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The NMR Spectra of Several *N*-(2-Biphenylyl)carboxamides

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During the course of an investigation of the structures of the photochemical decomposition products of several 1-acylbenzotriazoles,[1] it was discovered that the NMR spectrum of *N*-(2-biphenylyl)-pivalamide exhibited two signals farther downfield than usual aromatic protons. In connection with this finding, we examined the NMR spectra of several *N*-(2-biphenylyl) carboxamides and found that the two peaks were observed for all the spectra so far studied.

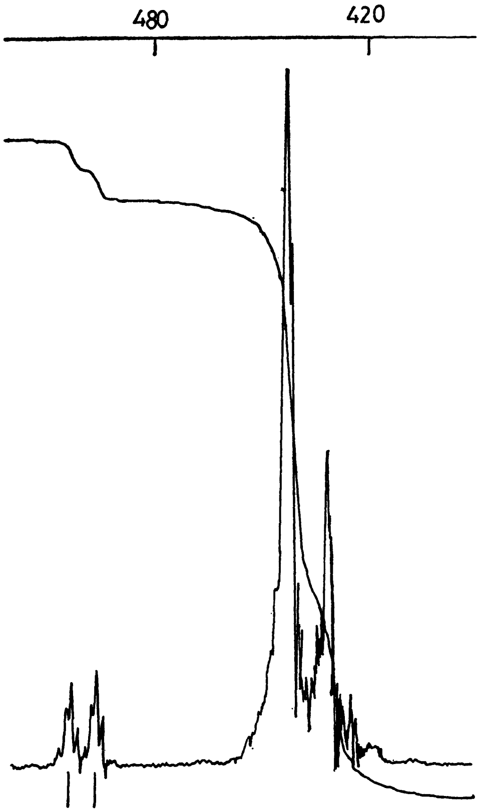
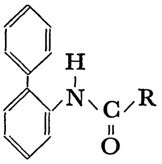
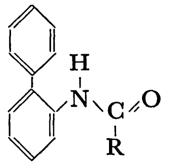


Fig. 1. The partial 60 MHz NMR spectrum of *N*-(2-biphenylyl)-pivalamide ($CDCl_3$) at room temperature.

Figure 1 shows the lower region of the spectrum of *N*-(2-biphenylyl)pivalamide. The two signals at 497 and 504 Hz from TMS at 60 MHz seemed assignable to the protons on the nitrogen atom of two geometrical isomers, **Ia** and **Ib**; this is in accord with the well-documented hindered rotation of amides.[2] Similar signals were also observed in the spectra of *N*-(2-biphenylyl) benzamide (II, 508 and 515 Hz) and *N*-(2-biphenylyl) acetamide (III, 490 and 497 Hz).


a


b

I $R=C(CH_3)$
II $R=ph$
III $R=CH_3$

Two conformations, **a** and **b**, were conceivable for the amide[2] from the viewpoint of steric factors, and the relative intensity of the two signals might reflect the relative abundance of the isomers (1:1). When the spectrum of I was measured in dimethyl sulfoxide-d_6, the two signals collapsed to a broad singlet which appeared at 519 Hz. This seemed to indicate that, in dimethyl sulfoxide, one of the two conformers became predominant and a strong hydrogen bonding between N–H and the solvent made the N–H signals deshielded.

On the other hand, no temperature dependence was observed for the spectrum of I in carbon tetrachloride in the range from room temperature to 150°C. Furthermore, the 220 MHz NMR spectrum of I (Fig. 2) exhibited the same intervals between the two signals as in the case of 60 MHz, suggesting that the two signals are caused by coupling. These phenomena were, however, inconsistent with the aforementioned assumption. Therefore, we carried out a decoupling experiment in order to clarify the cause of the two signals. When the aromatic protons at 435 Hz were irradiated, the two signals collapsed to singlet peak. Similarly, the shape of signals of aromatic protons markedly changed on irradiation at the center of the signals. These facts clearly demonstrated that the lowfield proton couples with the aromatic protons, the coupling constant being 7.2 Hz. Although a great number of works on long-range coupling, including a favourable coupling path in a planar zig-zag arrangement,[3] have been reported, only a few reports have been concerned with couplings between the proton on the nitrogen atom and the other protons across more than four bonds.[3-5] However, such a large coupling constant as 7.2 Hz has never been reported.

The presence of a five-bond coupling to the N–H proton seemed so unlikely that we looked for other explanations. One possibility was that the signals at

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[2] a) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonace," McGraw-Hill Book Co., New York (1959), p. 365. b) T. H. Siddall, III, and C. A. Prohaska, *J. Amer. Chem. Soc.*, **88**, 1172 (1966).

[3] S. Sternhell, *Pure and Appl. Chem.*, **14**, 15 (1964).

[4] R. F. Abraham and H. F. Bernstein, *Can. J. Chem.*, **37**, 1056 (1969).

[5] S. Sternhell, *Quart. Rev.*, **23**, 236 (1969).

