Bis(morpholine)-substituted 1,3,5-Triazines Derivatives: Synthesis and Structural Study

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Abstract

New 4,4'-[6-(o-carboranylalkoxy)-1,3,5-triazine-2,4-diyl]dimorpholine derivatives have been prepared by reacting 4,4'-[6-(alkynyloxy)-1,3,5-triazine-2,4-diyl]dimorpholines with decaborane and N,N-dimethylaniline as base. The intermediate compounds, 4,4'-[6-(alkynyloxy)-1,3,5-triazine-2,4-diyl]dimorpholines, have been prepared by reacting 4,4'-[6-chloro-1,3,5-triazine-2,4-diyl]dimorpholines with prop-2-yn-1-ol, but-3-yn-1-ol, and pet-4-yn-1-ol, and potassium tert-butoxide (t-BuOK) as base. The structure of these compounds has been confirmed by IR, ^{1}H, ^{11}B, and ^{13}C NMR and X-ray crystallographic studies.

1. Introduction

1,3,5-Triazine derivatives have been well known[1] for a long time and continue to be the subject of interest in various fields. Nitrogen heterocycles are biologically relevant as model nucleobases due to their H-acceptor abilities[2]. Triazine derivatives have found applications as pharmaceuticals[3], liquid crystals[4], building blocks for supramolecular chemistry[5], reactive dyes[6], organic light-emitting diodes (OLEDs)[7], and chemical reagents for selected transformations[8].

The symmetrical nature of the triazine core renders it an optimal scaffold that can be conveniently functionalized with a variety of elements. The scaffold has a plannar structure, but unlike benzene, exists as an irregular hexagon with two different bond angles yet identical bond lengths.[1c] The symmetrical bond lengths reflect the aromaticity of the 1,3,5-triazine core, although the calculated aromaticity is slightly lower than that of benzene[9]. The reduced aromaticity is due to the polarity of the C=N bond, which results in an increased electron density on the ring nitrogen atoms. This charge distribution across the 1,3,5-triazine ring explains much of the reactivity of this ring system, particularly the susceptibility to electrophilic attack at nitrogen and nucleophilic attack at carbon[10].

The generation of diverse libraries of trifunctionalized triazines has relied on the nucleophilic addition to triazine carbon atoms. The ease of displacement of the chlorine atoms in cyanuric chloride, coupled with its commercial availability and low cost, make this reagent an ideal starting material for the preparation of substituted 1,3,5-triazines. Sequential substitution of the three chlorine atoms with N-, S-, and O-nucleophiles can generate highly diverse chemical libraries. Herein, we describe the synthesis and structural studies of 4,6-dimorpholine substituted 1,3,5-triazines containing ether-linked o-carborane. These unique carborane products were analyzed by IR, ^{1}H, ^{11}B, and ^{13}C NMR spectroscopy and X-ray crystallography where appropriate.

2. Experimental

2.1. General Considerations

All manipulations were performed under either a dry nitrogen atmosphere using either standard Schlenk techniques or inside a KK-011AS glove box. Tetrahydrofuran (THF) and toluene were purchased from Samchun Pure Chemical Company and dried over sodium/benzophenone before use. Glassware, syringes, magnetic stirring bars, and needles were dried overnight in a con-

