Reversible Photochemistry of 10,10′-Dimethylbiacridan: Internal and External Heavy Atom Effects, and the Structure of Photoisomer F

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An extensive study of the photochemistry of 10,10′-dimethyl- (3a), 1,1′,10,10′-tetramethyl- (3b), and of 2,2′,7,7′-tetrabromo-10,10′-dimethyl-biacridan (3c) revealed the formation of two light-stable photoisomers E and F, from the fundamental modification A. The photoisomerization quantum yields $\phi_{A\rightarrow E}$ and $\phi_{A\rightarrow F}$ are enhanced by oxygen, xenon, alkyl halides and also by carbon disulphide. Flash photolysis studies of both direct and sensitized photoisomerization A ⟶ E suggest that E is formed through the triplet manifold. The formation of the E isomer involves rotation by 180° about the 9,9′-double bond as well as additional rotation of the benzene rings about the single bonds attached to the central double bond. ^{1}H N.m.r. spectra of photoisomer F measured at low temperatures, and geometry calculations by the CFF-π electron-CI method suggest that compared with A the structure of F involves torsion about both the central double bond and about the single bonds attached to it.

THE advent of powerful techniques such as low temperature n.m.r. and computational conformational analysis has made possible the recent elucidation of the molecular structures of the labile modifications of bianthrones (1),[1] responsible for the well known photochromic and thermochromic phenomena.[2] Within the

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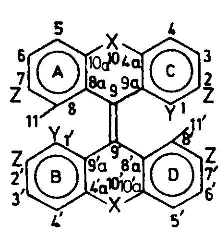
[1] R. Korenstein, Sh. Sharafi-Ozeri, and K. A. Muszkat, *J. Amer. Chem. Soc.*, 1973, **95**, 6177.

[2] T. Bercovici, R. Korenstein, K. A. Muszkat, and E. Fischer, *Pure Appl. Chem.*, 1970, **24**, 531.

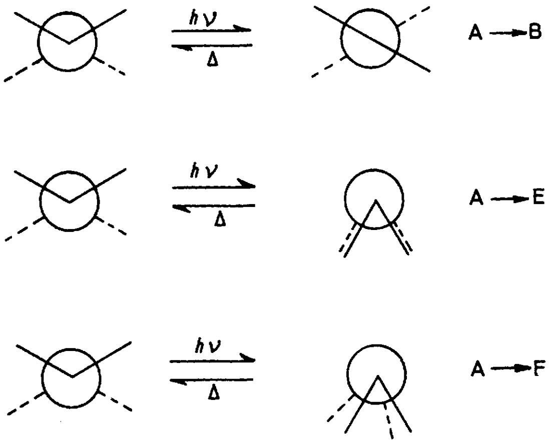
framework of a comprehensive investigation of the labile modifications in the bridged tetra-arylethylene series we have recently completed studies of the unstable photoisomers of dixanthylidene (2),[3,4] dithioxanthylidene (6),[5] and the dianthrylidenes (4) and (5).[6] In this paper we describe in detail the photochemistry of biacridans * (3a—c) leading to the formation of the recently reported E photoisomers[8] in (3a and c) and the new photoisomer F observed in (3b).



	X	Y	Z
(1)	CO	H	H
(2)	O	H	H
(3a)	NCH_3	H	H
(3b)	NCH_3	CH_3	H
(3c)	NCH_3	H	Br
(4)	CH_2	H	H
(5)	CHOH	H	H
(6)	S	H	H

Thus far neither photochromism nor thermochromism have been observed for biacridans in solution, though (3a) absorbed on magnesium oxide has been reported to be thermochromic.[7]

The configuration of molecules (1)—(6) and of their unstable modifications is determined by the interplay between the tendency towards coplanarity of the whole molecule and the repulsions between the 1,8′ and 1′,8 positions which prevent such a coplanar arrangement.



SCHEME 1

These repulsions can be relieved in various ways, as shown in the Newman projections (Scheme 1) along the 9,9′ bonds for the A, B, E, and F † modifications thus far observed in the bridged tetra-arylethylenes (1)—(6).

