Conformation of Thianthren and 2,7-Dichlorothianthren partially oriented in a Nematic Phase

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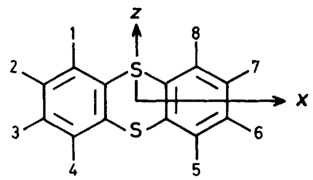
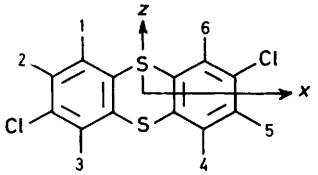
The ^1H n.m.r. spectra of thianthren and 2,7-dichlorothianthren dissolved in the Merck Nematic Phase IV were analysed and the structural parameters obtained. These molecules in solution adopt a folded conformation about the axis connecting the two sulphur heteroatoms. The angle of folding is 140.6° for thianthren and 139.8° for 2,7-dichlorothianthren. The correspondent standard deviations are ±0.4 and ±0.7°, respectively.

THE most interesting geometrical parameter of tricyclic molecules such as dibenzo-*p*-dioxin, thianthren, phenothiazine, *etc.*, is the angle of folding, ϕ, about the axis which joins the two heteroatoms. The angle of folding is defined as the dihedral angle between the two aromatic rings. In a previous paper [1] we have used n.m.r. spectroscopy in nematic solvents [2,3] for the determination of the molecular structure of dibenzo-*p*-dioxin, which was shown to exist in a folded conformation (ϕ 165.6°). In this study we have extended this method to thianthren (1). It is known that thianthren and its derivatives adopt a folded conformation about the S–S axis. The crystal structure of (1) has been fully analysed by *X*-ray diffraction, which gave an angle of folding of 128°.[4,5] This value was also predicted by Chandra [6] in a theoretical study using the LCAO-MO method. Aroney *et al.*[7] obtained, from dipole moment and molar Kerr constant measurements of thianthren in benzene solution, angles of folding of 144 ± 8 and 140 ± 10°, respectively. The marked difference between the values in solution and in the solid state was explained by the latter authors as an effect of ' flapping ' which induces the molecule to adopt in solution all folded structures with angles ranging from 180° to less than 128°, with a mean value of *ca.* 140°.



(1)



(2)

In this study we have analysed the ^1H spectrum of thianthren dissolved in an orienting medium in order to obtain an accurate value for the angle of folding in solution. In addition we have also examined 2,7-dichlorothianthren (2) to evaluate the effect of the substituents on the angle of folding.

RESULTS AND DISCUSSION

Thianthren (1).—The oriented spectrum of thianthren has been interpreted in terms of ten dipolar couplings and two chemical shifts. The energy barrier of the ring inversion process has been predicted by Chandra [6] to be 6—7 kcal mol^{-1} using the LCAO-MO method. This barrier was also estimated from dielectric polarization [8] and dielectric relaxation [9] studies to be 5.0 and 6.2 kcal mol^{-1}, respectively. Such a barrier to ring planarity is relatively high, suggesting that the molecule exists mainly in two equivalent interconverting folded conformations (the probability of occurrence of the planar form is of an order of magnitude of 10^{-5}). Since the two conformers in equilibrium have the same orientational parameters and the same interproton distances, the calculations were performed as if the molecule existed in a single rigid bent conformation. The bent molecule has C_{2v} symmetry. The proton geometry can be described by five distances; in addition, two orientational parameters are required to describe the orientation. Thus, with one distance (r_{23}) assumed to scale the geometry, there are six independent parameters to be determined from ten different dipolar coupling constants.

The experimental data and the results of the geometrical calculations, performed with the program SHAPE,[10] are given in Table 1. The agreement between the calculated and the experimental D_{ij} values is satisfactory for the folded conformation, although several direct couplings show deviations exceeding the experimental error. These discrepancies may be due to the assumption that the molecule interconverts only between two rigid bent conformers, whereas the dynamic averaging should include a number of states with slightly different geometries. Also the vibrational averaging effects are probably not negligible, as shown by Bechtold *et al.*[11] for naphthalene.

