Note

NMR Chemical Shifts of Common Laboratory Solvents as Trace Impurities

Hugo E. Gottlieb, Vadim Kotlyar, and Abraham Nudelman

	$CDCl_3$	$(CD_3)_2CO$	$(CD_3)_2SO$
solvent residual peak	7.26	2.05	2.50
H_2O	1.56	2.84	3.33
acetic acid	2.10	1.96	1.91
acetone	2.17	2.09	2.09
acetonitrile	2.10	2.05	2.07
benzene	7.36	7.36	7.37
chloroform	7.26	8.02	8.32
cyclohexane	1.43	1.43	1.40

More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Links to the 125 articles that cite this article, as of the time of this article download
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

View the Full Text HTML

NMR Chemical Shifts of Common Laboratory Solvents as Trace Impurities

Hugo E. Gottlieb,* Vadim Kotlyar, and
Abraham Nudelman*

*Department of Chemistry, Bar-Ilan University,
Ramat-Gan 52900, Israel*

Received June 27, 1997

In the course of the routine use of NMR as an aid for organic chemistry, a day-to-day problem is the identification of signals deriving from common contaminants (water, solvents, stabilizers, oils) in less-than-analytically-pure samples. This data may be available in the literature, but the time involved in searching for it may be considerable. Another issue is the concentration dependence of chemical shifts (especially ^{1}H); results obtained two or three decades ago usually refer to much more concentrated samples, and run at lower magnetic fields, than today's practice.

We therefore decided to collect ^{1}H and ^{13}C chemical shifts of what are, in our experience, the most popular "extra peaks" in a variety of commonly used NMR solvents, in the hope that this will be of assistance to the practicing chemist.

Experimental Section

NMR spectra were taken in a Bruker DPX-300 instrument (300.1 and 75.5 MHz for ^{1}H and ^{13}C, respectively). Unless otherwise indicated, all were run at room temperature (24 ± 1 °C). For the experiments in the last section of this paper, probe temperatures were measured with a calibrated Eurotherm 840/T digital thermometer, connected to a thermocouple which was introduced into an NMR tube filled with mineral oil to approximately the same level as a typical sample. At each temperature, the D_2O samples were left to equilibrate for at least 10 min before the data were collected.

In order to avoid having to obtain hundreds of spectra, we prepared seven stock solutions containing approximately equal amounts of several of our entries, chosen in such a way as to prevent intermolecular interactions and possible ambiguities in assignment. Solution 1: acetone, *tert*-butyl methyl ether, dimethylformamide, ethanol, toluene. Solution 2: benzene, dimethyl sulfoxide, ethyl acetate, methanol. Solution 3: acetic acid, chloroform, diethyl ether, 2-propanol, tetrahydrofuran. Solution 4: acetonitrile, dichloromethane, dioxane, *n*-hexane, HMPA. Solution 5: 1,2-dichloroethane, ethyl methyl ketone, *n*-pentane, pyridine. Solution 6: *tert*-butyl alcohol, BHT, cyclohexane, 1,2-dimethoxyethane, nitromethane, silicone grease, triethylamine. Solution 7: diglyme, dimethylacetamide, ethylene glycol, "grease" (engine oil). For D_2O. Solution 1: acetone, *tert*-butyl methyl ether, dimethylformamide, ethanol, 2-propanol. Solution 2: dimethyl sulfoxide, ethyl acetate, ethylene glycol, methanol. Solution 3: acetonitrile, diglyme, dioxane, HMPA, pyridine. Solution 4: 1,2-dimethoxyethane, dimethylacetamide, ethyl methyl ketone, triethylamine. Solution 5: acetic acid, *tert*-butyl alcohol, diethyl ether, tetrahydrofuran. In D_2O and CD_3OD nitromethane was run separately, as the protons exchanged with deuterium in presence of triethylamine.

