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CONFORMATIONAL STUDIES OF 7-MEMBERED CYCLIC SULFITES. 3-OXO-2,4,3-DIOXATHIEPIN AND 3-OXO-2,4,3-BENZODIOXATHIEPIN

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Abstract—The conformational and dynamic properties of the 7-membered cyclic sulfites **1** and **2** were investigated by ^1H and ^{13}C DNMR as well as by IR spectroscopy. Compound **1** showed two spectral modifications at low temperature for both ^1H (100 MHz) and ^{13}C (22.6 MHz) spectra while for compound **2** a single ^1H spectral change has been observed and resolved at 300 MHz. Analysis of the low temperature NMR spectra together with the IR frequencies for the stretching vibration of the S=O bond indicate that **1** exists as a 1:1 mixture of C-a and TB conformations in CHF_2Cl. Less polar solvents increase the proportion of the C-a form. In contrast, compound **2** is found to exist very predominantly as the TB form in CHF_2Cl at $-160°$, whereas in the less polar CCl_4 solvent a small amount of C-a form is found to be present at room temperature from the IR data. The conformational and dynamic properties determined for **1** and **2** are discussed in light of current theories relating to $n \rightarrow \sigma^*$ stereoelectronic lone pair donation and dipole–dipole interactions. Furthermore the results for **1** and **2** are used as the basis for a new conformational interpretation of published IR data for dimethyl sulfite. Finally, the differences in properties of **1** and **2** are discussed.

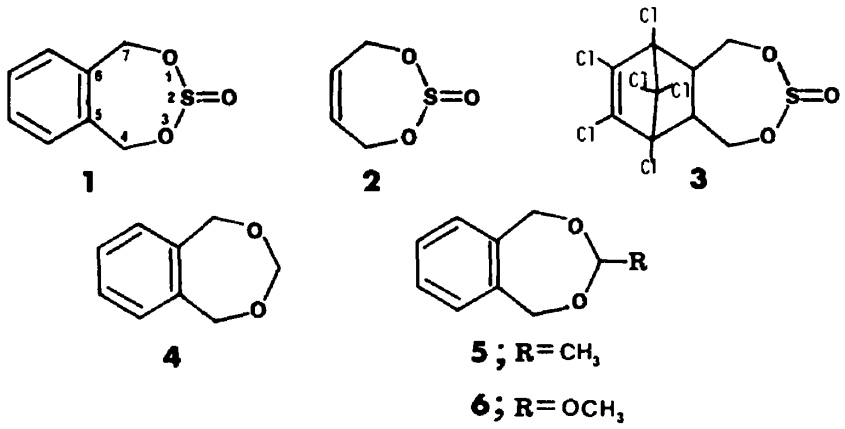
The Sulfites, esters of sulfurous acid,[2] constitute a class of compounds which has been the focus of much interest over the years because of the consequences of the stereochemical rigidity of the pyramidal S atom. Cyclic sulfites, mainly 5-[3,4] and 6-membered[5–10] rings, have been extensively investigated while only a few studies of larger rings have been reported.[11–13] Among the latter, the 7-membered cyclic sulfites **1** and **2** were first studied[11a] as models to obtain information pertinent to the conformations of the two stereoisomers of the insecticide thiodan (**3**).[11b]

It is now well established that the most stable conformation of trimethylene sulfite (3-oxa-1,3,2-dioxathian) is a chair form[14] containing an axially oriented S=O bond (C-a). This conformational preference over the equatorial orientation has been estimated to involve about 2 kcal/mole[15] in CCl_4. Further insight into the stereochemical properties of the sulfite function has been gained from studies of various alkyl-substituted 6-membered cyclic derivatives.[9,11] Examples of compounds existing as chairs with an equatorial[16] S=O bond (C-e) and others in twist-boat (TB) forms[17] have been found. Conformational conclusions for ethylene sulfites are much less precise owing to the great flexibility of the 5-membered ring.[3,4] On the other hand, remarkably little is known about the 7-membered sulfites. The early suggestion that **1** and **2** existed as chair forms with equatorial S=O bonds[11a] was indirectly discredited when the two stereoisomers of thiodan were assigned chair conformations with axial S=O bonds.[12]

Altogether many experimental techniques have been used to study the sulfites: IR,[5,10] ^1H and ^{13}C NMR[1–9] spectroscopic methods, ultrasonic absorption,[18] electron diffraction,[19] X-ray diffraction[14,16,17] and dipole moment measurements.[6,11a] However, when mixtures of conformations have been invoked, no direct observations of distinct NMR signals for each conformer and no dynamic NMR investigation appear to have been reported.

Because of the limited knowledge of the conformational behavior of the sulfite function and of the 7-membered cyclic molecules we chose to investigate 2-oxo-1,3,2-benzodioxathiepin (**1**) and 2-oxo-1,3,2-dioxathiepin (**2**)[20] which in a preliminary communication[21] were shown to exhibit characteristics suitable for a DNMR investigation. Further interest in these molecules arose from the recent report[22] that **4** exists as a mixture of C and TB forms while **5** and **6** exist as single but different conformations, namely the C-e and TB forms respectively. It was therefore important to find out if some similarity exists between **1** and **6** in order to gain a better understanding of the properties of the sulfite moiety. Also, through a comparative study of **1** and **2**, the effects produced by the replacement of a double bond by a benzo group in 7-membered rings could be determined experimentally.

Herein we report the results of ^1H and ^{13}C DNMR investigations of solutions of **1** and **2** as well as of IR studies of these compounds. Our observations are relevant to the question of the preferred orientation(s) of the S=O bond of the sulfite function in flexible



systems; they contribute to the identification of the underlying electronic interactions and their stereodynamic consequences. Furthermore we believe that our conclusions should be useful to understand the conformational properties of flexible larger cyclic sulfites as well as acyclic ones. In fact, our observation for **1** and **2** led us to reinterpret recent IR results for dimethyl sulfite[23] and to suggest a new geometry for the most stable conformation of the mixture detected.

RESULTS

NMR spectral analysis. The ^1H and ^{13}C NMR spectra (100 MHz and 22.6 MHz respectively) of compound **1** both showed spectral changes at low temperatures as illustrated in Fig. 1.

The ^{13}C NMR spectrum of **1** at room temperature showed only three signals which are assigned in Table 1. Fig. 1 (left hand side) illustrates the spectral change

