Structures of 1,6-Dioxa-6aλ^4-thiapentalene and of 1,6,6aλ^4-Trithiapentalene: C_s or C_{2v} Symmetry?

Charles L. Perrin,* Yeong-Joon Kim, and Joshua Kuperman

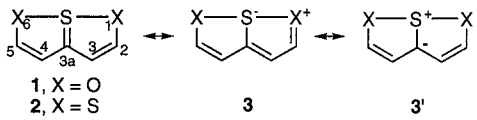
Department of Chemistry, University of California—San Diego, La Jolla, California 92093-0358

Received: October 1, 2001

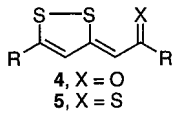
Do 1,6-dioxa-6aλ^4-thiapentalene (**1**) and 1,6,6aλ^4-trithiapentalene (**2**) have C_s symmetry, with a double-well potential, or C_{2v} symmetry, with a single-well potential? The long-standing question of their structure in solution is answered unequivocally using the NMR method of isotopic perturbation. Statistical mixtures containing zero, one, and two deuteriums were synthesized and observed by ^{13}C NMR spectroscopy. The isotope shifts of C5 are +15 in **1**-α-***d*** and −70 ppb in **2**-α-***d***, which are small and correspond simply to an intrinsic isotope shift ($^5\Delta_0$). Since there is no large downfield equilibrium isotope shift, both **1** and **2** are symmetric, with the motion of the central sulfur described by a single-well potential. The symmetry of **2** is not reduced by added mercury(II) chloride.

Introduction

Bonding in Trithiapentalene and Related Compounds. There has long been interest in the structure of 1,6-dioxa-6aλ^4-thiapentalene (**1**) and 1,6,6aλ^4-trithiapentalene (**2**), for which the resonance forms **3** and **3′** (with further delocalization of plus or minus charges) can be included.[1]



After many misassignments, structures **4** and **5** (R = CH_3) were eventually proposed on the basis of the IR spectrum of the former[2] and on an X-ray structure for the latter.[3] Static structure **4** is correct, but **5** shows equal S−S distances. Also the ^{1}H NMR spectrum of **5** shows equivalent methyls and equivalent methines.[4] Moreover, the two S−S distances in the parent 1,6,6aλ^4-trithiapentalene **2** are equal, and the SSS angle is 178°.[5] It was therefore proposed that these molecules are



symmetric, with electron pairs delocalized from sigma bonds.[3] This is then an unusual case of no-bond single-bond resonance between two equivalent C_s resonance forms. Indeed, the S−S distances in **2** are 2.363 Å, much shorter than the 3.7-Å sum of the van der Waals radii.

The question addressed here is whether these molecules really have a C_{2v}-symmetric structure (Figure 1), whose nuclear motion is described by a single-well potential. The alternative is a rapid interconversion of two valence tautomers, each of C_s symmetry, via the C_{2v} structure as transition state. In this case the motion of the central sulfur would be described by a double-well potential, and "dioxathiapentalene" and "trithiapentalene" would

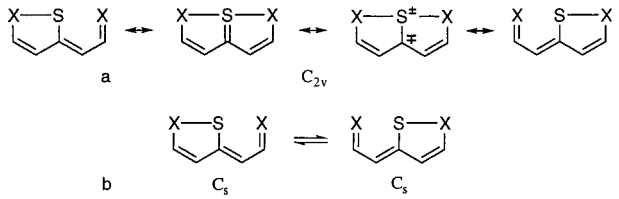
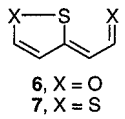


Figure 1. Proposed structures of 1,6-dioxa-6aλ^4-thiapentalene (**1**, X = O) and 1,6,6aλ^4-trithiapentalene (**2**, X = S): (a) C_{2v}-symmetric structure described by a single-well potential. (b) C_s-symmetric structure described by a double-well potential.

be misnomers for (3H-1,2-oxathiol-3-ylidene)acetaldehyde (**6**) and (3H-1,2-dithiol-3-ylidene)thioacetaldehyde (**7**).



One advantage of C_{2v} symmetry is aromatic stabilization from the 10 pi electrons.[6] The alternative C_s symmetry has the advantage of avoiding hypervalent sulfur. In principle, the hypervalent sulfur in resonance form **1**, **2**, or **3** could be avoided through resonance form **3′**. This is common when the charge separation is favorable, as in dimethyl sulfoxide, $Me_2S^+-O^-$. It is less so when the formal negative charge resides on carbon, as in a sulfur ylide, which is a reactive intermediate. The calculated charge densities at sulfur are +1.089 and +0.263 in **1** and **2**, respectively,[7] which is consistent with **3′** (but −0.677 and +0.422 at C3a, which is consistent for **1** but not for **2**). However, **3′** lacks aromaticity, owing to its 12 pi electrons, including the lone pair on the pyramidal sulfur that overlaps with the pi system.[6] The observation that the middle sulfurs of **1** and **2** are planar indicates that pyramidal $Me_2S^+-O^-$ is not a good model. This planarity confers sigma character on the sulfur lone pair and decreases the pi electron count from 12 to 10, but it then does require hypervalent sulfur, which may be unavoidable in C_{2v} symmetry.

