
Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: NA1276). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1997). **C53**, 496–498

13-Phenyl-11,13,15-triazatricyclo-[8.5.2.0^{11,15}]heptadec-16-ene-12,14-dione

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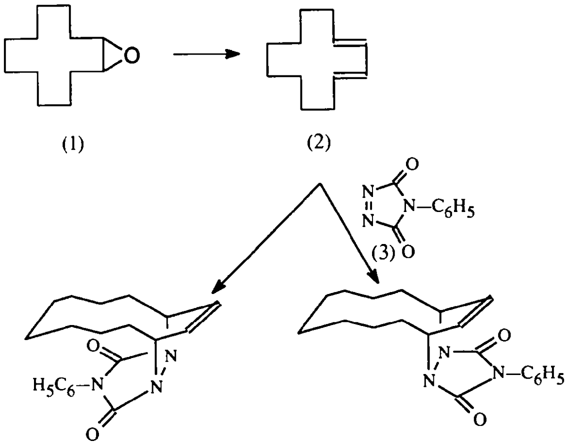
Abstract

The title compound, $C_{20}H_{25}N_3O_2$, has been assigned an *endo* structure on the basis of its X-ray analysis. In the *N*-phenyl-1,2,4-triazoline-3,5-dione moiety, the N—N and average C—O bond distances have values of 1.424 (3) and 1.208 (2) Å, respectively. The closest intermolecular contact of 3.306 (4) Å is between a phenyl C atom and an O atom of the 1,2,4-triazoline-3,5-dione moiety.

Comment

The Diels–Alder reaction of 1,3-cyclooctadiene with *N*-phenyl-1,2,4-triazoline-3,5-dione (PTAD) results in a cyclo-adduct with an almost planar hydrazine moiety (Brock, Demir & Watt, 1995). The molecule is one of the most planar of the 1,3-diene adducts of PTAD found in version 5.07 of the Cambridge Structural Database (Allen, Kennard & Taylor, 1983). The dihedral angle between the triazoline ring and the bridging moiety increases with increasing length of the bridge (Agmon, Kaftory, Nelson & Blakstock, 1986). By a conversion reaction of epoxide to 1,3-diene, we obtained a 1,3-cyclododecadiene. The Diels–Alder adduct with *N*-phenyl-1,2,4-triazoline-3,5-dione was identified as the title compound, but it was impossible to identify the structure as *endo* or *exo* on the basis of ^{1}H and ^{13}C NMR spectral data. The present X-ray crystal structure determination resolved this ambiguity and showed it to be the *endo* product, *i.e.* *endo*-(4).



(1) (2)

exo-(4) *endo*-(4)

In the cyclododecene part of the molecule, there is only one C=C double bond, namely, C10=C11; all the other C—C bond lengths have values in the single-bond range, with C9—C10 and C11—C12 being C_{sp^2}—C_{sp^3} bonds, while the rest are C_{sp^3}—C_{sp^3} (Table 1). The C12—N2 and C9—N3 bonds are C_{sp^3}—N_{sp^3}, and are longer than the other C—N bonds. The dihedral angle between the phenyl and triazoline-3,5-dione rings is 57.8 (1)°. The ring N3—C9—C10—C11—C12—N2 is in a boat conformation, with the C9 and C12 atoms −0.378 (3) and −0.607 (3) Å, respectively, from the least-squares plane through atoms N2, N3, C10 and C11.

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The dihedral angle between the ring N1—C7—N2—N3—C8 and the plane through N2, C12, C9 and N3 is 29.5 (2)°, which fits the trend described by Agmon *et al.* (1986). The closest intermolecular contact is 3.306 (4) Å, between the C3($-x$, $1-y$, $-z$) atom of the phenyl ring and the O2 atom of the 1,2,4-triazoline-3,5-dione moiety.

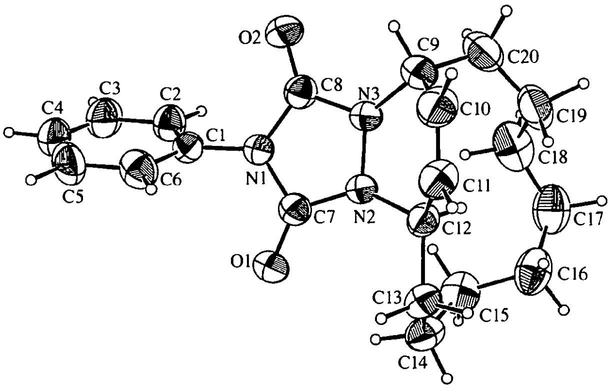

Fig. 1. The molecular structure of *endo*-(4) (*ORTEP*II; Johnson, 1976) with the atomic numbering scheme. The displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small circles of arbitrary radii.

