26a). Ketone **25** (or **25**-d_2) was reduced with lithium aluminum hydride as described for the preparation of **16s** and **16a**. Vpc analysis of the product (5 ft × 0.25 in. column, 30% SE-30, 150°) gave two peaks, area 3:2. The products were collected and identified as **26s** and **26a**, respectively. For **26s**: nmr τ 2.95 (4 H, s, arom), 3.67 (2 H, br m, vinyl), 6.15 (2 H, br m), 7.93 (1 H, br m), 8.63 (1 H, s), 9.10 (1 H, br m); in **26s**-d_2, the signals at τ 7.93 and 8.63 were absent, and the signal at τ 9.10 sharpened to a singlet; ir (CCl$_4$) 3600, 3100, 2950, 1400, 1250, 1060 cm^{-1}. A small sample of **26s** was converted to its acetate (as in the preparation of **12s**), whose nmr spectrum showed an acetyl methyl peak at τ 8.22. For **26a**: nmr τ 2.95 (4 H, s, arom), 3.42 (2 H, br m, vinyl), 6.05 (2 H, br m), 8.00 (1 H, br m), 8.07 (1 H, s), and 8.75 (1 H, m); in **26a**-d_2, the signals at τ 8.00 and 8.07 were absent, and the signal at τ 8.75 sharpened to a singlet; ir (CCl$_4$) 3600, 3100, 2950, 1400, 1250, 1050 cm^{-1}. A small sample of **26a** was converted to its acetate (as in the preparation of **12s**), whose nmr spectrum showed an acetyl methyl peak at τ 8.07.

Jones oxidation of the epimeric mixture of **26s** and **26a**, as described for **21s**, gave a quantitative yield of **25**.

Irradiation of 26s. A solution of **26s** (123 mg) in acetone (3 ml) in a Pyrex test tube sealed with a septum was deoxygenated with a N$_2$ stream for 30 min. An aliquot withdrawn before irradiation, injected into a vpc column (5 ft × 0.25 in., 20% FFAP, 185°), showed two peaks with retention times 3.5 and 21 min, due to naphthalene and **26s**, respectively. Irradiation was carried out in a Rayonet reactor fitted with 300-nm tubes. Product peaks appeared at retention times 18 and 27 min, area ratio 1:7; conversion was complete in 85 hr. The minor product was not identified. The major product was *syn*-6,7-benzotricyclo[3.3.0.0^{2,8}]oct-6-en-4-ol (**27s**). For the nmr spectrum, see the structure and the text. Ir (CCl$_4$): 3590, 3490, 3050, 2950, 1480, 1400 cm^{-1}.

6,7-Benzotricyclo[3.3.0.0^{2,8}]oct-6-en-4-one (28). Jones oxidation of **27s**, as described for **21s**, gave a quantitative yield of **28**: nmr see structure; ir (CCl$_4$) 3080, 2980, 1738, 1480, 1265 cm^{-1}; uv (EtOH) $\lambda_{\max}$ 285 nm (ϵ 12,000), 235 (33,000,s h), 209 (17,500); *m/e* 170 (P), 128 base).

Anal. Calcd for $C_{12}H_{10}O$: C, 84.68; H, 5.92. Found: C, 84.75; H, 6.02.

Lithium aluminum hydride reduction of **28**, as described for **16s** and **16a**, gave a quantitative yield of alcohol identical (ir, nmr) with **27s**.

Irradiation of 26a. A solution of **26a** (97 mg) in acetone (3 ml) was irradiated in the same manner as **26s**. A single product with vpc retention time of 34 min was formed. It was identified as *anti*-6,7-benzotricyclo[3.3.0.0^{2,8}]oct-6-en-4-ol (**27a**): nmr spectrum, see structure and the text; ir (CCl$_4$) 3590, 3400, 3050, 2950, 1480 cm^{-1}. Jones oxidation of **27a**, as described for **21s**, gave a quantitative yield of **28** identical (ir, nmr) with the oxidation product of **27s**.[24]

Acknowledgment. We are grateful to the National Science Foundation and the National Institutes of Health for their generous financial support. G. M. Love also thanks the Phillips Petroleum Company for a fellowship held during the summer of 1969.

[24] During the time this manuscript was being prepared for publication, another example of a remote group controlling the regiospecificity of the di-π-methane photoisomerization was described by I. Murata and Y. Sugihara, *Tetrahedron Lett.*, 3785 (1972).

Photochemical Reactivity of Some Benzoylthiophenes. I. Electronic Absorption and Emission Spectra[1]

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Abstract: The ultraviolet absorption and phosphorescence emission spectra of 2- and 3-benzoylthiophene and their *p*-cyano and *p*-methoxy derivatives have been measured. Partial state diagrams are drawn. The lowest energy absorption in every case is the carbonyl $n \rightarrow \pi^*$ transition. The $\pi \rightarrow \pi^*$ transition associated with the 2-thienoyl chromophore is at considerably longer wavelength than the corresponding transition of the 3-thienoyl chromophore. The lowest triplet of the 2-benzoylthiophene derivatives has π,π^* character and is assigned to the 2-thienoyl moiety. The 3-benzoylthiophene derivatives have an n,π^* triplet.

Photochemistry is one of the most versatile tools available for organic synthesis. However, in order fully to exploit the unusual reactivity of molecules in an excited state there is a need to define the generalizations governing this reactivity. This is a nontrivial matter, more complex than for ground-state molecules, since there are several possible electronic configurations for both singlet and triplet excited states and the rates of internal conversion and intersystem crossing can be competitive with rates of reaction. Furthermore, the same product may arise from more than one state and, in fact, by more than one mechanism involving the same state so that several sets of generalizations may well be necessary.

The most extensively studied functional group in photochemistry is the carbonyl group, and several generalizations with regard to carbonyl photochemical reactivity have been put forth. For example, hydrogen abstraction, both intra- (*e.g.*, Norrish type II) and intermolecular, is a general reaction of the n,π^* singlet and triplet states of ketones and aldehydes. The carbonyl n,π^* singlet and triplet states also generally add to olefins to form oxetanes. Both of these reactions have been studied with a large number of substituted acetophenone and benzophenone derivatives;[3] some limitations to reactivity have been defined and the results are largely, *post facto*, interpretable.

The question should now be asked, can these generalizations be applied to predict the photochemical

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[1] Contribution No. 56 from the Photochemistry Unit.

[2] Alfred P. Sloan Fellow, 1972–1974.

[3] Pertinent reviews include: (a) D. R. Arnold, *Advan. Photochem.*, **6**, 301 (1968); (b) D. C. Neckers, "Mechanistic Organic Photochemistry," Reinhold, New York, N. Y., 1967 Chapter 7; (c) A. Schönberg, "Preparative Organic Photochemistry," Springer-Verlag, New York, N. Y., 1968, Chapters 22 and 41; (d) P. J. Wagner, *Accounts Chem. Res.*, **4**, 168 (1971).

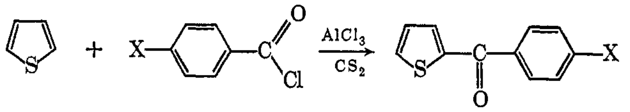
behavior of other similar carbonyl compounds? To answer this question, we have studied the photochemical reactivity of several benzoylthiophenes. We reasoned (in retrospect perhaps naively) that the substitution of thiophene for phenyl could be treated as a small and predictable perturbation of benzophenone; for example, the benzoylpyridines behave quite analogously to benzophenone upon irradiation.[3a,4] Furthermore, we were attracted by the synthetic utility of the possible photochemical reactions incorporating thiophene.

