

Contribution from the Laboratoire de Chimie de Coordination, Université Cadi-Ayyad, Boulevard de Safi, Marrakech, Morocco

Atropisomerism in *o*-Aryl-Substituted Borazines

Smail Allaoud, Touriya Zair, Abdallah Karim, and Bernard Frange*[†]

Received May 16, 1989

The fact that aromatic rings of *N,N',N''*-triaryl- (*B,B',B''*-triaryl-) substituted borazines are perpendicular to the plane of the borazine ring is now well documented, in solution¹ but also in the solid state.² As a direct consequence of such a conformation, existence of atropisomers is to be expected for such compounds provided the phenyl ring bears a substituent in the ortho (or meta) position. Those isomers were indeed observed by means of ¹H NMR in the case of (B(*o*-tolyl)N₂)₃.³ Quite unexpectedly, in our previous work on the closely related *B,B',B''*-trimethyl-*N,N',N''*-tri-*o*-tolylborazine, the sole symmetric isomer (*C_{3v}* group) could be obtained.⁴ During the course of this study, evidence for atropisomerism in a boron-nitrogen heterocycle was reported in a quite elegant work by two other groups.^{5,6} The above results,³ at variance with ours, prompted us to investigate in a systematic way, which was the aim of this paper, the existence of atropisomerism in the case of *N,N',N''*-triarylborazines (*o*-YC₆H₄NBX)₃ (Y = H, F, Cl, Br, Me; X = H, F, Cl, Br, Me) by using high-resolution ¹³C NMR and (eventually) ¹⁹F NMR.

Experimental Section

General Data. The solvents were refluxed and distilled from CaH₂. Diethyl ether was distilled over (C₆H₅)₂CO/Na prior to use. All reactions were carried out under a dry argon atmosphere. Routine ¹³C NMR spectra were recorded on a Varian HT 80A spectrometer: 20.0 MHz; solvent and reference CHCl₃ (chemical shifts converted to Me₄Si reference by using δ(Me₄Si) = δ(CHCl₃) + 77.2 ppm); spectra run in 10-mm-diameter tubes with a 5-mm coaxial tube containing D₂O for the lock. Accurate ¹³C NMR spectra were performed on a Bruker AM 300 instrument: 75.4 MHz; solvent CDCl₃; reference SiMe₄. ¹⁹F NMR spectrum were obtained on a Bruker WH 90 instrument: 84.7 MHz; solvent C₆D₆; external reference CF₃COOH.

Preparation of *B,B',B''*-Trifluoro-*N,N',N''*-triarylborazines. These compounds were prepared according to an established procedure⁷ by adding Et₂OBF₃ to the appropriate aniline in presence of a hindered tertiary amine (*N,N*-diethylaniline). Thus, boron trifluoride-diethyl ether (11.70 mL, 0.093 mol), 2-fluoroaniline (3.40 g, 0.0306 mol), and *N,N*-diethylaniline (9.14 g, 0.0613 mol) in 80 mL of benzene lead to brown, moisture-sensitive crystals of crude *B,B',B''*-trifluoro-*N,N',N''*-tris(2-fluorophenyl)borazine, yield 3.30 g (90%). The same workup was applied to 2-chloro, 2-bromo, and 2-methylaniline to give the corresponding borazines (*o*-YC₆H₄NBF)₃ (Y = Cl, Br, Me; yield 93%, 88%, and 75%, respectively).

Preparation of *B,B',B''*-Trimethyl-*N,N',N''*-triarylborazines. To a diethyl ether solution of methylmagnesium iodide, prepared from magnesium turnings (2 g, 0.0822 mol) and a slight excess of methyl iodide (11.85 g, 0.0835 mol), crude (*o*-FC₆H₄NBF)₃ (3.30 g, 0.0275 mol) was added by small portions. After being refluxed for 1 h, the mixture was cooled with an ice bath and quenched with a solution of NH₄Cl in water. Addition of methanol to the diethyl ether solution gave white crystals of (*o*-FC₆H₄NBMe)₃ (I): mp 201–202 °C for a 15/85 cis/trans mixture; yield 2.56 g (80%). Attempted separation of both isomers with a Florisil column (SiO₂/MgO, 85/15) was unsuccessful.

