J. Am. Chem. Soc. **1988**, *110*, 1025-1032

Triplet Ground-State Benzoylphenylmethylene and Its Quintet Ground-State Triplet–Triplet Radical Pair

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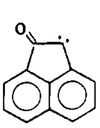
Abstract: Photolysis of crystalline azibenzil powder at 77 K and $\lambda \geq 345$ nm generates a complex ESR spectrum consisting of four components, namely a strong triplet, a weak triplet, a quintet, and a doublet. The strong triplet has been previously assigned to ground-state benzoylphenylmethylene and the quintet to the ground state of a radical pair formed between two triplet benzoylphenylmethylenes. On the basis of the similar values exhibited by the zero-field splitting parameters, the strong and weak triplet signals are assigned here to the *s-Z* and *s-E* isomers of the ground state of benzoylphenylmethylene, respectively. The *s-Z* conformer is more abundant and less stable than the *s-E*, and on annealing, the decay of both signals follows first-order kinetics. Above 90 K the quintet radical pair also decays with first-order kinetics to yield a new triplet diradical, which is stable at $T < 120$ K but disappears with first-order kinetics above 120 K. The Arrhenius parameters have been determined for all decay reactions and utilized in their mechanistic interpretation. The carrier of the structureless, broad doublet signal observed appears to be generated from the secondary photolysis of the triplet benzoylphenylmethylene. The assignment of the quintet spectrum to a radical pair is also supported by the absence of this spectrum in the photolysate of dilute azibenzil solutions in glassy matrices. Under such conditions, in addition to the spectrum of benzoylphenylmethylene and its doublet photolysis products, a new triplet diradical appears with a kinetics of formation suggesting that it is formed by the decay of the quintet. However, its identity has not been established.

Ketocarbenes are common intermediates in the decomposition of α-diazo ketones, α-diazo esters, and vinylene thioxocarbonates, in the oxidation of acetylenes, and in other synthetic, industrial, and biological reactions.[1-14] In spite of their frequent involvement as reactive intermediates, reports on the direct observation of ketocarbenes are still relatively sparse. Ab initio MO calculations predict the parent formylmethylene to have a triplet ground state, and probably most ketocarbenes have triplet ground states as well.[15,16]

Benzoylphenylmethylene (BPhM), PhCO$\ddot{C}$Ph (**1**), was the first ketocarbene to be stabilized by Trozzolo and Fahrenholtz[17] in the low-temperature photolysis of azibenzil in organic matrices and detected in its triplet ground state by ESR spectroscopy. Moreover, they found deoxybenzoin, formed via hydrogen abstraction, to be the major final product in organic matrices (methylcyclohexane, 2-methyltetrahydrofuran) as opposed to the photolysis at room temperature in which diphenylketene, the Wolff rearrangement product, becomes predominant. Subsequently, the isolation and ESR spectroscopic identification of several ketocarbenes, Table I, were also reported. For the cyclic ketocarbenes **2–4**, Chapman and co-workers[10] also obtained and described the visible optical spectra and IR spectra. The IR spectra detected earlier in the argon matrix isolated photolysis of hexafluoro-2-diazo-3-butanone and initially assigned by Strausz, Torres, and co-workers[27] to perfluoroacetylmethylmethylene was, however, somewhat later shown by Lemal et al.[28] to be actually due to the α-ketodiazirene isomer of the diazo ketone substrate. Finally, thioformylmethylene and iminoformylmethylene have been predicted to have triplet ground states[29-31] and some of their derivatives have been prepared.[32-34]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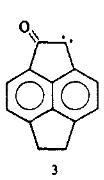
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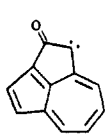
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That substituted carbenes can exist as geometric isomers or conformers has been shown by Trozzolo, Wasserman, and Yager on naphthylmethylenes[35] and further illustrated by the example of vinylmethylenes,[24,36] carbalkoxymethylenes,[18] quinolylmethylenes,[37] and dicarbomethoxymethylenes by Roth et al.[38] Other carbenes for which the existence of geometrical isomers

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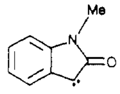
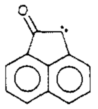
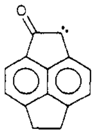
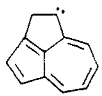
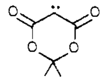
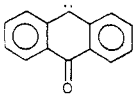
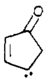
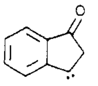
Table I. Triplet Ketocarbenes Characterized by ESR

species	matrix	config	D, cm^{-1}	E, cm^{-1}	ref
$Ph\ddot{C}COPh$	organic glasses		0.3815	0.0489	17
	polycrystal	*s-Z*	0.3916	0.0518	this work
		s-E	0.3123	0.0519	
$\ddot{C}HCOOMe$	methylcyclohexane	*s-Z*	0.663	0.030	18
		s-E	0.617	0.053	
$\ddot{C}HCOOEt$	methylcyclohexane	*s-Z*	0.661	0.031	18
		s-E	0.616	0.053	
$(CH_3)_3C\ddot{C}COC(CH_3)_3$	polycrystal	*s-Z*	0.500	0.074	19
$CF_3\ddot{C}COCF_3$	polycrystal	*s-Z*	0.605	0.034	20
		s-E	0.572	0.079	
$CF_3\ddot{C}COCF_2CF_3$	polycrystal	*s-Z*	~0.564	~0.039	21
		s-E	0.563	0.080	
$CF_3CF_2\ddot{C}COCF_3$	polycrystal	*s-Z*	~0.558	~0.029	21
		s-E	0.553	0.091	
	organic glasses	*s-E*	0.38		22
	argon matrix	*s-E*	0.407	0.0270	10
	argon matrix	*s-E*	0.401	0.0253	10
	argon matrix	*s-E*	0.427	0.0179	10
$PhCO\ddot{C}COPh$	polycrystal		0.0801	0.0232	23
			0.029		
$MeOCO\ddot{C}COOMe$	organic glasses		0.615	0.034	24
			0.604	0.031–0.051	
		*s-E,s-E*	0.578	0.035	24
	polycrystal		0.3638	0.0176	25, 26
			0.384	0.0247	10
			0.387	0.0152	10

has been shown include iminocyclohexadienylidene[34] and perfluoroacetylmethylmethylene.[20]

