

- FRASSON, E., PANATTONI, C. & ZANNETTI, R. (1959). *Acta Cryst.* **12**, 1027–1031.
- GODYCKI, L. E. & RUNDLE, R. E. (1953). *Acta Cryst.* **6**, 487–495.
- HAMILTON, W. C. (1964). *Statistics in Physical Science*, p. 216. New York: Ronald Press.
- HARA, Y., SHIROTANI, I. & ONODERA, A. (1976). *Solid State Commun.* **19**, 171–176.
- HARTLEY, F. R. (1973). *The Chemistry of Platinum and Palladium*, pp. 121, 501. London: Applied Science Publishers.
- IBERS, J. A. (1962). *International Tables for X-ray Crystallography*, Vol. III, p. 202, Table 3.31A. Birmingham: Kynoch Press.
- IBERS, J. A. & HAMILTON, W. C. (1964). *Acta Cryst.* **17**, 781.
- JOHNSON, G. L. (1966). *Inorg. Synth.* **8**, 242.
- PFLUGER, C. E., HARLOW, R. L. & SIMONSEN, S. H. (1970). *Acta Cryst.* **B26**, 1631–1633.
- WILLIAMS, D. E., WOHLAUER, G. & RUNDLE, R. E. (1959). *J. Am. Chem. Soc.* **81**, 755–756.

Acta Cryst. (1979). **B35**, 633–639

The Crystal and Molecular Structure of *N*-(2-Chlorophenyl)-3,6-dithiacyclohexene-1,2-dicarboximide

BY M. BUKOWSKA-STRZYŻEWSKA*

Institute of General Chemistry, Technical University, 36 Żwirki, 90-924 Łódź, Poland

AND B. PNIEWSKA

Institute of Chemistry, Pedagogical University, Siedlce, Poland

(Received 23 June 1978; accepted 30 September 1978)

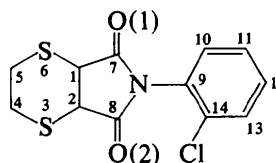
Abstract

Crystals of *N*-(2-chlorophenyl)-3,6-dithiacyclohexene-1,2-dicarboximide are monoclinic, space group $P2_1$, with $a = 8.226$ (1), $b = 16.056$ (2), $c = 14.604$ (2) Å and $\beta = 91.97$ (2)°. The three-dimensional intensity data (2770 independent reflections) were obtained with a Syntex $P2_1$ automated four-circle diffractometer. The structure was solved by direct methods and refined to a conventional R value of 6.2%. The unit cell contains three symmetrically independent molecules which are different optical isomers and have different deformations of individual rings and somewhat different bond lengths. The conformations of the 3,6-dithiacyclohexene rings are half-chair in molecules (I) and (III) and midway between sofa and half-chair in molecule (II). The asymmetry parameters of these rings are $\Delta C_2(\text{I}) = 0.7^\circ$, $\Delta C_2(\text{II}) = 15.1^\circ$, $\Delta C_s(\text{II}) = 14.1^\circ$ and $\Delta C_2(\text{III}) = 2.5^\circ$. The chlorophenyl and imide rings are planar in molecule (I) and the angle between their planes is 76.7° . The imide ring is not planar in molecule (II) and the dihedral angle between its best plane and the phenyl-ring plane is 84.1° . The imide and phenyl rings in molecule (III) are nearly planar but are more corrugated than in molecule (I). Bond distances, angles

and conformations of the three independent molecules are compared with those of molecules of DTTHP (3,6-dithia-3,4,5,6-tetrahydrophthalimide) and *N*-(4-chlorophenyl)-3,6-dithiacyclohexene-1,2-dicarboximide.

Introduction

The present work is part of a study of *N*-substituted derivatives of 3,6-dithiacyclohexene-1,2-dicarboximide (Bukowska-Strzyżewska, Dobrowolska & Pniewska, 1978; Bukowska-Strzyżewska & Pniewska, 1979). These compounds, which are related to thalidomide, show pharmacological activity which can be related to their stereochemistry. The atom-numbering system of the title compound is shown below.



The aim of this work was to obtain new data concerning the conformation of the 3,6-dithiacyclohexene ring and to determine the influence of the 2-chlorophenyl substituent on the conformation of the imide ring and the spatial shape of the molecule.

* Author to whom correspondence should be addressed.

Experimental

Single crystals of the title compound were kindly provided by Dr B. Rybczyński and Professor W. Hahn. A preliminary survey of film data collected with a Weissenberg camera indicated that the compound crystallized with monoclinic symmetry. The systematic absences ($0k0$ with k odd) suggest the possible space groups $P2_1/m$ (C_{2h}^2) and $P2_1$ (C_2). As the crystals show a piezoelectric effect, $P2_1$ was chosen. A small crystal approximately $0.15 \times 0.15 \times 0.25$ mm (glued to a glass fiber and mounted on a Syntex $P2_1$ diffractometer) was used to measure the cell constants and intensities. Unit-cell dimensions determined from preliminary Weissenberg photographs were refined by a least-squares procedure applied to measurements of 15 reflections. The density was measured by flotation in aqueous KI solution.