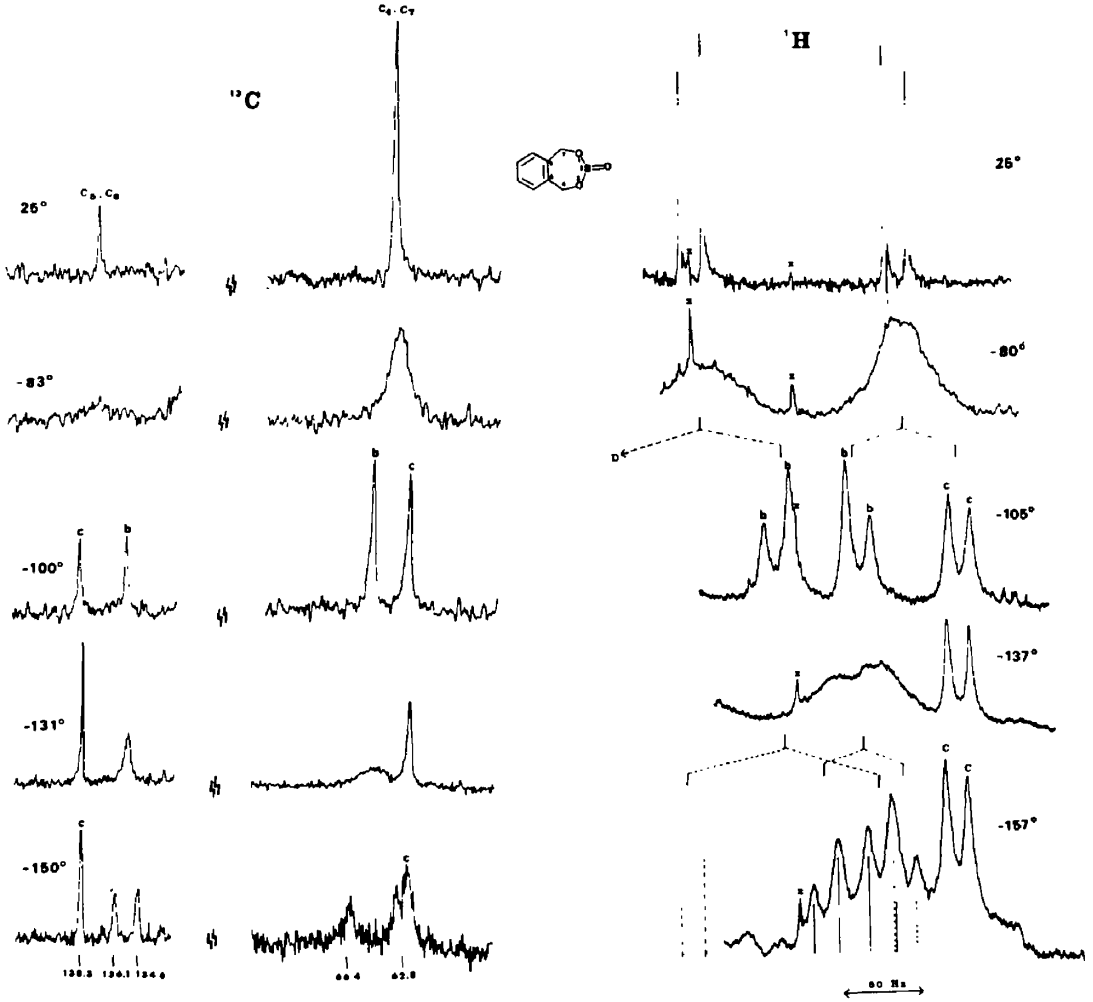


Fig. 1. Partial 22.6 MHz ^{13}C NMR (left hand side) and 100 MHz ^1H NMR (right hand side) spectra of **1** in CHF_2Cl at several temperatures. The meaning of the letters a, b and D is given in the text. Impurity signals are denoted by X.

observed for the C-5,6 and C-4,7 signals. It is shown that each line splits into a doublet with components of near equal intensity at $-100°$. At still lower temperatures, only one line from each doublet (those labelled *b*) further separates into additional doublets of equal intensity. The two lines labelled *c* remain unchanged throughout this temperature range. Thus, the partial ^{13}C spectrum at $-150°$ contains six lines, of which the two taller *c* lines are of equal intensity and the four other smaller lines are also of equal intensity. Furthermore, it is interesting to observe that, at $-150°$, the three upfield lines arising from the protonated benzylic carbons (C-4,7) are broader than those of the non-protonated C-5,6 owing to relaxation effects. Very similar and complementary results were observed in $CHFCl_2$ at $-103°$.

The ^{13}C NMR spectrum of **1** in dimethyl ether at $-103°$ also showed doublets for the C-5,6 and C-4,7 signals but with a ratio of *c*:*b* line intensity of 65: 35; this ratio is very similar to the 5:2 value reported in a preliminary communication[21] for a solution in *m*-fluorotoluene. A summary of the pertinent data together with activation parameters calculated at the coalescence temperature[24] is given in Table 1.

The 100 MHz ^1H NMR spectrum of **1** in CHF_2Cl at room temperature showed an AB pattern corresponding to the benzylic protons whose parameters are given in Table 2. This benzylic protons signal gave two spectral modifications at low temperature as shown on the right hand side of Figure 1. The single AB pattern observed at ambient temperature changes into the two AB patterns observe at $-105°$; these are labelled *b* and *c* in accordance with the convention established for the ^{13}C NMR spectra. Because the lowfield half of the AB pattern labelled *c* overlapped with solvent peaks, only its position is indicated by the letter D in Fig. 1. A chemical shift of 6.43 ppm for this doublet was obtained from a 250 MHz spectrum recorded at $-100°$. Below $-120°$, another spectral change takes place whereby only the inner AB pattern (labelled *b*) splits into two additional AB quartets for which the lowest field doublet is not shown because it also overlapped with solvent peaks. A splitting pattern and a "stick" diagram illustrate clearly the details of the second spectral modification for which the position of the lowest field doublet is indicated by means of the "stick" diagram. Accordingly, one AB pattern is identified by the solid lines while the broken lines

Table 1. Carbon-13 chemical shift and dynamic data for compounds **1** and **2** in several solvents at high and low temperatures[a]

Compounds; Solvent	Temperature °C	C-4, C-7	C-5, C-6	C-8 to C-11	$\Delta G^{\ddagger}$ (Tc) kcal/mole
1 CHF_2Cl	25°	63.91	137.74	129.55	8.9 (−83°)[b]
	−100°	62.49(c)[c]	135.59(b)	128.38, 129.20	
		64.86(b)	138.56(c)	d , 130.97	6.6 (−136°)[e]
	−150°	62.57(c)	134.72	128.51, 129.24	
		63.09	136.15	130.24, 130.97	
		66.41	138.35(c)		
1 $CHFCl_2$	−103°	61.92(c)	134.72(b)	127.73, 128.51	
		64.30(b)	137.70(c)	129.50, 130.32	
1 CH_3OCH_3	25 °	63.13	138.13	129.20, 129.33	
	−103°	61.62(c)[f]	136.06(b)	128.08, 128.63	
		63.91(b)	139.21(c)	129.29, 130.45	
2 CHF_2Cl	25°[g]	61.13	129.30		

a) The spectra were taken at 22.63 MHz with TMS as internal reference.

b) This value was calculate from the splitting of the C-4,7 line using a transmission coefficient of 1/2. A value of 8.8 was similarly calculated for the C-5,6 signal.

c) The labels b and c are defined in the text. In CHF_2Cl and $CHFCl_2$ the c : b ratio is about 1:1.

d) This line was obscured by a solvent signal.

e) This value was calculated for the b lines of the C-5,6 signal using a transmission coefficient of one. The value 6.7 (−131°) was obtained from the C-4,7 signal.

f) The ratio of c : b is 65 : 35 in CH_3OCH_3.

g) Resolved spectra were not obtained below coalescence for this compound.

