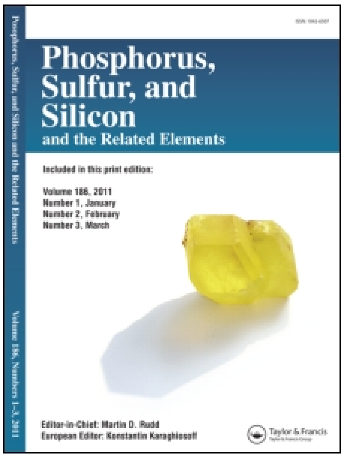

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CONFORMATIONAL INVESTIGATION OF SOME SYMMETRICALLY SUBSTITUTED DIALKYL MONO-SULFIDES AND DISULFIDES BY IR SPECTROSCOPY

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CONFORMATIONAL INVESTIGATION OF SOME SYMMETRICALLY SUBSTITUTED DIALKYL MONOSULFIDES AND DISULFIDES BY IR SPECTROSCOPY.

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Several infrared and Raman studies have been performed on compounds containing the disulfide group in the region of C-S and S-S stretching modes (1-4) in order to get a better insight of the correlations between molecular conformation and peculiar geometry parameters of the dihedral angle CS-SC.

In this context aimed also by the interest of providing structural models suitable for understanding the physico-chemical properties of polymers containing S-S chromophor both in the side and in the main chain, symmetrically substituted dialkyl disulfides R-S-S-R [R= $i\mathrm{C}_3\mathrm{H}_7$(I), $n\mathrm{C}_3\mathrm{H}_7$(II), $n\mathrm{C}_4\mathrm{H}_9$(III), $i\mathrm{C}_4\mathrm{H}_9$(IV) and $\mathrm{CH}_2\overset{*}{\mathrm{C}}\mathrm{H}(\mathrm{CH}_3)\mathrm{C}_2\mathrm{H}_5$(V)] as well as their analogous monosulfides have been investigated by IR spectroscopy.

Unlike previous studies we focused our attention on the spectral region between 1500 and 700 cm^{-1} where the spectral patterns are very sensitive to the conformations assumed by the alkyl groups.

The present investigation was based on the following statements:

a) possibility of obtaining crystalline samples by a tecnique got ready in our laboratories (5);

b) strong analogy between the spectra of alkyl bromides and alkyl disulfides in the liquid state;

c) extension to mono and disulfides of the results of conformational investigations performed on corresponding alkyl halides by normal frecuency calculation.

The spectral patterns of the alkyl bromides, examined in the liquid and crystalline state are very different, in particular a marked decrease of the number of the bands is observed in going from liquid to crystalline state, with the only exception of isopropyl bromide which, as expected, does not give rise to conformational isomerism.

The same situation takes place in (I), in fact the spectra recorded in the liquid, glass and crystalline state do not show any significant difference.

In contrast with this close analogy is the behaviour shown by the homologous derivatives (II-V) and corresponding alkyl bromides. The former in fact display a spectral complexity comparable both in crystalline and liquid state which is very similar to that observed on the spectra of the corresponding alkyl bromides in liquid phase. This aspect can be reasonably related to the existence of stable conformers, characterized by a different conformational situation of the two alkyl groups, present in the crystalline state and still dominant in the liquid state.

Therefore, assuming that the equilibrium value of the CS-SC dihedral angle for open chain disulfides is about ± 90°, it is easily understood on the basis of molecular models,the existence in the above compounds of symmetry elements of a helical structure in which the two alkyl groups assume different conformations.

In particular this situation should be cooperatively stabilized by nonbonded interactions reliable thanks to the presence of sulfur lone pairs in directional orbitals interacting with syn-hydrogen of βcarbon atom.

This hypothesis is independently supported by the high value of the optical rotation of (V) $\{[\Phi]_D^{25} + 204$ (neat)$\}$ and by the large differential dichroic absorption $\Delta\varepsilon_{265} = + 0.12$ (heptane) in the correspondence of the longest wavelength $n \rightarrow \sigma^*$ electronic transition of the disulfide chromophore.

In fact both values are very unusual in open chain compounds unless they are characterized by a severely limited number of conformers.

On the contrary corresponding monosulfides present a completely different behaviour. Their spectra in the crystalline state result simplified and very similar to the spectra of the corresponding alkyl chlorides recorded in the same conditions.

In this case the sulphur atom does not seem capable of influencing the conformational assembling of the alkyl groups, and the behaviour of this series of compounds seems to be very similar to that of the corresponding paraffins.

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