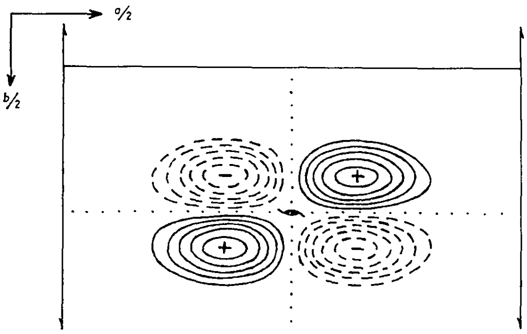

Fig. 2. Part of actual anti-symmetrical Fourier (zero contour, dotted) corresponding to the calcium displacements shown in the top left quarter of Fig. 1(*a*).

symmetrical component of a Fourier or Patterson map also may be advantageous in cases other than the one envisaged here, *e.g.* in structures showing pseudosymmetry of type (*b*) noted in the introduction.

5. Practical application

The use of the anti-symmetrical Patterson and Fourier functions has been very successful in the two-dimensional refinement of the structure of conichalcite, $CaCu(AsO_4)OH$ (Qurashi & Barnes, in the press). For this mineral, only a few, relatively weak, reflections, forbidden in *Pnma*, were observed, namely, eight $0kl$ for which $k+l=2n+1$, and nine $hk0$ for which $h=2n+1$. By ignoring these reflections, however, the principal features of the structure were first established in *Pnma* (Qurashi & Barnes, 1954). Small displacements of some of the metal and oxygen atoms from *Pnma* positions then were deduced from the ΔP syntheses and anti-symmetrical Fourier syntheses based on data for the forbidden reflections alone. Modification of the atomic coordinates by these shifts gave immediate improvement in R for all observed reflections in the three principal zones; for the most important zone, R was reduced from 0·22 to 0·12. Knowledge of these small shifts made successful refinement of the structure possible by standard methods in the true space group $P2_12_12_1$.

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Molecular Shapes of Thianthrene and Related Heterocyclic Compounds

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From data so far accumulated on three-membered heterocyclic compounds derived by replacing anthracene *meso* CH groups by atoms *A* and *B*, it is pointed out that molecules are planar if both *A* and *B* are any of C, N or O, but folded if at least one of *A* and *B* is S, Se or Te. This difference is explained by taking account of *d* orbitals in S and S-like atoms. The folding of the molecule is due to the 'natural' valency angle of a S atom, as was pointed out by Lynton & Cox in the case of thianthrene. The folding angle is not much affected in α and β thianthrene dioxide and thianthrene tetraoxide.

Introduction

Many kinds of three-membered heterocyclic compounds are derived if either or both of two anthracene *meso* CH groups are replaced by other kinds of atoms or atomic groups. Crystal structures of these compounds have been thoroughly or partly analysed by various authors, and enough data seem to have already been accumulated to allow us to discuss some essential characteristic features of atomic bondings in these compounds. Especially interesting is the fact that some molecules are planar whereas others are folded, and it is interesting to explain such features in terms of electron configuration.

The crystal structure of thianthrene was fully analysed by X-ray diffraction and its molecule was found to be folded on the S–S line, so that the two benzene rings lie in two planes at an angle of 128° (Lynton & Cox, 1956; Rowe & Post, 1958). The folded molecular structure was also reported for two isomers of thianthrene dioxide (Fig. 1, 2) (Hosoya & Wood, 1957; Hosoya, 1958*a*) and on thianthrene tetraoxide or diphenylene disulphone (Fig. 3) (Hosoya, 1958*b*). Di-

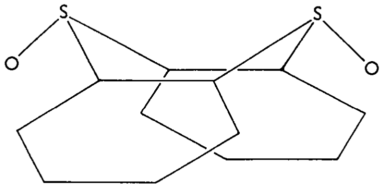

Fig. 1. α Thianthrene dioxide.

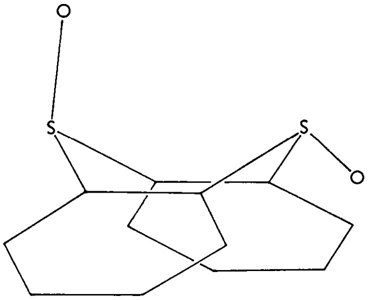

Fig. 2. β Thianthrene dioxide.

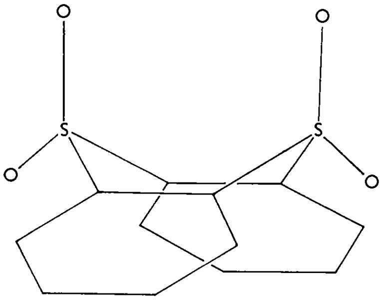

Fig. 3. Thianthrene tetraoxide (diphenylene disulphone).

hedral angles for these three compounds were determined as described in the next section.

Dihedral angles of three oxides of thianthrene

In the case of α and β thianthrene dioxide, one cycle of three-dimensional least-squares refinements with anisotropic temperature factors has been carried out by the author (Hosoya, 1958*c*), after the preliminary results were reported (Hosoya & Wood, 1957; Hosoya, 1958*a*). With the use of these data, the dihedral angle for each compound was calculated after determining the best fit planes for two benzene rings by the method of Blow (1960). It was also found, for comparison, that a less accurate but simpler method, where the secular equation does not come in (Hosoya & Satake, 1961), gave results which are not appreciably different from those by the method of Blow. For thianthrene tetraoxide, for which only one projection was refined, the dihedral angle was estimated from the shape of the two benzene rings, as already reported (Hosoya, 1958*b*).

