

THE REVERSIBLE PHOTOCHEMISTRY OF DIXANTHYLIDENES: TEMPERATURE, EXTERNAL SPIN-ORBIT PERTURBATION EFFECTS AND STRUCTURE OF THE C AND F PHOTOISOMERS

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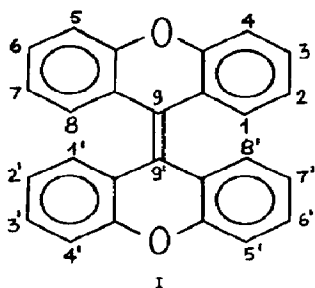
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Summary

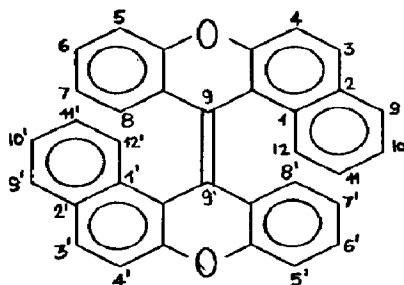
An extensive photochemical study of dixanthylidenes shows the existence of three unstable isomers: B, F and C. The C isomer was shown by low temperature proton n.m.r. to be a photocyclization product at the 1 and 1' positions. The structure of the F isomer was shown to involve both rotation of 180° about the central double bond and additional torsion about the four single bonds attached to it. The quantum yields for the A → B process are enhanced by external spin-orbit perturbers. The B isomer was shown to be formed from the triplet state. The formation of C, B and F are temperature controlled. Fluorescence quantum yields in these systems are strongly temperature dependent.

Introduction

Recently we have performed a detailed experimental study of the photochemistry of dixanthylidene (I) [1] showing the existence of three photoisomers, B, C and P, all of which revert thermally to the parent compound A. The recently established structure of the B isomer [2] in related systems involves torsion of ~57° about the 9-9' double bond, whereas the C isomer is a 1-1' photocyclization product of a 4a, 4b-dihydrophenanthrene type [1, 3]. We have briefly reported [4] on the photochemistry of VIII and IX. We wish to present here the detailed complex reversible photochemistry of dixanthylidene derivatives (II - X), the way it is dependent upon substitution, the type and structure of photoisomers formed and their mechanism of formation.



dixanthylidene	I
2,4,2',4'-tetramethyl-I	II
2,2' - dichloro-I	III
3,3' - dichloro-I	IV
2,2' - diphenyl-I	V
3,3' - dibromo-I	VI
4,4' - dimethoxy-I	VII
1,4,1',4' - tetramethyl-I	IX
1,1' - dichloro-4,4'-dimethyl-I	X



Photoformation of the B, C, D and F isomers

Irradiation of IIA* in a methylcyclohexane (MCH)/2-methylpentane (2-MP) 1:1 mixture at -190°C produces an isomer, denoted as IID (Fig. 1a, curve D). IID undergoes conversion to the IIB isomer (Fig. 1a, curve B) by a thermal process with a half-life value ($\tau_{1/2}$) of ~ 20 min at -190°C . The D \rightarrow B process involves a 50 nm blue-shift in the absorption spectrum. The IIB photoisomer reverts thermally to the parent compound (A isomer) at temperatures higher than -120°C . The activation energy E_a and the frequency factor A involved in the B \rightarrow A process are respectively 13 ± 0.5 kcal/mol and 10^{14} s^{-1} . The rate constants $k_{B \rightarrow A}$ for this process and the quantum yields $\Phi_{A \rightarrow B}$ for the photochemical process are $k_{B \rightarrow A} = 3.7 \times 10^{-5} \text{ s}^{-1}$ at -124°C ; $4.6 \times 10^{-4} \text{ s}^{-1}$ at -115°C ; $\Phi_{A \rightarrow B} = 0.001$ at -140°C , and 0.0006 at -170°C .

Irradiation of III, IV, V and VI yields only the B isomers. The quantum yields A \rightarrow B at the temperatures indicated are: III, 0.0013 (-130° to -180°C); IV, 0.001 (-140° to -180°C); V, 0.001 at -140°C ; VI, 0.013 at -140°C . Irradiation of VII produces two photoisomers (VIIB and VIIC)

*The modifications are designed by attaching capitals to the Roman numerals denoting the derivatives formulae. A denotes the fundamental modification; B the modification twisted about the 9-9' double bond [2]; D is the low temperature variant of B [5], and C is the cyclic photoisomer [3].

