BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 44, 3158—3160 (1971)

A Dianthr[14]annulene

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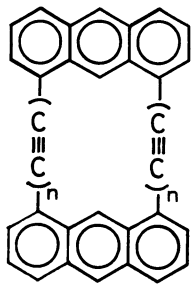
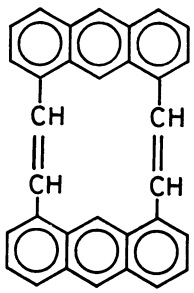
(Received May 28, 1971)

1,2,3,4,5:8,9,10,11,12-Di(1′,8′-anthr)[14]annulene (III) has been synthesized by the Wittig reaction of 1,8-diformylanthracene (IV) and the bis-ylide (VIII) derived from 1,8-bis(bromomethyl)anthracene (VI).

We previously reported the syntheses and properties of dianthratetradehydro[18]- and dianthroctadehydro-[26]annulenes (I and II).[1,2] It seemed to be of interest to synthesize dianthrannulene and compare its properties with those of dianthradehydroannulenes (I and II). On inspection of a molecular model of the dianthr[14]annulene (III), we realized that the molecule should be twisted owing to the steric repulsion between the hydrogen atoms at 9′-positions of the aromatic nuclei and those of the ethylenic bonds. Thus, a comparison of the electronic spectra of III and related compounds seemed to be of considerable interest. We wish to report the synthesis of the dianthr[14]annulene (III), a lower analogue of I and II.



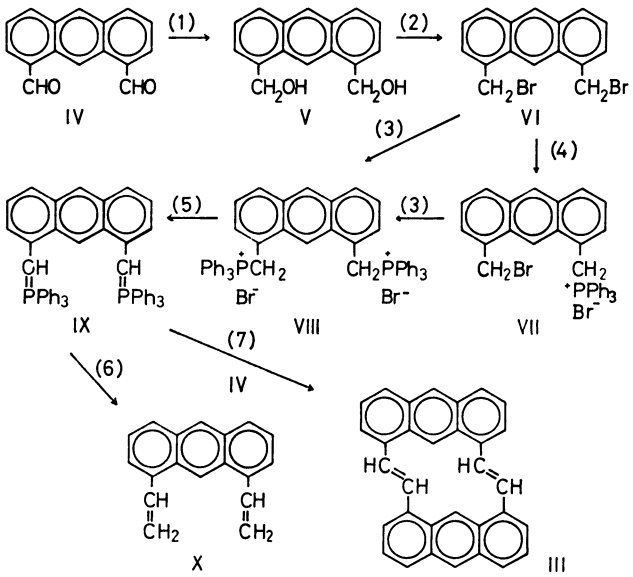
I n=2, II n=4



III

Synthesis. Preparation of III was performed according to an analogous sequence of the reaction used in the synthesis of 1,2,3:6,7,8-di(1′,8′-naphth)[10]-annulene.[3]

1,8-Diformylanthracene (IV)[2] was reduced by means of sodium borohydride to give 1,8-bis(hydroxymethyl)-anthracene (V). Glycol (V) was converted quantitatively to bis-bromomethyl derivative (VI). Bis-triphenylphosphonium salt (VIII) was obtained in a high



Scheme. Synthesis of dianthr[14]annulene and 1,8-divinylanthracene.
(1) $NaBH_4$/THF; (2) PBr_3-pyridine/THF; (3) Ph_3P/DMF; (4) Ph_3P/benzene; (5) PhLi/toluene; (6) $(CHO)_n$/toluene; (7) toluene.

1) S. Akiyama, S. Misumi, and M. Nakagawa, This Bulletin, **33**, 1293 (1960).

2) S. Akiyama, S. Misumi, and M. Nakagawa, *ibid.*, **35**, 1826 (1962).

3) R. H. Mitchell and F. Sondheimer, *J. Amer. Chem. Soc.*, **90**, 530 (1968).

yield by treatment of VI with 3 molar equivalents of triphenylphosphine in dimethylformamide at *ca.* 100°C. The reaction of the phosphine in benzene gave exclusively monophosphonium salt (VII) which could be converted to VIII in a good yield by further treatment with the phosphine in dimethylformamide. Phenyllithium in toluene transformed VIII to bis-ylide (IX). The Wittig reaction of 1,8-diformylanthracene IV and bis-ylide IX in toluene afforded dianthr[14]annulene III as bright yellow needles in a moderate yield. The crystals of III exhibit light green fluorescence. III gave satisfactory results of elemental analysis and the mass spectrum of III gave a molecular ion peak (M^+=404) exactly corresponding to the molecular weight of III.

