

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)
$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	U _{eq}
Cl(1)	1.2593 (1)	1/4	-0.53474 (4)	0.0693 (2)
N(1)	0.7727 (5)	0.1887 (5)	-0.4616 (2)	0.063 (1)
C(1)	0.8101 (5)	0.262 (1)	-0.3835 (2)	0.0609 (9)
C(2)	0.6135 (6)	0.2025 (6)	-0.3349 (2)	0.055 (1)
C(3)	0.6485 (5)	0.268 (1)	-0.2544 (2)	0.060 (1)
C(4)	0.4546 (6)	0.2097 (8)	-0.2042 (2)	0.059 (1)
C(5)	0.4815 (6)	0.276 (1)	-0.1237 (2)	0.059 (1)
C(6)	0.2874 (6)	0.2106 (7)	-0.0750 (2)	0.054 (1)
C(7)	0.3089 (6)	0.277 (1)	0.0066 (2)	0.058 (1)
C(8)	0.1148 (6)	0.2108 (7)	0.0546 (2)	0.057 (1)
C(9)	0.1345 (5)	0.2761 (9)	0.1359 (2)	0.057 (1)
C(10)	-0.0594 (6)	0.2076 (7)	0.1840 (2)	0.056 (1)
C(11)	-0.0446 (6)	0.274 (1)	0.2646 (2)	0.068 (1)
C(12)	-0.2387 (8)	0.210 (1)	0.3119 (2)	0.082 (2)

Table 2. Selected geometric parameters (Å, °)

N(1)—C(1)	1.492 (5)	C(6)—C(7)	1.526 (5)
C(1)—C(2)	1.507 (5)	C(7)—C(8)	1.505 (5)
C(2)—C(3)	1.510 (5)	C(8)—C(9)	1.517 (5)
C(3)—C(4)	1.509 (5)	C(9)—C(10)	1.510 (5)
C(4)—C(5)	1.510 (5)	C(10)—C(11)	1.508 (5)
C(5)—C(6)	1.510 (5)	C(11)—C(12)	1.491 (6)
N(1)—C(1)—C(2)	110.9 (4)	C(6)—C(7)—C(8)	114.3 (3)
C(1)—C(2)—C(3)	112.7 (3)	C(7)—C(8)—C(9)	114.8 (3)
C(2)—C(3)—C(4)	113.9 (4)	C(8)—C(9)—C(10)	114.6 (3)
C(3)—C(4)—C(5)	115.4 (3)	C(9)—C(10)—C(11)	115.3 (3)
C(4)—C(5)—C(6)	113.8 (4)	C(10)—C(11)—C(12)	115.3 (4)
C(5)—C(6)—C(7)	114.8 (3)		
N(1)—C(1)—C(2)—C(3)	178.0 (5)		
C(1)—C(2)—C(3)—C(4)	-179.8 (5)		
C(2)—C(3)—C(4)—C(5)	-178.9 (5)		
C(3)—C(4)—C(5)—C(6)	-178.6 (5)		
C(4)—C(5)—C(6)—C(7)	-179.4 (5)		
C(5)—C(6)—C(7)—C(8)	-179.8 (5)		
C(6)—C(7)—C(8)—C(9)	179.9 (5)		
C(7)—C(8)—C(9)—C(10)	-179.5 (5)		
C(8)—C(9)—C(10)—C(11)	-179.0 (5)		
C(9)—C(10)—C(11)—C(12)	178.8 (5)		

The scan width was $(1.37 + 0.35 \tan \theta)^\circ$ with an ω -scan rate of $16.0^\circ \text{ min}^{-1}$. The weak reflections [$I < 25.0\sigma(I)$] were rescanned (maximum of four rescans) and the counts were accumulated to ensure good counting statistics. Stationary background counts were recorded on each side of the reflection. The ratio of peak counting time to background counting time was 2:1.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1993). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BK1118). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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An Almost Planar Hydrazine Moiety in a Diels–Alder Adduct

