BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 48 (9), 2496—2501 (1975) [Vol. 48, No. 9

Substituent Effect on the Anomeric Effect in 1,3,5-Trithiane Derivatives

Michinori Ōki, Toshiyuki Endo, and Tadashi Sugawara

Department of Chemistry, Faculty of Science, The University of Tokyo, Tokyo 113

(Received April 30, 1975)

Anomeric effect in a series of 2-alkylthio- and 2-arylthio-1,3,5-trithianes has been studied by PMR spectroscopy to investigate the substituent effect on the anomeric effect. A remarkable steric effect is found in 2-*t*-butylthio-1,3,5-trithiane: the equatorial conformer is slightly favored over the axial one. The electron-withdrawing substituent in 2-arylthio-1,3,5-trithiane enhanced the anomeric effect. The origin of the steric and electric-electronic effect has been discussed on the ground of conformational analysis.

Anomeric effect[1] has drawn attention of many investigators and, to date, various factors affecting the anomeric effect have been discussed. In contrast to the *A* values[2] of the methoxy (0.55) and the chloro (0.53) groups in cyclohexane series, the axial forms of the methoxy and the chloro groups in pyranose rings are favored over the equatorial form by 1.5[3] and 2.7 kcal/mol,[4] respectively. Pierson and Runquist have reported that the magnitude of the anomeric effect is linearly related with the Taft σ^* values of the substituents.[5] Thus the electric-electronic effect of the substituent is important in determining the extent of the anomeric effect. The enhanced axial preference of benzoates over the acetates of pyranosides may be taken as another example of this effect.[6]

In contrast to the large electric-electronic effect, the steric effect is considered to be of minor importance. The axial form of the 2-alkoxyoxanes is present to the extent of 0.77, 0.76, 0.75 and 0.70 in terms of molar fractions for methoxy, ethoxy, isopropoxy, and *t*-butoxy compounds, respectively.[7] The similar trend is also observed in alkyl tri-*O*-benzoyl-β-D-ribopyranosides.[8] The 2-alkylthiooxanes, where alkyl may be methyl, ethyl, isopropyl or *t*-butyl, give practically the same free energy difference for a given equatorial-axial pair irrespective of the size of the alkyl group.[9] Indeed, comparison of the electric-electronic effects for various substituents was possible by assuming little steric effect of the substituted alkyl part of various RO groups.[5]

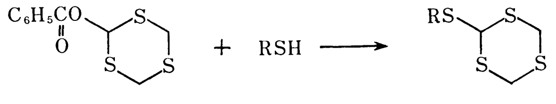
We have been interested in anomeric effect in 1,3,5-trithiane series for some time and have found that the phenylthio group exerts the stronger effect than the methylthio group: the enthalpy difference is found to be 1.3 kcal/mol in favor of the axial form for 2-phenylthio-1,3,5-trithiane in chloroform-*d*-carbon disulfide, whereas the difference is only 0.9 kcal/mol for 2-methylthio-1,3,5-trithiane.[10]

Trithiane represents a series different from those of cyclohexane and oxane. Since the bond length within the ring is one of the important factors in determining the 1,3-diaxial interaction and the steric effect exerted by the 1,3-diaxial interaction opposes the electric-electronic effect,[11] the longer C–S bond and a little flatter conformation of the trithiane ring should produce different extent of the substituent effect for a given substituent. It was felt that a systematic study would lend help in understanding the substituent effect on the anomeric effect in 1,3,5-trithianes. In addition, this kind of study may reveal the extent of the steric effect which has been neglected in the past studies.

This paper describes the results of a study on the electric-electronic effect in a series of 2-arylthio-1,3,5-trithianes and discusses the steric effect which is found in 2-*t*-butylthio-1,3,5-trithiane.

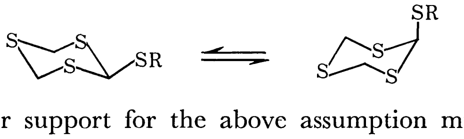
Results and Discussion

Steric Effects. It may be assumed that changing the alkyl group in 2-alkylthio-1,3,5-trithianes affects only the size of the substituent, to a good approximation, because ionization constants of alkanethiols are known to be relatively unaffected by the change of alkyl groups.[12] Thus 2-alkylthio-1,3,5-trithianes were synthesized by alkanethiolysis of 2-benzoyloxy-1,3,5-trithiane and their conformational equilibria were studied.



