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NON-BONDED INTERACTIONS AND THE RELATIVE CONFORMATIONS OF TRIPHENYL-s-TRIAZINE AND TRI-2-PYRIDYL-s-TRIAZINE STUDIED BY NMR

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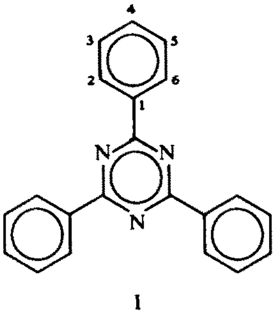
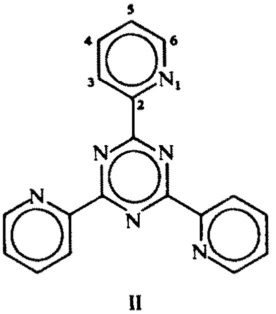
Abstract—A study of the proton chemical shifts of triphenyl-s-triazine (I) and tri-2-pyridyl-s-triazine (II) has shown that the latter is effectively more nearly planar than the former. This, in turn, means that for these compounds an *ortho-ortho* N...N interaction is less repulsive than a corresponding CH...N interaction.

INTRODUCTION

IN THIS PAPER we report the proton NMR spectra of triphenyl-s-triazine (I) and tri-2-pyridyl-s-triazine (II) in various solvents and use the chemical shifts to obtain information on the relative conformations of these compounds and, consequently, on the nature and relative strength of *ortho-ortho* N...N and CH...N interactions.



I



II

The discussion will be similar to that of Murrell *et al.*[1] on azabiphenyls and of Castellano *et al.*[2] on 2,2′-bipyridyl. The former authors briefly mentioned the spectra of I and II but no detailed interpretation was given. By considering the effects of neighboring ring magnetic anisotropy, of *ortho–ortho* interactions, of differences in π-electron distribution, and of solvent on the proton chemical shifts of azabiphenyls, they concluded that the averaged effective dihedral angle between the two ring nuclear planes decreases in the order biphenyl, 2-phenyl-pyridine, 2-phenylpyrimidine and 2,2′-bipyridyl, the latter being mainly *trans* at room temperature. This in turn, shows that in these compounds an *ortho–ortho* CH...N interaction is less repulsive than a corresponding CH...HC interaction.

As for the nature and relative strength of an N...N interaction no experimental evidence is known, as far as we are aware. The strong electric dipole moments associated with the nitrogen electron lone pairs would tend to make an N...N interaction more repulsive than CH...N or CH...HC; but, on the other hand, the steric hindrance is much less for the N...N interaction. The relative importance of these two opposing factors will be reflected in the relative conformations of molecules I and II, and these will, in turn, show up as specific differences in the NMR spectra.

RESULTS AND DISCUSSION

The proton chemical shifts relative to TMS as internal reference (τ-values) of I and II obtained from first-order analysis are shown in Table 1. In the case of I such an analysis reduces the accuracy of τ_3, τ_4 and τ_5 considerably. Table 2 shows the interproton coupling constants of II, neutral and protonated, also obtained from first-order analysis.

Table 1. τ-Values for triphenyl-s-triazine (I) and tri-2-pyridyl-s-triazine (II) in various solvents

	CCl_4	$(Me)_2CO$	MeOH	TFA
I $\tau_{2,6}$	1·30	1·22	1·18[a]	1·32
$\tau_{3,4,5}$	2·50 ± 0·05	2·42 ± 0·05	2·30 ± 0·05[a]	2·18 ± 0·08
II τ_3	1·03	1·13	0·91	0·40
τ_4	2·08	1·92	1·85	0·93
τ_5	2·55	2·37	2·30	1·23
τ_6	1·16	1·13	1·15	0·53

[a] These values are for a mixed solvent—65% (mole) MeOH + 35% (mole) $(Me)_2CO$—in view of the very low solubility of I in MeOH.

We begin the discussion by considering the results for the comparatively inert solvent CCl_4. The observed effect, Δ, of the remaining rings on the proton chemical shifts of a given phenyl (in I) or pyridyl (in II) ring is as follows:

$$\text{I} \quad \Delta_{2,6} = -1{\cdot}46 \text{ p.p.m.} \quad \Delta_{3,4,5} = -0{\cdot}26 \pm 0{\cdot}05 \text{ p.p.m.}$$

$$\text{II} \quad \Delta_3 = -1{\cdot}79 \text{ p.p.m.} \quad \Delta_4 = -0{\cdot}37 \text{ p.p.m.}$$

$$\Delta_5 = -0{\cdot}27 \text{ p.p.m.} \quad \Delta_6 = -0{\cdot}33 \text{ p.p.m.}$$

These Δ-values are the differences between the τ-values for I or II and those for the corresponding positions in benzene or pyridine molecules, respectively, in the same medium.

