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# Mercapto-*N*-phenylformimidoyl-1-ethyl-3-(2-morpholinoethyl)benzimidazolinium inner salt

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**Key indicators**

Single-crystal X-ray study
*T* = 100 K
Mean $\sigma$(C–C) = 0.007 Å
*R* factor = 0.074
*wR* factor = 0.183
Data-to-parameter ratio = 12.6

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



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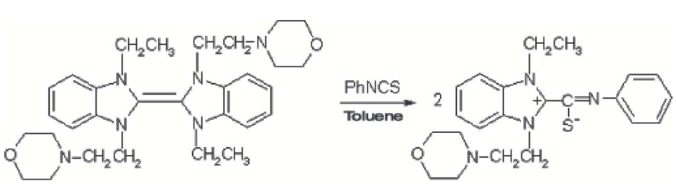
In the title compound {alternative name: [1-ethyl-3-(2-morpholinoethyl)benzimidazoliumyl](phenylimino)methanethiolate}, $C_{22}H_{26}N_4OS$, the morpholine ring has a chair conformation. The dihedral angle between the benzimidazole ring system and the phenyl ring is 0.5 (2)°. The crystal structure is stabilized by intermolecular C—H···O contacts.

## Comment

Electron-rich olefins, especially tetraaminoethylenes, are highly reactive compounds. They have been used as powerful reducing agents (Lappert, 1988), sources of carbene transition metal complexes (Çetinkaya *et al.*, 1994; Küçükbay *et al.*, 1996), and catalysts for acyloin type C—C coupling reactions (Çetinkaya & Küçükbay, 1995). They have an extensive organic chemistry; in particular, electron-rich olefins that contain imidazolidine or benzothiazolidine groups have long been known, but there are a limited number of studies of electron-rich olefins contain benzimidazolidine groups. Electron-rich olefins react with phenyl isothiocyanate in a 1:2 molar ratio to yield stable dipoles (Hocker & Merten, 1972). The objective of the present study was to elucidate the crystal structure of the title compound, (2), and compare it with those of related benzimidazole derivatives reported previously.




(1) (2)

The molecular structure of (2) is shown in Fig. 1 and selected bond lengths and angles are given in Table 2. The S1—C10 bond length of 1.701 (4) Å compares with the value of 1.6933 (19) Å in the similar structure of mercapto-*N*-phenylformimidoyl-1-methyl-3-(2-phenylethyl)benzimidazolinium inner salt (Öztürk *et al.*, 2004). All geometric parameters are comparable to those reported for similar structures (Öztürk *et al.*, 2003, 2004; Akkurt *et al.*, 2004; Allen *et al.*, 1987).

The benzimidazole ring system of (2) is planar, with maximum deviations of −0.017 (6) and 0.020 (5) Å for atoms C4 and C6, respectively. The dihedral angle between the least-squares planes of the benzimidazole ring system (N1/N2/C1–C6) and the phenyl ring (C11–C16) is 0.5 (2)°. The morpholine ring adopts a chair conformation [puckering parameters: $Q_T$ = 0.570 (5) Å, $\theta$ = 1.8 (5)° and $\varphi$ = 162°; Cremer & Pople, 1975].

The crystal structure of (2) is stabilized by intermolecular C—H···O contacts (Fig. 2).

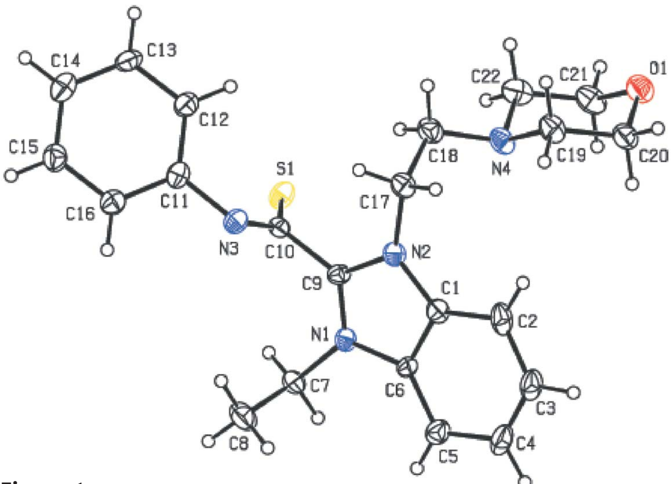



**Figure 1**
A plot of the molecule of (2), showing the atom-numbering scheme and 30% probability displacement ellipsoids

