

Photodimerization of enaminoketonatoboron difluorides

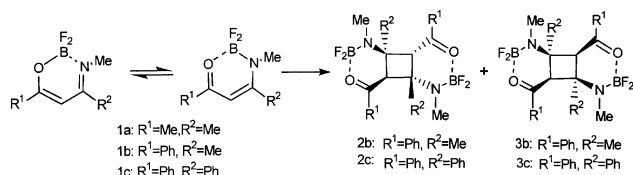
Kuniaki Itoh,* Miki Fujimoto and Masao Hashimoto

Department of Chemistry, Faculty of Science, Kobe University, Nada-ku, Kobe 657-8501, Japan.
E-mail: kuitoh@kobe-u.ac.jp

Received (in Montpellier, France) 30th November 2001, Accepted 20th March 2002
First published as an Advance Article on the web

Irradiation of enaminoketonatoboron difluorides (complexes) in solution in the presence of benzophenone gave two stereoisomeric dimers: *syn* head-to-tail (H-T) and *anti* H-T. The observed stereochemical control can be understood on the basis of steric energies calculated by molecular mechanics. However, in the crystalline state the complexes selectively afforded an *anti* H-T dimer. X-Ray analysis of the complex confirms that this reaction proceeds according to known topochemical principles. The cyclobutane ring formed shows planar and puckered forms in the *syn* H-T and *anti* H-T dimers, respectively.

The photochemical cycloaddition of 1,3-diketones to olefins¹ is a useful method in natural product synthesis.² However, the photoreaction of the corresponding carbonyl compound containing a β -enamine group has been hardly investigated.³ These compounds are expected to yield photoadducts able to serve as potential intermediates for the synthesis of various nitrogen-containing substances. However, irradiation of mixtures of some typical enaminoketones and olefins in organic solvents yielded no photoadducts. Hence, following the enhanced reactivity of 1,3-diketone BF₂ complexes toward olefins as demonstrated by Chow and Cheng,⁴ we prepared a number of enaminoketonatoboron difluorides (complexes, **1a–c**) by reaction with boron trifluoride. In earlier work we showed that the photoreactions of the complexes **1a–c** with cyclic olefins, besides resulting in some complex olefin adducts,⁵ yielded two photoproducts (**2a–c** and **3b, c**) as by-products. These latter compounds are also produced by photochemical reaction of the complex alone in solvent (hexane, benzene, etc.) or in the solid state.



We report herein the results of our investigation of the photodimerization of the complexes in solution and the solid state, and the structures of the product dimers.

Results and discussion

Photochemistry of the complexes in solution

A benzene solution of the complex (**1a–c**) was irradiated with a medium pressure mercury lamp in the presence of benzophenone ($E_T = 68 \text{ kcal mol}^{-1}$) through a pyrex filter to give the photoproducts. Whereas the complex **1a** gave only one product **2a**, the complexes **1b** and **1c** gave two products **2b, 3b** and **2c, 3c**, respectively. Results of the reactions are given in Table 1. On the other hand, when **1a** was irradiated under the same conditions in the absence of benzophenone, the same product (**2a**) was obtained, but the yield was low (trace

Table 1 Photochemical reactions of the complexes **1a–c** in the presence or in the absence of benzophenone

Substrate	Yield ^a	
	With benzophenone	Without benzophenone
1a	84.8 (2a) ^b	Trace (2a)
1b	45.1 (2b), 10.4 (3b)	46.5 (2b), 11.0 (3b)
1c	4.6 (2c), 4.1 (3c)	4.6 (2c), 4.1 (3c)

^a Irradiation of 0.05 M complex with or without 1 equiv. of benzophenone for 10 h. ^b Irradiation time 2 h.

amounts). Naphthalene ($E_T = 60 \text{ kcal mol}^{-1}$) also quenched the formation of **2a**. These results indicate that the product **2a** is produced *via* the triplet state ($E_T = 60\text{--}64 \text{ kcal mol}^{-1}$). In contrast, **1b** and **1c** gave similar yields in photoproducts with or without benzophenone. Unfortunately, the mass spectra (CI, EI) of each of these photoproducts showed identical molecular ion signals as the initial monomer. Furthermore, other spectra (¹H-NMR, ¹³C-NMR and IR) did not yield sufficient useful information to allow the structure of the photoproducts to be assigned. Therefore, we turned to single crystal structure analysis by X-ray diffraction to show that these products are the *anti* head-to-tail (H-T) dimer (**2**) and *syn* H-T dimer (**3**) of the parent compounds (Figs. 1–4).