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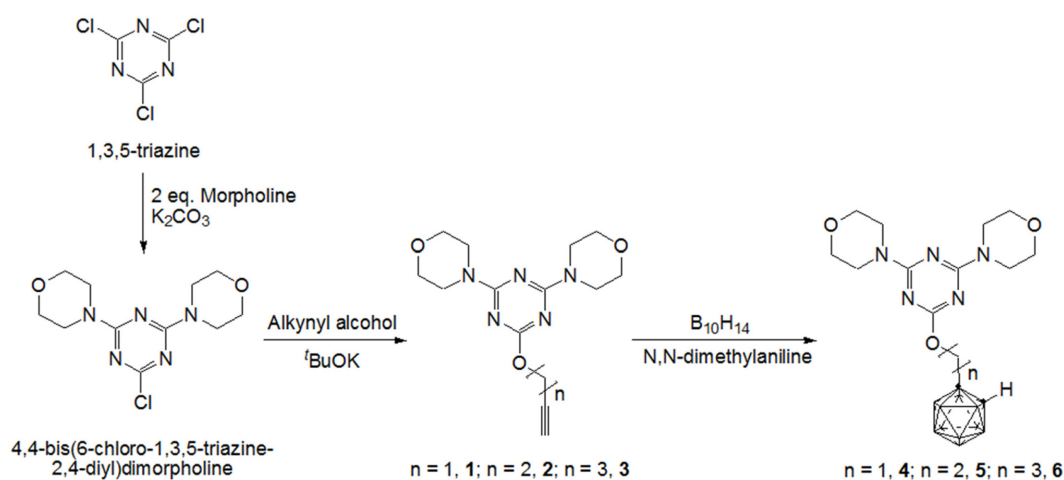
Scheme 1. Preparation of compounds **1**−**6**.

vection oven. Decaborane was purchased from Katchem and used after sublimation. Morpholine, cyanuric chloride, potassium tert-butoxide (t-BuOK), prop-2-yn-1-ol, but-3-yn-1-ol, pent-4-yn-1-ol and N,N-dimethylaniline were purchased from Aldrich Chemicals. IR spectra were recorded on an Agilent Cary 600 Series FT-IR spectrometer using KBr disks. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 300 spectrometer operating at 300.1 and 75.4 MHz, respectively. All proton and carbon chemical shifts were measured relative to the internal residual CHCl$_3$ from the lock solvent (99.9% CDCl$_3$). Elemental analysis (Carlo Erba Instruments CHNS-O EA1108 analyzer) and HR-MS (FAB) (Jeol LTD JMS-HX 110/110A) were performed by the Ochang branch of the Korean Basic Science Institute.

2.2. Synthesis of 4,4'-[6-(Alkynyloxy)-1,3,5-triazine-2,4-diyl]dimorpholine (1).

General Procedure. Prop-2-yn-1-ol (6 mmol) and excess t-BuOK as base were added to a stirred solution of (1,3,5-triazine-2,4-diyl)dimorpholine (5 mmol) in THF (30 mL) at 0°C. The resulting mixture was stirred at room temperature for 1 h, and at 70°C for an additional 6 h. The progress of the reaction was monitored by thin layer chromatography (TLC). After completion of the reaction, the mixture was cooled to room temperature and quenched with distilled water (50 mL×3). The mixture was subsequently extracted with ethyl acetate (50 mL×3). The organic layer was washed with distilled water (30 mL×3), dried with anhydrous MgSO$_4$,

filtered, and then concentrated in vacuo. The residue was purified by flash column chromatography (ethyl acetate:n-hexane = 1:1) to give **1**.

Compound **1**: Yield: 1.3 g (85%). White powders. m.p. 125−126°C. IR (KBr pellet, cm^{-1}) ν(C−H) 3047, 2983, 2980, ν(C≡C) 2105, ν(C=N) 1583. ^{1}H NMR (CDCl$_3$, ppm) δ 2.42 (t, *J* = 3.0 Hz, 1H), 3.69 (t, *J* = 5.0 Hz, 8H), 3.78 (t, *J* = 5.0 Hz, 8H), 5.17 (d, *J* = 2.5 Hz, 2H). ^{13}C NMR (CDCl$_3$, ppm) δ 43.9 (N*C*H$_2$ in morpholine), 54.1 (O*C*H$_2$), 66.8 (O*C*H$_2$ in morpholine), 74.5 (terminal *C*H), 78.6 (internal *C*), 166.0, 170.0 (triazine ring).

Compound **2**: Yield 1.4 g (84%). White powder. m.p. 119−120°C. IR (KBr pellet, cm^{-1}) ν(C−H) 3065, 2985, 2975, ν(C≡C) 2117, ν(C=N) 1580. ^{1}H NMR (CDCl$_3$, ppm) δ 2.00 (t, *J* = 2.5 Hz, 1H), 2.66 (m, 2H), 3.69 (t, *J* = 5.0 Hz, 8H), 3.77 (t, *J* = 5.0 Hz, 8H), 4.38 (t, *J* = 7.5 Hz, 2H). ^{13}C NMR (CDCl$_3$, ppm) δ 19.2 (*C*H$_2$), 43.9 (N*C*H$_2$ in morpholine), 64.3 (O*C*H$_2$), 66.8 (O*C*H$_2$ in morpholine), 70.0 (terminal *C*H), 80.3 (internal *C*), 166.1, 170.3 (triazine ring).