X-Ray analysis[9] of the fundamental modification A of (1) indicates folding of the two anthrone units about the 9,10 axis so that rings A and D are displaced to one side of the plane of the central double bond and rings B and C to the other side. The strong repulsion between the 1,8′ positions can be relieved in two other ways: (*a*) torsion about the 9,9′ double bond and (*b*) rotation of 180° about the 9,9′ double bond accompanied by additional rotation of rings A—D around the single bonds connected to the 9,9′ double bond system. We have shown that the structure[1] of photoisomer B found in (1) and (2) involves molecular deformation of type (*a*). The deduction of this structure was based on (i) ^{1}H n.m.r. measurements at low temperature, (ii) calculations of minimum strain energy conformations, and (iii) molecular orbital calculations of electronic excitation energies. Recently we have shown[8] that low temperature irradiation of (3a) and (4)—(6) produces a different photoisomer denoted E instead of the B isomer produced in (1) and (2). Both B and E are formed *via* the triplet manifold of the respective A forms. Here too, low temperature ^{1}H n.m.r. measurements and minimum strain energy calculations suggested that the structure of the E isomer (Figure 1a) involves deformation of type (*b*).

In this paper we describe the formation of the E isomers of (3a and c) in detail, and in addition a new type of photoisomer, F, observed in compound (3b). The structure of F (Figure 1b) was elucidated by means of the experimental and theoretical methods previously applied to the determination of the structure of E.[8]

(A) *Photoformation of the E and F Isomers.*—10,10′-Dimethylbiacridan (3a) and its derivatives (3b and c) photoisomerize in solution at temperatures down to −180°. Compounds (3b and c) yield an isomer denoted as the E form whose first absorption band is shifted from 420 in (3aA) to 360 nm in (3aE) (Figure 2a) and from 455 in (3cA) to 388 nm in (3cE). Compound (3b) gives rise to a different type of photoisomer, denoted F. The positions of the absorption maxima of (3bF) and (3bA) are almost identical, but absorption intensity in E is lower and the half-width of the absorption band is higher (Figure 2b). Both photoisomers E and F are light-stable, so that complete conversion of A into each of the photoisomers can be achieved. E and F revert thermally to A in first-order reactions. The Arrhenius parameters for (3c) in a methylcyclohexane (MCH)–3-methylpentane (3-MP) were E_a 14.7 ± 0.5 kcal mol^{-1}, log A 13.3 ± 0.5.

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* Compound (3a) and its derivatives are known as biacridans or biacridylidenes.[7] (1) and (2) are known as either bianthrone and bixanthylidene or as dianthrone and dixanthylidene.

† A is the fundamental modification, B the 9,9′ twisted modification,[1] C is the cyclic (4a,4b-dihydrophenanthrene type) modification,[10] and E and F are as described.

[3] R. Korenstein, K. A. Muszkat, M. A. Slifkin, and E. Fischer, *J.C.S. Perkin II*, 1976, 438.

[4] R. Korenstein, K. A. Muszkat, and E. Fischer, *J. Photochem.*, 1976, **5**, 447.

[5] R. Korenstein, K. A. Muszkat, and E. Fischer, *J. Photochem.*, 1976, **5**, 345.

[6] R. Korenstein, K. A. Muszkat, and E. Fischer, *J.C.S. Perkin II*, 1977, 564.

[7] G. Kortüm, W. Theilacker, and G. Schreyer, *Z. phys. Chem.* (*Frankfurt*), 1957, **11**, 182.

[8] R. Korenstein, K. A. Muszkat, and G. Seger, *J.C.S. Perkin* 1976, 1536.

[9] E. Harnik and G. M. J. Schmidt, *J. Chem. Soc.*, 1954, 3295.

[10] R. Korenstein, K. A. Muszkat, and E. Fischer, *Helv. Chim. Acta*, 1970, **53**, 2102.

The formation and decay of E were measured at temperatures from 25 to −50° by flash photolysis, and at lower temperatures under steady illumination conditions. In (3a and b) the photoisomerization efficiency decreases slowly with the temperature over a wide temperature range while in (3c) the photoisomerization is an unactivated process. Thus the quantum yield $\phi(A \longrightarrow E)$ in MCH-3-MP solutions of (3a) decreases from 0.002 5 at 25° to 0.001 6 at −30° and 0.000 5 at −100°, but remains unchanged on further cooling, down to −160°. $\phi(A \longrightarrow E)$ did not vary with the concentration of (3a) in the range 5×10^{-5}—5×10^{-4}M.