Another interesting observation made in the ESR spectroscopy study of the photolysis of polycrystalline azibenzil was the detection of a set of absorptions consisting of at least ten lines and assigned to a quintet radical pair (Q_0) formed between two close neighbor triplet ground-state benzoylphenylmethylenes $(BPhM(T_0))$.[39,40] Since then, similar characteristic spectra have been found in the case of three other ketocarbenes, namely anthranylidene,[26] perfluoroacetylmethylmethylene,[20] and (trimethylacetyl)-*tert*-butylmethylene.[19] They were all generated by the low-temperature photolysis of their respective polycrystalline diazo ketone precursors. As far as can be assessed, these quintet species still represent the only known examples of stable quintet-state radical pairs, although the mutual annihilation of triplet excitons in organic molecular crystals to give singlet exitons via triplet pairs has been reported[41] and many high-spin-state organic polycarbene

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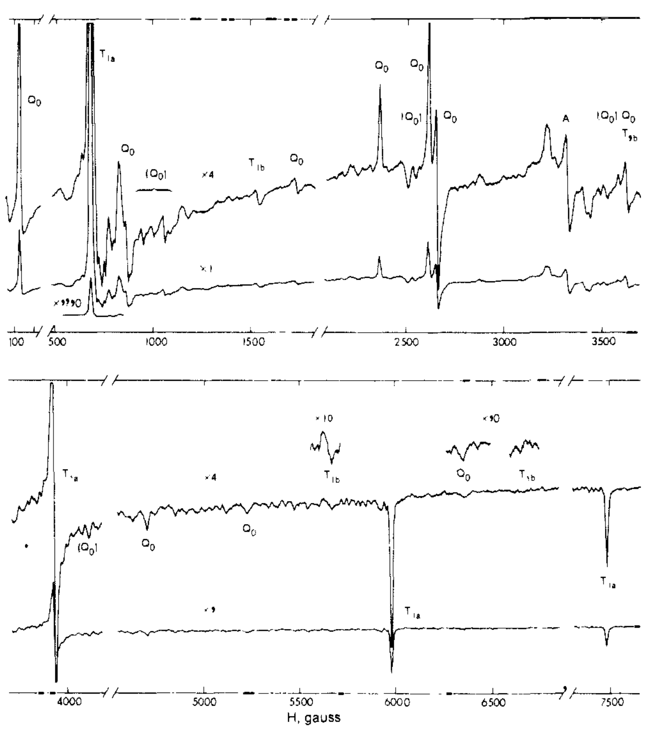


Figure 1. Complete ESR spectrum generated in the λ ⩾ 345 nm photolysis of azibenzil polycrystal at 77 K: A, doublet radical; T_{1a}, (*s*-*Z*)-benzoylphenylmethylene; T_{1b}, (*s*-*E*)-benzoylphenylmethylene; Q_0, quintet state triplet–triplet BPhM(T_0) radical pair. The klystron frequency was 9.169 GHz.

molecules have been identified up to nonet multiplicity in the past two decades.[42-49]

In the present paper we wish to give a more detailed account of the ESR spectroscopy of the photolysis of both polycrystalline and glassy matrix solutions of azibenzil.

Experimental Section

Azibenzil[50] crystals were finely powdered and filled into a 3-mm-i.d. Suprasil ESR tube, degassed under vacuum, and sealed. For glassy matrices ~10^{-2} M solutions of azibenzil in the appropriate solvent (methylcyclohexane–isopentane (4:1), ethanol, methanol, perfluorobenzene, benzene) were degassed by thaw–freeze cycles and sealed. Benzophenone glasses were obtained by rapidly cooling the benzophenone solution (323 K) to 77 K. In some experiments the benzophenone glasses were allowed to warm to room temperature, during which the glass underwent a phase change to polycrystal, and then the polycrystal was finely pulverized. For photolysis at 77 K, a Hanovia water-cooled 450-W medium-pressure mercury lamp equipped with a uranium glass filter (λ ⩾ 345 nm) was used as light source, and the sample was placed in a quartz Dewar filled with liquid nitrogen. For measurement below 77 K and variable-temperature measurements, the light source was a Hanovia 150-W medium-pressure mercury lamp with a λ ⩾ 340 nm cutoff filter. The sample was inserted into a Cryogenic Dewar Model LTD-3-110A Heli Tran. transfer system provided by Air Products and Chemicals installed inside the ESR cavity. A variable-temperature Dewar (Bruker) was used to study the decay kinetics and Curie's law. The sample temperature was monitored at the upper position of the sample inside the Cryogenic Dewar by a thermocouple of chromel versus gold 0.07 atom % iron. The ESR spectra were recorded on a Bruker ER-420 X-band spectrometer equipped with 100-kHz modulation in which the magnetic field was controlled by a Varian Fieldial V-FR 2503 and monitored by an Alpha digital NMR gauss meter Model 9093. The microwave frequency was determined with a Hewlett-Packard Model X532B frequency meter.

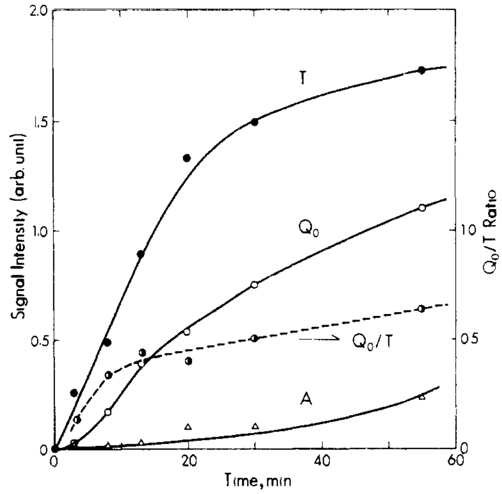


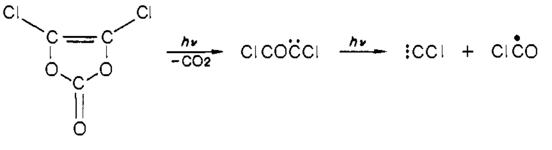
Figure 2. Intensity versus irradiation time of the ESR signals (doublet, A; triplet **1a**, T; quintet radical pair, Q_0).

Results and Discussion

Photolysis of Azibenzil in Polycrystalline Matrices. On irradiation, the polycrystalline sample yielded a complex ESR spectrum (Figure 1), which could be deconvoluted into four distinct spectra: (1) a signal A with no hyperfine structure at $g = 2.003$; (2) a set of strong absorptions which has been previously assigned to **1**[17] and now specifically assigned to the *s*-*Z* isomer of **1**, **1a** (vide infra); (3) another set of weak absorptions which gives zero-field splitting (ZFS) parameters very similar to those of **1a** and what we assign here to the *s*-*E* geometric isomer of **1**, **1b**; and (4) a set of complex absorptions occurring in the 0–6400-G range, which has been assigned to Q_0.

