factory. In order to examine the magnitude of the pseudo π bonding, the p_z–p_z' overlap populations[14] (n_π) were calculated at equilibrium bond length for each value of θ. These results are also shown in Figure 3. For the normal tetrahedral bond angle a substantial value of $n_\pi = 0.335$ is calculated, and in accord with the above reasoning this value increases as θ decreases.

In order to compare R_e with the s character calculated for the carbon–carbon bond, it is most convenient to consider the overlap populations of the carbon 2s orbital. If n (i, j) is the overlap population between orbitals i and j, then the extent (X_s) to which the 2s orbital on C_1 is involved in the total overlap population in the C_1–C_2 σ bond is given by [15]

$$X_s = \frac{n(C_12s, C_22s) + n(C_12s, C_22p_x)}{n(C_12s, C_22s) + n(C_12s, C_22p_x) + n(C_12p_x, C_22p_x)}$$

If this were a perfect criterion of hybridization, then a value of 0.25 would be expected for sp^3 hybrid orbitals and 0.33 for sp^2 orbitals, etc. Figure 3 shows F_s and X_s as a function of θ. It can be seen that there is a direct correlation between X_s and n_π thus making it extremely difficult to separate the two effects on a purely experimental basis. As a result, the conclusion of Maksić and Randić,[6] which neglected the pseudo π contributions, cannot be taken as an argument in support of bond shortening being the result of σ bond hybridizations. On the contrary, because of the close parallelism between X_s and n_π, the data are consistent with the conclusions of Miyazaki.[5]

It should be emphasized, however, that we do *not* claim to have established that the bond length variations are dependent *solely* upon the π or pseudo π bond order. On the contrary, because of the parallelism between this quantity and the fractional s character in the σ bond, it will be difficult to determine, on an experimental basis, which of these two quantities is responsible for the phenomenon.[18]

Registry No.—Ethane, 74-84-0.

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(14) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1841 (1955). Bond orders are strictly incompatible with the INDO approximations. The use of bond indice, however, leads to identical conclusions.

(15) The conclusions in this work are independent of the particular choice of definition of s character. For alternative definitions, see ref 16 and 17.

(16) C. Trindle and O. Sinanoglu, *J. Amer. Chem. Soc.*, **91**, 853 (1969).

(17) P. C. Van der Voorn and R. S. Drago, *ibid.*, **88**, 3255 (1966).

(18) NOTE ADDED IN PROOF.—W. R. Moore and C. R. Costin, *ibid.*, **93**, 4910 (1971), have recently presented dramatic evidence for the existence of pseudo π bonding in a bis(1-bicyclo[1.1.0]butyl) system. This molecule which lacks a formal chromophore shows an unusually long wavelength absorption (*ca.* 190 nm) and undergoes facile electrophilic addition to yield a 1,4-addition product in a manner analogous to that found in butadienes.

Notes

Quinoxaline Studies. XIX.[1] The Chiralities of the Bridge Carbon Atoms of (+)- and (−)-*trans*-Decahydroquinoxalines

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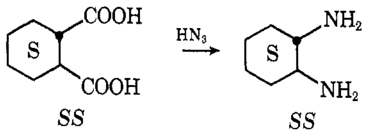
Discussion

The purpose of this publication, an epilogue of earlier work[2] and a prologue to future work, is to elucidate the chiralities of the bridge carbon atoms (C-9 and C-10) of the *trans*-decahydroquinoxalines, compounds which were earlier reported[2] and resolved. Applequist and Werner[3] and Mislow and coworkers,[4] reporting the chiralities of C-1 and C-2 of (+)-*trans*-cyclohexane-1(*S*),2(*S*)-dicarboxylic acid, bestowed feasibility upon this project.

