correlation between the calculated and experimental quenching rate constants by phenol (C) and indole (D).

actual electron-transfer process occurs, reorientation accompanying the change in charge distribution is precluded by the Franck–Condon principle; nonetheless, electronic rearrangements can still take place. The latter will be dependent upon the polarizability of the solvent molecules. Hence, the experimental rate constants can be correlated with the solvent properties by means of the Taft model by using a set of simultaneous equations of the type in eq 2.

$$\ln k_{\text{exp},j} = a\alpha_j + b\beta_j + c\pi_j^* \quad (2)$$

where α is an index of solvent HBD (hydrogen bond donor) acidity, β is an index of solvent HBA (hydrogen bond acceptor) basicity, and π^* is a measure of solvent polarity/polarizability. The coefficients a , b , and c for phenol and indole can be obtained by solving the corresponding simultaneous equations (eq 2), using the known

(26) (a) Abbott, A. P.; Rusling, J. F. *J. Phys. Chem.* **1990**, *94*, 8910. (b) Kamlet, M. J.; Dickinson, C. Taft, R. W. *Chem. Phys. Lett.* **1981**, *77*, 69.

TABLE 1. Solvent Parameters (Taft model) and Experimental Rate Constants for Electron Transfer from Phenol or Indole to BT Triplet

solvent (j)	α	β	π^*	phenol $\ln k_{\text{exp}}$	indole $\ln k_{\text{exp}}$
methanol	0.98	0.66	0.60	17.91	22.52
dichloromethane	0.13	0.10	0.82	21.56	21.42
acetonitrile	0.19	0.40	0.75	18.76	20.21

α , β , and π^* values for the three solvents (j), namely methanol, dichloromethane, and acetonitrile²⁷ (Table 1). The results are shown in eqs 3 and 4.

$$\text{phenol: } \ln k_j = 5.28\alpha_j - 4.32\beta_j + 25.98\pi_j^* \quad (3)$$

$$\text{indole: } \ln k_j = 7.54\alpha_j + 0.28\beta_j + 24.88\pi_j^* \quad (4)$$

Figures 4C and 4D show the correlation between the experimental $k_{\text{exp},j}$ and the calculated k_j from eqs 3 and 4. It can be clearly seen that for both phenol and indole the correlation using the Taft model is quite satisfactory.

A clear consequence of these equations is that the contribution of solvent polarity/polarizability (π_j^*) is by far the most important factor determining the value of the quenching rate constants for both phenol and indole. The equations also indicate some contribution of hydrogen bonding by HBD solvents (α_j). Interestingly, contribution of hydrogen bonding of the quencher to HBA solvents (β_j) is very small for indole ($b = 0.28$) and becomes even negative in the case of phenol ($b = -4.32$). The last finding agrees well with retardation of bimolecular phenolic hydrogen abstraction by the BT triplet due to the basicity of the solvent as expected from a decreased concentration of free phenol. Similar effects are observed in the rate constants for phenolic hydrogen abstraction by benzophenones.^{28,29}

Leigh et al.²⁹ have proposed that the key mechanistic feature of hydrogen abstraction from phenol by triplet aromatic ketones is hydrogen bonding between the excited triplet ketone and the phenol, which has the effect of adjusting the reduction and oxidation potentials of the reactants to the extent where electron transfer becomes thermodynamically favorable. A similar rationalization would be applicable to the photoreaction between BT and phenol or indole, as the actual electron-transfer step would be endergonic according to the Weller equation.^{30,31} This would be more than counterbalanced by the acidity of phenol or indole radical cation and the basicity of the ketone anion radical.³² Such effect appears to be less

(27) Marcus, Y. *Chem. Soc. Rev.* **1993**, 409.

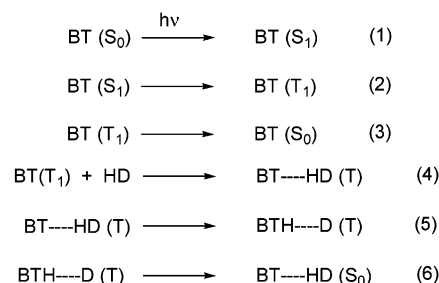
(28) Das, P. K.; Encinas, M. V.; Scaiano, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 4154.

(29) Lathioor, E. C.; Leigh, W. J.; Pierre, M. J. S. *J. Am. Chem. Soc.* **1999**, *121*, 11984.

(30) Rehm, D.; Weller, A. *Isr. J.* **1970**, *8*, 259.

(31) The E_0 values for phenol and indole, measured by cyclic voltammetry, are 1.4 and 1.1 V vs SCE, respectively. The E_0 of the 2-benzoylthiophene is -1.8 V vs SCE. The triplet energy of BT is 62.7 kcal/mol.^{11a} By fitting these data into the Weller equation,³⁰ the free energy changes (ΔG_{et}) associated with the electron-transfer step would be ca. +11 (phenol) and +4 (indole) kcal/mol, neglecting the Coulombic contribution to ΔG_{et} .

