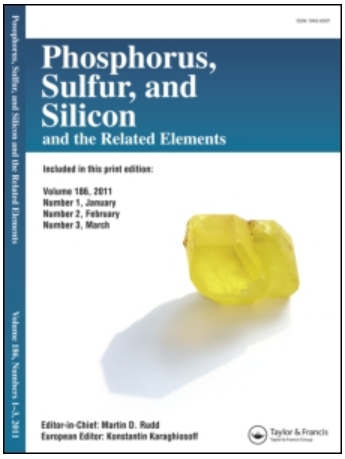

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CONFORMATIONAL DEPENDENCE OF THE ELECTRON ACCEPTOR CHARACTER OF ALKYLTHIOGROUPS IN ORGANIC RADICALS

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CONFORMATIONAL DEPENDENCE OF THE ELECTRON ACCEPTOR CHARACTER OF ALKYLTHIOGROUPS IN ORGANIC RADICALS.

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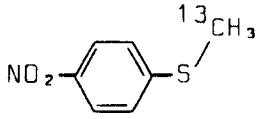
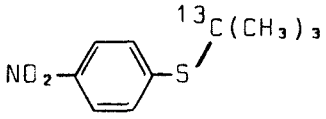
We have found that in the radical anions and nitroxides from p-alkylthionitrobenzenes, the alkylthiogroups behave as electron-withdrawing substituents and that their electron-acceptor character increases along the series methyl, ethyl, t-butyl. This behaviour could be explained in terms of a change of conformation of the SR substituent. Actually the ESR spectra of the radicals from the following isotopically substituted derivatives,



(I)



(II)

show very different hyperfine splitting constants at the ^{13}C: large and practically temperature independent in the case of the t-butylthionitrobenzene (II), and much smaller and strongly dependent on temperature with the methylthio analog (I). This finding provides evidence that in the latter derivative the methyl group deviates slightly from coplanarity with the aromatic ring, while the more stable conformation of (II) is that one placing the t-butyl group above the molecular plane with the Cp-S-^{13}C plane perpendicular to the aromatic system.

In the latter case, overlap between the π-system of the nitrobenzene moiety and the SR σ bond is at maximum, and therefore we may expect electron release from the π orbital containing the unpaired electron to the σ^* vacant orbital of the sulphur-carbon bond, since their energy separation is sufficiently small; this

implies that the whole -SR group acts as π acceptor.

INDO calculations showing that the electron transfer to the alkylthio substituent increases by progressively removing the R group from the molecular plane, strongly support the above explanation.