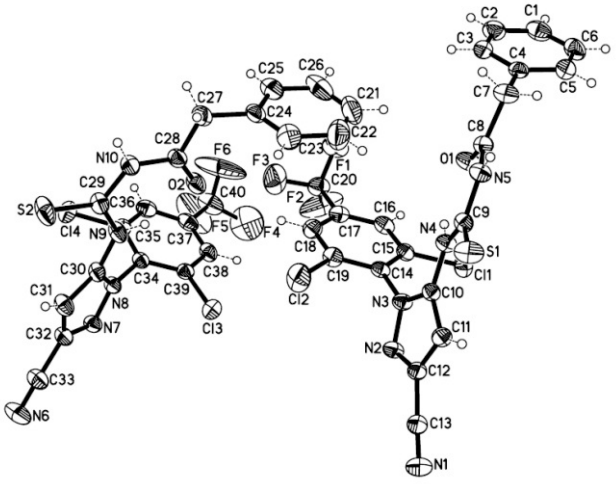
Crystal structure of *N*-[1-(2,6-dichloro-4-trifluoromethyl)phenyl-3-cyano-1*H*-pyrazol-5-yl]-*N*'-4-phenylacetyl thiourea, $C_{20}H_{12}Cl_2F_3N_5OS$

Li Xu[I], Pengfei Zhu[I], Huamei Xie[I], Xiao-Hong Zhang[*, I] and Ping Zhong[*, I, II]

[I] College of Chemisty and Materials Science, Wenzhou University, Wenzhou 325027, Zhejiang Province, P. R. China
[II] Oujiang College, Wenzhou University, Wenzhou 325027, Zhejiang Province, P. R. China

Received December 06, 2011, accepted July 19, 2012, available online July 26, 2012, CCDC no. 1267/3805



Abstract

$C_{20}H_{12}Cl_2F_3N_5Os$, triclinic, $P\bar{1}$ (no. 2), a = 12.300(3) Å, b = 14.379(3) Å, c = 14.496(3) Å, α = 69.511(4)°, β = 72.163(4)°, γ = 70.491(4)°, V = 2211.0 Å^3, Z = 4, $R_{gt}(F)$ = 0.0611, $wR_{ref}(F^2)$ = 0.1679, T = 298 K.

Table 1. Data collection and handling.

Crystal:	colourless blocks, size 0.31×0.33×0.35 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	4.36 cm^{-1}
Diffractometer, scan mode:	Bruker APEX CCD, φ and ω
$2\theta_{max}$:	50.24°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	11649, 7687
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 5866
$N(param)_{refined}$:	577
Programs:	SHELXS-97 [9]

Source of material

Following the method given in [1], the reaction of 2,6-dichloro-4-trifluoro methylamine (0.01 mol) with a suspension of nitrosyl sulfuric acid, followed by reaction with a solution of ethyl 2,3-dicyano propionate (0.01 mol) in acetic acid, gave 5-amino-3-cyano-1-(2,6-dichloro-4-trifluoromethylphenyl)-pyrazole (about 0.005 mol) (prodcut 1). Furthermore, according to reference [2], phenylacetyl chloride(0.007 mol) with dry potassium thiocyanate (0.1mol) was refluxed in anhydrous CH_3CN for two h at a temperature 80°C, which was then filtrated to obtain the acylisothiocyanate solution (2). The obtained products 1 and 2 were then reacted in anhydrous CH_3CN for about 4 h to get the title compound. Single crystals suitable for *X*-ray analysis were obtained by slow evaporation of the solution of acetone (m.p. 431-433 K).

IR (KBr, ν cm^{-1}): 3168, 2245 (CN), 1695 (CO), 1576 (phenyl), 1308 (C=S);
^{1}H NMR (CD_3COCD_3, δ, p.p.m.): 13.0 (s, 1H), 10.95 (s, 1H), 8.10 (s, 2H), 7.60 (s, 1H),7.31(m,5H), 3.81(2H),
^{13}C NMR (CD_3COCD_3, δ, p.p.m.): 179.3, 175.0, 172.3, 140.9, 136.8, 135.2 (q, J = 33,5Hz), 130.4, 130.1, 129.3, 129.1, 128.1, 127.6, 123.1 (q, J=272Hz), 113.8, 104.8, 44.2.

