The Structure of N-(4-Methoxyphenyl)-3,6-dithiacyclohexene-1,2-dicarboximide*

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Abstract

N-(4-Methoxyphenyl)-3,6-dithiacyclohexene-1,2-dicarboximide, $C_{13}H_{11}NO_3S_2$, crystallizes in the monoclinic system, $a = 12.31$ (2), $b = 12.68$ (2), $c = 8.56$ (1) Å, $\beta = 104.0$ (5)°, space group $P2_1/c$, $Z = 4$, $D_x = 1.50$, $D_m = 1.47$ Mg m⁻³, $F(000) = 608$, $\lambda(Cu\ K\alpha) = 1.5418$ Å. The structure was solved from three-dimensional X-ray data by direct methods and refined by least-squares methods with anisotropic temperature factors to a final $R = 0.089$ for 1124 observed reflections. The 3,6-dithiacyclohexene ring has the half-chair conformation, with the asymmetry parameter $\Delta C_2(1,2) = 1.4°$. The imide and phenyl rings are perfectly planar. The dihedral angle between the best planes of the imide and phenyl rings is 51.1 (7)°. The methoxy group is nearly coplanar with the phenyl ring.

Introduction

The structure of N-(4-methoxyphenyl)-3,6-dithiacyclohexene-1,2-dicarboximide was investigated as part of the research on the structures of N-substituted derivatives of 5,6-dihydro-1,4-dithiin-2,3-dicarboximide and 1,4-dithiane-2,3-dicarboximide obtained from the Institute of Organic Chemistry, University of Łódź, in the search for new heterocyclic compounds with potential biological activity (Hahn & Rybczyński, 1971, 1976). Preliminary pharmacological investigations have shown that imides in which the N atom is bound to phenyl or substituted phenyl groups are slightly toxic and act depressively on the central nervous system. The determination of the conformations of the heterocyclic rings and the influence of the N substituent on the hybridization of the N orbitals was the main aim of the work.

Experimental

The title compound crystallizes from acetic acid in the monoclinic system. The cell dimensions were determined from Weissenberg photographs taken with Cu

radiation. The density of the crystal was measured by the flotation method in a mixture of benzene and CH₃I. Intensity data were collected by means of a multiple-film pack on a Weissenberg camera. The intensities were visually estimated with a calibrated intensity scale. No absorption correction was made.

Determination of the structure

The structure was solved by the symbolic addition procedure using programs of the XRAY system

Table 1. *Final atomic positions ($\times 10^4$) with e.s.d.'s in parentheses*

	x	y	z	B (Å²)*
S(3)	1892 (2)	8895 (2)	−1588 (4)	4.17 (9)
S(6)	4381 (2)	8574 (3)	1465 (4)	4.35 (9)
O(1)	4425 (5)	6106 (6)	1666 (9)	4.1 (2)
O(2)	1172 (6)	6514 (6)	−2099 (9)	4.5 (2)
O(3)	1907 (6)	1759 (6)	587 (11)	4.9 (3)
N(9)	2744 (6)	5979 (6)	−274 (10)	4.0 (3)
C(1)	3472 (8)	7646 (8)	417 (13)	3.4 (3)
C(2)	2527 (9)	7778 (9)	−677 (13)	3.8 (3)
C(4)	2989 (10)	9833 (9)	−866 (14)	4.7 (4)
C(5)	3517 (10)	9746 (10)	886 (16)	5.2 (4)
C(7)	3676 (8)	6519 (8)	742 (13)	3.5 (3)
C(8)	2027 (8)	6718 (9)	−1150 (12)	3.8 (3)
C(10)	2516 (8)	4883 (8)	−115 (12)	3.2 (3)
C(11)	3303 (9)	4146 (10)	−190 (16)	5.1 (4)
C(12)	3074 (9)	3084 (9)	88 (16)	4.9 (4)
C(13)	2029 (9)	2798 (8)	323 (13)	3.8 (3)
C(14)	1259 (8)	3558 (9)	353 (13)	3.9 (3)
C(15)	1482 (8)	4613 (9)	131 (14)	3.9 (4)
C(16)	866 (10)	1425 (10)	816 (16)	5.5 (5)
H(41)	3594	9741	−1470	
H(42)	2676	10574	−1098	
H(51)	2891	9736	1452	
H(52)	3986	10389	1228	
H(111)	4045	4359	−432	
H(121)	3668	2525	83	
H(141)	504	3350	551	
H(151)	898	5175	153	
H(161)	691	1776	1782	
H(162)	239	1585	−153	
H(163)	866	632	1004	

