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Structure of 2,2′-Bis(4-chlorophenyl)-5,5′-dimethyl-[3,3′-bi-1,3-thiazolidine]-4,4′-dione, $C_{20}H_{18}Cl_2N_2O_2S_2$

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Abstract. $M_r = 453{\cdot}4$, monoclinic, $P2_1/n$, $a = 13{\cdot}857\,(2)$, $b = 12{\cdot}527\,(2)$, $c = 12{\cdot}199\,(2)$ Å, $\beta = 94{\cdot}58\,(3)°$, $Z = 4$, $U = 2110{\cdot}8\,(6)$ Å^3, $D_m = 1{\cdot}41$ (flotation), $D_x = 1{\cdot}426$ g cm^{-3}, $\mu(\text{Mo } K\alpha) = 5{\cdot}2$ cm^{-1}, $F(000) = 936$, room temperature. Final conventional R value is 0·069 ($R_w = 0{\cdot}058$) for 1178 diffractometer-measured intensities. The molecular structure is characterized by the intramolecular interaction between the two parallel phenyl groups (mean distance 3·3 Å) and by the different conformations of the two thiazolidine rings, half-chair and envelope. Both enantiomers 2*R*,5*S*,2′*S*,5′*S* and 2*S*,5*R*,2′*R*,5′*S* are present in the structure.

Introduction. Substituted 2-aryl-4-thiazolidinones exhibit several interesting therapeutical properties. In particular some of them have antibacterial, antifungal, antitubercular, myorelaxant, and antiviral activity. In addition, when the H atom bound to the nitrogen in position 3 of the pentaatomic ring is substituted by the nitrogen of another 2-aryl-4-thiazolidinone ring the compound obtained exhibits properties like those of an anti-inflammatory drug instead of those previously quoted (Fenech, 1972–73). The crystal and molecular structure of the title compound (F2TD2, hereinafter) has been determined as part of an investigation of the structural features of some substituted thiazolidinones, which we are examining in an attempt to correlate molecular conformation and pharmacological activity.

Experimental. Colourless single crystals of F2TD2, suitable for an X-ray analysis, obtained by slow evaporation of their ethanolic solution; approximate unit-cell parameters estimated from preliminary Weissenberg and precession photographs, crystal size 0·2 × 0·2 × 0·3 mm, Siemens–Stoe four-circle diffractometer, graphite monochromator, Mo $K\alpha$ radiation ($\lambda = 0{\cdot}71069$ Å), accurate unit-cell parameters and crystal-orientation matrices (together with their estimated standard errors) obtained from least-squares refinement of the 2θ, ω, χ and φ values of 20 carefully centred high-angle (θ range 6–12°) reflections; ω/θ scan, scan width 1·4°, scan speed 0·04° s^{-1}, 2θ range 6–50°, two standard reflections (154 and $\bar{5}01$)

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Table 1. *Fractional atomic coordinates* (×10^4), *and equivalent and isotropic thermal parameters* (×10^3) *for non-*H *atoms with e.s.d.'s in parentheses*

$U_{eq} = \frac{1}{3}\sum_i\sum_j a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$ (for values marked with an asterisk).

