The Structure of 1,6,4aλ^4-Trithiapentalene and 1,6-Dioxa-6aλ^4-thiapentalene studied by Means of Nuclear Magnetic Resonance Spectroscopy in Nematic Phase and in Isotropic Solution

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1,6,6aλ^4-Trithiapentalene and 1,6-dioxa-6aλ^4-thiapentalene have, by means of ^{1}H n.m.r. spectroscopy in a nematic phase, been shown to possess C_{2v} symmetry in solution. Quantitative structural parameters have been obtained for both compounds. A detailed structure of 1,6-dioxa-6aλ^4-thiapentalene has been obtained by combination of the n.m.r. data with data from *X*-ray and microwave studies. The ^{1}H and ^{13}C n.m.r. spectral data of the latter compound are reported and discussed.

1,6,6aλ^4-TRITHIAPENTALENE (1) and 1,6-dioxa-6aλ^4-thiapentalene (2) belong to a group of compounds containing hypervalent sulphur atoms. The structure of these compounds has attracted considerable interest during the last two decades mainly as a result of the unusual type of bonding involved.[1,2]

The issue is whether the molecule has a C_{2v} symmetric, single minimum electronic ground state, as implied in Figure 1 or, whether it should rather be considered as an equilibrium ' mixture ' of so-called valence tautomers undergoing more or less rapid tautomerization as in Figure 2.

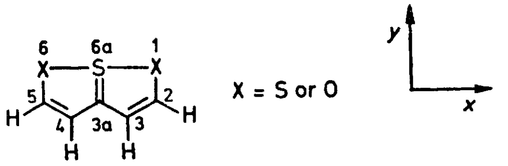


FIGURE 1

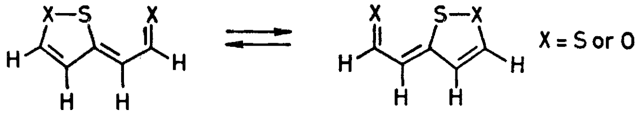


FIGURE 2

We shall present evidence in favour of the first of these possibilities in the following.

Numerous *X*-ray diffraction studies of (1) and its symmetrically substituted derivatives indicate a symmetrical structure.[3,4] Electron diffraction (ED),[5] and ESCA studies [6] as well as theoretical calculations [7] all agree on a very flat single-minimum C_{2v} structure, and thus a large number of low-lying vibrational states. Further, ^{1}H and ^{13}C n.m.r. spectra in isotropic solutions [8-11] support these findings, which we thus consider as firmly established.

Recently the microwave rotational spectrum of (2) was interpreted,[12] and the evidence obtained indicated beyond doubt that the compound has C_{2v} symmetry in the gas phase. Dalseng *et al.* determined the structure of the 2,5-dimethyl derivative [13] to which we shall return below. The ^{1}H n.m.r. spectroscopic results in isotropic solution [14] also agree with the gas-phase results so that the C_{2v} structure is firmly established.

In order to obtain quantitative structural information pertaining to the liquid phase the n.m.r. spectra of compounds (1) and (2) were examined in anisotropic solution. The basic theory of the n.m.r. spectra of molecules dissolved in liquid crystals has recently been reviewed by Emsley *et al.*[15] For a molecule possessing C_{2v} symmetry the expression for the dipole–dipole coupling, D_{ij}, is given by equation (1) in which γ_i and

$$D_{ij} = \frac{\hbar\gamma_i\gamma_j}{2\pi}\left\{\tfrac{1}{2}S_{zz}\left(\frac{1}{r_{ij}^{\,3}}\right) - \tfrac{1}{2}(S_{xx} - S_{yy})\left(\frac{\Delta X_{ij}^{\,2}}{r_{ij}^{\,5}} - \frac{\Delta Y_{ij}^{\,2}}{r_{ij}^{\,5}}\right)\right\} \qquad (1)$$

γ_j are magnetogyric ratios of the two nuclei and $\vec{r}_{ij} = (\Delta X_{ij}, \Delta Y_{ij}, \Delta Z_{ij})$ are the internuclear vectors and $r_{ij} = |\vec{r}_{ij}|$. S_{xx}, S_{yy}, and S_{zz} are ordering parameters describing the average orientation of the molecules in the nematic phase. The orientation of the molecular co-ordinate system is defined as having the *z* axis perpendicular to the plane of the molecule and the *y* axis parallel to the C_2 axis. In case of symmetry lower than C_{2v} the dipole–dipole couplings would have been related to the geometry through at least three-ordering parameters.

