Crystal structure of 3-(4-bromobenzoyl)-1,1-diphenylthiourea, $C_{20}H_{15}BrN_2OS$

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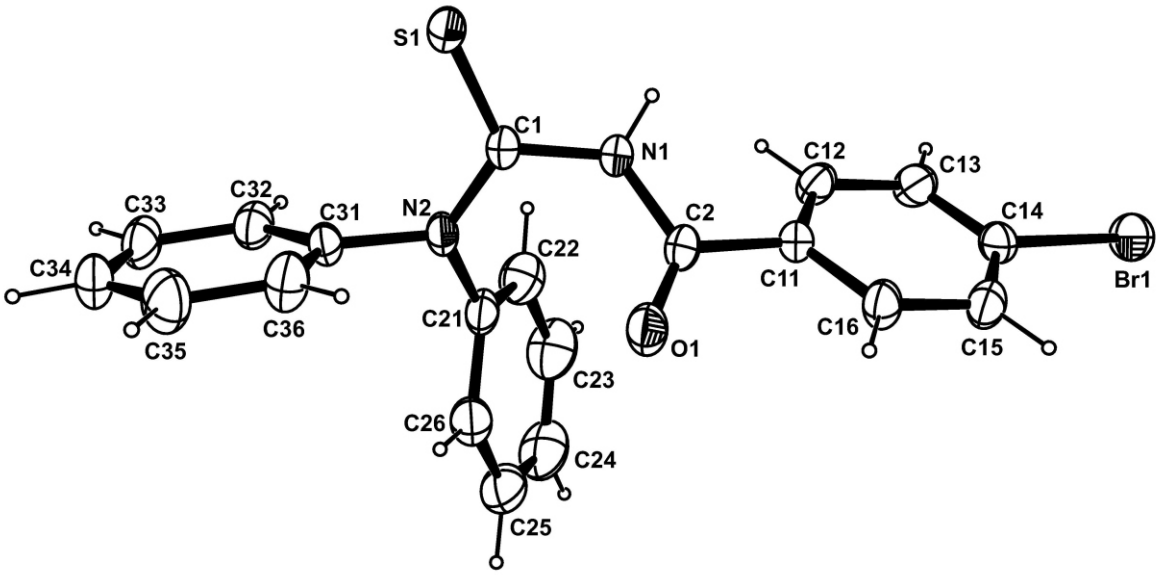

Abstract

$C_{20}H_{15}BrN_2OS$, triclinic, $P\bar{1}$ (no. 2), a = 6.7850(5) Å, b = 9.9640(7) Å, c = 13.4260(9) Å, α = 89.123(3)°, β = 79.952(3)°, γ = 89.816(3)°, V = 893.6 Å^3, Z = 2, $R_{gt}(F)$ = 0.049, $wR_{ref}(F^2)$ = 0.151, T = 200 K.

Source of material

The compound was prepared upon reacting 4-bromobenzoyl chloride with equimolar amounts of potassium thiocyanate and diphenylamine in refluxing acetone for four hours. After filtration, the solution was left for evaporation upon which a crystalline solid was obtained.

Experimental details

Carbon-bound H atoms were placed in calculated positions with d(C—H) = 0.95 Å and were included in the refinement in the riding model approximation with U(H) = 1.2 U_{eq}(C). The nitrogen-bound H atom was located on a difference Fourier map and refined freely.

Discussion

1,3-Diketonic and mixed 1,3-*O*- and *S*-ketonic molecules have found widespread use as ligands in coordination chemistry. Upon introduction of an amine group instead of a methylene group connecting the two sp^2-hybridized C atoms, an easy way of generating anionic, chelating ligands by means of deprotonation is available. For comparative studies in envisioned coordination compounds, we determined the crystal structure of the title compound. Structural analyses for similar compounds applying diethylamine- as well as di-*n*-propylamine substituents on the C=S-moiety are apparent in the literature [1,2].