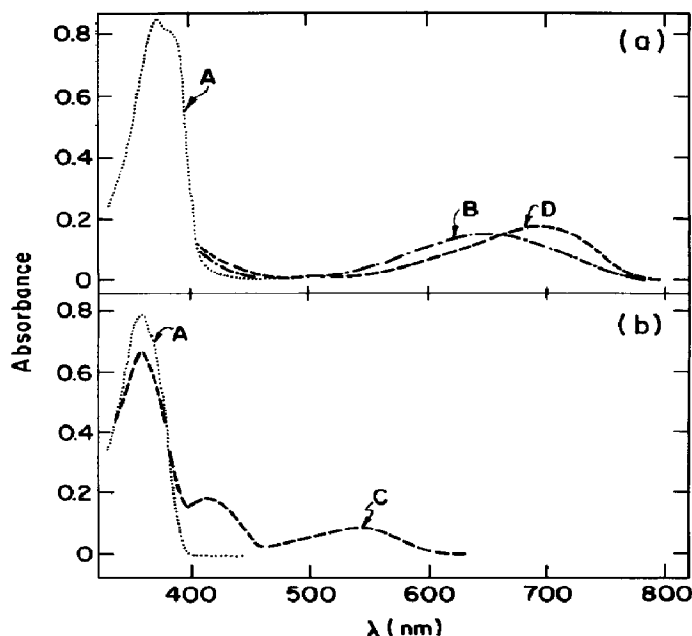


Fig. 1. (a) Absorption spectra of IIA, IIB and IID in MCH/2-MP mixture, $4 \times 10^{-5} M$. A, A at -190°C ; D, D isomer, formed by irradiation with 366 nm light at -190°C ; B, B isomer formed from D isomer by thermal decay at -190°C . (b) Absorption spectra of A and C isomers of VII in MCH/2-MP at -30°C . A, A form; C, C form at the photo-stationary concentration.

(Fig. 1b, curve C). The $\Phi_{A \rightarrow B}$ values for this process are 0.012 at -130°C and 0.007 at -170°C .

The photochemistry of VIII and IX has been recently described [4]. VIIIA photoisomerizes to the B modification (Fig. 2a, curve 2) $\Phi_{A \rightarrow B} = 0.28$ at -180°C . At higher temperatures it decays thermally chiefly to A and also to a minor extent to another isomer (VIIIF) (Fig. 2a, curve 3). At temperatures higher than -150°C the F modification is the only isomer formed, $\Phi_{A \rightarrow F}$ being 0.25 at -150°C . The respective values of E_a and A for the $F \rightarrow A$ process are $E_a = 14 \pm 0.5 \text{ kcal/mol}$ and $A = 10^{12} \text{ s}^{-1}$. The rate constants for this process are 11.5 s^{-1} at -10°C and 0.4 s^{-1} at -40°C . The rate constants for the $B \rightarrow A$ process are $1 \times 10^{-5} \text{ s}^{-1}$ at -175°C and 8.5×10^{-4} at -170°C .

IXA photoisomerizes to the B modification (Fig. 2b, curve 2) $\Phi_{A \rightarrow B} = 0.003$ below -175°C . When warmed up to above -175°C , it decays thermally to the IXF modification (Fig. 2b, curve 3), which can also be obtained ($\Phi_{A \rightarrow F} = 0.03$) by irradiation at temperatures from -150° to -170°C . IXF reverts thermally to the A form at temperatures above -140°C . Irradiation of IXA at temperatures from -130° to -60°C produces still another modification, IXC (Fig. 2b, curve 4), which is photolabile unlike the photostable F and B isomers. The quantum yields Φ_1 and Φ_2 for the $A \xrightarrow{\Phi_1} C$ process are respectively 0.9 and 0.2.

