BORON—NITROGEN COMPOUNDS

LXXVI *. (HEXAFLUOROISOPROPYLIDENIMINO)BORANES

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Summary

The compound $(CF_3)_2C=N-B[N(CH_3)_2]_2$ has been synthesized and spectroscopic data on species of the type $(CF_3)_2C=N-BR_2$ have been evaluated; the data substantiate a linear arrangement for the central C=N—B moiety of the compounds.

Introduction

Monomeric iminoboranes containing the basic skeleton $\supset C=N-B\subset$ can be viewed as isoelectronic analogs of allenes, $\supset C=C=C\subset$, provided one assumes back-bonding of π-electrons from the nitrogen to the vacant p_z-orbital of boron in the former species. However, experimental data on such iminoboranes are relatively scarce [2] and are not all in consonance. An X-ray study on $(C_6H_5)_2$-C=N—BR$_2$ (R = mesityl) seems to substantiate an allene-like structure for the compound with a C=N—B bond angle of 170° [3] and LCAO calculations result in a B—N bond order of 1.59 for the cited compound [4]. The limited available dipole moment data [5,6] do not appear to be convincing evidence to dispute the linearity of the C=N—B skeleton and a population analysis [7] seems to favor an allene-like structure. Vibrational spectroscopic as well as ^{11}B NMR data on iminoboranes appear to be yet inconclusive.

The compound $(CF_3)_2C=N-B(CH_3)_2$ has recently been synthesized and preliminary data on the species substantiated the existence of a linear C=N—B skeleton for the compound [8]. These data are now elaborated on in detail and, in conjunction with data obtained for the new compound $(CF_3)_2C=N-B[N-(CH_3)_2]_2$ and some additional related species, appear indeed to be best interpreted in terms of a linear allene-like skeleton for compounds of the type $(CF_3)_2C=N-BR_2$.

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* For part LXXV see ref. 1.

Results and discussion

Hexafluorisopropylideniminobis(dimethylamino)borane (I), $(CF_3)_2C=N-B-[N(CH_3)_2]_2$, is readily obtained when N-lithiohexafluoroisopropylidenimine, $(CF_3)_2C=NLi$ [9], is treated with bis(dimethylamino)chloroborane, $ClB[N-(CH_2)_2]_2$. The slightly yellow liquid I has an absorption band at 309 nm with an extinction coefficient of about 400. The mass spectrum of the compound features a parent peak (appearance potential: 5.6 ± 0.3 eV) at m/e 263 (40% relative intensity of the base peak at m/e 99). In contrast to the mass spectrum of tris(dimethylamino)borane, $B[N(CH_3)_2]_3$, which is characterized by fragmentation with the preferential loss of methyl and dimethylamino groups, the mass spectral fragmentation of I is dominated by the loss of CF_3 and $(CF_3)_2CN$ from the parent ion. The proton NMR spectrum of I (50% solution in CH_2Cl_2 exhibits) only one singlet with δ 2.54 ppm; two singlets observed in the ^{13}C NMR spectrum of the compound (50% solution in C_6D_6 vs. TMS) with δ 39.3 and 38.5 ppm, respectively, are assigned to the carbon atoms of the dimethylamino groups. This observation suggests a slight distortion from coplanarity of the latter groups. The multi-line vibrational spectrum of the compound is not readily assigned; however, a medium intensity absorption near 1768 cm^{-1} seems to be typical for the type of compound under consideration, i.e., involving a C=N—B moiety. Additional spectroscopic data of I are discussed below.

A C=N stretching frequency has been assigned for $(CF_3)_2C=NH$ at 1701 cm^{-1} [10]; only very minor frequency shifts are observed for this absorption if the N-bonded hydrogen is replaced by D, CH_3, or C_2H_5 to 1694, 1704, and 1698 cm^{-1}, respectively [11]. On the other hand, N-borylation causes a rather drastic shift of this mode to 1820 cm^{-1} for $(CF_3)_2C=N-BR_2$ with R = CH_3 and to 1841 cm^{-1} when R = C_6H_5. These data illustrate the influence of N-borylation on this particular vibration which in these (hexafluoroisopropylidenimino)boranes seems unlikely to be a pure C=N stretch. Rather, the data suggest that the observed band assumes a C=N—B group character in the iminoboranes. The assignment of a symmetric group stretching frequency in the spectrum of $(CF_3)_2C=N-B(C_6H_5)_2$ at 1098 cm^{-1} [11] seems to support this conclusion, especially since this separation of the symmetric and antisymmetric modes is almost identical to that observed for allene [12].