1: R=CH_3 **2**: R=C_2H_5
3: R=$(CH_3)_2CH$ **4**: R=$(CH_3)_3C$

PMR spectra of **1**, **2**, and **3** at room temperature show almost the same chemical shift differences, *ca.* 0.9 ppm, for the ring methylene protons (see Table 1 and Fig. 1), whereas that of **4** shows a smaller chemical shift difference. As these compounds exist as a mixture of ring-inversion isomers at room temperature, the observed chemical shift differences must be the averaged values of the individual isomers. Then almost the same chemical shift differences for compounds **1**—**3** mean that the population ratios of the equatorial and axial isomers are almost the same for these compounds, if the chemical shifts of each proton (δ_a and δ_e) are equal. The last assumption seems to be valid because the molecules are similar and the main moieties which affect the chemical shifts are equal.



Further support for the above assumption must be obtained by analyzing the population ratio in more detail. PMR spectra of these compounds at low temperatures gave two sets of signals due to ring protons and the methine proton at 2-position, respectively, as reported for the case of compound **1**.[10] These signals are assigned by taking the anisotropy effect of the C–S

TABLE 1. CHEMICAL SHIFT DIFFERENCES ($\Delta\delta$) BETWEEN TWO RING METHYLENE PROTONS OF 2-ALKYLTHIO-1,3,5-TRITHIANE AT VARIOUS TEMPERATURES AND EQUILIBRIUM CONTASNTS (K=a/e) IN $CDCl_3$-CS_2 (1: 1 v/v)

Compound							
	T °C	61	49	39	26	17.5	−83
1	$\Delta\delta$ ppm	0.84	0.86	0.88	0.92	0.94	a 1.56 e 0.46
	K	1.8	1.9	2.0	2.2	2.3	3.5[a]
	T °C	61	49	39	31	15	−83
2	$\Delta\delta$ ppm	0.84	0.88	0.90	0.92	0.97	a 1.55 e 0.47
	K	1.9	2.0	2.1	2.2	2.5	4.9[a]
	T °C	61	49		31	15	−83
3	$\Delta\delta$ ppm	0.80	0.84		0.89	0.98	a 1.56 e 0.47
	K	1.7	1.8		2.0	2.5	7.0[a]
	T °C	61	49	39		15	−83
4	$\Delta\delta$ ppm	0.26	0.25	0.24		0.23	a 1.55 e 0.54
	K	0.62	0.61	0.60		0.58	0.5[a]

a) Obtained by direct integration (±0.3).

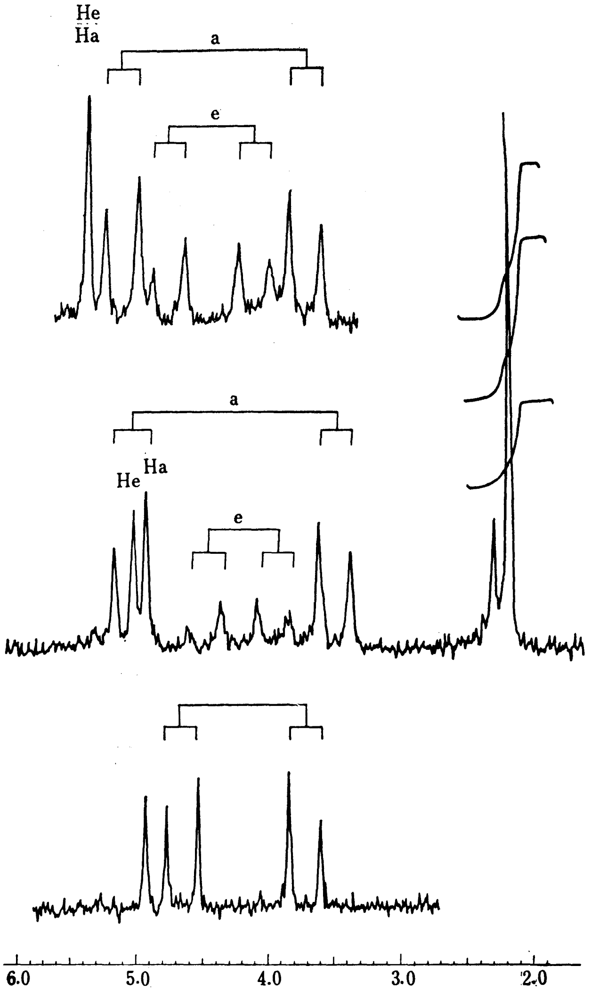


Fig. 1. PMR spectra of 2-methylthio-1,3,5-trithiane at 34 °C in $CDCl_3$-CS_2 (bottom), at −83 °C in $CDCl_3$-CS_2 (middle), and at −83 °C in $CDCl_3$-acetone-d_6 (1: 1 v/v) (top).

