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78. Flash Photolysis Studies of Reversible Photoprocesses V. Photochromism and Triplet States in the Dianthrone System

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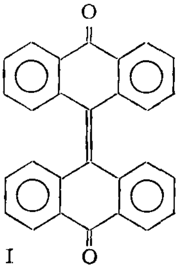
Summary. The kinetics of the formation of the photochromic forms B and C of tetramethyldianthrone has been studied in triacetin and methylcyclohexane/2-methylpentane at several temperatures. A flash spectroscopy method was developed, which allows the recording of the transient behaviour of the sample as function of both – wavelength and time – using a single photoflash for excitation. The results show that the photochromic forms B and C are directly populated from the excited singlet state. In addition a new triplet-triplet absorption band in the near infrared region was detected.

Introduction. – During the last two decades the reversible photochemical behaviour of the dianthrone (I) system has been the subject of many investigations. Even though many questions have been answered in the course of time there still remain unresolved aspects. *Fischer* gave an excellent survey with a large number of references at the 1970 IUPAC Photochemistry Symposium [1]. Our group applied the methods of flash spectroscopy to the tetramethyldianthrone TMD (II) systems and in an earlier paper [2] we reported the absorption spectrum of the TMD triplet state.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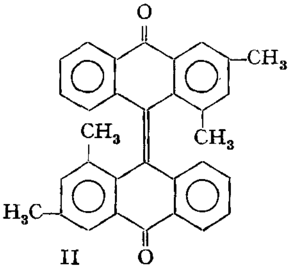


II

The triplet state has an absorption peak at 20,400 cm^{-1} and a tail reaching into the infrared region. Its lifetime at 77 K in a rigid glass is in the order of 100 ms. The formation of the various photochromic forms and their lifetimes depend strongly on the viscosity, polarity, and temperature of the solution. Three different forms which were given the names B, C, and D have been reported. An energy scheme is given in Fig. 1. The form B absorbs strongly at 15,500 cm^{-1} and is mainly responsible for the observed visible change in the colour of TMD solutions. In polar solvents an isomer C is produced in substantial amounts. It can be bleached by irradiation in its main absorption bands near 16,000 and 22,000 cm^{-1} [3]. An additional isomer D has been found

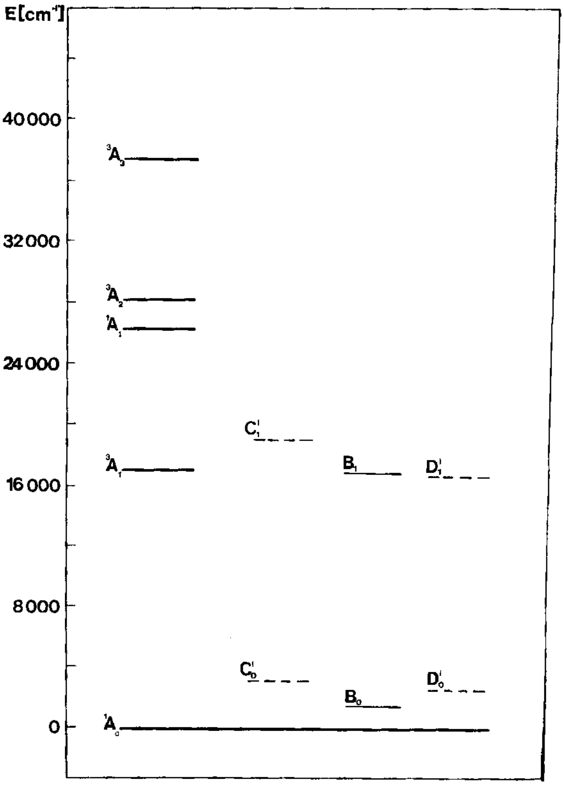


Fig. 1. *Electronic states in the TMD system.* The energy levels of the forms C_0' and D_0' relative to the ground state are chosen arbitrarily.

by *Bercovici & Fischer* [4] with an absorption maximum at 14,000 cm^{-1}. This form is reported to be seen in a narrow viscosity range only; in fluid solution it is immediately transformed into the isomer B.