(32) The $\text{p}K_{\text{a}}$ values for the radical cations of phenol and indole have been found to be -8.1 (Jennings, P.; Jones, A. C.; Mount, A. R.; Thomson, A. D. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 3791) and +4.9 (Bordwell, F. G.; Cheng, J. *J. Am. Chem. Soc.* **1991**, *113*, 1736), respectively. The $\text{p}K_{\text{a}}$ of the ketyl radical has been found to be 9.3 for the benzophenone analogue (Hayon, E.; Iбата, T.; Lichtin, N. N.; Simic, M. *J. Phys. Chem.* **1972**, *76*, 2072).

SCHEME 2. Processes Involved in the Photoactivation–Deactivation of BT in the Absence and in the Presence of a Hydrogen Donor (DH)

important in the case of indole. The difference in reactivity between indole and phenol toward BT triplet might arise from the lower ionization potential and acidity of indole.^{22a,23,33}

Theoretical Calculations. The mechanism of the reaction between photoactivated BT and phenol or indole was theoretically studied using density functional theory (DFT) methods. Excitation of BT results in formation of the excited singlet state (S_1), which undergoes fast intersystem crossing (ISC) to the lower lying excited triplet state (T_1). Subsequent radiationless decay would lead to the ground state (S_0) (Scheme 2). In the presence of a donor (DH), hydrogen abstraction can in principle take place from the excited triplet state. Therefore, the mechanism of photoinduced hydrogen abstraction between triplet BT and a phenol molecule was studied. The UB3LYP/6-31G* total and relative energies of the reactants and intermediates are given in Table 2, while the corresponding energy profile is represented in Figure 5. The geometries of the optimized triplets are given in Figure 6 (see Computational Methods in Experimental Section).

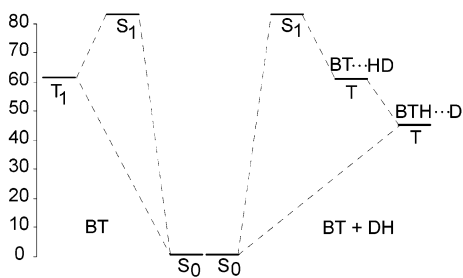
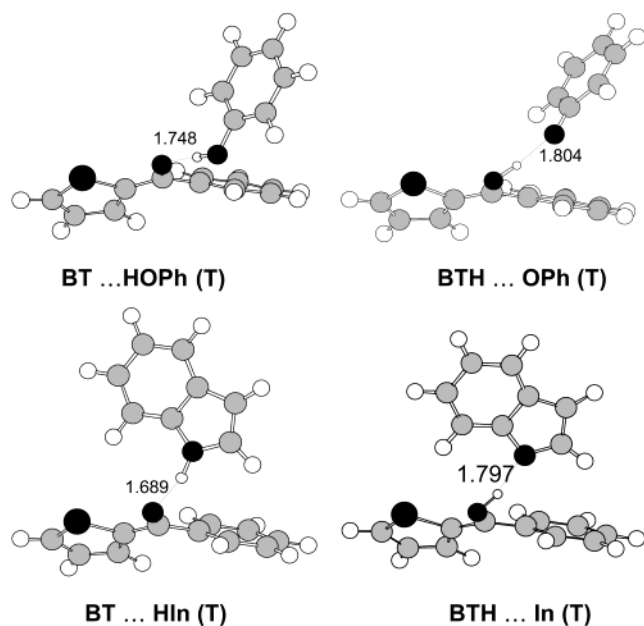
The UB3LYP/6-31G* energy for vertical excitation of the BT chromophore to the singlet state S_1 is 82.0 kcal/mol. The excited triplet state T_1 (61.2 kcal/mol relative to the ground-state S_0) lies ca. 20 kcal/mol below. These results are in reasonable agreement with the literature data.^{11a} In the presence of a phenol molecule hydrogen-bonded to the carbonyl oxygen atom of BT, hydrogen abstraction by BT (T_1) to give the triplet radical pair BTH \cdots OPh can be envisaged. This intermediate can be converted into BT \cdots HOPh (S_0) by hydrogen back-donation to the phenoxy radical. The BT \cdots HOPh (T) is 0.5 kcal/mol lower in energy than BT (T_1). It is remarkable that the triplet radical pair BTH \cdots OPh (T) lies ca. 16 kcal/mol below BT \cdots HOPh (T); this supports the feasibility of the proposed hydrogen abstraction from the BT triplet state. All attempts to locate the corresponding transition state for hydrogen abstraction were unsuccessful. These results suggest that this is a barrierless process from the triplet state. The analogous reaction was also studied for indole, obtaining similar results. The energies of the hydrogen-bonded triplets BT \cdots HIn (T) and

(33) (a) Canonica, S.; Hellrung, B.; Wirz, J. *J. Phys. Chem. A* **2000**, *104*, 1226. (b) Lagier, C. M.; Olivieri, A. C.; Harris, R. K. *J. Chem. Soc., Perkin Trans. 2* **1998**, *104*, 1791. (c) Barbou, N.; Feitelson, J. *J. Phys. Chem.* **1984**, *88*, 1065. (d) Dixon, W. T.; Murphy, D. *J. Chem. Soc. Faraday Trans. 2* **1976**, *72*, 1221. (e) Yagil, G. *Tetrahedron* **1967**, *23*, 2855.

