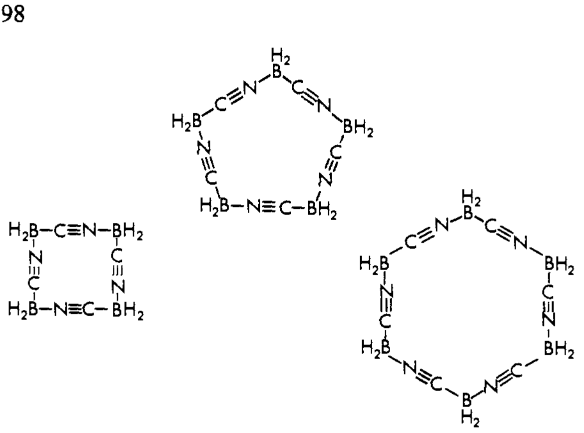

Figure 1. Macrocyclic cyanoboranes.

boron nuclei are in the same four-coordinate environment and have two hydrogens attached to each boron.[3] The ambient temperature proton spectrum in $DCCl_3$ with decoupled boron is a single signal at δ 2.03. These nmr data are consistent only with a cyclic structure. The infrared spectrum includes strong absorption bands at 2469, 2441, and 2429 and at 2295 cm^{-1} (BH_2 and $C\equiv N$ stretching, respectively), as well as an intense broad band at 1089 cm^{-1}, and several weaker ones at lower wave numbers. The appearance of only one $C\equiv N$ absorption at such a high frequency is consistent with the presence of a single, bridging cyano group[4] as required in a cyclic oligomer. The number and frequencies of the BH stretching bands fit that expected for a single type of BH_2 with four-coordinate boron.[5] No absorption characteristic of CH or NH is observed. The preliminary crystal data for $(BH_2CN)_5$ are as follows[6]: space group $P2_1/c$, monoclinic; $a = 9.46$, $b = 8.88$, $c = 16.04$ Å; $\beta = 106° 5'$; $V = 1295$ Å^3; if $Z = 4$, $D_{calcd} = 0.998$ and $D_{measd} = 1.00 \pm 0.2$ g/cm^3. Thus all the data are consistent with a cyclic species as shown in the figure. It is also interesting to note that for $(BH_2CN)_5$, a planar species would have an NBC bond angle of 108°, close to the normal tetrahedral angle of 109° 28'.

It is also possible, by means of fractional sublimation techniques, to obtain samples enriched in $(BH_2CN)_n$ where $n = 6, 7, 8$, with purities (as determined by glc analysis) of 80, 40, and 56%, respectively. All of these samples exhibit ^{11}B nmr and infrared spectra which are very similar to that of $(BH_2CN)_5$. In view of the very close similarities in the nmr and infrared spectra, as well as very similar mass spectral cracking patterns and intense parent ion envelopes for all of these species, the data are consistent with macrocyclic species rather than linear structures. In addition, on standing in solution, no change in relative concentrations of the various species is noticed. Linear species would be expected to undergo further polymerization.

These compounds are resistant to hydrolysis even in boiling water; in air over long periods, boric acid is deposited. Bases such as trimethylamine cause depolymerization of the cyclic oligomers as well as of the nonvolatile polymeric mass. An isolable 1:1 amine adduct is formed. We have also identified cyanoborane as a product of the reaction of HCN with THF–borane. The compound $(BH_2CN)_x$ as "a clear glassy solid" has been reported as one of the products of the thermal decomposition of $H_3SiCNBH_3$ or $Me_3SiCNBH_3$.[7] The solid residue was identified by material balance and elemental analysis. However, the infrared spectrum included absorption bands at 3450 and 1630 cm^{-1}, which were assigned to NH stretch and CN or NH bending, respectively. These absorptions are absent from the spectrum of cyanoborane, *vide supra*.

Studies on the purification, X-ray structure determinations, and further chemistry of the macrocyclics are underway. We are also interested in the nature of the nonvolatile polymeric mass.

Acknowledgment. We wish to thank the U. S. Army Research Office—Durham for support of this research.