The kinetic aspects of the formation of photochromism are less clear and considerable discrepancies exist in the literature. *Huber* [2] and *Dombrowski* [5] observed in rigid solvent a strong triplet-triplet and a rather weak photochromic absorption. In addition *Huber* pointed out that in an intermediate viscosity range, where the triplet state is still observable, the coloured forms B and C have no triplet precursor. They are formed independently and 'instantaneously' ($< 5\ \mu s$) from the first electronic excited singlet state $^1A_1$. These findings are supported by oxygen quenching experiments in low viscosity solvents which revealed that the presence of O_2, even at a pressure of 2 atmospheres [5] [6], has no influence on the quantum yield of the B and C photocolouration. The reaction scheme reflecting this situation would therefore be:

$$\begin{tikzcd} & & {}^3A_1 \arrow[dr] & \\ {}^1A_0 \arrow[r, "h\nu"] & {}^1A_1 \arrow[ur] \arrow[r] \arrow[dr] & B \arrow[r] & {}^1A_0 \\ & & C \arrow[ur] & \end{tikzcd} \qquad (1)$$

On the other hand an experiment carried out by *Dombrowski* [5] showed that the phosphorescence of biacetyl can be quenched by dianthrone and that sensitized photochromism can be observed in deaerated solutions. This would support the view of *Fischer's* group that the photochromic states D and B are formed through a triplet state:

$$\begin{tikzcd} {}^1A_0 \arrow[r, "h\nu"] & {}^1A_1 \arrow[r] & {}^3A_1 \arrow[r] \arrow[rrr, bend right] & D \arrow[r] & B \arrow[r] & {}^1A_0 \end{tikzcd} \qquad (2)$$

Bercovici & Fischer [1] [7] performed flash photolysis experiments on TMD in a 1:1 mixture of methylcyclohexane/2-methylpentane at –170° and they observed the following behaviour: The absorption at 20,400 cm^{-1}, which is mostly due to the triplet state, decays with a lifetime of 1.20 ms. Simultaneously an absorption at 14,000 cm^{-1}, due to the photochromic form D, is generated with a time constant of 1.34 ms. This photochromic form decays slowly with a lifetime of 273 ms to the form B. Its formation, monitored at 16,000 cm^{-1}, has a time constant of 300 ms. We have reinvestigated the kinetics of formation of the photochromic forms B and C in order to support either the kinetic scheme 1 or 2.

At very low temperatures only the triplet absorption may be observed. At room temperature only photochromic absorption is seen. The study of the formation of the photochromic forms thus requires experiments at intermediate temperatures. A series of such experiments is difficult to perform since after each single flash an appreciable amount of very long lived photochronism is formed. In order to create identical initial conditions for further experiments the sample has to be warmed up and refrozen after each flash. This is an awkward and time consuming process which is not very reproducible. Former investigators monitored the kinetic behaviour of the system at a few selected wavelength positions. Due to overlapping spectral absorptions the interpretation of the data was difficult.

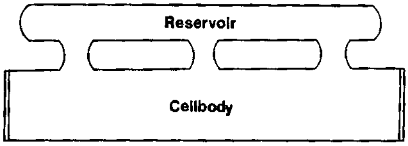


Fig. 2. *Low temperature cell.*

For part of our work a large *Hilger* quartz-glass spectrograph was modified and a step motor was attached which moved the photographic plate during exposure. With one excitation flash the complete spectral and kinetic information about the system to be studied was obtained. A similar system using a spectrograph and a rotating photosensitive cylinder had been described by *Metras, Mossé & Wippler* [8].

Experimental Part. – Tetramethyldianthrone II was synthesized from 1,3-dimethylanthrachinone as described by *Kortüm* [9]. It was recrystallized from butanol and ethylacetate and chromatographically purified using toluene and ethylacetate as solvents. All operations were performed in the dark.

The solvent triacetin (glycerol triacetate), 2-methylpentane, and methylcyclohexane were obtained from *Fluka*, Buchs SG (Switzerland) and were fractionally distilled. Immediately before use they were passed through a column of alox.

The flash photolysis apparatus was a slightly modified version of the apparatus described by *Vallotton & Wild* [10]. An electrical energy of 2000 J was discharged through a 85 cm long double wall quartz tube producing a light pulse having a gaussian time profile with a half width of 4 μs. The total number of photons emitted in the range from 50,000 to 25,000 cm^{-1} was $5.6 \cdot 10^{19}$.

A main problem in low temperature flash photolysis consists in the preparation of a clear transparent organic glass without cracks. This is not an easy problem and several cell types and methods of cooling have been tested [11]. The new cell type shown in fig. 2 proved to be very reliable. Its optically active length was 16 cm and its diameter 2 cm. The cell was mounted in the center of a transparent quartz dewar and was brought into direct contact with cold nitrogen gas. A reservoir of sufficient capacity was connected to the cell. This reservoir and its connections were in contact with an electrical element which could be heated in order to keep the solution in the reservoir liquid. This permitted compensation for the large volume contraction which occurred in the cell during the cooling procedure, and inhibited the formation of cavities. The flow of the cool nitrogen gas was controlled by the power applied to a heating element in the liquid nitrogen storage vessel. Using a regulator, a temperature stability of $\pm 2°$ could be achieved. After the experiment the dewar was purged with warm air and the reservoir was heated with maximum power. While the bulk of the solution is still in its contracted low temperature glass state a thin film of liquid solution, at the inner quartz surface, reduced the danger of breaking the quartz cell during the heating and expanding process of the content. The whole low temperature cell assembly with the surrounding dewar is shown in Fig. 3.

