

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)
$$U_{eq} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
N1	0.7783 (2)	0.2679 (2)	0.3461 (1)	0.0344 (7)
C2	0.8711 (2)	0.2374 (3)	0.4337 (2)	0.0361 (9)
N3	0.7862 (2)	0.2432 (2)	0.5279 (1)	0.0360 (7)
C4	0.6290 (2)	0.2804 (3)	0.4989 (2)	0.0313 (8)
C5	0.6226 (2)	0.2965 (3)	0.3865 (2)	0.0299 (8)
C6	1.0484 (3)	0.2059 (4)	0.4248 (3)	0.051 (1)
C7	0.4962 (2)	0.2837 (3)	0.5824 (2)	0.0342 (8)
C8	0.4838 (2)	0.3345 (3)	0.3120 (2)	0.0331 (8)
N20	0.5131 (2)	0.4581 (2)	0.7019 (1)	0.0314 (7)
C21	0.3855 (2)	0.4357 (3)	0.7812 (2)	0.0388 (9)
C22	0.4140 (3)	0.2696 (4)	0.8366 (2)	0.054 (1)
C23	0.2809 (5)	0.2510 (5)	0.9159 (3)	0.077 (2)
O50	0.8313 (2)	0.3740 (2)	0.7795 (1)	0.0498 (8)
O51	1.0318 (2)	0.7434 (3)	0.8535 (2)	0.0515 (8)
O52	0.8269 (3)	0.0874 (4)	0.9068 (2)	0.068 (1)

Table 2. Selected geometric parameters (Å, °)

N1—C2	1.343 (3)	O51—H511	0.79 (3)
N1—C5	1.388 (2)	O51—H512	0.96 (3)
N1—H11	1.02 (3)	O52—H521	1.00 (3)
C2—N3	1.323 (3)	O52—H522	0.57 (3)
C2—C6	1.495 (3)	O50...N3	2.774 (2)
N3—C4	1.391 (2)	O50...N20	2.905 (2)
C4—C5	1.363 (3)	O50...O51	2.803 (3)
C4—C7	1.496 (3)	O50...O52	2.856 (4)
C5—C8	1.507 (3)	O51...O50	2.803 (3)
C7—N20	1.480 (2)	O51...O52	2.854 (3)
C8—N20 ⁱ	1.481 (3)	O51...N1	2.851 (3)
N20—C21	1.473 (3)	O51...O52	2.824 (3)
C21—C22	1.517 (4)	O52...O50	2.856 (4)
C22—C23	1.499 (5)	O52...O51	2.854 (3)
O50—H501	1.04 (3)	O52...O51	2.824 (3)
O50—H502	0.93 (3)		
C2—N1—C5	107.6 (2)	N1—C5—C8	123.0 (2)
N1—C2—N3	111.3 (2)	C4—C5—C8	131.2 (2)
N1—C2—C6	123.4 (2)	C4—C7—N20	114.8 (2)
N3—C2—C6	125.2 (2)	C5—C8—N20 ⁱ	116.6 (1)
C2—N3—C4	106.0 (2)	C7—N20—C21	110.4 (1)
N3—C4—C5	109.2 (2)	C7—N20—C8 ⁱ	111.6 (2)
N3—C4—C7	120.7 (2)	C21—N20—C8 ⁱ	112.1 (2)
C5—C4—C7	129.9 (2)	N20—C21—C22	114.1 (2)
N1—C5—C4	105.9 (2)	C21—C22—C23	112.3 (2)

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

All H atoms were located in difference Fourier maps and subsequently refined.