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Cotton Effects of the Benzene Chromophore in the 300–185-nm Spectral Region

Sir:

The benzene ring today is the most widely studied chromophoric group, but, in spite of the extensive experimental and theoretical work made, several open questions remain unanswered concerning its chiroptical properties.

To date, there has not been published a CD spectrum covering the spectral range in which the three major $\pi \rightarrow \pi^*$ transitions of a single, chirally perturbed benzene chromophore occur. Although many attempts have been made, only the Cotton effect in the 260-nm region has been, until now, characterized in phenylalkanes.[1-3]

The failure to detect Cotton effects at shorter wavelengths than 240 nm is due to the weak CD with respect to the absorption. Moscowitz has pointed out that the low optical activity in a planar hydrocarbon π system can be associated with the fact that there is no convenient source of magnetic dipole character[4] for the three transitions in question. Moreover, it also has to be considered that in flexible compounds the observed CD is the average of the CD associated with each conformation.

An examination of models indicated that the chiral 2-phenyl-3,3-dimethylbutane (I) should be a suitable molecule with restricted conformational freedom to investigate the CD of the benzene chromophore.

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(+)-(*S*)-I was prepared starting from (+)-(*S*)-2-phenyl-3,3-dimethylbutanoic acid;[5] the latter was reduced by $LiAlH_4$ to (−)-(*S*)-2-phenyl-3,3-dimethyl-1-butanol which, *via* tosylate and treatment with LiCl in DMF,[6] afforded (−)-(*S*)-2-phenyl-3,3-dimethyl-1-chlorobutane. The corresponding Grignard reagent was hydrolyzed to I. The relationship between rotatory power and optical purity was established for I[5,6] and the optical purity of the sample used in the present investigation was 97%.

The uv spectrum of I in hydrocarbon solution (Figure 1) is characterized by three major absorption bands with fine structure and the maxima at 258, 209, and 188 nm. The position and the intensity pattern of the bands are in general agreement with those of alkyl-substituted benzenes.[7,8] In particular it has been recently reported for toluene[8] that the relative weak band at about 260 nm is assignable to a $^1B_1 \leftarrow {}^1A_1$ ($^1B_{2u} \leftarrow {}^1A_{1g}$ in benzene) transition, the band at about 210 nm to a $^1A_1 \leftarrow {}^1A_1$ ($^1B_{1u} \leftarrow {}^1A_{1g}$ in benzene) transition,[9] while the intense band near 190 nm is derived from the doubly degenerate electric dipole allowed $^1E_{1u} \leftarrow {}^1A_{1g}$ transition in benzene.

Correspondingly, the CD spectrum of I shows three fine structured bands with position and vibrational spacings analogous to those of the absorption bands.

All the CD bands have positive sign with the $\Delta\epsilon_{max}$ of the shortest wavelength band being ten times larger than that of the 210-nm band and one hundred times that of the 260-nm band. The Cotton effect in the 260-nm region is considerably large when compared to that shown by similar open-chain phenyl derivatives[1,2,10] and of the same order of magnitude as those displayed by cyclic compounds like (*S*)-1-methyl-1,2,3,4-tetrahydronaphthalene[3] and by coisotactic copolymers of an optically active α-olefin with styrene having a helical conformation with one prevailing screw sense.[11]

The rotational strength of the 260-nm transition remains, in practice, constant with lowering the temperature to −100° and using a more polar solvent like trifluoroethanol. For the latter, only a blue shift of about 1 nm is observable both in uv and CD. In addition, a clear correspondence can be established among the bands of the ir spectra of I in liquid, glass, and crystalline[12] phases.

The aforementioned results indicate that the positions of the conformational equilibria are not substantially shifted in different conditions and suggest that a strongly preferred conformation should already exist at 27°.