Results

Proton Spectra (Table 1). A sample of 0.6 mL of the solvent, containing 1 μL of TMS,[1] was first run on its own. From this spectrum we determined the chemical shifts of the solvent residual peak[2] and the water peak. It should be noted that the latter is quite temperature-
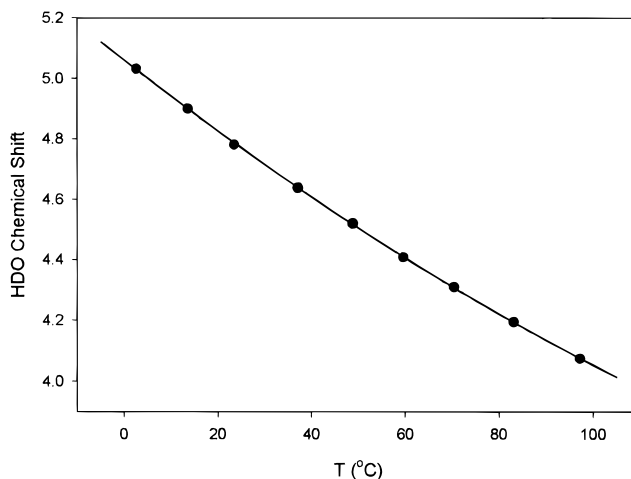

Figure 1. Chemical shift of *H*DO as a function of temperature.

dependent (*vide infra*). Also, any potential hydrogen-bond acceptor will tend to shift the water signal downfield; this is particularly true for nonpolar solvents. In contrast, in *e.g.* DMSO the water is already strongly hydrogen-bonded to the solvent, and solutes have only a negligible effect on its chemical shift. This is also true for D_2O; the chemical shift of the residual HDO is very temperature-dependent (*vide infra*) but, maybe counterintuitively, remarkably solute (and pH) independent.

We then added 3 μL of one of our stock solutions to the NMR tube. The chemical shifts were read and are presented in Table 1. Except where indicated, the coupling constants, and therefore the peak shapes, are essentially solvent-independent and are presented only once.

For D_2O as a solvent, the accepted reference peak (δ = 0) is the methyl signal of the sodium salt of 3-(trimethylsilyl)propanesulfonic acid; one crystal of this was added to each NMR tube. This material has several disadvantages, however: it is not volatile, so it cannot be readily eliminated if the sample has to be recovered. In addition, unless one purchases it in the relatively expensive deuterated form, it adds three more signals to the spectrum (methylenes 1, 2, and 3 appear at 2.91, 1.76, and 0.63 ppm, respectively). We suggest that the residual HDO peak be used as a secondary reference; we find that if the effects of temperature are taken into account (*vide infra*), this is very reproducible. For D_2O, we used a different set of stock solutions, since many of the less polar substrates are not significantly water-soluble (see Table 1). We also ran sodium acetate and sodium formate (chemical shifts: 1.90 and 8.44 ppm, respectively).

Carbon Spectra (Table 2). To each tube, 50 μL of the stock solution and 3 μL of TMS[1] were added. The solvent chemical shifts[3] were obtained from the spectra containing the solutes, and the ranges of chemical shifts

(1) For recommendations on the publication of NMR data, see: IUPAC Commission on Molecular Structure and Spectroscopy. *Pure Appl. Chem.* **1972**, *29*, 627; **1976**, *45*, 217.

(2) *I.e.*, the signal of the proton for the isotopomer with one less deuterium than the perdeuterated material, *e.g.*, C*H*Cl$_3$ in CDCl$_3$ or C$_6$D$_5$*H* in C$_6$D$_6$. Except for CHCl$_3$, the splitting due to J_{HD} is typically observed (to a good approximation, it is 1/6.5 of the value of the corresponding J_{HH}). For CHD$_2$ groups (deuterated acetone, DMSO, acetonitrile), this signal is a 1:2:3:2:1 quintet with a splitting of *ca.* 2 Hz.

(3) In contrast to what was said in note 2, in the ^{13}C spectra the solvent signal is due to the perdeuterated isotopomer, and the one-bond couplings to deuterium are always observable (*ca.* 20–30 Hz).