Compound **3**: Yield 1.35 g (81%). White powder. m.p. 112−114°C. IR (KBr pellet, cm^{-1}) ν(C−H) 3090, 2984, 2980, ν(C≡C) 2120, ν(C=N) 1581. ^{1}H NMR (CDCl$_3$, ppm) δ 1.94 (t, *J* = 2.5 Hz, 1H), 1.97 (m, 2H), 2.35 (m, 2H), 3.69 (t, *J* = 5.0 Hz, 8H), 3.77 (t, *J* = 5.0 Hz, 8H), 4.36 (t, *J* = 7.5 Hz, 2H). ^{13}C NMR (CDCl$_3$, ppm) δ 14.4, 27.9 (*C*H$_2$), 43.8 (N*C*H$_2$ in morpholine), 65.2 (O*C*H$_2$), 66.9 (O*C*H$_2$ in morpholine), 68.8 (terminal *C*H), 83.7 (internal *C*), 166.1, 170.9 (triazine ring).

2.3. Synthesis of 4,4'-[6-(o-Carboranylalkoxy)-1,3,5-triazine-2,4-diyl]dimorpholines (4).

General Procedure. Compounds **1** (5 mmol) in toluene (10 mL) was added to a stirred solution of decaborane (0.73 g, 6 mmol) and 1.2 equiv of N,N-dimethylaminoaniline in dry toluene (30 mL) at 0°C, through a cannula over a period of 60 min. The reaction mixture was maintained at 0°C for 30 min, and warmed slowly to room temperature. Subsequently, the reaction mixture was heated under reflux for 12 h. After cooling, the insoluble materials were removed by filtration through Celite®. The filtrate was diluted with CH_2Cl_2 (50 mL) then washed with distilled water (30 mL×3), dried with anhydrous $MgSO_4$, filtered, and then concentrated in *vacuo*. The residue was purified by flash column chromatography (ethyl acetate:n-hexane = 1:1) to give **4**.

Compound **4**: Yield 1.1 g (51%). Pale yellow crystals. m.p. $157-158^{\circ}$C. IR (KBr pellet, cm^{-1}) ν(B−H) 2588, ν(C−H) 3021, 2997, ν(C=N) 1587. ^{1}H NMR (CDCl$_3$, ppm) δ 3.55 (t, $J = 6.0$ Hz, 8H), 3.74 (t, $J = 6.0$ Hz, 8H), 4.45 (br s, 1H), 4.83 (s, 2H). ^{13}C NMR (CDCl$_3$, ppm) δ 47.5, 48.8 (NCH_2 in morpholine), 66.0 (OCH_2), 70.5, 70.8 (OCH_2 in morpholin), 73.0 (*C*H in carborane), 165.8, 169.3 (triazine ring).

Compound **5**: Yield 1.1 g, (49%). Pale yellow crystals. m.p. $137-139^{\circ}$C. IR (KBr pellet, cm^{-1}) ν(B−H) 2596, ν(C−H) 3005, 2991, ν(C=N) 1576. ^{1}H NMR (CDCl$_3$, ppm) δ 2.69 (t, $J = 6.0$ Hz, 2H), 3.56 (t, $J = 5.1$ Hz, 8H), 3.75 (t, $J = 5.1$ Hz, 8H), 3.89 (br s, 1H), 4.34 (t, $J = 6.0$ Hz, 2H). ^{13}C NMR (CDCl$_3$, ppm) δ 36.2 (*C*H$_2$Cab), 47.6, 48.0 (NCH_2 in morpholine), 63.7 (OCH_2), 70.6, 70.9 (OCH_2 in morpholine), 72.3 (*C*H in carborane), 165.9, 169.5 (triazine ring).

