Molecular and crystal structure of 3-(4-chlorophenylthio)-1-(2,4-dinitrophenylamino)-pyrrolidine-2,5-dione

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3-(4-Chlorophenylthio)-1-(2,4-dinitrophenylamino)-pyrrolidine-2,5-dione, $C_{16}H_{11}N_4C10_6S$, was obtained in the addition reaction of 4-chlorobenzenethiol and 2,4-dinitrophenyl-aminomaleimide. It forms orthorhombic crystals; the final R = 0.048 for 1083 unique observed reflections. The molecule consists of three rigid rings connected by single bonds. A synclinal conformation of the terminal phenyl rings (A and C) with respect to the central pyrrolidine ring (B) is observed in the crystal, with rings A and C close to one another. An intramolecular hydrogen bond N(2) · · · O(4) of 2.593(7) Å is observed. The structure of the title compound was also investigated by IR, ¹H—NMR and M.S.

Introduction

The present work is the first part of our X-ray study of the cyclic imides of succinic acid. This group of compounds was synthesized in the Department of Organic Chemistry, Medical Academy, Poznań. The main interest in the structures studied is in the conformations of the molecules that consist of several rigid rings connected by single chemical bonds, as well as in the intermolecular interactions and ability of the molecules to form hydrogen bonds.

Experimental

General procedure

The melting point was determined on a Boetius apparatus, and the IR spectrum was obtained as a potassium bromide pellet, using a Perkin-Elmer 180 spectrometer. The ¹H--NMR spectrum was recorded on a Varian EM-360(90 MHz) spectrometer in deuteriated DMSO, with TMS as internal standard. The mass spectrum was obtained on an EAI MS-900 mass spectrometer. To prepare the title compound, a mixture of equimolar amounts of 2,4-dinitrophenylaminomaleimide (Baloniak, 1968), 4-chlorobenzenethiol, and triethylamine was refluxed in acetone for 2 hr. Then, the solvent was removed and the dry residue was crystallized from ethanol.

Yellow crystals, mp 452.5 - 454.5 K. M.S.: m/z 422.00868(M^{++}) (Calcd. 422.00851). IR (cm⁻¹): 3355 (NH), 1795, 1730 (CO), 1540 - 1525, 1337 - 1315 (NO₂).

¹H-NMR: $\delta = 10.36(1H, s)$, 8.93(1H, d, J = 2Hz), 8.33(1H, dd, J = 2 Hz, J = 9 Hz), 7.65(2H, d, J = 9 Hz), 7.48(2H, dd, J = 9 Hz), 7.11(1H, broad singlet), 4.78(1H, q, ³J = 4.8 Hz, ³J = 9.0 Hz), 3.58(1H, dd, ²J = 18.4 Hz, ³J = 4.8 Hz), 2.90(1H, dd, ²J = 18.4 Hz, ³J = 9.0 Hz).

Anal.: Calcd. for $C_{16}H_{11}N_4C10_6S$ (422.79): C:45.4, H:2.6, N:13.2. Found: C:45.3, H:2.8, N:13.4. Crystal data are shown in Table 1.

X-ray analysis

Yellow single crystals of the title compound suitable for X-ray investigation were obtained by a slow evaporation of its ethanol solution, at room temperature. The crystal selected for data collection had the dimensions 0.25, 0.20, 0.46 mm. Measurements were carried out on a Syntex $P2_1$ diffractometer, using graphite

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Table 1. Crystal data

Space $a = 2$	e group <i>Pcca</i> 20.418(4) Å
b = 1	17.212(4) Å
V = 1	$3641(1) Å^3$
$Z = \delta$	$\frac{3}{1.54}$ some $\frac{-3}{1.54}$ (by θ_{-4-4} is a
$D_m = D_r =$	1.54 gcm (by notation) $1.55(5) \text{ gcm}^{-3}$
λ Μο	$K\alpha = 0.71069$ Å
μ(Mo <i>F(</i> 000	$K\alpha$ = 3.13 cm ⁻¹
R = 0	0.048 for 1083 unique observed reflections

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monochromated Mo $K\alpha$ radiation. The unit-cell parameters were determined by a least-squares fit to 10 automatically centered reflections (2θ 8.1 to 12.5°). Two control reflections monitored after each 200 intensity measurements showed no systematic change in intensity. The θ -2 θ scan method with a variable scan speed (from 2.0 to 29.3°/min.) was used; 3854 reflections were collected up to $2\theta = 50^{\circ}$, their indicies being h 0/25, k 0/20, l 0/13.