Experimental details

The H atoms were positioned geometrically and allowed to ride on their parent atoms at distances of Csp^2–H = 0.93 Å with U_{iso} = 1.2 U_{eq} (parent atom), Csp^3–H = 0.96 Å with U_{iso} = 1.5 U_{eq} (parent atom). The low U_{eq} of C20 and C40 as compared to neighbours may be attributed to the three disordered fluorine atoms. Attempts to refine the structure taking into account this disorder, were not successful.

Discussion

In recent years, close attention has been paid to acyl thiourea derivatives owing to their chemical properties and their biological activities [3, 4]. For example, some thiourea derivatives have been found to be useful as insecticides, herbicides and so on [5, 6]. On the other hand, pyrazole derivatives possessing fluorine-containing groups, for example, fipronil [5-amino-1-[2,6-dichloro-4-(trifluoromethyl)-phenyl]-4-trifluoromethylsulfinyl-l*H*-pyrazole-3-carbonitrile] is effective against a host of agricultural and household pests including grass hoppers, boll weevils, rice insects, termites, houseflies and thrips [7, 8]. So we surmised that the acylthiourea derivatives bearing a pyrazole moiety might have high biological activities. The title compound was synthesized based on the starting material 5-amino-3-cyano-1-(2,6-dichloro-4-trifluoromethylphenyl)pyrazole and phenylacetyl chloride. The molecular structure of the title compound is shown in the figure with the atom-numbering scheme. It is an acylthiourea with an overall U-shape and exhibiting a dimeric structure. The dimer was overlapped by 9.0° between the CF_3 phenyl group and the phenylacetyl group. In the crystal structure, the intramolecular dihedral angle between the pyrazole with attached phenyl ring and the phenylacetyl is 7.7°, 106.6°, 83.3°, and 96.4°, respectively. Moreover, an intramolecular N4–H4–O1 hydrogen bond with an N4–O1 seperation of 2.621(4) Å and N9–H9–O2 hydrogen bond with an N9–O2 seperation of 2.603(4) Å make the dimer more stable.

* Correspondence author (e-mail: zhongp0512@163.com)

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

Atom	Site	x	y	z	U_{iso}
H(4)	2*i*	0.6840	0.5219	0.0939	0.052
H(5)	2*i*	0.5661	0.3314	0.1835	0.055
H(9)	2*i*	0.7463	0.8010	0.5062	0.064
H(10)	2*i*	0.6532	0.6263	0.6909	0.062
H(1)	2*i*	1.2154	0.0696	0.0513	0.085
H(2)	2*i*	1.1473	0.1277	0.1922	0.081
H(3)	2*i*	0.9491	0.1941	0.2448	0.067
H(5A)	2*i*	0.8838	0.1388	0.0193	0.073
H(6)	2*i*	1.0849	0.0719	–0.0338	0.087
H(7A)	2*i*	0.7211	0.1943	0.1450	0.070
H(7B)	2*i*	0.7443	0.1948	0.2452	0.070
H(11)	2*i*	0.4115	0.6953	0.0114	0.057
H(16)	2*i*	1.0238	0.6040	0.0279	0.059
H(18)	2*i*	0.8288	0.6869	0.2778	0.064
H(21)	2*i*	0.9029	0.3700	0.2700	0.127
H(22)	2*i*	0.7076	0.4445	0.3114	0.128
H(23)	2*i*	0.6341	0.5106	0.4505	0.098
H(25)	2*i*	0.9571	0.4184	0.5038	0.086
H(26)	2*i*	1.0285	0.3540	0.3645	0.116
H(27A)	2*i*	0.6606	0.5077	0.6096	0.081
H(27B)	2*i*	0.7875	0.4742	0.6308	0.081
H(31)	2*i*	0.5243	1.0125	0.6036	0.067
H(36)	2*i*	1.1456	0.8231	0.4561	0.069
H(38)	2*i*	1.0391	0.8717	0.2045	0.066