The angle of folding has been calculated through equation (1). A value of 140.6° was obtained, in good

$$\phi = 180 - 2\arctan (y_2 - y_1)/(x_2 - x_1) \quad (1)$$

agreement with the angle determined from the dipole moments and the molar Kerr constants. The standard deviation of ϕ, derived from the standard deviations of the proton co-ordinates, is ± 0.4°. The deviations between the calculated and the experimental D_{ij} values are very sensitive to changes in the angle of folding. For instance, the calculations performed in the case of the rigid planar structure (ϕ 180°) show exceedingly large deviations for the inter-ring direct coupling constants (see Table 1). These results show that a significant flattening occurs for thianthren in anisotropic solution with respect to the solid state, confirming the results already found [7] in isotropic solvents. The effect of crystal packing observed for dibenzo-*p*-dioxin is opposite to that determined for thianthren. In fact dibenzo-*p*-dioxin is essentially planar in the solid state and puckered in solution (ϕ 165.6°).

TABLE 1

Experimental and computed data of thianthren (1) [a,b]

Parameter	Experimental value	$D_{calc} - D_{exp}$ (folded conformation)	$D_{calc} - D_{exp}$ (planar conformation)	Geometrical parameters
D_{12}	$-1\,011.47 \pm 0.05$	0.01	0.14	$r_{12}/r_{23} = 1.004 \pm 0.006$
D_{13}	-56.97 ± 0.06	−0.01	0.01	$r_{13}/r_{23} = 1.742 \pm 0.007$
D_{14}	6.52 ± 0.37	−0.61	−0.64	$r_{14}/r_{23} = 2.025 \pm 0.01$
D_{15}	-38.17 ± 0.39	−0.82	−8.63	$r_{15}/r_{23} = 2.859 \pm 0.008$
D_{16}	-40.79 ± 0.07	0.13	−4.41	$r_{16}/r_{23} = 3.223 \pm 0.006$
D_{17}	-70.99 ± 0.06	−0.04	−3.52	$r_{17}/r_{23} = 2.892 \pm 0.006$
D_{18}	-220.22 ± 0.29	0.05	18.82	$r_{18}/r_{23} = 2.018 \pm 0.003$
D_{23}	59.42 ± 0.38	0.13	−0.08	$r_{26}/r_{23} = 3.779 \pm 0.006$
D_{26}	-30.96 ± 0.38	0.17	−4.74	$r_{27}/r_{23} = 3.644 \pm 0.006$
D_{27}	-38.37 ± 0.30	−0.94	−6.47	
ν_1-ν_2 (Hz)	7.14 ± 0.68			
				ϕ [d] $= 140.6 \pm 0.4°$
R.m.s. (Hz)		0.14	3.27	
S_{xx} [c]		$0.230\,40 \pm 0.002\,16$	$0.178\,96 \pm 0.000\,14$	
S_{zz}		$-0.007\,54 \pm 0.000\,04$	$-0.007\,57 \pm 0.000\,04$	

[a] The indirect coupling constants were assumed according to ref. 13 (see Experimental section). [b] The direct coupling constants are in Hz. [c] Order parameters are determined with r_{23} 2.481 Å. [d] Angle of folding defined as the dihedral angle between the two aromatic rings.

2,7-*Dichlorothianthren* (2).—The molecule of 2,7-dichlorothianthren has C_2 symmetry and requires nine direct couplings to describe the relative proton positions and the three orientational parameters. Since nine different dipolar couplings are available, the problem is exactly determined and a solution with zero root mean square error has been obtained. As this solution led to an unacceptably distorted geometry for the aromatic rings, some assumptions must be introduced to decrease the number of the independent variables. We have thus assumed that H-1 (H-4) and H-3 (H-6) are related by a plane of symmetry, which means that the geometrical deformations induced by the chlorine atoms on H-1 and -3 are equal. Consequently the number of independent variables is reduced to seven and the problem becomes overdetermined.

