SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF 1-(4-METHYLBENZOYL)-3,3-DIMETHYLTHIOUREA

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ABSTRACT

Crystal and molecular structure of 1-(p-methylbenzoyl)-3,3-dimethylthiourea has been determined by means of spectroscopic techniques such as IR, ^{1}H, ^{13}C NMR and X-ray diffraction. Crystals are monoclinic, space group $P2_1/c$; a=12.703(5), b=5.577(5), c=17.389(5)Å, ß=103.93(1)°; Z=4. The compound was synthesized by a conventional procedure.

RESUMEN

La estructura cristalina y molecular de la 1-(p-metilbenzoil)-3,3-dimetiltiourea fue determinada por métodos espectroscópicos IR, RMN-^{1}H, ^{13}C y difracción de rayos X. Los cristales son monoclínicos con grupo espacial $P2_1/c$; a=12.703(5), b=5.577(5), c=17.389(5)Å, ß=103.93(1)°; Z=4. El compuesto fue sintetizado utilizando procedimientos convencionales.

INTRODUCTION

Among organic sulphur compounds, thioureas and its derivatives are of relevant importance. These compounds have been introduced almost in every branch of chemistry. They are commercialized as dyes, photographic films, elastomers, plastics and textiles (1).

In scientific research works they are thoroughly used as intermediates in the synthesis and characterization of organic compounds and in the separation of branched hydrocarbons in organic mixtures (2), (3).

Structural studies of a number of benzoylthioureas have proved them to be in the thioamidic form and to possess an intramolecular hydrogen bond between N-H and the benzoyl oxygen (4), (5).

The present paper describes the molecular structure of 1-(p-methylbenzoyl)-3,3-dimethylthiourea in order to have a

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better comprehension of the above mentioned properties and applications.

EXPERIMENTAL

The synthesis of 1-(p-methylbenzoyl)-3,3-dimethylthiourea was performed by means of the conventional method described by Douglas and Dains (6).

30 mmoles of amonium thiocyanate dissolved in 25 mL of dried acetone were added dropwise with stirring to an equimolar quantity of 4-methylbenzoylchloride dissolved in 15 mL of the same solvent. Next, 40 mmoles of dimethylamine dissolved in 15 mL of dried acetone were added slowly and with agitation to the mixture. Finally the contents were poured on 600 mL of cold water. Yield 53%, m.p. 125-128°C. **IR** (KBr) cm^{-1}: 3180 (NH), 1690 (C=O), 1610 (C=C), 1550 (band I, N-C=S), 1385 (band II N-C=S); 1125 (band III N-C=S); 975 (band IV N-C=S). **^{1}H-NMR**-($CDCl_3$) δppm: 8.32 (1H, s, NH), 7.27-7.70 (4H, AA'BB', ArH), 3.27, 3.51 (3H, s, CH_3), 2.42 (3H, s, CH_3). **^{13}C-NMR** ($CDCl_3$) δppm: 180.5 (C=S), 163.9 (C=O), 142.3 (C-5), 130.1 (C-8), 128.9 (C-7, C-9), 128.1 (C-6, C-10), 43.1, 43.4 (CH_3), 21.0 (CH_3). **UV** λmax nm: 249 ($\varepsilon.10^{-4}$: 2.01).

The infrared spectra were recorded in a Phillips Analytical Pu 9600 FT IR spectrometer. The ^{1}H NMR and ^{13}C NMR spectra were run in a Bruker AC F(250-^{1}H,-62.0-^{13}C) using TMS as internal standard and $CDCl_3$ as solvent. TLC chromatography was carried out employing silicagel-G-60 plates as stationary phase.

