ORGANIC LIGHT-SENSITIVE COMPOUNDS. IV.*

MECHANISM OF SENSITIZATION OF LIGHT-SENSITIVE POLYMERS BY PYRYLIUM SALTS

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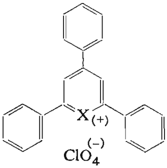
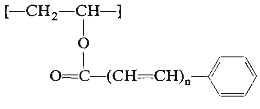
Photochemical properties of polyesters of cinnamic and cinnamylideneacetic acids, and mechanisms of their sensitization by 2,4,6-triphenylpyrylium and 2,4,6-triphenylthiopyrylium salts are discussed on the basis of spectral and quantum chemical LCI-SCF data.

The dimerization of cinnamic acid under ultraviolet irradiation was reported long ago[1]. Much later[2,3], when compounds became available which greatly increased the sensitivity of polyvinyl cinnamate, its photochemical dimerization[4,5] was applied in a light-sensitive medium to photomechanical reproduction. Phosphorescence spectra of cinnamic acid and its sensitizers[6-10], ESR measurements[11], and other physical properties[12] prove that the mechanism involves the energy transfer in a triplet state, as with many other photochemical reactions[13]. Therefore the compounds used as sensitizers are those which are easily excited by light to a triplet state, *e.g.*, carbonyl compounds[14,15] and pyrylium salts.

The spectral properties of 2,4,6-triphenylpyrylium and thiopyrylium salts (*I* and *II*) and their sensitization efficiency in layers of polyesters of cinnamic acid (*III*) and cinnamylideneacetic acid (*IV*) were described in our earlier paper[16]. The present paper extends this study to a discussion of the sensitization mechanism, making use of spectral measurements and LCI-SCF calculations.



I, X = O
II, X = S



III, *n* = 1
IV, *n* = 2

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EXPERIMENTAL

Spectral measurements. Electronic spectra were measured in ethanol on an Optica Milano CF 4 spectrophotometer. Fluorescence and phosphorescence spectra were measured in the laboratory of Prof. Z. R. Grabowski (Inst. Phys. Chem., Polish Acad. Sci., Warsaw) on equipment constructed there.

Quantum chemical calculations. These were of the PPP type using the variable β approximation. The procedure is described in detail in our earlier paper[17], and the parameters adopted summarized in Table I. Theoretical quantities not published in this paper are available from the authors on request. The calculations were performed on a National Elliott 503 computer, using the programs written in the Group for Applied Quantum Chemistry of the J. Heyrovský Institute of Physical Chemistry and Electrochemistry, Prague.

RESULTS AND DISCUSSION

Figs 1*a*,*b* present molecular diagrams for cinnamic and cinnamylideneacetic acids. For the former an analogous calculation was performed by Nakamura and Kikuchi[18] with γ integrals evaluated according to Pariser and Parr, whereas our calculation is based on the Mataga and Nishimoto approximation. The two calculations agree in electron distributions for S_0 ground states, but differ in molecular diagrams for excited states. Our diagram for T_1 corresponds to the diagram for S_1 of the paper cited. The calculation predicts that the bond order are not getting uniform on $S_0 \rightarrow S_1$ excitation, in contrast to the $S_0 \rightarrow T_1$ excitation. The differences between diagrams for S_1 and T_1 states are due to different weights of individual configurations in LCI wave functions (*vide infra*). In the photochemical reaction of cinnamic acid, coupling occurs in positions 7 and 8, with cyclobutane ring formation. Assigning to T_1 the

TABLE I

Semiempirical Parameters Used in LCI-SCF Calculations

Group	Atom	I_μ, eV	$\gamma_{\mu\mu}$, eV	$\beta_{C\mu}$, eV	Z_μ
		PPP singlet states			
—	C	11·42	10·84	−2·318	1
C—O—H	O	21·00	11·50	−2·318	2
C=O	O	13·60	11·30	−2·318	1
		PPP triplet states[18]			
—	C	8·80	8·20	−2·500	1
C—O—H	O	18·38	8·86	−2·500	2
C=O	O	10·98	8·66	−2·500	1

highest free valencies in positions 7 and 8, our calculation is consistent with the finding that the reaction proceeds in the triplet state.

With cinnamylideneacetic acid, the molecular diagrams for triplet and singlet states do not differ considerably; in both states the bond orders of the polymethine chain are getting uniform on excitation. The highest free valencies in the T_1 state are predicted for positions 7 and 10, which indicated that the photochemical reaction should result in formation of an eight-membered ring. This, however, has not yet been confirmed experimentally.