* The positional parameters correspond to anisotropic refinement. Isotropic temperature factors are from the last cycle of isotropic refinement with $R = 0.124$.

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* Alternative name: N-(4-methoxyphenyl)-5,6-dihydro-1,4-dithiin-2,3-dicarboximide.

(Stewart, Kundell & Baldwin, 1970) on a RIAD 32 computer. A three-dimensional Fourier synthesis located the remaining 10 heavy atoms. Refinement of the positional parameters, isotropic temperature factors and a scale factor was carried out by the block-diagonal least-squares method. The positions of the H atoms were determined from geometric considerations. The parameters of the H atoms were not refined. They were included in the last cycle of refinement with isotropic temperature factors equal to those of the bonded atoms. The final R value for all observed reflections was 0·089. Form factors for neutral C, N, S and O atoms were taken from Doyle & Turner (1968), and for H atoms from *International Tables for X-ray Crystallography* (1962).

The final positional parameters with their e.s.d.'s are listed in Table 1.*

Results and discussion

A view of the molecule projected on the xy plane and the numbering of the atoms are given in Fig. 1. The 3,6-dithiacyclohexene ring has a half-chair conformation but the S atoms are not ideally coplanar with the planar imide ring. The dihedral angle between the imide and phenyl planes is 51·1 (7)°. The methoxy group is nearly coplanar with the phenyl ring. Bond lengths and angles with standard deviations in parentheses are listed in Table 2.

The 3,6-dithiacyclohexene ring

The half-chair conformation of this ring is somewhat deformed. The torsion angles φ, $|\varphi|_{av}$ and the asymmetry parameter (Duax & Norton, 1975) are given in Fig. 2. The asymmetry parameter in relation to the twofold axis is small, $\Delta C_2(1,2) = 1\cdot4°$. The ring is not more corrugated than in other dithiacyclohexene

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34975 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
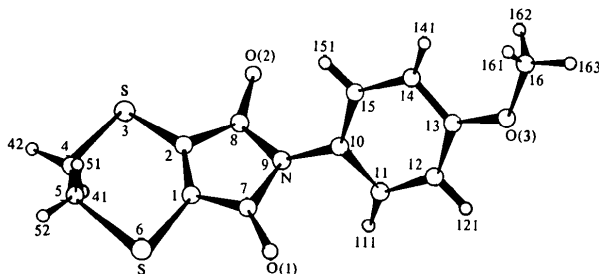

Fig. 1. A view of the molecule showing the atom numbering.

Table 2. Bond lengths (Å) and angles (°)

S(3)—C(2)	1·711 (11)	C(8)—N(9)	1·379 (12)
S(3)—C(4)	1·794 (12)	N(9)—C(10)	1·431 (13)
S(6)—C(1)	1·720 (10)	C(10)—C(11)	1·359 (16)
S(6)—C(5)	1·824 (12)	C(11)—C(12)	1·408 (17)
C(1)—C(2)	1·316 (13)	C(12)—C(13)	1·396 (17)
C(4)—C(5)	1·487 (17)	C(13)—C(14)	1·356 (15)
C(1)—C(7)	1·465 (15)	C(14)—C(15)	1·388 (16)
C(2)—C(8)	1·493 (15)	C(15)—C(10)	1·382 (15)
C(7)—O(1)	1·183 (11)	C(13)—O(3)	1·351 (13)
C(8)—O(2)	1·192 (11)	O(3)—C(16)	1·408 (16)
C(7)—N(9)	1·435 (12)		