The doublet spectrum, A, has a peak-to-peak width of ~14 G. It is assigned to some unidentified doublet radicals produced by secondary photolysis because its intensity, relative to that of the spectrum of **1a**, increases with increasing exposure time (Figure 2) and also when Vycor (λ > 210 nm) instead of uranium glass (λ > 345 nm) filtered light is used for photolysis. This absorption apparently corresponds to the signal at $g = 2.003$ observed by earlier workers[51] who mistakenly assigned it to the assumed ground singlet state of BPhM.

A similar doublet spectrum has been observed in all our ESR studies of triplet-state ketocarbenes showing a similar kinetic behavior as well. It appears to be likely that these featureless, broad, secondary doublet spectra arise from the secondary photolysis of the primary triplet ketocarbenes, in the present instance **1a** and **1b**. In agreement with this we found that in the gas-phase, room-temperature flash photolysis of dichlorovinylene carbonate, chloromethylidyne, :CCl, was a readily detectable product by



optical spectroscopy.[52] Therefore, in the present case the doublet spectrum can be due to some combination of the phenyl, phenylketyl, phenylmethylidyne, benzoyl, phenyloxirenyl, and ben-

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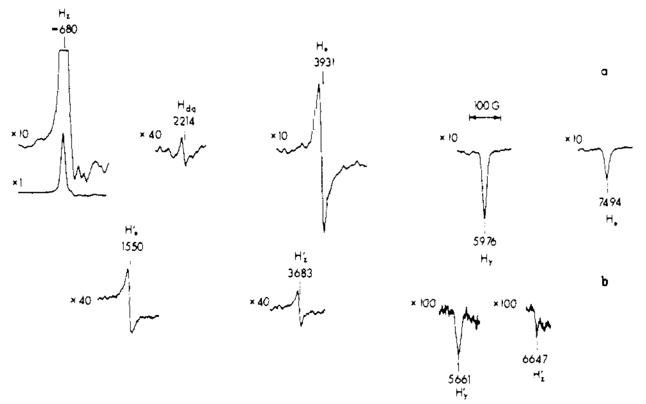
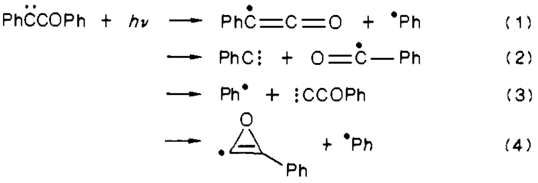


Figure 3. ESR signals of BPhM: (a) *s-Z* isomer **1a**; (b) *s-E* isomer **1b**.

zoylmethylidyne radicals (reactions 1–4) formed in the photolysis of **1a** and **1b**:


$$Ph\ddot{C}COPh + h\nu \rightarrow Ph\dot{C}{=}C{=}O + {}^{\bullet}Ph \quad (1)$$
$$\rightarrow PhC\!: + O{=}\dot{C}{-}Ph \quad (2)$$
$$\rightarrow Ph^{\bullet} + :CCOPh \quad (3)$$

In the photolyses of **1**, diphenyl ketene may also be formed (eq 5), or alternatively, it may be formed as a primary product of the photolysis of azibenzil itself (eq 6):

$$Ph\ddot{C}COPh + h\nu \rightarrow Ph_2C{=}C{=}O \qquad (5)$$

$$PhCN_2COPh + h\nu \rightarrow N_2 + Ph_2C{=}C{=}O \qquad (6)$$

According to Trozzolo,[17] product analysis after the low-temperature photolysis of azibenzil in organic glasses (methylcyclohexane, tetrahydro-2-methylfuran) showed, after warm-up, the presence of benzil (0–12%), deoxybenzoin (74–80%), and diphenylketene (0–12%), whereas when the photolysis of azibenzil was carried out at room temperature, diphenylketene was formed in 85–90% yield. We have observed, however, that low-temperature photolysis of azibenzil argon matrix isolated at 10 K resulted in the formation of diphenylketene as the only major product.

(1) The Geometric Isomers of BPhM(T_0). The spectrum of **1a** is shown in Figure 3a and the ZFS parameters obtained from the spectrum are listed in Table I along with the literature values obtained in organic glass matrices. Initially the signal intensity grows linearly with exposure time and **1a** is stable up to ~150 K, above which temperature it decays with good first-order kinetics (Figure 4). The Arrhenius plot (Figure 5) obtained from the rate constants measured in the temperature range 152–171 K gives an activation energy of 9.9 kcal/mol and log A (s^{-1}) = 10.4.

A slight intensity growth in the dark observed immediately after cessation of irradiation is probably due to a physical relaxation in the trapping site. A double quantum transition (H_{dq}) of **1a** was also detected, and its assignment is supported by the fact that the intensity of the signal diminishes much more rapidly than that of the other signals when the microwave power is attenuated.[53]

The spectrum of **1b** is also shown in Figure 3b, and the D and E values are given in Table I. The signal intensity, relative to that of **1a**, is less than 0.1, and it is not obvious whether **1b** is produced in the primary photolysis or not. When the photolysate was warmed to temperatures higher than 130 K, a slight narrowing and intensity growth of the lines of **1b** took place irreversibly. This can probably be attributed to the slight reorientation of the initial conformation of this triplet molecule or its settling into a more stable position during the annealing of the photolysate. No decay of **1a** was observed during this annealing, which indicates that thermal conversion of **1a** to **1b** was not taking place.

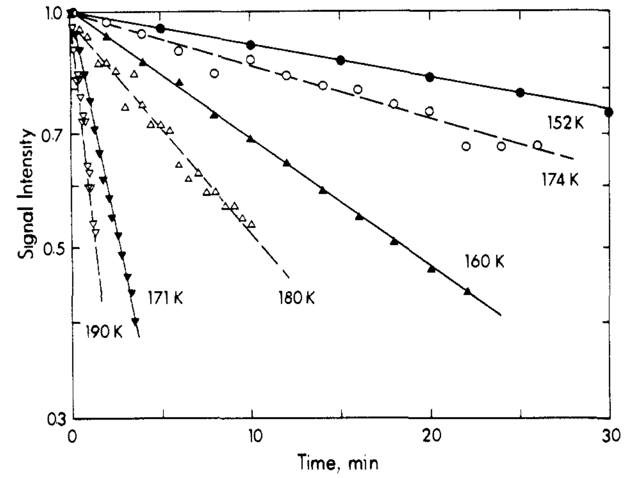


Figure 4. Semilogarithmic plot of the first-order decay of **1a** (●, ▲, ▼) and **1b** (○, △, ▽).

