structure towards complete stereospecificity.

Further studies on these lines are under active investigation.[12]

References and Notes

(1) U. Eder, G. Sauer, and R. Wiechert, *Angew. Chem., Int. Ed. Engl.*, **10**, 496 (1971).
(2) Z. G. Hajos and D. R. Parrish, *J. Org. Chem.*, **39**, 1615 (1974).
(3) (a) W. S. Knowles and M. J. Sabacky, *Chem. Commun.*, 1445 (1968); (b) W. S. Knowles, M. J. Sabacky, and B. D. Vineyard, *J. Chem. Soc., Chem. Commun.*, 10 (1972); (c) W. S. Knowles, M. J. Sabacky, B. D. Vineyard, and D. J. Weinkauff, *J. Am. Chem. Soc.*, **97**, 2567 (1975).
(4) (a) T.-P. Dang and H. B. Kagan, *Chem. Commun.*, 481 (1971); *J. Am. Chem. Soc.*, **94**, 6429 (1972); (b) J. C. Poulin and H. B. Kagan, *J. Organomet. Chem.*, **91**, 105 (1975); (c) G. Gelbard, H. B. Kagan, and R. Sern, *Tetrahedron*, **32**, 233 (1976).
(5) T. Hayashi, T. Mise, S. Mitachi, K. Yamamoto, and M. Kumada, *Tetrahedron Lett.*, 1133 (1976).
(6) (a) J. D. Morrison and H. S. Mosher, "Asymmetric Organic Reactions", Prentice-Hall, Englewood Cliffs, N.J., 1971; (b) J. W. Scott and D. Valentine, Jr., *Science*, **184**, 943 (1974); (c) L. Marko and B. Heil, *Catal. Rev.*, **8**, 269 (1973); (d) R. E. Harmon, S. K. Gupta, and D. J. Brown, *Chem. Rev.*, **73**, 21 (1973).
(7) Satisfactory (a) spectral and (b) analytical data were obtained for this substance.
(8) The effect of triethylamine on the optical yield for substrate **8b**, an ester, is not understood at this time.
(9) W. S. Knowles, M. J. Sabacky, and B. D. Vineyard, *Ann. N. Y. Acad. Sci.*, **172**, 232 (1970).
(10) Asymmetric hydrogenation of (*Z*)-α-methylcinnamic acid under the same conditions gave (*S*)-α-methyl-β-phenylpropionic acid in a 15% optical yield.
(11) J. P. Greenstein and M. Winitz, "Chemistry of the Amino Acids", Wiley, New York, N.Y., 1961, p 2037.
(12) The author thanks emeritus professor S. Yamada, University of Tokyo, for his encouragement.

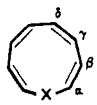
Kazuo Achiwa
Faculty of Pharmaceutical Sciences, University of Tokyo
Bunkyo-ku, Tokyo 113, Japan

Received June 24, 1976

An Examination of the Heteronins by ^{13}C Nuclear Magnetic Resonance

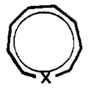
Sir:

Careful analysis of a wide variety of physicochemical data recently secured in these laboratories has led to the classification of certain hetero[9]annulenes (heteronins)[1] as polyenic (**1**) and others as "aromatic" (**2**), while a third subgroup, namely the *N*-alkylheteronins, e.g., **3**, emerged as nondescript under the same criteria. In an attempt to more accurately probe the stereoelectronic changes attending the development of "aromaticity" in this family of π-excessive heterocycles, we have examined certain representative members by ^{13}C NMR and are now in position to offer description and interpretation of this information.



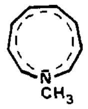
1

a; X = CH$_2$
b; X = O
c; X = NCOOEt



2

a; X = NH
b; X = N$^-$K$^+$



3

4

Table I.[a] ^{13}C NMR Constants of the Olefinic Centers of Select Heteronins and *cis*^{4}-Cyclononatetraene

Compound	Temp[b] (°C)	Solvent	Chemical shift[c] (ppm)	Coupling constant[d] (Hz)	Assignment
1a	−37.0	Acetone-d_6	131.04	158	α
			128.70	~157	—
			128.56	~157	—
			128.36	~157	—
1b	−34.0	Acetone-d_6	141.33	193	α
			129.78	156	γ or δ
			124.26	159	γ or δ
			110.93	156	β
1c	−34.5	Acetone-d_6	130.13[e] }	157	γ or δ
			127.92 }	157	
			125.87		—
			125.68		—
			125.28		—
			122.54[e] }	156	β
			110.39 }	154	
2a	−34.5	Acetone-d_6	119.46	172	α
			117.76	152	γ or δ
			117.47	153	γ or δ
			100.48	155	β
	+30	Me$_2$SO-d_6	118.06	172	α
			116.86	152	γ or δ
			116.54	~152	γ or δ
			99.56	155	β
2b	+30	Me$_2$SO-d_6	124.09	154	α
			114.88	138	γ or δ
			112.68	142	γ or δ
			112.33	143	β
3	−34.5	Acetone-d_6	129.68	172	α
			122.31	153	γ or δ
			121.18	153	γ or δ
			101.22	156	β