Crystal data

$C_{12}H_8ClNO_2S_2$	Space group $P2_1$
$a = 8.226$ (1) Å	$M_r = 297.78$
$b = 16.056$ (2)	$F(000) = 912$
$c = 14.604$ (2)	$D_x = 1.539$ Mg m $^{-3}$
$\beta = 91.97$ (2)°	$D_m = 1.54$ Mg m $^{-3}$
$V = 1927.71$ Å 3	$\mu(\text{Cu } K\alpha) = 5.646$ mm $^{-1}$
$Z = 6$	

Intensity data were collected by the θ - 2θ scan technique at a scan rate of 2° min^{-1} with monochromatized Cu $K\alpha$ ($\lambda = 1.5418$ Å) radiation. Two standard reflections were monitored frequently to check the stability of the system. No significant changes in the intensities of these reflections were observed. Structure amplitudes were derived in the usual manner for 2770 unique observations for which $F_o^2 \geq 3\sigma(F_o^2)$. Absorption corrections were ignored.

Determination and refinement of the structure

The structure was solved by multisolution weighted tangent-formula refinement (Germain, Main & Woolfson, 1971) of 382 reflections with $E > 1.4$. Approximate scale and overall isotropic temperature factors ($B = 4.83$ Å 2) were evaluated by the Wilson method. The values of the statistical averages of calculated normalized structure factors were 0.870 and 0.780 for $\langle |E| \rangle$ and $\langle |E^2 - 1| \rangle$ respectively, which indicated the lower space symmetry ($P2_1$). An E map based on the solution with the highest figure of merit ABSFOM (1.22) and the lowest RESID index (33.3) revealed clearly the positions of almost all the non-hydrogen atoms of two of the three independent molecules. The remaining non-hydrogen atoms were located by successive Fourier syntheses. Refinement of

the positional parameters, isotropic temperature factors and scale factors were carried out by the block-diagonal least-squares method [program *CRYLSQ* of the XRAY system (Stewart, Kundell & Baldwin, 1970)]. The R index was reduced from 0.384 to 0.109. Anisotropic refinement of temperature factors further reduced R to 0.068, but C(4), C(5), C(24), C(25), C(34) and C(35) showed particularly high temperature factors. A difference map revealed the positions of most of the H atoms as peaks of maximum density $0.35 \text{ e } \text{Å}^{-3}$. No maxima that could correspond to a partial inversion of the 3,6-dithiacyclohexene rings in individual molecules were observed. Instead of using the H coordinates from the difference map, positional parameters for 24 H atoms were calculated (C-H bond length 1.08 Å, sp^3 geometry in dithiacyclohexene rings, sp^2 in aromatic rings). A further refinement including H atoms with isotropic temperature factors equal to those of the bonded atoms and changing only the parameters of the non-hydrogen atoms reduced R to 6.2%. The weighting scheme was $w = 1/\sigma^2(F)$. The neutral-atom scattering factors for non-hydrogen atoms were taken from Doyle & Turner (1968) and for H atoms from *International Tables for X-ray Crystallography* (1962). The largest parameter shifts in the last cycle of refinement were less than 0.3 of their estimated standard deviations. A final difference Fourier map indicated no unaccounted for electron density. The positional parameters are given in Table 1.*

Discussion

The crystal structure consists of three somewhat different discrete molecules. Their packing in the unit

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33984 (55 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

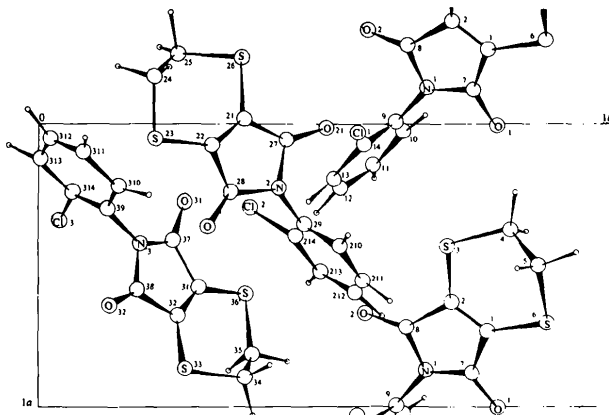


Fig. 1. A drawing of the three symmetrically independent molecules of *N*-(2-chlorophenyl)-3,6-dithiacyclohexene-1,2-dicarboximide viewed along the unit-cell c axis.

cell is shown in Figs. 1 and 2. The bond lengths and angles are shown in Table 2. (The numbering of atoms in the first molecule is from 1 to 14, in the second from 21 to 214, in the third from 31 to 314.) The maximal differences between analogous bond lengths in molecules (I)–(III) are from 3σ to 8σ . In the individual molecules one can observe different conformations for the 3,6-dithiacyclohexene rings, slightly different conformations for the imide rings and different lengths for some bonds.

