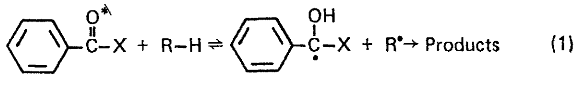
Assignment of Carbon-13 N.M.R. Lines using CIDNP

By H. Michael Maurer, Gian Piero Gardini, and Joachim Bargon*
(*IBM Research Laboratory, San Jose, California* 95193)

Summary ^{13}C N.m.r. resonance lines in aromatic aldehydes, ketones, and phenols can be assigned using photoreduction reactions which produce CIDNP; the technique is illustrated for acetophenone.

The assignment of ^{13}C n.m.r. lines in aromatic compounds is sometimes difficult and even a combination of techniques[1] such as $^{13}C\{^1H\}$ off-resonance noise decoupling, $^{13}C\{^1H\}$ selective decoupling, and interpretation of ^1H-coupled spectra does not always lead to a conclusive answer. We here demonstrate that additional information gained from chemically induced dynamic nuclear polarization (CIDNP) can assist in the assignment of the carbon resonance lines.

As an example we have chosen the study of aromatic aldehydes and ketones, where the assignment of *ortho* and *meta* carbons remains ambiguous in some cases. It is well established that photoexcited carbonyl ($>C{=}O^*$) compounds can reversibly abstract a hydrogen atom for instance from a benzylic hydrocarbon,[2] secondary alcohol,[3] or phenol;[4,5] see equation (1). For R=phenoxy both radicals



(1)

formed during the reversible reaction are odd alternate radicals, and thus have an alternating spin density in the aromatic ring, as is confirmed by molecular orbital calculations using, *e.g.*, the INDO method.[6] Since the signs of the CIDNP polarizations follow the signs of the hyperfine coupling constants, the alternating spin density should result in an alternating polarization of the n.m.r. lines measured during the photoreaction. This fact is found to be very general and has been observed previously during photoexcitation of acetophenone–phenol in the proton CIDNP spectrum.[4]

The ^{13}C n.m.r. spectrum of acetophenone has been reported by several investigators.[7–12] The chemical shift difference of the carbon atoms in the *ortho* and *meta* positions is only 0·3 p.p.m.; therefore, these two resonance lines could previously not be assigned conclusively.[7–9] The resonance at higher field (128·3 p.p.m.) was assigned to the *meta* carbon and that at 128·6 p.p.m. to the *ortho* carbon without a detailed justification being given,[10,11] while the reverse assignment of these lines was deduced from low temperature spectra.[12]

We irradiated a solution of acetophenone (0·2 mol/l) and benzene-1,3,5-triol (0·05 mol/l) in methanol inside the modified probe of a Varian CFT-20 spectrometer from the side *via* a lightguide, with u.v. radiation from a 1000 W high-pressure mercury–xenon lamp, filtered through aqueous $NiSO_4$–$CoSO_4$.[13] Benzene-1,3,5-triol was chosen because of its symmetry. It gives rise to only two resonance lines, which are located outside the chemical shift range of the ring carbons of acetophenone. The Figure shows the proton decoupled ^{13}C n.m.r. spectrum during the irradiation. A strong emission for the carbonyl carbon (A) as well as a weaker emission for lines C and E, and an enhanced absorption for lines B and D are observed. The assignment of lines A, B, and C to carbonyl, quaternary, and *para* carbons, respectively, is unambiguous. In accordance with the sign rule of CIDNP[14] the *para* and the carbonyl carbons are observed in emission, whereas the quaternary carbon exhibits absorption. From the alternating sign pattern of the spin density and the correct prediction of the sign of the resonances above it must be concluded that line D (129·5 p.p.m.) belongs to the *meta* carbon and line E (129·2 p.p.m.) to the *ortho* carbon of acetophenone. These findings reverse the assignment given in refs. 10 and 11. The benzene-1,3,5-triol shows emission from the carbon carrying the hydroxy group and absorption for the other carbon.