In this paper (part I), we report the synthesis and spectroscopic characterization of several substituted (4-phenyl) 2- and 3-benzoylthiophenes. The energy and electron configuration of the lowest excited singlet and triplet states are assigned, and partial state diagrams can be drawn. Part II of this series will describe the reactivity of these molecules upon irradiation in the presence of olefins and will compare the observed reactivity with predictions based on the state diagrams. In Part III the influence of methyl substitution, ortho to the carbonyl group of 2-benzoylthiophene, on the reactivity of the excited state will be described and compared with the behavior of *o*-methylbenzophenone.

It will become obvious that with the benzoylthiophenes, predictions of photochemical reactivity based on the reactivity of closely related model compounds (*e.g.*, benzophenone or the benzoylpyridines); or, based on the knowledge of the electron configuration and energy of the lowest excited states; or, even on the extrapolation from one type of "characteristic" excited-state reactivity to another, all fall short of being useful.

Results

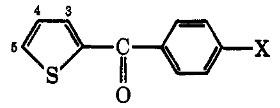
Synthesis of the Benzoylthiophenes. The synthesis of the 2-benzoylthiophenes was carried out using the Friedel–Crafts acylation reaction of thiophene with the benzoic acid chloride.[5] Ketones Ia[5] and Ib[6] have been prepared previously (eq 1) and the properties of our



Ia, X = H (1)
b, X = OCH_3
c, X = CN

products are in agreement with those reported; Ic is a new compound. Ia–c are substituted at the 2 position of thiophene consistent with the expected preferred position for electrophilic attack on thiophene and confirmed by the nmr spectrum which clearly shows the typical coupling pattern for the remaining thiophene protons (Table I).[7]

Table I. Chemical Shifts (ppm) and Coupling Constants (Hz) for the Protons on Thiophene of Some 2-Benzoylthiophenes



	Ia (X = H)	Ib (X = OCH_3)	Ic (X = CN)
H_3	7.64	7.62	7.61
H_4	7.14	7.11	7.18
H_5	7.59	7.60	7.78
$J_{3,4}$	5.0	5.0	4.0
$J_{3,5}$	1.5	1.2	1.2
$J_{4,5}$	4.0	4.0	4.2

Synthesis of the 3-benzoylthiophenes utilized several different routes (Scheme I) in an attempt to obtain reasonable yields. 3-Benzoylthiophene (IIa) was a known compound and was prepared by the established procedure.[8] Both IIb and IIc are new compounds. The position of substitution for IIa–c is established not only by the methods of synthesis, but, by an analysis of the nmr spectra summarized in Table II.

Scheme I

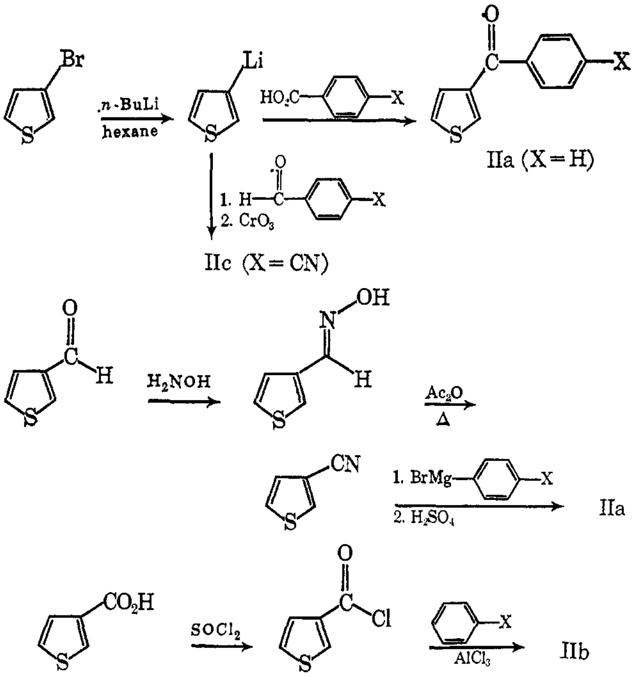
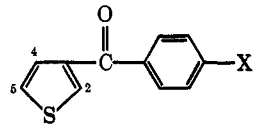


Table II. Chemical Shifts (ppm) and Coupling Constants (Hz) for the Protons on Thiophene of Some 3-Benzoylthiophenes



	IIa (X = H)	IIb (X = OCH_3)	IIc (X = CN)
H_2	7.86	7.86	8.18
H_4	7.31	7.33	7.76
H_5	7.56	7.54	7.77
$J_{2,4}$	3.0	3.3	3.3
$J_{2,5}$	1.4	1.5	1.4
$J_{4,5}$	5.2	5.0	5.4

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[4] (a) M. R. Kegelman and E. V. Brown, *J. Amer. Chem. Soc.*, **75**, 4649 (1953); (b) W. L. Bencze, C. A. Burckhardt, and W. L. Yost, *J. Org. Chem.*, **27**, 2865 (1962); (c) P. Traynard and J.-P. Blanchi, *J. Chim. Phys. Physicochim. Biol.*, **69**, 284 (1972). (d) 3-Hydroxypryido-[1,2-α]indole is formed upon irradiation of 2-benzoylpyridine in *aqueous solution*. Benzophenone is stable under these conditions: C. R. Hurt and N. Filipescu, *J. Amer. Chem. Soc.*, **94**, 3649 (1972).

[5] W. Minnis, "Organic Syntheses" Collect. Vol. II, Wiley, New York, N. Y., 1943, p 520.

[6] L. Kaper and Th. J. de Boer, *Spectrochim. Acta, Part A*, **26**, 2161 (1970).

[7] L. M. Jackman and S. Sternhall, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y., 1969, pp 209 and 307

[8] E. Campaigne and H. L. Thomas, *J. Amer. Chem. Soc.*, **77**, 5365 (1955).

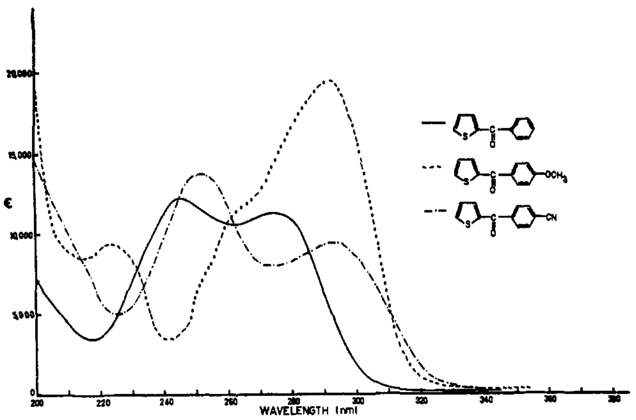


Figure 1. Ultraviolet absorption spectra of some 2-benzoylthiophenes in hexane.

