Tetrahedron. Vol. 31, pp. 2931 to 2935. Pergamon Press 1975. Printed in Great Britain

10-METHYL-9-PHOSPHAANTHRACENE[a]

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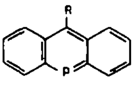
(*Received in UK* 13 *January* 1975; *Accepted for publication* 19 *June* 1975)

Abstract—The synthesis of 10-methyl-9-phosphaanthracene (**1b**) is described. Its stability is found to be intermediate between that of the unsubstituted parent compound (**1a**) and of the 10-phenyl derivative (**1c**). The electronic structure of this new phosphaaromatic system is studied, especially by photoelectron spectroscopy. As inductive and/or conjugative effects of the substituents are shown to be of minor importance, it is concluded that mainly steric effects stabilize the 9-phosphaanthracene system.

INTRODUCTION

9-Phosphaanthracene (**1a**), the parent compound and first representative[1] of tricyclic phosphaaromatic heterocycles, could not be isolated due to its high reactivity. However, 10-phenyl-9-phosphaanthracene (**1c**) proved to be an isolable compound of considerable stability in the absence of oxygen.[2] In a similar fashion, the 9-phosphaphenanthrene system[3,4] and the 9-arsaanthracene system[5,6] were considerably stabilized by a 10-phenyl substituent.



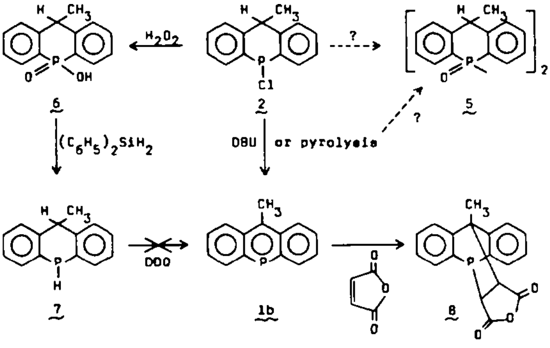
1a : R = H
1b : R = CH_3
1c : R = C_6H_5

Starting from the working hypothesis[4,7] that the enhanced stability of **1c** relative to **1a** is due to steric inhibition of polymerization reactions by the phenyl group we undertook the synthesis of 10-methyl-9-phosphaanthracene (**1b**) hoping that the Me substituent is sizable enough to achieve the same end. The concept proved partially successful leading to the first isolable alkyl substituted phosphaanthracene derivative of intermediate thermal stability and to the possibility of obtaining insight into the electronic structure of the new phospha-aromatic system by photoelectron spectroscopy.

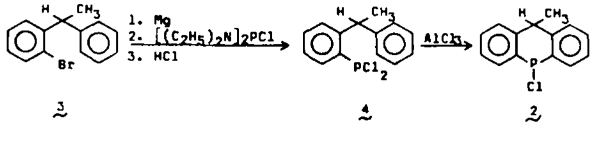
Synthesis of **1b**. The general approach to the synthesis of **1b** was similar to that applied earlier.[1,2] The starting material for the aromatization step, 9-chloro-10-methyl-9,10-dihydro-9-phosphaanthracene (**2**), was obtained by reacting the Grignard reagent of 1-(2-bromophenyl)-1-phenylethane[8] (**3**) with bis(diethylamino)-chlorophosphine, followed by treatment with gaseous hydrogen chloride to yield **4**, which was cyclized with aluminum chloride.

The dehydrohalogenation of **2** was carried out by two different procedures, i.e. with the tertiary nitrogen base 1,5-diazabicyclo[5.4.0]undec-5-ene (DBU) and by pyrolysis at *ca* 500°; both procedures gave **1b** in 10–30% yield, but **1b** was difficult to purify from byproducts. In the base-induced reaction, dimeric products were obtained, whereas in the pyrolysis much unreacted **2** was present.