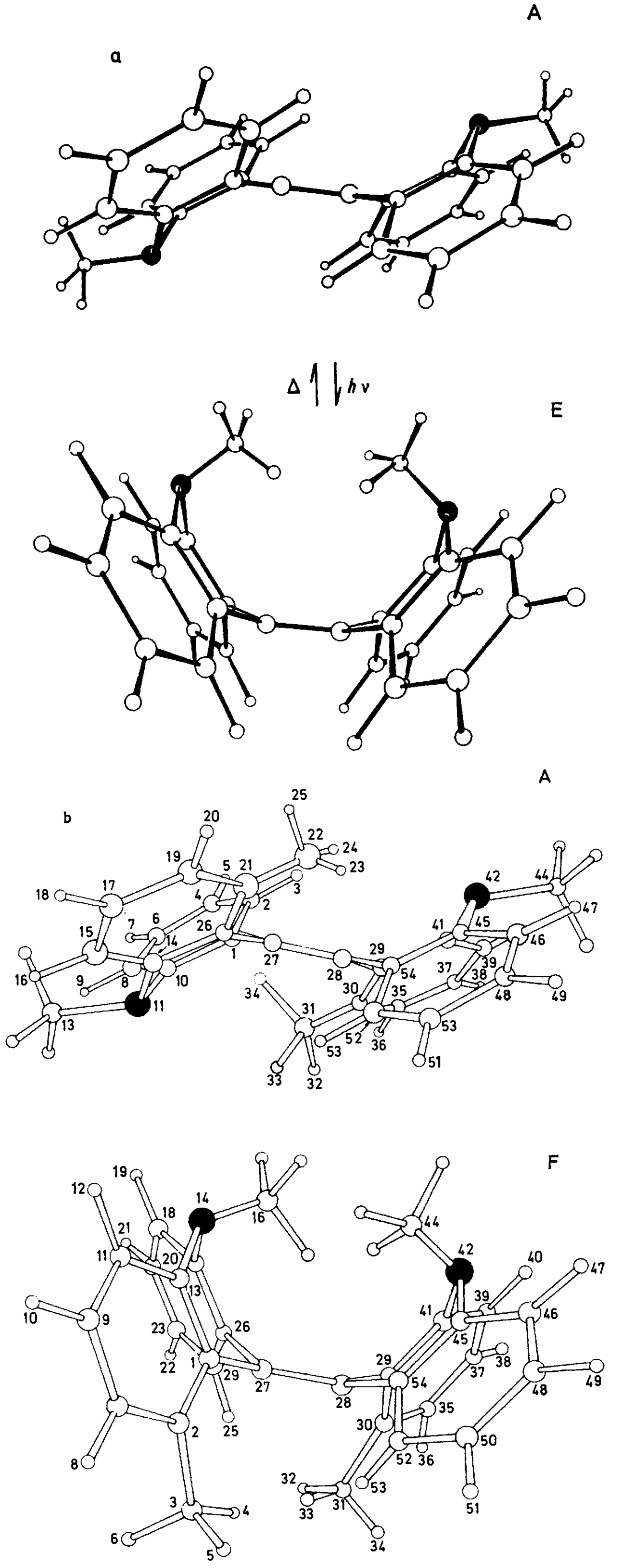

FIGURE 1 a, Calculated molecular structures of (3aA) and of (3aE); b, calculated molecular structures of (3bA) and (3bF)

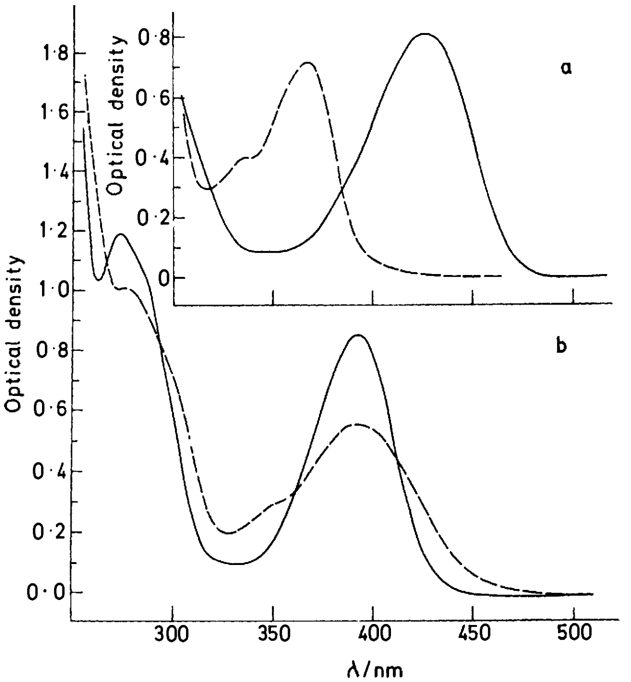

FIGURE 2 a, Absorption spectra of (3aA) (full curve) and (3aE) (broken curve); b, Absorption spectra of (3bA) (full curve) and (3bF) (broken curve)

(B) *Internal and External Heavy Atom Effects.*—The $A \longrightarrow E$ quantum yield of the dibromo-derivative (3c) did not vary with the temperature, and at −100° was 10^2 times higher than $\phi_{A \rightarrow E}$ of (3a) (Table 1). This may be considered as a rather high internal heavy atom effect. External spin–orbit coupling perturbations[11-14]

TABLE 1

Quantum yields of $\phi_{A \rightarrow E,F}$ of deaerated solutions of (3a—c) at −100°, as a function of increasing spin–orbit perturbation

Compound	MCH	Bu^{n}Br	C_2H_5I	CS_2
(3a)	0.000 5	0.002 1	0.032	0.3
(3b)	0.001 4	0.007	0.019	0.18
(3c)	0.05			0.08 *

* In the presence of 1.6M-CS_2.

