(s, 2 H), 3.90–3.47 (m, 3 H), 3.23 (dd, $J_1 = J_2 = 9$ Hz, 1 H), 2.13–1.40 (m, 5 H), 1.04 (s, 3 H), 0.97 (d, $J = 7$ Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 138.9, 128.2, 127.5, 127.3, 84.3, 73.1, 72.8, 67.2, 42.8, 35.9, 25.9, 22.5, 13.9; IR (film) 1060 cm^{-1}; MS (CI) *m/z* 235 ($M^+ + 1$, 100%). Reduction of the mixture of diols **45a** and **46a** using reduction Method E affords diols **45b** and **46b** after flash chromatography (60% ethyl acetate in hexane elution; 70% yield). Comparison of the mixture spectroscopically with authentic samples of **45b** and **46b** prepared as depicted in the Supplementary Material shows that the inversion selectivity is greater than 95% (**45b**:**46b** > 20:1). By conversion of the mixture of **45b** and **46b** to their respective tetrahydrofurans **45b** and **46b** (1.1 equiv TsCl/Et_3N/CH_2Cl_2) it is shown that the selectivity for inversion of configuration in the formation of hydration products is on the order of 98% (**43b**:**44b** = 62:1). Spectroscopic data for authentic samples of diols **45b** and **46b** are as follows. **45b**: ^{1}H NMR (90 MHz, $CDCl_3$) δ 7.26 (s, 5 H), 4.46 (s, 2 H), 4.10–2.50 (b, 2 H), 3.75–3.32 (m, 4 H), 2.21–1.75 (m, 1 H), 1.75–1.35 (m, 4 H), 1.15 (s, 3 H), 0.95 (d, $J = 7$ Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 137.5, 128.4, 127.8, 127.7, 74.4, 73.5, 63.5, 42.6, 34.3, 27.0, 25.4, 12.9; IR (film) 3400 cm^{-1}; MS (CI) *m/z* 235 (100%). **46b**: ^{1}H NMR (90 MHz, $CDCl_3$) δ 7.26 (s, 5 H), 4.46 (s, 2 H), 4.15 (b s, 1 H), 3.71–3.41 (m, 4 H), 3.35 (b s, 1 H), 2.15–1.79 (m, 1 H), 1.88–1.42 (m, 4 H), 1.07 (s, 3 H), 0.82 (d, $J = 7$ Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 137.4, 128.5, 127.8, 74.6, 73.7, 73.6, 63.4, 40.2, 38.2, 26.6, 22.3, 13.0; IR (film) 3400 cm^{-1}; MS (CI) *m/z* 193 ($M^+ - C_3H_7O$), 91 (100%).

Lactonization of [α,α,α]-Bicyclo[4.1.0]heptane-3-carboxylic Acid (48). Stereoisomerically pure (>98.0%) acid **48** is prepared as depicted schematically in the Supplementary Material: mp 35–36.5 °C; ^{1}H NMR (90 MHz, $CDCl_3$) δ 2.53–2.13 (m, 1 H), 2.13–1.48 (m, 4 H), 1.48–0.80 (m, 4 H), 0.80–0.43 (m, 1 H), 0.08 (dd, $J_1 = 5$ Hz, $J_2 = 10$ Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 183.1, 40.1, 27.0, 22.9, 22.7, 10.6, 9.9, 7.8; MS (EI) *m/z* 140 (M^+), 95 (100%); IR (film) 3000, 1710 cm^{-1}. Anal. Calcd for $C_8H_{12}O_2$: C, 68.57; H, 8.57. Found: C, 68.52; H, 8.78.

Cyclization of acid **48** using lactonization Method A (5 days/25 °C/CCl_4) affords γ-lactone **50** in only 14% yield after flash chromatography (40% ethyl acetate in hexane elution): ^{1}H NMR (90 MHz, $CDCl_3$) δ 4.51 (d, $J = 6$ Hz, 1 H), 2.74–1.14 (m, 8 H), 2.05 (d, $J = 5$ Hz, 2 H); IR (film) 1785 cm^{-1}. Lactone **50** is reduced to diol **51** using reduction Method F (LAH) in 60–70% yield after flash chromatography (ethyl acetate): ^{1}H NMR (80 MHz, $CDCl_3$) δ 3.90–3.62 (m, 1 H), 3.52 (d, $J = 5$ Hz, 2 H), 2.24–1.07 (m, 10 H), 0.92 (d, $J = 7$ Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 71.9, 68.0, 38.4, 34.4, 32.7, 29.3, 23.5, 12.2; IR (film) 3350 cm^{-1}. Exact mass calcd for $C_8H_{16}O_2$: 144.1150. Found 114.1157.

Alternatively, direct reduction of the crude lactone product using reduction Method F (LAH) affords diol **51** and a trace amount of an isomeric diol (GC-MS *m/z* 144; the relative retention times of **51** and the impurity are 1.14 and 1.00, respectively; 15:1 ratio). Flash chromatography (ethyl acetate elution) affords the two diols in 35% overall yield from acid **48**.

We note that acidification (48% HBR) of the basic aqueous layer remaining after cyclization workup, followed by the usual extractive workup, affords only traces (<5%) of material corresponding to hydroxy acids **49a,b**. Also, neither **50** nor **51** are rigorously characterized by correlation with authentic samples; they are distinguishable spectroscopically and gas chromatographically from their closely related isomeric counterparts, **29** and **31**, respectively.

Acknowledgment. We would like to thank Cornell University, the donors of the Petroleum Research Fund, administered by the American Chemical Society, the National Institutes of Health (GM 30875-01), the E. I. du Pont de Nemours Co., Dr. Alfred Bader, and Dr. M. Farahati for their generous financial support of this work. Acknowledgement is made to the National Science Foundation Instrumentation Program (CHE 7904825 and PCM 8018643) for support of the Cornell Nuclear Magnetic Resonance Facility.