In the title crystal structure, the molecule is present in its *O*- and *S*-diketonic tautomeric form. Due to mesomeric interactions, the bond length d(C(=S)—N) with only 1.346(3) Å is significantly shorter than both C—N bond lengths stemming from the central NH group. The NH group is nearly in plane with the *O*-keto group while the *O*-keto and the *S*-keto group adopt a staggered conformation. The least-squares planes defined by the C atoms of the 4-bromophenyl group on the one hand and the C(=O)–N_{NH} moiety on the other hand intersect at an angle of 27.3(2)° while for the least-squares plane defined by the C(=S)–N_{NH} moiety an intersection angle of 77.9(1)° is observed. The planes of the phenyl groups on the diphenylamine moiety enclose an angle of 87.2(1)°. In the crystal structure, two types of intermolecular interactions can be observed: first, N–H···S hydrogen bonds which connect two molecules to centrosymmetric dimers. Second, C–H···O contacts whose range falls by more than 0.3 Å below the sum of van-der-Waals radii of the respective atoms. These contacts appear between one of the H atoms in *ortho*-position to the Br atom of the 4-bromophenyl moiety and the double-bonded O atom. The latter contacts connect the dimeric units to tubes along (100) where the C–H···O contacts run as antidromic chains along the outside of these tubes. In terms of graph-set analysis [3,4], the descriptor for the hydrogen bonds is $R_2^2(8)$ on the unitary level while the descriptor for the C–H···O contacts is $C_1^1(6)$ on the same level. π-Stacking is not a prominent feature of the crystal structure with the closest distance between two aromatic systems found at 4.142(2) Å.

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Table 1. Data collection and handling.

Crystal:	colourless rod, size 0.13 × 0.25 × 0.55 mm
Wavelength:	Mo K_α radiation (0.71069 Å)
μ:	24.27 cm^{-1}
Diffractometer, scan mode:	Bruker APEX-II CCD, φ/ω
$2\theta_{max}$:	56°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	14718, 4210
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3645
$N(param)_{refined}$:	230
Programs:	SHELXS-97, SHELXL-97 [5], ORTEP-3 [6], Mercury [7], PLATON [8]

Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{iso}
H(71)	2*i*	0.092(6)	1.037(4)	0.390(3)	0.038(9)
H(12)	2*i*	–0.0740	1.0910	0.2584	0.035
H(13)	2*i*	–0.2609	1.2517	0.1864	0.039
H(15)	2*i*	0.2106	1.5069	0.1495	0.041
H(16)	2*i*	0.3981	1.3451	0.2207	0.036
H(22)	2*i*	0.1148	0.7932	0.2307	0.048
H(23)	2*i*	0.1248	0.7930	0.0552	0.062
H(24)	2*i*	0.4260	0.8221	–0.0549	0.065
H(25)	2*i*	0.7199	0.8485	0.0083	0.059
H(26)	2*i*	0.7152	0.8534	0.1824	0.046
H(32)	2*i*	0.3688	0.5638	0.3329	0.039
H(33)	2*i*	0.5821	0.3967	0.3772	0.046
H(34)	2*i*	0.8800	0.4555	0.4296	0.051
H(35)	2*i*	0.9552	0.6816	0.4477	0.057
H(36)	2*i*	0.7414	0.8494	0.4046	0.045

