Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71377 (13 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AB1085]

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Acta Cryst. (1993). C**49**, 1980–1982

Intramolecular Interactions in Dimethyl 2,2′-Bipyridine-3,3′-dicarboxylate

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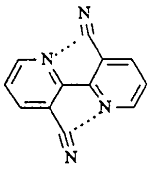
(*Received* 8 *April* 1993; *accepted* 11 *June* 1993)

Abstract

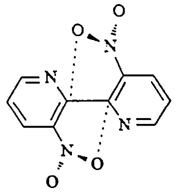
The title compound crystallizes from acetone with the pyridine rings arranged at 53° to each other in a *trans* conformation. There are intramolecular interactions between the alkoxy O atoms of the ester groups and the C2 atoms of the opposite rings, similar to those observed in the 3,3′-dinitro analogue. There are no significant intramolecular interactions between ring N atoms and ester carbonyl C atoms, although similar 1,5 interactions have been observed in other cases.

Comment

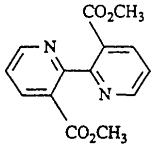
Intramolecular interactions in 3,3′-disubstituted 2,2′-bipyridines control the conformations observed in the solid state. In the dinitrile (1), attractive interactions between each pyridine N atom and the nitrile C atom of the opposite ring lead to the molecule adopting a *trans* conformation with an angle of only 23.6 (1)° between the best planes of the two heterocyclic rings. These short N$\cdots$C contacts have been proposed as a model for an early stage in the addition of a nucleophile to a nitrile group. Indeed, the molecule shows in-plane distortions that widen the angle of approach of the nucleophilic centre to $C\equiv N$ to 108° (Baxter, Connor, Povey & Wallis, 1991). In contrast, in the dinitro analogue (2), intramolecular interactions between the nitro O atoms and the electron-deficient C2 atoms of the opposite rings lead the molecule to deviate much further from a *trans* coplanar conformation. In this case, the inter-ring angle is 42.9 (1)° (Rice, Wallis & Povey, 1992). Although intramolecular interactions between the amino N-atom lone pairs and nitro groups have been observed in *peri*-substituted naphthalenes (Egli, Wallis & Dunitz, 1986), in (2) each pyridine N atom is only just in van der Waals contact with the nitro N atom attached to the opposite ring and, more significantly, the axes of the N-atom lone pairs are very poorly aligned for interaction with the nitro groups.



(1)



(2)



(3)

We have determined the X-ray crystal structure of the 3,3′-dicarboxylic ester (3) to investigate whether replacement of the nitro groups of (2) with more electrophilic ester groups induces a return to the type of interaction seen in (1). There are many examples of attractive interactions between electron-rich N atoms and carbonyl groups (Bürgi, Dunitz & Shefter, 1973; Schweizer, Procter, Kaftory & Dunitz, 1978).

The molecular conformation of (3) is illustrated in Figs. 1 and 2. Only half of the molecule is crystallographically unique; the two substituted pyridine rings are related by a twofold axis parallel to the *b* axis of the unit cell. The molecular conformation resembles that of the dinitro analogue (2) rather than the dinitrile (1). Thus, there are intramolecular interactions between the two halves of the molecule *via* ester O atoms and the ring C2 atoms, while the pyridine N atoms and carbonyl C atoms are only just in van der Waals contact.

The best planes through the two pyridine rings lie at 53.2 (1)° from the *trans* coplanar conformation. The rings are very slightly folded about the C3$\cdots$C6 vector, but the maximum deviation of a ring atom from the best plane is very small [C6 = 0.009 (2) Å]. The ester groups lie at 39.7 (1)° to their respective pyridine rings, so that the alkoxy O atom of each

Acta Crystallographica Section C
ISSN 0108-2701 ©1993

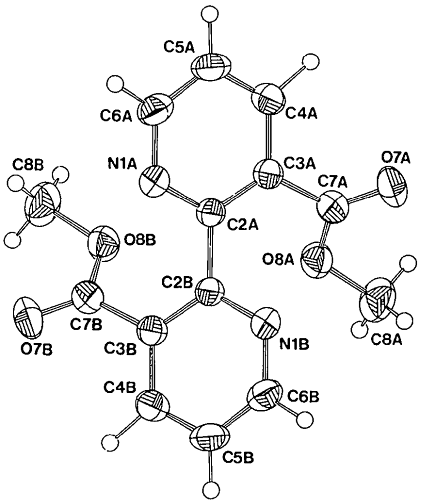


Fig. 1. Molecular structure of (3) with atomic displacement parameters drawn at the 50% probability level (Spek, 1991); only half of the molecule is crystallographically unique.