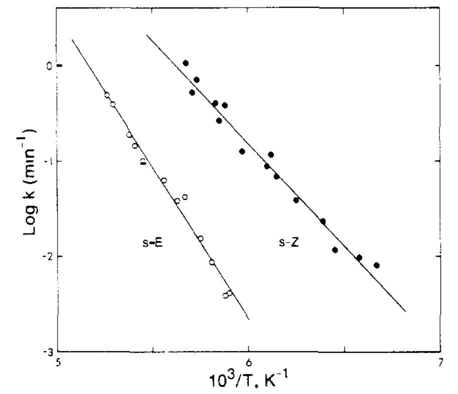
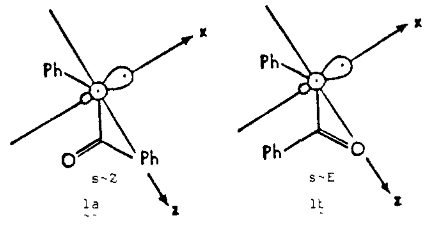


Figure 5. Arrhenius plots of the first-order rate constant for **1a** (●) and **1b** (○).

1b is somewhat more stable than **1a** and decays at temperatures above 170 K. This decay also obeys good first-order kinetics (Figure 4). The Arrhenius plot (Figure 5) gives an activation energy of 14.6 kcal/mol and log A (s^{-1}) = 14.7. **1b** was not detected in glass matrices, probably because of line-broadening effects.

Assignment of **1a** and **1b** to the *s-Z* and *s-E* isomers of BPhM, respectively, is based on their relative D and E values according to Roth's well-established criteria[24,36,37] ($D_{s\text{-}Z} > D_{s\text{-}E}$ and $E_{s\text{-}Z} < E_{s\text{-}E}$), which have been applied previously for the assignment of the *s-E* and *s-Z* isomers of analogous ketocarbenes.[18,20,21]



In the kinetic data concerning **1a**, the small A factor implies that this reaction takes place via $T_0 \rightarrow S_1$ intersystem crossing (Table II). In contrast, the large A factor for the decay of **1b**, which is close to the theoretical limit for a unimolecular reaction, does not involve intersystem crossing. The measured preexponential factor (log A (s^{-1}) = 14.7 at ~170 K) appears to be too large even for geometrical isomerization. If this is so, then the only plausible reaction channel that would be available is the adiabatic isomerization to the triplet ketene.

The measured value of E_a (**1a**) of 9.9 kcal mol^{-1} should be close to the triplet–singlet energy splitting in benzoylphenylmethylene, $\Delta(S_1\text{-}T_0) \simeq$ 9.9 kcal mol^{-1}, which is close to the average value of 4–6 kcal mol^{-1} [54] in acyclic carbenes. Recent ab initio molecular

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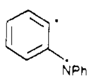
[53] Wasserman, E.; Snyder, L. C.; Yager, W. A. *J. Chem. Phys.* **1964**, *41*, 1763–1772.

Table II. Arrhenius Parameters for the Decay of Triplet Carbenes

carbene	config	K, kcal mol^{-1}	A (log A (s^{-1}))	temp range, K	ref
$CF_3\ddot{C}COCF_3$	*s-E*	5.0	6.5	105–123	20
$Ph\ddot{C}COPh$	*s-Z*	9.9	10.4	150–190	this work
	s-E	14.6	14.7		
$Q_0 \rightarrow$ **5**		5.8	10.2	93–103	this work
5 $\rightarrow S_0$		7.0	7.9	122–138.5	this work
[$Ph\ddot{C}CSPh$]		5.4	9.1	88–105.5	32
		5.2	6.5	104–124	34

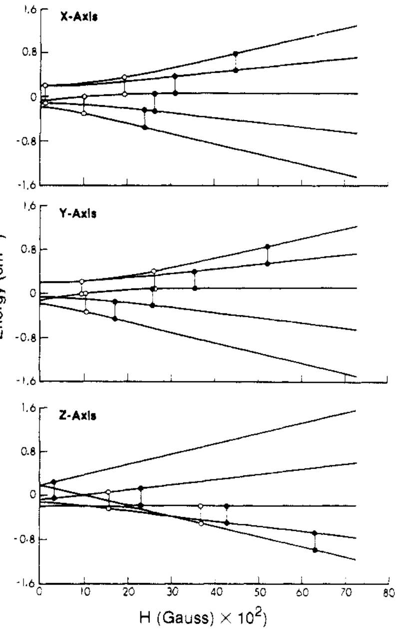


Figure 6. Quintet axial resonances for varying H with D = 0.0943 cm^{-1} and E = 0.0077 cm^{-1}: (●–●) Δm = 1 transitions; (○–○) Δm = 2 transitions.

orbital calculations[15] predict a planar diradical structure for the lowest triplet and singlet formylmethylene, with the singlet 1.3 kcal mol^{-1} above the ground-state triplet.

The same trend of decay was observed in the case of perfluoroacetylmethylmethylene geometric isomers;[20] namely, the *s-Z* isomer fades faster than the *s-E* isomer. In this case, the reaction of the *s-Z* isomer is also believed to involve the direct Wolff rearrangement and not the *s-Z* → *s-E* isomerization.

The other possible candidate for the decay of the triplet benzoylphenylmethylene is the reaction between the ketocarbene and azibenzil. This reaction, which may produce an azine (>C=N—N=C<) bond as reported in the case of the photolysis of diphenyldiazomethane,[55] could also provide a small value for the A factor and cannot be completely eliminated. However, Trozzolo did not report azines to be among the final reaction products nor could we detect any. The predominance of the *s-Z* isomer suggests that in the precursor azibenzil crystal the azibenzil molecule is present mainly in the *s-E* form due to the large steric interaction of two phenyl groups. Indeed that this is the case was confirmed by X-ray crystallographic studies.[56]

(2) The Quintet-State Triplet–Triplet Radical Pair (Q_0). Spectrum 4 was analyzed with the Hamiltonian

$$\mathcal{H} = g\beta\vec{H}\cdot\vec{S} + D\left\{S_z^2 - \frac{S(S+1)}{3}\right\} + E(S_x^2 - S_y^2)$$

Table III. Calculated and Observed Quintet Absorptions (Gauss)

calcd^a						
x axis		y axis		z axis		
Δm = 1	Δm = 2	Δm = 1	Δm = 2	Δm = 1	Δm = 2^b	obsd
	100					123
				350		
			950			823
			960			(942)^c
	1000					(1053)^c
		1200				
					1530	1738
	1950					
				2350		2364
2400						
		2550				2615
			2600			(~2500)^c
2650						2664
3100						
		3500				(3590)^c
					3650	3634
				4300		(4060)^c
4500						4712
		5225				5228
				6350		6352

^{a}Based on D = 0.0943 cm^{-1} and E = 0.0077 cm^{-1}. ^{b}One of the Δm = 2 transitions does not exist because the corresponding $\Delta E > h\nu$. ^{c}Tentative.

