92. *Molecular Polarisability. The Apparent Conformations of Thianthren and of Three of its Oxides as Solutes in Benzene.*

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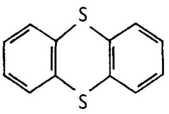
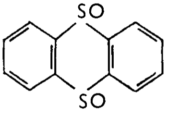
Dipole moments and molar Kerr constants are recorded for thianthren (1·41 D and -182×10^{-12}), α-thianthren dioxide (1·70 D and -195×10^{-12}), β-thianthren dioxide (4·88 D and -1640×10^{-12}), and thianthren tetroxide (5·11 D and -2810×10^{-12}), as solutes in benzene at 25°. The data are interpreted in terms of "equivalent" conformations for these flexible molecules; the apparent angle of fold about the S–S line is, in each case, greater than that reported on the basis of *X*-ray analysis for the solid-state configuration.

IT has been shown that thianthren (I),[1,2] its two dioxides (II),[3,4] and its tetroxide (III) [5] all have folded structures in the crystal state, the folding being about a line passing through the sulphur atoms. Hosoya [6] reviewed this work and listed the following dihedral angles: thianthren, 128°; α-thianthren dioxide, 123°; β-thianthren dioxide, 122°; thianthren tetroxide, 127°. In the present Paper we interpret the apparent polarities and electric birefringences of these compounds, examined in benzene solutions at 25°, in terms of their average conformations in this state.



(I)



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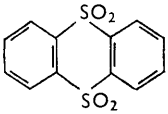

(III)

EXPERIMENTAL

Materials, Apparatus, etc.—Thianthren had m. p. 158° (from benzene). α-Thianthren dioxide [7] had m. p. 285° (from glacial acetic acid) (Found: C, 57·9; H, 3·3. Calc. for $C_{12}H_8O_2S_2$: C, 58·0; H, 3·2%). β-Thianthren dioxide [8] had m. p. 252° (Found: C, 57·9; H, 3·4%). Thianthren tetroxide [9] had m. p. *ca.* 325° (Found: C, 51·7; H, 3·0. Calc. for $C_{12}H_8O_4S_2$: C, 51·4; H, 2·9%).

Apparatus, techniques, symbols, and methods of calculation have been described before.[10,11] The quantities $\Delta\varepsilon$, Δd, Δn, and ΔB are the differences found between the dielectric constants, densities, refractive indexes, and Kerr constants, respectively, of benzene as solvent and of solutions containing weight fractions w_2 of solute. The following data apply at 25° to benzene: $\varepsilon_1 = 2{\cdot}2725$; $d_1 = 0{\cdot}87378$; $(n_1)_D = 1{\cdot}4973$; $10^7B_1 = 0{\cdot}410$; $10^{12}{}_sK_1 = 0{\cdot}0756$. Observations and results are summarised in Tables 1 and 2.

Previous Measurements.—The M.I.T. Tables [12] list five determinations of the dipole moment of thianthren ranging from 1·41 to 1·7 D. The value 1·41 D, which agrees with the present work, was obtained [13] in benzene at both 25° and 50° using thianthren which had been

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[1] Lynton and Cox, *J.*, 1956, 4886.

[2] Rowe and Post, *Acta Cryst.*, 1958, **11**, 372.

[3] Hosoya and Wood, *Chem. and Ind.*, 1957, 1042.

[4] Hosoya, *Chem. and Ind.*, 1958, 159.

[5] Hosoya, *Chem. and Ind.*, 1958, 980.

[6] Hosoya, *Acta Cryst.*, 1963, **16**, 310.

[7] Fries and Vogt, *Ber.*, 1911, **44**, 756.

[8] Krafft and Lyons, *Ber.*, 1896, **29**, 435.

[9] Cohen and Skirrow, *J.*, 1899, 889.

[10] Le Fèvre, "Dipole Moments," Methuen, London, 3rd edn., 1953.

[11] Le Fèvre and Le Fèvre, (*a*) *Rev. Pure Appl. Chem.* (*Australia*), 1955, **5**, 261; (*b*) ch. XXXVI in "Physical Methods of Organic Chemistry," ed. Weissberger, Interscience, New York, London, 3rd edn., Vol. 1, p. 2459.

[12] Wesson, "Tables of Electric Dipole Moments," Technology Press, M.I.T., 1948.

