

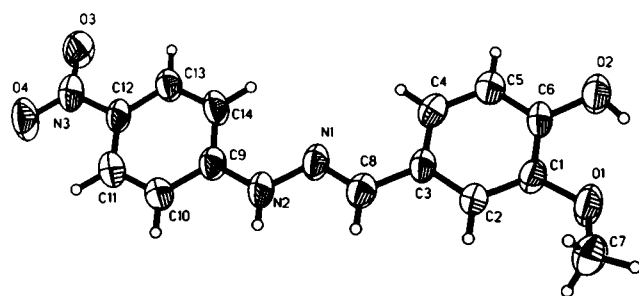
Crystal structure of 4-hydroxy-3-methoxybenzaldehyde-4-nitrophenylhydrazone, $C_{14}H_{13}N_3O_4$

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Abstract

$C_{14}H_{13}N_3O_4$, monoclinic, $P12_1/n1$ (No. 14), $a = 12.593(2)$ Å, $b = 6.9910(9)$ Å, $c = 15.765(2)$ Å, $\beta = 107.661(6)^\circ$, $V = 1322.5$ Å³, $Z = 4$, $R_g(F) = 0.043$, $wR_{\text{ref}}(F^2) = 0.096$, $T = 291$ K.

Source of material

The title compound was synthesized by condensation of equimolar ratio of 4-hydroxy-3-methoxybenzaldehyde and 4-nitrophenylhydrazine in ethanol solution. Some drops of acetic acid were added as a catalyst according to known procedure [1]. Both starting materials are commercially available. The orange crystals are obtained from the dark red ethanol solution by cooling. The product was isolated and recrystallized from glacial acetic acid (mp 505 K – 506 K). The crystals were grown by slow evaporation from glacial acetic acid within two days.

Experimental details

For the methyl group, hydrogen atoms were placed in calculated positions with U_{iso} constrained to be $1.5 \times U_{\text{eq}}$ of the carrier atom, and for the remaining hydrogen atoms $1.2 \times U_{\text{eq}}$ of the corresponding carrier atom.

Discussion

In the course of our investigations on organic nonlinear optical (NLO) materials we now determined the crystal structure of the title compound. The asymmetric unit of the crystal contains one formula unit $C_{14}H_{13}N_3O_4$. The molecule is nearly planar with distances and angles in the normal range. The molecules are linked by O—H...O, N—H...O and C—H...O hydrogen bonds ($d(\text{O2}—\text{H2} \cdots \text{O4}) = 2.892(2)$ Å, $\angle \text{O}—\text{H} \cdots \text{O} = 162^\circ$; $d(\text{N2}—\text{H2A} \cdots \text{O3}) = 3.105(3)$ Å, $\angle \text{N}—\text{H} \cdots \text{O} = 166^\circ$; $d(\text{C10}—\text{H10} \cdots \text{O2}) = 3.372(3)$ Å, $\angle \text{C}—\text{H} \cdots \text{O} = 160^\circ$).

Table 1. Data collection and handling.

| | |
|---|---|
| Crystal: | orange plate, size $0.2 \times 0.4 \times 0.5$ mm |
| Wavelength: | Mo K_α radiation (0.71073 Å) |
| μ : | 1.08 cm^{-1} |
| Diffractometer, scan mode: | Nonius KappaCCD, 208 frames, $\Delta\omega = 1^\circ$ |
| $2\theta_{\text{max}}$: | 50.44° |
| $N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$: | 7615, 2353 |
| Criterion for I_{obs} , $N(hkl)_{\text{gt}}$: | $I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 897 |
| $N(\text{param})_{\text{refined}}$: | 192 |
| Programs: | SHELXS-97 [2], SHELXTL-Plus [3], SHELXL-97 [4], PARST95 [5] |

Table 2. Atomic coordinates and displacement parameters (in Å²).

| Atom | Site | x | y | z | U_{iso} |
|-------|------|--------|--------|--------|------------------|
| H(2) | 4e | 0.8167 | 0.1290 | 1.1891 | 0.083 |
| H(2A) | 4e | 1.0624 | 0.3026 | 0.7596 | 0.071 |
| H(2B) | 4e | 1.0525 | 0.3160 | 1.0507 | 0.059 |
| H(4) | 4e | 0.7870 | 0.0976 | 0.8662 | 0.063 |
| H(5) | 4e | 0.7047 | 0.0324 | 0.9754 | 0.066 |
| H(7A) | 4e | 1.1313 | 0.1798 | 1.2078 | 0.102 |
| H(7B) | 4e | 1.1130 | 0.2912 | 1.2885 | 0.102 |
| H(7C) | 4e | 1.1151 | 0.4023 | 1.2026 | 0.102 |
| H(8) | 4e | 1.0554 | 0.3026 | 0.8967 | 0.064 |
| H(10) | 4e | 1.0802 | 0.3372 | 0.6157 | 0.066 |
| H(11) | 4e | 1.0088 | 0.2850 | 0.4649 | 0.067 |
| H(13) | 4e | 0.7394 | 0.0374 | 0.5019 | 0.062 |
| H(14) | 4e | 0.8108 | 0.0860 | 0.6533 | 0.065 |

