# Cyclopropylboranes and the Carbonium Ion Analogy

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Abstract: The synthesis of the compounds tricyclopropylborane, cyclopropyldimethylborane, cyclopropyldifluoroborane, and cyclopropyldichloroborane is described. The nmr and optical spectra of these compounds have been determined in order to investigate the possibility of conjugation between the cyclopropyl moiety and the vacant B(2p) orbital. Although the ^{11}B and ^{19}F nmr chemical shifts could be taken to infer the order of conjugative ability vinyl > cyclopropyl > alkyl toward boron, the low-temperature nmr spectra of cyclopropyldimethylborane and cyclopropyldifluoroborane give no evidence for the "bisected" cyclopropyl conformation. The observation that cyclopropylboranes do not exhibit intramolecular charge-transfer bands in the 2000–4000-Å range also differentiates these compounds from their isoelectronic carbonium ion counterparts. Tricyclopropylborane is a stronger Lewis acid than triisopropylborane since it will form complexes with $(CH_3)_3N$ and tertiary phosphines.

There is a considerable current interest in the ability of the cyclopropane ring to conjugate with π orbitals. This effect manifests itself in a variety of chemical and physical properties[1] such as solvolysis rates, thermodynamic stabilities, and electronic spectra. Structural studies have established that the "bisected" cyclopropyl conformation (**1**) represents a conformational energy minimum for the dimethylcyclopropyl-

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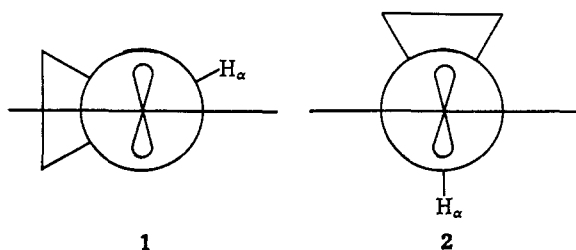
carbonium ion,[2] cyclopropylcarboxaldehyde,[3] cyclopropyl methyl ketone,[4] cyclopropylcarboxylic acid chloride,[5] phenylcyclopropane,[6] vinylcyclopropane,[7] and cyclopropylsemidiones.[8] These observations can be rationalized particularly well by invoking the Walsh model of cyclopropane[9] since the "bisected" conformation affords maximum overlap of the extraannular 2p electron with the 2p electrons of a π system or a carbonium ion.[10] It should also be pointed out, however, that the "symmetrical" conformation (**2**) is preferred in certain cyclopropyl-substituted anion radicals.[11] Here the cyclopropyl ring is behaving as an *acceptor*, and conjugation *from* the external p orbital to the in-

traannular orbitals results in the observed conformation.

In view of the interesting results obtained with the above organic systems, it became important to test the possibility that the cyclopropyl (c-C_3H_5) moiety might conjugate with the vacant 2p orbital of boron. Accordingly, we have synthesized $(c$-$C_3H_5)_3B$,[12] c-C_3H_5-$B(CH_3)_2$, c-$C_3H_5BF_2$, and c-$C_3H_5BCl_2$ and examined these compounds spectroscopically with a view to testing this hypothesis. The selection of these compounds was based on the concept that boranes and carbonium ions (where cyclopropyl conjugation is optimum) are isoelectronic. The ground-state functional similarity of these species has been demonstrated by their reactions with *e.g.*, diazoalkanes.[13] The electronic spectral similarities of boranes and carbonium ions have also been noted and the ultraviolet transitions of each interpreted on the basis of a ligand $\rightarrow$ 2p(vacant) intramolecular charge-transfer model.[14,15]

Experimental Section

All volatile materials were handled in high-vacuum manifolds with U-traps interconnected by Stock-type mercury float valves or chlorofluorocarbon-greased stopcocks. Molecular weights were measured by the Regnault method, and vapor pressures were determined in an immersible tensimeter. Materials of low volatility were handled under a dry nitrogen atmosphere or in a helium-filled drybox.