bond into consideration. If the C–S bond at 2-position is axially oriented, it should give the large deshielding effect to the axial protons at 4- and 6-positions. Thus the axial conformer will give a larger chemical shift difference between the equatorial and axial protons than that of 1,3,5-trithiane itself. On the other hand, the axial protons of the substituent-equatorial conformer suffer the small shielding effect from the C–S bond of the substituent to cause little change in the chemical shift difference of the AB protons from the corresponding ones in 1,3,5-trithiane.

Thus the AB protons showing the chemical shift difference of *ca.* 1.6 ppm can be assigned to the axial conformer and those with *ca.* 0.5 ppm difference to the equatorial conformer. This assignment is supported by a fact that the population of a conformer assigned to the equatorial form increases in the more polar media. Namely, the ratios of two conformers become *ca.* 1.1 in acetone-d_6 for compounds **1**—**3**, the conformer of larger chemical shift separation for the methylene being slightly favored. Compound **4** even failed to show any signals due to the conformer of larger separation of the methylene signals under the similar conditions. This solvent effect is accepted as the characteristics in anomeric equilibria and must be the result arising from the fact that the equatorial conformer is more polar than the axial.

Comparison of the peak intensities at −83 °C reveals that axial conformers are favored in the cases of **1** through **3**, whereas the equatorial conformer prevails in **4** (see Table 1). Using these chemical shifts, we may calculate the populations of the conformers at above the coalescence temperatures by the following equation.

$$\Delta\delta = N_a\Delta\delta_a + N_e\Delta\delta_e$$

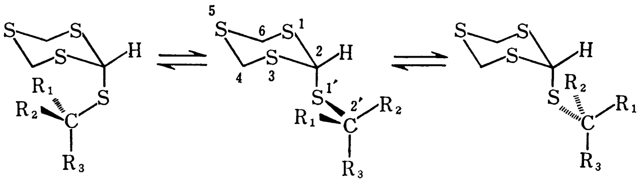
where N_a and N_e are the molar fractions of axial and equatorial conformers, respectively, and $\Delta\delta$, $\Delta\delta_a$, and $\Delta\delta_e$ are the observed chemical shift difference at above the coalescence temperature, that of the axial conformer, and that of the equatorial conformer, respectively. Then the study on temperature dependence of the equilibria affords thermodynamic parameters as shown in Table 2.

TABLE 2. THERMODYNAMIC PARAMETERS FOR THE EQUILIBRIUM (a$\rightleftharpoons$e) OF 2-ALKYLTHIO-1,3,5-TRITHIANE

Compound	ΔG kcal/mol (±0.05)	ΔH kcal/mol (±0.1)	ΔS e.u. (±0.2)
1	0.44	0.9	1.5
2	0.48	1.1	2.1
3	0.46	1.3	2.8
4	−0.33	−0.12	0.6

Inspection of the data in Table 2 indicates that, while the axial conformer of **1**—**3** is more stable than the equatorial conformer by about 0.5 kcal/mol, the equatorial conformer is slightly preferred over the axial in the case of **4**. This striking contrast must be caused by combination of steric and electric-electronic effect. Although the electric-electronic effect may arise as a result of preference or rejection of one or more conformers as a secondary effect, it may be considered to be almost the same for the series of compounds, to the first approximation, due to the fact that they are all 2-alkylthio-1,3,5-trithianes. Then the steric effect becomes the prime importance. We shall forcus the discussion on the steric effect and then extend to the electric-electronic effect later.

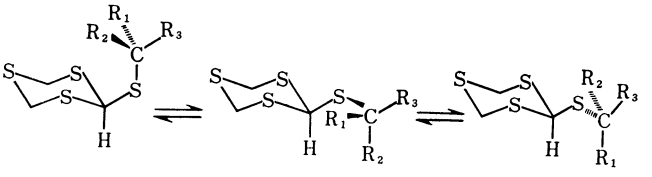
Among the axial conformers, three rotamers, a_1, a_2, and a_3, may be considered. The polarity of these compounds are equal.



