

FUNGAL RESISTANCE OF SOUTHERN PINE IMPREGNATED WITH METHYL FLUOROPHENYL CARBAMATES OR REACTED WITH FLUOROPHENYL ISOCYANATES

George C. Chen, Roger M. Rowell, and W. Dale Ellis

Chemists

U.S. Department of Agriculture, Forest Service
Forest Products Laboratory¹
Madison, WI 53705-2398

(Received January 1989)

ABSTRACT

Fluorine substituents in the phenyl ring of methyl fluorophenyl carbamates and fluorophenyl isocyanates were varied to determine the influence of fluorine substituents on fungal resistance of wood containing them. In southern pine impregnated with methyl fluorophenyl carbamates, increased fluorine substitution of the phenyl ring increased fungal resistance. Methyl pentafluorophenyl carbamate and methyl meta-trifluoromethylphenyl carbamate were the most effective preservatives, whereas methyl 4-fluorophenyl carbamate was the least effective.

Pine reacted with fluorophenyl isocyanates to form bonded carbamates *in situ* was effective in preventing attacks by fungi but required a much higher molar ratio of chemicals than did wood impregnated with methyl fluorophenyl carbamates. The fluorophenyl carbamyl groups in reacted wood are more stable than carbamates impregnated in wood and less subject to loss by hydrolysis.

Keywords: Fluorophenyl isocyanates, methyl fluorophenyl carbamates, modified wood, fungal resistance, southern pine.

INTRODUCTION

The most common method to protect wood from attack by fungi, termites, bacteria, and other organisms is to treat wood with a toxic chemical so as to minimize leaching and maximize toxicity to a broad scope of organisms. The chemicals are neither organism specific nor completely leach resistant.

Another method of protecting wood from attacking organisms is to attach a toxic chemical to wood in such a way that it is released at a rate necessary to control the growth of a target organism. This is usually done by impregnating wood with a reactive biocidal monomer and polymerizing the monomer *in situ* to an insoluble polymer within the wood structure. Fungicides and herbicides have been esterified to acrylate or vinyl monomers and polymerized *in situ* (Garg et al. 1977; Mendoza 1977; Montemarano and Dyckman 1975; Pittman et al. 1978, 1982; Rowell 1983; Harris 1985; Harris et al. 1976, 1977; Harris and Post 1974, 1975). The nature of the esterified biocide and the polymer backbone determine the release rate and effectiveness of the biocide. Results from these two

¹The Forest Products Laboratory is maintained at Madison, WI, in cooperation with the University of Wisconsin. This article was written and prepared by U.S. Government employees on official time, and it is therefore in the public domain and not subject to copyright.

methods of wood protection have yielded much information on chemical structures and fungus toxicity relationships, information vital to the development of specific toxins for specific applications.

A third method of protecting wood from attacking organisms is to chemically block hydroxyl groups in wood cell-wall polymers (Rowell 1984b). The bonded chemical need not be toxic to be effective in preventing attack because the mechanism is based on lowering the cell-wall moisture content and changing the molecular configuration of the polymers.

Bonding bioactive components to wood cell-wall polymer hydroxyl groups is also possible, a concept different from controlled release biocides previously described. In this case the biocide is not released but retains its toxicity while still bonded to the wood (Rowell 1984a). This approach to wood protection combines all the information gained by the previously described procedures: structural relationship to toxicity, mechanism of effectiveness, and bonding techniques.

In a preliminary study with bonded bioactive chemicals, we synthesized chlorinated phenyl isocyanates and reacted them with wood (Rowell and Chen 1983). We found that tetrachlorophenyl isocyanate, bonded to wood at a level of 15% by weight, reduced the attack of wood by the brown-rot fungus *Gloeophyllum trabeum* (Pers. ex Fr.) Murr. (Madison 617). The mechanism of effectiveness, however, was principally substrate blocking and not retained toxicity of the chlorinated aromatic (Rowell 1984a).

The purpose of the present research was to determine the fungal toxicity of fluorophenyl isocyanates² reacted with wood. Methyl fluorophenyl carbamates were also synthesized and impregnated into wood to compare bonded and non-bonded toxicity.