The ^{14}N NMR spectrum of $(CF_3)_2C=NH$ shows a single resonance line with a chemical shift δ 24 ppm (vs. external aqueous $NaNO_3$) with a half-maximum peak width of 250 Hz; for $(CF_3)_2C=N-B(CH_3)_2$, $\delta(^{14}N)$ 7 ppm. The resonance signal of the former compound is observed at very low field as compared to amines; this is readily interpreted in terms of the CN double bond as well as the inductive effect of the CF_3 groups. The quite similar shielding of the nitrogen in the latter compound is likely to be caused by two opposing factors. The BN π-interaction should promote a low field shift which is, however, opposed by a change in geometry about the nitrogen, assuming a linear C=N—B arrangement in the compound, which should result in a high field shift. Hence, the ^{14}N NMR data would tend to support an allene-like structture of $(CF_3)_2-C=N-B(CH_3)_2$. Additional NMR data on species of the type $(CF_3)_2C=N-BR_2$ are compiled in Table 1.

The ^{19}F NMR spectra show only single resonance lines for the $(CF_3)_2C=$

TABLE 2

SELECTED NMR DATA ON SPECIES OF THE TYPE $(CF_3)_2C=NBR_2$ [a]

R	CH_3	C_6H_5	$N(CH_3)_2$	
$\delta(^{19}F)$	—71.3	—75.0	—71.7	
$\delta(^{13}CF_3)$	117.0	116.5	117.1	
$\delta(^{11}B)$	46.3	52.0	27.0	

[a] Chemical shifts δ in ppm, positive values indicating downfield from the reference; references: ^{19}F = internal $CFCl_3$, ^{13}C = external $Si(CH_3)_4$, ^{11}B = external $(C_2H_5)_2OBF_3$.

N—BR$_2$ species whereas the ^{19}F spectrum of $(CF_3)_2C=NH$ shows two distinct signals (quartets) for the fluorine atoms [13]. These observations indicate that the fluorine atoms of the boron derivatives are all in equivalent environment thus lending credence to molecular structures involving linear C=N—B skeletons. This interpretation is further substantiated by the observation of only a single ^{13}C resonance signal (quartet) for the carbon atoms of the CF$_3$ groups, whereas two such signals are observed in the spectrum of $(CF_3)_2C=NH$. Also, the ^{11}B NMR data do not dispute π-type interaction between nitrogen and boron in the species; indeed, the ^{11}B resonance signals of the $(CF_3)_2C=N—BR_2$ compounds closely parallel those of the corresponding aminoboranes, $R'_2N—BR_2$, where π-interaction and multiple NB bond character is generally recognized.

In conclusion, the available spectroscopic data clearly suggest that in compounds of the type $(CF_3)_2C=N—BR_2$ the central CNB moiety is linear due to NB π-bonding. The compounds may be viewed as semi-inorganic analogs of allenes and may well lend themselves to allene-type chemical reactions.

Experimental

All reactions and transfers were carried out under an argon atmosphere. Solvents were dried by conventional methods and freshly distilled before use.