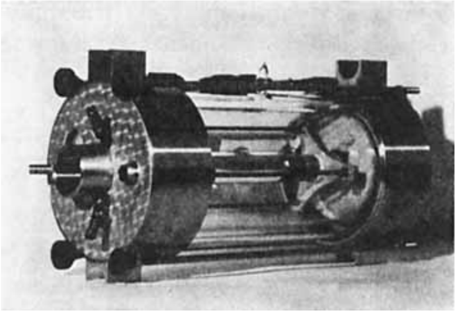


Fig. 3. *Complete low temperature assembly*

The TMD solutions were degassed, and at least six freeze-thaw cycles were performed before the cell was sealed.

A 100 W iodine quartz lamp served as the spectroscopic light source. The light passed through the low temperature cell in the direction of the long axis and was focussed on the vertical entrance slit of a modified *Hilger* Automatic *Littrow* Quartz-glass spectrograph. The handwheel which was provided to raise or lower the plate holder slide was replaced by a powerful high torque step motor which was able to move the slide from the top to the bottom within one second. Two micro switches activated by the slide in its end positions removed the driving frequency from the step motor control unit and prevented damage due to excessive torque. A third micro switch in between served to trigger the photoflash after a preselected time interval. Calibration of the time scale was achieved by means of a stroboscope focussed directly on the slit. The time resolution obtained with this method is determined by the speed of the slide and by the width of a horizontal slit which was placed as close as possible to the photographic plate surface. With a slit width of 0.3 mm and the maximum speed of the slide a time resolution of 5 ms could be achieved. Both the spectral sensitivity of the photographic plate and the dispersion of the spectrograph are strong functions of the wavelength. The vertical entrance slit was adjusted such that the photographic plate was sufficiently exposed in the wavelength region of interest. The wavelength calibration was accomplished by an after-exposure with a cadmium spectral lamp. The vertical slit width was left unchanged and the width of the Cd lines on the plate represent a record of the spectral slit width used. From the two-dimensional information on the plate, traces could be taken with a

Joyce Loebl MK IIIC double beam microdensitometer keeping either the time or the wavelength axis constant. Since our main interest was on the qualitative behaviour of the flash excited sample no additional corrections were applied to these traces. The spectra were recorded on *Ilford* HP 3 hypersensitive panchromatic plates. They have very high sensitivity from 40,000 to 15,000 cm^{-1} where the light response drops sharply. The plates were developed at 22° for $4^1/_2$ minutes using *Kodak* D-19 developer. For corresponding studies in the near infrared region *Kodak* Type I-N plates were used, and the same developing procedure as above was applied.