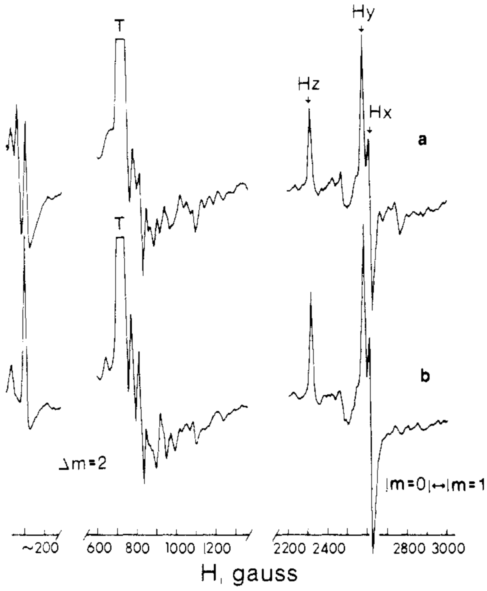


Figure 7. ESR spectrum of the quintet, Q_0, at 77 K (klystron frequency 9.166 GHz): (a) recorded immediately after 5-min photolysis; (b) after allowing the sample to relax for 23 min after photolysis.

where the higher order terms (S_i^4 or $S_i^2S_j^2$, $i, j = x, y, z$) are assumed to be negligible. The exact energy levels of $\mathcal{H}$ for a quintet state were obtained numerically by diagonalizing the corresponding matrices for the three principal axis orientations (Figure 6). The zero-field splitting parameters, D and E, were then determined from the two highest resonance absorption fields, which are equal to $H_0 + 3D/g\beta$ and $H_0 + 3(D + 3E)/2g\beta$, respectively, from first-order perturbation approximation. The values D = 0.0943 cm^{-1} and D = 0.0077 cm^{-1} were obtained, and the transitions reproduced on the basis of them are quite compatible with the appearance of the experimental spectrum on the whole (Table III, Figure 1).[57]

In Figure 1, absorption lines at 123, 823, 1738, 2364, 2615, 2664, 3634, 4712, 5228, and 6352 G have been assigned to the

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(54) Closs, G. L.; Rabinow, B. E. *J. Am. Chem. Soc.* **1976**, *98*, 8190–8198. Eisenthal, K. B.; Turro, N. J.; Aikawa, M.; Butcher, J. A.; DuPuy, C.; Hefferon, G.; Heatherington, W.; Korenowski, G. M.; McAuliffe, M. J. *J. Am. Chem. Soc.* **1980**, *102*, 6563–6565. DuPuy, C.; Korenowski, G. M.; McAuliffe, M.; Heatherington, M. W.; Eisenthal, K. G. *Chem. Phys. Lett.* **1981**, *77*, 272–274.

(55) Doetschman, D. C.; Hutchison, C. A., Jr. *J. Chem. Phys.* **1972**, *56*, 3964–3982.

(56) Cowie, M.; Gauthier, M. D. *Can. J. Chem.* **1981**, *59*, 1463–1469.

(57) In Figure 6, one of the Δm_z = 2 transitions does not exist because the corresponding $\Delta E > h\nu$. A similar situation has been commonly observed in the ESR of ketocarbenes,[10,18-21] where two of the Δm = 1 transitions are usually not observed for the same reason.

Table IV. Secondary Triplets Generated in the Photolysis of Azibenzil[a]

species	matrix	D, cm^{-1}	E, cm^{-1}
5	polycrystal	0.0189	0.0008
6	MCH/i-P	0.0134	≤0.0005
6	benzene	0.0132	≤0.0005
6	ethanol	0.0137	≤0.0005
6	C_6F_6	0.0141[b]	
6	benzophenone glass	0.0135	≤0.0005
6	benzophenone polycrystal	0.0137	≤0.0005
5	benzophenone polycrystal	0.0188	≤0.0005

[a] $g = 2.0023$ was used for the best fit. [b] Approximate value obtained from x,y lines.

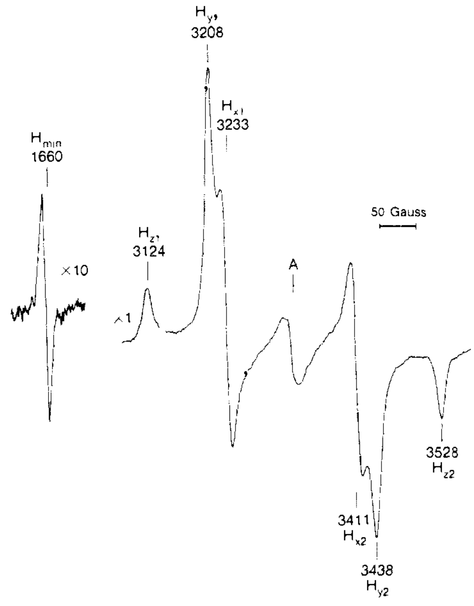


Figure 8. ESR signals of **5** recorded at 82 K. The klystron frequency was 9.312 GHz.

quintet on the basis of their parallel growth and thermal decay. There are also additional weak absorption lines at 942, 1053, 2500, 3590, and 4060 G but the fact that they overlap partially with the **1a** or **5** triplet signals makes their assignment to the quintet spectrum difficult. A line at ~350 G, if of weak intensity, may have been obscured by the background.

Following irradiation of the azibenzil sample, some spectral changes were observed in the dark for several minutes immediately after cessation of irradiation of which the growth of the Q_0 signals (Figure 7) was the most significant. In Figure 7, the lowest absorptions below 1200 G (at ~100 G and in the wing of the strong absorption of the triplet **1a** at ~800 G) are assigned to $\Delta m = 2$ transitions. The three sharp lines observed between 2300 and 2650 G are assigned to the z, y, and x lines of the $|m| = 0 \leftrightarrow |m| = 1$ transition of the lower field side. These strong lines were used for the purpose of kinetic measurements in all kinetic studies. Even at 9 K, slow growth of the Q_0 signals in the dark was observed. This initial change may be explained by the reorientation of the initially formed pairs of triplets in the trapping site to a more stable configuration of the quintet state.

These Q_0 signals were found not to be formed in the primary photolytic step after careful examination of the intensity growth profile in prolonged photolysis. This secondary origin supports the positive assignment of the spectra to a T_0–T_0 radical pair of **1a**.

The Q_0 spectrum is stable for hours at 77 K but fades above 90 K. This stability at 77 K eliminates the possibility of an excited quintet state. The decay of this signal follows good first-order kinetics and during the decay a new triplet-state ESR signal (Figure 8) having small ZFS parameters (Table IV) grows in clearly. The growth of this new triplet **5** signal is coincidental with the decay of the Q_0 signal as shown in Figure 9. The new triplet signal also features a $\Delta m = 2$ transition at half magnetic field. Triplet **5** decays at temperatures above 120 K, also obeying good first-order kinetics as shown in Figure 10, while **1a** and **1b**, as mentioned before, are stable up to 150 K.