[a] Spectra were uniformly recorded at 20 MHz on a Varian CFT-20 spectrometer equipped with a 5-mm probe. All determinations were made in vacuum-sealed NMR tubes; tetramethylsilane was employed as internal standard throughout. [b] Measured by thermocouple. [c] The term here denotes downfield shift from Me$_4$Si. [d] The values given refer to one-bond ^{13}C–H coupling. [e] The observed splitting is due to substituent-induced molecular asymmetry.

The ^{13}C NMR data (collected in Table I) were utilized to compare the various chosen members in terms of (i) chemical shift (a reliable measure of electron density) and (ii) ^{13}C–H coupling constant (a well-documented probe of hybridization). For obvious reasons, attention along these lines of comparison was focused primarily on the γ and δ carbons of each molecule, i.e., the two centers least likely to be influenced by direct interaction with the heteroatomic unit. The choice of models among available nine-membered rings proved to be straightforward with the heavily localized 1,3,5,7-cyclononatetraene (**1a**) elected as the "polyenic" reference and its well-delocalized anion **4**[2] chosen as the "aromatic" counterpart.

Since ^{13}C NMR chemical shift is primarily a function of electron density one may, in a molecule such as **1** (**2**,**3**), directly correlate properly chosen chemical shift differences with lone pair delocalization and hence the ability of a given member to realize its aromatic potential. In fact, bearing in mind that model **1a** ($\delta^3(\gamma,\delta)$ 128.54 ppm) has no available lone pair, while **4** (δ 109.5 ppm)[2] has a fully delocalized one[4] and assuming the relationship between ^{13}C chemical shift and electron density at carbon to be roughly linear, one may, for comparison purposes, readily translate chemical shift differences, $\Delta\delta(\gamma,\delta)$, between a given member of the family and **1a** or **4** into percent lone pair delocalization. Direct use of the chemical shift data collected in Table I thus yields $\Delta\delta(\gamma,\delta)$ terms which readily translate to ~8% lone pair delocalization in **1b** and **1c**, ~35% in **3**, ~58% in **2a**, and ~77% in **2b**.[4] Significantly, the observed increase of lone pair participation into the π system, on passing from **1b** or **1c** to **3** to **2a** and finally to **2b**, closely parallels the development of diatropic character previously deduced from ^{1}H NMR data.[1] In other words, when taken in conjunction with earlier ^{1}H NMR data the present ^{13}C NMR information offers previously unavailable *explicit* demonstration that the development of diatropism, and hence aromaticity, in the heteronins bears direct relation to lone pair delocalization.

Variations in ^{13}C–H coupling constants are chiefly reflective of hybridization differences at the carbon end of the bond which are themselves indicative of changes in bond angle and thus molecular shape. In the present instance, one finds the models to possess significantly different ^{13}C–H coupling constants, a drop of ca. 20 Hz being observed on passing from puckered-localized **1a** (J = 157 Hz) to planar-delocalized **4** (J = 137 Hz).[2] This rather dramatic reduction in the magnitude of J is best and perhaps uniquely reasoned in terms of the enhancement in the "p" character of the C–H carbon hybrid which the nine-membered frame must experience to accommodate the widening of the C–C–C angle (120° → 140°) attending the change from heavily buckled (**1a**) to D_{9h}-flat (**4**).[5] Upon applying this line of reasoning to the heteronins one is gratified to witness a similar downward trend of $J_{\gamma,\delta}(^{13}C–H)$[6] on going from the "polyenic" to the "aromatic" members of the family. Specifically, one finds this constant to change from 157.5 Hz in **1b** to 157 Hz[7] in **1c** to 153 Hz in **3** to 152.5 Hz in **4a** to 140 Hz in **2b**, the first and last of these values being so significantly similar to those of **1a** and **4**, respectively, as to unequivocally point to a heavily puckered oxonin and a virtually flat azoninyl anion.

Briefly summarizing the most significant aspects of the findings described in this report, we stress that what has been *explicitly* established with the use of ^{13}C NMR is that lone pair participation exerts controlling influence on the molecular shape of a heteronin, an increase in overall π density sharply enhancing the molecule's ability to flatten and thus benefit from "aromatic" delocalization.

Acknowledgment. We are grateful to the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work. The NMR spectrometer employed in this study was purchased under NSF instrument Grant MPS75-06106.

References and Notes

(1) For reviews on the subject see (a) A. G. Anastassiou, *Acc. Chem. Res.*, **5**, 281 (1972); (b) *Pure Appl. Chem.*, **44**, 691 (1975).