Compound **6**: Yield 0.9 g. (40%). Pale yellow powder. m.p. $131-133^{\circ}$C. IR (KBr pellet, cm^{-1}) ν(B−H) 2591, ν(C−H) 2998, 2989, ν(C=N) 1580. ^{1}H NMR (CDCl$_3$, ppm) δ 1.89 (m, 2H), 2.35 (t, $J = 8.8$ Hz, 2H), 3.53 (t, $J = 5.9$ Hz, 8H), 3.63 (br s, 1H), 3.73 (t, $J = 5.9$ Hz, 8H), 4.20 (t, $J = 6.0$ Hz, 2H). ^{13}C NMR (CDCl$_3$, ppm) δ 28.7 (*C*H$_2$Cab), 35.0 (*C*H$_2$CH$_2$), 47.6, 47.9 (NCH_2 in morpholine), 64.7 (OCH_2), 70.6, 71.0 (OCH_2 in morpholine), 74.8 (*C*H in carborane), 165.9, 170.1 (triazine ring).

2.5. Crystal Structure Determination

Crystals of **4** and **5** were obtained from dichloromethane (CH_2Cl_2), sealed in glass capillaries under argon, and mounted on the diffractometer. Preliminary examination and data collection were performed using a Bruker SMART CCD detector system single-crystal X-ray diffractometer equipped with a sealed-tube X-ray source (40 kV×50 mA) using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Preliminary unit cell constants were determined with a set of 45 narrow-frame (0.3° in ω) scans. The double-pass method of scanning was used to exclude any noise. The collected frames were integrated using an orientation matrix determined from the narrow-frame scans. The SMART software package was used for data collection, and SAINT was used for frame integration[11]. Final cell constants were determined by a global refinement of *xyz* centroids of reflections harvested from the entire data set. Structure solution and refinement were carried out using the SHELXTL-PLUS software package[12].

2.6. Supporting Information

CCDC 1815582 and 1815583 contains the supplementary crystallographic data of **4** and **5** for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

3. Results and Discussion

As outlined in Scheme 1, the starting 4,4'-(6-chloro-1,3,5-triazine-2,4-diyl)dimorpholine was prepared by reacting 2,4,6-trichloro-1,3,5-triazine with morpholine in a 1 : 2 stoichiometry using K_2CO_3 as base in THF for 12 h at 0°C and the product was purified by flash column chromatography. Under these conditions, two morpholine units completely displaced two chloride atoms to yield the disubstituted 1,3,5-triazine product. TLC was used to follow the disappearance of the starting material, which occurred after 6 h of vigorous stirring at 0°C. 4,4'-(6-Chloro-1,3,5-triazine-2,4-diyl)dimorpholine is moderately stable in air and can be purified by flash column chromatography. Since this simple step synthesis is high yielding (>80%), multi-gram quantities of the 4,4'-(6-chloro-1,3,5-triazine-2,4-diyl)dimorpholine can be produced with little effort. The new compound was characterized by ^{1}H and ^{13}C NMR. The ^{1}H

NMR spectrum of the 4,4'-(6-chloro-1,3,5-triazine-2,4-diyl)dimorpholine showed resonances at δ 3.68 and 3.75 due to the ethylene protons in the NCH_2CH_2O of morpholine units. Peaks at δ 43.9 and 66.6 (NCH₂CH₂O) and δ 164.5 and 170.0 (triazine ring) were observed in the ^{13}C NMR spectrum of 4,4'-(6-chloro-1,3,5-triazine-2,4-diyl)dimorpholine.

As shown in Scheme 1, 4,4'-(6-Chloro-1,3,5-triazine-2,4-diyl)dimorpholine was then treated with 1.2 equiv of alkynyl alcohol and t-BuOK as base in THF at room temperature for 12 h to generate, after flash column chromatography, 4,4'-[(6-alkynyloxy)-1,3,5-triazine-2,4-diyl]dimorpholine (1−3) in good yields (1 84%, 2 84%, 3 81%), respectively. The disappearances of the starting materials was monitored by TLC. Compounds 1−3 exhibit characteristic absorption bands in the infrared spectra at around 2105~2120 and 3047~3090 cm^{-1} reflecting the C≡C and C−H bond of the alkynyl groups. The ^{1}H NMR spectrum of 1−3 show resonances at around δ 1.97~2.42 due to the alkynyl CH protons and at around δ 3.69~3.78 due to the ethyl protons in the NCH_2CH_2O unit of the morpholine moieties. The ^{13}C NMR spectrum of 1−3 exhibit resonances at around δ 43.8~43.9 (NCH₂), 66.8~66.9 (OCH₂), and 74.5 (1), 70.0 (2) and 68.8 (3) due to the alkynyl CH, respectively.

