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Orthorhombic and Triclinic Forms of 2-Chloro-5-*p*-toluoylamino-*N*-*p*-tolyl-4-*p*-tolylamino-6-pyrimidinecarboxamide and 2-Chloro-5-(*p*-chlorobenzoylamino)-*N*-*p*-tolyl-4-*p*-tolylamino-6-pyrimidinecarboxamide

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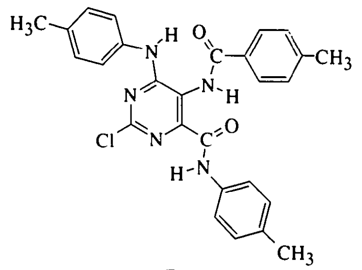
Abstract

2-Chloro-5-*p*-toluoylamino-*N*-*p*-tolyl-4-*p*-tolylamino-6-pyrimidinecarboxamide, $C_{27}H_{24}ClN_5O_2$, crystallizes in two forms: orthorhombic (I) and triclinic (I*a*). The orthorhombic form is almost isomorphous with the crystals of *N*-*p*-tolyl-5-benzoylamino-2-chloro-4-*p*-tolylamino-6-pyrimidinecarboxyamide. The triclinic form is almost isomorphous with the crystals of 2-chloro-5-(*p*-chlorobenzoylamino)-*N*-*p*-tolyl-4-*p*-tolylamino-6-pyrimidinecarboxamide, $C_{26}H_{21}Cl_2N_5O_2$ (II). The molecules of (I), (I*a*) and (II) are almost planar but are slightly bowed: the near-planarity is due to the intramolecular hydrogen bonds which are almost identical in all these structures, with N—H amide groups participating in intramolecular hydrogen bonds as donors, while each carbonyl O atom and one pyrimidine N atom are acceptors. In crystals of (I) the molecules are arranged in polymeric chains running along the *a* axis. In crystals of (I*a*) and (II) the molecules are arranged in dimers linked across crystallographic inversion centres by weak intermolecular hydrogen bonds.

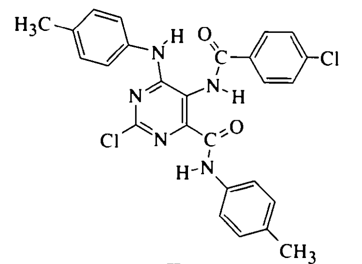
Comment

Several compounds with an amide moiety bound to an aromatic or heteroaromatic ring system may become potentially active agents influencing the central nervous system. The present structures belong to this class of compounds which act by blocking the dopamine D_2 receptor (Kebabian & Calne, 1979; Van Tol *et al.*, 1991). An earlier structural study of this class of compounds showed that the conformation of the molecules in the solid state is approximately planar and that the molecules form a network of intramolecular hydrogen bonds, which make pseudo-rings between amide groups fused to aromatic rings (De Winter, Verlinde, Blaton, Peeters & De Ranter, 1990; De Winter, Blaton, Peeters & De Ranter, 1990; Ueda, Marubayashi, Hayano, Murakami & Tahara, 1991).

The two present compounds do not differ significantly, the difference between them being in the *para* position of the aromatic substituents in the fifth position of the pyrimidine ring (Figs. 1 and 3). The structure of (I) is almost isomorphous with *N*-*p*-tolyl-5-benzoylamino-2-chloro-4-*p*-tolylamino-6-pyrimidinecarboxyamide (Mazurek, Lis & Jasztold-Howorko, 1995), and the structure of (I*a*) is almost isomorphous with the structure (II).



(I)



(II)

The compounds are built from four different blocks connected to the pyrimidine ring: the Cl atom, the *p*-tolylamine group, the *p*-toluylamine group [in (I) and (I*a*)] or the *p*-chlorobenzoylamine group [in (II)] and the tolylamide group. In all three structures the bond lengths and the values of the angles are almost the same, and the most significant differrence is observed for the C45—C46 bond length [1.343 (4), 1.385 (4) and 1.390 (4) Å for (I), (I*a*) and (II), respectively].

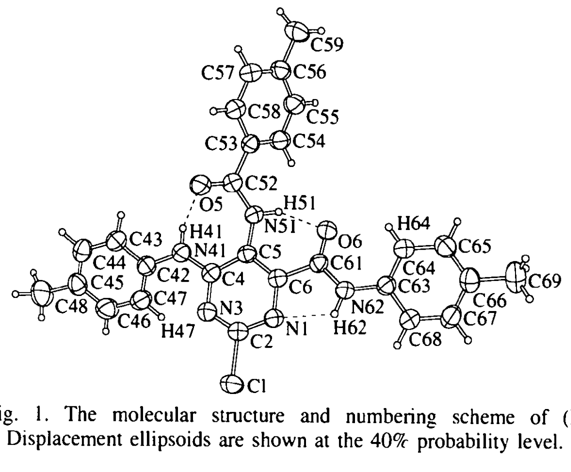


Fig. 1. The molecular structure and numbering scheme of (I). Displacement ellipsoids are shown at the 40% probability level.

