Observation of N.m.r. Spectra of ^{13}C in Natural Abundance

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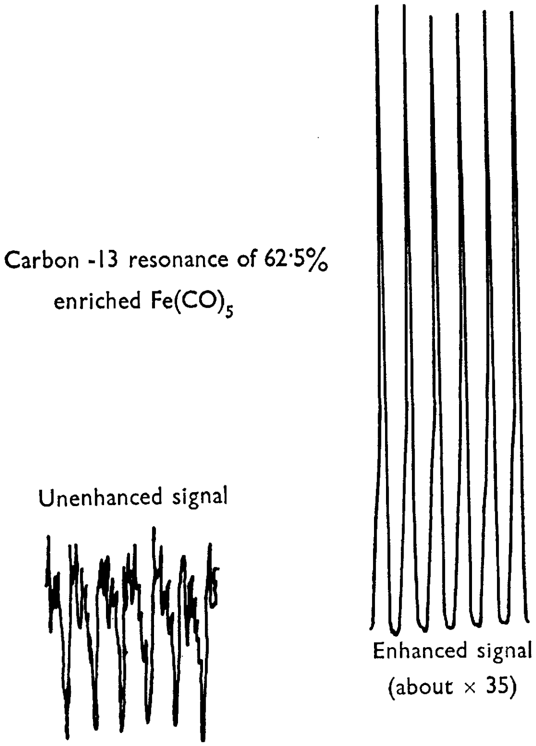
WE have used the nuclear-electron Overhauser effect[1,2] to observe magnetic resonances from ^{13}C nuclei in natural abundance (1·1%).

The apparatus used had a permanent magnetic field strength of 3300 gauss which corresponds to a ^{13}C resonance frequency of 3·5 Mc./sec. and an electron resonance frequency of 9·125 kMc./sec.[3] The probe consisted of a cylindrical microwave cavity which was operated in the H_{011} mode and had an n.m.r. coil of 20 turns (diameter 4 mm.) located at its centre. The effective sample size was about 35 mm.[3] All samples contained the 2,4,6-tri-t-butylphenoxy-radical.[2]

The ^{13}C resonance of a 62·5% enriched sample of $Fe(CO)_5$ was found to be negatively enhanced about 35 times (Figure 1), and the enhancement factor obtained by extrapolating to infinite microwave power[2] was -50. The spin–lattice relaxation time of the ^{13}C nuclei in this solution was 1·5 sec. Figure 2 shows the enhanced resonances obtained from the ^{13}C nuclei of benzene, of chloroform, and of a 40 : 60 mixture of benzene and chloroform. Figure 3 shows the positively enhanced ^{13}C resonance of a concentrated solution of the radical precursor (2,4,6-tri-t-butylphenol) in benzene. In all cases the spin–lattice relaxation times of the ^{13}C nuclei were reduced to a few seconds by addition of the free radical.

Triple irradiation experiments indicated that a strong three spin effect[4–6] was operative in solutions of benzene, cyclohexane, chloroform, bromoform, and hexafluorobenzene containing less than