MATERIALS AND METHODS

Impregnation

Procedures for synthesizing 2,4,6-trifluorophenyl isocyanate, pentafluorophenyl isocyanate, and methyl fluorophenyl carbamates were reported previously (Chen and Rowell 1984; Rowell and Chen 1983). Other fluorophenyl isocyanates (4-fluorophenyl isocyanate, para-trifluoromethylphenyl isocyanate, and meta-trifluoromethylphenyl isocyanate) were purchased from chemical suppliers. Infrared spectra of wood modified with fluorophenyl isocyanate were recorded on an infrared spectrometer using KBr pellets.

For fungal evaluations, 0.26 M solutions of methyl fluorophenyl carbamates in ethanol were prepared corresponding to 4.7%, 5.8%, 6.1%, and 6.7% by weight of solution for methyl 4-fluorophenyl carbamate, methyl 2,4,6-trifluorophenyl carbamate, methyl meta-trifluoromethylphenyl carbamate, and methyl pentafluorophenyl carbamate, respectively. The solutions for each chemical were further diluted with ethanol 1/10, 2/10, and 6/10. Pentachlorophenol (0.14 M, 4.5% by weight of solution) in ethanol was diluted 1/3, 1/6, and 1/30.

²This publication reports research involving pesticides. It does not contain recommendations for their use, nor does it imply that the uses discussed here have been registered. All uses of pesticides must be registered by appropriate state and/or federal agencies before they can be recommended.

Southern pine (*Pinus* sp.) sapwood blocks (1.9 by 1.9 by 1.9 cm in radial, longitudinal, and tangential directions) were used for fungal tests. Preparation, impregnation, and conditioning of wood blocks were performed according to American Society for Testing and Materials (ASTM) Standard D 1413-76 (ASTM 1976). Ethanol was used as a solvent for fungal tests. Impregnation procedures were modified as follows: blocks were placed in a vacuum (5-40 mmHG) and impregnated with the ethanol solutions by soaking for 30 min; they were then dried for 3 days at room temperature prior to conditioning.

Chemical modification of wood

Five Southern Pine sapwood blocks (1.9 by 1.9 by 1.9 cm) were reacted with 4 ml of 2,4,6-trifluorophenyl isocyanate in 80 ml of acetone for 2 h at 110 C, 150 lb/in². After reaction, the blocks were air dried for 24 h and then oven-dried at 75 C overnight. The blocks were then extracted with acetone for 6 h in a Soxhlet extractor, air dried, and then oven-dried at 75 C overnight. The blocks were then conditioned at 27 C and 30% relative humidity for 3 weeks prior to soil-block testing.

This procedure was used for bonding other fluorophenyl isocyanates to wood. Three levels of weight percent gain of chemicals in wood, 1% to 1.5%, 2.5% to 3.0%, and 5% to 9%, were obtained by adjusting the concentrations of fluorophenyl isocyanate solutions (around 2%, 5%, and 10%, weight of chemical/weight of acetone) or reacting for a longer time (4 and 6 h).

Fungal decay test

Fungal decay tests were performed for 12 weeks according to ASTM standard (ASTM 1976) using the brown-rot fungus, *Gloeophyllum trabeum*. The number of replicate blocks used in fungal decay tests were five and four, respectively, for impregnated and reacted wood. The extent of fungal attack was determined by weight loss of the blocks.

RESULTS AND DISCUSSION

Bond formation between meta-trifluoromethylphenyl isocyanate and wood was evidenced by the characteristic carbamate infrared absorption of the modified wood. The spectrum for unmodified wood in the region of 1,730 cm⁻¹ showed a weak carbonyl stretching vibration compared with a strong absorption near 1,650 cm⁻¹ (Fig. 1). The absorption at 1,730 cm⁻¹ is due to carbonyl stretching vibration of acetyl and carboxylic acid of hemicelluloses, and absorption near 1,650 cm⁻¹ is due to H-O-H deformation vibration (1,635 cm⁻¹) of adsorbed water and carbonyl stretching vibration (1,670 cm⁻¹) of lignin (Marchessault 1962; Marchessault and Liang 1962). After bonding meta-trifluoromethylphenyl isocyanate to wood to 7.3% weight gain, the carbonyl absorption band at 1,730 cm⁻¹ became stronger (Fig. 1 B), and at 11.4% weight gain this band (Fig. 1 C) was as intense as that at 1,650 cm⁻¹. The increase in carbonyl absorption at 1,730 cm⁻¹ (Socratic 1980) in modified wood is due to the formation of carbamate bonds between wood and meta-trifluoromethylphenyl isocyanate. Other characteristic carbamate

