

2-Formylbenzonitrile

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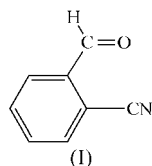
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The title compound, C_8H_5NO , has an intramolecular $O\cdots CN$ contact involving an $O\cdots C$ distance of 2.797 (2) Å and a $C-N$ bond angle of 174.5 (2)°, both indicative of a weak nucleophilic attack of the aldehyde O atom on the electrophilic C atom in the nitrile group. Calculations at the B3LYP density functional level using the 6-31G* basis set support this interpretation; natural bond-order analysis indicates an $n_{O1} \rightarrow \pi_{CN}^*$ delocalization energy of 6.3 kJ mol⁻¹. Similar results were obtained from density functional calculations on three related molecules. The 2-formylbenzonitrile molecules pack in sheets as a consequence of $C-H\cdots N$ and $C-H\cdots O$ hydrogen bonds.

Comment

In three *o*-nitrobenzonitrile derivatives (5-chloro-, 6-chloro- and 6-methyl-) there are weak electrophilic nucleophilic (or Lewis acid–base) interactions between a nitro O atom and the nitrile C atom (Britton & Cramer, 1996). This situation is indicated by a short $O\cdots C$ distance and a bending of the $C-CN$ group away from the interacting O atom. The study of 2-formylbenzonitrile, (I), reported here was undertaken to ascertain whether the same (expected) interaction occurred.



The atom labeling and displacement ellipsoids are shown in Fig. 1, which also shows the $O\cdots C$ interaction. The $O1\cdots C7$ distance is 2.797 (2) Å, which can be compared with the van der Waals distance of 3.22 Å (Bondi, 1964; Rowland & Taylor, 1996). The $C1-C7-N1$ angle is 174.54 (17)° and the CN group bends away from atom O1. This configuration is similar to those in the *o*-nitrobenzonitriles, except that the $O\cdots C$ distance is about 0.2 Å longer in the aldehyde. This difference is reasonable since the aldehyde O atom has no formal charge, while the nitro O atom has a formal charge of $-\frac{1}{2}$. The other bond angles and distances in the molecule are normal.

The molecules pack in sheets parallel to (10 $\bar{2}$) (Fig. 2). The molecules are tilted by 7.8 (1)° with respect to the sheets.

There are three weak $C-H\cdots X$ interactions with $H\cdots X$ distances less than 2.70 Å. These interactions give rise to three different rings, as can be seen in Fig. 2. Using graph-set notation (Etter, 1990; Bernstein *et al.*, 1995), there is an $R_2^2(10)$ ring involving two H6 atoms, an $R_3^3(10)$ ring involving atoms H3, H6 and H5, and an $R_4^4(22)$ ring involving two H3 and two H5 atoms. The geometric data for these interactions are given in Table 1.

The Cambridge Structural Database (Allen, 2002) contains three additional structures with short $O\cdots CN$ interactions, *viz.* 2-cyanobenzophenone, (II) (Preut *et al.*, 1992), 9-oxo-1-thioxanthencarbonitrile, (III) (Abboud *et al.*, 1990), and 5-cyano-7-methoxy-2,2-dimethyl-4-oxochroman-6-yl acetate, (IV) (Clegg, 2003); these are shown in Fig. 3 and relevant experimental data for these compounds are given in Table 2, where they are compared with electronic structure calculations.

To provide further insight into interactions between the potentially interacting carbonyl and nitrile groups in (I)–(IV), electronic structure calculations were carried out at the density functional level (Cramer, 2004) using the 6-31G* basis set (Hehre *et al.*, 1986) and the hybrid B3LYP functional (Becke, 1988, 1993; Lee *et al.*, 1988; Stephens *et al.*, 1994). All structures were fully optimized without the imposition of any symmetry constraints. The optimized densities were employed in the computation of interatomic bond orders according to

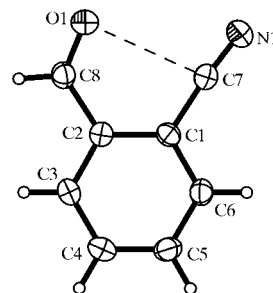


Figure 1

A view of the title molecule, with displacement ellipsoids drawn at the 50% probability level. The $O\cdots C-N$ interaction is shown as a dashed line.

