

Dynamic Stereochemistry of 10-Substituted 9-Mesityl-9,10-dihydro-9-boraanthracene Compounds

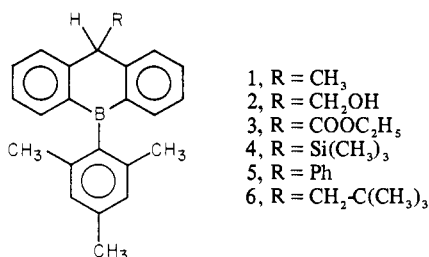
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Abstract: The free energies of activation for rotation around the B-C (mesitylenic) bond have been determined by ¹H NMR spectroscopy in a series of several substituted 9-mesityl-9,10-dihydro-9-boraanthracenes. These molecules, both in solution and in the solid state, adopt a ground-state conformation in which the mesityl ring is nearly perpendicular to the boraanthracene ring. The free energies of activation of the topomerization process observed have been found to depend on the solvent employed, which has a major influence on the coalescence temperature. A comparison between the energy barriers for rotation in our molecules and related systems, i.e., triarylboranes, 9-arylfluorenes, and 9-arylphanthenes, is also made.

Introduction

In a previous paper² van Veen and Bickelhaupt reported the synthesis and characterization of several derivatives of 9-mesityl-9,10-dihydro-9-boraanthracene substituted in the C-10 position, as depicted.



In continuation of our studies³⁻⁷ dealing with the static and dynamic stereochemistry of propeller-like molecules, we turned our attention to the investigation of the dynamic aspects of the isomerism in compounds 1-6 with the double purpose of (i) ascertaining the effect of the R group on the inhibition to rotation around the B-C (mesitylenic) bond and (ii) comparing the values of the free energies of activation of the isomerization process in such molecules with those already reported in the literature for similar unclamped molecules (i.e., triarylboranes),³ and for 9-arylfluorenes⁸ and 9-arylphanthenes.^{8,9}

In order to accomplish this task we resorted to a systematic dynamic NMR study of the above-mentioned arylboraanthracene derivatives.

Results and Discussion

The variable-temperature ¹H NMR spectra of compounds 1-6 all show two equally intense singlets arising from the mesitylenic *o*-methyl groups, whose position and difference in chemical shift depend upon the solvent employed.

Such behavior indicates that in such compounds rotation around the B-C (mesitylenic) bond is kinetically restricted on the NMR time scale at the temperatures in which two *o*-methyl signals are

Table I. Hindered Rotation around the B-C Bond

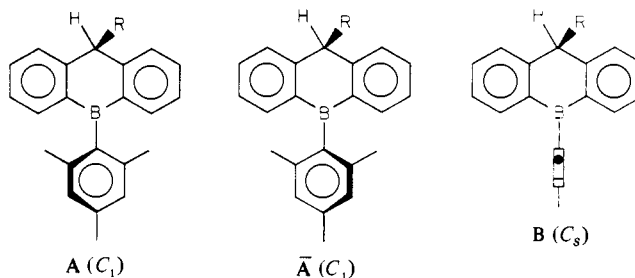
| compd | solvent | $\Delta\delta$ (<i>o</i> -CH ₃) ^a | T _c , °C | ΔG^\ddagger , kcal/mol ^b |
|-------|---------------------------------|---|---------------------|---|
| 1 | CS ₂ | 2.33 | -38 | 12.9 |
| 1 | <i>o</i> -dichlorobenzene | 2.22 | -12 | 14.4 |
| 2 | CS ₂ | 10.0 | -8 | 13.8 |
| 2 | <i>o</i> -dichlorobenzene | 2.2 | +112 | 21.5 |
| 2 | CDCl ₃ | <i>c</i> | | |
| 2 | CD ₂ Cl ₂ | 3.0 | -23 | 13.6 |
| 3 | CS ₂ | 2.33 | +4 | 15.3 |
| 3 | <i>o</i> -dichlorobenzene | 5.67 | +68 | 18.3 |
| 3 | pyridine- <i>d</i> ₅ | <i>c</i> | | |
| 4 | <i>o</i> -dichlorobenzene | 34.2 | >120 | >20 |
| 4 | CDCl ₃ | 20.4 | | |
| 5 | 1,2,4-trichlorobenzene | 8.5 | +156 | 22.9 |
| 6 | CCl ₄ | 9.0 | | |