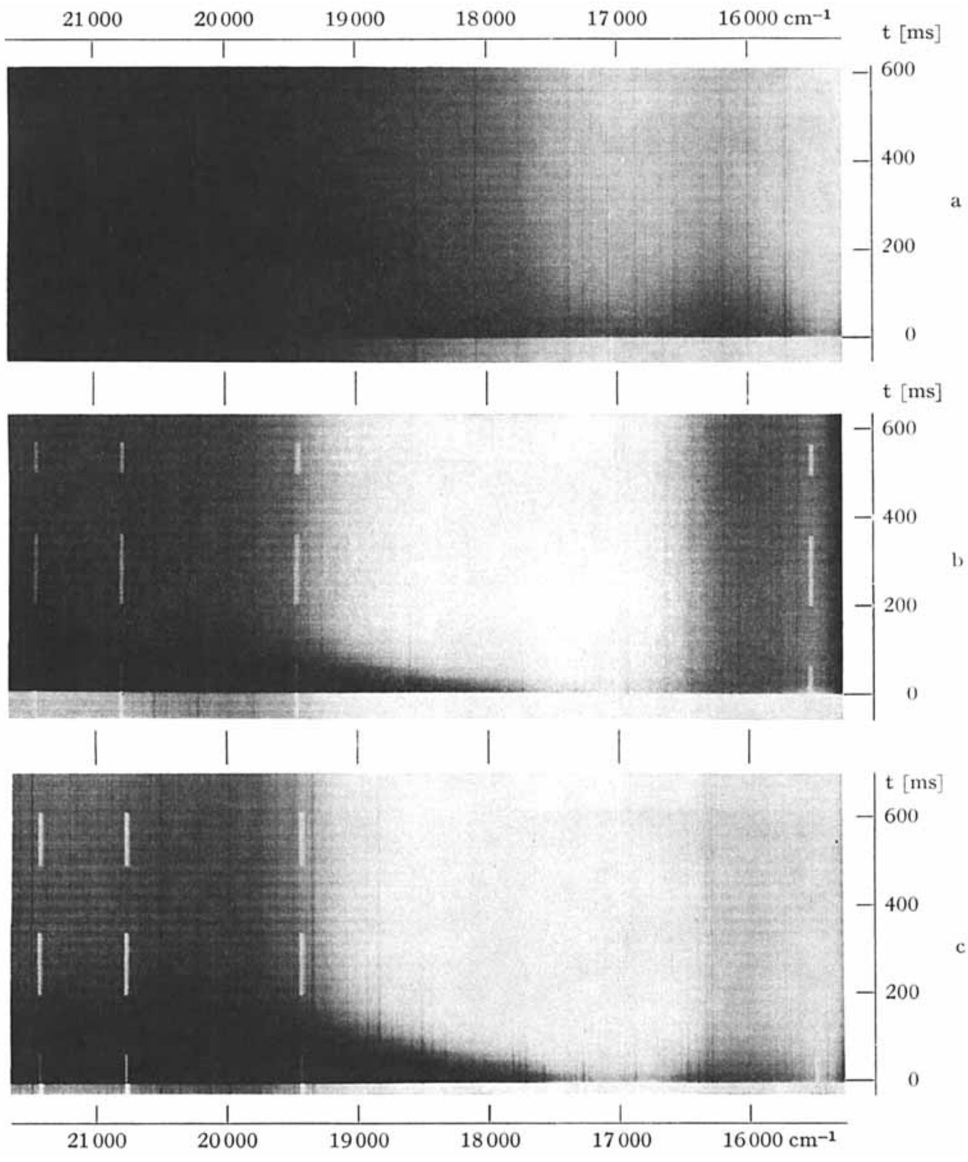


Fig. 4. ***Spectral survey of the time behaviour of a 5.4 · 10^{-5}M TMD solution in triacetin at*** a) room temperature, b) −57°, c) −60°. The bright Cd-calibration lines can be seen.

For the sake of comparison and verification, a series of conventional kinetic flash experiments were also performed.

The appropriately filtered analyzing light of a 6 V, 4.5 A tungsten lamp penetrated the solution and was detected photoelectrically with a nitrogen cooled 56 CVP photomultiplier, of S-1 response, positioned at the exit slit of a *Heath* monochromator and set at the desired wavelength. The signal was recorded on a *Tektronix* 549 oscilloscope and photographed on Polaroid film.

Results and Discussion. – From the numerous plates produced in the course of this investigation two series of three characteristic plates are reproduced. Each

