Chemistry of Heterocyclic Compounds, Vol. 29, No. 12, 1993

PYRYLOCYANINES.
32.* FREE RADICALS OF A SERIES OF TERT-BUTYL-SUBSTITUTED PYRYLOCYANINES AND THEIR HETEROANALOGS

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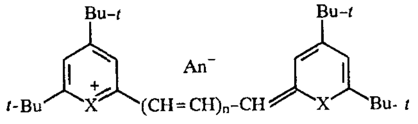
The one-electron reduction of tetra-tert-butyl-substituted pyrylo- and thiapyrylocyanines of the α- and γ-series was investigated by ESR spectroscopy and electrochemistry. The free radicals formed from cations of the indicated dyes were characterized.

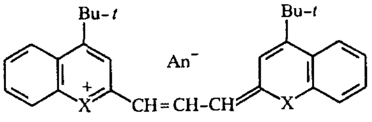
Interest in the study not only of the spectral but also of the chemical and redox properties of polymethine dyes is now increasing [2-4].

Earlier [3, 4] phenyl-substituted 2- and 4-pyrylocyanines were investigated. However, the selection of such objects for ESR spectroscopy is not entirely successful. Hyperfine interaction with the protons of the phenyl rings leads to a significant broadening of the lines in the ESR spectra or greatly complicates the spectral picture. As a result, an unambiguous interpretation frequently is impossible. It is also known that the angle of rotation of phenyl substituents to the plane of the chromophore depends on the nature of the heteroatom in the terminal groups [5]. This in turn hinders the disclosure of the patterns of distribution of spin density within the series studied.

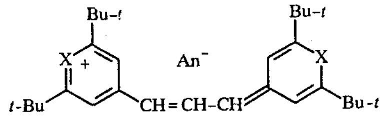
In this work ESR method was used to study free radicals of a series of tert-butyl-substituted pyrylocyanines and their heteroanalogs. Radicals were produced by chemical reduction of the corresponding dye cations I-X by alkali metals in THF.



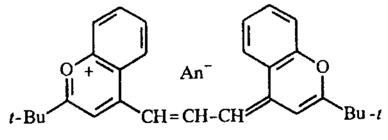
I-V



VI, VII



VIII, IX



X

I n=0, X=O; II n=1, X=O; III n=2, X=O; IV n=1, X=S; V n=1, X=NMe;
VI X=O; VII X=S; VIII X=O; IX X=S

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*For Communication 32, see [1].

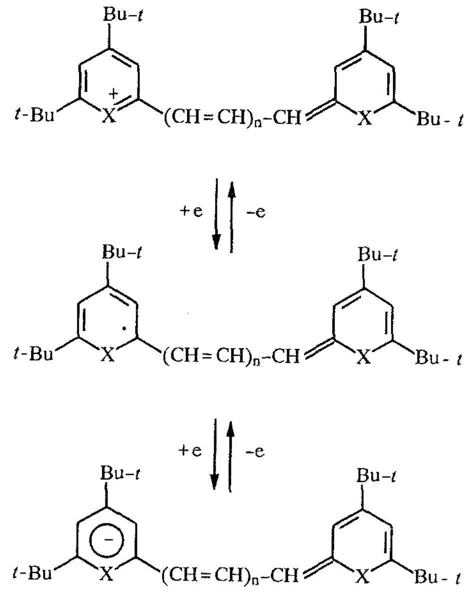
Institute of Organic Chemistry, Academy of Sciences of the Ukraine, Kiev-94, 253660. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 12, pp. 1638-1641, December, 1993. Original article submitted October 25, 1993.

0009-3122/93/2912-1414$12.50

TABLE 1. HFI Constants a_H (mT) and Spin Densities on Carbon Atoms (in parentheses)

Compound	X	n	α	β	γ	3,3′	5,5′
I	O	0	0,19(-0,07)			0,23(-0,08)	0,06(-0,06)
II	O	1	0,19(-0,07)	0,74(0,20)		0,19(-0,07)	
III	O	2	0,20(-0,05)	0,62(0,19)	0,24(-0,07)	0,15(-0,06)	
IV	S	1	0,24(-0,09)	0,61(0,19)		0,18(-0,05)	0,06(-0,06)
VI	O	1	0,24(-0,07)	0,70(0,20)		0,17(-0,06)	
VII	S	1	0,25(-0,09)	0,64(0,21)		0,23(-0,06)	
VIII	O	1	0,28(-0,07)	0,72(0,20)		0,10(-0,05)	0,07(-0,05)
IX	S	1	0,28(-0,07)	0,55(0,20)		0,14(-0,05)	0,10(-0,05)
X	O	1	0,29(-0,07)	0,69(0,21)		0,23(-0,05)	

The formation of radicals occurs according to the following scheme:



This scheme is analogous to that described in [4].

