

3-Amino-5,6-dicyano-1-phenylimino-1*H*-isoindole

Tor Dahl

Department of Chemistry, University of Tromsø,
N-9037 Tromsø, Norway

Correspondence e-mail: tor.dahl@chem.uit.no

Key indicators

Single-crystal X-ray study

$T = 100$ K

Mean $\sigma(\text{C}-\text{C}) = 0.003$ Å

R factor = 0.053

w R factor = 0.138

Data-to-parameter ratio = 16.0

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

The title compound, $\text{C}_{16}\text{H}_9\text{N}_5$, crystallized as thin needles from a 1:1 methanol solution of aniline and 1,2,4,5-tetracyanobenzene. Various kinds of short intermolecular contacts link the molecules together in chains along the needle axis. Some of these contacts seem difficult to explain.

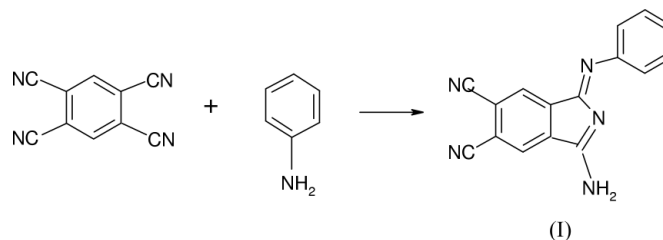
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Comment

The title compound, (I), was formed as a result of an attempt to crystallize a molecular complex between aniline and 1,2,4,5-tetracyanobenzene. This attempt was part of a systematic study of stacking interactions in this type of complexes (Dahl, 2000). It appears from the discussion in the *Experimental* section that stacking interactions may be involved in the initial step of the unexpected formation of the title compound. Among the observed intermolecular interactions in the title compound, discussed in this section, there is also a stacking interaction. The present report is therefore considered to be important for a study of stacking interactions as well as other kinds of intermolecular interactions.



The numbering of the atoms is shown in Fig. 1. The atoms of the isoindole ring system are all nearly coplanar, the largest deviation from the least-squares plane being 0.016 (2) Å. In the other benzene ring (C11–C16), the corresponding largest deviation is 0.011 (2) Å. The dihedral angle between these two ring systems is 49.4 (1)°. All bond distances and angles are as expected. The geometry of the $\text{C}-\text{C}\equiv\text{N}$ groups is not significantly different from that observed in crystalline 1,2,4,5-tetracyanobenzene (Lefebvre *et al.*, 1989).

The thin needle-shaped crystals are very easily cleaved along the needle axis. This indicates that the intermolecular interactions are much stronger along this axis, the b axis, than in other directions. Analysis of the intermolecular contacts shows that the molecules are linked together in chains along this axis. One such chain is shown in Fig. 2 and consists of alternating dimers held together by $\text{N31}-\text{H31}\cdots\text{N2}$ hydrogen bonds, and dimers of parallel overlapping molecules. In each of these dimers, the molecules are related by a centre of symmetry. The interplanar distance between the overlapping

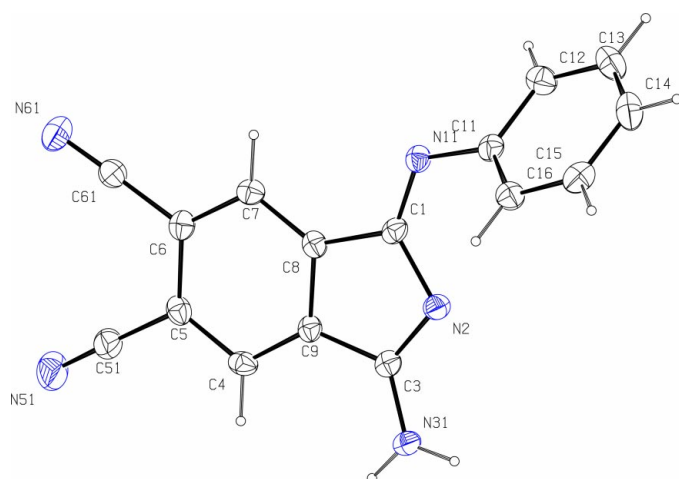


Figure 1
The title compound with the atom-labelling scheme, showing 50% probability displacement ellipsoids, viewed perpendicular to the plane of the isoindole ring system.

dimers is 3.336 (2) Å, and the shortest intermolecular C...C distance is 3.369 (3) Å. These distances are shorter than expected if only ordinary van der Waals interactions were present between these molecules. Many examples have been reported earlier of short interplanar distances between stacked molecules, which seem difficult to explain (Dahl, 1994). It may be worth considering if the molecules form a charge-transfer self-complex, where the five-membered ring is the electron donor and the benzene ring of the isoindole system the electron acceptor. The observed colour of the crystals may indicate a charge-transfer interaction. A similar self-complex formation has been suggested for various naphthoquinones (Gaultier *et al.*, 1969). It is, however, surprising that there is overlap not only of the 'donor' and the 'acceptor' ring, but also a considerable overlap of the 'donor' rings (Fig. 2).

In the chain, there is also a short intermolecular contact between the C61≡N61 group and the overlapping C3 atom of the corresponding molecule in the neighbouring cell (Fig. 2). The C61...C3 distance is 3.316 (4) Å. This short distance is difficult to explain.