The background and integrated intensity for each reflection were calculated according to the profile-analysis method of Lehmann and Larsen (1974). Of 2672

Table 2. Fractional atomic coordinates (*10⁴) and anisotropic thermal parameters^{*a*} (*10³) of non-hydrogen atoms and the H-atom positions (*10³). All the H-atoms were assigned $U_{iso} = 0.06$ Å²

Atom	x	у	Z	U_{11}	<i>U</i> ₂₂	U ₃₃	U ₁₂	<i>U</i> ₁₃	U ₂₃
s	2991(1)	2519(1)	1894(2)	72(1)	52(1)	38(1)	8(1)	-15(1)	3(1)
Cl	3575(1)	4914(1)	6314(2)	132(2)	65(2)	78(2)	20(2)	-27(2)	-24(1)
N(4)	4540(4)	3254(5)	9611(7)	63(5)	59(5)	51(5)	-13(5)	9(4)	-8(4)
O(5)	4608(3)	3927(4)	9278(6)	126(6)	56(4)	82(5)	-24(5)	-31(4)	-5(4)
O(6)	4711(3)	3001(3)	10667(5)	85(5)	78(5)	39(3)	-26(4)	-4(3)	-3(3)
C(9)	4259(4)	2702(4)	8699(7)	38(5)	39(5)	35(5)	-5(4)	-8(4)	-7(4)
C(8)	4130(3)	2959(4)	7463(7)	40(5)	38(5)	44(5)	0(4)	-1(4)	-5(4)
C(7)	3897(3)	2429(4)	6555(6)	44(5)	46(5)	23(4)	-5(5)	0(3)	11(4)
C(6)	3773(3)	1651(4)	6890(7)	39(5)	43(5)	25(4)	-4(4)	3(4)	0(4)
C(11)	3885(3)	1434(4)	8173(7)	42(5)	34(4)	31(4)	1(4)	7(4)	1(4)
C(10)	4131(3)	1961(5)	9058(7)	36(5)	52(6)	31(4)	3(5)	5(4)	4(4)
N(3)	3736(3)	657(4)	8654(6)	53(5)	41(4)	37(4)	2(4)	0(4)	4(4)
O(4)	3563(3)	157(3)	7877(5)	130(6)	46(4)	41(3)	-18(4)	-10(4)	1(3)
O(3)	3790(2)	528(3)	9813(5)	76(4)	62(4)	32(3)	-3(3)	-9(3)	18(3)
N(2)	3544(3)	1139(3)	5978(5)	57(4)	42(4)	24(3)	-15(4)	-1(3)	5(3)
N(1)	3587(3)	1348(3)	4682(5)	51(5)	41(4)	23(3)	1(4)	-3(4)	-4(3)
C(5)	4192(5)	1317(4)	4030(7)	46(6)	39(5)	39(5)	5(5)	10(5)	-1(4)
0(2)	4702(3)	1142(3)	4540(5)	40(4)	99(5)	58(4)	4(3)	-9(3)	15(4)
C(4)	4047(4)	1543(4)	2652(7)	63(6)	42(5)	37(5)	4(5)	9(5)	9(4)
C(3)	3302(4)	1609(4)	2554(7)	47(5)	42(5)	30(4)	8(4)	-6(4)	-1(4)
C(2)	3030(4)	1448(4)	3900(7)	41(6)	40(5)	44(5)	0(5)	-7(5)	0(4)
0(1)	2491(3)	1415(3)	4278(5)	42(4)	90(4)	59(4)	-4(4)	5(3)	1(5)
C(12)	3426(5)	4275(4)	5058(8)	95(8)	31(5)	46(5)	9(5)	-20(6)	-7(5)
C(13)	3905(4)	4096(5)	4201(8)	62(7)	36(5)	64(6)	10(5)	-9(5)	1(5)
C(14)	3785(4)	3562(4)	3239(8)	55(6)	45(5)	51(5)	7(5)	4(5)	9(5)
C(15)	3177(4)	3196(4)	3158(7)	56(7)	37(5)	36(4)	4(4)	-3(5)	3(4)
C(16)	2686(4)	3383(5)	4032(8)	50(6)	48(6)	69(6)	2(5)	4(5)	4(5)
C(17)	2817(5)	3917(5)	4992(9)	94(9)	47(6)	56(6)	15(6)	13(6)	-14(5)
Atom	x	у	Z						
H(8)	421	356	717						
H(7)	381	262	558						
H(10)	422	178	1004						
H(5)	334	59	626						
H(41)	427	209	243						
H(42)	423	110	200						
H(3)	313	119	185						
H(16)	438	437	427						
H(17)	416	343	255						
H(13)	221	312	396						
H(14)	245	406	570						

