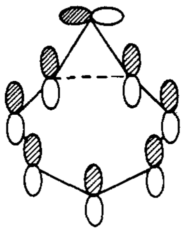
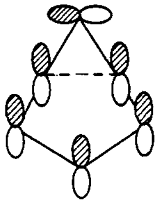




Möbius aromatic while the 6π bicyclo[3.1.0]hexenyl cation might equally well be termed Möbius antiaromatic.

It should be noted that the two alternative descriptions lead to the same conclusion. Thus, homotropylium is stabilized through aromatic conjugation, either *via* six π electrons in a Hückel ring or eight in a Möbius arrangement. Correspondingly, applying either model, bicyclo[3.1.0]hexenyl is seen to suffer in stability from its antiaromatic character. The description of choice would seem to depend heavily upon geometrical arguments: that is, a fully formed cyclopropane ring favoring a Hückel polyene and a more open structure, the Möbius arrangement. In actual practice both mechanisms for electron delocalization are no doubt operative.

Acknowledgments. The author acknowledges and thanks Professors Berson (Yale), Hoffmann (Cornell), Salem (Paris), and Schleyer (Princeton) for their comments and criticism on the manuscript, and the Centre de Recherches Roussel-Uclaf for a generous fellowship.

[12] Direct all correspondence to: Department of Chemistry, University of California, Irvine, Calif. 92664.

[13] The Laboratoire de Chimie Théorique is part of the Laboratoire de Physico-Chimie des Rayonnements and is associated with the CNRS.

Warren J. Hehre[12]
Laboratoire de Chimie Théorique[13] *(490)*
Université de Paris-Sud
Centre D'Orsay, 91405 Orsay, France
Received March 8, 1973

Electronic Structure and Reactivity of Small Ring Compounds. VI. Carbon–Carbon Coupling Constants in 1-Cyanobicyclo[1.1.0]butane[1]

Sir:

The considerable strain in the bicyclo[1.1.0]butane ring system[2,3] has prompted numerous calculations of the electronic structure at all levels of sophistication.[4–10] By employing the Muller–Pritchard relationship between hybridization and ^{13}C–H coupling constant,[11,12] these calculations are, at least for hybridization, subject to experimental verification. The observed coupling constants in bicyclobutane[13] therefore suggest the C_1–H orbital is $sp^{1.44}$, the C_2–H_{exo} orbital is $sp^{2.27}$, and the C_2–H_{endo} orbital is $sp^{1.96}$. Analogous results have been obtained for 1-cyanobicyclo[1.1.0]butane.[14]

A similar type of linear correlation between hybridization and ^{13}C–^{13}C coupling constants was suggested by Frei and Bernstein.[15] The relationship was justified theoretically by Pople and Santry[16] and used by Roberts[17] in the form

$$J_{^{13}C-^{13}C} = 550(S_{1(2)})(S_{2(1)}) \qquad (1)$$

where $S_{1(2)}$ and $S_{2(1)}$ are the s characters of the hybrid orbitals comprising the C_1–C_2 bond on carbons 1 and 2, respectively. Thus, for example, the ^{13}C–^{13}C coupling constant of 34.6 Hz in ethane[18] corresponds to s characters of 0.25 or sp^3 hybridization. Recently an alternative equation has been suggested, but it requires the bond overlap, *S*, calculated using the maximum overlap approximation.[12] It has also been used with maximum overlap derived hybridizations to predict coupling constants. It is important to point out that these coupling constant–hybridization relationships probably do not apply to highly strained small ring systems. Roberts,[17b] and more recently Schulman and Newton,[19] have suggested that the problem is due to contributions from terms other than the contact term.

In this communication we wish to report the ^{13}C–^{13}C coupling constants in 1-cyanobicyclobutane and compare these values to those predicted by the calculations. In addition the possibility of inserting these values into the coupling constant–hybridization equations and comparing the hybridizations to those calculated is discussed.

The nmr spectra were obtained on a Varian XL-100 FT spectrometer operating at 25.2 MHz with complete proton decoupling. The sample of 1-cyanobicyclobutane and about 30% of acetonitrile-d_3 were codistilled into a 12-mm nmr tube at 10^{-5} Torr, degassed and sealed. The peak corresponding to carbons 2 and 4 showed a single coupling constant to carbons 1 and 3 of 22 ± 0.5 Hz. This is in excellent agreement with the value of 21 Hz reported recently by Grant and Allred and coworkers for bicyclobutane itself.[20] Because of the symmetry of the system these authors were unable to obtain a value for the C_1–C_3 coupling constant. The value for the C_1–C_3 coupling constant, obtained from the side bands of both the C_1 and C_3 resonances of cyanobicyclobutane was 16 ± 0.5 Hz. In addition C_1 and C_3 were coupled by 22 Hz to C_2 and C_4.