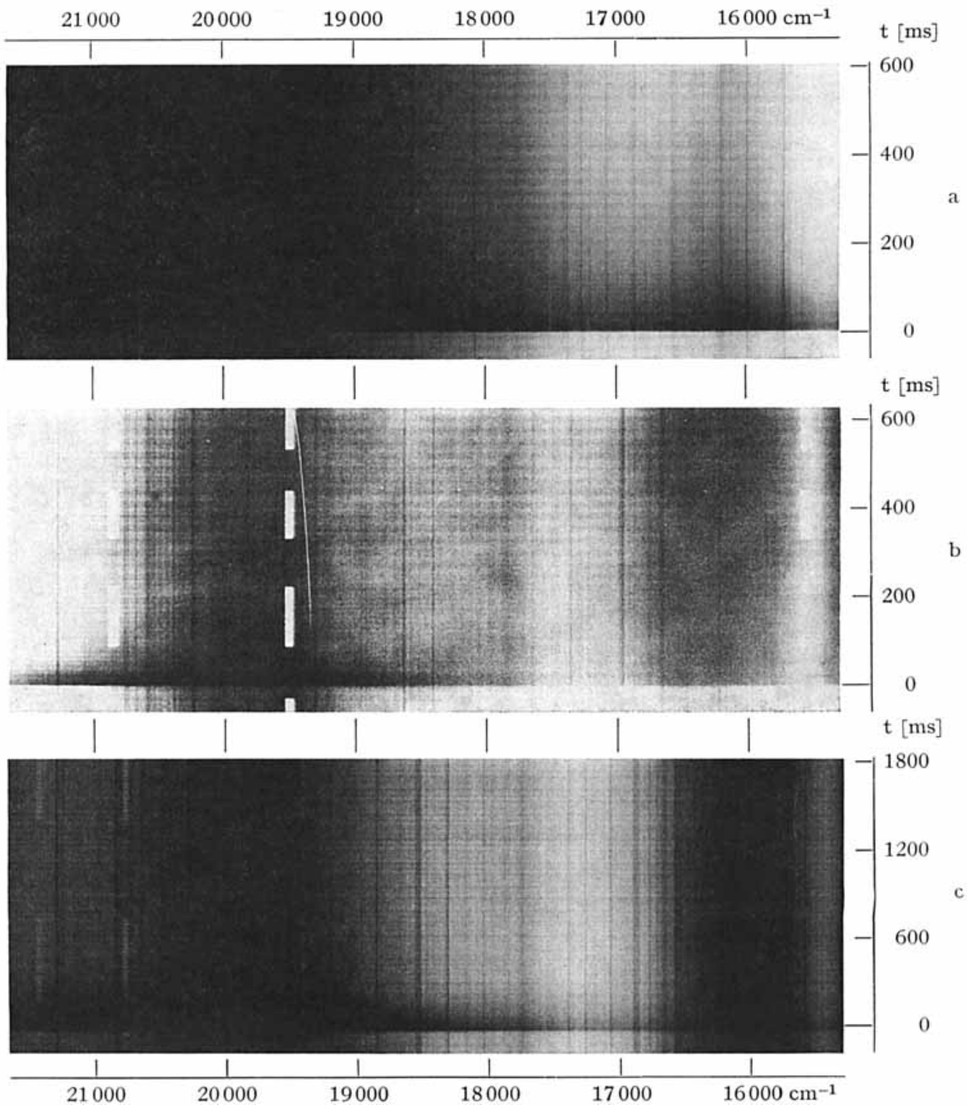


Fig. 5. *Spectral survey of the time behaviour of a 2.7 · 10^{-5}* M *TMD solution in MCH/2-MP at* a) room temperature, b) −170°, c) −173°.

series consists of a plate taken at room temperature where only photochromic changes are visible, a plate recorded at a temperature where both triplet and photochromic absorption can be seen, and a final plate taken at a slightly lower temperature where the triplet state absorption is predominant. In the first series (Fig. 4) the polar solvent triacetin and in the second one (Fig. 5) an apolar 1:1 mixture of methylcyclohexane/2-methylpentane has been used. This allows a comparison with the findings cited in the literature [1].

The changes which occur in the absorption spectra, upon flash illumination of a $5.4 \cdot 10^{-5}$ M solution of TMD in triacetin at room temperature, are shown in Fig. 4a. An increase in optical density extending over the whole region from 21,500 to 15,000 cm^{-1} can be observed immediately after the flash at time zero. The absorption near 20,000 cm^{-1} is mostly due to the photochromic form C, the absorption near 16,000 cm^{-1} results from the form B. It should be noted that the effective sentitivity of the plate has its highest values near 17,000 and 15,500 cm^{-1}. The band near 16,000 cm^{-1} is therefore much broader than it appears at first glance. The lifetimes of the photochromic forms are in the order of 100 ms and in good agreement with the values of *Huber* [2]. The $2.7 \cdot 10^{-5}$ M solution of TDM in the apolar solvent at room temperature shows a quite similar behaviour (Fig. 5a).

The plate 4b recorded at −57° in triacetin and the one taken at −170° in the apolar solvent mixture are of greatest interest for the elucidation of the photochromism

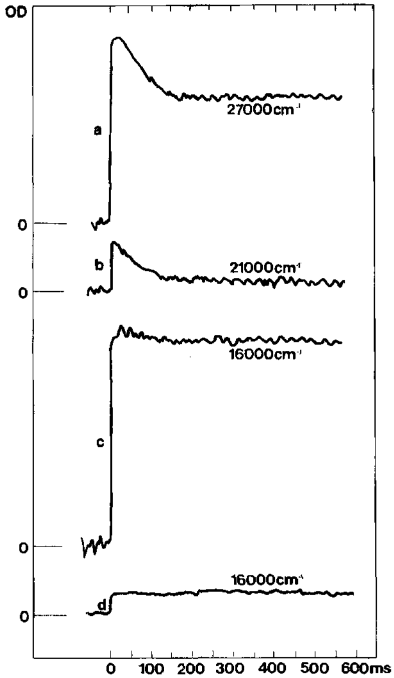


Fig. 6. *Microdensitometer traces*
a & b recorded at 21,000 cm^{-1} from fig. 4b and 5b respectively;
c & d recorded at 16,000 cm^{-1} from fig. 4b and 5b respectively.
The optical density OD. given in arbitrary units is that of the photographic plate.

