Tetrahedron Letters No. 22, pp. 1499-1500, 1963. Pergamon Press Ltd.
Printed in Great Britain.

THE NMR SPECTRUM OF PURINE

Sadao Matsuura and Toshio Goto
Department of General Education (S.M.)
and Faculty of Science (T.G.),
Nagoya University, Nagoya, Japan

(Received 17 June 1963; in revised form 16 July 1963)

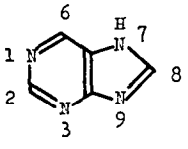
RECENTLY, Pullman (1) criticized Miller and Lykos' SCMO calculations of the charge densities of the purine molecule (2). His arguments were mainly based on the NMR evidence of Jardetzky and Jardetzky (3), who made an assumption that the most shielded proton belongs to the C_6 atom because the C_6 atom is bonded to a carbon and a nitrogen atom, while both the C_2 and the C_8 atoms are bonded to two nitrogen atoms.

TABLE 1

NMR of purine

(Chem. Shift, ppm from ext. C_6H_6)

Position			Solvent
H_2	H_6	H_8	
-2.08	-2.21	-1.83	D_2O
-1.99	-2.18	-1.70	1.0N NaOD
-2.88	-3.07	-2.62	1.2N DCl



Our results on pteridines (4), however, indicated that this assumption would not always be correct: in the case of the unsubstituted pteridine the least shielded proton belongs to the C_4 atom which corresponds to the C_6 atom of the purine. We therefore examined the NMR spectra of purine and 2-, 6-deuteriopurine to make unambiguous assignments. Surprisingly, the results were entirely different from that of Jardetzky: the proton on the C_6 atom was actually the least shielded one (table 1).

The observed order H_6-H_2-H_8 from the lower field is the same to the order of the electron densities of the carbon atoms calculated by Miller and Lykos (2), but is reverse to that of the Pullman's Hückel calculation (1). If Pullman's assumption (1) that the most shielded proton belongs to the carbon with the greatest charge density is correct, contrary to the Pullman's statement (1) Miller and Lykos' SCMO charge densities seem to be rather better than that of HMO, but for final decision we must consider the ring current anisotropy effect of the rings. The proton attached to the C_6 atom is close to the imidazole ring, the ring current of which would deshield the proton.

Recently, Reddy et al. (5) assigned the three signals of the purine to the order H_2-H_6-H_8 from the lower field without experimental evidence. This is also erroneous and should be changed to the order H_6-H_2-H_8. This would account for the large shift (-18.8 cps) of the lowest signal of purine when it is acetylated at the N_7, since the proton on the C_6 and an acetyl group at the N_7 are very close to each other.

2-Deuteriopurine (m.p. 212-213°) was synthesized from 4,5-diamino-2-chloropyrimidine (6) by reduction with deuterium and palladium on charcoal as catalyst and condensation with formic acid. 6-Deuteriopurine (m.p. 212-213°) was obtained from 4,5-diamino-6-chloropyrimidine (7) by the same procedure as above. The spectra were recorded on a Nihondenshi JNM-3 Spectrometer (60 Mc). Each solution was made by dissolving 20 mg of each sample in 0.4 ml of D_2O, 1.2N DCl, or 1.0N NaOD. Accuracy is ca. $\pm$0.01 ppm. The corresponding signal of each deuterio derivative diminished markedly.

REFERENCES

1 B. Pullman, Tetrahedron Letters, 231 (1963).
2 R.L. Miller and P.G. Lykos, Tetrahedron Letters, 493 (1962).
3 C.D. Jardetzky and O. Jardetzky, J. Amer. Chem. Soc. 82, 222 (1960).
4 S. Matsuura and T. Goto, J. Chem. Soc. 1773 (1963).
5 G.S. Reddy, L. Mandell, and J.H. Goldstein, J.Chem.Soc. 1414 (1963).
6 A. Albert, D.J. Brown, G. Cheeseman, J. Chem. Soc. 474 (1951).
7 A. Albert, D.J. Brown, G. Cheeseman, J. Chem. Soc. 4219 (1952).