P-108

THE STRUCTURE OF ALKOXYFLUOROALKYL RADICALS AS STUDIED BY M.O. AND COMPUTER SIMULATION OF POLYCRYSTALLINE SPECTRA

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A novel approach to the structure of Alkoxyfluoroalkyl radicals (1,2), based on the analysis of the anisotropy of polycrystalline ESR spectra and on M.O. calculations to the INDO level of approximation, is presented. Polymeric primary and secondary perfluoroalkoxyalkyl radicals of type $ROCF_2\cdot$ and $ROCF(CF_3)$ were prepared by UV photolysis at 77 K of peroxidic perfluoropolyethers (2) and their ESR spectra were analyzed by computer simulation with the spin Hamiltonian (3):

$$\mathcal{H} = \beta S \cdot g \cdot H + \Sigma_i I_i \cdot A_i \cdot S - g_n B_n H \cdot I_i$$

A satisfactory computer simulation of $ROCF_2\cdot$ polycrystalline spectrum was obtained by assuming a pyramidal structure with a degree of bending of~19° and with an axially symmetric h.f. tensor with principal values:

$A_{/\!/}\ (F_\alpha) = 243.2$ (G) $\quad A_\perp\ (F_\alpha) = 68.1$ (G)

$ROCF_2\cdot$

$T_{/\!/}\ (F_\alpha) = 116.8$ (G) $\quad T_\perp = -58.4$ (G) $\quad A_{iso}\ (F_\alpha) = 126.5$ (G)

The ESR spectrum of the $RO\dot{C}F(CF_3)$- radicals was accounted for in terms of a pyramidal radical centre with a degree of bending of about 11° and a locked orientation of the CF_3 group with a Fluorine in the eclipsed position in respect to the half filled orbital. The pertinent h.f. tensors are:

F_α $\quad A_{/\!/} = 225$ (G) $\quad A_\perp = 20$ (G) $\quad A_{iso} = 88.3$ (G)

$RO\dot{C}F(CF_3)$ $\quad T_{/\!/} = 136.6$ (G) $\quad T_\perp = -68.3$ (G)

F_β (eclipsed) $A_{/\!/} = 70$ (G) $\quad A_\perp \sim 5$ (G)

A_{iso} (Free rotations) = 12.2 (G)

INDO calculations, performed to match the experimental anisotropic components of the h.f. tensor, by using the formula (4)

$$T_{i,j}(N) = g \cdot \beta \cdot \gamma_N \cdot \hbar \cdot \textstyle\sum_{\mu,\nu} \varrho_{\mu,\nu} \langle \varphi_\mu \cdot \varphi_\nu \,|\, \tau_{i,j}(N) \rangle$$

support the above conclusions and further show that a major contribute (>90%) to the dipolar tensor t_{ij} arises from the one-centre integrals of the F-2p orbitals, followed by (<10%) the two-centre integrals related to the u.s. population at the hybrid orbital of the adjacent carbon atom. The coefficients C(2p)=0.33 and C(2s)=0.086 for the Fluorine orbitals in the LCAO of the u. electron M.O. have been obtained, for radicals $ROCF_2\cdot$.

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