

S2—C1	1.775 (3)	N2—C6	1.333 (3)
S3—C1	1.668 (3)	N2—C7	1.468 (4)
S4—C6	1.661 (3)	N2—C9	1.474 (4)
S2—C11—S1	116.9 (2)	S3—C1—S2	122.5 (2)
C6—S1—C11	102.12 (14)	N2—C6—S4	125.0 (2)
C1—S2—C11	102.65 (14)	N2—C6—S1	112.9 (2)
N1—C1—S3	124.1 (2)	S4—C6—S1	122.1 (2)
N1—C1—S2	113.4 (2)		

The systematic extinctions ($0k0$: $k = 2n + 1$) indicate two possible space groups, $P2_1$ (No. 7) and $P2_1/m$ (No. 11). The non-centrosymmetric space group was chosen since the cell contains two molecules, each formed by two *N,N*-diethylthiocarbamate moieties, closely related by a twofold symmetry axis and not by a mirror plane (see *Comment*). The structure was solved by standard Fourier and Patterson methods. The refinement was carried out with anisotropic displacement parameters for all non-H atoms, while H atoms were refined isotropically. The *U* displacement parameters of the methylene and methyl H atoms were fixed at, respectively, 1.2 and 1.5 times the U_{eq} of the atom to which they are bonded. In addition, the C—H distances were constrained to be 0.97 Å for methylene and 0.96 Å for methyl groups.

Data collection: Philips PW1100/20 software. Cell refinement: locally modified Philips PW1100/20 software. Data reduction: *RIFLUP80* (Biagini *et al.*, 1980). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEPII* (Johnson, 1976).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1097). Services for accessing these data are described at the back of the journal.

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Five 3,4-Dihydro-2*H*,5*H*-pyrano[3,2-*c*][1]-benzopyran-5-one Derivatives

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Abstract

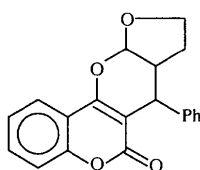
The molecular structures of five 3,4-dihydro-2*H*,5*H*-pyrano[3,2-*c*][1]benzopyran-5-one derivatives, namely, *cis,anti*-7,7*a*,8,9-tetrahydro-7-phenyl-6*H*,10*aH*-furo[2',3':2,3]pyrano[5,6-*c*][1]benzopyran-6-one [C₂₀H₁₆O₄, (I)], *cis*-2-ethoxy-3,4-dihydro-4-furyl-2*H*,5*H*-pyrano[3,2-*c*][1]benzopyran-5-one [C₁₈H₁₆O₅, (II)], *cis*-2-ethoxy-3,4-dihydro-4-phenyl-2*H*,5*H*-pyrano[3,2-*c*][1]benzopyran-5-one [C₂₀H₁₈O₄, (III)], *cis*-2-ethoxy-3,4-dihydro-4-(2-nitrophenyl)-2*H*,5*H*-pyrano[3,2-*c*][1]benzopyran-5-one [C₂₀H₁₇NO₆, (IV)] and methyl *cis*-2-ethoxy-3,4-dihydro-5-oxo-4-phenyl-2*H*,5*H*-pyrano[3,2-*c*][1]benzopyran-4-carboxylate [C₂₂H₂₀O₆, (V)] have been studied by single-crystal diffractometry. The conformation of the dihydropyran ring is compared with that found in 36 entries in the Cambridge Structural Database [version of 28 February 1997; Allen & Kennard (1993). *Chem. Des. Autom. News*, **8**, 31–37]. A scatterplot of the conformation of 46 independent molecules is shown. These molecules present a more or less distorted half-chair conformation, with few exceptions; in particular,

it seems that molecules with a second ring fused to the dihydropyran moiety adopt a diplanar conformation.

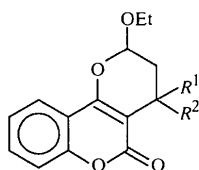
Comment

The pyranocoumarins, where the pyran ring is fused to the etherocyclic ring of 2*H*-1-benzopyran-2-one (coumarin), are well known compounds. Indeed, many of the products arising from *ortho*-phenylation followed by cyclization have been found in secondary metabolites of plants (Murray *et al.*, 1982) and are of pharmacological interest (Appendino *et al.*, 1988). Accordingly, warfarin, cyclocoumarol and their derivatives, which are structurally related to pyranocoumarins, possess anticoagulant and rodenticidal activities (Manolov & Danchev, 1995). Previous studies aimed at elucidating the chemistry of coumarin derivatives led to the development of new procedures for the synthesis of heterocyclic adducts (Appendino *et al.*, 1990, 1991, 1994, 1996; Annunziata *et al.*, 1995, 1997).

