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^{1}H NMR study of 2,4,6-trichlorophenyl-4'-nitrophenyl ether and related compounds

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2,4,6-Trichlorophenyl-4'-nitrophenyl, 2,4-dichlorophenyl-4'-nitrophenyl ether and related chemicals were prepared and their ^{1}H NMR spectra were measured and assigned. The substituent chemical shifts on diphenyl ethers with mono substituent were estimated as compared with ^{1}H NMR spectra of diphenyl ether. The chemical shifts of the prepared chemicals were calculated by the use of the substituent chemical shifts. The deviations occurred on 6-H or 6'-H NMR chemical shifts when the chemicals are 4'-nitrodiphenyl ether derivatives with 2-substituent.

2,4,6-Trichlorophenyl-4'-nitrophenyl (Chlornitrofen, CNP) and 2,4-dichlorophenyl-4'-nitrophenyl (Nitrofen, NIP) were used as herbicide that is divided into nitrodiphenyl ether group. 2,4,6-Trichlorophenyl-4'-nitrophenyl ether was developed in Japan and large amounts of this chemical material were employed over paddy rice fields in Japan in the period of 1965 to 1996. However, it has been found that this chemical brought serious consequences to the human who worked in the rice fields such as gallbladder cancer[1], and the doubt such as one of Endocrine-Disrupting chemicals happened on it. The pollution in fields is now pointed out although this herbicide is not employed at present. In fact nitro group in 2,4,6- trichlorophenyl-4'-nitrophenyl ether is reduced to amino group in soil and the reduced amino derivative stays behind in field.

In this work in order to obtain the information of chemical structures 2,4,6-trichlorophenyl-4'-nitrophenyl, 2,4-dichlorophenyl-4'-nitrophenyl ether and related compounds were prepared. The ^{1}H NMR spectra for those compounds were measured and assigned. Substituent chemical shifts were also estimated for the assignment and interpretation of the ^{1}H NMR signals.

Experimental

Except for diphenyl ether and 4-aminodiphenyl ether, all compounds were prepared by the Ullmann reaction or by one of its well-known modifications[2−4]. This synthesis involves the coupling of potassium phenolate substituted chlorines with halogenated nitrobenzene in the presence of a copper catalyst. The reaction was usually carried out without a solvent or a high-boiling solvent was used such as dimethyl sulfoxide. The compound was gained after the reaction mixture was

chromatographed over silica gel and recrystallized for purification. The prepared chemicals were listed with corresponding chlorinated phenols and halogenated nitrobenzenes in Table 1. Here the abbreviated names were also described. Diphenyl ether and 4-aminodiphenyl ether were gained as commercial chemicals.

The identification of prepared compounds was carried out by measurements of infrared spectra and elemental analysis. The infrared spectra were taken by the use of Bio-Rad FTS30 and FTS60A FT IR spectroscopy in KBr tablets and in CS_2 solutions. The analytical data of some prepared compounds were obtained by use of CE Instruments EA 1110. The analytical data were shown in Table 2.

Table 1. Corresponding Phenols and Halogenated Benzenes

Diphenyl Ethers		Phenols	Halogenated benzenes
4'-nitro diphenyl ether	(4'N)	Phenol	4-fluoronitrobenzene
2-chloro-4'-nitro diphenyl ether	(2C4'N)	2-chlorophenol	4-fluoronitrobenzene
3-chloro-4'-nitro diphenyl ether	(3C4'N)	3-chlorophenol	4-fluoronitrobenzene
4-chloro-4'-nitro diphenyl ether	(4C4'N)	4-chlorophenol	4-fluoronitrobenzene
2,4-dichloro-4'-nitro diphenyl ether	(24C4'N)	2,4-dichlorophenol	4-fluoronitrobenzene
2,5-dichloro-4'-nitro diphenyl ether	(25C4'N)	2,5-dichlorophenol	4-fluoronitrobenzene
2,6-dichloro-4'-nitro diphenyl ether	(26C4'N)	2,6-dichlorophenol	4-fluoronitrobenzene
2,4,6-trichloro-4'-nitro diphenyl ether	(246C4'N)	2,4,6-trichlorophenol	4-fluoronitrobenzene
4-amino-4'-nitro diphenyl ether	(4A4'N)	4-aminophenol	4-fluoronitrobenzene
4-nitro-4'-nitro diphenyl ether	(4N4'N)	4-nitrophenol	4-fluoronitrobenzene
2',4'-dinitro diphenyl ether	(2'4'N)	Phenol	2,4-dinitrochlorobenzene
2-chloro-2',4'-dinitro diphenyl ether	(2C2'4'N)	2-chlorophenol	,4-dinitrochlorobenzene
3-chloro-2',4'-dinitro diphenyl ether	(3C2'4'N)	3-chlorophenol	2,4-dinitrochlorobenzene
4-chloro-2',4'-dinitro diphenyl ether	(4C2'4'N)	4-chlorophenol	2,4-dinitrochlorobenzene
2,4-dichloro-2',4'-dinitro diphenyl ether	(24C2'4'N)	2,4-dichlorophenol	2,4-dinitrochlorobenzene
2,5-dichloro-2',4'-dinitrodiphenyl ether	(25C2'4'N)	2,5-dichlorophenol	2,4-dinitrochlorobenzene
2,6-dichloro-2',4'-dinitro diphenyl ether	(26C2'4'N)	2,6-dichlorophenol	2,4-dinitrochlorobenzene
2-chloro-2'-nitro diphenyl ether	(2C2'N)	2-chlorophenol	2-chloronitrobenzene
4-chloro-2'-nitro diphenyl ether	(4C2'N)	4-chlorophenol	2-chloronitrobenzene
3',4'-dinitro diphenyl ether	(3'4'N)	Phenol	3,4-dinitrochlorobenzene
4-chloro-3',4'-dinitro diphenyl ether	(4C3'4'N)	4-chlorophenol	3,4-dinitrochlorobenzene
2,4-dichloro-3',4'-dinitro diphenyl ether	(24C3'4'N)	2,4-dichlorophenol	3,4-dinitrochlorobenzene