Registry No. 2, 87433-66-7; **3a**, 87433-86-1; **3b**, 2865-82-9; **4a**, 87433-63-4; **4b**, 87433-64-5; **4c**, 87433-65-6; **5a**, 87433-67-8; **5b**, 87433-68-9; **5c**, 87433-69-0; **6a**, 87433-88-3; **6b**, 87433-90-7; **7a**, 87433-87-2; **7b**, 87433-89-4; **8a**, 69492-28-0; **8b**, 87434-21-7; **9a**, 87433-70-3; **9b**, 87433-71-4; **9c**, 87433-72-5; **10a**, 87433-73-6; **10b**, 87433-74-7; **10c**, 87433-75-8; **11a**, 87433-91-8; **11b**, 87433-95-2; **12a**, 87433-92-9; **12b**, 87433-96-3; **13a**, 87433-93-0; **13b**, 87433-97-4; **14a**, 87433-94-1; **14b**, 87433-98-5; **16a**, 87433-76-9; **16b**, 87433-77-0; **16c**, 87433-78-1; **17a**, 87433-79-2; **17b**, 87433-80-5; **17c**, 87433-81-6; **18a**, 87433-99-6; **18b**, 39638-67-0; **19a**, 87434-06-8; **19b**, 55013-32-6; **22**, 87434-03-5; **23**, 87434-04-6; **24**, 87434-02-4; **25**, 87434-05-7; **26**, 87434-00-2; **27**, 87434-01-3; **28a**, 87433-82-7; **28b**, 87433-83-8; **29**, 87434-07-9; **30**, 87434-08-0; **31**, 87434-09-1; **32**, 87434-10-4; **42**, 87434-22-8; **43a**, 87434-11-5; **43b**, 87434-15-9; **44a**, 87434-12-6; **44b**, 87434-16-0; **45a**, 87434-13-7; **45b**, 87434-17-1; **46a**, 87434-14-8; **46b**, 87434-18-2; **48**, 87433-85-0; **50**, 87434-19-3; **51**, 87434-20-6; $Hg(NO_3)_2$, 10045-94-0; $Hg(O_2CCF_3)_2$, 13257-51-7; $Hg(ClO_4)_2$, 7616-83-3; [$\alpha,\beta,$-α]-3-(hydroxymethyl)bicyclo[4.1.0]heptane, 87433-84-9.

Supplementary Material Available: Schematics for the preparation of all starting materials and authentic samples of **3b**, **6b**, **7b**, **11b–15b**, **18b**, **19b**, **22–25**, **31**, **32**, **43b**, and **44b** (5 pages). Ordering information is given on any current masthead page.

Methano-Bridged Compounds. 1. Correlation of the ^{13}C Nuclear Magnetic Resonance Shift Average and Shift of the Bridge Carbon with the Average π-Electron Density of Methano-Bridged and Homoaromatic Compounds

Ronald J. Hunadi[1]

Contribution from R. J. Consultants, 4524 Tobias Avenue, Sherman Oaks, California 91403.

Received August 2, 1982

Abstract: It was shown that the shift of the bridge carbon and ^{13}C NMR chemical shift average of methano-bridged and homoaromatic systems correlates well with the average π-electron density. The following equations were developed from the plot of the shift of the bridge carbon vs. electron density: $\delta_{\text{bridge}} = 51.97\rho_{\text{av}} - 16.40$ with $r = 0.942$ for methano-bridged systems and $\delta_{\text{bridge}} = 81.68\rho_{\text{av}} - 34.68$ with $r = 0.931$ for homoaromatic systems. Also developed were the following equations for the ^{13}C NMR shift average vs. π-electron density: $\delta_{\text{av}} = 275.85 - 145.71\rho_{\text{av}}$ with $r = 0.90$ for methano-bridged systems and $\delta_{\text{av}} = 234.52 - 117.40\rho_{\text{av}}$ with $r = 0.948$ for homoaromatic systems. If the slopes for the ^{13}C NMR chemical shift average vs. electron density are indicative of the degree of aromaticity, then the order of aromaticity is [0]bridged > methano-bridged > homoaromatic systems (161 > 146 > 117 ppm/e$^-$) as would be expected.

Although various studies have been reported on the properties and characterization of methano-bridged systems,[2] none of these studies resulted in a correlation between the $^{13}C_{\text{av}}$ NMR chemical shift and electron density of the system and/or the ^{13}C NMR

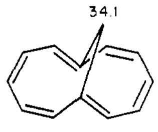
0002-7863/83/1505-6889$01.50/0 © 1983 American Chemical Society

chemical shift of the bridge carbon and average π-electron density. Initial studies by Vogel and Günther[2a] indicated that a diamagnetic ring-current effect does exist for the ^{13}C NMR shifts of methano-bridged compounds, but it is masked, in most cases, by other factors including structural ones. From their results they concluded that ^{13}C NMR spectroscopy is not suitable for probing the magnetic properties of π systems.

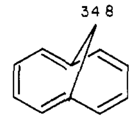
The Spiesecke–Schneider[3] correlation of ^{13}C NMR chemical shifts vs. average π-electron density is well documented and gives a straight line for acyclic, aromatic, and fused-aromatic systems.[4] We now report that a good correlation also exists between the ^{13}C NMR chemical shift average and the average π-electron density of fully conjugated, methano-bridged systems. Also and possibly more important, we have found that the ^{13}C NMR shift of the bridge carbon of fully conjugated, methano-bridged systems is sensitive to the average electron density of the system. Finally, we would like to present our studies on homoaromatic systems and the correlations derived from this work.