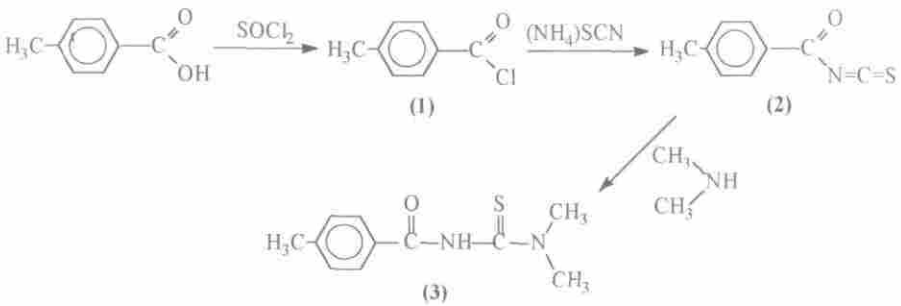
Crystals suitable for X-ray analysis were obtained by slow evaporation from acetone solution. The structure was solved using direct methods SHELXL 86 program. Most of the non-hydrogen atoms were located in the electron density map, and the remaining were found in a subsequent difference electron density map. They were refined on F^2(hkl) by full matrix least squares, originally with isotropic and latter anisotropic temperature factors. All the H- atoms were calculated at the idealized positions based on the molecular geometry with C-H = 0.96Å, except for H(1) whose coordinates were located in the electron density map. Isotropic temperature factors were set at 1.2 times Beq with respect to the corresponding atom to which they are bonded. Hydrogen atom coordinates were refined in subsequent least square cycles. Refinement was continued until all shift error ratios were <0.1.

Least-squares refinement was performed minimizing the function $R=\Sigma w_1 (|Fo|-|Fe|^2)$, where w=1, in the early stages of refinement and $w=1/[\sigma^2 (Fo^2)]$ in the final cycles. Neutral-atom scattering factors were used. All programs used are part of the SHELXT-Plus package (7). Diffractometer Siemens R3.

RESULTS AND DISCUSSION

The synthetic method employed consist of three steps, Scheme 1.

Infrared studies of the title compound show a band in the region of 3180cm^{-1} that sometimes appeared as a doublet and which is assigned to the bond vibration of the NH group. The band observed in the region of 1690 cm^{-1} corresponds to the bond vibration of the carbonyl group. The low value is due to the conjugation of



Scheme 1. *Synthesis of 1-(4-methylbenzoyl)-3.3-dimethylthiourea.*

the carbonyl group with the benzenic ring. The characteristic bands of the thioureid group, named as band I, II, III, IV were observed in the region reported by Moshen (8), i.e. at 1550 cm^{-1} (band I, N-C=S); 1385 cm^{-1} (band II, N-C=S); 1125 cm^{-1} (band III, N-C=S) and 975 cm^{-1} (band IV, N-C=S).

The ^{1}H-NHR spectrum of 3 showed signals for aromatic protons at δ 7.27-7.70 ppm and two singlets at δ 3.27 and 3.51 ppm for the methyl groups. The signal at δ 8.32 ppm was assigned to the proton attached to the nitrogen. This value is characteristic for this type of compounds in CDCl$_3$ (9). The ^{13}C-NHR spectrum was consistent with structure 3. Signals at δ 142.3, 128.1, 128.9 and 130.1 ppm were assigned to C-5, C-6, C-7 and C-8, respectively. Methyl carbons appeared at δ 40.9 and 41.8 ppm. Carbonylic and thiocarbonilic carbons resonated at 163.9 and 180.5 ppm, respectively.

Tables I, II and III summarize the crystal data and the data collection, the atomic coordinates and the temperature factors, bond lengths and angles obtained from X-ray diffraction studies for 1-(4-methylbenzoyl)-3,3 dimethylthiourea, respectively.

The intramolecular hydrogen bond N-H....S is present in this structure. The values of the hydrogen bond are N(1)-H(1): 0.900 Å, N(1)...S: 3.401 Å and the angle N(1)-H(1)...S: 122.09°. These values are in correspondence with the reported in the literature (10), (11).

The torsion angles O-C(1)-C(5)-C(6) and N(1)-C(1)-C(5)-C(6) are -36.98° and 143.94° respectively. These values are three times greater than those reported by Dago et al (12), in this case the effect of the substituent deviates the molecule from planarity. The acylthioureid group is present in the thiourea in a "*quasi S*" conformation (13).

Supplementary chemical and crystallographic data of this paper are available from the X-ray Laboratory of the National Center for Scientific Research, Havana, Cuba.

Figure 1 shows 1-(4-methylbenzoyl) thiourea in its preferential conformation.

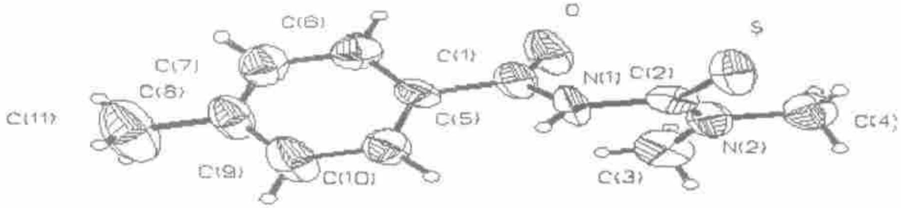


Figura 1. Molecular structure of $C_{11}H_{14}N_2OS$.