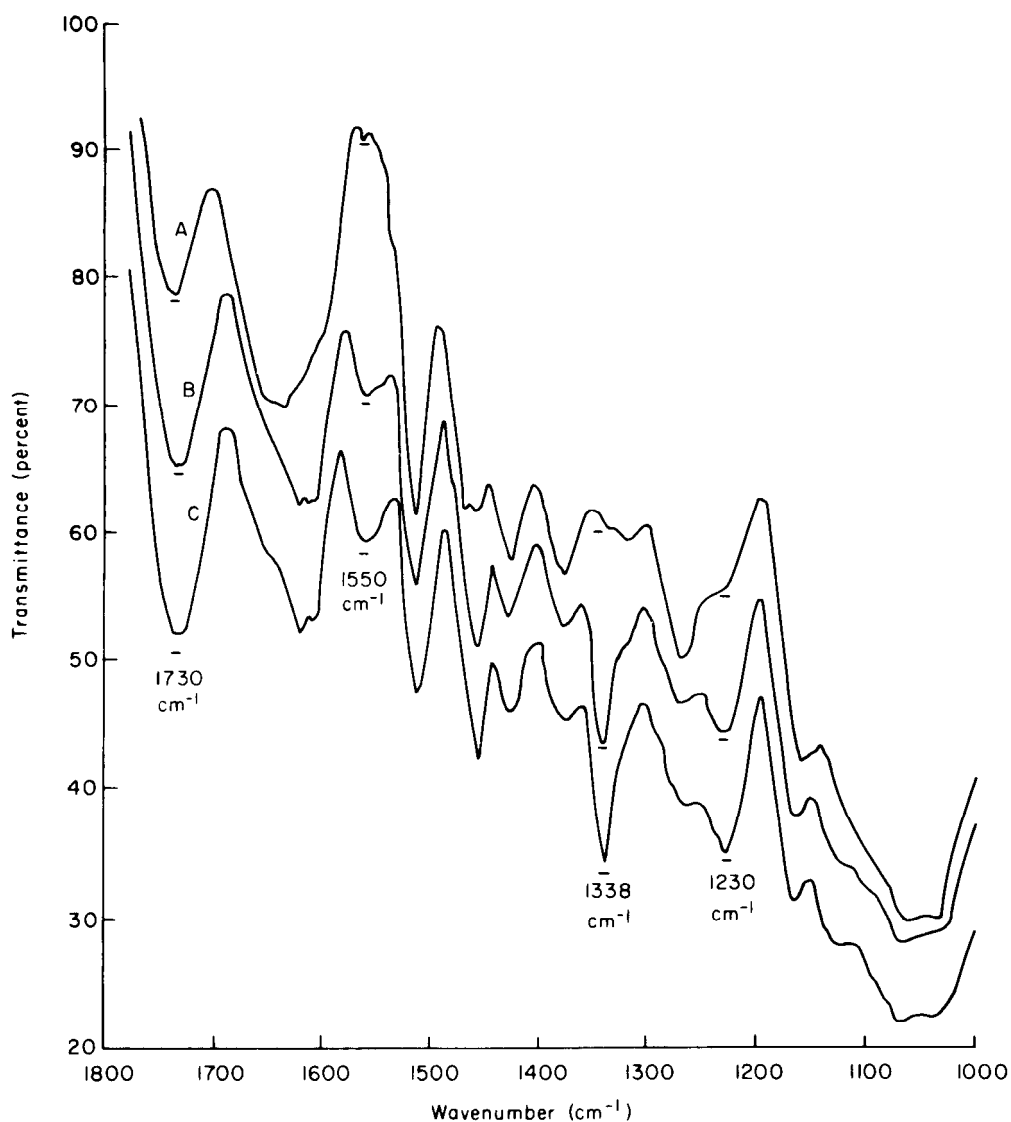


FIG. 1. Infrared spectra of control wood and wood bonded with meta-trifluoromethylphenyl isocyanate. A, control; B, 7.3% carbamate; C, 11.4% carbamate (ML88 5902).

absorption in modified wood are N-H deformation ($1,550\text{ cm}^{-1}$) and aromatic C-N stretching vibration ($1,230\text{ cm}^{-1}$) (Socratic 1980). The trifluoromethyl group of the aromatic ring in modified wood showed one characteristic absorption at $1,338\text{ cm}^{-1}$ due to stretching vibration of C-CF (Yadav and Singh 1985). Similar results of carbamate bond formation between wood and methyl isocyanate were reported (Rowell and Ellis 1980). Wood modified by methyl isocyanate showed the carbamate absorption including carbonyl stretching vibration ($1,730\text{ cm}^{-1}$), N-H deformation ($1,550\text{ cm}^{-1}$), and C-N stretching vibration ($770\text{--}780\text{ cm}^{-1}$).