Results

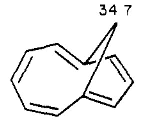
Bridge-Carbon Shift vs. Average π-Electron Density for Methano-Bridged Systems. Before proceeding to the data for correlating the ^{13}C NMR shift of the methano-bridged carbon to the electron density of methano-bridged systems, it will first be necessary to show, in the systems we are examining, that structural and geometric effects need not be as important as the average electron density. It is interesting to note the similarity of the ^{13}C NMR shifts of the bridge carbon of 1,7-methano[12]annulene (**1**),[2b] 1,6-methano[10]annulene (**2**),[2h] and 1,5-methano[10]annulene (**3**).[2f] In these three cases the average electron density is 1.0 and the three bridge shifts are all within 0.7 ppm. We feel that the major reason for this similarity is that the bridge carbon is very sensitive to the electron density of the ring over which it is located. *We propose that in fully conjugated, methano-bridged systems (if the ring sizes are not too dissimilar and the systems are planar), structural effects play a minor role in determining the ^{13}C NMR chemical shift of the bridge carbon and that the average electron density is the most important factor.*



1

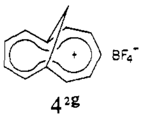
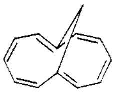
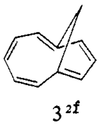
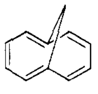
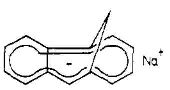
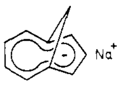
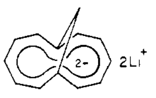


2



3

Table I. ^{13}C NMR Shifts of the Bridge Carbon of Methano-Bridged Systems vs. the Corresponding Average π-Electron Density

compound	δ_{bridge}	ρ_{av}
 **4**[2g]	32.6	0.909
 **1**[2c]	34.1	1.000
 **3**[2f]	34.7	1.000
 **2**[2h]	34.8	1.000
 **5**[2i,j]	39.8	1.077
 **6**[2j,k]	42.1	1.111
 **7**[2e]	44.6	1.167

"Theoretical studies and previous experimental evidence[4d,5a,b] show that the magnetic shielding constant σ of the ^{13}C nucleus is influenced mainly by the immediate electronic environment and the paramagnetic contribution to the shielding".[2a,5c]

In Table I we have compiled the available ^{13}C NMR shifts of bridge carbon vs. the average π-electron density of methano-bridged systems.[5i] The data were plotted and are displayed graphically in Figure 1. As can be seen from these data, a good correlation does exist between the ^{13}C NMR chemical shift of the bridge carbon and the *absolute value* of the average electron density. A least-squares analysis of these data gave the following equation[6a,b]

$$\delta_{\text{bridge}} = 51.97\rho_{\text{av}} - 16.40 \qquad (1)$$

This equation would predict a ^{13}C NMR shift of 29.7 for the bridge at the 1,6-position of the dication of *syn,syn*-1,6:8,17:10,15-trismethano[18]annulene (**8**).[5h] The actual shift is 32.8 with $\Delta_{^{13}\text{C}} = 3.1$ ppm. A good portion of this difference is due to deshielding effects of the carbon bridging the 8,17-position of **8** which must be taken into account. This equation would also

---

(1) This work was initiated at the Hydrocarbon Research Institute, University of Southern California.

(2) (a) Günther, H.; Schmickler, H.; Königshofen, H.; Recker, K.; Vogel, E. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 243. (b) Günther, H.; Schmickler, H.; Brinker, V. H.; Nachtkamp, K.; Wassen, J.; Vogel, E. *Ibid.* **1973**, *12*, 760. (c) Vogel, E.; Königshofen, H.; Müllen, K.; Oth, J. F. M. *Ibid.* **1974**, *13*, 281. (d) Vogel, E.; Mann, M.; Sakata, Y.; Müllen, K.; Oth, J. F. M. *Ibid.* **1974**, *13*, 283. (e) Oth, J. F. M.; Müllen, K.; Königshofen, H.; Mann, M.; Sakata, Y.; Vogel, E. *Ibid.* **1974**, *13*, 285. (f) Masamune, S.; Brooks, D. W. *Tetrahedron Lett.* **1977**, (*37*), 3239. (g) Kemp-Jones, A. V.; Jones, A. J.; Sakai, M.; Beeman, C. P.; Masamune, S. *Can. J. Chem.* **1973**, *51*, 767. Grimme, W.; Hoffmann, H.; Vogel, E. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 354. (h) Vogel, E.; Roth, H. D. *Ibid.* **1964**, *3*, 228. (i) Hunadi, R. J.; Helmkamp, G. K. *J. Org. Chem.* **1978**, *43*, 1586. (j) Hunadi, R. J. *J. Org. Chem.* **1982**, *47*, 1940. (k) Takahashi, K.; Kagawa, T.; Takase, K. *Chem. Lett.* **1979**, 701. (l) Destro, R.; Simonetta, M. *Acta Crystallogr., Sect. B* **1979**, *B35*, 1846.

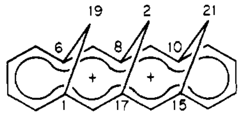
(3) (a) Spiesecke, H.; Schneider, W. G. *Tetrahedron Lett.* **1961**, 468. (b) Fraenkel, G.; Carter, R. E.; Mc Lacklar, A.; Richards, J. H. *J. Am. Chem. Soc.* **1960**, *82*, 5846.

(4) (a) O'Brien, D. H.; Hart, A. J.; Russel, C. R. *J. Am. Chem. Soc.* **1975**, *97*, 4410. (b) Olah, G. A.; Mateescu, G. D. *Ibid.* **1970**, *92*, 1430. (c) Lauterbur, P. C. *Ibid.* **1961**, *83*, 1838. (**d**) Stothers, J. B. "Carbon-13 NMR Spectroscopy"; Academic Press: New York, 1972; p 91. (e) As pointed out by one of the referees, Vogel's work,[2] as well as this study, indicates that there is no predominant factor that determined the average ^{13}C NMR shift for neutral bridged annulenes. This would indicate that for these systems, other effects (structural) will exhibit a significant influence on the average chemical shift. Although the average ^{13}C NMR shifts of **1**, **2**, **3**, **12**, **14**, and **15** are spread over a range of 13 ppm (13 ppm between **2** and **3**), compounds **1** and **3**, both being nonbenzeoid, differ by only 3.3 ppm, and the benzenoid compounds **2**, **5**, **12**, and **14** have a spread of 3.9 ppm. This indicates that the average shift of neutral methano-bridged compounds is influenced by the benzenoid or nonbenzenoid nature of the system.

