

## Rotational Isomers in Polyfluoroalkylaromatic Compounds

By R. D. CHAMBERS,\* J. A. JACKSON, and W. K. R. MUSGRAVE  
(University Science Laboratories, South Road, Durham)

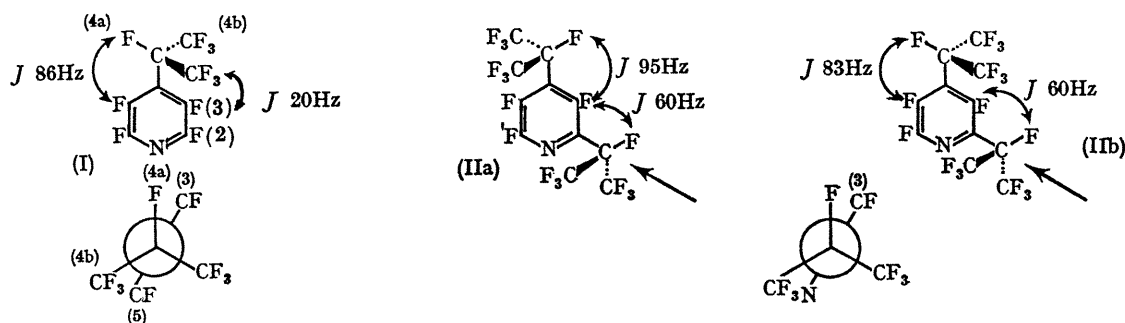
and L. H. SUTCLIFFE and G. J. T. TIDDY

(Department of Inorganic and Physical Chemistry, University of Liverpool)

THE synthesis of polyfluoroalkyl-pyridines has been described.<sup>1</sup> We report that large differences in the energy between various conformations of these systems allows the easy identification of rotational isomers by <sup>19</sup>F n.m.r. spectroscopy.

constant between the adjacent (4a) and (5a) fluorines could not be determined.

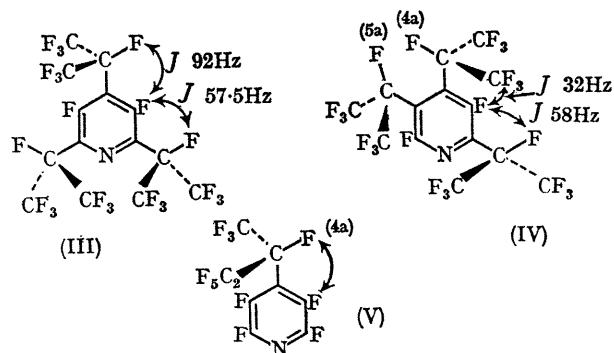
Perfluoro-s-butyl appears to have a larger barrier to rotation because, even at +30°, the spectrum of (V) indicated that the conformer shown is highly populated;



At 22° the n.m.r. spectra of perfluoroisopropylpyridines show broad lines which obscure the fine structure of the resonances. At low temperatures (−30° to −40°) the resonance lines are sharp and the splitting patterns can be observed. The low-temperature spectrum of the mono-substituted compound (I) showed six distinct resonances, including a single resonance from the CF<sub>3</sub> groups. A very large through-space coupling was observed between the 4a-fluorine and the eclipsed 3-fluorine with zero coupling with the corresponding 5-fluorine. Complementary coupling was observed for the CF<sub>3</sub> groups (4b) and must arise from the conformer shown (I). At +150° the 3- and 5-fluorines became chemically equivalent.

Also at −40°, the di-substituted compound showed two sets of resonances, ratio 1:2, which arise from conformers (IIa) and (IIb) respectively. The fixed conformation of the 2-perfluoroisopropyl group is attributable to the lower steric requirement of ring nitrogen than C–F, in interaction with CF<sub>3</sub>. The spectra of the trisubstituted compounds (III) and (IV) indicated a single conformation in each case, at −40°, pointing to interaction between the adjacent perfluoroisopropyl groups in (IV). These groups, unfortunately, have identical chemical shifts and so the coupling

between the 4a-fluorine and only the 3-fluorine occurred although at +150° the 3- and 5-fluorines became identical.



These systems appear to have abnormally large barriers to internal rotation and work is proceeding to determine accurate thermodynamic parameters and the sign of the "through-space" <sup>19</sup>F coupling.

(Received, December 4th, 1968; Com. 1659.)

\* R. D. Chambers, J. A. Jackson, W. K. R. Musgrave, and R. A. Storey, *J. Chem. Soc. (C)*, 1968, 2221.