In preliminary tests (Chen and Rowell 1986), methyl 2,4,6-trifluorophenyl carbamate impregnating wood was shown to be effective against fungal and termite

TABLE 1. Effect of methyl fluorophenyl carbamates on decay of pine by *Gloeophyllum trabeum*.

Treatment	Treatment effect (% w/w)	
	Retention	Weight loss*
Methyl 4-fluorophenyl carbamate	0.06	56.3
	0.30	60.2
	0.58	40.0
	1.81	9.2
	2.98	3.7
Methyl 2,4,6-trifluorophenyl carbamate	0.07	58.6
	0.34	45.7
	0.67	25.3
	2.02	5.7
	3.35	3.6
Methyl pentafluorophenyl carbamate	0.08	51.8
	0.41	33.5
	0.72	23.5
	2.29	0.9
	3.76	1.4
Methyl meta-trifluoromethylphenyl carbamate	0.07	59.6
	0.33	52.9
	0.69	26.2
	2.06	0.8
	3.40	1.0
Control		66.4
Solvent (ethanol)		63.7

* Mean of five replicates.

attack, while bromo and chloro analogs were not effective. For the fluoro compound at 0.56% retention, weight loss by *G. trabeum* was 18.9%, while for the bromo and chloro analogs and the control sample, weight loss was nearly twice as much.

In the present tests of pine blocks impregnated with methyl fluorophenyl carbamates, increased fluorine substitution of the phenyl ring increased fungal resistance. Blocks treated with methyl pentafluorophenyl carbamate (retention of 2.3%, 10 mmoles/ 100 g wood) lost 0.9% weight by *G. trabeum*, whereas blocks treated with methyl 2,4,6-trifluorophenyl carbamate (retention of 2.0%, 10 mmoles/ 100 g wood) and methyl 4-fluorophenyl carbamate (retention of 1.8%, 11 mmoles/ 100 g wood) had 5.7% and 9.2% weight losses, respectively. Wood treated with methyl meta-trifluoromethylphenyl carbamate (retention of 2.1%, 10 mmoles/ 100 g wood) had a very small (0.8%) weight loss (Table 1).

Wood reacted with 4-fluorophenyl isocyanate (weight gain of 3%, 42 mmoles/ 100 g wood) had a small weight loss (1.3%) by *G. trabeum*. The trifluoro and pentafluoro analogs (weight gain of 3.2%, 19 mmoles/100 g wood, and weight gain of 3.1%, 26 mmoles/100 g wood) had 5.5% and 8.0% weight losses, respectively. Wood reacted with para-trifluoromethylphenyl isocyanate (weight gain of 5.6%, 30 mmoles/100 g wood) had no weight loss (Table 2).

To determine the permanence of fluoro compounds in impregnated and reacted wood, wood impregnated with methyl 4-fluorophenyl carbamate and methyl pen-

TABLE 2. *Effect of reacted fluorophenyl isocyanates on decay of pine by Gloeophyllum trabeum.*

Treatment	Treatment effect (% w/w)	
	Weight gain of chemicals	Weight loss*
4-fluorophenyl isocyanate	2.97	1.3
	7.94	1.2
2,4,6-trifluorophenyl isocyanate	1.26	12.3
	3.22	5.5
	5.66	3.4
Pentafluorophenyl isocyanate	1.56	19.4
	3.06	8.0
Methyl meta-trifluoromethylphenyl isocyanate	2.97	16.6
	9.30	0
Methyl para-trifluoromethylphenyl isocyanate	1.09	17.5
	5.66	0
Control		66.4

* Mean of four replicates.

tafluorophenyl carbamate was analyzed for fluorine content after a 12-week soil-block fungal decay test. Fluorine analysis after the decay test showed that wood impregnated with methyl 4-fluorophenyl carbamate lost 54% of carbamate (from 0.203% to 0.094%) and the pentafluoro analog lost 79% of carbamate (from 0.95% to 0.20%) (Table 3). The loss of carbamates from treated wood may be due to hydrolysis and evaporation. The greater loss of pentafluoro compound from impregnated wood, compared with loss of the 4-fluoro compound, probably can be attributed to instability of the pentafluoro substituents containing the carbamate bond in the phenyl ring. The pentafluorophenol group, being a stronger electron-withdrawing group than the monofluoro group, was hydrolyzed more readily than the monofluoro analog.