1,8-Divinylanthracene (X), a reference substance of III, was prepared by the reaction of bis-ylide (XI) with an excess of paraformaldehyde in toluene.

Properties. Dianthr[14]annulene III thus prepared was found to be an extremely stable compound. It decomposed above 360°C. Annulene III is sparingly soluble in common organic solvents. The solubility in chlorobenzene was found to be 20 mg per 100 m*l* at room temperature. The configuration of ethylenic bonds in III was confirmed to be *trans*, because, as is shown in Fig. 1, the infrared spectrum of III exhibits a band at 975 cm^{-1} which is characteristic of *trans*-ethylene linkage.

The electronic spectrum of III is recorded in Fig. 2 together with those of the related compounds. The spectra of 1,8-diethynyl-[1] and 1,8-divinylanthracenes

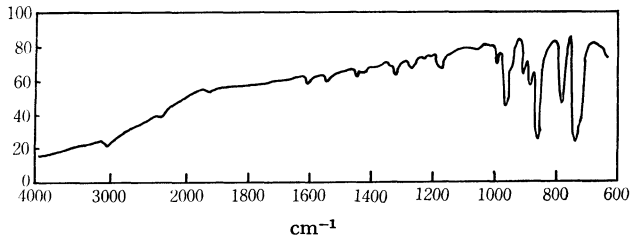


Fig. 1. The infrared spectrum of dianthr[14]annulene.

exhibit distinct vibrational fine structure characteristic of anthracene derivatives. However, disappearance of the fine structure and broadening of both absorption bands (250 nm and 340—450 nm regions) were observed in the spectrum of III. Broadening of the fine structure in the spectrum of X as compared with that of 1,8-diethynylanthracene can reasonably be attributed to the steric hindrance between the hydrogen atoms at 2- and/or 9-positions of anthracene nucleus and those of olefinic linkage. The same trend has been observed in the spectrum of 1,2-di-1′-anthrylethylene,[4] *i.e.*, the ethylene exhibits a broad spectrum in contrast to that of 1,1′-dianthrylacetylene[5] which shows a well-defined fine structure. The electronic spectrum of I also exhibits a sharp fine structure,[1] and vibrational sub-peaks are still observed in the broad and intense absorption bands of II.[2] Thus, the broadening and disappearance of the fine structure in the spectrum of III seem to be attributed mainly to the non-planar geometry of the annelated[14]annulene (III).

