

of the pesticides was not tested, the absence of CO₂ formation from the chemical in aerobic conditions is good evidence for cometabolism. Moreover, the patterns of metabolism previously noted for monuron (Tillmanns et al., 1978) and chlorobenzilate (Miyazaki et al., 1969, 1970) are consistent with the view that the substrates are cometabolized.

The data show that monuron, diuron, and linuron were mineralized at the lower concentrations (10 or 0.5 µg/L) but not at the higher concentration. At the higher levels, monuron (10 mg/L), but not diuron or linuron (2.0 mg/L), was converted to organic products; these products possibly included (4-chlorophenyl)urea and 4-chloroaniline. It is not clear why monuron behaved differently from the other two phenylureas. Although it is not known why mineralization occurs at one concentration and cometabolism takes place at another or why mineralization occurs in waters containing sediment and cometabolism takes place in sediment-free waters, different organisms may be involved. In this regard, Rubin et al. (1982) suggested that phenol was mineralized at different concentrations by two different kinds of organisms, oligotrophs at the lower concentration and eutrophs at the higher concentration.

Cunninghamella echinulata was reported to convert monuron to (4-chlorophenyl)urea and 3-(4-chlorophenyl)-1-methylurea (Tillmanns et al., 1978). Kearney and Kaufman (1965) did not find 4-chloroaniline to be formed when monuron was used as the substrate for bacterial enzymes. Nevertheless, in the present studies, 4-chloroaniline and (4-chlorophenyl)urea appeared to be products generated from monuron in sewage, at least on the basis of cochromatography. A *Pseudomonas* sp. was found to mineralize 4-chloroaniline (Zeyer and Kearney, 1982). Little attention has been given to the metabolism of chlorobenzilate by microorganisms, although Miyazaki et al. (1969) reported the conversion of 4,4'-dichlorobenzilic acid to 4,4'-dichlorobenzophenone. The present findings indicate more extensive degradation inasmuch as CO₂ was generated from ring-labeled chlorobenzilate.

Registry No. Chlorobenzilate, 510-15-6; diuron, 330-54-1; monuron, 150-68-5; linuron, 330-55-2.

LITERATURE CITED

- Boethling, R. S.; Alexander, M. *Appl. Environ. Microbiol.* **1979**, *37*, 1211.
- Edwards, C. A. In "Pesticides in Aquatic Environments"; Khan, M. A. Q., Ed.; Plenum Press: New York, 1977; pp 11-38.
- El-Dib, M. A.; Aly, O. A. *Water Res.* **1976**, *10*, 1055.
- Hill, G. D.; McGahen, J. W.; Baker, H. M.; Finnerty, D. W.; Bingeman, C. W. *Agron. J.* **1955**, *47*, 93.
- Jacobson, S. N.; O'Mara, N. L.; Alexander, M. *Appl. Environ. Microbiol.* **1980**, *40*, 917.
- Johnson, H. D.; Ball, R. C. In "Fate of Organic Pesticides in the Aquatic Environment"; American Chemical Society: Washington DC, 1972; pp 1-10.
- Kearney, P. C.; Kaufman, D. D. *Science (Washington, D.C.)* **1965**, *147*, 740.
- Miyazaki, S.; Boush, G. M.; Matsumura, F. *Appl. Microbiol.* **1969**, *18*, 972.
- Miyazaki, S.; Boush, G. M.; Matsumura, F. *J. Agric. Food Chem.* **1970**, *18*, 87.
- Morley, H. V. In "Pesticides in Aquatic Environments"; Khan, M. A. Q., Ed.; Plenum Press: New York, 1977; pp 53-74.
- Rubin, H. E.; Subba-Rao, R. V.; Alexander, M. *Appl. Environ. Microbiol.* **1982**, *43*, 1133.
- Sheets, T. J. *J. Agric. Food Chem.* **1964**, *12*, 30.
- Subba-rao, R. V.; Rubin, H. E.; Alexander, M. *Appl. Environ. Microbiol.* **1982**, *43*, 1139.
- Tillmanns, G. M.; Wallnoefer, R. R.; Engelhardt, G.; Olie, K.; Hutzinger, O. *Chemosphere* **1978**, *7*, 59.
- Wang, Y. S.; Subba-Rao, R. V.; Alexander, M. *Appl. Environ. Microbiol.* **1984**, *47*, 1195.
- Zeyer, J.; Kearney, P. C. *Pestic. Biochem. Physiol.* **1982**, *17*, 215.