Table 2. Proton coupling constants of II in MeOH, TFA and HCl (in Hz)

	J_{34}	J_{35}	J_{36}	J_{45}	J_{46}	J_{56}
MeOH	7·8	1·3	0·9	7·8	1·8	4·8
TFA	8·0	1·2	0·5	8·0	1·4	6·0
HCl 2M	7·9	1·2	0·5	7·9	1·2	5·9

Particularly interesting are the Δ-values for the protons *ortho* to the inter-ring bonds. They are mainly due to (a) the magnetic anisotropy of the neighbouring ring, (b) the electric field effects associated with the nitrogen lone pairs in *ortho–ortho* CH...N interactions and (c) to changes in π-electron density, as already considered for azabiphenyls;[1,2] a minor part (d) is due to effects of the more distant rings.

In the case of triphenyltriazine, the latter contribution stems essentially from the magnetic anisotropy of the phenyl rings. Calculations of the π-electron current effects of two phenyl rings on the chemical shift of the *ortho* protons of the third one have been performed for various conformations. The dipole approximation[3] and the value $(\chi_\pi)_{zz} = -42 \times 10^{-6}$ cm[3,4,5] for the magnetic susceptibility of the π system along the axis perpendicular to the ring nuclear plane were used. The results for various dihedral angles θ between the triazine ring and the phenyl ring planes are as follows: $\theta = 90°$, $+0{\cdot}08$ p.p.m.; $\theta = 45°$, $-0{\cdot}08$ p.p.m.; $\theta = 20°$, $-0{\cdot}16$ p.p.m.; $\theta = 0°$, $-0{\cdot}19$ p.p.m.; the result for $\theta = 45°$ and $\theta = 20°$ are averages over all conformations corresponding to the same θ.

These values may be compared with the difference, $-0{\cdot}28$, between the $\Delta_{2,6}$ value of I ($-1{\cdot}46$) and that for 2-phenylpyrimidine ($-1{\cdot}18$),[1] taking in due account the fact that part of it arises from changes in π-electron densities. For an averaged effective angle $\theta = 45°$, $-0{\cdot}28-(-0{\cdot}08) = -0{\cdot}20$ p.p.m. would thus have to be ascribed chiefly to differences in π-electron density on the *ortho* positions on going from 2-phenylpyrimidine to molecule I. The study of azabiphenyls shows, however, that such a value is much too big. We must therefore conclude that $\theta < 45°$ in agreement with the conclusions of ref 1 for 2-phenylpryimidine.

Regarding contribution d for tripyridyltriazine, in addition to the ring-current effect by any two pyridyl groups on the Δ-values of the third one, there will be the long-range effects of the magnetic anisotropy and electric dipole of the corresponding nitrogen atoms. However, calculations identical to those for pyridine[6] show that, due to the large distance, these additional factors are quite unimportant; the larger effect is that of the electric dipole which is $-0{\cdot}06$ p.p.m. at the maximum ($\theta = 0°$).

The Δ-values for the *ortho* protons of I and II are, therefore, essentially determined by the same factors. On the other hand, all these factors a, b, c[1] and d make contributions to Δ that are more negative the more nearly planar the molecule. Consequently, the fact that Δ_3 for II is appreciably more negative than $\Delta_{2,6}$ for I clearly shows that the tri-2-pyridyl-s-triazine must be effectively more planar than triphenyl-s-triazine. The difference observed, $-0{\cdot}33$ p.p.m., must reflect an appreciable decrease of the averaged effective dihedral angle θ; possibly of the order of 10°–15°.

Such a conformational change can hardly be explained by considerations of π-electron delocalization energy and its variation with θ; this is corroborated by MO calculations to be described elsewhere. Nor can it be due to any weak attraction between a N atom of a pyridyl ring and an *ortho* H atom of another, atoms that are more than 4 Å apart. It must, therefore, mean that an *ortho–ortho* N…N interaction in II is less repulsive than a CH…N interaction in I or II.

This conclusion is confirmed by the spectra in TFA. If N…N is less repulsive than CH…N, it is likely less repulsive than NH…N. Therefore, protonation of the pyridyl ring N atoms should increase the effective dihedral angle θ. Consideration of the τ-values of II in TFA (Table 1) clearly shows[7] that protonation takes place preferentially at the pyridyl N atoms. Such a protonation should affect τ_3 and τ_5 equally if there was no conformational change; what we note, however, is that proton 5 is shifted to low field more than proton 3. This can only mean that the effective angle θ has increased upon protonation.

No attempt is here made to interpret the much smaller changes observed on going from CCl_4 to $(Me)_2CO$ or MeOH as solvents. Also, no striking features are encountered within the set of coupling constants shown in Table 2.

EXPERIMENTAL

The spectra were run at room temperature on a Varian spectrometer HA-100. The chemical shifts were obtained from solutions of 5 mg/ml except for I in the mixed solvent MeOH/acetone and II in CCl_4 because of low solubility; the spectra of the corresponding saturated solutions were obtained with the aid of a time averaging computer (CAT). The proton coupling constants were obtained from the spectra of solutions of 30 mg/ml.

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