C(2)—S(3)—C(4)	99·7 (5)	C(2)—C(8)—N(9)	107·2 (8)
C(1)—S(6)—C(5)	98·8 (5)	C(8)—N(9)—C(7)	108·6 (8)
C(2)—C(1)—S(6)	129·4 (8)	C(8)—N(9)—C(10)	126·6 (7)
S(6)—C(1)—C(7)	120·5 (7)	C(7)—N(9)—C(10)	123·5 (7)
C(2)—C(1)—C(7)	110·0 (9)	N(9)—C(10)—C(11)	120·3 (9)
S(3)—C(2)—C(1)	131·2 (9)	C(11)—C(10)—C(15)	122·0 (10)
S(3)—C(2)—C(8)	120·5 (7)	N(9)—C(10)—C(15)	117·7 (9)
C(1)—C(2)—C(8)	108·3 (9)	C(10)—C(11)—C(12)	118·4 (11)
S(3)—C(4)—C(5)	114·1 (9)	C(11)—C(12)—C(13)	120·1 (10)
S(6)—C(5)—C(4)	114·7 (9)	C(12)—C(13)—O(3)	114·9 (10)
C(1)—C(7)—N(9)	105·9 (8)	C(14)—C(13)—O(3)	125·6 (11)
C(1)—C(7)—O(1)	129·0 (9)	C(12)—C(13)—C(14)	119·4 (10)
O(1)—C(7)—N(9)	125·0 (9)	C(13)—C(14)—C(15)	121·3 (10)
O(2)—C(8)—N(9)	124·6 (10)	C(10)—C(15)—C(14)	118·6 (10)
C(2)—C(8)—O(2)	128·2 (9)	C(13)—O(3)—C(16)	117·3 (9)

rings: $|\varphi|_{av} = 31\cdot3°$, where $|\varphi|_{av}$ of this ring in other structures (Bukowska-Strzyżewska & Pniewska, 1979a,b; Kirfel, Will & Fickentscher, 1975) was found to range from 28·1 to 33·4°. The torsion angle S(3)—C(2)—C(1)—S(6) = 5·8 (2)° is relatively large and indicates some non-planarity of these four atoms which should be planar for a typical half-chair conformation. The lengths of the S—C(sp^2) bonds are 1·711 (11) and 1·720 (10) Å and are shorter than a typical single bond, C(sp^2)—S = 1·77 Å (Argay, Kálmán, Nahlovski & Ribár, 1975). Shortening of these bonds indicates some π delocalization between not-perfectly-planar S—C—C—S atoms. The S—C(sp^3) bond lengths are 1·794 (12) and 1·824 (12) Å and are typical for this bond. In the known structures they are from 1·795 (24) to 1·843 (2) Å (Kalff & Romers, 1965, 1966; Marsh, 1955; Carey, Smith, Maher & Bryan, 1977; McPhail, Onan & Koskimies, 1976; Bukowska-Strzyżewska & Pniewska, 1979a,b; Chao & McCullough, 1960; Kobayashi & Iitaka, 1977; Dobrowolska & Bukowska-Strzyżewska, 1980a,b). The C(sp^3)—C(sp^3) distance is 1·487 (17) Å and is shorter than a typical C—C single-bond length. Shortening of this bond is often observed in 3,6-dithiacyclohexene rings with a half-chair conformation (Bukowska-Strzyżewska & Pniewska, 1979b; Kirfel, Will & Fickentscher, 1975). The C(1)—C(2) distance is 1·316 (13) Å and is typical for a C—C double bond. The mean C—S—C valency angle = 99·3 (4), S—C(sp^3)—C(sp^3) = 114·4 (6) and S—C(sp^2)—C(sp^2) = 130·3 (6)°; these agree well with literature data.
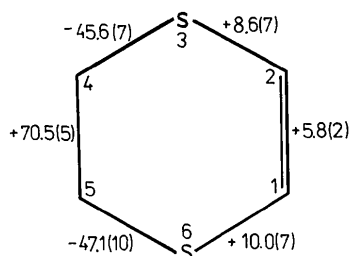
Fig. 2. Torsion angles (°). $[\Delta C_2(1,2) = 1.4°; |\varphi|_{av} = 31.3°.]$

The imide ring

The imide ring is ideally planar within experimental error, which for two degrees of freedom gives a significance level $\chi^2 = 0.1, p = 0.95$.

