Table I. ^{1}H NMR Parameters[a]

compd	C9-H[b]	Ar-CH$_3$	*C*-alkyl	Ar-H
8	4.65, 3.97	2.35, 2.52	3.62	6.8-7.6
9		2.37, 2.55	1.20,[c] 4.08[d]	6.9-7.8
10	3.91, 4.31		3.60	7.2-7.8
11			0.93,[c] 4.02[d]	7.2-7.9

[a] Deuteriochloroform solvent; 36 °C. Chemical shifts in parts per million downfield from internal Me$_4$Si.
[b] Chemical shifts for H$_A$ and H$_B$ of a pair of AB doublets calculated by using $|\nu_A - \nu_B| = (|\nu_1 - \nu_4| \times |\nu_2 - \nu_3|)^{1/2}$; $J = 18$ Hz. The broader resonance (Ha′) is given first.
[c] CH$_2$CH$_3$; $J = 7$ Hz. [d] CH$_2$CH$_3$; $J = 7$ Hz.

group (and the sulfinyl group bonded to halogens) is greater than that of the dialkylmalonyl residues under dicussion.

Experimental Section[9]

9,9-Dideuterio-1,4-dimethylthioxanthene (7). 1,4-Dimethylthioxanthene (1.5 g, 6.6 mmol) was added to 20 mL of CH$_3$OD which had been reacted with a pea-sized piece of sodium; the reaction mixture was refluxed for 48 h. The solvent was then removed and the residue washed with deuterium oxide and dried to afford 1.5 g (6.6 mmol, 100%) of the desired product, mp 78–80 °C. The ^{1}H NMR exhibited only those peaks due to aryl H and aryl CH$_3$.

Diethyl Diazomalonate. This compound was prepared according to literature methods[10] in 69% yield.

Dimethyl Diazomalonate. This compound was prepared similarly to diethyl diazomalonate and was obtained in 77% yield.[10,11]

9,9-Dideuteriothioxanthenium Bis(carbethoxy)methylide (11).[12] A mixture of 9,9-dideuteriothioxanthene[13] (2.0 g, 10.2 mmol), diethyl diazomalonate (1.7 g, 9.3 mmol), and anhydrous copper(II) sulfate was heated for 4 h at 90–95 °C. After the solution was cooled, chloroform was added and the insoluble residue removed by filtration. The solvent was then removed (nitrogen stream) and the residue recrystallized from benzene/ethyl acetate (2:1) to afford 1.5 g (4.2 mmol, 45%) of colorless crystals, mp 191–192 °C.[14]

9,9-Dideuterio-1,4-dimethylthioxanthenium Bis(carbethoxy)methylide (9).[12] A mixture of 9,9-dideuterio-1,4-dimethylthioxanthene (1.1 g, 5.0 mmol), diethyl diazomalonate (1.8 g, 9.9 mmol), toluene (1 mL), and anhydrous copper sulfate (200 mg) was heated for 4 h at 100 °C under a nitrogen atmosphere. After the mixture was cooled, the product was suspended in chloroform and filtered. The filtrate was concentrated to a brown oil and then triturated with hexane (15 × 2 mL) and methanol (2 × 1 mL) to afford 230 mg (12%) of **9**, mp 160–162 °C.

Thioxanthenium Bis(carbomethoxy)methylide (10).[12] A mixture of thioxanthene (2.0 g, 10 mmol), dimethyl diazomalonate (3.5 g, 22 mmol), and anhydrous copper(II) sulfate (0.060 g, 0.38 mmol) was heated at 90–95 °C for 3 h. After the solution was cooled, the reaction mixture was triturated with chloroform and the insoluble residue removed by filtration. Removal of the solvent (nitrogen stream) followed by recrystallization of the residue (2:1 benzene/ethyl acetate) afforded 0.64 g (2.0 mmol, 20%) of **10**, as colorless crystals, mp 203–204 °C.

1,4-Dimethylthioxanthenium Bis(carbomethoxy)methylide (8).[12] A mixture of 1,4-dimethylthioxanthene (3.0 g, 13 mmol), dimethyl diazomalonate (4.0 g, 25 mmol), naphthalene (2.0 g), and anhydrous copper sulfate (100 mg) was heated for 4 h at 100 °C under a nitrogen atmosphere. After the mixture was cooled, the solvent (naphthalene) was removed by trituration with hexane (6 × 20 mL). The resulting green solid was suspended in chloroform and filtered. After evaporation of the solvent, the residue was triturated with hexane (6 × 50 mL) and then recrystallized from benzene/ethyl acetate (2:1) to afford 1.6 g (4.5 mmol, 35%) of **8** as fine white crystals; mp 194–198 °C. Further trituration with hexane (4 × 2 mL) raised the mp to 198–199 °C.[15]

Acknowledgment. This research was supported by Grant Y-484 to A.L.T. from the Robert A. Welch Foundation. Purchase of the HA-100 was supported, in part, by a grant from the Research Corporation. We are grateful to W. Watson and G. Martin for valuable discussions.

