Triclinic
$P\bar{1}$
$a = 8.0599\,(10)$ Å
$b = 8.4190\,(10)$ Å
$c = 8.4446\,(8)$ Å
$\alpha = 78.078\,(9)°$
$\beta = 78.886\,(11)°$
$\gamma = 61.473\,(7)°$
$V = 489.63\,(10)$ Å^3
$Z = 2$
$D_x = 1.472$ Mg m^{-3}
D_m not measured

Cell parameters from 47
   reflections
$\theta = 4.96$–$13.60°$
$\mu = 0.615$ mm^{-1}
$T = 295\,(2)$ K
Prism
$0.67 \times 0.30 \times 0.25$ mm
Pale yellow–white

Data collection

Siemens *P4* diffractometer
$2\theta/\omega$ scans
Absorption correction: none
4432 measured reflections
2240 independent reflections
1896 reflections with
   $I > 2\sigma(I)$
$R_{int} = 0.022$

$\theta_{max} = 27.50°$
$h = -9 \rightarrow 10$
$k = -10 \rightarrow 10$
$l = -10 \rightarrow 10$
3 standard reflections
   every 97 reflections
   intensity decay: 6%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.084$
$S = 1.051$
2239 reflections
158 parameters
All H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.0478P)^2 + 0.0644P]$
   where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.009$
$\Delta\rho_{max} = 0.293$ e Å^{-3}
$\Delta\rho_{min} = -0.220$ e Å^{-3}
Extinction correction: none
Scattering factors from
   *International Tables for
   Crystallography* (Vol. C)

The approximate positions of the chloride anions and the six atoms of the 'pyridyl' ring were obtained by the heavy-atom method, while successive Fourier syntheses yielded the positions of the remaining non-H atoms. The structure was refined by the full-matrix least-squares method to anisotropic convergence, after which the positions of the H atoms were found in a difference map calculated using low-angle data ($\theta \leq 20°$). The H atoms were refined isotropically without any constraints. All computations were carried out on a Pentium PC using the Siemens *SHELXTL/PC* package (Sheldrick, 1994).

Data collection: *P4* (Siemens, 1995). Cell refinement: *P4*. Data reduction: *P4*.

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

N1—C2	1.325 (2)	C5—C6	1.358 (2)
N1—C9	1.374 (2)	C5—C10	1.415 (2)
N2—C8	1.454 (2)	C6—C7	1.409 (2)
C2—C3	1.386 (2)	C7—C8	1.367 (2)
C3—C4	1.360 (2)	C8—C9	1.412 (2)
C4—C10	1.415 (2)	C9—C10	1.413 (2)
C2—N1—C9	122.63 (13)	C7—C8—N2	120.16 (13)
N1—C2—C3	121.08 (14)	C9—C8—N2	120.09 (12)
C4—C3—C2	119.15 (14)	N1—C9—C8	122.32 (12)
C3—C4—C10	120.67 (14)	N1—C9—C10	118.11 (13)
C6—C5—C10	120.31 (14)	C8—C9—C10	119.57 (12)
C5—C6—C7	120.56 (14)	C9—C10—C4	118.35 (13)
C8—C7—C6	120.74 (14)	C9—C10—C5	119.07 (13)
C7—C8—C9	119.74 (13)	C4—C10—C5	122.58 (14)

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1A$\cdots$Cl1	0.88 (2)	2.16 (2)	3.002 (1)	158 (2)
N2^i—H22$^i\cdots$Cl1	0.85 (2)	2.26 (2)	3.073 (1)	159 (2)
C2^{ii}—H2A$^{ii}\cdots$Cl1	0.89 (2)	2.89 (2)	3.486 (2)	126 (1)
C4^{iii}—H4A$^{iii}\cdots$Cl1	0.98 (2)	2.78 (2)	3.508 (2)	131 (2)
N2—H21$\cdots$Cl2	0.91 (2)	2.17 (2)	3.057 (2)	163 (2)
N2^{iv}—H23$^{iv}\cdots$Cl2	0.86 (2)	2.23 (2)	3.090 (1)	174 (2)
C5^v—H5A$^v\cdots$Cl2	0.95 (2)	2.88 (2)	3.640 (2)	138 (2)
C6^{vi}—H6A$^{vi}\cdots$Cl2	0.92 (2)	2.90 (2)	3.628 (2)	138 (2)

