Synthesis of Various(Amino)diacetatoboranes*

G. J. Barrett and D. T. Haworth

The halogen substituted bis-(amino)diacetatoboranes, $[B(O_2CCl_3)_2NH_2]_2$, $[B(O_2CHCl_3)_2NH_2]_2$, $[B(O_2CCH_2Cl)_2NH_2]_2$, $[B(O_2CCBr_3)_2NH_2]_2$, $[B(O_2CCH_2Br)_2NH_2]_2$, $[B(O_2CCF_3)_2NH_2]_2$, and $[B(O_2CCH_2F)_2NH_2]_2$ have been prepared by the reaction of B-trichloroborazine with the appropriate haloacetic acids. The shift of the carbonyl absorption in the infrared spectra and the shift of the NH_2 absorption in the ${}^1H$-nmr spectrum are discussed in comparison to the parent compound, $[B(O_2CCH_3)_2NH_2]_2$. Explanations are given for carbonyl singlets and doublets appearing in the infrared spectra.

Introduction

In attempting to find a suitable solvent for substitution reactions on borazine, Schaeffer[1] observed that B-trichloroborazine reacts with glacial acetic acid to yield an aminoborane dimer. Support for a cyclic structure

$$2B_3Cl_3N_3H_3 + 12CH_3COOH \rightarrow 3[(CH_3CO_2)_2BNH_2]_2 + 6HCl \quad (1)$$
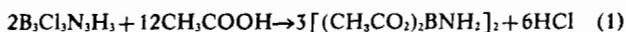
came from its infrared spectrum, which showed a boron-nitrogen stretching frequency at 960 cm^{-1} as compared to monomer's stretch at 1350-1500 cm^{-1}.[2] Recently we have reported on the reaction of B-trichloroborazine with AgO$_2$CCH$_3$ to yield B-triacetatoborazine (borazinyl esters of acetic acid).[3] Unsymmetrically substituted borazine esters have since been reported by Beachley.[4] This paper describes related studies dealing with the reaction of various halogen substituted acetic acids with B-tricholoroborazine to give corresponding (amino)diacetatoborane dimers and spectral and magnetic properties which bear on the structure of these complexes.

Experimental Section

The infrared spectra were measured on a Beck-

man IR-12 using Nujol and hexachloro-1,3-butadiene mulls in CsI plates for all compounds except $[B(O_2-CCHF_2)_2NH_2]_2$, for which a KBr pellet was used.

^1H-nmr spectra were measured on a Varian A-60, using acetic acid as solvent with TMS as internal standard.

The experimental molecular weights were determined by cryoscopy in acetic acid. Elemental analyses were be Alfred Bernhardt Microanalytisches Laboratorium and Chemalytics, Inc.

B-trichloroborazine[5] was prepared by the reaction of NH$_4$Cl with the adduct of CH$_3$CN:BCl$_3$.

A typical preparation method was as follows. To a solution of 2.00 g of B$_3$Cl$_3$N$_3$H$_3$ in 20 ml of anhydrous (C$_2$H$_5$)$_2$O at 0°C (N$_2$ atmosphere) was added 7.45 g CF$_3$CO$_2$H in 20 ml of ether. The mixture was stirred at 0°C for 15 min. and then refluxed for twelve hours. Removal of the solvent gave white crystals; 6.48 g (78.5%). Analytical data are given in Table I.

Results and Discussion

The infrared frequencies and assignments of the prepared halogen substituted (amino)diacetatoborane dimers are given in Tables II and III. The N–H stretching absorption in all of the infrared spectra is either broad, broad with a shoulder, or a doublet in the 3190-3260 cm^{-1} region with intensity ranging from medium to strong. This is indicative of the primary NH$_2$ group in the four-membered ring of the aminoborane dimers. For $[B(O_2CCH_2Br)_2NH_2]_2$, two absorptions appeared in the N–H scissoring region. Both absorptions were assigned to N–H scissoring, and the correct assignment is in question. The B–O stretching frequency is in the 1350-1310 cm^{-1} region of the spectrum[6] except for $[B(O_2CCHF_2)_2]_2$. This assignment is given to a shoulder at 1340 cm^{-1}.