If one assumes that the C_1–C_3 bond is symmetrical, that is the CN group exerts only a minimal perturbation, then eq 1 suggests the hybridization is $sp^{4.85}$–$sp^{4.85}$ (*i.e.*, 17.1% s character in each orbital.)

---

[1] Part V: M. Pomerantz, R. N. Wilke, G. W. Gruber, and U. Roy, *J. Amer. Chem. Soc.*, **94**, 2752 (1972).

[2] K. B. Wiberg, G. M. Lampman, R. P. Ciula, D. S. Conner, P. Schertler, and J. Lavanish, *Tetrahedron*, 21, 2749 (1965).

[3] R. B. Turner, P. Goebel, B. J. Mallon, W. von E. Doering, J. F. Coburn, Jr., and M. Pomerantz, *J. Amer. Chem. Soc.*, **90**, 4315 (1968).

[4] M. Pomerantz and E. W. Abrahamson, *ibid.*, **88**, 3970 (1966).

[5] Z. Maksić, L. Klasinc, and M. Randić, *Theor. Chim. Acta*, **4**, 273 (1966).

[6] M. D. Newton and J. M. Schulman, *J. Amer. Chem. Soc.*, **94**, 767 (1972).

[7] J. M. Schulman and G. J. Fisanick, *ibid.*, **92**, 665 (1970).

[8] D. R. Whitman and J. F. Chiang, *ibid.*, **94**, 1126 (1972).

[9] K. B. Wiberg, *Tetrahedron*, **24**, 1083 (1968).

[10] T. Yonezawa, K. Simizu, and H. Kato, *Bull. Chem. Soc. Jap.*, **41**, 2336 (1968).

[11] N. Muller and D. E. Pritchard, *J. Chem. Phys.*, 31, 768, 1471 (1959).

[12] See also Z. B. Maksić, M. Eckert-Maksić, and M. Randić, *Theor. Chim. Acta*, **22**, 70 (1971).

[13] K. Wüthrich, S. Meiboom, and L. C. Synder, *J. Chem. Phys.*, **52**, 230 (1970).

[14] M. Pomerantz and D. F. Hillenbrand, results to be submitted for publication.

[15] K. Frei and H. J. Bernstein, *J. Chem. Phys.*, **38**, 1216 (1963).

[16] J. A. Pople and D. P. Santry, *Mol. Phys.*, **8**, 1 (1964).

[17] (a) F. J. Weigert and J. D. Roberts, *J. Amer. Chem. Soc.*, **89**, 9562 (1967); (b) F. J. Weigert and J. D. Roberts, *ibid.*, **94**, 6021 (1972).

[18] R. M. Lynden-Bell and N. Sheppard, *Proc. Roy. Soc., Ser. A*, **269**, 385 (1962).

[19] J. M. Schulman and M. D. Newton, unpublished results.

[20] R. D. Bertrand, D. M. Grant, E. L. Allred, J. C. Hinshaw, and A. B. Strong, *J. Amer. Chem. Soc.*, **94**, 997 (1972).

In support of the contention that a CN groups exerts only a small effect is that in both the ethane–propionitrile and ethylene–acrylonitrile pairs the CN causes about a 5% change in J_{cc}: 34.6[18] and 33 Hz[21] for the former and 67.6 and 70.6 Hz for the latter pair, respectively. In addition the nitrile group on bicyclobutane changes the C_1–C_2 coupling from 21[20] to 22 Hz or also about 5%. In the subsequent discussion the effect of the nitrile group on the coupling constant will therefore be ignored.

By using the C_2–H_{exo} and C_2–H_{endo} coupling constants of 158.3 and 174.0 Hz, respectively,[14] the Muller–Pritchard relationship,[11] and assuming the equivalence of the C_1–C_2 and C_2–C_3 bonds, it can readily be shown that the orbitals on C_2 bonding to C_1 and C_3 contain 16.8% s character each. From the observed coupling constant of 22 Hz and eq 1 the orbitals on carbon 3 (and 1) bonding to C_2 and C_4 contain 23.8% s character.[22] This means, therefore, that the peripheral bonds are $sp^{3.20}$–$sp^{4.95}$ and C_2 and C_4 are cyclopropane like. Now since J_{C_3-H} = 207.8 Hz[14] and the total s character around C_3 = 1.00 this would leave 10.8% s character for the C_3 orbital bonding to C_1, or $sp^{8.26}$. Once again the "direct" measurement (assuming the validity of the hybridization–coupling constant equations) gives 17.1% s character or $sp^{4.85}$. Thus there is a 6% error in the value calculated using unity for total s character as compared with that obtained directly. Errors of this magnitude are often observed in other compounds.[23] Thus estimates of the s character of an orbital from the sum of s characters of the other orbitals around a carbon atom obtained from coupling constants should be done with due caution.[20]

The above discussion assumed the validity of the coupling constant–hybridization relationships and pointed up the error involved in extrapolating from several known to an unknown hybridization. Of utmost importance are the suggestions that these equations are inappropriate to highly strained small ring systems.

