Chemically-induced Dynamic Polarization of ^{19}F from Spin-delocalized Radicals

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Summary CIDNP of the ^{19}F n m r spectra are observed for the coupling products from the reaction of *p*-fluorobenzyl chloride and n-butyl-lithium

THE observation of chemically induced dynamic nuclear polarization (CIDNP) in the ^{1}H n m r spectra of products from reactions which proceed through radical intermediates has become common[1] since the original observations [2] We now report the observation of polarized ^{19}F n m r spectra for the coupling products from the reaction of *p*-fluorobenzyl chloride and n-butyl-lithium These spectra provide the first reported examples of CIDNP for ^{19}F nuclei and for distant nuclei in products arising from a spin-delocalized radical intermediate

Samples 1 0M in *p*-fluorobenzyl chloride and 1 6M in n-butyl-lithium in hexane were prepared and their reaction initiated in the n m r spectrometer by adding a small amount of diethyl ether Under these conditions the major products are *pp'*-difluorobibenzyl and *p*-fluoropentylbenzene [3] The spectrometer was adjusted to the fluorine resonance frequency expected for these products† and the spectrum scanned 5 sec after ether addition Typical spectra shown in Figures 1a and 2 demonstrate the intense polarization observed for both products The multiplet effect‡ predominates in Figure 1a, although in Figure 2a multiplet effect and a strong emission are superimposed The polarization of the *p*-fluorine nucleus five atoms removed from the reaction site is an expected consequence of spin delocalization in the benzyl radical (relative spin densities for α, *ortho-*, *meta-*, and *para*-carbon atoms are *ca* 1 0 : 3 : — 0 1 : 0 4),[8] but is not observed for aromatic ^{1}H nuclei in this reaction nor in the analogous reaction of unsubstituted benzyl chloride, and is apparently without precedent The greater sensitivity of ^{19}F as compared with ^{1}H probably results from its participation in the π molecular orbital containing the unpaired electron Polarized ^{19}F spectra are also observed for products from the analogous reactions of *meta-* and *ortho*-fluorobenzyl chlorides [9]

CIDNP is potentially a powerful tool for studying the

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† ^{19}F chemical shifts relative to fluorobenzene are 4 5^4 p p m for *pp'*-difluorobibenzyl and 5 1 p p m for *p* fluoropentylbenzene (measured in this work with authentic material)

‡ Nuclear polarization effects can be classified[5] as those in which the transitions for a single set of equivalent nuclei exhibit both emission (*E*) and enhanced absorption (*A*) but with the net magnetization equalling the equilibrium magnetization (the multiplet effect) [6 7] and those in which either emission or absorption with a net change in magnetization occurs Whether either effect is observed depends in an ill defined manner on the reaction mechanism and the electron and nuclear relaxation times

mechanism of radial reactions, and it is to be noted that use of a π-delocalized fluorophenyl group as a probe in such studies would afford several advantages. The effects are large and sensitive to the mechanism by which products form (*e.g.*, compare Figures 1a and 2), the spectra are not masked by normal solvent resonances, the large chemical-shift range for ^{19}F allows ready assignment of observed spectra, and essentially the same spin system exists for each product.

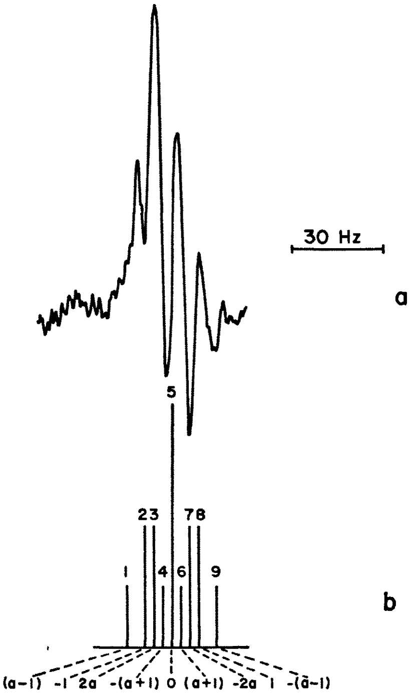

FIGURE 1. (a) *Polarised* ^{19}F *spectrum of bis*(p-*fluoro*)*bibenzyl*; (b) *Stick diagram simulation of equilibrium spectrum and predicted relative intensities for polarised transitions.*