Table 2. Elemental Analysis for Diphenyl Ethers

	Observed value	Calculated value		Observed value	Calculated value
2C4'N	H : 3.1001%	H : 3.2299%	4C2'4'N	H : 2.3020%	H : 2.3946%
	C : 57.390%	C : 57.733%		C : 48.687%	C : 48.916%
	N : 5.7000%	N : 5.6105%		N : 9.7671%	N : 9.5074%
4C4'N	H : 3.1121%	H : 3.2299%	24C2'4'N	H : 1.7022%	H : 1.8377%
	C : 57.561%	C : 57.733%		C : 43.830%	C : 43.796%
	N : 5.7128%	N : 5.6105%		N : 8.7024%	N : 8.5123%
24C4'N	H : 2.4424%	H : 2.4835%	25C2'4'N	H : 1.8942%	H : 1.8377%
	C : 50.382%	C : 50.733%		C : 43.823%	C : 43.796%
	N : 4.8861%	N : 4.9303%		N : 9.1028%	N : 8.5123%
25C4'N	H : 2.3818%	H : 2.4835%	26C2'4'N	H : 1.7906%	H : 1.8377%
	C : 50.118%	C : 50.733%		C : 43.801%	C : 43.796%
	N : 4.7633%	N : 4.9303%		N : 9.1085%	N : 8.5123%
26C4'N	H : 2.4512%	H : 2.4835%			
	C : 50.567%	C : 50.733%			
	N : 4.7046%	N : 4.9303%			

The ^{1}H NMR spectra for all compounds were recorded at room temperature on JEOL JMN-GX 270 and for some of them on JEOL ALPHA 400 spectroscopy. The concentrations of all compounds in $CDCl_3$ were approximately 20mg/ml in a 5mm diameter tube. All ^{1}H NMR chemical shifts were referenced to the signal of internal tetramethylsilane (TMS).

Results and Discussion

As mentioned above the ^{1}H NMR spectra of all compounds were measured on JEOL JMN-GX 270. Most of them were easily assignable by first order rules. Some compounds, however, gave complicated spectra that were of second order. In those cases the spectra were measured on ALPHA 400 spectroscopy. The observed spectra were of first order. The assignments of the ^{1}H NMR spectra of the compounds were carried out. The chemical shifts were listed in Table 3. The abbreviated term, DE, in this table means to be diphenyl ether.

Table 3. ^{1}H NMR Chemical Shifts of Diphenyl Ethers (ppm from TMS)

	H-2	H-3	H-4	H-5	H-6	H-2'	H-3'	H-4'	H-5'	H-6'
DE	7.00	7.31	7.09	7.31	7.00	7.00	7.31	7.09	7.31	7.00
4'N	7.09	7.43	7.26	7.43	7.09	7.01	8.20	-	8.20	7.01
2C4'N	-	7.52	7.25	7.35	7.17	6.95	8.20	-	8.20	6.95
3C4'N	7.10	-	7.24	7.36	6.99	7.05	8.23	-	8.23	7.05
4C4'N	7.04	7.40	-	7.40	7.04	7.02	8.21	-	8.21	7.02
24C4'N	-	7.53	-	7.32	7.10	6.96	8.21	-	8.21	6.96
25C4'N	-	7.45	7.23	-	7.16	6.99	8.23	-	8.23	6.99
26C4'N	-	7.44	7.22	7.44	-	6.92	8.21	-	8.21	6.92
246C4'N	-	7.46	-	7.46	-	6.91	8.21	-	8.21	6.91
2'4'N	7.14	7.49	7.33	7.49	7.14	-	8.83	-	8.31	7.03
2C2'4'N	-	7.56	7.33	7.41	7.26	-	8.89	-	8.32	6.85
3C2'4'N	7.16	-	7.31	7.41	7.04	-	8.84	-	8.36	7.10
4C2'4'N	7.09	7.45	-	7.45	7.09	-	8.83	-	8.34	7.05
24C2'4'N	-	7.57	-	7.38	7.19	-	8.87	-	8.33	6.87
25C2'4'N	-	7.48	7.30	-	7.25	-	8.86	-	8.35	6.91
26C2'4'N	-	7.48	7.29	7.48	-	-	8.91	-	8.32	6.75
2C2'N	-	7.49	7.19	7.29	7.08	-	7.99	7.19	7.49	6.85
4C2'N	6.97	7.33	-	7.33	6.97	-	7.95	7.23	7.52	7.03
3'4'N	7.08	7.43	7.25	7.43	7.08	6.94	-	-	7.94	7.15
4C3'4'N	7.01	7.38	-	7.38	7.01	6.96	-	-	7.93	7.19
24C3'4'N	-	7.53	-	7.30	7.06	6.79	-	-	7.97	7.19
4N4'N	7.17	8.29	-	8.29	7.17	7.17	8.29	-	8.29	7.17
4A	6.86	6.66	-	6.66	6.86	6.92	7.27	7.00	7.27	6.92
4A4'N	6.89	6.71	-	6.71	6.89	6.95	8.16	-	8.16	6.95