Neighbouring chains are linked together in sheets by a C—H...N hydrogen bond and a short C—H...N contact, both to N51 (Table 1). The hydrogen bond is quite short, whereas the other contact is only slightly shorter than the van der Waals distance. If the latter contact is classified as a hydrogen bond, N51 is thus involved in a bifurcated hydrogen bond. The shape and the nature of the crystals indicate, however, that this bond is much weaker than the interactions involved in the chain along the *b* axis. This seems to be the most significant conclusion which can be drawn from the packing analysis of this structure.

Experimental

By evaporating the solvent in daylight from a 1:1 methanol solution of aniline, obtained from Merck KGaA, and 1,2,4,5-tetracyano-

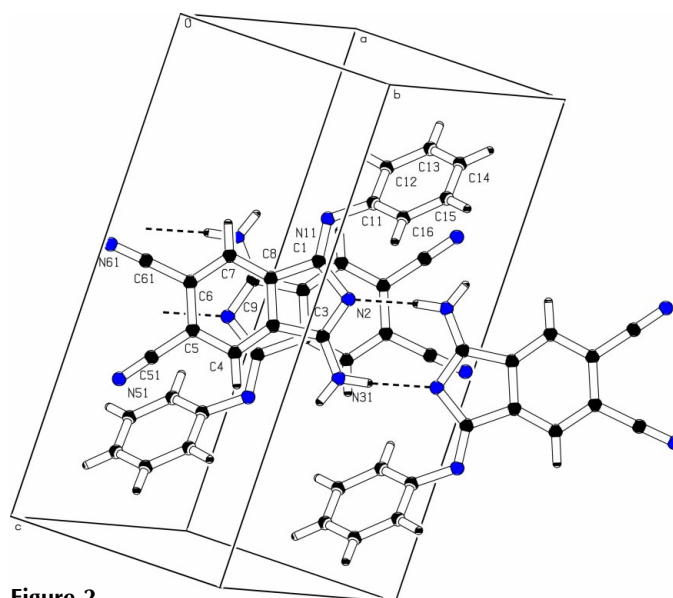


Figure 2
Chains of alternating hydrogen-bonded and overlapping dimers viewed perpendicular to the plane of the isoindole ring system.

benzene, obtained from Fluka Chemie AG, the title compound, rather than the expected molecular complex, was formed (see Scheme). Ito *et al.* (1997) have obtained a similar isoindole derivative as the final product from benzyl cyanide and 1,2,4,5-tetracyanobenzene after a series of reaction steps. The first step gave a 2:1 molecular complex, and the final product was obtained after irradiation of the complex and subsequent dissolution of the photocoupling product in certain solvents, such as ethanol or acetone. As the formation of the title compound might possibly be a result of similar reactions, a crystallization of the starting compounds was also made in darkness with dichloromethane as solvent. The crystals obtained in this way were of poor quality and consisted of pseudo-merohedral twins. They were considered unsuitable for a complete crystal structure analysis. Although they had the same colour and shape as those of the title compound, preliminary investigations by film methods showed that they had a different unit cell. Oscillation photographs about the needle axis showed some very strong reflections in the second layer line. This kind of reflections is typical for 1:1 molecular complexes with mixed stacks. These crystals were relatively easily soluble in dichloromethane, whereas those of the title compound were not. By recrystallization from methanol in daylight, the crystals of the title compound were obtained. All these observations indicate that the compound obtained from dichloromethane in darkness is not the same as the title compound, and that this probably is the 1:1 molecular complex of the starting materials.

Crystal data

C₁₆H₉N₅
M_r = 271.28
 Monoclinic, *P*₂₁/*n*
a = 11.571 (3) Å
b = 7.180 (3) Å
c = 15.530 (5) Å
 β = 95.94 (4)°
V = 1283.3 (8) Å³
Z = 4

D_x = 1.404 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 25 reflections
 θ = 4.2–12.1°
 μ = 0.09 mm⁻¹
T = 100 (2) K
 Needle, orange-brown
 0.60 × 0.15 × 0.15 mm

Data collection

Enraf–Nonius CAD-4
diffractometer
 ω -2 θ scans
Absorption correction: Gaussian
(*PLATON*; Spek, 1998)
 $T_{\min} = 0.986$, $T_{\max} = 0.988$
4052 measured reflections
3047 independent reflections
1542 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.021$
 $\theta_{\text{max}} = 28.0^\circ$
 $h = -1 \rightarrow 15$
 $k = -1 \rightarrow 9$
 $l = -20 \rightarrow 20$
2 standard reflections
frequency: 60 min
intensity decay: 1%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.053$
 $wR(F^2) = 0.138$
 $S = 0.93$
3047 reflections
190 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0642P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.003$
 $\Delta\rho_{\text{max}} = 0.26 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\text{min}} = -0.26 \text{ e } \text{Å}^{-3}$

Table 1

Hydrogen-bonding geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N31—H31 \cdots N2 ⁱ	0.88	2.02	2.896 (3)	172
C4—H4 \cdots N51 ⁱⁱ	0.95	2.34	3.250 (3)	159
C12—H12 \cdots N51 ⁱⁱⁱ	0.95	2.63	3.422 (4)	141

Symmetry codes: (i) $1-x, -y, 1-z$; (ii) $\frac{3}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z$; (iii) $x-\frac{1}{2}, \frac{3}{2}-y, \frac{1}{2}+z$.

All H atoms were located in a difference map. Attempts were made to refine the positions of the amino H atoms without assuming the amino group to be planar. The best R values were, however, obtained when these H atoms were constrained to be in ideal positions appropriate for an sp^2 -hybridized N atom and were allowed to ride on this atom. All the other H atoms were refined in a similar way.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *XCAD4* (Harms, 1996); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 1998); software used to prepare material for publication: *SHELXL97*.

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