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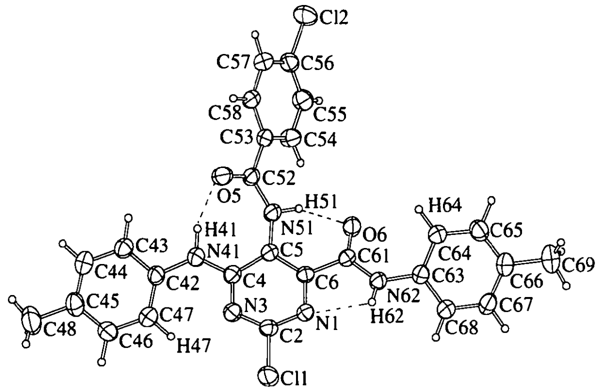

Fig. 2. The molecular structure and the numbering scheme of (II). Displacement ellipsoids are shown at the 40% probability level.

In (I), (I*a*) and (II) the pyrimidine ring deviates from strict planarity being slightly boat-shaped with C2 and C5 at the 'bows'; in all three cases, the largest deviations from the pyrimidine ring plane occur for C5 and are −0.028 (1), −0.032 (1) and −0.033 (2) Å for (I), (I*a*) and (II), respectively. This feature was observed previously for simple derivatives of pyrimidine (Furberg & Aas, 1975; Furberg, Grøgaard & Smedsrud, 1979). The inductive effect of the Cl atom at position 2 could explain the shortening of the N1—C2 bond length [1.308 (3), 1.308 (3) and 1.314 (3) Å for (I), (I*a*) and (II), respectively] and widening of the N1—C2—N3 angle [129.9 (2), 130.0 (2) and 129.4 (3)° for (I), (I*a*) and (II), respectively] in relation to the unsubstituted pyrimidine, as was observed for 2-chloropyrimidine (Furberg & Aas, 1975). The resonance between the free-electron pair on N41 and the pyrimidine ring could explain the elongation of the C4—C5 bond length [1.433 (3), 1.429 (3) and 1.430 (3) Å for (I), (I*a*) and (II), respectively] in comparison with that in the unsubstituted pyrimidine (Furberg & Aas, 1975) and the shortening of the C4—N41 bond length [1.351 (3), 1.347 (3) and 1.352 (3) Å for (I), (I*a*) and (II), respectively] in relation to single C—N amine bonds (Allen *et al.*, 1991). A similar effect was observed in the 2-aminopyrimidines and in other aminopyrimidines (Furberg & Aas, 1975; Dattagupta, Kröger & Saenger, 1977; Korbonits, Simon & Kolonits, 1991). The rest of the geometrical parameters of these molecules are not significantly different from those in other amide aromatic compounds.

The almost planar conformation of these molecules is the result of the intramolecular hydrogen-bonding network and two short intramolecular distances between aromatic H atoms and heteroatoms, namely H47···N3 and H64···O61. The amine and amide N atoms are utilized as donors and each carbonyl O atom and pyrimidine N1 atom are acceptors in the intramolecular hydrogen bonds. The intramolecular hydrogen bonds form three pseudo-rings fused with pyrimidine: O5 is linked to N41 forming the seven-membered pseudo-ring, O6 is linked to N51 forming the six-membered pseudo-ring, and N1 is linked to N62 forming the five-membered pseudo-ring. In (I*a*) and (II) the distances are a little shorter for O6···N51 and for N1···N62 and a little longer for O5···N41 than in (I). The angles *D*—H···*A* are almost the same for these molecules. The amide hydrogen H62 atom is used in bifurcated hydrogen bonds (Taylor, Kennard & Versichel, 1984): one of these contacts is strong and intramolecular, shorter than 2.7 Å, while the other is weak and intermolecular with the *D*—H···*A* angle *ca* 140°. This contact is particularly weak in the triclinic form (*D*···*A* > 3 Å).

The conformation of the title molecules in the solid state is a little different for the triclinic and orthorhombic forms. Fig. 3 shows a superposition of the three structures centred on the pyrimidine ring. In (I), all rings except the *p*-toluyl ring are almost coplanar. In (I*a*) and (II) the substituent rings are much more twisted in relation to the pyrimidine ring. The aromatic rings from the *p*-tolylamine and amide groups are more twisted in relation to the pyrimidine ring than in (I) or in *N*-*p*-tolyl-5-benzoylamino-2-chloro-4-*p*-tolylamino-6-pyrimidinecarboxyamide (Mazurek *et al.*, 1995). The phenyl rings from the *p*-toluylamine in (I*a*) and the *p*-chlorobenzoylamine in (II) are in the *gauche* position to the pyrimidine ring as in (I), but the angle between them and the pyrimidine ring is greater. The largest distortion from planarity is observed for (II). For all three structures the relation between the angles of the aromatic rings from *p*-toluylamine or *p*-chlorobenzoylamine and *p*-tolylamine, and from *p*-toluylamine or *p*-chlorobenzoylamine and the amide group is almost the same. The angles between the aromatic rings in all three molecules are listed in Table 10.

