ORGANIC COMPOUNDS

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N,*N*′-Dicyano-4,7-indanquinone Diimine†

Ekkehart Tillmanns*‡ and
Franz Schwabenländer

*Mineralogisches Institut der Universität Würzburg,
Am Hubland, W-8700 Würzburg, Germany*

Stefan Güssregen, Siegfried Hünig and
Tobias Metzenthin

*Institut für Organische Chemie der Universität Würzburg,
Am Hubland, W-8700 Würzburg, Germany*

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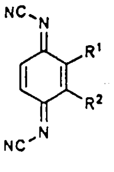
Abstract

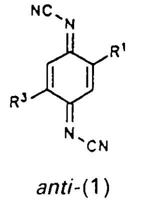
The title compound, $C_{11}H_8N_4$, has a *syn* configuration in the solid state in contrast to *syn*/*anti* isomerization in solution. The structural details help to explain the influence of the anellated five-membered ring on the properties of the quinoid π system.

Comment

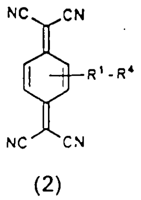
N,*N*′-Dicyanoquinone diimines [DCNQI (1)] have attracted worldwide interest as electron acceptors in electrically conducting charge-transfer (CT) complexes (Erk, Hünig, Klebe, Krebs & von Schütz, 1991) and radical anion salts (Hünig *et al.*, 1991; Kato, Kobayashi & Kobayashi, 1989). Their electron affinity, as well as their stereochemistry (*syn*/*anti* isomerism of two cyanoimine units), can be controlled using different substituents with an appropriate substitution pattern (Aumüller & Hünig, 1986). Comparative structure investigations of various tetracyanoquinodimethanes [TCNQ (2)] and DCNQI's demonstrate that the planarity of the π system is reduced in TCNQ derivatives with anellated six-membered rings, whereas DCNQI's with the same substitution pattern are planar (Schubert, Hünig & Aumüller, 1985). However, the reduction in steric demand due to five-membered rings does not affect the planarity of TCNQ acceptors (Kobayashi & Mazaki, 1988).



syn-(1)

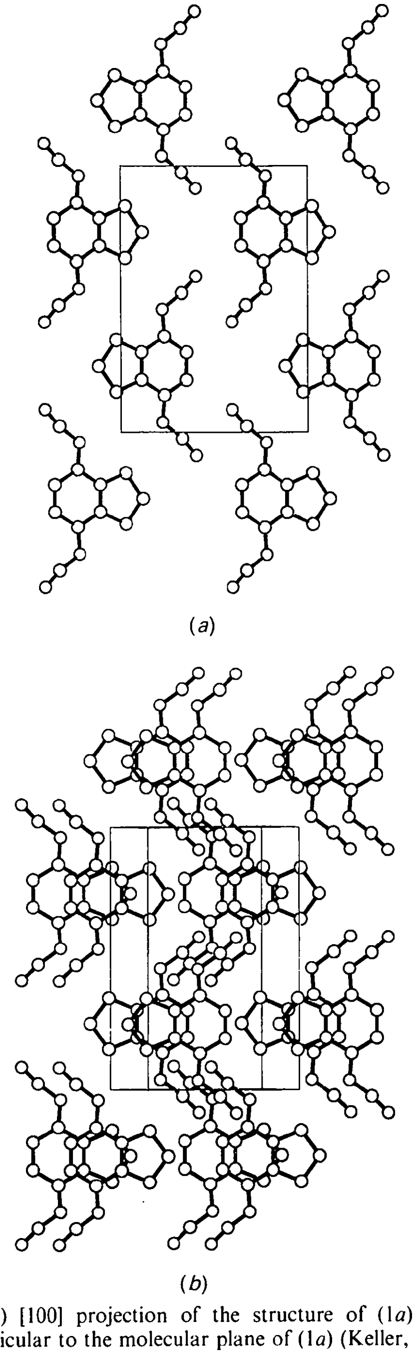


anti-(1)



(2)

In order to evaluate the effect of an anellated (strained) pentacycle on the stereochemistry, redox


(*a*)

(*b*)

Fig. 1. (*a*) [100] projection of the structure of (1*a*); (*b*) view perpendicular to the molecular plane of (1*a*) (Keller, 1988).