The same procedure was applied to the crude borazines (*o*-YC₆H₄NBF)₃ (Y = Cl, Br, Me) thus leading to the related (*o*-YC₆H₄NBMe)₃. Data for II, Y = Cl: mp 214–216 °C for a 17/83 cis/trans mixture; yield 90%. Data for III, Y = Br: mp 222–223 °C for a 32/68 cis/trans mixture; yield 90%. Data for IV, Y = Me: mp 165–167 °C for a 33/67 cis/trans mixture (lit.¹ mp 158–160 °C for the cis/trans mixture (?); lit.⁴ mp 168–170 °C for the cis isomer); yield 60%.

Preparation of *N,N',N''*-Triarylborazines. These compounds were obtained by pyrolysis of a mixture of the desired aniline with Et₃NBH₃ according to a classical method.⁸ In a typical reaction, 2-fluoroaniline (8.67 g, 0.078 mol) was slowly added to 8.98 g (0.078 mol) of Et₃NBH₃

Table I. ¹³C Chemical Shifts^a for (*o*-YC₆H₄NBCH₃)₃

carbon atom ^b	δ(I) ^c	J _{CF}	δ(II)	δ(III) ^d	δ(IV) ^d
1	135.8	13.4	145.5	147 (0.0)	147.4 (−0.3)
2	158.0	245.1	132.5	124 (+1.1)	133.9 (−0.5)
3	115.9	21.0	129.6 ^e	132.7 (−0.4)	130.3 (+0.1)
4	126.6	7.5	126.4	126.6 (−0.4)	125.1 (+0.2)
5	130.3	1.3	127.3 ^e	128 (−0.3)	126.6 (0.0)
6	124.1	4.0	129.8	129.6 (+0.7)	128.2 (−0.6)
7					18.3 (0.0)
B-CH ₃	1.0 (br)		1.0 (br)	1.0 (br)	0.9 (br)

^aThe reported chemical shifts are in fact mean values (see text); J_{CF} values in Hz are mean values as well. ^bThe numbering is the same as for the starting aniline, carbon 7, if any, corresponding to the ortho substituent. ^cThe assignments are rather straightforward because of the ranking of the ¹³C_{CF} coupling constant with *n*,¹¹ the presence of the electronegative nitrogen substituent, ortho to the fluorine atom, resulting in a decrease of the corresponding ¹³C_{CF}.¹² ^dThese assignments were deduced from 2D NMR data concerning related molecules,¹³ the values in parentheses measuring the observed deviation in ppm. Hence, the previously proposed attribution for IV is to be corrected.¹⁴ ^eThese assignments may be reversed.

Table II. ¹³C Chemical Shifts^a for (*o*-YC₆H₄NBH₃)₃

carbon atom	δ(V)	J _{CF}	δ(VI)	δ(VIII)
1	135.5	11.5	145	147.0 (+0.1)
2	156.8	245.9	130.7	132.9 (+0.5)
3	116.1	20.9	129.8 ^b	130.6 (−0.2)
4	126.5	7.6	126.6	125.5 (−0.2)
5	128.3	1.0	127.3 ^b	126.6 (+0.0)
6	124.2	4.1	128.4 ^b	127.3 (+0.3)
7				19.0 (−0.7)

^aThe reported chemical shifts are exact values; J_{CF} is in Hz. ^bThese assignments may be reversed.

at 100 °C with magnetic stirring. The temperature was then gradually raised to 200 °C with evolution of Et₃N and kept at 200 °C overnight. After cooling, recrystallization (C₆H₆/hexane) gave white crystals of (*o*-FC₆H₄NBH₃)₃ (V): mp 154 °C; yield 5.28 g (56%). The same procedure applied to 2-chloroaniline gave only 20% of (*o*-ClC₆H₄NBH₃)₃ (VI), mp 126.5 °C (lit.⁹ mp 126–128 °C), and despite repeated crystallizations and/or sublimations no fine structure could be obtained for the latter compound by ¹³C NMR spectroscopy. Similar difficulties were met with 2-bromoaniline, the expected borazine (*o*-BrC₆H₄NBH₃)₃ (VII) being contaminated by increasing amounts of polymeric materials whereas 2-methylaniline easily led to (*o*-CH₃C₆H₄NBH₃)₃ (VIII): mp 90 °C; yield 75%. However, by reaction with CH₃MgI, all these compounds were directly converted to the above quoted (*o*-YC₆H₄NBCH₃)₃ (Y = F (I), Cl (II), Br (III), Me (IX)) as mixtures of both isomers, 16/84 for (I) and 36/64 for (IV). The related yields were 80%, 90%, 90%, and 60%, respectively.