A calculational approach to this question is ongoing, but it has been noted that the conclusion depends on the level of

10.1021/jp013660e CCC: $20.00
Published on Web 11/15/2001

approximation.[8] According to Hartee−Fock calculations, the most stable structure of 1,6,6aλ^4-trithiapentalene (**2**) has C_s symmetry, with the C_{2v} structure 8.7 or 10.7 kcal/mol higher in energy.[9] However, correction for electron correlation reverses the order, rendering the C_{2v} structure more stable by 7 kcal/mol. Similar results were obtained for 1,6-dioxa-6aλ^4-thiapentalene (**1**).[9,10]

Various experimental data support a single C_{2v} structure rather than two equivalent C_s structures undergoing rapid interconversion. The ^{13}C chemical shift of C3a in **2** is downfield of that expected for **7**,[11] and that of C2 in **1** is upfield of the corresponding carbon of **4**.[12] No decoalescence in the ^{1}H NMR spectrum of **1** is seen even at −90 °C, and there is no IR absorption attributable to C=O.[13] Electron-diffraction data for **1** and **2** are consistent with C_{2v} symmetry,[14] and studies of **1** by microwave spectroscopy found no evidence of valence tautomerism.[15] X-ray photoelectron spectroscopy indicates that the two outer sulfurs of **2** have the same ionization potential.[16] The long-wavelength absorption responsible for the orange color of **2** has been attributed to admixture of $\sigma-\sigma^*$ excitations associated with the S−S−S fragment.[17] Infrared spectroscopy of **2** and its 2,5-dimethyl derivative, sometimes in argon matrix or in stretched polyethylene, as well as normal-coordinate analysis, supports a C_{2v} structure, especially a 153-cm^{-1} mode associated with the S−S−S fragment.[18]

There is scant evidence against structure **1** or **2**. The S−S distance in **2** is longer than S−S single bonds in cyclic disulfides.[5] The C3a−S6a distance in **2**, 1.748 Å, is longer than the 1.684 Å for C2−S1, which is inconsistent with the C−S double bond in resonance form **1** or **2**. Moreover, **1** shows unequal S−O distances,[19] some derivatives of **5** have unequal S−S distances,[1] and a metal derivative is also C_s.[20] Such variations could be a consequence of crystal-packing forces, but so could the short S−S distances. Besides, the stability of the 10-pi-electron structure cannot be dominant, since both 1,2-dithiol-3-ylidene acetaldehyde (**4**, R = H)[21] and 1,3-dithiol-2-ylidene acetaldehyde[22] are monocyclic, despite attractive S−O interactions, and a 1,5 S−O attraction is seen in the antibiotic leinamycin, which is not aromatic.[23]

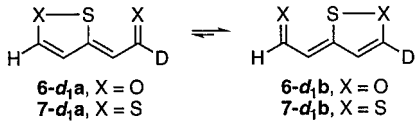
Although most experimental data do seem to be in agreement with C_{2v} symmetry, a rapid interconversion could give many of the same results. Nearly all of the experimental methods are incapable of distinguishing a C_{2v} structure from a rapidly interconverting pair of C_s structures. For example, the interatomic distances measured for **1** and **2** in a liquid crystal are consistent with either a symmetric structure or a tautomeric interconversion with a rate constant of 10^{10} s^{-1}.[24] The situation is reminiscent of that of the hydrogen bonds in dicarboxylic acid monoanions, which are symmetric in crystals and according to high-level calculations but are found to be a mixture of two asymmetric tautomers in solution, perhaps because of the disorder of the solvation environment.[25]

In summary, experimental data and high-level calculations convincingly indicate that **2** is symmetric. Direct evidence for **1** is scanty, and it is puzzling that the similar **4** is a static C_s structure. The instability of C=S double bonds could be responsible for destabilizing **7**, and the stability of C=O for stabilizing **4**, but then why is **1**, also with C=O, symmetric? Is it really? Is **2** really symmetric, even in solution?