For the thermal process $C \rightarrow A$, $E_a = 12.5 \pm 0.5 \text{ kcal/mol}$, and $A = 10^9 \text{ s}^{-1}$. The rate constants for this process are $k_{C \rightarrow A} = 4.7 \times 10^{-5} \text{ s}^{-1}$ at -70°C

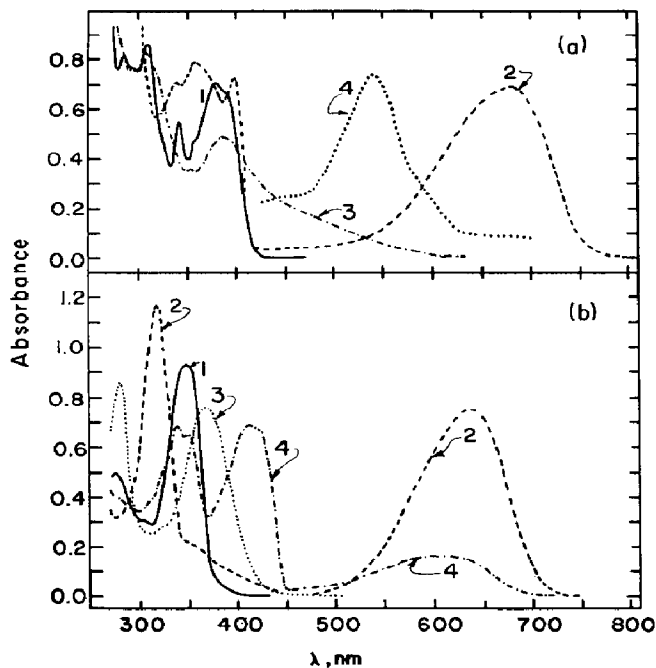


Fig. 2. (a) Absorption spectra of VIIIA, VIIB and VIIF in MCH/2-MP mixture, 5×10^{-5} M. 1, A at -180°C ; 2, B isomer obtained by irradiation with 366 nm light; 3, F isomer obtained by irradiation of the original solution to completion with 366 nm light; 4, triplet-triplet absorption spectrum obtained by flash photolysis at -196°C . (b) Absorption spectra of IXA, IXB, IXF and IXC in MCH/2-MP mixture, 3.5×10^{-5} M. 1, IXA at -190°C ; 2, B isomer, as above, formed by irradiation to completion with 366 nm light. 3, F isomer obtained by irradiation to completion at -160°C of original solution with 366 nm light and cooled to -180°C ; 4, C isomer formed by irradiation of original solution at -90°C and cooling to -180°C .

and $5.7 \times 10^{-4} \text{ s}^{-1}$ at -50°C . X photoisomerizes to the B isomer, $\Phi_{A \rightarrow B} = 0.25$ at -190°C . XB decays thermally to the A isomer above -180°C , e.g., $k_{A \rightarrow B} = 8.5 \times 10^{-4} \text{ s}^{-1}$ at -170°C and $1 \times 10^{-4} \text{ s}^{-1}$ at -175°C . Thus in this system the $\Phi_{A \rightarrow B}$ values, and the thermal rate constants, $k_{B \rightarrow A}$, are the highest observed in the I - X series.

Helixanthene is formed in deaerated solutions of X when irradiated above -160°C , whereas it is formed inefficiently in compounds I - IX even at room temperature, indicating that the photochemical elimination of the elements of HCl during the irreversible photocyclization process is very efficient. This situation is characteristic of cyclizations involving the elimination of chlorine and hydrogen, and was observed in 2,6-dichlorocinnamic acid and its esters [6].

Enhancement of $\Phi_{A \rightarrow B}$ by external spin-orbit perturbation

The rate of the $A \rightarrow B$ photoisomerization is effectively enhanced by molecular oxygen and by carbon disulphide [7]. The results are summarized in Table 1.

TABLE 1

Enhancement of $\Phi_{A \rightarrow B}$ by O_2 and CS_2 at $-140^\circ C$ in MCH/2-MP 1:1 mixture; $[CS_2] = 1.6 M$; $[O_2] = 1 \times 10^{-2} M$

Compound	$\Phi_{A \rightarrow B}^{Argon}$	$\Phi_{A \rightarrow B}^{O_2}$	$\Phi_{A \rightarrow B}^{CS_2}$
I	0.001	0.05	0.127
II	0.001	0.093	0.27
III	0.013	0.032	0.074
IV	0.001	0.037	0.02
V	0.001	0.021	0.13
VI	0.013	0.048	0.075
VII	0.012	0.044	0.018
VIII	0.43*	0.4*	0.4*

* $\Phi_{A \rightarrow F}$

These measurements were performed at $-140^\circ C$ because of the thermal instability at higher temperatures. At this temperature the solvent viscosity, 10^2 cP, is not enough to influence markedly the perturbation by oxygen or carbon disulphide. This perturbation was shown to depend on diffusional encounters between excited molecules $^1A^*$ and the perturber within the lifetime of $^1A^*$.