Preparation of *B,B',B''*-Trichloro- (bromo-) *N,N',N''*-triarylborazines. These compounds were prepared from BCl₃ (BBr₃) and the required aniline in boiling benzene.¹⁰ Direct addition of CH₃MgI in excess to this

- (1) Gerrard, W.; Mooney, E. F.; Pratt, D. E. *J. Appl. Chem.* **1963**, *13*, 127–133. (b) Butcher, I. M.; Gerrard, W.; Leane, J. B.; Mooney, E. F. *J. Chem. Soc.* **1964**, 4528–4531.
- (2) Schwarz, W.; Lux, D.; Hess, H. *Cryst. Struct. Commun.* **1977**, *6*, 431–436.
- (3) Johnson, P. M.; Mellon, E. K. *Inorg. Chem.* **1974**, *13*, 2769–2772.
- (4) Allaoud, S.; Frange, B. *Inorg. Chem.* **1985**, *24*, 2520–2523.
- (5) Köster, R.; Seidel, G.; Kersch, S.; Wrackmeyer, B. *Z. Naturforsch.* **1987**, *42b*, 191–194.
- (6) Köster, R.; Seidel, G.; Boese, R.; Wrackmeyer, B. *Chem. Ber.* **1987**, *120*, 669–683.
- (7) Harris, J. J.; Rudner, B. *Inorg. Chem.* **1969**, *6*, 1258–1262.
- (8) Köster, R.; Bellut, H.; Hattori, S. *Liebigs Ann. Chem.* **1968**, *720*, 23–31.
- (9) Atkinson, I. B.; Clapp, D. B.; Beck, C. A.; Currell, B. R. *J. Chem. Soc., Dalton Trans.* **1972**, 182–185.
- (10) Grosz, S. J.; Stafiej, S. F. *J. Am. Chem. Soc.* **1958**, *80*, 1357–1360.
- (11) Pugmire, R. I.; Grant, D. M. *J. Am. Chem. Soc.* **1971**, *93*, 1880–1887.
- (12) Weigert, F. J.; Roberts, J. D. *J. Am. Chem. Soc.* **1971**, *93*, 2361–2369.
- (13) Ernst, L.; Lincoln, D. N.; Wray, V. J. *Magn. Reson.* **1976**, *21*, 115–128.
- (14) Wray, V.; Ernst, L.; Lustig, E. J. *Magn. Reson.* **1977**, *27*, 1–21.
- (15) Wasylshen, R.; Schaefer, T. *Can. J. Chem.* **1972**, *51*, 961–973.
- (16) Allaoud, S.; Bitar, H.; Frange, B.; Faure, R. *Magn. Reson. Chem.* **1989**, *27*, 809–811.
- (17) Allaoud, S.; Bitar, H.; El Mouhtadi, M.; Frange, B. *J. Organomet. Chem.* **1983**, *248*, 123–130.

[†] Present address: Laboratoire de Physicochimie Minérale I, 43 boulevard du 11 novembre 1918, 69622 Villeurbanne, France.