One of the dimers could be isolated after exposure of the products to air and moisture and was identified as **5**. It is not clear whether **5** was formed from unreacted **2** in a dimerization reaction analogous to that described by Quin and Anderson,[9] or by radical processes involving **2** and/or **1b** or in a base catalyzed dimerization from **1b** analogous to the dimerization of acridine.[10] In an attempted alternative approach to **1b** we prepared 10-methyl-9,10-dihydro-9-phosphaanthracene (**7**) by reducing the corresponding phosphinic acid **6**. Dehydrogenation of **7** did not generate any **1b** traces of which would have been detected by its UV spectrum.



Compound **1b** was isolated from the base-induced reaction by crystallization (Experimental). It could not be purified by sublimation, as it decomposed on heating; in an inert atmosphere at room temperature, it decomposed in solution and to some extent even in the solid state.



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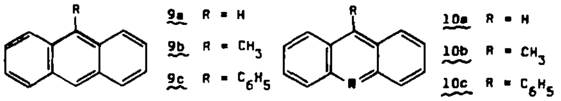
[a] In the sequence of a continuing series of papers on theory and application of photoelectron spectroscopy by A. Schweig *et al.*, this paper will be regarded as part 58 by that laboratory.

The identity of **1b** was proven by elemental analysis, by its UV spectrum which was very similar to that of **1a**[1] and **1c**,[2] by mass spectroscopy,[11] by its reaction with maleic anhydride to yield the Diels-Alder adduct **8**, and by reduction with potassium metal to the radical anion of **1b**,[12] the ESR spectrum of which showed two sets(a_p = 33·5 G) of four lines ($a_H^{CH_3}$ = 6·5 G). Both values must be considered as typical for (phospha) aromatic systems. For other phosphorin radical anions a_p has been reported to fall in the range of 23–36 G[12,13,*] [compare a_p = 8·4 G for $(C_6H_5)_2PK$[14]]; similarly, though less clear cut, a_H = 6·5 G resembles more that of the radical anion of 9-methylanthracene ($a_H^{CH_3}$ = 4·3 G)[15] than that of diphenylmethane ($a_H^{CH_2}$ = 2·2 G),[16] thereby making dimeric structures such as **5** rather unlikely. However, the most convincing proof for the electronic structure of **1b** was derived from photoelectron spectroscopy.

***Photoelectron spectrum and electronic structure of* 1b.** Fig. 1 shows the photoelectron (PE) spectra of **1b**, 9-methylanthracene (**9b**) and 9-methylacridine (**10b**).



The correlation diagram for the highest occupied MO's of these compounds using experimental and calculated values is displayed in Fig. 2. The calculations were carried out by the extended CNDO/S method[17] invoking the validity of Koopmans' theorem.[18] The orbital sequence of the respective MO's in anthracene (**9a**)[19–21] and **9b**[22] has previously been established [for an illustration of the four relevant occupied π MO's, π_1 to π_4, which belong to the b_{2g}, b_{3g}, a_u and b_{2g} (b_1, a_2, a_2 and b_1) irreducible representations of point group $D_{2h}(C_{2v})$, see below]. The assignment of bands in the PE spectra of **9b** and **10b**

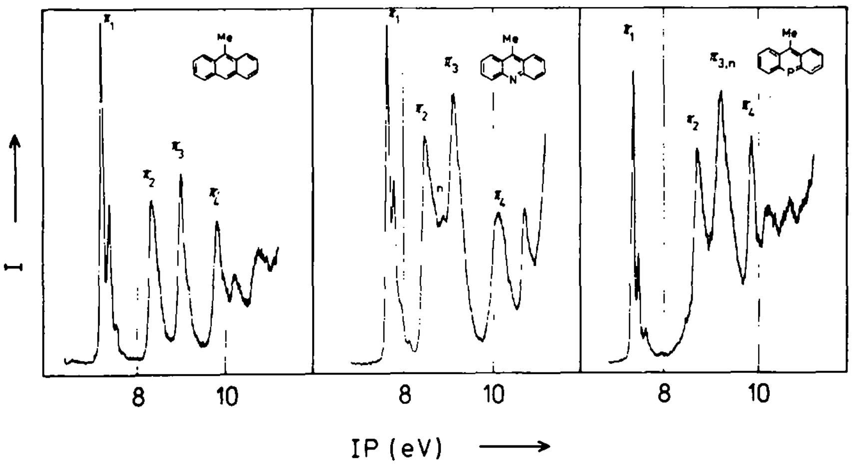


Fig. 1. Sections of the PE spectra of 9-methylanthracene (**9b**), 9-methylacridine (**10b**) and 10-methyl-9-phosphaanthracene (**1b**) with interpretation. For the measured vertical ionization potentials see Fig. 2.

