Stereodynamics of Enantiomerization in Bis(diisopropylamino)aminoboranes

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Abstract: Bis(diisopropylamino)alkylaminoboranes, $RR'NB\{N(i\text{-}C_3H_7)_2\}_2$, possess helically chiral configurations which are stereochemically rigid at low temperatures. NMR line shape analysis indicates that these molecules enantiomerize by correlated B–N rotations through transition states in which the substituents attached to two of the nitrogens are in the plane of the BN_3 unit while those on the third nitrogen are perpendicular to this plane. When $R = R'$ molecular symmetry only allows the determination of the barrier to the exchange in which one of the $N(i\text{-}C_3H_7)_2$ groups is coplanar with, while the other is perpendicular to, the BN_3 plane. $\Delta G^{\pm}$ for this process is in the range 8–9 kcal/mol. In principle, when $R = R'$ three different barriers can be determined for the three possible nondegenerate routes by which the enantiomerization can take place. For a series in which $R = H$ and $R' = $ alkyl the $\Delta G^{\pm}$ for these are 13–15, 8–9, and $\lesssim 5$ kcal/mol. The barriers seem to arise from a combination of B–N π bonding and steric effects.

Introduction

The stereodynamical behavior of aminoboranes has been a topic of longstanding and continuing interest, largely because the B–N bond possesses π bond character arising from delocalization of the nitrogen "lone pair" into the empty 2p orbital on boron.[1-3] Barriers to B–N bond rotation in a variety of monoaminoboranes, R_2NBX_2, have been determined; these usually lie in the range of 17–24 kcal/mol.[4] Several bis(amino)boranes, $(R_2N)_2BX$, have also been investigated and the B–N torsional barrier in them is almost invariably lower, typically being about 10–11 kcal/mol.[2,4c] This difference has been rationalized by postulating that the π bond order of an individual B–N bond would be less in a bis(amino)borane than in a similar mono(amino)borane because in the former two nitrogen lone pairs must compete for overlap with the empty boron orbital.

If such an argument is valid the introduction of a third amine should further decrease the π bond order in a given B–N linkage resulting in even lower rotational barriers. In view of this, the first reported[2] B–N torsional barrier in a tris(amino)borane (12.7 kcal/mol in $(Me_2N)_2BNMePh)$) was unexpectedly high. Dewar and Rona postulated that in this molecule the bulky *N*-methylphenyl group is forced into a position nearly perpendicular to the BN_3 plane.[2] In this orientation the lone pair on the nitrogen is nearly orthogonal to the empty boron orbital and therefore does not take part in B–N π bonding. The remainder of the molecule is analogous to a bis(dimethylamino)borane and shows a rotational barrier which is comparable to those in other bis(amino)boranes. More recently high B–N rotational barriers have also been observed in some bis(amino)boranes containing *N*-trimethylsilyl substituents,[5] and a similar steric deformation has been postulated to account for the apparent anomaly in barrier heights.

From a different standpoint, the tris(amino)boranes are interesting because they are stereochemically correspondent with triaryl compounds of general formulas Ar_3X. The stereochemistry and dynamics of the latter systems have been extensively studied.[6] The Ar_3X molecules have been shown to be chiral with a propeller-like ground state and the nature of the rotational isomerization processes which occur in them has received much theoretical and experimental attention.[6,7] The tris(amino)boranes offer the opportunity to study isomerization and dynamical processes in systems which are topologically identical with but electronically very different from the triaryl compounds.

In order to obtain further information on the stereochemical and dynamical properties of tris(amino)boranes, we have in-

vestigated a series of bis(diisopropylamino)alkylaminoboranes, consisting of bis(diisopropylamino)dimethylaminoborane,

I, R = R' = Me	III, R = H; R' = Me
II, R = R' = Et	IV, R = H; R' = Et
	V, R = H; R' = *i*-Pr
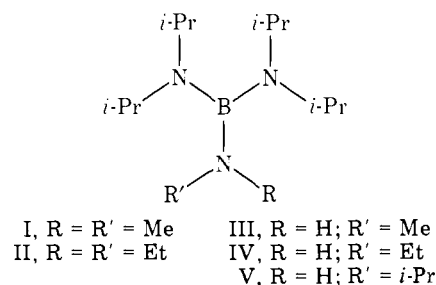
$[(i\text{-}Pr_2N)_2BNMe_2]$, I; bis(diisopropylamino)diethylaminoborane, $[(i\text{-}Pr_2N)_2BNEt_2]$, II; bis(diisopropylamino)methylaminoborane, $[(i\text{-}Pr_2N)_2BNHMe]$, III; bis(diisopropylamino)ethylaminoborane, $[(i\text{-}Pr_2N)_2BNHEt]$, IV; and bis(diisopropylamino)isopropylaminoborane, $[(i\text{-}Pr_2N)_2BNHiPr]$, V. The conclusions drawn from the results of this study may be cause for a reexamination of the interpretation of other stereochemical and stereodynamical studies on aminoboranes. A preliminary account of the results obtained on I and II has already appeared as a communication.[8]

Experimental Section

Syntheses. The tris(amino)boranes were prepared by previously reported synthetic methods[9] and purified by vacuum distillation or, in the case of IV, vacuum sublimation.

Spectra. NMR spectra were obtained on a Varian XL-100 spectrometer equipped with variable temperature accessories. Temperature measurements were made using a probe calibrated against water/ice and dry ice/acetone, and are believed to be accurate to within ±2 °C. The ^1H NMR samples were ~20% v/v solutions in CF_2Cl_2 with about 10% CD_2Cl_2 present. The ^{13}C NMR samples were ~20% v/v solutions in CF_2Cl_2 only. ^1H NMR spectra were taken using an internal ^2H lock; ^{13}C spectra were taken using an external ^{19}F lock. Chemical shifts for both ^{13}C and ^1H NMR are reported relative to external Me_4Si. Chemical shifts and spin–spin coupling constants at fast exchange and in the slow exchange regions are given in Tables I–IV.

Nuclear Overhauser Effect. A nuclear Overhauser effect experiment was performed on a sample of bis(diisopropylamino)methylaminoborane in CF_2Cl_2 solution. The sample was degassed on the vacuum line before sealing. Enhancements were determined by Xeroxing and cutting out and weighing the peaks from three spectra taken (not consecutively) at various power levels. Nuclear Overhauser effect enhancement is reported as the percentage increase in peak weight over that obtained while irradiating off-resonance (at a point in the spectrum where there are no peaks).