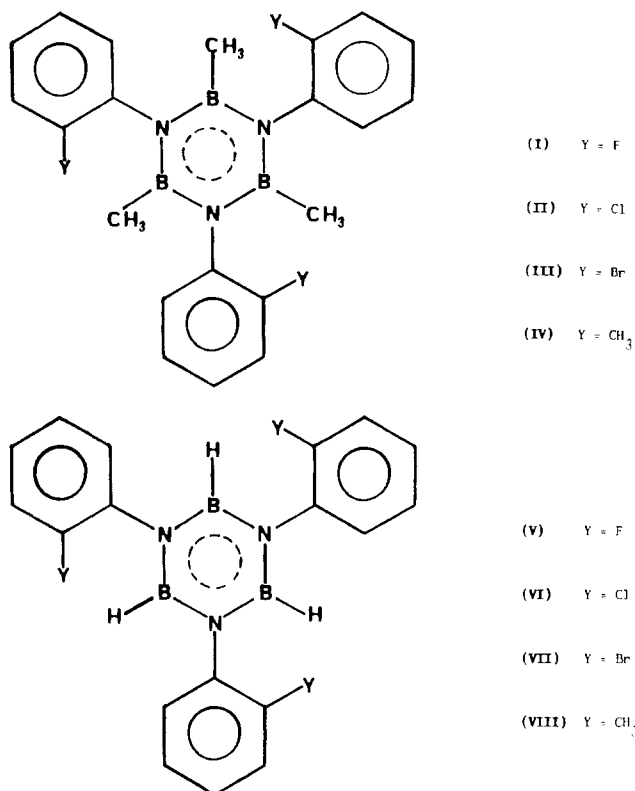


Figure 1. Formulas.

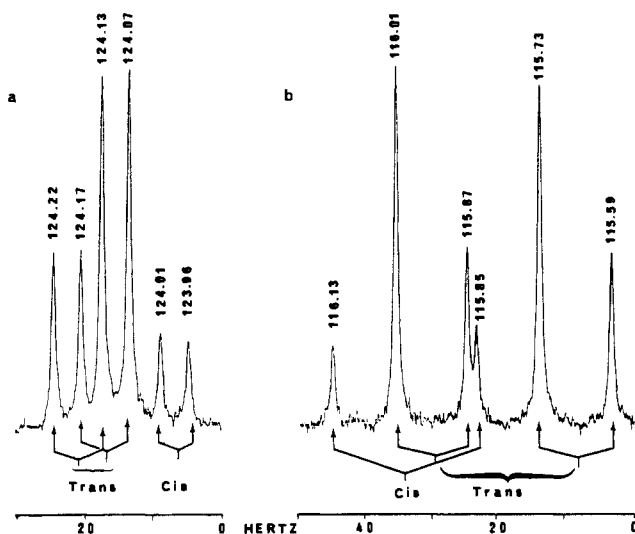


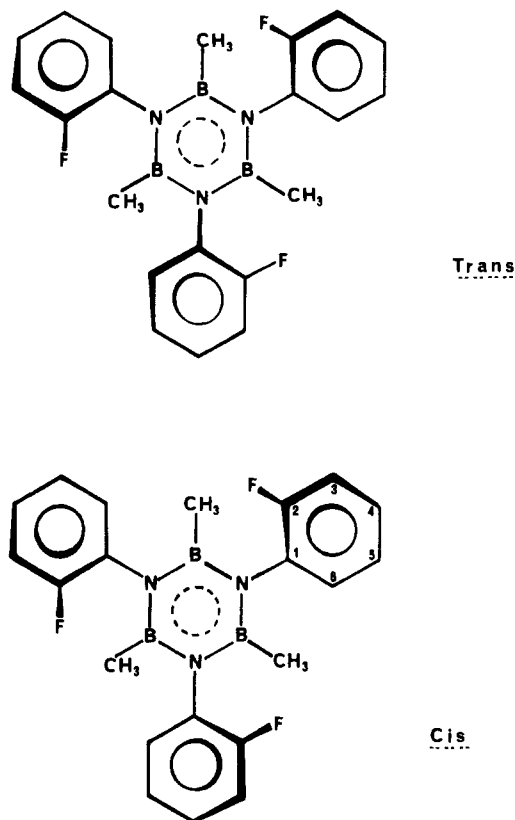
Figure 2. Partial aromatic section of the ¹H broad-band-decoupled ¹³C NMR spectrum of (*o*-FC₆H₄NBCH₃)₃: (a) carbon 6; (b) carbon 3. The numbering is the same as in Figure 1. The hertz frequency scale is arbitrary; chemical shifts are in ppm from TMS.

benzene solution allowed isolation of I as a mixture of both isomers (yield 75% with BCl₃ and 60% with BBr₃, after the same workup as earlier described).