^a In Hz. ^b Measured at the coalescence temperature. ^c Signals accidentally isochronous in the temperature range investigated (+30 to -50 °C).

in evidence; when the temperature is increased, the two singlets are gradually seen to coalesce to a single broad peak which becomes sharper on further increasing the temperature. Also in this process, as shown in Table I, the coalescence temperature is solvent dependent, being higher particularly in aromatic solvents.

The coalescence process observed reflects an exchange of environments of the diastereotopic *o*-methyl groups: the Gutowsky-Holm equation¹⁰ was used to calculate the rate constant for this site exchange and the Eyring equation to derive the free energy of activation for the stereoisomerization process under investigation. These values are reported in Table I.

For our compounds, two alternative, symmetry-differentiable conformations (A and B) seem the most probable structures on steric grounds.



In conformation A the mesityl ring is twisted by 0° < φ < 90° around the B-C (mesitylenic) bond; this structure is chiral and would admit two enantiomeric forms (A and \bar{A}) with C₁ point group symmetry. In conformation B the mesityl ring lies per-

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(2) R. van Veen and F. Bickelhaupt, *J. Organomet. Chem.*, **77**, 153 (1974).

(3) J. F. Blount, P. Finocchiaro, D. Gust, and K. Mislow, *J. Am. Chem. Soc.*, **95**, 7019 (1973).

(4) P. Finocchiaro, D. Gust, and K. Mislow, *J. Am. Chem. Soc.*, **96**, 2165, 2176, 3198, 3205 (1974).

(5) K. Mislow, D. Gust, P. Finocchiaro, and R. J. Boettcher, *Fortschr. Chem. Forsch.*, **47**, 1 (1974).

(6) P. Finocchiaro, D. Gust, W. D. Hounshell, J. P. Hummel, P. Maravigna, and K. Mislow, *J. Am. Chem. Soc.*, **98**, 4945 (1976); P. Finocchiaro, W. D. Hounshell, and K. Mislow, *ibid.*, **98**, 4952 (1976).

(7) P. Finocchiaro, V. Librando, P. Maravigna, and A. Recca, *J. Organomet. Chem.*, **125**, 185 (1977).

(8) W. T. Ford, T. B. Thompson, K. A. J. Snoble, and J. M. Timko, *J. Am. Chem. Soc.*, **97**, 95 (1975), and references cited therein.

(9) S. V. McKinley, P. A. Grieco, A. E. Young, and H. H. Freedman, *J. Am. Chem. Soc.*, **92**, 5900 (1970).

(10) H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1956).

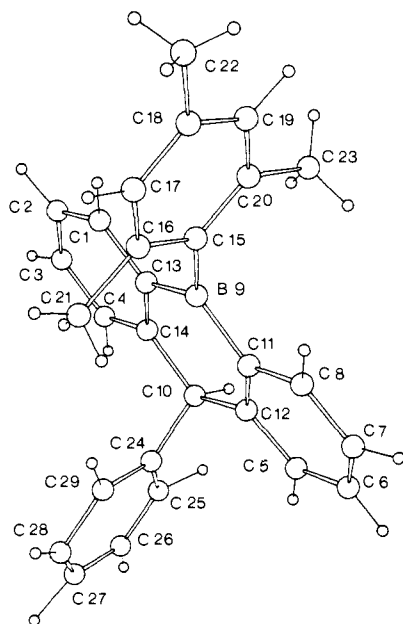


Figure 1. Perspective view of the molecule with numbering of the heavy atoms as used in the X-ray study.