(+)-*trans*-Cyclohexane-1(*S*),2(*S*)-dicarboxylic acid (**1**) was stereospecifically degraded *via* the Schmidt reaction to (+)-*trans*-cyclohexane-1(*S*),2(*S*)-diamine dihydrochloride (**2b**) in low yield (Scheme I). After the chiralities of C-1 and C-2 of **2b** had been established,

SCHEME I



1, (+), as free acid

2a, (+), as free base
b, (+), as dihydrochloride salt
c, (−), as (−)-tartrate salt

2c was more readily obtained by resolution of commerical 1,2-diaminocyclohexane with (−)-tartaric acid. Logistics dictated that the relatively large amounts of optically active *trans*-cyclohexane-1,2-diamine needed for preparation of the corresponding optically active *trans*-decahydroquinoxaline be obtained by resolution of 1,2-diaminocyclohexane with the cheaper (+)-tartaric acid. Scheme II displays the steps which related (−)-*trans*-cyclohexane-1(*R*),2(*R*)-diamine (**3a**) to (+)-*trans*-9(*R*),10(*R*)-decahydroquinoxaline (**5**).

With the chiralities of the bridge carbon atoms of **5** established, the chimera of a shorter, simpler route to this end then beckoned. This abbreviated route was based upon the reported reductive cycloalkylation[5] of

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(1) Paper XVIII of this series: H. R. Moreno and H. P. Schultz, *J. Org. Chem.*, **36**, 1158 (1971).

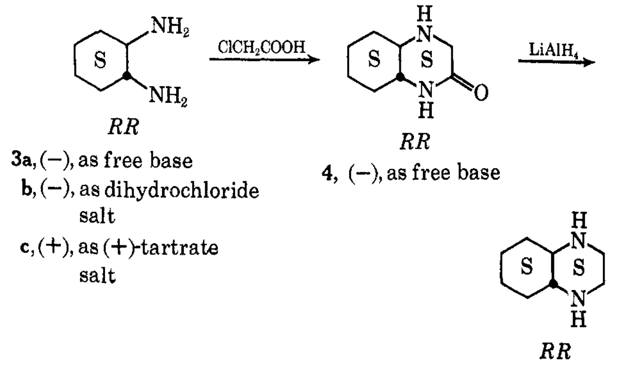
(2) E. Brill and H. P. Schultz, *ibid.*, **28**, 1135 (1963).

(3) D. E. Applequist and N. D. Werner, *ibid.*, **28**, 48 (1963).

(4) P. Laur, H. Häuser, J. E. Gurst, and K. Mislow, *ibid.*, **32**, 498 (1967).

(5) E. Brill and H. P. Schultz, *ibid.*, **29**, 579 (1964).

Scheme II



RR

3a, (−), as free base
b, (−), as dihydrochloride salt
c, (+), as (+)-tartrate salt

RR

4, (−), as free base

RR

5, (+), as free base

(±)-*trans*-cyclohexane-1,2-diamine with glyoxal to (±)-*trans*-decahydroquinoxaline.

To this earlier report is now added the observation that, with the conditions previously utilized,[5] **3a** was reductively cycloalkylated with glyoxal to optically active **5**. This success not only simplified the preparation of **5**, but also provided a measure of insight into the mode of formation of **5** *via* the reductive cycloalkylation of **3a**.

If the reductive cycloalkylation of **3a** to **5** had proceeded *via* either the intermediate addition compound (aminol) or dehydration compound (5,6,7,8,9,10-hexahydroquinoxaline), chiral integrities of the bridge carbon atoms of **5** would be expected to have been preserved. However, if formation of **5** in whole or part resulted from the intermediate, aromatic 5,6,7,8-tetrahydroquinoxaline (which could conceivably form by dehydrogenation of the hexahydroquinoxaline), then **5** would have been in part, at least, a racemic mixture. The result of this experiment indicates that the aromatic tetrahydroquinoxaline was not significantly present during the reductive cycloalkylation of **3a** to **5**.

