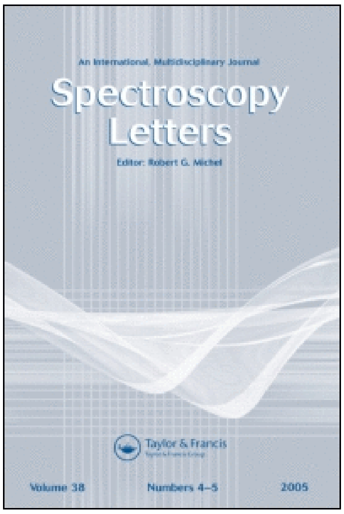

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Solution Structures of Pyrophthalones, III: Complementary Application of $^{14}N/^{16}N$-NMR Spectroscopy to Study Solution Structures of Pyrophthalones

Erhard T. K. Haupt[a]; Michael Eggers[a]
[a] Institut für Anorganische und Angewandte Chemie, Universität Hamburg, Hamburg

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Solution Structures of Pyrophthalones, III [1]

COMPLEMENTARY APPLICATION OF ^{14}N / ^{15}N-NMR SPECTROSCOPY TO STUDY SOLUTION STRUCTURES OF PYROPHTHALONES

Key Words: ^{14}N / ^{15}N-NMR, Pyrophthalones

Erhard T.K. Haupt [#] and Michael Eggers

Institut für Anorganische und Angewandte Chemie, Universität Hamburg,
Martin-Luther-King-Platz 6, D-20146 Hamburg 13, FRG

Abstract:

The solution structures of nine pyrophthalone-type substances are determined by ^{14}N / ^{15}N-NMR-spectroscopy. Mostly depending on the conditions (solvent, solubility, chemical nature of the compound), both isotopes can be used complementary to obtain reliable data. Additionally,

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[#] Author to whom correspondence should be addressed.
E-Mail: erhard_haupt@public.uni-hamburg.de

for some compounds ^{15}N solid state NMR data are available and demonstrate the structural identity in solution and the solid state.

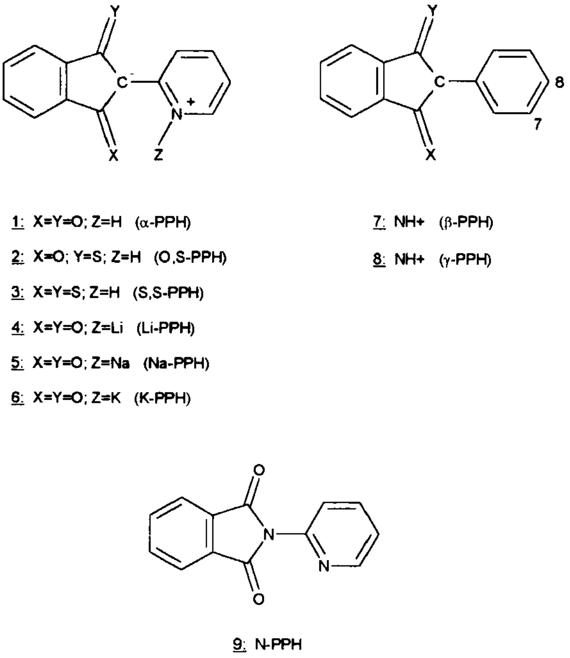
Introduction:

The constitution of pyrophthalone type compounds (scheme 1) is a matter of discussion since the first synthesis of α-PPH 1 [2]. More or less depending on the analytical method, the labile proton has been described to be located at several positions in the molecule [3].

Additionally, recent NMR-studies [1,3] have demonstrated, that a strong solvent dependence has to be obeyed and rotational isomerism around the central C-C-bond is observed, with consequences for the analysis and interpretation of spectroscopic data. Thus, for extended investigations of these compounds it is necessary to have a reliable method to determine the present constitution of the molecules subject to the conditions.

We have demonstrated earlier [1], that ^{15}N-NMR in principle is a valuable tool to fulfill these requirements. The characteristic chemical shift areas allow a fast and sure distinction between pyridinium (ca. 165 ppm) and pyridine-structures (ca. 290 ppm), which is important for their chemical and spectroscopic behaviour.

Generally, ^{15}N is the preferred nitrogen isotope for NMR spectroscopy because of its sharp lines as a consequence of the spin 1/2. Nevertheless, its application is restricted by its reduced sensitivity, which



1: X=Y=O; Z=H (α-PPH)
2: X=O; Y=S; Z=H (O,S-PPH)
3: X=Y=S; Z=H (S,S-PPH)
4: X=Y=O; Z=Li (Li-PPH)
5: X=Y=O; Z=Na (Na-PPH)
6: X=Y=O; Z=K (K-PPH)

7: NH+ (β-PPH)
8: NH+ (γ-PPH)

9: N-PPH

Scheme 1: Structural formulas of compounds (1) - (9)

also proves right for the badly soluble compounds discussed in this contribution. Advantages by the use of DEPT- or INEPT-sequences [4] or inverse experiments [4] depend on the existence of an effective proton-coupling, which is just the matter of discussion in our case. If available, these experiments are very helpful for the characterization, which has been demonstrated with the proton-coupled ^{15}N-NMR-spectra of iminopyrophthalone [1]. But, the obvious idea of simply measuring the ^{15}N-NMR spectrum often fails in this class of compounds. An unsuccesful measurement may have several reasons (solubility, absence of proton-coupling etc.) and thus gives no reliable hint about the constitution. Therefore, we demonstrate in this contribution that ^{14}N-NMR can be choosen successfully as an alternative, because the linewidths of the signals are moderate especially in those cases, where ^{15}N-NMR fails.