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† Alternative name: 4,7-indandiylidenedi(cyanamide).

‡ Present address: Institut für Mineralogie und Kristallographie der Universität, Dr. Karl Lueger-Ring 1, A-1010 Wien, Austria.

potential and electron-acceptor properties of the DCNQI system, we prepared the title compound (1*a*). Details of the synthetic and electrochemical work will be published elsewhere. NMR spectra reveal that (1*a*), although 2,3-substituted, exists as a mixture of *syn* and *anti* isomers in chloroform or toluene solution (Metzenthin, 1991). However, the solid structure of (1*a*) only exhibits *syn*-configured planar acceptor molecules, which should have a resulting dipole moment which is mutually compensated by the arrangement of the molecules in the crystal (Fig. 1*a*).

The view perpendicular to the molecular plane shows uniform stacks of acceptor molecules with the saturated five-membered ring being situated above the quinoid ring of the adjacent acceptor molecule (Fig. 1*b*). The crystal structure of a 5,6-unsubstituted quinoid system anellated to a five-membered ring in the 2,3-position is as yet unknown. Due to the strain of the pentacycle, the adjacent C=C double bond of the quinoid system is slightly lengthened and the angles at C3 differ markedly from the 120° angle for an idealized sp^2-hybridized C atom. While the angle C1—C3—C5 is considerably wider [126.8 (1)°], C3′—C3—C5 decreased to 112.2 (1)°, which is very close to the geometry of a tetrahedrally substituted (sp^3-hybridized) C atom. This distortion of the usual bond lengths is accompanied by a modulation of the chemical and physical properties of the adjacent aromatic, or in this case *quinoid*, nucleus. Since its discovery (Mills & Nixon, 1930) the so-called Mills–Nixon effect has stimulated theoretical and experimental work (Stanger, 1991). The increased electron affinity of quinoid molecules with anellated small rings was explained with a rehybridization of the substituted C atom (C3) (Streitwieser, Ziegler, Mowery, Lewis & Lawler, 1968). Streitwieser's useful model has been supported recently by molecular-orbital calculations (Eckert-Maksic, Lesar & Maksic, 1992) and paramagnetic resonance spectra (Davies & Ng, 1992). Among the *N*,*N*′-dicyanoquinone diimines as a new class of acceptor molecules, (1*a*) is now the first example to demonstrate this relationship between molecular geometry and electron-acceptor properties. While the cyanoimine unit of (1*a*) does not exhibit unusual bond lengths and angles in comparison to other DCNQI derivatives (Andreetti, Bradamante, Bizzari & Pagani, 1985), the whole quinoid system of (1*a*) is expected to have a higher electron affinity than ordinary 2,3-substituted DCNQI's, as a result of the distorted substitution geometry at C3. So (1*a*) readily forms crystalline charge-transfer complexes with electron donors like tetrathiafulvalene (TTF), with a powder conductivity of 3×10^{-3} S cm^{-1} (Metzenthin, 1991).

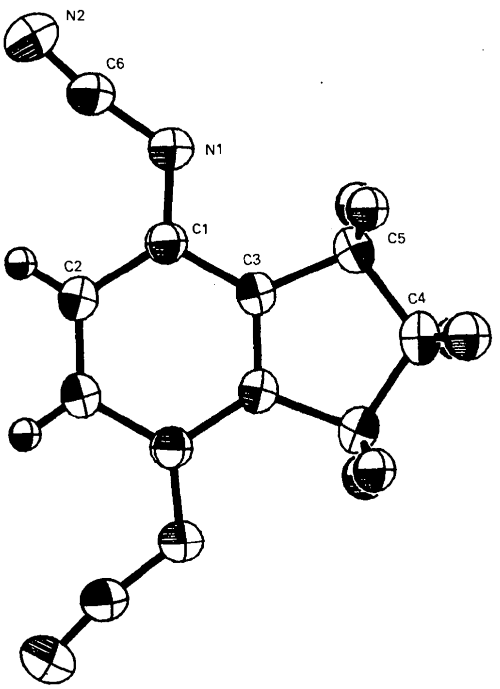

Fig. 2. View of *N*,*N*′-dicyano-4,7-indanquinone diimine with labeling of the non-H atoms. Displacement ellipsoids are shown at 50% probability levels (Johnson, 1976).

