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THE STRUCTURE AND CONFORMATION OF 3-METHYLPHOSPHACYMANTRENE

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Summary

The proton NMR spectrum of 3-methylphosphacymantrene in a nematic solvent has been interpreted in terms of the molecular structure and conformation. The preferred conformation of the molecule appears to be the one where a C–H bond of the methyl group is perpendicular to the ring plane. The results are in accord with the bond polarisation hypothesis.

Introduction

A study of phosphacymantrene dissolved in a nematic solvent indicated that the ring was essentially planar [1]. Replacement of a hydrogen by a methyl group leads to an interesting problem concerning the preferred conformation of the methyl group. NMR spectroscopy of oriented molecules has been applied to a number of such cases in the past [2]. However, in most of these cases, the number of derived dipolar couplings (D_{ij}'s between interacting nuclei i and j) was larger than the sum of the structural and the order (S_{ij}) parameters required to be derived, and so it was easy to find the preferred conformation from the quality of the fit of the dipolar couplings and of the geometrical and order parameters for the various conformational possibilities. On the other hand in a case such as 3-methylphosphacymantrene the number of HH dipolar couplings is the same as the sum of the structural and the order parameters, and hence for each conformational possibility the fit between the dipolar couplings and the structural and the order parameters is expected to be perfect, and hence derivation of the preferred conformation using this procedure is not possible. A comparison of the geometrical results obtained with available data

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on similar systems may give an indication on the preferred conformation. Results on 3-methylphosphacymantrene are described below.

Experimental

The proton magnetic resonance spectrum of 3-methylphosphacymantrene was recorded on a Bruker WH-270 FT-NMR spectrometer at 21° C. A 3 weight per cent solution of the compound in *N*-(*p*′-ethoxybenzylidene)-*p*-n-butylaniline (EBBA) was studied. Two hundred and forty free induction decays (FID's) were accumulated with the help of a BNC-12 computer having a core memory of 20k. The accumulated FID was Fourier transformed to obtain the frequency domain spectrum shown in Fig. 1.

The spectral analysis was achieved iteratively with the help of the LEQUOR programme [3] on a DEC-1090 computer. The number of lines fitted was 166, and a

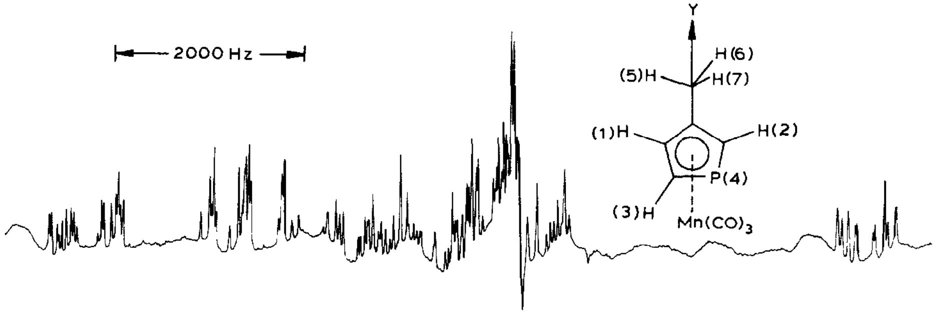

Fig. 1. Proton NMR spectrum of 3-methylphosphacymantrene oriented in the nematic phase of EBBA. Solute concentration: 3 weight per cent; temperature: 21° C; spectrometer: WH-270; number of scans: 240.