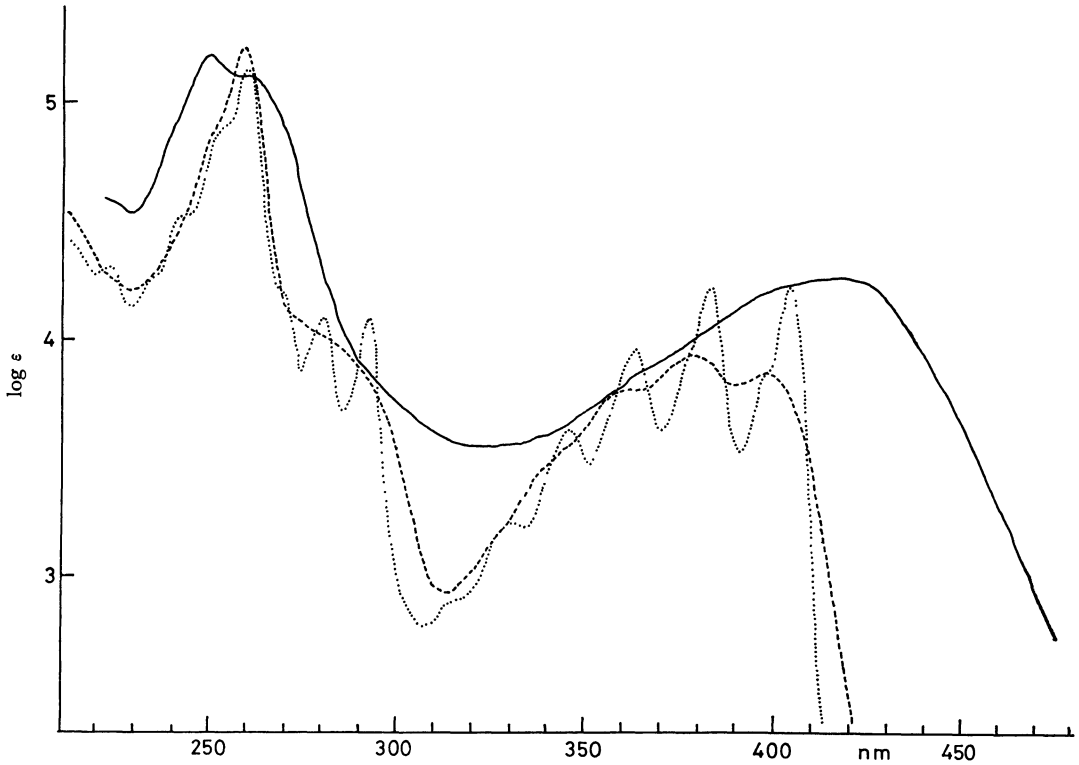


Fig. 2. The electronic spectra of dianthr[14]annulene (III, ——), 1,8-divinylanthracene (X, ——), and 1,8-diethynylanthracene (-----).

4) Unpublished result.

5) S. Akiyama, K. Nakasuji, and M. Nakagawa, This Bulletin, **44**, 2231 (1971).

The NMR spectrum of III could not be measured owing to the poor solubility of III in various NMR solvents.

Experimental

All melting points are uncorrected. The electronic spectra were obtained on a Hitachi EPS-3T spectrophotometer. The infrared and the mass spectra were measured on a Hitachi EPI-2 spectrophotometer and a Hitachi RMU-6D mass spectrometer, respectively.

1,8-Bis(hydroxymethyl)anthracene (V). The dialdehyde[2] (IV, 11.72 g, 0.05 mol) was reduced by means of sodium borohydride (1.90 g, 0.05 mol) in tetrahydrofuran (150 m*l*) employing a Soxhlet technique. Reflux was continued for 4 hr. Water was then added to deposit yellow crystals in a quantitative yield. Glycol V thus prepared was found to be identical with the specimen previously prepared.[2]

1,8-Bis(bromomethyl)anthracene (VI). To a stirred mixture of the diol (V, 2.38 g, 0.01 mol), pyridine (0.40 g, 5 mmol) and tetrahydrofuran (50 m*l*), was added a solution of phosphorus tribromide (4.07 g, 0.015 mol) in tetrahydrofuran (10 m*l*) over a period of 20 min. After stirring for further 2 hr at room temperature, cracked ice was added to the reaction mixture. The organic layer was separated, and worked up according to the usual procedure. The solvent was evaporated under reduced pressure. The residue was collected by filtration, and washed successively with an aqueous solution of sodium hydrogen carbonate and water. The yellow crystals obtained in a quantitative yield were recrystallized from benzene to afford yellow needles, mp 230—232°C (dec.). Found: C, 52.94; H, 3.31; Br, 43.69%. Calcd for $C_{16}H_{12}Br_2$: C, 52.78; H, 3.32; Br, 43.90%.

1-Bromomethyl-8-triphenylphosphoniomethylanthracene Bromide (VII). A solution of dibromide (VI, 3.64 g, 0.01 mol) and triphenylphosphine (3.90 g, 0.015 mol) in dry benzene (120 m*l*) was refluxed for 3 hr. The precipitate formed was collected, washed with benzene, and then dried to yield VII, mp 260—265°C (dec.), 6.05 g (97%). Found: C, 66.20; H, 4.34%. Calcd for $C_{34}H_{27}Br_2P$: C, 65.20; H, 4.34%. Unsatisfactory results in the analysis of carbon might be due to contamination with a small amount of bis-phosphonium salt VIII.