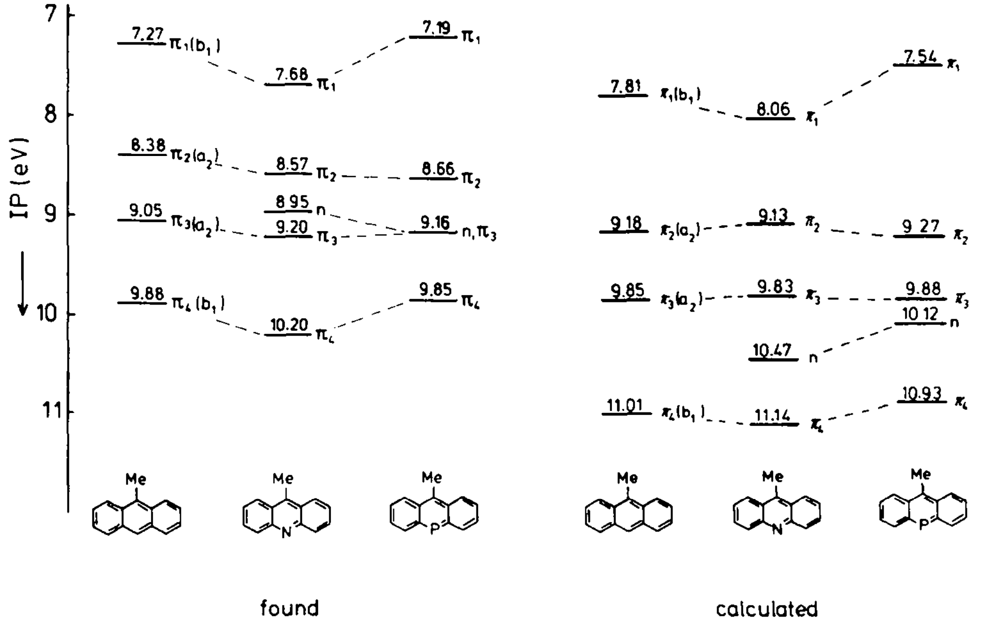


Fig. 2. Found and calculated correlation diagram for the highest occupied MOs of 9-methylanthracene (**9b**), 9-methylacridine (**10b**) and 10-methyl-9-phosphaanthracene (**1b**). The numbers above the levels are vertical ionization potentials (in eV).

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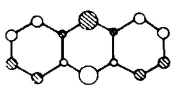
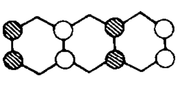
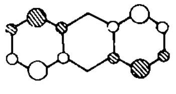
*The radical anions of **1a** and **1c** show a_p = 35 G and a_p = 36 G, respectively; C. Jongsma, unpublished results.



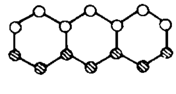
$\pi_1\ (b_{2g};b_1)$



$\pi_2(b_{3g},a_2)$



$\pi_3(a_u;a_2)$



$\pi_4\ (b_{2g},b_1)$

stems: (i) from the close correspondence between experimental and theoretical values (the strong calculated rise of the lone pair (n) level in going from **10b** to **1b** is probably not an artifact of the present calculations but a manifestation of the different orbital relaxation of nitrogen and phosphorus lone pair MO's[23] which is not taken into account in the calculations), (ii) from the observed (see Figs. 3–5 and discussion in text below) slight influence of the Me substituent in **1b**, **9b** and **10b** on the highest occupied MO's of anthracene (**9a**), acridine (**10a**) and 9-phosphaanthracene (**1a**) (ensuring that the orbital sequence in the parent and substituted systems is all the same) and (iii) from the generally found close correspondence of π ionization of phospha-aromatics and parent aromatics on the one hand and of the n ionization in analogous phospha- and aza-heterocycles on the other (for these two useful generalisations see ref. 24).

