

Dicyanodurene–*p*-tetrafluorodiiodobenzene (1/1)Doyle Britton^{a*} and William B. Gleason^b^aDepartment of Chemistry, University of Minnesota, Minneapolis, MN 55455, USA, and^bDepartment of Laboratory Medicine and Pathology, University of Minnesota, Minneapolis, MN 55455, USA

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Key indicators

Single-crystal X-ray study

T = 173 K

Mean $\sigma(\text{C}-\text{C}) = 0.004 \text{ \AA}$

R factor = 0.026

wR factor = 0.073

Data-to-parameter ratio = 18.6

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

In the crystal structure of the 1:1 complex between dicyanodurene (2,3,5,6-tetramethyl-1,4-benzodicyanide) and *p*-tetrafluorodiiodobenzene (2,3,5,6-tetrafluoro-1,4-diiodobenzene), $\text{C}_{12}\text{H}_{12}\text{N}_2 \cdot \text{C}_6\text{F}_4\text{I}_2$, there are two major types of intermolecular interaction. The planar molecules are stacked alternately in the common charge-transfer arrangement with molecules 3.53 (3) Å apart. In addition, the molecules form linear chains, driven by $\text{CN} \cdots \text{I}$ interactions, with a distance of 3.061 (3) Å. The dicyanodurene and tetrafluorodiiodobenzene molecules lie on centers of symmetry.

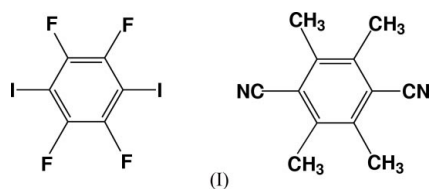
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Comment

Significant intermolecular $\text{CN} \cdots \text{I}-\text{C}$ interactions are well known. In the earliest work on ICN (Ketelaar & Zwartsenberg, 1939) and ICCCN (Borgen *et al.*, 1962), the $\text{CN} \cdots \text{I}$ distances are less than 3.0 Å. In *p*-iodobenzonitrile (Schlemper & Britton, 1965; see also Desiraju & Harlow, 1989) and similar compounds with aromatic rings between the I and the CN [for a summary, see Table 4 in Ojala *et al.* (1999)], the distances are nearer 3.2 Å, which is still shorter than the expected van der Waals distance of about 3.4 Å.



It was conjectured that *p*-dicyanobenzene and *p*-diiodobenzene might form a solid-state complex with similar interactions, but attempts in this laboratory to prepare crystals of such a complex by evaporating solutions that were equimolar in the two components produced only a mixture of crystals of the starting materials. The recent results of Cardillo *et al.* (2000), which showed that fluorinated diiodides interact strongly with a number of dibasic nitrogen compounds, suggested that replacing the *p*-diiodobenzene with *p*-tetrafluorodiiodobenzene would give a better chance of success. However, attempts to prepare a complex of *p*-tetrafluorodiiodobenzene and *p*-dicyanobenzene again led to mixtures of the two starting materials.

As Cardillo *et al.* (2000) have shown, replacement of H with F in the diiodides makes the I atoms stronger Lewis acids. In a similar fashion, replacement of H with CH_3 in the dicyanides should make the cyanide groups stronger Lewis bases. Accordingly, the preparation of the title compound, (I), was attempted and was successful. The structure of (I) is reported here.

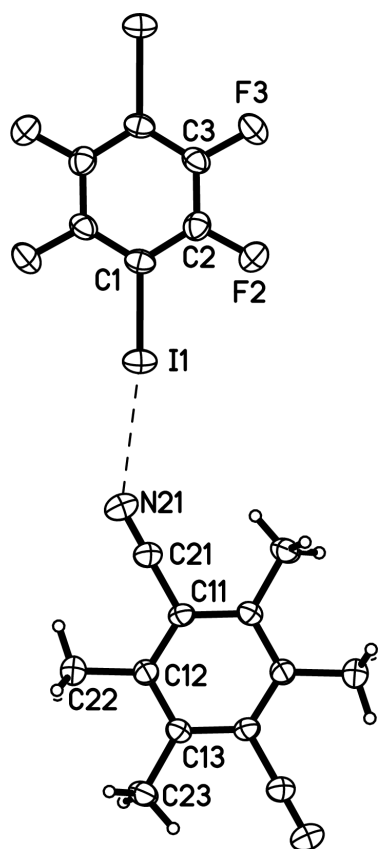


Figure 1

The title complex, with displacement ellipsoids shown at the 50% probability level. Unlabeled atoms are related to the labeled atoms by centers of symmetry. The dashed line shows the short CN...I contact.

