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Mercapto-*N*-phenylformimidoyl-1-methyl-3-(2-phenylethyl)benzimidazolinium inner salt

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Key indicators

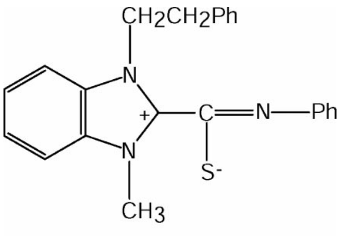
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.004 Å
Disorder in main residue
R factor = 0.039
wR factor = 0.104
Data-to-parameter ratio = 14.3

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The molecular conformation of the title compound {alternative name: [1-methyl-3-(2-phenylethyl)benzimidazolinio]-(phenylimino)methanethiolate}, $C_{23}H_{21}N_3S$, is non-planar. The molecule includes one benzimidazole ring system and two phenyl rings. The dihedral angles between the least-squares planes of the two phenyl rings is 85.65 (1)°.

Comment

Olefins with four electron-donating substituents react as strong nucleophiles and they are referred to as electron-rich olefins (Hocker & Merten, 1972). Electron-rich olefins are readily converted by aryl isothiocyanates to stable mercapto-*N*-arylformimidoylimidazolinium inner salts in high yield. However, there are few studies on phenyl isothiocyanate dervatives of electron-rich olefins containing a benzimidazole moiety (Küçükbay *et al.*, 1995) and there is no information about the crystal structures of these benzimidazole-type compounds. The aim of this study was to elucidate the crystal structure of the recently synthesized title compound, (I) (Küçükbay *et al.*, 2003), and compare it with those of related benzimidazole derivatives reported previously (Aydın *et al.*, 1998; İngeç *et al.*, 1999; Aydın *et al.*, 1999; Öztürk *et al.*, 2001; Akkurt *et al.*, 2003; Öztürk *et al.*, 2003).



(I)

Electron-rich olefins are extremely reactive, powerful π-bases. Characteristic reactions of the olefins with electrophiles that proceed *via* cleavage of the molecule are those with azides to form monoaza and/or triaza compounds, and with isothiocyanates to form stable dipoles or thiohydantoin derivatives (Hocker & Merten, 1972). Electron-rich olefins as a carbene source attack the relatively positively charged C atom of the phenyl isothiocyanate and the carbon–sulfur double bond opens to the relatively negatively charged S atom, forming a stable 1,3-dipolar system. According to the literature, these compounds undergo cycloaddition with suitable dipolarophiles, including aliphatic and aromatic isocyanates, aliphatic isothiocyanates, and multiple C—C bonds. Hydrolysis of cycloaddition products gives 1,3-di-

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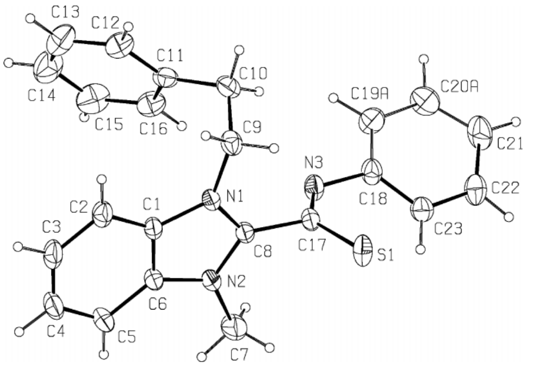

Figure 1
An *ORTEP*-3 plot (Farrugia, 1997) of (I), with the atom-numbering scheme. Displacement ellipsoids for non-H atoms are drawn at the 20% probability level. Only disordered atoms with high occupancy are shown.

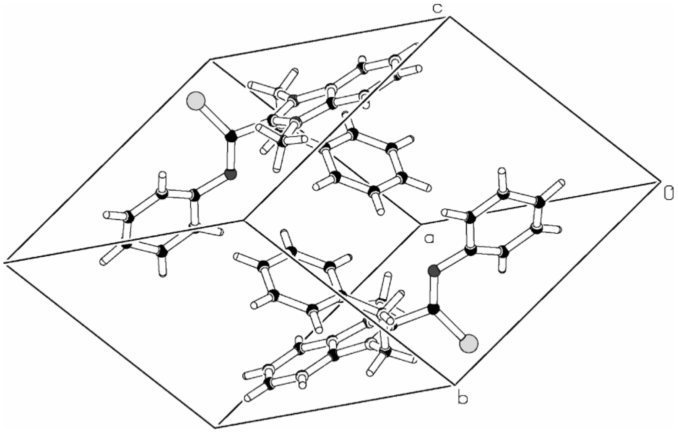

Figure 2
A view of the molecular packing of (I) in the unit cell. Only disordered atoms with high occupancy are shown.

phenylurea, confirming the assigned 1,3-dipolar structure of the compounds such as (I) (Winberg & Coffman, 1965).

Fig. 1 shows the molecular structure of the title compound, (I); bond lengths and angles are given in Table 1. The S1—C17 bond length is 1.6933 (19) Å. In similar studies, this length has been reported to be 1.694 (4) Å (İngeç *et al.*, 1999) and 1.6645 (19)–1.6556 (19) Å (Akkurt *et al.*, 2004). The N1—C8 and N2—C8 bond lengths in the imidazole ring agree with those reported for related structures (Öztürk *et al.*, 2003). All the bond lengths and angles in (I) have normal values.