[13] Walls and Smyth, *J. Chem. Phys.*, 1933, **1**, 337.

TABLE 1.

Incremental Kerr effects, refractive indexes, dielectric constants, and densities of solutions in benzene at 25°.

Thianthren

$10^5 w_2$	980·2	1023	2032	2192	3456	3508
$-10^7 \Delta B$	0·049	0·050	0·094	0·099	0·155	0·149

whence $\Sigma 10^7 \Delta B / \Sigma w_2 = -4{\cdot}52$.

$10^5 w_2$	451·9	777·7	875·6	980·2	1004	1334	1528	2032	3022	3456	4045
$10^4 \Delta n$	—	11	—	14	—	20	24	30	44	50	60
ε^{25}	2·2789	2·2844	2·2859	—	2·2877	2·2924	2·2953	—	—	—	—
d_4^{25}	0·87521	0·87615	—	—	—	0·87776	0·87829	—	0·88265	—	0·88577

whence $\Sigma \Delta n / \Sigma w_2 = 0{\cdot}147$; $\Sigma \Delta \varepsilon / \Sigma w_2 = 1{\cdot}50$; $\Sigma \Delta d / \Sigma w_2 = 0{\cdot}297$.

α-Thianthren dioxide

$10^6 w_2$	2400	4378	4468	4856	5381	5657	5805
$-10^7 \Delta B$	—	0·018	0·019	—	0·021	0·022	0·026
$10^4 \Delta n$	—	6	6	—	—	8	8
ε^{25}	2·2773	2·2804	2·2807	2·2799	2·2821	2·2823	2·2822
d_4^{25}	0·87461	—	0·87531	0·87557	0·87569	0·87589	0·87573

whence $\Sigma 10^7 \Delta B / \Sigma w_2 = -4{\cdot}13$; $\Sigma \Delta n / \Sigma w_2 = 0{\cdot}138$; $\Sigma \Delta \varepsilon / \Sigma w_2 = 1{\cdot}74$; $\Sigma \Delta d / \Sigma w_2 = 0{\cdot}354$.

β-Thianthren dioxide

$10^6 w_2$	599	1157	1355	1424	1474	1552	1782	2205	2437	2629
$-10^7 \Delta B$	—	0·042	—	0·043	—	—	0·059	—	0·082	0·094
$10^4 \Delta n$	—	—	—	—	1	—	2	3	4	4
ε^{25}	2·2793	—	2·2874	—	2·2883	2·2888	2·2927	2·2965	—	—
d_4^{25}	0·87400	0·87417	0·87424	—	0·87430	—	0·87439	0·87458	—	0·87472

whence $\Sigma 10^7 \Delta B / \Sigma w_2 = -33{\cdot}9$; $\Sigma \Delta n / \Sigma w_2 = 0{\cdot}133$; $\Sigma \Delta \varepsilon / \Sigma w_2 = 10{\cdot}9$; $\Sigma \Delta d / \Sigma w_2 = 0{\cdot}352$.

Thianthren tetroxide

$10^6 w_2$	356	536	961	1081	1494	1804
$-10^7 \Delta B$	0·021	—	0·052	0·061	0·072	0·093
$10^4 \Delta n$	—	—	1	1	—	2
ε^{25}	2·2761	2·2772	2·2827	2·2836	—	2·2928
d_4^{25}	0·87392	0·87402	0·87418	0·87421	0·87437	0·87451

whence $\Sigma 10^7 \Delta B / \Sigma w_2 = -52{\cdot}5$; $\Sigma \Delta n / \Sigma w_2 = 0{\cdot}104$; $\Sigma \Delta \varepsilon / \Sigma w_2 = 10{\cdot}5$; $\Sigma \Delta d / \Sigma w_2 = 0{\cdot}406$.

TABLE 2.

Polarisations, dipole moments, and molar Kerr constants (from observations in benzene at 25°).