TABLE 2. UB3LYP/6-31G* Total and Relative Energies, Geometrical Parameters of the Reactants and Intermediates, and Charge Transfer at the BT Fragment in the Triplet States and the Triplet Radical Pairs, after Excitation/Deactivation of BT in the Absence and in the Presence of Hydrogen Donors

chemical entity	total energy (au)	ΔE (kcal/mol)	BT–H (Å)	D–H (Å)	D1 ^a (degree)	D2 ^a (degree)	CT ^b (e)
BT (S ₀)	–897.389704						
BT (S ₁)	–897.259024	82.0					
BT (T ₁)	–897.292160	61.2					
BT–HOPh (S ₀)	–1204.869927		1.851				
BT–HOPh (T)	–1204.773139	60.7	1.748	0.986	6.9	29.5	–0.02
BTH–OPh (T)	–1204.798473	44.8	0.986	1.804	13.6	23.7	–0.05
BT–HIn (S ₀)	–1261.217229		1.961				
BT–HIn (T)	–1261.125197	57.8	1.689	1.041	5.7	30.8	–0.28
BTH–In (T)	–1261.141127	47.8	0.997	1.797	12.6	24.9	–0.06

^a D1 and D2 are the (O–C–C–S) and (O–C–C–C) dihedral angles, respectively. ^b Charge transfer located at the BT(H) fragment.

**FIGURE 5.** Energy profile (in kcal/mol) for the photoactivation/deactivation of BT in the absence and in the presence of a donor (DH) molecule.**FIGURE 6.** Structures of the triplet states. The lengths of the hydrogen-bonds are given in angstroms.

BTH...In (T) are 57.8 and 47.8 kcal/mol, respectively, above the ground-state BT...HIn (S₀). When compared with the case of phenol, the hydrogen abstraction process for indole is 5.9 kcal/mol less exothermic (10.0 vs 15.9 kcal/mol).

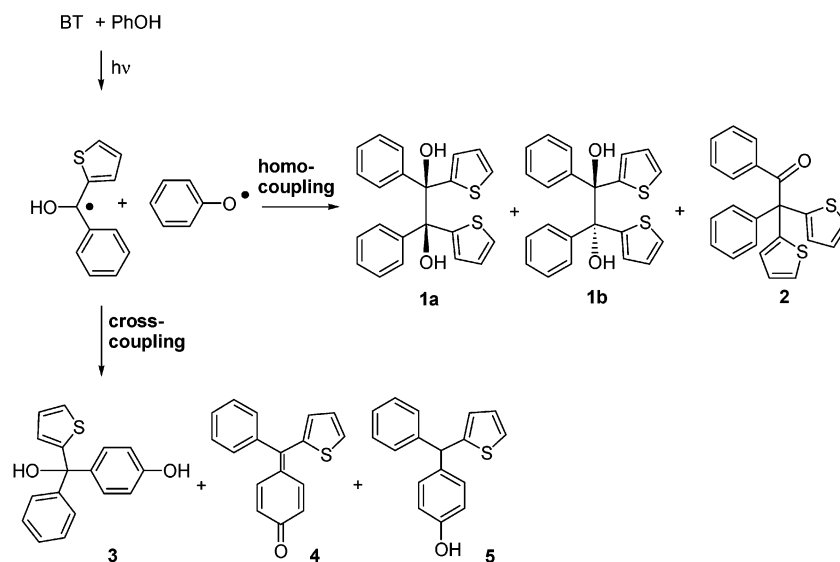
Figure 6 shows the geometries of the species relevant to hydrogen abstraction by BT from phenol and indole. The most significant data are the distances between the acidic hydrogen of phenol and indole and the carbonyl oxygen atom of BT (BT–H), as well as the distances

between this hydrogen and the oxygen or nitrogen atoms of the donors (D–H). For the excited triplet states BT...HOPh (T) and BT...HIn (T) these distances are 1.748 and 1.689 Å (BT–H) and 0.986 and 1.041 Å (D–H), respectively. These BT–H distances are shorter than those found at the ground states BT...HOPh (S₀) and BT...HIn (S₀) (1.851 and 1.961 Å, respectively). The shorter BT–H distance found for BT...HIn (T) as compared with BT...HOPh (T) agrees with the larger stabilization for the former. In the case of the triplet radical pairs BTH...OPh (T) and BTH...In (T) the corresponding distances are 0.986 and 0.997 Å (BT–H), and 1.804 and 1.797 Å (D–H), respectively. The shorter BT–H distances found in these species confirm that the hydrogen atom has been transferred from the donor to the BT triplet, while the PhO and In radicals are now hydrogen bonded to the BTH radical. The D₁ (O–C–C–S) and D₂ (O–C–C–C) dihedral angles (see Table 2) show that the thiophene and benzene rings are twisted with respect to the plane of the carbonyl group of BT. This deviation from the planar arrangement of the two aromatic rings is a consequence of the steric hindrance between the ortho hydrogen atoms. In the BT...HD (T) states D₁ is smaller than D₂, indicating that conjugation of the carbonyl group with the thiophene ring is larger than with the benzene ring. In the BTH...D (T) state D₁ increases while D₂ decreases, indicating a higher participation of the phenyl group in the delocalization of the system. In the isolated BT molecule, in the absence of any interaction with DH donors, the carbonyl group is π -conjugated (and almost coplanar) with the thiophene ring, while the degree of twisting of the benzene ring is ca. 71° in the ground state.³⁴