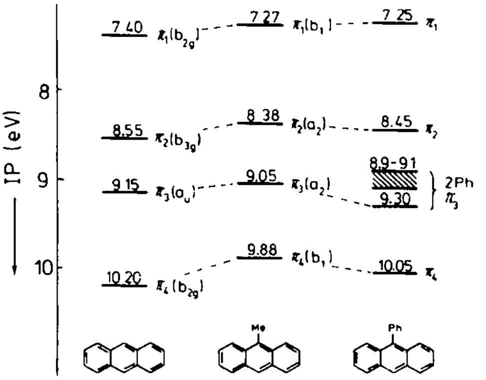


Fig. 3. Found correlation diagram for the highest occupied MOs of anthracene (**9a**), 9-methylanthracene (**9b**) and 9-phenylanthracene (**9c**). The two phenyl π ionization of **9c** are designated by 2 Ph. The numbers above the levels are vertical ionization potentials (in eV).

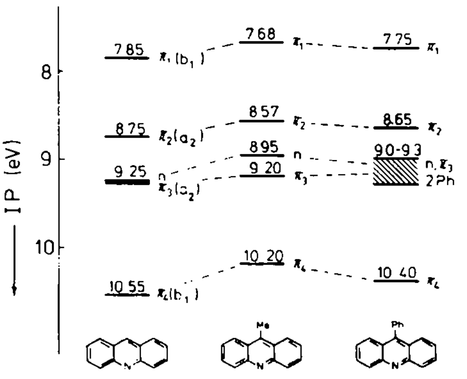


Fig. 4. Found correlation diagram for the highest occupied MOs of acridine (**10a**), 9-methylacridine (**10b**) and 9-phenylacridine (**10c**). The two phenyl π ionizations of **10c** are designated by 2 Ph. The numbers above the levels are vertical ionization potentials (in eV).

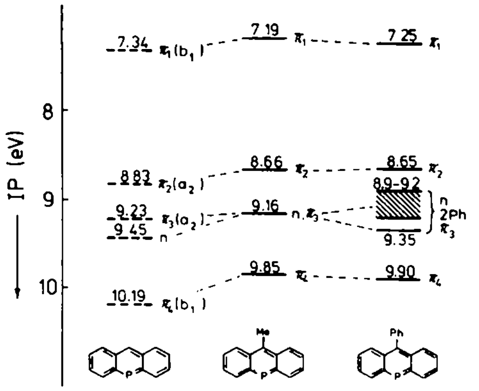


Fig. 5. Found correlation diagram for the highest occupied MOs of 9-phosphaanthracene (**1a**), 10-methyl-9-phosphaanthracene (**1b**) and 10-phenyl-9-phosphaanthracene (**1c**). The two phenyl π ionizations of **1c** are designated by 2 Ph. The levels for **1a** are drawn in dashed line to indicate that they have been obtained by use of an extrapolation procedure (see text). The numbers above the levels are vertical ionization potentials (in eV).

Figs. 3–5 represent the observed correlation diagrams for the highest occupied MO's of molecules **9a**, **9b** and **9c**, **10a**, **10b** and **10c** and **1a**, **1b** and **1c**, respectively using data for **9a** and **10a** from own measurements and the previously published [25] data for **1c**, **9c** and **10c**. The values given for **1a** were extrapolated on the base of the data from **1b** and the corresponding anthracene and acridine cases. As seen from these diagrams the methyl and phenyl substituent effects on the highest occupied MO's are very small (in the range of 0·1–0·2 eV) and nearly the same for both substituents. This result is in accordance with the assumption that the phenyl group in **1c**,[4] **9c**[26] and **10c** has a perpendicular orientation relative to the tricyclic system. Bearing this result in mind it is—in harmony with the working hypothesis[4,7] mentioned in the introduction—hardly conceivable that electronic (conjugative and/or inductive) effects of the methyl or phenyl groups play any significant role in determining the enhanced stability of **1b** or **1c** relative to the unsubstituted 9-phosphaanthracene (**1a**).