The absolute values of the hyperfine interaction constants, confirmed by a theoretical reconstruction of the spectra, are presented in Table 1. For the investigated compounds we calculated the distribution of spin density on the carbon atoms according to the MacLachlan method ($\lambda = 1.2$). An analysis of the ESR spectra and the results of the calculations showed that the unpaired electron is delocalized over the entire conjugated system of the molecule. In contrast to analogous pyrylo-4-cyanines [6], the radicals of pyrylo-2-cyanines II and III do not exhibit hyperfine interaction with protons in positions 5 and 5′ of the terminal groups. The ESR spectrum of radical II is a doublet of quintuplets. The intensity ratio in the quintuplets (1:2:3:2:1) differs from a binomial distribution, evidently on account of the contribution of the spectral line ($\delta = 0.08$ mT) of substituents in the 4,4′-positions of the heterocycles to the individual width. The shape of the spectrum does not depend on the temperature, varied in the range +25...−80°C. Replacement of the oxygen atoms in the rings by sulfur atoms (dye IV) leads to the appearance of hyperfine splitting on the protons in positions 5, 5′, explainable by the fact that, like the case of the corresponding cations of the dyes [7], in the radicals obtained from them the methine groups of the thiapyran rings are more involved in the general coupling system than those of the pyran rings.

From the data of Table 1 it is evident that in compounds containing three or five methine groups in the chain, the HFI constants a_H differ greatly for adjacent positions. The values of a_H for carbon atoms in odd positions are close to the values of the HFI constant in the meso-position of the monomethine dye I. The values of a_H for the atoms in the even positions of the chain are also close for all three trimethine dyes; they are somewhat decreased when the chain is lengthened and when the oxygen atom is replaced by a sulfur atom in the heterocycle.

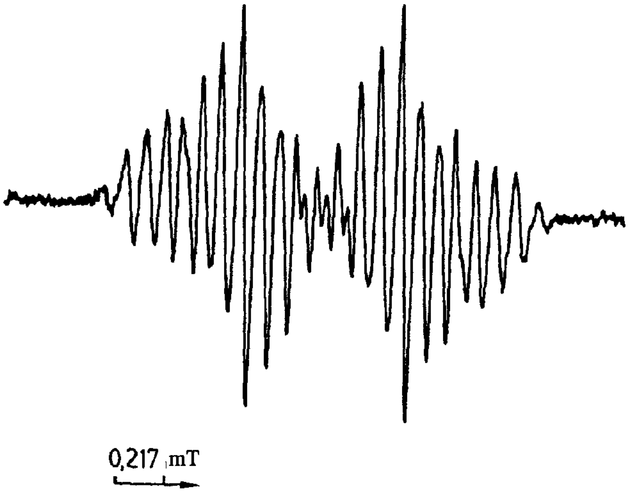


Fig. 1. ESR spectrum of the radical of the dye VI.

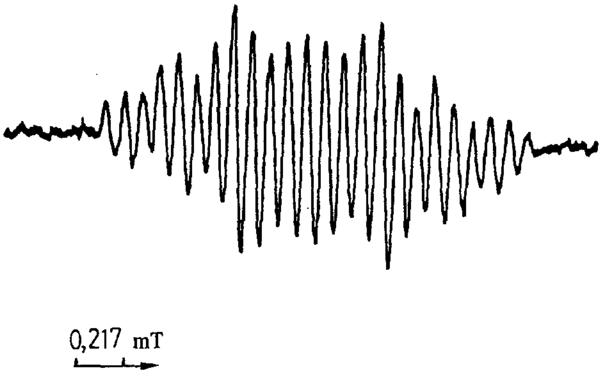


Fig. 2. ESR spectrum of the radical of the dye VII.

The results of the calculations predict a strong alternation of the values of the spin density, so that in the odd positions they have a negative sign, and in the even positions they have a positive sign; in the even positions the absolute value of the spin density is significantly greater. Such a picture of the distribution of spin density is due to the fact that the unpaired electron is found on orbitals whose nodes are situated close to the atoms in odd positions, as usual for symmetrical polymethines [8].

Annelation of the terminal groups does not introduce any substantial changes into the distribution of spin density, both for the α- and for the γ-isomers. In all cases HFI with the protons of the annelated rings is observed (Figs. 1, 2), and in radicals of the dyes VI and VII the unpaired electron interacts with four protons, whereas in the radical of the dye X it interacts with eight. This is evidence of the involvement of the entire heteroresidue in the general conjugation system.

Reduction of pyrido-2-carbocyanine V does not lead to a stable radical. The data of cyclic voltammetry show that the process is irreversible, and the reduction peaks are extremely weak.

EXPERIMENTAL

The ESR spectra were recorded on an SE/X-2543 radiospectrometer. The solutions were preliminarily evacuated to $4.5 \cdot 10^{-3}$ mm Hg. The solvent was purified according to the usual procedure.

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