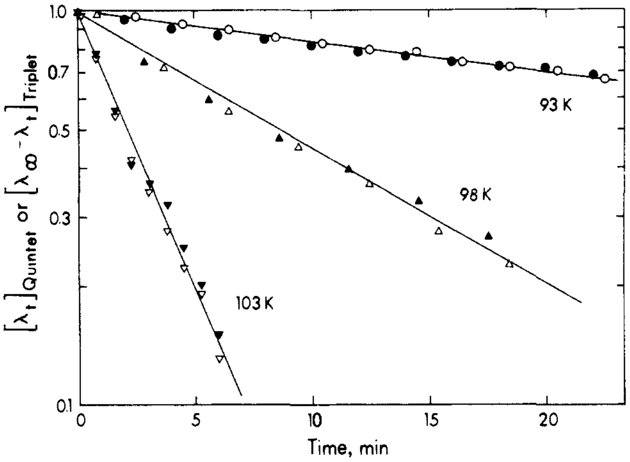


Figure 9. Typical first-order kinetic semilogarithmic plots of the quintet → triplet conversion obtained from ESR spectra of photolyzed azibenzil powder. Decay of the quintet (●, ▲, ▼) and growth of the new triplet (○, △, ▽). The corresponding λ_t values represent the signal intensities of the quintet and triplet spectrum at time = t. $[\lambda_t]_{quintet}$ and $[\lambda_\infty - \lambda_t]_{triplet}$ are normalized to 1.0 at $t = 0$.

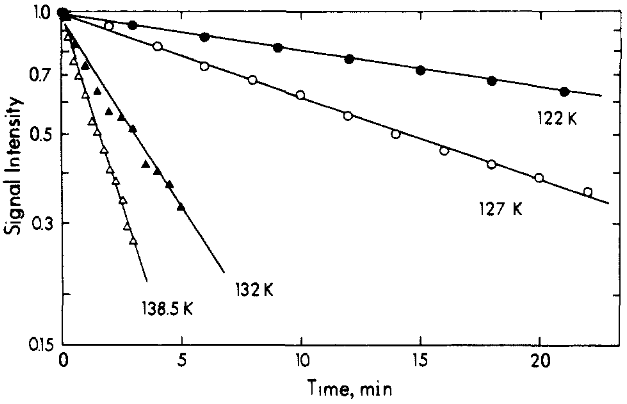
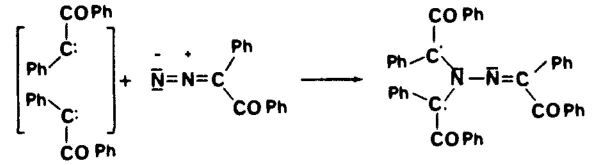


Figure 10. Typical first-order decay semilogarithmic plots of the new triplet **5** arising from the quintet.

The ratio of the initial signal intensity of Q_0 before the decay to the finally achieved signal intensity of **5** was found to be constant in the temperature range of 90–103 K. This may be taken as an indication that the $Q_0 \rightarrow$ **5** triplet conversion takes place exclusively. The ZFS parameters of **5** are similar to those of the large 1,5-diradical triplets reported by Closs and Kaplan,[58] and the mean separation of the two electrons computed from the D values of **5** in terms of point spin approximation is ~5.2 Å.

For the decay of Q_0 two basic routes may be considered: (a) collapse of the quintet radical pair to a triplet biradical via a single, intramolecular covalent bond formation between the two radicals in the pair, or (b) the addition of the quintet radical pair to a substrate molecule, e.g.



The occurrence of step b is difficult to envision for it would require a concerted attack by the two carbenes on the diazo group, which would be severely restricted in a crystalline solid matrix by the entropy requirements, and nonconcertedness would lead to azine and a BPhM(T_0) formation and thus could not account for the

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(58) Closs, G. L.; Kaplan, L. R. *J. Am. Chem. Soc.* **1969**, *91*, 2168–2169.

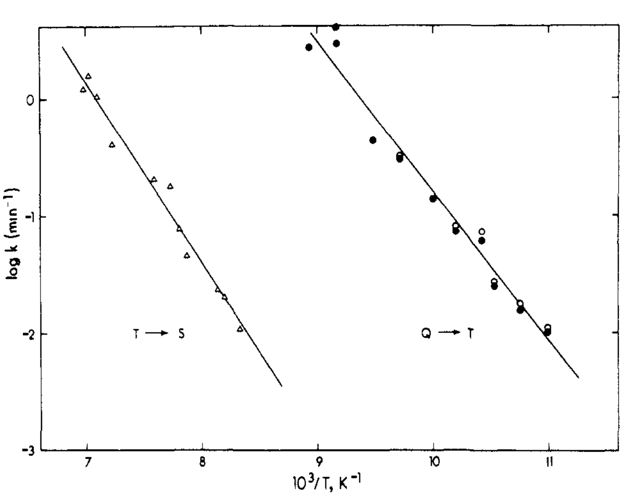


Figure 11. Arrhenius plots of the first-order rate constant for the quintet → triplet (●) and the triplet → singlet (△) conversion. (○) indicates the rate constants obtained from the growth of the new triplet.

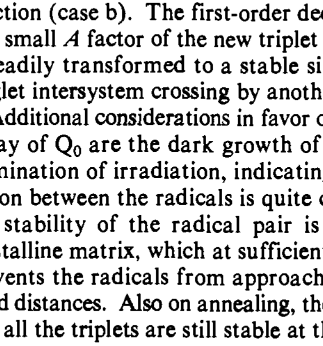
appearance of the new triplet biradical spectrum. Also, azine formation between BPhM tied up in a radical pair and the parent diazo ketone should be less likely and kinetically less favorable than with free BPhM and the rate of free BPhM decay in the system is slower than the decay of Q_0. Therefore, the decay of the quintet should be due to case a above, and case b can be ignored.

The Arrhenius plots for the decay of the Q_0 and the growth of **5** are shown in Figure 11 along with the plot for the decay of **5**. These plots give an activation energy of 5.8 kcal/mol and log A (s^{-1}) = 10.2 for the $Q_0 \rightarrow$ **5** conversion reaction and 7.0 kcal/mol and log A (s^{-1}) = 9.1 for the decay of the new triplet species, **5**.

The small activation energy and A factor of the $Q_0 \rightarrow$ **5**(T) conversion are reasonable for a unimolecular intersystem crossing corresponding to a covalent bond formation but this A factor value would be too large for a spin-forbidden, concerted, combination reaction (case b). The first-order decay, small activation energy, and small A factor of the new triplet also indicate that this triplet is readily transformed to a stable singlet product via triplet-to-singlet intersystem crossing by another chemical bond formation.

