303. *Infrared and Raman Spectra of the Isomeric 1,4-Dithian 1,4-Dioxides.*

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The infrared and Raman spectra of the isomeric 1,4-dithian 1,4-dioxides are recorded, and discussed in relation to the conformations of these compounds.

For substituents, X, in a cyclohexane ring in the chair conformation, equatorial C–X bonds are associated with infrared stretching frequencies somewhat higher than those of the corresponding axial bonds.[1] This generalisation seems to be established for a number of substituents, and an interpretation of the effect has been suggested,[1,2] namely, that the normal vibration which is described approximately as a C–X stretching vibration involves also some motion of the ring-atoms. In the case of an axial bond the additional motion is related to a ring-bending deformation, whereas for an equatorial bond the more strongly resisted ring-stretching and compression is involved.

It is of interest to know whether this difference exists for bonds of other types. The gross stereochemical features of the S=O bond in sulphoxides are similar to those of the C–X bonds attached to saturated carbon, and hence the isomeric 1,4-dithian 1,4-dioxides should provide information in this connection. These compounds were first prepared by Bell and Bennett;[3] from their crystalline forms, the α-isomer was designated as having

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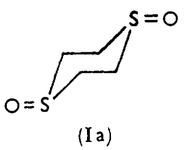
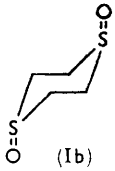
[1] Barton, Page, and Shoppee, *J.*, 1956, 331; Cole, Jones, and Dobriner, *J. Amer. Chem. Soc.*, 1952, **74**, 5571; Page, *J.*, 1955, 2017; Corey, Green, Danaher, Young, and Rutledge, *Chem. and Ind.*, 1954, 1294.

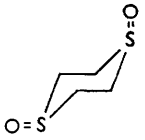
[2] de la Mare, Klyne, Millen, Pritchard, and Watson, *J.*, 1956, 1813.

[3] Bell and Bennett, *J.*, 1927, 1798.

the *trans*-, and the β- the *cis*-configuration. The assignment is now known to be correct through *X*-ray-crystallographic examination of the α-isomer,[4] which in the crystal adopts the diaxial (Ib) rather than the diequatorial (Ia) conformation. The β-isomer must therefore be represented as structure (II), on the assumption that chair rather than boat (or other non-chair) conformations will be adopted.


(Ia)


(Ib)


(Ic)

With these considerations in mind, the infrared and Raman spectra of the 1,4-dithian 1,4-dioxides have been examined.

EXPERIMENTAL

In the first instance the 1,4-dithian 1,4-dioxides were prepared from 1,4-dithian by oxidation with hydrogen peroxide in acetic acid, following Bell and Bennett's method.[3] The less soluble α-isomer crystallised from 90% ethanol as rhombs which decomposed at 265—270°. The more soluble β-isomer crystallised from ethanol as needles with an indefinite decomposition point, *ca.* 235—253°. Neither of these materials gave a satisfactory analysis for oxygen and sulphur. It was feared that they might contain a little 1,4-dithian 1,1,4-trioxide, since, from the least soluble fraction of a similar preparation, we obtained this material which, after recrystallisation from water, decomposed at 284—290° (beginning to darken at *ca.* 250°) (Found: C, 29·6; H, 4·9; O, 27·7; S, 37·6. Calc. for $C_4H_{18}S_2O_3$: C, 28·6; H, 4·8; O, 28·6; S, 38·0%). Consequently we prepared the dioxides by oxidation of 1,4-dithian with t-butyl hydroperoxide[5] in benzene. Dithian (2 g.) was dissolved in benzene (*ca.* 100 ml.) containing ether (10 ml.),

Infrared and Raman spectra of the isomeric 1,4-dithian 1,4-dioxides and of related compounds.

Frequencies in cm.$^{-1}$ (infrared range, 600—1500 cm.$^{-1}$; Raman range, 270—1400 cm.$^{-1}$); nj = Nujol.