Experimental

Cyclododecadiene (656 mg, 4 mmol, 1.4 equivalents) was dissolved in 30 ml of CH_2Cl_2 and triazoline dione (612.5 mg, 3.5 mmol) was added to this solution. The mixture was stirred at room temperature for 18 h (the red colour of the reaction mixture disappeared). The solvent was evaporated and the crude product was purified by column chromatography (silica gel 60, EtOAc/hexane, 2:1) resulting in a colourless solid (830 mg, 70%) which was recrystallized from EtOAc/hexane (2:1) (m.p. 435–436 K). IR (KBr): 2900–2870, 1760, 1704, 1597, 1503, 1428, 1407 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 1.16–2.31 (*m*, 15H, CH_2), 2.78–2.96 (*m*, 1H, CH_2), 4.38–4.50 (*m*, 1H, NCH), 5.0–5.11 (*m*, 1H, NCH), 6.05–6.38 (*m*, 2H, olefinic H), 7.25–7.56 (*m*, 5, Ar–H). Analysis calculated for $C_{20}H_{25}N_3O_2$: C 70.76, H 7.43, N 12.38%; found: C 70.85, H 7.38, N 12.46%.

Crystal data

$C_{20}H_{25}N_3O_2$
$M_r = 339.441$
Orthorhombic
Pbca
$a = 23.986\,(3)$ Å
$b = 14.076\,(2)$ Å
$c = 10.493\,(2)$ Å
$V = 3543.0\,(7)$ Å^3
$Z = 8$
$D_x = 1.2726$ Mg m^{-3}
D_m not measured

Mo *Kα* radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 10.20$–$18.11°$
$\mu = 0.078$ mm^{-1}
$T = 295$ K
Prism
0.50 × 0.40 × 0.35 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical *via* ψ scans (*MolEN*; Fair, 1990)
$T_{\min} = 0.961$, $T_{\max} = 0.973$
3784 measured reflections
3700 independent reflections

2063 reflections with $I > \sigma(I)$
$R_{\rm int} = 0.012$
$\theta_{\max} = 25.7°$
$h = -29 \rightarrow 0$
$k = 0 \rightarrow 17$
$l = 0 \rightarrow 12$
3 standard reflections
frequency: 120 min
intensity decay: −1.02%

Refinement

Refinement on *F*
$R = 0.052$
$wR = 0.056$
$S = 0.86$
2063 reflections
226 parameters
H atoms: see text
$w = 1/[\sigma^2(F) + (0.02F)^2 + 0.7]$

$(\Delta/\sigma)_{\max} = 0.00018$
$\Delta\rho_{\max} = 0.234$ e Å^{-3}
$\Delta\rho_{\min} = -0.118$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Selected geometric parameters (Å, °)*

O1—C7	1.206 (3)	C9—C20	1.537 (5)
O2—C8	1.211 (3)	C10—C11	1.312 (4)
N1—C1	1.430 (4)	C11—C12	1.497 (4)
N1—C7	1.405 (3)	C12—C13	1.518 (4)
N1—C8	1.387 (4)	C13—C14	1.526 (4)
N2—N3	1.424 (3)	C14—C15	1.516 (5)
N2—C7	1.357 (4)	C15—C16	1.515 (5)
N2—C12	1.470 (4)	C16—C17	1.522 (5)
N3—C8	1.377 (4)	C17—C18	1.532 (5)
N3—C9	1.495 (4)	C18—C19	1.536 (5)
C9—C10	1.497 (5)	C19—C20	1.527 (5)
C1—N1—C7	124.8 (2)	C9—C10—C11	121.3 (3)
C1—N1—C8	123.9 (2)	C10—C11—C12	117.2 (3)
C7—N1—C8	111.0 (2)	N2—C12—C11	108.1 (2)
N3—N2—C7	109.9 (2)	N2—C12—C13	114.9 (2)
N3—N2—C12	114.1 (2)	C11—C12—C13	116.9 (3)
C7—N2—C12	130.6 (2)	C12—C13—C14	115.0 (3)
N2—N3—C8	107.5 (2)	C13—C14—C15	116.1 (3)
N2—N3—C9	118.9 (2)	C14—C15—C16	117.2 (3)
N1—C7—N2	104.9 (2)	C15—C16—C17	113.8 (3)
N1—C8—N3	105.9 (2)	C16—C17—C18	116.7 (3)
N3—C9—C10	109.5 (3)	C17—C18—C19	115.1 (3)
N3—C9—C20	114.4 (3)	C18—C19—C20	115.1 (3)
C10—C9—C20	115.4 (3)	C9—C20—C19	119.6 (3)

H atoms were placed geometrically 0.95 Å from their parent C atoms. The H atoms of cyclododecadiene were refined for a few cycles and then a riding model was used for all H atoms, with $U_{\rm eq}({\rm H}) = 1.3U_{\rm eq}({\rm C})$.