Data collection: *CAD-4 Software* (Enraf-Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *Xtal AD-DREF SORTREF* (Hall, Flack & Stewart, 1992). Program(s) used to solve structure: *Xtal*. Program(s) used to refine structure: *Xtal CRYLSQ*. Molecular graphics: *PLATON93* (Spek, 1993), *PLUTON92* (Spek, 1992). Software used to prepare material for publication: *Xtal BONDLA CIFIO*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and contact distances have been deposited with the IUCr (Reference: NS1004). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Baumann, G. C., Summers, M. F., Hutchinson, J. P., Zubieta, J. & Marzilli, L. G. (1984). *Inorg. Chem.* **23**, 3104–3108.
- Berndt, D. C. (1970). *J. Org. Chem.* **35**, 1129–1131.
- Bouwman, E., Driessen, W. L. & Reedijk, J. (1990). *Coord. Chem. Rev.* **104**, 143–172.
- Breslow, R. (1991). *Acc. Chem. Res.* **24**, 317–324.
- Enraf-Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf-Nonius, Delft, The Netherlands.
- Geue, R. J., Höhn, A., Ralph, S. F., Sargeson, A. M. & Willis, A. C. (1994). *J. Chem. Soc. Chem. Commun.* pp. 1513–1515.
- Hall, S. R., Flack, H. D. & Stewart, J. M. (1992). Editors. *Xtal3.2 User's Manual*. Universities of Western Australia, Australia, Geneva, Switzerland, and Maryland, USA.
- Karunakaran, S. & Kandaswamy, M. (1994). *J. Chem. Soc. Dalton Trans.* pp. 1595–1598.
- Mendoza-Díaz, G., Driessen, W. L. & Reedijk, J. (1994). Unpublished results.
- Spek, A. L. (1992). *PLUTON92. Molecular Graphics Program*. University of Utrecht, The Netherlands.
- Spek, A. L. (1993). *PLATON93. Program for the Automated Analysis of Molecular Geometry*. University of Utrecht, The Netherlands.
- Stocker, F. B., Kurtz, J. L., Byron, L. G. & Forsyth, D. A. (1970). *J. Org. Chem.* **35**, 883–887.
- Teo, S.-B., Ng, C.-H. & Tiekink, E. R. T. (1993). *J. Coord. Chem.* **29**, 57–63.

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3-(6-Methoxy-2-benzimidazolyl)benzothiazolin-2-imine

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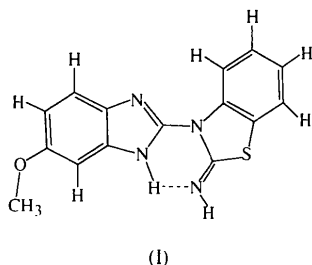
Abstract

The title compound, C₁₅H₁₂N₄OS, was unexpectedly isolated from the reaction of *N*-[2-(6-methoxy-1*H*-benzimidazol-2-ylthio)phenyl]thiourea with dicyclohexylcarbodiimide. The compound showed considerable anti-cancer activity *in vitro*. The benzimidazole and iminobenzothiazoline rings are coplanar *via* hydrogen bonding between the N atom of the imino group of benzothiazole and the H—N bond of benzimidazole. The whole molecule has a planar structure.

Comment

During our studies towards the synthesis of 1,3,5-thiadiazepine for potential biological applications (Vec-

chia, Dellureficio, Kisis & Vlattas, 1983), the reaction of *N*-[2-(6-methoxy-1*H*-benzimidazol-2-ylthio)phenyl]thiourea with dicyclohexylcarbodiimide unexpectedly afforded the title compound (I). This compound showed



considerable anti-cancer activity *in vitro*. The molecular structure shows that the compound contains benzimidazole and iminobenzothiazoline rings that are coplanar *via* two intramolecular hydrogen bonds (N3—H···N4 and C7—H···N2). The displacement of all atoms contained in the molecule, except some H atoms, is less than 0.125 (1) Å from the least-squares plane. Therefore the whole molecule, except the methyl group, has a π -conjugated system. All other numerical parameters are normal. There are three weak intermolecular hydrogen bonds in the crystal.

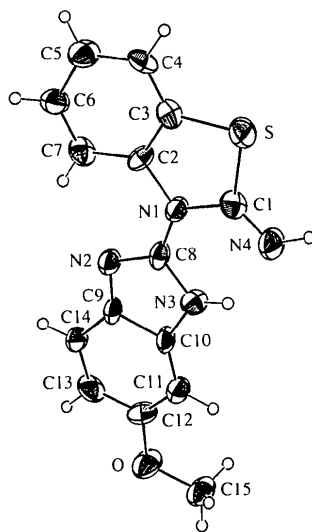


Fig. 1. Molecular structure showing 50% probability displacement ellipsoids.

Experimental

To a mixture of *N*-[2-(6-methoxy-1*H*-benzimidazol-2-ylthio)phenyl]thiourea and dicyclohexylcarbodiimide, acetonitrile was introduced. The solution was heated under reflux for 1 h. The precipitate of dicyclohexylthiourea produced during the reaction was filtered off. The filtrate was evaporated *in vacuo*

to yield a white solid. The product was purified on a silica gel column (*n*-hexane:ethyl acetate = 1:1, $R_f = 0.55$) and recrystallized from an acetonitrile/dioxane solution (yield 83%, m.p. 456–457 K).

