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Bis(9-triptycyl)amines, a Missing Link between the Corresponding Methanes and Ethers. An Unconventional Synthesis and Influence of Nitrogen Configurational Inversion on the Coupled Disrotatory Trajectory[1]

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As a part of our continued effort to uncover the unique stereoisomerism (phase isomerism) in bis(9-triptycyl)X compounds, three bis(9-triptycyl)amines **1** have been prepared by thermolysis of the corresponding neat 1,3-bis(9-triptycyl)triazenes **4**, obtained in turn from reaction of 9-triptycyllithiums with 9-triptycyl azides. The synthetic route was fairly efficient, and the overall yields from 9-bromotriptycenes were ca. 40%. The amine **1c** bearing chlorine atoms at carbons 2 and 3′ comprises one meso and one *dl* instead of three *dl* isomers by NMR and by HPLC evidence. This finding indicates rapid exchange of the hydrogen and of the unshared electron pair on nitrogen. The exchange due to configurational inversion of the nitrogen, as in typical secondary amines, was not slowed down at low temperature as shown by the lack of any spectral change in NMR spectra. In spite of the extreme overcrowding in these systems, there appears to be minimal interference between the coupled disrotation and the configurational inversion. The barrier for the interconversion of the meso and *dl* isomers of **1b** having chloro substituents at carbons 2 and 2′ was measured as 39.1 kcal mol^{-1} and lies between those of the analogous ethers and methanes. This observed trend is explicable solely from the relevant molecular constants such as C–X bond lengths, C–X stretching, and C–X–C bending force constants; invoking a contribution from nitrogen inversion is not required.

In previous papers of this series,[2] we described unique stereochemical consequences of tight meshing of two 9-triptycyl groups connected by an oxygen atom or by a methylene group. In these systems, two torsional degrees of freedom about the bonds from the bridgehead carbons to the central atom lose their independence. They become strictly coupled into disrotation. Labeling at least one of the three benzene rings of each triptycyl moiety gives rise to stereoisomers differing only in the phase relationship of the labeled benzene rings and this despite rapid rotation. In the simplest labeling pattern, one of the three benzene rings in each triptycyl unit is labeled identically to generate racemic (*dl*) and optically inactive (meso) isomers. In the former, the labeled benzene rings bite each other once in a full rotational cycle whereas in the latter they never come next to each other.

Although meso and *dl* isomers are expected to show minute differences in physical properties, they were effectively separated through HPLC.[2b,e] Separation of the *dl* isomers into the optical antipodes was also performed with the chiral stationary phase developed by Yuki and Okamoto.[2d] Separation and assignment of the nine stereoisomers resulting from a more complex labeling pattern, in bis(2,6-dichloro-9-triptycyl)methane, was undertaken, and a preliminary result has been published.[2g]

In spite of apparent congestion, coupled disrotation is almost unhindered and by no means slow. Molecular mechanical calculations predict barriers to the process—literally molecular cogwheeling—of 0.18 and 0.93 kcal mol^{-1} for the methane[3e] and for the ether,[2h] respectively. The barrier for the latter was recently determined experimentally as 4.2–4.8 kcal mol^{-1} from exciplex fluorescence dynamics of the *dl* isomer of 2,3-benzo-9-triptycyl 2-[(dimethylamino)methyl]-9-triptycyl ether.[2i] The system was extended to doubly geared ethers[2f] and methanes.[4]

The rate for interconversion of the meso and the *dl* isomers through molecular gear slippage is strongly dependent on the nature of the central atoms connecting two 9-triptycyl groups. The barrier was measured as 32–33 and 42–43 kcal mol^{-1} for the methanes and the ethers, respectively.[2e] In the case of bis(3-chloro-9-triptycyl)silane, physical separation of the phase isomers becomes impossible at room temperature. A barrier height below 20 kcal mol^{-1} was estimated from NMR line shape analyses.[5]

In order both to investigate the effect of the central atom on the gear slippage and to obtain more experimental insight into its mechanism, we have set about to prepare a series of bis(9-triptycyl)X compounds where X differs from CH_2, O, and SiH_2. In the present paper, we report preparation of the amines (X = NH), a hitherto missing link between CH_2 and O. Relevance of configurational inversion at nitrogen to the coupled disrotation and gear slippage process is also discussed.

Molecular Design and Synthesis

Except for bis(9-triptycyl) nitroxide, the bis(9-triptycyl)amine skeleton had never been reported in the literature. Kaur et al. generated the nitroxide through addition of the 9-triptycyl radical to 9-nitrosotriptycene, and they observed its ESR signals.[6] The nitroxide might have enough stability to be made on the preparative scale. Its reduction to the amine **1a**, however, did not seem to us promising, since considerable difficulties were encoun-

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† Ibaraki University.

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(1) Part 11 of the series. See ref 2j for part 10.

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(3) (a) Hounshell, W. D.; Johnson, C. A.; Guenzi, A.; Cozzi, F.; Mislow, K. *Proc. Natl. Acad. Sci. U.S.A.* **1980**, *77*, 6961. (b) Cozzi, F.; Guenzi, A.; Johnson, C. A.; Mislow, K.; Hounshell, W. D.; Blount, J. F. *J. Am. Chem. Soc.* **1981**, *103*, 957. (c) Johnson, C. A.; Guenzi, A.; Mislow, K. *Ibid.* **1981**, *103*, 6240. (d) Johnson, C. A.; Guenzi, A.; Nachbar, R. B., Jr.; Blount, J. F.; Wennerström, O.; Mislow, K. *Ibid.* **1982**, *104*, 5163. (e) Bürgi, H.-B.; Hounshell, W. D.; Nachbar, R. B., Jr.; Mislow, K. *Ibid.* **1983**, *105*, 1427. (f) Guenzi, A.; Johnson, C. A.; Cozzi, F.; Mislow, K. *Ibid.* **1983**, *105*, 1438.