Symmetry codes: (i) $1 - x, 1 - y, 1 - z$; (ii) $1 - x, -y, 1 - z$; (iii) $x - 1, 1 + y, z$; (iv) $1 - x, 1 - y, 2 - z$; (v) $2 - x, -y, 2 - z$; (vi) $x - 1, y, z$.

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1-Difluoroboronyloxy-3-(N-methylimino)-1-phenyl-1-butene and its Two Photoproducts

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Abstract

The title compound, $C_{11}H_{12}BF_2NO$, was found to be converted by irradiation to the *anti* and *syn* head-to-tail dimers {1,3-bis(difluoroboronyloxy)-2,4-bis[1-(*N*-methylimino)ethyl]-1,3-diphenylcyclobutane, $C_{22}H_{24}B_2F_4N_2O_2$}. The enaminoketone group of each complex takes a ring structure chelated through the BF_2 group.

Comment

One may consider from various spectra that β-enamino-ketones (β-EKs) exist in keto and enol tautomeric forms in several solvents (Bertolasi *et al.*, 1991; Olivieri *et al.*, 1993; Silvea & Ferrao, 1988). We have investigated photochemical reactions of some boron difluoride complexes of β-EKs because we found them to be more reactive reagents than the corresponding β-EKs (Itoh *et al.*, 1992). The title compound, (1), was irradiated with cyclic olefins to give, besides the complex olefin adducts, two photoproducts, (2) and (3), as side products, which could be obtained later by photochemical reaction of (1) alone in solvents. Complexes (1), (2) and (3) gave identical mass spectra when a CI or EI mode was used.

Fig. 1. The molecular structure of (1) showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

(1)

(2)   (3)

Complexes (2) and (3) were proved to be dimers of (1) and to have the *anti* and *syn* head-to-tail forms, respectively. The enaminoketone groups in the complexes take a ring structure chelated through the BF$_2$ group. The B—N distance in (1) [1.543 (6) Å] indicates weak bonding, and those in (2) [1.598 (4) Å] and (3) [1.591 (7) and 1.602 (8) Å] indicate further weaker bonding. On the other hand, the O—B distances in (2) [1.452 (6) and 1.426 (3) Å] and (3) [1.426 (7) and 1.422 (9) Å] are comparable with the reported B—O distances (on average 1.46 Å) (Singh *et al.*, 1986). These observations indicate that the monomer and the dimers adopt structures close to enol tautomers.

It is remarkable that the unit cells of (1) and (2) are similar and that the C(7)—C(8) bonds in adjacent molecules of (1) are related by a centre of symmetry; the intermolecular C(7)···C(8′) [and C(8)···C(7′)] distances are 3.835 (6) Å. These observations suggest a stereospecific formation of the dimer through a solid-state photochemical reaction. In fact, the formation of the *anti* form in high yield was confirmed by a preliminary solid-state irradiation.