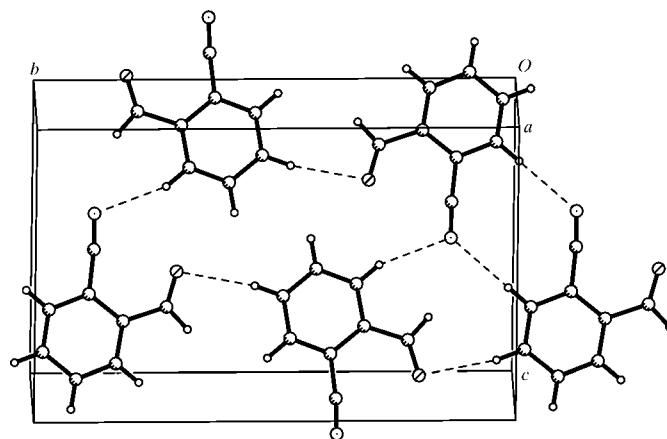


Figure 2

A view of the packing of molecules normal to (10 $\bar{2}$). $C-H\cdots N$ and $C-H\cdots O$ interactions are shown as dashed lines.

the scheme of Mayer (1983). In addition, the energetic stabilization associated with the $n_{O1} \rightarrow \pi_{CN}^*$ interaction was quantified by second-order perturbation theory in the natural bond orbital (NBO) basis (Reed *et al.*, 1988). CM3 partial atomic charges (Winget *et al.*, 2002) were also examined, but charges on the nitrile N atoms in (I)–(IV) varied negligibly.

Although the calculated gas-phase and experimental solid-state structures should not be expected to match completely, key trends in the two sets of structures are manifest. Most noteworthy is the increasing deviation of the nitrile N atom from collinearity with the nitrile C atom and the *ipso*-C atom of the aromatic ring as the distance between the carbonyl O and the nitrile C atoms decreases. If the carbon–oxygen interaction were purely repulsive, the nitrile group would be expected to be displaced away from the O atom, but that does not require bending at the nitrile C atom.

The presence of substantial repulsion is certainly supported by other geometric parameters. For instance, as the O–C–C–C torsion angle is reduced, the C–C–O angle increases to maintain separation from the nitrile C atom. In the case of (I), where conjugation evidently favors coplanarity of all of the exocyclic functionality, the C–C–O bond angle increases to 125.3°.

Analysis of the B3LYP densities provides in each case some support for an incipient nucleophilic interaction between the carbonyl O atom and nitrile C atom. That interaction is not sufficient to lead to any significant Mayer bond order developing between the two atoms. Instead, NBO analysis suggests that there is a stabilization associated with an $n_{O1} \rightarrow \pi_{CN}^*$ interaction that increases steadily with decreasing O–C

distance and concomitant decreasing C–C–N angles. The bending of the nitrile group facilitates this delocalization by increasing the amplitude of the π^* orbital on the side of the bond adjacent to the carbonyl O atom. This effect does lead to a small reduction in the C–N Mayer bond order as the bond angle increasingly deviates from linearity.

Experimental

The title compound was obtained from Aldrich. The crystal used for diffraction analysis was grown from chloroform.

Crystal data

| | |
|-------------------------------|---|
| C_8H_5NO | $Z = 4$ |
| $M_r = 131.13$ | $D_x = 1.374 \text{ Mg m}^{-3}$ |
| Monoclinic, $P2_1/c$ | Mo $K\alpha$ radiation |
| $a = 3.7889 (9) \text{ \AA}$ | $\mu = 0.09 \text{ mm}^{-1}$ |
| $b = 15.580 (4) \text{ \AA}$ | $T = 173 (2) \text{ K}$ |
| $c = 10.759 (3) \text{ \AA}$ | Needle, colorless |
| $\beta = 93.73 (3)^\circ$ | $0.50 \times 0.05 \times 0.05 \text{ mm}$ |
| $V = 633.8 (3) \text{ \AA}^3$ | |

Data collection

| | |
|--|---------------------------------------|
| Siemens SMART area-detector diffractometer | 1115 independent reflections |
| ω scans | 974 reflections with $I > 2\sigma(I)$ |
| 3166 measured reflections | $R_{int} = 0.041$ |
| | $\theta_{max} = 25.0^\circ$ |