	x	*y*	*z*	U_{eq}, U_{iso}(Å^2)
Cl(1)	9246 (2)	4094 (3)	12323 (2)	95 (2)*
Cl(2)	7077 (2)	1944 (3)	12417 (3)	112 (3)*
S(1)	4701 (2)	4166 (3)	7826 (3)	81 (2)*
S(2)	9175 (2)	3688 (3)	6679 (3)	80 (2)*
O(1)	6624 (5)	2797 (5)	5595 (6)	63 (4)*
O(2)	6522 (5)	5350 (5)	5971 (6)	74 (5)*
N(1)	7360 (5)	3671 (6)	7061 (6)	48 (5)*
N(2)	6476 (5)	4110 (6)	7333 (6)	50 (5)*
C(9)	8596 (9)	2012 (11)	5300 (12)	161 (12)*
C(13)	4566 (9)	5969 (9)	6533 (9)	103 (10)*
C(7)	8235 (6)	4273 (8)	7451 (7)	47 (3)
C(8)	8351 (8)	3061 (10)	5663 (10)	78 (4)
C(10)	7346 (8)	3145 (9)	6067 (10)	59 (3)
C(11)	6070 (7)	4872 (9)	6595 (9)	56 (3)
C(12)	4981 (8)	4908 (10)	6636 (10)	83 (4)
C(14)	5801 (7)	3391 (8)	7832 (8)	57 (3)
C(1)	8485 (6)	4215 (8)	8659 (7)	44 (3)
C(2)	8648 (7)	3251 (8)	9203 (8)	52 (3)
C(3)	8880 (7)	3196 (9)	10312 (9)	60 (3)
C(4)	8957 (6)	4157 (9)	10870 (8)	58 (3)
C(5)	8813 (7)	5122 (8)	10374 (8)	57 (3)
C(6)	8584 (7)	5150 (8)	9288 (8)	52 (3)
C(15)	6142 (6)	3044 (8)	8977 (8)	44 (3)
C(17)	6310 (6)	3759 (8)	9831 (8)	50 (3)
C(18)	6605 (7)	3450 (8)	10894 (8)	62 (3)
C(19)	6700 (7)	2374 (9)	11062 (9)	62 (3)
C(20)	6525 (7)	1633 (9)	10288 (9)	66 (3)
C(21)	6239 (7)	1958 (8)	9217 (8)	55 (3)

Table 2. *Final interatomic distances* (Å) *and bond angles* (°) *with e.s.d.'s in parentheses*

Cl(1)–C(4)	1·79 (1)	N(1)–C(10)	1·38 (1)
Cl(2)–C(19)	1·78 (1)	N(2)–C(11)	1·40 (1)
S(1)–C(12)	1·79 (1)	N(2)–C(14)	1·46 (1)
S(1)–C(14)	1·81 (1)	C(8)–C(10)	1·52 (1)
S(2)–C(7)	1·82 (1)	C(8)–C(9)	1·44 (1)
S(2)–C(8)	1·80 (1)	C(11)–C(12)	1·51 (1)
O(1)–C(10)	1·20 (1)	C(12)–C(13)	1·45 (1)
O(2)–C(11)	1·19 (1)	C(7)–C(1)	1·49 (1)
N(1)–N(2)	1·41 (1)	C(14)–C(15)	1·50 (1)
N(1)–C(7)	1·48 (1)		
C(1)–C(6)	1·40 (1)	C(15)–C(17)	1·38 (1)
C(1)–C(2)	1·39 (1)	C(17)–C(18)	1·38 (1)
C(2)–C(3)	1·37 (1)	C(18)–C(19)	1·37 (1)
C(3)–C(4)	1·38 (1)	C(19)–C(20)	1·33 (1)
C(4)–C(5)	1·36 (1)	C(20)–C(21)	1·40 (1)
C(5)–C(6)	1·34 (1)	C(21)–C(15)	1·40 (1)
S(2)–C(7)–N(1)	103·3 (6)	S(1)–C(14)–N(2)	103·5 (7)
C(7)–N(1)–C(10)	118·8 (8)	C(14)–N(2)–C(11)	116·8 (8)
N(1)–C(10)–C(8)	112 (1)	N(2)–C(11)–C(12)	110 (1)
C(10)–C(8)–S(2)	107·1 (9)	C(11)–C(12)–S(1)	107·0 (9)
C(8)–S(2)–C(7)	95·2 (5)	C(12)–S(1)–C(14)	92·5 (5)
S(2)–C(7)–C(1)	111·9 (7)	S(1)–C(14)–C(15)	111·2 (7)
C(7)–N(1)–N(2)	115·6 (7)	C(14)–N(2)–N(1)	117·0 (8)
N(1)–C(10)–O(1)	123 (1)	N(2)–C(11)–O(2)	124 (1)
S(2)–C(8)–C(9)	117·4 (9)	S(1)–C(12)–C(13)	115·8 (9)
C(10)–N(1)–N(2)	116·3 (8)	C(11)–N(2)–N(1)	115·4 (8)
C(7)–C(1)–C(2)	122·2 (8)	C(14)–C(15)–C(17)	122 (1)
C(1)–C(2)–C(3)	122 (1)	C(15)–C(17)–C(18)	123 (1)
C(2)–C(3)–C(4)	117 (1)	C(17)–C(18)–C(19)	116 (1)
C(3)–C(4)–C(5)	124 (1)	C(18)–C(19)–C(20)	125 (1)
C(4)–C(5)–C(6)	119 (1)	C(19)–C(20)–C(21)	119 (1)
C(5)–C(6)–C(1)	122 (1)	C(20)–C(21)–C(15)	120 (1)
C(6)–C(1)–C(2)	118 (1)	C(21)–C(15)–C(17)	118 (1)
C(3)–C(4)–Cl(1)	117 (1)	C(20)–C(19)–Cl(2)	118 (1)