Received for review September 7, 1984. Accepted January 7, 1985. This project was supported by funds provided by the U. S. Department of Agriculture under Agreement No. USDA-TPSU-CU-2057-261 and the U. S. Environmental Protection Agency under assistance agreement CR809735-02-0. The text has not been subjected to EPA's required peer and administrative review and therefore does not necessarily reflect the views of the Agency, and no official endorsement should be inferred.

Diphenyl Ether Herbicides: Assignment of the Proton and Carbon-13 Nuclear Magnetic Resonance (NMR) Spectra of Acifluorfen, Acifluorfen Methyl, and Bifenox with Two-Dimensional NMR

G. H. Lee

A complete assignment of the proton and carbon-13 nuclear magnetic resonance (NMR) spectra of three diphenyl ether herbicides, i.e., acifluorfen [sodium 5-[2-chloro-4-(trifluoromethyl)phenoxy]-2-nitrobenzoate], acifluorfen methyl [methyl 5-[2-chloro-4-(trifluoromethyl)phenoxy]-2-nitrobenzoate], and bifenox [methyl 5-(2,4-dichlorophenoxy)-2-nitrobenzoate], has been achieved based on data generated from coupling and two-dimensional NMR experiments.

INTRODUCTION

Derivatives of benzoic acid, e.g., dicamba and phenoxy acids, e.g., 2,4-D, have long been used as agronomically

important herbicides. The search for a synthesized herbicidal activity between these two classes of chemicals has led to the discovery of several new diphenyl ether type herbicides, e.g., nitrofen and bifenox. Further refinement of the activity has led to the discovery of a new and very potent selective herbicide—acifluorfen (Johnson et al., 1978). Since the recent introduction of acifluorfen, numerous patents disclosing newer generations of this type of herbicide have appeared in the literature (Cartwright

Analytical and Information Sciences Department, Applied Research and Development, Sun Refining and Marketing Company, Marcus Hook, Pennsylvania 19061-0835.

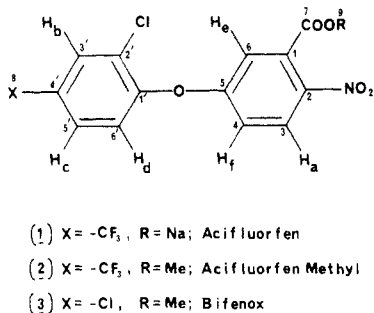


Figure 1. Structures of the diphenyl ether herbicides examined.

and Collins, 1979, 1981; Barton et al., 1981; Grove, 1981; Lee, 1983a, 1983b; Heiba, 1983; Steffens and Heiba, 1983; Gough et al., 1983). Some of them have even been taken into the advanced testing stages. Despite its efficacy and commercial success, the complete proton and carbon-13 nuclear magnetic resonance (NMR) spectra of acifluorfen have not yet been reported. One of the reasons could be that an unequivocal assignment cannot always be realized with only the spectra of limited numbers of analogues by using double resonance experiments.

The recent introduction of various two-dimensional NMR techniques (Bax, 1982) has provided organic chemists with a powerful new tool, for structural elucidations and NMR assignments can be made without the need for a large number of analogues. The application of these new methods in agrochemical research, however, has been very limited so far (Schwartz and Cutnell, 1983). Since the new generation of diphenyl ether herbicides can be considered to be derivatives of acifluorfen, it is believed that the complete assignment of a few representative diphenyl ethers with two-dimensional NMR techniques will be of value to researchers in herbicide syntheses, residue metabolism, and formulation studies. The compounds examined are indicated in Figure 1.

EXPERIMENTAL SECTION

Analytical grade acifluorfen acid, acifluorfen methyl, and bifenox were kindly supplied by Dr. Frank A. Norris of Rhone-Poulenc, Inc. (Monmouth Junction, NJ). Acifluorfen solution was prepared by dissolving acifluorfen acid into a deuterium oxide (D₂O) solution containing sodium dueteroxide (NaOD, 4%) and TSP (sodium 3-(trimethylsilyl)propionate-2,2,3,3-*d*₄, Merck). Acifluorfen methyl and bifenox were dissolved in deuterated acetone and deuterated chloroform for proton and carbon-13 NMR measurements.

The one- and two-dimensional NMR spectra were obtained with a GE/Nicolet NT-300 (7.1 tesla) wide-bore FT NMR spectrometer operating at 300.072 MHz for proton and 75.46 MHz for carbon-13 measurements. All experiments were performed at ambient temperature (ca. 293 K) under conditions generated by a Nicolet 293C pulse programmer and Nicolet NMC-1280 software (V no. 30615).

