

Spectral Assignments and Reference Data

¹⁷O NMR data of phenoxyethyl derivatives

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¹⁷O NMR data for 52 phenoxyethyl derivation have been
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KEYWORDS: ¹⁷O chemical shifts; phenoxyethyl derivatives;
substituent effects

INTRODUCTION

Although ¹⁷O is a quadrupolar nucleus, ¹⁷O NMR spectroscopy has
attracted some attention.¹ As long as the molecular weight is not
too high and the molecules are mobile in a not too viscous solvent,
then ¹⁷O resonance signals with line widths lower than 1 kHz can
be recorded. In the present communication we report data for 52
phenoxyethyl derivatives (Scheme 1).

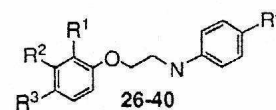
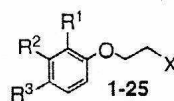
EXPERIMENTAL

All compound syntheses have been described before.²
¹⁷O NMR spectra were recorded in non-deuterated toluene
at 343 K on a Bruker DRX-500 spectrometer (11.74 T, ¹⁷O carrier
frequency 67.78 MHz) in the direct pulse mode using a broad-band
probehead without locking. Field homogenization was achieved
by initial measurement of pure D₂O; the same sample was used
as an external reference with $\delta = -3$, corresponding to $\delta = 0$ for
H₂O. Concentrations were 0.4 to 1.9 M, depending on the solubility
of the compounds. The numbers of scans were 30 000 to 524 000,
depending on the concentration and the ¹⁷O line width. The pulse
width was 25 μ s (*ca* 90° flip angle); the delay time after the pulse for
suppressing acoustic ringing was 70 μ s in general and was 30 μ s for
spectra with very broad signals. The spectral width was *ca* 27.1 kHz,
corresponding to 400 ppm, but was 47.6 kHz, corresponding to
700 ppm, for nitro or acetyl derivatives. FIDs were recorded using
4K data points and Fourier transformation was executed without
zero-filling. This resulted in acquisition times of 0.076 or 0.043 s per
transient respectively, and the digital resolution was 13.2 Hz/point
or 33.1 Hz/point respectively. Total recording times were between
1 and 11 h. Line broadening by exponential multiplication for noise
suppression was 200 Hz.

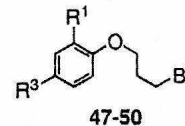
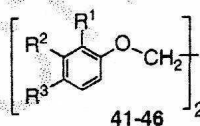
RESULTS AND DISCUSSION

All ¹⁷O chemical shifts are collected in Table 1. The ¹⁷O chemical
shifts of the oxygen attached to the phenyl group are between $\delta = 60$

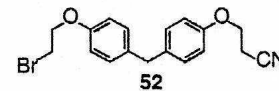
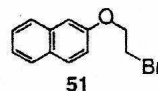
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	R ¹	R ²	R ³	X		R ¹	R ²	R ³	R ⁴
1	H	H	H	Br	26	H	H	H	H
2	Me	H	H	Br	27	H	NO ₂	H	H
3	Ph	H	H	Br	28	H	H	Me	H
4	Bz	H	H	Br	29	H	H	Br	H
5	I	H	H	Br	30	H	H	NO ₂	H
6	NO ₂	H	H	Br	31	H	H	OMe	H
7	OMe	H	H	Br	32	Br	H	Cl	H
8	H	H	Me	Br	33	H	H	H	Me
9	H	H	CO-Me	Br	34	H	H	OMe	Br
10	H	H	Ph	Br	35	H	H	H	Cl
11	H	H	Bz	Br	36	H	H	H	NO ₂
12	H	H	Br	Br	37	H	H	H	OMe
13	H	H	Cl	Br	38	NO ₂	H	H	OMe
14	H	H	NO ₂	Br	39	H	OMe	H	OMe
15	H	H	OMe	Br	40	H	H	Cl	OMe
16	Br	H	Cl	Br					
17	Br	H	Br	Br					
18	H	H	H	I					
19	H	NO ₂	H	I					
20	H	H	OMe	I					
21	H	H	Br	I					
22	Br	H	Cl	I					
23	Ph	H	H	CN					
24	H	H	Ph	CN					
25	Br	H	Me	CN					