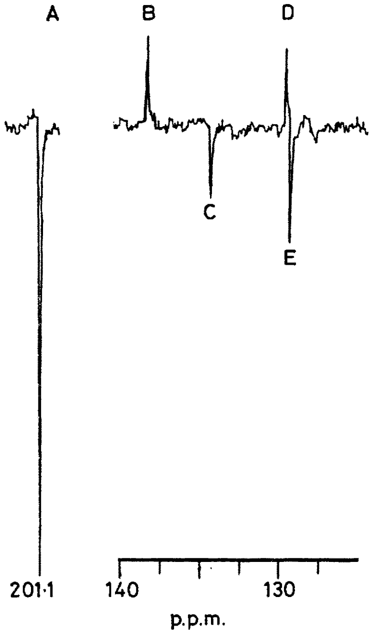


Figure. Proton decoupled pulse Fourier transform ^{13}C n.m.r. spectrum of a solution of acetophenone (0·2 mol/l) and benzene-1,3,5-triol (0·05 mol/l) in methanol during u.v.-irradiation; chemical shifts are given downfield from internal Me_4Si, 1200 accumulations.

Preliminary results using derivatives of acetophenone, benzophenone, and acetyl-naphthalenes show that these reactions can also be used to assign the resonance lines of the ring carbons in these compounds. In some special cases the hydroxy and carbonyl functions may also belong to the same molecule as, for example, in vanilline.

In the dark spectrum recorded under the same conditions, only the resonance lines of the *ortho* and *meta* carbons of acetophenone are seen clearly; thus the lines show a strong signal enhancement in the CIDNP spectrum (*ca.* 10—50). This 'amplification' may be used to advantage in order to obtain within a reasonable measuring time the ^{13}C n.m.r. spectra of such phenols or carbonyl compounds that have a low solubility or are available in small quantities only. The same approach has been used before in ^{1}H n.m.r. investigations of peptides and proteins.[15]

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[1] F. W. Wehrli and T. Wirthlin, 'Interpretation of Carbon-13 NMR Spectra,' Heyden, London, 1978, and references therein.

[2] G. L. Closs and L. E. Closs, *J. Amer. Chem. Soc.*, 1969, **91**, 4550.

[3] J. A. den Hollander, A. J. Hartel, and P. H. Schippers, *Tetrahedron*, 1977, **33**, 211.

[4] S. M. Rosenfeld, R. G. Lawler, and H. R. Ward, *J. Amer. Chem. Soc.*, 1973, **95**, 946.

[5] H.-D. Becker, *J. Org. Chem.*, 1967, **32**, 2140.

[6] J. A. Pople and D. L. Beveridge, 'Approximate Molecular Orbital Theory,' McGraw-Hill, New York, 1970.

[7] G. L. Nelson, G. C. Levy, and J. D. Cargioli, *J. Amer. Chem. Soc.*, 1972, **94**, 3089.

[8] L. Ernst, *J. Magnetic Resonance*, 1976, **22**, 279.

[9] L. F. Johnson and W. C. Jankowski, 'Carbon-13 NMR Spectra,' Wiley, New York, 1972.

[10] M. J. Loots, L. R. Weingarten, and R. H. Levin, *J. Amer. Chem. Soc.*, 1976, **98**, 4571.

[11] D. W. Beistel and W. D. Edwards, *J. Phys. Chem.*, 1976, **80**, 2023.

[12] T. Drakenberg, J. M. Sommer, and R. Jost, *Org. Magnetic Resonance*, 1976, **8**, 579.

[13] M. Kasha, *J. Opt. Soc. Amer.*, 1948, **38**, 929.

[14] R. Kaptein, *Chem. Comm.*, 1971, 732.

[15] K. A. Muszkat and C. Gilon, *Nature*, 1978, **271**, 685; R. Kaptein, K. Dijkstra, and K. Nicolay, *ibid.*, **274**, 293.