This conclusion is in agreement with recent results in the arsaanthracene series where it has been found that chlorine, bromine and methoxy as substituents in position 10 give no substantial stabilization.[27]

EXPERIMENTAL

M.ps are uncorrected. Mass spectra were recorded with a Varian MAT CH5 and ^{1}H NMR spectra with a Varian A-60 spectrometer. Chemical shifts are given in δ (ppm) from internal TMS. The IR spectra were recorded with a Perkin-Elmer 237 and the UV spectrum with a Perkin-Elmer spectrophotometer, model 137. The ESR spectrum was recorded with a Varian E-3 EPR spectrometer. The He(I)PE spectra (584 Å) were recorded with a Perkin-Elmer PS 18 spectrometer. Elemental analyses were performed under supervision of Mr. W. J. Buis at the Microanalytical Department of the Institute for Organic Chemistry TNO, Utrecht, The Netherlands.

1-(2-Dichlorophosphosphinophenyl)-1-phenylethane (**4**). The solution of the Grignard compound, prepared from **3**[8] (106 mmole) and Mg (127 mmole) in dry THF (80 ml) was added to a mixture of bis(diethylamino)-chlorophosphine (100 mmole) in dry THF (100 ml), which was cooled at −80°. After boiling for 4 hr the THF was distilled off and the residue was extracted with dry cyclohexane (175 ml). After filtration under N_2, the soln was saturated with gaseous HCl and after renewed filtration and evaporation of the filtrate, the residue was vacuum destilled and yielded **4** (19·1 g, 64%), b.p. 140°/0·01 mm. NMR (CCL_4): 8·72–8·38 (m, 1, aromatic proton); 8·11–7·25 (m, 8, aromatic protons); 5·42 (quintet, 1, $^3J_{H-H} = 7{\cdot}2$ Hz, $^4J_{P-H} = 7{\cdot}2$ Hz, methine proton); 2·14 (d, 3, $^3J_{H-H} = 7{\cdot}2$ Hz, CH_3).

9 - *Chloro* - 10 - *methyl* - 9,10 - *dihydro* - 9 - *phosphaanthracene* (**2**). A soln of **4** (64 mmole) in dry CS_2 (250 ml) was added under N_2 to a stirred suspension of $AlCl_3$ (74 mmole) in dry CS_2 (150 ml) and after refluxing for 20 hr pyridine (77 mmole) was added. The soln was filtered under N_2 and after evaporation to dryness the residue was stirred with cyclohexane (250 ml) and after filtration the solvent was evaporated. The residue yielded on vacuum destillation **2** (8·2 g, 52%), mp.p. 121–123° [Found: C, 67·75; H, 5·08; P, 12·36; Cl, 14·15; $C_{14}H_{12}PCl$ (M = 246·66) requires: C, 68·17; H, 4·91; P, 12·56; Cl, 14·37%]. **2** consists of two stereoisomers, A and B in the ratio 3:2, which have not been separated. NMR ($CDCl_3$): isomer A: 8·54–8·00 (m, 2, aromatic protons); 8·00–7·66 (m, 6, aromatic protons); 4·61 (octet, 1, $^3J_{H-H} = 7{\cdot}4$ Hz, $^4J_{P-H} = 2$ Hz, methine proton); 2·13 (d, 3, $^3J_{H-H} = 7{\cdot}4$ Hz, CH_3), isomer B: 4·78 (octet, 1, methine proton); 1·82 (d, 3, $^3J_{H-H} = 7{\cdot}1$ Hz, CH_3). Mass spectrum *m/e* (%): 248 (34), 246 (100), 233 (27), 231 (78), 211 (24), 210 (51), 196 (64), 180 (31), 178 (33), 165 (80).