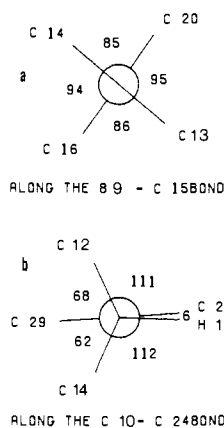


Figure 2. Newman projection along the B(9)-C(15) bond (a) and the C(10)-C(24) bond (b).

pendicular to the 9-boraanthracene plane; this form belongs to the C_s point group and therefore is achiral.

Two ortho mesityl methyl signals will be observed whether the ground state is achiral (B) or whether it is chiral (A/\bar{A}), and, in the latter case, whether enantiomerization is rapid on the NMR time scale or not. In principle, an attempt to distinguish between the two alternative conformations could be made introducing a prochiral group in the C-10 position of the boraanthracene ring.¹¹ In fact, in derivative **2** the CH_2OH protons are enantiotopic¹² in B, but diastereotopic¹² in A/\bar{A} , under the conditions which prevent the enantiomerization process.

The 1H NMR spectra of compound **2**, in a variety of solvents and under conditions in which the rotation around the B-C (mesitylenic) bond is kinetically restricted, do not indicate any nonequivalence of the methylenic CH_2OH protons.

This result, disregarding accidental isochronies, could mean either that **2** adopts the achiral ground state B or that in **2** the enantiomerization process ($A \rightleftharpoons \bar{A}$) is rapid under the conditions of observation.

In order to have more information on the ground-state geometry of our compounds we turned to an X-ray structure determination of derivative **5**.

Table II. Bond Lengths (Å) for **5** with Standard Deviations in Parentheses

| | | | |
|-------------|-----------|-------------|-----------|
| C(1)-C(2) | 1.379(7) | C(13)-C(14) | 1.406(9) |
| C(1)-C(13) | 1.412(6) | C(15)-C(16) | 1.398(6) |
| C(2)-C(3) | 1.374(9) | C(16)-C(17) | 1.391(9) |
| C(3)-C(4) | 1.385(7) | C(16)-C(21) | 1.508(6) |
| C(4)-C(14) | 1.398(6) | C(17)-C(18) | 1.381(6) |
| C(5)-C(6) | 1.377(7) | C(18)-C(19) | 1.371(7) |
| C(5)-C(12) | 1.397(6) | C(18)-C(22) | 1.525(10) |
| C(6)-C(7) | 1.386(9) | C(19)-C(20) | 1.390(9) |
| C(7)-C(8) | 1.377(7) | C(20)-C(15) | 1.403(6) |
| C(8)-C(11) | 1.414(6) | C(20)-C(23) | 1.517(8) |
| B(9)-C(11) | 1.547(7) | C(24)-C(25) | 1.401(9) |
| B(9)-C(13) | 1.545(6) | C(25)-C(26) | 1.380(8) |
| B(9)-C(15) | 1.570(10) | C(26)-C(27) | 1.346(10) |
| C(10)-C(12) | 1.524(6) | C(27)-C(28) | 1.383(11) |
| C(10)-C(14) | 1.514(7) | C(28)-C(29) | 1.475(9) |
| C(10)-C(24) | 1.518(7) | C(29)-C(24) | 1.373(7) |
| C(11)-C(12) | 1.400(9) | | |

Table III. Bond Angles among the Heavy Atoms (deg) for **5** with Standard Deviations in Parentheses