 ${}^{a}T = \exp\left[-2\pi^{2}(U_{11}h^{2}a^{*2} + U_{22}k^{2}b^{*2} + U_{33}l^{2}c^{*2} + 2U_{12}hka^{*}b^{*} + 2U_{13}hla^{*}c^{*} + 2U_{23}klb^{*}c^{*})\right].$



Fig. 1. ORTEP (Johnson, 1965) diagram of the molecule, viewed perpendicular to group C(3)-S-C(12). The thermal ellipsoids are drawn at the 50% probability level. H-Atoms have been omitted for clarity. The intramolecular hydrogen bond is indicated with the dashed line.

unique reflections, 1083 had $I \ge 1.96\sigma(I)$ and were used in the structure refinement. Only Lp corrections were applied. The structure was solved using MULTAN-80 (Main et al., 1980). After the refinement of the nonhydrogen atoms with anisotropic temperature factors, all hydrogen atoms were calculated from the geometry of the molecule ($d_{C-H} = 1.08$ Å) and assigned isotropic temperature factors (U) of 0.06 Å². Their coordinates were recalculated after each cycle of refinement, following the shifts of their carriers. The function minimized was $\Sigma w(|F_0| - |F_c|)^2$, where $w = [\sigma^2 F_0 + 0.0003]$ $|F_0|^2$]⁻¹. The final cycles of the full-matrix least-squares refinement gave R = 0.0480, wR = 0.0438 and S =0.75. For all the refined parameters, the final Δ/σ was smaller than 0.04, the highest peak on the final ΔF -map was 0.32 e Å⁻³, the minimum -0.21 e Å⁻³. The final atomic parameters are listed in Table 2. Atomic scattering factors from the International Tables for X-ray

Table 3. Bond lengths (Å) and valency angles (°)

N(4)-O(5) 1.2	216(8)	C(5)-O(2)	1.206(8)
N(4)-O(6) 1.2	29(8)	C(5) - C(4)	1.509(10)
N(4) - C(9) = 1.4	58(9)	C(4) - C(3)	1.529(9)
C(9)-C(8) 1.4	06(10)	C(3) - C(2)	1.520(10)
C(8)-C(7) 1.3	75(9)	C(2) = O(1)	1.189(9)
C(7)-C(6) 1.4	06(9)	C(2) - N(1)	1.390(8)
C(9)-C(10) 1.3	54(9)	C(3) - S	1.822(7)
C(10)-C(11) 1.3	84(9)	S-C(12)	1.793(7)
C(11)-C(6) 1.3	99(9)	C(12) - C(13)	1.388(10)
C(11)-N(3) 1.4	60(8)	C(13) - C(14)	1.381(10)
N(3)-O(3) 1.2	26(7)	C(14) - C(15)	1.390(10)
N(3)-O(4) 1.2	30(7)	C(15)-Cl	1.732(8)
C(6)-N(2) 1.3	74(8)	C(15)-C(16)	1.354(11)
N(2) = N(1) 1.3	93(7)	C(16)-C(17)	1.378(10)
N(1) = C(5) 1.4	08(9)	C(17)-C(12)	1.395(10)
O(5)-N(4)-O(6)	124.0(6)	N(1) = C(5) = O(2)	123.8(6)
O(5) = N(4) = C(9)	117.2(6)	C(2) = N(1) = C(5)	115.5(6)
O(6) - N(4) - C(9)	118.8(6)	O(2) - C(5) - C(4)	130.4(6)
N(4) = C(9) = C(10)	120.8(6)	N(1) - C(5) - C(4)	105.8(6)
N(4) - C(9) - C(8)	118.1(6)	C(5) - C(4) - C(3)	106.1(6)
C(8) = C(9) = C(10)	120.8(6)	C(4) - C(3) - C(2)	106.0(6)
C(9) - C(8) - C(7)	118.2(6)	C(3) - C(2) - N(1)	105.9(6)
C(8) = C(7) = C(6)	122.0(6)	O(1) - C(2) - C(3)	130.0(6)
C(7) - C(6) - C(11)	117.3(6)	C(2) - C(3) - S	112.2(5)
C(6) = C(11) = C(10)	120.9(6)	C(4) - C(3) - S	115.8(5)
C(11) - C(10) - C(9)	120.3(6)	C(3) = S = C(12)	102.2(3)
C(10) - C(11) - N(3)	116.7(6)	S = C(12) = C(17)	121.8(5)
C(6) = C(11) = N(3)	122.3(6)	S-C(12)-C(13)	118.3(5)
C(11) = N(3) = O(4)	118.8(5)	C(13) - C(12) - C(12)	17) 119.9(7)
C(11) - N(3) - O(3)	118.5(5)	C(12) - C(17) - C(17)	16) 120.2(7)
O(3) = N(3) = O(4)	122.7(5)	C(17) - C(16) - C(16)	15) 119.8(7)
C(11) - C(6) - N(2)	122.5(6)	C(16) - C(15) - C(15)	14) 120.9(8)
C(7) = C(6) = N(2)	120.2(5)	C(15) - C(14) - C(14)	13) 120.2(7)
C(6) = N(2) = N(1)	118.4(5)	C(14) - C(13) - C(13)	12) 119.0(7)
N(2) = N(1) = C(2)	122.9(5)	C(16) - C(15) - Cl	120.7(6)
N(1) = C(2) = O(1)	124.1(7)	C(14) - C(15) - Cl	118.4(6)
N(2) = N(1) = C(5)	120.4(5)		

