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THE STRUCTURE OF PHOSPHACYMANTRENE

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Summary

Proton NMR spectra of phosphacymantrene (π-phospholyl manganese tricarbonyl) orientated in the nematic phases of liquid crystals have been investigated. The derived H—H and H—P direct dipolar coupling constants have been used to determine the relative proton—proton and proton—phosphorus distances. A comparison of the geometrical data of various 5-membered aromatic heterocycles shows that the relative distances between the protons closest to the heteroatom increase with the van der Waals radius of the heteroatom. The results suggest that NMR spectroscopy of orientated molecules can be used to determine van der Waals radii.

Introduction

The technique of NMR spectroscopy of orientated molecules has been used by various workers for the determination of the molecular geometry of 5-membered aromatic ring systems containing heteroatoms such as O, N, S, Se, Te [1—5]. The ring system with phosphorus as a heteroatom has not previously been examined because such compounds were unknown until phosphacymantrenes (phospholylmanganese tricarbonyls) were synthesized [6,7]. The structure, properties and uses of these compounds have still not been well investigated. In the present communication, the results of a study of the structure of one such system, namely, π-phospholylmanganese tricarbonyl, determined by the technique of NMR spectroscopy of orientated molecules, are reported. A comparison of the geometrical data for various 5-membered aromatic ring systems containing a heteroatom indicates a correlation between the size of the atom and the relative distances of the protons closest to the heteroatom.

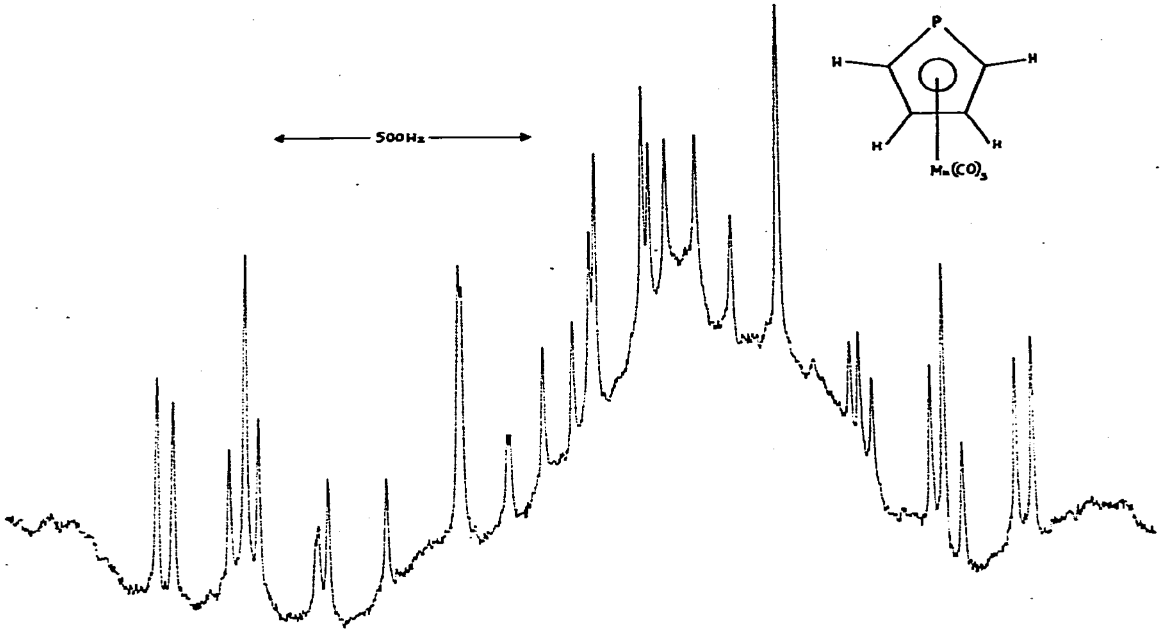


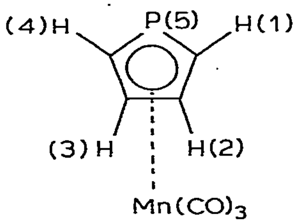
Fig. 1. Proton magnetic resonance spectrum of phosphacymantrene oriented in Merck Phase IV. Solute concentration: 3 mol %, temperature: 27° C, spectrometer frequency: 90 MHz, number of transients accumulated: 1000.