As part of this study, 3,4-dihydro-2-alkoxy-4-substituted pyranocoumarins, *i.e.* the 3,4-dihydro-2*H*,5*H*-pyrano[3,2-*c*][1]benzopyran-5-one derivatives, 7,7*a*,8,9-tetrahydro-7-phenyl-6*H*,10*aH*-furo[2',3':2,3]-pyrano[5,6-*c*][1]benzopyran-6-one, (I), 2-ethoxy-3,4-dihydro-4-furyl-2*H*,5*H*-pyrano[3,2-*c*][1]benzopyran-5-one, (II), 2-ethoxy-3,4-dihydro-4-phenyl-2*H*,5*H*-pyrano[3,2-*c*][1]benzopyran-5-one, (III), 2-ethoxy-3,4-dihydro-4-(2-nitrophenyl)-2*H*,5*H*-pyrano[3,2-*c*][1]benzopyran-5-one, (IV), and methyl 2-ethoxy-3,4-dihydro-5-oxo-4-phenyl-2*H*,5*H*-pyrano[3,2-*c*][1]benzopyran-4-carboxylate, (V), were synthesized starting from 4-hydroxycoumarin and the appropriate carbonyl compound. When carried out using aldehydes and α -ketoesters, this reaction gives 3-arylidene-3-pyranochromandiones, which were found to combine *in situ* with a variety of enol-ethers to afford the title compounds. The difficulty in elucidating the relative configurations of the moieties on the dihydropyran ring from NMR spectra suggested the X-ray single-crystal analysis of these compounds.



(I)

(II) $R^1 = \text{furyl}; R^2 = \text{H}$ (III) $R^1 = \text{Ph}; R^2 = \text{H}$ (IV) $R^1 = 2\text{-NO}_2\text{Ph}; R^2 = \text{H}$ (V) $R^1 = \text{Ph}; R^2 = \text{COOMe}$

The ellipsoid plots of molecules (I)–(V) are shown in Figs. 1–5, respectively. The adopted numbering scheme for the 3,4-dihydro-2*H*,5*H*-pyrano[3,2-*c*][1]benzopyran-5-one nucleus is the same for all five compounds in order to facilitate their comparison.

The geometries of the studied compounds do not present any unusual features. In fact, the differences between chemically equivalent bonds are quite in line with their s.u.'s; the maximum difference exceeds 0.02 Å only for the O12—C13 distance [1.457 (6) and 1.434 (2) Å in (I) and (III), respectively]. On the other hand, it should be noted that the chemical environments of atoms O12 and C13 in compound (I) are different from those in the other four molecules. In the case of (I), these atoms are part of a hindered tetrahydrofuran ring, while they are part of an ethoxy group in the other four molecules.

The tetrahydrofuran ring in (I) is *syn*-fused with the dihydropyran ring; the junction is equatorial for O12 and

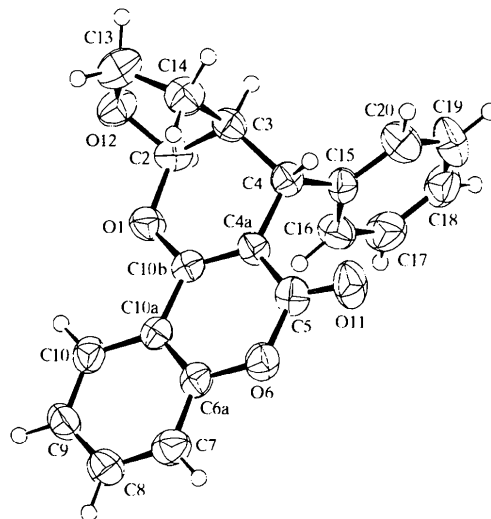


Fig. 1. An ORTEP (Johnson, 1976) plot of (I). Displacement ellipsoids are plotted at the 50% probability level and H atoms are shown as circles of arbitrary radii.