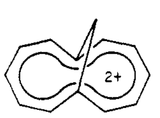
(5) (a) Mooney, E. F.; Winson, P. H. *Annu. Rep. NMR Spectrosc.* **1969**, *2*, 153. (b) Breitmaier, E.; Jung, G.; Voelter, W. *Angew. Chem.* **1971**, *83*, 659; *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 673. (c) For earlier work on ring-current effects on ^{13}C nuclei, ref 5d–g. (d) Burke, J. J.; Lauterbur, P. C. *J. Am. Chem. Soc.* **1964**, *86*, 1870. (e) Jones, A. J.; Alger, T. D.; Litchman, W. M. *Ibid.* **1970**, *92*, 2386. (f) Jones, A. J.; Gardner, P. P.; Grant, D. M.; Litchman, W. M.; Boekelheide, V. *Ibid.* **1970**, *92*, 2395. (g) Doddrell, D.; Caughey, W. S. *Ibid.* **1972**, *94*, 2510. (h) Deger, H. M.; Müllen, K.; Vogel, E. *Angew. Chem.* **1978**, *90*, 990. (i) The π-electron densities were calculated by using the simple equation for Hückel charge density (ρ_{av}) = the number of π-electrons/number of carbon atoms in the ring. (The number of carbons atoms does not, of course, include the bridge carbon.)

(6) (a) The least-squares analyses were performed on a HP-97 programmable calculator. (b) The correlation coefficient $r = 0.942$.

predict a ^{13}C NMR shift of 26.9 for the dication of 1,7-methano[12]annulene (**9**)[8] for which a ^{13}C NMR shift has not been reported. In this relationship it does not matter if the system is aromatic or antiaromatic, only the average electron density matters.

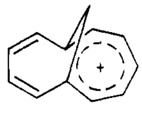


8

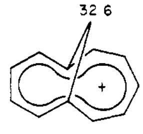


9

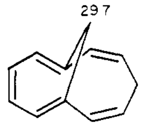
After examination of these data, the argument given by Masamune et al.[2g] concerning their conclusion that the cation of 1,6-methano[11]annulene (**11**) exists as **10** rather than **4** is not necessarily correct. They based their argument on the fact that



10



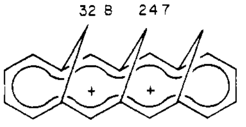
4



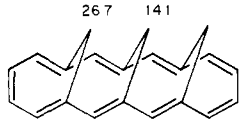
11

little change is seen in the chemical shift (^{13}C) of the bridge carbon on conversion of precursor **11** to ion **4**. They indicated that no unequivocal shielding effects by ring currents on ^{13}C NMR chemical shifts had been observed for any system at the time their study was completed. They felt that this may be due to the bridge being in a "null" shielding region and not in a shielding cone. Concrete support for the 1,6-methano[11]annulene cation existing as structure **4** and not **10** comes from the recently reported X-ray crystallographic studies performed by Destro and Simonetta. In their work they discovered that the large transannular distance between C-1 and C-6 (2.30 Å) indicated that homoaromatic delocalization was not important in this ion.[21]

If the bridged cation **8**, perpared from **12** by Vogel et al.,[5h] is examined, we see that although it is a 16π system, the same downfield shift of the bridge carbon (C-19) is observed as was seen for the conversion of **11** to **4**. Again, it can be argued that



8



12

the electron density of the system is what is most important. Masamune[2g] indicated that if the absolute value of the ring-current effect is independent of the nucleus involved, then the effects in the ^{13}C spectra would be outweighed by shifts due to changes in geometry and local charge. Since we showed that geometry changes need not always be the most important factor affecting the ^{13}C NMR shift, *then the local charge or charge density can be the most important factor affecting the ^{13}C NMR shift of the bridge carbon in methano-bridged systems.*

The equation we have derived for correlating the shift of the bridge carbon versus average electron density of methano-bridged systems will receive further verification as more ^{13}C NMR data on bridged 10π and 14π-systems becomes available.

^{13}C NMR Chemical-Shift Average vs. Average Electron Density of Methano-Bridged Systems. Several correlations on ^{13}C NMR chemical shift averages vs. electron density have been reported[4] and lend additional support to the validity of the Spiesecke–Schneider relationship[3] but, to the best of our knowledge, no one has systematically examined a series of methano-bridged compounds. Since these systems contain quaternary carbons, corrections may be required to achieve a good fit, but first we will examine the original uncorrected data to determine if we can develop a simple relationship.

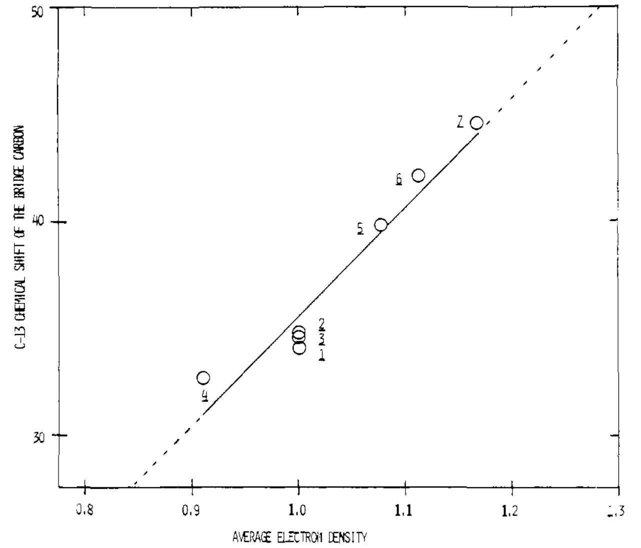


Figure 1. Correlation of the ^{13}C NMR shift of the bridge carbon with the π-electron density of methano-bridged systems.