(4) Kawada, Y.; Iwamura, H., unpublished results.

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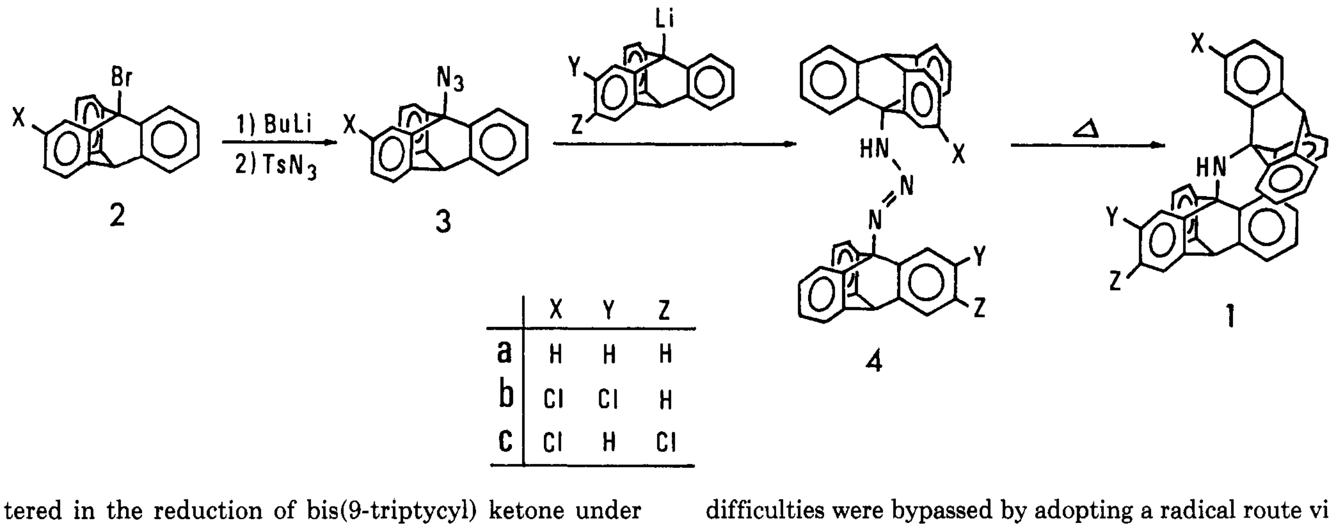
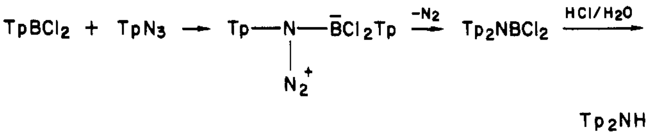
Scheme I



	X	Y	Z
a	H	H	H
b	Cl	Cl	H
c	Cl	H	Cl

tered in the reduction of bis(9-triptycyl) ketone under various conditions.[7]

Few of the known preparations of secondary amines seemed applicable to the synthesis of **1**. Firstly, nucleophilic substitution at the first row element next to the bridgehead carbon as well as at the bridgehead carbon itself is extremely difficult.[8] Secondly, 9-triptycyl organometallics rarely undergo substitution reactions with first row electrophiles,[9,10] although they behave normally in addition reactions.[11,12] Consider the example of Brown's method in which alkyl azides are treated with organoboranes.[13] A probable scheme would be as follows.



$$\mathrm{TpBCl_2} + \mathrm{TpN_3} \rightarrow \mathrm{Tp}\text{—}\underset{\substack{|\\ \mathrm{N_2^+}}}{\mathrm{N}}\text{—}\bar{\mathrm{B}}\mathrm{Cl_2Tp} \xrightarrow{-\mathrm{N_2}} \mathrm{Tp_2NBCl_2} \xrightarrow{\mathrm{HCl/H_2O}} \mathrm{Tp_2NH}$$

(Tp = 9-triptycyl)

This reaction sequence was, however, not adopted because we were uncertain of the relative ease of migration of the 9-triptycyl group on the boron atom to the electron-deficient nitrogen and of the rearrangement of the other 9-triptycyl group on nitrogen to a homotriptycyl (tribenzo-[3.2.2]nonatrien-2-yl) skeleton.[14,15] Difficulties were also anticipated in preparing the starting (dichloro-9-triptycyl)borane (vide supra). While bis(1- and 2-anthryl)amines have been known for some time,[16] bis(9-anthryl)amine is not a known compound. Even if this amine were prepared, addition of benzyne in the desired manner might compete strongly with an electrophilic reaction of benzyne with the lone pair on nitrogen.[17] These difficulties were bypassed by adopting a radical route via thermolysis of 1,3-bis(9-triptycyl)triazenes.

Formation of amines by thermolysis of triazenes is well-known. For instance, we have reported formation of *N*-methyl-*p*-toluidine in 11–13% yields via collapse of the *p*-tolylaminyl methyl radical pair in the thermolysis of 1-(*p*-tolyl)-3-methyltriazene in fluid solution.[18] However, the main reaction was hydrogen abstraction from solvent molecules by the aminyl radical to give *p*-toluidine. Use of triazenes for the synthesis of secondary amines has yet to be established. Currently, triazenes are widely used as alkylating agents[19] and as intermediates for preparation of aryl halides,[20] but ionic mechanisms prevail in these reactions.