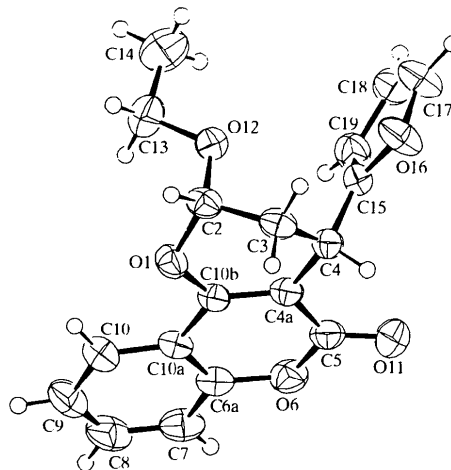


Fig. 2. An ORTEP (Johnson, 1976) plot of (II). Displacement ellipsoids are plotted at the 50% probability level and H atoms are shown as circles of arbitrary radii.

axial for C14. This ring and the phenyl group bonded to C4 are in an *anti* conformation. In the other four compounds, the ethoxy group and the aromatic ring bonded to C4 are in a *syn*-axial conformation.

The scatterplot shown in Fig. 6 reports the dihydropyran-ring conformation of the five title molecules, together with 41 other molecules taken from 36 entries for 3,4-dihydro-2*H*,5*H*-pyrano[3,2-*c*][1]benzopyran-5-one derivatives included in the Cambridge Structural Database (version of 28 February 1997; Allen & Kennard, 1993); the conformation is expressed by θ_2 and φ_2 according to Nardelli (1983). As can be seen, the dihydropyran ring in coumarin derivatives, with few

exceptions, presents a more or less deformed half-chair conformation. The only systematic deviation from this rule seems to be connected with the presence of a second fused ring on the dihydropyran ring, since these molecules show a diplanar conformation. The scatterplot gives prominence to these molecules, denoting them by small circles.

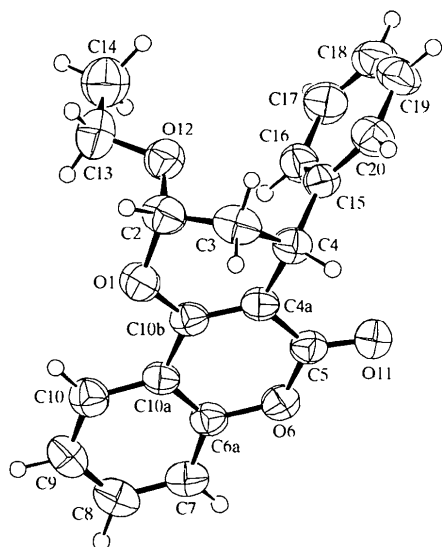


Fig. 3. An ORTEP (Johnson, 1976) plot of (III). Displacement ellipsoids are plotted at the 50% probability level and H atoms are shown as circles of arbitrary radii.

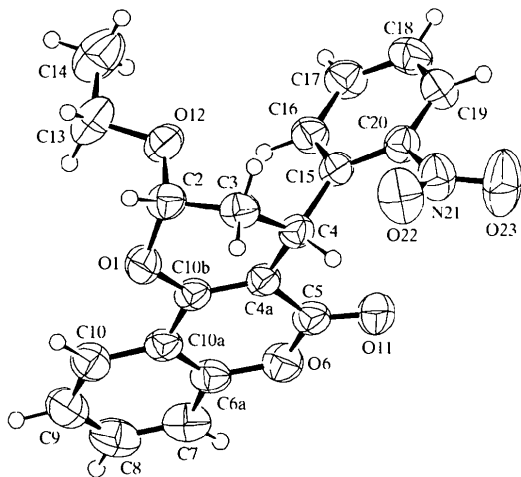


Fig. 4. An ORTEP (Johnson, 1976) plot of (IV). Displacement ellipsoids are plotted at the 50% probability level and H atoms are shown as circles of arbitrary radii.