The C(7)—C(8′) [and C(8)—C(7′)] bond length in (2) [1.593 (3) Å] and the corresponding ones in (3) [1.579 (7) and 1.581 (7) Å] are considerably longer than the standard value of a C—C single bond length.
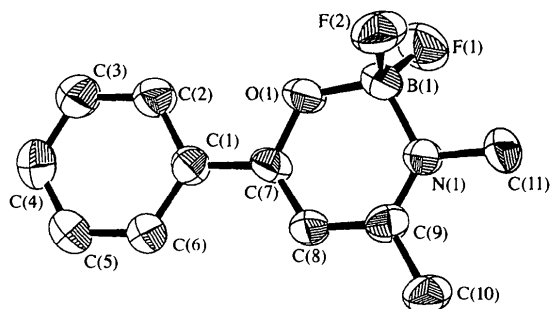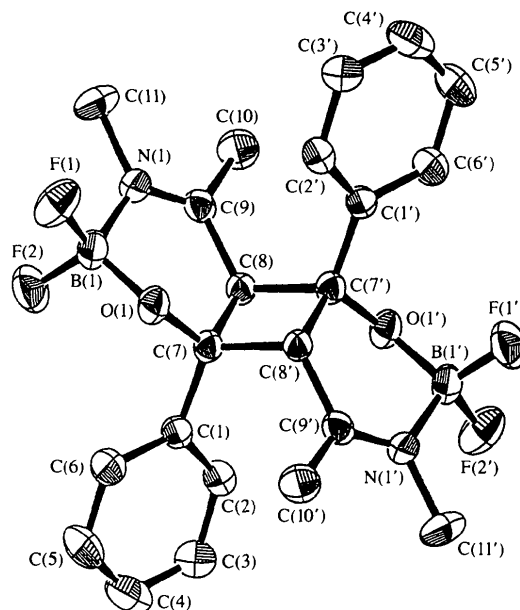

Fig. 2. The molecular structure of (2) showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity.
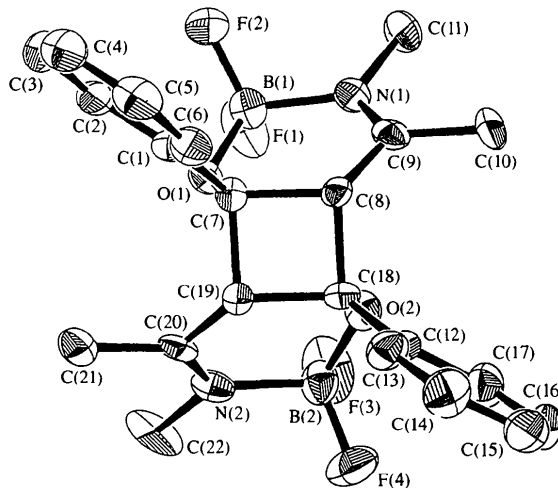

Fig. 3. The molecular structure of (3) showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

Moreover, the four-membered ring of (2) is planar, indicating a considerable strain. These findings seem consistent with the fact that (2) dissolved in dichloromethane returned to the parent compound, (1), after a few hours at room temperature, while (3) did not, at least after a few days at the same temperature.

Experimental

The title compound, (1), was prepared from boron trifluoride etherate and β-EK obtained according to the method described by Tokutomi & Hayashi (1977). Complex (1) in benzene was irradiated with a high-pressure mercury lamp through a Pyrex filter for 10 h to give a white solid [a mixture of (2) and (3)]. Complex (2) was recrystallized from dichloromethane–hexane solutions and (3) was separated from the filtrate by silica-gel column chromatography. X-ray quality crystals of (1), (2) and (3) were obtained by slow diffusion of hexane into their dichloromethane solutions.

Compound (1)

Crystal data

$C_{11}H_{12}BF_2NO$
$M_r = 223.03$
Monoclinic
$P2_1/n$
$a = 7.185\,(1)$ Å
$b = 11.3264\,(8)$ Å
$c = 13.443\,(1)$ Å
$\beta = 93.48\,(1)°$
$V = 1092.0\,(2)$ Å^3
$Z = 4$
$D_x = 1.357$ Mg m^{-3}
$D_m = 1.33$ Mg m^{-3}
D_m measured by flotation
in KI

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 25
reflections
$\theta = 13.1–15.0°$
$\mu = 0.108$ mm^{-1}
$T = 294.2$ K
Prismatic
$0.40 \times 0.30 \times 0.30$ mm
Colourless

Data collection

AFC-5R diffractometer
$\omega/2\theta$ scans
Absorption correction: none
2852 measured reflections
2650 independent reflections
1272 reflections with
$I > 3\sigma(I)$
$R_{int} = 0.009$