In Scheme I is outlined our synthetic route to the amines **1**. 9-Bromotriptycenes **2** were converted to 9-triptycyl azides **3** according to the literature procedure with slight modification.[15] Addition of 9-triptycyllithiums to the azides proceeded normally to give triazenes **4** in good yields after aqueous workup. Less than a few hundred mg of the triazenes **4** were pyrolyzed in the absence of any solvent. Darkening of the sample with evolution of nitrogen started at around 200 °C, and the decomposition became very rapid at ca. 250 °C. As with synthesis of the ethers,[2e] the yield was highest in the case of the unsubstituted amine (**1a**, nearly quantitative; **1b**, 60%; **1c**, 70%). Large scale pyrolysis gave significantly lower yields, possibly due to inadequate dissipation of evolved heat resulting in local overheating. Much higher yields, as compared to solution-phase pyrolysis of less hindered triazenes, can be ascribed mainly to generation of bulky 9-triptycyl and 9-triptycylaminyl radicals face-to-face with each other in a rigid environment, leading to efficient cage-recombination.

Separation of the Isomers and Kinetics of Isomerization. Differences in solubility of the meso and *dl* isomers of **1b** and **1c** are much larger than those for the corresponding isomers of the methanes and the ethers. The meso isomers are less soluble. Thus repeated recrystallization of the reaction mixture from either chloroform/hexane or dichloromethane/hexane gave considerably meso-enriched samples, and *dl*-rich samples were

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[7] Crumrine, D.; Iwamura, H., unpublished results.

[8] Wilt, J. W.; Malloy, T. P. *J. Org. Chem.* **1972**, *37*, 2781.

[9] Bis(9-triptycyl)X compounds prepared through double nucleophilic substitutions of X(halogen)$_2$ are TpSiH$_2$ and Tp$_2$Hg.[10] Thus X are limited to the atoms belonging to second or lower row in the periodic table. Tp$_2$S and Tp$_2$PH could not be prepared by application of similar methods. There is some evidence to show that it is the second substitution that does not occur easily. Tp$_2$PCl$_2$ was cleanly obtained from 9-triptycyllithium and phosphorous trichloride.[11]

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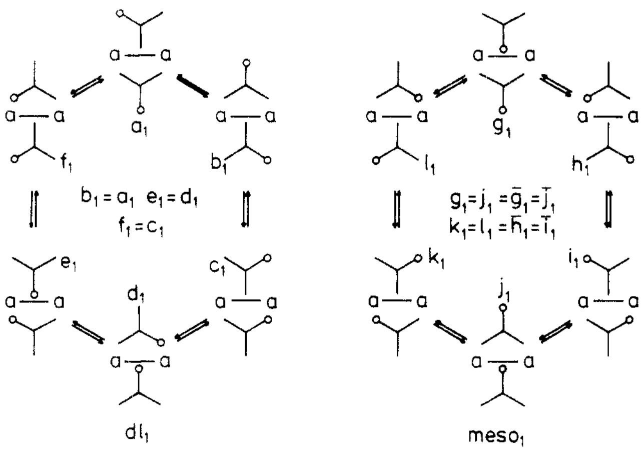

Figure 1. Conformational gearing circuits for bis(9-triptycyl)X molecules in which the tetrahedral atom X carries two identical substituents and one of the benzene rings on each triptycene unit is labeled identically. The nonidentical labeling gives rise to isomers dl_2 and meso_2 (one of the labels is now ● instead of ○ in the above figures). In the latter, $g_2 = \bar{g}_2$, $j_2 = \bar{j}_2$, $k_2 = \bar{i}_2$ and $l_2 = \bar{h}_2$.

obtained as later fractions of column chromatography on silica gel of the *dl*-rich mother liquor of recrystallization. However, complete separation of the meso and *dl* isomers required HPLC on microsilica, as was performed on **1b**.

Unambiguous assignment of the meso and *dl* isomers was based on the ratio of the amounts of the two isomers obtained and on their ^{13}C NMR spectra. HPLC showed the presence of the two isomers in almost statistical ratio (1:2) in the crude pyrolysate. This suggested that the minor isomers, eluted first, are, as with all the single-geared methanes and ethers, the meso isomers. The ^{13}C NMR spectra of the meso isomer of **1b** show 12 signals in the aromatic region. In sharp contrast, 18 lines were observed for the *dl* isomers: the two unlabeled benzene rings are diastereotopic. Similarly, most of the theoretically predicted 24 and 36 carbon signals of the meso and *dl* isomers, respectively, of **1c** were observed. These observations firmly supported the assignment.

The interconversion of the separated meso and *dl* isomers of **1b** was performed, as in the earlier work in *o*-dichlorobenzene,[2e] in the temperature range 176–276 °C. From the Arrhenius plots of the rates of isomerization (Table I) the activation energy is 39.1 ± 0.5 kcal mol^{-1}, and log $A = 12.4 \pm 0.2$. The equilibrium constant defined as *dl*/meso was 1.82 throughout the whole temperature range, thus slightly favoring the meso isomer as is always the case for the hitherto known bis(9-triptycyl)X compounds.

Discussion

Relevance of the Configurational Inversion of the Nitrogen to the Coupled Disrotatory Trajectory. The number of possible phase isomers depends not only on the pattern of labeling benzene rings but also on the nature of the substituents on the central atom.[3a,b,f] Let us consider the case in which only one of the three benzene rings in each triptycene unit is labeled and in which the central atom has tetrahedral configuration. When the two substituents a and b on the central atom are identical, one meso and one *dl* isomer are formed, irrespective of whether the labeled benzene rings are identical (meso_1 and dl_1 in Figure 1) or not (meso_2 and dl_2 in Figure 1). To the contrary, different substituents on the central atom ($a \neq b$) give rise to one meso and one *dl* or to three *dl* isomers, depending on whether the unique benzene rings are equally labeled (meso_3 and dl_3 in Figure 2a) or not (dl_4, dl_5, and dl_6 in Figure 2b).