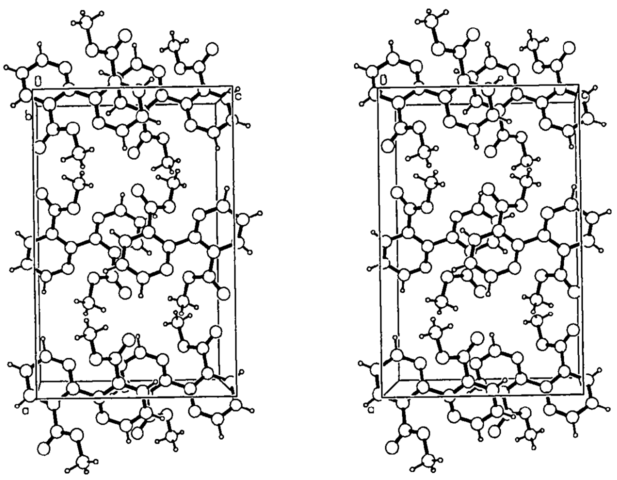


Fig. 2. Stereoview of the crystal packing of (3) (Spek, 1991).

ester group lies close to the C2 atom of the opposite ring [O8*A*···C2*B* = 2.849 (3) Å]. The O8*A*···C2*B*—C3*B* angle is 116.1 (2)° and the torsion angles about the O8···C2 vector are C7*A*—O8*A*···C2*B*—C3*B* = 157 (1)° and C8*A*—O8*A*···C2*B*—C3*B* = −84 (1)°. If the non-bonding valence electrons on the alkoxy ester group are described as two sp^3 lone pairs, one lone pair would then lie at 28° to the O8*A*···C2*B* vector. Alternatively. if they are described as sp^2 and *p* lone pairs, the axis of the former would then make an angle of 56° with the O8*A*···C2*B* vector. As in the case of the nitro analogue, the geometry of this interaction is similar to that for an incipient Michael addition to the C2—C3 bond. Indeed, the C2*A* atom deviates from the plane defined by its three bonded neighbours towards O8*B* by 0.035 (2) Å. This results in the molecule having a slight *cis* bend about the inter-ring bond. Although ester groups often make interactions with electrophilic centres (*e.g.* hydrogen bonds) *via* the carbonyl O atoms, interactions involving the alkoxy O atoms should not be overlooked.

Each pyridine N atom lies 3.001 (3) Å from the opposite carbonyl C atom, only just within van der Waals contact (3.2 Å). Furthermore, the axis of each N-atom lone pair is not directed towards the opposite carbonyl C atom, but makes an angle of 57.2 (1)° with the corresponding N1*A*···C7*B* vector [*cf.* 51-52° for (2)]. There are no short intermolecular interactions.

Experimental

Crystal data

$C_{14}H_{12}N_2O_4$
M_r = 272.28
Orthorhombic
Pbcn
a = 15.885 (4) Å
b = 7.804 (1) Å
c = 10.504 (1) Å
V = 1302.1 (4) Å^3
Z = 4
D_x = 1.39 Mg m^{-3}
M.p. = 423 K

Mo $K\alpha$ radiation
λ = 0.7106900 Å
Cell parameters from 500 reflections
θ = 4-25°
μ = 0.097 mm^{-1}
T = 291 K
Flawless blocks
0.35 × 0.30 × 0.27 mm
Colourless

Data collection

Enraf-Nonius FAST TV area detector diffractometer
Collection method: *SADONL* and *MADNES* (see below)
Absorption correction: none
5430 measured reflections
1057 independent reflections

5669 observed reflections [$I > 3\sigma(I)$]
$R_{\rm int}$ = 0.07
$\theta_{\rm max}$ = 25.2°
$h = 0 \rightarrow 17$
$k = 0 \rightarrow 9$
$l = 0 \rightarrow 12$

Refinement

Refinement on F
Final R = 0.033
wR = 0.035
S = 0.62
669 reflections
115 parameters
All H-atom parameters refined
$w = [\sigma^2F + 0.0001(F^2)]^{-1}$

$(\Delta/\sigma)_{\rm max}$ = 0.026
$\Delta\rho_{\rm max}$ = 0.14 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.14 e Å^{-3}
Extinction correction: none
Atomic scattering factors from Cromer & Mann (1968) (O, N, C) and Stewart, Davidson & Simpson (1968) (H)

Data collection: *SADONL* (Danopoulos, Wilkinson, Hussain-Bates & Hursthouse, 1991); *MADNES* (Pflugrath & Messerschmidt, 1989). Standard reflections are not relevant to this mode of data collection. Data reduction and cell refinement: *SADONL*. The structure was solved by direct methods using *SHELXS86* (Sheldrick, 1986) and refined with *SHELX76* (Sheldrick, 1976), including H atoms located from a difference Fourier map. Molecular graphics: *PLATON* (Spek, 1990); *PLUTON* (Spek, 1991). Software used to prepare material for publication: *PARST* (Nardelli, 1982).