Results and Discussion

The *B,B',B''*-trihalo-*N,N',N''*-triarylborazines (*o*-YC₆H₄NBX)₃ (Y = F, Cl, Br, Me; X = F, Cl, Br) being most sensitive to moisture were directly methylated by means of CH₃MgI. Thus, the present study is mainly concerned with the methyl compounds (*o*-YC₆H₄NBCH₃)₃ (Y = F (I), Cl (II), Br (III), Me (IV)) and the related borazines (*o*-YC₆H₄NBH)₃ (Y = F (V), Cl (VI), Br (VII), Me (VIII)) (Figure 1). For both sets of compounds, the ¹³C chemical shifts are summarized in Tables I and II, respectively.

From the above-reported data one can notice a nearly constant chemical shift for carbon 4 throughout the halogen series (Y = F, Cl, Br). Furthermore, the carbon 1 chemical shift steadily

Figure 3. Cis and trans isomers of (*o*-FC₆H₄NBCH₃)₃.Table III. ¹³C Chemical Shifts for (*o*-FC₆H₄NBCH₃)₃

carbon atom	δ	J _{CF} (c) ^a	J _{CF} (t)
2	159.64 (c), ^b 159.60 (t), 159.56 (t)	245.0	244.1
	156.40 (c), 156.36 (t), 156.32 (t)		244.1
1	135.87 (c), 135.83 (t), 135.79 (t)	13.6	13.5
	135.69 (c), 135.65 (t), 135.61 (t)		13.4
5	130.59 (c), 130.37 (t), 130.18 (t)	1.3	1.4
	130.57 (c), 130.35 (t), 130.17 (t)		1.4
4	126.68, ^c 126.66	7.5	7.5
	126.58, 126.56		
6	124.22 (t), 124.13 (t), 124.01 (c)	4.1	3.9
	124.17 (t), 124.07 (t), 123.96 (c)		4.0
3	116.13 (c), 116.01 (t), 115.87 (t)	20.9	21.1
	115.85 (c), 115.73 (t), 115.59 (t)		21.1

^a J_{CF}, in Hz, is measured for the cis isomer (c) and the trans one (t).

^b Every line is related to a triplet structure with two signals for the trans isomer (t) and one signal for the cis (c); the boron-bonded carbon 7 (B-CH₃) does not present fine structure. ^c There is accidental overlapping of the three signals.

increases with the steric bulk of Y as a consequence of changes in ring anisotropy caused by variation in the interplanar angle θ. Similar trends were observed in biphenyl derivatives¹⁵ and were used to estimate the angle of twist in these compounds.

However, the most interesting feature can be observed in the ¹H broad-band-decoupled ¹³C NMR spectrum of I. Thus, every aromatic carbon of the latter appears as a doublet of triplets (Figure 2). If the doublet structure results of the spin value 1/2 for the fluorine atom, the observed triplet brings definitive support to the existence of atropisomers in (*o*-FC₆H₄NBCH₃)₃.¹⁶ Two configurations are indeed expected for this compound (Figure 3): the cis isomer with all three of the fluorine atoms on one side of the borazine ring plane (C_{3v} symmetry) and the trans isomer with two fluorine atoms on one side of the borazine ring plane and the

(15) Roberts, R. M. G. *Magn. Reson. Chem.* **1985**, *23*, 52-54.

(16) Additional proof of this atropisomerism may be derived from the ¹⁹F NMR spectrum of I where three signals are observed: -46.88, -47.54, and -48.20 ppm.

third on the opposite side (C_2 symmetry). Therefore, every aromatic carbon should display three signals: a singlet for the cis isomer and two singlets, with a resonance line being twice the intensity of the other, for the trans isomer (Table III). A careful integration of the above-quoted signals gives a ratio of 15% for the cis isomer and 85% for the trans one (the statistical ratio would be 25/75). Furthermore, the splitting into triplet of every aromatic carbon may bring useful albeit empirical information for the assignments of some carbon atoms. For example, in the ^{13}C NMR spectrum of (I), carbon 4 appears as a doublet of doublets (instead of a doublet of triplets) probably because this carbon belongs to the aryl group rotation axis and is therefore rather insensitive to the above atropisomerism. The same triplet pattern was observed for the aromatic carbons of II–IV, supporting the existence of cis/trans isomers in these three compounds.