The 3,6-dithiacyclohexene rings

The torsion angles φ and the asymmetry parameters Δ and $|\varphi|_{av}$ of these rings in molecules (I)–(III) are shown in Fig. 3. The asymmetry parameters, calculated as $\Delta C_2 = [\sum_{i=1}^2 (\varphi_i - \varphi'_i)^2/2]^{1/2}$ and $\Delta C_3 = [\sum_{i=1}^3 (\varphi_i -$

$\varphi'_i)^2/3]^{1/2}$, yield a measure of the deformation of a ring from ideal symmetry. They define precisely conformations of the rings relative to the ideal conformation and relative to any other ring of similar composition. From the data in Fig. 3 it follows that the dithiacyclohexene rings in molecules (I) and (III) have a half-chair conformation. The half-chair in molecule (III) is slightly flatter and more deformed. The opposite signs of the torsion angles for the two rings indicate that they are different enantiomers, although their inversion is not conditioned by the symmetry of the crystal lattice. The dithiacyclohexene ring in the second molecule has a conformation midway between half-chair and sofa. The asymmetry parameter in relation to the twofold axis perpendicular to a double bond is 15.1° here, whereas the asymmetry parameter in relation to the plane of symmetry through C(2) and C(5) is 14.1° . C(sp³)–S bond lengths in all three molecules are identical within

Table 1. Atomic positional parameters ($\times 10^4$, for H $\times 10^3$) with e.s.d.'s in parentheses

	x	y	z		x	y	z
Cl(1)	413 (4)	5567 (2)	2511 (2)	C(12)	2348 (17)	5220 (10)	83 (9)
Cl(2)	2983 (4)	3654 (2)	3028 (2)	C(13)	2041 (16)	5140 (8)	1014 (9)
Cl(3)	3425 (5)	354 (2)	826 (2)	C(14)	821 (15)	5660 (8)	1350 (7)
S(3)	-5774 (4)	7119 (2)	1928 (3)	C(21)	-282 (12)	3605 (7)	5101 (7)
S(6)	-3028 (4)	8834 (2)	2120 (3)	C(22)	763 (12)	3005 (6)	5348 (7)
S(23)	499 (4)	2019 (2)	5759 (2)	C(24)	-1724 (14)	1992 (10)	5780 (10)
S(26)	-2406 (3)	3559 (2)	5043 (2)	C(25)	-2649 (19)	2431 (10)	5071 (11)
S(33)	8743 (4)	2586 (3)	2235 (2)	C(27)	565 (13)	4346 (6)	4778 (7)
S(36)	5965 (4)	3602 (2)	668 (2)	C(28)	2441 (13)	3327 (7)	5220 (7)
O(1)	107 (10)	7966 (6)	1334 (7)	C(29)	3547 (13)	4629 (7)	4523 (7)
O(2)	-3303 (10)	5747 (5)	1277 (5)	C(31)	5711 (13)	2761 (6)	1383 (7)
O(21)	104 (9)	4999 (5)	4504 (5)	C(32)	6742 (13)	2401 (7)	1968 (7)
O(22)	3676 (9)	2942 (5)	5299 (6)	C(34)	8976 (21)	3609 (13)	1704 (13)
O(31)	2806 (10)	2524 (6)	1012 (6)	C(35)	8141 (17)	3699 (13)	799 (12)
O(32)	6392 (12)	1215 (6)	2993 (6)	C(37)	4070 (13)	2356 (6)	1444 (7)
N(1)	-1258 (10)	6727 (6)	1184 (6)	C(38)	5836 (15)	1711 (7)	2433 (8)
N(2)	2283 (10)	4155 (5)	4942 (6)	C(39)	3002 (15)	1191 (6)	2374 (8)
N(3)	4244 (11)	1737 (5)	2092 (6)	C(210)	4286 (16)	5232 (7)	4999 (8)
C(1)	-2726 (14)	7835 (7)	1754 (8)	C(211)	5579 (15)	5683 (8)	4590 (9)
C(2)	-3714 (13)	7191 (8)	1708 (8)	C(212)	5969 (15)	5509 (8)	3697 (9)
C(4)	-6204 (16)	8216 (9)	2035 (9)	C(213)	5180 (15)	4876 (8)	3210 (8)
C(5)	-5017 (14)	8700 (9)	2619 (9)	C(214)	3963 (14)	4437 (7)	3609 (7)
C(7)	-1139 (14)	7536 (8)	1396 (9)	C(310)	2240 (16)	1357 (9)	3217 (8)
C(8)	-2865 (14)	6446 (7)	1368 (7)	C(311)	1062 (17)	774 (9)	3478 (8)
C(9)	-20 (13)	6214 (7)	826 (7)	C(312)	528 (19)	161 (9)	2948 (9)
C(10)	338 (16)	6286 (10)	-106 (9)	C(313)	1226 (16)	-12 (8)	2105 (9)
C(11)	1535 (15)	5783 (10)	-454 (9)	C(314)	2471 (14)	545 (8)	1867 (7)
H(10)	-31	672	-54	H(241)	-208	134	575
H(11)	186	582	-118	H(242)	-209	225	643
H(12)	322	480	-23	H(251)	-391	229	518
H(13)	269	470	144	H(252)	-226	218	442
H(41)	-739	827	231	H(310)	253	190	362
H(42)	-616	847	134	H(311)	57	82	417
H(51)	-554	930	274	H(312)	-49	-22	317
H(52)	-488	837	326	H(313)	86	-53	167
H(210)	390	537	570	H(341)	1025	372	161
H(211)	625	614	496	H(342)	847	407	217
H(212)	688	588	335	H(351)	842	435	57
H(213)	558	472	251	H(352)	870	328	34