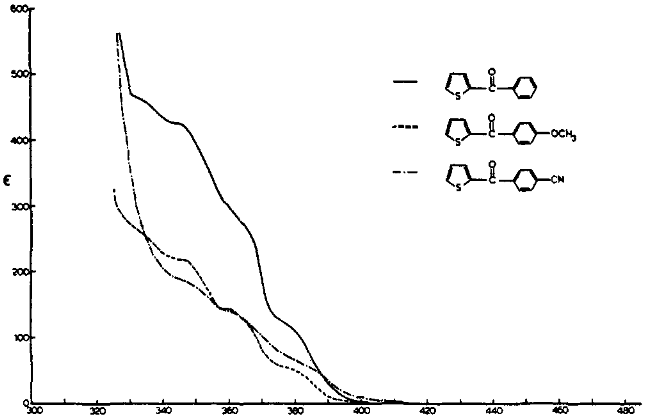


Figure 2. Long wavelength detail of the ultraviolet absorption spectra of some 2-benzoylthiophenes in hexane.

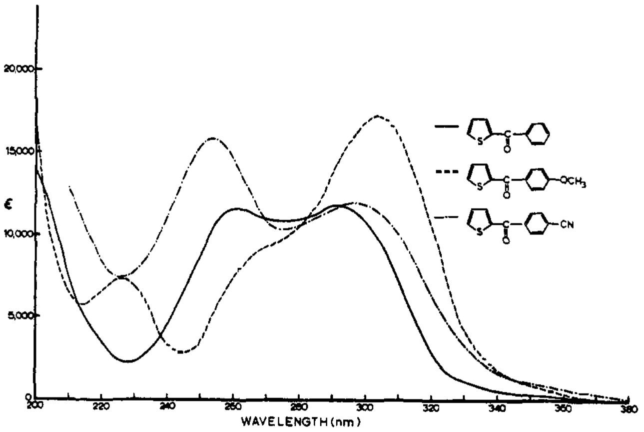


Figure 3. Ultraviolet absorption spectra of some 2-benzoylthiophenes in 95% ethanol.

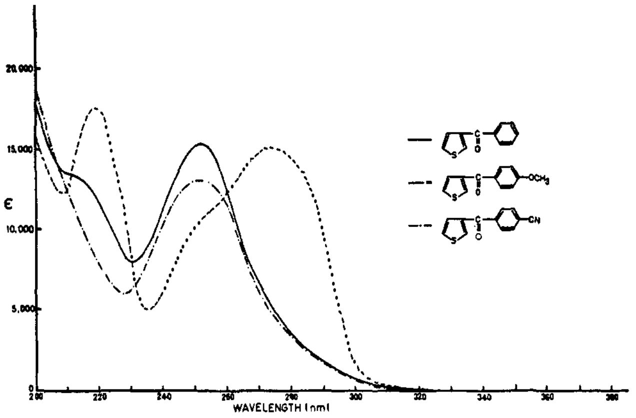


Figure 4. Ultraviolet absorption spectra of some 3-benzoylthiophenes in hexane.

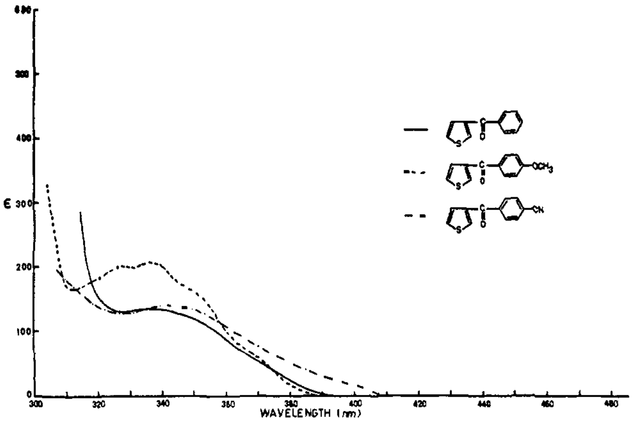


Figure 5. Long wavelength detail of the ultraviolet absorption spectra of some 3-benzoylthiophenes in hexane.

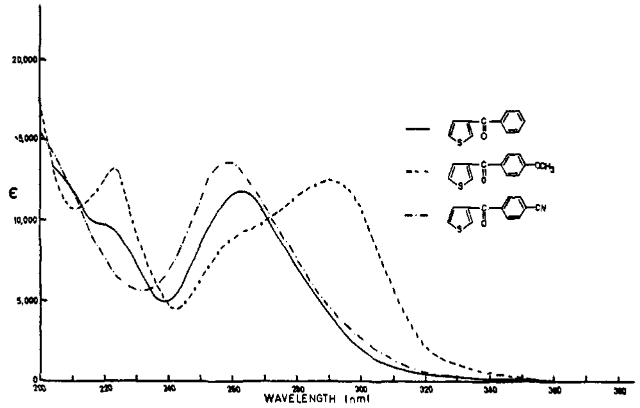


Figure 6. Ultraviolet absorption spectra of some 3-benzoylthiophenes in 95% ethanol.

Ultraviolet Absorption and Phosphorescence Emission Spectra. The ultraviolet absorption spectra of Ia–c were measured in hexane (Figures 1 and 2) and in ethanol (Figure 3). Figure 2 shows the long wavelength (>320 nm) region of the hexane solutions with a higher concentration of the ketone than in Figure 1 so that the weak structured absorption could be seen in detail. No structured absorption was observed with ethanol solutions at higher concentrations of ketone than were used for Figure 3. Figures 4–6 are the ultraviolet absorption spectra of IIa–c. Here again, long wavelength structured absorption was observed only in hexane solution (Figure 5).

The ultraviolet absorption spectra of benzophenone, 4,4′-dimethoxybenzophenone, and 4,4′-dicyanobenzophenone, all in ethanol solution, are shown for comparison in Figure 7.

The phosphorescence emission spectra from Ia–c and IIa–c were measured in EPA (diethyl ether–isopentane–ethanol, 5 : 5 : 2 v/v) at 77°K. Figure 8 shows the emission spectra observed for Ia. The emission

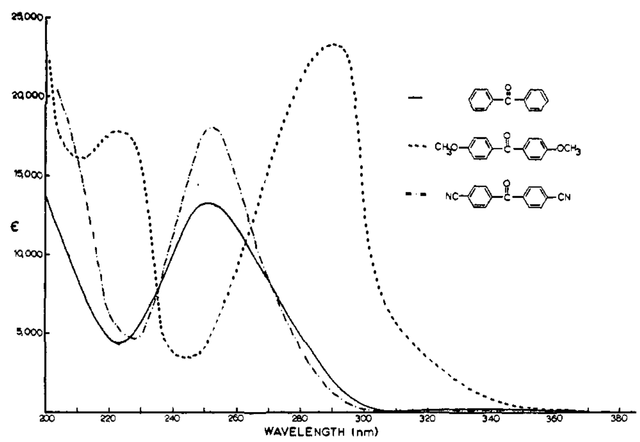


Figure 7. Ultraviolet absorption spectra of some benzophenones in 95% ethanol.