Solute	$\alpha\varepsilon_1$	β	γ	δ	${}_{\infty}P_2$ (c.c.)	R_D (c.c.)	μ (D) *	$10^{12}{}_{\infty}({}_{m}K_2)$
Thianthren ...	1·50	0·340	0·098	−11·0	109·7	66·0	1·41	−182
α-Dioxide ...	1·74	0·405	0·092	−10·1	131·6	69·1	1·70	−195
β-Dioxide ...	10·9	0·403	0·089	−82·7	559·6	68·6	4·88	−1640
Tetroxide ...	10·5	0·465	0·069	−128·0	604·7	66·9	5·11	−2810

* Calculated on the assumption that ${}_{D}P = 1{\cdot}05\, R_D$.

fractionally crystallised nine times. Other relevant measurements included in these tables are: μ (α-thianthren dioxide) = 1·7 D and μ (β-thianthren dioxide) = 4·2 D, both of which were determined in benzene solution at 19°.[14] The lower melting point of the β-isomer (246°) [14] than that found for our product, may explain the discrepancy in the moments. There appear to be no previous estimates of the dipole moment of thianthren tetroxide.

DISCUSSION

The folded configuration of thianthren was first suggested [14] to account for the dipole moment observed in solution. Later workers [15,16] tried unsuccessfully to resolve various thianthren derivatives into optically isomeric forms. Keats [16] concluded that, in solution,

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[14] Bergmann and Tschudnovsky, *Ber.*, 1932, **65**, *B*, 457.

[15] Bennett, Lesslie, and Turner, *J.*, 1937, 444.

[16] Keats, *J.*, 1937, 1592.

the thianthren molecule is not rigid but oscillates rapidly through a mean planar position. More recently, the dielectric relaxation time of thianthren in benzene solution at 25° [(2·30 ± 0·15) × 10^{-11} sec.] has been explained in terms of " enantiomorphic-inverse collapse " of the molecule.[17] Chandra [18] deduced, from an LCAO–MO study of thianthren, that the molecule is folded about the S–S axis and that the energy barrier for inversion through the planar form is relatively low (6—7 kcal./mole). Thus, available evidence indicates that the thianthren molecule is not rigid in solution but is capable of " flapping " about the line joining the sulphur atoms. It seems reasonable to expect that the oxides of thiantren are also non-rigid. This appears to be borne out by the fact that the second *cis*-dioxide described by Taylor [19] has not been isolated despite the stability of the tetroxide. Clearly, both *cis*-arrangements (cf. ref. 19) would be only two of the conformations contributing to an oscillating system. Hence, the following discussion relates to the " average conformations " of these molecules in the experimental medium.

Dipole Moments.—Theoretical dipole moments for conformations defined by angles of fold ϕ (see Fig. 1) have been calculated for thianthren and its oxides by vector addition of bond and group components. The following parameters have been used: $\mu(\mathrm{Ph_2S}) = 1{\cdot}50 \pm 0{\cdot}20$ (ref. 20); $\mu(\mathrm{Ph_2SO_2}) = 4{\cdot}97 \pm 0{\cdot}60$ (ref. 21); μ(S–O) for sulphoxides = 3·2 ± 0·3 (refs. 21 and 22); $\angle \mathrm{X_1SX_2} = \angle \mathrm{X_3SX_4} = 123 \pm 8°$ (ref. 23). In Fig. 2, for the α-dioxide $\mathrm{X_1 = X_4 = O}$ and $\mathrm{X_2 = X_3}$ = lone-pair, for the β-dioxide $\mathrm{X_1 = X_3 = O}$ and $\mathrm{X_2 = X_4}$ = lone-pair. The relatively large errors have been allowed to take into account the effects of possible changes in bond angles and bond orders in the application of these data to the thianthren series. The calculations are summarised in Table 3. The predicted moment of β-thianthren dioxide acts in the XZ-plane at an angle α° to the Z-axis; for each of the other compounds the resultant moment is located along the Z-direction. The angle CSC is calculable from ϕ using the relationship $\sin(\angle \mathrm{CSC}/2) = \sin(\phi/2) \cos 30$. Comparison of the calculated values with the observed moments of Table 2 leads to the following average angles of fold (∠CSC in parentheses): thianthren, 144 ± 8 (111 ± 4); α-dioxide, 139 ± 10 (108 ± 5); β-dioxide, 130 ± 10 (103 ± 6); tetroxide, 140 ± 8 (109 ± 4).

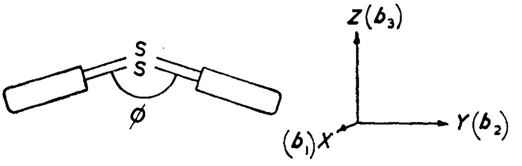

FIG. 1.

