Table 1. *Selected geometric parameters (°)*

N1—C7—C4	112.8 (5)	N2—C22—C19	110.9 (5)
N1—C7—C8	108.7 (5)	N2—C22—C23	108.8 (5)
O1—C9—N1	123.4 (5)	O2—C24—N2	121.2 (5)
O1—C9—C10	121.5 (5)	O2—C24—C25	122.7 (5)
N1—C9—C10	115.1 (4)	N2—C24—C25	116.0 (5)
C11—C10—C12	58.6 (4)	C26—C25—C27	58.4 (4)
C10—C11—C12	60.2 (4)	C25—C26—C27	61.0 (4)
C10—C12—C11	61.2 (4)	C25—C27—C26	60.6 (4)
O1—C9—N1—C7	−4.4 (8)	C7—N1—C9—C10	173.3 (5)
O2—C24—N2—C22	2.9 (9)	C8—C7—N1—C9	−148.3 (5)
N1—C7—C4—C3	20.8 (8)	C17—C18—C19—C22	−178.4 (6)
N1—C7—C4—C5	−161.4 (5)	C18—C19—C22—C23	−70.4 (8)
N2—C22—C19—C18	52.4 (8)	C19—C22—N2—C24	70.4 (7)
N2—C22—C19—C20	−127.6 (6)	C20—C19—C22—C23	109.5 (6)
C3—C4—C7—C8	−101.5 (7)	C21—C20—C19—C22	178.2 (6)
C5—C4—C7—C8	76.2 (7)	C22—N2—C24—C25	−178.0 (5)
C6—C5—C4—C7	−178.2 (7)	C23—C22—N2—C24	−164.1 (6)

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H27···O1	0.91	2.03	2.933 (4)	172
N1—H9···O2^{i}	1.00	1.96	2.879 (6)	151

Symmetry code: (i) $-1-x, y-\frac{1}{2}, -\frac{3}{2}-z$.

H atoms were found in electron-density difference maps, but were replaced in calculated positions and allowed to refine as riding models on their appropriate C atoms.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1996). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1998). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1401). Services for accessing these data are described at the back of the journal.

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3-Ethyl-5-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-naphthylmethylene)thiazolidine-2,4-dione

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Abstract

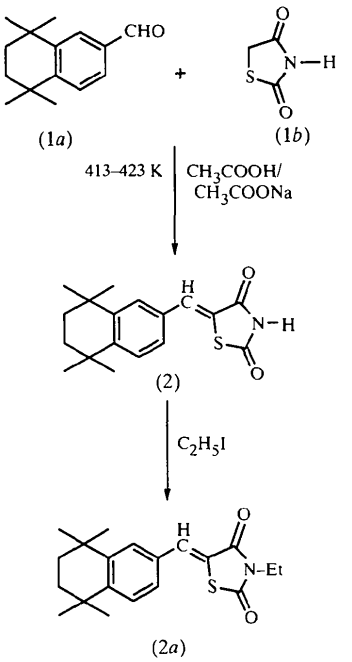
The title compound, $C_{20}H_{25}NO_2S$, is under investigation for potential retinoid-receptor activity. The molecular conformation is approximately planar, with five methyl groups projecting from the mean plane. Twofold disorder of the methylene groups of the tetrahydrotetramethyl residue was detected and satisfactorily modelled.

Comment

Retinoic acid and its biological isosteres play important roles in a variety of biological processes including regulation of cell growth/differentiation and lipid peroxidase inhibition (Hiramatsu & Packer, 1990). The physiological effects of retinoids have emerged in their application in chemotherapy in several cancer treatments (Smith *et al.*, 1992; Vokes *et al.*, 1993) although they have significant side effects, due in part to their high hydrophobicity (Shimasaki *et al.*, 1995) and their ability to activate multiple retinoid receptors (Orfanos *et al.*, 1987). As part of our search for new antioxidant drugs, we have been studying retinoidal compounds bearing the 5,6,7,8-tetrahydro-5,5,8,8-tetramethyl moiety as potential inhibitors of cytochrome P450 isozymes and we have reported a potent antioxidant activity of a tetrahydrotetramethylbenzimidazol compound (Ates *et al.*, 1997). On the other hand, the thiazole moiety is found in many anticancer compounds as well as antioxidants (Schumaker *et al.*, 1997; Herbert *et al.*, 1993). Previously, it was reported that inclusion of the thiazolidine ring into the retinoic acid side-chain led to good retinoidal activity towards human promyelocytic leukaemia HL-60 cells (Tashima *et al.*, 1997).