Mechanism of the A \rightarrow B photoisomerization

Compound VIII, because of its high photoisomerization quantum yield even at low temperatures (*e.g.*, $\Phi_{A \rightarrow B} = 0.28$ at $-180^\circ C$) was chosen for studies of the mechanism of formation of the B isomer. Flash photolysis at $-196^\circ C$ reveals the existence of a short lived transient with an absorption peak at 540 nm (Fig. 2a, curve 4), $\tau_{1/2} \sim 0.03$ s. Parallel e.s.r. experiments revealed a transient at a field of 1528 G with the same $\tau_{1/2}$ value, ~ 0.03 s. This signal corresponds to a $\Delta m = 2$ transition of triplet A. A $\Delta m = 1$ transition with tenfold lower intensity was observed at 3124 G.

Flash experiments at $-170^\circ C$ on solutions of VIII indicate that during the thermal decay of the absorption at 540 nm there is a parallel build-up of the B isomer (680 nm, Fig. 3).

These flash experiments clearly show that the B isomer is formed from the triplet state of A. This conclusion is supported by the observed enhancement of the A $\xrightarrow{h\nu}$ B process by external spin-orbit perturbers such as oxygen or carbon disulphide. The same mechanism was found for the formation of the B isomer in bianthrone [5].

Fluorescence quantum yields and their temperature dependence

The fluorescence quantum yields, Φ_F , were measured at temperatures below 20° down to $-180^\circ C$ in argon flushed MCH/2-MP 1:1 mixtures.

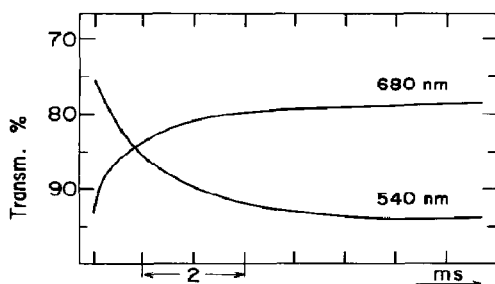


Fig. 3. Flash photolysis of VIII, $5 \times 10^{-5} M$ in MCH/2-MP solvent mixture, at $-170^\circ C$. Kinetics of the decay of triplet VIII, at 540 nm and corresponding appearance of the B isomer at 680 nm.

Φ_F was measured relative to 9,10-diphenylanthracene [8]. The dependence of Φ_F on temperature in compounds II - IX is given in Fig. 4. All compounds studied except VIII show strong increase of Φ_F on cooling to $-140^\circ C$. Further cooling is either without noticeable effect or results in lowered fluorescence quantum yields.

This behaviour may be attributed to the existence of activated and non-activated radiationless processes. Two approaches have been employed to interpret such behaviour: the first approach implies that the temperature dependence is due to two intersystem crossing processes: a slow non-activated process $S_1 \rightarrow T_1$, the T_1 state being below the S_1 state and a fast activated process $S_1 \rightarrow T_2$ to the T_2 state (or to some higher state). The second approach is based on the phonon coupling model [9] and its application is described elsewhere [10].

Experimentally, the observed temperature dependence can be described by a $\log(\Phi_F^{-1} - 1) \propto T^{-1}$ law at temperatures higher than a discontinuity value which in the case of II (Fig. 5) is at $-155^\circ C$.