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[11] R. Korenstein and K. A. Muszkat, in 'Environmental Effects on Molecular Structures and Properties,' ed. B. Pullman, Reidel, Dordrecht, Holland, 1976, pp. 561—571; R. Korenstein, K. A. Muszkat, and E. Fischer, *Chem. Phys. Letters*, 1975, **36**, 509.

[12] D. Gegiou, K. A. Muszkat, and E. Fischer, *J. Amer. Chem. Soc.*, 1968, **90**, 3907.

[13] D. O. Cowan and J. C. Koziar, *J. Amer. Chem. Soc.*, 1975, **97**, 249 and references cited therein.

[14] G. Fischer and E. Fischer, *Mol. Photochem.*, 1974, **6**, 463.

were investigated through the effect of external agents on $\phi(A \longrightarrow E)$ and $\phi(A \longrightarrow F)$ in a wide range of concentrations of the perturbers O_2, Xe, C_2H_5I, Bu^nBr, and CS_2 (Figures 3 and 4). A comparative study of $\phi(A \longrightarrow E,F)$ in a series of solvents with increasing external spin–orbit perturbation effect is given in Table 2. The increase in $\phi(A \longrightarrow E)$ or in $\phi(A \longrightarrow F)$ along the series MCH, Bu^nBr, C_2H_5I is as expected from an effect of the nuclear charge of the heavy atom on spin–orbit coupling,[16] but CS_2 despite the low atomic number of S, is exceptionally effective (Table 1, Figure 3). Molecular oxygen is the most effective spin–orbit perturber [14] (Figures 3 and 4), followed by xenon.

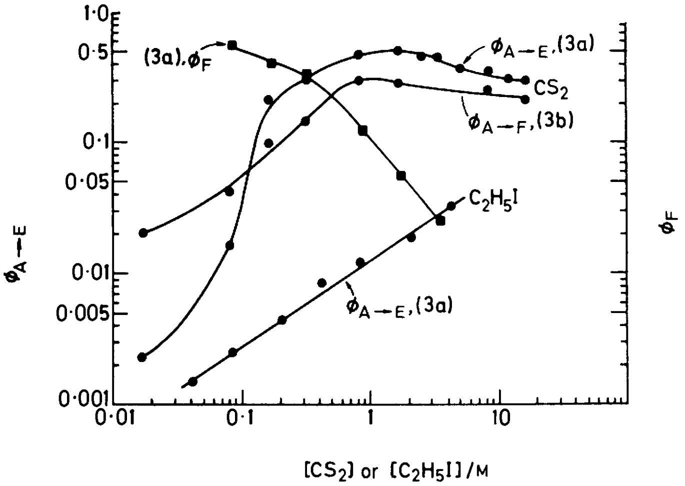

FIGURE 3 Variation of $\phi_{A \rightarrow E}$, $\phi_{A \rightarrow F}$, and ϕ_F with the concentration of CS_2 and C_2H_5I. Solutions in MCH of (3a and b) (*ca.* 5×10^{-5}M) at −100°