The normal one-dimensional proton NMR spectra were obtained with a 5- μ s (55°) pulse, 3-KHz spectral window, quadrature detection, and 32 K data points to give 0.1-Hz/point digital resolution. Free induction decays were weighted to 0.1-Hz line broadening. Proton chemical shifts reported are referenced to Me₄Si (0.00 ppm) or TSP (0.00 ppm). The normal one-dimensional carbon-13 NMR spectra, the APT (attached proton test) spectra, and the gated decoupled spectra were obtained by using an 8- μ s (33°) pulse, bilevel (1 and 4 W) MLEV64 (Levitt et al., 1982) decoupling, 20-KHz spectral window, quadrature detection, and 32 K data points to give 0.6-Hz/point digital

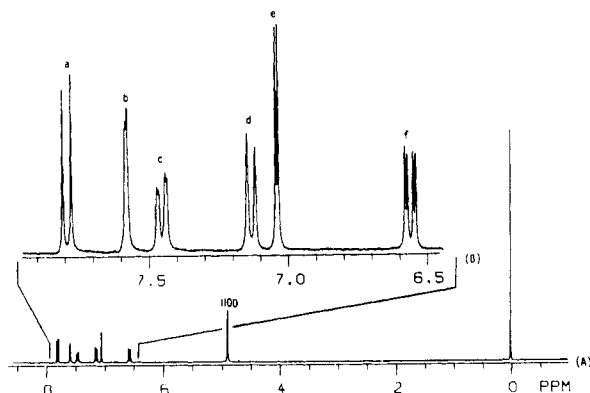


Figure 2. 300-MHz proton NMR spectrum of acifluorfen (A) and the expanded aromatic region (B).

resolution. Free induction decays were weighted to 1-Hz line broadening. Chemical shifts reported were referenced to Me₄Si (0.00 ppm) or TSP (0.00 ppm).

The proton homonuclear shift-correlated (*J* correlated, COSY) spectra and the proton-carbon-13 shift-correlated (CSCM) spectra were obtained by using the COSY and the CSCM pulse sequences supplied in the NMC-1280 software package. Heteronuclear long-range couplings were determined with the 2DJHET pulse sequence provided by Dr. Regina Shuck of GE/Nicolet Magnetics Corporation (Offenbach, West Germany).

The COSY spectra were obtained by using a sweep width of 639 Hz, 1 K data points, 8.3- μ s (90°) pulse, and a 2-s repetition rate. A total of 512 spectra were collected to provide the equivalent of a 639-Hz sweep width in the second frequency dimension. Free induction decays in both dimensions were resolution enhanced with sine multiplications. The absolute values of the spectra were calculated and the contour plot was obtained from the symmetrized two-dimensional NMR data (Baumann et al., 1981). The CSCM spectra were obtained by using a sweep width of 7 KHz, 8 K data points, a 2-s repetition rate, and 31.5- μ s (90°) and 63- μ s (180°) pulses. A total of 128 spectra were obtained to provide the equivalent of a 974-Hz sweep width in the proton frequency dimension. Free induction decays in the proton dimension were zero filled to 512 data points before Fourier transformation. The spectra were displayed in the absolute value mode. Long-range proton-carbon-13 couplings were determined with the method reported by Bax and Freeman (1982). The selective decoupler 180° pulse was determined from a chloroform sample by population inversions (Pachler and Wessels, 1973). The spectra were obtained by using a sweep width of 6 KHz, 16 K data points, and an 8-s preparation period. A total of 128 spectra were obtained to provide the equivalent of a 20-Hz (\pm 10 Hz) sweep width in the second frequency dimension. A complete two-dimensional spectrum was not computed, but only those F₁ traces which carry the desired coupling information were transposed. These transposed traces were zero filled to 8 K data points before Fourier transformation, and the result were displayed in the phase-sensitive mode.