Table 2. Spectral parameters of the benzylic protons for compounds 1 and 2 at high and low temperatures[a]

Compounds; Solvent	Temperatures °C	δ_A ppm	δ_B ppm	$-^2J_{AB}$ (Hz)
1 CHF_2Cl	25°	5.91	4.64	14.1 ± 0.2
	-105°	6.43[b] (c)[c]	4.33 (c)	d
		5.46 (b)	4.98 (b)	
	-152°	~ 6.4 (c)	4.4 (c)	d
		5.2 (b_1)[e]	4.9 (b_1)	
		6.0 (b_2)	4.8 (b_2)	
1 $CHFCl_2$	25°	5.93	4.67	14.0
	-103°	6.45 (c)	4.39 (c)	d
		5.49 (b)	5.04 (b)	
2 CHF_2Cl	25°	4.91	4.42	14.0
	-160°	4.83 (b_1)[f]	4.47 (b_1)	
		5.48 (b_2)	4.29 (b_2)	

a) The spectra of 1 were recorded at 100 MHz while those of 2 were recorded at 300 MHz.

b) The chemical shift of this AB pattern was determined at 250 MHz.

c) The label b and c are defined in the text and have the same meaning as in Table I.

d) The broad lines at low temperatures did not permit the measurement of precise coupling constant. They are similar to that measured at room temperature.

e) The number 1 and 2 identify each of the two AB patterns observed at low temperatures and identified by the "stick" diagram (Fig. 1).

f) The number identify each of the two AB patterns observed at -160° (Fig. 2).

identify the other one. The pertinent ^1H NMR spectral parameters are given in Table 2.

A series of ^1H NMR spectra of 2 taken at 100 MHz revealed a complex spectral change for the allylic protons below $-155°$, which because of appreciable overlap could not be analyzed confidently. This compound was therefore examined at 300 MHz. Thus, at room temperature, the spectrum of 2 in CHF_2Cl reveals a triplet at 5.77 ppm (separation = 2.2 Hz) for the olefinic protons and an AB pattern with fine structure owing to various couplings and second order effects. At $-135°$, line broadening removes the smaller couplings so that the four lines of the AB pattern are clearly seen as shown in Fig. 2. A spectral change takes place at lower temperatures such that at $-160°$ four broad signals are clearly visible. Better resolution showing the splitting due to the large geminal coupling, could not be achieved. Nevertheless the spectrum at $-160°$ clearly reveals four about equally intense peaks in accord with signals of unresolved multiplicities arising from four different proton environments. (i.e. two AB patterns with coupling to the olefinic protons). The chemical shifts are assigned by analogy with 1 and the spectral parameters are given in Table 2. A splitting pattern illustrating the spectral change is drawn above the last spectrum of Fig. 2. Coalescence temperatures were not searched for at 300 MHz. On the other hand, the 100 MHz spectra showed that the lowfield splitting occurred at about $-160 \pm 5°$, thus permitting an estimate of 5.3 kcal/mole for the free energy of activation characterizing the averaging process.

The ^{13}C NMR spectra of 2 in CHF_2Cl both at 22.6 and 75.4 MHz did not reveal any resolved spectral change at low temperatures. However, the spectra at 75.4 MHz revealed extensive broadening for the C-4,7 line in the spectrum recorded at about $-160°$ while the C-5,6 line also showed significant broadening. Thus at about $-160°$, the C-4,7 line width at half-height is many times broader than TMS (i.e. about 175 Hz compared to a few Hz).

This observation is compatible with the fact that more than one allylic carbon signal would be observed at still lower temperatures as suggested by the ^1H spectrum.

IR spectral description. The frequencies of the stretching vibration[10] of the S=O bonds (ν_{SO}) in the region between 1175 to 1250 cm^{-1} have been measured from IR spectra taken for 0.05 M solutions of 1 and 2 in CCl_4 and in CH_3CN. The spectral appearance of the bands observed for each compound was shown in a preliminary communication[21] and only a brief description of peak frequencies and relative intensities is required for our present purpose. Thus for

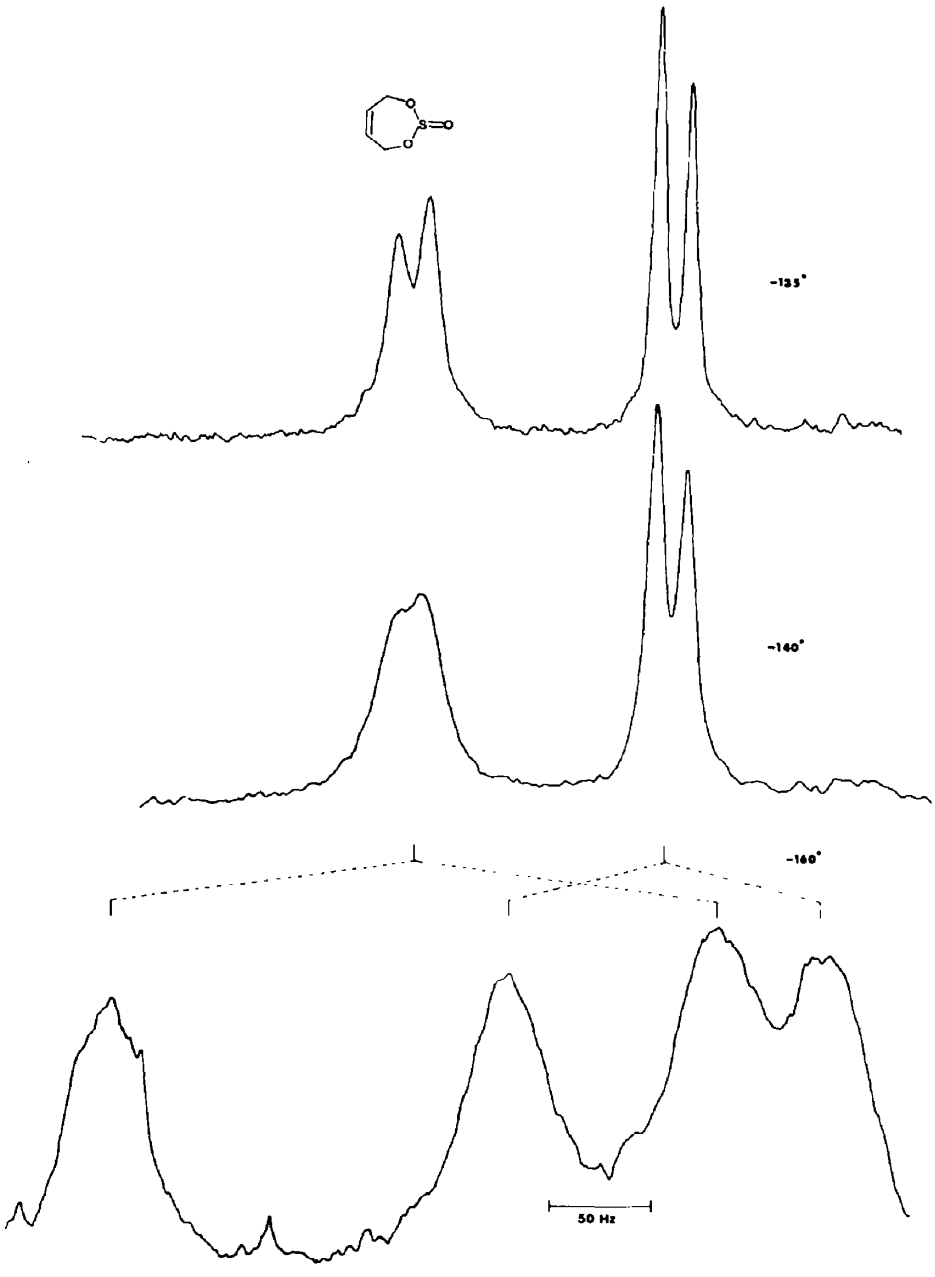


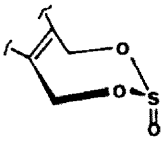
Fig. 2. The 300 MHz ^{1}H NMR spectra of the allylic protons of **2** in CHF_2Cl at several temperatures.