We observed that the H-T dimer was formed despite the fact that the photochemical reaction should lead to head-to-head (H-H) dimers according to MO perturbation theory.⁶ We considered frontier orbital control as a possible explanation for the stereochemical behavior of the complex. The energy gap between the frontier orbitals indicates that the best interaction occurs between the HSOMO of the excited triplet state and the LUMO of the fundamental singlet state (Table 2). However, the atomic coefficient data suggests the formation of the H-T dimer at HOMO/LSOMO, but cannot indicate the formation behavior at LUMO/HSOMO (Table 3). We concluded that the observed stereochemistry cannot be fully explained on this basis. In order to shed some light on this problem, we attempted molecular mechanics calculations using the MMFF 98 method,^{7,8} taking into account the steric effects suggested by Epitotis.^{6b} The results are given in Table 4. We observed a completely different trend for H-T and H-H

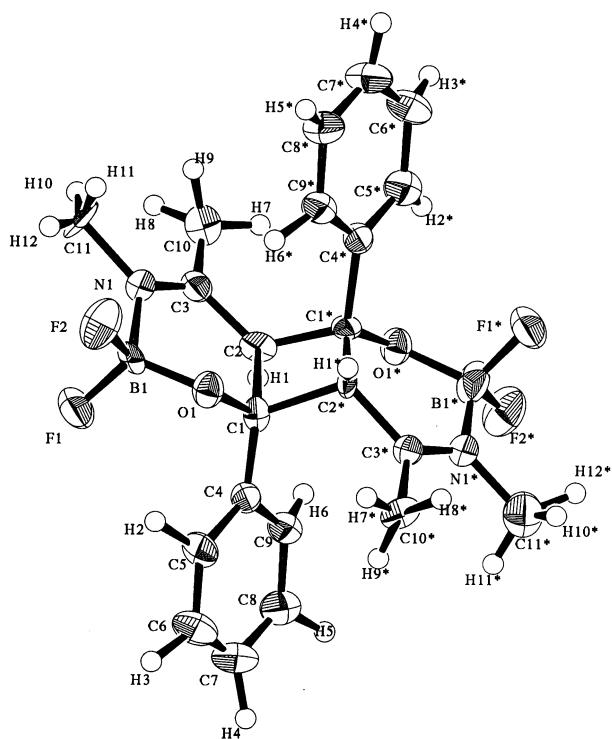


Fig. 1 Molecular structure of dimer 2b.

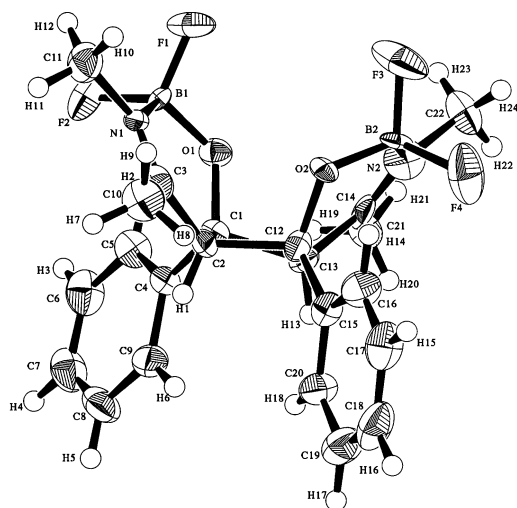


Fig. 2 Molecular structure of dimer 3b.

dimers. The H-T dimers of **1b** had steric energies of 1.9 (*anti*) and 3.4 (*syn*) kcal mol⁻¹, while the H-H dimers had values of 52.4 (*anti*) and 58.9 (*syn*) kcal mol⁻¹. The dimers of **1a** and **1c** followed similar trends. These results indicate that H-T dimers