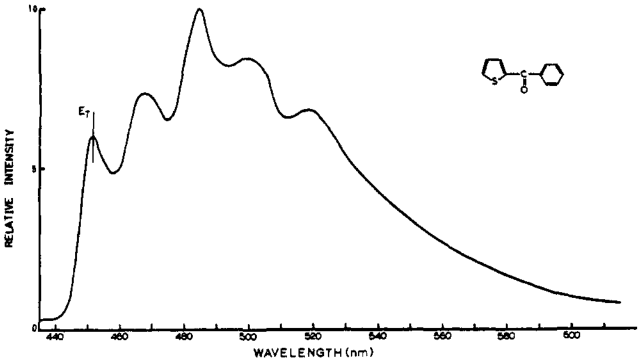
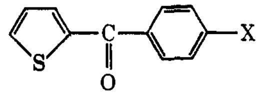
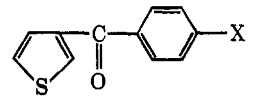


Figure 8. Emission spectrum of 2-benzoylthiophene in EPA at 77°K.

from Ia–c are very similar in gross features, showing small substituent effects on position and lifetime. The emission from IIa–c are also similar to one another, but are very different from that from Ia–c. The emission from IIa is shown in Figure 9. The triplet energies gleaned from the 0–0 band of the emission and the triplet lifetime taken by measuring the decay of the emission are listed in Table III.

Table III. Triplet Energies and Lifetimes for Some Benzoylthiophenes

				
X	E_T[a]	τ[b]	E_T[a]	τ[b]
—OCH_3	63.63	1.18×10^{-1}	70.70	11×10^{-3}
—H	63.30	1.41×10^{-1} (1.78×10^{-1})[c]	70.62	6×10^{-3}
—CN	62.69	1.35×10^{-1}	70.34	9×10^{-3}

[a] Triplet energy (kcal mol^{-1}). [b] Lifetime (sec). [c] T. S. Cantrell, *J. Chem. Soc., Chem. Commun.*, 155 (1972).

Discussion

Several groups of workers have studied the electronic absorption of benzoylthiophenes, and the suggestion has been made that the total spectrum results from transitions within five, more or less independent, chromophores[6,9] (Figure 10). It is possible to assign transitions to the various chromophores available to the benzoylthiophenes on the basis of comparison with model compounds.

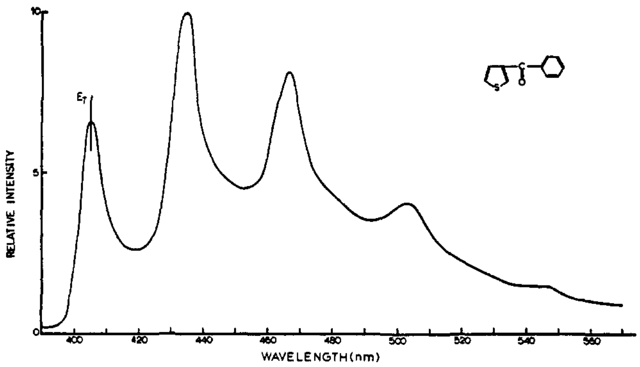


Figure 9. Emission spectrum of 3-benzoylthiophene in EPA at 77°K.

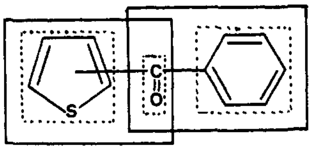


Figure 10. The total absorption of the benzoylthiophenes can be divided into transitions within five more or less independent chromophores.

The absorption spectrum of benzophenone (Figure 7) has a $\pi \rightarrow \pi^*$ transition assigned to the benzoyl chromophore at 252 nm (max). The absorption spectrum of 4,4′-dicyanobenzophenone is quite similar with this transition maximum shifted to 260 nm. 4,4′-Dimethoxybenzophenone has this band, now due to the 4-methoxybenzoyl chromophore, shifted to 280 nm (max) and the appearance of another transition assigned to the methoxyphenyl chromophore at 221 nm (max). All of these $\pi \rightarrow \pi^*$ transitions are observed in the absorption specta of the correspondingly substituted 2- and 3-benzoylthiophene.

The absorptions due to the 2-thienoyl and 3-thienoyl chromophores are considerably different from one another. These transitions can be assigned, in the spectra of the benzoylthiophenes, by comparison with the absorption spectra of the 2- and 3-alkyl thiophene ketones. 2-Acetylthiophene[6] has absorption maxima at 260 and 283 nm due to the thienyl and 2-thienoyl chromophores, respectively, while 3-propionylthiophene[9a] has only one maximum due presumably to the superposition of both the thienyl and 3-thienoyl chromophores at 244 nm.

In the π,π^* excited state the thienoyl chromophore will have considerable charge transfer character as is represented by the valence bond structures in Figure 11. Both double bonds of the thiophene ring are involved in the case of the 2-thienoyl chromophore while with 3-thienoyl only one double bond is used. For ordinary α,β-unsaturated ketones an additional double

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(9) (a) B. Bonini and J. Degani, *Bull. Sci. Fac. Chim. Ind. Bologna*, **20**, 115 (1962); (b) H. H. Szmant and A. J. Basso, *J. Amer. Chem. Soc.*, **73**, 4521 (1951); (c) A. Mangini and A. Tundo, *Z. Electrochem.*, **64**, 694 (1960); (d) L. Kaper, J. U. Veenland, and Th. J. de Boer, *Spectrochim. Acta, Part A*, **23**, 2605 (1967); (e) Y. Sugimoto, S. Nishimura, and E. Imoto, *Bull. Univ. Osaka Prefect.*, **8**, 71 (1959).

bond extending the conjugation results in a 40-nm bathochromic shift,[10] very close to that observed in this case.

The ultraviolet absorption spectra of the 2-benzoylthiophenes can thus be separated into components. Consider first the spectra in hexane shown in Figure 1. The spectrum of 2-benzoylthiophene (Ia) shows absorption maxima due to the thienyl and benzoyl chromophores at 245 nm and the 2-thienoyl chromophore at 275 nm (max). The spectrum of 2-(4-methoxybenzoyl)thiophene (Ib) shows the large shift of the benzoyl absorption maximum to 292 nm caused by conjugation with the *p*-methoxyl. There are two shoulders on this absorpton at 254 and 270 nm which can be assigned to the thienyl and 2-thienoyl chromophores, respectively, and an absorption maximum at 224 nm due to the methoxyphenyl chromophore. 2-(4-Cyanobenzoyl)thiophene (Ic) has an absorption maximum at 252 nm due to the thienyl and *p*-cyanobenzoyl chromophores and another at 293 nm due to the 2-thienoyl chromophore. The weak long wavelength absorption (Figure 2), present in all three derivatives, is the carbonyl n $\rightarrow$ π^* transition which is not greatly affected by substitution; the 0–0 band is near 380 nm in each case.

Considering the spectra of the 3-benzoylthiophenes, again in hexane (Figure 4), 3-benzoylthiophene (IIa) shows an absorption maximum at 252 nm which includes the thienyl, benzoyl, and 3-thienoyl chromophores. The 4-methoxy derivative (IIb) has an absorption maximum at 275 nm due to the *p*-methoxybenzoyl chromophore and a shoulder at 255 nm due to the thienyl and 3-thienoyl chromophores. The maximum at 220 nm is assigned to the methoxyphenyl chromophore. The 4-cyano derivative (IIc) has just one absorption maximum at nearly the same wavelength (250 nm) as in the unsubstituted compound. The carbonyl n $\rightarrow$ π^* transitions are observed at long wavelengths (Figure 5). The 0–0 bands are not as distinct in these spectra; however, from the overall shape of the absorption manifold, they occur at approximately 380 nm.