1, two bands are clearly visible in each solvent (i.e. at 1220 (M) and 1184 (S) cm^{-1} in CCl_4 vs 1210 (S) and 1179 (M) cm^{-1} in CH_3CN); the reversal of intensities observed is such that the band at higher frequency is the least intense in CCl_4 and the most in CH_3CN. By comparison two bands are observed for **2** in CCl_4 (i.e. at 1219 (S) and 1184 (W) cm^{-1}) whereas in CH_3CN only one band at 1204 cm^{-1} is clearly resolved although a shoulder could be present on the lower frequency side.

DISCUSSION

The ^{1}H and ^{13}C NMR spectra of **1** each revealed two spectral modifications at low temperature whereas only one spectral change was observed clearly in the ^{1}H NMR spectra of **2**. Because it is reasonable to assume that all conformational averaging processes for **1** and **2** have been slowed down on the NMR time scale,[22] the lowest temperature spectra recorded should provide direct information on the nature of the most stable conformation(s). In this context, the more complex spectra of **1** are potentially more informative since they indicate the existence of two conformations, one corresponding to the *b* lines in Tables 1 and 2 and the other one associated with the *c* lines. It is therefore more instructive to begin our analysis with the spectra of **1**.

Stable conformations of **1** *in solution.* Because the ^{13}C spectra are simpler to analyse, they are considered first.



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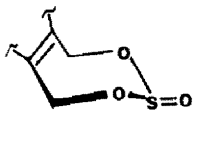

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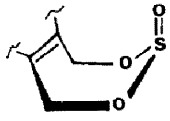

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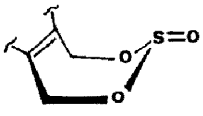

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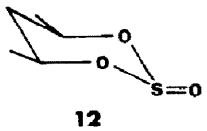
The three ^{13}C lines observed for each of the C-5,6 and C-4,7 signals of **1** at $-150°$ (Fig. 1 and Table 1) and their intensity distribution identify the existence of a mixture of two conformations of different symmetry. The more intense lines labelled *c* can be assigned to a conformation containing a plane of symmetry making C-4 and C-7 equivalent as well as C-5 equivalent to C-6. For the other conformer, each of these C atoms gives a distinct signal in accord with the absence of a symmetry element. The examination of the five possible conformations for **1** (i.e. **7**–**11**) shows that all forms except TB (**9**) possess a plane of symmetry. The TB form is then identified as the conformation characterized by the *b* lines in Fig. 1.

The ^1H NMR spectrum of **1** at $-157°$ (Fig. 1) confirms the identity of TB as one of the conformers detected. Thus the two AB patterns identified by the line diagram under the bottom spectrum arise from the nonequivalent benzylic methylene groups of TB whereas the single AB pattern labelled *c* must be associated with the other symmetrical conformation. The ^1H and ^{13}C NMR chemical shift of the signals belonging to the symmetrical form suggest a C-a geometry as discussed next.

Firstly, it is known that the S=O substituent effect (i.e. replacement of CH_2 by S=O) on ^{13}C chemical shift is stereodependent. For example, the replacement of the 2-CH_2 in 1,3-dioxane by S=O produces an upfield shift of 11.6 ppm on C-4,6 for solutions in $CDCl_3$ (i.e. the difference in the chemical shift of 67.7 ppm 1,3-dioxane[25] and 57.1 for trimethylene sulfite[26]). This large upfield shift is a consequence of the gauche relationship between C-4 (and C-6) and the axial S=O bond. In order to determine the magnitude a similar substituent effect for 7-membered rings, the appropriate reference parameter to be used is the 76.25 ppm shift for C-4,7 of the chair form of **4** obtained at $-130°$ in CHF_2Cl.[22] Thus, a 13.7 ppm upfield displacement is determined for the symmetrical form of **1** (i.e. difference with the 62.57 ppm for C-4,7 at $-150°$ in CHF_2Cl, Table 2).



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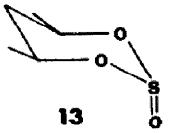

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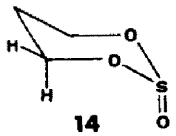

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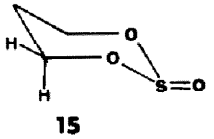

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The *anti* relationship of C-4 and C-6 with an equatorial S=O group, in trimethylene sulfite results in the $CH_2 \rightarrow S{=}O(eq)$ substitution effect being a much smaller upfield shift ($\sim$2.5 ppm) as revealed from a comparison of the C-4,6 signals of **12** and 1,3-dioxane. As a consequence, the difference in chemical shift between the C-4,6 signals of **12** and **13** is 9.1 ppm, the signal of **13** being at higher field.[26] Therefore, among the symmetrical conformations of **1**, neither the C-e or B-e forms, for which C-4 and C-7 are *anti* to the S=O bond, are acceptable conformations. It is thus shown that the C-a form for **1** is able to account for the S=O substituent effect on the C-4,7 signal. But the B-a form, for which a gauche relationship exists between C-4,7 and the S=O bond, cannot be rejected from the above argument.

It is relevant to point out that the ^{13}C chemical shifts of the TB form of **1** also reflect the geometrical relationships between the benzylic carbons and the S=O bond orientation. The low temperature ^{13}C data show that, relative to the TB signal of **4** (70.38 ppm at $-130°$ in CHF_2Cl),[22] the *syn* and *anti* benzylic carbons of **1** (i.e. C-7 and C-4 respectively in **9**) are displaced upfield by 7.29 and 3.97 ppm respectively. These values are very similar to those determined for the TB conformation of **6** which are 7.81 and 2.54 ppm.[22]

The analysis of ^1H chemical shifts also provides conformationally discriminating information. Several groups of workers[7,8,27] have shown that the S=O bond in sulfites exerts a strongly differentiating effect on the chemical shifts of axial and equatorial protons of methylene groups adjacent to the ring O atom whereby a chemical shift difference of -1.14 ppm has been observed between the two protons shown in structure **14**; the negative sign indicates that the equatorial proton is more upfield than the axial one. The reversal of sign, compared to the $+0.48$ ppm differentiating axial and equatorial protons in cyclohexane,[28] suggest that a global effect of approximately -1.15 ppm is produced by the electric field and magnetic anisotropy effects of the axial S=O bond. Contrastingly, the equatorial S=O bond, as in **15**, leads to a small chemical shift difference for the methylene protons as deduced from derivatives of trimethylene sulfite and sulfites derived from decalin.[27]

For the 7-membered rings, reference chemical shift differences for the benzylic methylene protons are provided by those characterizing the chair forms of benzocycloheptene and of **4** which were found to be -0.106 and -0.119 ppm respectively.[29,22] Thus the very large absolute value of 2.1 ppm characterizing the AB pattern labelled *c* in the spectrum of **1** at $-105°$ (Table 2) is compatible with a C-a form for which the effect of the S=O bond on the methylene protons would be amplified by the greater puckering of the seven-membered chair form.[29]

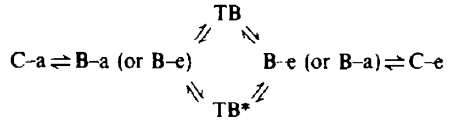
As for the ^{13}C parameter analysis, the B-a form cannot be ruled out rigorously by the ^1H parameters. Fortunately the dynamic features revealed by the spectra of **1** can. Accordingly, if a mixture of B-a and TB forms existed for **1**, then only one spectral change would be observed as a result of the slowing down of TB ⇆ B-a, the only process possible (*vide-infra*). Thus, the symmetrical conformation of **1** must have the C-a geometry which together with TB can account for the two spectral changes observed.