The presence of one meso and one *dl* isomer and the failure to detect three *dl* isomers for **1c** (a = H and b = unshared electron pair) both in NMR spectra and HPLC indicate a rapid configurational exchange of the hydrogen atom and the unshared electron pair on the nitrogen without loss of phase relationships at ambient temperature. Both ^1H and ^{13}C NMR spectra measured on the practically pure meso isomer at low temperature (down to −90 °C) showed no sign of slow-down of the exchange process, which should have appeared as a change from magnetic equivalence to nonequivalence of the two unlabeled benzene rings of each 9-triptycyl group. The 9-triptycyl group and the hydrogen atom differ greatly in their reduced masses and moments of inertia. Bis(9-triptycyl)X molecules are rather unique, in that small deviations from the coupled disrotatory trajectory cause steep increases of the potential energy.[2h,3e] Hence, minimal movement of the triptycyl groups is required. Therefore, the most likely mechanism for the exchange is a simple permutation of the hydrogen atom and the lone pair of electrons via a planar transition state at the nitrogen either by a proton tunneling and/or through vibrationally excited states as in dimethylamine.[21]

The ground-state conformation of the bis(9-triptycyl)X molecules in the solution phase is not clear. Mislow et al. prefer C_2 to C_s conformations for X = CH_2 based on molecular mechanical calculations[3e] and the X-ray data on bis(9-triptycyl)methane.[3d] The latter conformation is considered to be the transition state for the interconversion of the two C_2 conformations through 60° coupled disrotation. In solid phase, bis(9-triptycyl) ether adopts the C_s conformation which can be reproduced by a molecular mechanical calculation employing slightly different parametrization.[2h] Thus it seems to differ from compound to compound which one might be its ground-state conformation. In the C_s conformation, the NH staggered form with respect to the three benzene rings of one triptycyl unit is the eclipse form with one benzene ring of the other triptycyl unit. Figure 3 shows the exchange process in Newman projection viewed down from the nitrogen to the bridgehead carbons assuming either the C_s or C_2 skeletal conformations. When the N–H group turns over from one side to the other in the C_s conformation, a new eclipsing interaction of the hydrogen with the benzene ring of one triptycyl group is generated in the transition state. A similar interaction with the other triptycyl group disappears when the configuration of the nitrogen changes from tetrahedral to trigonal. In the C_2 conformation, the N–H bond holds the 30° dihedral angle with the benzene rings of either triptycene unit. As inversion of the configuration at nitrogen starts, the hydrogen atom has to pass over the benzene rings of either triptycyl group at the same time in the early stage of the inversion process. Accordingly, the inversion in the C_2 conformation may be slightly disfavored. It is to be noted though that the two conformations are separated by small barriers only.[22] Nonbonded interactions involving the hydrogen on the nitrogen will raise the inversion barrier a little. On the other hand, the intrinsic inversion barrier is considered to be lowered by increase in the C–N–C angle which is presumably the case in **1** as found in the di-9-triptycylmethanes (129.3–129.5°)[3] and di-9-triptycyl ether (135.8°).[2h] Therefore, the barrier height should not be much larger than those reported for

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(22) Empirical force field calculations predict the C_s transition state for dynamic gearing to be 0.2 kcal mol^{-1} above the C_2 ground state of the methane.[3d] The C_2 conformation is a second energy minimum 0.24 kcal mol^{-1} higher in steric energy than the C_s form of the ether.[2h]