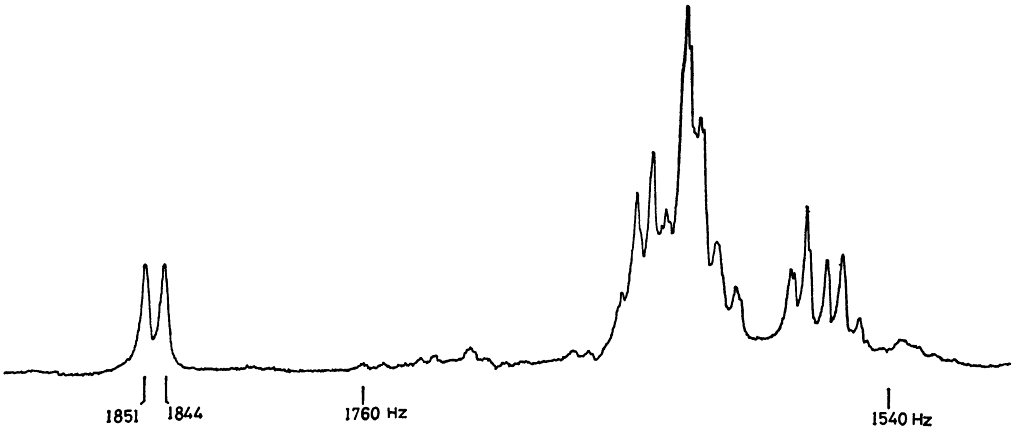

Fig. 2. The partial 220 MHz NMR spectrum of *N*-(2-biphenylyl)-pivalamide ($CDCl_3$) at room temperature.

497 and 504 Hz were due to one of the aromatic protons. In order to clarify this point, deuterium exchange was carried out. The sample recrystallized from methanol-d_4 - deuterium oxide showed a strong N–D absorption at 2400cm^{-1} in its IR spectrum; its NMR spectrum exhibited the two unchanged signals at the same positions, but the shapes of the signals of the usual aromatic protons changed markedly. This result indicated that the N–H proton which was obscured by the intense signals of the aromatic protons and that the two distinct signals at the downfield is probably due to an aromatic proton.

Since neither *N*-phenylbenzamide nor *N*-(4-biphenylyl)-carboxamides shows such spectral features, steric factors in *N*-(2-biphenylyl) carboxamides must be responsible for this remarkable deshielding effect.

On the basis of the aforementioned facts, it was deduced that the pivaloylamino group must lay on the same plane as that of the phenyl ring and that the anisotropy of the carbonyl group[6] might cause such a big deshielding effect on the proton at the ortho position to the amino group.[7] Steric effects and intramolecular π-NH hydrogen bonding were conceivable as factors fixing the conformation of the amino group as **a** in the scheme.

The spectrum of II was measured in a $CDCl_3$ solution to which a few drops of dimethyl sulfoxide has been added. The spectrum's two signals and the N–H signal moved up- and down-field respectively. Finally, the spectrum measured in dimethyl sulfoxide did not exhibit the two signals, but showed a broad singlet at 595 Hz which disappeared on deuterium exchange. These phenomena can be explained on the basis of the aforementioned conclusion; that is, the strong hydrogen bonding between the solvent and N–H proton would destroy the coplanarity of the carbonyl group, and hence the negative anisotropy effect on the ortho-proton would disappear to give the signals in the usual aromatic region.

Experimental

All the melting points are uncorrected. The NMR spectra were measured on JEOL JNM-3H60 or Varian HR 220-MHz spectromerters in a ca. 20% solution in either chloroform-*d* ($CDCl_3$) or dimethyl sulfoxide-d_6, with TMS as the internal standard.

N-(2-Biphenylyl)pivalamide (I). A solution of pivaloyl chloride (3.0 g) in methylene chloride (30 m*l*) was stirred, drop by drop, into a solution of *o*-biphenylamine (4.2 g) in methylene chloride (20 m*l*) and cooling with ice-water. To the reaction mixture we then added a solution of triethylamine (3.0 m*l*) in methylene chloride, after which the mixture was stirred for half an hour at room temperature. The mixture containing precipitates was washed with water (100 m*l*) three times and dried over anhydrous sodium sulfate. The subsequent evaporation of the solvent gave *N*-(2-biphenylyl) pivalamide (3 g). After recrystalization from ethanol, it had a mp of 69.7—70.1°C.

Found: C, 80.45; H, 7.44; N, 5.61%. Calcd for $C_{17}H_{19}ON$: C, 80.57; H, 7.56; N, 5.53%.

IR(KBr) 3260(NH), 1640(C=O), 770, 740, 700 cm^{-1} (benzene ring)

N-(2-Biphenylyl)benzamide(II) and N-(2-Biphenylyl)acetamide(III). The same experimental technique was used as that reported for *N*-(2-biphenylyl)pivalamide. The identification was made by a comparison of IR spectra of these products with the standard IRDC cards.[10]

N-(2-biphenylyl)benzamide mp 86.7—87.0°C (lit, 85—86°C).[8]

N-(2-biphenylyl)acetamide mp 116°C (lit, 117°C.)[9]

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