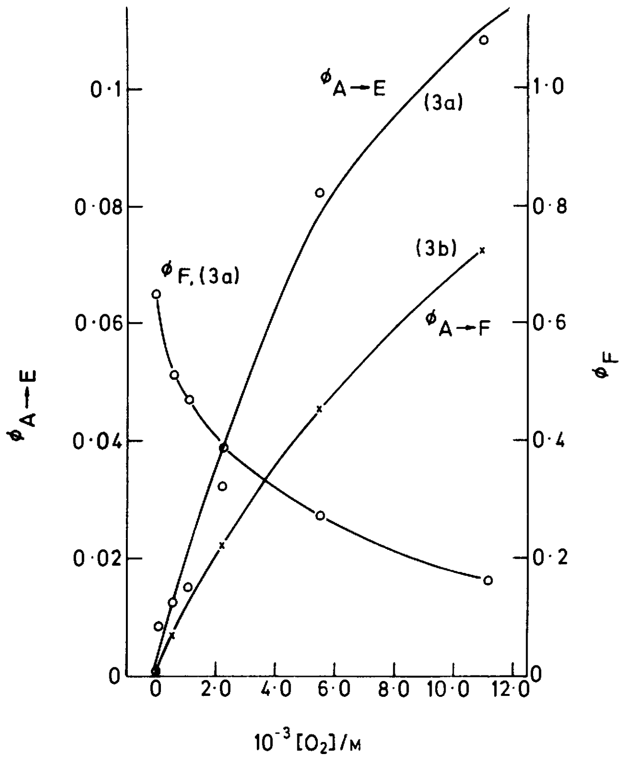

FIGURE 4 Dependence of $\phi_{A \rightarrow E}$, $\phi_{A \rightarrow F}$, and ϕ_F on concentration of oxygen. Compound (3a) at −120° and (3b) at −60°, both 5×10^{-5}M in MCH–methylcyclopentane (1 : 1)

TABLE 2

Quantum yields $\phi_{A \rightarrow E}$ and $\phi_{A \rightarrow F}$ of (3a—c) at −100° in MCH saturated * with argon, oxygen, and Xe at −20°

Compound	Argon $\phi_{A \rightarrow E,F}$	O_2 $\phi_{A \rightarrow E,F}$	Xe $\phi_{A \rightarrow F}$
(3a)	0.000 5	0.11	0.1
(3b)	0.001 4	0.07	
(3c)	0.05	0.1	

* For solubility data see ref. 15.

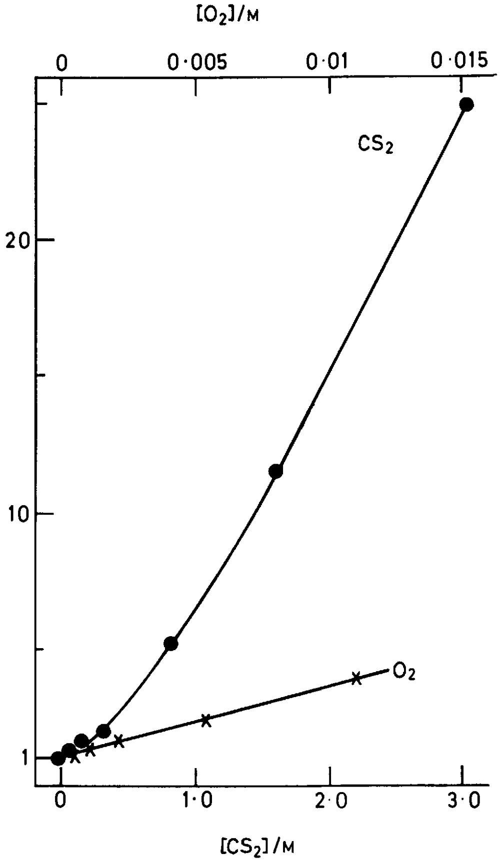

FIGURE 5 Stern–Volmer plot of fluorescence quenching in (3aA) and (3bA) by molecular oxygen and by carbon disulphide in MCH

The fluorescence of (3a) is effectively quenched both by oxygen and by CS_2. Linear Stern–Volmer plots are obtained for O_2, while those for CS_2 are nonlinear, probably because of efficient static quenching [17] (Figure 5), besides the normal dynamic quenching. Within the

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[15] W. P. Linke and A. Seidell, ' Solubilities: Inorganic Compounds,' Van Nostrand, Princeton, 1958, vol. 1, p. 3.

[16] S. P. McGlynn, T. Azumi, and M. Kinoshita, ' Molecular Spectroscopy of the Triplet State,' Prentice-Hall, Englewood Cliffs, 1969.

[17] A. A. Lamola and N. J. Turro in ' Techniques of Organic Chemistry, Vol. XIV,' ' Energy Transfer and Organic Photochemistry,' Wiley, New York, 1969.

limited concentration range available for oxygen, its quenching action is predominantly dynamic.

The emission and absorption spectra of the A forms and their corresponding photoisomers E and F are given in Figures 6a and b. The fluorescence quantum yields ϕ_F were measured over a wide temperature range in evacuated or argon-flushed solutions relative to 1,6-diphenylhexatriene (ϕ_F 0.8)[18] and to 1,1,4,4-tetraphenylbutadiene (ϕ_F 0.4).[18] The ϕ_F values are virtually constant from room temperature down to $-180°$, and amount to 0.40 for (3aA) and (3bA), and 0.28 for (3cA). The attenuation of ϕ_F by air yields a value of 11.5 ns for the lifetime of the emitting singlet state of (3a) and 12.5 ns for that of (3b). The ϕ_F value of the E and F forms is only *ca.* 0.05 at temperatures from -100 to $-180°$.