10 - *Methyl* - 9 - *phosphaanthracene* (10 - *methyldibenzo*[*b*, *e*]*phosphorin*, **1b**). To a refluxing soln of **2** (3·7 mmole) in dry toluene (50 ml) under N_2, DBU (3·7 mmole) was slowly added in 1 hr. After a few drops of DBU the soln turned yellow and later white crystals of DBU·HCl (IR, NMR) precipitated in 95% yield (titration). The mixture was refluxed for 2 hr, filtered under N_2 and evaporated. The residue was extracted with dry cyclohexane (30 ml) and evaporated to 10 ml. Cooling the vessel yielded yellow crystals of **1b** (180 mg, 23%), m.p. *ca* 120° (dec) [Found: C, 78·86; H, 5·46; $C_{14}H_{11}P$ (M = 210·11), requires: C, 79·99; H, 5·28%]. UV (ether) λ_{max} (log ϵ): 431 (3·79), 407 (3·74), 388 (3·56), 370 (3·23), 274 (4·78). Mass spectrum *m/e* (%): 210 (100), 209 (14), 207 (28), 183 (20), 178 (100), 165 (16), 152 (14), 105 (8).

9,9′ - *Dioxo* - 10,10′ - *dimethyl* - 9,9′,10,10′ - *tetrahydro* - 9,9′ - *biphosphaanthryl* (**5**). Compound **2** (2·3 mmole) and DBU (3·1 mmole) were refluxed in dry benzene (70 ml) under N_2 for 30 min and then H_2O (5 ml) was added. The mixture was worked up under air and decolourized at once. The benzene layer was separated and washed with H_2O, dried and evaporated to dryness. The residue was crystallized from alcohol/water yielding **6** (220 mg, 30%) and **5** (112 mg, 11%), m.p. 246–248° [Found: C, 74·03; H, 5·57; P, 13·77; $C_{28}H_{24}P_2O_2$ (M = 454·11), requires: C, 74·00; H, 5·33; P, 13·63%]. NMR (D6-DMSO): 8·0–7·7 (m, 2, aromatic protons); 7·7–7·3 (m, 6, aromatic protons); 4·28 (quartet, 1, $^3J_{H-H} = 7$ Hz, methine proton); 1·53 (d, 3, $^3J_{H-H} = 7$ Hz, CH_3). IR (KBr) $_{\nu max}$ in cm^{-1}; 1180 (s) P = 0. Mass spectrum *m/e* (%): 454 (44), 244 (88), 227 (29), 212 (58), 211 (100), 210 (46), 196 (25), 183 (25), 178 (36), 165 (35).

9 - *Hydroxy* - 9 - *oxo* - 10 - *methyl* - 9,10 - *dihydro* - 9 - *phosphaanthracene* (**6**). H_2O_2 was added slowly to a boiling suspension of **2** (1·1 mmole) in 2 N NaOH (15 ml). After refluxing for 1 hr the mixture was filtered. **6** was precipitated by adding 2 N HCl and was recrystallized (EtOH) yielding white crystals (204 mg, 75%), m.p. 298–304° [Found: C, 68·11; H, 5·63; P, 12·65; $C_{14}H_{13}PO_2$ (M = 244·21), requires: C, 68·85; H, 5·36; P, 12·68%]. NMR (D6-DMSO): 8·35 (s, 1, OH); 8·22–7·50 (m, 2, aromatic protons); 7·50–7·05 (m, 6, aromatic protons); 4·47 (octet, 1, $^3J_{H-H} = 7$ Hz, $^4J_{P-H} = 1{\cdot}7$ Hz, methine proton); 1·55 (d, 3, $^3J_{H-H} = 7$ Hz, CH_3). IR (KBr) ν_{max} in cm^{-1}: 2060 (m) P–OH, 1150 (s) P=O, 950 (s) P–OH. Mass spectrum *m/e* (%): 244 (100), 229 (92), 226 (40), 165 (40).

