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 $J_{\gamma,\delta}(^{13}C\text{–}H)$[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: $J^{13}C_\gamma\text{–}H + J^{13}C_\delta\text{–}H/2$

(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

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

Sir:

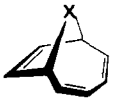
The pronounced skeletal rigidity of the title frame (**1**), coupled with the presence of a heteroatomic bridge in tandem with two formally isolated π ribbons, clearly renders this system suitable as a model for the study of the possible influence that a π excessive heteroatomic unit might have on the 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

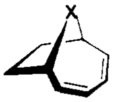
Compound	Chemical shift (ppm)[b]	Coupling constant (Hz)[c]	Assignment
1a	141.10	156	Butadiene
	124.01	155	Butadiene
	119.28	169	Ethylene
	61.42	149	C(1)
1b	138.59	158	Butadiene
	125.13	156	Butadiene
	120.59	168	Ethylene
	49.79	146	C(1)
1c	134.17	~171	Butadiene
	125.92	163	Butadiene
	117.86	175	Ethylene
	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.

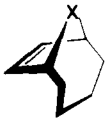
Examination of the ^{13}C NMR information collected in Table I reveals a number of interesting features. One notes, for example, that of the various carbon centers it is those associated with the molecule's ethylene function which experience the most pronounced chemical shift differential on passing 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



1



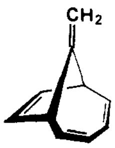
2



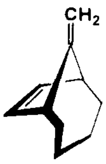
3

4

a; X = NH
b; X = S
c; X = NCN
d; X = O



5



6

for **1a**, 3.7 ppm for **1b**, 2.2 ppm for **1c**, and 1.9 ppm for **1d**. Now, since hydrocarbon **5** and heterobicycle **1** share a common basic skeleton, we may safely attribute these residual differences chiefly, if not exclusively, to lone pair-induced enhancement of the ethylene group's π electron density.[5] We conclude, therefore, that the lone pair in **1** does partake in nonbonded interaction and, judging from the relative magnitude of the above-noted $\Delta\Delta\delta$ terms, that the extent of such interaction increases in the order $O \sim NCN < S < NH$.

Continuing our analysis of the data we now make note of the fact that the chief influence that nonbonded lone pair transfer is expected to exert on the heteroatomic bridge of a molecule such as **1** is to enhance its effective electronegativity. Translated into ^{13}C NMR observables, this anticipated increase in heteroatom electronegativity should manifest itself primarily as an increase in the magnitude of the ^{13}C–H coupling constant of the "bridgehead" position, C(1), i.e., the carbon center directly linked to the bridge.[6] In fact, by following the change of this ^{13}C NMR constant during the structural transition of the 9-heterononabicyclo[4.2.1] frame from saturated **4** to partially unsaturated **2, 3** and, finally to fully unsaturated **1**, it becomes possible to gain knowledge about the mechanism of nonbonded interaction and draw inference about its dependence on the nature of the bridging unit. To begin with, one notes that the fully saturated **4** does manifest the expected dependence of J C(1)–H on heteroatom electronegativity, the recorded ΔJ (**4**) differential between the two extreme cases, i.e., for X = NH and X = O, rising to an impressive 11 Hz. Similar trends are also observed with the partially saturated models **2** and **3**, the corresponding differential between extreme cases (a and d) being here 7 and 12 Hz, respectively. Turning now to the key trienic frame **1** we discover that azabicycle **1a** fails to properly correlate with the other three members of the series due to a sharp increase in the magnitude of J C(1)–H over and above that expected on the basis of values obtained from model transformations. Specifically, one finds the increase in this constant to be significantly greater (100%+) in the transformation **4a** to **1a** (11 Hz) than the *combined* differential (5 Hz) associated with model changes $\mathbf{4a} \rightarrow \mathbf{2a}$ (3 Hz) and $\mathbf{4a} \rightarrow \mathbf{3a}$ (2 Hz)! In distinct contrast to this discrepancy in ΔJ between *model* and *actual* transformation when X = NH, one finds the other members of the series, i.e., those with X = S, NCN, and O, to be associated with virtually identical (within 1 Hz) *actual* ($\mathbf{4} \rightarrow \mathbf{1}$) and *model* ($\mathbf{4} \rightarrow \mathbf{2} + \mathbf{4} \rightarrow \mathbf{3}$) ΔJ differentials. Recalling now that heteroatom electronegativity in **1** must have decisive influence on the magnitude of J C(1)–H (vide supra) we interpret the discrepancy in $\Delta\Delta J$ observed between **1a** and **1(b,c,d)** to mean that when exposed to the π environment of **1**, the molecule's heteroatomic bridge experiences a decisive surge in electronegativity for X = NH but not for X = S, NCN, or O. Translating this information to nonbonded interaction, one is drawn to the inevitable conclusion that: *among the four heterotrienes examined here, only azabicycle* **1a** *is endowed with what might safely be termed a bicycloconjugated frame.*[8] The lone pair participation deduced for **1b, 1c,** and **1d** on the basis of the "chemical shift" differential (vide supra) must thus be attributed chiefly to homoconjugative interaction[9] between lone pair and, judging from the direction of electron transfer, ethylene appendage.