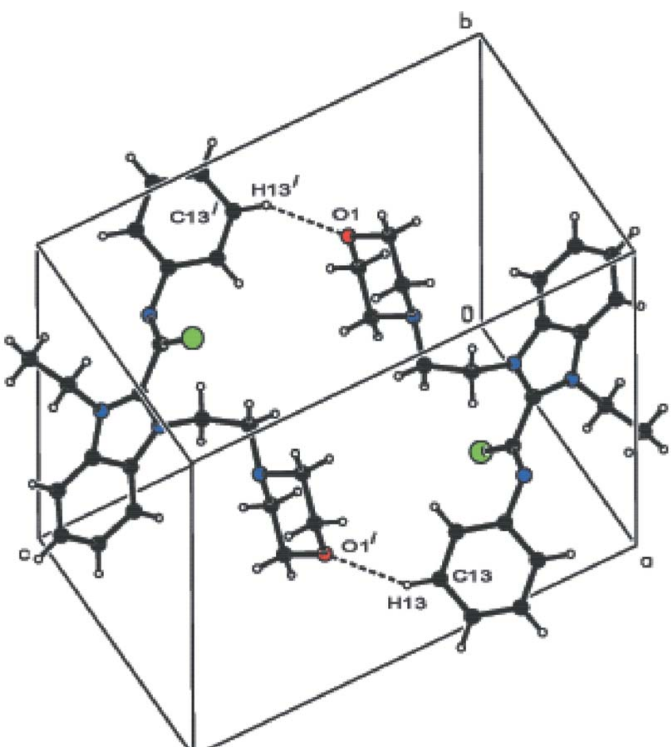



**Figure 2**
View of the packing and intermolecular C—H···O contacts (dashed lines) of (2). The symmetry code is as in Table 2.

## Experimental

To a solution of bis[1-ethyl-3-(2-morpholinoethyl)benzimidazolidine-2-ylidene], (1) (0.5 g, 0.97 mmol), in toluene (10 ml) was added PhNCS (0.3 ml, 2.49 mmol). When the mixture was stirred at room temperature, an exothermic reaction soon took place. All volatile materials were then removed *in vacuo* and the yellow crude product was crystallized from ethanol (yield: 0.62 g, 82%; m.p. 383–384 K). $^1$H NMR ($CDCl_3$): $\delta$ 1.6 (*t*, –$CH_2$—$CH_3$, 3H), 2.5 (*s*, morpholine –$CH_2$—$CH_2$–, 4H), 3.0 (*q*, –$CH_2CH_3$, 2H), 3.6 (*s*, morpholine –$CH_2$—$CH_2$—, 4H), 4.6 (*m*, N—$CH_2$—$CH_2$—N, 4H), 7.0–7.7 (*m*, Ar—H, 9H). $^{13}$C NMR ($CDCl_3$): $\delta$ 14.55, 41.25, 43.52, 53.83, 56.96, 66.86, 112.44, 112.88, 122.52, 123.96, 126.16, 129.90, 130.13, 130.90, 149.88, 150.33, 165.91. Analysis calculated for $C_{22}H_{26}N_4OS$: C 67.01, H 6.60, N 14.21, S 8.12%; found: C 66.80, H 6.57, N 13.87, S 8.37%.

*Crystal data*

| | |
|---|---|
| $C_{22}H_{26}N_4OS$ | $Z = 2$ |
| $M_r = 394.54$ | $D_x = 1.289$ Mg m$^{-3}$ |
| Triclinic, $P\overline{1}$ | Mo $K\alpha$ radiation |
| $a = 8.9037$ (16) Å | Cell parameters from 7037 reflections |
| $b = 9.1916$ (15) Å | $\theta = 2.5$–27.1° |
| $c = 13.950$ (2) Å | $\mu = 0.18$ mm$^{-1}$ |
| $\alpha = 105.927$ (12)° | $T = 100$ K |
| $\beta = 91.443$ (13)° | Plate, colorless |
| $\gamma = 110.871$ (14)° | 0.54 × 0.36 × 0.11 mm |
| $V = 1016.2$ (3) Å$^3$ | |

*Data collection*

| | |
|---|---|
| Stoe IPDS-II diffractometer | 3213 independent reflections |
| $\omega$ scans | 1957 reflections with $I > 2\sigma(I)$ |
| Absorption correction: refineme from $\Delta F$ (*XABS2*; Parkin *et al.*, 1968) | $R_{int} = 0.000$ |
| $T_{min} = 0.909$, $T_{max} = 0.980$ | $\theta_{max} = 26.0°$ |
| 4337 measured reflections | $h = -10 \rightarrow 10$ |
| | $k = -11 \rightarrow 11$ |
| | $l = -15 \rightarrow 15$ |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | H-atom parameters constrained |
| $R[F^2 > 2\sigma(F^2)] = 0.074$ | $w = 1/[\sigma^2(F_o^2) + (0.0925P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| $wR(F^2) = 0.183$ | $(\Delta/\sigma)_{max} < 0.001$ |
| $S = 1.01$ | $\Delta\rho_{max} = 0.31$ e Å$^{-3}$ |
| 3213 reflections | $\Delta\rho_{min} = -0.27$ e Å$^{-3}$ |
| 254 parameters | |