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}
Cl(1)	2*i*	0.85596(9)	0.62736(8)	–0.07905(7)	0.0623(6)	0.0738(7)	0.0612(6)	–0.0150(5)	–0.0078(5)	–0.0315(5)
Cl(2)	2*i*	0.59710(9)	0.7426(1)	0.25369(9)	0.0489(6)	0.125(1)	0.0785(8)	–0.0042(6)	0.0037(5)	–0.0503(7)
Cl(3)	2*i*	0.79400(9)	0.94745(8)	0.25513(7)	0.0685(6)	0.0667(6)	0.0535(5)	–0.0149(5)	–0.0193(5)	–0.0156(5)
Cl(4)	2*i*	0.9381(1)	0.89550(9)	0.58720(8)	0.0878(8)	0.0832(8)	0.0544(6)	–0.0185(6)	–0.0230(5)	–0.0224(5)
S(1)	2*i*	0.39952(8)	0.50434(8)	0.14608(8)	0.0351(5)	0.0601(6)	0.0763(7)	–0.0133(4)	–0.0006(4)	–0.0047(5)
S(2)	2*i*	0.5500(1)	0.80941(9)	0.73012(9)	0.111(1)	0.0662(7)	0.0679(7)	–0.0461(7)	0.0431(7)	–0.0346(6)
F(1)	2*i*	1.1108(2)	0.5253(2)	0.2085(2)	0.073(2)	0.074(2)	0.143(3)	0.007(1)	–0.062(2)	–0.033(2)
F(2)	2*i*	1.1233(3)	0.6752(3)	0.1300(3)	0.105(2)	0.184(4)	0.178(4)	–0.102(3)	–0.094(3)	0.081(3)
F(3)	2*i*	1.0322(3)	0.6418(3)	0.2794(3)	0.092(2)	0.159(3)	0.155(3)	0.003(2)	–0.069(2)	–0.088(3)
F(4)	2*i*	1.2481(3)	0.8207(4)	0.1745(4)	0.093(3)	0.245(6)	0.154(4)	–0.001(3)	0.050(3)	–0.073(4)
F(5)	2*i*	1.2994(3)	0.8622(4)	0.2635(5)	0.059(2)	0.204(5)	0.343(7)	–0.058(3)	0.057(3)	–0.164(5)
F(6)	2*i*	1.2795(3)	0.7181(3)	0.3022(4)	0.102(3)	0.084(3)	0.303(6)	0.044(2)	0.099(3)	0.042(3)
O(1)	2*i*	0.7964(2)	0.3897(2)	0.1089(2)	0.036(1)	0.042(1)	0.085(2)	–0.009(1)	–0.009(1)	–0.012(1)
O(2)	2*i*	0.7889(3)	0.6736(2)	0.4765(2)	0.081(2)	0.047(2)	0.052(2)	–0.020(1)	0.015(1)	–0.018(1)
N(1)	2*i*	0.3556(3)	0.9776(3)	–0.0986(3)	0.079(3)	0.065(2)	0.092(3)	0.014(2)	–0.042(2)	–0.018(2)
N(2)	2*i*	0.5881(2)	0.8131(2)	0.0101(2)	0.042(2)	0.038(2)	0.063(2)	–0.004(1)	–0.016(1)	–0.011(1)
N(3)	2*i*	0.6349(2)	0.7126(2)	0.0525(2)	0.035(1)	0.039(2)	0.057(2)	–0.005(1)	–0.015(1)	–0.011(1)
N(4)	2*i*	0.6097(2)	0.5456(2)	0.0946(2)	0.031(1)	0.041(2)	0.058(2)	–0.007(1)	–0.012(1)	–0.013(1)
N(5)	2*i*	0.6079(2)	0.3754(2)	0.1557(2)	0.039(2)	0.039(2)	0.054(2)	–0.013(1)	–0.003(1)	–0.009(1)
N(6)	2*i*	0.5264(4)	1.2919(3)	0.4844(3)	0.083(3)	0.051(2)	0.116(3)	0.003(2)	–0.012(2)	–0.030(2)
N(7)	2*i*	0.7401(3)	1.0804(2)	0.4354(2)	0.051(2)	0.040(2)	0.050(2)	–0.010(1)	–0.005(1)	–0.011(1)
N(8)	2*i*	0.7671(2)	0.9771(2)	0.4561(2)	0.043(2)	0.036(2)	0.042(2)	–0.011(1)	0.001(1)	–0.011(1)
N(9)	2*i*	0.6975(3)	0.8306(2)	0.5505(2)	0.057(2)	0.045(2)	0.051(2)	–0.022(1)	0.015(1)	–0.020(1)
N(10)	2*i*	0.6764(3)	0.6683(2)	0.6346(2)	0.061(2)	0.042(2)	0.044(2)	–0.022(1)	0.007(1)	–0.011(1)
C(1)	2*i*	1.1348(4)	0.0951(3)	0.0733(4)	0.056(2)	0.053(2)	0.080(3)	–0.006(2)	0.003(2)	–0.015(2)
C(2)	2*i*	1.0944(4)	0.1304(3)	0.1566(3)	0.061(3)	0.056(2)	0.082(3)	–0.002(2)	–0.026(2)	–0.017(2)
C(3)	2*i*	0.9756(3)	0.1699(3)	0.1881(3)	0.064(2)	0.047(2)	0.052(2)	–0.003(2)	–0.018(2)	–0.016(2)
C(4)	2*i*	0.8950(3)	0.1745(2)	0.1376(2)	0.054(2)	0.034(2)	0.043(2)	–0.009(2)	–0.005(2)	–0.005(1)
C(5)	2*i*	0.9365(4)	0.1373(3)	0.0544(3)	0.076(3)	0.053(2)	0.057(2)	–0.018(2)	–0.018(2)	–0.013(2)
C(6)	2*i*	1.0574(4)	0.0971(3)	0.0223(3)	0.093(3)	0.054(2)	0.055(2)	–0.013(2)	0.010(2)	–0.025(2)
C(7)	2*i*	0.7652(3)	0.2193(3)	0.1722(3)	0.050(2)	0.044(2)	0.067(2)	–0.010(2)	–0.006(2)	–0.006(2)
C(8)	2*i*	0.7281(3)	0.3348(3)	0.1418(2)	0.042(2)	0.043(2)	0.042(2)	–0.009(2)	–0.005(2)	–0.010(2)
C(9)	2*i*	0.5445(3)	0.4773(2)	0.1312(2)	0.040(2)	0.044(2)	0.042(2)	–0.011(1)	–0.003(1)	–0.014(2)
C(10)	2*i*	0.5691(3)	0.6512(2)	0.0577(2)	0.034(2)	0.040(2)	0.046(2)	–0.007(1)	–0.008(1)	–0.014(1)
C(11)	2*i*	0.4737(3)	0.7138(3)	0.0180(3)	0.039(2)	0.050(2)	0.057(2)	–0.008(2)	–0.016(2)	–0.016(2)
C(12)	2*i*	0.4910(3)	0.8118(3)	–0.0103(3)	0.039(2)	0.048(2)	0.049(2)	–0.000(2)	–0.012(2)	–0.017(2)
C(13)	2*i*	0.4170(3)	0.9061(3)	–0.0594(3)	0.055(2)	0.056(2)	0.061(2)	0.001(2)	–0.020(2)	–0.022(2)
C(14)	2*i*	0.7392(3)	0.6855(2)	0.0896(3)	0.035(2)	0.034(2)	0.054(2)	–0.009(1)	–0.010(2)	–0.010(2)
C(15)	2*i*	0.8486(3)	0.6482(2)	0.0333(3)	0.043(2)	0.038(2)	0.050(2)	–0.013(1)	–0.007(2)	–0.013(2)
C(16)	2*i*	0.9502(3)	0.6277(3)	0.0664(3)	0.032(2)	0.044(2)	0.066(2)	–0.009(1)	–0.004(2)	–0.017(2)
C(17)	2*i*	0.9411(3)	0.6430(3)	0.1574(3)	0.042(2)	0.041(2)	0.066(2)	–0.014(2)	–0.019(2)	–0.008(2)
C(18)	2*i*	0.8335(3)	0.6780(3)	0.2161(3)	0.051(2)	0.056(2)	0.053(2)	–0.013(2)	–0.013(2)	–0.015(2)
C(19)	2*i*	0.7332(3)	0.6995(3)	0.1813(3)	0.037(2)	0.055(2)	0.055(2)	–0.011(2)	–0.002(2)	–0.017(2)
C(20)	2*i*	1.0525(4)	0.6215(3)	0.1911(4)	0.058(2)	0.059(3)	0.083(3)	–0.015(2)	–0.030(2)	–0.013(2)
C(21)	2*i*	0.8738(8)	0.3952(4)	0.3262(4)	0.170(7)	0.073(4)	0.078(4)	–0.047(4)	0.005(4)	–0.038(3)
C(22)	2*i*	0.7581(7)	0.4399(5)	0.3501(4)	0.145(6)	0.112(5)	0.088(4)	–0.049(4)	–0.028(4)	–0.040(4)
C(23)	2*i*	0.7141(5)	0.4793(4)	0.4336(4)	0.085(3)	0.082(3)	0.081(3)	–0.022(3)	–0.015(3)	–0.027(3)
C(24)	2*i*	0.7892(4)	0.4719(3)	0.4907(3)	0.074(3)	0.036(2)	0.054(2)	–0.015(2)	–0.005(2)	–0.012(2)
C(25)	2*i*	0.9058(4)	0.4248(3)	0.4651(4)	0.075(3)	0.053(2)	0.079(3)	–0.014(2)	–0.007(2)	–0.020(2)
C(26)	2*i*	0.9488(5)	0.3860(4)	0.3817(5)	0.100(4)	0.056(3)	0.108(4)	–0.022(3)	0.028(3)	–0.033(3)
C(27)	2*i*	0.7406(4)	0.5147(3)	0.5804(3)	0.097(3)	0.043(2)	0.053(2)	–0.016(2)	–0.004(2)	–0.013(2)
C(28)	2*i*	0.7396(3)	0.6253(3)	0.5564(3)	0.051(2)	0.043(2)	0.049(2)	–0.010(2)	–0.001(2)	–0.014(2)