population mechanism. Both plates show a transient absorption of the lifetime in the order of 50 ms extending from 22,000 to 18,000 cm^{-1} which is assigned to the triplet state of TMD. As an example the microdensitometer traces of plate 4b and 5b at 21,000 and at 16,000 cm^{-1} are given in Fig. 6. The periodic variation in the optical density is due to the stepwise motion of the slide drive which produces a somewhat uneven exposure. The triplet transient absorption with the 50 ms lifetime can be clearly seen in Fig. 6a and 6b. The remaining absorption which is mostly due to the photochromic form C is much stronger in the case of the triacetin solvent. This underlines the fact that in polar solvents the formation of the form C is preferred. For the time scale used the forms B and C are practically nondecaying and their overlapping absorptions cover the entire visible spectrum. The region around 16,000 cm^{-1} where triplet absorption can be neglected shows directly that the photochromic absorption is fully developed immediately after the flash. The corresponding microdensitometer traces (Fig. 6c and 6d) indicate no further increase or decrease in optical density.

The final plates 4c and 5c of the series taken at the lowest temperature display the absorption due to the triplet state. Only very little photochromism is produced and the absorption spectra after 300 ms are practically identical with the preflash spectra.

Corresponding experiments using the infrared sensitive plates exhibit exactly the same behaviour as described above. In addition a new transient absorption with a maximum at 11,200 cm^{-1} could be observed on the plate given in Fig. 7.

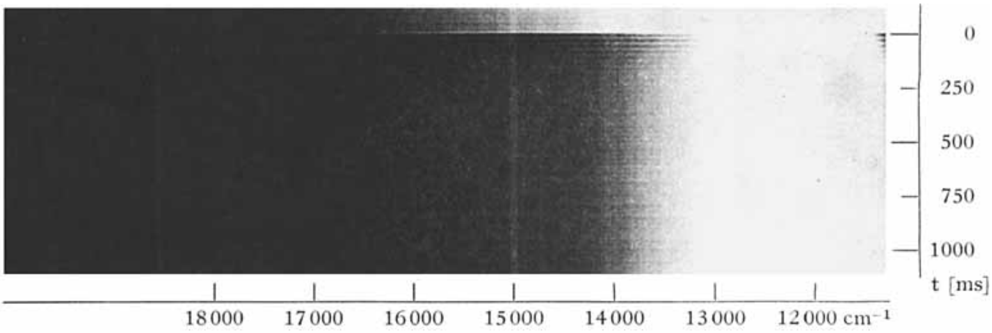
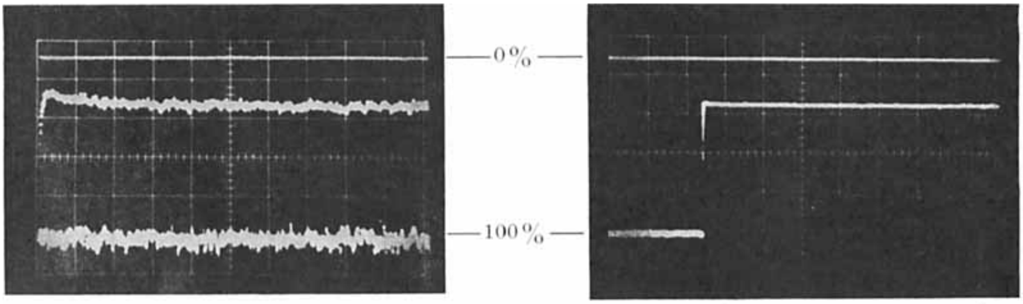


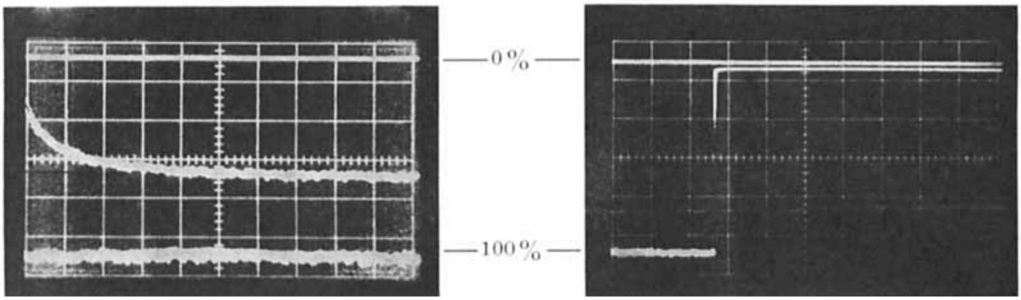
Fig. 7. *Spectral survey of the time behaviour of a 5.4 · 10^{-5}*M *TMD solution in triacetin* at – 68° recorded on a *Kodak* I-N plate.

