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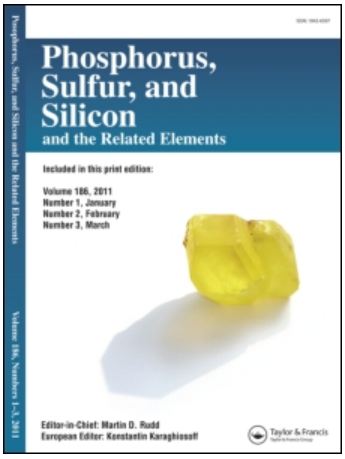

Phosphorus, Sulfur, and Silicon and the Related Elements

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Phosphorus-31 Fluorine-19 N.M.R. Through-Space Coupling

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PHOSPHORUS-31 FLUORINE-19 N.M.R. THROUGH-SPACE COUPLING

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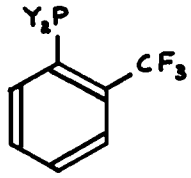
Through-space coupling, which may be observed when NMR active nuclei are close in space, is additive to any through-bond coupling. The magnitude of the coupling via the through-space mechanism varies according to the element, its valency and the distance between the coupled atoms - independently of the number of bonds separating the coupled atoms. The couplings between carbon-bound fluorine and phosphorus (in its three valent three coordinate state) have been studied using a series of o-(trifluoromethyl)phenylphosphanes (1). The phosphorus-fluorine coupling is lowest (29.6Hz) for the primary phosphine (1, Y = H). It is 43 Hz for the diethylamino derivative (1, R = Et_2N), rising to 53-56 Hz when Y is phenyl, heteroaromatic, alkyl and ethoxy groups, and then to 63 and 68 Hz for the phenoxy and fluoro derivatives. The PF coupling is largest (85-88 Hz) for the dichloro and dibromo compounds. The coupling constants are zero or close to zero for the corresponding salts, oxides and sulphides. The changes in the magnitude of the phosphane couplings are discussed in terms of conformational and electronic influences on a through-space spin-spin coupling mechanism.



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