Experimental

Crystal data

$C_{11}H_8N_4$
M_r = 196.21
Monoclinic
$P2_1/m$
a = 4.038 (1) Å
b = 12.840 (3) Å
c = 9.355 (2) Å
β = 99.91 (2)°
V = 477.8 Å^3
Z = 2
D_x = 1.36 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.7107 Å
Cell parameters from 25 reflections
θ = 8–21°
μ = 0.08 mm^{-1}
T = 293 K
Column shaped
0.35 × 0.10 × 0.10 mm
Light red-brown
Crystal source: chloroform solution

Data collection

Enraf–Nonius CAD-4 diffractometer
ω-2θ scans [θ-scan width (0.8 + 0.35tanθ)°; rate 1-5° min^{-1} in ω]
Absorption correction: none
1648 measured reflections
1449 independent reflections

1045 observed reflections [$F_o^2 > 2\sigma(F_o^2)$]
$R_{\rm int}$ = 0.039
$\theta_{\rm max}$ = 30°
$h = 0 \rightarrow 5$
$k = 0 \rightarrow 18$
$l = -13 \rightarrow 12$
3 standard reflections
frequency: 120 min
intensity variation: none

Refinement

Refinement on F
R = 0.045
wR = 0.057
S = 2.7

$w = 4F_o^2/\sigma^2(F_o^2)$
$(\Delta/\sigma)_{\rm max}$ = 0.01
$\Delta\rho_{\rm max}$ = 0.34 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.36 e Å^{-3}

1045 reflections
88 parameters
Only coordinates of H atoms refined
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$B_{eq} = (1/3)\Sigma_i\Sigma_j B_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
C1	0.4443 (3)	0.6395 (1)	0.2319 (1)	2.88 (2)
C2	0.6375 (3)	0.8022 (1)	0.3514 (1)	3.16 (2)
C3	0.2590 (3)	0.8025 (1)	0.1111 (1)	2.78 (2)
C4	−0.0579 (5)	3/4	−0.1172 (2)	4.05 (4)
C5	0.0579 (3)	0.8467 (1)	−0.0250 (1)	3.46 (3)
C6	0.6012 (3)	0.4770 (1)	0.3259 (2)	3.73 (3)
N1	0.4286 (3)	0.53800 (9)	0.2224 (1)	3.61 (2)
N2	0.2648 (4)	0.5851 (1)	0.5979 (2)	5.19 (3)

Table 2. *Selected geometric parameters* (Å, °)

C1—N1	1.307 (2)	C3···C5′	2.365 (2)
C1···C1′	2.839 (2)	C3···C1′	2.434 (2)
C1···C5	2.637 (2)	C3···C4	2.390 (2)
C1···C6	2.310 (2)	C3′···C4	2.390 (2)
C2—C2′	1.340 (2)	C3···N1	2.346 (2)
C2—C1	1.456 (2)	C5—C4	1.538 (2)
C2···C1′	2.434 (2)	C5′—C4	1.538 (2)
C2···C3	2.491 (2)	C5···C5′	2.483 (2)
C2···C3′	2.831 (2)	C5···N1	2.932 (2)
C2···C6	2.847 (2)	N1—C6	1.344 (2)
C2···N1	2.455 (2)	N2—C6	1.142 (2)
C3—C3′	1.347 (2)	N2···N1	2.478 (2)
C3—C5	1.499 (2)		
C2—C1—N1	125.3 (1)	C1—C3—C5	126.8 (1)
C2′—C2—C1	121.0 (1)	C3′—C3—C1	121.0 (1)
C3′—C3—C5	112.2 (1)	C5—C4—C5′	107.7 (1)
N2—C6—N1	171.2 (1)	C1—N1—C6	121.3 (1)