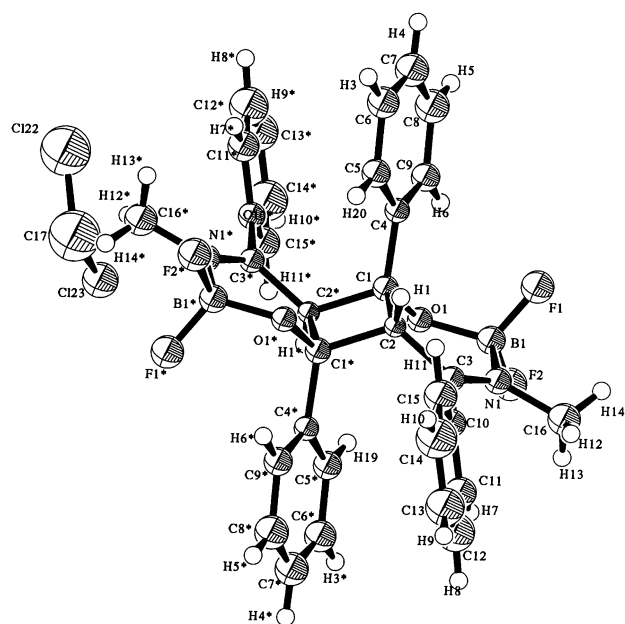


Fig. 3 Molecular structure of dimer 2c.

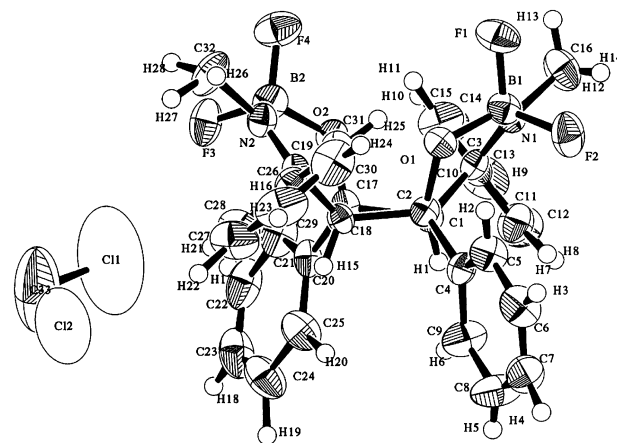


Fig. 4 Molecular structure of dimer 3c.

Table 2 The energy gap (eV) between the fundamental state and the excited state

Substrate	HOMO-LSOMO	LUMO-HSOMO
1a	1.313	0.886
1b	1.310	0.605
1c	0.828	0.797

Table 3 Atomic coefficients of HOMO and LUMO of S₀, and SOMO of T₁

Substrate	HOMO			LSOMO			LUMO			HSOMO		
	C1	C2	C3	C1	C2	C3	C1	C2	C3	C1	C2	C3
1a	0.25	0.56	0.00	0.50	0.11	-0.47	0.44	-0.01	-0.50	0.39	-0.58	0.33
1b	0.21	0.54	0.02	0.50	0.09	-0.30	0.42	-0.08	-0.40	0.11	-0.50	0.55
1c	0.20	0.50	0.02	0.50	0.21	-0.38	0.35	-0.04	-0.38	0.24	-0.49	0.07

(-O-) (R-) C1-C2 (-H1)-C3 (-R') (-N-).

Table 4 Steric energy^a (kcal mol⁻¹) of the complexes **1a–1c**

Substrate	<i>anti</i> -H-T	<i>syn</i> -H-T	<i>anti</i> -H-H	<i>syn</i> -H-H	substrate
1a	-43.4	-50.1	-19.0	-12.5	-4.2
1b	1.9	3.4	52.4	58.9	22.3
1c	66.9	67.7	115.7	122.9	48.3

^a The molecular mechanics calculation were performed using the MMFF98 method.⁸

are more stable than the H-H dimers and the large energy difference explains the exclusive formation of the former. Furthermore, the molecular mechanics results allow us to explain the stereochemistry (*anti*/*syn* forms) of the photochemical reaction. The energy differences between the *anti* and *syn* forms are 6.7 kcal mol⁻¹ for the dimer of **1a**, 1.5 kcal mol⁻¹ for the dimer of **1b**, and 0.8 kcal mol⁻¹ for the dimer of **1c**. These values reflect quite well the observed product yields and ratios.

It is well known that the yield of the dimers and the stereomer ratio of the *anti*/*syn* forms is related to the dielectric constant of the solvent used.⁹ To confirm the effect in the present case, we performed the photodimerization using several different solvents. The results are shown in Table 5. For the complexes **1a–1c**, the decrease in dimer yield appears to be correlated with an increasing solvent dielectric constant.¹⁰ Hoffman *et al.*¹¹ observed a remarkable solvent effect on photodimerization whereby only the *anti* H-H dimer is formed in nonpolar solvents while both *syn* and *anti* H-H dimers are formed in polar media. On the other hand, the stereomer ratio of the *anti*/*syn* forms is correlated by a single straight line in a Kirkwood–Onsager plot¹² with the dielectric constant of the solvent. For the complex **1b**, we could not find a definite straight line. The excited triplet state lifetime is known to decrease with increasing solvent polarity.^{11,13} Therefore, it is reasonable that the dimer yield from photoreaction of complex **1a** in the presence of benzophenone decreases in polar solvents.