Methodology. The NMR method of isotopic perturbation of equilibrium[26] can give a clear answer to the question of whether these are really symmetric molecules or are a mixture of two rapidly interconverting valence tautomers. This method relies on the observation of isotope shifts, $^n\Delta$, the change of the chemical shift δ of nucleus X due to isotopic substitution n bonds away (eq 1).[27] The heavier isotope usually produces an upfield shift, corresponding to $^n\Delta < 0$. There are always intrinsic shifts $^n\Delta_0$ associated with the mere presence of the isotope, and these decrease as n increases.

$$^n\Delta = \delta X_{\text{heavier}} - \delta X_{\text{lighter}} \tag{1}$$

Isotopic perturbation can most effectively be provided by monodeuterium substitution at the α position of **1** or **2**. The goal of this study is to measure the ^{13}C NMR chemical-shift difference between C5 of an alpha-deuterated molecule and C2-(5) of undeuterated (eq 2). If **1** or **2** is a mixture of valence tautomers **6-*d*$_1$a** and **6-*d*$_1$b** or **7-*d*$_1$a** and **7-*d*$_1$b**, then an equilibrium isotope shift Δ_{eq} will be observed in addition to the intrinsic isotope shift $^5\Delta_0$. In contrast, if **1** or **2** has C_{2v} symmetry, then only $^5\Delta_0$ will contribute.



6-*d*$_1$a, X = O
7-*d*$_1$a, X = S

6-*d*$_1$b, X = O
7-*d*$_1$b, X = S

$\Delta_{obs} = \delta_{C5(\alpha\text{-}d)} - \delta_{C2(5)(d_0)} = \Delta_{eq} + {}^5\Delta_0$

$$\Delta_{\text{obs}} = \delta_{\text{C5}}(\alpha\text{-}\boldsymbol{d}) - \delta_{\text{C2(5)}}(\boldsymbol{d_0}) = \Delta_{\text{eq}} + {}^5\Delta_0 \tag{2}$$

It is possible to estimate Δ_{eq} for the case of two valence tautomers. Under conditions of rapid interconversion, separate peaks for **a** and **b** are not seen, but only an average, whose chemical shift can be compared with that of unlabeled material. It is readily shown that Δ_{eq} is given by eq 3, where K is the equilibrium constant [**b**]/[**a**] and D is the difference between chemical shifts of −CH=O and =CH−O or between −CH=S and =CH−S. The CH stretching frequency of an aldehyde is 2770 cm^{-1} and that of an enol is 3020 cm^{-1}.[28] The zero-point energy for **6-*d*$_1$a** is (3020+2770/2$^{1/2}$)/2 cm^{-1} and that for **6-*d*$_1$b** is (2770+3020/2$^{1/2}$)/2 cm^{-1}. From the energy difference of 37 cm^{-1}, K is estimated to be 1.2 at 25 °C. Similarly, from C−H stretching frequencies of 2990 and 3040 cm^{-1} respectively for the −CH=S of thioformaldehyde and the =CH−S of 1,3-dithiol-2-one,[29] **7-*d*$_1$b** has a 7.3-cm^{-1} lower zero-point energy than **7-*d*$_1$a**, corresponding to K = 1.04 at 25 °C. In both cases the equilibrium favors tautomer **b**, with D on the higher frequency bond. Moreover, D can be estimated as ca. 20 ppm for **6**, as judged from solid-state HOCH=CPh-CH=O,[30] or 115 ppm for **7**, from 2,4,6-tri-*tert*-butylthiobenzaldehyde (δ 250)[31] and triarylethenethiol (δ 135).[32] Therefore Δ_{eq} is expected to be ca. 1 ppm (downfield) in both cases. Similarly, in the ^{1}H NMR spectrum, where D is ca. 2 ppm, we may expect a Δ_{eq} of ca. 0.1 ppm for **1**, but only 0.02 ppm for **2**.

$$\Delta_{\text{eq}} = D(K-1)/2(K+1) \tag{3}$$

The ^{13}C Δ_{eq} is large because ^{13}C chemical shifts are quite sensitive to environment. It is large enough to be resolvable and to permit distinguishing between a single symmetric structure and two asymmetric valence tautomers. Moreover, the sign is diagnostic. An equilibrium between two tautomers produces a large positive Δ_{eq}. In contrast, in C_{2v} symmetry there will be no Δ_{eq} and only the intrinsic $^n\Delta_0$ will be observed. This latter is usually a small negative (upfield) shift, which is readily distinguishable from the positive (downfield) equilibrium isotope shift.

We now report that both **1** and **2** show only small isotope shifts. Therefore we conclude that they are C_{2v} symmetric,

despite an admonition that "[if] the energy barrier is too low ..., distinctions between real or time-averaged C_{2v} symmetry may be impossible".[9]

Experimental Section

Partially Deuterated 1,6-Dioxa-6aλ^4-thiapentalene. Chelidonic acid was *O*-deuterated with excess D_2O and then decarboxylated to 4-pyrone.[33] ^{1}H NMR showed distorted doublets at both δ 8.15 and δ 6.33, owing to CH groups with neither exclusive H nor exclusive D at the adjacent position. Therefore deuterium had been introduced not only at Cα by decarboxylation but also at Cβ by acid-catalyzed exchange. After deuterium was removed from Cβ by heating in water,[34] the NMR spectrum showed a symmetrical doublet at δ 8.15 and a weaker distorted doublet at δ 6.33, corresponding to deuteration only at Cα. 4-Pyrone-α-*d* was then thionated with P_2S_5 in benzene,[35] and rearranged to 1,6-dioxa-6aλ^4-thiapentalene-α-*d* with $Tl(O_2CCF_3)_3$.[36]

Partially Deuterated 1,6,6aλ^4-Trithiapentalene. Partially deuterated 1,6,6aλ^4-trithiapentalene was obtained if thioacetamide-d_2 was used in the final step of rearranging the adduct between 1,2-dithiole-3-thione and propiolic acid.[37]

Effect of $HgCl_2$. The partially deuterated 1,6,6aλ^4-trithiapentalene (35 mg) was dissolved in 1 mL THF-d_8. Mercury(II) chloride (50 mg) was added, leaving undissolved solid, and the NMR spectrum was obtained.