To understand the electronic features of step 5 in Scheme 2, the degree of charge transfer at the BT...HD (T) and BTH...D (T) species was analyzed. The natural atomic charges have been shared between the BT/HD and the BTH/D fragments. The results given in Table 2 suggest that the mechanism for the hydrogen abstraction step is different for phenol and indole. Thus, while for phenol both species present a similar (and almost negligible) charge, suggesting that the hydrogen atom, one electron, and one proton are transferred along the process, in the case of indole a larger charge transfer is found in BT...HIn (T) (0.28 e). This indicates that for indole electron-transfer precedes proton transfer and is

(34) (a) Abu-Eittah, R.; Hilal, R. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 2718. (b) Cheng, C. L.; John, I. G.; Ritchie, G. L. D.; Gore, P. H.; Farnell, L. *J. Chem. Soc., Perkin Trans. 2* **1975**, 744.

SCHEME 3. Product Formation in the Photoreaction of BT and PhOH



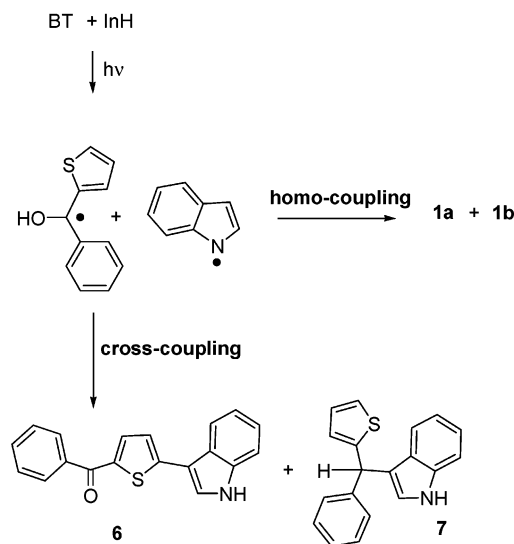
in agreement with the fact that indole is better electron-donor than phenol, explaining the lower energy found for the species $\text{BT}\cdots\text{HIn}$ (T).

Steady-State Studies. Irradiation of a deaerated acetonitrile solution of benzoylthiophene and phenol, using the Pyrex-filtered light from a medium-pressure mercury lamp, led to a complex mixture containing the known pinacols **1**³⁵ along with minor amounts of pinacolone **2** (from rearrangement of the pinacols)^{35b} and cross-coupling products with M^+ 264, 266, and 282. Analysis of the isolated pinacols by ¹H NMR allowed a reliable structure assignment by comparison with the data reported for analogous compounds (Et-BT pinacol diastereoisomers).¹⁷ On the other hand, the spectral data agreed with structures **3**, **4**, and **5**³⁶ for the cross-coupling photoproducts with M^+ 282, 264, and 266, respectively (Scheme 3). Such assessment was confirmed by comparison of their spectra with those of similar products obtained upon irradiation of Et-BT in the presence of the 2,6-di-*tert*-butylphenol. An easy interconversion (dehydration/hydration) was observed between products **3** and **4**.

Likewise, irradiation of BT in the presence of indole, led to a complex mixture consisting mainly of the BT pinacols. However, in this case compounds **6** (M^+ 303), and **7** (M^+ 289) were also present in the photomixtures as minor products (Scheme 4).

The structural assignment of **5**, **6**, and **7** was confirmed by unambiguous synthesis, using well-established methods.³⁷ Thus, compound **5** was synthesized by sodium borohydride reduction of fuchsonone **4** (Scheme 5a). The synthesis of compound **6** was accomplished through benzoylation of the thienyl group of 3-thien-2-yl-1*H*-indole, which was obtained in one step by adding thien-2-yllithium to a refluxing mixture of isatin in ether, followed by treatment with LiAlH_4 , (Scheme 5b). Com-

SCHEME 4. Product Formation in the Photoreaction of BT and InH



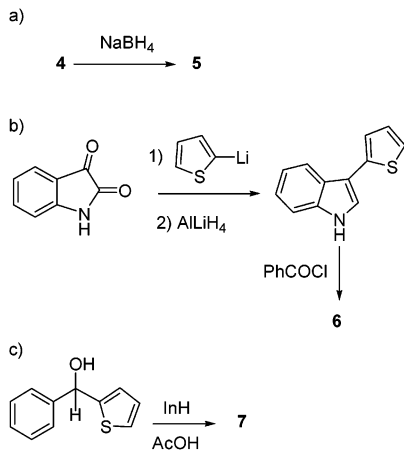
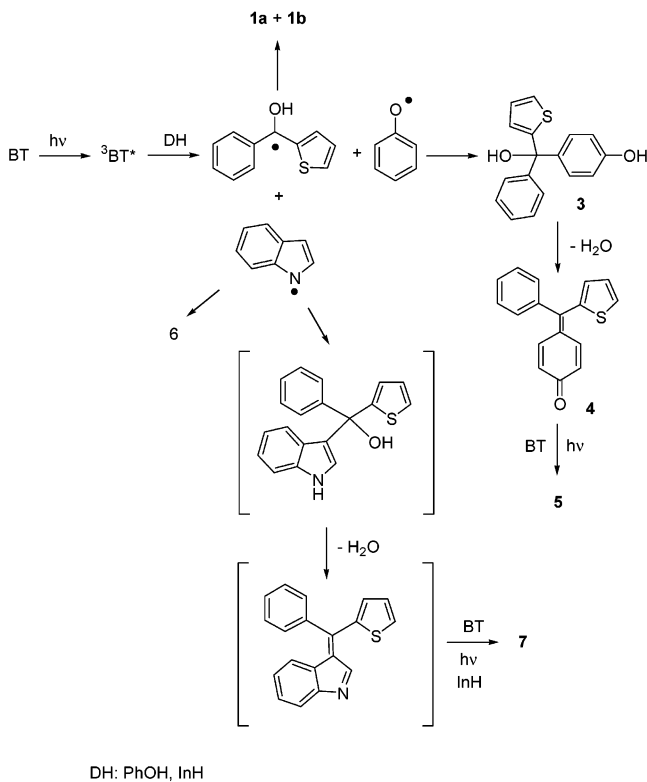
pound **7** was obtained by acid-catalyzed condensation of phenyl(thien-2-yl)methanol with indole (Scheme 5c).