a_1 a_2 a_3

From the steric grounds, however, a_1 will be eliminated because of the severe steric effect between the *S*-alkyl group and the ring. This effect will be operative irrespective to the size of the alkyl group. In conformations of a_2 and a_3, there are two diaxial interactions if the C_2–$S_{1'}$–$C_{2'}$ bonds are considered as a part of the chair ring: in a_2 conformation, C_2–S_3 and $C_{2'}$–R_1 bonds are in this relation and the relation between C_2–H and the $C_{2'}$–R_2 bonds is another case. Similarly the relation of C_2–S_1 and $C_{2'}$–R_2 bonds and that of C_2–H and $C_{2'}$–R_1 bonds are also diaxial in a_3. If the alkyl in alkylthio groups bears two hydrogens, the effect of these 1,3-diaxial interaction may be minimized by taking an appropriate conformation. Namely, the conformations a_2 and a_3 will be most stable when R_1 and R_2 are hydrogens in the case of **2**. When the alkyl group is an isopropyl, the increase in the 1,3-diaxial interaction is unavoidable. However, the severe interaction may be avoided by taking the a_2 conformation in which the C_2–H and $C_{2'}$–CH_3 bonds interact in 1,3-diaxial manner and C_2–S_3 and $C_{2'}$–H bonds interact similarly. A similar conformation is possible for a_3 also. Accordingly, it is possible for the isopropyl group in **3** to take a conformation in which repulsive force is not much higher than the corresponding methyl or ethyl compounds: in the latter two compounds also, the C–S/C–H interaction is unavoidable.

The situation of the *t*-butyl compound **4** is different from those of other alkylthio compounds. Since all the hydrogens of 2′-carbon are substituted by methyls, 1,3-diaxial interactions of the C–CH_3/C–S type become inevitable.* The axial conformation of **4** is thus drastically destabilized as compared with other cases.



e_1 e_2 e_3

Now comparison of the energy levels of equatorial conformers becomes necessary. From the stand point of the steric effect, there seem to be some differences in the stability of the three forms, e_1, e_2, and e_3. In e_1 conformation, there are two 1,3-diaxial interactions of the C–S/C–R type, whereas the 1,3-diaxial interactions are C–S/C–R and C–H/C–R types in e_2 and e_3. If the alkyl is either the methyl or the ethyl, the destabilization of the e_1 form due to 1,3-diaxial interaction may not become severe by taking an appropriate conformation. The e_1 form of **3** is destabilized because at least one C–S/C–C diaxial interaction is unavoidable, although this destabilization may be lessened by rotating the isopropyl group about the $S_{1'}$–C_2 bond. On the other hand, the e_1 conformation of **4** is definitely unstable due to the presence of two C–S/C–C diaxial interactions. e_2 and e_3 conformations of **1**, **2**, and **3** are neither specially stabilized nor destabilized on the steric ground, if they are compared with another conformation e_1, because they will have only C–S/C–H and C–H/C–H interactions in **1** and **2** or C–H/C–C and C–S/C–H interactions in **3** in favorable conformations. The e_2 and e_3 conformations of **4** involve C–S/C–C and C–H/C–C interactions which are less severe than the 1,3-interactions in the e_1 form.

On the electric grounds, e_1 form is most favored because the dipole formed by the substituent partly compensates that of the ring, whereas in the other forms (e_2 and e_3), the dipole made by the substituent is nearly parallel to that of the ring. At the same time, both lone pairs of electrons on the sulfur atom of the substituent are anti-parallel to the C–S bonds of the ring in e_1 conformation. This conformation is favorable for stabilization by the resonance effect.[11d]

Summarizing the steric effect and the electric-electronic effect of the equatorial forms, we may conclude that the e_1 form predominates in compounds **1**—**3**,** whereas e_2 and e_3 forms predominate in compound **4**. Then the discussion on the stability of axial and equatorial conformers is reduced to comparison of stabilities of a_2(a_3) and e_1 in the cases of **1**—**3**, whereas it is comparison of the stabilities of a_2(a_3) and e_2(e_3) in the case of **4**.

In the a_2 and a_3 conformations of **1** and **2**, the 1,3-diaxial interactions are C–H/C–S and C–H/C–H types, whereas those are two C–H/C–S types in e_1 conforma-

---

* The methyl axial-conformation is less stable than the methyl-equatorial conformation by 2.4 kcal/mol in the 1,3,5-trithiane system, as studied by equilibration of *cis* and *trans* forms of 2,4,6-trimethyl-1,3,5-trithiane. M. Fukunaga, Ph. D. thesis, The University of Tokyo, 1972.