Photochemistry of the BF₂ complexes in the solid state

The solid state photoaddition was studied in the crystal prepared from dichloromethane on the outer surface of a pyrex test tube. After irradiation (10 h) the reaction mixture was examined using ¹H-NMR spectroscopy. Photodimerization

Table 5 Photodimerization of the complexes **1a–c** in various solvents

Substrate	Solvent ^b	Yield/%		
		2	3	2/3
1a ^a	Hexane	No reaction		
	Benzene	82.0		
	Chloroform	70.6		
	Acetone	35.7		
	Methanol	26.5		
1b	Hexane	No reaction		
	Benzene	45.1	10.4	4.3
	Chloroform	10.1	3.7	2.7
	Acetonitrile	0.78	0.30	2.6
	Acetone	0.34	0.10	3.4
	Methanol	0.25	0.045	5.5
1c	Hexane	—	(90) ^c	—
	Benzene	4.6	4.1	1.1
	Methanol	0.79	0.57	1.4

^a In the presence of benzophenone. ^b Solvent dielectric constants: hexane 1.88, benzene 2.27, chloroform 4.81, acetone 20.56, methanol 32.66, acetonitrile 35.90.¹⁰ ^c Insoluble in hexane, solid state photoaddition.

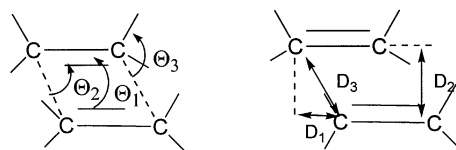
Table 6 Geometrical parameters^a of molecules **A–C'**

Molecule	$\theta_1/^\circ$	$\theta_2/^\circ$	$\theta_3/^\circ$	$D_1/\text{\AA}$	$D_2/\text{\AA}$	$D_3/\text{\AA}$
A, A'	—	—	—	—	—	4.635, 4.801
B (2b type)	0	85.52	109.50	0.299	3.819	3.831
B' (3b type)	—	—	—	—	—	> 6
C (2c type)	0	84.43	88.23	0.363	3.723	3.741
C' (3c type)	0.37	83.91	78.59	0.371	3.483	3.503
Optimal data ^b	0	90	90	0	D3	< 4.2

^a Geometrical parameters from ref. 15. ^b Schmidt's rule, ref. 14.

of complex **1b** gave the dimer **2b** (55%) as the sole product, and the complex **1c** gave only dimer **2c** (54%). But in the case of **1a**, no dimer could be obtained. The structures of the dimers were found to be *anti* H-T by comparison with the previous product spectra.

It is noteworthy that the yield and selectivity of dimer formation reflect the topology of the parent substances. Thus, the photodimerization in the solid state depends on the relative geometry of reactant molecules in the crystal lattice: the center-to-center distance and angle between the nearest neighbor double bonds.¹⁴ The geometrical parameters of **1a–1c** obtained from single crystal X-ray structure analysis¹⁵ are shown in Table 6. To achieve a [2 + 2] topochemical photocycloaddition, not only the center-to-center distance (less than *ca.* 4.2 Å) but also the best overlap of the reaction partner π orbitals are important.¹⁴ Hence the reaction depends on such geometrical parameters (θ_1 , θ_2 , θ_3 and D_1) shown in Fig. 5. The optimal values¹⁴ of these parameters are 0°, 90°, 90° and 0 Å respectively. In **1a** crystals, the distance between the double bonds of the two reactive partners is 4.64 and 4.80 Å in the molecules **A** and **A'**, respectively. In the crystal of **1b**, the distance between the two adjacent molecules **B'** (corresponding to *syn* H-T, **3b** type) is > 6.0 Å. The molecules **A**, **A'** and **B'** are thus located unfavorably for the photoreaction as the distance of the separation is larger than 4.2 Å. On the other hand, the distances between molecules **B**, **C**, and **C'** are shorter than 4.2 Å. However, in molecule **B**, the bond angle ($\theta_3 = 109.50^\circ$) is far from the optimal angle (90°), but the crystal reactivity is based on the availability of free space around the reaction site.¹⁶ We could not obtain the molecule **C'** (*syn* H-T, **3c** type). In this molecule, the bond angle ($\theta_3 = 78.59^\circ$) is far from the optimal angle (90°) and the torsional angle ($\theta_1 = 0.37^\circ$) is also slightly different from the optimal angle (0°). However, these factors appear to be insufficient to explain the photoreactivity. It is interesting to ponder the reason for the absence of reaction between centrosymmetrically related, sterically close monomers. The relative orientation of the related molecular pair is shown in Fig. 6. The situation is favorable for the formation of dimer **2c**. The monomer **C** and its centrosymmetrically related partner only need to do a parallel translation, so the formation of the dimer **2c** is facile. However, the formation of dimer **3c** is difficult. The monomer **C'** and its partner are not favorably positioned for the reaction. One may assume that the motion of the monomer pair to achieve maximum π -overlap will be accompanied by steric hindrance from the surrounding substituent groups. Therefore, the molecular **C'** does not undergo photodimerization because mobility of molecules will be highly restricted in the crystal. Thus, the X-ray results