| | | | |
|-------------------|----------|-------------------|----------|
| C(2)-C(1)-C(13) | 121.5(3) | C(4)-C(14)-C(13) | 119.2(3) |
| C(1)-C(2)-C(3) | 119.5(4) | C(10)-C(14)-C(13) | 122.6(3) |
| C(2)-C(3)-C(4) | 120.7(4) | B(9)-C(15)-C(16) | 121.5(3) |
| C(3)-C(4)-C(14) | 120.7(3) | B(9)-C(15)-C(20) | 120.0(3) |
| C(6)-C(5)-C(12) | 120.7(3) | C(16)-C(15)-C(20) | 118.5(2) |
| C(5)-C(6)-C(7) | 120.5(4) | C(15)-C(16)-C(17) | 120.0(3) |
| C(6)-C(7)-C(8) | 119.2(4) | C(15)-C(16)-C(21) | 120.8(3) |
| C(7)-C(8)-C(11) | 121.7(3) | C(17)-C(16)-C(21) | 119.2(3) |
| C(11)-B(9)-C(13) | 116.7(2) | C(16)-C(17)-C(18) | 121.2(3) |
| C(11)-B(9)-C(15) | 121.0(4) | C(17)-C(18)-C(19) | 118.9(3) |
| C(13)-B(9)-C(15) | 122.3(3) | C(17)-C(18)-C(22) | 120.3(4) |
| C(12)-C(10)-C(14) | 116.9(2) | C(19)-C(18)-C(22) | 120.8(4) |
| C(12)-C(10)-C(24) | 110.4(3) | C(18)-C(19)-C(20) | 121.5(4) |
| C(14)-C(10)-C(24) | 110.5(3) | C(15)-C(20)-C(19) | 119.9(3) |
| C(8)-C(11)-B(9) | 121.1(2) | C(15)-C(20)-C(23) | 120.1(3) |
| C(8)-C(11)-C(12) | 118.0(3) | C(19)-C(20)-C(23) | 120.0(4) |
| B(9)-C(11)-C(12) | 121.0(3) | C(10)-C(24)-C(25) | 118.7(4) |
| C(5)-C(12)-C(10) | 118.0(2) | C(10)-C(24)-C(29) | 120.4(3) |
| C(10)-C(12)-C(11) | 122.2(3) | C(24)-C(25)-C(26) | 122.5(5) |
| C(5)-C(12)-C(11) | 119.8(4) | C(25)-C(26)-C(27) | 116.1(4) |
| C(1)-C(13)-B(9) | 121.1(2) | C(26)-C(27)-C(28) | 126.6(5) |
| C(1)-C(13)-C(14) | 118.4(4) | C(27)-C(28)-C(29) | 116.2(6) |
| B(9)-C(13)-C(14) | 120.5(3) | C(24)-C(29)-C(28) | 117.7(4) |
| C(4)-C(14)-C(10) | 118.2(2) | C(25)-C(24)-C(29) | 120.9(3) |

The X-ray structure determination of compound **5** indicates that in the solid state the mesitylene ring is nearly perpendicular to the boraanthracene ring. This is visualized in Figure 1 and can be judged from the Newman projection along the B(9)-C(15) bond (Figure 2a); from a least-squares plane it follows that the angle between the anthracene and mesitylene ring is 84.8° .

The boraanthracene moiety is nearly planar; its three rings make angles of 3 and 1° , respectively, and are themselves planar within the limits of accuracy. The benzene ring, substituted at carbon atom C(10), is also nearly perpendicular to the boraanthracene ring as follows from the Newman projection in which C(29) bisects the dihedral angle between C(12) and C(14) (see Figure 2b).

The bond lengths and angles are given in Tables II and III, respectively. It can be seen that most of them have their normal values, with the exception of those belonging to the benzene ring. However, these anomalous lengths are most probably due to partial disorder, which also induces large thermal parameters.

On the basis of these findings we propose, for the ground-state geometry of our molecules, a time-average C_s structure, in which the mesityl and boraanthracene ring systems are essentially orthogonal. Under these conditions it is therefore plausible to admit that the two enantiomeric structures A and \bar{A} would rapidly equilibrate in solution, even at very low temperatures.

Based on the evidence for the time-average perpendicular B conformation, the exchange of the diastereotopic ortho mesityl methyl groups observed in our compounds at high temperatures is a topomerization process which occurs by a rotation through π radians around the B-C bond, through a planar transition state.

(11) We are grateful to Professor K. Mislow for having suggested to us the possibility of observing diastereotopicity in methylene protons of compound **2**.

(12) K. Mislow and M. Raban, *Top. Stereochem.*, **1**, 1 (1967).

