methylcyclohexane or *n*-heptane, while the bis-$P(C_6H_5)_3$ adduct was prepared in $(C_2H_5)_2O$. Tensiometric titrations at 0° established stoichiometries of reactions involving the volatile ligands. Elemental analyses established compositions of all of the adducts. Thermal stabilities are in the following order of ligands

$$P(C_6H_5)_3 > P(CH_3)_3 \gg N(CH_3)_3$$

The phosphine adducts are stable at 100°, while the amine adduct decomposes noticeably at room temperature under vacuum after a period of about 1 day. With the exception of the bis-$P(C_6H_5)_3$ adduct, which is significantly more stable than its counterpart with B_5H_9, thermal stabilities parallel those of the $B_5H_9L_2$ analogs.[9] The boron-11 nmr spectrum of B_6H_{10}-$[P(CH_3)_3]_2$ at 32 MHz consists of three peaks in the area ratio 2:2:2 (a doublet at 2.5 ppm, J_{BH} = 114 Hz; a singlet at 19.4 ppm; and a triplet at 50.2 ppm, J_{BH} = 105 Hz). The boron-11 nmr spectrum of B_6H_{10}-$[N(CH_3)_3]_2$ consists of two peaks in an area ratio of 4:2 (an asymmetric singlet at +21.6 ppm and a doublet at −2.1 ppm, J_{BH} = 96 Hz). All chemical shifts are given with respect to $BF_3 \cdot O(C_2H_5)_2$.

Attempts to produce a 1:1 adduct involving $N(CH_3)_3$ and B_6H_{10} always showed that the apparent reaction is in a 2:1 ratio of amine to B_6H_{10}. Thus, when equivalent amounts of $N(CH_3)_3$ and B_6H_{10} were placed in THF solution, the boron-11 nmr spectrum at −60° revealed the presence of $B_6H_{10}[N(CH_3)_3]_2$ and unreacted B_6H_{10} in apparently equal amounts. Addition of excess KH to the system at −78° produced 0.5 equiv of H_2 which came from the unreacted B_6H_{10}, since $B_6H_{10}[N(CH_3)_3]_2$ in THF does not react with KH in the temperature range −78 to −45°.

The $B_6H_9^-$ ion does not react with $N(CH_3)_3$ at low temperature in solution.

Acknowledgment. We wish to acknowledge, gratefully, support of this research through Grants No. GP-7557X and GP-8321 by the National Science Foundation.

[9] M. L. Denniston and S. G. Shore, Abstracts, 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1969, No. INOR 104.

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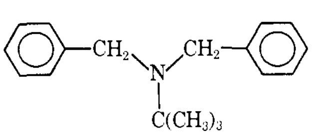
Nonequivalent Methylene Protons in Neopentylamines and Benzylamines[1]

Sir:

Two groups of workers have recently reported that separate proton-resonance lines are observed from the two methylene protons on each benzyl of dibenzylmethylamine at low temperatures.[2,3] In both cases the results were interpreted in terms of a slow nitrogen inversion, although Bushweller and O'Neil[2] point out that their observations could also be explained by a hindered rotation about the carbon–nitrogen bond. However, this explanation was rejected because the barrier to rotation for trimethylamine had been reported to be 4.4 kcal/mol[4] which was significantly smaller than the 6.0 ± 0.5 kcal/mol[5] estimated from the coalescence temperature for dibenzylmethylamine. Actually the two barriers are not comparable since the former is $\Delta H^{\ddagger}$ and the latter $\Delta G^{\ddagger}_{127}$. We wish to present some results from a continuing study of benzyl- and neopentylamines which suggest that it may be hindered rotation rather than slow inversion which gives rise to the proton nonequivalence.

Proton resonance spectra were obtained on a Varian Associates HA 100D spectrometer. At very low temperatures where concentrations were limited by solubility, spectra were sometimes obtained by the Fourier transform technique.[6] Exchange rates were determined by comparison with theoretical spectra which were calculated as previously described.[7] From these results it was possible to calculate enthalpies and entropies of activation for the process producing equivalence of the methylene protons. All errors listed are standard deviations.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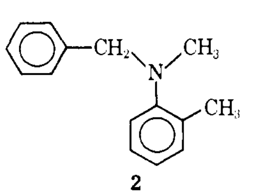
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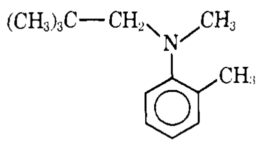
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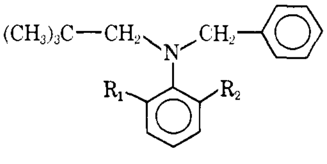
4a, $R_1 = H$; $R_2 = CH_3$
4b, $R_1 = R_2 = H$
4c, $R_1 = R_2 = CH_3$