It is apparent that specificity for binding at the active sites of different retinoid receptors must eventually depend on the conformational properties of the individual molecules. The size and conformational flexibility of the retinoid molecules obtained from X-ray studies are important factors for the future design of retinoid-type

compounds. In our continuing search for antitumour and antioxidant agents bearing the 5,6,7,8-tetrahydro-5,5,8,8-tetramethylnaphthalene moiety (as part of a retinoidal molecular pathway), we have synthesized a new thiazolidine compound, (2*a*), and describe its X-ray structure.



The molecular structure of (2*a*) is shown in Fig. 1. The cyclohexene ring adopts a half-chair conformation. The adjacent methylene groups are each disordered over two positions; for clarity, only the major components C132 and C142 are shown in Fig. 1.

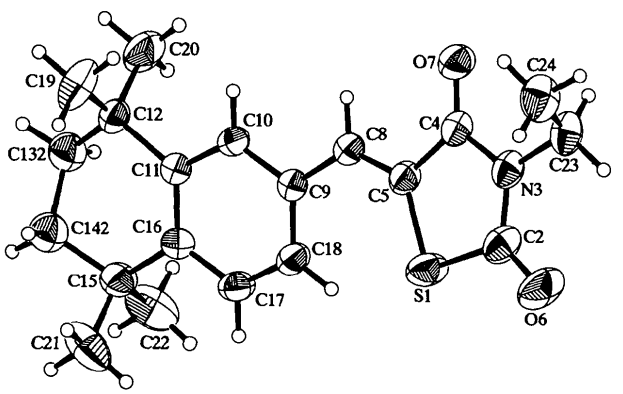


Fig. 1. Molecular structure showing 50% probability displacement ellipsoids for non-H atoms. For H atoms, spheres of arbitrary radii are drawn. Atoms C131 and C141 and their H atoms, which comprise the other disorder component to C132 and C142 and their H atoms, are omitted for clarity.

The nearly coplanar relationship between the phenyl and thiazolidinedione rings is maintained by an attractive intramolecular interaction C18—H18···S1 [C···S 3.272 (2) Å, C18—H18···S1 129.0 (2)°]. The ethyl substituent is oriented out of the thiazolidinedione ring plane. Molecules of (2*a*) pack in a layered arrangement with their average molecular planes parallel to, and located midway between, the (202) crystal planes.

Experimental

Compound (2) was synthesized by Knoevenagel condensation (Lima *et al.*, 1992). A mixture consisting of 1 mmol each of 5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-naphthalenecarboxaldehyde, (1*a*) (Boehm *et al.*, 1994), 2,4-thiazolidinedione (1*b*) (Lima *et al.*, 1992) and sodium acetate in glacial acetic acid (2 ml) was heated at 413–423 K for 20 h. The crude product (2) was crystallized from EtOH/H_2O to give the title compound in 70% yield; m.p. 465 K. ^{1}H NMR ($CDCl_3$), (δ p.p.m.): 1.29 (*s*, 6H, CH_3), 1.31 (*s*, 6H, CH_3), 1.72 (*s*, 4H, CH_2), 7.25–7.45 (*m*, 3H, aromatic), 7.80 (*s*, 1H, =CH), 8.50 (*s*, 1H, NH). Analysis calculated for $C_{18}H_{21}NO_2S$: C 68.57, H 6.66, N 4.44, S 10.15%. Found: C 68.58, H 7.18, N 4.33, S 10.08%. MS: 315 (M^+), 317 ($M+2$).