Related photochemical reactions of phenols with aromatic ketones have been previously studied.^{17,37b} Thus, photolysis of aromatic ketones in the presence of 2,6-disubstituted phenols, followed by coupling of the generated ketyl and phenoxy radicals and tautomerization gives rise to triaryl carbinols. These carbinols are converted into 3,5-disubstituted fuchsones in a nonphotochemical process. Furthermore, Becker has demonstrated that benzophenone (BP) sensitizes secondary photochemical reactions of the generated fuchsones such as reduction. Thus, the fuchsonone triplet state can abstract hydrogen atoms from the solvent or oxidize phenols, ultimately leading to the triarylmethyl radical. Dimerization of this intermediate (a reaction analogous to formation of pinacols) does not occur due to steric hindrance; instead, it disproportionates to fuchsonone and triarylmethane. Analogous reaction steps would explain formation of all the products obtained in the photoreac-

(35) (a) Foulatier, P.; Salaun, J. P.; Caultet, C. *C. R. Acad. Sc. Paris* **1974**, *279*, 779. (b) Kegelman, M. R.; Brown, E. V. *J. Am. Chem. Soc.* **1953**, *75*, 5961.

(36) Lapkin, I. I.; Belonovich, M. I. *Metody Poluch. Khim. Reaktivov Prepr.* **1969**, *142*. *Chem. Abstr.* **1971**, *74*, 1414126h.

(37) (a) Bergman, J. *Acta Chem. Scand.* **1971**, *25*, 1277. (b) Becker, H. D. *J. Org. Chem.* **1967**, *32*, 2115.

SCHEME 5. Alternative Synthesis of Photoproducts 5, 6, and 7**SCHEME 6. Mechanistic Proposal for the Product Formation in the Photoreaction of 2-Benzoylthiophene with Phenol and Indole.**

tion of BT with phenol and indole, except ketone **6**. The latter would originate from coupling of the delocalized ketyl radical, through the thienyl 5-position, with the indolyl radicals generated in the process (Scheme 6). Remarkably, analysis of the product distribution revealed some differences between the reactions with phenol and indole. Thus, the compound analogous to the ketone **6**, isolated in the reaction with indole, was hardly detected as traces by GC/MS in the case of phenol.

Conclusion

Our results demonstrate that photoreduction of BT in the presence of phenol or indole generates BT ketyl

radicals with high rate constants and quantum yields close to 1. However, long irradiation times are needed (mainly in the case of indole) to achieve important conversions in the steady-state irradiation experiments. These data indicate that ketyl and phenoxy or indolyl radicals largely react to regenerate starting materials, as it has been proposed for the photoreactions of benzophenones with phenols and amines. Moreover, the efficiency of radical formation reflects that when electron-transfer precedes proton transfer in the exciplex (as with indole), subsequent back electron transfer is slow as compared with proton transfer.

The different trends observed for the solvent-dependence of the quenching rate constants, together with DFT theoretical studies, indicate fundamental differences between the mechanisms of the reaction of BT triplet with phenol and indole. Thus, for the BT/phenol pair, data agree with the involvement of a hydrogen-bonded exciplex, where concerted electron and proton transfer leads to the radical pair. Conversely, in the case of indole electron-transfer precedes proton transfer. This marked reactivity difference must arise from the lower ionization potential and acidity of indole, together with the lower acidity of the indole radical cation, when compared to the corresponding values for phenol and its radical cation.

Finally, it is remarkable that C–C cross-coupling products have been isolated and characterized in the irradiation of BT in the presence of phenol and indole. The structures of the products have been confirmed by alternative synthesis where needed.

Experimental Section

General. ^1H and ^{13}C NMR spectra were recorded in a 300 MHz spectrometer; chemical shifts (δ) are reported in ppm relative to TMS. The coupling constants (J) are in hertz (Hz). Column chromatography was performed on silica gel (230–400 mesh). HPLC was carried out using a C-18 Bondapack column or a Silica column. High-resolution mass spectra were conducted at the SCSIE in Valencia, Spain.