In contrast, wood reacted with fluorophenyl isocyanates lost fluorophenyl carbamyl groups from reacted wood less readily than wood impregnated with methyl fluorophenyl carbamates. This was indicated by fluorine analysis of wood reacted with 4-fluorophenyl isocyanate after the decay test. The ratio of actual and theoretical (based on weight gain of chemicals in wood) fluorine content of this modified wood was 2.03 for the blocks with decay test and 1.76 for the blocks without decay test. This showed a 27% loss of fluorine from decayed blocks. The loss of 27% fluorine from wood reacted with 4-fluorophenyl isocyanate was less than the 54% loss of fluorine from wood impregnated with methyl 4-fluorophenyl carbamate (Table 3). In the fluoro-modified wood, actual fluorine content was higher than fluorine content based on chemical weight gain in wood. For example, wood reacted with 4-fluorophenyl isocyanate had 1.03 times more actual fluorine than fluorine content based on chemical weight gain in wood. This was because the loss of acetone-soluble extractives was not considered in calculating the weight percent gain of chemicals in wood. The acetone-soluble extractives were lost from wood during reaction as well as during extraction using acetone as a solvent.

For wood reacted with pentafluorophenyl isocyanate, the ratio of actual and theoretical (based on weight gain of chemical in wood) fluorine content was 1.80 for blocks without decay test and 1.74 for blocks with decay test. This indicated

TABLE 3. Percent fluorine in pine blocks treated with methyl fluorophenyl carbamates or reacted with fluorophenyl isocyanates before and after a 12-week soil-block decay test.

Treatment	Weight gain of chemicals in wood (%)	Fluorine in wood (%)			Fluorine loss of decayed blocks (%)
		Theoretical	Nondecay blocks	Decayed blocks*	
Wood impregnated					
Methyl 4-fluorophenyl carbamate	1.84	0.203	—	0.094	54
Methyl pentafluorophenyl carbamate	2.42	0.95	—	0.20	79
Wood reacted					
4-fluorophenyl isocyanate	3.38	0.46	—	0.81	27
	3.04	0.40	0.81	—	
Pentafluorophenyl isocyanate	2.82 ^b	1.24 ^b	—	2.17 ^b	6
	2.47	1.09	1.96		
Control			0.004		

* 12-week soil-block decay test.

^b Mean of three replicates.

that wood reacted with pentafluorophenyl isocyanate lost only 6% of fluorine as a result of 12-week fungal decay test (Table 3). This small loss of fluorine from pentafluoro-reacted wood indicated that pentafluorophenyl isocyanate formed a stable carbamate bond with wood polymers.

CONCLUSION

Wood impregnated with methyl fluorophenyl carbamates showed that increased fluorine substitution of the phenyl ring increased fungal resistance. Methyl pentafluorophenyl carbamate and methyl meta-trifluoromethylphenyl carbamate were the most effective preservatives, and methyl 4-fluorophenyl carbamate was the least effective.

In general, wood reacted with fluorophenyl isocyanates was shown to be effective in preventing fungal attacks but required much higher molar ratio of chemicals than wood impregnated with methyl fluorophenyl carbamates. However, fungicidal fluorophenyl carbamyl groups in reacted wood are more stable than those in impregnated wood because in the case of wood reacted with fluorophenyl isocyanates, loss of fluorophenyl carbamyl groups from wood due to hydrolysis is smaller, and losses due to evaporation do not occur. Reacting wood with fluorophenyl isocyanates may be an effective method for protecting wood from fungal attack.