Crystal data

$C_{15}H_{12}N_4OS$
 $M_r = 296.35$
 Triclinic
 $P\bar{1}$
 $a = 7.424 (1) \text{ \AA}$
 $b = 7.325 (1) \text{ \AA}$
 $c = 13.959 (1) \text{ \AA}$
 $\alpha = 78.67 (1)^\circ$
 $\beta = 75.15 (1)^\circ$
 $\gamma = 63.98 (1)^\circ$
 $V = 656.3 (1) \text{ \AA}^3$
 $Z = 2$
 $D_x = 1.500 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation
 $\lambda = 0.71073 \text{ \AA}$
 Cell parameters from 25 reflections
 $\theta = 10.0\text{--}13.0^\circ$
 $\mu = 0.251 \text{ mm}^{-1}$
 $T = 293 (2) \text{ K}$
 Tetragonal rod
 $0.40 \times 0.38 \times 0.30 \text{ mm}$
 Colourless

Data collection

CAD-4 diffractometer
 $\omega/2\theta$ scans
 Absorption correction: none
 2502 measured reflections
 2306 independent reflections
 2229 observed reflections
 $[I > 2\sigma(I)]$

$R_{int} = 0.0294$
 $\theta_{max} = 26.27^\circ$
 $h = -8 \rightarrow 9$
 $k = 0 \rightarrow 9$
 $l = -17 \rightarrow 17$
 3 standard reflections
 frequency: 60 min
 intensity decay: 0.03%

Refinement

Refinement on F^2
 $R(F) = 0.0376$
 $wR(F^2) = 0.0996$
 $S = 1.108$
 2306 reflections
 238 parameters
 H-atom treatment: see below
 $w = 1/[\sigma^2(F_o^2) + (0.0568P)^2 + 0.1971P]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = -0.002$
 $\Delta\rho_{max} = 0.192 \text{ e \AA}^{-3}$
 $\Delta\rho_{min} = -0.315 \text{ e \AA}^{-3}$
 Extinction correction: none
 Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

$$U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i\cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
S	0.22847 (7)	0.85987 (9)	0.19819 (4)	0.0498 (2)
C1	0.2406 (3)	0.8272 (3)	0.32500 (13)	0.0381 (4)
N1	0.4407 (2)	0.7797 (2)	0.33426 (10)	0.0335 (3)
C2	0.5823 (3)	0.7560 (2)	0.24304 (12)	0.0319 (3)
C3	0.4893 (3)	0.7954 (3)	0.16125 (13)	0.0371 (4)
C4	0.6010 (3)	0.7790 (3)	0.06521 (14)	0.0433 (4)
C5	0.8086 (3)	0.7210 (3)	0.05022 (14)	0.0451 (4)
C6	0.9028 (3)	0.6769 (3)	0.13064 (14)	0.0449 (5)
C7	0.7919 (3)	0.6942 (3)	0.22767 (14)	0.0397 (4)
C8	0.4935 (2)	0.7582 (2)	0.42670 (12)	0.0318 (4)
N2	0.6744 (2)	0.7254 (2)	0.43907 (10)	0.0362 (3)
C9	0.6499 (3)	0.7178 (3)	0.54241 (12)	0.0337 (4)
C10	0.4504 (3)	0.7480 (3)	0.58862 (12)	0.0334 (4)
C11	0.3801 (3)	0.7498 (3)	0.69124 (13)	0.0379 (4)
C12	0.5221 (3)	0.7211 (3)	0.74664 (12)	0.0371 (4)
C13	0.7238 (3)	0.6913 (3)	0.70156 (14)	0.0409 (4)
C14	0.7902 (3)	0.6884 (3)	0.60024 (14)	0.0413 (4)

N3	0.3527 (2)	0.7722 (2)	0.51237 (11)	0.0366 (3)
O	0.4814 (2)	0.7164 (2)	0.84870 (9)	0.0507 (4)
C15	0.2781 (3)	0.7524 (4)	0.8981 (2)	0.0516 (5)
N4	0.0938 (2)	0.8444 (3)	0.39842 (13)	0.0481 (4)

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N,N-Dimethyl-2,4-dinitroaniline

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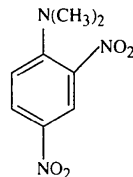
Abstract

The title compound, C₈H₉N₃O₄, has both the *o*-nitro group and the 1-dimethylamino group twisted out of the plane of the benzene ring, whereas the *p*-nitro group is almost coplanar with the ring.