10 - *Methyl* - 9,10 - *dihydro* - 9 - *phosphaanthracene* (**7**). A mixture of **6** (20·4 mmole) and diphenylsilane (48 mmole) was heated at 250° for 2 hr under N_2 and afterwards vacuum destilled yielding **7** (1·7 g, 39%), m.p. 103–106° [Found: C, 78·48; H, 6·29; P, 14·18; $C_{14}H_{13}P$ (M = 212·12) requires: C, 79·23; H, 6·17; P, 14·60%]. NMR ($CDCl_3$): 7·75–7·02 (m, 8, aromatic protons); 5·15 (broad s, 1, PH); 4·07 (quartet, 1, $^3J_{H-H} = 7{\cdot}5$ Hz, methine proton); 1·41 (d, 3, $^3J_{H-H} = 7{\cdot}5$ Hz, CH_3). IR (KBr) ν_{max} in cm^{-1}: 2230, 2275 (m) P–H. Mass spectrum *m/e* (%): 212 (63), 210 (6), 197 (100), 196 (30), 178 (18), 165 (42).

Attempt to prepare 10 - *methyl* - 9 - *phosphaanthracene* (**1b**) *from* 10 - *methyl* - 9,10 - *dihydro* - 9 - *phosphaanthracene* (**7**). In a vacuum UV tube **7** (0·6 mmole), DDQ (0·55 mmole) and dry toluene (22 ml) were filled at −196° under N_2. The tube was sealed off after evacuation and was allowed to warm up to 25°. No **1b** could be detected by its UV spectrum.

10 - *Methyl* - 9,10 - *dihydro* - 9,10 - *ethano* - 9 - *phosphaanthracene* - 11,12 - *dicarboxylic anhydride* (**8**). DBU (1·4 mmole) was added under N_2 to a refluxing soln of **2** (1·3 mmole) in dry benzene (60 ml). After 2 hr a soln of maleic anhydride (1·4 mmole) in dry benzene (10 ml) was added. The yellow soln first decolourized and then turned red. The mixture was filtered and evaporated to dryness, yielding crude **8** (280 mg, 70%). Recrystallization from alcohol opened the anhydride, but from chloroform pure **8**, m.p. 271–274° was obtained [Found: C, 69·97; H, 4·38; P, 9·77; $C_{18}H_{13}PO_3$ (M = 308·25), requires: C, 70·13; H, 4·25; P, 10·05%]. NMR (D6-DMSO): 8·05–7·02 (m, 8, aromatic protons), 3·90 [d of d, 1, $^3J_{H-H} = 9{\cdot}5$ Hz, $^2J_{P-H} = 3{\cdot}1$ Hz, H(11)], 3·47 [d of d, 1, $^3J_{H-H} = 9{\cdot}5$ Hz, $^3J_{P-H} = 1{\cdot}7$ Hz, H(12)], 2·34 (s, 3, CH_3). IR (KBr) ν_{max} in cm^{-1}: 1760 (s), 1850 (s) anhydride. Mass spectrum *m/e* (%): 308 (3), 210 (100), 178 (32).

Compound **2** (0·25 mmole) in a vacuum vessel was sublimed through a pyrex tube of *ca* 500°. After cooling the vessel dry toluene (8 ml) was added and the UV spectrum of the yellow soln was recorded and indicated the formation of **1b** (±40% from extinction coefficients). Adding maleic anhydride (0·33 mmole) in dry THF (1 ml) decolourized the soln in a few min. The vessel was opened and 0·1 N KOH (5 ml) was added; the toluene layer was separated, neutralized, dried and evaporated, leaving after drying at 90°/0·1 mm a residue of **8** (30 mg, 39%), identified by its m.p. and IR spectrum. To the water layer 2 N HCl was added and **6** precipitated (12 mg, 20%).

The radical anion of 10 - *methyl* - 9 - *phosphaanthracene.*[12] A vacuum vessel with an ESR tube, a UV cell and a potassium mirror was filled under N_2 with **1b** (0·07 mmole) and dry THF (7·5 ml). After evacuation the vessel was sealed off. The UV spectrum of **1b** was measured and then the soln was brought into contact with the potassium mirror for 5 min and the soln turned green. The ESR spectrum was poorly resolved.

Acknowledgements—The investigations were supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for the Advancement of Pure Research (ZWO) and the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. The calculations were carried out using the TR4 computer at the Rechenzentrum der Universität Marburg.

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