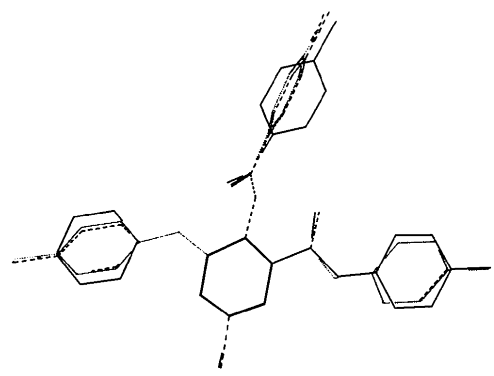

Fig. 3. A comparison of structures (I) (solid line), (I*a*) (dashed line) and (II) (dotted line). The common reference is the pyrimidine ring.

In (I) (Fig. 2) the molecules are arranged in layers parallel to the *ac* plane, with weak intermolecular hydrogen bonds between layers. Each molecule is linked to two other symmetry-related molecules by hydrogen bonds in which the amide N62 atom is a donor of hydrogen and the carbonyl atom O5 is an acceptor.

In the crystal structures of (I*a*) and (II), molecules are arranged in layers parallel to the *bc* plane. The molecules are joined in dimers by the weak hydrogen bonds through the symmetry centre: these involve N62 as the donors and O5 as the acceptors of the hydrogen bond, respectively.

Experimental

The compounds were obtained by the method described previously (Jasztold-Howorko *et al.*, 1992). Crystals of (I) were obtained by slow evaporation of methylene chloride. Crystals of (I*a*) and (II) were obtained by slow evaporation of dimethylformamide.

Compound (I)

Crystal data

$C_{27}H_{24}ClN_5O_2$
$M_r = 485.96$
Orthorhombic
Pbca
$a = 11.851\ (6)$ Å
$b = 15.298\ (9)$ Å
$c = 27.347\ (15)$ Å
$V = 4958\ (5)$ Å^3
$Z = 8$
$D_x = 1.302\ (2)$ Mg m^{-3}
$D_m = 1.30$ Mg m^{-3}
D_m measured by flotation in an aqueous solution of $Pb(NO_3)_2$

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 25 reflections
$\theta = 10$–$20°$
$\mu = 1.639$ mm^{-1}
$T = 303\ (2)$ K
Hexagonal plate
0.82 × 0.60 × 0.22 mm
Yellow

Data collection

Kuma KM4 automatic diffractometer
Profile data from $\omega/2\theta$ scans
Absorption correction: analytical (*SHELX*76; Sheldrick, 1976)
$T_{min} = 0.418$, $T_{max} = 0.727$
5887 measured reflections
5254 independent reflections

3247 observed reflections [$I > 2\sigma(I)$]
$R_{int} = 0.0239$
$\theta_{max} = 80°$
$h = 0 \rightarrow 14$
$k = 0 \rightarrow 19$
$l = 0 \rightarrow 34$
3 standard reflections monitored every 100 reflections
intensity decay: 3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0425$
$wR(F^2) = 0.1161$
$S = 1.039$
3247 reflections
413 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.082P)^2 + 1.00P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = -0.14$