2σ limits and their mean value is 1.819 (7) Å, which agrees well with the values found for C(sp^3)-S^{II} single bonds in other structures. The lengths of the C(sp^2)-S bonds show greater variation in individual molecules (from 1.705 to 1.748 Å) and are always shorter than a typical single bond C(sp^2)-S = 1.77 Å (Argay, Kálmán, Nahlovski & Ribár, 1975). The shortening of these bonds is connected with the delocalization of π electrons within the central nearly planar part of the molecule. These bonds are longest in the second molecule where (see Table 3) the imide ring is not planar and deviations of the S atoms from its 'best' plane are greater than in the other two molecules. In the structure investigated one can observe a clear shortening of the C(sp^3)-C(sp^3) bonds in all three independent

molecules [the mean length of the bond for three rings is 1.471 (13) Å]. It seems that the shortening is only apparent, since the very high temperature factors of C(4) and C(5) observed in all three rings suggest statistical disorder of the atoms about the assigned equilibrium positions. In the crystal structure of *N*-(4-chlorophenyl)-3,6-dithiacyclohexene-1,2-dicarboximide, however, in which a close parallel stacking of 3,6-dithiacyclohexene rings occurs, C(4) and C(5) do not show markedly high temperature factors and the length observed for C(4)-C(5) (1.551 Å) is a typical single-bond value. On the basis of the present structural data, dithiacyclohexene rings seem to show great flexibility and are susceptible to deformation and inversion.