Broadening and separation of the methylene signal for **1** dissolved in CF_2Cl_2 was observed in the temperature range 163–123°K (δ_{AB} = 0.56 ppm, $\Delta H^{\ddagger}_{298}$ = 3.7 ± 0.4 kcal/mol, $\Delta S^{\ddagger}_{298}$ = −19 ± 18 eu). Similar results were found for **2** (δ_{AB} = 0.60 ppm, $\Delta H^{\ddagger}_{298}$ = 3.7 ± 0.2 kcal/mol, $\Delta S^{\ddagger}_{298}$ = −21 ± 7 eu). The coalescence temperature of **1** is 130°K with $\Delta G^{\ddagger}_{127}$ = 6.1 kcal/mol; for **2**, 133°K with $\Delta G^{\ddagger}_{127}$ = 6.2 kcal/mol; compared with 127°K and $\Delta G^{\ddagger}_{127}$ = 6.0 kcal/mol[2] and 136°K and $\Delta G^{\ddagger}$ = 6.5 kcal/mol[3] for dibenzylmethylamine. The lines from the neopentyl methylene protons of solutions of **3** and **4a** dissolved in CS_2 broadened and split in the temperature range 200–160°K. For **3**, δ_{AB} = 0.69 ppm with $\Delta H^{\ddagger}_{298}$ = 8.5 ± 0.2 kcal/mol, $\Delta S^{\ddagger}_{298}$ = 1 ± 5 eu. For **4a**, δ_{AB} = 0.59 ppm with $\Delta H^{\ddagger}_{298}$ = 7.7 ± 0.4 kcal/mol, $\Delta S^{\ddagger}_{298}$ = −5 ± 9 eu. At low temperatures separate signals were observed for each of the methylene protons of the

[1] Issued as NRCC No. 11700.

[2] C. H. Bushweller and J. W. O'Neil, *J. Amer. Chem. Soc.*, **92**, 2159 (1970).

[3] M. J. S. Dewar and W. B. Jennings, *Tetrahedron Lett.*, 339 (1970).

[4] D. R. Lide and D. E. Mann, *J. Chem. Phys.*, **28**, 572 (1958).

[5] Dewar and Jennings[3] give 6.5 kcal/mol.

[6] R. R. Ernst and W. A. Anderson, *Rev. Sci. Instrum.*, 37, 93 (1966).

[7] S. Brownstein, E. C. Horswill, and K. U. Ingold, *Can. J. Chem.*, **47**, 3243 (1969).

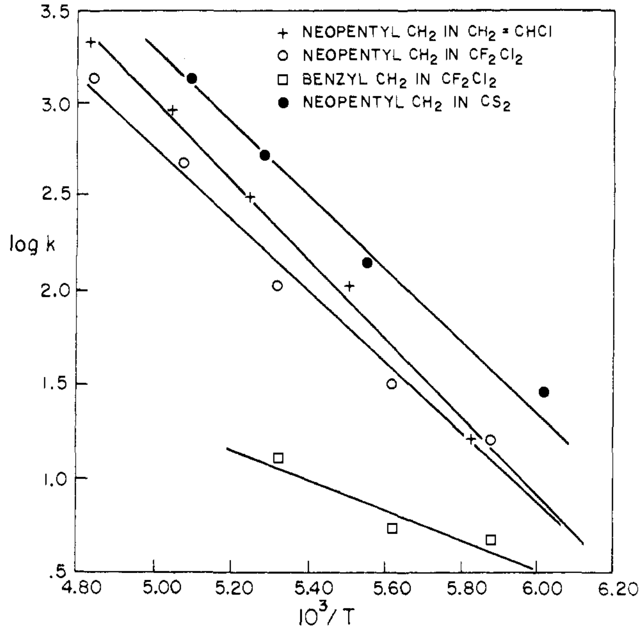

Figure 1. Rates of inversion about the neopentyl and benzyl nitrogen bonds in **4a**.

neopentyl and benzyl groups of **4a** dissolved in CF_2Cl_2. For the neopentyl methylene, $\Delta H^{\ddagger}_{298} = 8.4 \pm 0.5$ kcal/mol and $\Delta S^{\ddagger}_{298} = -4 \pm 8$ eu while for the benzyl methylene $\Delta H^{\ddagger}_{298} = 3.1 \pm 0.8$ kcal/mol and $\Delta S^{\ddagger}_{298} = -36 \pm 13$ eu. These results are plotted in Figure 1.

If the process causing nonequivalence of the methylene protons was due to slow nitrogen inversion one would expect similar barriers for **2** and **3**, which would be different from **1** and different again from dibenzylmethylamine. This is not observed.