Registry No. 4, 261-31-4; 5, 24624-33-7; 6, 17394-13-7; 7, 72844-60-1; 8, 72844-61-2; 9, 72844-62-3; 10, 72447-77-9; 11, 72844-63-4; diethyl diazomalonate, 5256-74-6; dimethyl diazomalonate, 6773-29-1.

---

(9) Melting points were obtained by using a Mel-Temp apparatus and a Büchi melting point device and are corrected. Boiling points are uncorrected. New compounds (8–11) gave satisfactory analyses (C, H, S) and their NMR spectra were completely consistent with assigned structures. Homogeneity was established by TLC (silica gel) or recrystallization to a constant melting point and NMR spectrum. NMR spectra were recorded on Varian Models T-60 and HA-100.

(10) Peace, B. W.; Carman, F. C.; Wulfman, D. S. *Synthesis* 1971, 658.

(11) Fieser, M.; Fieser, L. F. "Reagents for Organic Synthesis", Wiley: New York, 1975; Vol. 5, p 244.

(12) The method is adopted from Ando, W.; Yagihara, T.; Tozune, S.; Imai, I.; Suzuki, J.; Toyama, T.; Nakaido, S.; Migita, T. *J. Org. Chem.* **1972**, *37*, 1721. We have observed significant increase in yields by using toluene as a "solvent" for this reaction.

(13) Prepared quantitatively, by reacting thioxanthene with an excess of CH$_3$OD and NaOCH$_3$.

(14) Since this work was completed, this structure conformation has been confirmed by X-ray crystallography (W. H. Watson and A. L. Ternay, Jr., in preparation).

(15) When conducted in the absence of solvent, the reaction afforded the isomeric dimethyl 9-(1,4-dimethylthioxanthenyl)malonate, mp 123–124 °C. The structure of this a′-substituted thioxanthene was established by X-ray crystallography (W. H. Watson, in preparation).

Natural-Abundance ^{15}N Nuclear Magnetic Resonance Spectroscopy. Unambiguous Evidence for Lack of Influence of Lone-Pair Orbital Orientation on Piperidine ^{15}NH Chemical Shifts

George T. Furst and Robert L. Lichter*

City University of New York, Department of Chemistry, Hunter College, New York, New York 10021

Friedrich W. Vierhapper*

Institut für Organische Chemie, Universität Wien, A-1090 Wien, Austria

Received November 5, 1979

Recently, Duthaler et al. reported that ^{15}N chemical shifts of *N*-methylpiperidines appear to depend on the configuration of the N substituent, but those of the NH-substituted piperidines do not.[1] The latter inference was based on the existence of a simple linear correlation between the piperidine ^{15}N shifts and the ^{13}C shifts of hydrocarbon analogues. Such a correlation might not have been expected because piperidines thought to have predominantly axial as well as those with predominantly equatorial N–H bonds were included among the data. However, because direct evidence for the N–H configurations was lacking, the above inference is uncertain.

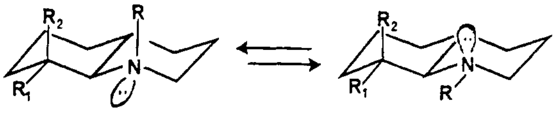
We report here explicit evidence that piperidine ^{15}N chemical shifts are indeed independent of N–H conformation. This conclusion is based on comparison of the 8-methyl-*trans*-decahydroquinolines 1 and 2[2] with the

---

(1) R. O. Duthaler, K. L. Williamson, D. D. Giannini, W. H. Bearden, and J. D. Roberts, *J. Am. Chem. Soc.*, **99**, 8406 (1977).

(2) (a) E. L. Eliel and F. W. Vierhapper, *J. Am. Chem. Soc.*, **96**, 2257 (1974); **97**, 2424 (1975); (b) *J. Org. Chem.*, **40**, 2729, 2734 (1975).