Table I. ^{1}H DNMR of $(i\text{-}Pr_2N)_2BNR_2$ Compounds

Compd Resonance	δ (appearance, J, rel no. of H's)^a	
	Ambient temp	Low temp
R = Me	30 °C	−124 °C
$CH(CH_3)_2$	3.58 (heptet, 7.0 Hz, 4 H)	3.59 (br, 2 H)
		3.36 (br, 2 H)
NCH_3	2.59 (s, 6 H)	2.49 (br, 6 H)
$CH(CH_3)_2$	1.21 (d, 7.0 Hz, 24 H)	1.17 (br, 24 H)
R = Et	30 °C	−100 °C
$CH(CH_3)_2$	3.58 (heptet, 7.1 Hz, 4 H)	3.55 (heptet, br. 2 H)
		3.30 (heptet, br, 2 H)
CH_2CH_3	2.93 (q, 7.1 Hz, 4 H)	2.7 ABX_3 ($\delta_A - \delta_B =$ 0.2 ppm, $J_{H_AH_B} =$ 13 Hz, 4 H)^b
$CH(CH_3)_2$	1.21 (d, 7.1 Hz, 24 H)	1.15 (d, br, 12 H)
		1.00 (d, br, 12 H)
CH_2CH_3	0.96 (t, 7.1 Hz, 6 H)	0.81 (t, br, 6 H)

^{a} Chemical shifts are in parts per million downfield from external Me$_4$Si. ^{b} Values for ($\delta_A - \delta_B$) and $J_{H_AH_B}$ were obtained at −100 °C by decoupling the ethyl methyl protons.

Table II. ^{13}C DNMR of $(i\text{-}Pr_2N)_2BNR_2$ Compounds

Compd Resonance	δ (appearance, J, rel no. of C's)^{a,b}	
	Ambient temp	Low temp
R = Me	30 °C	−125 °C
$CH(CH_3)_2$	61.47 (d, 91.00 Hz, 4 C)	62.43 (2 C)
		62.08 (2 C)
NCH_3	53.37 (q, 95.45 Hz, 2 C)	53.28 (2 C)
$CH(CH_3)_2$	38.48 (q, 95.43 Hz, 8 C)	41.83 (2 C)
		41.21 (2 C)
		37.78 (2 C)
		37.08 (2 C)
R = Et	30 °C	−105 °C
$CH(CH_3)_2$	61.82 (d, 125 Hz, 4 C)	62.35 (4 C)
CH_2CH_3	53.90 (t, 125 Hz, 2 C)	53.19 (2 C)
$CH(CH_3)_2$	38.75 (q, 115 Hz, 8 C)	41.21 (2 C)
		41.6 (2 C)
		37.78 (2 C)
		37.08 (2 C)
CH_2CH_2	27.48 (q, 120 Hz, 2 C)	28.18 (2 C)

^{a} Chemical shifts are in parts per million downfield from external Me$_4$Si. ^{b} The proton–carbon-13 coupling constants were obtained from spectra with protons not decoupled. All other parameters are from noise decoupled spectra.

Line Shape Analyses and Thermodynamic Calculations. The rate constants for the observed processes at variable temperatures were obtained by complete line shape analysis of suitable portions of the ^{13}C NMR spectra in the intermediate exchange regions. For the process having a 13–15 kcal/mol barrier, a program which treats a two-site exchange utilizing the density matrix formalism described by Lynden-Bell was used.[10a] For the processes having barriers of 8–9 kcal/mol, a program treating exchange among four sites by setting up and solving for the absorption mode line shape of the Block equations, including chemical exchange effects between sites, was used. Both programs require as input the maximum peak height and the line width (or T_2) in the absence of exchange, which were measured directly from the spectra at each temperature, and the peak positions in the absence of exchange, taken from slow exchange spectra.

The rate of exchange at coalesence of isopropyl methines in I was calculated from the formula $k = \frac{1}{2}(\sqrt{2}\pi\Delta)$ where k is the exchange rate and Δ is the peak separation (in hertz) at slow exchange.[10b]

Thermodynamic parameters $\Delta H^\ddagger$, $\Delta S^\ddagger$, and $\Delta G_c^\ddagger$ were determined by using calculated exchange lifetimes (τ) in an unweighted least-squares plot of $\ln (1/\tau)$ vs. $(1000/T)$.

Molecular Orbital Calculations. INDO calculations were performed using the program CNINDO obtained from the Quantum Chemistry
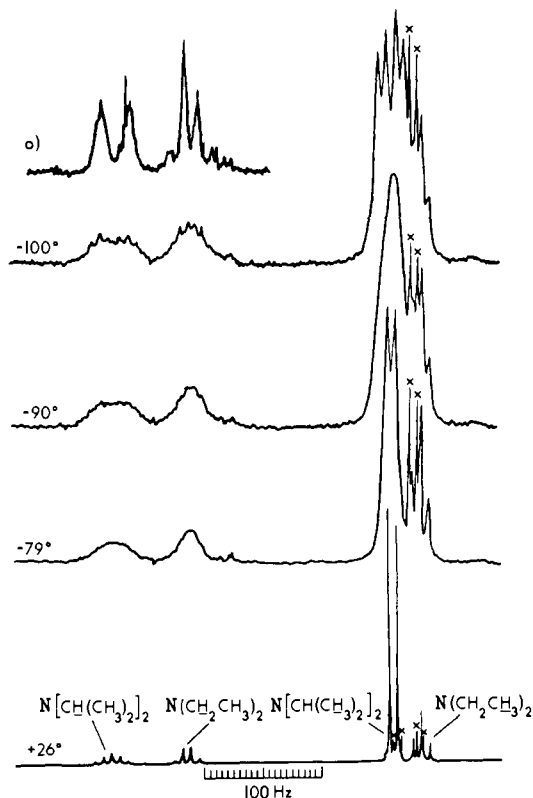

Figure 1. ^{1}H DNMR spectra of bis(diisopropylamino)diethylaminoborane (II). Insert "a" shows the −100 °C spectrum with methyl protons decoupled. Peaks marked "X" arise from an impurity.

Program Exchange, University of Indiana. The following fixed parameters were used throughout the calculations: B–N distance = 1.43 Å; N–H distance = 1.00 Å; N–B–N angle = H–N–H angle = H–N–B angle = 120°.