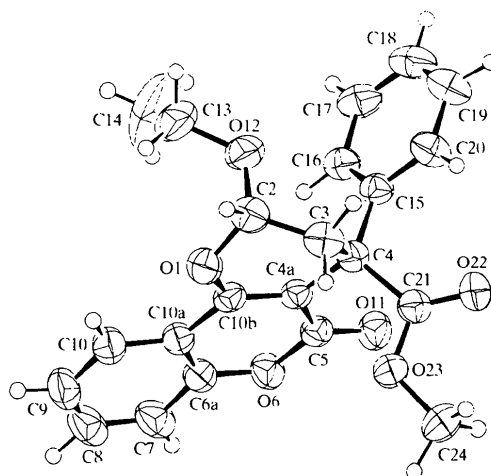


Fig. 5. An ORTEP (Johnson, 1976) plot of (V). Displacement ellipsoids are plotted at the 50% probability level and H atoms are shown as circles of arbitrary radii.

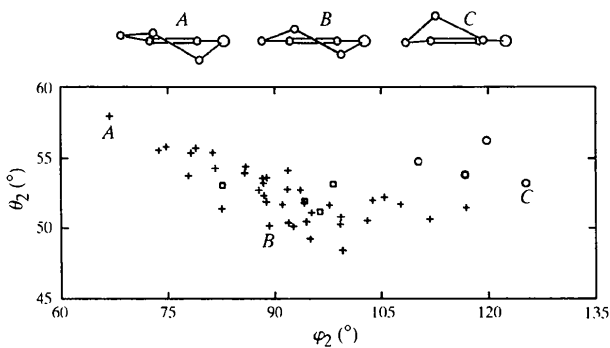


Fig. 6. Scatterplot of the conformation of 46 3,4-dihydropyran ring systems (see *Comment*). Small circles indicate molecules with two rings fused to the dihydropyran system. The schematic projections above the scatterplot show three limit conformations [A = FEGPEM, B = FEGPAI (molecule 2) and C = KAPBUY].

Experimental

The title compounds were recrystallized by slow diffusion of either ethyl ether or isopropyl ether into saturated dichloromethane solutions.

Compound (I)

Crystal data

C₂₀H₁₆O₄
M_r = 320.344

Mo K α radiation
 λ = 0.71073 Å

Monoclinic

$P2_1$
 $a = 8.664 (1) \text{ \AA}$
 $b = 10.640 (2) \text{ \AA}$
 $c = 8.822 (1) \text{ \AA}$
 $\beta = 108.38 (1)^\circ$
 $V = 771.8 (2) \text{ \AA}^3$
 $Z = 2$
 $D_x = 1.378 \text{ Mg m}^{-3}$
 D_m not measured

Data collection

Siemens *P4* diffractometer
 $2\theta/\omega$ scans
 Absorption correction: none
 1377 measured reflections
 1285 independent reflections
 937 reflections with
 $I > 2\sigma(I)$
 $R_{\text{int}} = 0.022$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.041$
 $wR(F^2) = 0.088$
 $S = 1.114$
 1285 reflections
 218 parameters
 H atoms not refined
 $w = 1/[\sigma^2(F_o^2) + (0.0342P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.143 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.162 \text{ e \AA}^{-3}$

Compound (II)**Crystal data**

$\text{C}_{18}\text{H}_{16}\text{O}_5$
 $M_r = 312.321$
 Monoclinic
 $P2_1/n$
 $a = 11.987 (2) \text{ \AA}$
 $b = 10.028 (2) \text{ \AA}$
 $c = 13.413 (2) \text{ \AA}$
 $\beta = 107.551 (8)^\circ$
 $V = 1537.3 (5) \text{ \AA}^3$
 $Z = 4$
 $D_x = 1.350 \text{ Mg m}^{-3}$
 D_m not measured

Data collection

Siemens *P4* diffractometer
 $2\theta/\omega$ scans
 Absorption correction: none
 3699 measured reflections
 3535 independent reflections
 2425 reflections with
 $I > 2\sigma(I)$
 $R_{\text{int}} = 0.012$

Cell parameters from 41

reflections
 $\theta = 3.98\text{--}9.89^\circ$
 $\mu = 0.096 \text{ mm}^{-1}$
 $T = 293 (2) \text{ K}$
 Elongated tablet
 $0.46 \times 0.20 \times 0.10 \text{ mm}$
 Colourless