Gratifyingly, the conclusions arrived at in the present study closely parallel those derived earlier from PES information.[1-3] We conclude by pointing to a striking parallel between bicycloconjugation in the 9-heterobicyclo[4.2.1]nona2,4,7-trienes and conventional conjugation in the heteronins.[10] In both cases heteroatomic participation is activated by the loosely held lone pair of nitrogen and inhibited by the more tightly bound counterpart of oxygen.

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(1) H. Schmidt, A. Schweig, A. G. Anastassiou, and H. Yamamoto, *J. Chem. Soc., Chem. Commun.*, 218 (1974).
(2) C. Muller, A. Schweig, A. G. Anastassiou, and J. C. Wetzel, *Tetrahedron*, **30**, 4089 (1974).
(3) H. Schmidt, A. Schweig, A. G. Anastassiou and J. C. Wetzel, *Tetrahedron*, **32**, 2239 (1976).
(4) R. W. Hoffmann, H. Kurz, M. T. Reetz, and R. Schuttler, *Chem. Ber.*, **108**, 109 (1975).
(5) These values ($\Delta\Delta\delta$) must be regarded as strictly minimal indicators of lone pair transfer into the ethylene, inasmuch as the upfield ^{13}C NMR shift of this appendage observed on passing from **6** to **5** (10.2 ppm) ought to be due in large measure to the transfer of electron density from the molecule's exomethylene unit; note that the ^{13}C NMR assigned to C(9) experiences a downfield shift of 8.7 ppm on going from **6** to **5**. For an analysis of ^{13}C NMR information relating to this system see R. W. Hoffmann and H. Kurz, *Chem. Ber.*, **108**, 119 (1975).
(6) For a general description of the relation between ^{13}C–H coupling constant and neighboring group electronegativity, see J. B. Stothers, "Carbon-13 NMR Spectroscopy", Academic Press, New York, N.Y., 1972, pp 332–348.
(7) As judged by the close similarity of the J C(1)–H term, the electronegativity of the NH unit in **1** is seen to be nearly as pronounced as that of its normally far more demanding counterparts NCN and O!
(8) The term bicycloconjugation is employed here to denote simultaneous interaction of the lone pair with the two formally isolated π appendages.
(9) The term homoconjugation is utilized here to describe the interaction of the lone pair with only one of the two formally isolated π segments, irrespective of whether the process operates through bonds or through space.
(10) For a review on the subject see A. G. Anastassiou, *Acc. Chem. Res.*, **5**, 281 (1972). See also A. G. Anastassiou and E. Reichmanis, *J. Am. Chem. Soc.*, preceding paper in this issue.

A. G. Anastassiou,* E. Reichmanis
Department of Chemistry, Syracuse University
Syracuse, New York 13210

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A Novel Base-Catalyzed Rearrangement. Formation of Dibenzo[*cd,gh*]pentalenide Dianion

Sir:

Molecular rearrangements are of great significance both as synthetic tools and in mechanistic studies. Most rearrangements, especially in the aromatic series, are acid-catalyzed and only a few are base-catalyzed.[1] A well-known base-catalyzed rearrangement in the aromatic series is the Smiles rearrangement[2] in which a carbanion in a system including a heteroatom is rearranged. For example, a system