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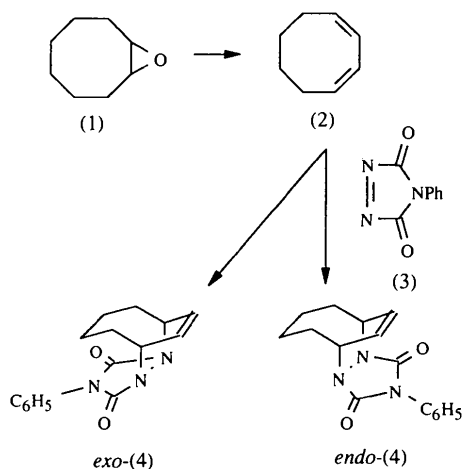
Abstract

The structure of the product of the reaction of 1,3-cyclooctadiene and *N*-phenyl-1,2,4-triazoline-3,5-dione has been identified as 4-phenyl-2,4,6-triazatricyclo-[5.4.2.0^{2,6}]tridec-12-ene-3,5-dione (C₁₆H₁₇N₃O₂). The distinction between *endo* and *exo* addition cannot be made because the hydrazine moiety in the product molecule is almost planar.

Comment

In the course of developing a new reaction for the direct conversion of epoxides to dienes, we investigated the thermal reaction of 1,2-epoxycyclooctane, (1), with

hexamethylphosphoramide. The expected product was (1Z,3Z)-1,3-cyclooctadiene, (2). Unfortunately, the isolated yield in the conversion of (1) to (2) was low as a consequence of the volatility of (2). To solve this problem, the crude product containing (2) was subjected to a Diels–Alder reaction with *N*-phenyl-1,2,4-triazoline-3,5-dione, (3) (hereafter PTAD) in order to produce the non-volatile adduct (4). As expected, a single Diels–Alder adduct was isolated, which was assigned the structure *endo*-(4) on the basis of spectral data and the pathway expected for cycloadditions. The chemical shift of the vinylic protons in the ^1H NMR spectrum of the adduct appeared, however, at higher field than anticipated for fully pyramidal N atoms. These shifts raised the possibility that the adduct was *exo*-(4) rather than *endo*-(4). A structure determination was undertaken to resolve the ambiguity.



The three bonds around N1 (see Fig. 1) are approximately coplanar, as are the three bonds around N3. The dihedral angle between the rings C1,N1,N3,C4 and N1,C2,N2,C3,N3 is $15.0(2)^\circ$. The angle α_{av} defined by Kaftory & Agmon (1984) is 119.6° . 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). There are only three other adducts having dihedral angles less than 25° and *R* factors less than 0.10 (see Adam, Klug, Peters, Peters & von Schnering, 1985; Krow, Lee, Szczepanski, Zacharias & Bailey, 1987).

The α_{av} value fits the trend described by Agmon, Kaftory, Nelsen & Blackstock (1986), who observed that α_{av} for PTAD-diene adducts increases with the length of the bridges. The molecule 4-phenyl-2,4,6-triazatetracyclo[6.3.2.0^{2,6}.0^{7,9}]trideca-10,12-diene-3,5-dione (Krow *et al.*, 1987) also has an α_{av} value very close to 120° .

The anisotropic displacement ellipsoids for atoms N1 and N3 are clearly elongated in the direction

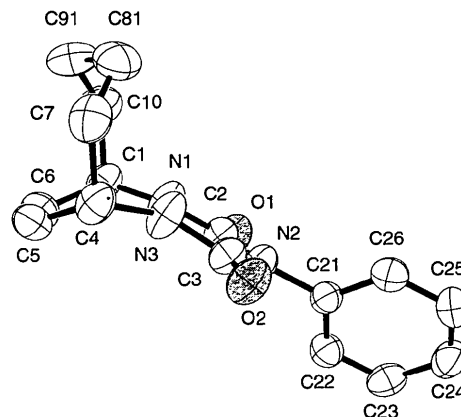


Fig. 1. Perspective drawing of the molecule showing the atom-numbering scheme. The shapes of the ellipsoids correspond to 50% probability contours of atomic displacement. The H atoms and the two C atoms of the minor conformer have been omitted for clarity.

perpendicular to the bonding plane and are larger than for other atoms at similar distances from the center of mass. Some closely related molecules (Agmon *et al.*, 1986) show the same feature, which can be interpreted in terms of the proximity of the structure to the transition state for double nitrogen inversion. It is also possible that both N atoms are slightly pyramidal. The smaller ellipsoids for adjacent C atoms would then imply that the displacements of the two N atoms relative to the mean plane are out of phase. These displacements might be correlated with the displacements of the disordered atoms C8 and C9 (see Fig. 2 and the *Experimental*).