$\theta_{\text{max}} = 22.99^\circ$
 $h = 0 \rightarrow 9$
 $k = -1 \rightarrow 11$
 $l = -9 \rightarrow 9$
 3 standard reflections
 every 97 reflections
 intensity decay: 4.45%

Extinction correction:
SHELXL93
 Extinction coefficient:
 0.019 (4)
 Scattering factors from
International Tables for
Crystallography (Vol. C)
 Absolute structure: Flack
 (1983)
 Flack parameter = 0 (2)

Mo $K\alpha$ radiation
 $\lambda = 0.71073 \text{ \AA}$
 Cell parameters from 44
 reflections
 $\theta = 5.10\text{--}14.03^\circ$
 $\mu = 0.099 \text{ mm}^{-1}$
 $T = 293 (2) \text{ K}$
 Triangular prism
 $0.50 \times 0.42 \times 0.28 \text{ mm}$
 Colourless

$\theta_{\text{max}} = 27.50^\circ$
 $h = 0 \rightarrow 15$
 $k = 0 \rightarrow 13$
 $l = -17 \rightarrow 16$
 3 standard reflections
 every 197 reflections
 intensity decay: 2.86%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.036$
 $wR(F^2) = 0.101$
 $S = 0.962$
 3535 reflections
 273 parameters
 All H atoms refined
 $w = 1/[\sigma^2(F_o^2) + (0.0597P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$

Compound (III)**Crystal data**

$\text{C}_{20}\text{H}_{18}\text{O}_4$
 $M_r = 322.36$
 Monoclinic
 $P2_1/n$
 $a = 11.682 (1) \text{ \AA}$
 $b = 11.101 (1) \text{ \AA}$
 $c = 12.610 (1) \text{ \AA}$
 $\beta = 93.660 (10)^\circ$
 $V = 1632.0 (3) \text{ \AA}^3$
 $Z = 4$
 $D_x = 1.312 \text{ Mg m}^{-3}$
 D_m not measured

Data collection

Siemens *P4* diffractometer
 $2\theta/\omega$ scans
 Absorption correction: none
 3921 measured reflections
 3743 independent reflections
 2268 reflections with
 $I > 2\sigma(I)$
 $R_{\text{int}} = 0.013$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.037$
 $wR(F^2) = 0.096$
 $S = 0.922$
 3743 reflections
 290 parameters
 All H atoms refined
 $w = 1/[\sigma^2(F_o^2) + (0.0514P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$

Compound (IV)**Crystal data**

$\text{C}_{20}\text{H}_{17}\text{NO}_6$
 $M_r = 367.357$

$\Delta\rho_{\text{max}} = 0.197 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.136 \text{ e \AA}^{-3}$
 Extinction correction:
SHELXL93
 Extinction coefficient:
 0.0023 (10)
 Scattering factors from
International Tables for
Crystallography (Vol. C)

Mo $K\alpha$ radiation
 $\lambda = 0.71073 \text{ \AA}$
 Cell parameters from 50
 reflections
 $\theta = 4.61\text{--}12.38^\circ$
 $\mu = 0.091 \text{ mm}^{-1}$
 $T = 293 (2) \text{ K}$
 Prism
 $0.46 \times 0.36 \times 0.32 \text{ mm}$
 Colourless

$\theta_{\text{max}} = 27.50^\circ$
 $h = 0 \rightarrow 15$
 $k = 0 \rightarrow 14$
 $l = -16 \rightarrow 16$
 3 standard reflections
 every 197 reflections
 intensity decay: 3.32%

$\Delta\rho_{\text{max}} = 0.141 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.123 \text{ e \AA}^{-3}$
 Extinction correction:
SHELXL93
 Extinction coefficient:
 0.0038 (11)
 Scattering factors from
International Tables for
Crystallography (Vol. C)

Mo $K\alpha$ radiation
 $\lambda = 0.71073 \text{ \AA}$

Monoclinic

$P2_1/c$
 $a = 8.276 (1) \text{ \AA}$
 $b = 15.024 (1) \text{ \AA}$
 $c = 14.448 (1) \text{ \AA}$
 $\beta = 98.68 (1)^\circ$
 $V = 1775.9 (3) \text{ \AA}^3$
 $Z = 4$
 $D_x = 1.374 \text{ Mg m}^{-3}$
 D_m not measured