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}
C(29)	2*i*	0.6453(3)	0.7702(3)	0.6343(3)	0.054(2)	0.050(2)	0.049(2)	–0.025(2)	0.006(2)	–0.017(2)
C(30)	2*i*	0.6815(3)	0.9359(3)	0.5274(2)	0.048(2)	0.044(2)	0.041(2)	–0.019(2)	0.004(2)	–0.015(2)
C(31)	2*i*	0.5944(3)	1.0155(3)	0.5556(3)	0.048(2)	0.055(2)	0.060(2)	–0.016(2)	0.010(2)	–0.025(2)
C(32)	2*i*	0.6347(3)	1.1023(3)	0.4961(3)	0.050(2)	0.042(2)	0.055(2)	–0.008(2)	–0.005(2)	–0.018(2)
C(33)	2*i*	0.5748(4)	1.2085(3)	0.4903(3)	0.057(2)	0.052(2)	0.072(3)	–0.007(2)	–0.004(2)	–0.022(2)
C(34)	2*i*	0.8818(3)	0.9243(2)	0.4130(2)	0.043(2)	0.033(2)	0.043(2)	–0.014(1)	–0.001(1)	–0.009(1)
C(35)	2*i*	0.9715(3)	0.8880(3)	0.4651(3)	0.055(2)	0.044(2)	0.047(2)	–0.017(2)	–0.009(2)	–0.011(2)
C(36)	2*i*	1.0857(3)	0.8479(3)	0.4204(3)	0.046(2)	0.049(2)	0.075(3)	–0.009(2)	–0.015(2)	–0.015(2)
C(37)	2*i*	1.1100(3)	0.8451(3)	0.3222(3)	0.046(2)	0.040(2)	0.072(3)	–0.013(2)	0.003(2)	–0.015(2)
C(38)	2*i*	1.0216(3)	0.8762(3)	0.2701(3)	0.062(2)	0.046(2)	0.047(2)	–0.016(2)	0.009(2)	–0.016(2)
C(39)	2*i*	0.9064(3)	0.9144(2)	0.3163(2)	0.050(2)	0.036(2)	0.042(2)	–0.012(1)	–0.005(2)	–0.007(1)
C(40)	2*i*	1.2353(4)	0.8073(4)	0.2731(4)	0.053(3)	0.066(3)	0.103(4)	–0.017(2)	0.025(3)	–0.019(3)