Additional considerations in favor of the suggested unimolecular decay of Q_0 are the dark growth of the ESR signal of Q_0 after termination of irradiation, indicating that the strength of interaction between the radicals is quite considerable. Undoubtedly, the stability of the radical pair is due to the rigidity of the crystalline matrix, which at sufficiently low temperature, <90 K, prevents the radicals from approaching one another to covalent bond distances. Also on annealing, the quintet is the first to decay, and all the triplets are still stable at the onset of the quintet decay temperature. This is in line with the relative ease with which covalent bond length can be achieved giving a delocalized twisted olefinic triplet diradical with free spin separation of ~5.2 Å.

The X-ray diffraction data[56] of azibenzil single crystal suggest two possible combinations of the nearest two azibenzil molecules to produce Q_0. In one case, two molecules exist in one unit cell and they are twisted to one another. The diazo groups are directed toward each other but somewhat inclined (**I**). In the other case, two molecules with identical orientations are aligned one above the other (II). The distances in the two conformations between the two diazo carbons are 6.1 and 5.6 Å, respectively. The other combinations of two molecules seem to be too far to have dipole–dipole interactions after the formation of two BPhM(T_0). This crystallographic result suggests that the triplet–triplet radical pair has a configuration of two divalent carbons facing each other or parallel to each other, and the first covalent bond formation by annealing probably takes place between two divalent carbons instead of the carbon–oxygen bond considered previously.[39] The diradical could be stabilized by getting frozen with a twisted or distorted configuration of two precursor frameworks in the rigid crystal lattice. Finally, a slight change of the molecular framework by further annealing would help to achieve planarity and double-bond formation in the diradical.



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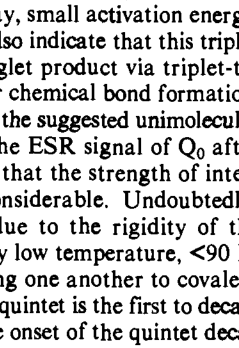

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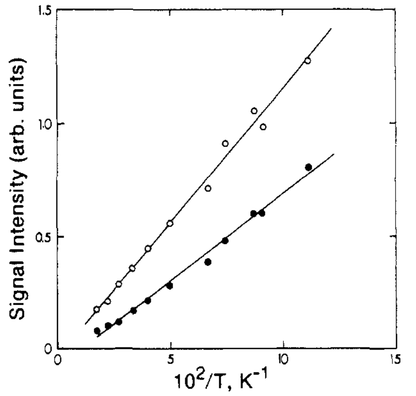
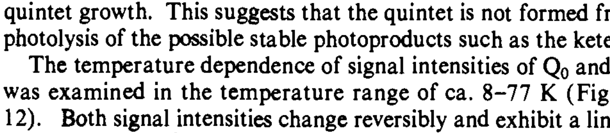


Figure 12. Signal intensities of the quintet (●) and **1a** (○) versus T^{-1}. The lines represent the best linear least-squares fit of the data.



(7)

The mechanism of Q_0 formation has not been elucidated in detail: nevertheless it has been shown that Q_0 is not a primary photoproduct. The sample, even if used repeatedly for a long period of time, exhibits identical behavior and the same spectral and kinetic characteristics, including the induction period for the quintet growth. This suggests that the quintet is not formed from photolysis of the possible stable photoproducts such as the ketene.

The temperature dependence of signal intensities of Q_0 and **1a** was examined in the temperature range of ca. 8–77 K (Figure 12). Both signal intensities change reversibly and exhibit a linear dependence on T^{-1} as expected for ground-state species if the Curie law is obeyed. This linear relationship does not, however, exclude the unlikely possibility of a near-degenerate S_0 of S_1 state.

Photolysis of Azibenzil in Organic Glasses. Irradiation of azibenzil (~10^{-2} mol/L) at 77 K in methylcyclohexane and isopentane (MCH/i-P (4/1)) mixture glass at 77 K using $\lambda \geqslant$ 345 nm light resulted in the appearance of three ESR spectra, which were assigned to the randomly oriented BPhM(T_0) (**1**), another triplet species having small ZFS parameters (**6**), and the ubiquitous structureless doublet radicals of secondary origin (A).

The ZFS parameters of **1** were determined to have values D = 0.385 and E = 0.052 cm^{-1} and line width at half-height ($\Delta H_{1/2}$) of the lowest magnetic field z line of 254 G in MCH/i-P glass as compared to $\Delta H_{1/2}$ = 13 G in azibenzil powder. This type of line broadening occurring in matrices other than the precursor's own crystal has been termed by Trozzolo, Wasserman, and Yager[59] as the "Shpolskii effect like" phenomenon. From comparison with the ZFS obtained in azibenzil powder, **1** apparently has, by and large, an *s-Z* conformation in organic glasses. It is a primary photoproduct (Figure 13), which fades on warming the photolysate to temperatures above 100 K.

The spectrum of **6** is shown in Figure 14, and the ZFS parameters are given in Table II. The small values of the ZFS

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(59) Trozzolo, A. M.; Wasserman, E.; Yager, W. A. *J. Chim. Phys.* **1964**, *61*, 1663–1665.

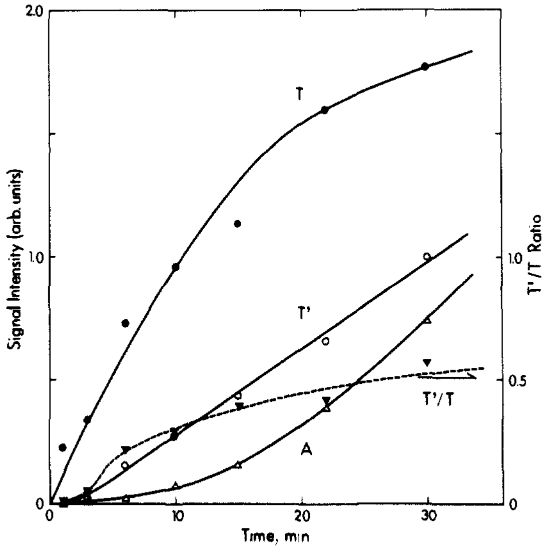


Figure 13. Time dependence of the ESR signal during photolysis of azibenzil in MCH/i-P glass at 77 K. T = 1; T′ = 6; A = doublet radical.