RESULTS

The ^{1}H n.m.r. spectra of compound (1) dissolved in *N*-(4-ethoxybenzylidene)-4-butylaniline (EBBA) at different concentrations were recorded. An example of the spectra obtained is shown in Figure 3. The iterative spectral analysis was performed in the usual way with a modified

TABLE 1

Dipole–dipole couplings [D_{ij}(Hz)] and relative distances in 1,6,6aλ^4-trithiapentalene (1)

	3.1 mol % in EBBA	3.9 mol % in EBBA	4.7 mol % in EBBA
D_{23}	$-1\,678.5 \pm 0.8$	$-1\,647.3 \pm 0.6$	$-1\,605.5 \pm 0.7$
D_{24}	-350.6 ± 1.1	-344.3 ± 0.8	-335.5 ± 0.9
D_{25}	-140.0 ± 0.8	-137.6 ± 0.6	-134.0 ± 0.6
D_{34}	$-2\,862.2 \pm 0.9$	$-2\,809.0 \pm 0.6$	$-2\,736.0 \pm 0.7$
r_{23}/r_{34}	1.013 ± 0.006	1.013 ± 0.007	1.012 ± 0.006
r_{24}/r_{34}	1.939 ± 0.003	1.939 ± 0.006	1.939 ± 0.005
r_{25}/r_{34}	2.734 ± 0.003	2.733 ± 0.003	2.733 ± 0.003
S_{xx} [a]	0.3605	0.3538	0.3446
S_{yy} [a]	-0.1642	-0.1605	-0.1606

[a] Based upon r_{34} = 2.473 Å (assumed value).