The absorption maximum for all the $\pi \rightarrow \pi^*$ transitions of the benzoylthiophenes show the expected bathochromic shift in alcohol relative to hydrocarbon solvent (Figures 3 and 6). The shift of the π,π^* maximum assigned to the 2-thienoyl chromophore is larger (18 nm for 2-benzoylthiophene) than that for the 3-thienoyl chromophore (10 nm for 3-benzoylthiophene). This is consistent with a greater contribution of the charge separated structure (Figure 11) to the excited state of the former. A large bathochromic shift (ethanol *vs.* hexane) is also observed for the *p*-methoxybenzoyl $\pi \rightarrow \pi^*$ transition very similar to the corresponding shift of this chromophore in 4,4′-dimethoxybenzophenone.[11]

The bathochromic shift of the longest wavelength $\pi \rightarrow \pi^*$ transition and the hypsochromic shift of the carbonyl n $\rightarrow$ π^* transition combine to obscure the latter under the long wavelength tail of the former in alcohol solution.

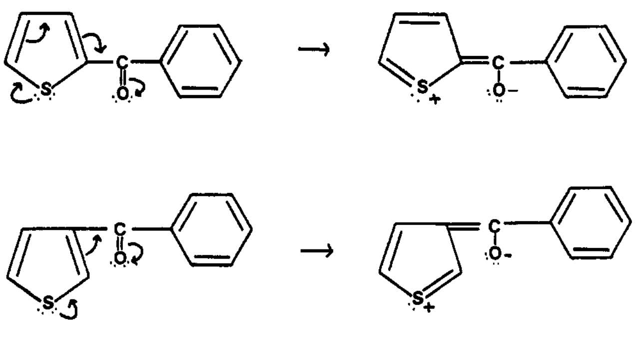

Figure 11. The π,π^* excited state of the thienoyl chromophore will have considerable charge transfer character.

At the beginning of this work there were no reports characterizing the lowest triplet state of any of the benzoylthiophenes from their emission spectra. Traynard and Blanchi had attempted to determine the triplet energy of 2-benzoylthiophene by studying the efficiency of its photoreduction in various solvents and assuming that the triplet energy lay between the carbon–hydrogen bond dissociation energy of the abstracted hydrogen for solvents in which it was efficiently reduced and for solvents in which it was inefficiently reduced.[12] This approach is less than convincing, particularly since they did not show that photoreduction had in fact occurred but looked only at the disappearance of starting ketone. As this work was in progress Cantrell published a triplet lifetime for 2-benzoylthiophene which is in agreement with our results; however, he did not report the triplet energy.[13]

The emission from the 2-benzoylthiophenes is structured with a prominent vibrational separation of 600 cm^{-1}. The triplet lifetimes, while short for a "typical" aromatic π,π^* triplet, are too long for an n,π^* state.[14] Furthermore, if the singlet–triplet splitting ($S_1 - T_1$) is taken as the energy difference between the longest wavelength maximum (shoulder) of the n $\rightarrow$ π^* absorption and the maximum of the shortest wavelength band of the emission, then the observed value (4300 cm^{-1}) is rather large for the emission to originate from the carbonyl n,π^* triplet. For example, $S_1 - T_1$ in benzophenone is only about 2200 cm^{-1}.[15]

The variation of triplet energy with substitution is small. If a π,π^* triplet of the benzene moiety were involved, such as the lowest triplet state of methyl benzoate, higher triplet energies and a larger effect of substituents would be expected. For example, compare the values in Table III with those for methyl benzoate, E_T = 77.9 kcal mol^{-1};[16] methyl *p*-anisate, 75.4 kcal mol^{-1};[17] and methyl *p*-cyanobenzoate, 72.0[16] kcal mol^{-1}. We tentatively assign to the lowest triplet of these 2-benzoylthiophenes a π,π^* configuration involving predominantly the thienoyl chromophore.

The shapes of the emission from the 3-benzoylthiophenes are typical of molecules having an n,π^* triplet. The emission has the characteristic "five fingered" pattern of vibrational structure separated by about

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(10) H. H. Jaffe and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," Wiley, New York, N. Y., 1962, p 215.

(11) G. Porter and P. Suppan, *Trans. Faraday Soc.*, **61**, 1664 (1965).

(12) P. Traynard and J.-P. Blanchi, *C. R. Acad. Sci., Ser. C*, **266**, 1492 (1968).

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

(14) S. P. McGlynn, T. Azumi, and M. Kinoshita, "Molecular Spectroscopy of the Triplet State," Prentice-Hall, Englewood Clifts, N. J., 1969, p 246.

(15) Reference 14, p 84.

(16) D. R. Arnold, J. R. Bolton, and J. A. Pedersen, *J. Amer. Chem. Soc.*, **94**, 2872 (1972).

(17) D. R. Arnold and K. V. Prabhu, unpublished results.

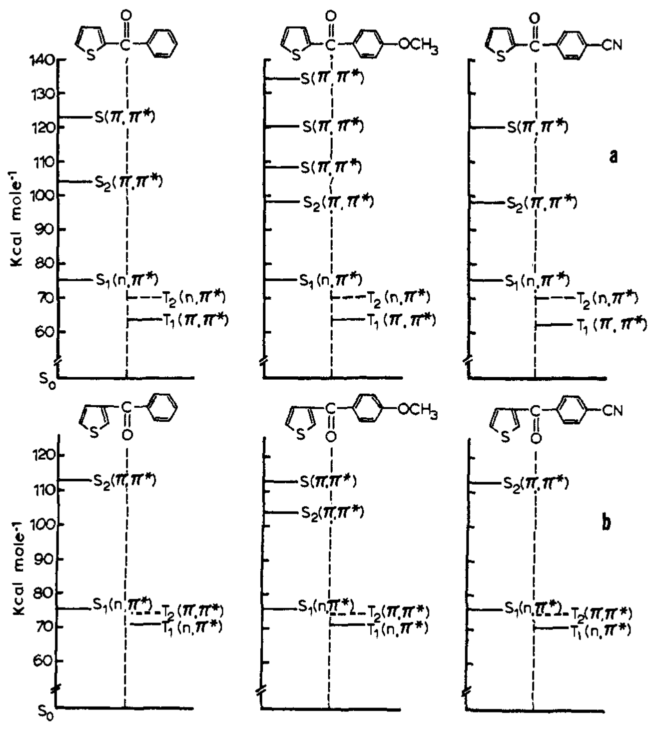

Figure 12. (a) Partial energy diagrams for the 2-benzoylthiophenes; (b) partial energy diagrams for the 3-benzoylthiophenes.