NMR Spectroscopy. The ^{1}H NMR and ^{13}C NMR spectra were recorded at 400 or 500 and 125.7 MHz, respectively, using a Varian Mercury-400 or Unity-500 FT-NMR spectrometer. ^{13}C NMR spectra were with ^{1}H decoupling using a heteronuclear broadband probe or an indirect detection probe. The ^{2}H-decoupled ^{13}C spectra were obtained when a synthesized signal generator was fixed to the deuterium frequency.

Mass Spectrometry. Mass spectra were obtained with a Hewlett-Packard 5971 GC/MS or by the High-Resolution Mass Spectrometry Facility at University of California—Riverside. The mass spectrum of pyrone-α-*d* was compared with that of unlabeled, so as to determine the deuterium content, corrected for the fragmentation pattern and for natural isotopic abundances. Results show a d_0:d_1:d_2 ratio of 33:46:22 for 4-pyrone, 38:45:17 for 4H-pyran-4-thione, and 36:45:19 for **1**. These isotopic abundances are in good agreement with the NMR integrations.

To reduce fragmentation in the mass spectrum of **2**, chemical ionization by methane was used. Additional peaks due to deprotonated parent ions interfered with the evaluation of the amounts of **2-*d*$_1$** and **2-*d*$_2$**. The extent of deuteration was instead determined using $C_5H_5S_2^+$ (dithiopyrone·H^+, m/z=129) and the $C_2H_5^+$ adduct of **2** (m/z = 189) peaks, both of which were free of nearby peaks. After correction for natural abundance the ratio of **2**:**2-*d*$_1$**:**2-*d*$_2$** is obtained as 27:46:27 from $C_5H_5S_2^+$ and 27:47:26 from $MC_2H_5^+$. The average of these is 27:46:27. This is close to the 25:50:25 for statistical monodeuteration, owing to a kinetic isotope effect that compensates for the excess of deuterium from thioacetamide-d_2 over protium from propiolic acid.

Results

Isotope Shifts of 1,6-Dioxa-6aλ^4-thiapentalene. The ^{13}C NMR peaks for **1** have been reported and assigned.[12] Table 1 lists chemical and intrinsic isotope shifts for **1** in 1:2 DMSO-d_6/$CDCl_3$. To aid in the assignment of the spectra, the sample of deuterated **1** was spiked with unlabeled **1**.

TABLE 1: ^{13}C Chemical Shifts and Isotope Shifts of Monodeuterated 1,6-dioxa-6aλ^4-thiapentalene (1) in 1:2 DMSO-d_6/$CDCl_3$ and 1,6,6aλ^4-Trithiapentalene (2) in $CDCl_3$

C	$\delta_{1,\text{ppm}}$	Δ(**1**-*d*), ppb	δ_2, ppm	Δ(**2**-α-*d*), ppb	Δ(**2**-β-*d*), ppb
2	167.8		161.9		-106 ± 3 ($^2\Delta_0$)
3	104.0	-143 ($^2\Delta_0$)	128.8	-158 ($^2\Delta_0$)	-219 ($^1\Delta_0$)
3a	175.0	$+39$ ($^3\Delta_0$)	177.7	$+46 \pm 3$ ($^3\Delta_0$)	-55 ($^2\Delta_0$)
4	104.0	-10 ($^4\Delta_0$)	128.8	-122 ($^4\Delta_0$)	-43 ($^3\Delta_0$)
5	167.8	$+15$ ($^5\Delta_0$)	161.9	-70 ± 3 ($^5\Delta_0$)	-39 ± 3 ($^4\Delta_0$)

Isotope Shifts of 1,6,6aλ^4-Trithiapentalene. In the ^{1}H NMR spectrum of partially deuterated **2**, the singlet from H3 of **2**-α-***d*$_1$** is seen between the components of the δ 7.96 doublet, which is due to H3(4) of **2**, H4 of **2**-α-***d*$_1$**, and H4 of **2**-β-***d*$_1$**. Likewise, the H2 singlet of **2**-β-***d*$_1$** appears between the components of the δ 9.17 doublet, which is due to H2(5) of **2**, H5 of **2**-α-***d*$_1$**, and H5 of **2**-β-***d*$_1$**. Separate ^{1}H NMR peaks for the four possible dideuterated compounds are not seen since the intensities are low and they are screened by monodeuterated compounds with the same chemical shifts. The integration ratio of δ 9.17:δ 7.96 signals is 59/41, which means that β deuteration is more extensive. The observed isotope shift is 0 ± 1 ppb for H2 and -1 ± 1 ppb for H3.