Compound (2*a*) was prepared by the procedure of Sohda *et al.* (1982). A mixture of (2) (1 mmol), Na_2CO_3 (1 mmol), C_2H_5I (2 mmol) and DMF (5 ml) was stirred at room temperature for 1 h, diluted with H_2O, filtered and crystallized from EtOH; m.p. 516 K. ^{1}H NMR ($CDCl_3$), (δ p.p.m.): 1.25 (*t*, 3H, CH_3), 1.28 (*s*, 6H, CH_3), 1.30 (*s*, 6H, CH_3), 1.72 (*s*, 4H, CH_2), 3.85 (*q*, 2H, NCH_2), 7.25–7.45 (*m*, 3H, aromatic), 7.85 (*s*, 1H, =CH). Analysis calculated for $C_{20}H_{25}NO_2S$: C 69.97, H 7.28, N 4.08, S 9.32%. Found: C 69.93, H 7.35, N 4.01, S 9.12%. MS: 343 (M^+), 345 ($M+2$).

Crystal data

$C_{20}H_{25}NO_2S$
M_r = 343.47
Monoclinic
$P2_1/c$
a = 10.412 (1) Å
b = 8.516 (1) Å
c = 21.556 (1) Å
β = 101.223 (10)°
V = 1874.8 (3) Å^3
Z = 4
D_x = 1.217 Mg m^{-3}
D_m = 1.17 Mg m^{-3}
D_m measured by flotation in aqueous KI

Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 6540 reflections
θ = 2.58–26.35°
μ = 0.184 mm^{-1}
T = 293 (2) K
Prism
0.35 × 0.30 × 0.25 mm
Yellow–orange

Data collection

Nonius Kappa CCD diffractometer
1° φ and ω scans
Absorption correction: none
6540 measured reflections
3642 independent reflections

2796 reflections with $I > 2\sigma(I)$
R_{int} = 0.019
θ_{max} = 26.35°
h = 0 → 13
k = −10 → 10
l = −25 → 24

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.052$
$wR(F^2) = 0.152$
$S = 1.093$
3642 reflections
219 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0976P)^2 + 0.3939P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = -0.005$
$\Delta\rho_{max} = 0.35$ e Å^{-3}
$\Delta\rho_{min} = -0.24$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

S1—C5	1.741 (2)	N3—C23	1.471 (3)
S1—C2	1.774 (2)	C4—C5	1.476 (3)
C2—N3	1.370 (3)	C5—C8	1.342 (2)
N3—C4	1.387 (2)	C8—C9	1.451 (2)
C5—S1—C2	91.77 (10)	N3—C4—C5	111.0 (2)
N3—C2—S1	110.80 (14)	C4—C5—S1	110.26 (13)
C2—N3—C4	116.2 (2)		

S1—C5—C8—C9	−2.3 (3)
C5—C8—C9—C18	−13.5 (3)
C16—C11—C12—C132	−14.7 (3)
C11—C12—C132—C142	47.6 (5)
C12—C132—C142—C15	−69.8 (5)
C132—C142—C15—C16	53.0 (4)
C12—C11—C16—C15	1.4 (3)
C142—C15—C16—C11	−20.7 (3)
C4—N3—C23—C24	74.1 (3)

Disorder was identified in the adjacent methylene groups and modelled in terms of two components – C131 and C141 with occupancy 0.467 (7), and C132 and C142 with occupancy 0.533 (7). Except for the disordered atoms, non-H atoms were refined anisotropically. U_{iso} values for the disordered atoms refined in the range 0.060–0.070 Å^2. H atoms were fixed in idealized positions with common U_{iso} values for chemically related groups (range 0.066–0.126 Å^2).

Data collection: *Collect Software* (Nonius BV, 1998). Cell refinement: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997). Data reduction: *DENZO* and *SCALEPACK*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ZORTEP* (Zsolnai & Pritzkow, 1994). Software used to prepare material for publication: *SHELXL*93 and *PARST*95 (Nardelli, 1995).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1315). Services for accessing these data are described at the back of the journal.

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3-(2-Hydroxyphenylamino)-5,5-dimethylcyclohex-2-enone

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Abstract

In the title compound, $C_{14}H_{17}NO_2$, the molecules are linked through two hydrogen bonds to form a two-dimensional network in the (100) plane. The carbonyl-O atom is involved in two intermolecular hydrogen

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