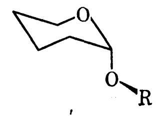
** This assumption is supported by a fact that the chemical shift of the axial 2-proton in these compounds is in a higher field than that of the equatorial. This phenomenon is contrary to the general consideration of the C–S bond anisotropy and has been attributed to the anisotropy effect of the C–S bond of the substituent in conformation e_1.[10] Similar situation occurs in 1,3-dioxane series also. The results of NOE experiment on *r*-2-methoxy-*t*-4,*t*-6-dimethyl-1,3-dioxane have been interpreted by assuming a conformation in which the methyl group in the methoxy lies nearly above the methine proton at 2-position, whereas the methoxy–methyl group of *r*-2-methoxy-*c*-4,*c*-6-dimethyl-1,3-dioxane seems to be away from the methine proton.[13]

tions of **1** and **2**. Thus a_2 and a_3 conformations of **1** and **2** are slightly favored over the e_1 form from the stand point of the steric effect in addition to the electric and electronic effects which are discussed frequently in explaining the anomeric effect. In the isopropyl compound **3**, a_2 and a_3 forms possess 1,3-interactions of C–H/C–S and C–H/C–C types, whereas e_1 has C–H/C–S and C–C/C–S types. Thus the steric effect favors the axial form in this compound. Combination of these steric, electric, and electronic factors seems to result the observed near coincidence of the difference in the stabilities of the equatorial and axial conformations.

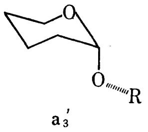
e_2 and e_3 forms of compound **4** are disfavored from the stand point of the electric and the electronic factors and they have the steric effect due to the presence of C–C/C–S and C–H/C–C interactions. On the other hand, a_2 and a_3 forms have the same 1,3-diaxial interactions of C–S/C–C and C–H/C–C types with the e_2 and e_3 forms, although they are favored from the electric and electronic effects. The observed result that the equatorial form is more stable than the axial by about 0.12 kcal/mol may indicate that the contribution of the electronic and electric effect is considered to amount about this magnitude.

The results presented above make the striking contrast to the anomeric effect in the oxane series in a sense that the bulkiness of the alkoxy group has little effect on the distribution of the anomers.[7–9] This contrast may be attributed to the presence of heteroatoms on both sides of the electronegative substituent for the following reasons.

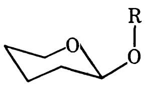
Since only one oxygen atom is present in the ring of oxane, the direction of dipole of the ring is not axial to the ring but is tilted. On electric grounds, this segregates two stable rotamers in oxane series, which are equivalent in trithianes. The energy levels of a_2' and a_3' of 2-alkoxyoxanes are different because two dipoles spearheaded by oxygens in a_3' are almost anti-parallel whereas those in a_2' have a definite value. Indeed, the calculated dipole moment and the observed are compared to draw a conclusion that the conformation of 2-alkoxyoxane can be taken as a_3' to the first approximation.[14]



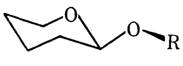
a_2'



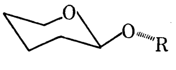
a_3'



e_1'



e_2'



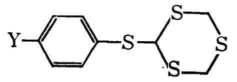
e_3'

Likewise, the conformation e_2' can be taken unstable. The equatorial form can be considered to be a mixture of e_1' and e_3' from the electric factor. Since the steric factor is unfavorable in e_1', however, the e_3' form will prevail in the equatorial conformations to the first approximation.

Quantum mechanical calculation has been carried out for the conformations of methanediol as a model for the anomeric center in the pyranose.[15] The results indicate that the axial conformer has a sharp minimum at a_3' form, whereas the equatorial has two equivalent minima corresponding to conformations e_2' and e_3' with somewhat lessened O_1–C_2–O_{sub}–C_{sub} dihedral angle of 35°. This calculation is consistent with the consideration of molecular dipoles presented above.

We may now compare the stabilities of a_3' and e_3' of 2-*t*-butoxyoxane. Since there are 1,3-diaxial interactions of C–H/C–C and C–O/C–C types in both forms, the steric factor is almost equal. This will make the electric-electronic factor important to cause the preference of the axial form. The preference of the axial forms to the similar degree in *t*-butoxyoxane, compared with other alkoxyoxanes, is not surprising, because the steric factors in axial a_3' and equatorial e_3' forms of these compounds can be similar also.