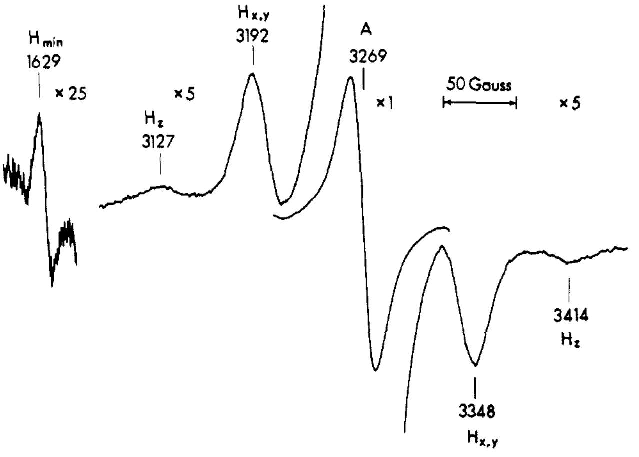


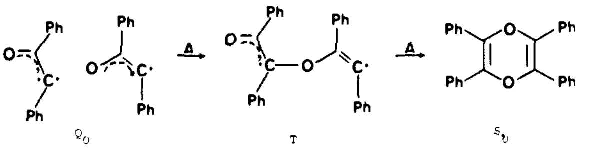
Figure 14. ESR spectrum of **6** ($H_{x,y}$, H_z, and H_{min}) and doublet radical (A) generated in the $\lambda \geq 345$ nm photolysis of azibenzil in MCH/i-P glass at 77 K. The klystron frequency was 9.313 GHz.

parameters imply that **6** is either a radical pair or a large diradical, with an average separation of the two spins of ~5.8 Å in terms of a point dipole approximation.

Similar spectra with similar D and E values (Table IV), were obtained in the photolyses of azibenzil in several different matrices. In benzene, which forms a polycrystal on cooling, the relative intensities of **1** (broad) and **6** (sharp) were approximately the same as in the MCH/i-P matrix. In ethanol the relative signal intensity of **6** appears to be somewhat weaker, and in hexafluorobenzene, which also forms a polycrystal matrix, the intensity of **6** is very weak. In benzophenone glass, the same results were obtained as in MCH/i-P glass, whereas microcrystalline powdered benzophenone solution yielded not only the signals of **6** but also the full spectrum that was obtained when azibenzil was photolyzed in neat powder form, including **1a**, **1b**, the quintet, and the doublet radicals. When the photolysate was annealed at 100 K, the quintet decayed and the new triplet, **5**, grew in superimposed on the signals of **6**. Upon further warming, the new triplet, **5**, from the collapse of the quintet faded at ca. 130 K while both **1a** and **6** decayed slowly at ca. 160 K. **6** appeared to be somewhat more stable than **1a**. **1b** faded at 180 K, at which temperature the doublet was still stable.

That **6** is not a primary photoproduct is indicated by its growth curve and the curve depicting its relative spectral intensity to **1** as a function of exposure time (Figure 13), which both closely resemble the analogous curves of the quintet radical pair formed in the polycrystalline phase (Figure 2). Therefore, one may be led to believe that **6** in the glass matrices is identical with the triplet species **5**, now formed from the thermal collapse of the quintet radical pair within the molecular cluster. However, the ZFS parameters of **6** are different, somewhat smaller (D = 0.013–0.014, $E \leq 0.0005$ cm^{-1}) for the glass matrices than for the powder sample (D = 0.0189, E = 0.0008 cm^{-1}). Since matrix effects will not account for the difference, important configurational changes would have to be invoked for **5** and **6** to be the same species.

Alternatively, the difference in the D and E values between **5** and **6** could be rationalized as being due to the thermal decay of the quintet via a different kind of bond formation between the two triplets. In the powder sample, carbon–carbon bond formation would take place as suggested (reaction 7), while carbon–oxygen bond formation may take place in the glass matrix cluster (reaction 8). However, efforts to stabilize a possible quintet at lower



(8)

temperatures (15 K) have not been successful, and it is certainly not easy to rationalize such regiospecificity. Alternative diradical structures may also be considered.

The possibility that **6** is a triplet-state doublet–doublet radical pair formed by H abstraction from the solvent is not likely either since its intensity does not follow the H-donor capability of the different matrices and also the ZFS parameters are not significantly affected by the different matrices. Proper assignment of the nature of triplet **6** must await the analysis of the final photolysis products.

In summary, photolysis of azibenzil powder at 77 K produces four paramagnetic intermediates, namely, the *s-Z* and *s-E* isomers of BPhM(T_0) in a 9:1 ratio, a Q_0, and a yet unidentified mixture of doublet radicals formed in the secondary photolysis of BPhM(T_0). The predominance of the *s-Z* isomer of BPhM(T_0) is simply the reflection of the main molecular structure, *s-E* of the precursor azibenzil in its crystal. Although both **1a** and **1b** will likely undergo Wolff rearrangement to the ketene, their decay kinetics indicate a more facile rearrangement for **1a** via

$$\mathbf{1a}(T_0) \xrightarrow{\text{ISC}} \mathbf{1a}(S_1) \xrightarrow{\text{WR}} \text{ketene}(S_1 \text{ or } S_0)$$

than for **1b** via

$$\mathbf{1b}(T_0) \xrightarrow{\text{WR}} \text{ketene}(T_1) \xrightarrow{\text{ISC}} \text{ketene}(S_0)$$

The triplet–triplet radical pair of Q_0 has a quintet ground state, and the kinetics indicate that the decay of Q_0 is via stepwise intersystem crossing $Q_0 \rightarrow T_0 \rightarrow S_0$. Thus, combination of the two BPhM(T_0) occurs on the quintet surface, which is the lowest energy surface at large internuclear distances of the carbene centers (~5 Å). On annealing, covalent bond formation occurs exclusively via intersystem crossing to the surface of the triplet olefin product, which at the reaction temperature is still frozen in the rigid matrix as a nonplanar triplet olefin. On further annealing, this leads to crossover to the planar S_0 ground-state surface of the olefin. Carbon–carbon bond formation between two BPhM is proposed for this reaction, but the sequences established here may provide a scheme for the general mechanism of triplet carbene recombination reactions.

On the other hand, photolysis of azibenzil in organic matrices produces triplet BPhM, a small D and E triplet **6**, and an unidentified mixture of doublet radicals with or without the spectrum observed in the powder form, depending on the structural state (glass versus crystal) of the matrix. Kinetics of the formation of the small D and E triplet suggest that it is formed by the thermal decay of the quintet. However, its nature has not been determined. Further work is in progress.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for continuing support.

Registry No. **1**, 74487-99-3; **5**, 112270-12-9; azibenzil, 3469-17-8; 2,3,5,6-tetraphenyl-1,4-dioxin, 6963-24-2; 1,2,3,4-tetraphenylbut-2-ene-1,4-dione, 7510-34-1.