Results

DNMR Studies. The ^{1}H and the ^{13}C spectra of I–V are temperature dependent. Figures 1–4 show representative spectra of II and IV. The spectral behavior of I is analogous to that of II, except that in I at −120 °C two equal intensity peaks arising from the isopropyl methine groups are present in the ^{13}C NMR spectrum. The temperature dependencies observed in the NMR spectra of III and V are analogous to those seen in IV. NMR parameters for I–V at ambient temperature and in the slow exchange regions are summarized in Tables I–IV.

In the ^{13}C NMR spectra of III–V, the diisopropylamino methyl peaks were not totally resolved at low temperatures. Analysis using computer-assisted deconvolution shows that at 120 °C, the isopropyl methyl region of IV contains three peaks.

Nuclear Overhauser Effect. Irradiation of the amine proton of III at −55 °C resulted in a maximum nuclear Overhauser effect enhancement of 13.6% in the intensity of the downfield isopropyl methine resonance and no significant enhancement of the upfield resonance.

Discussion

Ground State Conformation of Tris(amino)boranes. Tris(dimethylamino)borane has been shown by infrared spectroscopy, photoelectron spectroscopy, electron diffraction, and ultraviolet spectroscopy and by theoretical calculations to possess a propeller-like conformation in which the amino moieties are rotated from the plane containing the boron and the three nitrogens.[11] Such a configuration is chiral and for I–V results in the following two enantiomers.[12]

Table III. ^{1}H DNMR of $(i\text{-}Pr_2N)_2BNHR$ Compounds

Compd Resonance	δ (appearance, J, rel no. of H's)		
	Ambient temp	Intermediate temp	Low temp
R = Me[a,c]	30 °C	−67 °C	−100 °C
CH(CH$_3$)$_2$	3.52 (heptet, 6.8 Hz, 4 H)	3.3 (br, 2 H)	3.5 (br, 1 H)
		3.11 (heptet, 6.6 Hz, 2 H)	3.19 (heptet, 2 H)
			3.1 (br, 1 H)
NCH_3	2.63 (d, 5.8 Hz, 3 H)	2.55 (d, 3 H)	2.5 (d, 3 H)
NH	f	2.05 (br, 1 H)	2.02 (q, 5.8 Hz, 1 H)
CH(CH_3)$_2$	1.13 (d, 6.8 Hz, 24 H)	1.04 (d, 7.0 Hz, 12 H)	0.97 (v br, 24 H)
		1.02 (d, 6.6 Hz, 12 H)	
R = Et[b,d]	30 °C	−40 °C	−100 °C
CH(CH$_3$)$_2$	3.48 (heptet, 6.7 Hz, 4 H)	3.6 (heptet, 6.9 Hz, 2 H)	3.9 (v br, 1 H)
		3.3 (heptet, 6.4 Hz, 2 H)	3.3 (br, 2 H)
			∼3.3 (v br, 1 H)
CH_2CH$_3$	3.0 (d of q, J_{HCCH} = J_{HNCH} = 7.0 Hz, 2 H)	3.0 (d of q, 2 H)	2.99 (br, 2 H)
NH	2.32 (v br, 1 H)	2.32 (br, 1 H)	2.32 (t, 7.0 Hz, 1 H)
CH(CH_3)$_2$[d]	1.12 (d, 6.7 Hz, 24 H)	1.13 (d, 6.9 Hz, 12 H)	1.09 (v br, 24 H)
		1.10 (d, 6.4 Hz, 12 H)	
R = i-Pr[a,e]	30 °C	−21 °C	−112 °C
N[CH(CH$_3$)$_2$]$_2$	3.42 (complex multiplet)	3.53 (heptet, 6.7 Hz, 3 H)	3.83 (v br, 1 H)
NCH(CH$_3$)$_2$		3.21 (heptet, br, 2 H)	3.15 (v br, 4 H)
NH	2.06 (br, 1 H)	1.99 (d, 11.5 Hz, 1 H)	1.89 (d, 1 H)
N[CH(CH_3)$_2$]$_2$	1.07 (d, 6.9 Hz, 24 H)	1.03 (d, 24 H)	0.97 (v br, 30 H)
NCH(CH_3)$_2$	1.03 (d, 6.4 Hz, 6 H)	0.99 (d, 6 H)	

[a] Chemical shifts are in parts per million downfield from external Me$_4$Si. [b] Chemical shifts are in parts per million downfield from internal Me$_4$Si. [c] Isopropyl methine chemical shifts at −100 °C were obtained with isopropyl methyl protons decoupled. [d] The ethyl methyl resonance is obscured by the isopropyl methyl resonance. [e] The monoisopropylamine methine resonance, which should be a doublet (J_{HNCH} = 11.5 Hz) of heptets (J_{HCCH} = 6.4 Hz), is obscured by the diisopropylamine methine signal. [f] The amine proton resonance is not observed at ambient temperature because of quadrupole broadening.
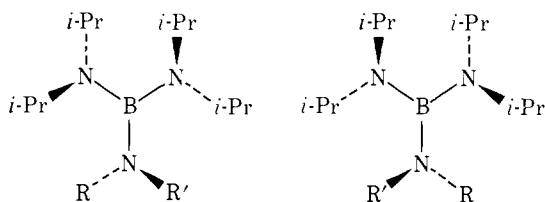
As predicted from the structures shown above, low-temperature ($\sim$−100 °C) ^{1}H and ^{13}C NMR spectra (Figures 1 and 2, Tables I and II) of I and II show two diastereotopic isopropyl groups. The R groups attached to the remaining nitrogen are equivalent, but prochiral methyl groups within each isopropyl (and ethyl methylene protons in II) are anisochronous. As shown in Figures 1 and 2 for II, the spectra are temperature dependent and at 30 °C nonequivalencies between prochiral groups and between isopropyl groups have disappeared. Obviously at ambient temperature I and II are no longer stereochemically rigid but are undergoing an enantiomerization which also effects an interchange between isopropyl group sites. While the limiting high-temperature spectra give little information on the nature of this process, its permutational characteristics can be obtained from spectra taken in the intermediate exchange region.