(2) The ^{13}C NMR spectrum of this substance was described by E. A. LaLancette and R. E. Benson, *J. Amer. Chem. Soc.*, **87**, 1941 (1965).

(3) The term here refers to the algebraic average of $\delta(C_\gamma)$ and $\delta(C_\delta)$.

(4) It was pointed out by one reviewer that judging from the obvious hybridization changes which the heteronin frame is subject to on passing from **1b** to **1c** to **2a** to **2b** the use of chemical shift to calculate lone pair delocalization constitutes a rather serious oversimplification. This is certainly a valid point which necessitates that we warn the reader against overinterpreting the given percentages; they are offered merely as qualitative indicators of an increasingly delocalized π frame on going from **1b** to **1c** to **2a** and, finally, to **2b**.

(5) H. E. Simmons, D. B. Chestnut, and E. A. LaLancette, *J. Am. Chem. Soc.*, **87**, 982 (1965).

(6) The term here refers to the average: $J^{13}C_\gamma$–H + $J^{13}C_\delta$–H/2

(7) Because of serious complication introduced by overlapping peaks, $J^{13}C_\delta$–H could not be determined for this compound. The value given is simply $J^{13}C_\gamma$–H.

A. G. Anastassiou,* E. Reichmanis

Department of Chemistry, Syracuse University
Syracuse, New York 13210

Received July 6, 1976

An Examination of the 9-Heterobicyclo[4.2.1]nona-2,4,7-trienes by ^{13}C Nuclear Magnetic Resonance

Sir:

The pronounced skeletal rigidity of the title frame (**1**), coupled with the presence of a heteroatomic bridge in tandem with two formally isolated π ribbons, clearly renders this system suitable as a model for the study of the possible influence that a π excessive heteroatomic unit might have on the development of nonbonded interaction. We have recently addressed ourselves to this question with the aid of photoelectron spectroscopy (PES)[1,2,3] and are now offering further insight into the matter with a description and analysis of pertinent ^{13}C NMR data.

Table I.[a] ^{13}C NMR Constants of the "Olefinic" and "Bridgehead" Centers of Select 9-Heterobicyclo[4.2.1]nona-2,4,7-trienes

Compound	Chemical shift (ppm)[b]	Coupling constant (Hz)[c]	Assignment
1a	141.10	156	Butadiene
	124.01	155	Butadiene
	119.28	169	Ethylene
	61.42	149	C(1)
1b	138.59	158	Butadiene
	125.13	156	Butadiene
	120.59	168	Ethylene
	49.79	146	C(1)
1c	134.17	~171	Butadiene
	125.92	163	Butadiene
	117.86	175	Ethylene
	64.59	151	C(1)
1d	137.09	157	Butadiene
	125.03	158	Butadiene
	119.06	172	Ethylene
	80.97	153	C(1)
2a	142.91	155	Butadiene
	123.62	156	Butadiene
	57.75	141	C(1)
2b	139.64	157	Butadiene
	124.41	155	Butadiene
	48.38	142	C(1)
2c	135.73	159	Butadiene
	125.34	158	Butadiene
	62.01	148	C(1)
2d	139.10	155	Butadiene
	124.60	156	Butadiene
	78.07	148	C(1)
3a	134.17	164	Ethylene
	62.98	140	C(1)
3b	134.46	164	Ethylene
	51.31	143	(C(1)
3c	130.27	170	Ethylene
	67.11	149	C(1)
3d	131.14	167	Ethylene
	83.05	152	C(1)
4a	57.56	138	C(1)
4b	48.53	~140	C(1)
4c	60.74	145	C(1)
4d	77.52	~148	C(1)

[a] Spectra were uniformly recorded at 20 MHz on a Varian CFT-20 spectrometer equipped with a 5-mm probe. All determinations were made in deaerated (N_2) benzene-d_6 at ca. 30°, employing Me_4Si as internal standard throughout. [b] The term here denotes downfield shift from Me_4Si. [c] The values given refer to one-bond ^{13}C–H coupling.

Examination of the ^{13}C NMR information collected in Table I reveals a number of interesting features. One notes, for example, that of the various carbon centers it is those associated with the molecule's ethylene function which experience the most pronounced chemical shift differential on passing from model **3** to the triene counterpart **1**. Specifically, this structural change is seen to generate upfield shifts of 12.08 ppm for X = O, 12.41 ppm for X = NCN, 13.87 ppm for X = S, and 14.89 ppm for X = NH. Direct comparison with hydrocarbon models, **5** (δ (ethylene) ~123.6 ppm)[4] and **6** (δ (ethylene) = 133.8 ppm)[4] in terms of this ^{13}C NMR differential allows one to estimate residual upfield shifts ($\Delta\Delta\delta$) of 4.7 ppm