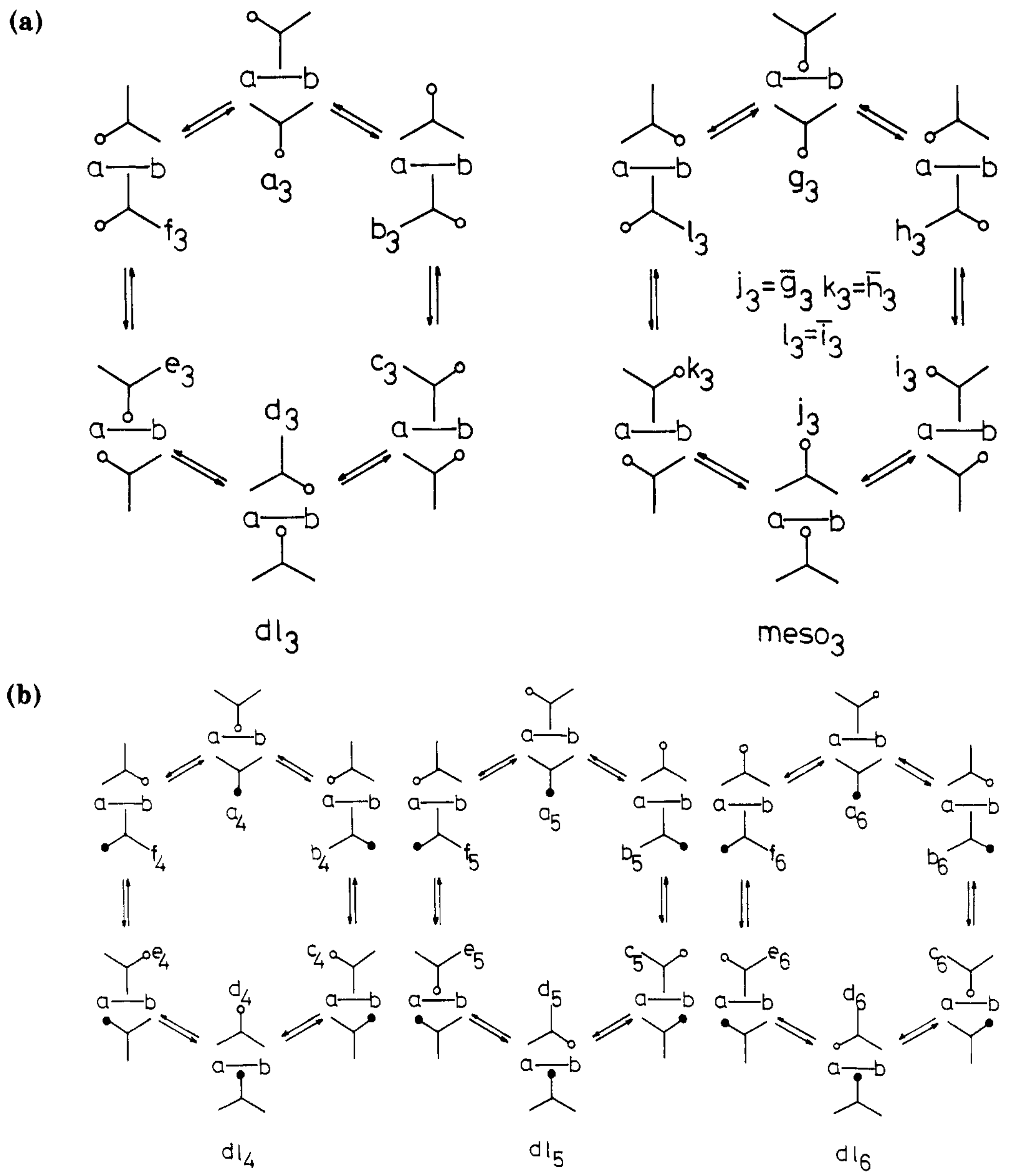

Figure 2. Conformational gearing circuits for bis(9-triptycyl)X molecules in which the tetrahedral atom X carries two different substituents a and b and one of the benzene rings on each triptycyl group is labeled identically (a) or differently (b).

ammonia and dimethylamine, 5.8[23] and 4.4 kcal mol^{-1},[21] respectively. Although the extent of magnetic nonequivalence due to the frozen nitrogen configuration in the present system is not easy to gauge, it is expected to be small. Low-temperature NMR measurements on **1c** did not show any spectral change, which was to be expected.

In Figure 4 are depicted the interconversions of dl_4 and its optical antipode (a) and of dl_5 and the optical antipode of dl_6 (b) through the proposed process, which newly give rise to one meso and one *dl* isomers, corresponding to the two observed isomers of **1c**, respectively. Similar stereochemical circuits for the case where two triptycyl groups cannot be differentiated (c) and to which **1b** belongs are shown in Figure 4. The inversion process is identical with either the 60° or 180° coupled rotation. Since the barrier to disrotation is expected not to be higher than that for inversion, the conventional methods for measuring the latter escape us.

Interconversion of the Meso and *dl* Isomers of 1b. Prior to this study, we had thought naively that possible nitrogen inversion might give rise to a looser gear in **1**. Now this was found not to be the case. The barrier to the interconversion of the meso and *dl* isomers of **1b** is intermediate between those of the corresponding methanes and ethers. When relevant molecular constants are compared, by using $(CH_3)_2X$ ($X = CH_2$, NH, and O) as model molecules, the following sequences result: bond lengths, C–C (1.526 Å)[24] > C–N (1.466 Å)[21] > C–O (1.410 Å);[25] stretching force constants, C–O (5.34 mdyn Å^{-1})[26] > C–N (3.02 mdyn Å^{-1})[27] > C–C (2.47 mdyn Å^{-1});[28] C–X–C bending force constants, C–O–C (1.22 mdyn Å)[26] > C–N–C (1.045 mdyn Å)[27] > C–C–C (0.711 mdyn Å).[28] Thus our experimental finding is reasonably explained in terms of these structural factors;[29,30] meshing of the molecular bevel

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(29) If we adopt the transition state similar to $C_s(2/2)$ (C in Figure 6) proposed by Mislow et al.,[3e] it is more easily understood that all of these constants more or less influence the barrier. The two benzene rings are squeezed together and tucked into the expanded notch between the two rings of the other triptycyl group. At the same time the C–C–C angle expands by ca. 7°, and the bond from the central carbon to the bridgehead of the latter triptycyl moiety is elongated by ca. 0.026 Å.

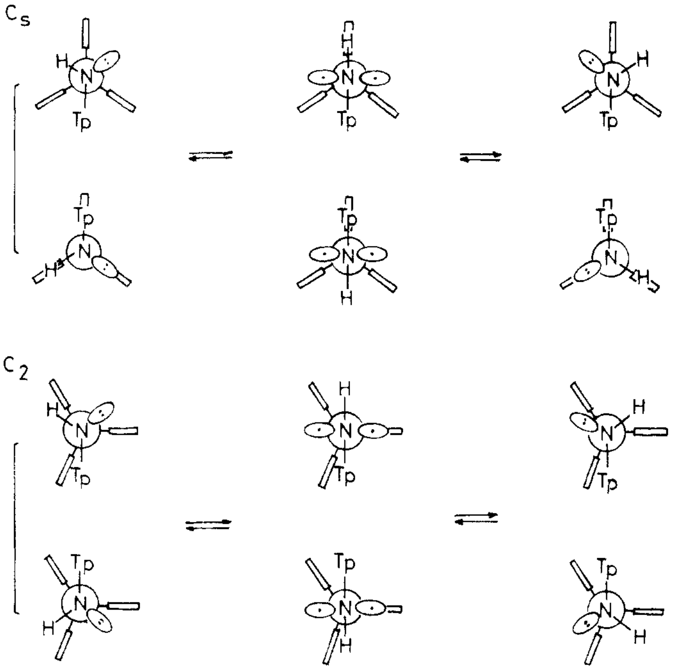

Figure 3. Newman projections of the exchange process between the hydrogen atom and the lone pair of electrons viewed down from the nitrogen to the bridgehead carbons of bis(9-triptycyl)amine in the C_s and C_2 skeletal conformations.