Mechanism of Enantiomerization. In principle either correlated or noncorrelated rotations about the B–N bonds could result in the interconversion of enantiomers. A noncorrelated process would be one in which the amino groups rotate independently of one another. However, in such a process not every rotation about a B–N bond would exchange enantiomers, since a chirality change requires torsion about all B–N bonds. Such a simultaneous rotation about all the B–N bonds would be a rare event in the noncorrelated case. Thus, considering the –B(N-i-Pr$_2$)$_2$ portion of I and II, if noncorrelated rotations are occurring the rate at which nonequivalent isopropyl groups become equivalent should exceed the rate at which enantiomers

interchange. Experimentally the rate of isopropyl group exchange can be measured from the behavior of methine signals in the intermediate exchange region and the rate of interconversion of enantiomers can be determined from the coalescence of signals arising from anisochronous prochiral groups. In I, at the coalescence temperature of the ^{13}C NMR methine signals (−121 °C), the rate of methine group exchange is calculated to be 20 s^{-1}, while the rate of methyl group exchange determined by line shape analysis of ^{13}C NMR spectra is 17 s^{-1}. The obvious conclusion is that I and II enantiomerize via correlated motions about the B–N bonds.
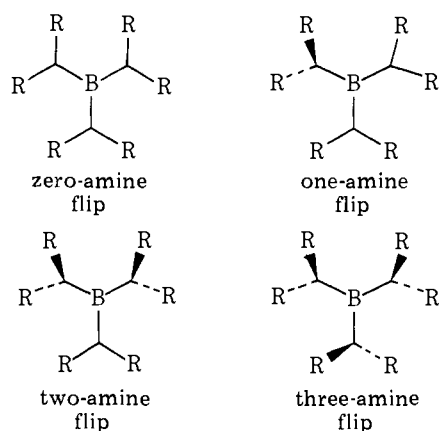
A number of pathways are available for enantiomerization if the amino groups move in a correlated fashion. Fortunately these have already been enumerated in detail by Mislow and co-workers for molecular propellers.[7a,b,d] The correlated rearrangements of these systems can be described in terms of "flip" mechanisms. When applied to the tris(amino)boranes, four such mechanisms are available. These correspond to correlated rotations in which zero, one, two, or all three of the amino groups rotate so that the substituents attached to the nitrogen pass perpendicular to the BN$_3$ plane. At the same time any remaining amino groups rotate so that their substituents pass through this plane. These rearrangements can thus be classified as zero-, one-, two-, or three-amine flips depending on the number of amino groups which rotate through an orientation perpendicular to the BN$_3$ plane. Idealized transition states for the four flip mechanisms are shown below.[13] In general the energies of each of the pathways will be different. The chirality of the tris(amino)borane will be reversed by any of these mechanisms; nonetheless they can be distinguished because they permute various sites within the molecule in different ways.

Table V summarizes the permutations within the isopropyl groups of I–V which are characteristic of each of the flip mechanisms. Note that when R = R' the following equivalencies exist between sites because of symmetry: a ≡ h, b ≡ g,

Table IV. ^{13}C DNMR of $(i\text{-}Pr_2N)_2$ BNRH Compounds

Compd Resonance	δ (appearance, J_{CH}, rel no. of C's)[a,b]		
	Ambient temp	Intermediate temp	Low temp
R = Me	30 °C	−40 °C	−120 °C
$CH(CH_3)_2$	60.41 (d, 90.97 Hz, 4 C)	60.06 (2 C)	60.59 (2 C)
		58.48 (2 C)	62.5 (1 C)
			56.71 (1 C)
NCH_3	62.00 (q, 93.21 Hz, 1 C)	60.94 (1 C)	62.00 (1 C)
$CH(CH_3)_2$	37.69 (q, 97.65 Hz, 8 C)	36.81 (4 C)	37.69 (4 C)
		36.57 (4 C)	~38 (2 C)
			~37 (2 C)
R = Et[c]	30 °C	−36 °C	−120 °C
$CH(CH_3)_2$	60.50 (d, 90.91 Hz, 4 C)	60.06 (2 C)	60.77 (2 C)
		58.30 (2 C)	62.53 (1 C)
			56.89 (1 C)
CH_2CH_3	52.3 (t, 95 Hz, 1 C)	51.25 (1 C)	52.49 (1 C)
$CH(CH_3)_2$	37.78 (q, 97.65 Hz, 8 C)	35.46 (4 C)	38.04 (4 C)
		36.9 (4 C)	~38 (2 C)
			36.97 (2 C)
CH_2CH_3	33.30 (q, 95.43 Hz, 1 C)	32.58 (1 C)	34.17 (1 C)
R = *i*-Pr	30 °C	−11 °C	−120 °C
$N[CH(CH_3)_2]_2$	59.35 (d, 90 Hz, 4 C)	60.06 (2 C)	61.12 (2 C)
		58.30 (2 C)	62.17 (1 C)
			56.71 (1 C)
$NCH(CH_3)_2$	56.89 (d, 90.97 Hz, 1 C)	56.71 (1 C)	57.94 (1 C)
$NCH(CH_3)_2$	40.51 (q, 93.19 Hz, 2 C)	40.51 (2 C)	41.92 (2 C)
$N[CH(CH_3)_2]_2$	36.99 (q, 95.43 Hz, 8 C)	37.0 (4 C)	38.22 (4 C)
		36.46 (4 C)	~38 (2 C)
			36.63 (2 C)

[a] Chemical shifts are in parts per million downfield from external Me_4Si. [b] Proton–carbon-13 coupling constants were obtained from spectra with protons not decoupled. All other parameters are from noise-decoupled spectra. [c] Computer-assisted deconvolution of the isopropyl methyl region of the −120 °C spectrum revealed the presence of three peaks, with calculated chemical shifts and relative intensities of 38.47 (2 C), 38.07 (4 C), and 36.99 (2 C).

zero-amine flip
one-amine flip
two-amine flip
three-amine flip

Table V

Exchange mechanism	Methyl sites permuted	Methine sites permuted
(0) flip	(ab) (cd) (ef) (gh)	(α) (β) (γ) (δ)
(1,2,3) flip	(af) (bd) (ch) (dg)	$(\alpha\gamma)$ $(\beta\delta)$
(1) flip	(ag) (bh) (ce) (df)	$(\alpha\delta)$ $(\beta\gamma)$
(2) flip	(ac) (bd) (ef) (gh)	$(\alpha\beta)$ (γ) (δ)
(3) flip	(ab) (cd) (eg) (fh)	(α) (β) $(\gamma\delta)$
(1,2) flip	(afdg) (bech)	$(\alpha\beta\gamma\delta)$
(1,3) flip	(agfd) (bhce)	$(\alpha\beta\gamma\delta)$
(2,3) flip	(ac) (bd) (eg) (hf)	$(\alpha\beta)$ $(\gamma\delta)$