measured every 120 min, 2150 data measured, 1178 with $I \geq 2{\cdot}5\sigma(I)$, corrections for Lorentz and polarization effects (absorption and extinction corrections ignored); trial structure obtained by direct methods (Germain, Main & Woolfson, 1971) and refined by full-matrix least-squares procedures, function minimized $\sum w(|F_o| - |F_c|)^2$, $w = 5{\cdot}4833/[\sigma^2(F_o) + 8{\cdot}8 \times 10^{-5}(F_o)^2]$; adequacy of the weighting scheme confirmed by an analysis of the variance of the mean $w\Delta^2$ with F_o and $\sin\theta/\lambda$; scattering factors from *International Tables for X-ray Crystallography* (1974); both the real and imaginary components of anomalous dispersion were included for chlorine only (*International Tables for X-ray Crystallography*, 1974); Cl, S, O, N and methyl C atoms anisotropic, remaining C atoms isotropic, H atoms in idealized calculated positions (C—H = 0·97 Å), final $R = 0{\cdot}069$, $R_w = 0{\cdot}058$; in final cycle $(\Delta/\sigma)_{max} = 0{\cdot}1$, final $\Delta\rho$ excursions $\leq|0{\cdot}2|$ e Å^{-3}. IBM 4331 computer of the University of Messina with *SHELX*76 (Sheldrick, 1976).

Discussion. The final structural parameters are given in Table 1,* and interatomic distances and interbond angles with e.s.d.'s calculated from the full variance–covariance matrix are in Table 2. A perspective view of the molecule with the atom-numbering scheme is presented in Fig. 1.

The present X-ray analysis demonstrates unequivocally that the product examined is 2,2′-bis(4-chlorophenyl)-5,5′-dimethyl-[3,3′-bi-1,3-thiazolidine]-4,4′-dione. Four C atoms of F2TD2, *i.e.* C(7), C(8), C(12) and C(14), exhibit chirality. The observed C(sp^2)—Cl distances of 1·78 (1) and 1·79 (1) Å are significantly longer not only than the expected C(aryl)—

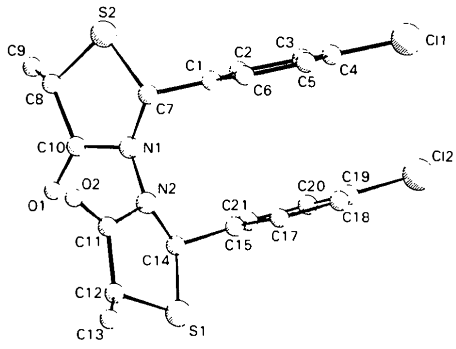

Fig. 1. A view down **b** of the F2TD2 molecule, with the atom-numbering scheme.

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* Lists of structure factors, anisotropic thermal parameters, least-squares-planes' data, torsion angles and ring-puckering coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39025 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Cl = 1·73 Å value but also than those (1·72–1·76 Å) usually found by X-ray diffraction in analyses of standard accuracy (Herbstein, 1979). Probably the e.s.d.'s are optimistic, so the differences appear significant. Bond lengths and valence angles of the phenyl rings range from 1·33 (1) to 1·40 (1) Å and from 116 (1) to 125 (1)° respectively. The mean of the bond lengths, 1·375 (1) Å, is shorter than the accepted value of 1·397 Å (Pauling, 1960). In contrast, the mean of the angles, 120 (1)°, represents the standard value. The mean planes through the two C_6 rings are approximately parallel, making an angle of about 3° with each other. In addition, a mean distance of about 3·3 Å (3·25–3·37 Å) between these planes is observed. These data, along with the overlap of the two phenyl rings (Fig. 2), indicate an intramolecular interaction between the phenyl groups, which would be responsible for the overall conformation of the F2TD2 molecule.