A further series of conventional flash experiments was performed in order to confirm our results. The temperature of the triacetin TMD solution was chosen such that the triplet lifetime was about 2 ms. Under these conditions, the T → D → B process, if it exists at all, should clearly be seen. The traces given in Fig. 8 must be interpreted in the following way:

The triplet state which absorbs at 20,400 cm^{-1} decays with a lifetime of 2 ms and the remaining absorption is mainly due to the form C. A trace taken at 14,000 cm^{-1}, where the form D is said to absorb strongly, reveals an intense and immediately formed absorption signal. Superimposed is a weak and shortlived red tail triplet



14,000 cm^{-1}, timebase 2 ms per unit 14,000 cm^{-1}, timebase 200 ms per unit



20,400 cm^{-1}, timebase 2 ms per unit 16,100 cm^{-1}, timebase 200 ms per unit

Fig. 8. *Time dependence of absorption signals at the wavelengths indicated.* 5.4 · 10^{-5}M TMD in triacetin at –52°.

absorption. No indication of the process D → B which would lead to an increase in transmittance could be seen during the observation period of 2 seconds. In accordance with this behaviour the B form absorption at 16,000 cm^{-1} is fully developed after the flash and shows no further growth during the 2 seconds period. All our data are in perfect agreement with the originally proposed kinetic Scheme 1.

The transient absorption observed at 11,200 cm^{-1} (Fig. 7) was further investigated by conventional kinetic flash spectroscopy. The choice of temperature (–68°) guaranteed a high and easily perceptible triplet population with a slow decay rate of about 120 ms.

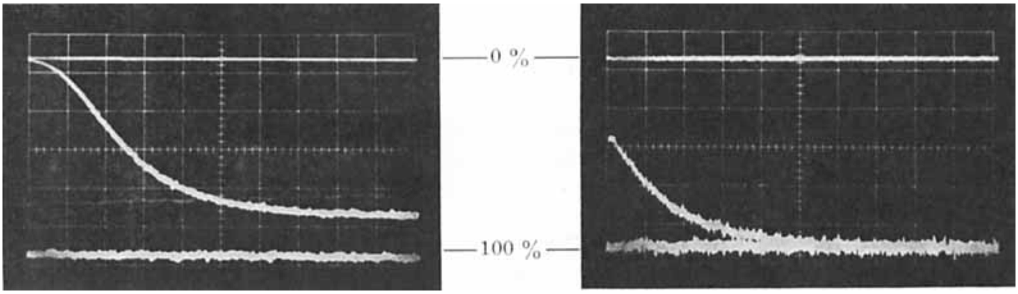


Fig. 9. *Time dependence of the TMD triplet-triplet absorption at 20,200 cm^{-1} (left) and 11,800 cm^{-1} (right).* 5.4 · 10^{-5}M TMD in triacetin at –68°. The timebase was 50 ms per unit.

The decay constants in the spectral region from 14,000 to 9,700 cm^{-1} revealed the same values as the original 20,400 cm^{-1} reference signal, thus establishing the transient absorption as one originating from a lower lying triplet TMD state. The Polaroid photographs in Fig. 9 may serve as examples.

From the optical densities extrapolated to time zero the triplet-triplet absorption spectrum figure 10 was derived. There is no doubt, that the spectrum is still incomplete concerning its extension toward the infrared. It is interesting that this behaviour is in good agreement with the calculated oscillator strengths (Table 1) of the allowed triplet-triplet transitions using the PPP-method [12].

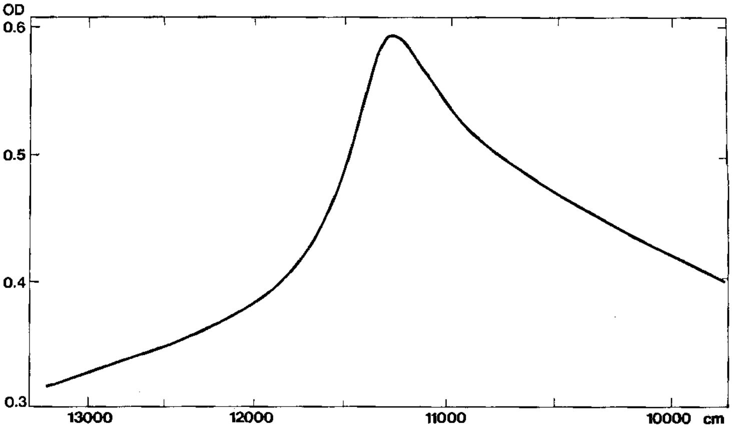


Fig. 10. *Near infrared triplet-triplet absorption of TMD in triacetin at* – 68°. 5.4 · 10^{-5} M.