Table 1. ^{1}H NMR Data

	proton	mult	CDCl$_3$	(CD$_3$)$_2$CO	(CD$_3$)$_2$SO	C$_6$D$_6$	CD$_3$CN	CD$_3$OD	D$_2$O
solvent residual peak			7.26	2.05	2.50	7.16	1.94	3.31	4.79
H$_2$O		s	1.56	2.84^a	3.33^a	0.40	2.13	4.87	
acetic acid	CH$_3$	s	2.10	1.96	1.91	1.55	1.96	1.99	2.08
acetone	CH$_3$	s	2.17	2.09	2.09	1.55	2.08	2.15	2.22
acetonitrile	CH$_3$	s	2.10	2.05	2.07	1.55	1.96	2.03	2.06
benzene	CH	s	7.36	7.36	7.37	7.15	7.37	7.33	
tert-butyl alcohol	CH$_3$	s	1.28	1.18	1.11	1.05	1.16	1.40	1.24
	OH^c	s			4.19	1.55	2.18		
tert-butyl methyl ether	CCH$_3$	s	1.19	1.13	1.11	1.07	1.14	1.15	1.21
	OCH$_3$	s	3.22	3.13	3.08	3.04	3.13	3.20	3.22
BHT^b	ArH	s	6.98	6.96	6.87	7.05	6.97	6.92	
	OH^c	s	5.01		6.65	4.79	5.20		
	ArCH$_3$	s	2.27	2.22	2.18	2.24	2.22	2.21	
	ArC(CH$_3$)$_3$	s	1.43	1.41	1.36	1.38	1.39	1.40	
chloroform	CH	s	7.26	8.02	8.32	6.15	7.58	7.90	
cyclohexane	CH$_2$	s	1.43	1.43	1.40	1.40	1.44	1.45	
1,2-dichloroethane	CH$_2$	s	3.73	3.87	3.90	2.90	3.81	3.78	
dichloromethane	CH$_2$	s	5.30	5.63	5.76	4.27	5.44	5.49	
diethyl ether	CH$_3$	t, 7	1.21	1.11	1.09	1.11	1.12	1.18	1.17
	CH$_2$	q, 7	3.48	3.41	3.38	3.26	3.42	3.49	3.56
diglyme	CH$_2$	m	3.65	3.56	3.51	3.46	3.53	3.61	3.67
	CH$_2$	m	3.57	3.47	3.38	3.34	3.45	3.58	3.61
	OCH$_3$	s	3.39	3.28	3.24	3.11	3.29	3.35	3.37
1,2-dimethoxyethane	CH$_3$	s	3.40	3.28	3.24	3.12	3.28	3.35	3.37
	CH$_2$	s	3.55	3.46	3.43	3.33	3.45	3.52	3.60
dimethylacetamide	CH$_3$CO	s	2.09	1.97	1.96	1.60	1.97	2.07	2.08
	NCH$_3$	s	3.02	3.00	2.94	2.57	2.96	3.31	3.06
	NCH$_3$	s	2.94	2.83	2.78	2.05	2.83	2.92	2.90
dimethylformamide	CH	s	8.02	7.96	7.95	7.63	7.92	7.97	7.92
	CH$_3$	s	2.96	2.94	2.89	2.36	2.89	2.99	3.01
	CH$_3$	s	2.88	2.78	2.73	1.86	2.77	2.86	2.85
dimethyl sulfoxide	CH$_3$	s	2.62	2.52	2.54	1.68	2.50	2.65	2.71
dioxane	CH$_2$	s	3.71	3.59	3.57	3.35	3.60	3.66	3.75
ethanol	CH$_3$	t, 7	1.25	1.12	1.06	0.96	1.12	1.19	1.17
	CH$_2$	q, 7^d	3.72	3.57	3.44	3.34	3.54	3.60	3.65
	OH	s^{c,d}	1.32	3.39	4.63		2.47		
ethyl acetate	CH$_3$CO	s	2.05	1.97	1.99	1.65	1.97	2.01	2.07
	C*H*$_2$CH$_3$	q, 7	4.12	4.05	4.03	3.89	4.06	4.09	4.14
	CH$_2$C*H*$_3$	t, 7	1.26	1.20	1.17	0.92	1.20	1.24	1.24
ethyl methyl ketone	CH$_3$CO	s	2.14	2.07	2.07	1.58	2.06	2.12	2.19
	C*H*$_2$CH$_3$	q, 7	2.46	2.45	2.43	1.81	2.43	2.50	3.18
	CH$_2$C*H*$_3$	t, 7	1.06	0.96	0.91	0.85	0.96	1.01	1.26
ethylene glycol	CH	s^e	3.76	3.28	3.34	3.41	3.51	3.59	3.65
"grease"^{f}	CH$_3$	m	0.86	0.87		0.92	0.86	0.88	
	CH$_2$	br s	1.26	1.29		1.36	1.27	1.29	
n-hexane	CH$_3$	t	0.88	0.88	0.86	0.89	0.89	0.90	
	CH$_2$	m	1.26	1.28	1.25	1.24	1.28	1.29	
HMPA^g	CH$_3$	d, 9.5	2.65	2.59	2.53	2.40	2.57	2.64	2.61
methanol	CH$_3$	s^h	3.49	3.31	3.16	3.07	3.28	3.34	3.34
	OH	s^{c,h}	1.09	3.12	4.01		2.16		
nitromethane	CH$_3$	s	4.33	4.43	4.42	2.94	4.31	4.34	4.40
n-pentane	CH$_3$	t, 7	0.88	0.88	0.86	0.87	0.89	0.90	
	CH$_2$	m	1.27	1.27	1.27	1.23	1.29	1.29	
2-propanol	CH$_3$	d, 6	1.22	1.10	1.04	0.95	1.09	1.50	1.17
	CH	sep, 6	4.04	3.90	3.78	3.67	3.87	3.92	4.02
pyridine	CH(2)	m	8.62	8.58	8.58	8.53	8.57	8.53	8.52
	CH(3)	m	7.29	7.35	7.39	6.66	7.33	7.44	7.45
	CH(4)	m	7.68	7.76	7.79	6.98	7.73	7.85	7.87
silicone grease^i	CH$_3$	s	0.07	0.13		0.29	0.08	0.10	
tetrahydrofuran	CH$_2$	m	1.85	1.79	1.76	1.40	1.80	1.87	1.88
	CH$_2$O	m	3.76	3.63	3.60	3.57	3.64	3.71	3.74
toluene	CH$_3$	s	2.36	2.32	2.30	2.11	2.33	2.32	
	CH(o/p)	m	7.17	7.1−7.2	7.18	7.02	7.1−7.3	7.16	
	CH(m)	m	7.25	7.1−7.2	7.25	7.13	7.1−7.3	7.16	
triethylamine	CH$_3$	t,7	1.03	0.96	0.93	0.96	0.96	1.05	0.99
	CH$_2$	q, 7	2.53	2.45	2.43	2.40	2.45	2.58	2.57