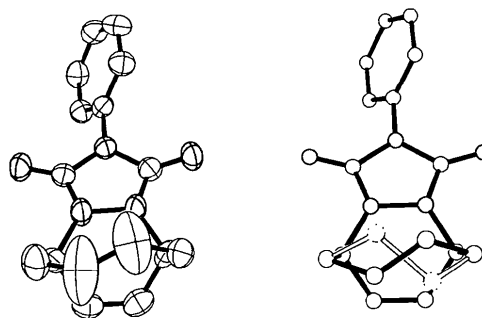


Fig. 2. Drawing showing (left) the atomic ellipsoids before inclusion of the disorder model (right).

Examination of packing diagrams (see Fig. 3) reveals two reasonably short (Desiraju, 1991) C—H...O=C interactions [O1...C5($x - \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} + z$) 3.316(3); O1...C23($-x, -y, -z$) 3.361(3) Å].

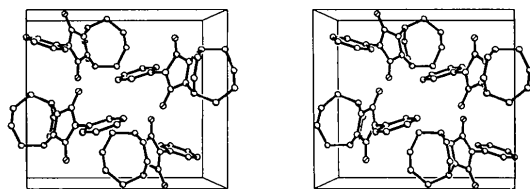


Fig. 3. Stereoscopic drawing of the unit cell. The *b* axis points from right to left, the *c* axis points downwards and the *a* axis points out of the plane of the paper.

Experimental

Crystals were grown by slow evaporation of ethyl acetate solutions.

Crystal data

C₁₆H₁₇N₃O₂
M_r = 283.33
 Monoclinic
*P*2₁/*n*
a = 10.3828 (7) Å
b = 12.2813 (7) Å
c = 10.9310 (9) Å
 β = 91.207 (6)°
V = 1393.54 (17) Å³
Z = 4
D_x = 1.350 Mg m⁻³

Mo *K*α radiation
 λ = 0.7107 Å
 Cell parameters from 19 reflections
 θ = 12.3–12.9°
 μ = 0.085 mm⁻¹
T = 295 (1) K
 Tablet (major faces are {10 $\bar{1}$ }, {11 $\bar{1}$ }, {010}, {111}, {101})
 Colorless

Data collection

Enraf–Nonius CAD-4-VAX diffractometer
 $\omega/2\theta$ scans
 Absorption correction: eight ψ scans (Flack, 1977)
 T_{\min} = 0.81, T_{\max} = 0.90
 2449 measured reflections
 2449 independent reflections

1412 observed reflections
 $[I > 2\sigma(I)]$
 θ_{\max} = 25.0°
 $h = 0 \rightarrow 13$
 $k = 0 \rightarrow 15$
 $l = -14 \rightarrow 14$
 3 standard reflections
 frequency: 60 min
 intensity decay: 0.6%

Refinement

Refinement on *F*²
 $R[F^2 > 2\sigma(F^2)] = 0.0415$
 $wR(F^2) = 0.0950$
 $S = 1.113$
 2448 reflections
 199 parameters
 H atoms riding
 $w = 1/[\sigma^2(F_o^2) + (0.0589P)^2 + 0.1185P]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = -0.012$
 $\Delta\rho_{\max} = 0.141 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.216 \text{ e \AA}^{-3}$
 Extinction correction: none
 Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} / <i>U</i> _{iso}
O1	0.0504 (2)	0.22120 (14)	0.04501 (14)	0.0597 (5)
O2	-0.0115 (2)	0.29088 (14)	-0.36598 (14)	0.0563 (5)
N1	0.1511 (2)	0.3316 (2)	-0.0931 (2)	0.0570 (6)