In the ^{13}C NMR spectrum, when deuterated compounds are present, additional signals are shown near those of the nondeuterated compound, as shown in Figure 2. The assignments are based on the relative intensities and the assumption that two-bond intrinsic isotope shifts ($^2\Delta_0$) are larger than those of more distant isotopic substituents. When deuterium is decoupled, C3 and $^1\Delta_0$ are observable for **2**-β-***d*$_1$**, and some broad peaks, especially those from carbons two bonds away from deuterium, are sharpened, but C2 and $^1\Delta_0$ for **2**-α-***d*$_1$** could not be observed. The isotope shifts for **2** in $CDCl_3$ are also included in Table 1, along with their assignments.

The NMR spectra in THF-d_8 are basically the same as those in $CDCl_3$. In the ^{1}H NMR spectrum, H2(5) appears at δ 9.29 and H3(4) at δ 8.08. The ^{13}C NMR signals are at δ 178.9, 163.2, and 130.1 for C3a, C2(5), and C3(4), respectively. The isotope shifts in both ^{1}H and ^{13}C NMR are the same as in $CDCl_3$. No change is observed after the addition of mercury (II) chloride.

Discussion

Regioselectivity of Deuteration. It might have been preferable to prepare **2** specifically deuterated at the α position. Unfortunately, this could not be obtained by hydrolysis and decarboxylation of 2,5-di(ethoxycarbonyl)trithiapentalene, even with DBr in acetic acid.[38] Instead we obtained a mixture of **2**-α-***d*** and **2**-β-***d*** because the [3+2] cycloaddition of propiolic acid onto 1,2-dithiole-3-thione is not regiospecific,[37] or else because the rearrangement and decarboxylation of that cycloadduct proceeds via an intermediate tha scrambles the positions that become α and β.[39] It is unfortunate that the relative proportions of the two possible cycloadducts could not be determined because the material is too insoluble. Fortunately, the presence of **2**-β-***d*** does not interfere, and it provides additional calibration of isotope shifts.

Structure of 1,6-Dioxa-6aλ^4-thiapentalene: The ^{13}C NMR data in Table 1 show very small isotope shifts for **1**, none larger than 150 ppb. Shifts of this magnitude are indicative of intrinsic rather than equilibrium isotope shifts. Since the predicted equilibrium isotope shift of +1 ppm was not observed, 1,6-dioxa-6aλ^4-thiapentalene exists as a single structure with C_{2v} symmetry.

Structure of 1,6,6aλ^4-Trithiapentalene. The ^{1}H NMR isotope shifts of H2 and H3 in **2-*d*$_1$** are very small, $\leq$1 ppb.