$\Delta\rho_{max} = 0.21$ e Å^{-3}
$\Delta\rho_{min} = -0.35$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.00046 (8)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (I)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	U_{eq}
Cl	0.03507 (5)	0.77797 (4)	0.07266 (2)	0.05868 (18)
N1	0.18352 (15)	0.82556 (12)	0.00806 (6)	0.0474 (4)
C2	0.16840 (18)	0.81448 (14)	0.05504 (7)	0.0449 (5)
N3	0.23763 (15)	0.82850 (12)	0.09155 (6)	0.0483 (4)
C4	0.34154 (18)	0.85598 (14)	0.08004 (7)	0.0455 (5)
C5	0.37356 (17)	0.86575 (13)	0.02981 (7)	0.0427 (5)
C6	0.28906 (17)	0.85220 (13)	−0.00418 (7)	0.0434 (5)
N41	0.41269 (18)	0.87953 (14)	0.11632 (7)	0.0563 (5)
C42	0.3950 (2)	0.88367 (16)	0.16726 (8)	0.0537 (6)
C43	0.4845 (3)	0.9112 (3)	0.19491 (11)	0.0866 (10)
C44	0.4740 (4)	0.9177 (3)	0.24569 (12)	0.0991 (13)
C45	0.3772 (3)	0.8965 (2)	0.26947 (9)	0.0745 (8)
C46	0.2906 (4)	0.8702 (3)	0.24137 (11)	0.0998 (13)
C47	0.2962 (3)	0.8638 (3)	0.19081 (10)	0.0905 (12)
C48	0.3654 (6)	0.9025 (5)	0.32448 (13)	0.1119 (16)
N51	0.47940 (14)	0.89642 (12)	0.01386 (7)	0.0467 (4)
C52	0.58314 (18)	0.87047 (14)	0.02840 (8)	0.0476 (5)
O5	0.59881 (14)	0.82804 (12)	0.06602 (6)	0.0639 (5)
C53	0.67856 (18)	0.89682 (14)	−0.00360 (8)	0.0486 (5)
C54	0.6652 (3)	0.92244 (16)	−0.05200 (8)	0.0537 (6)
C55	0.7579 (3)	0.94294 (18)	−0.08016 (9)	0.0610 (6)
C56	0.8655 (3)	0.93976 (18)	−0.06096 (11)	0.0665 (7)
C57	0.8784 (3)	0.9142 (3)	−0.01315 (13)	0.0818 (9)
C58	0.7867 (3)	0.8928 (2)	0.01561 (11)	0.0681 (7)
C59	0.9659 (4)	0.9643 (4)	−0.0922 (2)	0.0966 (13)
C61	0.30620 (18)	0.87113 (14)	−0.05775 (7)	0.0463 (5)
O6	0.37820 (14)	0.92326 (11)	−0.07164 (6)	0.0603 (5)
N62	0.23681 (18)	0.82760 (14)	−0.08745 (6)	0.0540 (5)
C63	0.2251 (3)	0.83582 (16)	−0.13893 (8)	0.0574 (6)
C64	0.3073 (4)	0.8729 (3)	−0.16835 (11)	0.0874 (10)
C65	0.2863 (5)	0.8795 (3)	−0.21841 (12)	0.1098 (15)
C66	0.1892 (5)	0.8507 (3)	−0.23952 (10)	0.1000 (13)
C67	0.1103 (4)	0.8127 (3)	−0.20974 (11)	0.0930 (11)
C68	0.1283 (3)	0.80473 (19)	−0.15992 (9)	0.0683 (7)
C69	0.1682 (10)	0.8609 (6)	−0.29398 (14)	0.155 (3)

Table 2. *Selected geometric parameters (Å, °) for (I)*

Cl—C2	1.744 (2)	C5—N51	1.408 (3)
N1—C2	1.308 (3)	C6—C61	1.507 (3)
N1—C6	1.357 (3)	N41—C42	1.410 (3)
C2—N3	1.310 (3)	N51—C52	1.352 (3)
N3—C4	1.339 (3)	C52—O5	1.231 (3)
C4—N41	1.351 (3)	C61—O6	1.228 (3)
C4—C5	1.433 (3)	C61—N62	1.334 (3)
C5—C6	1.382 (3)	N62—C63	1.420 (3)
C2—N1—C6	114.0 (2)	N41—C4—C5	120.7 (2)
N1—C2—N3	129.9 (2)	C6—C5—N51	119.1 (2)
N1—C2—Cl	115.9 (2)	C6—C5—C4	115.9 (2)
N3—C2—Cl	114.2 (2)	N51—C5—C4	124.6 (2)
C2—N3—C4	116.6 (2)	N1—C6—C5	123.2 (2)
N3—C4—N41	119.0 (2)	N1—C6—C61	114.9 (2)
N3—C4—C5	120.1 (2)	C5—C6—C61	121.8 (2)
N1—C6—C61—O6	153.3 (3)	O5—C52—C53—C58	−16.4 (4)
N1—C6—C61—N62	−26.1 (3)	N51—C52—C53—C54	−19.0 (4)
C5—C6—C61—O6	−23.4 (4)	N51—C52—C53—C58	163.1 (3)
C5—C6—C61—N62	157.2 (2)	O6—C61—N62—C63	−4.9 (4)
C5—N51—C52—O5	−16.2 (4)	C61—N62—C63—C64	19.5 (5)
O5—C52—C53—C54	161.5 (3)	C61—N62—C63—C68	−161.1 (3)

Table 3. *Hydrogen-bonding geometry (Å, °) for (I)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N41—H41···O5	0.81 (3)	1.99 (3)	2.716 (3)	148 (3)
N51—H51···O6	0.87 (3)	1.89 (3)	2.660 (3)	147 (3)
N62—H62···N1	0.84 (3)	2.28 (3)	2.687 (3)	110 (3)

C47—H47···N3	0.94 (4)	2.27 (4)	2.853 (3)	119 (3)
C64—H64···O6	0.92 (4)	2.41 (4)	2.880 (4)	112 (3)
N62—H62···O5[i]	0.84 (3)	2.18 (3)	2.947 (3)	153 (3)

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

Compound (Ia)