^{a} In these solvents the intermolecular rate of exchange is slow enough that a peak due to HDO is usually also observed; it appears at 2.81 and 3.30 ppm in acetone and DMSO, respectively. In the former solvent, it is often seen as a 1:1:1 triplet, with $^2J_{H,D} = 1$ Hz. ^{b} 2,6-Dimethyl-4-*tert*-butylphenol. ^{c} The signals from exchangeable protons were not always identified. ^{d} In some cases (see note a), the coupling interaction between the CH$_2$ and the OH protons may be observed ($J = 5$ Hz). ^{e} In CD$_3$CN, the OH proton was seen as a multiplet at δ 2.69, and extra coupling was also apparent on the methylene peak. ^{f} Long-chain, linear aliphatic hydrocarbons. Their solubility in DMSO was too low to give visible peaks. ^{g} Hexamethylphosphoramide. ^{h} In some cases (see notes a, d), the coupling interaction between the CH$_3$ and the OH protons may be observed ($J = 5.5$ Hz). ^{i} Poly(dimethylsiloxane). Its solubility in DMSO was too low to give visible peaks.

show their degree of variability. Occasionally, in order to distinguish between peaks whose assignment was ambiguous, a further 1−2 μL of a specific substrate were added and the spectra run again.

Table 2. ^{13}C NMR Data^a

		CDCl$_3$	(CD$_3$)$_2$CO	(CD$_3$)$_2$SO	C$_6$D$_6$	CD$_3$CN	CD$_3$OD	D$_2$O
solvent signals		77.16 ± 0.06	29.84 ± 0.01	39.52 ± 0.06	128.06 ± 0.02	1.32 ± 0.02	49.00±0.01	
			206.26 ± 0.13			118.26 ± 0.02		
acetic acid	CO	175.99	172.31	171.93	175.82	173.21	175.11	177.21
	CH$_3$	20.81	20.51	20.95	20.37	20.73	20.56	21.03
acetone	CO	207.07	205.87	206.31	204.43	207.43	209.67	215.94
	CH$_3$	30.92	30.60	30.56	30.14	30.91	30.67	30.89
acetonitrile	CN	116.43	117.60	117.91	116.02	118.26	118.06	119.68
	CH$_3$	1.89	1.12	1.03	0.20	1.79	0.85	1.47
benzene	CH	128.37	129.15	128.30	128.62	129.32	129.34	
tert-butyl alcohol	C	69.15	68.13	66.88	68.19	68.74	69.40	70.36
	CH$_3$	31.25	30.72	30.38	30.47	30.68	30.91	30.29
tert-butyl methyl ether	OCH$_3$	49.45	49.35	48.70	49.19	49.52	49.66	49.37
	C	72.87	72.81	72.04	72.40	73.17	74.32	75.62
	C*C*H$_3$	26.99	27.24	26.79	27.09	27.28	27.22	26.60
BHT	C(1)	151.55	152.51	151.47	152.05	152.42	152.85	
	C(2)	135.87	138.19	139.12	136.08	138.13	139.09	
	CH(3)	125.55	129.05	127.97	128.52	129.61	129.49	
	C(4)	128.27	126.03	124.85	125.83	126.38	126.11	
	CH$_3$Ar	21.20	21.31	20.97	21.40	21.23	21.38	
	*C*H$_3$C	30.33	31.61	31.25	31.34	31.50	31.15	
	C	34.25	35.00	34.33	34.35	35.05	35.36	
chloroform	CH	77.36	79.19	79.16	77.79	79.17	79.44	
cyclohexane	CH$_2$	26.94	27.51	26.33	27.23	27.63	27.96	
1,2-dichloroethane	CH$_2$	43.50	45.25	45.02	43.59	45.54	45.11	
dichloromethane	CH$_2$	53.52	54.95	54.84	53.46	55.32	54.78	
diethyl ether	CH$_3$	15.20	15.78	15.12	15.46	15.63	15.46	14.77
	CH$_2$	65.91	66.12	62.05	65.94	66.32	66.88	66.42