Table 4. Selected torsion angles (deg).

Crystallography (1974) were used. Most of the calculations were performed with SHELX-76 (Sheldrick, 1976) on a RIAD-32 computer.

Discussion

The molecular conformation and labeling of the atoms and rings are presented in Fig. 1. The bond distances and valency angles are listed in Table 3. The molecule consists of three rigid fragments: the phenyl rings are almost planar; χ^2 for ring A is 15.6 and for ring C is 2.2. The 5-membered ring B is not strongly

distorted from planarity, its χ^2 equals 136.9 (all the atoms of ring *B* are closer than 0.06 Å from its best plane). Atoms O(1) and O(2) are 0.103(6) and 0.171(6) Å off this plane, respectively. The distance of atom S to this plane is -1.353(2) and of atom N(2) 0.065(6) Å. The nitro groups are planar: C(11)-NO₂ ($\chi^2 = 0.01$), C(9)-NO₂ ($\chi^2 = 2.57$) and they are at 6.7(7) and 7.0(7)°, respectively, to the plane of phenyl ring *A* (see Table 4).

The molecule consists of three planar rings, and its conformation can be described with the torsion angles along the single bonds with which the rings are connected (Table 4). The angles between the planes of the rings are: ring A to ring B—77.0(7)°, ring A to ring C—109.5(6)°, ring B to ring C—125.0(6)°. All the bond lengths and valency angles agree very well with the expected values. A short intramolecular hydrogen bond between N(2) and O(4) of 2.593(7) Å was observed, distance H(2)···O(4) is 1.89 Å and angle N(2)—H(2)···O(4) is 119.2° (the position of H(2) was calculated from the geometry of the molecule skeleton).

The synclinal conformation of the molecule (see Fig. 1) causes no short intramolecular contacts between the atoms of rings A and C. The shortest intramolecular distance is $C(7) \cdot \cdot \cdot C(13) 3.77(1)$ Å, all the others are longer than 3.8 Å. The molecular packing of the molecules in the crystal is shown in Fig. 2. No other intermolecular contacts other than van der Waals' interactions are observed in this structure.



Fig. 2. Stereoscopic view of the unit-cell contents (Motherwell and Clegg, 1978). Hydrogen bonds are represented by the dashed lines, H-atoms have been omitted for clarity.

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Structure factor data have been deposited with the British Library, Boston Spa, Wetherby, West Yorkshire, UK as supplementary publication No. 60679 (6 pages).