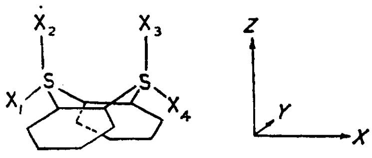

FIG. 2.

TABLE 3.

Calculated values of the resultant dipole moments.

ϕ	∠CSC	μ(thianthren)	μ(α-dioxide)	μ(β-dioxide)	α	μ(tetroxide)
180°	120°	0	5·6 ± 0·8	0	—	0
150	114	1·23 ± 0·2	2·7 ± 0·9	3·4 ± 0·4	43 ± 6°	4·1 ± 0·5
140	109	1·53 ± 0·2	1·8 ± 0·9	4·2 ± 0·5	43 ± 6	5·1 ± 0·6
130	103	1·77 ± 0·2	1·0 ± 0·9	4·9 ± 0·6	43 ± 6	5·9 ± 0·7
120	97	1·96 ± 0·2	0·3 ± 0·9	5·4 ± 0·7	43 ± 6	6·5 ± 0·8
90	75	2·32 ± 0·3	1·1 ± 0·9	6·4 ± 0·8	43 ± 6	7·7 ±0 ·9

Molar Kerr Constants.—Le Fèvre and Le Fèvre [11a] reported the molar Kerr constant of thianthren, measured in carbon tetrachloride solution at 20°, as —194 × 10^{-12}, from which they inferred that, though the molecule is non-planar, the degree of folding cannot

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[17] Fischer, *Commun. Fac. Sci. Univ. Ankara*, 1957, **9**, 43.
[18] Chandra, *Tetrahedron*, 1963, **19**, 471.
[19] Taylor, *J.*, 1935, 625.
[20] Aroney, Le Fèvre, and Saxby, *J.*, 1963, 1167.
[21] Aroney, Fisher, and Le Fèvre, *J.*, 1963, 4450.
[22] Cumper and Walker, *Trans. Faraday Soc.*, 1956, **52**, 193.
[23] Cumper and Vogel, *J.*, 1959, 3521.

be considerable otherwise the Kerr constant would be positive. The extent to which inter-ring conjugation occurs in this molecule is not known, so the usual calculations (ref. 11*b*, p. 2486) involving C–S bond and C_6H_4 group polarisability data derived from dimethyl sulphide [20] and benzene,[24] respectively, cannot be accurately applied. Hence, an alternative approach is used initially to specify the polarisability ellipsoid semi-axes of the group $C_6H_4S_2$ in thianthren and from such values the theoretical molar Kerr constants are calculated for various angles of fold. Wood and Crackston [25] measured the principal refractive indexes ($n_{\alpha,\beta,\gamma}$) of crystalline thianthren (see also ref. 1), from which can be estimated the corresponding molar refractions (eqn. 1) and thence molecular polarisabilities (eqn. 2) using $d = 1{\cdot}44$ g./c.c. (ref. 1) and $M = 216{\cdot}3$.

$$R = (n^2 - 1)M/(n^2 + 2)d \tag{1}$$

$$_{\mathrm{E}}P = 0{\cdot}95R = 4\pi Nb/3 \tag{2}$$

	α	β	γ		α	β	γ		α	β	γ
n ...	1·646	1·759	1·950	$_{\mathrm{E}}P$ ...	51·79	58·66	68·92	b	2·053	2·325	2·732

From the location of the molecules in the unit cell [1,25] we have, to a good approximation,

$$b_\alpha = b_1 \cos^2 59 + b_3 \cos^2 31 \tag{3}$$

$$b_\beta = b_1 \cos^2 31 + b_3 \cos^2 59 \tag{4}$$

$$b_\gamma = b_2, \tag{5}$$

where b_1, b_2, and b_3 are the principal polarisabilities of the thianthren molecule (see Fig. 1). It follows that $b_1 = 2{\cdot}479$; $b_2 = 2{\cdot}732$; $b_3 = 1{\cdot}899$.* Lynton and Cox [1] and Rowe and Post [2] found that for the crystal state the angle of fold (ϕ) is 128°; hence, b_{L}, b_{T}, and b_{V} for the $C_6H_4S_2$ group (see Fig. 3) are calculable from equations (6)—(8) as 1·496, 1·240, and 0·819, respectively.