diglyme	CH$_3$	59.01	58.77	57.98	58.66	58.90	59.06	58.67
	CH$_2$	70.51	71.03	69.54	70.87	70.99	71.33	70.05
	CH$_2$	71.90	72.63	71.25	72.35	72.63	72.92	71.63
1,2-dimethoxyethane	CH$_3$	59.08	58.45	58.01	58.68	58.89	59.06	58.67
	CH$_2$	71.84	72.47	17.07	72.21	72.47	72.72	71.49
dimethylacetamide	CH$_3$	21.53	21.51	21.29	21.16	21.76	21.32	21.09
	CO	171.07	170.61	169.54	169.95	171.31	173.32	174.57
	NCH$_3$	35.28	34.89	37.38	34.67	35.17	35.50	35.03
	NCH$_3$	38.13	37.92	34.42	37.03	38.26	38.43	38.76
dimethylformamide	CH	162.62	162.79	162.29	162.13	163.31	164.73	165.53
	CH$_3$	36.50	36.15	35.73	35.25	36.57	36.89	37.54
	CH$_3$	31.45	31.03	30.73	30.72	31.32	31.61	32.03
dimethyl sulfoxide	CH$_3$	40.76	41.23	40.45	40.03	41.31	40.45	39.39
dioxane	CH$_2$	67.14	67.60	66.36	67.16	67.72	68.11	67.19
ethanol	CH$_3$	18.41	18.89	18.51	18.72	18.80	18.40	17.47
	CH$_2$	58.28	57.72	56.07	57.86	57.96	58.26	58.05
ethyl acetate	*C*H$_3$CO	21.04	20.83	20.68	20.56	21.16	20.88	21.15
	CO	171.36	170.96	170.31	170.44	171.68	172.89	175.26
	CH$_2$	60.49	60.56	59.74	60.21	60.98	61.50	62.32
	CH$_3$	14.19	14.50	14.40	14.19	14.54	14.49	13.92
ethyl methyl ketone	*C*H$_3$CO	29.49	29.30	29.26	28.56	29.60	29.39	29.49
	CO	209.56	208.30	208.72	206.55	209.88	212.16	218.43
	*C*H$_2$CH$_3$	36.89	36.75	35.83	36.36	37.09	37.34	37.27
	CH$_2$*C*H$_3$	7.86	8.03	7.61	7.91	8.14	8.09	7.87
ethylene glycol	CH$_2$	63.79	64.26	62.76	64.34	64.22	64.30	63.17
"grease"	CH$_2$	29.76	30.73	29.20	30.21	30.86	31.29	
n-hexane	CH$_3$	14.14	14.34	13.88	14.32	14.43	14.45	
	CH$_2$(2)	22.70	23.28	22.05	23.04	23.40	23.68	
	CH$_2$(3)	31.64	32.30	30.95	31.96	32.36	32.73	
HMPA^b	CH$_3$	36.87	37.04	36.42	36.88	37.10	37.00	36.46
methanol	CH$_3$	50.41	49.77	48.59	49.97	49.90	49.86	49.50^c
nitromethane	CH$_3$	62.50	63.21	63.28	61.16	63.66	63.08	63.22
n-pentane	CH$_3$	14.08	14.29	13.28	14.25	14.37	14.39	
	CH$_2$(2)	22.38	22.98	21.70	22.72	23.08	23.38	
	CH$_2$(3)	34.16	34.83	33.48	34.45	34.89	35.30	
2-propanol	CH$_3$	25.14	25.67	25.43	25.18	25.55	25.27	24.38
	CH	64.50	63.85	64.92	64.23	64.30	64.71	64.88
pyridine	CH(2)	149.90	150.67	149.58	150.27	150.76	150.07	149.18
	CH(3)	123.75	124.57	123.84	123.58	127.76	125.53	125.12
	CH(4)	135.96	136.56	136.05	135.28	136.89	138.35	138.27
silicone grease	CH$_3$	1.04	1.40		1.38		2.10	
tetrahydrofuran	CH$_2$	25.62	26.15	25.14	25.72	26.27	26.48	25.67
	CH$_2$O	67.97	68.07	67.03	67.80	68.33	68.83	68.68
toluene	CH$_3$	21.46	21.46	20.99	21.10	21.50	21.50	
	C(*i*)	137.89	138.48	137.35	137.91	138.90	138.85	
	CH(*o*)	129.07	129.76	128.88	129.33	129.94	129.91	
	CH(*m*)	128.26	129.03	128.18	128.56	129.23	129.20	
	CH(*p*)	125.33	126.12	125.29	125.68	126.28	126.29	
triethylamine	CH$_3$	11.61	12.49	11.74	12.35	12.38	11.09	9.07
	CH$_2$	46.25	47.07	45.74	46.77	47.10	46.96	47.19