As shown in Scheme 1, target compounds 4−6 can be easily prepared using a modified procedure of a previously reported method[13]. Thus, treatment of 1 with decaborane (B$_{10}$H$_{14}$) and N,N-dimethylaniline in toluene produced target compounds 4, in moderate yields (4 51%, 5 49%, 6 40%). Compounds 4−6 show characteristic B−H vibration absorption bands in the infrared (IR) spectrum at 2588 (4), 2596 (5) and 2591 cm^{-1} (6). The diagnostic signals of the cage C−H unit of the carborane for compounds 4−6 were observed at δ 4.25 (4), 3.89 (5) and 3.63 (6) in the ^{1}H NMR spectra, and at δ 73.0 (4), 72.3 (5) and 74.8 (6) in the ^{13}C NMR spectra, respectively. The alkynyl C−H unit signals at δ 2.42 (1), 2.00 (2) and 1.94 (3) in the ^{1}H NMR spectra of the starting materials move downfield upon cyclization; moreover, the spectra of compounds 4−6 contained a broad signal caused by B−H peaks of the o-carborane units from δ 0.5~3.4. To authenticate the assignments of the final compounds made on the basis of NMR spectral data, an X-ray structural study of 4 and 5 were undertaken to confirm the molecular structure shown in Fig. 1 and 2.

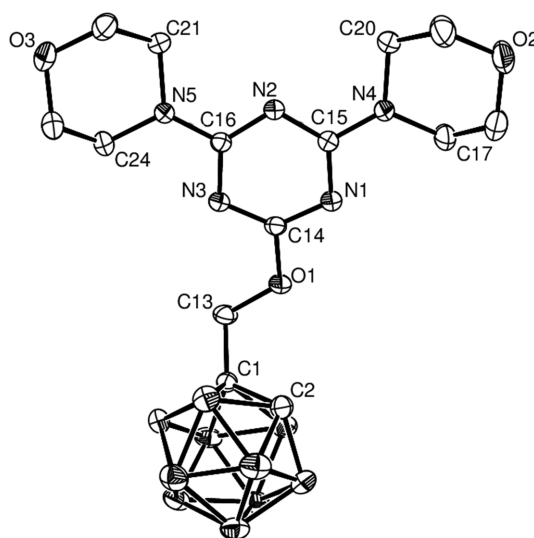**Fig. 1.** Molecular structure of 4 with thermal ellipsoids drawn at the 30% level. Hydrogen atoms are omitted for clarity.
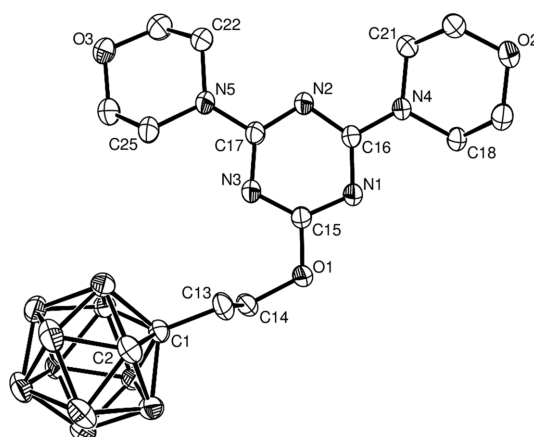

Fig. 2. Molecular structure of 5 with thermal ellipsoids drawn at the 30% level. Hydrogen atoms are omitted for clarity.