Materials. Trimethylphosphine was prepared by the reaction of CH_3MgBr with PCl_3 in diethyl ether solution. The $(CH_3)_3P$ was stabilized as the complex $[(CH_3)_3PAgI]_4$ by reaction with AgI in aqueous KI solution.[16,17] The trimethylphosphine was freed from the complex by heating. The compound was identified by its vapor tension (161 mm at 0°) and by its characteristic infrared spectrum.[18] Published procedures were used to prepare triisopropylborane,[19] $(CH_3)_3B$,[20,21] dicyclopropylmercury,[22] and $(CH_3)_2$-

(1) For reviews see M. Y. Lukina, *Russ. Chem. Rev.* (English Transl.), 419 (1962); W. A. Bernett, *J. Chem. Educ.*, **44**, 17 (1967).
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(3) L. S. Bartell, J. P. Guillory, and A. P. Parks, *J. Chem. Phys.*, **43**, 647 (1965).
(4) L. S. Bartell, J. P. Guillory, and A. P. Parks, *ibid.*, **43**, 654 (1965).
(5) L. S. Bartell, J. P. Guillory, and A. P. Parks, *J. Phys. Chem.*, **69**, 3043 (1965).
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(7) G. R. DeMare and J. S. Martin, *ibid.*, **88**, 5033 (1966).
(8) G. A. Russell and H. Malkus, *ibid.*, **89**, 160 (1967).
(9) A. D. Walsh, *Trans. Faraday Soc.*, **45**, 179 (1949).
(10) The alternative "bent-bond" model with "sp⁵" extra-annular hybrids does not preclude conjugation of this kind. However, the sp⁵–p overlap is both smaller than pure p overlap and less sensitive to changes of dihedral angle; see W. A. Bernett, *J. Chem. Educ.*, **44**, 17 (1967), and references therein.
(11) N. L. Bauld, R. Gordon, and J. Zoeller, Jr., *J. Am. Chem. Soc.*, **89**, 3948 (1967).

(12) A synthesis of this compound has been described previously in a brief communication; see P. Binger and R. Koester, *Angew. Chem.*, **74** 652 (1963).
(13) J. E. Leffler and B. G. Ramsey, *Proc. Chem. Soc.*, 117 (1961); H. Whitlock, *J. Am. Chem. Soc.*, **84**, 3807 (1962).
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(17) F. G. Mann and A. F. Wells, *ibid.*, 708 (1938).
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(19) E. Krause and P. Nobbe, *Ber.*, **64**, 2112 (1931).
(20) H. C. Brown, *J. Am. Chem. Soc.*, **67**, 376 (1945).
(21) W. J. Lehmann, C. O. Wilson, Jr., and I. Shapiro, *J. Chem. Phys.*, **28**, 777 (1958).

BCl.[23] Cyclopropyl bromide, BCl_3, BF_3, $B(OCH_3)_3$, and Li metal were obtained commercially. Boron trichloride was freed from traces of HCl by passage through a $-112°$ trap. The other materials were used without further purification.

Cyclopropyllithium.[24] Cyclopropyl bromide (0.4 mole) was added dropwise over a period of 1 hr to a mixture of clean Li wire and 200 ml of ether in a 1-l. three-necked flask equipped with a dropping funnel, condenser, and mechanical stirrer. The reaction mixture was maintained at 0° throughout the addition, and the appropriate provisions were made to ensure a nitrogen atmosphere. Stirring was continued for an additional hour to permit completion of the reaction.

Tricyclopropylborane. A solution of 0.1 mole of $(CH_3O)_3B$ in 50 ml of ether was added dropwise to the cyclopropyllithium reagent. Following this the reaction mixture was gently refluxed overnight. The excess lithium reagent was hydrolyzed with 100 ml of freshly prepared, degassed 2.5 N NaOH solution. After filtration the ether layer was separated and dried over anhydrous Na_2SO_4 for 24 hr. After evaporation of the solvent the residual liquid was fractionally distilled to give ~9 g of a clear colorless liquid (~75% yield) boiling at 32° (1.5 mm). Anal.[25] Calcd for $C_9H_{15}B$: C, 80.65; H, 11.28. Found: C, 80.55; H, 11.11. Principal ir peaks (cm^{-1}) were at 3085, 3010, 1460, 1373, 1200, 1150, 1023, 965, 912, 862, 851, and 660. Table I shows the volatility of tricyclopropylborane at various temperatures and pressures.