Data collection

Siemens P4 diffractometer
 $2\theta/\omega$ scans
 Absorption correction: none
 3354 measured reflections
 3127 independent reflections
 1874 reflections with
 $I > 2\sigma(I)$
 $R_{\text{int}} = 0.011$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.033$
 $wR(F^2) = 0.079$
 $S = 0.851$
 3127 reflections
 301 parameters
 H atoms treated by a
 mixture of independent
 and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0413P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$

Cell parameters from 52

reflections
 $\theta = 4.97\text{--}11.38^\circ$
 $\mu = 0.103 \text{ mm}^{-1}$
 $T = 293 (2) \text{ K}$
 Square tablet
 $0.38 \times 0.36 \times 0.15 \text{ mm}$
 Colourless

$\theta_{\text{max}} = 25.00^\circ$
 $h = 0 \rightarrow 9$
 $k = 0 \rightarrow 17$
 $l = -17 \rightarrow 16$
 3 standard reflections
 every 97 reflections
 intensity decay: 4.02%

$(\Delta/\sigma)_{\text{max}} = 0.002$
 $\Delta\rho_{\text{max}} = 0.131 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.128 \text{ e \AA}^{-3}$
 Extinction correction:
SHELXL93
 Extinction coefficient:
 0.0072 (7)
 Scattering factors from
International Tables for
Crystallography (Vol. C)

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.040$
 $wR(F^2) = 0.100$
 $S = 1.014$
 2993 reflections
 322 parameters
 H atoms treated by a
 mixture of independent
 and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0458P)^2 + 0.0483P]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} = 0.004$
 $\Delta\rho_{\text{max}} = 0.140 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.140 \text{ e \AA}^{-3}$
 Extinction correction:
SHELXL93
 Extinction coefficient:
 0.0063 (10)
 Scattering factors from
International Tables for
Crystallography (Vol. C)

Crystals of compounds (I) and (V) were very small and of poor quality, and this led to the decision not to measure data above $\theta = 23$ and 24° , respectively. Cu radiation or low-temperature equipment would have provided better measurements but were unavailable for these studies. The H atoms of compound (I) were placed in calculated positions; the reduced number of Friedel-related reflections and, moreover, the small values of the anomalous scattering factors made it impossible to establish the absolute configuration of this molecule with sufficient reliability. In compounds (IV) and (V), the methyl C14 atom exhibits quite high thermal motion and it was impossible to refine the relative H-atom positions.

For compounds (I)–(V), data collection: *XSCANS* (Fait, 1991); cell refinement: *XSCANS*; data reduction: *XSCANS*; structure solution: *SIR92* (Altomare *et al.*, 1994); structure refinement: *SHELXL93* (Sheldrick, 1993); computer graphics: *ORTEPII* (Johnson, 1976); preparation of material for publication: *SHELXL93*; other programs used include *PARSTCIF* (Nardelli, 1991).

We wish to thank Professor Giovanni Palmisano who suggested this work and for helpful discussions.

Compound (V)

Crystal data

C₂₂H₂₀O₆
 $M_r = 380.38$
 Monoclinic
 $P2_1/n$
 $a = 10.392 (1) \text{ \AA}$
 $b = 17.192 (1) \text{ \AA}$
 $c = 11.193 (1) \text{ \AA}$
 $\beta = 107.394 (6)^\circ$
 $V = 1908.3 (3) \text{ \AA}^3$
 $Z = 4$
 $D_x = 1.324 \text{ Mg m}^{-3}$
 D_m not measured

Mo $K\alpha$ radiation
 $\lambda = 0.71073 \text{ \AA}$
 Cell parameters from 43
 reflections
 $\theta = 3.40\text{--}12.27^\circ$
 $\mu = 0.097 \text{ mm}^{-1}$
 $T = 293 (2) \text{ K}$
 Irregular prism
 $0.42 \times 0.40 \times 0.30 \text{ mm}$
 Colourless

$\theta_{\text{max}} = 24.00^\circ$
 $h = -11 \rightarrow 11$
 $k = 0 \rightarrow 19$
 $l = -12 \rightarrow 12$
 3 standard reflections
 every 97 reflections
 intensity decay: 3.75%

Data collection

Siemens P4 diffractometer
 $2\theta/\omega$ scans
 Absorption correction: none
 5977 measured reflections
 2993 independent reflections
 2011 reflections with
 $I > 2\sigma(I)$
 $R_{\text{int}} = 0.030$

Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1342). Services for accessing these data are described at the back of the journal.