1,8-Bis(triphenylphosphoniomethyl)anthracene Dibromide (VIII). *1) From the Monophosphonium Salt (VII):* A mixture of VII (2.10 g, 3.35 mmol), triphenylphosphine (1.30 g, 5 mmol) and dimethylformamide (15 m*l*) was refluxed for 30 min. The precipitate formed by the addition of benzene (10 m*l*) was collected and then washed with a small amount of benzene, resulting in yellow fine cubes, 2.48 g (84%). The second crop (0.17 g, 6%) was obtained from the mother liquor. Decomposition of VIII was observed above 360°C.

2) From the Dibromide (VI): A solution of VI (0.364 g, 1 mmol) and triphenylphosphine (0.786 g, 3 mmol) in dimethylformamide (2 m*l*) was heated on a boiling water-bath for 2 hr. The precipitate formed on cooling the reaction mixture in an ice-water bath was collected by filtration and washed with a small amount of benzene. Bis-phosphonium bromide VIII, thus prepared, showed an identical IR spectrum with that of VIII derived from VII and decomposed also above 360°C. Found: C, 70.04; H, 4.78; Br, 17.49%. Calcd for $C_{52}H_{42}Br_2P_2$: C, 70.28; H, 4.76; Br, 17.98%.

1,2,3,4,5:8,9,10,11,12-Di(1',8'-anthr)[14]annulene (III). To a suspension of the bis-phosphonium salt (VIII, 5.334 g, 6 mmol) in toluene (200 m*l*), was added an ethereal solution of phenyllithium (0.85 N, 14.1 m*l*, 12 mmol) at 80°C over a period of 15 min under nitrogen atmosphere. After the mixture had been stirred for 15 min at 80°C, a solution of the dialdehyde (IV, 1.404 g, 6 mmol) in toluene (210 m*l*) was added, and stirred for 2 hr at the same temperature. The insoluble material was collected by filtration, and washed with water and alcohol successively to remove triphenylphosphine oxide. The residue was then digested repeatedly with boiling chlorobenzene (total 1.2 *l*). A brown resinous powder insoluble in chlorobenzene (*ca.* 0.7 g) remained. The hot extract was passed through a column of alumina (60 g) to give yellow filtrate with green fluorescence. The solvent was removed under reduced pressure to afford yellow needles, 0.412 g (17%). The original filtrate of the reaction mixture was passed through a thin layer of alumina (10 g), and the filtrate was concentrated *in vacuo* to afford the second drop of III (0.101 g, 4%). The slightly crude crystals of III thus obtained were dissolved in chlorobenzene and passed through a short column of alumina, affording pure III as bright yellow fine needles with green fluorescence. III was found to decompose above 360°C. Found: C, 94.78; H, 5.00%. Calcd for $C_{32}H_{20}$: C, 95.02; H, 4.98%. IR: 975 cm^{-1} (*trans* double bond). Mass: 404 (M^+), Calcd 404.5. The ratio of $M^+/M^+ + 1$ was found to be consistent with the theoretical value (obs. 0.331. theor. 0.349). UV: $\lambda_{max}^{tetrahydrofuran}$ (ε) 249 (157900), 257 (131300), and 418 (18300) nm.

1,8-*Divinylanthracene (X).* To a stirred solution of the bis-ylide IX [from VIII, 1.778 g, 2 mmol and phenyllithium, 4 mmol in toluene (50 m*l*)], was added a large excess of paraformaldehyde [dried over phosphorus pentoxide for 3 days] at 70°C. Rapid disappearance of the characteristic red color of the ylide solution was observed. After stirring for 2 hr the solvent was evaporated under reduced pressure and extracted with cyclohexane (150 m*l*). The extract was percolated through a thin layer of alumina (3 g), affording a faint yellow solution with blue-violet fluorescence. Concentration of the solvent under reduced pressure resulted in pale yellow plates, 0.270 g (57%), mp 68—70°C. The material was recrystallized twice from methanol to give analytical specimen, mp 70—71.5°C. Found: C, 93.66; H, 6.06%. Calcd for $C_{18}H_{14}$: C, 93.87; H, 6.13%. IR: 1240, 910 ($=CH_2$), 990 ($=C\langle_H$) cm^{-1}. Mass: 230 (M^+), Calcd 230. UV: $\lambda_{max}^{n\text{-hexane}}$ (ε) 256 (165600), 360 (6100), 378 (8700), and 398 (7300) nm.