For most saturated systems the orbital and dipolar terms are small and for unstrained systems the contact term is large and positive and predominates.[24] However, recently Schulman and Newton[19] have refined their original INDO calculations[6] and shown that for bicyclobutane, 1-cyanobicyclobutane, and benzvalene the 1,3 bond is abnormal in that the contact term is not large and positive but rather small and perhaps negative as are the dipolar and orbital terms. Thus Schulman and Newton calculate a value of +23.4 Hz for the C_1–C_2 coupling constant in bicyclobutane and −7.9 Hz for the C_1–C_3 coupling constant. The corresponding calculated value for the C_1–C_3 coupling constant in 1-cyanobicyclobutane is −8.0 Hz.[25] Other calculations predict a positive value for the C_1–C_3 coupling constant and in particular the maximum overlap method[5,12] predicts 17.8 Hz. The corresponding calculated C_1–C_2 coupling constant[5,12] is 19.4 Hz. It is amusing to point out that the simplest calculations[4] predict a C_1–C_2 coupling constant of 20 and 15 Hz for the sp^2 and sp model, respectively, and a C_1–C_3 coupling constant of 27 and 15 Hz for these respective bicyclobutane models assuming the validity of eq 1.

In conclusion, since the contact term for the C_1–C_2 bonds in bicyclobutane is rather normal according to the INDO calculations, the calculated value for the coupling constant by most methods agrees with that observed. On the other hand these more sophisticated calculations show an abnormality in the C_1–C_3 contact term and suggest a negative coupling constant as opposed to other calculations, such as maximum overlap, which predicts a positive sign. We plan to obtain the sign of the coupling constant experimentally. Of course if J is indeed negative the coupling constant–hybridization relationships cannot therefore apply to these highly strained microcyclic systems.

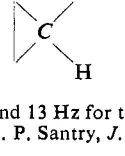
Acknowledgment. We wish to thank Dr. S. C. Cherkofsky of E. I. du Pont de Nemours for a generous gift of the cyanobicyclobutane M. P. wishes to thank the Chemistry Department of the University of Wisconsin for their hospitality and support during the fall of 1972 while a Visiting Professor and Professor J. M. Schulman for informative discussions and results of unpublished calculations.

---

(21) G. E. Maciel, J. W. McIver, Jr., N. S. Ostlund, and J. A. Pople, *J. Amer. Chem. Soc.*, **92**, 11 (1970).

(22) See ref 18 for a discussion of the C_1–C_2 bonds in bicyclobutane itself.

(23) The sum of the s character of the bonds around the italicized carbon atom is given in parentheses. The value should be compared to unity: PhC≡*C*H (1.07);[15] PhC≡*C*CH$_3$ (1.04);[15] and



(using 161 Hz for the C–H and 13 Hz for the C–C coupling,[17] 0.95).

(24) A. C. Blizzard and D. P. Santry, *J. Chem. Phys.*, **55**, 950 (1971).

(25) It should be pointed out that the observation that the calculated values for $J_{C_1-C_3}$ do not differ supports the idea that the nitrile group exerts only a minimal pertubation on the ring system.

(26) Author to whom correspondence should be addressed at Yeshiva University. Alfred P. Sloan Foundation Research Fellow.

Martin Pomerantz,*[26] David F. Hillenbrand
Department of Chemistry, The University of Wisconsin
Madison, Wisconsin 53706
Belfer Graduate School of Science, Yeshiva University
New York, New York 10033

Received May 26, 1973

Solution Behavior of a Synthetic Myoglobin Active Site

Sir:

We recently described[1] the synthesis of a section of the myoglobin active site[2,3] which is capable of binding oxygen as a solid material. The compound and its derivatives are shown in Figure 1.

We now report the rather spectacular solution behavior of this compound. The hemin II was dissolved in 3 ml of methylene chloride at about 10^{-4} *M* concentration. This solution was shaken at 25° with 0.05 ml of a (pH 7) phosphate buffer containing an excess of sodium dithionite. The resulting solution had a broad band centered at 545 nm which is remarkably similar to that of deoxymyoglobin.[3] Cooling this solution to

---

(1) C. K. Chang and T. G. Traylor, *Proc. Nat. Acad. Sci. U. S.*, in press.

(2) (a) J. H. Wang in "Oxygenases," O. Hayaishi, Ed., Academic Press, New York, N. Y., 1962, p 502; (b) J. H. Wang in "Heamatic Enzymes," Part 1, J. E. Falk, R. Lemberg, and R-K. Morton, Ed., Pergamon Press, New York, N. Y., 1961, p 98.

(3) E. Antonini and M. Brunori, "Hemoglobin and Myoglobin in Their Reactions with Ligands," North Holland Publishing Co., Amsterdam, 1971, p 76.