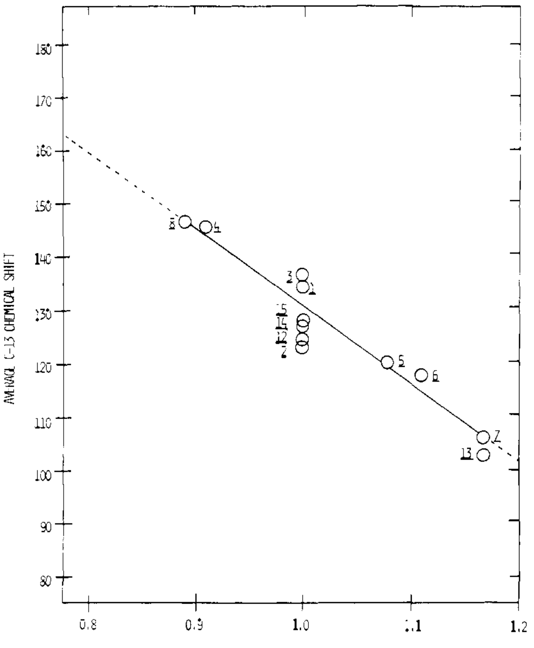


Figure 2. Correlation of the ^{13}C NMR chemical shift average with the π-electron density of methano-bridged systems.

In Table II, we have assembled a series of ^{13}C NMR chemical shift averages of methano-bridged systems along with their corresponding average electron densities. These data are presented in graphic form in Figure 2. As with neutral, polycyclic aromatic compounds,[9] the neutral benzenoid, methano-bridged compounds fall below the line in Figure 2 (that is, their average chemical shift is less than the value predicted on charge density alone) while the chemical shift averages of 1,5-methano[10]annulene (**3**)[2g] and 1,7-methano[12]annulene (**1**)[2c] lie above the line obtained after least-squares analysis.[6a] From the data in Table II we have derived the following equation

$$\delta_{av} = 275.85 - 145.71\rho_{av} \qquad (2)$$

with the correlation coefficient $r = 0.90$ and a slope of 145.71

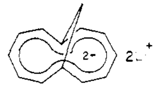
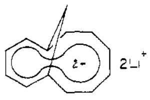
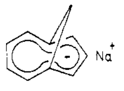
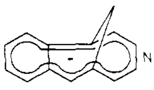
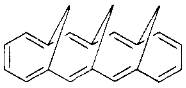
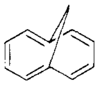
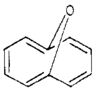
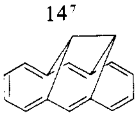
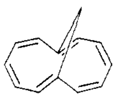
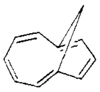
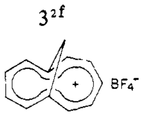
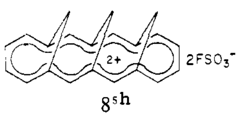
---

[7] (a) Hunadi, R. J., unpublished results. (b) This compound has been included for comparison purposes only and its ^{13}C NMR shift average has not been included in the analysis for the determination of eq 2.

[8] Masamune, S.; Brooks, D. W.; Morio, K.; Sobezak, R. L. *J. Am. Chem. Soc.* **1976**, *98*, 8277.

[9] Stothers, J. B. "Carbon-13 NMR Spectroscopy"; Academic Press: New York, 1972; Chapter 3.

Table II. ^{13}C NMR Chemical Shift Average of Methano-Bridged Systems vs. the Corresponding Average π-Electron Density

compound	δ_{av}	ρ_{av}
 $7^{2e,15}$	106.4	1.167
 $13^{2e,15}$	102.8	1.167
 $6^{2j,k}$	118.3	1.111
 $5^{2l,j}$	120.3	1.077
 12^{5h}	123.8	1.000
 2^{2h}	124.8	1.000
 14^{7}	126.9	1.000
 15^{2a}	127.7	1.000
 1^{2c}	134.5	1.000
 3^{2f}	137.8	1.000
 4^{2g}	145.5	0.909
 8^{5h}	146.4	0.888

ppm/e$^-$. This relationship is not as precise as the relationships uncovered by O'Brien et al.[4a] ($\delta_{av} = 289.5 - 156.3\rho_{av}$, $r = 0.996$) and Olah et al.[4b] ($\delta_{av} = 288.5 - 159.5\rho_{av}$) for nonbridged systems. The scatter in the neutral methano-bridged systems is responsible for a lower correlation coefficient.[4c] Nonetheless, the analysis does show that a linear relationship exists with the uncorrected data and that eq 2 can be used for meaningful analyses without recourse to correction factors for most situations.

^{13}C NMR Chemical-Shift Average vs. Average Electron Density of Homoaromatic Systems. After examination of methano-bridged systems, we felt that a logical extension of these initial studies would be to include the examination of homoaromatic systems. Again, to the best of our knowledge, no one has reported a study on the correlation of ^{13}C NMR chemical shift averages of homoaromatic systems vs. their corresponding average electron density. We will restrict the study to mono- and bishomoaromatic systems that contain no other interruptions in the carbon skeleton except for methylene or methyne groups bridging the perimeter of the molecule. Unfortunately, ^{13}C NMR data for these compounds are scarce for two reasons: first, there are a limited number of truely homoaromatic compounds that have been characterized; second, ^{1}H NMR spectroscopic studies instead of ^{13}C NMR studies were conducted on most of these systems.

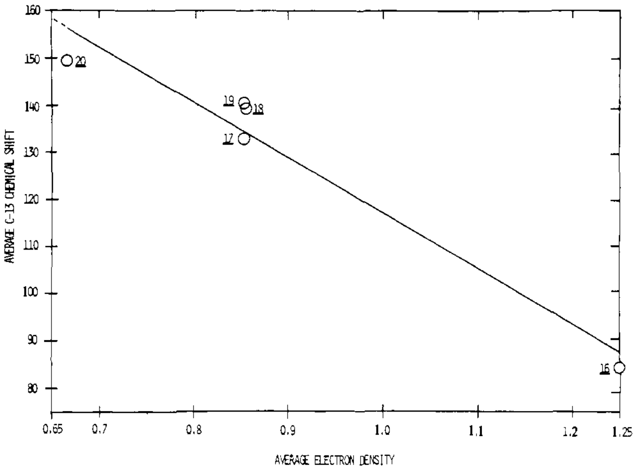


Figure 3. Correlation of the ^{13}C NMR chemical shift average with the π-electron density of homoaromatic systems.