Laser Flash Photolysis. Laser flash photolysis experiments were carried out by using the third harmonics (355 nm) of a pulsed Nd:YAG laser. The pulse duration was 10 ns, and the energy of the laser beam was 10 mJ/pulse, respectively. A Lo255 Oriol xenon lamp was employed as detecting light source. The laser flash photolysis apparatus consisted of the pulsed laser, the Xe lamp, a 77200 Oriol monochromator, and an Oriol photomultiplier (PMT) system made up of 77348 side-on PMT, 70680 PMT housing, and a 70705 PMT power supply. The oscilloscope was a TDS-640A Tektronix. The output signal was transferred to a personal computer for data analysis.

The molar absorption coefficients of BT triplet excited state in MeCN were determined by a comparative method (eq 5), using the triplet absorption of benzophenone (BP) in MeCN as an actinometer:

$$\phi_{\text{isc}}^{\text{BT}} = \phi_{\text{isc}}^{\text{BP}} \times \Delta A^{\text{BT}} \times \epsilon_{525}^{\text{BP}} / \Delta A_{525}^{\text{BP}} \times \epsilon^{\text{BT}} \quad (5)$$

where ΔA^{BT} and $\Delta A_{525}^{\text{BP}}$ values refer to the net absorbances of the BT triplet excited state at 350 or 600 nm and BP triplet state at 525 nm, respectively. The BP molar absorption coefficient ($\epsilon_{525}^{\text{BP}}$) and triplet yield ($\phi_{\text{isc}}^{\text{BP}}$) in acetonitrile were taken to be $6500 \text{ M}^{-1} \text{ cm}^{-1}$ and 1, respectively. The BT triplet yield in MeCN ($\phi_{\text{isc}}^{\text{BT}} = 1$)²⁵ has also been described. Hence, BT molar absorption coefficients of ca. $2900 \text{ M}^{-1} \text{ cm}^{-1}$ at 600 nm and ca. $4800 \text{ M}^{-1} \text{ cm}^{-1}$ at 350 nm were obtained. Similar values were calculated for dichloromethane and methanol as solvents.

On the other hand, molar absorption coefficients of BT ketyl radical (BTH) were also determined by a comparative method, using two solutions with the same absorbance (0.3) at 355 nm: BP in MeCN and BT containing indole (4×10^{-4} M) in dichloromethane (ca. 95% of BT triplet quenching). The quantum yield for the formation of indolyl radical (ϕ_{In}) was calculated by using eq 6:

$$\phi_{In} = \phi_{isc}^{BP} \times \Delta A_{460}^{In} \times \epsilon_{525}^{BP} / \Delta A_{525}^{BP} \times \epsilon_{460}^{In} \quad (6)$$

where ΔA_{460}^{In} and ϵ_{460}^{In} ($850 \text{ M}^{-1} \text{ cm}^{-1}$) are the net absorbance and the molar absorption coefficient of In radical at 460 nm. It was assumed that BTH radical does not absorb at 460 nm. Thus, for ϕ_{In} a value of ca. 0.95 in dichloromethane was calculated. Then, since $\phi_{In} = \phi_{BTH}$, eq 7 allowed for the calculation of the molar absorption coefficients of BTH radical:

$$\phi_{BTH} = \phi_{isc}^{BP} \times \Delta A_{580}^{(BTH+In)} \times \epsilon_{525}^{BP} / \Delta A_{525}^{BP} \times \epsilon_{580}^{(BTH+In)} \quad (7)$$

where ΔA_{580} value refers to the net absorbance of the ketyl and indolyl radicals at 580 nm. Thus, the BTH molar absorption coefficient was found to be ca. $2100 \text{ M}^{-1} \text{ cm}^{-1}$ at 580 nm.

By the same methodology following eq 8, a value of ca. 0.95 was calculated for ϕ_{BTH} in a dichloromethane solution of BT containing 4×10^{-3} M phenol (ca. 95% of BT triplet quenching):

$$\phi_{BTH} = \phi_{isc}^{BP} \times \Delta A_{580}^{(BTH)} \times \epsilon_{525}^{BP} / \Delta A_{525}^{BP} \times \epsilon_{580}^{(BTH)} \quad (8)$$

In this case, ΔA_{580} refers only to the BT ketyl radicals since phenoxy radicals have no absorption at this wavelength.

Computational Methods. Density functional theory³⁸ calculations have been carried out using the B3LYP or UB3LYP³⁹ exchange-correlation functional, together with the standard 6-31G* basis set.⁴⁰ The geometry optimizations were carried out using the Berny analytical gradient optimization method.⁴¹ For minimized triplet states, the UB3LYP wave functions showed no spin contamination ($\langle s^2 \rangle$ ca. 2.0). A recent investigation of *Z/E* isomerization of polyenes has shown that DFT methods (UB3LYP/6-31G**) give relaxed triplet energies that are close to experimental values and compare well with results from high level ab initio methods.⁴² Atomic charges were obtained using the natural bond orbital (NBO) method.⁴³ All calculations were carried out with the Gaussian 98 suite of programs.⁴⁴

Lamp Irradiation of 2-Benzoylthiophene in the Presence of Phenol. (a) A degassed acetonitrile solution of BT (188 mg, 1 mmol) and phenol (94 mg, 1 mmol) in a Pyrex tube was irradiated for 27 h with a 125-W medium-pressure mercury lamp inside a quartz immersion well, under continuous magnetic stirring. After evaporation of the solvent, the residue was chromatographed in a silica gel column (hexane/ethyl acetate, 10/1) and then submitted to semipreparative HPLC, to give 2-benzoylthiophene (18 mg, 6.4%), 1,2-diphenyl-1,2-dithien-2-ylethane-1,2-diol (**1a** and **1b**) (33 mg, 11.8%),

4-[hydroxy(phenyl)thien-2-ylmethyl]phenol (**3**), and [phenyl-(thien-2-yl)]methylidencyclohexa-2,5-dien-1-one (**4**) (4 mg, 1.4% in weight).