The deviations of the atoms from the least-squares plane are given in Table 3. It should be noted that almost all atoms connected to the atoms of this ring show considerable deviations from its plane. The deviations of S atoms from the imide-ring best plane are a consequence of the deformed half-chair conformation of the 3,6-dithiacyclohexene ring. The deviation of O(1) from the plane results from the molecular packing [shortening of the three O(1)—H distances (see Fig. 3)]. The deviation of C(10) is of the order of 20σ and indicates the partial sp^3 hybridization of the N atom.

The angle between the C(7)—C(8)—N(9) plane and the N(9)—C(10) bond is 9.7 (6)°. The measurements of absorption spectra, dipole moments and theoretical calculations of energy levels and charge densities of cyclic imides derived from anhydrides indicate that the hybridization of the N orbitals changes from sp^3 to sp^2,
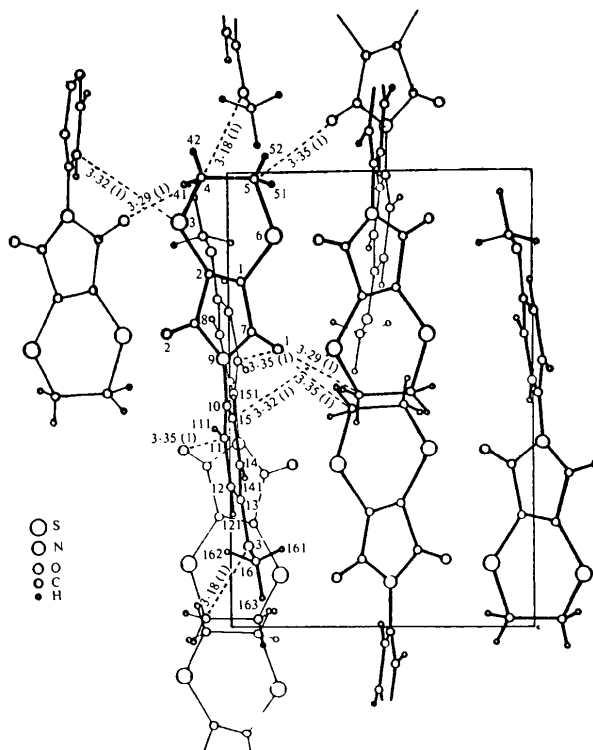
Table 3. *Deviations (Å) of the atoms from the least-squares planes*

The imide ring

$$0.6878X - 0.0500Y - 0.7242Z = -2.1477$$

C(1)	−0.002 (12)	*O(1)	−0.027 (9)
C(2)	0.002 (12)	*O(2)	−0.007 (8)
C(7)	0.000 (12)	*S(3)	0.072 (4)
C(8)	−0.002 (12)	*S(6)	−0.071 (7)
N(9)	0.001 (9)	*C(10)	−0.241 (11)
		*C(13)	−0.847 (11)
$\chi^2 = 0.1$ $p = 0.95$		*O(3)	−1.081 (9)

The phenyl ring

$$0.1324X + 0.1076Y + 0.9853Z = -0.9738$$

C(10)	0.012 (10)	*O(3)	0.042 (9)
C(11)	−0.021 (14)	*C(16)	0.007 (14)
C(12)	0.018 (14)	*N(9)	0.072 (9)
C(13)	−0.006 (11)		
C(14)	−0.004 (11)	$\chi^2 = 6.6$	
C(15)	0.001 (12)	$0.05 < p < 0.1$	

* Atoms not included in the calculation of the plane.