Crystal data

$C_{27}H_{24}ClN_5O_2$
$M_r = 485.96$
Triclinic
$P\bar{1}$
$a = 7.375$ (2) Å
$b = 11.888$ (6) Å
$c = 14.103$ (6) Å
$\alpha = 101.34$ (4)°
$\beta = 94.75$ (3)°
$\gamma = 91.20$ (3)°
$V = 1207.2$ (9) Å^3
$Z = 2$
$D_x = 1.337$ Mg m^{-3}
$D_m = 1.33$ Mg m^{-3}
D_m measured by flotation in acetone/CCl_4

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 25 reflections
$\theta = 10$–22°
$\mu = 1.683$ mm^{-1}
$T = 298$ (2) K
Prism
0.40 × 0.15 × 0.10 mm
Yellow

Data collection

Kuma KM4 automatic diffractometer
Profile data from $\omega/2\theta$ scans
Absorption correction: none
5168 measured reflections
4649 independent reflections
3165 observed reflections [$I > 2\sigma(I)$]

$R_{int} = 0.0395$
$\theta_{max} = 80°$
$h = -9 \rightarrow 7$
$k = -15 \rightarrow 15$
$l = -17 \rightarrow 17$
3 standard reflections monitored every 100 reflections intensity decay: 3.7%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0393$
$wR(F^2) = 0.1083$
$S = 1.048$
3165 reflections
412 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.072P)^2 + 0.26P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.11$
$\Delta\rho_{max} = 0.17$ e Å^{-3}
$\Delta\rho_{min} = -0.29$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 4. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (Ia)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Cl	0.01272 (10)	0.85314 (5)	0.53968 (5)	0.0659 (3)
N1	0.1484 (3)	0.65386 (14)	0.49220 (12)	0.0443 (4)
C2	0.1031 (3)	0.72793 (17)	0.56721 (16)	0.0449 (5)
N3	0.1168 (3)	0.72267 (15)	0.65973 (13)	0.0463 (5)
C4	0.1785 (3)	0.62464 (18)	0.68173 (15)	0.0437 (5)
C5	0.2230 (3)	0.53274 (16)	0.60656 (15)	0.0409 (5)
C6	0.2124 (3)	0.55464 (16)	0.51375 (15)	0.0403 (5)
N41	0.1990 (3)	0.61477 (17)	0.77548 (13)	0.0525 (5)
C42	0.1781 (4)	0.69755 (19)	0.85998 (15)	0.0476 (5)
C43	0.1260 (4)	0.6569 (3)	0.94031 (17)	0.0528 (6)
C44	0.1156 (4)	0.7316 (3)	1.02774 (18)	0.0596 (7)
C45	0.1548 (4)	0.8474 (3)	1.03859 (17)	0.0605 (7)
C46	0.2045 (5)	0.8863 (3)	0.9578 (2)	0.0693 (8)
C47	0.2167 (5)	0.8132 (3)	0.86955 (19)	0.0625 (7)
C48	0.1497 (8)	0.9284 (4)	1.1359 (3)	0.0932 (12)
N51	0.2941 (3)	0.42841 (15)	0.62280 (13)	0.0451 (4)
C52	0.2334 (3)	0.35843 (17)	0.68003 (15)	0.0446 (5)
O5	0.1129 (3)	0.38464 (14)	0.73444 (13)	0.0593 (5)
C53	0.3229 (3)	0.24649 (17)	0.67180 (14)	0.0431 (5)
C54	0.4845 (4)	0.2223 (2)	0.63011 (19)	0.0551 (6)
C55	0.5572 (4)	0.1150 (3)	0.6238 (2)	0.0615 (7)
C56	0.4699 (4)	0.02883 (19)	0.65834 (17)	0.0551 (6)
C57	0.3100 (4)	0.0542 (3)	0.70082 (19)	0.0609 (7)
C58	0.2373 (4)	0.1610 (2)	0.70758 (18)	0.0555 (6)
C59	0.5458 (6)	−0.0892 (3)	0.6494 (3)	0.0771 (9)
C61	0.2761 (3)	0.47198 (17)	0.42875 (14)	0.0413 (5)
O6	0.3628 (3)	0.38721 (13)	0.43899 (11)	0.0540 (4)
N62	0.2321 (3)	0.50146 (15)	0.34281 (13)	0.0446 (4)
C63	0.2769 (3)	0.44316 (18)	0.25039 (15)	0.0441 (5)
C64	0.2900 (4)	0.3252 (2)	0.22741 (18)	0.0539 (6)
C65	0.3239 (4)	0.2734 (3)	0.13469 (19)	0.0590 (6)
C66	0.3467 (4)	0.3358 (3)	0.06273 (17)	0.0547 (6)
C67	0.3350 (4)	0.4534 (3)	0.08775 (18)	0.0582 (6)
C68	0.3008 (4)	0.5074 (3)	0.18037 (17)	0.0540 (6)
C69	0.3767 (6)	0.2771 (4)	−0.0387 (3)	0.0771 (9)