Table I. Volatility of Tricyclopropylborane

$(\text{Log } P = 7.481 - 2143.2/T)$
$(t_{760} = 192.7;$ Trouton constant $= 21.04$ eu)

Temp, °C	81.90	75.50	71.80	62.30	58.80	42.50	30.00
P_{obsd}, mm	28.53	21.26	17.72	12.07	10.59	5.35	3.28
P_{calcd}, mm	27.85	21.58	18.54	12.37	10.59	4.91	2.59

Cyclopropyldimethylborane. A mixture of 6.4 mmoles of $(CH_3)_2BCl$ and 7.0 mmoles of dicyclopropylmercury was allowed to warm slowly from $-196°$ in an evacuated, sealed Pyrex tube. Reaction took place suddenly as evidenced by the formation of a white solid. Fractionation of the volatiles with U-traps held at -78, -112, and $-196°$ yielded 6.0 mmoles of clear, colorless cyclopropyldimethylborane in the $-112°$ trap. Anal. Calcd for $C_5H_{11}B$: C, 73.28; H, 13.53; mol wt, 81.95. Found: C, 73.20; H, 13.27; mol wt, 82.3. Principal ir peaks (cm^{-1}) were at 3106, 3020, 1363, 1305, 1110, and 910. Volatility data are given in Table II.

Table II. Volatility of Cyclopropyldimethylborane

$(\text{Log } P = 7.4916 - 1552.1/T)$
$(t_{760} = 63.5;$ Trouton constant $= 21.09$ eu)

Temp, °C	36.10	29.40	26.20	21.50	17.30	12.00
P_{obsd}, mm	297.30	231.05	200.65	167.65	141.06	112.30
P_{calcd}, mm	297.10	230.02	202.74	167.58	140.63	111.88

Cyclopropyldichloroborane was prepared in an analogous manner by the action of 8.0 mmoles of BCl_3 on 8.6 mmoles of dicyclopropylmercury. Fractionation of the volatiles with traps at -78, -100, and $-196°$ yielded 4.0 mmoles of cyclopropyldichloroborane in the $-100°$ trap. Anal. Calcd for $C_3H_5BCl_2$: C, 29.43; H, 4.10; Cl, 57.75; mol wt, 122.8. Found: C, 29.11; H, 4.16; Cl, 57.67; mol wt, 123.7. Principal ir peaks (cm^{-1}) were at 3110, 3040, 1360, 1190, 1137, 1130, 1047, 995, 955, 920, 910, and 535. Volatility data are given in Table III.

Cyclopropyldifluoroborane. Either of the following methods can be used to prepare this compound. In both cases, however, the

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(24) D. Seyferth and H. M. Cohen, *J. Organometal. Chem.*, **1**, 15 (1963).

(25) All elemental analyses were performed by Alfred Bernhardt Mikroanalytisches Laboratorium, Max-Plank-Institut für Kohlenforschung, Mülheim (Ruhr), West Germany.

Table III. Volatility of Cyclopropyldichloroborane

$(\text{Log } P = 7.8674 - 1819.3/T)$
$(t_{760} = 91.68°;$ Trouton constant $= 22.8$ eu)

Temp, °C	0.9	13.00	19.9	29.50	35.70	41.2
P_{obsd}, mm	17.30	32.80	45.00	72.15	95.70	119.70
P_{calcd}, mm	16.95	32.34	45.66	71.85	94.86	120.26

yields are disappointing (~10%) due to the formation of considerable quantities of involatile materials.