Refinement

| | |
|---------------------------------|--|
| Refinement on F^2 | $w = 1/[\sigma^2(F_o^2) + (0.038P)^2 + 0.26P]$ |
| $R[F^2 > 2\sigma(F^2)] = 0.042$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| $wR(F^2) = 0.101$ | $(\Delta/\sigma)_{max} = 0.001$ |
| $S = 1.08$ | $\Delta\rho_{max} = 0.15 \text{ e \AA}^{-3}$ |
| 1115 reflections | $\Delta\rho_{min} = -0.17 \text{ e \AA}^{-3}$ |
| 91 parameters | |
| H-atom parameters constrained | |

Table 1

Distances^a and angles (\AA , $^\circ$) in the C–H···X–C contacts.

| C–H···X–C | C–H···X | H···X | H···X–C | C···X |
|--|---------|-------|---------|-----------|
| C3–H3···N1 ⁱ –C7 ⁱ | 152 | 2.67 | 110 | 3.540 (2) |
| C5–H5···O1 ⁱⁱ –C8 ⁱⁱ | 169 | 2.60 | 95 | 3.532 (2) |
| C6–H6···N1 ⁱⁱⁱ –C7 ⁱⁱⁱ | 157 | 2.64 | 127 | 3.533 (2) |

Note: (a) all C–H distances are 0.95 \AA . Symmetry codes: (i) $x - 1, -y + \frac{1}{2}, z - \frac{1}{2}$; (ii) $-x + 1, y + \frac{1}{2}, -z + \frac{3}{2}$; (iii) $-x + 2, -y + 1, -z + 2$.

Table 2

Experimental and computed (\AA , $^\circ$) values for the substituted aryl nitriles (I)–(IV).

| | (I) | (II) | (III) | (IV) |
|---|-----------|-----------|-----------|-----------|
| Experimental | | | | |
| O···C | 2.797 (2) | 2.837 (4) | 2.607 (3) | 2.758 (4) |
| C–C–N | 174.5 (2) | 176.8 (4) | 174.0 (2) | 174.4 (5) |
| C–C–O | 124.9 (2) | 119.9 (3) | 118.8 (2) | 123.4 (4) |
| O–C–C–C ^a | 10.1 (3) | 42.6 (4) | 12.1 (3) | 7.4 (5) |
| Computed | | | | |
| O···C | 2.806 | 2.858 | 2.665 | 2.758 |
| C–C–N | 173.0 | 174.7 | 171.4 | 172.9 |
| C–C–O | 125.3 | 119.0 | 120.2 | 123.6 |
| O–C–C–C ^a | 0.0 | 39.7 | 17.0 | 6.0 |
| O···C bond order | 0.022 | 0.005 | 0.023 | 0.023 |
| C–O bond order | 1.908 | 1.829 | 1.811 | 1.841 |
| C–N bond order | 2.765 | 2.784 | 2.759 | 2.766 |
| NBO $n_{O1} \rightarrow \sigma_{CN}^*$ kJ mol ⁻¹ | 6.3 | 2.5 | 9.6 | 7.9 |

Note: (a) torsion angle of the CCO group with respect to the mean plane of the C₆ ring.

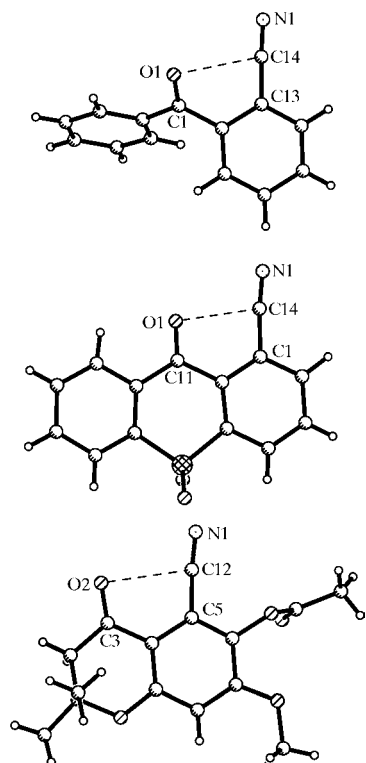


Figure 3
Views of (II) (top), (III) (middle) and (IV) (bottom); see *Comment*. Intramolecular O···C interactions are shown as dashed lines.

H atoms were introduced at calculated positions, with C—H distances of 0.95 Å, and refined using a riding model [$U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$].

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINTE* (Bruker, 2002); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ3013). Services for accessing these data are described at the back of the journal.

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