Table 5. *Selected geometric parameters (Å, °) for (Ia)*

Cl—C2	1.743 (2)	C5—N51	1.409 (3)
N1—C2	1.308 (3)	C6—C61	1.507 (3)
N1—C6	1.359 (3)	N41—C42	1.410 (3)
C2—N3	1.314 (3)	N51—C52	1.361 (3)
N3—C4	1.342 (3)	C52—O5	1.227 (3)
C4—N41	1.347 (3)	C61—O6	1.231 (2)
C4—C5	1.429 (3)	C61—N62	1.343 (3)
C5—C6	1.380 (3)	N62—C63	1.419 (3)
C2—N1—C6	114.3 (2)	N41—C4—C5	120.7 (2)
N1—C2—N3	130.0 (2)	C6—C5—N51	119.0 (2)
N1—C2—Cl	114.6 (2)	C6—C5—C4	116.3 (2)
N3—C2—Cl	115.4 (2)	N51—C5—C4	124.3 (2)
C2—N3—C4	116.2 (2)	N1—C6—C5	122.7 (2)
N3—C4—N41	119.0 (2)	N1—C6—C61	114.6 (2)
N3—C4—C5	120.3 (2)	C5—C6—C61	122.7 (2)
N1—C6—C61—O6	168.5 (2)	O5—C52—C53—C58	16.0 (4)
N1—C6—C61—N62	−10.2 (3)	N51—C52—C53—C54	15.8 (4)
C5—C6—C61—O6	−9.7 (4)	N51—C52—C53—C58	−163.6 (2)
C5—C6—C61—N62	171.6 (2)	O6—C61—N62—C63	−0.6 (4)
C5—N51—C52—O5	−7.4 (4)	C61—N62—C63—C64	33.1 (4)
O5—C52—C53—C54	−164.5 (4)	C61—N62—C63—C68	−149.6 (3)

Table 6. *Hydrogen-bonding geometry (Å, °) for (Ia)*

D—H···A	D—H	H···A	D···A	D—H···A
N41—H41···O5	0.87 (3)	1.96 (3)	2.732 (3)	146 (3)
N51—H51···O6	0.89 (3)	1.85 (3)	2.635 (3)	146 (3)
N62—H62···N1	0.88 (3)	2.14 (3)	2.620 (3)	114 (2)
C47—H47···N3	0.96 (3)	2.52 (3)	2.968 (3)	109 (3)
C64—H64···O6	0.90 (3)	2.49 (3)	2.931 (3)	111 (2)
N62—H62···O5[i]	0.88 (3)	2.45 (3)	3.124 (3)	134 (2)

Symmetry code: (i) $-x, 1 - y, 1 - z$.

Compound (II)

Crystal data

$C_{26}H_{21}Cl_2N_5O_2$
$M_r = 506.38$

Cu $K\alpha$ radiation
$\lambda = 1.54180$ Å

Triclinic
$P\overline{1}$
$a = 7.411$ (2) Å
$b = 11.784$ (2) Å
$c = 13.989$ (4) Å
$\alpha = 101.61$ (2)°
$\beta = 94.29$ (2)°
$\gamma = 92.15$ (2)°
$V = 1191.6$ (5) Å^3
$Z = 2$
$D_x = 1.411$ Mg m^{-3}
$D_m = 1.400$ Mg m^{-3}
D_m measured by flotation in acetone/CCl_4

Cell parameters from 25 reflections
$\theta = 10$–27°
$\mu = 2.737$ mm^{-1}
$T = 294$ (1) K
Prism
0.30 × 0.25 × 0.08 mm
Yellow

Data collection

Kuma KM4 automatic diffractometer
Profile data from $\omega/2\theta$ scans
Absorption correction: none
5378 measured reflections
3278 independent reflections
3061 observed reflections [$I > 2\sigma(I)$]

$R_{int} = 0.0367$
$\theta_{max} = 76°$
$h = -9 \rightarrow 9$
$k = -14 \rightarrow 14$
$l = -17 \rightarrow 17$
3 standard reflections monitored every 100 reflections intensity decay: 3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0460$
$wR(F^2) = 0.1232$
$S = 1.068$
3278 reflections
401 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.088P)^2 + 0.24P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.05$