Finally, the two AB patterns characterizing the TB form in the ^1H NMR spectrum of **1** at $-157°$ (Fig. 1) show markedly different chemical shift differences for the nonequivalent benzylic methylene groups which are 0.3 and 1.2 ppm. The examination of molecular models of the TB form (**9**) shows that the CH_2 group *syn* to the S=O bond is expected to show a greater proton chemical shift difference than the *anti* CH_2 group for which the smaller 0.3 ppm is compatible with the small value found for the *anti* relationship in **15**.

Having determined unambigously that the two conformations of **1** are of the C-a and TB forms, it now possible to confirm that the IR stretching frequencies of the S=O bonds (ν_{SO}) in the region of 1175–1250 cm^{-1} reveals a behavior similar to that empirically defined for 6-membered cyclic sulfites, for which extensive investigation[10] has led to the definition of representative frequency domains characteristic of the three conformations C-a, C-e and TB forms as summarized in Table 3. Furthermore, it has been shown[10] that low concentration (0.05 M or less) minimizes molecular association effects.

The IR spectra of **1** revealed two characteristic bands for both CCl_4 and CH_3CN solutions. In the less polar CCl_4 solvent, the bands at 1184 cm^{-1} is more intense than the one at 1220 cm^{-1}. The NMR observation that the C-a form of **1** predominates in solvent of lower polarity, such as dimethyl ether, and the use of Table 3 shows that the band at 1184 cm^{-1} arises from the C-a form while the TB form gives the band at 1220 cm^{-1}. The solvent induced frequency shifts $\Delta\nu(CCl_4\text{–}CH_3CN)$, being 5 cm^{-1} for C-a and 10 cm^{-1} for TB, are in good agreement with expectations. The IR method, therefore, appears to be a useful probe for the spatial arrangements of the sulfite moiety in this family of 7-membered rings. The small deviations between the C-a frequencies for **1** and those for SO_a in Table 3 could reflect the fact that the 7-membered chair form is more puckered[29] while the TB form being more flexible allows the sulfite function to take up very similar dispositions for both ring sizes.

Conformational dynamics of **1**. The conformational interconversion pathways characterizing the cycloheptene ring differ from those possible for cycloheptane because the introduction of the double bond requires four carbon atoms to remain coplanar. This contraint imparts rigidity to the chair form which can no longer undergo the pseudorotation motion which interconverts the chair and twist-chair conformations of cycloheptane.[30] Consequently, the cycloheptene conformations interconvert through two basic molecular motions consisting of a C ⇆ B transformation and a B ⇆ TB pseudorotation cycle. The standard interconversion scheme[31] must be modified slightly for **1** by taking into account the pyramidal nature of the S atom and the orientation of the S=O bond. The appropriate conformational interconversion pathways are represented in Scheme 1 where the * indicates an inverted (or mirror image) conformation.



Scheme 1.

It is seen that C-a can be transformed directly into B-a while C-e can become B-e by flipping the unsaturated end of the molecule as prevailing evidence indicates for benzocycloheptene.[32,33] On the other hand, when the flipping of the sulfite end of the molecule is considered, the C-a is transformed into B-e while C-e changes into B-a. This dual possibility is accounted for in Scheme 1 by indicating the alternate forms in parenthesis. Furthermore it is seen that the

Table 3. Frequency domains [a] for the S=O bond stretching vibration in six-membered cyclic sulfites

Type of S=O [b]	$\nu_{SO}(CCl_4)$	$\nu_{SO}(CH_3CN)$	$\Delta\nu(CCl_4\text{–}CH_3CN)$
SO_a	1191 ± 3	1185 ± 3	7 ± 3
SO_i	1220 ± 2	1209 ± 1	11 ± 2
SO_e	1242 ± 2	1225 ± 1	17 ± 2

a) The values (cm^{-1}) reported in this table are taken from ref. 10 for the whole group of alkyl derivatives studied.

b) The three types of S=O environment considered are : a = axial, e = equatorial, i = isoclinal as in twist-boat forms.

TB to TB* process (TB inversion) can in principle proceed by two pathways, one involving the B-a form and the other the B-e form.

The ^1H and ^{13}C spectral changes observed for **1** near $-130°$ and below (i.e. at the lower temperatures) involve only the TB signals and therefore arises from the slowing down of TB inversion on the NMR time scale. At $-100°$, this process is rapid whereas the C-a and TB conformational interconversion process is still slow because separate signals are observed for each form. At room temperature both processes are rapid so that averaging of the C-a and TB signals is observed. As a result, the room temperature spectrum reveals an average plane of symmetry even though the TB form is chiral.

It is interesting to observe that the free energy activation barriers for the TB inversion of **1** (6.6 kcal/mole) is very similar to that observed for **6** (6.7 kcal/mole).[22] On the other hand, the barrier for the C-a to TB interconversion of **1** (9.0 kcal/mole) is significantly lower than the corresponding value of 10.9 kcal/mole for benzocycloheptane but higher than the 8.0 kcal/mole determined for **4**.[22] The lower interconversion barrier of **1** relative to that of benzocycloheptene could be interpreted in terms of a change in the nature of the prefered molecular motion whereby, for **1**, the sulfite end of the molecule could flip so that C-a would be transformed into B-e in Scheme 1. It is not easy to explain why this should happen. Alternatively it is conceivable that the presence of heteroatoms could reduce torsional strain in the transition state resulting from the flipping of the benzo end of the molecule. Furthermore it could be argued that the two ring O atoms are better able to support angular strain in either transition state by a rehybridization to SP^2. Finally, the smaller O–S–O angle ($\sim 101°$)[34] in the chair form of **1** relative to the O–CH_2–O angle of **4**, which is probably similar to that reported for the chair form of 1,3-dioxepane (~ 116),[35] could explain the slightly higher barrier of **1** relative to **4** for either of the two types of motions. Convincing support in favor of one of these rationals does not appear to be available at present.

Conformational properties of **2** *in solution.* The four broad peaks in the ^1H NMR spectrum of **2** at about $-160°$. (Fig. 2) each represent non resolved halves of two AB patterns with coupling to the olefinic protons. The close to near equality of the area of each peak suggests the presence of four different proton environments close to equally populated. The splitting pattern illustrated in Fig. 2 is very similar to that characterizing the lower temperature spectral change of the inner AB pattern in the spectrum of **1** at $-100°$ (Fig. 1) as are the chemical shift differences for each of AB pattern labelled b_1 and b_2 in Table 2. These observations indicate that TB inversion is responsible for the spectral modification observed for **2** and the predominant conformation of **2** in solution must therefore be the TB form. A near equimolar mixture of C-a and TB forms is thus excluded and only a minor amount of C-a form could be present because its small signals, which would be on both sides of the TB signals as suggested by the *c* lines of **1**, have not been detected in the spectrum at $-160°$.