$c \equiv f$, $d \equiv e$, $\alpha \equiv \delta$, and $\beta \equiv \gamma$. Thus there are only four distinct isopropyl methyl sites and two distinct methine sites in I and II. If the number in parentheses is taken to denote the amino moiety(ies) which pass perpendicular to the BN_2 plane in the idealized transition state, inspection of Table V reveals that complete interchange of diastereotopic groups in I and II can be achieved only by a (1,2) or the equally energetic (1,3) flip *or* by a combination of (2) and (3) flips which are equivalent in I and II and would thus occur at equal rates. Unfortunately the permutations between the four methyl sites and between the two methine sites are exactly the same for a (1,2) + (1,3) two-amine flip process or for the (2) + (3) one-amine flip process. The line shape observed in the intermediate exchange region can be closely duplicated using these permutations (Figure 5). While this demands that the molecules are isomerizing by a (1,2) + (1,3) and/or (2) + (3) process, it does not reveal which of these or whether a combination of the two is actually occurring. Thermodynamic parameters for the exchange process seen in I and II are given in Table VI.

While the NMR data give no information on the details of the motions of the NR_2 group, it is important to notice that if a (1) flip, or a (2,3) flip were still occurring at the temperatures at which the (2) + (3) or (1,2) + (1,3) flips are slow, the molecules would possess time-average mirror symmetry through a plane defined by BN_3 and through a plane perpendicular to BN_3 and containing the R_2N–B bond. As a consequence the observed anisochronicity between prochiral groups would not occur. The clear conclusion is that the lower limit for the activation energy of a (1) flip and/or (2,3) flip is the observed barrier to the (2) + (3) and/or (1,2) + (1,3) processes. Since there is no reason to expect all the one-amine flips
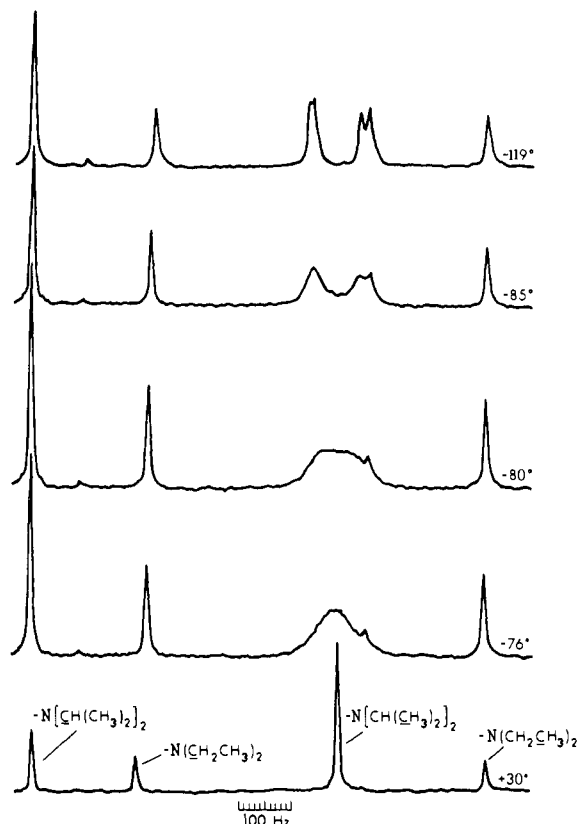
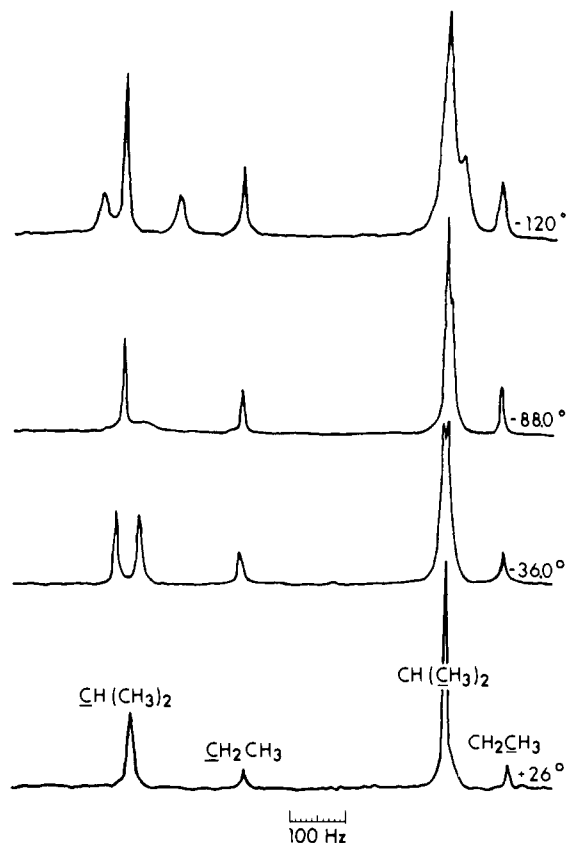**Figure 2.** ¹³C DNMR spectra of bis(diisopropylamino)diethylaminoborane (II).

Figure 4. ¹³C DNMR spectra of bis(diisopropylamino)ethylaminoborane (IV).
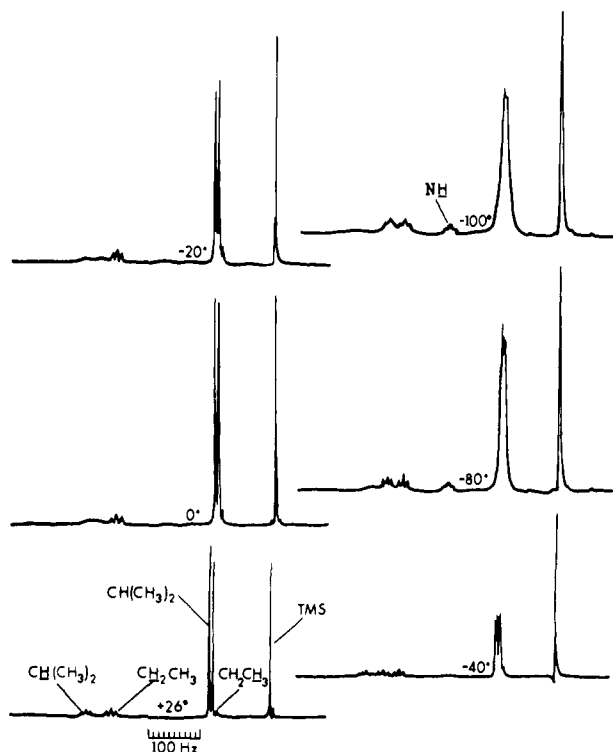

Figure 3. ¹H DNMR spectra of bis(diisopropylamino)ethylaminoborane (IV).