RESULTS AND DISCUSSION

The normal one-dimensional 300-MHz proton NMR spectrum of acifluorfen (1) is shown in Figure 2A and the aromatic region is expanded in Figure 2B. Assignment of this spectrum was achieved first by determining the absorptions due to protons on each phenyl ring with a homonuclear shift-correlated (*J* correlated; COSY) (Jeener, 1971; Bax, 1982) experiment where through-bond connectivity is indicated by the presence of off-diagonal peaks

Table I. Proton NMR Data for Acifluorfen, Acifluorfen Methyl, and Bifenox^a

proton	acifluorfen methyl (2) in							
	acifluorfen (1) in D ₂ O		CDCl ₃		CD ₃ COCD ₃		bifenox (3) in CDCl ₃	
	chem shifts	coupling constants	chem shifts	coupling constants	chem shifts	coupling constants	chem shifts	coupling constants
H _a	7.79	(d) $J = 9.1$	8.04	(d) $J = 8.8$	8.48	(dd) $J = 8.5, 0.86$	8.03	(d) $J = 8.9$
H _b	7.58	(d) $J = 1.8$	7.81	(d) $J = 2.1$	8.01	(ddq) $J = 2.2, 0.74, 0.3$	7.55	(d) $J = 2.5$
H _c	7.45	(dd) $J = 8.6, 1.8$	7.62	(dd) $J = 8.1, 2.2$	7.84	(ddq) $J = 8.5, 2.3, 0.72$	7.35	(dd) $J = 8.7, 2.4$
H _d	7.13	(d) $J = 8.4$	7.24	(d) $J = 7.4$	7.60	(ddq) $J = 8.6, 0.92, 0.3$	7.12	(d) $J = 8.7$
H _e	7.04	(d) $J = 2.7$	7.12	(d) $J = 2.7$	7.41	(dd) $J = 2.7, 0.9$	7.06	(d) $J = 2.3$
H _f	6.56	(dd) $J = 9.1, 2.7$	7.08	(dd) $J = 8.8, 2.7$	7.39	(dd) $J = 8.4, 2.7$	7.03	(dd) $J = 8.7, 2.7$
H(CH ₃)			3.92	(s)	3.87	(s)	3.92	(s)

^a Recorded in D₂O, CDCl₃ or CD₃COCD₃ solutions. Chemical shifts are given in ppm relative to internal standard either TSP (acifluorfen) or Me₄Si (acifluorfen methyl and bifenox); coupling constants are given in Hz.

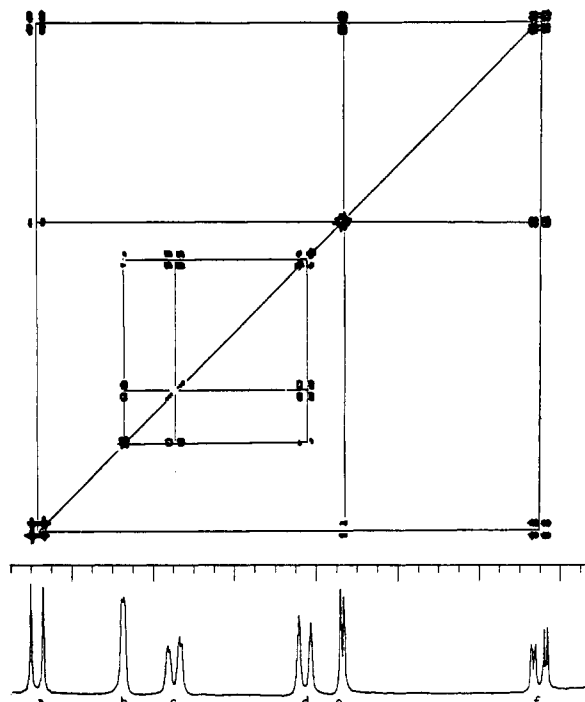


Figure 3. Contour plot of the aromatic region of the proton J correlated (COSY) spectrum of acifluorfen.

(see Figure 3). It is quite clear that absorptions a, e, and f are resonances from the nitrobenzoic ring while b-d are those from the other since there were not cross peaks between these two groups of absorptions. Similar results were obtained for acifluorfen methyl (2) and bifenox (3). The proton NMR spectroscopic data for all three compounds are summarized in Table I. We have also included the proton NMR data for acifluorfen methyl in deuterated acetone solution in Table I because the long-range fluorine-proton couplings were reasonably well resolved in that solvent.

The use of two-dimensional NMR techniques simplifies the assignment of the proton NMR spectra of these compounds at high field. However, the assignments also can be analyzed with simple first-order approximations and double-resonance results. Assignments of the protons (a, e, and f) in the NMR spectra on the nitrobenzoic rings of these three compounds with this approach have recently been reported (Draper and Casida, 1983). The advantages of these two-dimensional methods, however, would become more significant if a lower field strength NMR instrument is employed.