N2	-0.0164 (2)	0.24111 (15)	-0.1592 (2)	0.0424 (5)
N3	0.1324 (2)	0.3524 (2)	-0.2186 (2)	0.0560 (6)
C1	0.2716 (2)	0.3601 (2)	-0.0305 (2)	0.0492 (6)
C2	0.0621 (2)	0.2597 (2)	-0.0564 (2)	0.0451 (6)
C3	0.0308 (2)	0.2945 (2)	-0.2617 (2)	0.0446 (6)
C4	0.2355 (2)	0.4032 (2)	-0.2868 (2)	0.0515 (6)
C5	0.3625 (2)	0.3678 (2)	-0.2347 (2)	0.0576 (7)
C6	0.3792 (2)	0.3479 (2)	-0.1170 (3)	0.0587 (7)
C7	0.2194 (3)	0.5269 (2)	-0.2880 (2)	0.0595 (7)
C81	0.1849 (5)	0.5796 (3)	-0.1646 (4)	0.0677 (14)
C91	0.2837 (5)	0.5693 (3)	-0.0616 (4)	0.071 (2)
C82†	0.2675 (13)	0.5861 (9)	-0.1774 (8)	0.060 (4)
C92†	0.1929 (12)	0.5558 (10)	-0.0618 (10)	0.073 (4)
C10	0.2667 (3)	0.4736 (2)	0.0248 (2)	0.0649 (8)
C21	-0.1277 (2)	0.1726 (2)	-0.1589 (2)	0.0398 (5)
C22	-0.1164 (2)	0.0664 (2)	-0.1211 (2)	0.0466 (6)
C23	-0.2244 (2)	0.0017 (2)	-0.1162 (2)	0.0534 (6)
C24	-0.3424 (2)	0.0430 (2)	-0.1485 (2)	0.0581 (7)
C25	-0.3528 (2)	0.1486 (2)	-0.1891 (2)	0.0605 (7)
C26	-0.2458 (2)	0.2140 (2)	-0.1936 (2)	0.0513 (6)

† Occupancy factor 0.254 (7) (see below).

Table 2. Selected geometric parameters (Å, °)

O1—C2	1.214 (3)	C5—C6	1.317 (3)
O2—C3	1.214 (3)	C7—C82	1.488 (9)
N1—C2	1.344 (3)	C7—C81	1.544 (5)
N1—N3	1.406 (2)	C81—C91	1.513 (6)
N1—C1	1.456 (3)	C91—C10	1.521 (5)
N2—C2	1.393 (3)	C82—C92	1.542 (12)
N2—C3	1.396 (3)	C92—C10	1.572 (9)
N2—C21	1.429 (3)	C21—C22	1.373 (3)
N3—C3	1.348 (3)	C21—C26	1.373 (3)
N3—C4	1.457 (3)	C22—C23	1.376 (3)
C1—C6	1.487 (3)	C23—C24	1.366 (3)
C1—C10	1.520 (3)	C24—C25	1.374 (4)
C4—C5	1.491 (3)	C25—C26	1.374 (3)
C4—C7	1.529 (3)		
C2—N1—N3	109.2 (2)	C5—C4—C7	112.8 (2)
C2—N1—C1	127.4 (2)	C6—C5—C4	121.7 (2)
N3—N1—C1	121.0 (2)	C5—C6—C1	121.1 (2)
C2—N2—C3	111.1 (2)	C82—C7—C4	116.4 (5)
C2—N2—C21	123.7 (2)	C4—C7—C81	115.9 (2)
C3—N2—C21	125.1 (2)	C91—C81—C7	116.7 (4)
C3—N3—N1	109.6 (2)	C81—C91—C10	116.2 (4)
C3—N3—C4	128.7 (2)	C7—C82—C92	112.5 (10)
N1—N3—C4	119.3 (2)	C82—C92—C10	113.7 (9)
N1—C1—C6	109.1 (2)	C1—C10—C91	117.1 (2)
N1—C1—C10	111.8 (2)	C1—C10—C92	111.7 (6)
C6—C1—C10	112.2 (2)	C22—C21—C26	120.3 (2)
O1—C2—N1	127.6 (2)	C22—C21—N2	119.8 (2)
O1—C2—N2	127.2 (2)	C26—C21—N2	119.9 (2)
N1—C2—N2	105.2 (2)	C21—C22—C23	119.8 (2)
O2—C3—N3	127.7 (2)	C24—C23—C22	120.1 (2)
O2—C3—N2	127.6 (2)	C23—C24—C25	119.9 (2)
N3—C3—N2	104.7 (2)	C24—C25—C26	120.3 (2)
N3—C4—C5	109.5 (2)	C21—C26—C25	119.5 (2)
N3—C4—C7	110.4 (2)		

Disorder in the four-atom bridge (C7—C10) was apparent from observation of elongated ellipsoids for atoms C81 and C91 (see Fig. 2) and a short C81—C91 distance. The disorder was modeled with isotropic atoms C82 and C92, which have occupancy factors of 0.254 (7). The bond length C82—C92 was restrained to a target value of 1.531 (12) Å and the lengths C82—C7 and C92—C10 to a value of 1.524 (14) Å (Allen *et al.*, 1987).