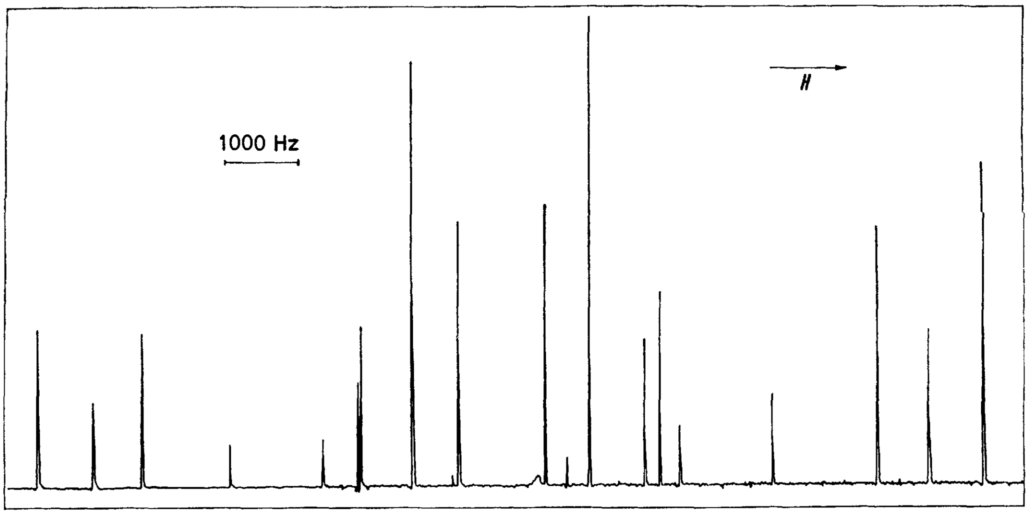


FIGURE 3 ^1H N.m.r. spectra of 1,6,6aλ^4-trithiapentalene (1) in EBBA

LAOCOON program named LAOCOON V [16]. The values of the dipole–dipole coupling constants obtained are given in Table 1. In these calculations the equalities: $D_{23} = D_{45}$, $D_{21} = D_{35}$, $\delta(2) = \delta(5)$ and $\delta(3) = \delta(4)$ has been introduced. This means that the molecule has been assumed to possess C_{2v} symmetry or existence of exchange between forms of lower symmetry. The values of the indirect coupling constants given by Pedersen *et al.*[9] have been fixed in these calculations. The r.m.s. errors in the final iterations were less than 0.9 Hz. This implies that the deviation between the experimental and the theoretical spectra are mainly due to uncertainties in the determination of the line positions. Thus, the C_{2v} configuration of the molecule is completely in agreement with the spectra.

The sign of the dipole–dipole coupling constants has so far been chosen to be negative in order to have the direction of the axis through H(2) and H(5) parallel to the magnetic field. The agreement between experimental and theoretical spectra were less pronounced for dipole–dipole coupling constants with a positive sign than for those with a negative sign.

TABLE 2

Dipole–dipole couplings [D_{ij}(Hz)] and relative distances in 1,6-dioxa-6aλ^4-thiapentalene (2)

	3.2 mol % in EBBA	4.2 mol % in EBBA	5.2 mol % in EBBA	5.0 mol % in MEBBA [a]	5.7 mol % in MEBBA [a]	4.1 mol % in DHAB [b]
D_{23}	−553.1 ± 0.4	−546.3 ± 0.3	−536.7 ± 0.3	−496.0 ± 0.3	−491.6 ± 0.9	−637.9 ± 0.6
D_{24}	−144.7 ± 0.5	−143.2 ± 0.3	−140.2 ± 0.4	−128.4 ± 0.3	−126.8 ± 1.2	−158.8 ± 0.6
D_{25}	−78.0 ± 0.4	−76.7 ± 0.2	−75.1 ± 0.3	−68.6 ± 0.3	−67.4 ± 0.9	−84.2 ± 0.5
D_{34}	−923.4 ± 0.5	−910.3 ± 0.2	−889.9 ± 0.3	−815.1 ± 0.5	−804.7 ± 1.4	−997.9 ± 0.6
r_{23}/r_{34}	0.902 ± 0.008	0.896 ± 0.003	0.896 ± 0.005	0.896 ± 0.004	0.894 ± 0.012	0.893 ± 0.05
r_{24}/r_{34}	1.759 ± 0.004	1.756 ± 0.002	1.756 ± 0.004	1.757 ± 0.002	1.757 ± 0.006	1.754 ± 0.003
r_{25}/r_{34}	2.279 ± 0.004	2.281 ± 0.003	2.280 ± 0.003	2.282 ± 0.003	2.286 ± 0.009	2.280 ± 0.003
S_{xx} [c]	0.1931	0.1903	0.1861	0.1704	0.1682	0.2086
S_{yy} [c]	−0.0241	−0.0307	−0.0293	−0.0255	−0.0276	−0.0256

[a] Mixture of *N*-(4-ethoxybenzylidene)-4-butylaniline (EBBA) (2 g) and *N*-(4-methoxybenzylidene)-4-butylaniline (MBBA) (1.18 g). [b] This spectrum was recorded at a temperature of 85 °C (DHAB = 4,4-dihexyloxyazoxybenzene). [c] Based upon r_{34} = 2.928 Å.

TABLE 3

^{13}C Chemical shifts (p.p.m.) and coupling constants (Hz) in 1,6-dioxa-6aλ^4-thiapentalene (2)

	(2) [a]	(1) [b, c]	(3) [c]	Furan
δ(C-2)	167.78	161.69	181.12	142.70 [d]
δ(C-3)	104.13	128.64	109.04	109.60 [d]
δ(C-3a)	175.63	177.45	172.04	
$^1J_{C-2,H-2}$	188.9	176.5	182.3	201.79 [e]
$^1J_{C-3,H-3}$	176.8	165.4	167.98	174.67 [e]
$^2J_{C-2,H-3}$	7.3	−4.6	7.19	11.03 [e]
$^2J_{C-3,H-2}$	15.6	3.6	22.3	13.79 [e]
$^3J_{H-2,H-3}$	2.6	6.31	1.68	
$^5J_{H-2,H-4}$	0.2	0.08	0.13	
$^6J_{H-2,H-5}$	0.0	0.35	0.0	
$^4J_{H-3,H-4}$	±0.4	0.30	−0.4	