**Fig. 5** Pictorial representation of $\theta_{1,2,3}$ and $D_{1,2,3}$ parameters.

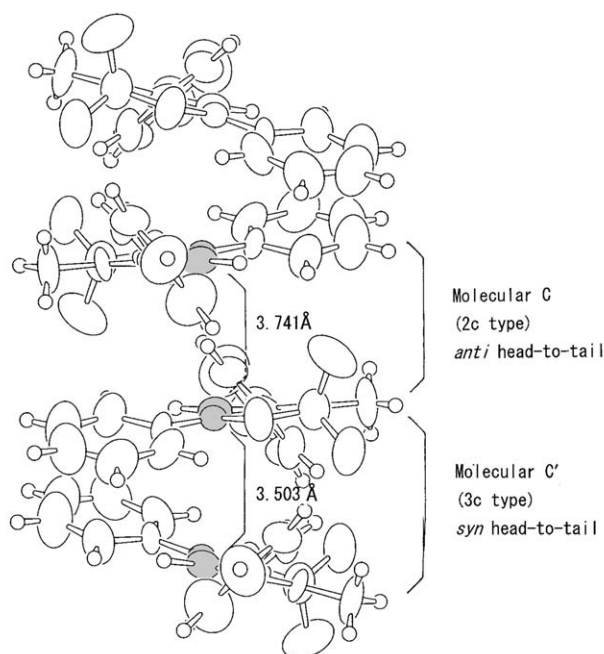


Fig. 6 Pairs of molecules of the complexes C and C'.

are consistent with our observations that the head-to-tail arrangements were preferred. This is in accordance with well-known topochemical principles.¹⁷

X-Ray structure analysis and thermal decomposition

In Table 7 we summarize selected structural parameters of dimers **2b**, **3b**, **2c** and **3c**. Unfortunately, single crystals of **2a** could not be prepared.¹⁸ In the crystals of these dimers (**2b**–**3c**), all the non-hydrogen atoms on both enamino-ketonato-boron rings are coplanar. It is well-known that the geometry of cyclobutane rings reflects the delicate balance between strain forces and repulsive interactions of vicinal substituents.¹⁹ Ring strain is minimized in the planar form, but increases in the puckered form. It may be thought that the bond angles are far from that of the sp^3 carbon atoms, but the total energy of the molecule results in a minimum by balancing the overlap of bonding electrons. For the dimer **2b** it is interesting that the cyclobutane ring is planar, and its bond distances (1.550, 1.589 Å) and torsion angle (0°) are similar to those of the normal planar cyclobutane ring.¹⁹ However, the bond angles (88.5 , 91.5°) are different from that of the general unsubstituted ring, and it takes on a slightly warped diamond-shaped

form. Also, the bond distance (1.589 Å) connecting the two halves is slightly longer than that (1.550 Å) of the enamino-ketone ring. In the dimer **3b** the bond distances of the cyclobutane ring (1.552, 1.575–1.587 Å) and its bond angles (86.8 – 87.2 , 90.8 – 91.1°) are similar to those reported for puckered cyclobutane rings,²⁰ but the torsion angle (16.4°) is remarkably different, being only about half of the normal value (29.6°). On the other hand, the bond distances (1.553–1.584 Å) and the bond angles (87.2 – 91.5°) in the cyclobutane rings of the dimers **2c** and **3c** are similar to those of **2b** and **3b**, respectively. However, the bond distances connecting the two halves of the dimer **3c** are longer (1.565–1.584 Å), presumably due to the highly crowded conformation around the cyclobutane ring.