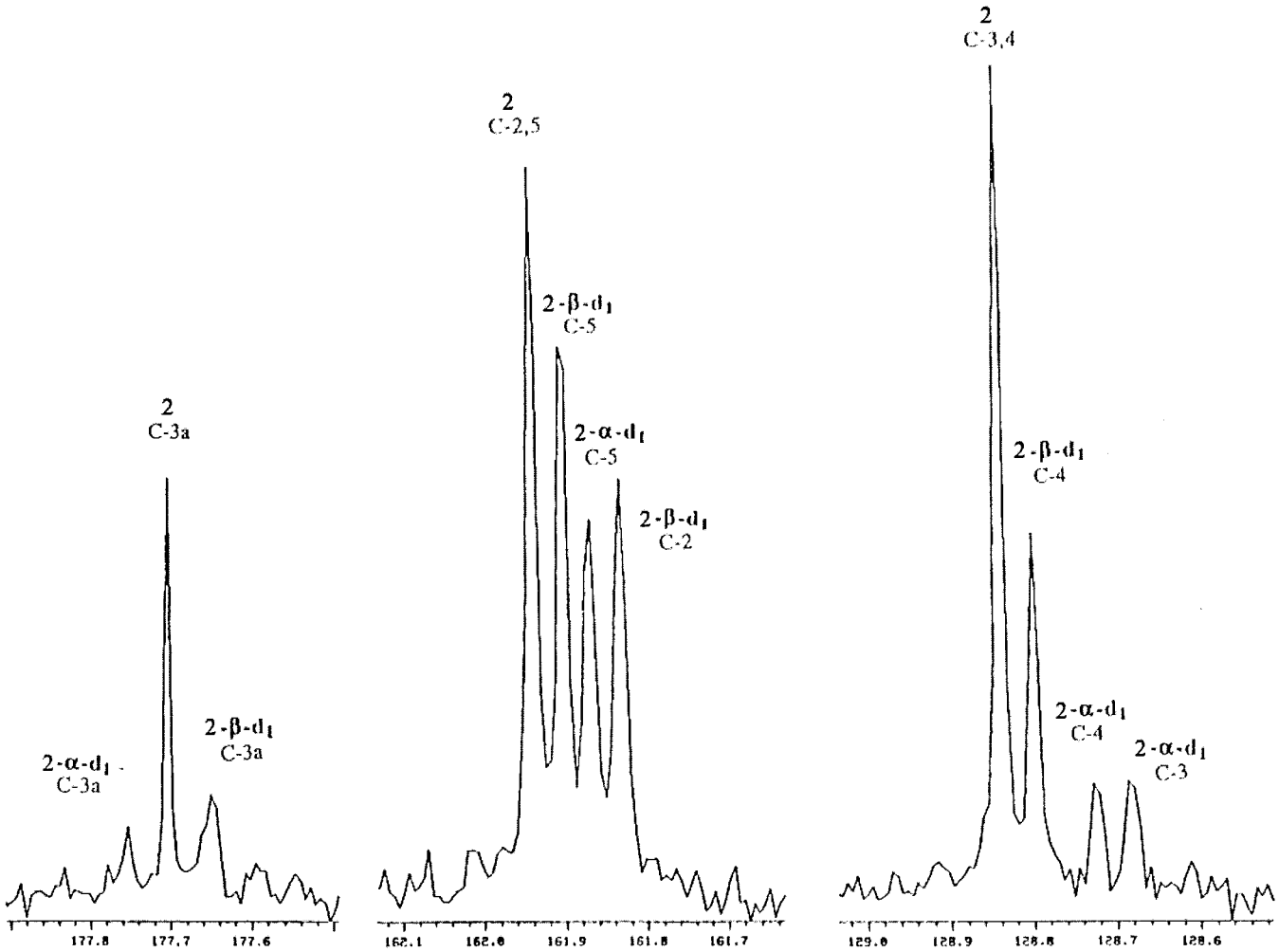


Figure 2. The ^{13}C NMR spectrum of the mixture of deuterated and nondeuterated **2**.

Moreover, according to the relative intensities the H2 signal arises from **2**-β-$\boldsymbol{d_1}$ and the H3 signal from **2**-α-$\boldsymbol{d_1}$. This means that these are intrinsic shifts $^3\Delta_0$. The absence of any Δ_{eq} verifies that **2** is symmetric, rather than existing as a mixture of two valence tautomers. However, the Δ_{eq} expected above is only 20 ppb, and ^{13}C NMR is more sensitive.

The ^{13}C NMR isotope shifts are small and negative, consistent with an intrinsic isotope shift. The isotope shifts for **2**-β-$\boldsymbol{d_1}$ provide no information about the symmetry of the molecule but are useful to assign intrinsic isotope shifts for **2**-α-$\boldsymbol{d_1}$. If there were C_s symmetry, the isotope shift at C5 of **2**-α-$\boldsymbol{d_1}$ would include a large positive equilibrium isotope shift of ca. +1000 ppb. Because there is no such shift, we can conclude that 1,6,-6aλ^4-trithiapentalene **2** has C_{2v} symmetry.

Since sulfur binds strongly to mercury, the C_{2v} structure of 1,6,6aλ^4-trithiapentalene might convert to the C_s structure in the presence of $HgCl_2$. Indeed, one of its sulfurs can be oxidized by aqueous mercuric acetate,[40] and its Au(I)Cl complex is monocyclic but fluxional.[41] Nevertheless, the chemical shifts and isotope shifts in the ^{13}C NMR spectrum of **2** are unchanged by adding $HgCl_2$. The aromaticity is apparently so strong that interaction between S and Hg cannot break the symmetry, in contrast to that with Au.

Positive Intrinsic Isotope Shifts. It is unusual that $^3\Delta_0$ for C3a in both **1** and **2** is positive, +39 or +46 ppb, and $^5\Delta_0$ for C5 in **1** is +15 ppb. The former carbon is on the symmetry axis and cannot be affected by any isotopic perturbation of equilibrium. The positive isotope shifts may be a consequence of the anti relationship between C and D, as in other instances.[42]

Conclusions

The long-standing question about the structures of 1,6-dioxa-6aλ^4-thiapentalene (**1**) and 1,6,6aλ^4-trithiapentalene (**2**) is answered unequivocally using the ^{13}C NMR method of isotopic perturbation of equilibrium. In solution the α-monodeuterated compounds show only small intrinsic isotope shifts of the distant carbon, whereas a rapidly interconverting mixture of two structures would have shown a large downfield isotope shift. Therefore we conclude that each of these thiapentalenes is a single structure with C_{2v} symmetry.