Table VI. Barriers to Exchange Processes in I–V

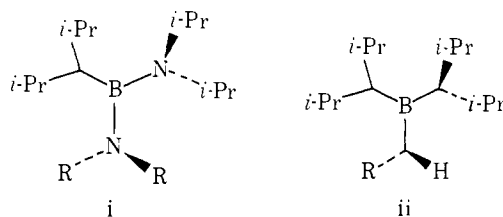|	Process[a]			
	(1) flip		(2) and (3) flips[b] or (2) flip[c]	
Compd	T_c, °C	$\Delta G_c^{\ddagger}$, kcal/mol[d]	T_c, °C	$\Delta G_c^{\ddagger}$, kcal/mol[d]
I	e	e	−110	7.91
II	e	e	−80	9.38
III	−7	13.56	−96	8.02
IV	−7	13.20	−89	8.28
V	16	14.36	−89	8.46

[a] For the assignment of barriers to specific processes, see the Discussion. [b] For R = R'. [c] For R = H. [d] From line shape analysis of ¹³C NMR spectra. [e] The (1) flip is not observable in I and II.

or all the two-amine flips to be of equal energies, and since the idealized transition states appear to contain quite dissimilar steric interactions, in all probability the (1) and/or (2,3) flips are of higher energy than the (2) + (3) and/or (1,2) + (1,3) process which is observed. Slowing of the (1) or the (2,3) flips

without slowing the (2) + (3) or the (1,2) + (1,3) flips would lead to no observable change in the NMR spectra of I or II and it is thus impossible to obtain a direct measure of the barrier to these processes from I and II.

Fortunately, the ambiguity between the one-amine and two-amine flip mechanisms can be resolved in compounds such as III–V where R ≠ R'. In these cases none of the eight methyl sites and four methine sites in the B(N-*i*-Pr₂)₂ portion of the molecules are equivalent by symmetry. Correspondingly the temperature dependency of the NMR spectra of III–V are more complex than those of I and II. Sample ¹³C and ¹H NMR spectra are shown for IV in Figures 3 and 4; those for III and V are quite similar. In these compounds two exchange processes slow between 30 and −120 °C. The first of these is evidenced by the broadening of the single isopropyl methyl and methine resonances which are observed at room temperature. By −40 °C these have resharpened and each appears as two new peaks. Obviously this is the result of the slowing of an

exchange between two equally populated isopropyl sites. Thermodynamic parameters to exchange between these sites are summarized in Table III. It should be noted that for III-V this barrier is about 13-14 kcal/mol. As the temperature is lowered below −40 °C one methyl and one methine peak do not change. The other methyl and methine resonance each broaden and finally resharpen to two new peaks. This results in a spectrum at −120 °C which contains three isopropyl sites populated in a 1:1:2 ratio. The thermodynamic parameters associated with this exchange are also reported in Table VI. Note that the barrier for the latter process in III-V is in the same range (8-9 kcal/mol) as the barrier for the process observed in I and II, which has been identified as either (2) + (3) flip, or a (1,2) + (1,3) flip.

An idealized transition state for the (1,2) or (1,3) flips in I and II (i) is almost identical with that for the corresponding (1,2) or (1,3) flips in III-IV (ii).

Thus, if enantiomerization in I-V occurs via two-amine flips, the 8-9 kcal process may reasonably be assigned as the (1,2) and/or (1,3) flips. The 13-14 kcal process in III-V must then be the remaining two-amine flip, the (2,3) flip. However, cessation of the (2,3) flip alone could not give rise to the −40 °C spectra in III-V, as rapid (1,2) and (1,3) flips would still interconvert all isopropyl methine sites (Table V). Hence, the two-amine flip mechanism cannot account for the spectral temperature dependencies observed in III-V.

On the other hand, if enantiomerization in I-V occurs via one-amine flips, all the spectral changes can be readily explained. As discussed above, the highest energy one-amine flip would be the (1) flip, which can be assigned as the 13-14 kcal/mol process. While slowing of the (1) flip in I and II could not be observed because of the symmetry of the molecules, its cessation in III-V renders the two diisopropylamino moieties nonequivalent. Since rapid (2) and (3) flips interconvert the isopropyl groups within the diisopropylamines, and enantiomerize the molecule (Table V), slowing only the (1) flip results in two separate isopropyl methyl and methine signals, as observed in the ^{1}H and ^{13}C spectra of III-V taken at −40 °C (Figures 3 and 4).

The 8-9 kcal process is attributable to the (2) and/or (3) flips. In I and II, these flips are equal in energy and will have equal rates. In III-V, the (2) and (3) flips are not likely to be equal in energy. The idealized transition state for the (2) flip is very similar to that of the (2) [and (3)] flip in I and II, while
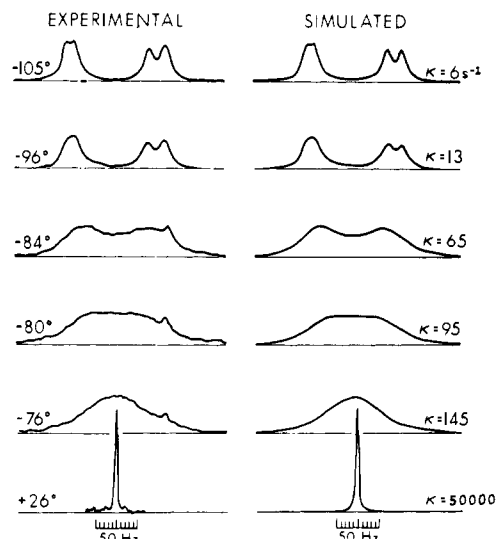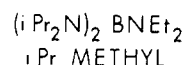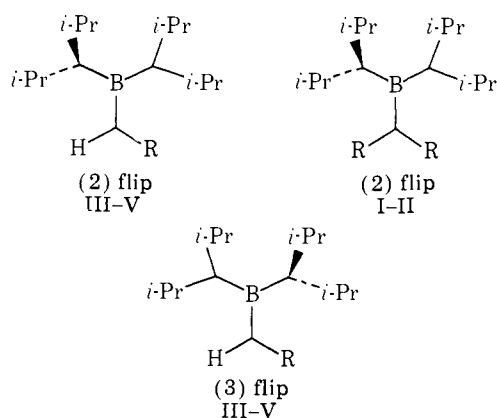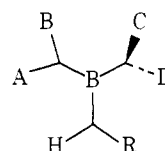

Figure 5. Experimental and calculated ^{13}C DNMR spectra of bis(diiso-propylamino)diethylaminoborane (II) in the isopropyl methyl region.

the (3) flip in III-V is less sterically hindered and thus should be the lowest energy of the one-amine flips in III-V.