There are two independent thiazolidine rings in the molecule: C(7)S(2)C(8)C(10)N(1) and C(14)S(1)-C(12)C(11)N(2) (hereinafter rings I and II, respectively). It is evident that they cannot be planar. In particular, the puckering amplitude Q, which defines quantitatively the degree of puckering (Cremer & Pople, 1975) is 0·20 (1) and 0·34 (1) Å, for rings I and II, respectively. Within ring I there is a pseudo mirror plane through C(7) and the mid-point of the C(8)–C(10) bond. Fig. 3(*a*) and the asymmetry parameter of Duax, Weeks & Rohrer (1976), ΔC_s [C(7)] = 3·7 (9)°, indicate that ring I assumes an envelope conformation. In addition, C(7) is 0·33 (1) Å out of the plane of S(2)N(1)C(8)C(10) on the side opposite the substituent groups. Within ring II there is a pseudo twofold axis through C(11) and the mid-point of the C(14)–S(1) bond. Fig. 3(*b*) and the value of ΔC_2 [C(11)] (Duax *et al.*, 1976) of 2·7 (9)° indicate that the conformation of ring II is half-chair. Finally C(13) is 0·55 (1) Å from the mean plane through the ring on the same side as the oxygen and the chlorophenyl group.

Though the rings differ conformationally the corresponding bond distances and angles agree very well. In addition, the molecular dimensions of the five-membered rings fall within the ranges of the observed distances and angles in accurate crystal-structure studies on thiazolidine rings (Parthasarathy, Paul & Korytnyk, 1976; Hickel, Leger, Carpy, Vigorita, Chimirri & Grasso, 1983).

The geometry of the bonds about N(1) and N(2) tends to be tetrahedral, the N atoms being about

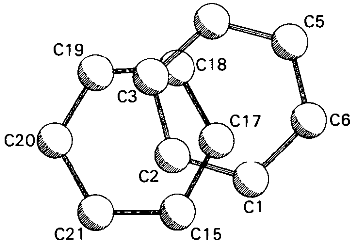

Fig. 2. Overlap of the phenyl rings in F2TD2.

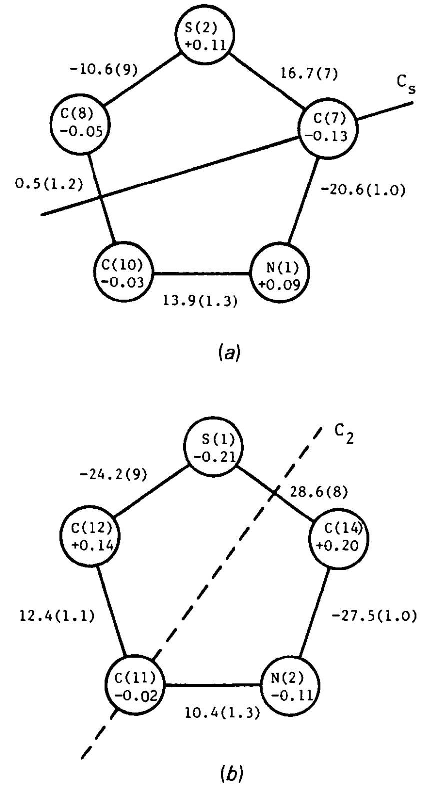

Fig. 3. The puckering of the five-membered rings (*a*) I and (*b*) II in F2TD2. In the circles the numerical values are the perpendicular displacements (Å) (average e.s.d. 7 × 10^{-3} Å) of the corresponding atoms of the mean plane through the ring. (Torsion angles in degrees.)

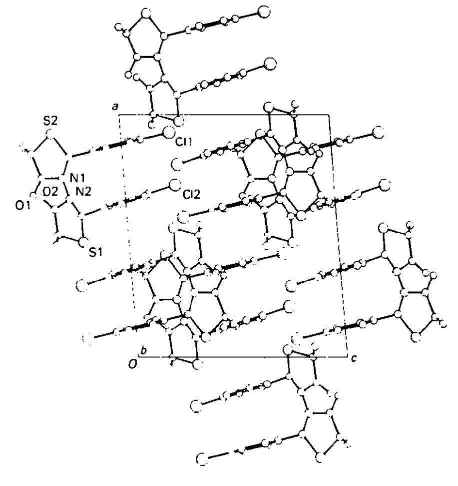

Fig. 4. The crystal packing as viewed down **b**.