The experimental data and the geometrical parameters are collected in Table 2. Some of the calculated D_{ij} values show rather large deviations with respect to the experimental value, which are probably due to the above assumption. Actually Diehl *et al.*[12] have found that both

TABLE 2

Experimental and computed data of 2,7-dichlorothianthren (2) [a,b]

Parameter	Experimental	$D_{calc} - D_{exp}$	Geometrical parameters
D_{12}	$-2\,502.15 \pm 0.10$	0.00	$r_{13}/r_{12} = 2.007 \pm 0.012$
D_{13}	49.92 ± 0.89	0.30	$r_{14}/r_{12} = 2.838 \pm 0.017$
D_{14}	14.97 ± 0.63	0.63	$r_{15}/r_{12} = 3.205 \pm 0.02$
D_{15}	-21.24 ± 0.08	−0.01	$r_{16}/r_{12} = 2.008 \pm 0.012$
D_{16}	-309.97 ± 1.46	1.27	$r_{23}/r_{12} = 1.729 \pm 0.011$
D_{23}	180.89 ± 0.80	−0.33	$r_{25}/r_{12} = 3.760 \pm 0.023$
D_{25}	-30.23 ± 0.54	0.03	$r_{26}/r_{12} = 2.878 \pm 0.018$
D_{26}	-121.42 ± 1.36	−2.49	$r_{36}/r_{12} = 2.838 \pm 0.017$
D_{36}	-107.04 ± 0.09	0.00	
$\nu_2 - \nu_1$ (Hz)	-9.29 ± 0.79		
$\nu_3 - \nu_1$ (Hz)	27.39 ± 0.56		ϕ [d] $= 139.8 \pm 0.7°$
R.m.s. (Hz)		0.12	
S_{xx} [c]		$0.329\,38 \pm 0.001\,31$	
S_{zz}		$-0.052\,41 \pm 0.000\,98$	
S_{xz}		$0.181\,49 \pm 0.001\,39$	

[a] The J_{ij} values were assumed constant (see Experimental section). [b] The direct coupling constants are in Hz. [c] Order parameters are determined with r_{13} 5.024 Å (thianthren value). [d] Angle of folding defined as the dihedral angle between the two aromatic rings.

proton and carbon geometries in monochlorobenzene are deformed from the hexagonal structure in anisotropic phases. The maximum deviation was observed for the r_{meta}/r_{ortho} ratio (*ca.* − 0.015). Since this deviation is of the same order of magnitude of the standard deviations determined for the internuclear distance ratios, we believe that the assumption used is valid within the reported accuracy.

The angle of folding of 2,7-dichlorothianthren obtained with this method is 139.8 ± 0.7°. This value is almost the same as that found for thianthren and shows that the two chlorine atoms do not significantly affect the conformation of this tricyclic system.

Molecular Orientation.—In both molecules S_{xx} is the largest positive order parameter, which indicates that the molecules are oriented preferentially along the x axis, as expected from the molecular shape. In the case of 2,7-dichlorothianthren the angle between the molecule-fixed x axis and the principal axis x' of the diagonalized ordering matrix was found to be 21.8°.

EXPERIMENTAL

The n.m.r. spectra of (1) and (2) were recorded with a Varian XL-100-15 spectrometer at the probe temperature (35°). The oriented spectra were analysed with the LAC-XLC iterative program on a Univac 1 100 computer. A 2 mole % solution of commercially available thianthren was prepared in 4-n-butyl-4′-methoxyazoxybenzene (Phase IV). A total of 340 lines were assigned by iterative analysis, which gave root mean square error of 1.0 Hz with a maximum deviation of 3.0 Hz. The indirect coupling constants were taken from the isotropic spectrum in $CDCl_3$[13] and were kept constant, J_{12} 7.9, J_{13} 1.3, J_{14} 0.3, and J_{23} 7.4 Hz. All the inter-ring coupling constants were assumed to be zero. The linewidth of the spectrum is 4 Hz.

2,7-Dichlorothianthren was synthetized according to ref. 14. The solubility in the nematic solvent Phase IV is very low and a 1—2 mole % solution was used. The indirect coupling constants were taken from the $CDCl_3$ spectrum and were kept constant, J_{12} 8.04 ± 0.13, J_{13} 2.40 ± 0.13 Hz, and J_{23} 0.25 ± 0.13 Hz. 116 lines (linewidth 4 Hz) were assigned by iterative analysis which gave a r.m.s. error of 0.6 Hz with a maximum deviation of 2.1 Hz.

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