These results are an informative contrast to a recent study using this same method of isotopic perturbation, where 3-hydroxy-2-phenylpropenal was found to be a mixture of two asymmetric tautomers.[43] Since **1** and **2** are here found to be symmetric, the method is capable of distinguishing symmetric species from asymmetric. The asymmetry cannot be attributed to an artifact of the presence of an isotope, a conclusion that is also guaranteed by the Born−Oppenheimer approximation.[44] Nor is asymmetry a necessary consequence of the disorder due to solvation, as proposed for some hydrogen bonds.[25]

Acknowledgment. This research was supported by NIH Grant GM44527 and by NSF Grants CHE94-20739 and CHE99-82103.

References and Notes

(1) Lozac′h, N. *Adv. Heterocycl. Chem*. **1971**, *13*, 161. Gleiter, R.; Gygax, R. *Top. Curr. Chem*. **1976**, *63*, 49. Lozac′h, N. In *Comprehensive Heterocyclic Chemistry*; Katritzky, A. R., Rees, C. W., Eds.; Pergamon Press: Oxford, 1984; Vol. 6, p 1049ff. Pedersen, C. T. *Phosphorus, Sulfur, Silicon* **1991**, *58*, 17. Genin, H.; Hoffmann, R. *J. Am. Chem. Soc*. **1995**, *117*, 12328.

(2) Guillouzo, G. *Bull. Soc. Chim. Fr*. **1958**, 1316.

(3) Bezzi, S.; Mammi, M.; Garbuglio, C. *Nature*, **1958**, *182*, 247. Bezzi, S.; Garbuglio, C.; Mammi, M.; Traverso, G. *Gazz. Chim. Ital*. **1958**, *88*, 1226.

(4) Bothner-By, A. A.; Traverso, G. *Chem. Ber*. **1957**, *90*, 453. Hertz, H. G.; Traverso, G.; Walter, W. *Liebigs Ann*. **1959**, *625*, 43.

(5) Hansen, L. K.; Hordvik, A. *Acta Chem. Scand*. **1973**, *27*, 411.

(6) Minkin, V. I.; Minyaev, R. M. *Chem. Rev*. **2001**, *101*, 1247.

(7) Nakano, M.; Yamada, S.; Yamaguchi, K. *Chem. Phys. Lett*. **1999**, *306*, 187.

(8) Takane, S.-Y.; Sakai, S. *J. Mol. Struct. Theochem* **1999**, *488*, 1.

(9) Cimiraglia, R.; Hofmann, H.-J. *J. Am. Chem. Soc*. **1991**, *113*, 6449.

(10) Saebø, S.; Boggs, J. E.; Fan, K. N. *J. Phys. Chem*. **1992**, *96*, 9268.

(11) Pedersen, C. T.; Schaumburg, K. *Org. Magn. Reson*. **1974**, *6*, 586.

(12) Jacobsen, J. P.; Hansen, J.; Pedersen, C. T.; Pedersen, T. *J. Chem. Soc., Perkin Trans. 2* **1979**, 1521.

(13) Reid, D. H.; Webster, R. G. *J. Chem. Soc., Perkin Trans. 1* **1975**, 775.

(14) Shen, Q.; Hedberg, K. *J. Am. Chem. Soc*. **1974**, *96*, 289. Hagen, K.; Saethre, L. J.; Pedersen, C. T. *Acta Chem. Scand*. **1988**, *A42*, 71.

(15) Pedersen, T.; Skaarup, S. V.; Pedersen, C. T. *Acta Chem. Scand. B* **1977**, *31*, 711.

(16) Saethre, L. J.; Svensson, S.; Mårtensson, N.; Gelius, U.; Malmquist, P. Å.; Basilier, E.; Siegbahn, K. *Chem. Phys*. **1977**, *20*, 431.

(17) Spanget-Larsen, J.; Erting, C.; Shim, I. *J. Am. Chem. Soc*. **1994**, *116*, 11433.

(18) Spanget-Larsen, J.; Fink, N. *J. Phys. Chem*. **1990**, *94*, 8423. Andersen, K. B.; Abildgaard, J.; Radziszewski, J. G.; Spanget-Larsen, J. *J. Phys. Chem. A* **1997**, *101*, 4475. Spanget-Larsen, J.; Andersen, K. B. *Phys. Chem. Chem. Phys*. **2001**, *3*, 908.

(19) Cohen-Addad, C.; Lehmann, M. S.; Becker, P.; Davy, H. *Acta Crystallogr*. **1988**, *B44*, 522.

(20) Yih, K.-H.; Lin, Y.-C.; Lee, G.-H.; Wang, Y. *J. Chem. Soc., Chem. Commun*. **1995**, 223.

(21) Pedersen, C. T.; Frandsen, E. G.; Schaumberg, K. *Org. Magn. Reson*. **1977**, *9*, 546.

(22) Frère P.; Belyasmine, A.; Gouriou, Y.; Jubault, M.; Gorgues, A.; Duguay, G.; Wood, S.; Reynolds, C. D.; Bryce, M. R. *Bull. Soc. Chim. Fr*. **1995**, *132*, 975.

