V. La réduction préparative a été effectuée avec une électrode de mercure à un potentiel fixé à $-2{,}10$ V. Le courant cathodique moyen de 1 A est tombé à 0,05 A après le passage de 1,7 F. L'analyse des produits réactionnels par chromatographie en phase gazeuse a révélé la présence de cyclopropanol par comparaison avec un échantillon authentique (rendement approximatif: 60%).

Partie experimentale. – *Généralités.* L'acétonitrile (*Fluka*) a été séché sur tamis moléculaires puis distillé sous azote sec. Le bromure de tétraéthylammonium (*Fluka*) a été recristallisé dans un mélange éthanol-acétate d'éthyle. Les électrolyses ont été faites, sous azote, à une cathode de mercure séparée d'une anode en platine par un diaphragme poreux (Diapor). Le potentiel de la cathode était fixé par rapport au couple Ag^0/Ag$^+$ (KCl sat.) à l'aide d'un potentiostat construit dans notre laboratoire. Les polarogrammes ont été relevés avec un appareil Polarecord *Metrohm* E 261 R à temps de goutte contrôlé.

Phénylcyclopropane: Une solution de 15 g (0,054 mole) de phényl-1-dibromo-1,3-propane [5] dans 400 ml d'acétonitrile-Et$_4$NBr (0,3 M) a été électrolysée sous un courant cathodique moyen de 1 A. Le potentiel de la cathode a été tout d'abord fixé à $-0{,}9$ V, puis à $-1{,}4$ V en fin d'électrolyse afin de maintenir un courant d'intensité convenable. L'électrolyse a été interrompue lorsque le courant est tombé en dessous de 0,1 A. On a enregistré le passage d'env. 9600 coulombs. La température a été maintenue entre 20–25° pendant la durée de l'électrolyse.

Environ 250 ml d'acétonitrile ont été chassés du mélange final par distillation. Après addition de 250 ml d'eau et extraction à l'éther, l'évaporation des extraits éthérés a abandonné un résidu qui a été distillé sous pression réduite. 4,3 g de phénylcyclopropane ont été receuillis à 60–61° 15 Torr sous forme d'un liquide incolore: $n_D^{20} = 1{,}5322$. La structure a été confirmée par comparaison du spectre de RMN. avec celui d'un échantillon authentique.

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251. Photochromism in Bianthrone and Related Compounds. Part VI. The Structure of the Photochromic Isomers of Bianthrones[1]

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(11. IX. 70)

Summary. The cyclic structure III is assigned to the **C** photochromic isomer of 1,8'-dimethylbianthrones on the basis of spectral and chemical evidence. Similar considerations indicate that this does not apply to the **B** photoisomers of bianthrones.

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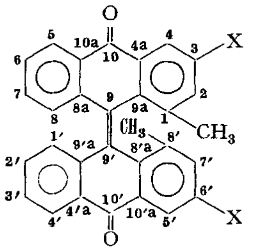
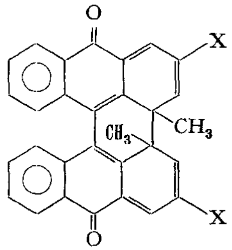
The molecular structure of the coloured forms of bianthrones has been a longstanding unsolved problem ([1], for recent references see [2]). In this note we wish to report new experimental results showing that the structure of the photochromic **C** modifications [2] [3] of 1,8′-dimethylbianthrone (I) and of 1,3,6′,8′-tetramethylbianthrone (II) may be represented respectively by IIIa (X = H) and by IIIb (X = CH_3).



I (X = H)
II (X = CH_3)



IIIa (X = H)
IIIb (X = CH_3)

However, for form **B**, a similar cyclic structure seems to be ruled out. The photochemical properties of I and of II, and of their two photochromic forms, **B** and **C**, are as follows: The **C** form is observed *only* in the two compounds I and II. Mixtures of the two photochromic forms, **B** and **C**, result on irradiation of solutions of I or of II. The ratio **B**/**C** is a function of the temperature, the wavelength of the light used for irradiation, the nature of the solvent, and to some extent its viscosity [3] [4]. The electronic spectra of the pure modifications **B** and **C** are given in Fig. 1 (cf. [3b]). In analogy with the *cis*-stilbene-4a,4b-dihydrophenanthrene systems [5], the **C** forms of I and of II undergo *photo*conversion into the starting compound. However, the **B** isomers of I and II, as well as those of bianthrone proper and of 1,8′-difluoro-, 1,8′-dimethoxy- and 1,2,7′,8′-dibenzo-bianthrone are completely light-stable. Contrary to the 4a,4b-dihydrophenanthrenes [5] [6], the **B** isomers are inert to oxidation by