(b) A degassed acetonitrile solution of BT (188 mg, 1 mmol) and phenol (94 mg, 1 mmol) in a Pyrex tube was irradiated for 8 h with a 125-W medium-pressure mercury lamp inside a quartz immersion well, under continuous magnetic stirring. Addition of 10 drops of concentrated HCl led to the precipitation of a solid (180 mg) which was filtered and chromatographed (hexane/ethyl acetate, 10/1) to give pinacolone **2** (50 mg, 17.8%) and BT. On the other hand, the filtrate was evaporated and column-chromatographed (dichloromethane/hexane, 10/1) to give pinacolone **2** (6 mg, 2.2%), BT and (4-hydroxyphenyl)-phenyl-(2-thienyl)methane (**5**, 2 mg, 0.9%).

1a: ¹H NMR (CDCl₃): δ 3.20 (s, 2 H), 6.82–6.86 (m, 2H), 6.94 (bb, 2H), 7.04–7.20 (m, 8H), 7.25–7.28 (m, 4H). ¹³C NMR (CDCl₃): δ 82.1 (s), 124.9 (d), 125.4 (d), 126.1 (d), 126.4 (d), 126.6 (d), 126.7 (d), 140.8 (s), 147.3 (s).

1b: ¹H NMR (CDCl₃): δ 3.36 (s, 2 H), 6.82–6.84 (m, 4H), 7.13–7.17 (m, 8H), 7.27–7.30 (m, 4H). ¹³C NMR (CDCl₃): δ 82.3 (s), 124.6 (d), 125.5 (d), 126.1 (d), 126.2 (d), 126.8 (d), 127.8 (d), 140.1 (s), 147.3 (s).

2: ¹H NMR (CDCl₃): δ 6.65 (dd, $J_1 = 3.6$, $J_2 = 1.1$ Hz, 2H), 6.83 (dd, $J_1 = 5.1$, $J_2 = 3.6$ Hz, 2H), 7.14 7.21 (m, 9H), 7.32 (t, $J = 7.4$, 1H), 7.55 (d, 2H, $J = 7.4$ Hz, 2H). ¹³C NMR (CDCl₃): δ 64.3 (s), 125.0 (d), 125.3 (d), 126.7 (d), 126.8 (d), 127.2 (d), 128.0 (d), 128.1 (d), 129.9 (d), 131.1 (d), 135.9 (s), 142.8 (s), 146.5 (s), 196.5 (s). MS *m/z* 360 (M⁺ 89), 283 (21), 255 (100), 221 (36).

3: ¹H NMR (CDCl₃): δ 2.85 (s, 1H), 5.05 (s, 1H), 6.68 (d, $J = 3.3$ Hz, 1H), 6.76 (d, $J = 8.4$ Hz, 2H), 6.91 (dd, $J_1 = 5.1$, $J_2 = 3.6$ Hz, 1H), 7.19–7.32 (m, 8H).

4: ¹H NMR (CDCl₃): δ 6.35 (dd, $J_1 = 9.3$, $J_2 = 2.1$ Hz, 1H), 6.48 (dd, $J_1 = 10.0$, $J_2 = 2.1$ Hz, 1H), 7.09–7.15 (m, 2H), 7.20–7.22 (m, 1H), 7.27 (d, $J = 6.8$ Hz, 2H), 7.39–7.46 (m, 3H), 7.62 (dd, $J_1 = 5.1$, $J_2 = 1.1$ Hz, 1H), 7.77 (dd, $J_1 = 10.0$, $J_2 = 2.7$ Hz, 1H). MS *m/z* 264 (M⁺ 100), 235 (59), 202 (29). HRMS Calcd for C₁₇H₁₂OS: 264.0609. Found: 264.0716

5: ¹H NMR (CDCl₃): δ 4.57 (s, 1H), 5.55 (s, 1H), 6.60–6.61 (m, 1H), 6.70 (d, $J = 8.7$ Hz, 2H), 6.86 (dd, $J_1 = 5.1$, $J_2 = 3.6$ Hz, 1H), 7.01 (d, $J = 8.7$ Hz, 2H), 7.12–7.15 (m, 3H), 7.20–7.23 (m, 2H). MS *m/z* 266 (M⁺ 100), 249 (6), 189 (56), 115 (6). HRMS Calcd for C₁₇H₁₄OS: 266.0765. Found: 266.0753.

Lamp Irradiation of 2-Benzoylthiophene in the Presence of Indole. A degassed acetonitrile solution of BT (188 mg, 1 mmol) and indole (117 mg, 1 mmol) in a Pyrex tube was irradiated for 100 h with a 125-W medium-pressure mercury lamp inside a quartz immersion well, under continuous magnetic stirring. After evaporation of the solvent, the residue was chromatographed in a silica gel column (hexane/ethyl acetate, 10/1) and then submitted to semipreparative HPLC, to give indole (22 mg, 7.2%), 1,2-diphenyl-1,2-dithien-2-ylethane-1,2-diol (**1a** and **1b**) (17.5 mg, 5.8%), 2-benzoylthiophene (84 mg, 27.7%), and [5-(1*H*-indol-3-yl)thien-2-yl]-(phenyl)methanone (**6**) (8.5 mg, 2.8%).