Experimental Section[6]

(+)-*trans*-**Cyclohexane-1(*S*),2(*S*)-dicarboxylic Acid (1)**.—(±)-*trans*-Cyclohexane-1,2-dicarboxylic acid[7] was resolved (68% yield) by the procedure of Applequist and Werner:[3] mp 183–185°, $[\alpha]^{26}\mathrm{D}$ +22.25° (*c* 1.88, Me_2CO) [lit.[3] mp 183.5–185°, $[\alpha]^{30}\mathrm{D}$ + 22.3° (*c* 5.3, Me_2CO)].

(+)-*trans*-**Cyclohexane-1(*S*),2(*S*)-diamine Dihydrochloride (2b)**.—This material (**2b**) was prepared (13% yield) *via* the Schmidt reaction utilized by Yashunskii,[8] as modified by Brill and Schultz,[2] for the preparation of the corresponding cis isomer: $[\alpha]^{24}\mathrm{D}$ +16.14° (*c* 0.21, H_2O) [lit.[9] $[\alpha]^{25}\mathrm{D}$ ±15.8° (*c* 20)]. *Vide infra* for the optical activity of the enantiomeric hydrochloride.

(−)-*trans*-**Cyclohexane-1(*S*),2(*S*)-diamine (−)-Tartrate (2c)**.—Commercial, redistilled 1,2-diaminocyclohexane[10] was resolved with (−)-tartaric acid (90% yield) by the procedure of Reinbold and Pearson[11] to give **2c**, $[\alpha]^{24}\mathrm{D}$ −18.05° (*c* 0.44, H_2O). Its antipodal (+)-tartrate salt (**3c**) had $[\alpha]^{24}\mathrm{D}$ +14.19° (*c* 0.32, H_2O) [lit.[11] $[\alpha]_{589}$ +12.1° (*c* 1, H_2O), lit.[12] $[\alpha]\mathrm{D}$ +12°].

(+)-*trans*-**Cyclohexane-1(*S*),2(*S*)-diamine (2a)**.—Solid potassium hydroxide was added to 50 ml of an aqueous, stirred solution containing 6.4 g of **2c** until two layers formed. The amine was separated and distilled from solid potassium hydroxide to give 2.25 g (81%) of colorless liquid **2a**, bp 104–110° (40 mm), $[\alpha]^{25}\mathrm{D}$ +35.47° (*c* 4.74, Me_2CO). The optical antipode (**3a**) had bp 105–110° (40 mm), $[\alpha]^{25}\mathrm{D}$ −35.20° (*c* 6.78, Me_2CO) [lit.[11] bp 75–80° (16 mm); lit.[13] bp 82° (14 mm), $[\alpha]\mathrm{D}$ −36°]. The hydrochloride salt (**3b**) obtained upon passing hydrogen chloride gas into a diethyl ether solution of (−)-*trans*-cyclohexane-1(*R*),2(*R*)-diamine (**3a**) had $[\alpha]^{24}\mathrm{D}$ −17.18° (*c* 0.51, H_2O) and $[\alpha]^{24}\mathrm{D}$ −15.58° (*c* 20, H_2O) [lit.[9] $[\alpha]^{25}\mathrm{D}$ ±15.8° (*c* 20)].

(−)-*trans*-**9(*R*),10(*R*)-Decahydroquinoxalin-2-one (4)**.—Compounds **3b** and **3c** were cyclized with chloroacetic acid to **4** in 30% yields by the procedure of Brill and Schultz,[2] except that potassium bicarbonate was used instead of ammonium hydroxide: mp 196–197.5°, $[\alpha]^{24}\mathrm{D}$ −70.33° (*c* 0.24, 95% EtOH).

Anal. Calcd for $C_8H_{14}N_2O$: C, 62.30; H, 9.15; N, 18.17. Found: C, 62.44; H, 9.12; N, 18.34.

The optical antipode of **4**, (+)-*trans*-9(*S*),10(*S*)-decahydroquinoxalin-2-one, was similarly prepared: mp 196–198°, $[\alpha]^{24}\mathrm{D}$ +71.17° (*c* 0.45, 95% EtOH).