The B–N ring stretching frequency of an aminoborane dimer is usually observed in the 900 cm^{-1} region of the spectrum.[2] This stretching frequency for the prepared dimers is observed in the range of 890-940 cm^{-1}. A much lower frequency (1500-1350 cm^{-1}) is observed for B–N stretching in monoaminoboranes. One can assume that the nitrogen is not sharing its free electron pair with boron and partial

* Presented in part at the 5th Great Lakes Regional Meeting of the American Chemical Society, Peoria, Illinois, June 10-11, 1971.
(1) G. L. Brennan, G. H. Dahl, and R. J. Schaeffer, *J. Am. Chem. Soc.*, **82**, 6248 (1960).
(2) K. Niedenzu and J. W. Dawson, «Boron-Nitrogen Compounds», Springer-Verlag, N.Y., page 52-53 (1965).
(3) D. T. Haworth and E. S. Matushek, *Chem. and Ind.* (London), 130 (1970).
(4) O. T. Beachley, Abstracts of papers presented at the 161st ACS National Meeting, Los Angeles, California, March 29-April 2, 1971, No. 79, Inorganic Division. See also, *J. Am. Chem. Soc.*, **93**, 5066 (1971).

(5) E. F. Rothergy and L. F. Hohnstedt, *Inorg. Chem.*, **6**, 1065 (1967).
(6) L. J. Bellamy, M. F. Gerrard, M. F. Lappert, and R. L. Williams, *J. Chem. Soc.*, 2412 (1958).

Table I. Percent Yield, Melting Point, Molecular Weight, and Element Analysis of the Halogen Substitued Bis-(Amino)diacetatoboranes.

Dimer	Percent Yield (%)	Melting Point (°C)	Mol. Wt. (g/mol) Calcd.	Found	%C Calcd.	Found	H% Calcd.	Found	N% Calcd.	Found
[B(O₂CCF₃)₂NH₂]₂	78.0	112-116	506	496	19.00	18.50	0.80	0.90	5.54	5.39
[B(O₂CHCF₂)₂NH₂]₂	76.4	102-106	434	440	22.15	20.90	1.86	2.20	6.46	6.89
[B(O₂CCCl₃)₂NH₂]₂	88.5	113-116	703	715	13.47	13.35	0.57	0.70	3.93	3.79
[B(O₂CCHCl₂)₂NH₂]₂	79.0	124-126	565	538	16.99	17.23	1.43	1.69	4.95	4.61
[B(O₂CCH₂Cl)₂NH₂]₂	85.7	154-156	428	403	22.47	21.92	2.83	2.91	6.55	6.11
[B(O₂CCBr₃)₂NH₂]₂	89.8	104-107	1237	1180	7.77	8.39	0.33	0.42	2.27	2.24
[B(O₂CCH₂Br)₂NH₂]₂	60.1	128-130	605	615	15.87	15.65	2.00	2.15	4.63	4.90

Table II. Infrared Frequencies (cm⁻¹) and Assignments of the Halogen Substituted Bis-(Amino)diacetatoboranes

Dimer	N-H Stret.	C-H Stret.	N-H Scissor	CH₂ Scissor	B-O Stret.	C-O Asymm. Stret.	C-O Symm. Stret.
[B(O₂CCF₃)₂NH₂]₂	3260		1560		1320	1240	1125
[B(O₂CCHF₂)₂NH₂]₂	3240		1550		1340(?)	1280	1130
[B(O₂CCCl₃)₂NH₂]₂	3240		1570		1310	1255	1135
[B(O₂CCHCl₂)₂NH₂]₂	3250 3215	3020	1547		1323	1215	1135
[B(O₂CCH₂Cl)₂NH₂]₂	3240 3200	3010 2965	1560	1415	1310	1335	1135
[B(O₂CCBr₃)₂NH₂]₂	3220 3190 (sh)		1570		1338	1250	1120
[B(O₂CCH₂Br)₂NH₂]₂	3230 3200	3020 2960	1580(?) 1560(?)	1406	1323	1258	1125

Table III. Infrared Frequencies (cm⁻¹) and Assignments of the Halogen Substituted Bis-(Amino)diacetatoboranes

Dimer	CF₃ Asymm. Stret.	CF₃ Symm. Stret.	CH₂Cl Wagg	CH₂Br Wagg	B-N Stret.	C-Cl Asymm. Stret.	C-Cl Symm. Stret.	C-Br Asymm. Stret.	C-Br Symm. Stret.
[B(O₂CCF₃)₂NH₂]₂	1180	1075			940				
[B(O₂CCHF₂)₂NH₂]₂	1280	1090			927				
[B(O₂CCCl₃)₂NH₂]₂					910	850	690		
[B(O₂CCHCl₂)₂NH₂]₂					920	830	695		
[B(O₂CCH₂Cl)₂NH₂]₂			1225		910		800		
[B(O₂CCBr₃)₂NH₂]₂					890			680	610
[B(O₂CCH₂Br)₂NH₂]₂				1190	910				570

B–N double bond character, as in the monoamino-boranes, is eliminated.