The values of dihedral angles which have so far been determined are listed in Table 1. The values shown there may be subject to slight changes on further refinement of the structures, but such changes will not affect the following qualitative arguments. It is remarkable that the dihedral angle should be so uniform throughout this series, despite the considerable changes in the environment of the S atom and the increasing steric congestion brought about by the addition of the oxygen atoms. These results suggest that the bond arrangement effected by sulphur atoms is comparatively stable. This characteristic is worth looking at in some detail from a wider point of view.

Table 1. *Dihedral angles*

Thianthrene	128°
α Thianthrene dioxide	123
β Thianthrene dioxide	122
Thianthrene tetraoxide	127

Planar molecules and folded molecules

If anthracene *meso* CH groups are replaced by atoms *A* and *B* (which may or may not be accompanied by other atoms), many compounds may be derived corresponding to the various possible combinations of different *A* and *B*. Some of the compounds already studied, including anthracene itself, are found to be

Table 2(*a*). *Planar molecules*

	A	*B*	
Anthracene	C(H)*	C(H)	(Robertson, 1933; Mathieson, Robertson & Sinclair, 1950; Cruickshank, 1956)
Acridine	C(H)	N	(Phillips, 1956)
Phenazine	N	N	(Herbstein & Schmidt, 1955)
Phenoxazine	N(H)	O	(Cullinane & Rees, 1940)
Diphenylene dioxide	O	O	(Cullinane & Rees, 1940)

* Atoms in ( ) accompany atoms not in ( ).

Table 2(*b*). *Folded molecules*

	A	*B*	
Phenothiazine	N(H)	S	(Cullinane & Rees, 1940)
Phenoxthionine	O	S	(Wood, McCale & Williams, 1941; Hosoya, 1958*c*)
Phenoxselenine	O	Se	(Wood, McCale & Williams, 1941; Thomas, 1956)
Phenoxtellurine	O	Te	(Wood, McCale & Williams, 1941; Thomas, 1956)
Thianthrene	S	S	(Lynton & Cox, 1956; Rowe & Post, 1958)
Selenanthrene	Se	Se	(Wood & Crackston, 1941)
α Thianthrene dioxide	S(O)	S(O)	(Hosoya & Wood, 1957)
β Thianthrene dioxide	S(O)	S(O)	(Hosoya, 1958*a*)
Thianthrene tetraoxide	S(O_2)	S(O_2)	(Hosoya, 1958*b*)

planar, as shown in Table 2(*a*), and others folded, as shown in Table 2(*b*).

From these data it may be concluded that the compounds are planar if the *A* and *B* atoms are any of C, N or O, and are folded if either or both of the atoms *A* and *B* are S, Se and Te. This difference seems to arise from the fact that *d* orbitals are used in the bonding of S or S-like atoms, but not in C, N or O. The shape of the folded molecules is understood by relating it to the fact that a bond angle X–S–X is substantially smaller than the angle X–O–X as discussed in the next section.

Bond angles

The fact that the angle X–O–X is larger than the angle X–S–X is borne out in all the published results for numerous compounds except for the case $X = \mathrm{S}$, as reviewed in papers by Allen & Sutton (1950) and by Abrahams (1956). Typical examples are shown in Table 3, together with the results on phenoxthionine (Hosoya, 1958*c*), where the C–O–C angle and C–S–C angle seem to be affected by the coexistence of O and S in the same middle ring.

Table 3

	X–O–X		X–S–X
H_2O	104·75°	H_2S	92·33°
Furan	107°	Thiophene	91°
1,4-Dioxane	108–112°	1,4-Dithian	99°
		Thianthrene	100°
		α Thianthrene dioxide	96–97°
		β Thianthrene dioxide	96–98°
Phenoxthionine	118–120°	Phenoxthionine	92–94°

The difference between the angles X–O–X and X–S–X as above seems to indicate essentially the participation of *d* orbitals in the bonding of S. Both oxygen and sulphur belong to group VI, and their ground states have the same outer configuration of electrons $(ns)^2(np)^4$, where $n = 2$ for O and $n = 3$ for S. The valence orbitals in atoms of the second period such as C, N and O, however, are limited to 2*s* and 2*p* or hybrids of these two. Sulphur, on the other hand, can be converted to the excited configuration $(3s)^2(3p)^3(3d)$.

A support for the above view was provided by Ohno, Mizuno & Mizushima (1958), who found that the admixture of the 3*d* orbitals is helpful in explaining the hyperfine structure of the spectroscopic data on H_2S.

In the discussion by Lynton & Cox of the folding of thianthrene, the participation of the 3*d* orbitals was assumed in the bonding. The same situation may safely be assumed, though the three oxides of thianthrene described here are much more complicated than thianthrene itself, because, according to the theoretical study by Moffitt (1950), the 3*d* orbitals play an important role in the formation of the S=O bond and the double-bond character may be more or less present in these oxides.

In conclusion, the variation of the X–S–X angle found for so many structures is in the range 93 to 100°, whereas the X–S–O angles lie in the range 102 to 108°. The combination of these two kinds of bond angles results in a folded molecule with stability enough to withstand the perturbing effects of the steric strains which may be present in the oxides.

There does not seem to be much information on the hybridization which occurs in these oxides. However, it appears most unlikely, despite the apparent constancy of the configuration, that the hybridization is the same throughout. It is possible that a spectroscopic study of them might afford valuable new information now that the structures are known.

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