BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 47(8), 2083—2084 (1974)

^{13}C Nuclear Magnetic Resonance Spectra of Unsymmetrical Naphthyridines

Minoru HIROTA, Hideyuki MASUDA, Yoshiki HAMADA* and Isao TAKEUCHI*

Department of Applied Chemistry, Faculty of Engineering, Yokohama National University, Minami-ku, Yokohama 233

**Faculty of Pharmacy, Meijo University, Showa-ku, Nagoya 468*

(Received May, 21, 1974)

Synopsis. ^{13}C Nuclear magnetic resonance spectra of some naphthyridines were measured and the chemical shifts were compared with those theoretically calculated by an SCF-MO method of π-electron system. Fairly good linear relationship is observed between these values.

In the course of the investigations on the syntheses of naphthyridines and related compounds by modified Skraup reactions,[1] some naphthyridines were obtained and their ^{13}C NMR spectra were measured. The ^{13}C chemical shifts of the naphthyridines are shown in Table 1, together with the electron densities obtained by simple-LCAO and SCF(Pariser-Parr-Pople approximation) MO calculations.[2] The unambiguous assignment of the chemical shifts were obtained by the selective heteronuclear decoupling.

TABLE 1. ^{13}C CHEMICAL SHIFTS AND π-ELECTRON DENSITIES OF 1,X-NAPHTHYRIDINES

Compound	Position of C atom	Chemical shift Obsd./ppm	π-electron density Simple-LCAO	π-electron density SCF
1,5-Naphthyridine	2, 6	−22.55	0.8989	0.8464
	3, 7	+4.25	0.9929	1.0202
	4, 8	−8.81	0.9448	0.9506
	9, 10	−15.41	0.9582	0.9403
1, 6-Naphthyridine	2	−26.26	0.8812	0.8034
	3	+5.99	1.0086	1.0572
	4	−7.06	0.9168	0.9331
	5	−24.39	0.8847	0.8294
	7	−18.42	0.9303	0.8698
	8	+4.83	1.0211	1.0380
	9	−21.92	0.9325	0.8597
	10	+6.38	1.0052	1.0601
1,7-Naphthyridine	2	−23.42	0.8951	0.8495
	3	+3.42	0.9927	1.0084
	4	−6.13	0.9346	0.9646
	5	+8.68	0.9973	1.0347
	6	−15.23	0.9487	0.9027
	8	−25.73	0.9088	0.8321
	9	−14.81	0.9606	0.9505
	10	−2.61	0.9774	0.9714
1,8-Naphthyridine	2, 7	−27.64	0.8827	0.8171
	3, 6	+5.70	1.0112	1.0516
	4, 5	−8.62	0.9218	0.9474
	9	−24.97	0.9123	0.8268
	10	+6.38	1.0035	1.0505

^{13}C Chemical shifts of aromatic hydrocarbons have been correlated approximately with the π-electron density by the following equation:[3]

$$\Delta\sigma_r = \alpha(q_r - 1)$$

where $\Delta\sigma_r$ is the chemical shift from benzene and α is a constant which is estimated to be 160 ppm by Lauterbur.[4] In order to examine the applicability of the equatoin to six-membered nitrogen heterocycles, the ^{13}C chemical shifts were plotted against the π-electron densities calculated by the SCF-MO method, and shown in Fig. 1. The full line in this figure illustrates the correlation line for $\alpha=160$ ppm. The best fit value for this series of compounds was estimated to be about 140 ppm by the least-square calculation of the most appropriate slope of the correlation line as illustrated by the dotted line in the figure, and this value is close to the α value for aromatic hydrocarbons.

The observed and the theoretical spectra of 1,6- and 1,7-naphthyridines were given in Fig. 2. The theoretical spectra were calculated by the equation with the best fit parameters (See Fig. 1). Thus, the less elaborate π-electron calculation is proven to be

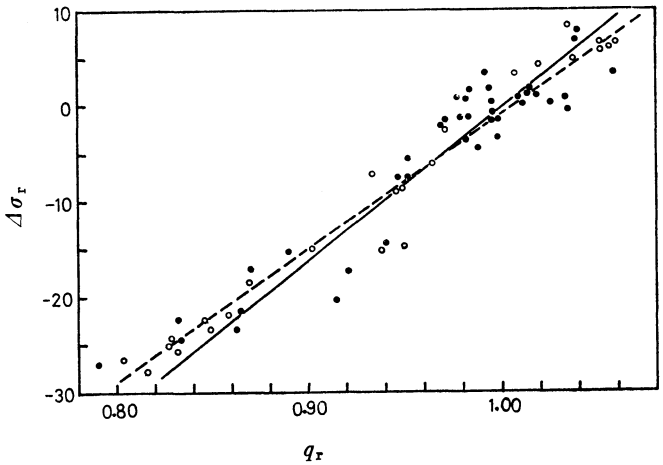

Fig. 1. ^{13}C Chemical shift *vs.* electron density plot. The full line in this figure corresponds to the equation $\Delta\sigma_r=160\ (q_r-1)$, and the broken line to the best fit equation $\Delta\sigma_r=139.8\,q_r-140.7$. The chemical shifts of naphthyridines investigated are illustrated by ○, and those of other six-membered aromatic nitrogen heterocycles by ●.

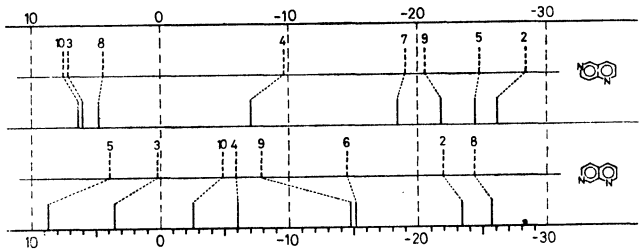

Fig. 2. Observed and calculated ^{13}C chemical shifts of 1,6- and 1,7-naphthyridines.

nearly as well useful as those including all valence shell electrons[5] to predict the ^{13}C chemical shifts of these heterocycles. The simple LCAO-MO calculation also predicts the ^{13}C chemical shifts of nitrogen heterocycles qualitatively. However, the correlation between the observed and the theoretical chemical shifts is poorer.

The authors are grateful to Dr. M. Imanari of the Japan Electron Optics Laboratories Co. for the measurement of ^{13}C NMR spectra.

References

1) Y. Hamada, I. Takeuchi, and M. Hirota, *Chem. Pharm. Bull. (Tokyo)*, **19**, 1751 (1971); *ibid.*, **22**, 485 (1974).
2) R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 767 (1953).
3) J. B. Stothers, *Quart. Revs.*, **1967**, 144.
4) P. C. Lauterbur, *Tetrahedron Lett.*, **1961**, 274.
5) The CNDO/2 calculations on symmetrical naphthyridines were compared with the ^{13}C chemical shifts in the following literature. A. C. Boicelli, R. Danieli and A. Mangini, *J. Chem. Soc. Perkin II*, **1973**, 1024.