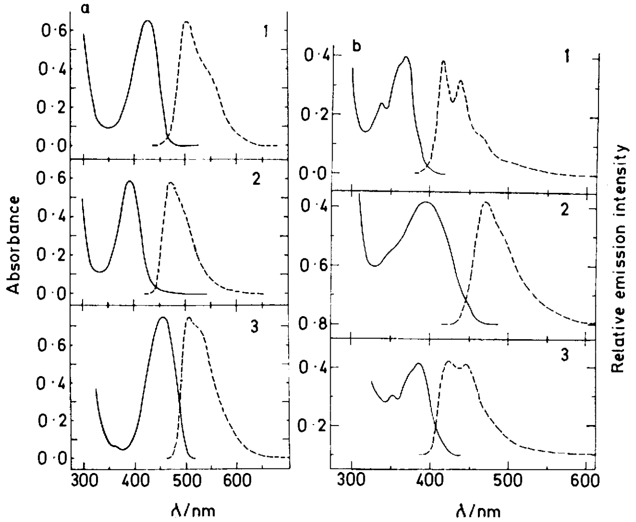
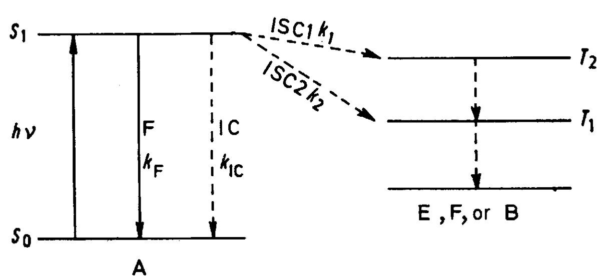


FIGURE 6 Absorption (——) and fluorescence (— — —) spectra of the A, E, and F forms of (3a—c) in MCH–methylcyclopentane mixture (1 : 1) at $-180°$: a, 1, (3aA); 2, (3bA); 3, (3cA); b, 1, (3aE); 2, (3bF); 3, (3cE)

The values of ϕ_F for the A forms are rather low, and the effect of bromination is small ($0.40 \longrightarrow 0.28$). Since the triplet formation is very inefficient in the absence of perturbing agents, we must conclude that internal conversion from the S_1 state is extensive. This is more so in the E and F forms.



SCHEME 2

In this context one should note that the relative effect of bromine on ϕ_F ($\phi_F^{(3c)}/\phi_F^{(3a)} = 0.7$) is much weaker than the effect on $\phi_{A\to E}$ (20). We shall consider here one simple case (Scheme 2) where such a situation would be anticipated. In Scheme 2 F denotes fluorescence, IC internal conversion, and ISC1 and ISC2 denote two intersystem crossing paths. The corresponding rate constants are k_F, k_{IC}, and k_1 and k_2. In (3a) intersystem crossing takes place through ISC1 but in (3c) the important path is ISC2. In both (3a and c) k_F is very much larger than k_1 and k_2. In (3a) k_1 is larger than k_2 ($k_2 \longrightarrow 0$) but in (3c) k_2 is much larger than k_1. For both compounds we thus have equation (1). Assuming

$$\phi_{A\to E}/\phi_F = (k_1 + k_2)/k_F \qquad (1)$$

that very roughly k_F and k_1 are the same for (3a and c) we get an estimate for $k_2^{(3c)}/k_1$, $k_2^{(3c)}/k_1 = (\phi_{A\to E}/\phi_F)_{(3c)}/(\phi_{A\to E}/\phi_F)_{(3a)} = 28$.

(C) *Mechanism of Photoisomerization*.—(a) *Flash photolysis of* (3a) *at low temperatures*. No transients were observed in solutions of (3a) in MCH-3-MP–toluene mixtures. However, in the presence of 1.6M-carbon disulphide, at $-175°$, a transient absorbing at 780 nm denoted as *780* was detected, whose decay kinetics were very similar to those of the appearance of E at 360 nm (Figure 7). These results suggest that *780* is a precursor of E, and that the formation of *780* is immediate (within the life-time of the flash pulse, *ca.* 20 μs).