Electric and Electronic Effects. The electric and electronic factors may be varied, by the introduction of various arylthio groups, without significant alteration of the steric effect. Thus a series of 2-arylthio-1,3,5-trithianes have been prepared by arenethiolysis of 2-benzoyloxy-1,3,5-trithiane.



5: X=OCH_3 **6**: X=H
7: X=Cl **8**: X=NO_2

The equilibrium constants and thermodynamic parameters were obtained as described earlier and are tabulated in Tables 3 and 4.

The results indicate that the higher is the electronegativity of the *para*-substituent, the more the axial conformer is preferred. When the free energy differences between the axial and the equatorial conformers of each compound were divided into enthalpy and entropy terms (Table 4), it has become clear that the tendency in the conformational equilibria is the result of enthalpy

TABLE 3. CHEMICAL SHIFT DIFFERENCES ($\Delta\delta$) BETWEEN TWO RING METHYLENE PROTONS OF 2-ARYLTHIO-1,3,5-TRITHIANE AT VARIOUS TEMPERATURES AND EQUILIBRIUM CONSTANTS (K=a/e) in $CDCl_3$-CS_2 (1: 1 v/v)

Compound						
	T °C	63	49	33		−83
5	$\Delta\delta$ ppm	0.80	0.84	0.88		a 1.61 e 0.48
	K	1.6	1.7	1.9		5.0[a)]
	T °C	63	49	33	15	−83
6	$\Delta\delta$ ppm	0.84	0.88	0.92	0.99	a 1.60 e 0.49
	K	1.8	1.9	2.1	2.4	8.2[a)]
	T °C	63	49	29		−83
7	$\Delta\delta$ ppm	0.83	0.86	0.92		a 1.55 e 0.49
	K	1.8	1.9	2.2		8.2[a)]
	T °C	63	49	29		−83
8	$\Delta\delta$ ppm	0.84	0.88	0.94		a 1.46 e 0.52
	K	2.2	2.4	2.8		[b)]

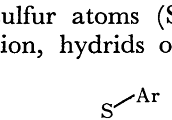
a) Obtained by direct integration (±0.3). b) Not measured because of the poor solubility.

TABLE 4. THERMODYNAMIC PARAMETERS FOR THE EQUILIBRIUM (a$\rightleftharpoons$e) OF 2-ARYLTHIO-1,3,5-TRITHIANE

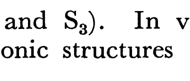
Compound	ΔG kcal/mol (± 0.05)	ΔH kcal/mol (± 0.1)	ΔS e.u. (± 0.2)
5	0.39	1.1	2.6
6	0.48	1.3	2.6
7	0.48	1.3	2.6
8	0.61	1.5	2.8

change rather than the entropy change. This result is the affirmation for the significance of the electric and electronic factors on the anomeric effect in this series.

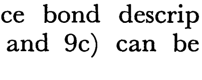
Interpretation of the observed tendency from the stand point of the dipole-dipole interaction involves some obscureness. Estimation of the contribution of the aryl group to the dipole moment of the whole molecule is rather complicated. Putting an electronegative aryl group instead of an alkyl in the substituent of the axial form will increase the component of the dipole which is anti-parallel to the component of the trithiane ring. Thus the axial conformations seem to be stabilized more in arylthio compounds with electronegative substituents. On the other hand, in e_1 conformation of arylthiotrithianes with electronegative substituents, the dipole moment of the molecule will increase to some extent, whereas those of e_2 and e_3 conformations will decrease. Thus populations of e_2 and e_3 forms increase. These factors make it difficult to estimate the electric factor quantitatively. Although the discussion given above tends to favor the axial forms to enhance the anomeric effect, separation of the electric effect from the electronic is not possible at present.



a_2

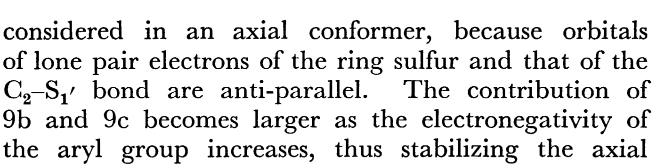


e_1



e_2

The observed results seem to be interpreted best by consideration of the resonance effect. As the electronegativity increases, the polarity of the C_2–S_1' increases to facilitate the donation of the lone pair electrons on sulfur atoms (S_1 and S_3). In valence bond descrip tion, hydrids of ionic structures (9b and 9c) can be