X-ray structural analysis of compounds 4 and 5 was consistent with the structures proposed based on the NMR assignments. Selected crystallographic data and selected bond lengths and angles are summarized in Table 1 and 2, respectively. The ORTEP diagram in Fig. 1 shows the molecular structure of 4 and confirms to be that of 4,4'-[6-(o-carboranylmethoxy)-1,3,5-triazine-2,4-diyl]dimorpholine. The morpholine rings adopt a chair conformation, as expected. The C−N dis-

Table 1. Crystal data and structure refinement for **4** and **5**.

Identification code	cnu1002	cnu1001
Empirical formula	$C_{14} H_{29} B_{1}0 N_5 O_3$	$C_{15} H_{30} B_{10} N_5 O_3$
Formula weight	423.52	436.54
Temperature	293(2) K	293(2) K
Wavelength	0.71073 A	0.71073 A
Crystal system, space group	Triclinic, P-1	Triclinic, P-1
Unit cell dimensions	$a = 7.03880(10)$ Å, $\alpha = 87.1180(10)°$	$a = 9.7505(3)$ Å, $\alpha = 88.224(2)°$
	$b = 9.7116(2)$ Å, $\beta = 88.4920(10)°$	$b = 11.1591(4)$ Å, $\beta = 74.390(2)°$
	$c = 16.9533(3)$ Å, $\gamma = 74.5480(10)°$	$c = 11.9630(4)$ Å, $\gamma = 67.088(2)°$
Volume	1115.49(3) Å^{-3}	1150.74(7) Å^{-3}
Z, D_{calc}	2, 1.261 g/cm^3	2, 1.260 g/ cm^3
m	0.079 mm^{-1}	0.079 mm^{-1}
$F(000)$	444	458
Crystal size	0.24 × 0.20 × 0.15 mm	0.26 × 0.22 × 0.19 mm
θ range for data collection	1.20 to 28.14°	1.77 to 28.34°
Limiting indices	−9≤h≤9, −10≤k≤12, −21≤l≤21	−13≤h≤13, −14≤k≤14, −15≤l≤15
Reflections collected / unique	16295 / 5176 [R(int) = 0.0292]	31151 / 5711 [R(int) = 0.0465]
Completeness to θ = 25.96	94.9%	99.8%
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	5176 / 0 / 289	5711 / 0 / 299
Goodness-of-fit on F^2	1.055	1.124
Final R indices [I>2s (I)]	R1 = 0.0528, wR2 = 0.1335	R1 = 0.0647, wR2 = 0.2064
R indices (all data)	R1 = 0.0829, wR2 = 0.1540	R1 = 0.0840, wR2 = 0.2238
Extinction coefficient		0.011(5)
Largest diff. peak and hole	0.205 and -0.272 e.Å^{-3}	0.807 and -0.360 e. Å^{-3}

[a]$R_1 = \Sigma||F_o|-|F_c||$ (based on reflections with $F_o^2 > 2sF^2$), [b]$wR_2 = [\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$; $w = 1/[\sigma^2(F_o^2)+(0.095P)^2]$;, $P = [max(F_o^2, 0)+2F_c^2]/3$ (also with $F_o^2 > 2\sigma F^2$)

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Table 2. Selected bond lengths (Å) and angles (°) for **4** and **5**.

	4		
C1−C2	1.627(2)	N1−C14	1.317(2)
O1−C14	1.358(2)	N1−C15	1.352(2)
O1−C13	1.429(2)	N3−C14	1.318(2)
N4−C15	1.348(2)	N3−C16	1.355(2)
N5−C16	1.350(2)	N2−C15	1.339(2)
C1 C13	1.520(2)	N2−C16	1.335(2)
C14−O1−C13	118.8(1)	C13−C1−C2	119.7(1)
O1−C13−C1	109.4(1)	N1−C14−N3	129.4(1)
N1−C14−O1	111.7(1)	N3−C14−O1	118.9(1)
N2−C15−N1	125.4(1)	N2−C16−N3	125.5(1)
	5		
C1−C2	1.638(3)	O1−C14	1.444(2)
O1−C15	1.351(2)	C13−C14	1.504(3)
C1−C13	1.531(2)	N1−C15	1.324(2)
N1−C16	1.349(2)	N2−C16	1.342(2)
N2−C17	1.336(2)	N3−C15	1.311(2)
N3− C17	1.347(2)		
C15−N3−C17	113.03(15)	C15−N1−C16	112.50(14)
C17−N2−C16	114.04(16)	C15−O1−C14	116.47(14)
C13−C1−C2	116.26(14)	C14−C13−C1	112.70(16)
O1−C14−C13	111.28(16)	N3−C15−N1	128.89(17)
N3−C15−O1	118.03(15)	N1−C15−O1	113.08(15)

