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# 2-[2-(Dimethylamino)ethylammoniomethyl]-4-nitrophenolate

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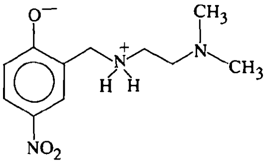
## Abstract

The structure of the title compound, $C_{11}H_{17}N_3O_3$, reveals that the intramolecular hydrogen-bonded phenolic H atom has shifted to the amino N atom so that there is an intermolecular hydrogen bond to the phenolic O atom of a neighbouring molecule [N···O 2.644 (3) Å], as well as an intramolecular hydrogen bond [N···O 2.662 (4) Å]. This proton-transfer process is due to the nitro substituent which facilitates the formation of a quinonoid structure for the substituted phenyl ring.

## Comment

X-ray structural analyses of salicylideneimine Schiff bases (Burr & Hobson, 1969; Kamwaya & Khoo, 1985) and their organotin adducts (Hazell, Hu & Khoo, 1996) revealed that the phenolic H atom shifts to the imine N atom and forms an N—H···O hydrogen bond instead of the usual O—H···N intramolecular hydrogen bond. Recently, this proton-transfer process (O—H···N → O···H—N) was observed for the saturated Schiff base analogues $2\text{-}HOC_6H_4CH_2NR_2$ using Fourier-transform IR continuum studies (Brzezinski, Maciejewska, Zundel & Kramer, 1990). Since definitive establishment of the bonding behaviour in these compounds must come from diffraction studies, we have carried out an X-ray crystal structure determination of the title compound, (I), in which the acidity of the phenolic OH group is increased by the nitro substituent.



(I)

The structure (Fig. 1) shows that the phenolic H atom is shifted to the amino N2 atom so that there are both intramolecular N2—H···O1 hydrogen bonds and intermolecular hydrogen bonds to the O1 atom of a neighbouring molecule, *i.e.* N2—H···O1($\frac{1}{2}-x$, $y-\frac{1}{2}$, $\frac{1}{2}-z$). This is further substantiated by the short C1—O1 bond distance and the quinonoid form of the phenyl group. The C—O(H) distance in $p\text{-}CH_3OC_6H_4N{=}CH\text{-}C_6H_4OH$ is 1.352 (4) Å (Yeap *et al.*, 1992) and in $2\text{-}HO\text{-}C_6H_4COOSnPH_3$ is 1.362 (3) Å (Vollano, Day, Rau, Chandrasekhar & Holmes, 1984). Other bond distances and angles have the expected values. The amine N3 atom is involved in neither the proton-transfer process nor the hydrogen bonding.

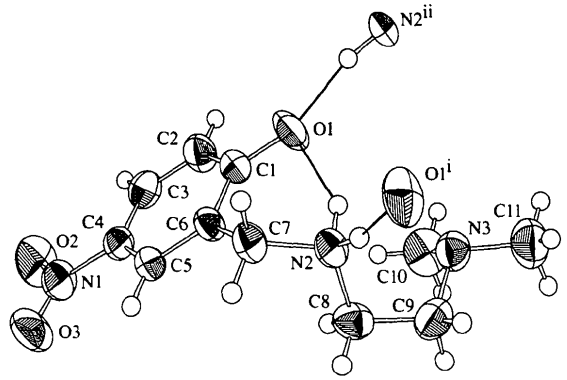


Fig. 1. View of the title molecule showing the labelling of the non-H atoms, the intermolecular hydrogen bonding to O1$^{\text{i}}$ and N2$^{\text{ii}}$, and the intramolecular hydrogen bonding. Displacement ellipsoids are shown at 50% probability levels and H atoms are drawn as small circles of arbitrary radii. [Symmetry codes: (i) $\frac{1}{2}-x$, $y-\frac{1}{2}$, $\frac{1}{2}-z$; (ii) $\frac{1}{2}-x$, $\frac{1}{2}+y$, $\frac{1}{2}-z$.]

## Experimental

The title compound was prepared by reducing the Schiff base analogue with $NaBH_4$ in boiling ethanol (Shukla, Bharadwaj, Hall & Whitmire, 1994). Yellow crystals (m.p. 431–432 K) suitable for X-ray analysis were obtained by recrystallization from methanol. Analysis found: C 55.31, H 7.504, N 17.562%; calculated for $C_{11}H_{17}N_3O_3$: C 55.22, H 7.16, N 17.56%.