Molecular models suggest that the barrier to rotation of the benzyl groups in **1**, **2**, **4a**, and dibenzylmethylamine should be small and should be very similar provided the phenyl ring remains perpendicular to the plane bisecting the benzylic protons. In fact, this common barrier should be no larger than that for the rotation of a methyl group (4.4 kcal/mol[4]). However, the restriction on the conformation of the benzyl group implies that rotation of a benzyl group will involve a large negative entropy of activation, as is observed.[8] There is no special orientation of the almost spherical neopentyl group which would allow it to rotate more easily and hence $\Delta S^{\ddagger}$ for rotation should be approximately zero for this group, again as observed. Furthermore, the barrier to rotation of the neopentyl groups in **3** and in **4a**, **4b**, and **4c** should be rather similar as is found.[9] For these reasons, we propose that the process causing nonequivalence of the methylene protons in the compounds discussed is hindered rotation[10] about the benzyl or neopentyl carbon–nitrogen bond. This must be true of the neopentyl group or else **4a** could not have different barriers for the neopentyl and benzyl groups. However, the possibility that inversion with $\Delta H^{\ddagger}_{298} \sim 3$–4 kcal/mol produces nonequivalence of the benzylic protons in these compounds cannot be entirely eliminated.

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[8] It is only because of the large negative entropy that the barrier to equivalence of the benzyl protons can be studied by nmr.

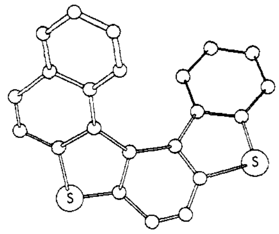
[9] For **4b** in CF_2Cl_2 $\Delta H^{\ddagger}_{298} = 6.0 \pm 0.4$ kcal/mol and $\Delta S^{\ddagger}_{298} = -10 \pm 12$ eu. For **4c** in CF_2Cl_2 $\Delta H^{\ddagger}_{298} = 6 \pm 2$ kcal/mol and $\Delta S^{\ddagger}_{298} = -1 \pm 9$ eu. The benzylic protons did not become nonequivalent in either compound.

[10] With hindered rotation as the rate-determining process rapid inversion is assumed each time a rotation occurs.[7]

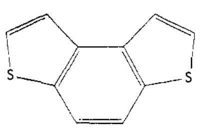
The Absolute Configuration of a Heterohelicene

Sir:

Recently the structure of the heterohelicene benzo[*d*]naphtho[1,2-*d'*]benzo[1,2-*b*:4,3-*b'*]dithiophene (I) has been elucidated by X-ray analysis.[1] The compound I along with a number of other heterohelicenes all having in common the benzo[1,2-*b*:4,3-*b'*]dithiophene moiety (II) have been resolved and the ORD and CD spectra have been measured.[2]



(-)- I



II

Knowing the structure of I we took the benzo[1,2-*b*:4,3-*b'*]dithiophene part of the molecule as a model compound[3] and applied the so-called dipole velocity method[4] to this molecule to calculate the absolute configuration. We found excellent agreement between the calculated and experimentally observed CD spectra (three longest wavelength bands). Our results showed that the (+)-heterohelicenes studied by us must have a right-handed helicity (a P configuration[5]). The absolute configuration of I has now been obtained independently by X-ray diffraction.

For the space group $P2_1$ of I, where the reflections *hkl* and $h\bar{k}l$ are Bijvoet pairs,[6] the intensities of the two members of a pair can be collected on one Weissenberg layer about the *a* or *c* axis. Structure factor calculations based on right-handed screws showed that clearly observable intensity differences should occur on the zero-, first-, and third-layer lines about the *c* axis, when taking the films with Cr radiation, $\Delta f''(\mathrm{s}) = 1.2$. The expected differences were indeed observed, but appeared to be opposite in sign from the calculated values in all cases where the difference was large. This clearly indicated the crystal to be composed of molecules having left-handed helicity (an M configuration[5]) in

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[2] H. Wynberg and M. B. Groen, *J. Amer. Chem. Soc.*, **90**, 5339 (1968), and forthcoming papers.

[3] This simplification finds its justification in the fact that the CD spectra of all our heterohelicenes, varying from hexahelicenes up to an undecahelicene, were essentially similar.

[4] (a) A. Moscowitz, Ph.D. Thesis, Harvard University, Cambridge, Mass., 1957; (b) C. M. Kemp and S. F. Mason, *Tetrahedron*, **22**, 629 (1966).

[5] R. S. Cahn, C. K. Ingold, and V. Prelog, *Angew. Chem., Int. Ed. Engl.*, **5**, 385 (1966).

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