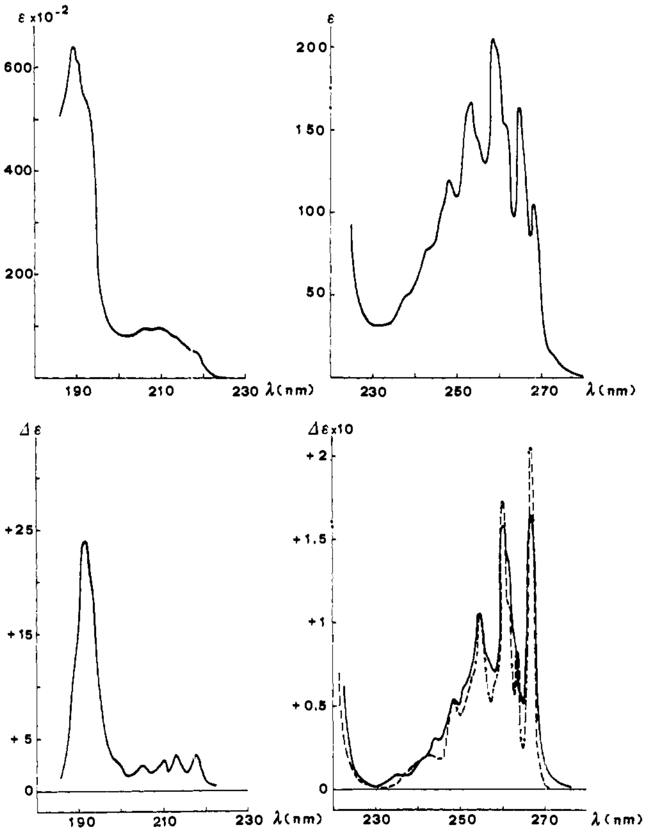
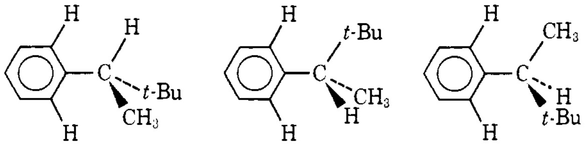


Figure 1. Uv spectrum of (+)-(*S*)-2-phenyl-3,3-dimethylbutane (I) (*n*-heptane, room temperature), determined by a Cary-14 spectrophotometer, and CD spectra (methylcyclohexane–isopentane, 1:3) at room temperature (——) and −100° (- - -), determined by a Roussel-Jouan II dichrograph. For the latter, the use of a 150-W xenon lamp gave spectral bandwidths of ~0.3 nm in the 260-nm region, ~0.2 nm in the 210-nm region, and ~0.5 nm in the 190-nm region.

Looking at the relative positions that the benzene ring can assume with respect to each group (H, CH_3, *t*-Bu) bound to the chiral carbon atom, the three conformations shown in Chart I can be considered to be the limiting cases.[13]

Chart I



Ia Ib Ic

The conformation Ic can be tentatively considered "not allowed" because of the very strong steric interactions, as shown by examination of molecular models. In addition, the sign observed for the CD bands is opposite to that predicted by the sector rules derived by Snatzke.[14]

Between Ia and Ib the former should be preferred in accordance with the results obtained in the determination of the crystal structure of isotactic polystyrene[15] and in the investigation by nmr of conformations of isopropylarenes.[16]

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In conclusion, I represents an interesting case of a very simple, open-chain phenylhydrocarbon in which the relatively strong CD observed is without doubt only attributable to the optically active electronic transitions connected with the π system of a single phenyl chromophore. Considering the restricted conformational freedom of the molecule, the well-resolved CD and uv spectra should provide the basis for an improvement of theoretical treatments.

Acknowledgment. The authors wish to express their particular thanks to Dr. Alex F. Drake for helpful discussion and to Professor Enzo Benedetti for his skillful assistance in obtaining the ir spectra.