### *Crystal data*

$C_{11}H_{17}N_3O_3$
$M_r = 239.27$
Monoclinic
$C2/c$
$a = 19.818\ (4)$ Å
$b = 6.676\ (2)$ Å
$c = 20.035\ (4)$ Å
$\beta = 109.044\ (11)°$
$V = 2506\ (1)$ Å$^3$
$Z = 8$
$D_x = 1.269$ Mg m$^{-3}$
$D_m$ not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 30 reflections
$\theta = 17.2\text{–}26.3°$
$\mu = 0.094$ mm$^{-1}$
$T = 294$ K
Hexagonal plate
0.475 × 0.475 × 0.070 mm
Yellow

### *Data collection*

Huber diffractometer
$\theta/2\theta$ scans

$R_{\text{int}} = 0.059$
$\theta_{\max} = 25°$

Absorption correction:
by integration
$T_{\min} = 0.965$, $T_{\max} = 0.994$
2653 measured reflections
2205 independent reflections
1534 reflections with
$I > \sigma(I)$
$h = -23 \rightarrow 20$
$k = 0 \rightarrow 7$
$l = 0 \rightarrow 23$
2 standard reflections
every 50 reflections
intensity decay: 5%

*Refinement*

Refinement on $F$
$R = 0.065$
$wR = 0.069$
$S = 1.28$
1534 reflections
163 parameters
H atoms: see below
$w = 1/\{[\sigma_{cs}(F^2) + 1.03F^2]^{1/2} - |F|\}^2$
$(\Delta/\sigma)_{\max} = 0.0010$
$\Delta\rho_{\max} = 0.13\,(3)$ e Å$^{-3}$
$\Delta\rho_{\min} = -0.12\,(3)$ e Å$^{-3}$
Extinction correction: Becker & Coppens (1974) type 1, Lorentzian isotropic
Extinction coefficient: $1.7\,(4) \times 10^4$
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

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

| | | | |
|---|---|---|---|
| O1—C1 | 1.295 (3) | N3—C10 | 1.448 (5) |
| C6—C7 | 1.491 (4) | N3—C11 | 1.451 (4) |
| C7—N2 | 1.499 (4) | N1—O2 | 1.229 (3) |
| N2—C8 | 1.476 (4) | N1—O3 | 1.232 (4) |
| C8—C9 | 1.512 (5) | N1—C4 | 1.438 (4) |
| C9—N3 | 1.450 (4) | | |
| O1—C1—C2 | 122.7 (3) | N2—C8—C9 | 109.3 (2) |
| O1—C1—C6 | 119.4 (3) | C8—C9—N3 | 112.8 (3) |
| C2—C1—C6 | 117.9 (3) | C9—N3—C10 | 111.7 (3) |
| C3—C4—N1 | 118.9 (3) | C9—N3—C11 | 110.6 (3) |
| N1—C4—C5 | 120.1 (3) | C10—N3—C11 | 110.0 (3) |
| C1—C6—C7 | 117.8 (2) | O2—N1—O3 | 122.2 (3) |
| C5—C6—C7 | 122.0 (3) | O2—N1—C4 | 119.1 (3) |
| C6—C7—N2 | 111.1 (3) | O3—N1—C4 | 118.6 (3) |
| C7—N2—C8 | 115.0 (2) | | |

Cell dimensions were determined from reflections measured at ±2$\theta$. All H atoms were located from a difference map and could be refined satisfactorily, however, in the final refinements, the H atoms not involved in hydrogen bonding were kept fixed in calculated positions (with C—H 0.95 Å and displacement factors 20% larger than those of the atoms to which they were attached) so as to increase the ratio of observations to variables.

Data collection: *MAD* (Allibon, 1995). Cell refinement: *MAD*. Data reduction: *KRYSTAL* (Hazell, 1995). Program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994) and *KRYSTAL*. Program(s) used to refine structure: modified *ORFLS* (Busing, Martin & Levy, 1962) and *KRYSTAL*. Molecular graphics: *ORTEP*III (Burnett & Johnson, 1996) and *KRYSTAL*.

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Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: AB1425). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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# *N*-Butylthiophene-3-carboxamide and 2-Benzylseleno-*N*-butylthiophene-3-carboxamide at 130 K

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## Abstract

In *N*-butylthiophen-3-carboxamide, $C_9H_{13}NOS$, the *N*-butylcarboxamide group is almost planar with the aromatic thiophene ring, with the amide N atom *cis* to C2. In the 2-benzylseleno derivative, $C_{16}H_{19}NOSSe$, the *N*-butylcarboxamide group adopts an orientation with the amide O atom *cis* to C2 and forming a close contact with the Se atom. In both compounds, the amide N atom is involved in hydrogen bonding with the O atom of an adjacent molecule forming zigzag chains.

## Comment

During the course of studies aimed at the preparation of thiophene-containing analogues of the anti-inflammatory compound ebselen, we had cause to prepare 2-benzyl-

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