Comment

In the absence of any specific electrostatic interaction, the *o*-nitro group in an *o*-nitrobenzene derivative, e.g. 2,4-(O₂N)₂C₆H₃X, (II), is twisted out of the plane of the aryl ring (Table 3). This is well illustrated by the amino compounds with X = (cyclohexyl)₂N (Punte & Rivero, 1991), X = (ⁱPr)₂N (Punte, Rivero, Socolovsky & Nudelman, 1989) and X = (cyclohexyl)(ⁱPr)N (Punte, Rivero, Socolovsky & Nudelman, 1991), in which not only are the *o*-nitro groups twisted out of the plane of the aryl rings [between 37.3(2) and 46.3(2)°], but so are the bulky amino groups [by 28.5(5) to 37.7(2)°].

In contrast, in the title compound (X = H₂N), (I), the *o*-nitro group and the NH₂ group are almost coplanar with the benzene ring (Prasad, Gabe & Le Page, 1982). This is the consequence of a hydrogen bond between the nitro and amino groups. The *o*-nitro and attached aryl ring are also nearly coplanar in *o*-nitroaryl sulfides, e.g. for X = SPh (Korp, Bernal & Martin, 1981), as a result of S—O interactions.



(I)

In order to investigate more closely the effect of the size of a non-electrostatically interacting X group on the planarity of the *o*-nitro group and its attached aryl ring, the structure determination of the title compound, (I) (X = NMe₂), was undertaken. Despite the amino group of

Table 2. Selected geometric parameters (Å, °)

S—C3	1.738 (2)	C2—C3	1.401 (2)
S—C1	1.759 (2)	C8—N2	1.308 (2)
C1—N4	1.269 (2)	C8—N3	1.359 (2)
C1—N1	1.404 (2)	N2—C9	1.400 (2)
N1—C8	1.403 (2)	C9—C10	1.392 (2)
N1—C2	1.413 (2)	C10—N3	1.378 (2)
C3—S—C1	92.26 (8)	N2—C8—N3	114.56 (15)
N4—C1—N1	123.9 (2)	N2—C8—N1	124.82 (15)
N4—C1—S	126.55 (14)	N3—C8—N1	120.62 (14)
N1—C1—S	109.54 (13)	C8—N2—C9	103.36 (14)
C8—N1—C1	122.32 (14)	C10—C9—N2	110.54 (14)
C8—N1—C2	123.39 (13)	C14—C9—N2	130.0 (2)
C1—N1—C2	114.29 (14)	N3—C10—C9	105.17 (14)
C7—C2—N1	128.3 (2)	N3—C10—C11	131.2 (2)
C3—C2—N1	112.19 (15)	C8—N3—C10	106.37 (14)

Table 3. Hydrogen-bonding geometry (Å, °)

D—H...A	H...A	D...A	D—H...A
C7—H7...N2	2.30 (2)	2.880 (2)	120 (2)
N3—H3...N4	2.02 (3)	2.617 (3)	129 (2)
C4—H4...O ⁱ	2.64 (3)	3.523 (3)	157 (2)
C14—H14...N4 ⁱⁱ	2.76 (2)	3.473 (3)	132 (2)
N4—H4...N2 ⁱⁱⁱ	2.78 (3)	3.472 (3)	138 (2)

Symmetry codes: (i) $x, y, z - 1$; (ii) $1 + x, y, z$; (iii) $x - 1, y, z$.

The structure was solved by direct methods using *SHELXS86* (Sheldrick, 1985) and difference Fourier techniques, and refined using *SHELXL93* (Sheldrick, 1993). Final full-matrix least-squares refinement was based on F^2 with anisotropic displacement parameters for all non-H atoms and isotropic displacement parameters for H atoms.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *MolEN* (Fair, 1990). Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *SHELXL93*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AS1188). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Enraf–Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
- Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis*. Enraf–Nonius, Delft, The Netherlands.
- Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures*. University of Göttingen, Germany.
- Sheldrick, G. M. (1993). *SHELXL93. Program for Crystal Structure Refinement*. University of Göttingen, Germany.
- Vecchia, L. D., Dellureficio, J., Kisis, B. & Vlattas, I. (1983). *Heterocycl. Chem.* **20**, 1287–1294.