Fig. 3. The molecular packing.

depending on the substituent of the N—R bond (sp^3 type for H and CH_3, sp^2 type for a phenyl group; Lumbroso & Dabard, 1959; Arcoria, Lumbroso & Passerini, 1959; Matsuo, 1965). This suggestion has not been confirmed by known structures. Structures of N-substituted 1,2-dicarboximides where R = o-Cl-phenyl, p-Cl-phenyl or CH_3 indicate that the deviations from planarity of the three N—C bonds are independent of the type of R group. In the structure of N-(2-chlorophenyl)-3,6-dithiacyclohexene-1,2-dicarboximide (Bukowska-Strzyżewska & Pniewska, 1979b) the planar distribution of the three N—C bonds is clearly deformed only for one of the three independent molecules. The angle between the C—C—N plane of the ring and the N—C bond to the substituent is here 20.1°. For the remaining two molecules this angle is smaller than 2° and indicates practical coplanarity of the three bonds. For the structures of 7-methyl-1,4-dithia-7-azaspiro[4.4]nonane-6,8-dione (containing two independent molecules) and N-methyl-1,4-dithiane-2,3-dicarboximide, where the N substituent is CH_3 in both compounds, the planarity of the three N—C bonds is not disturbed in two molecules whereas for the third molecule the angle between the C—C—N ring plane and the N—C substituent bond is about 10°. For comparable rings a distinctly deformed planar distribution of the three N—C bonds was observed for six rings where the N substituent was o-Cl-phenyl, α-glutarimide, —S—S—

$C(CH_3)_3$, p-methoxyphenyl, CH_3, and p-I-phenyl (Bukowska-Strzyżewska & Pniewska, 1979b; Allen & Trotter, 1971; Mazhar-ul-Haque & Behforouz, 1979; Dobrowolska & Bukowska-Strzyżewska, 1980b; Ribár, Stanković, Herak, Halasi & Djurić, 1974). Maximal deformation was observed for an o-Cl-phenyl substituent. In the other rings with the same or different, but equally aromatic or aliphatic, substituents the distribution of N—C bonds is perfectly planar (Sheldrick & Trotter, 1979; Dobrowolska & Bukowska-Strzyżewska, 1980a; Bukowska-Strzyżewska & Pniewska, 1979a; Kaftory, 1978; Petersen, 1969). It appears that the non-planarity of the three N—C bonds is to a high degree a consequence of the molecular packing.

The $C(sp^2)$—$C(sp^2)$ bond lengths are 1·493 (15) and 1·465 (15) Å and are the same as in the other structures mentioned above. The $C(sp^2)$—N bond lengths are 1·379 (12) and 1·435 (12) Å. The difference here is of the order of 5σ. This could be due to the deviation of the O(1) atom from the ring plane [the distance of O(1) from the imide-ring plane is 0·027 (9) Å]. Thus the delocalization of the lone-electron pair of the N atom and the C—O(1) bond through the N(9)—C(7)—O(1) atoms is more difficult.

The 4-methoxyphenyl ring

The phenyl ring is nearly planar, $\chi^2 = 6·6$, $0·05 < p < 0·1$. The distances of atoms from the best plane of this ring are given in Table 3. The average C—C bond length is 1·382 (8) Å and the average C—C—C bond angle is 120·0 (5)°. The maximum differences between extreme values of bond lengths and angles are of the order of 3σ. The dihedral angle between the planes of the phenyl and imide rings is 51·1 (7)°. The methoxy group and the phenyl ring are nearly coplanar. The distance of O(3) of this group from the plane of the phenyl ring is 0·042 (9) Å; however, C(16) is situated perfectly in this plane. The C(13)—O(3) bond length of 1·351 (13) Å indicates partial double-bond character and compares well with the average calculated value of 1·360 Å for similar bonds (Pauling, 1960). It would appear that the tendency of the group Ph—O(3)—C(16) towards planarity has resulted in some close contacts between C(16) – C(14) and the H attached to them, which have been relieved by increasing the angle C(14)—C(13)—O(3) from 120° to 125·6 (11)° and the angle C(13)—O(3)—C(16) to 117·3 (9)°.