$\theta_{max} = 27.5°$
$h = 0 \rightarrow 9$
$k = 0 \rightarrow 14$
$l = -17 \rightarrow 17$
3 standard reflections
every 100 reflections
intensity decay: -1.05%

Refinement

Refinement on F
$R = 0.057$
$wR = 0.038$
$S = 3.140$
1272 reflections
146 parameters
H atoms not refined
Weighting scheme based
on measured s.u.'s
$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.19$ e Å^{-3}
$\Delta\rho_{min} = -0.29$ e Å^{-3}
Extinction correction:
Zachariasen type 2
Gaussian isotropic
Extinction coefficient:
0.0274
Scattering factors from International Tables for X-ray Crystallography (Vol. IV)

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

O(1)—C(7)	1.329 (4)	C(1)—C(7)	1.476 (5)
O(1)—B(1)	1.452 (6)	C(7)—C(8)	1.336 (5)
N(1)—C(9)	1.298 (4)	C(8)—C(9)	1.415 (5)
N(1)—B(1)	1.543 (6)		

Compound (2)

Crystal data

$C_{22}H_{24}B_2F_4N_2O_2$
$M_r = 446.06$
Monoclinic
$P2_1/c$
$a = 6.043\,(2)$ Å
$b = 11.192\,(2)$ Å
$c = 15.715\,(2)$ Å
$\beta = 99.76\,(1)°$
$V = 1047.5\,(3)$ Å^3
$Z = 2$
$D_x = 1.414$ Mg m^{-3}
$D_m = 1.415$ Mg m^{-3}
D_m measured by flotation
in KI

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 25
reflections
$\theta = 13.6–14.9°$
$\mu = 0.113$ mm^{-1}
$T = 294.2$ K
Prismatic
$0.40 \times 0.20 \times 0.20$ mm
Colourless

Data collection

AFC-5R diffractometer
$\omega/2\theta$ scans
Absorption correction: none
2775 measured reflections
2544 independent reflections
1573 reflections with
$I > 3\sigma(I)$
$R_{int} = 0.015$

$\theta_{max} = 27.49°$
$h = 0 \rightarrow 7$
$k = 0 \rightarrow 14$
$l = -20 \rightarrow 20$
3 standard reflections
every 150 reflections
intensity decay: -1.87%

Refinement

Refinement on F
$R = 0.052$
$wR = 0.037$
$S = 1.64$
1572 reflections
182 parameters
H atoms not refined
Weighting scheme based
on measured s.u.'s
$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.23$ e Å^{-3}
$\Delta\rho_{min} = -0.17$ e Å^{-3}
Extinction correction:
Zachariasen type 2
Gaussian isotropic
Extinction coefficient:
0.0410
Scattering factors from International Tables for X-ray Crystallography (Vol. IV)

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

O(1)—C(7)	1.406 (3)	C(1)—C(7)	1.520 (3)
O(1)—B(1)	1.426 (3)	C(7)—C(8)	1.551 (3)
N(1)—C(9)	1.283 (3)	C(7)—C(8^i)	1.593 (3)
N(1)—B(1)	1.598 (4)	C(8)—C(9)	1.486 (3)
O(1)—C(7)—C(8)	113.7 (2)	C(7)—C(8^i)—C(7^i)	91.5 (2)
O(1)—C(7)—C(8^i)	108.5 (2)	C(7)—C(8)—C(9)	118.3 (2)
C(8)—C(7)—C(8^i)	88.5 (2)	C(7^i)—C(8)—C(9)	116.9 (2)

Symmetry code: (i) $1 - x, -y, 2 - z$.