In the benzimidazole ring system, the dihedral angle between the least-square planes through the benzene and imidazole rings is 1.92 (1)° [with atom C8 deviating from the mean plane passing through the remaining atoms in that ring by 0.023 (1) Å]. The dihedral angle between the least-squares planes of the two phenyl rings (C11–C16 and C18–C23) is 85.65 (1)° and those between these phenyl rings and the benzimidazole ring system are 45.06 (1) and 49.82 (1)°.

Experimental

All experiments were performed under argon using freshly distilled dry solvents. To a solution of bis[1-(2-phenylethyl)-3-methylbenzimidazolidin-2-ylidene], (0.5 g, 0.06 mmol) in toluene (15 ml), PhNCS (0.25 ml, 2.12 mmol) was added. When the mixture was stirred at room temperature an exothermic reaction soon took place. All volatiles were then removed *in vacuo* and the yellow crude product was crystallized from CHCl$_3$–Et$_2$O (4:1) (yield: 0.70 g, 89%; m.p.: 406–407 K). ^{1}H NMR (CDCl$_3$): δ 3.5 (*t*, CH$_2$CH$_2$Ph, 2H), 4.1 (*s*, CH$_3$, 3H), 4.8 (*t*, CH$_2$CH$_2$Ph, 2H), 7.2–7.7 (*m*, Ar-H, 14H). ^{13}C NMR (CDCl$_3$): δ 32.24, 36.03, 47.99, 112.67, 112.76, 122.87, 124.38, 126.63, 126.69, 127.60, 129.17, 129.31, 129.41, 130.54, 137.43, 150.11, 151.01, 166.47. Analysis calculated for C$_{23}$H$_{21}$N$_3$S: C 74.39, H 5.66, N 11.32%; found: C 74.77, H 5.88, N 10.88.

Crystal data

C$_{23}$H$_{21}$N$_3$S
$M_r = 371.50$
Triclinic, $P\bar{1}$
$a = 9.3894$ (8) Å
$b = 10.8881$ (11) Å
$c = 11.6658$ (12) Å
$\alpha = 67.191$ (7)°
$\beta = 83.696$ (8)°
$\gamma = 67.040$ (7)°
$V = 1011.07$ (19) Å^3
$Z = 2$
$D_x = 1.220$ Mg m^{-3}
Mo Kα radiation
Cell parameters from 9837 reflections
$\theta = 1.9$–29.0°
$\mu = 0.17$ mm^{-1}
$T = 293$ K
Prism, yellow
0.68 × 0.37 × 0.20 mm

Data collection

Stoe IPDS-II diffractometer
ω scans
Absorption correction: by integration (*X-RED*32; Stoe & Cie, 2002)
$T_{\min} = 0.923$, $T_{\max} = 0.973$
11523 measured reflections
3983 independent reflections
2562 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.029$
$\theta_{\max} = 26.0°$
$h = -11 \rightarrow 11$
$k = -13 \rightarrow 13$
$l = -14 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.104$
$S = 0.94$
3983 reflections
279 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0584P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.16$ e Å^{-3}
$\Delta\rho_{\min} = -0.26$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

S1—C17	1.6933 (19)	N2—C7	1.465 (4)
N1—C1	1.396 (3)	N2—C8	1.331 (2)
N1—C8	1.336 (2)	N3—C17	1.288 (2)
N1—C9	1.460 (3)	N3—C18	1.411 (3)
N2—C6	1.390 (3)		
C1—N1—C8	108.61 (15)	N1—C8—N2	109.09 (16)
C1—N1—C9	126.32 (16)	N1—C8—C17	126.09 (17)
C8—N1—C9	125.05 (16)	N2—C8—C17	124.79 (17)
C6—N2—C7	126.42 (19)	N1—C9—C10	112.39 (16)
C6—N2—C8	109.05 (17)	S1—C17—N3	134.86 (16)
C7—N2—C8	124.46 (19)	S1—C17—C8	112.82 (13)
C17—N3—C18	121.99 (16)	N3—C17—C8	112.32 (16)
N1—C1—C2	131.8 (2)	N3—C18—C19*A*	115.8 (3)
N1—C1—C6	106.62 (17)	N3—C18—C23	126.49 (18)
N2—C6—C1	106.62 (18)	N3—C18—C19*B*	115.0 (5)
N2—C6—C5	131.4 (2)		

All H atoms, apart from H19*A*, H19*B*, H20*A* and H20*B* [C—H = 0.95 (6)–1.03 (7) Å], were positioned geometrically and refined with a riding model; for the methyl group, $U_{\rm iso} = 1.5U_{\rm eq}$ of the carrier atom, and C—H = 0.96 Å, and for the other atoms $U_{\rm iso} = 1.2U_{\rm eq}$ and C—H = 0.93–0.98 Å. Two of the six atoms of the phenyl ring (C19 and C20) are disordered, with a nearly statistical distribution over two sites (0.60:0.40).

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED*32 (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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