

Nucleosides and nucleotides: part 28 [1]. ^{13}C -NMR spectra of 2'-deoxycytidine and 3-deaza-2'-deoxycytidine

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Submitted May 9, 1988

3-Deaza-2'-deoxycytidine (d(3-deazaC)) is a structural analogue of 2'-deoxycytidine (dC) and was shown to react in a different manner as a 5'-triphosphate [2] and as a template nucleotide [3] on *in vitro* polymerization. In this connection the tautomeric equilibrium of d(3-deazaC) with its imino-enol form was investigated by ^{13}C -NMR spectroscopy. Using solvents with gradually changing hydration properties (dimethyl sulfoxide/water mixtures) d(3-deazaC) was measured and compared to dC the tautomeric equilibrium of which is mostly on the amino-lactam side in both solvents (*cf.* Figure and Table).

The assignments of the ^1H -decoupled signals are based on ^1H , ^{13}C heteronuclear correlation spectra (data not shown) and on ^{13}C -NMR spectra of cytidine from the literature. The assignment of C(4) and C(2) of d(3-deazaC) was confirmed by a fully coupled ^{13}C -NMR spectrum in d_6 -dimethyl sulfoxide ($J_{\text{CH}}(163.05 \text{ ppm}) = 6.2 \text{ Hz}$, broadened doublet; $J_{\text{CH}}(157.74 \text{ ppm}) = 9.7 \text{ Hz}$, doublet).

The ^1H -NMR spectrum of d(3-deazaC) in d_6 -dimethyl sulfoxide shows two amino protons at 6.1 ppm (not shown). Therefore, due to the relatively small differences between the curves of the same carbon atom of both substrates (Figure) it is concluded that no substantial shift of the tautomeric equilibrium towards the imino-enol form of d(3-deazaC) takes place through the replacement of dimethyl sulfoxide with water.

I thank Prof. Ch. Tamm for his interest in these investigations. They were supported by the Swiss National Science Foundation.

References: [1] Part 27: Charczuk, R. & Tamm, Ch. (1987) *Helv. Chim. Acta* 70, 717-725. [2] Wachtl, M., Kohler, P. & Tamm, Ch. (1980) *Helv. Chim. Acta* 63, 2495-2502. [3] Charczuk, R., Tamm, Ch., Suri, B. & Bickle, Th. A. (1986) *Nucleic Acids Res.* 14, 9530.

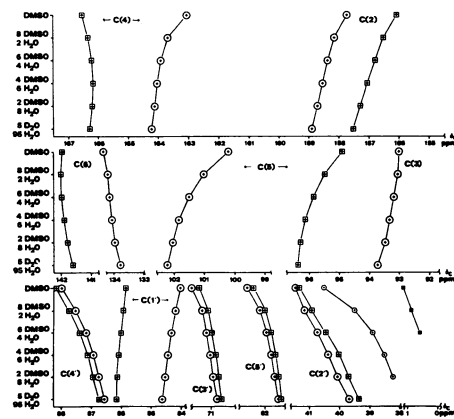


Figure. ^{13}C -NMR chemical shifts of d(3-deazaC) and of dC in different solvent mixtures (recorded on a Varian VXR 400 (99.95 MHz)).

Table. ^{13}C -NMR Data of dC (I) and of d(3-deazaC) (II). (^1H -decoupled signals in ppm relative to external TMS.)

I	II	DMSO 100 H ₂ O 0	8 2	6 4	4 6	2 8	0 100
C(4)		166.53	166.34	166.22	166.17	166.20	166.28
	C(4)	163.05	163.99	163.92	164.04	164.11	164.22
C(2)		156.09	156.54	156.81	157.07	157.30	157.53
	C(2)	157.74	156.16	156.38	156.55	156.17	156.90
C(3)		141.94	142.00	141.98	141.89	141.77	141.80
	C(3)	134.34	134.20	134.14	134.06	133.96	133.78
C(5)		94.90	95.47	95.85	96.13	96.29	96.36
	C(5)	100.20	101.01	101.50	101.84	102.04	102.21
C(2')		93.01	93.05	93.18	93.32	93.47	93.72
	C(4')	88.17	87.74	87.38	87.11	86.82	86.73
	C(4')	87.98	87.83	87.17	86.92	86.74	86.56
C(1')		85.85	85.93	86.00	86.06	86.12	86.16
	C(1')	84.04	84.20	84.33	84.44	84.53	84.63
C(3')		71.41	71.13	70.99	70.86	70.77	70.67
	C(3')	71.66	71.31	71.17	71.04	70.95	70.82
C(5')		62.38	62.00	61.80	61.65	61.56	61.45
	C(5')	62.58	62.16	61.94	61.78	61.67	61.56
C(2')		41.26	40.92	40.66	40.03	39.71	39.26
	C(4')	41.47	41.17	40.76	40.37	40.07	39.89
C(DMSO)		40.51	39.50	38.90	38.50	38.22	--
C(internal TMS)		1.12	0.86	0.58	b)	b)	b)

a) δ_{C} relative to TMS(CH_3) $_2\text{SQ Na}$ at -2.596 ppm relative to external TMS.
b) TMS insufficiently soluble in solvent.