Table 3. Geometric parameters of the hydrogen bond geometry (Å, º) for **4** and **5**.

D−H···A	D−H	H···A	D···A	D−H···A
		4		
C2−H2···O2[i]	1.10	2.27	3.143	135
C13−H13A···N2[ii]	0.97	2.58	3.521	163
C13−H13B···N3	0.97	2.23	2.687	108
C17−H17B···N1	0.97	2.33	2.754	105
C20−H20A···N2	0.97	2.35	2.765	105
C21−H21B···N2	0.97	2.35	2.758	105
C24−H24A···N3	0.97	2.36	2.751	103
		5		
C2−H2···O3[iii]	1.10	2.13	3.163	156
C13−H13A···N1	0.97	2.53	3.038	113
C18−H18B···N2	0.97	2.33	2.771	107
C21−H21A···N3	0.97	2.31	2.753	107
C22−H22A···N3	0.97	2.37	2.790	106
C25−H25A···N1	0.97	2.32	2.754	106

Symmetry codes: (i) 1+x, y, z; (ii) −x, 1−y, −z; (iii) −1+x, y, z

tances of C_3N_3 ring are in the double bond range (average 1.33 Å). This value is similar to the mean bond distances reported in other (1,3,5-triazine-2,4-diyl)dimorpholine derivatives, e.g. 1.34 Å for 2-chloro-4,6-dimorpholino-1,3,5-triazine[14], 1.34 Å for 4,6-dimorpholino-N-(2,4,4-trimethylpentan-2-yl)-1,3,5-triazin-2-amine[15]. The C1−C2 bond length of carborane is within the normal range [1.627(2) Å]. This value is similar to the C1−C2 bond length of the parent compound [1.629(6) and 1.630(6) Å][16] and is somewhat longer than that of our previous result [1.614(3) Å][17]. The B−C bond lengths lie between 1.686(3) and 1.713(3) Å, while the B−B bond lengths range from 1.762(3) to 1.782(3) Å. The five-membered C13−O1−C14−N3−H13B ring, containing the triazine ring and the C13−H13B···N3 hydrogen bond, is 0.051(1) Å and nearly coplanar with the 1,3,5-triazine ring, with a dihedral angle of 1.18(1)º. As shown in Table 3, the remainder of the inter- and intramolecular hydrogen bonds are of non-classical fashion and weak, and occur between the heteroatom (O2, N1, and N2), the carborane C2−H2 and morpholine C−H units, with C···N distances varying from 2.687 to 3.521 Å. As shown in Fig. 3, these hydrogen bonds appear to play an important role in controlling the molecular conformation of compound **4**. Interestingly, all C−N−C bond angles are around 113º and all N−C−N bond angles are around 127º; for example, a C14−N1−C15
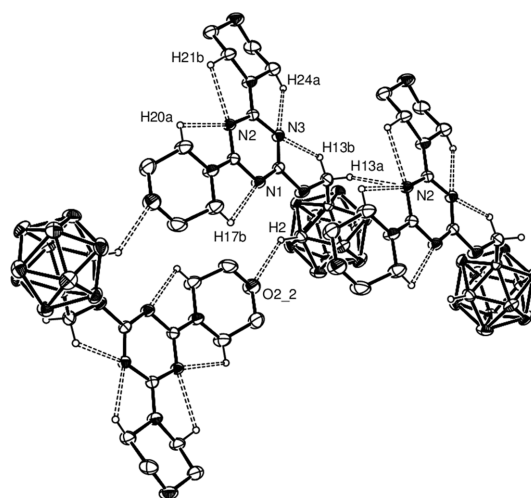

