

27% *anti*-9 isomers. By mass spectrometry these fractions contained 0.649, 0.947, and 0.046 atom excess D, respectively. By pmr the two compound mixture contained 73% 2 and 27% *syn*-9 isomers. The product distribution in Table III was calculated by assuming that only deuterated material was formed from the Grignard reagent.

1-Trimethylsilylbenzonorbornadiene was isolated from the preceding mixture (A) >95% pure and identified by its pmr, ir, and mass spectra.

2- and *syn*-9-trimethylsilylbenzonorbornadiene were isolated from mixture A as a 77:23 mixture (by pmr) and identified by their pmr, ir, and mass spectra.

anti-9-Trimethylsilylbenzonorbornadiene was isolated from the diene cycloaddition >95% pure and identified by its pmr, ir, and mass spectra.

1-trimethylsilylbenzonorbornadiene-*anti*-9-*d* was isolated from mixture B and identified by its pmr spectrum, which showed a reduction in area and broadening of the $H_{9a,9s}$ signal but no other change from the data given in Table V. It contained 0.649 atom excess D by mass spectrometry. The *anti*-9-*d* configuration was assumed by analogy to other examples in this paper.

2- and *syn*-9-trimethylsilylbenzonorbornadiene-*anti*-9-*d* were isolated as a 73:27 mixture from run B and were identified by their combined pmr spectra, which were identical with those presented in Table V except for a slightly narrower H_1 , H_4 , multiplet and an H_{9a} , H_{9s} singlet equivalent to 0.75 H. The mixture contained 0.947 atom excess D by mass spectrometry. The *anti*-9-*d* configuration in the 2 isomer was assumed by analogy to previous examples.

Addition of benzyne to *tert*-butylcyclopentadienes on a 4.7-mmol scale gave a 57% yield by glpc of *tert*-butylbenzonorbornadienes. Separation and analysis with column D at 225° gave 33% 1 (retention time 21 min) and 67% 2 (15 min) isomers.

Analysis of the mixture prior to glpc by areas of *tert*-butyl peaks in its pmr spectrum indicated 34% 1 and 66% 2 isomers.

Anal. (of the isomeric mixture). Calcd for $C_{15}H_{18}$: C, 90.85; H, 9.15. Found: C, 90.74; H, 8.89.

1- and 2-*tert*-butylbenzonorbornadiene as isolated by glpc were each >95% pure and were identified by their pmr, ir, and mass spectra.

Addition of Benzyne to *tert*-Butylcyclopentadienylmagnesium Chloride.—On a 19-mmol scale the Grignard reagent (pmr δ 1.20, s, 9 H; 5.79, AA'BB', 4 H) was generated in 12 hr. After deuterolysis a yield of 29% *tert*-butylbenzonorbornadiene was found by glpc. Analysis and separation on column D gave 12% 1 and 88% 2 isomers which contained 0.724 and 0.898 atom excess D, respectively. The product distribution in Table IV was calculated by assuming that the distribution of deuterated material was identical with that formed *via* Grignard.

1-*tert*-Butylbenzonorbornadiene-*anti*-9-*d* was isolated >95% pure and identified by its pmr, ir, and mass spectra.

2-*tert*-Butylbenzonorbornadiene-*anti*-9-*d* was isolated >95% pure and identified by its pmr, ir, and mass spectra. Its pmr spectrum showed a broad peak at δ 2.14 for H_{9s} and a much weaker half of an AB spectrum for residual H_{9a} compared to its undeuterated analog.

Registry No.—4, 31893-09-1; 9, 31893-10-4; 10, 31893-11-5; benzyne, 462-80-6.

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Pseudo π Bonding in Saturated Hydrocarbons

GRAHAM R. UNDERWOOD* AND JO-ANNA M. IORIO¹

Department of Chemistry, New York University, University Heights, Bronx, New York 10453

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INDO MO calculations on a number of geometries of ethane lead us to conclude that the fraction of s character in the C-C "single" bond is directly proportional to the pseudo π bond order between the two atoms. This and previous results suggest that the length of the C-C "single" bond may be determined primarily by the π bond order.

The question as to the extent to which the carbon-carbon bond length depends upon π bond order or upon the hybridization in the σ bond has been the subject of considerable debate for several years.²⁻⁶ Many studies have involved attempts to define appropriate models for single bonds resulting from the overlap of different types of hybrid atomic orbitals (sp^n , different n) in unsaturated and strained saturated hydrocarbons.