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3,4-Dimethyltetrathiafulvalene†

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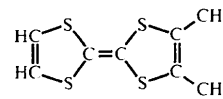
Abstract

The title compound consists of C₃H₈S₄ molecules where the tetrathiafulvalene backbone is nearly planar, and bond angles and distances are in accord with other TTF derivatives. The C—S—C angles for the five-membered rings of the TTF moiety average 95.83 (15)° for the ring containing the methyl groups and 94.37 (17)° for the unsubstituted ring. The molecules are stacked in pairs about an inversion center, with intermolecular S··S distances of 3.932 (2) Å between adjacent molecules.

Comment

Organic molecules such as tetrathiafulvalene (TTF) and its derivatives are important precursors in the design of new conducting, optical and magnetic materials. These planar molecules can be readily oxidized both chemically and electrochemically to produce radical cations which, when associated with suitable electron acceptors such as 7,7,8,8-tetracyanoquinodimethane (TCNQ), form segregated stacks that allow for electrical conductivity due to the overlap of their π orbitals (Ferraris *et al.*, 1973). These donor molecules have also been observed to form salts with large metal-

based cluster anions that exhibit remarkably variable properties, differences that are attributed to the size and shape of the organic donor and inorganic acceptors, as well as their redox properties. Fourmigué & Batail (1992) have shown that methyl-TTF derivatives such as the title compound can be used to prepare a series of multidentate TTF–phosphine ligands, including 3,4-dimethyl-3',4'-bis(diphenylphosphino)tetrathiafulvalene (*ortho*-P2). The structure of 3,4-dimethyltetrathiafulvalene, (I), has been undertaken in order to compare the geometrical features with those of related TTF derivatives and the structures of the *ortho*-P2 ligand and its metal complexes (Uzelmeier *et al.*, 1998).



(I)

The central core (S1–S4, C3 and C4) of the title molecule is nearly planar, with a maximum deviation of 0.016 (2) Å for C3, and an r.m.s. deviation of 0.010 Å. The dihedral angle between planes C5, C6, S4, S3 and S1–S4, C3, C4 is 0.60 (13)°, while the angle between planes C1, C2, S2, S1 and S1–S4, C3, C4 is 1.88 (16)°. This is in contrast to the analogous dihedral angles in the neutral and cationic TTF crystal structures, where both fulvalene rings exhibit the same out-of-plane bend. For neutral tetrathiafulvalene, the value is 2.1° for both five-membered rings (Cooper *et al.*, 1971), whereas for cationic TTF, the corresponding dihedral angles between the planes are 2.2° (Kistenmacher *et al.*, 1974). Bond distances and angles within the TTF core of (I) are comparable to other TTF molecules. The C=C bond at the center of the molecule is 1.340 (4) Å, and S··S distances within the molecule are 2.967 (2) Å for S1··S2 and 2.945 (1) Å for S3··S4. It should be noted that this value for the central C=C distance is equivalent to that in neutral TTF [1.349 (3) Å], but shorter than that found in cationic TTF [1.369 (4) Å]. The bond lengths of the external C atoms in (I) are 1.308 (5) Å for C1=C2 and 1.338 (4) Å for C5=C6. This lengthening of C5=C6 renders it indistinguishable from C3=C4, a situation that has also been observed in 3,3'-dimethyl-4,4'-bis(diphenylphosphino)tetrathiafulvalene (Fourmigué *et al.*, 1997). Another manifestation of the presence of methyl substituents is differences in the S—C distances. The five-membered ring that contains the methyl groups exhibits S—C distances that are essentially all equivalent, but on the opposite side of the molecule; the sulfur to bridging-carbon distances are longer than the sulfur to exterior-carbon distances by 0.024 (4) Å.

Typically, neutral TTF stacks in a parallel orientation with respect to the *b* axis, with intermolecular S··S contacts of 3.62 Å; the TTF cation in TTF–TCNQ also

† Alternative name: 2-(2*H*-1,3-dithiol-2-ylidene)-4,5-dimethyl-2*H*-1,3-dithiole.