**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| S1—C10 | 1.701 (4) | N2—C9 | 1.356 (5) |
| O1—C20 | 1.430 (6) | N2—C17 | 1.460 (6) |
| O1—C21 | 1.420 (6) | N3—C10 | 1.302 (6) |
| N1—C6 | 1.401 (5) | N3—C11 | 1.426 (6) |
| N1—C7 | 1.494 (6) | N4—C18 | 1.470 (7) |
| N1—C9 | 1.303 (6) | N4—C19 | 1.465 (6) |
| N2—C1 | 1.383 (5) | N4—C22 | 1.468 (7) |
| | | | |
| C20—O1—C21 | 108.9 (4) | N1—C7—C8 | 109.9 (4) |
| C6—N1—C7 | 123.5 (4) | N1—C9—N2 | 109.7 (3) |
| C6—N1—C9 | 110.2 (3) | N1—C9—C10 | 126.2 (3) |
| C7—N1—C9 | 126.2 (3) | N2—C9—C10 | 124.1 (4) |
| C1—N2—C9 | 107.8 (4) | S1—C10—N3 | 134.3 (3) |
| C1—N2—C17 | 126.9 (4) | S1—C10—C9 | 114.9 (3) |
| C9—N2—C17 | 125.2 (4) | N3—C10—C9 | 110.8 (4) |
| C10—N3—C11 | 119.8 (4) | N3—C11—C12 | 122.4 (4) |
| C18—N4—C19 | 111.4 (4) | N3—C11—C16 | 117.1 (4) |
| C18—N4—C22 | 109.3 (4) | N2—C17—C18 | 114.2 (4) |
| C19—N4—C22 | 108.1 (4) | N4—C18—C17 | 115.2 (4) |
| N2—C1—C2 | 131.6 (4) | N4—C19—C20 | 110.2 (4) |
| N2—C1—C6 | 107.5 (3) | O1—C20—C19 | 112.0 (4) |
| N1—C6—C1 | 104.7 (3) | O1—C21—C22 | 112.7 (4) |
| N1—C6—C5 | 132.1 (4) | N4—C22—C21 | 110.3 (4) |

**Table 2**
Hydrogen-bond geometry (Å, °).

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| C13—H13···O1$^i$ | 0.93 | 2.57 | 3.363 (7) | 144 |

Symmetry code: (i) $-x+1, -y+1, -z+1$.

H atoms were positioned geometrically and refined using a riding model, with C—H = 0.93–0.97 Å and $U_{iso}$(H) = 1.2 or 1.5 times $U_{eq}$(C). The crystal was twinned by a twofold rotation axis perpendicular to (001). Reflection data were measured for the two twin domains, scaled and combined together, but overlapping reflections could not be satisfactorily measured and were discarded, leading to a data completeness of only slightly over 80%.

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED32* (Stoe & Cie, 2002); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP3* for Windows (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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## References

Akkurt, M., Öztürk, S., Küçükbay, H., Orhan, E. & Büyükgüngör, O. (2004). *Acta Cryst.* E**60**, o219–o221.
Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.
Altomare, A., Burla, M. C., Camalli, M., Cascarano, G. L., Giacovazzo, C. Guagliardi, A., Moliterni, A. G. G ., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.
Çetinkaya, E., Hitchcock, P. B., Küçükbay, H., Lappert, M. F. & Al-Juaid, S. (1994). *J. Organomet. Chem.* **481**, 89–95.
Çetinkaya, E, & Küçükbay, H. (1995). *Turk. J. Chem.* **19**, 24–30.
Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Hocker, J. & Merten, R. (1972). *Angew. Chem. Int. Ed. Engl.* **11**, 964–973.
Küçükbay, H., Çetinkaya, B., Guesmi, S. & Dixneuf, P. H. (1996). *Organometallics*, 15, 2434–2439.
Lappert, M. F. (1988). *J. Organomet. Chem.* **358**, 185–214.
Öztürk, S., Akkurt, M., Küçükbay, H., Okuyucu, N. & Fun, H.-K. (2003). *Acta Cryst.* E**59**, o1014–o1016.
Öztürk, S., Akkurt, M., Küçükbay, H., Orhan E. & Büyükgüngör, O. (2004). *Acta Cryst.* E**60**, o936–o938.
Parkin, S., Moezzi, B. & Hope, H. (1995). *J. Appl. Cryst.* **28**, 53–56.
Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
Stoe & Cie (2002). *X-AREA* (Version 1.18) and *X-RED32* (Version 1.04). Stoe & Cie, Darmstadt, Germany.