$\Delta\rho_{max} = 0.31$ e Å^{-3}
$\Delta\rho_{min} = -0.33$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0041 (7)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 7. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (II)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Cl1	0.00390 (11)	0.85296 (6)	0.54222 (5)	0.0639 (3)
N1	0.1453 (3)	0.65492 (17)	0.49315 (14)	0.0418 (5)
C2	0.1004 (4)	0.7299 (3)	0.56942 (17)	0.0426 (6)
N3	0.1173 (3)	0.72485 (18)	0.66264 (14)	0.0445 (5)
C4	0.1816 (3)	0.6275 (3)	0.68392 (16)	0.0411 (5)
C5	0.2251 (3)	0.5348 (3)	0.60764 (16)	0.0392 (5)
C6	0.2111 (3)	0.5567 (2)	0.51421 (16)	0.0376 (5)
N41	0.2070 (4)	0.6184 (2)	0.77876 (15)	0.0507 (6)
C42	0.1873 (4)	0.7036 (3)	0.86393 (17)	0.0458 (6)
C43	0.1253 (4)	0.6655 (3)	0.94345 (19)	0.0506 (6)
C44	0.1150 (4)	0.7419 (3)	1.0312 (2)	0.0562 (7)
C45	0.1625 (4)	0.8579 (3)	1.0421 (2)	0.0591 (7)
C46	0.2239 (5)	0.8954 (3)	0.9617 (3)	0.0650 (8)
C47	0.2372 (5)	0.8189 (3)	0.8732 (3)	0.0598 (8)
C48	0.1548 (9)	0.9419 (6)	1.1389 (4)	0.0898 (13)
N51	0.2964 (3)	0.43012 (19)	0.62327 (15)	0.0436 (5)
C52	0.2342 (4)	0.3589 (3)	0.68010 (17)	0.0422 (6)
O5	0.1140 (3)	0.38481 (16)	0.73542 (15)	0.0570 (5)
C53	0.3201 (4)	0.2453 (3)	0.67088 (16)	0.0408 (6)
C54	0.4804 (4)	0.2207 (3)	0.6278 (3)	0.0524 (7)
C55	0.5491 (5)	0.1121 (3)	0.6196 (3)	0.0594 (8)
C56	0.4561 (4)	0.0279 (3)	0.65505 (19)	0.0521 (7)
C57	0.2970 (5)	0.0510 (3)	0.6994 (3)	0.0560 (7)
C58	0.2305 (4)	0.1599 (3)	0.70736 (19)	0.0507 (6)
Cl2	0.53678 (12)	−0.11000 (6)	0.64291 (6)	0.0728 (3)
C61	0.2735 (3)	0.4734 (3)	0.42766 (16)	0.0396 (5)
O6	0.3604 (3)	0.38865 (16)	0.43722 (13)	0.0512 (5)
N62	0.2284 (3)	0.50260 (19)	0.34158 (14)	0.0430 (5)
C63	0.2716 (3)	0.4441 (3)	0.24744 (16)	0.0416 (6)
C64	0.2853 (4)	0.3253 (3)	0.2240 (2)	0.0521 (7)
C65	0.3226 (4)	0.2744 (3)	0.1301 (3)	0.0563 (7)
C66	0.3440 (4)	0.3373 (3)	0.05871 (18)	0.0522 (7)
C67	0.3306 (4)	0.4558 (3)	0.0844 (2)	0.0556 (7)
C68	0.2953 (4)	0.5102 (3)	0.17776 (19)	0.0508 (6)
C69	0.3754 (6)	0.2786 (5)	−0.0440 (3)	0.0710 (10)

Table 8. *Selected geometric parameters (Å, °) for (II)*

Cl1—C2	1.737 (2)	C6—C61	1.511 (3)
N1—C2	1.314 (3)	N41—C42	1.416 (3)
N1—C6	1.349 (3)	N51—C52	1.358 (3)
C2—N3	1.314 (3)	C52—O5	1.231 (3)
N3—C4	1.337 (3)	C56—Cl2	1.733 (3)
C4—N41	1.352 (3)	C61—O6	1.232 (3)
C4—C5	1.430 (3)	C61—N62	1.340 (3)
C5—C6	1.380 (3)	N62—C63	1.424 (3)
C5—N51	1.411 (3)		
C2—N1—C6	114.6 (2)	N41—C4—C5	120.3 (3)
N1—C2—N3	129.4 (3)	C6—C5—N51	119.3 (3)
N1—C2—Cl1	114.9 (2)	C6—C5—C4	116.0 (3)
N3—C2—Cl1	115.8 (2)	N51—C5—C4	124.5 (2)
C2—N3—C4	116.3 (3)	N1—C6—C5	123.0 (3)
N3—C4—N41	119.1 (3)	N1—C6—C61	114.7 (2)
N3—C4—C5	120.5 (2)	C5—C6—C61	122.3 (2)
N1—C6—C61—O6	169.2 (3)	O5—C52—C53—C58	15.6 (4)
N1—C6—C61—N62	−9.4 (3)	N51—C52—C53—C54	15.4 (4)
C5—C6—C61—O6	−9.3 (4)	N51—C52—C53—C58	−163.9 (3)
C5—C6—C61—N62	172.2 (3)	O6—C61—N62—C63	−0.5 (4)
C5—N51—C52—O5	−8.3 (4)	C61—N62—C63—C64	32.7 (4)
O5—C52—C53—C54	−165.1 (3)	C61—N62—C63—C68	−149.0 (3)

Table 9. *Hydrogen-bonding geometry (Å, °) for (II)*

D—H···A	D—H	H···A	D···A	D—H···A
N41—H41···O5	0.90 (4)	1.94 (4)	2.746 (3)	147 (3)
N51—H51···O6	0.91 (4)	1.83 (4)	2.632 (3)	145 (4)
N62—H62···N1	0.84 (4)	2.20 (4)	2.616 (3)	111 (3)
C47—H47···N3	0.98 (4)	2.52 (4)	2.985 (4)	109 (3)
C64—H64···O6	0.99 (3)	2.43 (3)	2.931 (3)	111 (3)
N62—H62···O5^i	0.84 (4)	2.46 (4)	3.127 (3)	137 (3)

Symmetry code: (i) $-x, 1-y, 1-z$.