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Table 3. Atomic coordinates and displacement parameters (in Å²).

| Atom | Site | <i>x</i> | <i>y</i> | <i>z</i> | <i>U</i> ₁₁ | <i>U</i> ₂₂ | <i>U</i> ₃₃ | <i>U</i> ₁₂ | <i>U</i> ₁₃ | <i>U</i> ₂₃ |
|-------|------|-----------|-----------|-----------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|
| O(1) | 4e | 0.9776(2) | 0.2603(3) | 1.1887(1) | 0.062(2) | 0.119(2) | 0.035(1) | −0.013(1) | 0.013(1) | −0.011(1) |
| O(2) | 4e | 0.7800(1) | 0.0861(3) | 1.1407(1) | 0.071(2) | 0.096(2) | 0.042(1) | −0.012(1) | 0.021(1) | −0.006(1) |
| O(3) | 4e | 0.7249(2) | 0.0683(3) | 0.3442(1) | 0.071(2) | 0.097(2) | 0.044(1) | −0.008(1) | 0.010(1) | −0.003(1) |
| O(4) | 4e | 0.8764(2) | 0.1817(3) | 0.3267(1) | 0.087(2) | 0.127(2) | 0.041(1) | −0.008(1) | 0.033(1) | 0.001(1) |
| N(1) | 4e | 0.9379(2) | 0.2098(3) | 0.7971(1) | 0.074(2) | 0.059(2) | 0.034(1) | 0.003(1) | 0.020(1) | 0.000(1) |
| N(2) | 4e | 0.9970(2) | 0.2532(3) | 0.7394(1) | 0.070(2) | 0.079(2) | 0.031(1) | −0.009(1) | 0.018(1) | −0.003(1) |
| N(3) | 4e | 0.8200(2) | 0.1349(3) | 0.3746(2) | 0.072(2) | 0.070(2) | 0.039(2) | 0.009(2) | 0.023(2) | 0.002(1) |
| C(1) | 4e | 0.9337(2) | 0.2200(4) | 1.1003(2) | 0.054(2) | 0.060(2) | 0.034(2) | −0.001(2) | 0.011(2) | −0.004(1) |
| C(2) | 4e | 0.9827(2) | 0.2582(3) | 1.0353(2) | 0.056(2) | 0.054(2) | 0.038(2) | −0.007(1) | 0.015(2) | −0.004(1) |
| C(3) | 4e | 0.9292(2) | 0.2115(3) | 0.9466(2) | 0.060(2) | 0.048(2) | 0.033(2) | 0.005(2) | 0.017(2) | 0.002(1) |
| C(4) | 4e | 0.8244(2) | 0.1277(3) | 0.9252(2) | 0.056(2) | 0.061(2) | 0.037(2) | 0.000(2) | 0.007(2) | −0.005(1) |
| C(5) | 4e | 0.7749(2) | 0.0886(3) | 0.9904(2) | 0.058(2) | 0.060(2) | 0.047(2) | −0.002(1) | 0.017(2) | −0.002(2) |
| C(6) | 4e | 0.8301(2) | 0.1333(4) | 1.0778(2) | 0.060(2) | 0.057(2) | 0.033(2) | 0.006(2) | 0.018(2) | 0.004(1) |
| C(7) | 4e | 1.0934(2) | 0.2854(3) | 1.2248(2) | 0.070(2) | 0.080(2) | 0.044(2) | −0.002(2) | 0.004(2) | 0.001(2) |
| C(8) | 4e | 0.9845(2) | 0.2490(3) | 0.8794(2) | 0.065(2) | 0.053(2) | 0.041(2) | 0.003(1) | 0.015(2) | −0.001(2) |
| C(9) | 4e | 0.9534(2) | 0.2189(4) | 0.6508(2) | 0.060(2) | 0.050(2) | 0.037(2) | 0.004(2) | 0.018(2) | 0.004(1) |
| C(10) | 4e | 1.0115(2) | 0.2771(3) | 0.5930(2) | 0.056(2) | 0.065(2) | 0.048(2) | −0.008(1) | 0.022(2) | −0.003(2) |
| C(11) | 4e | 0.9690(2) | 0.2472(3) | 0.5031(2) | 0.063(2) | 0.066(2) | 0.046(2) | 0.003(2) | 0.028(2) | 0.003(2) |
| C(12) | 4e | 0.8661(2) | 0.1599(4) | 0.4698(2) | 0.063(2) | 0.056(2) | 0.028(2) | 0.004(2) | 0.017(2) | 0.002(1) |
| C(13) | 4e | 0.8077(2) | 0.0985(3) | 0.5252(2) | 0.060(2) | 0.056(2) | 0.044(2) | 0.001(2) | 0.023(2) | 0.004(2) |
| C(14) | 4e | 0.8503(2) | 0.1273(3) | 0.6156(2) | 0.068(2) | 0.061(2) | 0.041(2) | 0.001(2) | 0.028(2) | 0.009(1) |

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