Low temperature proton n.m.r. spectra of the C photoisomer of IX

The 90 megacycles proton n.m.r. spectra of IXA and of a mixture of IXC-IXA measured at $-90^\circ C$ in CD_2Cl_2 are given in Fig. 6. In the A \rightarrow C process the 1- and 1'-methyls are deshielded, moving from 1.31 p.p.m. to 2.8 p.p.m. while the 4- and 4'-methyls are shielded and are shifted from 2.42 to 2.32 p.p.m. In the aromatic region the 8,8'-protons are transferred from the highest field $\delta = 6.52$ p.p.m. to the lowest field region at 7.35 p.p.m. A new absorption is observed at 6.29 p.p.m. These changes due to the A \rightarrow C process suggest a 4a,4b-dihydrophenanthrene type structure for C, e.g., A \rightarrow C involves photocyclization between the 1- and 1'-positions. In the fundamental modification (A), the resonance of the 1- and 1'-methyl protons occurs at the highest field (1.31 p.p.m.) because of the shielding by the opposite aromatic rings (for detailed discussion see refs. [2] and [3]). In the cyclic modification these protons are far apart from the opposite benzene rings and thus have their resonances shifted to lower field. The 4- and 4'-methyl protons are

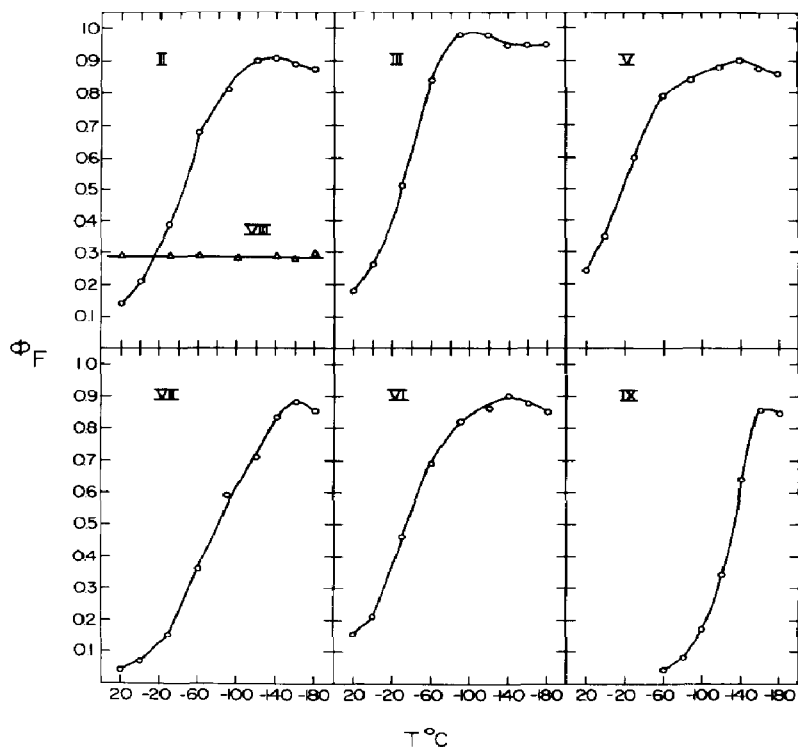


Fig. 4. Temperature dependence of fluorescence quantum yields (Φ_F) for II - IX, $\sim 2 \times 10^{-5} M$, in MCH/2-MP solvent mixture.

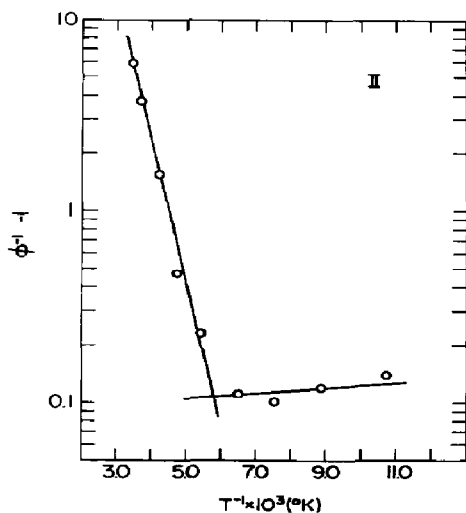


Fig. 5. Temperature dependence of fluorescence quantum yields of II plotted as $\log(\Phi_F^{-1} - 1)$ against $1/T$.

aromatic in A but vinylic in C and thus their position is shifted to a higher field (6.29 p.p.m.). The extent of conversion as seen from n.m.r. intensities