α-1,4-Dithian 1,4-dioxide		β-1,4-Dithian 1,4-dioxide		1,4-Dithian 1,1,4-trioxide	Dithian
Infrared	Raman	Infrared	Raman	Infrared	Infrared
620w	290mw	599w	276vs	625m	660s
719w	438mw	627m	306vw	671w	725w
872m	600vs	662w	458mw	713m	892s
887m	633s	684w	566m	870m	903s
901m	818s	719w	606m	888s	942w
1010vs	912s	818w	641m	897sh	999w
1020vs	1022s	873w	682m	935w	1149s
1075w	1097mw	887sh	820mw	1005s	1163w
1114m	1125m	900m	913m	1012s	1271m
1127m	1168mw	927s	1014m	1029sh	1299w
1171w	1212m	1012vs	1067m	1116s	1379s, nj
1316w	1248m	1032vs	1127s	1143m	1408m
1377s, nj	1398s	1047s	1190m	1218w	1458s, nj
1397w		1086s	1238m	1272s	
1408w		1115m	1308vw	1304m	
1453s, nj		1125m	1353vw	1326m	
1464s, nj		1172w	1397m	1374s, nj	
		1205w		1395w	
		1300w		1408w	
		1374s, nj		1451s, nj	
		1401m		1460s, nj	
		1453s, nj			

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[4] Shearer, *J.*, 1959, 1394.

[5] Bateman and Hargrave, *Proc. Roy. Soc.*, 1954, *A*, **224**, 389, 399; Barnard, *J.*, 1956, 489.

and t-butyl hydroperoxide (L. Light & Co.; 65—72%) was added. The mixture was set aside for 2 months at room temperature. The solution was then decanted. Two types of crystal were apparent in the residues, rhombs and needles. A sample of the rhombs, sorted by hand, was recrystallised from 90% ethanol. The α-dioxide obtained in this way shrank and darkened at 260° but began to decompose sharply at 270° (Found: C, 31·8; H, 5·4; O, 21·3; S, 41·8. Calc. for $C_4H_8O_2S_2$; C, 31·6; H, 5·3; O, 21·0; S, 42·1%). Despite its much more satisfactory analysis, its infrared spectrum was very little different from that of the material obtained by Bell and Bennett's method.

The residues from the preparation of the α-dioxide were allowed to crystallise slowly from slightly aqueous ethanol, and successive fractions were removed. From the more soluble material there was obtained the β-dioxide which had m. p. 252—255° (decomp.; darkens 240°, sinters 248°) (from ethanol) (Found: C, 31·6; H, 5·4; O, 21·2; S, 42·0%). Its infrared spectrum was characteristically different from that of the α-dioxide and of the trioxide, but again was very similar to that of the apparently less pure material prepared by oxidation with hydrogen peroxide in acetic acid.

The results are given in the Table. The infrared spectra are for Nujol mulls of material prepared by oxidation with t-butyl hydroperoxide, and are in good accord with those determined on material prepared by Bell and Bennett's method. They were recorded by using a Grubb-Parsons G.S.2A grating spectrophotometer.

The Raman spectra, which were recorded some time ago, are of material prepared by Bell and Bennett's method; they refer to aqueous solutions, the spectra having been excited by the mercury line at 4358 Å, and were recorded on OaO plates by using an F/4 Hilger E5 spectrograph; frequencies were evaluated from microphotometer readings.

DISCUSSION

A detailed spectroscopic assignment of the frequencies recorded in the Table is not attempted, since their number is too large to allow definite decisions to be made about the origins of many of them. Some simplification of the problem is provided by molecular symmetry, but, even in the more favourable case of the *trans*-centrosymmetric isomer (I), of point-group C_{2h}, the number of vibrations belonging to the various symmetry classes is still large, *viz.*, 12 A_g, 10 A_u, 9 B_g, and 11 B_u.