REFERENCES

- ASTM. 1976. Standard method of testing wood preservatives by laboratory soil-block cultures. D 1413-76. American Society for Testing and Materials, Philadelphia, PA.
- CHEN, G. C., AND R. M. ROWELL. 1984. Polyhalogenated phenyl isocyanate synthesis with excess phosgene and either triethylamine or tetramethylurea. U.S. Patent No. 4,477,389. Oct. 16, 1984.
- , A. N. D. —. 1986. Approaches to the improvement of biological resistance of wood through controlled release technology. Pages 75-76 in Proc. 13th International Symposium on Bioactive Materials. Controlled Release Society, Inc., Lincolnshire, IL.
- GARG, B. K., J. CORREDOR, AND R. V. SUBRAMANIA. 1977. Copolymerization of tri-n-butyltin acrylate and tri-n-butyltin methacrylate monomers with vinyl monomers containing functional groups. J. Macromol. Sci. Chem. A1 1(9): 1567-1601.

- HARRIS, F. W. 1985. Synthesis and hydrolysis of polymers containing pendent herbicide substituents. Pages 3-4 in Proc. 1985 International Symposium on Controlled Release of Bioactive Materials. Controlled Release Society, Inc., Lincolnshire, IL.
- HARRIS, F. W., AND L. K. POST. 1974. Synthesis of polymers containing aquatic herbicides as pendent substituents. Pages 17.1 -17.4 in Proc. 1974 Controlled Release Pesticide Symposium. Controlled Release Society, Inc., Lincolnshire, IL.
- , A. N. D. —. 1975. Synthesis of polymers containing pendent herbicide substituents. Polym. Preprints 16(1):622-627.
- , A. E. AUDABAUGH, R. D. CASE, M. K. DYKES, AND W. A. FELD. 1976. Controlled release polymer formulations, polymers containing pendent herbicide substituents: Preliminary hydrolysis studies. In D. R. Paul and F. W. Harris. eds. ACS Symposium Series 33(18):222-230. American Chemical Society, Washington, DC.
- , M. K. DYKES, J. A. BAKER, AND A. E. AUDABAUGH. 1977. Polymers containing pendant herbicide constituents: Hydrolysis Study II. Pages 102-111 in A. B. Scher, ed. Controlled release pesticides. American Chemical Society, Washington, DC.
- MARCHESSAULT, R. H. 1962. Application of infrared spectroscopy to cellulose and wood polysaccharides. Pure Appl. Chem. 5:107-129.
- , AND C. Y. LIANG. 1962. The infrared spectra of crystalline polysaccharides. XIII. Xylan. Polym. Sci. 59:357-378.
- MENDOZA, J. A. 1977. Wood preservation by *in situ* polymerization of organotin monomers. M.S. thesis, Washington State University, Pullman, WA.
- MONTEMARANO, J. A., AND E. J. DYCKMAN. 1975. Performance of organometallic polymers as antifouling materials. J. Paint Technol. 47(600):59-61.
- PITTMAN, C. U., JR., K. S. RAMACHANDRAN, AND K. R. LAWYER. 1982. Synthesis of fungicidal monomers, polymers, and latices. J. Coatings Technol. 54(690):27-40.
- , G. A. STAHL, AND H. WINTERS. 1978. Synthesis and mildew resistance of vinyl acetate and ethyl acrylate films containing chemically anchored fungicides. J. Coatings Technol. 50(636):49-56.
- ROWELL, R. M. 1983. Bioactive polymer-wood composites. Pages 347-357 in T. J. Roseman and S. Z. Mansdorf, eds. Controlled release delivery systems. Marcel Dekker, Inc., New York.
- , 1984a. Bonding of toxic chemicals of wood. Applied Biochem. Biotechnol. 9:447-453.
- , 1984b. Penetration and reactivity of wood cell wall components. Pages 175-210 in ACS Advances in Chemistry Series 207. American Chemical Society, Washington, DC.
- , AND G. C. CHEN. 1983. Synthesis of polyhalogenated phenyl isocyanates. 186th Am. Chem. Soc. Meeting, Polymeric Materials Science and Engineering Proc., Aug. 28-31, 1983, Washington, DC.
- , AND W. D. ELLIS. 1980. Bonding of isocyanates to wood. In K. N. Edwards, ed. Urethane chemistry and applications. ACS Symposium Series, Am. Chem. Soc. 172(19):262-284. American Chemical Society, Washington, DC.
- SOCRATIC, G. 1980. Infrared characteristic group frequencies. John Wiley and Sons, New York.
- YADAV, R. A., AND I. S. SINGH. 1985. Vibrational studies of trifluoromethyl benzene derivatives. III. Para-trifluoromethyl aniline. Spectrochimica Acta 4(12):191-197.