1700 cm^{-1} (the carbonyl stretching frequency). The $S_1 - T_1$ splitting is much smaller, 1600–2000 cm^{-1}, with these derivatives than in the 2-benzoyl series and is in accord with that expected for a carbonyl n,π^* triplet. Furthermore, the lifetimes, although rather long in the case of IIb, are consistent with an n,π^* assignment. The triplet energies of these derivatives fall between benzophenone (69.1 kcal mol^{-1}) and acetophenone (74.1 kcal mol^{-1}). The effect of the substituents on triplet energy is small but is in the expected order for an n,π^* triplet, since electron-withdrawing substituents in the para position lower the n,π^* triplet energy of acetophenone and benzophenone.[18]

From the spectroscopic characterization of the excited states of these ketones, it is now possible to construct diagrams (Figure 12) showing the relative position of the excited states. The π,π^* singlet energy levels are taken from the maxima (or shoulders) of the ultraviolet absorption spectra in hexane; they are therefore maximum values but are useful for comparison. The n,π^* singlet energy levels are taken from the 0–0 band of the n $\rightarrow$ π^* absorption spectrum in hexane. The lowest triplet levels are taken from the 0–0 band of the emission spectra in EPA.

The change in the configuration of the lowest triplet state of the 2- and 3-benzoylthiophene derivatives makes the upper triplet states of considerable interest. It is possible to estimate the approximate energy and nature of the T_2 levels. The only chromophore of the benzoylthiophene molecule for which it is difficult to assign an approximate triplet energy is the thienyl ring. The widely quoted value of 69 kcal mol^{-1} [19] is probably incorrect since Heckman was later unable to observe phosphorescence from thiophene.[20]

In the case of the 3-benzoylthiophene, the T_2 state is assigned a π,π^* configuration of either the 3-thienoyl or the benzoyl moiety; both of these chromophores should have approximately 74 kcal mol^{-1} triplet energy. This estimate for 3-thienoyl is based on the assumption that a similar singlet–triplet splitting exists for the 3- and the 2-thienoyl chromophores. The π,π^* triplet energy of the benzoyl moiety is assumed to be approximately the same as that observed for acetophenone.[21] The T_2 level of the 2-benzoylthiophene is probably the carbonyl n,π^* triplet. A normal carbonyl n,π^* singlet–triplet separation (2000 cm^{-1}) would place this state at about 70 kcal mol^{-1}.

The electronic configuration of the lowest triplet levels, π,π^* for the 2-benzoylthiophenes and n,π^* for the 3-benzoylthiophenes, would have been difficult to predict on the basis of structure alone. The ultraviolet absorption spectra are of some help. The large bathochromic shift of the thienoyl $\pi \rightarrow \pi^*$ singlet transition of the 2-benzoylthiophene is consistent with a lowest π,π^* triplet in this case and might have suggested (but by no means would require) the observed inversion of triplet states.

Armed with the knowledge embodied in these energy diagrams we are now in a position to make predictions of photochemical reactivity.

Experimental Section

General. The melting points were observed on a Thermolyne hot-stage microscope and are uncorrected. The analyses were performed by Chemalytics, Inc., Tempe, Ariz. 3-Bromothiophene and 4-cyanobenzaldehyde were obtained from the Aldrich Chemical Co., and 3-thenaldehyde was obtained from the Columbia Organic Chemicals Co.

The infrared spectra were run in chloroform solution on either a Beckman Model IR 7 or IR 10 spectrometer using sodium chloride cells. The spectra were calibrated using the 1602-cm^{-1} absorption band of polystyrene.

The nmr spectra were run in a dilute solution in deuteriochloroform using tetramethylsilane as an internal reference. The spectra were obtained on a Varian HA-100 spectrometer. The chemical shifts are taken as the center of multiplets and the coupling constants are the result of first-order analysis.

The ultraviolet absorption spectra were run on a Cary 14 spectrometer in *n*-hexane (B. D. H., spectral grade) and 95% ethanol (redistilled) using 1-cm quartz cells. The spectra were recorded as absorption against wavelength and were replotted manually as extinction coefficient against wavelength.

The emission spectra were measured on a spectrometer comprised of a Hanovia 150-W Xenon source, the light from which was passed through a Bausch and Lomb 0.25-m monochromator and focused onto the sample, in a quartz Dewar kept at liquid nitrogen temperature, by a quartz lens. The emission at right angles from the sample was passed through a Jarrel-Ash spectrophotometer into an EMI 9558 QD photomultiplier (S-20 response), cooled with Dry Ice. The output from the photomultiplier was fed, *via* a timing amplifier (Ortec Model 454)and a fast discriminator (Ortec Model 417), to a multichannel analyzer (Geos Model 7010) with 1024 channels. The signal was displayed on an oscilloscope and then recorded on an Infotronic stepping recorder.

Emission spectra were recorded using all 1024 channels with a dwell time of 1 sec/channel and a scan rate of 125 Å /min.

Lifetimes were measured using a nanopulse light source (Xenon Corporation Model 437) rather than the Hanovia Xenon source. The decay curves were recorded using 256 of the analyzer channels and a dwell time of 10^{-3} or 10^{-4} sec/channel. The signal was displayed on an oscilloscope but recorded on a teletype both as printout and punched tape. The data were fed into the PDP-10 computer, and lifetimes were obtained from the decay curves.

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[18] D. R. Arnold, *Advan. Photochem.*, **6**, 331 (1968).

[19] R. V. Newman, Ph.D. Thesis, University of California, Berkeley, 1947.

[20] (a) R. C. Heckman, *J. Mol. Spectrosc.*, **2**, 27 (1958); (b) see also D. F. Evans, *J. Chem. Soc.*, 3885 (1957).

[21] M. Koyanagi, R. J. Zwarich, and L. Goodman, *J. Chem. Phys.*, **56**, 3044 (1972).

The samples for emission measurements were purified by multiple recrystallization. It should be noted that the samples for the emission spectra of the 3-benzoylthiophenes were prepared by three different routes thus eliminating one of the possibilities of emission from a common impurity. The emission spectra were measured at a concentration of 1 mg/1 ml of ketone in EPA (American Instrument Co., Inc., Silver Springs, Md) at 77°K, after degassing the solutions by three freeze–pump–thaw cycles.

Synthesis of the 2-Benzoylthiophenes. Thiophene (0.18 mol) and the acid chloride (0.17 mol) were dissolved in carbon disulfide (250 ml) with stirring. Aluminum chloride (0.34 mol) was added in portions at room temperature, the evolution of hydrogen chloride being allowed to subside in between each addition. After stirring for 0.5 hr (in the case of the cyano derivative the reaction mixture was refluxed for 0.5 hr), the reaction mixture was poured into cold water (1 l.) and stirred for a further 0.5 hr to hydrolyze the ketone–aluminum chloride complex. The carbon disulfide layer was separated and the aqueous layer extracted with two further portions of carbon disulfide (100 ml). The combined carbon disulfide extracts were washed with two portions of 10% aqueous potassium hydroxide (250 ml) followed by three portions of water (500 ml) and dried over anhydrous sodium sulfate. Removal of the carbon disulfide left the product either as a brown oil or solid.

2-Benzoylthiophene. Removal of the carbon disulfide gave a brown oil. Distillation of this oil gave a light yellow oil (bp 96–100° (0.15 mm)) which crystallized when cooled in ice. Recrystallization from methanol-benzene yielded 15.16 g (46%) of 2-benzoylthiophene as colorless crystals: mp 55.3–55.5° (lit.[5] 55–56°); ir $\nu_{\max}^{\mathrm{CHCl_3}}$ 1635, 1603, 1580, and 1513 cm^{-1}.