(a) **The Reaction of Tricyclopropylborane and BF_3.** In a typical reaction a mixture of 4.0 mmoles of tricyclopropylborane and 8.0 mmoles of BF_3 was allowed to warm slowly from $-196°$ in an evacuated 500-ml bulb. After standing for 1 hr at ambient temperature, the bulb was opened and the volatiles were transferred into the vacuum system. Fractionation through traps held at -50, -100, -150, and $-196°$ yielded approximately 0.4 mmole of cyclopropyldifluoroborane in the $-150°$ trap. Anal. Calcd for $C_3H_5BF_2$: C, 40.09; H, 5.61; mol wt, 89.88. Found: C, 40.19; H, 5.65; mol wt, 90.1. The vapor tension of the pure material is 4 mm at $-78°$. Attempts to improve the yield of cyclopropyldifluoroborane by varying reaction times and rate of warming of the reagents were not successful. Principal ir peaks (cm^{-1}) were at 3100, 3020, 1420, 1360, 1352, 1230, 1222, 915, 910, 677, and 515.

(b) **The Reaction of Dicyclopropylmercury with BF_3.** Essentially the same procedure was adopted as that described for the preparation of cyclopropyldichloroborane.

Infrared Spectra. Most of the infrared spectra were measured on a Perkin-Elmer Model 337 grating spectrophotometer. Some spectra were recorded on a Beckman I.R.-7 spectrophotometer equipped with NaCl and CsI optics. Vapor samples were run at 10 mm pressure in a 100-mm path length cell equipped with KBr windows. Less volatile samples were run as neat liquid films between KBr plates.

Nmr Spectra. Ambient-temperature ^1H spectra were recorded on a Varian A-60 instrument. ^{11}B, ^{19}F, and low-temperature ^1H spectra were measured on a Varian HA-100 spectrometer.

Ultraviolet Spectra. A Cary Model 14 recording spectrophotometer was employed for ultraviolet spectra in the 2000–4000-Å range. Most samples were run in a quartz gas cell of 10-mm path length. The vacuum ultraviolet spectrum of tricyclopropylborane was determined[26] in a 10-cm stainless steel cell equipped with LiF windows on a McPherson Model 218 spectrophotometer. This instrument employs a 0.3-m, F/5.3 plane grating vacuum scanning monochromator together with a Model 665 double-beam attachment.

Results

(a) **Nmr.** The ^1H nmr spectrum of c-$C_3H_5B(CH_3)_2$ (20% solution in CH_2Cl_2) consisted of a complex cyclopropyl resonance at τ 9.4 and a methyl singlet at τ 9.7. No splitting of the methyl resonance was observed down to $-100°$ of either the CH_2Cl_2 solution sample or a neat sample. The ^{19}F nmr spectrum of c-$C_3H_5BF_2$ consisted of a quartet at -39.4 ppm (relative to external BF_3) with $J_{BF} = 72$ Hz (Figure 1a). Upon cooling, the quartet broadened and collapsed to a singlet (Figure 1b). The ^{11}B, ^{19}F, and ^1H chemical shifts of the cyclopropylboranes are shown in Tables IV, V, and VI, respectively, along with some pertinent data from other laboratories.

(b) **Ultraviolet Spectroscopic Studies.** Tricyclopropylborane vapor caused no detectable absorption of uv radiation in the 2000–4000-Å range. In the vacuum uv range (1400–2000 Å) a broad, featureless absorption was detected between 1500 and 1800 Å with λ_{max} at 1690 Å. c-$C_3H_5BF_2$ was also transparent in the 2000–4000-Å range. c-$C_3H_5BCl_2$ and c-$C_3H_5(CH_3)_2$ displayed "end absorption" at ~1950 Å with ϵ 1700 and 1500, respectively. However, the latter data should

(26) The authors wish to express their gratitude to Dr. S. E. Webber for performing this experiment.

Table IV. ^{11}B Nmr Chemical Shifts

Compound	^{11}B chemical shift[a]	Ref
$C_2H_5BCl_2$	−45.2	31
$(c\text{-}C_3H_5)BCl_2$	−41.1	This work
$C_6H_5BCl_2$	−35.9	b
$CH_2{=}CHBCl_2$	−35.9	31, c
BCl_3	−29.4	31
$C_2H_5BF_2$	−10.3	31
$(c\text{-}C_3H_5)BF_2$	−9.98	This work
$CH_2{=}CHBF_2$	−5.0	31
$(CH_3)_3B$	−68.2	b, c
$(c\text{-}C_3H_5)B(CH_3)_2$	−63.5	This work
$CH_2{=}CHB(CH_3)_2$	−57.7	c

[a] Relative to $(CH_3O)_3B$ external standard. [b] W. D. Phillips, H. C. Miller, and E. L. Muetterties, *J. Am. Chem. Soc.*, **81**, 4496 (1959). [c] C. D. Good and D. M. Ritter, *ibid.*, **84**, 1162 (1962).