With the limited data available to us, we have constructed a plot of the ^{13}C NMR chemical shift averages vs. average electron density and these data are presented in Figure 3 (listed in Table III). Least-squares analysis of the data[6a] allowed us to derive the following equation

$$\delta_{av} = 234.52 - 117.40\rho_{av} \qquad (3)$$

with the correlation coefficient $r = 0.948$. Here the slope is 117 ppm/e$^-$ as compared to 146 for methano-bridged and 156–161 ppm/e$^-$ for nonbridged systems[4a,d] (see Appendix I for data on fused aromatic systems) which may be an additional piece of data supporting the concept of homoaromatic compounds being less aromatic than unbridged aromatic compounds. Also, this would suggest that methano-bridged aromatic systems are "more aromatic" than homoaromatic systems. Again, as with methano-bridged molecules, eq 3 will receive further verification as additional ^{13}C NMR data on homoaromatic systems become available.

Bridge-Carbon Shift vs. Average Electron Density for Homoaromatic Systems. Since we were able to obtain a good correlation between the bridge carbon of methano-bridged systems and the average electron density, we decided to determine if a similar correlation could be obtained for homoaromatic compounds. We restricted the correlation to systems containing only methylene interruptions in the carbon perimeter. In Table IV we have

---

(10) (a) Barfield, M.; Bates, R. B.; Beavers, W. A.; Blackburg, I. R.; Brenner, S.; Mayall, B. I.; McCullock, C. S. *J. Am. Chem. Soc.* **1975**, *97*, 900. (b) Ley, S. V.; Paquette, L. A. *Ibid.* **1974**, *96*, 6770. (c) Paquette, L. A.; Ley, S. V.; Traynor, S. G.; Martin, J. T.; Geckler, J. M. *Ibid.* **1976**, *98*, 8162.

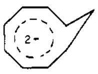
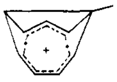
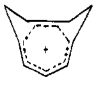
(11) Paquette, L. A.; Broadhurst, M. J. *J. Org. Chem.* **1973**, *38*, 1893.

(12) (a) Paquette, L. A.; Broadhurst, M. J.; Warner, P.; Olah, G. A.; Liang, G. *J. Am. Chem. Soc.* **1973**, *95*, 3386. (b) Warner, P.; Winstein, S. *Ibid.* **1971**, *93*, 1284. (c) Rosenberg, J. L.; Mahler, J. E.; Pettit, R. *Ibid.* **1962**, *84*, 2842. Keller, C. E.; Pettit, R. *Ibid.* **1966**, *88*, 604. Holmes, J. D.; Pettit, R. *Ibid.* **1963**, *85*, 2531. Winstein, S.; Kaesz, H. D.; Kreiter, C. G.; Freidrich, E. C. *Ibid.* **1965**, *87*, 3267. Warner, D. L.; Harris, D. L.; Bradley, C. H.; Winstein, S. *Tetrahedron Lett.* **1970**, 4013.

(13) Olah, G. A.; Staral, J. S.; Liang, G. *J. Am. Chem. Soc.* **1974**, *96*, 6233. Olah, G. A.; Staral, J. S.; Spear, R. J.; Liang, G. *Ibid.* **1975**, *97*, 5489.

(14) (a) Olah, G. A.; Prakash, G. K. S.; Rawdah, T. N.; Whittaker, D.; Rees, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 3935. (b) Müllen, K.; Oth, J. F. M.; Engels, H.-W.; Vogel, E. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 229.

Table III. ^{13}C NMR Chemical Shift Average of Homoaromatic Systems vs. the Corresponding Average π-Electron Density

compound	δ_{av}	ρ_{av}
 16^{10}	84.3	1.250
 17^{11}	132.5	0.857
 $18^{12a,b}$	139.4	0.857
 $19^{12a,c}$	140.4	0.857
 20^{13}	149.2	0.666

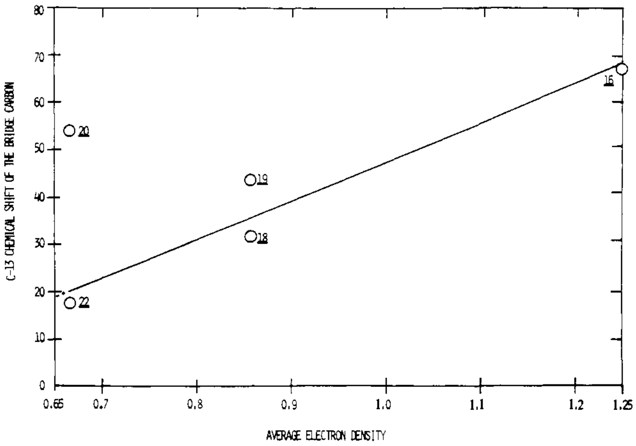
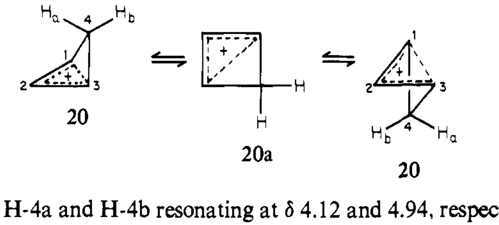


Figure 4. Correlation of the bridge carbon shift with the π-electron density of homoaromatic systems.

assembled the ^{13}C NMR bridge shifts vs. average π-electron density and these data are presented graphically in Figure 4.

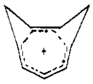
If we include the homocyclopropenyl cation (**20**)[13] in our correlation, we do not obtain a good fit (r = 0.294 after least-squares analysis). The shift of the sp^2 carbon of **20** is 54.0 ppm, and the reason for such high deshielding may be due to steric strain and the geometry of this system since bending of the methylene carbon is required to achieve overlap at C-1 and C-3. Since the homocyclopropenyl cation (**20**) is such a small, strained system, the methylene carbon shift may not be representative of a homoaromatic 2π system.