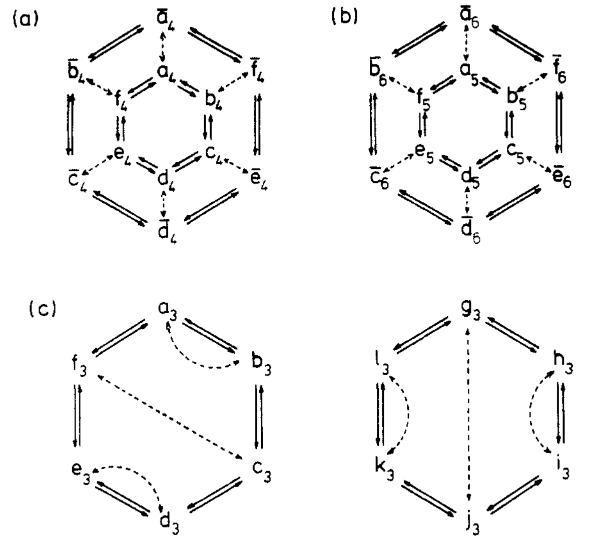

Figure 4. Interconversions of the stereoisomers through the exchange of the substituents a and b on atom X of bis(9-triptycyl)X compounds. Arrows ⇌ and ↔ indicate the coupled disrotation and the exchange, respectively. As to the naming of the conformations, see Figures 1 and 2. The bar on the letter indicates the antipode of the original letter.

gear should be tightest for the ethers and become looser as we ascend the periodic table for the central atom X. There seems to be no reason to invoke other factors in the gear slippage pathway of the amines.

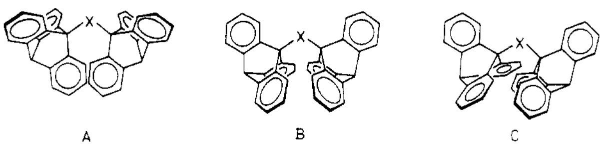

Figure 5. Possible transition-state structures for the gear-slipping process proposed by Mislow et al.[3a,e]

Gear slippage via a transition state (A in Figure 5, where X is an NH group) similar to that proposed by Mislow et al.[3a] for the gear slippage of the methane in their early molecular mechanical calculation would be conceivable. These transition states differ only in the kind and configuration of the central atom. An extremely high energy (ca. 75 kcal mol^{-1}) was calculated recently by Mislow et al. for the above transition state A.[3e] Such a value is not expected to be reduced to less than 40 kcal mol^{-1} by the change C(sp^3) → N(sp^2). Thus even at temperatures as high as 300 °C contribution of such a process is doubtful. It might be possible that the nitrogen atom assumes a trigonal configuration also in the transition state corresponding to C, which was proposed as the most reasonable alternative for A and B.[3e] However, it seems unnecessary to consider this process C as a composite of nitrogen inversion and of the deformations which cause gear slippage in the methanes and in the ethers.

Conclusions

Bis(9-triptycyl)amines **1** were prepared efficiently by the thermolysis of neat 1,3-bis(9-triptycyl)triazenes **4**. The method may give access to some hindered secondary and tertiary amines difficult to obtain otherwise. The presence of one meso and one *dl* isomer for **1c** is an unequivocal evidence for the rapid exchange of the unshared electron pair and the hydrogen atom on the nitrogen. The rate process was not slowed down at −90 °C, and is explicable by the permutation of the hydrogen and the lone pair of electrons without concomitant displacement of the two heavy triptycyl groups. In spite of severe congestion, it seems to interfere little with the coupled disrotation, and its barrier is considered to be no more than those of simple secondary amines. The activation energy for the isomerization of the meso and *dl* isomers of **1b** is closely related to the barrier height for the gear slippage process. The value $E_a = 39.1$ kcal mol^{-1} with $\log A = 12.4$ lies between those of the similarly substituted di-9-triptycylmethane ($E_a = 32.2$ kcal mol^{-1})[2e] and di-9-triptycyl ether ($E_a = 42.0$ kcal mol^{-1}).[2e] These values are reasonable from the orders of the relevant bond lengths and the stretching and bending force constants. It seems unnecessary to invoke the contribution of the nitrogen inversion.

Experimental Section

General Methods. ^{1}H NMR spectra were obtained on Hitachi R-20 (60 MHz), JEOL FX-100 (99.6 MHz), and JEOL GX-400 (398.4 MHz) spectrometers. Chemical shift values (δ) are reported in ppm downfield from internal tetramethylsilane. ^{13}C NMR spectra were measured on JEOL FX-100 (25.0-MHz) and JEOL GX-400 (100-MHz) spectrometers with tetramethylsilane as an internal standard. In FT measurements on the spectrometers other than R-20, standard parameters were employed. When higher resolution in the aromatic region was required in the ^{13}C measurements at 25 MHz, 8K data points were applied to 800-Hz spectral width. Chloroform-*d* (99.8%) was used as a solvent unless specified. Infrared spectra were recorded on a Hitachi 295 infrared spectrophotometer.