	R ¹	R ²	R ³		R ¹	R ³
41	H	H	H	47	H	Cl
42	H	OMe	H	48	H	OMe
43	H	H	OMe	49	NO ₂	H
44	H	H	Ph	50	H	Br
45	Br	H	Me			
46	Br	H	Cl			



Scheme 1. Structures of the phenoxyethyl derivatives 1-52.

and 93 ppm, whereas those of methoxy groups are always smaller
($\delta = 38$ -54 ppm) due to the smaller inductive effect. There is a clear
dependence of $\delta(^{17}\text{O})$ on the inductive and mesomeric effects of
para-substituents, e.g. $\delta = 93$ ppm for *p*-NO₂ (14), $\delta = 88$ ppm for *p*-
C=O-CH₃ (9), $\delta = 73$ ppm for *p*-CH₃ (8) and $\delta = 67$ ppm for *p*-OCH₃
(15). Such dependence vanishes if the substituent is in the meta-
position (27,39 and 42). In the ortho-position, the nitro substituent
(6) loses its deshielding effect, probably because it cannot adopt a
coplanar orientation with respect to the phenyl ring due to steric
interference; however, *o*-OCH₃ (7) is still shielded ($\delta = 60$ ppm). All
this is reminiscent of related data of substituted phenol derivatives.³

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Table 1. ^{17}O NMR chemical shift δ (ppm) of the phenoxyethyl derivatives 1–52; line widths in parentheses

Compound	δ (O–Ph)	δ (OMe)	δ (NO ₂)	δ (C=O)
1	77 (190)			
2	73 (300)			
3	71 (440)			
4	74 (500)			
5	93 (220)			
6	74 (490)		618 (310)	
7	60 (260)	38 (160)		
8	73 (250)			
9	88 (490)			552 (500)
10	77 (730)			
11	74 (640)			
12	77 (400)			
13	79 (320)			
14	93 (490)		576 (870)	
15	67 (570)	43 (450)		
16	80 (360)			
17	81 (410)			
18	83 (310)			
19	81 (320)		620 (230)	
20	75 (360)	45 (210)		
21	84 (320)			
22	88 (420)			
23	68 (800)			
24	72 (1010)			
25	72 (440)			
26	72 (460)			
27	81 (290)		577 (910)	
28	67 (780)			
29	72 (530)			
30	90 (700)		574 (1000)	
31	64 (900)	44 (420)		
32	77 (610)			
33	71 (370)			
34	61 (710)	42 (400)		
35	71 (510)			
36	69 (600)		559 (670)	
37	72 (370)	39 (450)		
38	71 (690)	39 (330)	617 (410)	
39	75 (1000)	54 (380)/39 (410)		
40	71 (740)	41 (430)		
41	71 (650)			

Table 1. (Continued)

Compound	δ (O–Ph)	δ (OMe)	δ (NO ₂)	δ (C=O)
42	72 (780)	53 (370)		
43	62 (570)	40 (710)		
44	75 (710)			
45	71 (830)			
46	75 (790)			
47	72 (370)			
48	64 (420)	43 (280)		
49	71 (480)		617 (260)	
50	73 (680)			
51	78 (410)			
52	67/73 ^a			

^a Two signals, only partially resolved; total band width: 1200 Hz.

The substituent X in the O–CH₂–CH₂–X chain has some γ_{anti} -effect on the phenoxy- ^{17}O ($\delta = 72$ ppm for X = N–Ph (26), 72 ppm for X = CN (24), 77 ppm for X = Br (1) and 83 ppm for X = I (18), but further substitution within the aniline moiety does not affect it further.

The chemical shifts of the nitro groups are between $\delta = 574$ and 620 ppm. No obvious trend can be extracted from the scattered data available.

Acknowledgements

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