Data collection: CAD-4 diffractometer software (Enraf–Nonius, 1988). Cell refinement: CAD-4 diffractometer software. Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CR1189). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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9 α -Fluoro-16 α -methyl-3,17-dioxoandrosta-1,4-dien-11 β -yl 2-Butynoate

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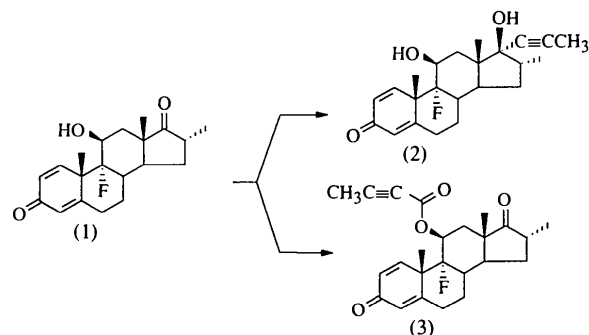
Abstract

The structure of the title compound, $C_{24}H_{27}FO_4$, which was an unexpected reaction product, was determined in order to establish its connectivity.

Comment

The title compound was supposedly produced in a reaction in which the lithium salt of propyne was added to 9 α -fluoro-11 β -hydroxy-16 α -methylandrosta-1,4-diene-3,17-dione, (1), in order to obtain the expected adduct 9 α -fluoro-11 β ,17 β -dihydroxy-16 α -methyl-17 α -propynylandrosta-1,4-diene-3-one, (2). Instead, com-

pound (3) was obtained unexpectedly. Efforts to identify the source of the one-carbon unit that comprises the carbonyl of the ester in (3) (*e.g.* adventitious DMF, *etc.*) proved uninformative. The mode of synthesis of (3) remains unexplained.



The combination of the rather flat steroid ring structure and the nearly cylindrical butynoate substituent might have been expected to be unfavorable for crystal packing, especially since the cylinder axis must make a fairly small angle with the plane normal. The displacement ellipsoids and the melting point, however, are both normal. The space group is common and there is one molecule in the asymmetric unit. The packing diagrams (Figs. 2 and 3) show that the butynoate substituents are aligned in columns by the translation along *a*. Columns fit together such that the butynoate stacks fit into cavities between steroid groups. The *a* axis is the morphological axis of the very long needles and there are fairly short (Desiraju, 1991) C—H...O=C distances in molecules related by this translation [C6...O1ⁱ 3.335 (4), C19...O1ⁱ 3.450 (4) and C24...O4ⁱ 3.627 (4) Å; symmetry code: (i) *x* − 1, *y*, *z*].

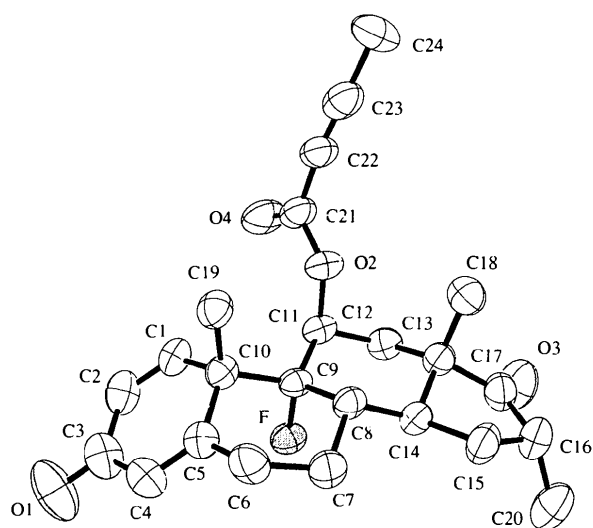


Fig. 1. Perspective drawing of the title molecule showing the atom-numbering scheme. The shapes of the ellipsoids correspond to 50% probability contours of atomic displacement. The H atoms have been omitted for clarity.