Maksić and Randić⁶ recently examined a number of saturated hydrocarbons, for which the structures are accurately known, and used the method of maximum overlap⁷ to calculate the hybridization of the atomic orbitals involved in the various bonds. These authors found a close correlation between the experimental

bond lengths and the amount of s character calculated for the hybrid orbitals forming the single bonds. Miyazaki,⁵ however, pointed out one of the dangers in using the localized bond approximation particularly for hybrid orbitals with little s character and came to the surprising conclusions that by neglecting the π overlap in ethylene and acetylene the calculated equilibrium bond lengths were essentially identical with those calculated for ethane. This would imply that π overlap is entirely responsible for the shortening of the carbon-carbon bond in the former two molecules. The question therefore arises: *If bond lengths are essentially independent of the hybridization in the σ bond, how does one explain the correlations of Maksić and Randić⁶ which were obtained for a large number of saturated hydrocarbons?*

Because of the many difficulties inherent in experimental approaches to this question, we considered it highly desirable to examine the problem from a theoretical point of view. The INDO⁸ approximate SCF MO method which has now been adequately tested and has been shown to give reliable results appeared to us to be most appropriate for this purpose. In this communi-

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(2) For a recent, concise review of the status of this controversy, see R. A. Alden, J. Kraut, and T. G. Traylor, *J. Amer. Chem. Soc.*, **90**, 74 (1968), and references cited therein.

(3) (a) R. S. Mulliken, *Tetrahedron*, **6**, 68 (1959); (b) M. J. S. Dewar and A. N. Schmeising, *ibid.*, **5**, 166 (1959).

(4) An Epistologue on Carbon Bonds, *ibid.*, **17**, 123 (1962).

(5) T. Miyazaki, *Tetrahedron Lett.*, 1363 (1970).

(6) Z. B. Maksić and M. Randić, *J. Amer. Chem. Soc.*, **92**, 424 (1970).

(7) L. Klasinc, Z. Maksić, and M. Randić, *J. Chem. Soc. A*, 755 (1966).

(8) J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Chem. Phys.*, **47**, 2026 (1967).

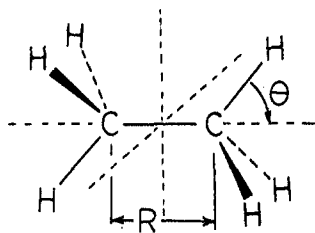


Figure 1.—The orientation of the reference ethane molecule in the Cartesian framework and the definition of R and θ .

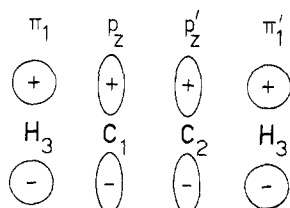


Figure 2.—The basis set of orbitals in ethane antisymmetric with respect to the XY plane.

cation we use the INDO method to show that both the above sets of data are compatible with the predominant effect on bond length being due to π bonding, and we describe a pseudo π bonding phenomenon which should be of general importance in studies involving strained σ systems.

For simplicity, we shall confine our initial discussion to the carbon-carbon bond length in ethane. We may form hypothetical ethane molecules with differently hybridized carbon atoms by locating the hydrogen nuclei in such a manner as to force the appropriate changes in hybridization. The fact that such distorted molecules have insignificantly short lifetimes is of no consequence. We have performed a large number of INDO MO calculations on these ethane molecules in both the staggered and eclipsed conformation. In all cases the C-H bond lengths were assumed to be 1.09 Å. The C-C internuclear distances were varied and the equilibrium bond lengths, R_e , were obtained by minimizing the energy of the molecule with respect to this parameter.

For convenience, we imagine these molecules to be located at the origin of a Cartesian coordinate framework with the two carbon nuclei lying equidistant from the origin on the X axis. The geometry will be discussed in terms of the parameters R and θ shown in Figure 1.

A limitation of the localized σ bond description of saturated molecules can be visualized as follows. Consider ethane to be composed of a basis set of six hydrogen 1s orbitals and two sets of carbon 2s, $2p_x$, $2p_y$, and $2p_z$ orbitals centered on the appropriate nuclei. The two sets of three hydrogen 1s orbitals are most conveniently expressed as three normalized group orbitals, one (σ_1) symmetric with respect to the X axis and the other two (π_1 , π_2) antisymmetric with respect to the XY XZ plane, respectively. Considering only those orbitals antisymmetric with respect to the XY plane, we obtain the picture shown in Figure 2.

These orbitals can be combined in the same manner as the four p_z orbitals in butadiene, with the same consequence: partial π bonding character between the two carbon atoms. A similar argument pertains to the orbitals antisymmetric with respect to the XZ plane.