0·27 (1) Å out of the plane through the three bonded atoms. The departure from the tetrahedral value may be explained by the ring strain. The observed N(1)—N(2) bond length of 1·41 (1) Å is very close to that found in the related compound diacetylhydrazine (Shintani, 1960) and falls within the range of distances observed for this bond in analogous systems (Jensen & Lingafelter, 1961; Karle & Karle, 1965). Packing is due mainly to van der Waals interactions and all intermolecular contacts agree with those predicted from radii-sum rules. The F2TD2 crystal structure, as viewed down **b**, is presented in Fig. 4.

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Structure of 1,3,5,7-Tetranitroadamantane,* $C_{10}H_{12}N_4O_8$

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Abstract. $M_r = 316\cdot23$, tetragonal, $P\bar{4}2_1c$, $a = b = 7\cdot874$ (2), $c = 10\cdot552$ (2) Å, $V = 654\cdot2$ (2) Å^3, $Z = 2$, $D_x = 1\cdot605$ Mg m^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1\cdot54178$ Å, $\mu = 1\cdot24$ mm^{-1}, $F(000) = 328$, $T = 300$ K. Final $R = 0\cdot027$ for 296 independent observed reflections. The molecule lies on a crystallographic $\bar{4}$ axis coincident with the axis through opposing secondary C atoms in the adamantane cage. The nitro groups are rotated approximately 15° from a symmetrical eclipsed position with the adjacent cage bonds to the C atoms on the $\bar{4}$ axis. The crystal symmetry is identical to that of the low-temperature form of the unsubstituted adamantane.

Introduction. The title compound (TNA) was provided by G. Sollott who first synthesized the material (Sollott & Gilbert, 1980). This compound was investigated as a part of a continuing program to examine the structures of high-density polynitro organic compounds. It is one of a series of nitroadamantanes examined (George & Gilardi, 1983) to provide a library of observed structural parameters for energetic organic substituents. These are used to evaluate and modify semi-empirical parameters used to predict the properties of nitro-organic compounds by methods of quantum chemistry or conformational energy analysis.

Experimental. Clear 0·65 × 0·65 × 0·75 mm crystal, m.p. 634–636 K. Automatic Picker four-circle diffractometer upgraded with Krisel Control automation, diffracted-beam graphite monochromator, Cu $K\alpha$. 20 centered reflections within $40 \le 2\theta \le 82°$ used for measuring lattice parameters. No absorption correction applied. $(\sin\theta/\lambda)_{\max} = 0\cdot56$ Å^{-1}, range of hkl: $0 \le h \le 6$, $-8 \le k \le 8$, $-11 \le l \le 11$; standards 220, $2\bar{2}0$ and 245 with maximum variation of 2, 2, and 4%, respectively over data collection; $\theta/2\theta$ scan mode, scan width 2°, scan rate a function of the count rate; 1854 reflections measured, 296 unique, $R_{\mathrm{int}} = 0\cdot029$, 296 observed with $I \ge 2\sigma(I)$. Structure solved by direct methods using *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980), H atoms located in difference maps; final refinement by full-matrix least-squares program *ORXFLS*3 (Busing, Martin, Levy, Ellison, Hamilton, Ibers, Johnson & Thiessen, 1975), function minimized $\sum w(|F_o|-|F_c|)^2$ where $w = 1/\sigma^2(F_o)$; standard deviation of the observed structure factor is $\sigma^2_F = QI/4\mathrm{Lp}\ [(\sigma_I/I)^2 + (\sigma_Q/Q)^2]$ where Lp is the Lorentz–polarization factor, Q is the attenuation factor used when source is attenuated for intense peaks, σ_I/I includes a counting statistics term and a term proportional to the intensity for random instrumental errors (0·02 in this work) (Gilardi, 1973). 63 parameters refined: all atom coordinates, anisotropic

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* Adamantane is tricyclo[3.3.1.1^{3,7}]decane.

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