The carbon-13 NMR spectrum of acifluorfen methyl (2) is shown in Figure 4A and the expansion of the aromatic portion is shown in Figure 4B. A total of 21 individual absorptions were observed. The assignment of the carbon

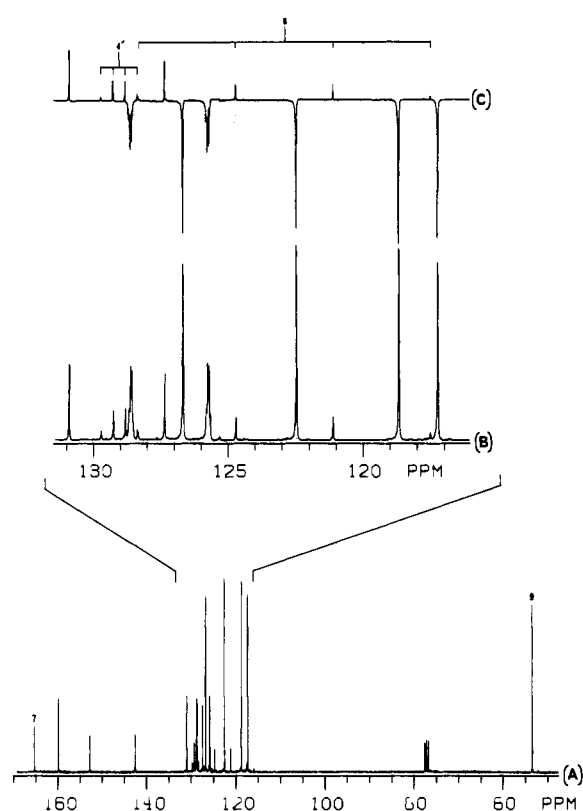


Figure 4. 75-MHz carbon NMR spectrum of acifluorfen methyl (A), the expanded aromatic region (B), and the J modulated APT spectrum of the aromatic region (C). The absorptions due to carbons 4', 7, 8, and 9 have been labeled.

spectrum is more complex than that of the proton spectrum. There are no unequivocal assignments that can be reached with simple empirical additivity calculations (Memory and Wilson, 1982). Actually, the results from simple empirical calculations would predict incorrect chemical shift sequences for most of the carbons on the phenyl rings.

Some of the 21 absorptions can be readily assigned due to their unique chemical environments. These include the carbonyl carbon (7, 165.00 ppm), the methyl carbon (9, 53.47 ppm, $J_{CH} = 148.2$ Hz), the trifluoromethyl carbon (8, 123.08 ppm, $J_{CF} = 272.4$ Hz), and the carbon bearing the trifluoromethyl group (4', 129.23 ppm, $J_{CCF} = 33.7$ Hz). The identification of the absorptions from the six hydrogen-bearing carbons (3, 4, 6, 3', 5', and 6') was aided with the J -modulated APT (attached proton test) (Patt and Shoolery, 1982) spectrum where absorptions of carbons with an uneven number of attached protons were rendered out-of-phase as shown in Figure 4C. Two of these absorptions showed long-range fluorine-carbon-13 couplings;