Our experiments therefore show that the triplet-triplet absorption spectrum of TMD has two strong peaks at 20,400 and at 11,200 cm^{-1}. In addition we find that in the solvents triacetin and MCH/2-MP the photochromic absorptions arround 20,000 and 16,000 cm^{-1} are formed within the time resolution of our apparatus.

Table I. *Calculated TMD triplet-triplet transition energies and oscillator strengths*

Transition	Energy [cm^{-1}]	Oscillator Strength	Transition	Energy [cm^{-1}]	Oscillator Strength
T_1–T_2	4,580	0.005	T_1–T_{11}	15,910	0.003
T_1–T_5	10,440	0.028	T_1–T_{14}	17,810	0.276
T_1–T_6	10,480	0.050	T_1–T_{15}	20,930	0.025
T_1–T_8	12,510	0.008	T_1–T_{19}	22,670	0.363
T_1–T_{10}	15,650	0.069	T_1–T_{20}	23,070	0.806

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REFERENCES

[1] *T. Bercovici, R. Kornstein, K. A. Muszkat & E. Fischer*, Pure and Appl. Chem. *24*, 531 (1970).
[2] *J. R. Huber, U. Wild & Hs. H. Günthard*, Helv. *50*, 841 (1967).
[3] *R. Kornstein, K. A. Muszkat & E. Fischer*, Israel J. Chemistry *8*, 273 (1970).

[4] *T. Bercovici & E. Fischer*, Israel J. Chemistry *7*, 127 (1969).
[5] *L. J. Dombrowski*, Thesis, Rensselaer Polytechnic Inst., Troy, New York (1968).
[6] *L. J. Dombrowski, C. L. Groncki, R. L. Strong & H. H. Richtol*, J. Phys. Chem. *73*, 3481 (1969).
[7] *T. Bercovici, G. Fischer & E. Fischer*, Israel J. Chemistry *8*, 277 (1970).
[8] *J.-C. Metras, M. Mosse & C. Wippler*, J. Chim. phys. 659 (1965).
[9] *G. Kortüm, W. Theilacker, H. Zeininger & H. Elliehausen*, Chem. Ber. *86*, 294 (1953).
[10] *M. Vallotton & U. P. Wild*, J. Phys. E. Sci. Instr. *4*, 417 (1971).
[11] *K. H. Gschwind*, Diss. Nr. 4745, 1971, ETH, Zürich.
[12] *R. Lorenz, U. Wild & J. R. Huber*, Photochem. Photobiol. *10*, 233 (1969).

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79. Die Struktur von Ovalicin

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(11. I. 73)

Summary. The structure of ovalicine, a metabolite of the fungus *Pseudeurotium ovalis* with immunosuppressive activity, has been determined to be **15**.

Dem aus dem Kulturfiltrat des Pilzes *Pseudeurotium ovalis Stolk*[1]) isolierten Sesquiterpen-methyläther Ovalicin[2]) konnte auf Grund verschiedener Abbau- und Umwandlungsreaktionen sowie durch die röntgenographische Analyse eines Derivates die Konstitution und partielle Konfiguration **1** zugeordnet werden [1]. *Sassa et al.* haben 1970 in einer Kurzmitteilung über die Isolierung des Pilzmetaboliten Graphinon referiert und auf Grund der spektroskopischen und physikalischen Eigenschaften die Identität von Graphinon und Ovalicin vorgeschlagen [2].

Wir berichten im folgenden über abschliessende Experimente, die die Ableitung der Struktur von Ovalicin erlauben.

Aus verschiedenen Mutterlaugen von Ovalicin wurden durch Chromatographie an Kieselgel zwei neue schwefelhaltige Verbindungen $C_{16}H_{26}O_5S$ (**2**) und $C_{16}H_{26}O_6S$ (**3**) isoliert, deren enge Verwandtschaft durch die oxydative Überführung von **2** in **3** bewiesen wurde.

2 ist ein optisch aktives Neutralprodukt ($[\alpha]_{D}^{20} = -36°$), besitzt aber die interessante immunosuppressive Aktivität von Ovalicin [3] nicht.

Auf Grund der Bruttoformel $C_{16}H_{26}O_5S$ könnte **2** formal als H_2S-Anlagerungsprodukt von Ovalicin **1** aufgefasst werden. Der Vergleich der spektroskopischen Daten (siehe Tab. 1) von **2** und **3** mit denen von **1** deuten auf das gleiche carbocyclische Grundgerüst hin.

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[1]) Die mikrobiologischen Arbeiten verdanken wir den Herren Dr. *E. Härri*, *Ch. Stoll* und *G. Poirel*.

[2]) Die Isolierung und Reinigung grösserer Mengen Ovalicin erfolgte unter der Leitung von Herrn *P. Furger*.