Unexpectedly, the ^{13}C NMR spectra of the N,N',N'' -triarylborazines ($o\text{-YC}_6\text{H}_4\text{NBH}$)₃ ($Y = \text{F}$ (V), CH_3 (VIII)) are quite different. Thus, the above splitting of aromatic carbons was observed with neither V nor VIII, every aromatic carbon resulting in sharp singlets for VIII or doublets for V. No conclusion could be drawn with compound VI as three of the primary aromatic carbons gave rather broad signals, the last primary aromatic carbon being attributed to carbon 4 on the basis of its unusual height (about three times the intensity of the other carbon atoms).

From our experimental results, one may conclude that during the methylation of ($o\text{-YC}_6\text{H}_4\text{NBX}$)₃ ($Y = \text{F}, \text{Cl}, \text{Br}, \text{Me}; \text{X} = \text{Me}, \text{H}$), the amount of cis/trans isomers obtained is a function of both substituents X and Y. Thus, the same ratios of ($o\text{-FC}_6\text{H}_4\text{NBCH}_3$)₃ were obtained either from ($o\text{-FC}_6\text{H}_4\text{NBF}$)₃ (15/85) or from ($o\text{-FC}_6\text{H}_4\text{NBH}$)₃ (16/84), the hydrogen and fluorine atoms having similar steric requirements. Similar results were observed with ($o\text{-CH}_3\text{C}_6\text{H}_4\text{NBCH}_3$)₃; the ratio of cis/trans isomers was 33/67 with ($o\text{-CH}_3\text{C}_6\text{H}_4\text{NBF}$)₃ and 36/64 with ($o\text{-CH}_3\text{C}_6\text{H}_4\text{NBH}$)₃, no trans isomer (100/0) being obtained if one started from the chloroborazine ($o\text{-CH}_3\text{C}_6\text{H}_4\text{NBCl}$)₃ in complete agreement with our earlier results.⁴ Furthermore, for a given substituent on boron, the amount of cis isomer increases with the steric bulk of the ortho substituent Y. For example, for methylation of ($o\text{-YC}_6\text{H}_4\text{NBF}$)₃ ($Y = \text{F}, \text{Cl}, \text{Br}, \text{Me}$), the amount of cis isomer were 15%, 17%, 32%, and 33%, respectively. Unfortunately, such correlations are limited to the lighter boron trihalides, the heavier ones (and especially BBr_3) giving rise to different heterocycles.^{17,18}

On the other hand, the difference in behavior between ($o\text{-YC}_6\text{H}_4\text{NBCH}_3$)₃ and ($o\text{-YC}_6\text{H}_4\text{NBH}$)₃ ($Y = \text{F}$ (V), Me (VIII)) can be interpreted in three different ways: (i) the reaction of Et_3NBH_3 with the aniline $o\text{-YC}_6\text{H}_4\text{NH}_2$ leads to the cis isomer of ($o\text{-YC}_6\text{H}_4\text{NBH}$)₃ alone; (ii) V and VIII are in fact a mixture of cis and trans isomers with rapid (on the NMR time scale) rotation about the CN bond; (iii) there is a slight puckering of the borazine ring in the case of ($o\text{-YC}_6\text{H}_4\text{NBH}$)₃, thus allowing free rotation of the aryl group. From literature data,^{9,19} concerning the borazine ring formation, the first hypothesis (i) may be ruled out. A free rotation of the aryl group in V and, a fortiori in VIII, seems unlikely. This can be demonstrated by the fact that in ($\text{C}_6\text{H}_5\text{NBCH}_3$)₃, isomeric with VIII, the signal observed in the ^1H NMR spectrum for the BCH_3 occurs at high field of TMS (-0.22 ppm, solvent CS_2), which was attributed to a hindered rotation of the aromatic groups, nearly perpendicular to the plane of the borazine ring.^{1b} Hence, the third hypothesis (iii) remains thus far the most attractive and requires further investigations. A related example has been reported in the literature with the four- π -electron heterocycle $\text{C}_4\text{H}_4\text{B}_2\text{F}_2$. The latter was shown to lie in a plane²⁰ whereas when the BF bonds were replaced by BH ones, the nido compound $\text{C}_4\text{H}_4\text{B}_2\text{H}_2$ was obtained.²¹

Acknowledgment. We are most grateful to Dr. M. Pasdeloup and Dr. J. P. Commenges for a generous gift of fluoroanilines and secondarily for ^{19}F NMR spectra (Laboratoire de Chimie de Coordination, Toulouse, France).