Table II. Carbon NMR Data for Acifluorfen, Acifluorfen Methyl, and Bifenox^a

C no.	acefluorfen (1) (D ₂ O)			acifluorfen methyl (2) (CDCl ₃)			bifenox (3) (CDCl ₃)		
	chem shifts		coupling constant	chem shifts		coupling constants	chem shifts		coupling constants
	calcd	obsd		calcd	obsd		calcd	obsd	
1	133.7	142.81	(d) $J = 5.04$	127.8	131.09	(d) $J = 5.95^b$	127.8	130.98	(d) $J = 5.97^b$
2	144.5	143.60	(dd) $J = 9.12, 3.21$	144.6	142.64	(dd) $J = 8.9, 3.4$	144.6	141.81	(ddd) $J = 8.95, 3.30$
3	125.7	129.38	(d) $J = 169.4$	125.8	126.85	(d) $J = 169.9$	125.8	126.67	(d) $J = 168.07$
4	123.4	120.15	(dd) $J = 167.4, 4.0$	124.9	118.83	(dd) $J = 167.5, 5.0$	124.9	117.80	(dd) $J = 167.22, 4.99$
5	163.3	163.10	(dt) $J = 10.1, 3.0$	163.4	160.03	(dt) $J = 10.15, 3.4$	163.4	160.64	(dt) $J = 13.47, 3.35$
6	121.4	118.34	(dd) $J = 166.5, 4.5$	121.5	117.39	(ddd) $J = 167.5, 4.8, 1.18^b$	121.5	116.30	(ddd) $J = 167.34, 5.03, 0.82^b$
1'	161.1	156.22	(m) $J = 7.2$	161.1	152.91	(m) $J = 10.25^b$	156.0	148.33	(ddd) $J = 10.21, 7.54, 3.86$
2'	126.0	129.50	(d) $J = 10.88$	126.0	127.54	(d) $J = 1.78^b$	127.0	127.84	(ddd) $J = 8.3, 4.27, 1.64$
3'	128.7	130.88	(dq) $J = 168.9, 4.3$	128.7	128.79	(ddq) $J = 169, 7.08^b, 3.7$	131.3	131.01	(ddd) $J = 171.5, 6.07, 1.06^b$
4'	115.8	131.10	(qd) $J = 33.5, 9.0$	115.8	129.23	(qdt) $J = 33.7, 9.0, 1.4$	131.0	131.99	(ddd) $J = 12.54, 4.68, 3.69$
5'	126.4	128.62	(dq) $J = 165.2, 3.5$	126.4	125.91	(dq) $J = 165, 3.5$	129.0	128.78	(ddd) $J = 169, 6.23, 0.93$
6'	121.1	125.03	(d) $J = 165.7$	121.1	122.66	(d) $J = 165.3$	122.1	123.63	(d) $J = 166$
7		175.00	(m) $J = 3.89$		165.50	(m)		165.62	(m)
8		126.00	(qm) $J = 272$		123.08	(qtd) $J = 272.4, 4.3, 1.1$			
9					53.47	(q) $J = 148.2$		53.39	(q) $J = 148.14$

^a Recorded in either D₂O or CDCl₃ solutions. Chemical shifts are given in ppm relative to internal standard either TSP (acifluorfen) or Me₄Si (acifluorfen methyl and bifenox); coupling constants are given in Hz. ^b Long-range coupling constants are either obtained or confirmed with a separate 2DJHET experiment.

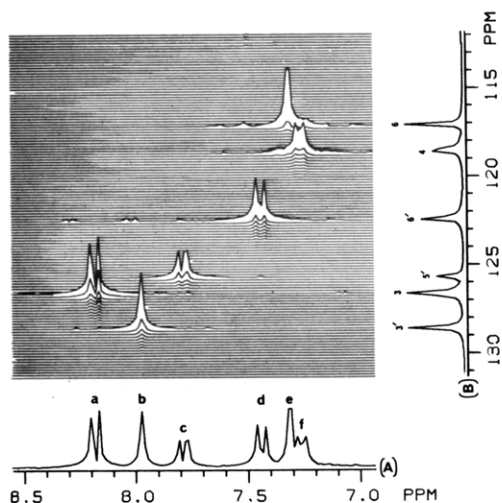


Figure 5. Stacked plot of the chemical shift-correlated (CSCM) spectrum of the aromatic region of acifluorfen methyl with projections along the proton frequency dimension (A) and the carbon frequency dimension (B).

therefore, they must be due to carbons 3' and 5'. Rather than perform six selective decoupling experiments, the individual assignment of these six absorptions was accomplished with a heteronuclear two-dimensional shift-correlated (CSCM) experiment (Maudsley et al., 1977; Bodenhausen and Freeman, 1977, 1978; Bax, 1982). Figure 5 is the stacked plot of the aromatic region of a CSCM experiment for acifluorfen methyl. Figure 5A is the projection along the aromatic proton frequency dimension, and 5B is the projection along the aromatic carbon-13 frequency dimension. Since the proton NMR spectrum of 2 has been fully assigned, the assignment of the absorptions for these six carbons can be readily recognized. The result is summarized in column 5 of Table II.