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

$$U_{eq} = \frac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
O7*A*	0.1774 (1)	0.1790 (2)	0.0307 (2)	0.0686 (7)
O8*A*	0.12290 (9)	0.0437 (2)	0.1996 (2)	0.0479 (6)
N1*A*	−0.0903 (1)	0.3627 (2)	0.1649 (2)	0.0443 (7)
C2*A*	−0.0150 (1)	0.2886 (2)	0.1827 (2)	0.0353 (7)
C3*A*	0.0343 (1)	0.2285 (2)	0.0831 (2)	0.0371 (7)
C4*A*	0.0043 (2)	0.2488 (3)	−0.0403 (2)	0.0477 (9)
C5*A*	−0.0724 (2)	0.3250 (3)	−0.0597 (3)	0.0516 (9)
C6*A*	−0.1177 (2)	0.3778 (3)	0.0443 (3)	0.0501 (9)
C7*A*	0.1190 (1)	0.1498 (3)	0.1004 (2)	0.0441 (9)
C8*A*	0.2057 (2)	−0.0233 (4)	0.2282 (4)	0.0657 (13)

Table 2. *Geometric parameters* (Å, °)

O7*A*—C7*A*	1.204 (2)	C2*A*—C2*B*	1.493 (2)
O8*A*—C7*A*	1.332 (2)	C3*A*—C4*A*	1.390 (3)
O8*A*—C8*A*	1.447 (3)	C3*A*—C7*A*	1.490 (2)
N1*A*—C2*A*	1.342 (2)	C4*A*—C5*A*	1.371 (3)
N1*A*—C6*A*	1.345 (3)	C5*A*—C6*A*	1.372 (3)
C2*A*—C3*A*	1.388 (2)		
O8*A*···C2*B*	2.849 (3)	N1*A*···C7*B*	3.001 (3)
O8*A*···N1*B*	2.913 (3)		
C7*A*—O8*A*—C8*A*	115.4 (2)	C4*A*—C3*A*—C7*A*	118.1 (2)
C2*A*—N1*A*—C6*A*	117.2 (2)	C3*A*—C4*A*—C5*A*	119.5 (2)
N1*A*—C2*A*—C3*A*	122.9 (2)	C4*A*—C5*A*—C6*A*	118.6 (2)
N1*A*—C2*A*—C2*B*	114.6 (2)	N1*A*—C6*A*—C5*A*	123.7 (2)
C3*A*—C2*A*—C2*B*	112.3 (2)	O8*A*—C7*A*—C3*A*	113.2 (2)
C2*A*—C3*A*—C7*A*	123.8 (2)	O7*A*—C7*A*—C3*A*	122.9 (2)
C2*A*—C3*A*—C4*A*	118.1 (2)	O7*A*—C7*A*—O8*A*	123.9 (2)

The diester (3) was obtained by oxidation of 1,10-phenanthroline to 2,2′-bipyridine-3,3′-dicarboxylic acid (Baxter, Connor, Povey, Powell & Wallis, 1992), esterification with methyl orthochloroformate/*N*-methylmorpholine (Rebek, Trend, Wattley & Chakravorti, 1979) and crystallization from acetone.

We thank Professor M. B. Hursthouse and the SERC X-ray Crystallography Service, University of Wales, Cardiff, for collecting the diffraction data, Professor J. A. Ballantine and the SERC Mass Spectrometry Service for some data and the University of Kent for a studentship (to CRR) and further financial help.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71395 (7 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AL1057]

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Acta Cryst. (1993). C**49**, 1982–1985

Structure of Pentaerythritol Tetrabenzoate

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(*Received* 30 *June* 1992; *accepted* 8 *April* 1993)

Abstract

Distances and angles about the central C atom are in agreement with literature values for pentaerythritol and its ester derivatives; three C—'central C'—C angles are < 109° while two are > 109°. The O···O distances are incompatible with metal complexation; this is consistent with unsuccessful attempts to form complexes with various metal cations.

Comment

This project was undertaken to explore the usefulness of the title compound (PETB) as a metal ligand. Atomic coordinates and isotropic thermal parameters are given in Table 1, bond lengths and angles in Table 2. The molecular structure with atom labelling is shown in Fig. 1.