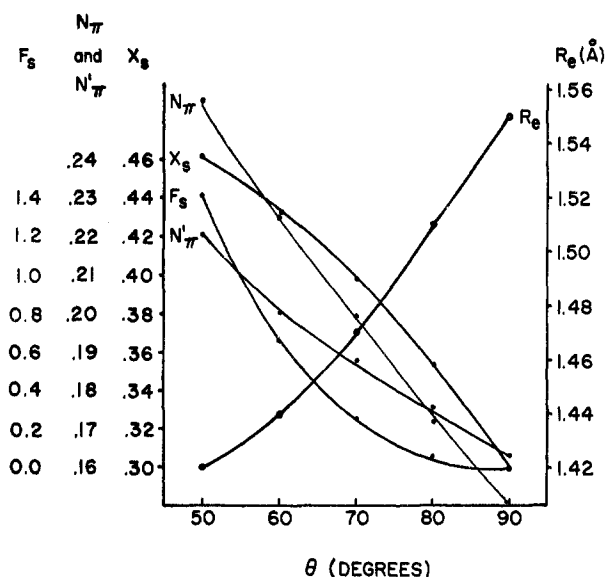


Figure 3.—The variation, as a function of the angle θ defined in the text, of (a) R_e , the calculated equilibrium bond length in Å, (b) N_{π} , the calculated pseudo π bond order between the two carbon atoms at the calculated equilibrium bond length, (c) N'_{π} , the calculated pseudo π bond order between the two carbon atoms at a constant separation of 1.50 Å, and (d) F_s and X_s , two different estimates of fractional s character in the C-C bond, as defined in the text.

The formal hybridization of the carbon atoms is changed by the relocation of the hydrogen atoms. The effect of decreasing θ is to increase the s character in the C-C σ bond. If we assume complete absence of bond bending,⁹ then the fractional s character (F_s) in the hybrid orbital on C_1 which is directed toward C_2 is given by¹⁰

$$F_s = 2 \cot^2 \theta$$

However, from Figure 2 it is apparent that the effect of decreasing θ is to decrease the π_1 - p_z and π'_1 - p'_z overlaps, and, since the mutual bond polarizability

$$\pi_{23,12} = \partial p_{23} / \partial \beta_{12}$$

is negative for butadiene,¹² this suggests that decreased π_1 - p_z overlap resulting from a decrease in θ should result in an increase in the pseudo π bonding between the two carbon atoms. Consequently, any attempt to change the hybridization at carbon by changing bond angles will also be accompanied by a change in the pseudo π bond order. Furthermore, increased s character is accompanied by an *almost parallel* increase in pseudo π bond order, and both these factors should be borne in mind when interpreting experimental data.

The situation is best illustrated by some of the results of the INDO calculations. It is found that, as θ decreases, the calculated equilibrium bond length, R_e , decreases, as expected.⁶ Figure 3 shows a plot of R_e vs. θ . It is noted that, for ethane ($\theta = 70^\circ$),¹³ R_e is somewhat smaller than the experimental value of 1.534 Å,¹³ but the agreement is, nevertheless, quite satis-

(9) C. A. Coulson and W. E. Moffitt, *Phil. Mag.*, **40**, 1 (1949).

(10) Alternatively, to account for bond bending, θ could be replaced by θ_0 , the angle between the x axis and the hybrid atomic orbital on carbon directed toward each hydrogen, and θ_0 could be estimated, for example, by the method of Mislow.¹¹

(11) K. Mislow, *Tetrahedron Lett.*, 1415 (1964).

(12) A. Streitwieser, "Molecular Orbital Theory for Organic Chemists," Wiley, New York, N. Y., 1961, pp 107, 108.

(13) H. C. Allen, Jr., and E. K. Plyler, *J. Chem. Phys.*, **31**, 1062 (1959).

factory. In order to examine the magnitude of the pseudo π bonding, the p_z - p_z' overlap populations¹⁴ (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_s 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 by¹⁵

$$X_s = \frac{n(C_1 2s, C_2 2s) + n(C_1 2s, C_2 2p_z)}{n(C_1 2s, C_2 2s) + n(C_1 2s, C_2 2p_z) + n(C_1 2p_x, C_2 2p_x)}$$

If this were a perfect criterion of hybridization, then a value of 0.25 would be expected for sp^3 hybrid orbitals

(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).

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.

(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

DOLORES GRACIAN AND HARRY P. SCHULTZ*

Department of Chemistry, University of Miami,
Coral Gables, Florida 33124

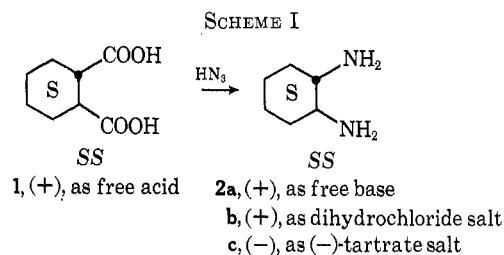
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Discussion

The purpose of this publication, an epilogue of earlier work² 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 reported² and resolved. Appiequist and Werner³ 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 di-

hydrochloride (**2b**) in low yield (Scheme I). After the chiralities of C-1 and C-2 of **2b** had been established,



2c was more readily obtained by resolution of commercial 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 cycloalkylation⁵ of

(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. Appiequist 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).