The assignment of the remaining five quaternary aromatic carbons (1, 2, 1', 2', and 4') has been challenging. One of the most powerful two-dimensional NMR techniques, the INADEQUATE experiment (Bax et al., 1980a, 1980b; Bax, 1982) is often used under these circumstances if the quaternary carbons involved are aliphatic. The two-dimensional INADEQUATE experiment (Bax et al., 1981a, 1981b; Marei and Freeman, 1982), however, would not be that useful since the sensitivity of the two-dimen-

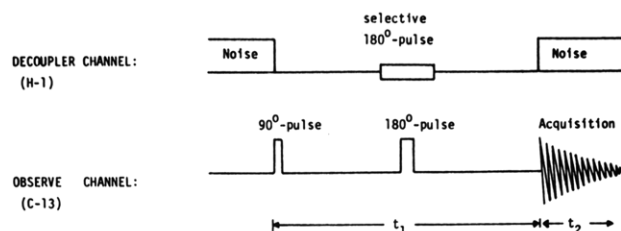


Figure 6. pulse sequence used in the determination of heteronuclear long-range couplings (2DJHET).

sional INADEQUATE experiment for quaternary aromatic carbons is quite poor (Berger, 1984). Obtaining the connectivity information through the attached protons with relayed coherence transfer spectroscopy (Bolton, 1982; Bax, 1983) was also ruled out based on the same considerations. A recent experiment allowing the measurement of long-range couplings (2DJHET) appears to be most useful for our purpose (Bax and Freeman, 1982). This experiment employs a selective 180° pulse on one proton, and the long-range coupling of carbons to this proton is measured in the second frequency dimension. The pulse program is shown in (Figure 6).

This technique was originally proposed for the measurement of allylic and longer-range proton-carbon-13 couplings. We believe that this technique could be adapted to assign the C-13 absorptions of quaternary aromatic carbons by measuring the long-range couplings of these quaternary carbons to selected protons. Figure 7 is the spectra obtained for acifluorfen methyl when proton a was flipped in a 2DJHET experiment. Figure 7A shows a meta coupling constant (J_{CCCH}) of 10.15 Hz from the peak at 160.03 ppm. Therefore, this peak must be due to carbon 5. By the same token, we can assign the peak at 131.09 ppm to carbon 1 with a meta coupling (J_{CCCH}) of 5.95 Hz as shown in Figure 7B. The absorption at 117.39 ppm by carbon 6 was also reconfirmed with a small four-bond coupling J_{CCCCH} of 1.18 Hz as shown in Figure 7C. Carbons 1', 2', and 3' were assigned by flipping proton c in a separate 2DJHET experiment, and the long-range coupling constants obtained are summarized in Table II. The above two 2DJHET experiments allowed the direct assignment of four (1, 5, 1', and 2') of the remaining five aromatic quaternary carbons. The only absorption left (142.64 ppm) must be due to carbon 2. This completes the assignment of the carbon-13 NMR spectrum of acifluorfen methyl.

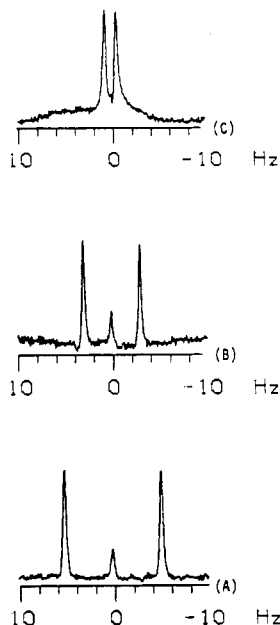


Figure 7. Long-range coupling spectra of acifluorfen methyl when proton a was flipped in a 2DJHET experiment.

The assignment of the carbon-13 NMR spectrum of bifenox (3) followed a similar course. The use of the CSCM technique there, however, was necessary since protons e and f overlap in the proton NMR spectrum, and selective decouplings would not have been fruitful at all. Assignment of the carbon-13 NMR spectrum of acifluorfen was based primarily on the APT, the CSCM experiments, and a comparison of the observed coupling pattern with that obtained for acifluorfen methyl in gated decoupled experiments. The acifluorfen solution we prepared was not concentrated enough, and the employment of the 2DJHET method would have consumed more than an overnight run time.

All the carbon NMR spectral results are summarized in Table II.

CONCLUSION

The NMR spectra of several agronomically important herbicides have been fully assigned with a combination of several two-dimensional NMR techniques: homonuclear shift correlated (COSY), heteronuclear shift correlated (CSCM), and heteronuclear long-range coupled (2DJHET). These methods allow quick and precise determination of nuclear connectivity without relying on empirical calculations or correlations among the spectra of analogues. The usefulness of these techniques has been demonstrated with the complete assignment of three diphenyl ether herbicides: acifluorfen, acifluorfen methyl, and bifenox.

Since two-dimensional NMR methods provide substantially better resolution and dispersion over two frequency domains, we anticipate these methods will become quite useful in agricultural process research, residue and metabolism (Lee and Ksenic, 1981), and formulation studies.