(+)-*trans*-**9(*R*),10(*R*)-Decahydroquinoxaline (5). A. From 4.**—Compound **4** was reduced to **5** with lithium aluminum hydride (50% yield) by the described procedure:[2] mp 176–177°, $[\alpha]^{24}\mathrm{D}$ +16.31° (*c* 0.46, H_2O), $[\alpha]^{24}\mathrm{D}$ +14.72° (*c* 0.4, 95% EtOH), and $[\alpha]^{24}\mathrm{D}$ +10.72° (*c* 0.48, $CHCl_3$) [lit.[2] mp 176–177°, $[\alpha]^{26}\mathrm{D}$ +10.4° (*c* 10, $CHCl_3$)]

Anal. Calcd for $C_8H_{16}N_2$: C, 68.52; H, 11.50; N, 19.98. Found: C, 68.79; H, 11.69; N, 20.35.

B. From 3a.—(−)-*trans*-Cyclohexane-1(*R*),2(*R*)-diamine was reductively cycloalkylated (30% yield) with glyoxal over platinum oxide catalyst by the earlier reported procedure.[5] The **5** obtainied had mp 176–177°, $[\alpha]^{24}\mathrm{D}$ +16.40° (*c* 0.38, H_2O).

Registry No.—**2a**, 21436-03-3; **2b**, 32044-18-1; **2c**, 32044-19-2; **3a**, 20439-47-8; **3b**, 32044-21-6; **3c**, 32044-22-7; (−)-**4**, 32044-23-8; (+)-**4**, 32044-24-9; **5**, 32044-25-0.

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[6] Melting points, uncorrected, were determined on a Thomas–Hoover apparatus. All optical activities were determined in a Rudolph Model 63 polarimeter using a 2-dm tube. Microanalyses were performed by PCR, Gainesville, Fla.

[7] C. C. Price and M. Schwarcz, *J. Amer. Chem. Soc.*, **62**, 2891 (1940).

[8] V. G. Yashunskii, *Zh. Obshch. Khim.*, **28**, 1361 (1958); *Chem. Abstr.*, **52**, 19979*f* (1958).

[9] R. G. Asperger and C. F. Liu, *Inorg. Chem.*, **4**, 1492 (1965).

[10] Aldrich Chemical Co.

[11] P. E. Reinbold and K. H. Pearson, *Talanta*, **17**, 391 (1970). Their salt was named D(−)-*trans*-1,2-diaminocyclohexane L(+)-tartrate, although neither reference to nor proof of a known absolute configuration for the diaminocyclohexane moiety is presented. As written by Eliel (E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill, New York, N. Y., 1962, p 90), the use of only one configurational symbol is inadequate for naming a compound having two asymmetric atoms, even if the two centers are alike, as they are in (−)-*trans*-cyclohexane-1,2-diamine.

[12] R. S. Treptow, *Inorg. Chem.*, **5**, 1593 (1966). The salt was named *l*-chn *d*-tartrate, indicating that it was the salt of the (−)-free amine base with (+)-tartaric acid. In point of fact, the salt *itself*, as cited in the experimental details above, had a (+) rotation.

[13] F. M. Jaeger and L. Bijkerk, *Proc. Kon. Ned. Akad. Wetensch.*, **40**, 12 (1937); *Chem. Zentr.*, **108** (II) 1196 (1937).

Reactions of 2-Dichloromethylene-3-oxazolin-5-ones with Toluene under Friedel–Crafts Conditions

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In our previous paper[1] it was reported that 2-isopropylidene-3-oxazolin-5-ones (I) react with benzene in the presence of anhydrous aluminum chloride to give 1:2 adducts, *N*-(α-phenylisobutyryl)-α-amino ketones (II), by 1,4 addition to the double bond system followed by ring opening.

It was of interest to determine what reaction would occur when related pseudoxazolones containing a di-

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[1] Y. Iwakura, F. Toda, and Y. Torii, *J. Org. Chem.*, **32**, 3202 (1967).