[a] This work. [b] Pedersen *et al.*[9] [c] Pedersen *et al.*[10] [d] E. Breitmaier and W. Voelter.[22] [e] Hansen *et al.*[21]

The ^1H n.m.r. spectra of compound (2) dissolved in nematic phases resemble those for (1), except for a pronounced difference in spectral width. In order to be able to obtain the values of the dipole–dipole couplings (Table 2) the indirect spin–spin coupling constants in the molecule were determined by a computer analysis of the ^1H n.m.r. spectra of compound (2) dissolved in deuteriochloroform. The values obtained are as given in Table 3. The analysis of the spectra of (2) in nematic phases were performed in a way similar to the one used in case of (1). The final r.m.s. error was less than 0.5 Hz in all cases.

Finally the dipole–dipole couplings have been analysed in terms of H–H distance ratios in Tables 1 and 2 using the relation of Diehl *et al.*[17] The geometrical relation between r_{24}, r_{25}, and r_{34} is included in these relations.

DISCUSSION

H–H Distance ratios obtained for compound (1) in Table 1 agree with those obtained in an ED study published by Shen *et al.*[5] The latter allowed two possibilities for the skeletal structure, but the hydrogen positions were poorly defined. If the ED results are combined with the values of the structural parameters in Table 1 it can be calculated that the structure possibility (B) (*cf.* ref. 5) with $r_{C(3)C(3a)} \neq r_{C(2)C(3)}$ is the most appropriate one. Furthermore, the reported value of $\angle C(2)C(3)H(3) = 122.0°$ seems to be too high. A value of 120.5 ° can be deduced from the combined ED and n.m.r. data. The *X*-ray structure of compound (1) [3] deviates to a small extent from the combined ED and n.m.r. structure, probably as a result of the distortion of the molecule in the crystalline phase. In view of the agreement between the structural parameters obtained by n.m.r. spectroscopy and those obtained from ED and *X*-ray studies there seems to be no evidence for the existence of a valence tautomerism in case of compound (1) in solution.

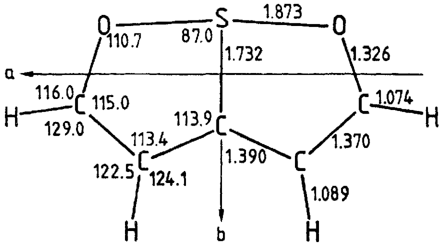


FIGURE 4

The H–H distance ratios for compound (2) may be rationalized in terms of the structure given in Figure 4, where a and b indicate the principal axes for the moment of inertia tensor. This structure is based on the evidence from three sources. (i) The *X*-ray diffraction study of 2,5-dimethyl-1,6-dioxa-6a-thiapentalene [13] established the skeletal structure. (ii) The positions of the 3-H and 4-H atoms with respect to the parent structure were established on the basis of the differences in the moments of inertia around the principal axes of inertia a and b shown in Figure 4: $\Delta I_a = I_a^* - I_a = 11.578\,636$ μÅ² and $\Delta I_b = I_b^* - I_b = 4.315\,834$ μÅ². Here I_g^* ($g = a, b$) refers to the moment of inertia of [3,4-$^2H_2$]-1,6-dioxa-6a-thiapentalene and I_g is the corresponding moment of inertia of the parent molecule. These moments of inertia are determined from the rotational constants obtained by analysis of the rotational spectra.[12] (I_a[μÅ²] = 505 376/A[MHz] *etc.*). This approach is known as the substitution method and was originally introduced by Costain.[18] The appropriate formalae for the a and b co-ordinates of atoms 3 and 4 are as follows: [19]

$$|a_3| = |a_4| = \left(\frac{\Delta I_b}{\Delta M}\right)^{\frac{1}{2}} = 1.464\ \text{Å}$$

$$|b_3| = |b_4| = \left(\frac{\Delta I_a}{\Delta M}\frac{M^*}{M}\right)^{\frac{1}{2}} = 2.417\ \text{Å}$$