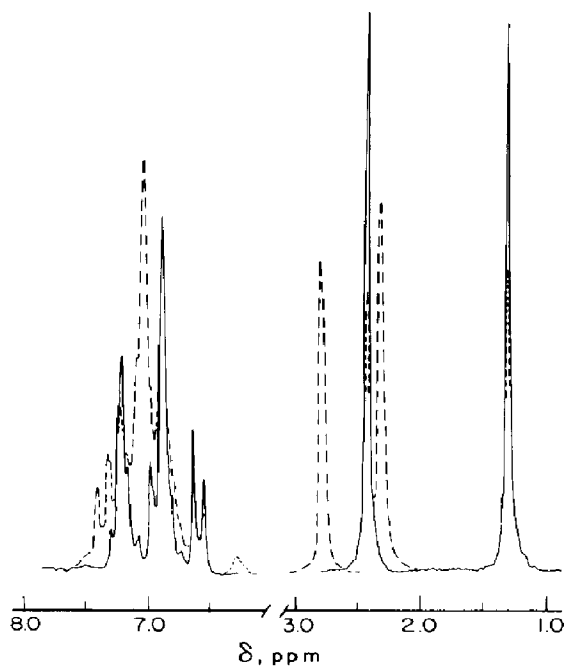
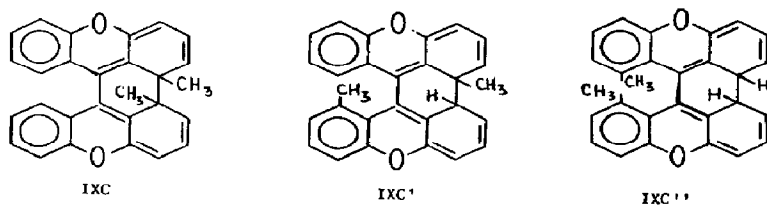


Fig. 6. 90 megacycle proton n.m.r. spectra of IXA (—) and of mixture of IXA and IXC (-----), both in CD_2Cl_2 , at -90°C .

is $\sim 50\%$ (where the maximal amount of $\text{A} \rightarrow \text{C}$ conversion is $\sim 80\%$) clearly indicates cyclization between the 1- and 1'-positions (IXC) and excludes 1-8' (IXC') or 8-8' (IXC'') cyclizations (cf. discussion in ref. [3]).



C isomers similar to IXC were found previously both in 1,1'-dimethylbianthrone and in 1,3,1',3'-tetramethylbianthrone. The explanation for the exclusive formation of IXC rests on the relative ground state energies of the three possible cyclization products. For 1,1'-dimethylbianthrone a detailed conformational analysis was carried out indicating that a IXC'' cyclization product is less stable than IXC by 27 kcal [11].

Low temperature proton n.m.r. of VIIF

The proton n.m.r. spectra of the VIIF and VIIF' isomers measured in CD_2Cl_2 solution at -90°C are given in Fig. 7. The broken curve in Fig. 7 represents the spectrum of pure VIIF, since VIIF is light stable and a com-

plete photoconversion of $A \rightarrow F$ could be obtained. This situation is different from that found in the photolabile IXC, where only a mixture of IXA and IXC could be studied. In the $A \rightarrow F$ process downfield shifts of the aromatic protons are observed. Thus the 8,12- and 8',12'-protons are shifted from the highest field (6.5, 6.57 p.p.m.) in A to the lowest region (8.38 p.p.m.) in F. In A these protons are highly shielded by the opposite benzene rings while in F this effect no longer operates.

The formation of the B isomer is common for compounds II - X, while the F isomer is formed only in VIII and IX. In these two derivatives severe non-bonding interactions exist between the 1-8' and 1'-8 positions. These interactions enable stabilization of the F conformation. Similar isomers of this type were observed in 1,1',10,10'-tetramethylbiacridan and in bithioxanthene [12]. Their structure was found to involve both torsion about the 9-9' double bond and about the four single bonds attached to it. Again, these isomers were detected only where the 1- and 1'-positions are