With the (1) flip already slow and the (3) flip still rapid, III-V assume the time-averaged conformation shown below

when the (2) flip slows. Isopropyl groups A and B are inequivalent to C and D because of the slow (1) flip. As the (2) flip slows, A becomes inequivalent to B while C and D remain equivalent to each other. Exactly this behavior is seen between −40 and −120 °C in the spectra of III-IV. There, in both the ^{1}H and ^{13}C spectra, one of the two methine peaks remains sharp while the other broadens to reappear as a doublet at low temperature.

Note that if this assignment is correct, isopropyl groups A and B should be assigned to the new peaks which appear in the −120 °C spectra. They, thus, should be the groups which give rise to the peaks in the −40 °C spectra which are temperature dependent between −40 and −120 °C. In fact this supposition is borne out by NOE experiments on III, where R' = CH₃, in which the amine proton was spin tickled and which resulted in a 13% signal enhancement in the isopropyl methine signal which gave rise to two peaks at −100 °C; during these NOE experiments no enhancement could be detected in the methine signal which did not change between −40 and −120 °C. Since NOE signal enhancement is proportional to $1/r$,[6] the isopropyl groups closest to the amine proton (i.e., A and B) are the ones for which maximal signal enhancement should occur.[14] The resonance which is temperature dependent between −40 and −120 °C can thus be confidently assigned to A and B while C and D must give rise to the peak which does not change over this temperature range.

In principle a third two-amine flip, the (3) flip, might also slow. However, we were unable to observe its cessation in these experiments; its barrier must be somewhat less than 5-6 kcal/mol. This is probably not too surprising since its idealized transition state appears to be far less sterically congested than those of either the (1) or (2) flip.

Table VII. Relative One-Amine Flip Transition State Energies in $B(NH_2)_3$

Flip mechanism	Energy,[a] kcal/mol
Zero-amine flip	0.00
One-amine flip	17.08
Two-amine flip	40.41
Three-amine flip	74.07

[a] The energy is reported relative to that of zero-amine flip transition state.

Molecular Orbital Calculations. Mislow and co-workers in a series of definitive studies have shown that triarylboranes, and related triaryl compounds which are stereochemically correspondent to the tris(amino)boranes, isomerize through a two-flip mechanism.[7] In these compounds the rearrangement mode appears to be a result primarily of steric effects as evidenced by the ability of empirical force field calculations both to predict a two-flip mechanism as the low-energy route of isomerization and to closely reproduce the observed barriers.[7c] The operation of the one-flip as the low-energy mode of isomerization in tris(amino)boranes indicates that other factors influence the relative activation energies for concerted rotations in these compounds. Intuitively, one would expect electronic effects to be much more significant in tris(amino)boranes than in the triaryl systems.

While in a planar X_2B-NR_2 unit the B–N bond contains significant double bond character, π bonding will be decreased when rotation takes place around the B–N bond to produce the nonplanar arrangement of NR_2 and X_2B units found in the chiral ground state geometries of the tris(amino)boranes. Upon isomerization, however, the opportunity is offered to some of the amino moieties to assume a conformation in the transition state which maximizes π interactions. The transition state of a two-amine flip, which by analogy to Mislow's results on the triaryl compounds would probably be the low-energy route to enantiomerization in I–V if steric effects alone are involved, places only one amino moiety in a position to maximize its π interaction to boron. The remaining two are approximately perpendicular to the BN_3 plane and are unable to π bond with the boron. The transition state for the one-amine flip, on the other hand, places only one amino group in the unfavorable perpendicular orientation while two are positioned to maximize the B–N π interaction.

In order to determine the electronic contributions to the relative stabilities of the flip mechanism transition states, we performed INDO calculations on the model compound $B(NH_2)_3$ in various conformations.[15] The results, as shown in Table VII, indicate that the one-amine flip is electronically favored by 23 kcal/mol over the two-amine flip. It is interesting that the zero-amine flip transition state is electronically even more stable than the one-amine flip transition state. Since the zero-amine flip is not the low-energy mode of enantiomerization, it must be destabilized by steric interactions to a greater degree than it is stabilized by electronic interactions. Hence the one-amine flip is the low-energy mode of enantiomerization because of a combination of electronic factors (which render it more stable than the two- or three-amine flips) and steric factors (which render it more stable than the zero-amine flip).

Previous Investigations. Previous stereodynamical studies of aminoboranes and of the isoelectronic and stereochemically correspondent guanidinium ions have not explicitly considered the consequences of correlated NR_2 motions or of possible helical molecular conformations. Of course, in some cases achiral conformations and noncorrelated motions may prevail. It is interesting, however, that several observations which have already been made can be rationalized in terms of stereodynamical processes similar to those observed in this study. For example, the barrier observed in $((CH_3)_2N)_2BN(CH_3)$-$(C_6H_5)^2$ can be attributed to the slowing of both of the one-amine flips which place a dimethylamino group perpendicular to the BN_3 plane. (Slowing of only one of these processes will not lead to a change in the NMR spectra.) With the methylphenylamino flip still rapid, the time-averaged conformation will be just that postulated by Dewar and Rona as the ground state conformation of this molecule.[2]