Fig. 3. Non-classical inter- and intramolecular hydrogen bond of **4**. Hydrogen bonds are shown by dashed lines, and hydrogen atoms not involved in hydrogen bonding omitted for clarity.

angle of 112.6(1)º and a N2−C16−N3 angle of 125.5(1)º. The torsion angle between the 1,3,5-triazine ring and the ether linkage is 178.9(3)º. The torsion angles of C20−N4−C15−N1 and C24−N5−C16−N3 are 175.0(2) and 179.4(2)º, respectively. The planes of C17−N4−C20 and C21−N5−C24 are nearly coplanar with the 1,3,5-triazine ring, with dihedral angles of 9.69(3) and
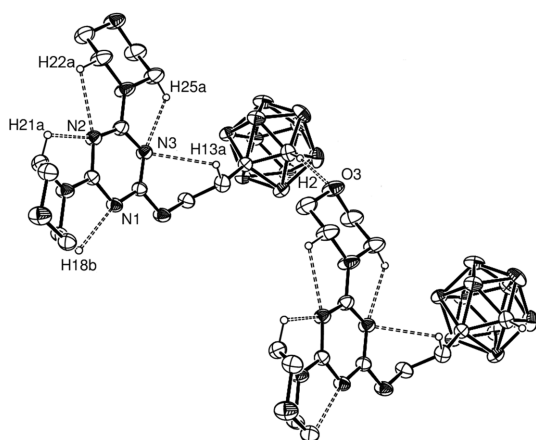
Fig. 4. Non-classical inter- and intramolecular hydrogen bond of **5**. Hydrogen bonds are shown by dashed lines, and hydrogen atoms not involved in hydrogen bonding omitted for clarity.

13.68(1)°, respectively.

Crystals of **5** that were suitable for single-crystal X-ray diffraction were cultured by slowly evaporating CH_2Cl_2 at room temperature and normal pressure. Compound **5** crystallizes in the triclinic space group, P−1. The C−N bond lengths in the 1,3,5-triazine ring vary from 1.311(2) to 1.349(2) Å, which are between the bond lengths of a C−N single bond (1.470 Å) and C=N double bond (1.250 Å). The C1−C2 bond length of carborane is in a normal range [1.638(3) Å][18]. The B−C bond lengths lie between 1.690(3) and 1.730(3) Å, while the B−B bond lengths range from 1.758(3) to 1.793(4) Å. As shown in Table 3, two kinds of hydrogen bonds exist in the crystal of **5**: a single intermolecular hydrogen bond (C2−H2···O2) and five intramolecular hydrogen bonds (C−H···N). Its packing structure is configured by the extensive hydrogen bonding interaction to form a 3D network (Fig. 4). Moreover, the bond angles of triazine ring, which are between 112.5(1) and 128.9(2)°, are close to 120°, confirming the tautomerism of 1,3,5-triazine rings. The torsion angles of C21−N4−C16−N1 and C22−N5−C17−N3 are −174.1(2) and 179.6(2)°, respectively. Moreover, the torsion angles of C14−O1−C15−N1, C1−C13−C14−O1, C15−O1−C14−C13, and C14−C13−C1−C2 are −175.8(2), 173.4(2), −80.5(2), and 167.8(2)°, respectively. The planes of C18−N4−C21 and C22−N5−C25 are nearly coplanar with the 1,3,5-triazine ring, with a dihedral angles of 4.50(4) and 7.01(2)°, respectively.

4. Conclusion

In conclusion, we described the first report of intra- and intermolecular hydrogen bond containing 6-o-carboranylalkoxy substituted (1,3,5-triazine)dimorpholine compounds. A combination of X-ray crystallographic and spectroscopic studies confirms the nature of these compounds. The X-ray crystallographic study of compounds **4** and **5**, as described above, provides the first structural data for the 4,4'-[6-(o-carboranylalkoxy)-1,3,5-triazine-2,4-diyl]dimorpholine compounds. Additionally, it has been shown that intra- and intermolecular hydrogen bonds has a significant influence not only on the stability of the compounds **4** and **5** but also on the formation of their 3D networks.

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