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N-Chloro-*N*-lithioaniline. Generation and Characterization of a Nitrenoid

Sir:

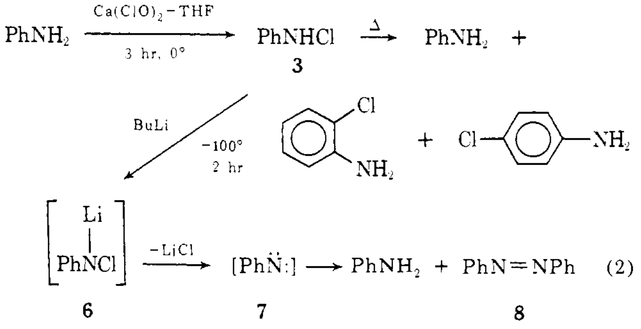
The similarities between nitrenes and carbenes are quite well known. Both intermediates can be generated by thermal or photochemical nitrogen elimination reactions: carbenes from diazo compounds and nitrenes from azides.[1] Another common method of producing carbenes is by the decomposition of α-chloroorganolithium compounds, carbenoids (RR′CLiX). Several of these carbenoids have been characterized at low temperatures.[2] The analogous nitrene generation *via* a "nitrenoid" intermediate (RNLiX) is not known.[3] The ready availability of amines has led us to investigate methods of efficiently producing nitrenes *via* α eliminations. This report deals with a proof of a nitrenoid intermediate and some nitrenium ion ($\mathrm{RN^+R'}$) reactions.

Our first attempt at generating a nitrene by way of an α elimination is shown in eq 1. We were successful in obtaining *N*-bromoaniline (**1**), but lithiation of **1** gave only *n*-butylaniline (**2**) rather than proton abstraction.

$$\mathrm{PhNH_2} \xrightarrow[\text{2. Br}_2]{\text{1. BuLi-THF}} \underset{\mathbf{1}}{\mathrm{PhNHBr}} \xrightarrow[-100^\circ]{\text{BuLi}} \underset{\mathbf{2}}{\mathrm{PhNHBu}} \qquad (1)$$

Using a modification of Haberfeld and Paul's procedure,[4] aniline was chlorinated with calcium hypochlorite in tetrahydrofuran (THF) to give *N*-chloroaniline. After removal of the excess hypochlorite, the crude product (kept at 0°) was divided into two parts. The one part was allowed to decompose and gave (by vpc analysis) 64% aniline, 25% *o*-chloroaniline, 10% *p*-chloroaniline, and 1% of an unidentified component, probably dichloroaniline. This sets the lower limit of *N*-chloroaniline production at about 35%. There actually could be considerably more formed since the nitrenium ion intermediate that is presumably formed during the conversion of **3** to **4** and **5** may also hydrogen abstract from the solvent to give aniline.[5] The decomposition of *N*-chloroaniline in THF has not been previously examined. Attempts to get quantitative results by titration of the iodine liberated from the reaction of **3** and KI have not been successful (due to very poor end points).[4] It is, therefore, not possible to say how much aniline comes from nonreaction and how much from decomposition of **3** and, thus, what the exact yield of **3** was.

The other portion of the crude product was treated at −100° with 1 equiv of *n*-butyllithium for 2 hr and allowed to warm to room temperature. The solution warms smoothly with no sudden exotherm as is frequently observed in carbene generation.[2] The product consisted of 81.5% aniline and 18.5% azobenzene (**8**) and a small amount of polymer (eq 2). The production of aniline and azobenzene confirms that phenylnitrene was produced in these reactions, since phenylnitrene produced by the thermal or photochemical decomposition of phenyl azide also gives the same two products.[6]



Most nitrenes will add to olefins to give aziridines: however, phenylnitrene generated by photolysis does not.[7] [Phenyl azide will thermally add to olefins without prior loss of nitrogen.[8]] If the reactions outlined in eq 2 were conducted in the presence of a large excess of cyclohexene, aniline, azobenzene, and polymer were still the only products formed. Thus, phenylnitrene generated by α elimination shows the same reactions as phenylnitrene generated from phenyl azide.

The question now arises as to whether phenylnitrenoid (**6**) is an intermediate in these reactions or whether **3** goes directly to **7** by means of a concerted elimination of HCl. We have attempted to trap **6** in several ways.[9] The method that we found most successful was trapping with trimethylchlorosilane. A control experiment showed that trimethylchlorosilane does not react with aniline, *N*-chloroaniline, or *o*- and *p*-chloroaniline, but, if *n*-butyllithium was added to *N*-chloroaniline prior to or in the presence of trimethyl-

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