Guanidinium ions, which are important biological compounds, are both stereochemically correspondent to and isoelectronic with tris(amino)boranes. An elegant investigation of the stereoisomerization of N,N,N',N',N''-pentamethyl-
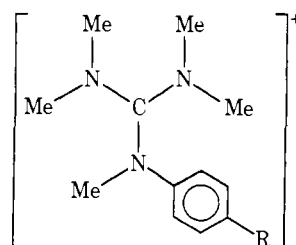
N''-phenylguanidinium ions has been reported.[16] While stipulating that the ground state for these ions is in fact probably not planar, Kessler and Leibfritz treated the dynamics of the problem from the standpoint of a planar ground state and independent rotations about the bonds between the nitrogens and the central carbon. Their experimental results may be at least equally well explained by postulating a chiral, propeller-like ground state geometry and exchange by means of concerted C–N rotations, specifically, one-amine flips.[17]

While there are little data to indicate whether similar behaviors would also be expected in bis(amino)boranes, Neilson and Wells have recently postulated that in compounds such as $((CH_3)_3Si)_2NB(C_6H_5)N(CH_3)_2$ the bulky bis(trimethylsilyl)amino group is rotated out of the BN_2 plane while the $-N(CH_3)_2$ moiety is coplanar with the boron and its two other substituents.[5] These results could also be explained if the ground state geometry of these molecules is chiral and the
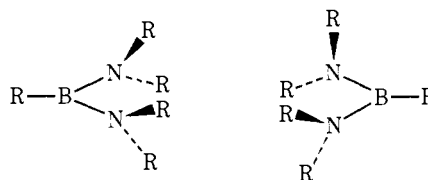
enantiomerization occurs by a correlated one-amine flip. If the one-amine flip in which the dimethylamino group goes perpendicular to the BN_2 plane is stopped, the time-average conformation of the molecule would be very close to the static conformation proposed by Wells. In $((CH_3)_3Si)((CH_3)_2$-$CH)NB(C_6H_5)N(CH_3)_2$, where two barriers to B–N motions could be detected, both of the one-amine flips which are possible if this molecule is helically chiral may have ceased. Such a stereochemically rigid chiral structure may be indicated by the anisochronicity of the prochiral isopropyl methyl groups which was observed in the ^1H spectra obtained at low temperatures.[5]

In summary, tris(amino)boranes have been shown to be helically chiral and to isomerize by means of concerted rotations of the amine groups. The one-amine flip is the low-energy mode of isomerization, as a result of combined steric and electronic effects. This is in contrast to stereochemically correspondent triaryl compounds which isomerize by means of two-flips, primarily as a result of steric considerations. The fact that two classes of stereochemically correspondent systems are

helically chiral molecular propellers and rearrange by means of concerted rotations of the substituents on the central atom strongly suggests that such behavior should be considered in studies of other stereochemically equivalent systems such as guanidinium ions.

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(13) The NMR data obtained in this study, of course, only give information on the permutational character of the enantiomerization. The idealized transition states represent geometric averages between the initial and final conformations and undoubtedly do not represent the actual transition states with absolute fidelity. Nonetheless the idealized states are pictorially useful and clearly illustrate the differences in the direction of B–N bond rotations which occur among the various flip mechanisms.

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Reaction of e_{aq}^- into Excited States of $Ru(bpy)_3^{2+}$ [1]

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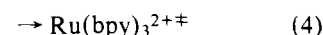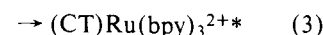
Abstract: In the reaction of e_{aq}^- with $Ru(bpy)_3^{3+}$ it was found that 38% of e_{aq}^- yields $(CT)Ru(bpy)_3^{2+*}$, the well-known, luminescent lowest charge transfer state of $Ru(bpy)_3^{2+}$. More than 55% of e_{aq}^- (that is, almost all of the remainder) yields another excited state or a coordinated radical complex, which is longer lived than $(CT)Ru(bpy)_3^{2+*}$ and does not convert to it. A very small fraction of e_{aq}^- (<7%) is transferred directly to the ground state. While $(CT)Ru(bpy)_3^{2+*}$ decays to the ground state both by first-order conversion and through quenching by $Ru(bpy)_3^{3+}$, the other product decays to $Ru(bpy)_3^{2+}$ almost solely (under our conditions) through a reaction with $Ru(bpy)_3^{3+}$. The lack of a significant direct reaction to the ground state is rationalized as an example of the slow electron transfers to be expected for highly exergonic reactions in the "inverted" region of the Marcus theory. H atoms, Cd^+, and $Ru(bpy)_3^+$ were found to react with $Ru(bpy)_3^{3+}$ to yield the divalent ground state directly.

Introduction

The reduction of $Ru(bpy)_3^{3+}$ (bpy = 2,2-bipyridine) by several reductants yields the lowest charge transfer state of $Ru(bpy)_3^{2+}$ (denoted $(CT)Ru(bpy)_3^{2+*}$).[2] This was shown to be the case for reduction of $Ru(bpy)_3^{3+}$ by OH^- ions,[3] by hydrazine,[4] and by various products of electrochemical reduction of $Ru(bpy)_3^{2+}$.[5] In all of these reactions chemiluminescence was observed, the spectrum of which was similar to the emission spectra obtained on excitation of $Ru(bpy)_3^{2+}$ by light to its lowest charge transfer state.[6] However, in most of these systems it is improbable that the chemiluminescence is a result of simple electron transfer from the reductant to $Ru(bpy)_3^{3+}$ since the thermodynamics of such a simple transfer are either unfavorable or marginally favorable. Recently, Martin et al.[7] have demonstrated that a relatively efficient chemiluminescence results when $Ru(bpy)_3^{3+}$ is reduced

by aquated electrons, e_{aq}^-. Since by nature of the reductant the most probable mechanism is a direct electron transfer to $Ru(bpy)_3^{3+}$ we considered it to be of some interest to study this reaction in detail.

Once an e_{aq}^- encounters $Ru(bpy)_3^{3+}$ and a precursor complex is formed[8] (reaction 1) the transferred electron might then find itself after vibrational relaxation in any of the following possible states:

$$Ru(bpy)_3^{3+} + e_{aq}^- \rightleftharpoons Ru(bpy)_3^{3+}|e_{aq}^- \quad (1)$$

$$Ru(bpy)_3^{3+}|e_{aq}^- \rightarrow Ru(bpy)_3^{2+} \quad (2)$$

$$\rightarrow (CT)Ru(bpy)_3^{2+*} \quad (3)$$

$$\rightarrow Ru(bpy)_3^{2+\ddagger} \quad (4)$$

Namely, either the ground state (reaction 2) or the lowest charge transfer state (reaction 3) or some other product such