9a 9b 9c

considered in an axial conformer, because orbitals of lone pair electrons of the ring sulfur and that of the C_2–S_1' bond are anti-parallel. The contribution of 9b and 9c becomes larger as the electronegativity of the aryl group increases, thus stabilizing the axial form. The anomeric effect becomes stronger in these cases. pK_a values of arenethiols are in accord with the consideration: pK_a's of *para*-substituted benzenethiols, as measured in 20% water–ethanol at 20 °C are *p*-methoxy 7.06, hydrogen 6.81, and *p*-chloro 6.53.[16] pK_a of *p*-nitrobenzenethiol has been measured in methanol as 8.4 when that of benzenethiol was 10.9.[17]

Hoffmann and coworkers proposed MO interpretation of the anomeric effect.[11c] According to the theory, the interaction takes place between the low-lying antibonding orbital of a polar bond and p-type orbital of the hetero atom to lower the latter level. Consequently the total energy of the molecule is lowered. This type of interaction occurs to a greater extent if the antibonding orbital is lower and the substituent is axial. The high electronegativity corresponds to the low antibonding orbital and the axial substituent means the better overlap of the orbitals concerned. The results presented here, therefore, give an experimental support to the MO interpretation.

Experimental

PMR Measurement. The PMR spectra were recorded on a Hitachi R 20B spectrometer equipped with a temperature variation accessory. Temperature was read by the chemical shift difference of methyl and hydroxy protons of methanol at the low temperature and those of ethylene glycol at room temperature or above.

Solvents. As the polarity of solvents was found to have a critical influence upon the anomeric equilibria, the solvent for measurements was picked up from a stock mixture of solvents ($CDCl_3$–CS_2 1: 1 v/v) in order to unify experimental conditions.

2-Methylthio-1,3,5-trithiane (1), mp 94—95 °C, was prepared from 2-benzoyloxy-1,3,5-trithiane and methanethiol as reported previously.[10]

2-Ethylthio-1,3,5-trithiane (2). A solution of 2 g (9 mmol) of 2-benzoyloxy-1,3,5-trithiane and 2 g (32 mmol) of ethanethiol in 30 ml of chloroform was heated for 3 hr in a reaction vessel equipped with a dry ice condenser. Benzoic acid produced during the reaction was removed by passing the solution through a potassium carbonate layer and the solvent was evaporated to give crude products (95%). This was purified by chromatography on neutral alumina. Elution with hexane–benzene (1: 1) afforded the desired product, mp 47—48 °C. Found: C, 30.56; H, 5.36; S, 64.27%. Calcd for $C_5H_{10}S_4$: C, 30.27; H, 5.08; S, 64.65%. PMR ($CDCl_3$, δ): 1.30 (t, 3H), 2.66 (q, 2H), 3.67 and 4.68 (q, J=14 Hz, 4H), 5.00 (s, 1H).

2-Isopropylthio-1,3,5-trithiane (3), mp 52—53 °C, was prepared from 2-benzoyloxy-1,3,5-trithiane and 2-propanethiol as described above. The crude product was purified by chromatography. Found: C, 34.18; H, 5.96; S, 60.15%. Calcd for $C_6H_{12}S_4$: C, 33.93; H, 5.70; S, 60.38%. PMR ($CDCl_3$, δ): 1.41 (d, 6H), 3.05 (sep, 1H), 3.69 and 4.70 (q, J=14 Hz, 4H), 5.04 (s, 1H).

*2-*t*-Butylthio-1,3,5-trithiane (4),* mp 94—95 °C, was prepared from 2-benzoyloxy-1,3,5-trithiane and 2-methyl-2-propanethiol. The crude product was purified by chromatography. Found: C, 37.21; H, 6.19%. Calcd for $C_7H_{14}S_4$: C, 37.13; H, 6.23%. PMR ($CDCl_3$, δ): 1.44 (s, 9H), 4.16 and 4.34 (q, J=14 Hz, 4H), 5.07 (s, 1H).

*2-(*p*-Methoxyphenylthio)-1,3,5-trithiane (5),* mp 129—131 °C, was prepared from 2-benzoyloxy-1,3,5-trithiane and *p*-methoxybenzenethiol.[18] The crude product was purified by chromatography. Found: C, 43.65; H, 4.28; S, 45.94%.

Calcd for $C_{10}H_{12}OS_4$: C, 43.45; H, 4.38; S, 46.39%. PMR ($CDCl_3$, δ): 3.80 (s, 3H), 3.82 and 4.68 (q, J=14 Hz, 4H) 5.18 (s, 1H), 6.83 and 7.50 (q, J=8.4 Hz, 4H).