Melting points were determined on a Laboratory Device Mel-Temp melting point apparatus and are uncorrected. For some compounds that had high melting points, a Du Pont 990 thermal analyzer was used in the differential scanning calorimetry (DSC) mode, and the extrapolated temperature of onset of an endothermic curve obtained with a scanning rate of 5 °C/min was taken as the melting point. Microanalyses were performed by M. Sekine of this Department at Ibaraki University by using a Yanako MT 2 CHN Corder.

Preparative chromatography was done with quartz columns (i.d. 22–32 mm) packed with either Wako C-200 or C-300 silica gel containing 0.7% fluorescence indicator using a varying mixture

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(30) We note that Urey–Bradley force constants are of approximate nature and suffer considerable change even among molecules of common structural features and that the interaction terms cannot be neglected.

of hexane and dichloromethane as an eluent. HPLC was performed on a Shimadzu LC-3A apparatus. For analytical purposes, a Du Pont Zorbax Sil column (4.6 mm × 25 cm) was used. Separation of the meso and *dl* isomers of **1b** was achieved on μ-Porasil ($^3/_8$ in. × 1 ft) and Develosil (10 mm × 25 cm) columns connected in series. Chloroform (4%)-hexane was used as an eluent under flows of 1.0 and 3.5 mL/min for analytical and preparative purposes, respectively.

All the reactions employing lithium reagents were carried out under dry nitrogen atmosphere on a standard Schlenk line.

Materials. All the chemicals were used as received except for drying when necessary. *p*-Toluenesulfonyl azide was prepared according to the literature procedure.[31] Preparation of 9-bromo-, 2-chloro-9-bromo-, and 3-chloro-9-bromotriptycenes (**2a**, **2b**, and **2c**, respectively) is fully described in a previous paper of this series.[3e]

9-Triptycyl Azide (3a). To the 9-triptycyllithium prepared as described previously from 10.0 g (33 mmol) of 9-bromotriptycene in a mixture of 250 mL of benzene and 500 mL of diethyl ether was added at −40 °C 5.9 g (30 mmol) of *p*-toluenesulfonyl azide in 50 mL of diethyl ether all at once. Stirring was continued overnight without the cooling bath. After quenching with 20% aqueous ammonium chloride, the organic layer was separated, washed once with water, and dried over magnesium sulfate. Evaporation of the solvent followed by recrystallization from benzene/hexane gave 4.8 g of the azide. The residue of the mother liquor was chromatographed on silica gel (120 g) with 20% dichloromethane/hexane as an eluent to give an additional 3.4 g of the azide; the total yield was 92%. In our hands, refluxing of the reaction mixture to effect thermolysis of the triazene salt (TpN=NNLiTp)[15] was unnecessary and resulted in lower yields: mp 187–189 °C; ^{1}H NMR (60 MHz) 5.41 (s, 1 H), 7.00–7.14 (m, 6 H), 7.32–7.44 (m, 3 H), 7.52–7.62 (m, 3 H); IR (KBr) 3060, 3010, 2950, 2110, 1455, 1295, 1275, 750, 740, 640, 625, 480 cm^{-1}.

1,3-Bis(9-triptycyl)triazene (4a). To 8.6 mmol of 9-triptycyllithium in benzene/diethyl ether (80 mL/160 mL) was added a solution of 2.54 g (8.6 mmol) of **3a** in 80 mL of benzene over a 30-min period at −40 °C. Stirring overnight at ambient temperature was followed by a similar workup as in the preparation of **3a**. Chromatography on silica gel (170 g) gave 2.07 g (44%) of **4a** as a second band: needles (dichloromethane/hexane), darkening started at around 200 °C; ^{1}H NMR (100 MHz) 5.74 (s, 2 H), 6.80–7.04 (m, 12 H), 7.30–7.50 (m, 6 H), 7.60–7.80 (m, 6 H), 9.90 (br s, 1 H); ^{13}C NMR 53.94, 71.64, 122.21, 123.58, 125.17, 125.53, 144.83, 145.18; IR (KBr) 3400, 3060, 2960, 2925, 1500, 1480, 1460, 1295, 1250, 1190, 1025, 750, 740, 640, 490, 480 cm^{-1}. Anal. Calcd for $C_{40}H_{27}N_3$: C, 87.40; H, 4.95; N, 7.64. Found: C, 87.28; H, 4.86; N, 7.55.

Bis(9-triptycyl)amine (1a). Two-hundred milligrams of **4a** was gradually heated to 250 °C and maintained at the temperature for 30 min in a 30-mL egg-shaped flask. The dark residue was chromatographed on silica gel (100 g) to give **1a** almost quantitatively along with a trace amount of triptycene: mp (DSC) 450 °C; ^{1}H NMR (60 MHz) 3.70 (s, 1 H), 6.70–7.05 (m, 12 H), 7.40–7.80 (m, 12 H); ^{13}C NMR (25 MHz) 54.49, 70.91, 123.26, 124.08, 124.62, 125.45, 145.14, 147.67; IR (KBr) 3450, 3060, 3010, 2950, 2920, 2850, 1450, 1295, 1270, 745, 700, 640, 615, 480 cm^{-1}. Anal. Calcd for $C_{40}H_{27}N$: C, 92.10; H, 5.22; N, 2.69. Found: C, 91.83; H, 5.28; N, 2.75.

Bis(2-chloro-9-triptycyl)amine (1b). Starting from **2b**, it was obtained in a similar procedure as described for the preparation of **1a**. The yields for the three steps were 93%, 70%, and 60%, respectively. Anal. Calcd for $C_{40}H_{25}NCl_2$: C, 81.35; H, 4.27; N, 2.37. Found: C, 81.19; H, 4.30; N, 2.40. Separation of the meso and *dl* isomers was achieved by HPLC.