Hence, hoping to understand the relation between ring strain and the stabilities of these dimers, we examined their thermal decomposition into their parent monomers. The dimer **2b** in deuterated chloroform solution was thermostatted at 45°C , and the relative ratio of the complex **1b** and the dimer **2b** measured by NMR spectrometry. The dimers **2b** showed a half-life of 75 min. That of dimer **2c** was 25 min. In other words, the cycloreversion rate of the dimer **2c** was three times faster than that of the dimer **2b**. However, at the same temperature (45°C), the dimers **3b** and **3c** were almost completely resistant to cleavage. The *anti* dimers (planar rings) split into monomers, but the *syn* dimers (puckered rings) did not cleave. It appears that the cycloreversion in solution may not be directly correlated to the ring structure in the solid state.

Experimental

Spectral measurements and X-ray structure determination

IR spectra were recorded on a Perkin Elmer 1600 spectrometer on KBr disks. ^1H and ^{13}C NMR spectra were taken on a JEOL JMN-GX 400 or Bruker DPX-250 spectrometer with tetramethylsilane as internal standard. Melting points were obtained on a Yanako micro apparatus and are uncorrected. Mass spectra were recorded on a Shimadzu GCMS-QP2000A. Irradiation was done by a 450 W high pressure mercury lamp (USHIO UM-452) through a pyrex filter.

X-Ray crystallographic analysis was carried out on a Rigaku AFC-5R four-circle diffractometer. Crystal data and details of data collection were summarized in Table 8. The structures were solved by direct methods with the programs SAPI91²¹ and SIR88²² and refined by full-matrix least-squares methods using the TEXSAN²³ package.

CCDC reference number 171762–171765. See <http://www.rsc.org/suppdata/nj/b1/b110975h/> for crystallographic files in CIF or other electronic format.

Table 7 Selected geometrical parameters of the dimers^a

Compound	2b	3b	2c	3c	Planar	Puckered
Distance/Å						
C1–C2	1.550(2)	1.552(8)	1.555(9)	1.561(6)	1.558	1.553
C1–CY	1.589(2)	1.575(8)	1.553(9)	1.584(6)	1.558	1.553
C2–CX	1.589(2)	1.587(8)	1.553(9)	1.565(6)	1.558	1.553
CX–CY	1.550(2)	1.552(8)	1.555(9)	1.560(6)	1.558	1.553
Bond angle/ $^\circ$						
C1–C2–CX	91.5(1)	90.8(5)	91.0(5)	91.5(3)	90	88
C2–C1–CY	88.5(1)	87.2(4)	89.0(5)	87.2(3)	90	88
C1–CY–CX	91.5(1)	91.1(5)	91.0(5)	90.8(3)	90	88
C2–CX–CY	88.5(1)	86.8(5)	89.0(5)	87.9(3)	90	88
Torsion angle/ $^\circ$						
C1–C2–CX–CY	0.00(1)	–16.4(5)	0.00(1)	–12.1(3)	0	29.6

^a Dimers **2b** and **2c**: CX = C1', CY = C2'; dimer **3b**: CX = C12, CY = C13; dimer **3c**: CX = 17, CY = C18. ^b ref. 19.

Table 8 Crystal data for structure determination of **2b**, **2c**, **3b** and **3c**

Compound	2b	3b	2c	3c
Formula	$C_{22}H_{24}B_2F_4N_2O_2$		$C_{32}H_{28}B_2F_4N_2O_2 \cdot CH_2Cl_2$	
Mol. wt.	446.06		655.13	
Space group	<i>P</i> 21/ <i>c</i>	<i>P</i> 21/ <i>a</i>	<i>P</i> 21/ <i>c</i>	<i>P</i> -1
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic
<i>a</i> /Å	6.043(2)	14.685(2)	13.936(4)	9.669 (3)
<i>b</i> /Å	11.192(2)	8.679(3)	8.744(2)	18.632(3)
<i>c</i> /Å	15.715(2)	17.769(3)	14.796(3)	9.416(2)
α /°	90	90	90	91.52(2)
β /°	99.76(1)	111.75(1)	109.60(1)	110.66(2)
γ /°	90	90	90	94.71(2)
<i>u</i> /Å ³	1047.5(3)	2103.4(7)	1698.5(7)	1579.0(6)
<i>Z</i>	2	4	2	2
Collected reflect.	2775	5352	4334	7685
Unique reflect.	2544	5157	4035	7681
Obsd reflect. ($> 1.0\sigma(F)$)	1820	2524	1842	4545
Final <i>R</i> /%	5.07	11.81	7.87	8.02
<i>R</i> _w /%	4.73	9.45	19.82	13.31

Materials

The enaminoketonatoboron difluorides (**1a–c**) were prepared from borontrifluoride methyletherate and the 1,3-enamino-ketones obtained by the method described by Tokutomi and Hayashi³ and by us.⁵

Photoaddition reactions

In solution. The benzene solution of the complex **1a–c** (0.05 M) out-gassed with nitrogen was irradiated for 2 h. After the solution was removed under reduced pressure, the residue was chromatographed on silica gel with hexane–ethyl acetate (5/1) and dichloromethane as eluent to yield the dimers as a colorless solid.