(23) Wu, S.; Greer, A. *J. Org. Chem*. **2000**, *65*, 4883.

(24) Bjorholm, T.; Jacobsen, J. P.; Pedersen, C. T. *J. Mol. Struct*. **1981**, *75*, 327.

(25) Perrin, C. L.; Thoburn, J. D. *J. Am. Chem. Soc*. **1989**, *111*, 8010. Perrin, C. L.; Thoburn, J. D. *J. Am. Chem. Soc*. **1992**, *114*, 8559. Perrin, C. L. *Science* **1994**, *266*, 1665. Perrin, C. L.; Nielson, J. B. *J. Am. Chem. Soc*. **1997**, *119*, 12734.

(26) Siehl, H.-U. *Adv. Phys. Org. Chem*. **1987** *23*, 63. Forsyth, D. A. *Isotopes in Organic Chemistry*; Buncel, E., Lee, C. C., Eds.; Elsevier: Amsterdam, 1987; Vol. 6, Chapter 1. Hansen, P. E. *Annu. Rep. NMR Spectrosc*. **1983**, *15*, 105. Hansen, P. E. *Prog. Nucl. Magn. Reson. Spectrosc*. **1988**, *20*, 207.

(27) Batiz-Hernandez, H.; Bernheim, R. A. *Prog. NMR Spectrosc*. **1967**, *3*, 63. Jameson, C. J.; Osten, H. J. *Ann. Rep. NMR Spectrosc*. **1986**, *17*, 1. Risley, J. M.; Van Etten, R. L. *NMR* **1990**, *22*, 81. Berger, S. *NMR* **1990**, *22*, 1. Hansen, P. E. *Magn. Reson. Chem*. **2000**, *38*, 1.

(28) Nakanishi, K.; Solomon, P. H. *Infrared Absorption Spectroscopy*, 2nd ed.; Holden-Day: San Francisco, 1977.

(29) Torres, M.; Clement, A.; Strausz, O. P.; Weedon, A. C.; de Mayo, P. *Nouv. J. Chem*. **1982**, *6*, 401. Torres, M.; Safarik, I.; Clement, A.; Strausz, O. P. *Can. J. Chem*. **1982**, *60*, 1187.

(30) Imashiro, F.; Madea, S.; Takegoshi, K.; Terao, T.; Saika, A. *J. Am. Chem. Soc*. **1987**, *109*, 5213.

(31) Ishii, A.; Ishida, T.; Kumon, N.; Fukuda, N.; Oyama, H.; Inamoto, N.; Iwasaki, F.; Okazaki, R. *Bull. Chem. Soc. Jpn*. **1996**, *69*, 709.

(32) Selzer, T.; Rappoport, Z. *J. Org. Chem*. **1996**, *61*, 5462.

(33) Pauson, P. L.; Proctor, G. R.; Rodger, W. J. *J. Chem. Soc*. **1965**, 3037.

(34) Mayo, D. W.; Sapienza, P. J.; Lord, R. C.; Phillips, W. D. *J. Org. Chem*. **1964**, *29*, 2682.

(35) Reid, D. H.; Webster, R. G.; *J. Chem. Soc., Perkin Trans. 1* **1972**, 1447.

(36) Reid, D. H.; Webster, R. G.; *J. Chem. Soc., Chem. Commun*. **1972**, 1283.

(37) Davy, H.; Vialle, J. *C. R*. **1972**, *C275*, 625. Caillaud, G.; Mollier, Y. *Bull. Soc. Chim. France* **1972**, 151.

(38) Dingwall, J. G.; McKenzie, S.; Reid, D. H. *J. Chem. Soc. (C)* **1968**, 2543.

(39) Davidson, S.; Leaver, D. *J. Chem. Soc., Chem. Comm*. **1972**, 540.

(40) Beer, R. J. S.; Carr, R. P.; Cartwright, D.; Harris, D.; Slater, R. A. *J. Chem. Soc. C* **1968**, 2490.

(41) Wang, S.; Fackler, J. P., Jr. *J. Chem. Soc., Chem. Commun*. **1988**, 22.

(42) Lambert, J. B.; Greifenstein, L. G. *J. Am. Chem. Soc*. **1974**, *96*, 5120. Saunders, M.; Kates, M. R. *J. Am. Chem. Soc*. **1977**, *99*, 8072. Gunther, H.; Seel, H.; Gunther, M.-E. *Org. Magn. Reson*. **1978**, *11*, 97. Aydin, R.; Gunther, H. *J. Am. Chem. Soc*. **1981**, *103*, 1301. Perrin, C. L.; Kim, Y.-J. *Inorg. Chem*. **2000**, *39*, 3902.

(43) Perrin, C. L.; Kim, Y.-J. *J. Am. Chem. Soc*. **1998**, *120*, 12641.

(44) Levine, I. N. *Quantum Chemistry*, 2nd ed.; Allyn & Bacon: Boston, 1974; p 289ff.