Table 10. *Angles (°) between selected planes for (I), (Ia) and (II)*

	Planes					
	A/B	*A/C*	*A/D*	*B/C*	*B/D*	*C/D*
(I)	8.6 (2)	18.3 (1)	9.4 (2)	25.7 (1)	15.1 (2)	22.1 (2)
(I*a*)	34.0 (1)	56.0 (1)	20.8 (1)	51.8 (2)	13.8 (1)	48.4 (2)
(II)	38.6 (1)	56.7 (1)	21.7 (1)	49.5 (2)	17.4 (1)	47.4 (2)

Planes: *A* N1,C2,N3,C4,C5,C6; *B* C42,C43,C44,C45,C46,C47; *C* C53,C54,C55,C56,C57,C58; *D* C63,C64,C65,C66,C67,C68.

The oscillation and Weissenberg photographs as well as preliminary diffractometer results suggested the isomorphism of the crystals (I) with crystals of *N*-*p*-tolyl-5-benzoylamino-2-chloro-4-*p*-tolylamino-6-pyrimidinecarboxyamide (Mazurek *et* *al.*, 1995) and the crystals (I*a*) with crystals (II). The structure of (I) was solved by taking the published coordinates of the non-H atoms (Mazurek *et al.*, 1995). The structure of (II) was solved by direct methods (*SHELXS*86; Sheldrick, 1990) and its refined coordinates were used as a starting model for (I*a*). In the structure of (II) we noted rather high values for the anisotropic displacement parameters of the atoms forming the tolyl groups, especially the value of 0.284 (10) for U_{11} of C69. We tried unsuccessfully to develop a satisfactory disorder model for this group.

Although compound (II) has a higher value of μ than compound (I), an absorption correction was applied to the latter only: this was because the much larger crystal results in a higher value of μR (where R is the mean crystal radius) for (I) (*ca* 0.8) compared with that for (II) (0.4).

For all compounds, data collection: *KM*4 (Kuma Diffraction, 1987); cell refinement: *KM*4; data reduction: *KM*4; program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *ORTEP*II (Johnson, 1976)

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry, together with a structural diagram of (I*a*), have been deposited with the IUCr (Reference: BM1069). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Redetermination of Cholesteryl *p*-Toluenesulfonate at 150 K

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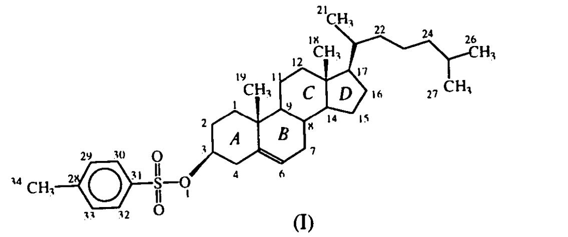
Abstract

Compared to a previous room-temperature study, the apparent shortening of the bond lengths in the C17 side chain of cholesteryl *p*-toluenesulfonate, $C_{34}H_{52}O_3S$, is much less pronounced at 150 K, and the uncertainties associated with the molecular geometry are much improved.

Comment

Room-temperature X-ray studies of cholesteryl derivatives may show bond-length anomalies or disorder in the C17 side chain (El-Shora, Palmer, Singh, Bhardwaj & Paul, 1984; Buchanan, Cox & Wardell, 1996*a*). We have recently used cholesteryl *p*-toluenesulfonate in the synthesis of metallated steroids (Buchanan, Cox & Wardell, 1996*b*) and have observed unusual geometries in this chain. The previously determined room-temperature crystal structure of the title compound (I) (Chandross & Bordner, 1977) exhibits such features but geometrical uncertainties are high. The current low-temperature study was performed to obtain a better molecular geometry of the steroid. The R value has improved from 0.092 to 0.049, the bond length uncertainties have decreased by a factor of about three and the apparent shortening of C—C bonds in the C17 side chain is less obvious at 150 K. For example, C24—C25 is 1.405 (26) Å at room temperature and 1.496 (7) Å at 150 K; the corresponding values for C25—C26 are 1.479 (32) and 1.505 (7) Å, respectively. It is probable that high anisotropic displacement parameters caused librational shortening of the C—C bonds lengths in the room-temperature study.



(I)