6: ¹H NMR (CDCl₃): 7.22–7.24 (m, 2H), 7.28 (d, $J = 3.9$ Hz, 1H), 7.36–7.53 (m, 4H), 7.55 (d, $J = 2.8$ Hz, 1H), 7.58 (d, $J = 3.9$ Hz, 1H), 7.82 (d, $J = 8.5$ Hz, 2H), 7.97–8.00 (m, 1H), 8.45 (bb, 1H). ¹³C NMR (CDCl₃): δ 111.9 (s), 112.1 (d), 120.4

(38) (a) Parr, R. G.; Yang, W. *Density Functional Theory of Atoms and Molecules*; Oxford University Press: New York, 1989. (b) Ziegler, T. *Chem. Rev.* **1991**, *91*, 651.

(39) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(40) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab initio Molecular Orbital Theory*; Wiley: New York, 1986.

(41) (a) Schlegel, H. B. *J. Comput. Chem.* **1982**, *3*, 214. (b) Schlegel, H. B. Geometry Optimization on Potential Energy Surface. In *Modern Electronic Structure Theory*; World Scientific Publishing: Singapore, 1994.

(42) (a) Brink, M.; Jonson, H.; Ottonson, C.-H. *J. Phys. Chem. A* **1998**, *102*, 6513. (b) Abu-Hasanayn, F.; Herstroeter, W. G. *J. Phys. Chem. Phys. A* **2001**, *105*, 1214.

(43) Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 735.

(44) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.6; Gaussian, Inc.: Pittsburgh, PA, 1998.

(d), 121.8 (d), 123.3 (d), 123.7 (d), 123.9 (d), 125.3 (s), 128.8 (d), 129.4 (d), 132.3 (d), 136.8 (d), 136.9 (s), 139.0 (s), 140.0 (s), 148.6 (s), 188.4 (s). MS m/z 303 (M^+ 100), 226 (50), 154 (33), 105 (11). HRMS Calcd for $C_{19}H_{13}NOS$: 303.071786. Found: 303.0717.

Synthesis of 5. To a solution of fuchsonone **4** (8 mg, 0.03 mmol) in methanol (7 mL) was added sodium borohydride (38 mg, 0.01 mmol). After 25 min, water was added, and the reaction mixture was extracted with ether and dried over anhydrous sodium sulfate. Solvent was removed, and the reaction crude was analyzed by 1H NMR showing the formation of **5** in a 30% yield.

Synthesis of 6. A solution of 3-thien-2-yl-1*H*-indole^{37b} (597 mg, 3 mmol) and benzoyl chloride (0.3 mL, 3 mmol) in dichloromethane (10 mL) at -10 °C was treated during 45 min with $AlCl_3$ (420 mg, 3 mmol), stirred for 12 h at room temperature and decomposed with ice and HCl, to give an oil which was column-chromatographed (hexane/ethyl acetate, 5/1) leading to **6** (89 mg, 10% yield).

Synthesis of 7. A mixture of phenyl(thien-2-yl)methanol^{35b} (190 mg, 1 mmol) and indole (234 mg, 2 mmol) in acetic acid (15 mL) was stirred at refluxing temperature for 4 h and then cooled by means of an ice bath. Subsequently, water was added, and the reaction mixture was extracted with ether and dried over anhydrous sodium sulfate. Solvent was removed, and the crude was chromatographed in a silica gel column (hexane/ethyl acetate, 5/1), to give 3-[phenyl(thien-2-yl)methyl]-1*H*-indole (**7**) (49 mg, 17%).

7: 1H NMR ($CDCl_3$): 1H NMR ($CDCl_3$): δ 5.82 (s, 1H), 6.71–6.73 (m, 2H), 6.86 (dd, $J_1 = 5.1$, $J_2 = 3.2$ Hz, 1H), 6.95 (t, $J = 6.4$ Hz, 1H), 7.10–7.12 (m, 2H), 7.18–7.30 (m, 7H), 7.90 (bb, 1H). ^{13}C NMR ($CDCl_3$): δ 44.4 (d), 111.5 (d), 119.9 (d), 120.1 (d), 120.3 (s), 122.6 (d), 123.9 (d), 124.4 (d), 126.0 (d), 126.9 (d), 127.0 (d), 127.1 (s), 128.8 (d), 128.9 (d), 137.0 (s), 144.2 (s), 148.7 (s). MS m/z 289 (M^+ 100), 256 (7), 212 (50), 171 (8). HRMS Calcd for $C_{19}H_{15}NS$: 289.0925. Found: 289.0925.

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Supporting Information Available: NMR spectra for compounds **1a**, **1b**, **2–7** and the B3LYP/6-31G* computed total energies and Cartesian coordinates for the stationary points BT(S_0), BT(T_1), BT \cdots HOPh (S_0), BT \cdots HOPH (T), BTH \cdots OPH (T), BT \cdots HIIn (S_0), BT \cdots HIIn (T), and BTH \cdots In (T) are included. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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