Table V. ^{19}F Nmr Chemical Shifts

Compound	^{19}F chemical shift[a]	Ref
BF_3	0	b
$C_6H_5BF_2$	−35	c
$CH_2{=}CHBF_2$	−38	b
$(c\text{-}C_3H_5)BF_2$	−39.4	This work
$n\text{-}C_3H_7BF_2$	−54	b

[a] Relative to BF_3 external standard. [b] T. D. Coyle and F. G. A. Stone, *J. Am. Chem. Soc.*, **82**, 6223 (1960). [c] J. P. Grivit, unpublished work cited by T. D. Coyle and F. G. A. Stone in "Progress in Boron Chemistry," Vol. 1, H. Steinberg and A. L. McClosky, Ed., Pergamon Press, Oxford, 1964, Chapter 2.

Table VI. Chemical Shifts of the α- and β-Hydrogens of Cyclopropane Derivatives

Compound	α-H[a]	β-H	Ref
Cyclopropane	9.78	9.78	b
Cyclopropyl bromide	7.16	9.05	c
Cyclopropylammonium ion	7.07	9.07	33
Tricyclopropylcarbonium ion	7.74	7.74	33
Cyclopropyldimethylcarbonium ion	6.3	6.3	33
Cyclopropyl methyl ketone	8.1	9.2	d
Tricyclopropylphosphine	9.6	9.6	34
Cyclopropyllithium	12.5	9.8	24
Cyclopropyldifluoroborane	10.2	9.48	This work
Tricyclopropylborane	10.3	9.4	This work
Cyclopropyldimethylborane	9.4	9.4	This work
Cyclopropyldichloroborane	9.1	8.98	This work

[a] In τ units. [b] K. B. Wiberg and B. J. Nist, *J. Am. Chem. Soc.*, **83**, 1226 (1961). [c] K. B. Wiberg and B. J. Nist, *ibid.*, **85**, 2788 (1963). [d] P. Yates and C. D. Anderson, *ibid.*, **80**, 1264 (1958).

be regarded as tentative since the Cary 14 slits are at wide aperature below about 2050 Å.

(c) Lewis Acidity Experiments. Proton magnetic resonance spectroscopy was employed as a tool for the Lewis acidity experiments. The data are shown in Table VII. It is evident that triisopropylborane does not complex with either $(CH_3)_3N$ or $(CH_3)_3P$ as shown by the lack of evidence for new peaks compared with either the free acid or the free base. Tricyclopropylborane forms 1:1 complexes with both $(CH_3)_3N$ and $(CH_3)_3P$ since in either system the most intense cyclopropyl ring peak moves upfield and the $(CH_3)_3P$ or $(CH_3)_3N$ peaks move downfield. Further, the J_{PCH} coupling increased from 1.86 to 8.30 Hz as the phosphorus atom undergoes complexation. No peaks attributable to the free acid or free base were detected in either the $(CH_3)_3N$ or $(CH_3)_3P$ system. As expected,
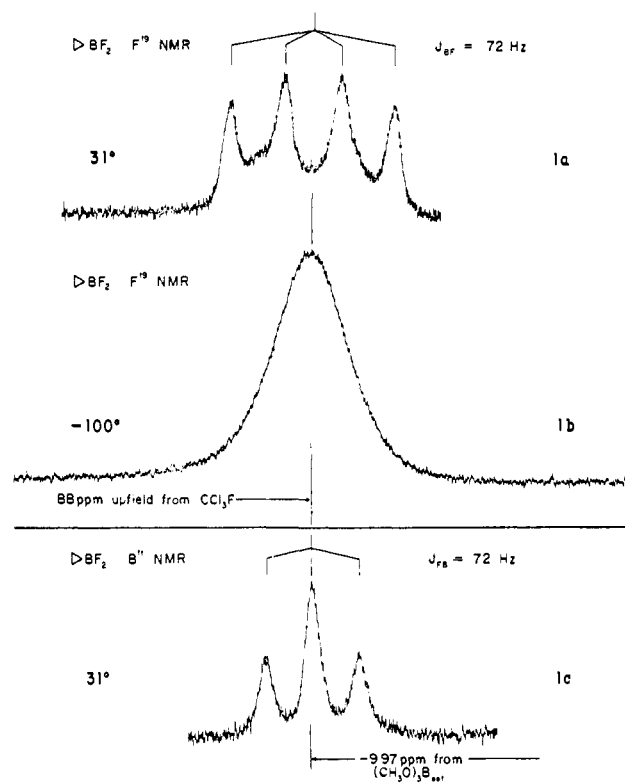