Compound (3)

Crystal data

$C_{22}H_{24}B_2F_4N_2O_2$
$M_r = 446.06$
Monoclinic
$P2_1/a$

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 25
reflections

$a = 14.685\ (2)$ Å
$b = 8.679\ (3)$ Å
$c = 17.769\ (3)$ Å
$\beta = 111.75\ (1)°$
$V = 2103.4\ (7)$ Å^3
$Z = 4$
$D_x = 1.408$ Mg m^{-3}
$D_m = 1.406$ Mg m^{-3}
D_m measured by flotation
  in KI

$\theta = 11.2–12.3°$
$\mu = 0.112$ mm^{-1}
$T = 289.2$ K
Prism
$0.25 \times 0.20 \times 0.20$ mm
Colourless

Data collection

Rigaku AFC-5R diffractom-
  eter
$\omega/2\theta$ scans
Absorption correction: none
4149 measured reflections
3986 independent reflections
2187 reflections with
  $I > 2\sigma(I)$

$R_{int} = 0.035$
$\theta_{max} = 25°$
$h = 0 \rightarrow 17$
$k = 0 \rightarrow 10$
$l = -21 \rightarrow 19$
3 standard reflections
  every 150 reflections
  intensity decay: -0.55%

Refinement

Refinement on F
$R = 0.085$
$wR = 0.052$
$S = 1.341$
2187 reflections
258 parameters
H atoms not refined
Weighting scheme based
  on measured s.u.'s
$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.37$ e Å^{-3}
$\Delta\rho_{min} = -0.42$ e Å^{-3}
Extinction correction:
  Zachariasen type 2
  Gaussian isotropic
Extinction coefficient:
  3.138×10^{-6}
Scattering factors from *Inter-
  national Tables for X-ray
  Crystallography* (Vol. IV)

Table 3. *Selected geometric parameters (Å, °) for (3)*

O(1)—C(7)	1.412 (6)	C(1)—C(7)	1.503 (6)
O(1)—B(1)	1.426 (7)	C(7)—C(8)	1.550 (7)
O(2)—C(18)	1.411 (6)	C(7)—C(19)	1.579 (7)
O(2)—B(2)	1.422 (9)	C(8)—C(9)	1.482 (6)
N(1)—C(9)	1.274 (7)	C(8)—C(18)	1.581 (7)
N(1)—B(1)	1.591 (7)	C(12)—C(18)	1.518 (7)
N(2)—C(20)	1.291 (7)	C(18)—C(19)	1.548 (7)
N(2)—B(2)	1.602 (8)	C(19)—C(20)	1.489 (7)
O(1)—C(7)—C(8)	110.9 (4)	O(2)—C(18)—C(8)	108.7 (5)
O(1)—C(7)—C(19)	108.1 (5)	O(2)—C(18)—C(19)	111.6 (5)
C(8)—C(7)—C(19)	86.9 (4)	C(8)—C(18)—C(19)	86.9 (4)
C(7)—C(8)—C(9)	119.1 (5)	C(7)—C(19)—C(18)	91.1 (4)
C(7)—C(8)—C(18)	91.0 (4)	C(7)—C(19)—C(20)	113.4 (4)
C(9)—C(8)—C(18)	117.2 (5)	C(18)—C(19)—C(20)	119.3 (5)

Date collection and cell refinement for all complexes: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Programs used to solve structure: *SIR*88 (Burla *et al.*, 1989) for (1) and (2), *SAPI*91 (Fan, 1991) for (3). Programs used to refine structure: *DIRDIF*92 (Beurskens *et al.*, 1992) for (1) and (3), *DIRDIF*94 (Beurskens *et al.*, 1994) for (2) and *TEXSAN* (Molecular Structure Corporation, 1992) for all complexes. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *TEXSAN*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DE1049). Services for accessing these data are described at the back of the journal.

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7-Methyl-3,7,11,17-tetraazabicyclo[11.3.1]-heptadeca-1(17),13,15-triene

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Abstract

The title compound, $C_{14}H_{24}N_4$, is known to act as a macrocyclic ligand and its conformation has been determined to facilitate future comparisons with its coordinated forms. The aliphatic macrocyclic strand is disordered with respect to a mirror plane perpendicular to the pyridine ring and contains an ordered tertiary