Comparison of the spectra with those of cyclohexane [6] and dioxan [7] indicates that the lines falling in the regions 1125—1250 and 1300—1400 cm.$^{-1}$ are probably to be assigned to CH_2-wagging and -twisting vibrations, respectively. At somewhat lower frequencies, both the S=O bond-stretching and the ring-stretching frequencies are expected to fall in roughly the same region; these will be discussed further in connection with the molecular configuration. The frequencies which appear at about 600—700 cm.$^{-1}$ are probably to be associated with the ring-stretching motions involving mainly C–S bond-stretching; analogous frequencies are observed for dithian, and they seem, by comparison with cyclohexane and dioxan, to be too high to be ring-bending frequencies, and on the other hand they are lower than the ring-stretching frequencies for these molecules. The low frequencies in the Raman spectra are probably to be assigned as ring-bending frequencies. The Raman-active ring-bending frequencies found for dioxan [7] at 283 and 486 cm.$^{-1}$ are quite similar to the frequencies found for α-1,4-dithian 1,4-dioxide.

In principle, the mutual exclusion rule of infrared and Raman activity for centrosymmetric molecules should enable a distinction to be made between the *cis*- and the *trans*-isomer. In fact, the rule is not of much direct help, partly because there are often symmetric and antisymmetric vibrational modes of similar frequencies in molecules such as these, and partly because the infrared spectra refer to the solids and the Raman spectra to aqueous solutions. Nevertheless, because of the differences in the molecular symmetries of the two isomers, the two spectra have quite different characters, from which it is immediately evident that the α-isomer has the *trans*-configuration. Both the infrared

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[6] Beckett, Spitzer, and Pitzer, *J. Amer. Chem. Soc.*, 1947, **69**, 2488.

[7] Malherbe and Bernsten, *J. Amer. Chem. Soc.*, 1952, **74**, 4408.

and the Raman spectra of the β-isomers are much richer in lines than are the corresponding spectra of the α-isomer. This is the result to be expected if the α-isomer has the higher molecular symmetry and consequently the more restrictive selection rules. The differences between the Raman spectra are especially noticeable. The very rich spectrum of the β-isomer has no particular outstanding features, but the spectrum of the α-isomer has four prominent lines (600, 633, 912, and 1022 cm.$^{-1}$), each of which is both strong and sharp. This is another indication that the α-isomer has the higher molecular symmetry, for it is a well known characteristic of Raman spectra of molecules having symmetry that sharp lines are frequently associated with the totally symmetric vibrations.

The *X*-ray crystallographic finding[4] that the α-isomer has the biaxial structure (Ib) makes it possible to interpret the changes in S=O stretching frequency which occur in passing from the α- to the β-isomer. Sulphoxides are characterised in their infrared spectra[8,9] by a very strong absorption near 1050 cm.$^{-1}$ Examination of the Table shows, therefore, that for the α-isomer either of the two bands at 1010 or 1020 cm.$^{-1}$ might be associated with S=O bond-stretching. The appearance of two bands may be the result of a crystal-field effect, or one of the bands may be due to a ring-stretching vibration. Whatever the explanation of the presence of two bands is, there can be little doubt that the asymmetric S=O stretching frequency for the α-isomer falls not far from 1020 cm.$^{-1}$. This must be attributed to the biaxial structure (Ib), since this is the molecular structure in the crystal,[4] and the infrared spectrum, having been examined in Nujol mull, is also that of the crystal.

In the infrared spectrum of the β-isomer there are three strong lines in the region where S=O stretching-frequencies are to be expected. One of these, at 1012 cm.$^{-1}$, is close to the S=O stretching-frequency for the α-isomer; the other two are somewhat higher, *viz.*, at 1032 and 1047 cm.$^{-1}$. It is clear, from the spectra, that the configurational change that occurs in passing from the α- to the β-isomer is not accompanied by the appearance of any new strong band in the region immediately below 1012 cm.$^{-1}$. So, presumably, either the band at 1032 cm.$^{-1}$ or that at 1047 cm.$^{-1}$ represents the other expected S=O stretching-frequency. Since the α-isomer has the biaxial conformation, such an upward frequency shift is readily understood in terms of the generalisation,[1,2] mentioned earlier, that higher stretching frequencies are to be associated with equatorial rather than with axial groups. In passing from the *cis*-structure (II) of the β-form with one axial and one equatorial group to the α-isomer with the biaxial configuration (Ib), a frequency associated with the stretching of an equatorial bond is expected to disappear from the infrared spectrum.