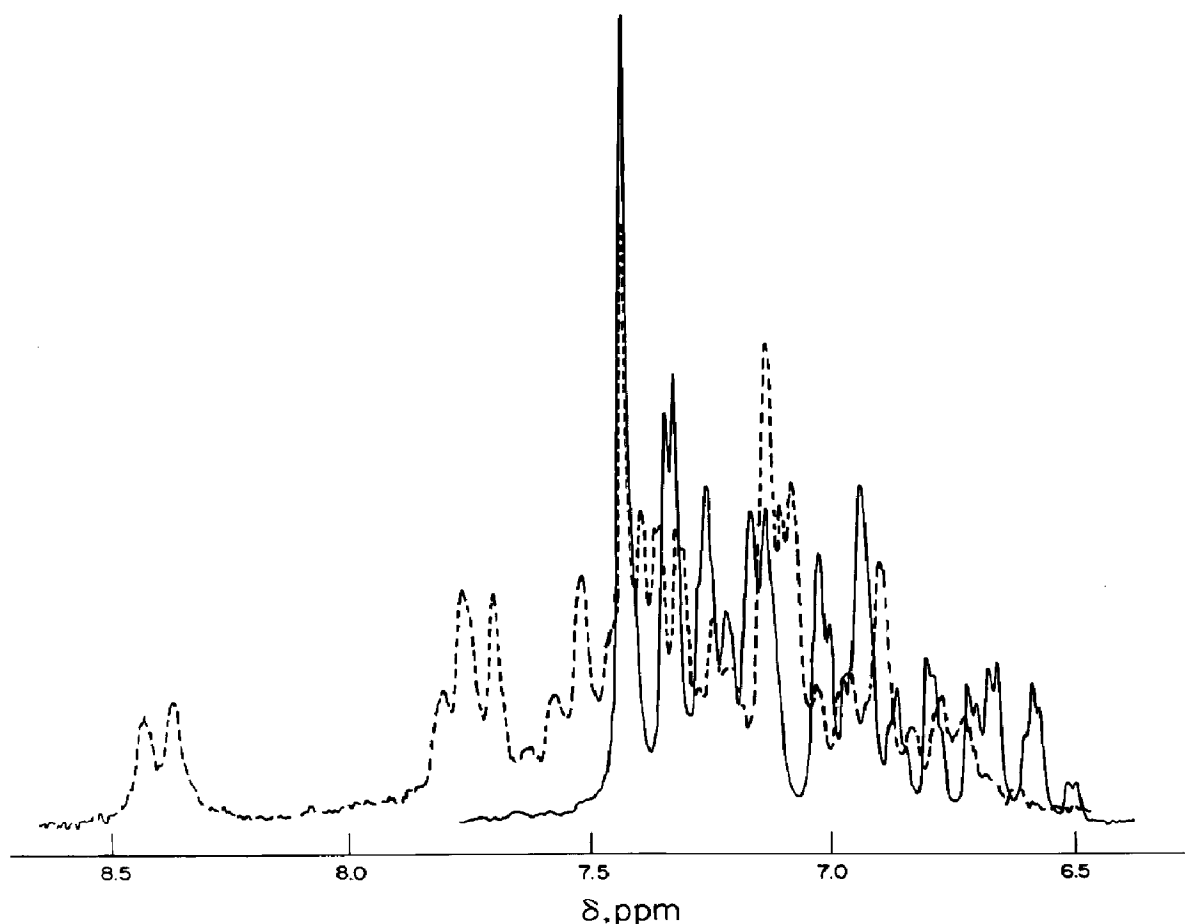


Fig. 7. 90 megacycle proton n.m.r. spectra of VIIIA (—) and of VIIIF (-----), both in CD_2Cl_2 at $-90^\circ C$.

substituted, resulting in strong non-bonding interactions. Based on the similarity of the spectral, photochemical and thermal properties of the F isomers in biacridan and those found in IX and VIII one is tempted to attribute the same type of molecular deformations to the IXC and VIIIF isomers.

Experimental

A solution of VIII in CD_2Cl_2 was irradiated at -90°C , inside the 90 megacycle proton n.m.r. probe [13] with light from a Xe/Hg lamp filtered by a 9863 Corning filter. The sample was irradiated for 30 min, during which the spectra were measured in the FT mode and u.v. irradiation was continued throughout the whole acquisition time (~ 30 min). IX was irradiated under the same conditions, except that the light was filtered through a 5970 Corning filter.

Absorption and emission spectra were recorded as described in the earlier publications [1, 5]. Oxygen and argon were bubbled through the solution at -20°C , thus minimizing solvent losses.

Compounds II - X were prepared according to the literature [14].

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