In the solid state. The complex **1a–c** was dissolved with a small amount of dichloromethane in a pyrex test tube. Slow evaporation of the solvent to dryness adhered on the tube surface while rotating the inclined tube produced crystals. The test tube containing the crystals was irradiated. The photolytic mixture was dissolved in deuterated chloroform, and the dimer yields were calculated based on the integrated ratio of ¹H-NMR signals.

Dimer characterization

Dimer of (N-B)-Z-2-difluoroboronyl-4-methylimino-2-pentene (1a). *Dimer 2a.* Mp 150.8–152.0 °C. MS: *m/z* 322, 281, 264, 238. IR: 1674, 1392, 1150 cm^{−1}. ¹H-NMR (CD₃CN): δ 1.36 (s, 6H), 2.34 (s, 6H), 3.34 (s, 6H), 3.37 (s, 2H); ¹³C-NMR (CD₃CN): δ 18.4, 21.7, 34.8, 50.4, 126.3, 183.6. Anal. found: C, 44.82, H, 6.55, N, 8.06%; calcd for C₁₂H₂₀N₂O₂B₂F₄: C, 44.82, H, 6.50, N, 8.06%.

Dimers of (N-B)-Z-2-difluoroboronyl-3-methylimino-1-phenyl-1-butene (1b). *Dimer 2b.* Mp 137.0–138.8 °C. MS: *m/z* 223 (M⁺/2), 222, 105, 77, 56. IR: 1674, 1366, 1152, 1084, 910, 882 cm^{−1}. ¹H-NMR (CDCl₃): δ 1.49 (s, 6H), 2.98 (s, 6H), 4.29 (s, 2H), 7.30–7.84 (m, 10H); ¹³C-NMR (CDCl₃): δ 21.7, 35.2, 76.0, 126.6, 127.7, 128.8, 129.0, 142.2, 181.4. Anal. found: C, 59.97, H, 5.41, N, 5.88%; calcd for C₂₂H₂₄N₂O₂B₂F₄: C, 59.24, H, 5.42, N, 6.28%.

Dimer 3b. Mp 142.0–144.0 °C. MS: *m/z* 223 (M⁺/2), 222, 105, 77, 56. IR: 1686, 1448, 1144, 1006, 940, 904 cm^{−1}. ¹H-NMR (CDCl₃): δ 2.02 (s, 6H), 3.24 (s, 6H), 3.84 (s, 2H),

7.30–7.84 (m, 10H); ¹³C-NMR (CDCl₃): δ 20.9, 34.0, 78.4, 126.5, 127.2, 128.0, 128.7, 144.6, 180.5. Anal. found: C, 59.25, H, 5.25, N, 6.00%.

Dimers of (N-B)-Z-2-difluoroboronyl-1,3-diphenyl-3-methylimino-1-propene (1c). *Dimer 2c.* Mp 126.0–127.0 °C. MS: *m/z* 285 (M⁺/2), 284, 149, 118, 105, 77, 56. IR: 1660, 1532, 1144 cm^{−1}. ¹H-NMR (CDCl₃): δ 3.12 (s, 6H), 4.80 (s, 2H), 6.55 (d, *J* = 7.4 Hz, 4H), 7.18–7.71 (m, 16H); ¹³C-NMR (CDCl₃): δ 37.4, 62.6, 127.3, 127.5, 127.7, 128.1, 128.6, 128.7, 129.2, 131.5, 141.8, 178.9. Anal. found: C, 67.49, H, 5.09, N, 4.99%; calcd for C₃₂H₂₈N₂O₂B₂F₄: C, 67.41, H, 4.95, N, 4.91%.