Otting and Neugebauer[10] have recently reported the infrared spectra in potassium bromide discs of the isomeric 1,3-dioxides of 2,2-diphenyl-1,3-dithian, and of related compounds. The isomer of m. p. 189° had a single strong S=O stretching frequency at 1052 cm.$^{-1}$, agreeing in position with the similar single frequencies observed for 2,2-diphenyl-1,3-dithian 1-oxide (1059 cm.$^{-1}$) and 2,2-diphenyl-1,3-dithian 1,1,3-trioxide (1063 cm.$^{-1}$). To this isomer they assigned the *cis*-configuration (III), which in any individual molecule has only one type of S=O group, either equatorial or axial, provided that chair forms are adopted in preference to non-chair forms. The other isomer, m. p. 177°, had two strong absorption bands attributable to S=O stretching vibrations, at 1058 and 1085 cm.$^{-1}$. This isomer was assigned the *trans*-configuration (IV), since one S=O group must be equatorial and the other axial.

These authors seem to regard the frequency at *ca.* 1060 cm.$^{-1}$ as attributable to equatorial and that at *ca.* 1085 cm.$^{-1}$ to axial S=O. Our assignment would be the reverse, and therefore we would regard the 2,2-diphenyl-1,3-dithian 1,3-dioxide of m. p. 177° as having the biaxial conformation (IIIb) and would think that the S=O groups in the corresponding 1-oxide and 1,1,3-trioxide are probably axial also. It would clearly be of great interest if the crystal structures of these compounds were determined to check the validity

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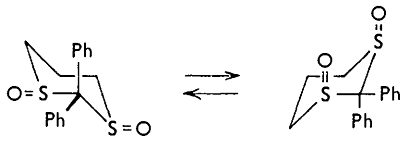
[8] Barnard, Fabian, and Koch, *J.*, 1949, 2442.

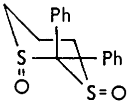
[9] Tamres and Searles, *J. Amer. Chem. Soc.*, 1959, **81**, 2100.

[10] Otting and Neugebauer, *Chem. Ber.*, 1962, **95**, 540.

and generality of our conclusions; the dipole moments of the isomeric dioxides are, as Otting and Neugebauer [10] noted, rather close, probably too close to be helpful.



(IIIa) (IIIb)



(IV)

It is interesting that the S=O stretching-frequencies in these 2,2-diphenyl 1,3-dioxides (1055 and 1085 cm.$^{-1}$) are displaced to frequencies appreciably higher than those observed in the 1,4-dioxides (1012, 1033, or 1047 cm.$^{-1}$). In the case of the 1,4-dioxide the molecular symmetry allows the larger sulphur atoms to be introduced into the ring while preserving tetrahedral angles, but for the 1,3-dioxide this is not so, and some strain in the ring arises. It seems likely that the increased rigidity of the ring modifies in the observed direction the stretching frequencies which involve some motion of the ring atoms.

The S=O stretching frequencies for 1,2-cyclic sulphites were found [2] to be at slightly higher frequencies than those for 1,3-cyclic sulphites, and this was ascribed to the coupling of these vibrations with the slightly more rigid 5-membered ring.* A difference of a similar magnitude is to be seen in the comparison of the infrared spectra of 2,2-diphenyl-1,3-dithiolan 1-oxide with 2,2-diphenyl-1,3-dithian 1-oxide, and of 2,2-diphenyl-1,3-dithiolan 1,1,3-trioxide with 2,2-diphenyl-1,3-dithian 1,1,3-trioxide.[10] For the dioxides, however, the differences are marginal, and the presence of what seem to be two S=O stretching frequencies in the spectra of both isomers of 2,2′-diphenyl-1,3-dithiolan 1,3-dioxide suggests that this ring is non-planar, so that the S=O groups can have more than one geometrical environment.

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* Recent work by Van Woerden (personal communication) suggests that equatorial and axial S=O bonds in cyclic sulphites have absorption bands at noticeably separated wavelengths, and that the value accepted for the S=O stretching frequency of 1,3-sulphites [2] is probably that of an axial S=O bond in this series.