^{a} See footnotes for Table 1. ^{b} $^2J_{PC}$ = 3 Hz. ^{c} Reference material; see text.

For D_2O solutions there is no accepted reference for carbon chemical shifts. We suggest the addition of a drop of methanol, and the position of its signal to be defined as 49.50 ppm; on this basis, the entries in Table 2 were recorded. The chemical shifts thus obtained are, on the whole, very similar to those for the other solvents. Alternatively, we suggest the use of dioxane when the methanol peak is expected to fall in a crowded area of the spectrum. We also report the chemical shifts of sodium formate (171.67 ppm), sodium acetate (182.02 and 23.97 ppm), sodium carbonate (168.88 ppm), sodium bicarbonate (161.08 ppm), and sodium 3-(trimethylsilyl)-propanesulfonate [54.90, 19.66, 15.56 (methylenes 1, 2, and 3, respectively), and −2.04 ppm (methyls)], in D_2O.

Temperature Dependence of HDO Chemical Shifts. We recorded the ^1H spectrum of a sample of D_2O, containing a crystal of sodium 3-(trimethylsilyl)propane-sulfonate as reference, as a function of temperature. The data are shown in Figure 1. The solid line connecting the experimental points corresponds to the equation

$$\delta = 5.060 - 0.0122\,T + (2.11 \times 10^{-5})\,T^2 \qquad (1)$$

which reproduces the measured values to better than 1 ppb. For the 0 - 50°C range, the simpler

$$\delta = 5.051 - 0.0111\,T \qquad (2)$$

gives values correct to 10 ppb. For both equations, T is the temperature in °C.

JO971176V