Ideally ^{13}C NMR could have provided more quantitative data because of greater spectral simplicity as was the case for **1**; but unfortunately only broadening of the C-4,7 and C-5,6 lines has been observed.

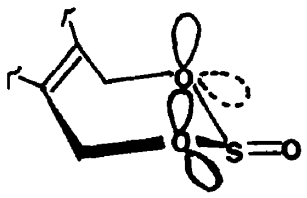
Confirmation of the above conclusion is provided from the IR data for **2**. As was shown with **1**, the stretching frequency of the S=O bond is a convenient conformational probe sensitive to the spacial arrangement of the sulfite moiety and consequently diagnostic of ring conformation for cyclic molecules. Accordingly the bands at 1219 and 1184 cm^{-1} and their relative intensities in the spectrum[21] of **2** in CCl_4 indicate that a mixture of C-a and TB forms exists in this relatively non polar solvent; the TB form responsible for the signal at 1219 cm^{-1} is predominant. On the other hand, the spectrum of **2** in the more polar CH_3CN solvent apparently shows only one peak at 1204 cm^{-1} characteristic of the TB form; however the small shoulder on the right hand side could indicate the presence of a small amount of the C-a form. Thus it is seen that an increase of solvent polarity decreases the amount of C-a form. This trend was also observed for **1** both by NMR and IR measurements.

It therefore appears that a minor amount of C-a form is possible for **2** in the polar solvent CHF_2Cl used in the NMR experiments. The fact that the NMR results are evaluated at $-160°$, however, suggests that very little of the C-a form would be present. This situation for **2** is to be contrasted to that of **1** for which significant amount of the two forms is always observed. There is therefore a greater tendency for **2** to adopt the TB form than for **1**.

Orientational preference of the S=O *bond.* The stronger conformational preference of the S=O bond for the axial position of the trimethylene sulfite chair form relative to that observed for pentamethylene sulfoxide has already been attributed to electronic origins analogous to the anomeric effect. Originally dipole–dipole interactions[36] were invoked and later a stereoelectronic interaction,[16] between axial lone pairs of the ring oxygen atoms and an antibonding orbital of the axial S=O bond, was used to explain the phenomenon.

Much basic information, useful to understand the conformational properties of ring systems, can be obtained from a consideration of the behavior of the individual bonds present. The theoretical foundation describing the factors affecting the rotation of polar bonds was set down clearly by Radom *et al.*[37] in their treatment of internal rotation potential functions through a Fourier component analysis; they concluded that changes in potential energy for the rotation of polar bonds involve at least three terms, namely a threefold energy barrier (V_3) as exists in ethane and methanol, a two fold energy barrier (V_2) involving lone pair donation and a onefold term (V_1) related to dipole-dipole interactions. Their works showed that such a decomposition facilitates the interpretation of internal rotation.

A closely similar theoretical view of the electronic interaction accounting for the twofold barrier in systems containing adjacent polar bonds and electron pairs has been proposed later by David *et al.*[38] who concluded that stabilization results from donation of the antiperiplanar (*app*) adjacent lone pair into the σ-anti-bonding orbital of the X–Y bond for –Ö–X–Y moiety (i.e. n–σ^* back-donation). Finally the need for a twofold barrier was also recognized in force field



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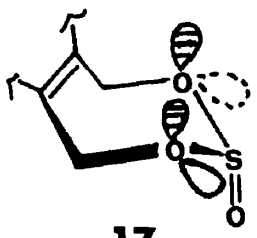

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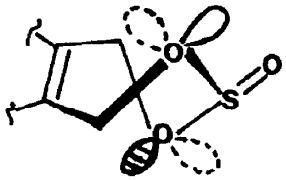

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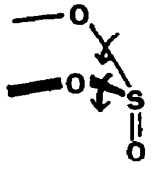


19

calculations.[39] Models for this type of stereoelectronic effect must take into consideration the hybridization state of the two lone pairs of oxygen as being either non-equivalent (P and SP^2) or equivalent (SP^3). As this question is not yet completely resolved, and because observed stereochemical effects appear to be predictable by the simple model using equivalent lone pairs for oxygen, this approach will be used in our work.[40,41]

For the illustration of the above concept in the conformational analysis of **1** and **2**, it is useful to consider the electron lone pair orientations for the three conformations of interest: **16** (C-e), **17** (C-a) and **18** (TB). While lone pair donation is involved between each –S–O-bond of the ring, it is with back-donation to the S=O bond that we are first concerned.[16] Thus it is seen that no *app* lone pair to the S=O bond are found in C-e whereas C-a contains two and TB one. It therefore follows that C-e should be the conformation least stabilized by this type of stereoelectronic back-donation.

As structural consequences of this effect for a —Ö—X—Y moiety, it has been calculated and demonstrated that an *app* lone pair to the polar X–Y bond shortens and strengthens the O–X bond while simultaneously lengthening and weakening the X–Y bond; moreover, when more than one *app* lone pair exists, the effect is cumulative.[41–43]

The examination of structures **16**, **17** and **18** together with Table 3 further reveals that a qualitative relationship exists between the characteristic frequency domains for the S=O stretching vibration and the number of *app* lone pairs present in the three conformations: C-e (0 *app*; 1242 cm^{-1}), TB (1 *app*; 1220 cm^{-1}) and C-a (2 *app*; 1191 cm^{-1}). The observed values for **1** and **2** are very similar to these, the only significant difference being 1184 cm^{-1} for C-a instead of 1191 cm^{-1} noted for the 6-membered ring. It therefore appears reasonable to expect that the S=O bond length and strength will be modified by lone pair donation and that as a consequence[44] the stretching frequency dependence on S=O orientation in C-a, C-e and TB is attributable (at least in part) to the stereoelectronic interaction involving *app* lone pairs. This origin therefore rationalizes the intermediate frequency for the TB form relative to those of the C-e and C-a forms. Furthermore, the solvent induced frequency shifts from a less polar (CCl_4) to a more polar (CH_3CN) medium are in line with the suggestion that a more polar solvent should decrease the degree of back-donation as the result of better *app* lone pair solvation.[38] Alkyl substitution on the C-a form of trimethylene sulfites does produce different sensitivity to solvation but the data are not systematic enough to support the above suggestion.[10]

The angular dependance of the stereoelectronic lone pair donation term has been given by the expression V_2 (1-cos 2Ø) where Ø is an appropriate dihedral angle.[37,45] It is therefore apparent that rotation of the sulfite bonds shown in structure **19** will modify the extent of $n \rightarrow \sigma^*$ donation and consequently the importance of the conformational stabilizing effect and the stretching frequency of the S=O bond.

In addition to the above contribution, calculations show that dipole–dipole interactions also constitute an important source of rotational energy[37,45,46] for polar bonds (i.e. the onefold term in the Fourier component analysis[37]) whereby bond arrangements with unfavorable dipole orientation (usually parallel or nearly so) are destabilized relative to those with more opposite orientations. A useful example is the anomeric effect for which relationalization uniquely in terms of this factor have been successful because this effect is very likely the result of a mutual balance between dipole–dipole interactions and stereoelectronic back-donation interactions.[46] The relative importance of each term is a function of the method of calculation and is not known with certainty even for

small molecules such as dimethoxymethane. Fortunately in the case of axial and equatorial positions for 2-substituted tetrahydropyran, both qualitative arguments based on either dipolar interactions or lone pair donation generally lead to the same conformational conclusion.