Infrared spectra of the neat liquids were obtained between CsI plates and vapor phase spectra were recorded using a 10 cm single-path gas cell equipped with CsI windows. All infrared spectra were obtained on a Perkin—Elmer Model 621 spectrometer under standard operating conditions as well as employing a 4X abscissa expansion (wavelength calibration with a polystyrene film). Raman spectra of the neat liquids were recorded with a Jarrell—Ash double-monochrometer Raman instrument using a 50 mW He—Ne laser as the exciting device. Proton NMR spectra (50% solution in CH_2Cl_2) were recorded on a Varian T-60 spectrometer using tetramethylsilane as internal reference. Boron-11 spectra (neat liquids) and fluorine-19 NMR spectra (50% in CH_2Cl_2 versus internal $CFCl_3$) were obtained on Bruker HX8 and 60-E instruments, respectively; the former spectra were obtained using external $B(OCH_3)_3$ as reference and chemical shift values were recalculated for $(C_2H_5)_2O \cdot BF_3$ as reference. Carbon-13 NMR spectra (50% solution in C_6D_6) were recorded on a Varian Model CFT-20 spectrometer using tetramethylsilane as reference. All chemical shift data are given in ppm with positive values indicating downfield from the indicated reference. Mass spectral data were obtained on a Perkin—Elmer—Hitachi RMU-7 instrument.

(CF$_3$)$_2$CNH [13], (CF$_3$)$_2$CNB(C$_6$H$_5$)$_2$ [14], (CF$_3$)$_2$CNB(CH$_3$)$_2$ [8], (CF$_3$)$_2$CNLi [9], ClB[N(CH$_3$)$_2$]$_2$ [15], and (CH$_3$)$_2$BBr [16] were prepared by literature procedures.

The mass spectrum of (CF$_3$)$_2$CNH (70 eV) was found to exhibit only three peaks at m/e (relative abundances in parentheses) 165 (5.0), 97 (2.7), and 96 (100). ^{13}C NMR spectrum: δ (in ppm) 154.6 septet (J(FCC) 39 Hz), 116.7 quartet (J(FC) 278.2 Hz), 115.5 quartet (J(FC) 281.0 Hz).

The 70 eV mass spectrum of (CH$_3$)$_2$BBr showed peaks (relative abundances (in parentheses) of greater than 5% only) at m/e 122 (8.3), 120 (8.7), 107 (7.2), 105 (6.8), 83 (6.1), 41 (100), 40 (37.4), 39 (26.4), 38 (9.1), 37 (14.3), 36 (6.8). ^{13}C NMR spectrum at −7°C: δ'(in ppm) 18.6 quartet (partially collapsed).

Besides the parent peak at m/e 205 (3.8% relative abundance) the 15 eV mass spectrum of (CF$_3$)$_2$C=N—B(CH$_3$)$_2$ showed peaks (relative abundances (in parentheses) of greater than 5% only) at m/e 165 (5.1), 140 (7.4), 136 (15.6), 96 (44.4), 83 (100), 82 (51.5), 81 (6.5), 69 (13.7), 43 (17.8), 42 (5.7), 41 (15.2), 40 (19.4). Vibrational spectrum (gas phase, 2 Torr): 3690vw, 3675vw, 3315vw, 2968vw, 2928(sh), 2858vw, (1829ms at 30 Torr), 1408(sh), 1389w, 1333w, 1262m, 1212ms, 1198ms, 970vw; lower region at 30 Torr: 968vs, 931vs, 904(sh), 778vw, 746(sh), 708 (PQR), 636w, 537m, 478m, 449wm. Raman (neat liquid): 2910s(p), 1820m(br,p), 1430w(br, dp), 1302wm(p), 1241vw, 1219(sh), 1202ms-(p), 1170vw(dp), 1135m(dp), 897m(p), 775w, 748w, 732s(p), 577wm(p), 538w(b), 450vw(b), 405m(p), 380vw(b), 347w, 331ms(p), 289wm(dp), 243vs-(p), 196ms(dp).

Hexafluoroisopropylideniminobis(dimethylamino)borane

A slurry of hexafluoroisopropylidenimino lithium (20.5 g, 120 mmol) in hexane was generated in situ in a 250 ml three-necked flask equipped with a magnetic stirrer, a reflux condenser (0°C), and an addition funnel. The flask was cooled to −30°C and a solution of 11 g (81 mmol) of bis(dimethylamino)-chlorobornae in approximately 30 ml of hexane was added dropwise over a period of about 30 minutes. The mixture was allowed to warm to room temperature during a period of 3 hours and was stored overnight. The reaction vessel was then attached to a vacuum line and hexane was stripped off at −30°C into a trap cooled to −196°C. The off-white pasty residue was heated in an oil bath of 40 to 50°C under a distillation set-up and a pressure of 4 × 10^{-2} Torr and approximately 20 ml of yellow distillate were collected in a −196°C receiving vessel. Two subsequent redistillations using a spinning band column gave 14.2 g (54% yield) of yellow liquid, boiling point 70 to 73°C/99 Torr, which was identified by its mass spectrum as the desired (CF$_3$)$_2$C=N—B[N(CH$_3$)$_2$]$_2$.