2-(4-Methoxybenzoyl)thiophene. Removal of the carbon disulfide gave a pale brown solid. Crystallization from methanol-benzene yielded 37 g (66.5%) of 2-(4′-methoxybenzoyl)thiophene: mp 73.5–74° (lit.[6] 75–76°); ir $\nu_{\max}^{\mathrm{CHCl_3}}$ 1635, 1603, 1578, and 1512 cm^{-1}.

2-(4-Cyanobenzoyl)thiophene. Removal of the carbon disulfide gave a dark tar which was chromatographed on Woelm neutral alumina (grade 1). 2-(4-Cyanobenzoyl)thiophene was eluted from the column by pure ether and gave a colorless solid upon removal of the solvent. Recrystallization from methanol–benzene gave 4 g (11%) of colorless crystals: mp 149°; ir $\nu_{\max}^{\mathrm{CHCl_3}}$ 2225, 1640, 1615, 1565, and 1513 cm^{-1}.

Anal. Calcd for $C_{12}H_7NOS$: C, 67.60; H, 3.31. Found: C, 67.73; H, 3.16.

Synthesis of the 3-Benzoylthiophenes. Reaction of 3-Lithiophene with Benzoic Acid. 3-Lithiothiophene was prepared by the method of Hornfeldt and Gronowitz;[22] 3-bromothiophene (8.15 g) in dry ether (10 ml) was added dropwise with stirring to 1.14 *N* *n*-butyllithium in hexane (50 ml) at −70° under a nitrogen atmosphere. After this mixture was allowed to warm to room temperature, a slurry of benzoic acid (3.2 g) in dry benzene (128 ml) was added over 0.5 hr. The reaction mixture was stirred overnight and then poured into ice water (1 l.); the organic layer was separated from the aqueous layer and was extracted with two portions of 10% aqueous potassium hydroxide (250 ml) followed by two portions of water (500 ml) and then dried over anhydrous sodium sulfate. Removal of the solvent gave a dark brown oil.

Distillation of this dark oil yielded a clear oil (bp 92–95°) (0.05 mm)) which crystallized upon vigorous trituration in Dry Ice. These crystals were recrystallized from methanol yielding 200 mg (2%) of 3-benzoylthiophene as colorless plates, mp 62–62.5° (lit.[8] 63–64°).

Reaction of 3-Cyanothiophene with Phenylmagnesium Bromide.[8] 3-Cyanothiophene was prepared from 3-thenaldehyde by conversion to the aldoxime[23] which was then dehydrated to give the nitrile.[24]

3-Thenaldehyde (11.5 g) was dissolved in ethanol (75 ml) and hydroxylamine (16 g) and pyridine (28 ml) were added. The reaction mixture was refluxed for 3 hr and then poured into water (300 ml). This gave a brown oil which solidified when cooled in the refrigerator overnight, and the crystals were filtered. Recrystallization from methanol yielded 10 g (79%) of 3-thenaldoxime as colorless needles. Further cooling of the aqueous solution yielded a further 1.25 g (10%) of 3-thenaldoxime.

3-Thenaldoxime (10 g) was added to acetic anhydride (25 ml) and heated carefully until a vigorous reaction started. The heat was removed until the reaction had subsided and the reaction mixture was then refluxed for 20 min and poured into cold water (300 ml). The product separated as an oil and was extracted from the water by three portions of ether (100 ml). The combined ether extracts were washed with two portions of 10% aqueous potassium hydroxide (100 ml) followed by two portions of water (150 ml) and dried over anhydrous sodium sulfate. Removal of the solvent gave a dark brown oil which was distilled at reduced pressure yielding 5.5 g (73%) of 3-cyanothiophene as a colorless oil, bp 58–59° (3 mm) (lit.[24] 59° (3 mm)).

Phenylmagnesium bromide was prepared[25] by placing dry bromobenzene (7 ml), dry magnesium turnings (5.4 g), and ether (15 ml) in a flask with a crystal of iodine and stirring until the reaction commenced. A solution of bromobenzene (17 ml) in ether (9 ml) was added at such a rate as to keep the reaction mixture refluxing, and when it had all been added the refluxing was continued for a further 0.5 hr. The solution of the phenylmagnesium bromide was cooled to room temperature and 3-cyanothiophene (5 g) in ether (40 ml) was added dropwise so that the reaction mixture started to reflux again. When the addition was completed the reaction mixture was refluxed for a further 4 hr and then allowed to stand overnight. The reaction mixture was hydrolyzed by pouring it onto a mixture of ice and dilute sulfuric acid. The organic layer was separated and a yellow solid at the ether–water interface was dissolved in 6 *N* sodium hydroxide and extracted with two portions of ether (150 ml). The ether extracts were combined, washed with two portions of water, and dried over anhydrous sodium sulfate. Removal of the ether gave a brown oil which was distilled under reduced pressure giving a light yellow oil (bp 85–86°)(0.03 mm) which crystallized upon triturating in Dry Ice. Recrystallization from methanol yielded 1 g (20%) of 3 benzoylthiophene as colorless leaflets: mp 62–62.5° (lit.[8] 63–64°); ir $\nu_{\max}^{\mathrm{CHCl_3}}$ 1643, 1600, 1580, and 1505 cm^{-1}.

Synthesis of 3-(4-Cyanobenzoyl)thiophene. 3-(4-Cyanobenzoyl)-thiophene was prepared by the addition of 3-lithiothiophene to 4-cyanobenzaldehyde to give 3-thienyl(4-cyanophenyl)carbinol followed by oxidation to the ketone.

3-Lithiothiophene was prepared using the method of Hornfeldt and Gronowitz;[22] 3-bromothiophene (3.26 g) in ether (5 ml) was added to 2.5 *N* *n*-butyllithium (8.7 ml) with stirring at −70°. This mixture was allowed to warm to room temperature and was then added in portions to 4-cyanobenzaldehyde (2.5 g) in a mixture of benzene (60 ml) and ether (20 ml) at 0°. The reaction was allowed to stand at room temperature for 10 min and was then poured into 10% aqueous ammonium chloride (200 ml). The organic layer was separated and the aqueous layer was extracted with two portions of ether (150 ml). The combined organic extracts were washed with water and dried over anhydrous sodium sulfate. Evaporation of the solvent gave a dark oil which was chromatographed on Woelm basic alumina to give the alcohol upon elution with 25% methanol–ether. The product had a strong hydroxyl absorption in the infrared and a singlet at 5.9 ppm in the nmr characteristic of the benzylic proton. It was not further characterized.

3-Thienyl(4-cyanophenyl)carbinol (1.3 g) was dissolved in acetone (10 ml), and a solution of chromium trioxide (0.6 g) in 35% aqueous sulfuric acid (2 ml) was added dropwise at 10° with stirring. After the addition was completed, the reaction was stirred for a further 5 min and was then poured into water (50 ml). A dark oil separated and was extracted from the aqueous layer with benzene (50 ml). The benzene extracts were washed with 10% aqueous sodium bicarbonate (100 ml), to remove the acid, followed by water (50 ml) and dried over anhydrous sodium sulfate. Removal of the solvent gave a dark brown tar which was sublimed (100° (0.05 mm)) giving yellow crystals. Recrystallization from methanol–benzene yielded 0.45 g (11%) of 3-(4-cyanobenzoyl)-thiophene: mp 118–118.3°; ir $\nu_{\max}^{\mathrm{CHCl_3}}$ 2250, 1657, 1605, 1585, and 1508 cm^{-1}. *Anal.* Calcd for $C_{12}H_7NOS$: C, 67.60; H, 3.31. Found: C, 67.60; H, 3.35.