Figure 1. Nmr spectra of cyclopropyldifluoroborane.

1:1:1 mixtures of $(i\text{-}C_3H_7)_3B$, $(c\text{-}C_3H_5)_3B$, and $(CH_3)_3N$ or $(i\text{-}C_3H_7)_3B$, $(c\text{-}C_3H_5)_3B$, and $(CH_3)_3P$ showed peaks corresponding to $(c\text{-}C_3H_5)_3BN(CH_3)_3$ or $(c\text{-}C_3H_5)_3\text{-}BP(CH_3)_3$ and free $(i\text{-}C_3H_7)_3B$.

Discussion

The low-temperature proton magnetic resonance results with cyclopropyldimethylborane are clearly different from those obtained by Pittman and Olah[2] with the isoelectronic dimethylcyclopropyl carbonium ion. These authors observed nonequivalent methyl groups for this cation at −60° and thus elegantly demonstrated that the "bisected" cyclopropyl group conformation (1) is preferred in this system. The plausible reasons for the lack of splitting of the CH_3 resonance of cyclopropyldimethylborane are: (a) any CH_3 group inequivalence is overshadowed by peak broadening due to boron quadrupolar relaxation; (b) a "symmetrical" cyclopropyl conformation is adopted (2); or (c) the cyclopropyl group is still rotating freely at −100°, thus placing an upper limit of ∼3.0 kcal/mole on the B–C rotational barrier. Evidence for ^{11}B quadrupolar relaxation can, in fact, be found in the low-temperature spectra of cyclopropyldifluoroborane (Figure 1b). The ambient temperature ^{19}F 1:1:1:1 quartet ($J_{^{11}B-^{19}F}$ = 72 Hz)[27] passes through a broad doublet-like structure and finally collapses to a broad singlet line at −100°. Similar observations have been made previously with the ^{19}F

(27) There is evidence of slight collapsing of the ^{19}F spectrum at ambient temperature (Figure 1a). Nevertheless, we take $J^{11}_{B}-^{19}_{F}$ to be the multiplet separation of this spectrum. The value thus obtained is in good agreement with that obtained from the ^{11}B spectrum (Figure 1c).

Table VII. ¹H Nmr Chemical Shift Data[a] for Tricyclopropylborane and Triisopropylborane Lewis Acidity Studies

System[b]	$(i\text{-}C_3H_7)_3B$[c]	$(c\text{-}C_3H_5)_3B$[c]	$(CH_3)_3P$	$(CH_3)_3N$	J_{PCH}, Hz
$(i\text{-}C_3H_7)_3B$	4.40	...	...	...	...
$(c\text{-}C_3H_5)_3B$	...	4.71			
$(CH_3)_3P$	...	...	4.32	...	1.86
$(i\text{-}C_3H_7)_3B + (CH_3)_3P$	4.44	...	4.25	...	1.82
$(c\text{-}C_3H_5)_3B + (CH_3)_3P$	...	5.29	4.10	...	8.30
$(i\text{-}C_3H_7)_3B + (c\text{-}C_3H_5)_3B + (CH_3)_3P$	4.43	5.26	4.08	...	8.40
$(CH_3)_3N$	...	...	...	3.20	...
$(i\text{-}C_3H_7)_3B + (CH_3)_3N$	4.41	...	...	3.16	...
$(c\text{-}C_3H_5)_3B + (CH_3)_3N$	...	5.14	...	3.82	...
$(i\text{-}C_3H_7)_3B + (c\text{-}C_3H_5)_3B + (CH_3)_3N$	4.39	5.12	...	2.83	...
$(i\text{-}C_3H_7)_3 + (c\text{-}C_3H_5)_3B$	4.40	4.70	...	...	...