Table I. Summary of crystal data and conditions for crystallographic data collection structure solution and refinement.

Crystal data			
Empirical Formula	$C_{11}H_{14}N_2OS$	Volume	1199.7 (5) Å^3
Formula weight	222.304	Z	4
Crystal system	Monoclinic	Density (Calculated)	1.235 Mg/m^3
Space group	$P2_1/c$	Absorption coefficient	0.25 mm^{-1}
Unit cell dimensions	a = 12.703(1) Å	F(000)	472.0
Determined from	b = 5.577(1)	Crystal size	0.40 x 0.23 x
32 reflections	c = 17.389(2)		0.07 mm
	β= 103.93(1)°		
Data collection			
Diffractometer	Siemens R3		
Radiation	MoKα(λ = 0.71069) *graphite monochromator*		
Temperature	293 K		
For data collection	θ *range*		
	1.50 to 20°	check reflections	1 measured every 100 refl.
h k l limits	-1/ 12, -1/ 5, -16/ 16	absorption correction	not applied
scan type	ω/2θ	reflections collected	1857
variable scan speed	min = 3 grade / min;	reflections unique	1126
	max = 30 grade/min	reflections observed	[I > 2s (I)] = 771
Refinement on F^2			
$R[F^2 > 2\sigma(F^2)] = 0.071$			
$wR(F^2) = 0.137$			

Table II. Atomic coordinates (x10^4) and temperature factors (Å^2 x 10^3).

Atom	x/a	y/b	z/c	Uequiv.
S	-1625(2)	1445(4)	4628(1)	69(1)
O	88(4)	1939(12)	2783(3)	81(3)
N1	116(4)	2616(11)	4115(3)	58(3)
N2	-1396(5)	4892(13)	3641(3)	57(3)
C1	506(6)	2077(16)	3438(5)	59(4)
C2	-990(6)	3045(14)	4084(4)	42(3)
C3	-810(6)	6584(17)	3275(4)	82(4)
C4	-2569(6)	5431(17)	3487(4)	78(4)
C5	1705(5)	1748(16)	3623(4)	47(3)
C6	2125(7)	30(17)	3204(4)	63(4)
C7	3253(7)	-202(19)	3338(4)	76(4)
C8	3931(6)	125.8(21)	3850(5)	79(5)
C9	3506(6)	3003(21)	4255(5)	92(5)
C10	2378(6)	3229(18)	3973(5)	64(4)
C11	5148(6)	1021(27)	4143(4)	151(7)

Table III. Selected bond lengths (Å) and bond angles ($(^0)$), (s.d. following Cruickshank, Internat. Tables, II, 1959, p.331).

Bond lengths (Å)		Bond Angles (^{0})		
	lengths		Angle	s.u
S-C2	1.645(8)	C1-N1-C2	123.29	0.55
N1-C1	1.414(10)	C2-N2-C3	126.90	0.68
N1-C2	1.414(9)	C2-N2-C4	120.05	0.63
N2-C2	1.315(10)	C3-N2-C4	113.05	0.59
N2-C3	1.441(11)	O-C1-N1	122.23	0.68
N2-C4	1.481(9)	O-C1-C5	124.73	0.68
C1-C5	1.490(10)	N1-C1-C5	113.03	0.60
C5-C6	1.386(12)	S-C2-N1	120.45	0.52
C5-C10	1.363(10)	S-C2-N2	125.77	0.57
C6-C7	1.401(12)	N1-C2-N2	113.59	0.62
C7-C8	1.353(13)	C1-C5-C6	118.36	0.68
C8-C9	1.384(15)	C1-C5-C10	120.94	0.66
C8-C11	1.515(11)	C6-C5-C10	120.49	0.72
C9-C10	1.404(11)	C5-C6-C7	119.01	0.78
O-C1	1.208(8)	C6-C7-C8	121.14	0.80
		C7-C8-C9	119.55	0.89
		C7-C8-C11	120.44	0.76
		C9-C8-C11	120.00	0.75
		C8-C9-C10	120.19	0.77
		C5-C10-C9	119.60	0.72

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