

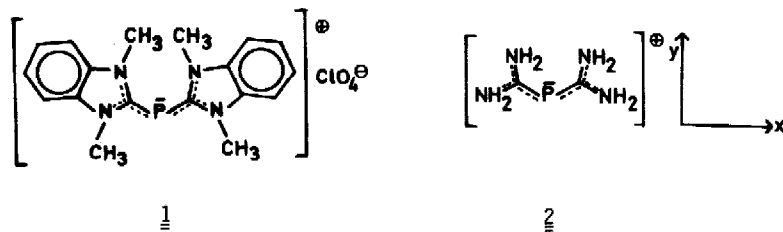
RADICALS FROM POLYMETHINE DYES, II. PHOSPHACYANINES ¹

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Polarographic investigations of phosphacyanine dyes² showed evidence of a reversible one-electron reduction³. In the case of Bis- [1.3-dimethyl-benzimidazole-(2)] -phosphacyanine-perchlorate 1 we were able to detect the ESR-signal of the neutral radical formed upon electrolytic reduction⁴



of a $5 \cdot 10^{-4}$ molar solution of 1 in DMF (supporting electrolyte tetrapropyl-ammonium-perchlorate in 0.05 molar concentration). Fig. 1 shows the ESR-spectrum (average of 8 scans).

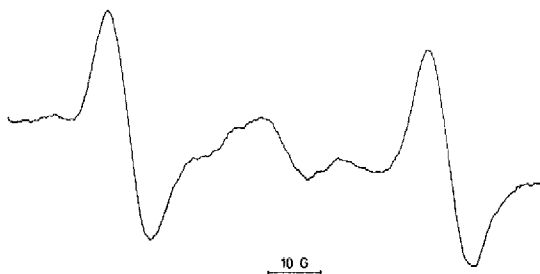


Fig. 1 ESR-spectrum of the neutral radical derived from 1.

Potentials lower than the polarographic half wave potential of -1.75 V ³ (Ag/AgCl/LiCl/CH₃CN reference electrode) were used. The radical is not very persistent. Its half-life is <30 sec.

The ESR-spectrum shows a doublet splitting due to the coupling of the unpaired electron with the ³¹P-nucleus. Hyperfine structure from coupling with protons or nitrogen atoms is not resolved. The weak signal in the central part of the spectrum arises from a radical formed in low concentration by reduction of the supporting electrolyte.

The value of $a^P = 63.8$ G is surprisingly high, as HMO-calculations show that the unpaired electron should occupy the antisymmetric $a_2-\pi$ -molecular orbital (MO) which has a node at the P-atom. In the corresponding case of the phosphorine-tri-anion radicals $a^P = 4.6$ G only.

Two mechanisms may be discussed to explain this phenomenon:

The value of a^P may be a consequence of the nonplanar structure of the molecule, as the two benzimidazole rings are twisted in opposite directions out of the molecular plane because of steric hindrance between two of the N-methyl groups. For the fragment 2, CNDO/2-calculations ⁷ show that in the twisted molecule there is a contribution of the phosphorus 3s atomic orbital (AO) to the $a_2-\pi$ -MO since the only element of symmetry is a twofold axis of rotation through the P-atom. To explain the value of a^P on the basis of these calculations an angle of twist $>60^\circ$ would be required. Steric interaction is expected to produce a twist of only 20° ⁸, so that either the CNDO/2 method gives too low a value for the 3s coefficient of the $a_2-\pi$ -MO or the radical is strongly twisted for some other reason. In this context it may be noteworthy that ¹H-NMR spectra of 1 show the existence of a dynamic process which renders the 4 N-methyl groups equivalent down to -100°C .⁹

The large value of a^P may also be due to an inversion of sequence of the first two antibonding π -MOs. With the unpaired electron in the symmetric $b_1-\pi$ -MO there would be a maximum of spin density at the P-atom.

In the phosphorine-mono-anion radicals ^{5,6} the unpaired electron occupies an orbital of this symmetry and in these radical anions $a^P = 29 - 35$ G, with spin densities at the P-atom $\rho_p \sim 0.5$. In the larger system 1 ρ_p cannot exceed this value. Inversion of sequence of antibonding π -MOs would therefore explain only part of the value of a^P .

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