Table IV. Fractional Coordinates of the Heavy Atoms for 5

| | | | |
|-------|------------|------------|------------|
| C(1) | 0.5493(4) | 0.3996(3) | 0.2401(3) |
| C(2) | 0.4192(5) | 0.3935(3) | 0.2715(3) |
| C(3) | 0.2636(5) | 0.2938(3) | 0.1986(4) |
| C(4) | 0.2358(4) | 0.2003(3) | 0.0933(3) |
| C(5) | 0.4427(4) | 0.0082(3) | -0.1921(3) |
| C(6) | 0.5719(5) | 0.0061(3) | -0.2220(3) |
| C(7) | 0.7360(5) | 0.1001(3) | -0.1481(3) |
| C(8) | 0.7690(4) | 0.1956(3) | -0.0434(3) |
| B(9) | 0.6767(4) | 0.3104(3) | 0.1052(3) |
| C(10) | 0.3254(4) | 0.1014(3) | -0.0591(3) |
| C(11) | 0.6386(4) | 0.2013(2) | -0.0111(3) |
| C(12) | 0.4742(4) | 0.1051(3) | -0.0870(3) |
| C(13) | 0.5268(4) | 0.3055(3) | 0.1347(3) |
| C(14) | 0.3653(4) | 0.2054(3) | 0.0588(3) |
| C(15) | 0.8598(4) | 0.4199(2) | 0.1881(3) |
| C(16) | 0.9934(4) | 0.4289(3) | 0.3108(3) |
| C(17) | 1.1560(4) | 0.5250(3) | 0.3792(3) |
| C(18) | 1.1885(5) | 0.6133(3) | 0.3288(4) |
| C(19) | 1.0568(5) | 0.6056(3) | 0.2096(4) |
| C(20) | 0.8930(4) | 0.5106(3) | 0.1382(3) |
| C(21) | 0.9631(5) | 0.3360(3) | 0.3714(4) |
| C(22) | 1.3688(6) | 0.7168(4) | 0.4043(5) |
| C(23) | 0.7509(6) | 0.5048(4) | 0.0063(4) |
| C(24) | 0.1625(4) | 0.0807(3) | -0.1877(3) |
| C(25) | 0.0169(5) | -0.0285(4) | -0.2497(4) |
| C(26) | -0.1347(6) | -0.0560(5) | -0.3687(5) |
| C(27) | -0.1358(7) | 0.0290(6) | -0.4221(5) |
| C(28) | -0.0016(8) | 0.1403(6) | -0.3693(5) |
| C(29) | 0.1594(6) | 0.1671(4) | -0.2426(4) |

The striking feature of this process is that the energetic barriers are strongly affected by the solvent employed and by the bulkiness of the R group present in the C-10 position, as could be inferred from Table I.

Apparently, only bulky groups introduce sufficient steric congestion—and, probably, difference in chemical shift of the *o*-methyl groups—for nonequivalence to become observable at room or higher temperatures. This effect is difficult to rationalize on the basis of simple model inspection, and the entropic factor could play a relevant role on the values of ΔG^\ddagger here determined at different coalescence temperatures. However, in view of the well-known inaccuracies in the determination of ΔS^\ddagger by dynamic NMR measurements^{13,14} we did not attempt to calculate ΔH^\ddagger and ΔS^\ddagger . Furthermore, the observed interactions between solvents and solute could influence our ΔG^\ddagger values, but a quantitative estimate of such an effect is worth further investigation, although a complexation phenomenon involving the nonbonding chlorine electrons of the solvent and the vacant p orbital on boron could play a major role. On the other hand, the high barrier to rotation in **2** (in *o*-dichlorobenzene) may be due to a tight coordination of the alcoholic oxygens to boron in a dimeric structure.¹⁵

Coming now to the comparison of the rotational barriers determined for compounds **1–6** and those already reported for some triarylboranes,³ we remark that in the former clamped systems these barriers are much higher than in the latter unclamped ones, with similar steric congestion.