Table 2. Bond distances (Å) and angles (°) with e.s.d.'s in parentheses

Cl(1)-C(14)	1.745 (12)	O(1)-C(7)	1.241 (15)	C(1)-C(2)	1.315 (16)	C(29)-C(214)	1.424 (16)
Cl(2)-C(214)	1.703 (13)	O(2)-C(8)	1.185 (14)	C(1)-C(7)	1.502 (18)	C(31)-C(32)	1.316 (17)
Cl(3)-C(314)	1.762 (15)	O(21)-C(27)	1.181 (12)	C(2)-C(8)	1.481 (16)	C(31)-C(37)	1.505 (15)
S(3)-C(2)	1.740 (12)	O(22)-C(28)	1.191 (13)	C(4)-C(5)	1.494 (20)	C(32)-C(38)	1.509 (17)
S(3)-C(4)	1.803 (16)	O(31)-C(37)	1.228 (15)	C(9)-C(10)	1.407 (18)	C(34)-C(35)	1.475 (26)
S(6)-C(1)	1.711 (12)	O(32)-C(38)	1.220 (16)	C(9)-C(14)	1.348 (17)	C(39)-C(310)	1.425 (18)
S(6)-C(5)	1.826 (16)	N(1)-C(7)	1.338 (16)	C(10)-C(11)	1.384 (21)	C(39)-C(314)	1.339 (16)
S(23)-C(22)	1.709 (11)	N(1)-C(8)	1.431 (15)	C(11)-C(12)	1.357 (21)	C(210)-C(211)	1.434 (19)
S(23)-C(24)	1.831 (12)	N(1)-C(9)	1.423 (15)	C(12)-C(13)	1.398 (19)	C(211)-C(212)	1.382 (19)
S(26)-C(21)	1.748 (11)	N(2)-C(27)	1.458 (14)	C(13)-C(14)	1.408 (19)	C(212)-C(213)	1.389 (19)
S(26)-C(25)	1.823 (16)	N(2)-C(28)	1.395 (13)	C(21)-C(22)	1.333 (15)	C(213)-C(214)	1.371 (18)
S(33)-C(32)	1.705 (13)	N(2)-C(29)	1.441 (15)	C(21)-C(27)	1.465 (15)	C(310)-C(311)	1.410 (20)
S(33)-C(34)	1.830 (21)	N(3)-C(37)	1.376 (14)	C(22)-C(28)	1.492 (15)	C(311)-C(312)	1.318 (20)
S(36)-C(31)	1.724 (11)	N(3)-C(38)	1.385 (16)	C(24)-C(25)	1.446 (22)	C(312)-C(313)	1.405 (21)
S(36)-C(35)	1.800 (14)	N(3)-C(39)	1.418 (15)	C(29)-C(210)	1.327 (16)	C(313)-C(314)	1.412 (18)
C(7)-N(1)-C(9)	126.8 (9)	C(27)-N(2)-C(29)	122.0 (8)	C(37)-N(3)-C(39)	125.9 (9)		
C(7)-N(1)-C(8)	108.9 (9)	C(27)-N(2)-C(28)	109.2 (8)	C(37)-N(3)-C(38)	110.1 (9)		
C(8)-N(1)-C(9)	124.3 (9)	C(28)-N(2)-C(29)	124.4 (9)	C(38)-N(3)-C(39)	124.0 (9)		
C(2)-C(1)-S(6)	131.0 (10)	C(22)-C(21)-S(26)	128.1 (9)	C(32)-C(31)-S(36)	130.5 (9)		
C(2)-C(1)-C(7)	105.9 (10)	C(22)-C(21)-C(27)	111.4 (9)	C(32)-C(31)-C(37)	109.3 (9)		
S(6)-C(1)-C(7)	123.1 (9)	S(26)-C(21)-C(27)	120.3 (8)	S(36)-C(31)-C(37)	120.1 (8)		
C(1)-C(2)-S(3)	130.3 (10)	C(21)-C(22)-S(23)	132.6 (9)	C(31)-C(32)-S(33)	131.8 (9)		
C(1)-C(2)-C(8)	110.8 (10)	C(21)-C(22)-C(28)	107.8 (9)	C(31)-C(32)-C(38)	107.3 (10)		
S(3)-C(2)-C(8)	118.8 (9)	S(23)-C(22)-C(28)	119.7 (8)	S(33)-C(32)-C(38)	120.8 (8)		
C(2)-S(3)-C(4)	98.4 (6)	C(22)-S(23)-C(24)	99.6 (6)	C(32)-S(33)-C(34)	100.0 (7)		
S(3)-C(4)-C(5)	115.5 (10)	S(23)-C(24)-C(25)	118.5 (11)	S(33)-C(34)-C(35)	114.5 (14)		
C(4)-C(5)-S(6)	114.2 (9)	C(24)-C(25)-S(26)	116.4 (11)	C(34)-C(35)-S(36)	121.2 (12)		
C(1)-S(6)-C(5)	99.0 (6)	C(21)-S(26)-C(25)	98.7 (6)	C(31)-S(36)-C(35)	98.3 (8)		
N(1)-C(7)-C(1)	109.5 (10)	N(2)-C(27)-C(21)	104.2 (8)	N(3)-C(37)-C(31)	106.3 (9)		
C(1)-C(7)-O(1)	125.3 (11)	C(21)-C(27)-O(21)	132.9 (10)	N(3)-C(37)-O(31)	125.4 (10)		
O(1)-C(7)-N(1)	125.2 (11)	O(21)-C(27)-N(2)	122.7 (9)	C(31)-C(37)-O(31)	128.3 (10)		
N(1)-C(8)-C(2)	104.9 (9)	N(2)-C(28)-C(22)	106.8 (9)	N(3)-C(38)-C(32)	107.0 (9)		
N(1)-C(8)-O(2)	123.9 (10)	N(2)-C(28)-O(22)	126.4 (10)	N(3)-C(38)-O(32)	126.1 (11)		
C(2)-C(8)-O(2)	131.2 (11)	C(22)-C(28)-O(22)	126.7 (10)	C(32)-C(38)-O(32)	127.0 (11)		
N(1)-C(9)-C(10)	119.0 (10)	N(2)-C(29)-C(210)	119.2 (10)	N(3)-C(39)-C(310)	118.6 (10)		
N(1)-C(9)-C(14)	122.2 (10)	N(2)-C(29)-C(214)	118.9 (9)	N(3)-C(39)-C(314)	122.9 (10)		
C(10)-C(9)-C(14)	118.9 (11)	C(210)-C(29)-C(214)	121.9 (10)	C(310)-C(39)-C(314)	118.5 (11)		
C(9)-C(10)-C(11)	118.9 (12)	C(29)-C(210)-C(211)	118.9 (11)	C(39)-C(310)-C(311)	115.9 (12)		
C(10)-C(11)-C(12)	121.2 (12)	C(210)-C(211)-C(212)	119.3 (12)	C(310)-C(311)-C(312)	123.8 (12)		
C(11)-C(12)-C(13)	121.5 (13)	C(211)-C(212)-C(213)	120.8 (12)	C(311)-C(312)-C(313)	121.6 (14)		
C(12)-C(13)-C(14)	116.0 (12)	C(212)-C(213)-C(214)	119.6 (11)	C(312)-C(313)-C(314)	114.4 (12)		
C(9)-C(14)-C(13)	123.5 (10)	C(29)-C(214)-C(213)	119.3 (10)	C(39)-C(314)-C(313)	125.5 (11)		
Cl(1)-C(14)-C(9)	119.8 (9)	Cl(2)-C(214)-C(29)	120.2 (9)	Cl(3)-C(314)-C(39)	117.8 (9)		
Cl(1)-C(14)-C(13)	116.7 (9)	Cl(2)-C(214)-C(213)	120.5 (9)	Cl(3)-C(314)-C(313)	116.7 (9)		