Experimental

π-Phospholylmanganese tricarbonyl was prepared as previously described [6,7]. PMR spectra of the compound dissolved in nematic solvents were

TABLE 1

SPECTRAL PARAMETERS FOR PHOSPHACYMANTRENE ORIENTED IN MERCK PHASE IV



Parameter	At 27° C, 90 MHz (data 1) (Hz)	At 21° C, 270 MHz (data 2) (Hz)
$D(12)$	84.89 ± 0.43	102.66 ± 0.42
$D(13)$	72.28 ± 0.43	76.44 ± 0.41
$D(14)$	84.90 ± 0.11	88.92 ± 0.07
$D(15)$	168.16 ± 0.16	177.53 ± 0.10
$D(23)$	450.50 ± 0.11	472.44 ± 0.09
$D(25)$	10.29 ± 0.16	12.66 ± 0.09
$(\nu_1 - \nu_2)$	49.50 ± 0.22	147.82 ± 0.14

Indirect proton—proton and proton—phosphorus coupling constants (in Hz) used are [6]: $J(12) = 4.67$; $J(13) = 1.10$; $J(14) = 1.77$; $J(15) = 35.80$; $J(23) = 3.04$; $J(25) = 5.30$.

recorded on Bruker WH-90 and WH-270 FT-NMR spectrometers. The solute concentrations were about 3 mol% in Merck Phase IV and the spectra were recorded at 27°C and 21°C respectively. A typical spectrum is shown in Fig. 1.

The spectra were analyzed with the help of the LAOCOONOR [8] program on an IBM 360/44 computer. Values of the derived parameters including the probable errors as given by the computer program are reported in Table 1. The values of the indirect spin—spin coupling constants reproduced in Table 1 were taken from the reported spectrum in isotropic medium [6].

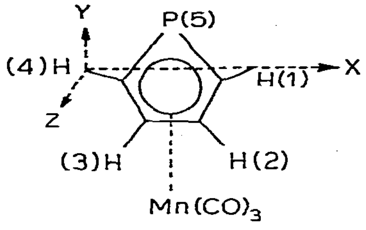
Results and discussion

Table 1 shows that the phospholyl moiety of phosphacymantrene provides six independent direct dipolar couplings. The planar skeleton of this moiety needs three geometrical parameters (to fix relative positions of the four protons and the phosphorus atom) and two order parameters. For such a situation, the system is over determined by one coupling constant. An acceptable fit between the experimental dipolar couplings and those calculated with the "best-fit" geometrical and the order parameters indicates that the molecule is essentially planar and provides the molecular geometry. However, if the phosphorus atom is out of the plane of the ring carbons, the system is under-determined by one coupling constant as far as the determination of the geometrical and the order parameters from the derived direct dipolar couplings is concerned; in this case four geometrical parameters are needed to define the relative positions of the four protons and the phosphorus atom and three parameters are essential for the description of the order of the ring moiety. A combination of the results in various solvents and/or various orientation conditions must, therefore, be used to establish whether the ring skeleton is planar or not. In the present case, the spectra were recorded in solutions at various temperatures and the derived geometrical and the order parameters using the "least-square-fit" programme SHAPE [9] are given in Table 2 for the planar ring moiety.