Acknowledgments. The authors thank the National Natural Science Foundation of China (no. 20972114), Zhejiang Provincial Natural Science Foundation of China (Y4100578).

References

1. Hatton, L. R.; Buntain, I. G.; Hawkins, D. W.; Parnell, E. W.; Pearson, C.J.; Roberts, D. A.: US Patent No.5232940 (1993).
2. Gong,Y.; Wang, Z.; Zhang, Z.; Chen, C.; Wang,Y.: Chinese Journal of Organic Chemisty. 3 (2006) 360-363.
3. Zhou,W. Q.; Leng, K. S.; Zhang,Y.; Lude, L.: J.Mol.Struct. **215** (2003) 657.
4. Koch,K.R. Coord. Chem. Rev. **473** (2001) 216-C217.
5. Madan,V.K.; Taneja, A.D.; Kudesia,V.P. J.: Indian Chem. Soc. **68** (1991) 162.
6. Xue, S. J.; Duan, L. P.; Ke, S. Y.; Zhu, J. M.: Chinese journal of organic chemistry. **24** (2004) 686-689.
7. Durham, E.W.; Scharf, M.E.; Siegfried, B.D.: Pestic. Biochem. Physiol. **71** (2001) 97.
8. Brennan, A.A.; Harwood, A.D.; You, J.; Landrum, P.F.; Lydy, M.J.: Chemosphere. **77** (2009) 22.
9. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112-122.