Table I. Rate Constants for Isomerization of 1b

T, K	k, s^{-1}	T, K	k, s^{-1}
176	2.31×10^{-7}	236	4.12×10^{-5}
196	1.61×10^{-6}	258	1.91×10^{-4}
215	8.98×10^{-6}	276	7.26×10^{-4}

meso: mp (DSC) 425 °C; ^{1}H NMR (100 MHz) 3.61 (s, 1 H), 5.48 (s, 2 H) 6.80–7.10 (m, 8 H), 7.25–7.70 (m, 14 H); ^{13}C NMR (25 MHz) 53.63, 70.59, 123.50, 123.89, 124.32, 124.75, 124.94, 125.33, 125.84, 130.52, 143.62, 144.63, 146.62, 149.64.

***dl*:** mp (DSC) 429 °C; ^{1}H NMR (100 MHz) 3.58 (s, 1 H), 5.48 (s, 2 H), 6.60–7.16 (m, 10 H), 7.30–7.76 (m, 12 H); ^{13}C NMR (25 MHz, 1,1,2,2-tetrachloroethane-d_2) 53.18, 70.33, 123.29, 123.52 (two overlapping signals), 123.68, 124.46, 124.53, 124.65, 124.81, 125.28, 125.55, 125.70, 130.46, 143.44, 144.26 (two overlapping signals), 145.67, 146.37, 149.88.

(2-Chloro-9-triptycyl)(3-chloro-9-triptycyl)amine (1c). It was obtained through thermolysis of 1-(2-chloro-9-triptycyl)-3-(3-chloro-9-triptycyl)triazene/1-(3-chloro-9-triptycyl)-3-(2-chloro-9-triptycyl)triazene (**4c**) (70%) which was obtained in turn by the reaction of 2-chloro-9-triptycyl azide (**3b**) with (3-chloro-9-triptycyl)lithium (66%). Anal. Calcd for $C_{40}H_{25}NCl_2$: C, 81.35; H, 4.27; N, 2.37. Found: C, 81.36; H, 4.19; N, 2.54. Although complete separation of the meso and *dl* isomers by HPLC was not tried, meso- and *dl*-rich fractions (90 and 98% enriched, respectively) were obtained through repeated recrystallization and column chromatography (see text).

meso: ^{1}H NMR (100 MHz), 3.60 (s, 1 H), 5.46 (s, 2 H), 6.64–7.26 (m, 10 H), 7.30–7.92 (m, 12 H); ^{13}C NMR (25 MHz) 53.53, 53.77, 70.38, 70.57, 123.09, 123.36, 123.49, 123.54, 123.58, 124.14, 124.42, 124.50, 124.69, 125.04, 125.35, 125.70, 125.73, 126.29, 130.73, 130.89, 143.64, 144.30, 144.58, 145.39, 146.10, 146.68, 147.19, 150.46.

***dl*:** ^{1}H NMR (100 MHz), 3.60 (s, 1 H), 5.46 (s, 2 H), 6.72–7.20 (m, 10 H), 7.40–7.84 (m, 12 H); ^{13}C NMR (25 MHz) 53.53, 53.73, 70.38, 70.53, 122.87, 123.34 (three overlapping signals), 123.58, 123.63, 123.74, 124.16, 124.31 (two overlapping signals), 124.42, 124.57, 124.60, 124.71, 124.78, 124.99, 125.19, 125.31, 125.58, 125.63, 125.70 (two overlapping signals), 130.58, 131.01, 143.53, 144.11, 144.36, 144.54, 144.56, 145.81, 145.98, 146.65, 146.69, 146.81, 147.08, 149.93.

Kinetics. Interconversion of the meso and *dl* isomers of **1b** was followed as previously described[3e] starting from the meso isomer dissolved in *o*-dichlorobenzene (3.4 mM) in the temperature range of 176–276 °C. The solvents and chemicals used for the constant-temperature baths were *n*-decane, *n*-undecane, *n*-dodecane, *n*-tridecane, biphenyl, and a mixture of biphenyl and anthracene. The temperatures were monitored by a chromel-alumel thermocouple directly immersed in the liquid (±1 °C).

The following equations were used for analysis of the data:

$$\text{meso} \underset{k}{\overset{kK}{\rightleftharpoons}} dl$$

$$k(K + l)t = \ln \frac{x_\infty(1 + x/\epsilon)}{x_\infty - x}$$

where k, K, $\epsilon = \epsilon_{dl}/\epsilon_{meso}$, and $x = A_{dl}/A_{meso}$ are the rate constant for isomerization from the *dl* to meso isomer, the equilibrium constant defined as C_{dl}/C_{meso}, the ratio of molar absorptivity at 254 nm, and the observed ratio of absorbance of the two isomers at the same wave length, respectively. The rate constants obtained as in Table I were used to make the Arrhenius plot. Parameters ϵ and K were determined as 1.08 and 1.82, respectively. The values of K remained constants within experimental errors throughout the temperature range.

Registry No. **1a**, 101225-59-6; *meso*-**1b**, 101225-60-9; *dl*-**1b**, 101313-06-8; *meso*-**1c**, 101225-61-0; *dl*-**1c**, 101399-08-0; **3a**, 58325-20-5; **3b**, 101225-63-2; **4a**, 101225-58-5; **4c**, 101225-62-1; 9-triptycyllithium, 59239-90-6; (3-chloro-9-triptycyl)lithium, 101225-64-3; *p*-toluenesulfonyl azide, 941-55-9.

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(31) Doering, W. von E.; DePuy, C. H. *J. Am. Chem. Soc.* **1953**, *75*, 5955.