Justification for the geometrical effects in the homocyclopropenyl cation (**20**) comes from Olah's analysis of the proton NMR data for this ion.[13] At −115 °C, the ring flipping was frozen out with H-4a and H-4b resonating at δ 4.12 and 4.94, respectively. The corresponding shifts for the homotropylium cation (**19**) are δ -0.67 and 5.10, respectively. In the case of the homocyclopropenium ion (**20**), the shielding encountered by the endo proton is substantially less than encountered in **19**. They reasoned that C-8 in the homotropylium ion (**19**) is bent further out of the C$_1$–C$_7$ plane than is C-4 from the C$_1$–C$_3$ plane of **20** and consequently H-8$_{endo}$ is further over the shielding region of the aromatic ring. This indicates that the ring strain present in **20**, due to the small ring size (it cannot distort to achieve the degree of homoaromaticity present in **19**), would exert a dramatic influence on the shift of C-4 making this shift nonrepresentative of an unstrained homoaromatic 2π system.



20 20a 20

Table IV. ^{13}C NMR Shift of the Bridge Carbon of Homoaromatic Systems vs. the Corresponding Average π-Electron Density

compound	δ_{bridge}	ρ_{av}
 16^{10}	66.6	1.250
 $18^{12a,b}$	43.7	0.857
 $19^{12a,c}$	31.5	0.857
 20^{13}	54.0	0.666
 22^{14a}	17.6	0.666

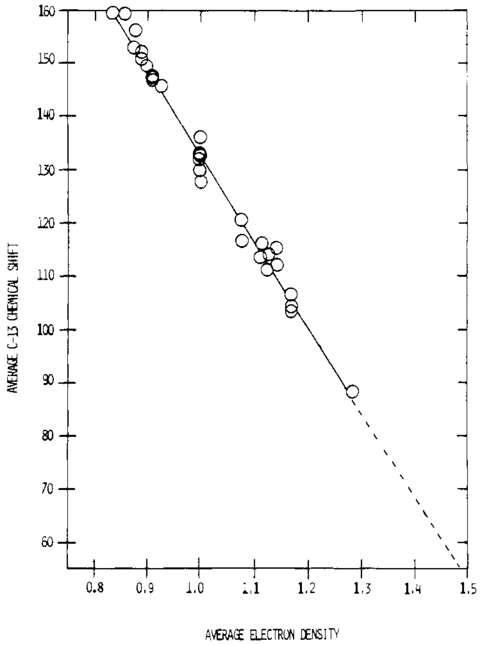
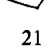
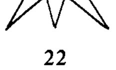


Figure 5. Correlation of the ^{13}C NMR chemical shift average with the π-electron density of [0]bridged systems.

A similar system where some of the strain might be relieved (and more flexibility would be present) would be the bishomocyclopropenyl cation (**21**), but unfortunately this cation had eluded isolation and characterization. The trishomocyclopropenyl cation (**22**) may be a suitable system for comparison, and since the ^{13}C NMR shifts have been reported, we will use **22** instead of the homocyclopropenyl cation (**20**) in our study. If we compare the ^{13}C NMR shift of **22** with the rest of the data presented in Table



21



22

Table V. ^{13}C NMR Chemical Shift Average of [0]Bridged Systems vs. the Corresponding Average π-Electron Density

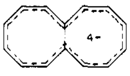
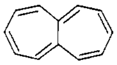
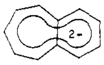
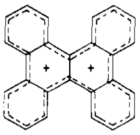
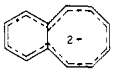
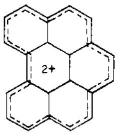
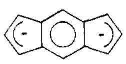
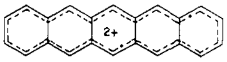
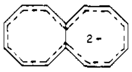
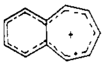
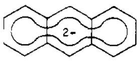
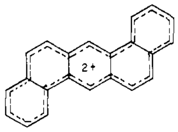
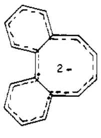
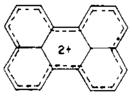
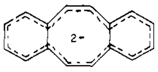
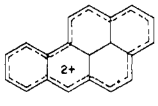
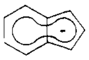
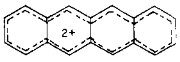
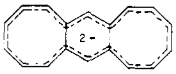
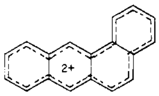
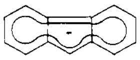
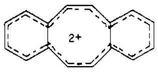
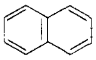
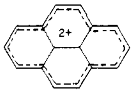
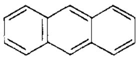
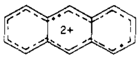
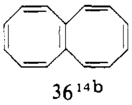
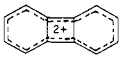
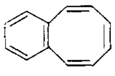
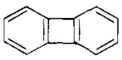
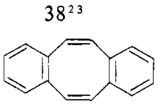
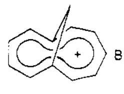
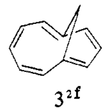
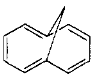
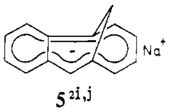
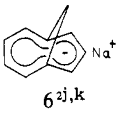
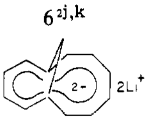
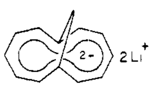
compound	δ_{av}	ρ_{av}	compound		ρ_{av}
 23[14b]	88.0	1.286	 40[15]	136.1	1.000
 24[15]	103.7	1.167	 41[24]	145.6	0.923
 25[16]	104.4	1.167	 42[24]	146.7	0.909
 26[17]	107.4	1.167	 43[24]	147.4	0.909
 27[14b]	111.9	1.143	 44[25]	146.9	0.909
 28[18]	115.1	1.143	 45[24]	147.5	0.909
 29[18]	111.4	1.125	 46[24]	144.8	0.900
 30[19a]	112.2	1.125	 47[24]	149.2	0.900
 31[20]	113.5	1.111	 48[24]	150.6	0.888
 32[16]	116.0	1.111	 49[24]	152.2	0.888
 33[2j,21]	116.7	1.077	 50[19b]	151.3	0.875
 34[22]	128.5	1.000	 51[24]	156.0	0.875
 35[9]	129.9	1.000	 52[24]	159.1	0.857
 36[14b]	132.6	1.000	 53[23]	160.9	0.833
 37[16]	131.8	1.000			
 38[23]	132.5	1.000			
 39[19b]	132.8	1.000			