It can be seen from Tables 1 and 2 that, even though the changes in the various dipolar couplings in the two different experiments are not proportional, the derived geometrical information in both cases is the same within experimental error. The r.m.s. error between the observed and the "best fit" calculated dipolar coupling constants in both cases is less than 0.05 Hz. The results indicate that the ring skeleton is essentially planar. In order to provide additional confirmation, similar experiments were performed in *N*-(*p*-methoxybenzylidene)-*p*-n-butylaniline. In this case too, the derived values of the ratios $r(12)/r(23)$, $r(14)/r(23)$ and $r(15)/r(23)$ agreed, within experimental error with those reported in Table 2. The results are, therefore, consistent with an essentially planar structure for the ring moiety of phosphacymantrene. X-ray crystallographic studies on a related compound, namely, 2-benzoyl-3,4-dimethylphospholylmanganese tricarbonyl indicate that the phospholyl ring is not strictly planar [7]; the dihedral angle between the carbon and the C—P—C planes is 2.15°. An inclusion of non-planar distortions of this magnitude in the present studies on phosphacymantrene indicate that the results are insensitive to such small deviations from planarity in the phospholyl moiety. However, the relative H—H and H—P dis-

TABLE 2

THE GEOMETRICAL AND THE ORDER PARAMETERS IN PHOSPHACYMANTRENE



Parameter	From data 1 of table 1	From data 2 of table 1
$r(12)/r(23)$	0.974 ± 0.004	0.977 ± 0.004
$r(14)/r(23)$	1.744 ± 0.002	1.745 ± 0.002
$r(15)/r(23)$	0.964 ± 0.001	0.964 ± 0.001
S_{xx} ^{a}	−0.07385 ± 0.00002	−0.07745 ± 0.00003
S_{yy} ^{a}	−0.0024 ± 0.0003	−0.0052 ± 0.0003

^{a} r_{23} = 2.70 Å (assumed).

tances do not change significantly whether or not such distortions are incorporated. The values are given in Table 2.

A comparison of the relative H—H distances, particularly $r(14)/r(23)$, was made for the various 5-membered aromatic ring systems such as furan, pyrrole, thiophene, selenophene, tellurophene and phosphacymantrene. Values determined for the first five compounds by NMR spectroscopic measurements in liquid crystals, have been reported and are 1.47 [1], 1.551 [2], 1.745 [3], 1.788 [4], and 1.840 [5] respectively. This ratio increases with the size of the heteroatom. A plot of the van der Waals radii of the heteroatoms O, N, S, Se, Te against the distance ratio $r(14)/r(23)$ in the 5-membered heterocycles is shown in Fig. 2. From this curve and Table 1, a value of 1.80 Å is obtained for the van der Waals radius of the phosphorus atom. This is the same as the litera-

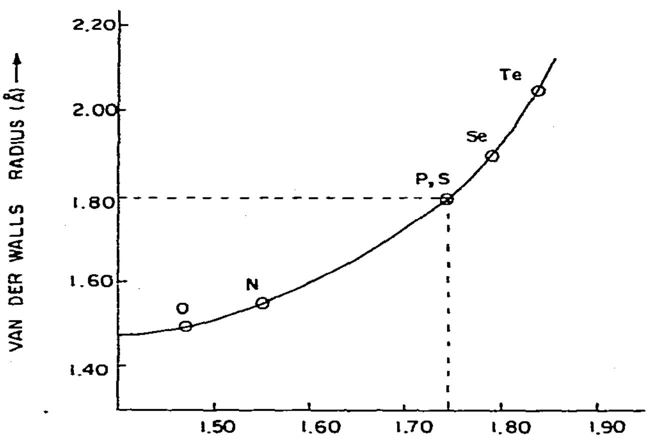


Fig. 2. Plot of van der Waals Radii of heteroatoms vs. the distance ratios $r(14)/r(23)$ in 5-membered aromatic heterocyclic ring systems.

ture value [10], and this indicates that NMR spectroscopy of oriented molecules can be used satisfactorily to determine van der Waals radii.

The order parameters (Table 2) expressed relative to a Cartesian coordinate system (having x and y axes in the ring plane and y coinciding with the c_2 symmetry axis of the ring moiety) show that the molecule orientates preferentially with the ring plane perpendicular to the direction of the magnetic field. The effect is similar to that observed for analogous π-complexes [11] such as π-cyclobutadiene iron tricarbonyl, π-cyclopentadienyl nickel nitrosyl, π-cyclopentadienyl manganese tricarbonyl, π-methylcyclopentadienyl manganese tricarbonyl and π-benzene chromium tricarbonyl.

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