The bond lengths and angles are normal. Fig. 1 shows one CN...I interaction. Since both molecules lie on centers of symmetry, these interactions lead to chains of molecules lying along the [102] direction. Adjacent molecules in these chains are tilted 2.1 (2)° away from being parallel to each other. The metric parameters of the CN...I interaction are: CN...I 143.4 (4)°, N...I 3.061 (3)° and N...I—C 172.6 (3)°.

The π - π interactions between molecules in adjacent chains are also significant. Fig. 2 shows the overlap between molecules, viewed perpendicular to the plane of the diiodide molecule. The perpendicular distance between the ring atoms in the molecules is 3.53 (3) Å. This is consistent with the findings of Dahl (1971, 1972, 1975) that complexes of hexafluorobenzene with *p*-xylene, mesitylene, durene, and hexamethylbenzene had inter-ring distances of 3.55, 3.56, 3.51 and 3.56 Å, respectively.

The combination of the CN...I and π - π interactions leads to layers of molecules perpendicular to the *b* axis, as shown in Fig. 3. I atoms in adjacent chains make van der Waals contacts of 4.247 (2) Å.

Experimental

The diiodide was obtained from Aldrich Chemical Co. Inc. The di-cyanodurene was prepared as described by Britton & van Rij (1991). The crystals grew as plates from acetonitrile.

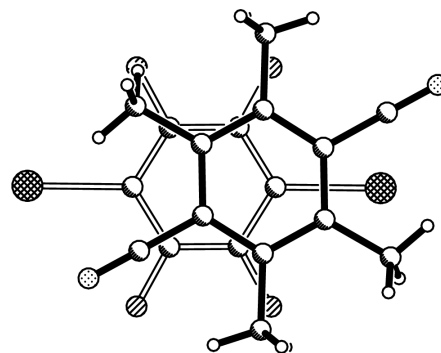


Figure 2

The π - π overlap between the molecules, viewed normal to the plane of the C₆F₄I₂ molecule.

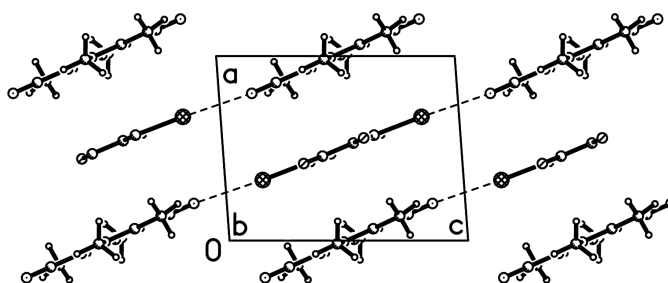


Figure 3

View along *b*, showing one layer formed by the combined CN...I and π - π interactions.

Crystal data

C₁₂H₁₂N₂·C₆F₄I₂
M_r = 586.10
 Monoclinic, *P*2₁/*n*
a = 7.447 (2) Å
b = 13.657 (4) Å
c = 9.642 (2) Å
 β = 94.19 (1)°
V = 978.0 (4) Å³
Z = 2

D_x = 1.990 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 2326 reflections
 θ = 3.0–27.4°
 μ = 3.26 mm⁻¹
T = 173 (2) K
 Plate, colorless
 0.50 × 0.20 × 0.05 mm

Data collection

Siemens SMART area-detector diffractometer
 ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 T_{\min} = 0.50, T_{\max} = 0.85
 9767 measured reflections

2234 independent reflections
 1903 reflections with $I > 2\sigma(I)$
 R_{int} = 0.034
 θ_{max} = 27.5°
 $h = -9 \rightarrow 9$
 $k = -17 \rightarrow 17$
 $l = -11 \rightarrow 12$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)]$ = 0.026
 $wR(F^2)$ = 0.073
 S = 1.02
 2234 reflections
 120 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.041P)^2 + 0.663P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}}$ = 0.009
 $\Delta\rho_{\text{max}}$ = 1.18 e Å⁻³
 $\Delta\rho_{\text{min}}$ = -0.49 e Å⁻³

All of the peaks higher than 0.5 e Å⁻³ in the final difference Fourier map lie about 1 Å from the I atom. The methyl H atoms were included at idealized positions, with the methyl groups allowed to rotate around the C—C bonds.

Data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1994); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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