Data collection: Enraf–Nonius CAD-4 computer controlled diffractometer. Cell constants and the orientation matrix for data collection were obtained from least-squares refinement, using setting angles measured by a computer controlled diagonal slit method of centering. All calculations were performed on a VAX computer using *SDP*/*VAX* (Frenz, 1978). Refinement was by full-matrix least squares.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71550 (20 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: SE1017]

References

Andreetti, G. D., Bradamante, S., Bizzari, P. C. & Pagani, G. A. (1985). *Mol. Cryst. Liq. Cryst.* **120**, 309–312.

Aumüller, A. & Hünig, S. (1986). *Liebigs Ann. Chem.* pp. 142–146.

Davies, A. G. & Ng, K. M. (1992). *J. Chem. Soc. Perkin Trans.* 2, pp. 1857–1858.

Eckert-Maksic, M., Lesar, A. & Maksic, Z. B. (1992). *J. Chem. Soc. Perkin Trans.* 2, p. 993.

Erk, P., Hünig, S., Klebe, G., Krebs, M. & von Schütz, J. U. (1991). *Chem. Ber.* **124**, 2005–2011, and references therein.

Frenz, B. A. (1978). *The Enraf–Nonius CAD-4 SDP – a Real-Time System for Concurrent X-ray Data Collection and Crystal Structure Solution, Computing in Crystallography*, edited by H. Schenk, R. Olthoff-Hazekamp, H. van Koningsveld & G. C. Bassi, pp. 64–71. Delft Univ. Press.

Hünig, S., Erk, P., Meixner, H., Metzenthin, T., Langohr, U., von Schütz, J. U., Werner, H.-P., Wolf, H. C., Burkert, R., Helber, H. W. & Schaumburg, G. (1991). *Adv. Mater.* **3**, 311–315.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Kato, R., Kobayashi, H. & Kobayashi, A. (1989). *J. Am. Chem. Soc.* **111**, 5224–5232.

Keller, E. (1988). *SCHAKAL*88. *Fortran Program for the Graphical Representation of Molecular and Crystallographic Models.* Univ. of Freiburg, Germany.

Kobayashi, K. & Mazaki, Y. (1988). *Synth. Met.* **27**, B309–B314.

Metzenthin, T. (1991). Dissertation, Univ. of Würzburg, Germany.

Mills, W. H. & Nixon, I. G. (1930). *J. Chem. Soc.* p. 2510.

Schubert, U., Hünig, S. & Aumüller, A. (1985). *Liebigs Ann. Chem.* pp. 1216–1222.

Stanger, A. (1991). *J. Am. Chem. Soc.* **113**, 8277–8280, and references therein.

Streitwieser, A., Ziegler, G. R., Mowery, P. C., Lewis, A. & Lawler, R. G. (1968). *J. Am. Chem. Soc.* **90**, 1357.

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A Cubic Modification of (Triphenylarsine)diiodine

S. Abbas, S. M. Godfrey, C. A. McAuliffe and R. G. Pritchard

Department of Chemistry, University of Manchester Institute of Science and Technology, PO Box 88, Manchester M60 1QD, England

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Abstract

Cubic packing has allowed (triphenylarsine)diiodine, $(C_6H_5)_3AsI_2$, to adopt strict C_3 point symmetry with the three phenyl rings arranged in the form of a propeller around the linear As—I—I chain [I—As—C—C 54 (2)°]. Donation of the arsenic lone pair to iodine [As—I 2.616 (3) Å] considerably weakens the I—I bond [I—I 3.014 (3) Å].

Comment

The cubic form of Ph_3AsI_2 (I) is a further example of the four-coordinate 'spoke' structure established for other crystallographic modifications of this compound (Beagley *et al.*, 1988) and for Ph_3PXX [X = Br (Bricklebank, Godfrey, Mackie, McAuliffe & Pritchard, 1992), I