In Figs *2a,b* the results of LCI-SCF calculations are compared with the observed spectra of cinnamic and cinnamylideneacetic acids. In both cases the agreement between calculation and observation, including absorption intensities, is good. In accordance with the calculation of Nakamura and Kikuchi[18], the main absorption band of cinnamic acid is assigned to two strongly allowed transitions $S_0 \rightarrow S_2$ and $S_0 \rightarrow S_3$, which can be characterized as 6 → 7 (77%) and 5 → 7 (79%) electron promotions. Our calculation gives in addition a weakly allowed transition $S_0 \rightarrow S_1$, arising by combination of 4 → 7 (46%), 6 → 8 (17%), and 5 → 8 (25%) electron

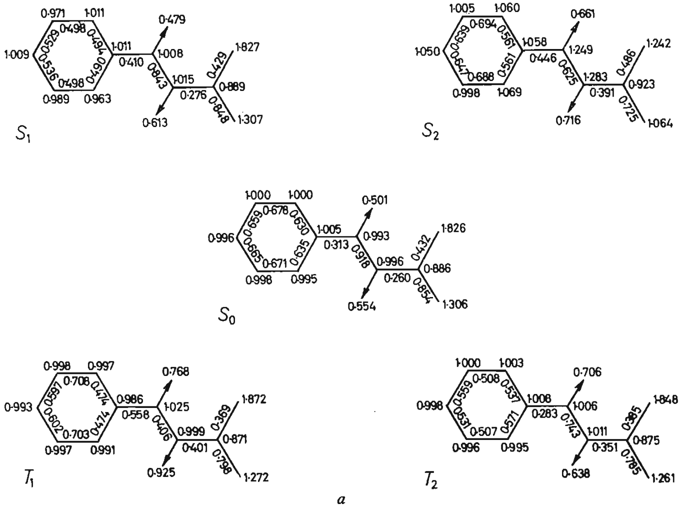
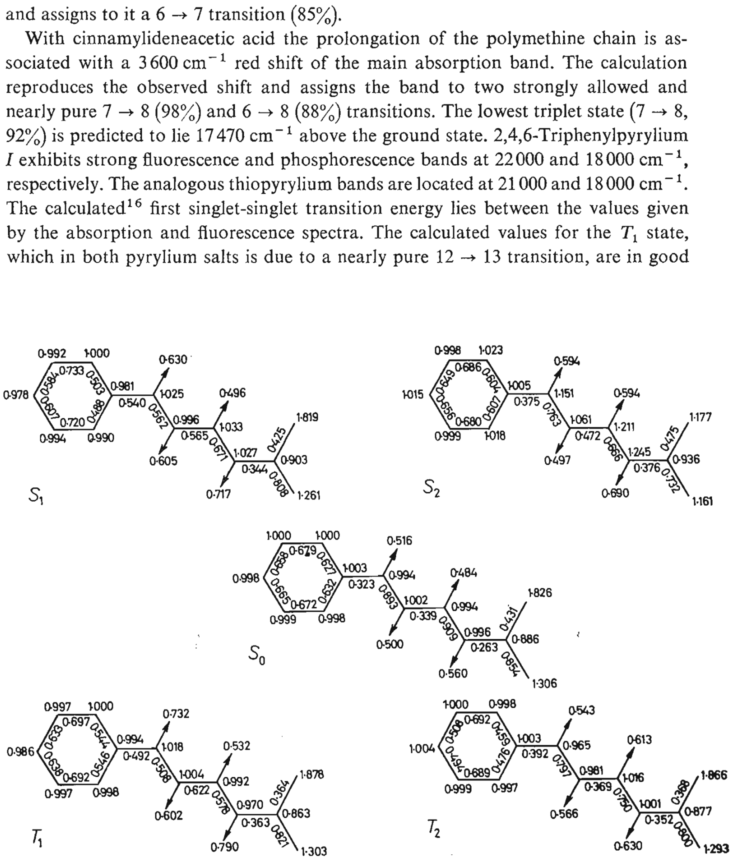


FIG. 1 Molecular Diagrams of Cinnamic (*a*)

promotions. The phosphorescence spectrum ($T_1 \rightarrow S_0$) of cinnamic acid[9] exhibits two clean-cut maxima at 20100 cm^{-1} and 18600 cm^{-1}, corresponding to 0–0 and 0–2 vibration transitions. Our calculation locates the T_1 state at 22000 cm^{-1} and assigns to it a 6 → 7 transition (85%).

With cinnamylideneacetic acid the prolongation of the polymethine chain is associated with a 3600 cm^{-1} red shift of the main absorption band. The calculation reproduces the observed shift and assigns the band to two strongly allowed and nearly pure 7 → 8 (98%) and 6 → 8 (88%) transitions. The lowest triplet state (7 → 8, 92%) is predicted to lie 17470 cm^{-1} above the ground state. 2,4,6-Triphenylpyrylium *I* exhibits strong fluorescence and phosphorescence bands at 22000 and 18000 cm^{-1}, respectively. The analogous thiopyrylium bands are located at 21000 and 18000 cm^{-1}. The calculated[16] first singlet-singlet transition energy lies between the values given by the absorption and fluorescence spectra. The calculated values for the T_1 state, which in both pyrylium salts is due to a nearly pure 12 → 13 transition, are in good