The evaluation of the importance of dipole–dipole interactions for **1** and **2** is even more difficult because the TB form must be considered. Dipole moment calculations[11a] for the sulfite function in 7-membered rings have suggested that C-a ≈ B-a have smaller values than C-e ≈ B-e. The benzo group and the double bond were neglected in these calculations. The smaller group dipole involved for this remote part of the molecules (i.e. 0.63 D) for benzocycloheptene[47]) suggests that this approximation is acceptable. A consideration of the group dipoles present in the sulfite geometries for C-a, TB and C-e suggests that TB ought to have an intermediate dipole moment and therefore is a more polar conformation than C-a. This order of polarity for the three dispositions of the sulfite moiety has been confirmed experimentally from dipole moment measurements for trimethylene sulfite (C-a) and for alkyl derivatives existing in the C-e and TB forms.[10] It therefore appears that the C-e form of **1** would be most destabilized by dipole–dipole interactions, C-a would be the least and TB would be intermediate.

Furthermore, in addition to the stereoelectronic stabilization from lone pair donation involving the S=O bond and the dipolar interactions described above, it is important, for molecules **1** and **2**, to consider the effect of other electronic interactions[41] such or those involving the O–S–O ring segment and back-donation of the sulfur lone pair to the –O–C– bonds of the ring. Finally a complete description should contain the effect of the threefold (V_3) term and would be rather complex for molecules such as **1**.

However, relative to benzocycloheptene (for which the chair is the only detected conformation), the stabilizing interaction between the ring oxygen, as exists in **4**, has been shown to be more important in the TB form[22] and responsible for the observation of 21% and 33% of TB for CHF_2Cl and CH_3OCH_3 solutions at −130°. Moreover, results for **6** have shown that the OCH_3 group does not preferably take up the axial position of the chair form because of steric repulsion, but instead adopts the isoclinal position of TB so that this form is the only one for which NMR signals were detected in CHF_2Cl.[22] Why, then, does **1** not exist exclusively in the TB form instead of the 1:1 mixture observed in CHF_2Cl? It appears that the longer O–S bonds of the ring of **1** compared to the O–C bonds of **6** (i.e. ~1.58 Å and ~1.43 Å respectively)[34,35] minimize any destabilizing steric interaction involving the axial S=O bond. In fact, the S=O bond in pentamethylene sulfoxide slightly prefers the axial position.

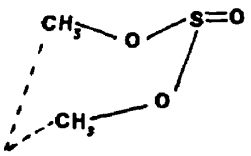
Solvent effect on the TB/C-a ratio. Solvent effects on conformational population usually follow a predictable pattern for systems governed by the anomeric effect[48] and the generalizations formulated in that context can be useful to understand the variation of the TB/C-a ratio of **1** for the solvents used. Thus, for 2-methoxytetrahydropyrans, the axial conformer is more predominant in non polar solvents than in polar ones. This observation has been rationalized by some workers as resulting from the reduction of stabilizing lone pair donation in the C-a form because of solvation of the *app* lone pairs[38] while others have invoked a perturbation of the dipolar interactions whereby, in the more polar solvents, dipolar destabilization is reduced so that the proportion of the more polar conformation (i.e. the equatorial form) increases.[49] Thus both rationals predict the same solvent induced conformational change for 2-substituted tetrahydropyrans. Although a more quantitative treatment of solvent effects should include quadrupole and higher order terms,[50] the simple approach combining both types of electronic interactions described above appears sufficient to explain qualitatively the trends observed for molecules such as **1** and **2**. Consequently an increase in solvent polarity is expected to lead to an increase in the proportion of the more polar TB form of **1** and **2** and therefore to an increase in the TB/C-a ratio as observed by NMR and IR. It is interesting to point out that for **4**, which contains no S=O bond, the solvent effect on the TB/C ratio is opposite[22] but still compatible with the above concepts applied to the –O–C–O– acetal moiety.

The above observations and the conclusions regarding the favorable orientations of the S=O bond for the sulfite moiety in the C-a and TB forms of **1** and **2** are useful to understand the conformational features of dimethyl sulfite as revealed from IR measurements published recently.[23] Two conformations, called I and II, were proposed for the simple molecule, that is one for each of the equally intense bands appearing at 1197 and 1219 cm^{-1} respectively in CCl_4. It was also observed that an increase in solvent polarity increases the proportion of conformer II relative to I.

Conformation II (characterized by the band at 1219 cm^{-1}) is very loosely defined by the authors[23] and is described as encompassing a large number of *gauche* or *anti* relationships while the illustration reported is identical to structure **20** for which both methyl groups are *anti* to the S=O bond but pushed apart slightly through small rotations to minimize steric repulsion. The dotted lines illustrate the fact that the sulfite disposition in **20** is very similar to that found in the C-e form and consequently should be relatively unfavorable because of unfavorable electronic interactions.

Conformation I (band at 1197 cm^{-1}) was defined as one containing both methyl groups *syn* to the S=O bond. Its description and illustration[23] do not permit a distinction to be made between arrangements with methyl and S=O groups eclipsed or gauche. Structure **21** illustrates a conformation in which both methyl groups are close to gauche and on the same side of the S=O bond. The sulfite disposition is similar to that existing in the C-a form except for slight rotations moving the methyl groups apart to minimize steric repulsiohn. The existence of significant stereoelectronic lone pair donation in this form is able to account for the IR frequency of 1197 cm^{-1} observed. However, the 120° rotation of one of the O–S bonds towards S=O produces another apparently acceptable form with both CH_3 groups *gauche* to S=O.

Because the solvent response of the TB/C-a conformational population ratio of **1** and **2** is quite similar to that of the II/I population ratio of dimethyl sulfite, we suggest a geometry for II which better reflects the conformational preference of the sulfite moiety as revealed from our results on **1** and **2**. This



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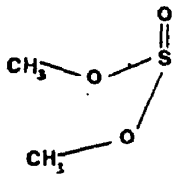

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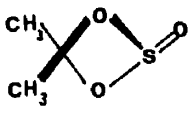

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new conformation is depicted by **22** which is seen to contain an arrangement of atoms similar to that found in the TB form of **1** or **2** for which one CH_3 is *anti* and the other is *gauche* to S=O. Thus the observed IR frequency[23] of 1219 cm^{-1} for II is compatible with **22** and with our understanding of the stereochemical and conformational dependance of the S=O stretching frequency described earlier. Finally, it is interesting to note that the disposition of the CH_3–O–S–O–CH_3 skeleton in **22** is identical to that found most stable for dimethoxymethane by electron diffraction.[51]

Comparison of **1** *and* **2**. Our objective here is to suggest plausible explanations for some of the major differences in the conformational and dynamic properties determined for compounds **1** and **2**.

Force field calculations on cycloheptene[32] have suggested that the energy difference between the C and TB conformations is relatively small and the value of 0.57 kcal/mole was reported. Experimentally only the C form has been detected but the free energy activation barrier of 5.0 kcal/mole determined by DNMR for the C inversion of cycloheptene-d_5[52] agrees very well with the value of 5.2 kcal/mole calculated for ΔH^* in the above work. Benzocycloheptene has also been shown experimentally to exist only in the chair form.[29,53]

A most important feature distinguishing benzocycloheptene from cycloheptene[32] (and other analogous pairs as well) is the nature of the torsional interactions at the allylic and benzylic bonds as illustrated for **1** and **2** in structures **23** and **24**. It is shown that **24** contains an H/H eclipsing of the type found in propene (1.98 kcal/mole rotational barrier) while **23** has a H/$C_{sp}2$ eclipsing of the type found in toluene (0.5 kcal/mole rotational barrier). The consequence of this difference on the dynamic properties as well as on the relative stabilities of the C and TB forms will be considered.

