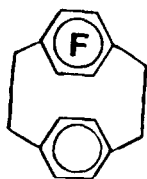


NON-BONDED INTERACTIONS BETWEEN PROXIMATE ARYL AND POLYFLUOROARYL RINGS

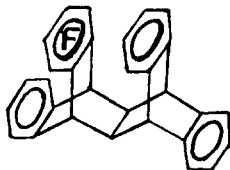
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As part of a larger study, we describe the preparation and use of model compounds with fixed geometries to assess non-bonded interactions between closely disposed phenyl and polyfluorophenyl groups. The ultraviolet and ^1H , ^{13}C , and ^{19}F nmr spectra of 4, 5, 7, 8-tetrafluoro [2.2] paracyclophane (I) have been compared with those for [2.2] paracyclophane (II) and octafluoro [2.2] paracyclophane (III). Studies are reported on competitive reactions between I and II and I and III. The results provide one basis for evaluating effects on chemical reactivity of transannular, inter-nuclear interactions in I. Similar studies on 1-phenyl-8-pentafluorophenyl naphthalene are in progress. The availability of tetrafluoro "vis-a-visene" (né "janusene") (IV) would provide an especially interesting model for further exploration.



(I)



(IV)

REACTION OF PERHALOALKANES BrCF_2X WITH NUCLEOPHILES. COMPETITIVE PROCESSES INITIATED BY ONE ELECTRON TRANSFER

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The condensation of various nucleophiles (enamines, ynamines, phenates, thiophenates, carbanions ...) with the perhaloalkanes BrCF_2X ($\text{X}=\text{Cl}$, Br , CF_2Br) gives haloperfluoroalkylketones, ethers, thioethers ... In the case of BrCF_2Cl the nature of the group introduced (CF_2Br or CF_2Cl) is a good indication of the mechanism involved: chlorodifluoromethyl compounds are formed by a radical chain process whereas bromodifluoromethyl products are the result of a carbenic chain mechanism. The reaction of phenates or thiophenates with $\text{BrCF}_2\text{CF}_2\text{Br}$, leading to bromotetrafluoroethylethers and thioethers, occurs with the formation of tetrafluoroethylene intermediate. All these competitive chain processes occur after an initial one electron transfer from nucleophiles to perhaloalkanes BrCF_2X giving a caged, intimate radical/anion radical pair.