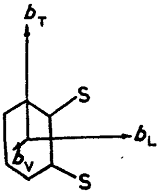

FIG. 3.

$$b_1 = 2b_{\mathrm{T}} \tag{6}$$

$$b_2 = 2(b_{\mathrm{L}} \cos^2 26 + b_{\mathrm{V}} \cos^2 64) \tag{7}$$

$$b_3 = 2(b_{\mathrm{L}} \cos^2 64 + b_{\mathrm{V}} \cos^2 26) \tag{8}$$

From these group polarisabilities can be predicted b_1, b_2, and b_3 for any conformation of thianthren defined by a particular value of ϕ, and, by use of the calculated moments of Table 3, the corresponding molar Kerr constant can be found. Comparison of the theoretical values in Table 4 with the experimental molar Kerr constant in benzene (-182×10^{-12}) indicates that the angle of fold is *ca.* 140°. The possible error in ϕ, though difficult to predict, can reasonably be taken as ±10°.

TABLE 4.

Calculated molar Kerr constants of thianthren.

ϕ	b_1	b_2	b_3	$10^{12}{}_{\mathrm{m}}K$	ϕ	b_1	b_2	b_3	$10^{12}{}_{\mathrm{m}}K$
180°	2·480	2·992	1·638	+70·1	130°	2·480	2·750	1·880	−225
150	2·480	2·901	1·729	−108	120	2·480	2·654	1·977	−232
140	2·480	2·834	1·796	−181	90	2·480	2·315	2·315	+50·4

Crystal data similar to those used for thianthren are not available for the three oxides examined. However, for thianthren tetroxide and α-thianthren dioxide, where the molecular symmetry is such that the locations of b_1, b_2, b_3, and μ(resultant) are known, an approximate calculation is possible. It has been shown [21,26] that for the series sulphide, sulphoxide, and sulphone, Σb(S–O) is approximately equal to Σb(lone-pair) so it seems reasonable to assume that the formation of S–O bonds (symmetrically) from thianthren will not seriously change the polarisability specifications for a particular conformation of this molecule, as these are governed in most part by the dispositions of the highly polarisable C_6H_4 groups. If, then, the b_1, b_2, b_3 values of Table 4 are used in conjunction

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* Molecular and group polarisabilities are quoted throughout in 10^{-23} c.c. units.

[24] Aroney and Le Fèvre, *J.*, 1960, 3600.

[25] Wood and Crackston, *Phil. Mag.*, 1941, **31**, 62.

[26] Price and Gillis, *J. Amer. Chem. Soc.*, 1953, **75**, 4750.

with the appropriate moments of Table 3, calculated molar Kerr constants are obtained which agree with the observed values if $\phi = ca.$ 130° for thianthren tetroxide, and *ca.* 138° for α-thianthren dioxide. The lower symmetry of the β-dioxide does not allow us to locate with precision the principal polarisability semi-axes or the resultant dipole moment, so that analogous calculations for this molecule would be highly speculative.

Conclusions.—The dipole moment and electric birefringence of thianthren in benzene solution can be analysed in terms of an " equivalent " conformation (having a dihedral angle approximately 142°) which is significantly different from the solid-state configuration (for which $\phi = 128°$). This appears compatible with the concept of a " flapping " * molecule for which ϕ adopts all values from 180° to less than 128°. However, conformations having $\phi < 128°$ would be energetically less favourable than those having $\phi > 128°$ owing predominantly to steric repulsions of the benzene rings. Analogous " equivalent " conformations specified for the α- and the β-dioxide and for the tetroxide of thianthren all have apparent angles of fold greater than those found for the crystal state, which suggests that these molecules, like the parent compound, are flexible in solution.

The award of a Commonwealth Research Scholarship to J. D. S. is gratefully acknowledged.

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* The effect of " flapping " on the mean square dipole moment and on the Kerr constant is difficult to estimate without a detailed knowledge of the operative steric, mesomeric, and bond-distortion effects, as well as those arising from solvent–solute interactions. However, it seems reasonable to assume that the probability of occurrence of conformations having ϕ considerably different from 142° is low. A potential barrier of 6—7 kcal./mole (ref. 18) results in a probability of occurrence less than 2×10^{-5} for the planar form ($\phi = 180°$), whilst small values of $\phi(<128°)$ would lead to appreciable steric interaction between the aromatic ring systems.