Materials and Methods:

The synthesis of the compounds was performed according to the literature [2,5-8]. The ^{15}N-NMR-spectra were recorded at 36 MHz and referenced, analysed and assigned as described in loc. cit. [1]. The ^{14}N-NMR spectra are recorded at 26 MHz using the same equipment, but a 10mm broadband probehead. Because of the low solubility, in all ^{14}N-NMR spectra we observed a signal at 313 ppm (DMSO, $W_{1/2}$ = 60-90 Hz) or 308 ppm ($CDCl_3$, $W_{1/2}$=50 Hz) respectively, which can be proven to be dissolved gaseous N_2 by measuring normal $CDCl_3$ bubbled with N_2 and afterwards with helium gas, whereto the signal vanishes. The solid state ^{15}N-NMR spectra are measured with the equipment described in loc. cit. [1] and referenced to the glycin-nitrogen at 33.75 ppm rel. to NH_{3liq}.

Results and Discussion:

The extension of our initial studies of α-PPH [3] to β,γ-PPH as well as similar compounds (scheme 1) affords an analytical method to determine unequivocally the constitutional behaviour of the samples, before reliable stereochemical conclusions are possible. The main reason is, that although betainic structures have been proposed in several cases [1,3], it is not sure that these are valid for all other compounds of this type, especially when the polarity of the solvent is varied. Because of the existence of one labile proton, the dominance of other tautomeric or mesomeric forms seems to be possible. Thus, this basic question has to be answered for any compound for all present conditions. In principle, this problem can be attacked via ^{1}H-NMR, but only in favourable cases the proton-nitrogen-bond to the pyridine-ring is stable enough to detect proton-proton-couplings to the pyridine-ring-protons or to perform successful ^{15}N-DEPT experiments. Also the stereochemical interpretation of the ^{1}H-NMR data depends strongly on the charge situation at the nitrogen and/or the neighboured X,Y atoms (scheme 1). Thus, it is necessary to determine the basic structure separately for every compound. As is shown in Table 1, ^{15}N-NMR is very helpful, but is not always available for all compounds under investigation, mainly due to the solubility of the substances. Nevertheless, we could achieve ^{14}N-NMR spectra of sufficient quality in all cases, where ^{15}N-NMR fails. We observe a moderate linewidth, which allows an easy measurement in approximately 1 hour (^{15}N: 64h). On the other hand, there are examples, e.g. the alkali salts, where ^{14}N-NMR fails. We expect, that this is due to a

TABLE 1: ^{14}N / ^{15}N-NMR Chemical Shifts of Compounds 1-9

Substance	Solvent	δ ^{15}N (ppm)	δ ^{14}N (ppm)	^{14}N Linewidth $W_{1/2}$ (Hz)
α-PPH (1)	DMSO-d_6	164.7	163	730
"	$CDCl_3$	160.1	155	364
"	*solid*	170.1		
β-PPH (2)	DMSO-d_6		208	318
γ-PPH (3)	DMSO-d_6		175	364
"	*solid*	172.0		
O,S-PPH (4)	DMSO-d_6		172	683
"	$CDCl_3$	166.6	164	296
"	*solid*	170.0		
S,S-PPH (5)	DMSO-d_6		185	524
"	$CDCl_3$		171	273
"	*solid*	171.0		
Li-PPH (6)	DMSO-d_6	276.4		
Na-PPH (7)	DMSO-d_6	292.0		
K-PPH (8)	DMSO-d_6	303.2		
N-Methyl-PPH [9]	$CDCl_3$		179	?
N-PPH (9)	DMSO-d_6	314.7 189.3		
"	$CDCl_3$	305.2	305 171	1001 1230

dramatically increased linewidth, obviously because the pyridine character prevails. This is concluded from the ^{15}N chemical shift and the comparison of the linewidth behaviour in N-PPH. In those cases, where spectra of both isotopes are available, the chemical shift discrepancies are within the borders of accuracy and good enough to make a sure structural decision. The chemical shifts confirm the assumption, that in most cases pyridinium-structures are present with the result of either reduced linewidth in ^{14}N-NMR as well as the availability of ^{15}N data in favourable cases. In contrast, the salts and N-PPH are preferably described with a saturated pyridine-moiety, which can be observed better in ^{15}N-NMR than in ^{14}N-NMR. For comparison, some ^{15}N-CPMAS-NMR data are included in Table 1 and demonstrate, that in the given examples the constitution is the same in the solid state and in solution.

Conclusion:

The characterization of the basic constitution of pyrophthalone-type compounds can be performed successfully, when both magnetically active nitrogen isotopes are applied and used for the analysis complementary. Despite the chemical shift, the availabilty of the spectra and the linewidth in the ^{14}N-spectra seem to yield additional hints for the structural features, while the ^{15}N spectra yield the better resolution and in favourable cases additional informations about proton-nitrogen couplings.

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