The imide and chlorophenyl rings

The imide rings in the molecules of the title compound are not perfectly planar. Table 3 gives the equations of their best planes (calculated without N atoms, but including O), deviations of the remaining atoms of the molecule from them and χ^2 and α values. The computed ratio $\sum_m d_m^2/\sigma^2$ [where d_m is the distance of atom m (defining the plane) from the plane] follows the χ^2 distribution, and from tabulated values (Korn & Korn, 1968) for three degrees of freedom it gives the probability α that a planar set of six atoms will have a ratio exceeding that found. It is assumed that if $\alpha < 0.01$ the set of six atoms is not rigorously planar within experimental error. The data from Table 3 indicate that

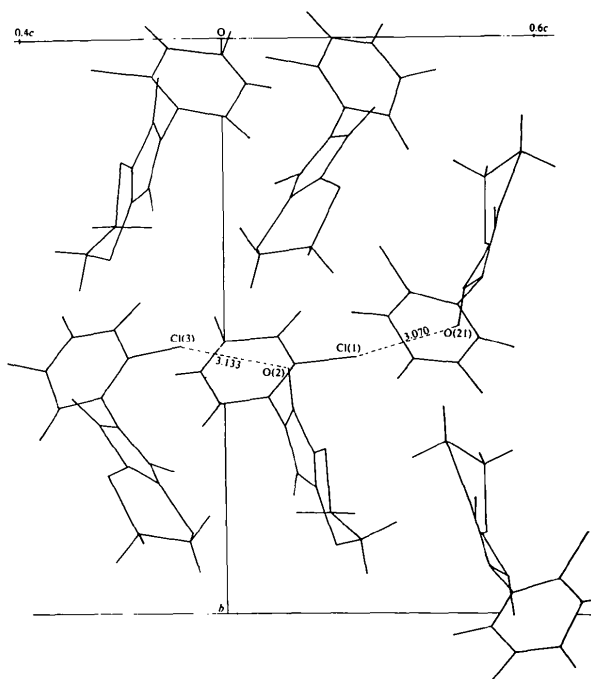


Fig. 2. The molecular packing viewed along the unit-cell a axis.

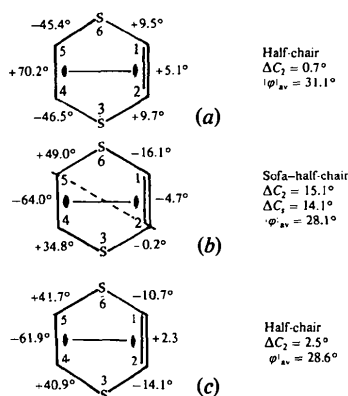


Fig. 3. Torsion angles ($^\circ$) of the 3,6-dithiacyclohexene for (a) molecule (I), (b) molecule (II) and (c) molecule (III).

only the imide ring of the third molecule can be considered planar, whereas that in the second molecule seems the most corrugated. The deviation of N(2) from the best plane of C(21), C(22), C(27), C(28), O(21) and O(22) is 0.151 Å; this indicates a partial tetrahedral hybridization of N(2). The average of six C—C single-bond lengths in the three molecules is 1.490 (7) Å and the average of five C(sp^2)—N bonds is 1.385 (7) Å, indicating some π delocalization. N(21)—C(27) = 1.458 (14) Å is the only typical single bond. C=O

Table 3. Least-squares planes of the imide and phenyl rings, and deviations of the atoms from the planes

(a) Equations of various planes in the standard orthogonal system in the form $AX + BY + CZ = D$

	A	B	C	D
Molecule (I)				
Imide ring	0.2585	-0.2291	0.9384	-1.1044
2-Chlorophenyl ring	0.6810	0.6965	0.2260	7.1868
Molecule (II)				
Imide ring	0.2840	0.3613	0.9320	9.0282
2-Chlorophenyl ring	-0.6608	0.6646	-0.3485	0.8648
Molecule (III)				
Imide ring	-0.2733	0.6324	0.7247	3.0186
2-Chlorophenyl ring	-0.6691	0.5864	-0.4565	-2.0220

(b) Distances (Å) of the atoms from the planes

	Molecule (I)	Molecule (II)	Molecule (III)
2-Chlorophenyl ring			
C(9)	-0.0048	-0.0043	-0.0116
C(10)	0.0007	0.0122	0.0314
C(11)	0.0059	-0.0158	-0.0353
C(12)	-0.0086	0.0118	0.0171
C(13)	0.0047	-0.0034	0.0042
C(14)	0.0020	-0.0004	-0.0058
*Cl(1)	0.0129	-0.0267	-0.0532
	$\chi^2 = 0.9$	$\chi^2 = 3.3$	$\chi^2 = 14.9$
	$\alpha = 0.8^\dagger$	$\alpha = 0.3^\dagger$	$\alpha < 0.01^\dagger$
Imide ring			
C(1)	0.0217	-0.0114	-0.0165
C(2)	-0.0137	0.0006	0.0119
C(7)	-0.0160	-0.0007	0.0062
C(8)	-0.0198	0.0516	0.0141
O(1)	0.0075	-0.0051	-0.0018
O(2)	0.0202	-0.0350	-0.0139
*N(1)	-0.0304	0.1507	0.0324
*S(3)	-0.1257	-0.0200	0.0370
*S(6)	0.0872	-0.1665	0.0133
*C(4)	-0.4764	-0.0592	0.4539
*C(5)	0.3909	-0.7897	-0.2364
*C(9)	-0.0652	-0.1139	0.0598
*C(10)	-1.2799	0.8999	1.3026
*C(11)	-1.3123	0.6363	1.2551
*C(12)	-0.2037	-0.6691	0.1853
*C(13)	1.0241	-1.7171	-1.0508
*C(14)	1.0282	-1.4583	-1.0195
*Cl(1)	2.5509	-2.7247	-2.5446
	$\chi^2 = 15.0$	$\chi^2 = 34.5$	$\chi^2 = 7.2$
	$\alpha < 0.01^\dagger$	$\alpha < 0.001^\dagger$	$\alpha = 0.1^\dagger$