The 1,5-cyclooctadiene and dibenzo-1,5-cyclooctadiene pair provides a most interesting analogy[54] in which the dibenzo derivative also gives a larger proportion of the C form than does the corresponding diene and recent force field calculations[55] suggest that the replacement of a benzo group by a double bond stabilizes the TB form relative to C most probably because the higher torsional strain about the allylic bond is relieved in the TB form. This factor is thus able to account in large part for the greater relative proportion of the TB form for **2** than for **1**.

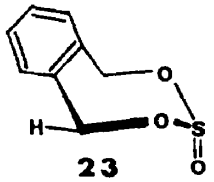
The dynamic features revealed by NMR spectral changes as function of temperature are determined both by the nature and number of stable conformations detected for a given molecule. It is now well known that the higher barrier for the C $\rightleftharpoons$ B step of the chair inversion of benzocycloheptene[32,33] relative to cycloheptene is a consequence of the difference in relief of H/H and H/$C_{sp}2$ eclipsing about the allylic and benzylic bonds as the unsaturated end of the molecule flips to reach the transition state. But as was pointed out earlier (Scheme 3), it is not evident that flipping of the benzo part of the C-a forms of **1** is the prefered molecular motion for this interconversion. Unfortunately, the absence of resolved C-a signals for **2** prevents the characterization of this process which would have permitted a comparison of **1** and **2** with the above parent compounds.

Because the TB inversion barrier has been calculated to be small for both cycloheptene and benzocycloheptene[32] the observed free energy barriers for the TB inversion of **1** and **2** merit comment. Furthermore, because attempts to measure them for model compounds such as **25** and **26** by ^1H NMR at 100 MHz failed at a temperature of about $-170°$, (**26** was also studied at 300 MHz down to about $-155°$), the suggested maxima for ΔG^* are about 5 kcal/mole for these model molecules.[56] Thus the TB inversion barriers for **1** (6.6 kcal/mole) and **2** ($\sim$5.3 kcal/mole) are higher than for the two model compounds and remarkably similar to the value of 6.7 kcal/mole determined[22] for **6**. This coincidence suggests a similar origin, perhaps of electronic nature. In fact, Anet and Yavari have shown that the generalized anomeric effect raises the rotation barrier of chloromethylmethyl ether relative to dimethyl ether.[57] It is therefore reasonable to assume that electronic effects in the sulfite bonds could raise the pseudorotation barrier of the TB form of **2** above the calculated value of 2.9 kcal/mole for cycloheptene.[32]

$$\underset{a_1^*}{TB^*} \rightleftharpoons \underset{a_1}{B\text{–}a\,(10)} \rightleftharpoons \underset{a_2}{TB\,(9)} \rightleftharpoons \underset{a_2^*}{B\text{–}e\,(11)} \rightleftharpoons TB^*$$

Scheme 2.

Two pathways are available for the TB inversion of **1** and **2** as illustrated in Scheme 2 where it is seen that the



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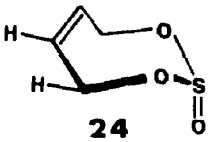

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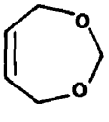

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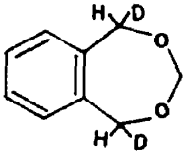

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TB form (9) can be transformed into its mirror image TB* (inverted form) by passing through either the B–a or B–e forms. The a_1 and a_2 forms have intermediate geometries with fine coplanar atoms.[3,2]

Because the ring O atoms have equivalent relationships in both B–a and B–e, the energy associated with their disposition relative to that in TB should contribute similarly to both pathways. On the other hand, stereoelectronic back-donation to S=O is expected to be more stabilizing in B–a while dipolar interactions of the whole sulfite function appear to be more strongly destabilizing[11a] in B–e so that TB inversion most likely should take place preferentially through the pathway involving B–a. The transformation of TB into B–a is accompanied by a *syn*-1,3 H/O=S interaction in a_1; therefore without precise and complete conformational calculations, it is impossible to describe the exact energy maximum as well as the relative contribution of all factors to the energy profile for the TB ⇄ B–a ⇄ TB* interconversion. However, the combined electronic effects describe above appear responsible in large part for the measurable free energy barriers for the TB pseudorotation of **1**, **2** and by extension of **6**.

EXPERIMENTAL

Microanalyses were carried out by: Le Service Central de Microanalyse, Division de Lyon, France.

Room temp analytical ^{1}H NMR spectra were recorded on a Varian T-60 spectrometer while ^{13}C NMR spectra were recorded on a Varian XL-100 spectrometer.

IR spectra were taken on a Perkin–Elmer Model 221 spectrometer using an expanded scale with a precision of 0.6 cm^{-1}. Concentrations of 0.05 M were used. The low temp 100 MHz ^{1}H NMR spectra were recorded on a JEOL JNM-4H-100 spectrometer while the 22,63 MHz ^{13}C NMR spectra were obtained with a Bruker WH-90 spectrometer under conditions previously described.[22]

The 300 MHz ^{1}H NMR and 75.4 ^{13}C NMR spectra were taken on a Bruker WH-300 spectrometer (located at Bellirica, New York, U.S.A.) operating in the standard FT mode. Cooling was done by boiling off liquid N_2 under control of the B-VT-1000 unit. Extreme care was taken to eliminate all leaks in the cooling system. The 250 MHz ^{1}H NMR spectra of **1** at −100° was taken on a Bruker WM-250 spectrometer located at Grenoble.

Preparation of **1** *and* **2**. Compounds **1** and **2** were prepared by the general reaction of alcohols or diols with thionyl chloride.[5,8]

Compound **1** was prepared by the reaction of phthalylalcohol (Aldrich, 1,2-benzenedimethanol) with thionyl chloride as previously described[11a]. The solid product (74%) obtained was purified by column chromatography using silica gel (Merck, 70–230 mesh).

^{1}H NMR in CCl_4: 7.1 ppm (4 H aromatic), 5.9 ppm (2 H) and 4.4 ppm (2 H); ^{13}C NMR in $CDCl_3$: 62.7 ppm (C-4,7) and 128.2 (C-5,6), as well as Tables 1 and 2 (Found: C, 52.24; H, 4.47; S, 17.14. Calc. for $C_8H_8O_3S$: C, 52.16; H, 4.38; S, 17.40%).

Compound **2** was prepared similarly by the reaction of 9.26 g of *cis* 2-butene-1,4-diol (Aldrich) and 11.9 g of thionyl chloride. The liquid product was purified by fractional distillation from which 11.5 g (68%) of **2** were obtained pure ^{1}H NMR in C_6D_6: 5.8 ppm (2 H, olefinic), 5.0 ppm (2 H) and 4.5 ppm (2 H); ^{13}C NMR in $CDCl_3$: 60.9 ppm (C-4,7) and 128.6 (C-5,6), as well as Tables 1 and 2 (Found: C, 35.99; H, 4.65; S, 23.23. Calc. for $C_4H_6O_3S$: C, 35.81; H, 4.51; S, 23.90).

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