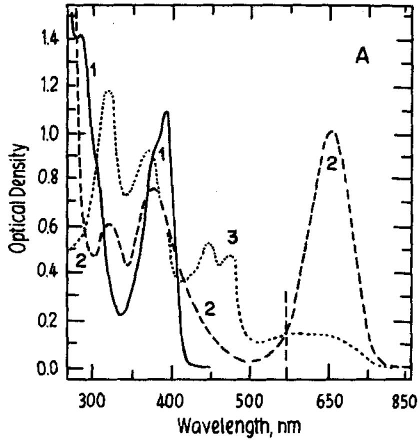


Fig. 1. *Absorption spectra of compound II in MTHF, ca.* 5×10^{-5} M, *at* −175°

Curve 1 – before irradiation; curve 2 – after complete conversion into the **B** form by 405 nm irradiation; curve 3 – **C** form (extrapolated) molecular oxygen. Forms **C** of I and of II, and all the **B** modifications, undergo thermal conversion to the parent bianthrone derivatives at temperatures higher than about –80° for the **B** forms, and about –50° for the **C** forms.

The thermochromism and the reversible and irreversible photoreactions of bianthrone proper (*i.e.* I without methyls) may be described as follows: Solutions of bianthrone in diphenyl ether have a single absorption band in the visible region, whose intensity increases with temperature ('thermochromism'). At 235° the peak is at 655 nm and shifts to 665 nm at 100°. This may be compared with the single peak observed for the **B** photoisomer in the photochromism of bianthrone in methyltetrahydrofuran (MTHF) (Fig. 2A). This photochromic peak is blue-shifted from 695 nm at –175° to 675 at –60°. There is thus good reason to believe that here, as in the case of the various derivatives of bianthrone investigated, the 'photochromic' coloured isomer **B** and the 'thermochromic' coloured isomer (*i.e.* formed at high temperatures in a thermal equilibrium) are identical. The absorption spectrum of such a solution of bianthrone in diphenyl ether is not affected by oxygen, even at 235°. The same holds for the **B** isomer formed by UV. irradiation of, e.g., a solution in 1-propanol/2-propanol at –160°. When such a solution, containing either virtually pure **B** isomer, or a mixture of starting material and **B**, is heated to –80° and oxygen

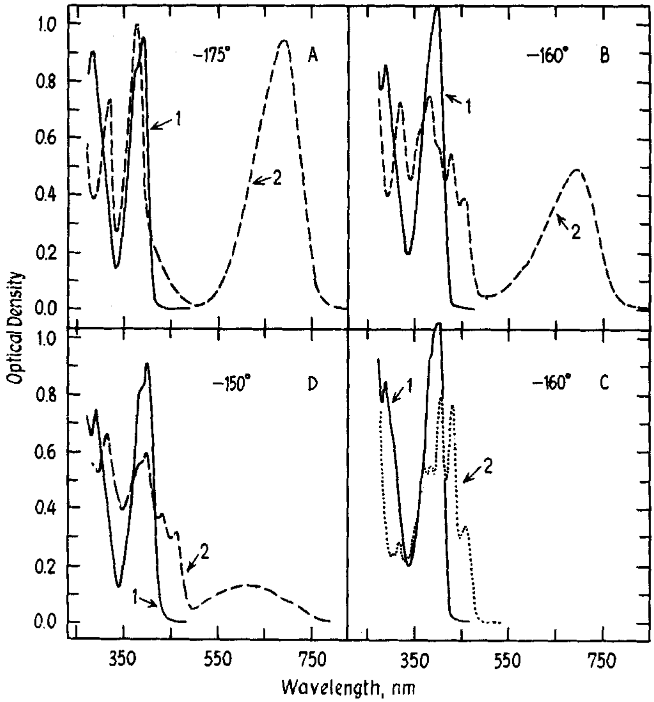
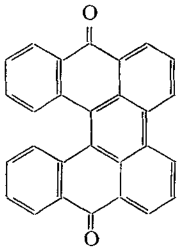


Fig. 2. *Absorption spectra of bianthrone in MTHF, ca. 5 × 10⁻⁵ M, at the temperatures indicated*

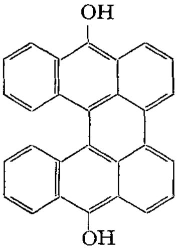
Full curves (1) – before 405 nm irradiation; dashed curves (2) – after irradiation. Curve 2 in 2C results from heating the irradiated solution of Fig. 2B to room temperature and recooling it to –160°.

bubbled through, no spectral change is observed. **B** thus does not undergo any thermal reaction, except the spontaneous reversion to the colourless starting isomer above about −80°.