(13) G. Binsch, *Top. Stereochem.*, **3**, 97 (1968).

(14) A. Allerhand, H. S. Gutowsky, J. Jonas, and R. A. Meinzer, *J. Am. Chem. Soc.*, **88**, 3185 (1966).

(15) We are grateful to a referee for having suggested to us this possibility.

This finding is not unexpected considering that in triarylboranes the threshold mechanism occurs through a two-ring flip,³ whereas in compounds **1–6** the transition state resembles more closely the zero-ring flip, which necessarily occurs with higher energy.³

The activation energies for rotation determined in our 10-substituted 9-mesityl-9,10-dihydro-9-boraanthracenes are comparable to those already found for 9-mesitylxanthenes^{8,9} and lower by about 10 kcal/mol with respect to those of the corresponding 9-mesitylfluorenes⁸ (although, in the latter class of compounds, the activation energies for rotation are very little affected by the solvent⁸). This effect could probably be ascribed to a greater flexibility of the xanthene or boraanthracene ring with respect to the fluorene ring.

Bulky substituents in the C-10 position could greatly reduce this flexibility, thus explaining the higher barriers observed for compounds **4–6** when compared with those of **1–3**.

Experimental Section

DNMR Measurements. The ¹H NMR spectra were recorded in a Perkin-Elmer R 32 90-MHz spectrometer, equipped with variable-temperature accessories.

Temperatures are considered to be accurate to ± 1 °C. Saturation of the NMR signals was avoided. NMR samples were ca. 15% v/v solutions containing tetramethylsilane as internal reference.

Crystallography. Crystals of compound **5** were triclinic with cell constants $a = 9.1996$ (4) Å, $b = 12.5711$ (10) Å, $c = 11.6633$ (6) Å, $\alpha = 102.162$ (5)°, $\beta = 114.717$ (4)°, $\gamma = 105.970$ (4)°, and from an inaccurate measurement of the density $Z = 2$ was derived.

The cell dimensions were measured on an Enraf-Nonius CAD4 diffractometer, using graphite-monochromated Cu K α radiation at room temperature. For the intensity measurements a crystal of size $0.03 \times 0.05 \times 0.09$ mm was used and a total of 2148 independent nonzero reflections ($I > 2.5\sigma$) were collected in the range $2.5 < \theta < 65^\circ$. No correction for absorption was made.

The 29 heavy-atom positions were found by using the interactive direct method program SIMPEL.^{16,17} From intensity statistics the space group $P\bar{1}$ was derived; as usually found in that space group, the Σ_2 consistency figure of merit (FOM) does not reveal the solution. Instead, a combination of FOM's Σ_1 criterion,¹⁸ negative quartet criterion,¹⁹ and Harker-Kasper criterion²⁰ selected a Σ_2 solution, which contained all atoms at the correct positions. The structure was refined by a block-diagonal least-squares procedure in the course of which the hydrogen atoms were located from a difference synthesis. In the final cycle anisotropic thermal parameters were used for the heavy atoms and isotropic ones for the hydrogens and the *R* value was 5.7%. In Table IV the final positional parameters of the heavy atoms are given.

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Supplementary Material Available: A listing of structure factor amplitudes, positional parameters of the hydrogen atoms, and atomic thermal parameters (19 pages). Ordering information is given on any current masthead page.

(16) A. R. Overbeek and H. Schenk in "Computing in Crystallography", H. Schenk, R. Olthof-Hazekamp, H. van Koningsveld, and G. C. Bassi, Eds., Delft University Press, Delft, 1978, p 108.

(17) A. R. Overbeek, Thesis, Amsterdam, 1980.

(18) A. R. Overbeek and H. Schenk, *K. Ned. Akad. Wet., Proc., Ser. B*, **79**, 341 (1976).

(19) H. Schenk, *Acta Crystallogr., Sect. A*, **30**, 477 (1974).

(20) H. Schenk and J. G. H. de Jong, *Acta Crystallogr., Sect. A*, **29**, 31 (1973).