The resonance has been scanned repeatedly

FIGURE 1

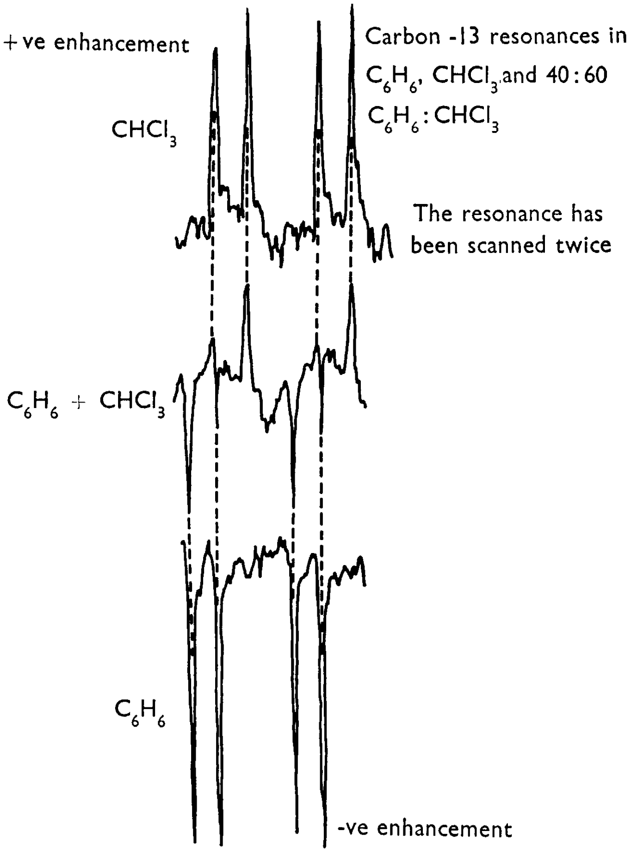


FIGURE 2

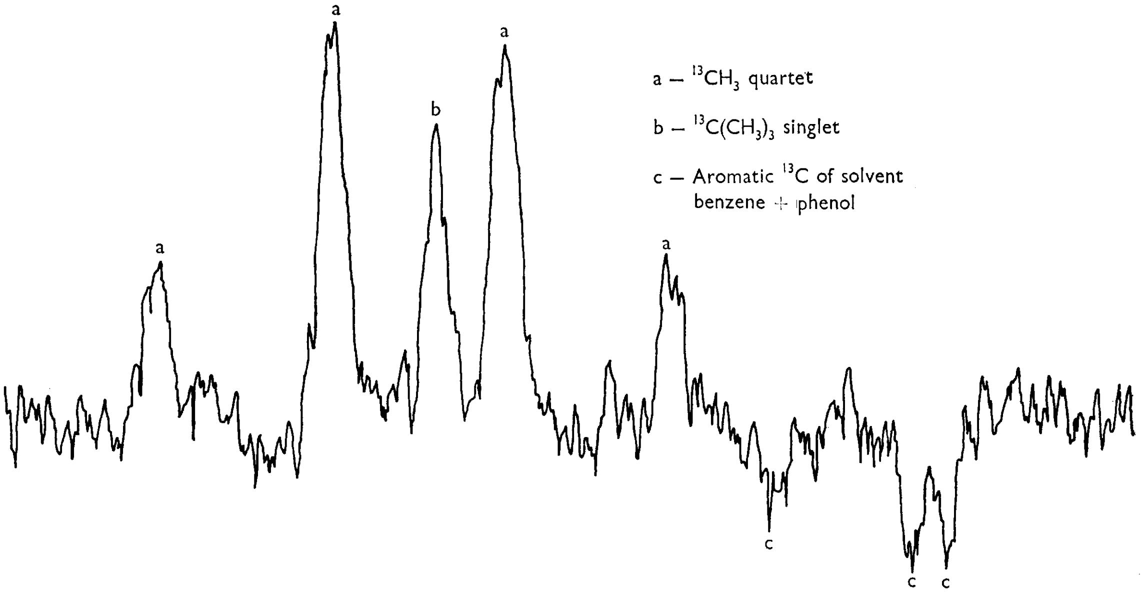


FIGURE 3

about 10^{-3}M of free radical. Decoupling the 3rd spin (H or F) produced a considerable increase in the signal to noise ratio. These results are in agreement with those obtained by other workers.[4,7–9]

The positive enhancements of the tertiary butyl ^{13}C nuclear resonance of the radical precursor are in agreement with the theory put forward to explain positively enhanced tertiary butyl proton resonances in this system[10] but the other positive enhancements are unexpected. Calculations[11] have indicated that scalar coupling between electrons and ^{13}C nuclei should be about twice as effective as between electrons and protons for a given amount of electron mixing but this does not seem sufficient to account for the strong positive enhancement. However, contact between a radical electron and a large halogen atom (as possessed by all the molecules whose ^{13}C resonances are positively enhanced) may great facilitate scalar coupling and give rise to the observed behaviour.

Attempts have been made to observe enhanced ^{13}C spectra in a magnetic field of 12,500 gauss. No spectra have been observed for ^{13}C nuclei in natural abundance, however an enriched sample of $Fe(CO)_5$ gave a ^{13}C resonance negatively enhanced about 4 times. This suggests that the electron correlation spectrum is near zero at this field.

TABLE

Solvent	Sign of enhancement	Notes
C_6H_6	—	Very strong
C_6F_6	—	Very strong
C_6D_6	—	
C_6H_5F	—	
C_6H_5–CH_3	—	
C_6H_5–CF_3	—	
C_6H_4–$(CH_3)_2$	—	
C_6H_{12}	—	
$Fe(CO)_5$	—	Enriched sample
$CHCl_3$	+	
$CHBr_3$	+	
CH_2Cl_2	+	
CH_2Br_2	+	
CH_2I_2	+	
CH_3I	—	
CCl_4	+	
$CFCl_3$		No resonance observed
CF_3CCl_3	—	
CH_3OH	—	
CH_3CN	—	—^{13}CN resonance very strong
$H{\cdot}CO_2{\cdot}CH_3$	—	
$CH_3{\cdot}CH_2{\cdot}OH$	—	
$(C_2H_5)_2CO$	—	
CS_2	—	
2,4,6-Tri-t-butylphenol	+ (t-butyl) — (aromatic)	Conc. solution in benzene

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[1] L. Solomon, *Phys. Rev.*, 1955, **99**, 559.

[2] R. A. Dwek, J. G. Kenworthy, D. F. S. Natusch, R. E. Richards, and D. J. Shields, *Proc. Roy. Soc.*, 1966, *A*, **291**, 487.

[3] J. G. Kenworthy and R. E. Richards, *J. Sci. Instr.*, 1965, **42**, 675.

[4] K. H. Hausser and F. Rheinbold, *Phys. Letters*, 1962, **2**, 53.

[5] D. F. S. Natusch and R. E. Richards, *Chem. Comm.*, 1966, 185.

[6] D. F. S. Natusch and R. E. Richards, *Mol. Phys.*, in the press.

[7] C. H. Holm, *J. Chem. Phys.*, 1957, **26**, 707.

[8] E. G. Paul and D. M. Grant, *J. Amer. Chem. Soc.*, 1961, **83**, 1838.

[9] J. P. Imbaud, *Compt. rend.*, 1965, **261**, 5442.

[10] R. A. Dwek, J. G. Kenworthy, and R. E. Richards, *Mol. Phys.*, in the press.

[11] M. C. R. Symons, *Adv. Phys. Org. Chem.*, 1963, **1**, 183.