Molecular packing

The molecular packing in the unit cell is given in Fig. 3. The deviation of the phenyl ring from the elongated molecular axis is here clearly shown. The shortened intermolecular contacts are marked. The deformation of the planar distribution of the N—C bonds is caused by the shortened distances O(3)—C(4) = 3·176 (15) and O(1)—C(11) = 3·351 (15) Å.

References

ALLEN, F. H. & TROTTER, J. (1971). *J. Chem. Soc. B*, pp. 1073–1079.
ARCORIA, A., LUMBROSO, H. & PASSERINI, R. (1959). *Bull. Soc. Chim. Fr.* pp. 754–760.
ARGAY, GY., KÁLMÁN, A., NAHLOVSKI, Á. & RIBÁR, B. (1975). *Acta Cryst.* B31, 1956–1961.
BUKOWSKA-STRZYŻEWSKA, M. & PNIEWSKA, B. (1979a). *Acta Cryst.* B35, 640–643.
BUKOWSKA-STRZYŻEWSKA, M. & PNIEWSKA, B. (1979b). *Acta Cryst.* B35, 633–639.
CAREY, F. A., SMITH, P. M., MAHER, R. J. & BRYAN, R. F. (1977). *J. Org. Chem.* 42(6), 961–967.
CHAO, G. Y. & MCCULLOUGH, J. D. (1960). *Acta Cryst.* 13, 727–732.
DOBROWOLSKA, W. & BUKOWSKA-STRZYŻEWSKA, M. (1980a). *Acta Cryst.* B36, 317–321.
DOBROWOLSKA, W. & BUKOWSKA-STRZYŻEWSKA, M. (1980b). *Acta Cryst.* B36, 462–464.
DOYLE, P. A. & TURNER, P. S. (1968). *Acta Cryst.* A24, 390–397.
DUAX, W. L. & NORTON, D. A. (1975). *Atlas of Steroid Structure*. New York, Washington, London: Plenum.
HAHN, W. E. & RYBCZYŃSKI, B. (1971). *Soc. Sci. Łodz. Acta Chim.* 16, 123–128.
HAHN, W. E. & RYBCZYŃSKI, B. (1976). *Rocz. Chem.* 50, 1523–1533.
International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.
KAFTORY, M. (1978). *Acta Cryst.* B34, 471–475.
KALFF, H. T. & ROMERS, C. (1965). *Acta Cryst.* 18, 164–168.
KALFF, H. T. & ROMERS, C. (1966). *Acta Cryst.* 20, 490–496.
KIRFEL, A., WILL, G. & FICKENTSCHER, K. (1975). *Acta Cryst.* B31, 1973–1975.
KOBAYASHI, Y. & IITAKA, Y. (1977). *Acta Cryst.* B33, 923–925.
LUMBROSO, H. & DABARD, R. (1959). *Bull. Soc. Chim. Fr.* pp. 749–753.
MCPHAIL, A. T., ONAN, K. D. & KOSKIMIES, J. (1976). *J. Chem. Soc. Perkin Trans.* 2, pp. 1004–1008.
MARSH, R. E. (1955). *Acta Cryst.* 8, 91–94.
MATSUO, T. (1965). *Bull. Chem. Soc. Jpn*, 38, 557–562.
MAZHAR-UL-HAQUE & BEHFOROUZ, M. (1979). *Acta Cryst.* B35, 845–848.
PAULING, L. (1960). *The Nature of the Chemical Bond*, pp. 275–276. Ithaca: Cornell Univ. Press.
PETERSEN, C. S. (1969). *Acta Chem. Scand.* 23, 2389–2402.
RIBÁR, B., STANKOVIĆ, S., HERAK, R., HALASI, R. & DJURIĆ, S. (1974). *Cryst. Struct. Commun.* 3, 669–672.
SHELDRICK, G. M. & TROTTER, J. (1979). B35, 250–253.
STEWART, J. M., KUNDELL, F. A. & BALDWIN, J. C. (1970). The XRAY 70 system. Computer Science Center, Univ. of Maryland, College Park, Maryland.