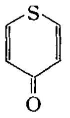
Moreover, if bianthrone is first converted completely into the **B** isomer by 405 nm irradiation at very low temperatures (Fig. 2A) and the irradiation then continued at −150°, no further changes are observed. If, however, bianthrone itself is irradiated directly at −150°, efficient irreversible reactions take place (Fig. 2D). This shows conclusively that the **B** isomer is light-stable, and therefore not a precursor in the sequence of the irreversible photoreactions. If a mixture of bianthrone and its **B** isomer (formed at −175° by partial conversion into **B** with 405 nm light) is irradiated at −80° with light at 546 + 578 nm, no reaction takes place. This shows that excited **B** molecules do not react under these conditions, but of course still allows for the possibility of a reaction between **B** and photoexcited bianthrone. When the same 1:1 mixture of bianthrone and its **B** isomer is irradiated at −150° with 405 nm light, a fast photodecomposition of bianthrone, similar to the one described for pure bianthrone, is observed, while the **B** isomer is not affected. All this indicates that in the efficient irreversible photoreactions of bianthrone, which do take place at all but the lowest temperatures [7] [8], the primary active units are excited bianthrone molecules, probably undergoing some reaction which *competes* with the formation of **B** and does not involve **B** at all.



IV



V



VI

On the other hand, it is very plausible that the efficient photo-oxidation of bianthrone to helianthrone (IV) involves a cyclic short-lived intermediate analogous to III, which has as yet not been detected, but is certainly not the **B** isomer. This intermediate is then dehydrogenated with oxygen or with bianthrone to form IV, possibly *via* dihydrohelianthrone (V). The latter is a major irradiation product of bianthrone in alcoholic or etheric solvents above about −120° (unpublished results from this Laboratory), and is easily oxidized to IV [7].

Bianthrones dissolve only to a limited extent in photochemically stable solvents. However, we have found that irradiation at 405 nm in solvents suitable for NMR. and IR. studies, such as CS_2, CH_2Cl_2, $CHCl_3$, and mixtures thereof, affords sufficiently high concentrations of forms **C** and **B** to obtain meaningful spectra, in particular for **C**. These solvents are not decomposed by irradiation at 405 nm.

The following signals (in ppm *vs.* tetramethylsilane) in the NMR. spectrum of a mixture of form **C** and of its starting compound I (Fig. 3) are due to **C**: 1.74 ppm (1,8′ methyls); 6.5–6.73 ppm (2,3,4,5′,6′,7′ olefinic protons); 8.18 ppm (aromatic

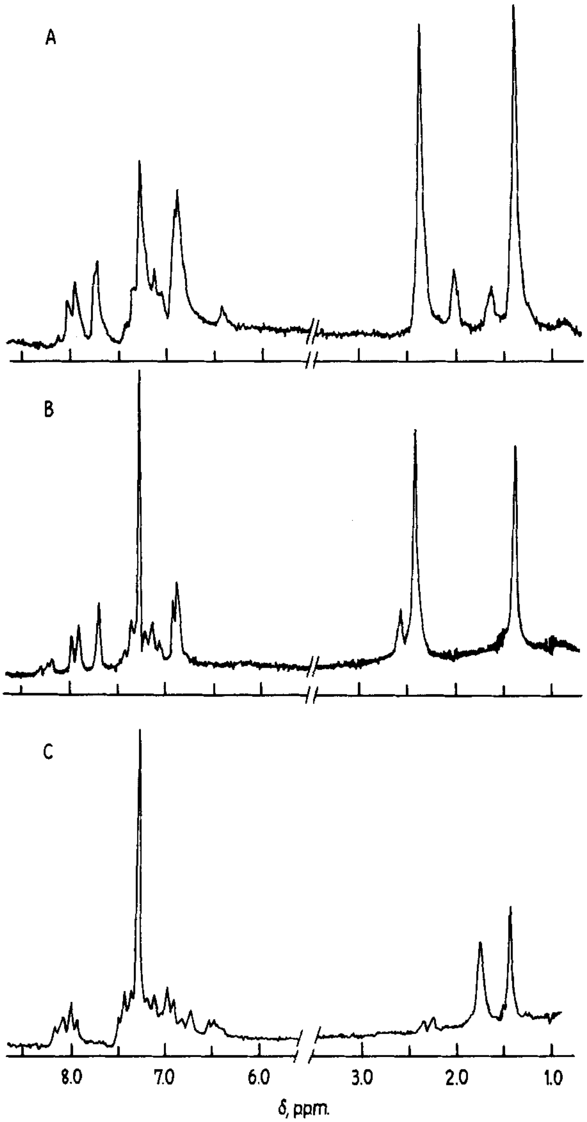


Fig. 3. *NMR. spectra of compounds II and I after partial conversion into* **B** *or* **C** *by irradiation at low temperatures*