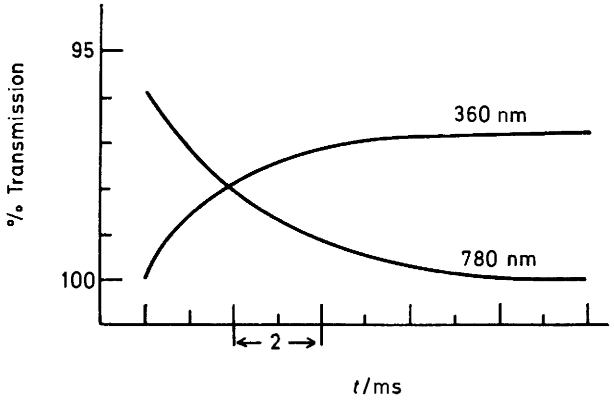


FIGURE 7 Kinetics of the decay of the 780 nm transient and corresponding appearance of isomer E (at 360 nm) in the flash photolysis of (3a) (5×10^{-5}M) in MCH–isohexane–toluene (5 : 5 : 1) (1.6M in CS_2) at $-170°$

CS_2 was added in these experiments as an external perturber because the rate of intersystem crossing (ISC) in (3c) in the absence of perturber, as manifested also by the low value of $\phi_{A\to E}$, is very low. As shown in Figure 3, $\phi_{A\to E}$ passes a maximum at a CS_2 concentration of 1.6M, indicating that a maximum in the steady state population of the triplet state is obtained at this CS_2 concentration.

(b) *Photosensitized conversion A* $\longrightarrow$ *E*. A solution of biacetyl as donor with (3a) as acceptor was flushed thoroughly with argon and flash-photolysed at temperatures from -20 to $-50°$. In all cases transients corresponding to the E isomer were observed. The decay kinetics of the transient formed by both direct

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[18] I. B. Berlman, 'Handbook of Fluorescence Spectra,' Academic Press, New York, 1971, 2nd edn.

excitation and sensitization paths were the same, k(E ⟶ A, first order) 1.5 s^{-1} at $-30°$.

Although the aim was to excite selectively only the biacetyl molecules, direct excitation of (3a) could not be completely avoided, since biacetyl absorbs in the same region as (3a). Nevertheless, it could be shown that the amount of transient formed by direct excitation of (3aA) is $<1\%$ of the total.

(D) *Minimum Energy Calculation of the Conformations of the A and F Forms.*—The exact conformation of the A and F forms in (3b) were calculated by the CFF–π-electron–CI method of Warshel and Karplus.[19] The potential energy surface was searched for a secondary minimum, in addition to that of the lowest energy form A. The calculated minimum energy structures of the A and F forms are given in Figure 1b. The initial co-ordinates for the A form were derived from those of 10,10′-dihydrobianthrylidene, and then were optimized by the above method. The initial co-ordinates of the F form were obtained by twisting the A form by 180° about the 9,9′ double bond. The calculated dihedral angles whenever different from 0 or 180° are in Table 3.

TABLE 3

Calculated dihedral angles in degrees for non-planar parts in (3bA) and (3bF)

Angle	Atoms	Dihedral angles (°) A	F	Δ
τ_A	9a, 9, 9′, 8′a	0	13	13
τ_B	1, 9a, 9, 9′	308	284	24
τ_C	9, 8a, 8, 11	355	355	
τ_D	10a, 8a, 9, 9′	135	113	22
τ_E	8a, 10a, 10, 4a	41	41	
τ_F	11, 8, 7, 6	187	188	

τ_B and τ_D are the torsion angles about the single bonds attached to the 9,9′ double bond. Both increase by 22 to 24° in the phototransformation of A to F, resembling the structural changes in the A ⟶ E process. The change in the value of τ_A from 0° in the A form to 13° in the F form, constitutes a torsion about the 9,9′ double bond, similar to the deformation in the B isomer.[1] By comparing the structure of the B and E isomers with that of F, one observes that the characteristic deformations in both B and E are present in the F isomer: (*a*) twisting of 13° about the 9,9′ double bond, (*b*) additional torsion about the four single bonds attached to the 9,9′ double bond. The three types of photoisomers can be described by Newman projections as shown in Scheme 1. The calculated difference of ground state energies between A and F is $E_F - E_A$ 13 kcal mol^{-1}.

The spectral changes which take place in the A ⟶ F process (Figure 1b) can be explained by considering the molecular deformations resulting from the photoisomerization process. (*a*) In the B isomer the torsion about the 9,9′ double bond results in a shift to the red in the first absorption band from 25 000 in A to *ca.* 16 000 cm^{-1} in B. (*b*) In the E isomer the considerable twist about the four single bonds attached to the 9,9′ double bond results in a blue shift in the first absorption band from 23 800 in A to *ca.* 27 800 cm^{-1} in E. In the A ⟶ F process both types of deformation are involved, and exert contrary effects on the energy of the first transition in F, thus explaining the fact that in the A ⟶ F process there is no shift but only a broadening of the first band.

