

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

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

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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

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Table I. C2/c Coordinates (*x*, *y*, *z*, and $U_{eq}^a \times 10^4$)

| atom | <i>x</i> | <i>y</i> | <i>z</i> | U_{eq} or <i>B</i> , Å ² |
|------|------------|------------|-----------|---------------------------------------|
| Ga | 0 | 398 (0.3) | 2500 | 423 (1) |
| Cl | 0 | 2221 (0.9) | 2500 | 814 (3) |
| N11 | 2603 (2) | -555 (2) | 3595 (1) | 495 (5) |
| N12 | 2054 (2) | 367 (2) | 3158 (1) | 482 (4) |
| N21 | 271 (2) | -1161 (2) | 3985 (1) | 481 (4) |
| N22 | -606 (2) | -449 (2) | 3474 (1) | 465 (4) |
| C13 | 3101 (3) | 1120 (3) | 3217 (2) | 577 (6) |
| C14 | 4320 (3) | 688 (3) | 3680 (2) | 662 (8) |
| C15 | 3972 (3) | -361 (3) | 3905 (2) | 646 (7) |
| C23 | -1789 (3) | -350 (3) | 3843 (2) | 604 (6) |
| C24 | -1673 (3) | -996 (3) | 4585 (2) | 687 (7) |
| C25 | -377 (3) | -1491 (2) | 4655 (2) | 608 (7) |
| B | 1667 (3) | -1586 (2) | 3677 (2) | 542 (7) |
| HBA | 2238 (28) | -2180 (24) | 4212 (17) | 6.5 (7) ^b |
| HBB | 1338 (23) | -1999 (19) | 3032 (15) | 4.4 (5) ^b |
| H13 | 2884 (30) | 1832 (25) | 3006 (18) | 6.3 (8) ^b |
| H14 | 5162 (30) | 1049 (25) | 3825 (18) | 6.3 (7) ^b |
| H15 | 4468 (31) | -896 (26) | 4228 (19) | 6.8 (8) ^b |
| H23 | -2538 (28) | 115 (23) | 3561 (17) | 5.6 (7) ^b |
| H24 | -2363 (31) | -1099 (25) | 4931 (19) | 6.6 (7) ^b |
| H25 | 140 (31) | -2003 (25) | 5054 (20) | 6.6 (8) ^b |

^a $U_{eq} = \frac{1}{3} \sum_i \sum_j [U_{ij}(a_i^* a_j^*) (\bar{a}_i \bar{a}_j)]$. ^b Isotropic displacement parameter, *B*.

to Ga, suggesting that these B-N bonds have been slightly rehybridized to reflect the different Ga-N distances, without disturbing the pyrazolyl rings. Another interesting result is a listing of the C-H bonds in the 3- and 5-positions of the pyrazolyl rings, the H-C-N angles being substantially smaller (118 (1)°) than H-C-C (133 (1)°). All C-H distances are equal to their average value (0.93 Å) within their esd's of 0.03 Å; B-H distances are 1.16 (3) and 1.11 (2) Å.

Supplementary Material Available: Tables SI-SIII, listing anisotropic U_{ij} 's for the heavy atoms and bond distances and angles (2 pages); a listing of observed and calculated *F*'s for the C2/c refinement (5 pages). Ordering information is given on any current masthead page.

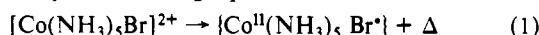
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Origin of the Solvent Effect on the Photolysis of $[\text{Co}(\text{NH}_3)_5\text{Br}]^{2+}$ at 254 nm in a Water-Acetonitrile Solvent System

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Charge-transfer excitation of $[\text{Co}(\text{NH}_3)_5\text{Br}]^{2+}$ causes an intramolecular redox reaction in which an electron is transferred from an orbital centered on the bromine ligand to an orbital centered on the cobalt metal.¹ The primary photoproduct is formed via homolytic fission of the Co-Br bond, and this product consists of a Br radical and a Co(II) species.^{2,3} The process may be described by the following equation



where Δ is the amount of light energy absorbed in excess of that required for homolytic dissociation. Prior to separation, the Br radical with the Co(II) fragment is referred to as a cage species.