The multiplet effect in Figure 1a is of further interest as it is more complex than any previously reported for a set of equivalent ^{1}H nuclei. Proton spectra exhibiting a multiplet effect change phase from absorption (*A*) to emission (*E*) only once (*i.e.*, *AE* or *EA* going from low to high field) whereas the phase of the polarization in Figure 1a changes at least five times. *p*-Fluorophenyl corresponds to an AA′BB′X spin system, however, and the ^{19}F nucleus (X) is distinguished from the previously studied protons by being coupled to two nonequivalent nuclei (H_o and H_m) which have hyperfine coupling constants of opposite sign.§ A qualitative understanding of Figure 1a can be gained by approximating the fluorine resonance as a triplet of triplets, as shown by the stick diagram in Figure 1b with *J*(F–H-*o*) 5·8 Hz and *J*(F–H-*m*) 8·7 Hz,[12] and considering the polarization of each triplet individually according to the predictions of Closs[6] and Kaptein and Oosterhoff.[7] Lines resulting from the F(H-*m*)$_2$ triplet (1,2,4; 3,5,7; and 6,8,9) are thus polarized with relative intensities $\pm\ 1 : 0 : \mp\ 1$, respectively; and those resulting from the F(H-*o*)$_2$ triplet (1,3,6; 2,5,8; and 4,7,9) have relative intensities $\mp$ a : 0 : $\pm$ a, respectively, where $a > 1$ since $|A_{o\text{-H}}| > |A_{m\text{-H}}|$. Summing the effects, selecting *EA* phasing for the F(H-*m*)$_2$ triplet and *AE* for the F(H-*o*)$_2$ triplet, yields the relative intensities indicated beneath Figure 1b, which closely reproduce the general features of the experimental spectrum.

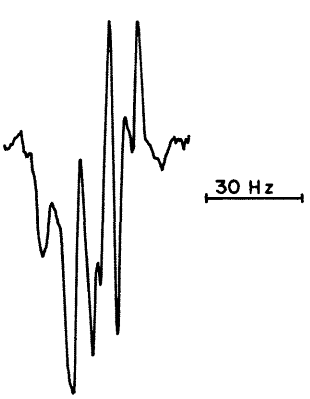

FIGURE 2. *Polarised* ^{19}F *spectrum of* p-*fluoropentylbenzene.*

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§ Theoretical predictions[10] concur with n.m.r. contact-shift measurements[11] for *p*-fluorophenyl groups in π-delocalized paramagnetic compounds which demonstrate that the nuclear hyperfine coupling constants A_F and $A_{m\text{-H}}$ are positive while $A_{o\text{-H}}$ is negative; the differences arising from the alternation of the sign of the spin density around the phenyl ring and the different mechanisms by which hydrogen and fluorine sense the spin density in the π-orbital of the contiguous carbon atom.

[1] *e.g.*, H. R. Ward, R. G. Lawler, and R. A. Cooper, *J. Amer. Chem. Soc.*, 1969, **91**, 746; *Tetrahedron Letters*, 1969, 527; A. R. Lepley, *Chem. Comm.*, 1969, 1460; A. Rieker, P. Niedener, and D. Leibfritz, *Tetrahedron Letters*, 1969, 4287; R. Kaptein, *Chem. Phys. Letters*, 1968, **2**, 261.

[2] H. R. Ward and R. G. Lawler, *J. Amer. Chem. Soc.*, 1967, **89**, 5519; J. Bargon and H. Fischer, *Z. Naturforsch*, 1967, **22a**, 1551.

[3] D. F. Hoeg and D. I. Lusk, *J. Organometallic Chem.*, 1966, **5**, 1.

[4] R. G. Pews and N. D. Ojha, *J. Amer. Chem. Soc.*, 1969, **91**, 5769.

[5] H. Fischer and J. Bargon, *Accounts Chem. Res.*, 1969, **2**, 110.

[6] G. L. Closs, *J. Amer. Chem. Soc.*, 1969, **91**, 4552.

[7] R. Kaptein and L. J. Oosterhoff, *Chem. Phys. Letters*, 1969, **4**, 195, 214.

[8] S. V. Kulkarni and C. Trapp, *Mol. Phys.*, 1969, **17**, 209.

[9] Unpublished work of Dr. D. T. Dix of this laboratory.

[10] A. J. Hinchliffe and J. N. Murrell, *Mol. Phys.*, 1968, **14**, 147; J. A. Pople, D. L. Beveridge, and P. A. Dobash, *J. Amer. Chem. Soc.*, 1968, **90**, 4201.

[11] D. R. Eaton, A. D. Josey, W. D. Phillips, and R. E. Benson, *Mol. Phys.*, 1962, **5**, 407.

[12] Values reported for *p*-fluorotoluene, T. Schaefer and W. G. Schneider, *Canad. J. Chem.*, 1959, **37**, 2078.