Low Temperature ^{1}H *N.m.r. Measurements of the F and A Forms.*—The low temperature 90 MHz ^{1}H n.m.r. spectra of F and A forms of (3b) (Figure 8) were recorded in the Fourier transform mode at $-50°$. In the spectrum of the A form (solid curve) the 1,1′-methyl groups are shielded by the opposite benzene ring and therefore appear at a high field (δ 1.26). The *N*-methyls appear at δ 3.48 and the aromatic protons at 6.5—7.5. Comparison of the spectrum of the A form (full curve) with that of the F form indicates the following changes in shielding during the A ⟶ F process. (1) The 1,1′-methyl groups undergo a downfield shift from δ 1.26 to 2.88. (2) The *N*-methyl protons are shifted upfield from δ 3.48 to 3.21. (3) The 8,8′-protons are shifted downfield from δ 6.55 to 7.5. These changes indicate that the process A ⟶ F removes the significant diamagnetic shielding observed in A of both the 1,1′-methyl groups and 8,8′-hydrogen atoms, by the opposite benzene ring. The shielding change on the *N*-methyl protons is identical to that resulting from the A ⟶ E process in (3a).[8] The increase in the diamagnetic shielding suggests that the *N*-methyl is close to the plane of the adjacent rings in A but further removed from these planes in F, *i.e.* the *N*-methyl is equatorial in A and axial in E (Figure 1).

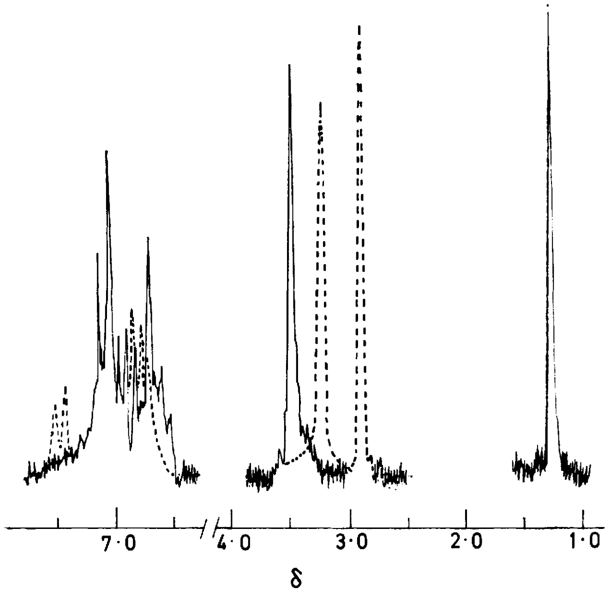

FIGURE 8 Low temperature ^{1}H n.m.r. spectra of (3aA) (full curve) and of (3bF) (broken curve) both in CD_2Cl_2 at $-50°$

EXPERIMENTAL

Low Temperature ^{1}H *N.m.r. Measurements.*—A solution of (3b) in CD_2Cl_2 was irradiated with the light from a

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[19] A. Warshel and M. Karplus, *J. Amer. Chem. Soc.*, 1972, **95**, 5612; 1974, **96**, 5677; A. Warshel and M. Levitt, Program QCFF/PI (QCPE No. 247), Quantum Chemistry Program Exchange.

Xe–Hg lamp filtered by a 5030 Corning glass filter (transmission maximum at 400 nm). The irradiation took place inside the n.m.r. probe,[20] following cooling of the sample to −50°. Before and following complete conversion of A into E the spectrum was recorded in the Fourier transform mode after 1 024 pulses. The sample was then removed from the n.m.r. probe, heated to +20° to achieve reconversion into A, and then re-cooled to −50°, at which temperature the spectrum was recorded again.

Low Temperature Photochemistry and Spectrophotometry.—Absorption and emission spectra were recorded as described in earlier publications.[2,3,12] Emission spectra are uncorrected, but the sensitivity change in the 400—500 nm range is <10%. Mixtures of nitrogen and oxygen were prepared in commercial containers by introducing each gas at the required pressure.[14] Argon containing <5 p.p.m. oxygen was used to achieve oxygen-free conditions. The gases or gas mixtures were bubbled through the solutions at low temperatures, where solvent losses through evaporation are negligible.

[6/557 *Received*, 22*nd March*, 1976]

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[20] K. A. Muszkat and M. Weinstein, *J.C.S. Perkin II*, 1976, 1072.