In the spectrum of [B(O₂CCHF₂)₂NH₂]₂, the broadness of the absorption at 1280 cm⁻¹ for [B(O₂CCHF₂)₂NH₂]₂ was attributed to C–F asymmetric and C–O asymmetric stretching, since they both absorb in this region. Since CH₂Cl wagging and C–O asymmetric stretching cause absorptions approximately in the same region, the strong, broad absorption at 1225 cm⁻¹ for [B(O₂CCH₂Cl)₂NH₂]₂ was assigned to CH₂Cl wagging and C–O asymmetric stretching.

The assigned carbonyl stretching absorptions (Table IV) are broad singlets except for [B(O₂CCCl₃)₂NH₂]₂, [B(O₂CCH₂Cl)₂NH₂]₂, [B(O₂CCBr₃)₂NH₂]₂ and [B(O₂CCH₂Br)₂NH₂]₂ which appear as a doublet. The doublets for [B(O₂CCH₂Cl)₂NH₂]₂ and [B(O₂CCH₂Br)₂NH₂]₂ may be attributed to cis and gauche rotational isomers of the acetato group.[7,8] The term cis is used here to indicate that the halogen atom is cis

Table IV. Carbonyl Stretching Frequencies.

Dimer	ν₁(cm⁻¹)	ν₂(cm⁻¹)	Average of ν₁ and ν₂(cm⁻¹)
[B(O₂CCF₃)₂NH₂]₂	1780	—	—
[B(O₂CCl₃)₂NH₂]₂	1760	1720	1740
[B(O₂CCBr₃)₂NH₂]₂	1832	1710	1721
[B(O₂CCHF₂)₂NH₂]₂	1772	—	—
[B(O₂CCHCl₂)₂NH₂]₂	1750	—	—
[B(O₂CCH₂Cl)₂NH₂]₂	1753	1710	1732
[B(O₂CCH₂Br)₂NH₂]₂	1740	1708	1724
[B(O₂CCH₃)₂NH₂]₂	1725[10]	—	—

(10) E.S. Matushek, M.S. Thesis, Marquette University, 1969.

to the carbonyl oxygen.

Cis Isomer   *Gauche* Isomer
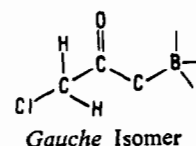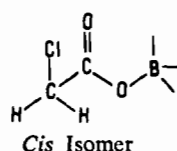
(7) T. L. Brown, *J. Am. Chem. Soc.*, **80**, 3513 (19-58).
(8) T. L. Brown, *Spectrochim. Acta*, **18**, 1615 (1962).