(21) Rudolph, R. W.; Pretzer, W. R. *Inorg. Chem.* 1972, 11, 1974–1978.

Contribution No. 8344 from the A. A. Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91125

The Crystal Structure of $[\text{H}_2\text{B}(\text{pz})_2]_2\text{GaCl}$: Corrigendum

Richard E. Marsh

Received October 10, 1989

The synthesis and crystal structure of this dihydrobis(pyrazolyl)borate complex of gallium have recently been reported.¹ The structure was refined in space group Cc (monoclinic; $a = 9.542$ (1) Å, $b = 12.022$ (2) Å, $c = 15.317$ (2) Å, $\beta = 98.67$ (2)°, $Z = 4$), to an R of 0.025. The authors reported that the structure “can also be described in the centrosymmetric space group $C2/c$ ” but that attempts to refine it in $C2/c$ led to unreasonably large “temperature factors” for the Ga and Cl atoms and to unreasonably low ones for the remaining atoms. Surprising results of the Cc refinement were large asymmetries in the trigonal-bipyramidal bonding about Ga, the two axial Ga–N distances being 2.180 (8) and 1.94 (1) Å and the two equatorial Ga–N distances being 1.994 (8) and 1.923 (9) Å; there were also surprising irregularities within the pyrazolyl rings, with N–N distances ranging from 1.26 to 1.46 Å. I have had no difficulty in refining in $C2/c$, and the resulting structure shows no such surprises (which undoubtedly resulted from the near-singularities inherent in non-centrosymmetric refinement of a centrosymmetric structure²).

Refinement in $C2/c$ was based on the 1504 F_o values (rather than the 1987 reported in ref 1) recovered from the supplementary material. The number of parameters totaled 143: coordinates and anisotropic U_{ij} 's for the 13 heavier atoms, coordinates and isotropic B 's for the 8 hydrogens, a scale factor, and an extinction coefficient (final value: 0.065 (14) $\times 10^{-6}$). The final R was 0.025, the same value as reported¹ for the Cc refinement, which was based on 215 parameters (no extinction coefficient was used, and the H atoms were not adjusted). The final $C2/c$ coordinates are given in Table I.

It is a reasonable presumption that the earlier failure¹ to obtain satisfactory refinement in $C2/c$ was due to incorrect atom multiplicities. In $C2/c$ the Ga and Cl atoms lie on 2-fold symmetry axes with site multiplicities of 4; the remaining atoms lie in general positions with multiplicities of 8. If all multiplicities had been set equal, least-squares refinement would attempt to compensate by increasing the “temperature factors” of Ga and Cl and reducing those of the remaining atoms, just as observed earlier.³

A final comment: it seems apparent that the intensity data were of excellent quality, and the final $C2/c$ structure is both of high precision and of high accuracy. Besides the large difference between the axial and the equatorial Ga–N bond lengths, 2.065 (2) vs 1.964 (2) Å, more subtle effects can be noted. For example, corresponding bond lengths in the two pyrazolyl rings are identical within their esd's (about 0.003 Å); however, the two N–B distances connecting the rings are unequal, at 1.544 (4) and 1.565 (3) Å. The shorter distance is to the pyrazolyl group that is axially bonded

(17) Blackborow, J. R.; Lockhart, J. C. *J. Chem. Soc., Dalton Trans.* 1973, 1303–1308.

(18) Allaoud, S.; El Mouhtadi, M.; Frange, B. *Nouv. J. Chim.* 1985, 9, 499–504.

(19) Bartlett, R. K.; Turner, H. S.; Warne, R. J.; Young, M. A.; Lawrenson, I. *J. Chem. Soc. A* 1966, 479–500.

(20) Timms, P. L. *J. Am. Chem. Soc.* 1968, 90, 4585–4589.

(1) Reger, D. L.; Knox, S. J.; Lebioda, L. *Inorg. Chem.* 1989, 28, 3092.

(2) Schomaker, V.; Marsh, R. E. *Acta Crystallogr.* 1979, B35, 1933.

(3) Professor Reger (private communication) has confirmed that the multiplicities were not reset when their Cc model was transformed to $C2/c$.