Dimer 3c. Mp 120.0–122.0 °C. MS: *m/z* 285 (M⁺/2), 284, 149, 118, 105, 77. IR: 1672, 1540, 1138 cm^{−1}. ¹H-NMR (CDCl₃): δ 3.32 (s, 6H), 4.14 (s, 2H) 7.18–7.71 (m, 20H); ¹³C-NMR (CDCl₃): δ 34.4, 96.0, 126.9, 127.5, 128.8, 130.8, 132.3, 132.7, 132.9, 133.3, 147.5, 171.3. Anal. found: C, 67.51, H, 5.07, N, 5.02%.

References

- P. de Mayo, H. Takeshita and A. B. M. A. Sattar, *Proc. Chem. Soc.*, 1962, 119; P. de Mayo, *Pure Appl. Chem.*, 1964, **9**, 567.
- G. Büchi, J. A. Carlson, J. E. Powell, Jr. and L.-F. Tietze, *J. Am. Chem. Soc.*, 1970, **92**, 2165; L.-F. Tietze, K.-H. Glüssenkamp, N. Nakane and C. R. Hutchison, *Angew. Chem., Int. Ed. Engl.*, 1983, **21**, 70; J. D. Winkler, C. M. Bowen and F. Liotta, *Chem. Rev.*, 1995, **95**, 2003.
- T. Tokumitsu and T. Hayashi, *Nippon Kagaku Kaishi*, 1997, 1338.
- Y. L. Chow and X. E. Cheng, *J. Chem. Soc., Chem. Commun.*, 1990, 1043.
- K. Itoh, K. Okazaki, A. Sera and Y. L. Chow, *J. Chem. Soc., Chem. Commun.*, 1992, 1608.
- (a) M. D'Auria and R. Racioppi, *Tetrahedron*, 1997, **53**, 17307; (b) N. D. Epitotis, *J. Am. Chem. Soc.*, 1973, **95**, 5624.
- Spartan v.'02 Windows, Wavefunction, Inc., Irvine, CA, USA.
- (a) G. Robinet, J. Devillers, C. de Bourayne, M. Riviere and M. Barthelat, *New. J. Chem.*, 1987, **11**, 51; (b) The structures calculated by molecular mechanics fit to within 2–3% of the structure determined by X-ray analysis.
- P. de Mayo, J.-P. Pete and M. Tchir, *Can. J. Chem.*, 1968, **46**, 2535.
- We were unable to investigate the reactions of the complexes **1a** and **1b** in hexane solution owing to solubility problems. For solvent dielectric constants, see *Solvents and Solvent Effects in Organic Chemistry*, ed. C. Reichardt, VCH, Weinheim, 1988.
- R. Hoffman, P. Wells and H. Morrison, *J. Org. Chem.*, 1971, **36**, 102.

- 12 R. Steinmetz, W. Hartman and G. O. Schenck, *Chem. Ber.*, 1965, **98**, 3854.
- 13 N. Ghoneim, A. Monbelli, D. Pillound and P. Suppan, *J. Photochem. Photobiol.*, 1996, **94**, 145.
- 14 M. D. Cohen and G. M. J. Schmidt, *J. Chem. Soc.*, 1964, 1996; M. D. Cohen, G. M. J. Schmidt and F. J. Sonntag, *J. Chem. Soc.*, 1964, 2000; G. M. J. Schmidt, *J. Chem. Soc.*, 1964, 2014; G. M. J. Schmidt, *Pure Appl. Chem.*, 1971, **27**, 647.
- 15 K. Itoh, M. Fujimoto and M. Hashimoto, *Acta Crystallogr., Sect. C*, 1998, **53**, 1324.
- 16 A. Gavezzotti, *J. Am. Chem. Soc.*, 1983, **105**, 5220.
- 17 M. Gnanaguru, K. N. Ramasubbu, K. Venkatesan and V. Ramamurthy, *J. Org. Chem.*, 1985, **50**, 2337.
- 18 Attempts to obtain a single crystal of **2a** of suitable quality were unsuccessful as polymerization or cycloreversion occurred during crystallization.
- 19 F. H. Allen, *Acta Crystallogr. Sect. B*, 1984, **40**, 64.
- 20 F. H. Allen, M. J. Doyle and T. P. E. Auf der Heyde, *Acta Crystallogr., Sect. B*, 1991, **47**, 412.
- 21 SAPI91: H. F. Fan, Structure Analysis Programs with Intelligent Control, Rigaku Corporation. Tokyo, Japan, 1991.
- 22 SIR88: M. C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, G. Polidori, R. Spagna and D. Vinerbo, *J. Appl. Crystallogr.*, 1988, **22**, 389.
- 23 TEXSAN Crystal Structure Analysis Package, Molecular Structure Corporation, The Woodland, TX, 1995.