The carbonyl doublet appearing in the spectra of $[B(O_2CCBr_3)_2NH_2]_2$ and $[B(O_2CCCl_3)_2NH_2]_2$ can not be explained by using rotational isomers. These doublets may be attributed to intramolecular hydrogen bonding between carbonyl oxygen and the hydrogen bonded to nitrogen. One carbonyl oxygen of an acetato group is hydrogen bonded while another carbonyl oxygen is not, thus resulting in the appearance of two carbonyl stretching frequencies; the lower frequency being assigned to the coordinated carbonyl.
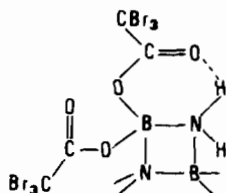
The two carbonyl frequencies of trivalent acyloxy derivatives of boron have also been explained on the basis of one carbonyl bonded to boron and the other is uncoordinated.[9] One would analogously expect a carbonyl doublet for the dimer $[B(O_2CCF_3)_2NH_2]_2$; however, only a carbonyl singlet is observed in the spectrum. This may be due to the fact that there is only intramolecular hydrogen bonding between the more electronegative fluorine and the hydrogen bonded to nitrogen. Thus, only one carbonyl stretching frequency will be observed, as opposed to two frequencies resulting from hydrogen bonding of the carbonyl oxygen.
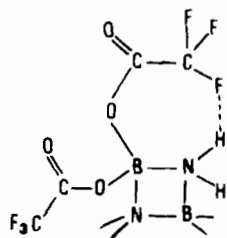
The carbonyl absorptions of $[B(O_2CCHF_2)_2NH_2]_2$ and $[B(O_2CCHCl_2)_2NH_2]_2$ are broad singlets. The dimer of $[B(O_2CCHF_2)_2NH_2]_2$ could have rotational isomers, thus resulting in a carbonyl doublet. Since only a singlet appears, this may indicate that there is intramolecular hydrogen bonding between a fluorine and hydrogen bonded to a nitrogen, thus hindering internal rotation of the acetato C–C bond and ultimately the *cis* and *gauche* rotational isomers. Also, the expected doublet resulting from the rotational isomers may not be resolved into a doublet. $[B(O_2CCHCl_2)_2NH_2]_2$ could have a carbonyl doublet resulting from rotational isomers, as well as a carbonyl doublet resulting from intramolecular hydrogen bonding between carbonyl oxygen and a hydrogen bonded to a nitrogen. These various carbonyl absorptions are probably not resolved and constitute the broad carbonyl singlet. In all cases where a carbonyl

(9) L. W. Duncanson, W. Gerrard, M. F. Lappert, H. Pyszoro, and R. Shafferman, *J. Chem. Soc.*, 3652 (1958).

doublet is observed, some weak hydrogen bonding is not precluded.

Table IV includes the carbonyl stretching frequencies for the aminodiacetato borane dimers prepared and that of the parent compound, $[B(O_2CCH_3)_2NH_2]_2$. There is a general trend in the increase in frequency for the mono-, di-, and tri-halogeno substituted dimers. For the trihalogeno substituted dimers, the carbonyl frequencies are 1721 cm^{-1}, 1740 cm^{-1}, 1780 cm^{-1} for the tribromo, trichloro, and trifluoro dimers, respectively. The values of the tribromo and trichloro substituted dimers are averages of the two carbonyl absorptions. If the two absorptions for the tribromo and trichloro dimers are taken individually, the values are 1732 and 1710 cm^{-1}, and 1760 and 1720 cm^{-1} respectively. These values also show a definite increase in carbonyl frequencies as more electronegative halogens are substituted. Analogously, there is an increase in carbonyl frequencies in the dihalogeno and monohalogeno series as more electronegative halogens are substituted. This shift in frequency is accounted for by the electron density of the polar C=O bond is closer to the oxygen in the parent compound. Halogen will inductively pull the electron density farther away from the carbonyl oxygen and closer to carbon resulting in a carbonyl bond more covalent; thus raising the carbonyl stretching frequency.

Table V. Delta (δ) Values of the N-H Absorption from ^{1}H-nmr

Dimer	N-H Absorption (p.p.m.)
$[B(O_2CCF_3)_2NH_2]_2$	—5.0+
$[B(O_2CCCl_3)_2NH_2]_2$	—5.9—
$[B(O_2CCBr_3)_2NH_2]_2$	—5.7
$[B(O_2CCHF_2)_2NH_2]_2$	—5.7
$[B(O_2CCHCl_2)_2NH_2]_2$	—5.6
$[B(O_2CCH_2Cl)_2NH_2]_2$	—5.4
$[B(O_2CCH_2Br)_2NH_2]_2$	—5.2
$[B(O_2CCH_3)_2NH_2]_2$	—5.1

The ^{1}H-nmr of all the dimers prepared were quite similar with respect to the broad (30-50 Hz) –NH$_2$ resonance (Table V) which shifted to low field relative to the parent compound depending on the halogen atom bonded to the α-carbon of the acetato group. For the parent compound, the –NH$_2$ absorption peaked at a delta value of —5.1 p.p.m. A shift to low field may be explained in terms of the electron withdrawing effect of the halogens which deshield the protons of –NH$_2$. For increased identical halogen substitution, the downfield shift increased, and it also increased for each mono-, di-, and trihalogeno substituted series. The shift is solvent independent, again suggesting intramolecular hydrogen bonding rather than intermolecular hydrogen bonding.