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Br(1)	2*i*	–0.19905(4)	1.52464(3)	0.11046(2)	0.0425(2)	0.0478(2)	0.0457(2)	0.0202(1)	–0.0001(1)	0.0189(1)
S(1)	2*i*	0.2429(1)	0.86627(6)	0.52052(5)	0.0421(4)	0.0269(3)	0.0266(3)	0.0104(2)	–0.0015(2)	0.0041(2)
O(1)	2*i*	0.4869(3)	1.1002(2)	0.2646(2)	0.0280(9)	0.0254(9)	0.054(1)	0.0000(7)	–0.0070(8)	0.0080(8)
N(1)	2*i*	0.2029(3)	1.0086(2)	0.3563(2)	0.031(1)	0.0203(9)	0.030(1)	0.0058(8)	–0.0001(8)	0.0056(8)
N(2)	2*i*	0.4122(3)	0.8228(2)	0.3303(2)	0.032(1)	0.0209(9)	0.026(1)	0.0092(8)	–0.0050(8)	0.0019(7)
C(1)	2*i*	0.2920(4)	0.8998(2)	0.3968(2)	0.029(1)	0.018(1)	0.028(1)	0.0034(8)	–0.0041(8)	0.0022(8)
C(2)	2*i*	0.3068(4)	1.1023(2)	0.2888(2)	0.031(1)	0.016(1)	0.030(1)	–0.0001(8)	–0.0064(9)	0.0010(8)
C(11)	2*i*	0.1787(4)	1.2033(2)	0.2477(2)	0.027(1)	0.020(1)	0.027(1)	0.0030(8)	–0.0034(8)	0.0017(8)
C(12)	2*i*	–0.0162(4)	1.1755(3)	0.2366(2)	0.031(1)	0.025(1)	0.031(1)	–0.0040(9)	–0.0042(9)	0.0061(9)
C(13)	2*i*	–0.1272(4)	1.2705(3)	0.1940(2)	0.025(1)	0.037(1)	0.035(1)	0.001(1)	–0.0063(9)	0.009(1)
C(14)	2*i*	–0.0415(4)	1.3927(3)	0.1627(2)	0.031(1)	0.031(1)	0.029(1)	0.011(1)	–0.0024(9)	0.0059(9)
C(15)	2*i*	0.1533(4)	1.4225(3)	0.1718(2)	0.035(1)	0.023(1)	0.042(1)	–0.000(1)	–0.005(1)	0.006(1)
C(16)	2*i*	0.2636(4)	1.3265(2)	0.2143(2)	0.029(1)	0.021(1)	0.042(1)	–0.0009(9)	–0.008(1)	0.0026(9)
C(21)	2*i*	0.4129(4)	0.8258(2)	0.2225(2)	0.040(1)	0.021(1)	0.027(1)	0.0069(9)	–0.007(1)	0.0020(8)
C(22)	2*i*	0.2380(5)	0.8061(3)	0.1856(2)	0.049(2)	0.035(2)	0.038(1)	–0.001(1)	–0.013(1)	0.000(1)
C(23)	2*i*	0.2447(6)	0.8053(4)	0.0814(3)	0.068(2)	0.049(2)	0.044(2)	0.000(2)	–0.028(2)	–0.001(1)
C(24)	2*i*	0.4229(7)	0.8220(4)	0.0161(2)	0.086(3)	0.048(2)	0.031(1)	0.010(2)	–0.016(2)	–0.001(1)
C(25)	2*i*	0.5966(6)	0.8387(3)	0.0537(2)	0.066(2)	0.044(2)	0.032(1)	0.014(2)	0.004(1)	0.005(1)
C(26)	2*i*	0.5945(5)	0.8412(3)	0.1568(2)	0.044(2)	0.035(1)	0.035(1)	0.010(1)	–0.004(1)	0.003(1)
C(31)	2*i*	0.5379(4)	0.7211(2)	0.3646(2)	0.031(1)	0.022(1)	0.026(1)	0.0084(9)	–0.0036(9)	0.0009(8)
C(32)	2*i*	0.4884(4)	0.5874(3)	0.3561(2)	0.042(1)	0.025(1)	0.030(1)	0.004(1)	–0.007(1)	0.0006(9)
C(33)	2*i*	0.6156(5)	0.4887(3)	0.3818(2)	0.056(2)	0.022(1)	0.035(1)	0.011(1)	–0.006(1)	0.001(1)
C(34)	2*i*	0.7910(5)	0.5233(3)	0.4141(2)	0.047(2)	0.038(2)	0.042(2)	0.019(1)	–0.006(1)	0.010(1)
C(35)	2*i*	0.8366(5)	0.6577(3)	0.4238(3)	0.036(2)	0.049(2)	0.061(2)	0.003(1)	–0.020(1)	0.012(2)
C(36)	2*i*	0.7099(5)	0.7574(3)	0.3985(2)	0.040(2)	0.028(1)	0.049(2)	–0.001(1)	–0.016(1)	0.006(1)

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