3A: II in $CDCl_3$ at −55° (**C** isomer); 3B: II in $CS_2/CDCl_3$ (2:1) at −85° (**B** isomer); 3C: I in $CDCl_3$ at −55° (**C** isomer).

protons). These signals are reversibly destroyed by heating or by irradiation at 436 or 546 nm.

The decision between 1–8′ or 1–1′ ring closure was made on the basis of the extent of conversion: Spectrophotometric observations had shown that the maximal extent of photoconversion into **C** under the prevailing experimental conditions was about 50% in II and 70% in I, immediately after irradiation. The manipulations necessary in connection with the NMR. measurements can only reduce this percentage, because of the partial thermal decay. However, the NMR. spectrum of I after irradiation indicates that 50% of the methyl groups in the mixture are of the new type (Fig. 3C). If 1–1′ were the irradiation product, only *complete* conversion could lead to this result. Since this is clearly impossible, we have to conclude that, if a cyclic structure is formed, it has to be 1–8′. Additional proof for structure III, *i.e.* ring closure at the 1–8′ positions, is provided by the fact that from the NMR. signals one sees that the number of protons at 1.74 ppm and at 6.5 + 6.73 ppm is approximately equal. This is as expected for III, while in the compound resulting from ring closure at the 1–1′ positions the ratio should be 1:2. A similar argument applies to the C photoproduct of compound II, and indeed the ratio between the number of protons proved that it also has structure III. This probably means that already in the starting compounds I and II the methyl groups are in the *cis* position with regard to the central double bond.

The infrared spectra of forms C of I (Fig. 4B) and of II (Fig. 4A) indicate that the carbonyl groups at 10 and 10′ (III) are intact in the C form (but probably not in the B form).

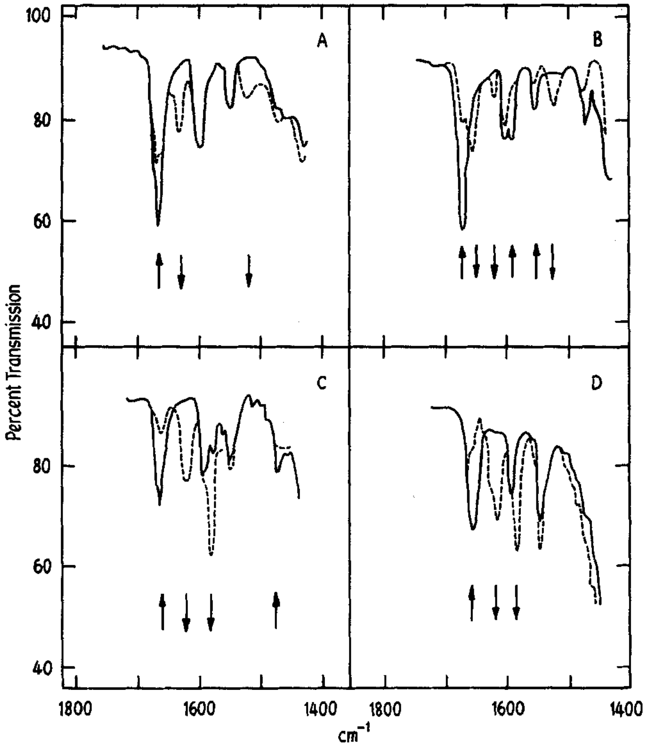


Fig. 4. *Infrared absorption spectra at low temperatures*

About 10^{-2}M solutions in methylene chloride in 0.1 mm cells. Full curves – before, dashed curves – after irradiation at 405 nm. 4A: II at –50° (C isomer); 4B: I at –80° (C isomer); 4C: 1,8′-dimethoxy-bianthrone at –95° (B isomer); 4D: 1,2,7′,8′-dibenzo-bianthrone at –90° (B isomer).