* Not included in the calculation of the plane.

† Probability that a truly planar set of six atoms will have χ^2 as large as that found.

bond lengths in the molecules differ within the 4σ limits and are from 1.181 (12) to 1.241 (15) Å. Shorter bonds can be observed in the more corrugated imide rings of the first and second molecules, where, because of some deviation from planarity, delocalization of π bonds is more difficult.

Phenyl rings in the first and second molecules can be considered perfectly planar within the observed errors whereas in the third molecule the ring is clearly corrugated and the Cl deviates from its best plane by 0.053 Å. The mean C—C bond length in the three phenyl rings is 1.386 (6) Å and agrees with the commonly observed value for aromatic rings. The C—Cl bond varies slightly: in the second molecule it is a little shorter [1.703 (13) Å] than in the other two molecules [(C—Cl)_{av} = 1.754 (9) Å].

A comparison of the structure of the title compound with those of the 4-chlorophenyl derivative and DTTHP

A comparison of the molecular structures of the three analogous compounds, differing in the type and structure of the substituent *R* at the N atom (*R* = 2-chlorophenyl, 4-chlorophenyl and H), can give an answer to the question as to whether or not (and to what extent) the substituent modifies the geometry of the whole molecule. It appears that in the structure of

the 2-chlorophenyl derivative one can observe a clearly different structure for one of the three symmetrically independent molecules. The second molecule in the elementary cell differs from the other two in the geometry of the imide and 3,6-dithiacyclohexene rings, in their orientation in relation to each other, and in the lengths of some bonds.

The structure of the 2-chlorophenyl derivative reveals a considerably looser arrangement of the molecules in the crystal than is present in the structure of the 4-chlorophenyl derivative; this is indicated by a comparison of the densities of both crystals (1.539 and 1.585 Mg m⁻³ respectively). The loose arrangement of molecules in the 2-chlorophenyl derivative is connected with their considerably less planar shape. The planarity of the molecules of the title compound is disturbed by (a) rotation of the phenyl ring in relation to the imide ring, conditioned by the steric hindrance between O atoms and the *ortho* substituent on the phenyl ring, and (b) deviations of C(*sp*³) atoms from the central plane of the molecule, resulting from the half-chair conformation of the dithiacyclohexene ring.

In the crystals investigated the angle between the planes of the phenyl and imide rings in the first molecule is 76.7°, in the second 84.1° and in the third 77.1°, whereas in the structure of the 4-chlorophenyl derivative it is only 50.5°. In addition, in all three molecules of the 2-chlorophenyl derivative the rotation

Table 4. Comparison of averaged bond lengths (Å) and molecular geometry in the structures of the title compound, the 4-chlorophenyl derivative and DTTHP

	Title compound	4-Chlorophenyl derivative*	DTTHP†
3,6-Dithiacyclohexene ring			
C(<i>sp</i> ³)—S	⑥ ‡ 1.819 (7)	② 1.823 (2)	② 1.823(4)
C(<i>sp</i> ²)—S	⑤ 1.718 (5), (II)§ 1.748 (11)	1.740 (2), 1.728 (2)	② 1.723 (2)
C(<i>sp</i> ³)—C(<i>sp</i> ³)	③ 1.471 (13)	1.551 (4)	1.499 (6)
C(<i>sp</i> ²)—C(<i>sp</i> ²)	③ 1.321 (9)	1.326 (3)	1.336 (3)
Conformation	(I) Half-chair, (II) sofa-half-chair, (III) half-chair	Half-chair	Half-chair
Asymmetry parameters	$\Delta C_2(I) = 0.7^\circ$, $\Delta C_2(II) = 15.1^\circ$, $\Delta C_2(III) = 14.1^\circ$, $\Delta C_2(III) = 2.5^\circ$	$\Delta C_2 = 9.9^\circ$	$\Delta C_2 = 4.2^\circ$
Imide ring			
C(<i>sp</i> ²)—C(<i>sp</i> ²)	⑥ 1.490 (7)	② 1.489 (2)	② 1.491 (2)
C(<i>sp</i> ²)—O	③ 1.230 (9), (I) 1.185 (14), ② (II) 1.181 (9)	② 1.205 (2)	1.216 (3), 1.201 (3)
C(<i>sp</i> ²)—N	⑤ 1.385 (7), (II) 1.458 (14)	② 1.384 (2)	② 1.384 (3)
<i>d</i> _N (Å)¶	(I) 0.030, (II) 0.151, (III) 0.032	0.067	0.010
Chlorophenyl ring			
C(<i>sp</i> ²)—N	③ 1.427 (9)	1.446	
C(<i>sp</i> ²)—C(<i>sp</i> ²)	① 1.386 (6), ④ 1.424 (10), ③ 1.331 (11)	④ 1.391 (2)	
C(<i>sp</i> ²)—Cl	⑤ 1.754 (9), (II) 1.703 (13)	1.764 (2)	
Dihedral angle (°)	(I) 76.7, (II) 84.1, (III) 77.1	50.5	
between imide- and phenyl-ring planes			

* Bukowska-Strzyżewska & Pniewska (1979).