b

and Cinnamylideneacetic (*b*) Acids

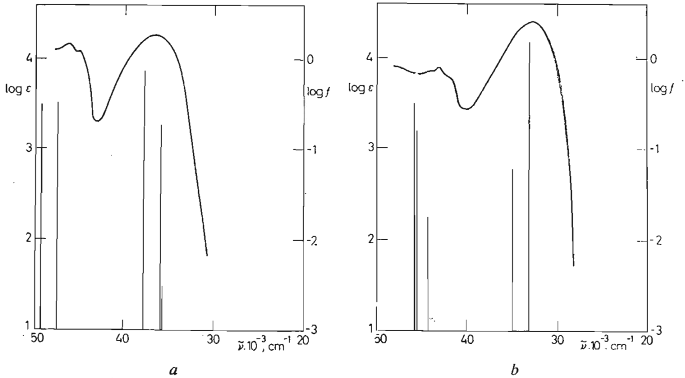


FIG. 2

Absorption Curves and LCI-SCF Transition Energies and Intensities in Cinnamic Acid (*a*) and Cinnamylideneacetic Acid (*b*)

agreement with the phosphorescence data. As with singlet states[16], theory predicts the next triplet state, T_2, to be close to T_1. The T_2 state is due to a 11 → 13 transition and probably makes a strong S → T intersystem crossing possible (*vide infra*).

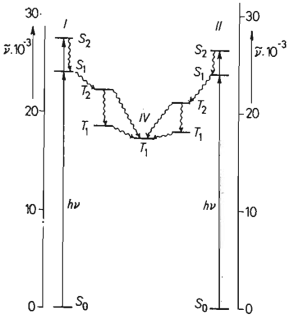


FIG. 3

Mechanism of Sensitization of Light-Sensitive Polymer *IV* by Pyrylium Salts *I* and *II*

On the basis of the spectral and quantum chemical data presented above, we suggest, in Fig. 3, the mechanism of sensitization of light-sensitive polymers *III* and *IV* by pyrylium salts *I* and *II*. The S_1 and T_2 states being sufficiently close in energy, the intersystem crossing is presumably due to these states. This also affords an explanation for the remarkable intensity of that transition, in contrast to other $^3\pi$–π states and in accordance with strong ^1n–$\pi \rightarrow {}^3n$–π transitions where the energy difference ranges[19] usually lie from 2000 to 5000 cm^{-1}. The subsequent energy transfer from a sensitizer molecule to the light-sensitive polymer can proceed from the T_2 state or from the T_1 state, or possibly both.

There is experimental evidence which supports the suggested mechanism. Unsubstituted 2,4,6-triphenylpyrylium salts, in which the T_1 and T_2 levels are very near the T_1 level in cinnamic acid, are the most powerful sensitizers for polyester *III*. With introduction of a methoxy group on the phenyl ring, the energy of excited states of pyrylium salts becomes lower than the T_1 level in cinnamic acid; this is associated with a considerable decrease in sensitization efficiency. In contrast, in the case of the polyester of cinnamylideneacetic acid *IV*, where the lowest triplet state is calculated to lie 4500 cm^{-1} lower, the methoxy substituted 2,4,6-triphenylpyrylium salts are much more efficient sensitizers than the unsubstituted compounds.

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REFERENCES

1. Stobbe H., Lehfeldt A.: Ber. *58*, 2415 (1925).
2. Minsk L. M., Smith J. G., Van Deusen W. P., Wright J. F.: J. Appl. Polymer Sci. *2*, 302 (1959).
3. Robertson E. M., Van Deusen W. P., Minsk L. M.: J. Appl. Polymer Sci. *2*, 308 (1959).
4. Nakamura K., Kikuchi S.: Tech. Assoc. Graphia Arts Japan *1968*, 10.
5. Sonntag F., Srinivasson R.: Tech. Reg. Conf. Soc. Plast. Eng. *1957*, 163.
6. Tsuda M.: J. Polymer Sci. B *2*, 1143 (1964).
7. Tsuda M.: Presented on the International Congress of Photographic Science, Tokyo 1967.
8. Tsuda M.: Bull. Chem. Soc. Japan *42*, 905 (1969).
9. Nakamura K., Kikuchi S.: Bull. Chem. Soc. Japan *41*, 1977 (1968).
10. Curme H. G., Natale C. C., Kelley D. J.: J. Phys. Chem. *71*, 767 (1967).
11. Nakamura K., Kikuchi S.: Bull. Chem. Soc. Japan *40*, 2684 (1967).
12. Tsuda M.: J. Polymer Sci. A *2*, 2907 (1964).
13. Noyes A., Hammond G. S., Pitts J. N.: *Advances in Photochemistry* 5, p. 21. Wiley, New York 1968.
14. Kosar J.: *Light-Sensitive Systems*, p. 144. Wiley, New York 1965.
15. Mistr A., Láznička V., Vávra M.: This Journal *36*, 150 (1971).
16. Mistr A., Vávra M., Skoupý J., Zahradník R.: This Journal *37*, 1520 (1972).
17. Hochman P., Zahradník R., Kvasnička V.: This Journal *33*, 3478 (1968).
18. Nakamura K., Kikuchi S.: Bull. Chem. Soc. Japan *40*, 1027 (1967).
19. Murrell J. N.: *The Theory of the Electronic Spectra of Organic Molecules*, p. 158. Methuen, London 1963.

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