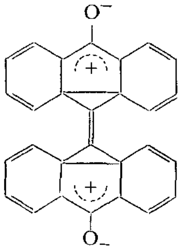
Studies in the 4000–2200 cm^{-1} spectral range indicate that no OH groups are formed during the process I or II $\xrightarrow{h\nu}$ **C**. Structure III for **C** is also supported by the following observations: (a) The resistance of **C** to oxidation by molecular oxygen, which is paralleled by the previously observed stability of 4a,4b-methyl-substituted 4a,4b-dihydrophenanthrene towards oxygen [5]; (b) Both the thermal and the photochemical processes **C** → I (or II) are analogous to similar processes in the *cis*-stilbene-4a,4b-dihydrophenanthrene system [5].

Our previous measurements and calculations of the electronic absorption spectra of 4a,4b-dihydrophenanthrenes [5] indicate that the presently reported spectrum of the **C** isomer of II is entirely compatible with structure III. The shift to longer wavelengths of the first band (475 nm in hexamethyldihydrophenanthrene [5] *vs.* 580 nm in the **C** form of II) would be the result of an extension of the chromophore part, while the decrease in intensity ($\varepsilon = 3100$ [5] *vs.* 2600 in **C**) would be due to a further deviation from planarity.

We have not yet reached a definite conclusion about the molecular structure of form **B**. The infrared spectrum (Fig. 4, C and D) indicates that the carbonyl group frequency is strongly modified. However we are unable at present to decide whether or not the new band at 1620 cm^{-1} is due to a modified C=O stretching vibration, as in γ-thiapyrone (VI) [9]. The **B** forms do not show any OH stretching frequencies in their IR. spectra.

The NMR. spectrum of the **B** form of II (Fig. 3B) shows a pronounced shift of the 1-methyl signal, from 1.4 ppm in II to 2.6 ppm in its **B** isomer. The 3-methyl signal remains unchanged, and no olefinic protons are observed. However, the extent of conversion into **B** was too low to allow accurate observations. Anyway, the above facts cannot be reconciled with a cyclic structure similar to III, and thus support the same conclusion reached earlier, on the basis of the stability of **B** towards oxidation and photochemical changes in general, including reversion to the starting compound. The NMR. results indicate that both methyl groups retain their aromatic character, with the 1-methyl group undergoing deshielding as a result of the transformation of II into **B**.

Very recently[4]) Prof. *O. L. Chapman* suggested a structure of type VII, which might be compatible with the observed optical absorption spectra and photostability, though perhaps not with the NMR. spectra. This suggestion certainly deserves further study.



VII

K. A. Muszkat wishes to express his indebtedness to Professor *E. Heilbronner* for his hospitality, and to the Bank *Julius Baer & Co.*, Zurich, and in particular to Mr. *W. J. Baer*, for the grant of a fellowship.

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252. Mass Spectrometric Studies of Mono- and Di-Haloacetylenes

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(12. X. 70)

Summary. The mass spectra of the four monohaloacetylenes X-C≡C-H with X = F, Cl, Br, I and the six dihaloacetylenes X-C≡C-Y with X, Y = Cl, Br, I have been recorded. The dissociation energies of the carbon-carbon triple bonds of these compounds have been determined from the appearance potentials of the CH^+ and CX^+ ions. The appearance potentials of the singly- and doubly-charged molecular ions are also reported.

Monohaloacetylenes, X–C≡C–H (X = F, Cl, Br, I), and dihaloacetylenes, X–C≡C–Y (X, Y = Cl, Br, I), have recently been the subject of a variety of physicochemical studies [1] [2]. The availability of these compounds in our laboratory gave us the opportunity to carry out some mass spectrometric studies of their thermodynamic properties. Our main interest was to determine the dissociation energies of the carbon-carbon triple bonds.

The bond dissociation energy (D) is defined as the difference in energy between the parent molecule (in its equilibrium configuration) and the two fragments (also in their equilibrium configurations) after bond breaking [3]. Therefore, the bond dissociation energy can be written as the difference between the heats of formation of the fragments and the heat of formation of the parent molecule:

$$D(\mathrm{A{-}B}) = \Delta H_f(\mathrm{A}) + \Delta H_f(\mathrm{B}) - \Delta H_f(\mathrm{AB}).$$

The determination of bond dissociation energies by electron impact is based upon the following considerations [4]. For the process

$$\mathrm{AB} \rightarrow \mathrm{A}^+ + \mathrm{B} + e$$

the appearance potential of A^+ is

$$AP(\mathrm{A}^+) = D(\mathrm{A{-}B}) + IP(\mathrm{A}) + E\,, \tag{1}$$

where E is the excess energy (both internal and translational) of the products. Many

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