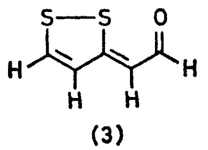
where M^* and M are the total molecular masses and $\Delta M = M^* - M$. It should be noted that these co-ordinates are *not* dependent on the actual structure of the ring, hence even if the ring structure is not known with the same accuracy (in the gas phase!) the distance $r_{34} = 2|a_3| = 2.928$ Å is well determined. (The uncertainty may amount to *ca.* 10^{-3} Å, and comes mainly from zero-point vibrational effects in the rotational constants, rather than from the experimental uncertainty, which is very much smaller.) (iii) Finally, the distance r_{34} is used in conjunction with the H–H distance ratios r_{25}/r_{34} and r_{23}/r_{34} obtained in this work (Table 2) to find the co-ordinates for atoms 2 and 5 and hence the whole structure.

We have only used the differences in moments of inertia above. It is found that all moments of inertia are reproducible to within 0.2%, which is as good as can be expected, the zero-point effects mentioned above being considered. Finally the structure seems reasonable, the C–H distances being *ca.* 1.08 Å and the O–C–H angle the same as for furan.

We therefore conclude that there is no indication of valence tautomerism in compound (2) in the liquid phase. The presence of transoid isomers equivalent to the ones reported to be formed during photolysis of substituted α-(1,2-dithiol-3-ylidene)ketones [20] can also be excluded.

The presence of isomers of these types would be expected to give rise to quite different structural parameters obtained upon analysis of the n.m.r. spectra at different temperatures since variations in the latter would lead to different isomer populations. As can be seen from Table 2 identical values of structural parameters were obtained at both 30 and 85 °C. This indicates a significant stability for structure (2). Furthermore, the ^1H n.m.r. spectrum of the molecule in isotropic solution at −90 °C is identical to the spectrum at room temperature. There was no indication of any ‘ freeze out ’ of more than one isomer.

The bicyclic structure of (2) can, in fact, explain other experimental observations as given in Table 3. Pedersen *et al.*[10] have reported the ^1H and ^{13}C n.m.r. spectra of various derivatives of α-(1,2-dithiol-3-ylidene)acetaldehyde (3) and shown that these molecules are likely to be of the monocyclic type with no S–O interaction. The ^{13}C chemical shift of C-2 in compound (2) is much smaller than that in compound (3) and much nearer to the corresponding value in furan. This is a consequence of the existence of S–O interaction in the former compound.



(3)

As would be expected the bicyclic character of compound (2) is also reflected in the values of the coupling constants. Both $^1J_{CH}$ coupling constants in compound (2) do, in fact, lie between the corresponding values for compound (3) [10] and furan.[21] The value of $^2J_{C-3,H-2}$ in (3) are typical for conjugated aldehydes.[22] The value for compound (2) is smaller but still greater than the value for furan. The increase of the value of $^3J_{H-2,H-3}$ observed between (3) and (2) is also a contribution to the evidence for the bicyclic character of (2). Since the value in (1) is still higher (6.31 Hz [9]), the pronounced difference in structure between (1) and (2) is seen to greatly influence the values of the coupling constants.

EXPERIMENTAL

The spectra in nematic solution were recorded on a JEOL FX60 FT n.m.r. spectrometer. The pulse lengths used were 20 μs corresponding to a 60° flip angle with a spectral width of 10 kHz for compound (1) and 5 kHz for compound (2). The FID was recorded for 16 K data points. The magnetic field was stabilized by an external deuterium lock. All the spectra except one were recorded at 25 °C.

1,6,6aλ^4-*Trithiapentalene*.—This compound was prepared according to the method of Davy and Vialle.[23]

1,6-*Dioxa*-6aλ^4-*thiapentalene*.—This compound was prepared according to the method of Reid and Webster.[24]

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