ACKNOWLEDGMENT

The management support is greatly appreciated. I also thank W. H. Stewart for his excellent technical assistance and S. S. Curren for the preparation of the manuscript. In addition, Dr. N. M. Page (Forbus) of Mobil Chemical Company (Princeton, NJ) and Dr. C. C. Ku of Merck, Sharp, and Dohme Research Laboratory (Three Bridges, NJ) kindly reviewed the manuscript and provided many helpful suggestions prior to submission for publication.

Registry No. 1, 50594-66-6; 2, 50594-67-7; 3, 42576-02-3.

LITERATURE CITED

- Barton, J. E. D.; Cartwright, D.; Collins, D. J.; Cox, J. M.; Griffin, D. A.; Parry, D. R. *Eur. Pat. Appl.* 23 392, 1981.
- Baumann, R.; Wider, G.; Ernst, R. R.; Wuthrich, K. *J. Magn. Reson.* 1981, 44, 402.
- Bax, A. "Two-Dimensional Nuclear Magnetic Resonance in Liquids": Delft University Press, D. Reidel Publishing Company: Boston, MA, 1982.
- Bax, A. *J. Magn. Reson.* 1983, 53, 149.
- Bax, A.; Freeman, R. *J. Am. Chem. Soc.* 1982, 104, 1099.
- Bax, A.; Freeman, R.; Frenkiel, T. A. *J. Am. Chem. Soc.* 1981a, 103, 2102.
- Bax, A.; Freeman, R.; Frenkiel, T. A.; Levitt, M. H. *J. Magn. Reson.* 1981b, 43, 478.
- Bax, A.; Freeman, R.; Kempell, S. P. *J. Am. Chem. Soc.* 1980a, 102, 4849.
- Bax, A.; Freeman, R.; Kempell, S. P. *J. Magn. Reson.* 1980b, 41, 349.
- Berger, S. *Org. Magn. Reson.* 1984, 22, 47.
- Bodenhausen, G.; Freeman, R. *J. Magn. Reson.* 1978a, 28, 471.
- Bodenhausen, G.; Freeman, R. *J. Am. Chem. Soc.* 1978b, 100, 320.
- Bolton, P. H. *J. Magn. Reson.* 1982, 48, 336.
- Cartwright, D.; Collins, D. J. *Eur. Pat. Appl.* 3416, 1979.
- Cartwright, D.; Collins, D. J. *Eur. Pat. Appl.* 23 100, 1981.
- Draper, W. M.; Casida, J. E. *J. Agric. Food Chem.* 1983, 31, 1201.
- Gough, S. T. D.; Heiba, E.-A. I.; Lee, G. H.; Borrod, G.; Chene, A. Belg. Pat. BE 893 939, 1983.
- Grove, W. S. Belg. Pat. BE 884 698, 1981.
- Heiba, E.-A. I. Belg. Pat. BE 893 940, 1983.
- Jeener, J., unpublished reports, 1971.
- Johnson, W. O.; Kollman, G. E.; Swithenbank, C.; Yih, R. Y. *J. Agric. Food Chem.* 1978, 26, 285.
- Lee, G. H. Belg. Pat. BE 893 028, 1983a.
- Lee, G. H. Belg. Pat. BE 893 941, 1983b.
- Lee, G. H.; Ksenic, G. A., unpublished results, 1981.
- Levitt, M. H.; Freeman, R.; Frenkiel, T. *J. Magn. Reson.* 1982, 50, 157.
- Mareci, T. H.; Freeman, R. *J. Magn. Reson.* 1982, 48, 158.
- Maudsley, A. A.; Muller, L.; Ernst, R. R. *J. Magn. Reson.* 1977, 28, 463.
- Memory, J. D.; Wilson, N. K. "NMR of Aromatic Compounds"; John Wiley and Sons, Inc.: New York, 1982; p 117.
- Pachler, K. G. R.; Wessels, P. L. *J. Magn. Reson.* 1973, 12, 337.
- Patt, S. L.; Shoolery, J. N. *J. Magn. Reson.* 1982, 46, 535.
- Schwartz, A. L.; Cutnell, J. D. *J. Magn. Reson.* 1983, 53, 398.
- Steffens, J. J.; Heiba, E.-A. I. Belg. Pat. BE 893 938, 1983.

Received for review August 27, 1984. Accepted January 7, 1985. This project was completed with an in-house method development fund (1983) from the Analytical and Information Sciences Department of Applied Research and Development, Sun Refining and Marketing Company.