Table VI. ^{1}H NMR Shifts of the Bridge Protons of Methano-Bridged Systems vs. the Corresponding Average π-Electron Density[a]

compound	δ_{bridge}	ρ_{av}
 4[2g]	−1.8; −0.3	0.909
 3[2f]	−0.95; −0.50	1.000
 2[2h]	−0.5; −0.5	1.000
 5[2i,j]	−0.84; −0.29	1.077
 6[2j,k]	−0.95; −0.45	1.111
 13[2e,15]	−6.08; −5.52	1.167
 7[2e]	−6.44; −6.44	1.167

[a] In ppm δ.

IV (excluding the data for **20**), we obtain a much better fit (after least-squares analysis) with $r = 0.931$ and the following equation

$$\delta_{\text{bridge}} = 81.68\rho_{\text{av}} - 34.68 \qquad (4)$$

defining the relationship between the bridge-carbon shift and the electron density.

The slope is steeper than that obtained with the methano-bridged systems, indicating that the sp^2 carbon of homoaromatic systems is more sensitive to changes in electron density. It may be difficult to justify the exclusion of the homocyclopropenyl cation (**20**) from our study solely on the basis of geometry and strain arguments, but it can be seen that a much better fit ($r = 0.931$) is obtained when it is excluded from the analysis ($r = 0.294$ when the homocyclopropenyl cation (**20**) is included in the analysis).

Conclusion

After careful analysis of the available ^{13}C NMR data for methano-bridged compounds, we have arrived at equations relating the electron density of the system to both the bridge carbon shift and the ^{13}C NMR chemical shift average (excluding the bridge carbon). We have obtained good correlation factors ($r = 0.942$ and 0.90, respectively) for these relationships without the introduction of correction factors or alteration of the original data. Similarly, we have derived equations for homoaromatic systems and again the correlation coefficients ($r = 0.931$ and 0.948, respectively) have indicated a good fit of the data although less ^{13}C NMR information was available for these systems. These equations, nonetheless, will be further refined when additional ^{13}C NMR data on homoaromatic systems become available.

Acknowledgment. I am grateful to Dr. G. K. Surya Prakash for his helpful comments on the manuscript and to Profs. G. Helmkamp and G. Olah for invaluable help before this manuscript was conceived.

Appendix I. ^{13}C NMR Chemical Shift Average vs. Average Electron Density of [0]Bridged Systems

In Table V we have assembled the ^{13}C NMR chemical shift averages and electron densities of a series of fused ring systems containing [0]bridges in order to perform a least-squares analysis and obtain an equation defining fused systems. The Spiesecke–Schneider[3] relationship has been extended to various systems, but we wanted a correlation for strictly fused systems which contained quaternary carbons. This would give us a slope which we could directly compare to methano-bridged and homoaromatic systems. A least-squares analysis[6a] of the data presented Table V (these data are plotted in Figure 5) gave the following equation

$$\delta_{\text{av}} = 293.67 - 160.94\rho_{\text{av}} \qquad (5)$$

with $r = 0.99$ and a slope of −160.94 ppm/e$^-$.

Appendix II. ^{1}H NMR Shift of the Bridge Protons of Methano-Bridged Systems vs. the Corresponding Average Electron Density

For comparison, in Table VI we have listed the ^{1}H NMR shifts of the bridge protons of methano-bridged compounds along with their corresponding average electron density. We have compiled these data in order to show that a *linear relationship* does not exist between the ^{1}H NMR shifts, the average of the shifts, or the combination of the shifts of the two bridge protons and the average electron density of the systems.

---

(15) Oth, J. F. M; Müllen, K.; Konigshofen, H.; Wassen, J.; Vogel, E. *Helv. Chim. Acta* **1974**, *57*, 2387.

(16) Paquette, L. A.; Ewing, G. D.; Traynor, S.; Gardlick, J. M. *J. Am. Chem. Soc.* **1977**, *99*, 6115.

(17) Edlung, U., disclosed in a letter to Prof. B. L. Shapiro, Sept. 27, 1979.

(18) Müllen, K. *Helv. Chim. Acta* **1978**, *61*, 1296.

(19) (a) Katz, T. J.; Yoshida, M.; Siew, L. C. *J. Am. Chem. Soc.* **1965**, *87*, 4516. (b) Olah, G. A.; Staral, J. S.; Liang, G.; Paquette, L. A.; Melega, W. P.; Carmondy, M. J. *J. Am. Chem. Soc.* **1977**, *99*, 3349.

(20) Stothers, J. B. "Carbon-13 NMR Spectroscopy"; Academic Press: New York, 1972; p 269.

(21) (a) Hunadi, R. J. Ph.D. Dissertation, University of California, Riverside, CA, 1977. (b) O'Brien, D. H.; Russel, C. R.; Hart, A. J. *J. Am. Chem. Soc.* **1979**, *101*, 633. (c) Edlung, U. *Org. Magn. Reson.* **1979**, *12*, 661.

(22) Alger, T. D.; Grant, D. M.; Paul, E. G. *J. Am. Chem. Soc.* **1966**, *88*, 5397.

(23) Olah, G. A.; Liang, G. *J. Am. Chem. Soc.* **1977**, *99*, 6045.

(24) Forsyth, D. A.; Olah, G. A. *J. Am. Chem. Soc.* **1976**, *98*, 4086.

(25) Bertelli, D. J.; Gerig, J. T.; Herbelia, J. M. *J. Am. Chem. Soc.* **1968**, *90*, 107.