2-Phenylthio-1,3,5-trithiane (6), mp 123.0—123.5 °C, was prepared from 2-benzoyloxy-1,3,5-trithiane and benzenethiol as reported previously.[10]

*2-(*p*-Chlorophenylthio)-1,3,5-trithiane (7)*, mp 126—129 °C, was prepared from 2-benzoyloxy-1,3,5-trithiane and *p*-chlorobenzenethiol[18] and the desired product crystallized on standing. The product was purified by recrystallization from benzene. Found: C, 38.63; H, 3.15; Cl, 12.82; S, 45.44%. Calcd for $C_9H_9ClS_4$: C, 38.49; H, 2.23; Cl, 12.62; S, 45.66%. PMR ($CDCl_3$, δ): 3.83 and 4.72 (q, J=14 Hz, 4H), 5.31 (s, 1H), 7.33 and 7.45 (q, J=9 Hz, 4H).

*2-(*p*-Nitrophenylthio)-1,3,5-trithiane (8)*, mp 174—175 °C, was prepared from 2-benzoyloxy-1,3,5-trithiane and *p*-nitrobenzenethiol[19] and the desired product crystallized on standing. The product was purified by recrystallization from benzene. Found: C, 37.25; H, 3.01; N, 4.74; S, 44.05%. Calcd for $C_9H_9NO_2S_4$: C, 37.00; H, 3.11; N, 4.81; S, 44.01%. PMR ($CDCl_3$, δ): 3.82 and 4.66 (q, J=14 Hz, 4H), 5.50 (s, 1H), 7.55 and 8.16 (q, J=8.4 Hz, 4H).

References

1) R. U. Lemieux, R. K. Kulling, H. J. Bernstein, and W. G. Schneider, *J. Amer. Chem. Soc.*, **80**, 6098 (1958).

2) F. R. Jensen, C. H. Bushweller, and B. H. Beck, *ibid.*, **91**, 344 (1969).

3) C. B. Anderson and D. T. Sepp, *Tetrahedron*, **24**, 1707 (1968).

4) C. B. Anderson, *J. Org. Chem.*, **32**, 607 (1967).

5) G. O. Pierson and O. A. Runquist, *ibid.*, **33**, 2572 (1968).

6) P. L. Durette and D. Horton, *Adv. Carbohyd. Chem. Biochem.*, **26**, 49 (1971).

7) E. L. Eliel and C. A. Giza, *J. Org. Chem.*, **33**, 3754 (1968).

8) P. L. Durette and D. Horton, *Carbohyd. Res.*, **18**, 289 (1971).

9) A. J. de Hoog and E. Havinga, *Rec. Trav. Chim.*, **89**, 972 (1970).

10) M. Ōki, T. Sugawara, and H. Iwamura, This Bulletin, **47**, 2457 (1974).

11) a) J. T. Edward, *Chem. & Ind.* (London), **1955**, 1102: b) R. O. Hutchins, L. D. Kopp, and E. L. Eliel, *J. Amer. Chem. Soc.*, **80**, 7174 (1968): c) S. David, J. O. Eisenstein, W. J. Hehre, L. Salem, and R. Hoffmann, *ibid.*, **95**, 3806 (1973): d) L. Radom, W. J. Hehre, and J. A. Pople, *ibid.*, **94**, 2371 (1972).

12) H. L. Loy and D. M. Himmelblau, *J. Phys. Chem.*, **65**, 264 (1961).

13) E. L. Eliel and F. Nader, *J. Amer. Chem. Soc.*, **91**, 536 (1969).

14) R. U. Lemieux, A. A. Pavia, J. C. Martin, and K. A. Watanabe, *Can. J. Chem.*, **47**, 4427 (1969): R. U. Lemieux and S. Koto, *Tetrahedron*, **30**, 1933 (1974).

15) G. A. Jeffrey, J. A. Pople, and L. Radom, *Carbohyd. Res.*, **25**, 117 (1972).

16) G. Chuchani and A. Frohlich, *J. Chem. Soc., B*, **1971**, 1471.

17) B. W. Clare, D. Cook, E. C. F. Ko, Y. C. Mac, and A. J. Parker, *J. Amer. Chem. Soc.*, **88**, 1911 (1966).

18) D. S. Tarbell and D. F. Fukushima, "Organic Synthesis," Coll. Vol. 3, p. 809 (1955).

19) L. B. Sebrell and C. E. Boord, *J. Amer. Chem. Soc.*, **45**, 2401 (1923).