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On assumption of simple sum rule for chemical shifts of the ^{1}H NMR spectra the substituent chemical shifts as compared with diphenyl ether were estimated. The results were shown in Table 4. Here chemical shifts of mono chlorine substituted diphenyl ethers were used in order to estimate the effects of chlorine atoms[5]. The estimated values were summarized in Table 4. By employing those values the ^{1}H NMR chemical shifts of nitrodiphenyl ethers with substituent taken up in this work were calculated. Experiential and calculated results were collected and correlated. The correlation was shown in Fig. 1.

Table 4. Substituent Effects on the ^{1}H NMR Chemical Shifts of Diphenyl Ether (ppm from TMS)

	H-2	H-3	H-4	H-5	H-6	H-2'	H-3'	H-4'	H-5'	H-6'
2C	-	+0.13	-0.03	-0.11	-0.02	-0.04	+0.01	±0.00	+0.01	-0.04
3C	-0.02	-	-0.06	-0.12	-0.14	±0.00	+0.01	+0.02	+0.01	±0.00
4C	-0.08	-0.04	-	-0.04	-0.08	-0.01	+0.02	+0.02	+0.02	-0.01
5C	-0.14	-0.12	-0.06	-	-0.02	±0.00	+0.01	+0.02	+0.01	±0.00
6C	-0.02	-0.11	-0.03	+0.13	-	-0.04	+0.01	±0.00	+0.01	-0.04
2'N	+0.05	+0.06	+0.07	+0.06	+0.05	-	+0.63	+0.12	+0.15	+0.02
4N	+0.01	+0.89	-	+0.89	+0.01	+0.09	+0.12	+0.17	+0.12	+0.09
4'N	+0.09	+0.12	+0.17	+0.12	+0.09	+0.01	+0.89	-	+0.89	+0.01
4A	-0.14	-0.65	-	-0.65	-0.14	-0.08	-0.04	-0.09	-0.04	-0.08

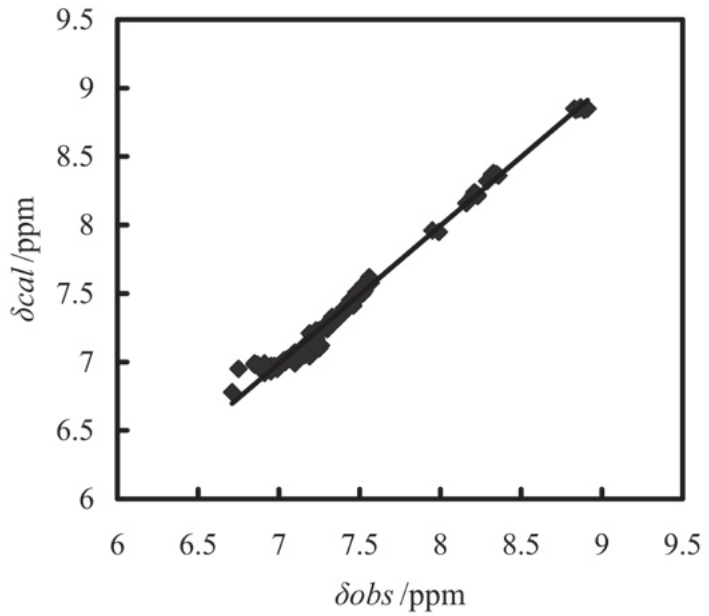

Fig. 1. The correlation between the observed and the calculated ^{1}H NMR chemical shifts.

The deviations occurred on 6-H or 6'-H NMR chemical shifts of the chemicals that have a 2-substituent. Configuration between the two aromatic rings in the chemicals appears to be an important factor for these deviations.

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