Synthesis of 3-(4-Methoxybenzoyl)thiophene. 3-(4-Methoxybenzoyl)thiophene was prepared by a Friedel–Crafts reaction between anisole and 3-thienoyl chloride which was prepared from 3-thenaldehyde.

3-Thenaldehyde was oxidized to 3-thenoic acid using the method

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(22) A. Hornfeldt and S. Gronowitz, *Acta Chem. Scand.*, **16**, 789 (1962).

(23) W. E. Bachmann and C. H. Boatner, *J. Amer. Chem. Soc.*, **58**, 2097 (1936).

(24) A. I. Vogel, "Practical Organic Chemistry," 3rd ed, Longsman, Green and Co., New York, N. Y., 1968, p 804.

(25) Reference 24, p 756.

of Campaigne and Le Suer.[26] 3-Thenoic acid (24 g) was then refluxed in thionyl chloride (100 ml) with two drops of pyridine until a homogeneous solution was obtained. The excess thionyl chloride was then removed by distillation leaving 28 g (100%) of crude 3-thienoyl chloride which was not further purified.

The crude 3-thienoyl chloride (8 g) was dissolved in anisole (150 ml) and aluminum chloride (13 g) was added in portions, with stirring. A slightly exothermic reaction occurred giving a deep red solution which was stirred for 15 min and then poured into water (500 ml). The organic layer was separated and the aqueous layer extracted with ether (2 × 150 ml). The ether extracts were washed twice with 10% aqueous potassium hydroxide and (250 ml) twice with water (500 ml) and then dried over anhydrous sodium sulfate. Evaporation of the solvent gave a brown solid. Recrystallization of this solid from methanol yielded 7.3 g (72%) of 3-(4-methoxybenzoyl)thiophene as colorless crystals: mp 67-67.5°; ir $\nu_{max}^{CHCl_3}$ 1640, 1600, 1574, and 1507 cm^{-1}.

Anal. Calcd for $C_{12}H_{10}O_2S$: C, 66.05; H, 4.62. Found: C, 66.12; H, 4.71.

Acknowledgment. This work was supported by a grant from the National Research Council of Canada.

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[26] E. Campaigne and W. M. Le Suer, "Organic Synthesis," Collect. Vol. IV, Wiley, New York, N. Y., 1963 p 919.

Photochemical Rearrangement Effected by Triplet Excitation Transmitted through a High Energy Moiety. Mechanistic and Exploratory Organic Photochemistry. LXXX[1,2]

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Abstract: 5,12-Dihydro-2,3-naphthacenobarrelene was synthesized. This is a molecule with a naphtho low triplet energy reservoir at one terminus which is attached by methylene groups to the benzo ring of the higher energy benzobarrelene moiety. Direct irradiation proved capable of selectively exciting the naphtho ring. Similarly, benzophenone sensitization delivered triplet excitation to the naphtho group. Fluorescence studies revealed only naphthalene-like emission. Parallel phosphorescence spectra also proved characteristic of a naphthalene chromophore. Yet both direct and sensitized photolyses afforded the corresponding semibullvalene. The quantum yields were $\phi = 0.36$. The similar reactivity in direct and sensitized runs suggests that rearrangement utilizes a triplet excited state. Thus, the 63 kcal/mol naphtho triplet excitation energy initially heavily localized at one end of the molecule proves available to the other end of the molecule as needed for vinyl–vinyl bonding in the di-π-methane rearrangement.

In previous studies we have shown that, like barrelene itself,[3] benzobarrelene,[4] 2,3-naphthobarrelene,[5] and 2,3-anthrabarrelene[2] all rearrange to give the corresponding substituted semibullvalene. Additionally, the rearrangements have been shown[2–5] to proceed by initial bridging of the two vinyl groups in the triplet excited states.

An intriguing question posed itself. This was whether in a molecule such as 5,12-dihydro-2,3-naphthacenobarrelene (**1**) triplet excitation delivered to the naphtho moiety could successfully effect the di-π-methane rearrangement.[3–5] Two impediments would seem to make such a result difficult. First, the vinyl–vinyl bridging occurs at a site quite remote from the excited naphtho group. Second, the triplet excitation would have to pass up an energy ladder through the benzo moiety; naphtho triplet excitation is slightly above 60 kcal/mol while the benzo moiety requires on the order of 80 kcal/mol for excitation.

Synthesis of Barrelene 1. An approach was selected which would generate dihydronaphthacyne (**9**). This could react with benzene to give barrelene **1**. We started with the readily available naphthalene-2,3-dicarboxylic anhydride.[6] This was condensed with tetralin by treating with aluminum chloride to give *o*-(1,2,3,4-tetrahydro-6-naphthoyl)naphthoic acid (**2**) which was cyclized to 1,2,3,4-tetrahydro-6,13-dioxopentacene (**3**) in hot sulfuric acid. Nitric acid oxidation of dione **3** to 5,12-dioxo-2,3-naphthacenedicarboxylic acid (**4**) was followed by cyclization with acetic anhydride to 5,12-dioxo-2,3-naphthacenedicarboxylic anhydride (**5**). Reaction of anhydride **5** with urea afforded 5,12-dioxo-2,3-naphthacenedicarboxyimide (**6**) which was converted to sodium 2-amino-5,12-dioxo-3-naphthacenecarboxylate (**7**) under Hofmann rearrangement conditions. Reduction of **7** with zinc under alkaline conditions furnished 2-amino-5,12-dihydro-3-naphthacenoic acid (**8**) which was then used as the dihydronaphthacyne precursor. An *in situ* method[7] employing isoamyl nitrite in benzene at 80° led to barrelene **1**, mp 285–287°, in yields ranging from 6 to 10% (note Chart I and the Experimental Section for the detailed synthetic procedure).

The structure assigned to barrelene **1** derives from

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[1] For paper LXXVIII see H. E. Zimmerman and W. Eberbach, *J. Amer. Chem. Soc.*, **95**, 3970 (1973).

[2] For paper LXXIX of the series, note H. E. Zimmerman and D. R. Amick, *J. Amer. Chem. Soc.*, **95**, 3977 (1973).

[3] H. E. Zimmerman, R. W. Binkley, R. S. Givens, G. L. Grunewald, and M. A. Sherwin, *J. Amer. Chem. Soc.*, **91**, 3316 (1969).

[4] H. E. Zimmerman, R. S. Givens, and R. M. Pagni, *J. Amer. Chem. Soc.*, **90**, 4191, 6096 (1968).

[5] H. E. Zimmerman and C. O. Bender, *J. Amer. Chem. Soc.*, **92**, 4366 (1970).

[6] (a) M. Freund and K. Fleischer, *Justus Liebigs Ann. Chem.*, **399**, 215 (1913); (b) K. Yogi, *J. Agr. Chem. Soc. Jap.*, **23**, 43 (1944); *Chem. Abstr.*, **45**, 5142 (1951).

[7] L. Friedman and F. M. Logullo, *J. Org. Chem.*, **34**, 3089 (1969).