Data collection: *CAD*-4 *Express* (Enraf–Nonius, 1993). Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SIR* in *MolEN*. Program(s) used to refine structure: *LSFM* in *MolEN*. Molecular graphics: *PLATON*92 (Spek, 1992) version of *ORTEP* (Johnson, 1976). Software used to prepare material for publication: *MolEN*.

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Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: AB1419). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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4,4′-Dimethyl-2,2′-bipyridine 1,1′-Dioxide

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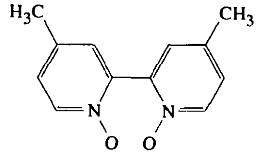
Abstract

There are four molecules in a unit cell of the title compound, $C_{12}H_{12}N_2O_2$, and the structure of only half a molecule has been determined because of its twofold rotational symmetry. The dihedral angle between the two pyridine rings is 61.3° and the non-bonded distance between O atoms in the *N*-oxide groups is 2.96 Å. The skew conformation of the skeleton is almost the same as that of the tetrakis(2,2′-bipyridine 1,1′-dioxide)-lanthanum(III) complex.

Comment

The bidentate ligand 2,2′-bipyridine 1,1′-dioxide (bpdo) forms a skewed seven-membered ring with a metal ion. Since the skew conformation produces a pair of enantiomers, a tris(bpdo) complex has four possible racemic pairs of conformational isomers. The tris-(bpdo)–Cr^{III} complex, however, crystallizes in one of the four isomers and then isomerizes and racemizes on dissolution in water (Kanno & Fujita, 1987). This indicates that the skewed bpdo-chelate ring is flexible and changes its conformation rather easily in solution. The dihedral angle between the pyridine rings, which seems to represent a distortion of the seven-membered ring, is 61.4° in the La^{III} complex (Al-Karaghouli, Day & Wood, 1978) and 53.7° in the U^{IV} complex (Alcock & Roberts, 1987). The present study was undertaken in order to estimate the dihedral angle between the pyridine rings of the bpdo molecule with methyl groups at the 4,4′-positions, (I).



(I)

The title molecule has a twofold rotational axis and the parameters of half of the molecule have been determined (Fig. 1). The pyridine ring is planar within 0.03 Å, but the O atom of the *N*-oxide group is slightly out of the plane (0.13 Å), away from the other O atom

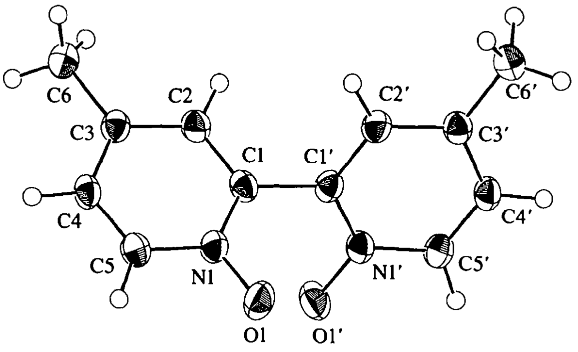


Fig. 1. *ORTEP* drawing (Johnson, 1965) of the whole title molecule, half of which is an asymmetric unit, showing the atomic numbering scheme. Displacement ellipsoids of the non-H atoms are shown at the 50% probability level. H atoms are shown as spheres of arbitrary radii.

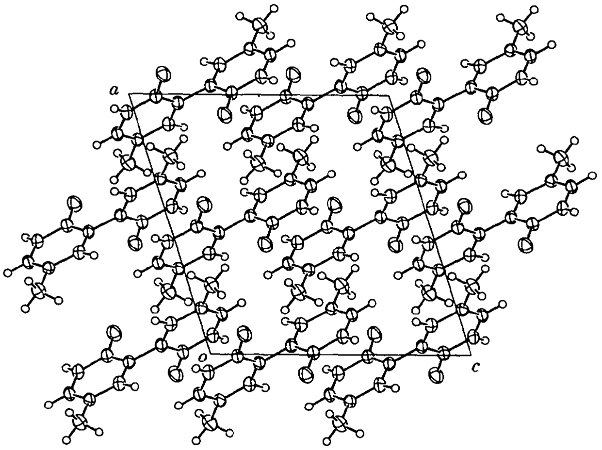


Fig. 2. The crystal structure of (I) viewed along the *b* axis.