Mass spectrum (70 eV, relative adundances (in parentheses) of greater than 6% only): m/e 263 (40.0), 262 (20.0), 260 (8.8), 194 (35.0), 169 (30.0), 168 (8.8), 143 (16.3), 126 (10.0), 117 (25.0), 115 (13.8), 103 (26.3), 100 (11.3), 99 (100), 98 (52.5), 97 (11.3), 96 (33.8), 94 (15.0), 93 (8.8), 92 (61.3), 91 (12.5), 85 (15.0), 84 (11.3), 83 (23.8), 81 (12.5), 74 (99.5), 73 (28.8), 71 (22.5), 70 (26.3), 69 (48.8), 58 (33.8), 57 (27.5), 56 (76.3), 55 (55.0), 54 (11.3), 51 (10.0), 45 (25.0), 44 (99.5), 43 (43.8), 42 (52.5), 41 (37.5), 40 (11.3), 39 (10.0), 29 (8.8), 28 (12.5), 27 (8.8). Vibrational spectrum: IR (neat liquid): 2998m, 2958(sh), 2929s, 2885s, 2871(sh), 2810m, 1773(sh), 1765m,

1546(sh, br), 1535(sh), 1531s, 1526(sh), 1519(sh), 1509(sh), 1495(sh), 1467(sh), 1461s, 1421(sh), 1419s, 1405vs, 1385s, 1368s, 1330vs, 1289(?), 1241vs, 1194-(sh), 1180vs, 1150(sh, br), 1118m, 1108(sh), 1072m, 1068(sh), 997m, 961ms, 910(sh), 906m, 865vw, 753w, 723s, 691m, 670(sh), 667w, 650w, 582w, 532vw, 520vw, 520w, 433w, 405vw, 325(sh, br), 309w, 302(sh), 289(sh). IR (gas phase, 7 Torr): 3005m, 2968m, 2933m, 2891s, 2877(sh), 2817m, 1773(sh), 1768m, 1561(sh), 1544(sh, br), 1535(sh), 1530s, 1524(sh), 1519(sh), 1509(sh), 1496-(sh, br), 1473(sh), 1463m, 1460(sh), 1421m, 1407s, 1372m, 1332s, 1288(?), 1248vs, 1237(sh), 1192vs, 1152(sh), 1145(?), 1123m, 1073w, 1034(?), 1000w, 965vs, 907vw, 867vw, 788w, 752w, 725m, 713(sh), 692w, 651vw, 581vw, 532vw, 521(sh, br), 439vw. Raman (neat liquid): 3002m(p), 2943s(p), 2920(sh), 2902s(p), 2872vs(p), 2814(sh), 2809m(p), 1772w(p), 1492(sh), 1466m(dp), 1460(sh), 1430w(dp), 1425(sh), 1377w(p), 1305vw(b), 1250vw(p), 1190(sh, br), 1157(sh), 1146(?), 1124vw, 1109(sh), 1077vw(dp), 1017(sh), 1003w(p), 976(sh), 914vw, 902(sh), 783w(p), 777(sh), 758(sh), 730vw, 701(vw(p), 698(sh), 677vw, 652vw, 610vw(p), 590w(p), 526w(p), 447vw(p), 414vw(p), 368w(p), 337w(p), 317w(p), 291w(p), 256vw, 216(sh), 186w(dp), 159(sh). ^{13}C NMR spectrum: δ (in ppm) 140.4 quintet, 117.1 quartet, 39.3 singlet, 38.5 singlet.

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