[a] Chemical shifts given in parts per million upfield from internal CH_2Cl_2. [b] Mixtures were 0.25 M in each component. [c] Position of most intense peak.

nmr spectra of BF_3[28] and BF_2H,[29] and the problem of quadrupolar relaxation has been treated theoretically.[30] Evidence for reason b, the preference for a symmetrical conformation (2), has been presented by Bauld and coworkers.[11] In cyclopropyl-substituted anion radicals the excess charge density at the proximate carbon atom is negative; hence in such cases the cyclopropyl group appears to play the unusual role of π acceptor.

To see if a distinction could be made between possibilites a, b, and c, other (and regrettably less direct) lines of evidence were sought. Since Coyle, Stafford, and Stone[31] have interpreted ¹¹B and ¹⁹F chemical shift data on the basis that such data support the idea of boron–carbon π bonding in vinylboranes, we have determined these parameters for the cyclopropylboranes. For three types of organoboranes (Table IV) the ¹¹B chemical shifts of the cyclopropyl derivatives adopt a position which is intermediate between vinyl- (or phenyl-) substituted boranes and alkylboranes. A similar trend is apparent in the ¹⁹F data of the difluoroboranes (Table V). Bearing in mind the obvious hazards of attempting to relate chemical shifts to π bonding,[32] it is nevertheless of interest to note that both the ¹¹B and ¹⁹F chemical shift data (Tables IV and V) suggest that the order of conjugative ability toward boron is vinyl > cyclopropyl > alkyl.

The chemical shifts of the α- and β-hydrogens of cyclopropyl groups have also been employed to infer delocalization effects. For instance, Deno, Richey, and coworkers[33] have noted that it is possible to distinguish between purely inductive withdrawal and concerted conjugative-inductive interactions. Thus, (Table VI) in cyclopropyl bromide or the cyclopropylammonium cation the α protons are shifted downfield by more than τ 2.5 from cyclopropane. By contrast the β protons are only moved downfield by

$\tau \sim 0.7$. In the cyclopropyl-substituted carbonium ions both the α protons and the β protons are shifted downfield by approximately the same extent due to conjugative delocalization of positive charge into both α and β positions. Uncharged species where both inductive and conjugative effects are operative, such as cyclopropyl methyl ketone, assume intermediate chemical shifts.

Recently[34] we have found that the α- and β-proton chemical shifts of tricyclopropylphosphine are equal and close to that of cyclopropane in accordance with the expectation of relatively nonpolar P–C bonds and minimal π bonding in this linkage. In cyclopropyllithium[24] the polarity of the lithium–carbon bond in the sense Li^+–C^- places an appreciable negative charge on the α-hydrogen atom but leaves the β-hydrogens relatively unaffected. Likewise in the cyclopropylboranes the α-proton is at higher field than the β-protons (or equal in the case of cyclopropyldimethylborane) presumably due to the B^+–C^- σ-bond polarity. However, the chemical shift differences between the α- and β-protons are not as large in the cyclopropylboranes as in cyclopropyllithium since boron is less electropositive than lithium. Any conjugative effects would be expected to counteract the polarity of the B–C σ bond, thus diminishing the τ values of both the α- and β-hydrogens. It may be significant, therefore, that among the cyclopropylboranes the smallest β-hydrogen τ value occurs with cyclopropyldichloroborane since qualitatively one might expect the most cyclopropyl→vacant B(2p) orbital π interaction with Cl substituents on boron. However, the observed trend with the cyclopropylboranes may relate to simple inductive effects which are operative at both the α- and β-hydrogens, although such an interpretation would not be in accord with Huheey's group electronegativities[35] which are in the order $BF_2 > BCl_2 > B(CH_3)_2$.