† Kirfel, Will & Fickentscher (1975).

‡ The number of bond lengths averaged within the 3σ range is circled.

§ The numbers of the independent molecules are denoted by (I), (II) and (III).

¶ *d*_N is the perpendicular distance of the N atom from the best plane of the imide ring.

of the $C(sp^3)-C(sp^3)$ bond and the rotation of the phenyl ring about the axis of the molecule are antiparallel, contrary to what is observed in the structure of the 4-chlorophenyl derivative. This results in considerable difficulties for the close arrangement of the molecules in the crystal lattice. The arrangement of the molecules in the structure investigated is illustrated in Fig. 2. No shortened $C-H\cdots O$ and $C-H\cdots S$ contacts can be observed here (unlike the structure of the 4-chlorophenyl derivative) and there is only a slight shortening of the intermolecular contacts $Cl(1)\cdots O(21) = 3.070(9)$ and $Cl(3)\cdots O(2) = 3.133(9)$ Å. Therefore, the presence of a different conformation for the dithiacyclohexene ring in the second molecule does not result from specific intermolecular interactions and should rather be attributed to the relatively loose arrangement of the rings in a crystal, and by their great flexibility and susceptibility to deformation.

It seems that the different conformation of the imide ring in the second molecule is mainly influenced by the nearly perpendicular position of the 2-chlorophenyl ring in relation to it. Even if nearly the same intramolecular $N\cdots Cl$ distance as in the first and the third molecules is preserved, $Cl(2)$ is here closer to the free p orbital of the N atom; this causes destabilization, and thus changes the type of hybridization of $N(2)$. The deviation from planarity of this imide ring excludes $N(21)$ from the area of delocalization of the π bonds. A lengthening of the bond $N(21)-C(27) = 1.458(14)$ Å to a single-bond value can be observed here. Table 4 presents mean lengths in the structures being compared (averaged within the 3σ range) and some selected characteristics of the geometries of individual molecules. In all five molecules compared, the 3,6-dithiacyclohexene ring has a conformation of a more or less deformed half-chair. In the second molecule of the 2-chlorophenyl derivative the conformation is precisely midway between sofa and half-chair. The imide ring is the least corrugated in the DTTHP (Kirfel, Will & Fickentscher, 1975) molecule and the most corrugated in the second molecule of the 2-chlorophenyl deriva-

tive. The first and third molecules in the present structure are different enantiomers. The molecules of the 2-chlorophenyl and 4-chlorophenyl derivatives are different rotation isomers. In all the molecules of the title compound rotations of the phenyl ring and the $C(sp^3)-C(sp^3)$ bond about the axis of the molecule are in opposite directions, whereas in the 4-chlorophenyl derivative the rotations are in the same direction. The data from Table 4 indicate that most of the corresponding bonds in individual structures and molecules agree within 3σ .

We thank Professor W. Hahn and Dr B. Rybczyński for supplying the crystals.

The intensities were measured in the Regional Laboratory of Unique Chemical Apparatus at the University of Poznań.

This research was supported by project MR I-9 from the Polish Academy of Science.

References

- ARGAY, G., KÁLMÁN, A., NAHLOVSKI, Á. & RIBÁR, B. (1975). *Acta Cryst.* **B31**, 1956–1961.
- BUKOWSKA-STRZYŻEWSKA, M., DOBROWOLSKA, W. & PNIEWSKA, B. (1978). *Rocz. Chem.* **52**, 1843–1845.
- BUKOWSKA-STRZYŻEWSKA, M. & PNIEWSKA, B. (1979). *Acta Cryst.* **B35**, 640–643.
- DOYLE, P. A. & TURNER, P. S. (1968). *Acta Cryst.* **A24**, 390–397.
- GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* **A27**, 368–376.
- International Tables for X-ray Crystallography* (1962). Vol. III. Birmingham: Kynoch Press.
- KIRFEL, A., WILL, G. & FICKENTSCHER, K. (1975). *Acta Cryst.* **B31**, 1973–1975.
- KORN, G. A. & KORN, T. M. (1968). *Mathematical Handbook for Scientists and Engineers*. New York, London, Sydney: McGraw-Hill.
- STEWART, J. M., KUNDELL, F. A. & BALDWIN, J. C. (1970). The XRAY 70 system. Computer Science Center, Univ. of Maryland, College Park, Maryland.