The Co portion of the cage species is labile and will undergo aquation in a stepwise fashion at rates in the microsecond time domain. The Br radical may either undergo primary recombina-

tion or escape from the solvent cage to form a solvent-separated radical pair. The competition between these two pathways for the bromine radical determines the overall quantum yield of Co(II), and the cage escape process can carry traces of the effects of initial excitation through the magnitude of Δ .

The competition is dependent upon the solvent used. As well, Endicott⁴ discovered that there is a dependence of the product quantum yield on the excitation wavelength (energy). The quantum yield of Co(II) increased upon decreasing the excitation wavelength. However, there is a limit to this increase in water. For $\lambda \leq 333$ nm, the quantum yield remains constant. It is especially interesting that this limit may be removed by changing the solvent. For example, in 80% acetonitrile, the quantum yield of Co(II) approaches unity upon decreasing the excitation wavelength.⁴ This phenomenon may be explained if the step involving competition between escape from the solvent cage and recombination follows a solvent-dependent step in which the system may be trapped in an unreactive state.^{2,5}

Experimental Section

Materials. $[\text{Co}(\text{NH}_3)_5\text{Br}]_2\text{Br}_2$ was synthesized according to a published procedure.⁶ $[\text{Co}(\text{NH}_3)_5\text{Br}](\text{NO}_3)_2$ was prepared by treating $[\text{Co}(\text{NH}_3)_5\text{Br}]_2\text{Br}_2$ with AgNO_3 . The AgBr was filtered out and the product isolated by freeze-drying. $[\text{Co}(\text{NH}_3)_5\text{Br}](\text{BPh}_4)_2$ was precipitated by addition of NaBPh_4 to aqueous $[\text{Co}(\text{NH}_3)_5\text{Br}]_2\text{Br}_2$. The product was isolated by filtration. In all cases, the solvent was distilled water.

Photolysis Experiments. The light source was a Rayonet photochemical reactor with a low-pressure 253.7-nm lamp. The intensity of the light was measured by ferrioxalate actinometry.⁷ Solutions of $[\text{Co}(\text{NH}_3)_5\text{Br}]^{2+}$, approximately 2.5×10^{-3} M, were irradiated to a conversion of less than 12% in all cases. The Co(II) formed was determined via spectrophotometric analysis of $\text{Co}(\text{SCN})^{4-}$ in acetone at 620 nm.⁸ An HP-8452A diode array spectrophotometer interfaced with an IBM-PC was used for all absorbance measurements. The quantum yield of Co(II) was calculated according to the method described in the literature.⁹ Spectrophotometric grade acetone and acetonitrile were purchased from Aldrich and used as received.

Results and Discussion

The composition of an acetonitrile-water solvent system was systematically varied so as to study the effects of the reaction medium upon the quantum yield of Co(II) when $[\text{Co}(\text{NH}_3)_5\text{Br}]^{2+}$ was irradiated at 253.7 nm. Due to solubility problems, two salts of $[\text{Co}(\text{NH}_3)_5\text{Br}]^{2+}$ had to be used. These were the nitrate salt and the tetraphenylborate salt. The nitrate salt was chosen as it is readily soluble in polar solvents and because the nitrate anion does not absorb light significantly at 253.7 nm at the concentrations involved in the photolysis. Therefore it does not interfere with the reaction system and the photochemistry of the system may be attributed to only the cationic complex. Unfortunately, $[\text{Co}(\text{NH}_3)_5\text{Br}](\text{NO}_3)_2$ is insoluble in neat acetonitrile. To overcome this problem, the tetraphenylborate salt was used. The tetraphenylborate anion (in the form of the sodium salt) absorbs strongly at 253.7 nm and is found to fluoresce. The fluorescence was quenched in the presence of the Co complex, exhibiting a linear Stern-Volmer plot with a slope equal to 6650 M^{-1} . A stoichiometric concentration of the cation in a 2.5×10^{-3} M solution of $[\text{Co}(\text{NH}_3)_5\text{Br}](\text{BPh}_4)_2$ quenches greater than 99% of the emission. Thus, it can be inferred that the tetraphenylborate anion sensitizes the cobalt complex and, as with the nitrate salt, the photochemistry is due only to the cationic complex.

The change from the nitrate to the tetraphenylborate salt occurs in the region where the quantum yield is essentially constant. This

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