Next we turned to optical spectroscopy to investigate the possibility of an intramolecular charge transfer between the cyclopropyl group and the vacant B(2p) orbital. Ramsey[14] has applied the well-known Mulliken expression[36] $E_{CT} = IP - EA - C + R$ to an interpretation of the ultraviolet spectra of a number of boranes and their isoelectronic carbonium ion analogs. The energy of the charge-transfer band, E_{CT}, was found to depend principally on the ionization potential, IP,

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of the donor (*i.e.*, the substituent on B or C⁺). The electron affinity of boron, EA, was taken to be zero. The resonance energy, R, was neglected, and the Coulomb electrostatic energy, C, was approximated for each system.

Using Ramsey's approach[14] in conjunction with the value 10.06 eV for the ionization potential of cyclopropane,[37] we predict λ_{max} for tricyclopropylborane at approximately 2400 Å. Support for a predicted transition in this region comes from the fact that the tricyclopropyl carbonium ion exhibits an intense absorption at 2700 Å with ϵ 22,600.[38] In view of the foregoing, therefore, it was somewhat surprising to find that tricyclopropylborane does not absorb in the expected region (2000–3500 Å). The 1690-Å absorption in the vacuum ultraviolet region is not necessarily the ligand → B(2p) charge-transfer band since it could be due to an absorption within the cyclopropyl moiety. For instance, cyclopropane[39] exhibits intense absorptions at 1202, 1449, and 1596 Å, and cyclopropyl chloride[40] is reported to show a smooth, broad absorption beginning at 1923 Å. While a certain amount of departure from the expected region could be ascribed to variations in the Coulombic term, C (as has been suggested for trivinylborane[14]), it is believed that tricyclopropylborane represents an exception to the charge-transfer hypothesis. In any event the electronic spectral data in no way support the idea of boron-carbon π bonding. End absorption was detected with cyclopropyldichloroborane and cyclopropyldimethylborane. However, as pointed out in the Experimental Section, these are to be regarded as preliminary data, and we defer further comment pending a more detailed spectroscopic investigation.

Another way of assessing π bonding in boron Lewis acids concerns the effect of such bonding on the Lewis acidity. The now classical "inverted" order of acidity, $BF_3 < BCl_3 < BBr_3$, is a case in point.[41] The most obvious experiment seemed to be to compare the Lewis acidities of triisopropylborane and tricyclopropylborane toward $(CH_3)_3N$ and $(CH_3)_3P$ since the isopropyl group is the open-chain counterpart of the cyclopropyl group. However, Brown[20] has already established that triisopropylborane will not complex with $(CH_3)_3N$ down to $-80°$. Our nmr data confirm this result and also indicate that this borane does not complex with $(CH_3)_3P$. By contrast tricyclopropylborane does form complexes with $(CH_3)_3N$ and $(CH_3)_3P$ (and tricyclopropylphosphine[34]). Although the steric requirements of cyclopropyl groups are admittedly less than those of isopropyl groups, it should be pointed out that the carbon atom hybridizations are approximately sp^3 and sp^2 in the isopropyl and cyclopropyl groups, respectively. The higher per cent s character and consequent larger electronegativity[42] of the cyclopropyl α-carbon atom would therefore also result in tricyclopropylborane being a stronger Lewis acid than triisopropylborane. On the other hand, conjugation between the cyclopropyl moiety and the vacant B(2p) orbital would serve to reduce the Lewis acidity of tricyclopropylborane. The present evidence does not permit a distinction to be made between steric and electronic factors.

In summary it can be said that the only indication of a π-type interaction between a cyclopropyl group and a vacant B(2p) orbital comes from the ^{11}B and ^{19}F chemical shift data of the cyclopropylboranes. Bearing in mind the inherent danger of relating chemical shifts to one factor such as π bonding, the most reasonable interpretation of the low-temperature ^1H and ^{19}F nmr data on cyclopropyldimethylborane and cyclopropyldifluoroborane is possibility c, *i.e.*, that the cyclopropyl group is still freely rotating at $-100°$ in these compounds. However, it would be desirable to have a microwave or electron diffraction study of a cyclopropylborane before making an unequivocal statement.

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