TABLE 1

SPECTRAL PARAMETERS IN 3-METHYLPHOSPHACYMANTRENE ORIENTED IN THE NEMATIC PHASE OF EBBA

Parameter	Value (Hz)	Parameter	Value (Hz)
J_{12}	1.46±0.62 (1.10) [a]	D_{15}	32.16±0.10
J_{13}	5.10±0.36 (4.67) [a]	D_{23}	121.70±0.31
J_{23}	2.89±0.72 (1.77) [a]	D_{24}	−52.52±0.13
$\nu_2-\nu_1$	230.31±0.32 [b]	D_{25}	−244.33±0.06
$\nu_3-\nu_1$	167.94±0.41 [b]	D_{34}	452.13±0.48
$\nu_5-\nu_1$	1134.13±0.31 [b]	D_{35}	−69.14±0.10
D_{12}	218.71±0.29	D_{45}	−63.70±0.10
D_{13}	−934.21±0.18	D_{55}	1391.75±0.05
D_{14}	15.64±0.48		

[a] Values for phosphacymantrene. [b] At 270 MHz other *J*-values used are [1]: $J_{14}=5.30$, $J_{24}=J_{34}=35.8$, $J_{15}=J_{25}=J_{35}=0.0$, $J_{45}=1.0$ Hz.

root-mean-square (rms) error of 1.2 Hz between the observed and the calculated line positions was obtained when the iterations were carried on the HH indirect couplings (J(HH)'s) between the ring protons the HH and the HP dipolar couplings (D_{ij}'s) and the chemical slift differences ($\nu_i - \nu_j$) between the protons. The indirect couplings between the ring and the methyl protons were taken as zero, and the indirect PH couplings were taken from the literature on the isotropic spectrum of phosphacymantrene. Values of the parameters derived are listed in Table 1.

Results and discussion

Table 1 shows that the values of the indirect HH couplings between the ring protons are similar within experimental error to those reported for phosphacymantrene in the isotropic phase [1]. The table also shows that 3-methylphosphacymantrene provides 11 independent direct dipolar couplings. For the planar ring skeleton of the molecule three of these are required for the specification of the molecular orientation. The remaining 8 dipolar couplings are just sufficient to fix the relative HH and HP distances for each mode of the rotation of the methyl group about the C–C bond. Therefore, a perfect fit between the derived dipolar couplings and the relative HH and HP positions and the order parameters is expected for any mode of methyl group rotation. The various modes of rotation considered were those in which (i) a C–H bond of the methyl group is in the ring plane, (ii) is perpendicular to it, or (iii) is free to rotate. The calculations were performed using a version of the SHAPE programme [4] modified to include the methyl group rotation in the calculations. Perfect fits for all the considered modes were obtained. The derived relative internuclear distances were the same in all cases except when a C–H bond of the methyl group was assumed to be perpendicular to the ring plane (referred to as possibility P). The values are reported in Table 2 along with the distance ratios derived for phosphacymantrene. A comparison of the results for phosphacymantrene and 3-methylphosphacymantrene shows that the agreement between the two is better for possibility P. There is thus an indication that the

TABLE 2

STRUCTURAL PARAMETERS FOR 3-METHYLPHOSPHACYMANTRENE

Parameter	Value		
	Possibility P	Other possibilities	Phosphacymantrene
r_{12}/r_{13}	1.700	1.657	1.732
r_{14}/r_{13}	1.457	1.407	1.480
r_{34}/r_{13}	0.996	0.977	0.992
r_{23}/r_{13}	1.814	1.770	1.841
X_1/r_{13} [a]	−1.117	−0.992	
Y_1/r_{13} [a]	−0.777	−0.765	
Y_3/r_{13} [a]	−1.770	−1.763	
r_{56}/r_{13}	0.694	0.696	

[a] X_i and Y_i are the X and Y coordinates of the i^{th} nucleus with respect to a Cartesian coordinate system with the centre of the triangle formed by the methyl proton as the origin; X and Z axes lie in the plane containing the methyl protons. Y is the axis of the methyl group rotation.

preferred conformation of 3-methylphosphacymantrene is that in which a C–H bond of the methyl group is orthogonal to the ring plane. This is in accord with the results on toluene [3] and π-methylcyclopentadienylmanganese tricarbonyl complex [5]. It can be interpreted in terms of the bond polarisation hypothesis [6] according to which the ring and the methyl C–H bonds try to keep as far apart as possible due to electrostatic repulsions between the bonds with similar polarities.

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