Table I. ^{15}N Chemical Shifts of 8-Substituted *trans*-Decahydroquinolines[a]



A B

		R = H			R = CH₃		
R_1	R_2	predomnt conformn[3]	compd	δ_N	predomnt conformn[2a]	compd	δ_N
H	CH_3	B	1	51.4	B	1m	45.8
CH_3	H	B	2	49.6	A	2m	26.0
H	$(CH_3)_3C$	B	3	55.7	B	3m	46.9
$(CH_3)_3C$	H	A	4	54.3	A	4m	28.2
H	H	B	5	54.3	B	5m	48.5

[a] In C_6H_6/C_6D_6, concentration 2-4 M. Chemical shifts were measured with respect to external $CH_3{}^{15}NO_2/CD_3NO_2$ and were converted to the anhydrous liquid ammonia scale via the relationship $\delta_{NH_3} = \delta_{CH_3NO_2} + 380.2$ ppm. Positive values denote diminished shielding relative to the reference.

corresponding 8-*tert*-butyl compounds **3** and **4**[3] and the parent compound **5** (Table I). From infrared studies, in which the Bohlmann-band C–H stretching region was carefully scrutinized, the 8-*tert*-butyl groups were shown to bias the N–H conformation and were predominantly (~80%) equatorial in **3** and predominantly (~80%) axial in **4**.[3] By the same criteria, a methyl group at C-8 is substantially less effective in influencing the N–H equilibria of **1** and **2**. The ^{15}N chemical shift difference between **1** and **2** is 1.8 ppm, and that between **3** and **4**, for which the conformational difference is considerably more profound, is even smaller, only 1.4 ppm. The possibility that this small shift difference may be attributed to major deviations of **3** and **4** from double chair conformations may be discounted because recent X-ray crystallographic studies indicate that the corresponding picrate salts exist in the double chair form.[4] This result leads to the conclusion that *N–H (hence lone-pair) conformation does not influence ^{15}N resonance positions in piperidines and conversely that ^{15}N chemical shift determinations are of little value in probing lone-pair orientations in these compounds.*

The remaining substituent effects on the ^{15}N chemical shifts can be interpreted in a relatively straightforward manner. The γ effect displayed by **1** and **2** relative to the parent **5** is configuration dependent and differs from that observed in the 3-methylpiperidines.[1] The deshielding δ effect introduced by 8-*tert*-butyl substitution is the same for both axial (4.3 ppm) and equatorial (4.7 ppm) configurations (**1** → **3** and **2** → **4**), again reflecting the absence of a lone-pair effect. In the tertiary series, infrared and ^{13}C NMR spectroscopic data reveal that the *N*-methyl groups in **1m** and **3m** are completely, and in **5m** >95%, equatorial.[3] The small ^{15}N chemical shift range in this series is similar to that for **1**, **3**, and **5**, but the magnitudes differ somewhat. Here, the conformation of the nitrogen substituent probably plays a significant role. Thus the **1m** → **3m** and **2m** → **4m** δ effects are about half those for **1** → **3** and **2** → **4**. The 8.5-ppm shielding of **1m** relative to **5** conforms to that expected for a γ-gauche C-8 methyl and an equatorial *N*-methyl group.[1,5] Similarly, **2m** is shielded but to a slightly lesser extent (–28.3 ppm relative to **5**) than is expected[5] from the substituent parameters. This may reflect a deviation of the equatorial C-8 γ-methyl group from the type of gauche relationship to nitrogen that an axial methyl would have; compounds with the latter geometry were used to derive the piperidine parameters.[5]

Further discussion of conformational preference is deferred to a full paper.

Experimental Section

Nitrogen chemical shifts were measured in the Fourier transform mode with broad-band proton decoupling by using a JEOL PFT-100 spectrometer equipped with the EC-100 data system and operating at 10.09 MHz. A sweep width of 5 kHz over 8K data points was used. For the N–H decahydroquinolines a pulse width corresponding to a tip angle of 30° and a repetition time of 2 s was employed; this was increased to 4 s for the methylated series. The N–H series required 5–10K transients, while the *N*-methyl compounds required 25K transients for an adequate signal-to-noise ratio. Samples were 2–4 M in C_6H_6/C_6D_6 solution. The reference signal was derived from a concentric capillary of ^{15}N-enriched nitromethane. Chemical shifts are reported in parts per million downfield from anhydrous liquid ammonia by using the expression $\delta_{NH_3} = \delta_{CH_3NO_2} + 380.2$.[6]

The preparation of the compounds used in this study has been reported.[2,3]

Acknowledgment is made (by R.L.L.) to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work. The authors are especially indebted to Dr. E. L. Eliel for his incisive and helpful comments.

Registry No. 1, 52761-68-9; **1m**, 52008-64-7; 2, 52730-00-4; **2m**, 55970-12-2; 3, 68367-00-0; **3m**, 68367-02-2; 4, 68366-99-4; **4m**, 68367-01-1; 5, 767-92-0; **5m**, 875-63-8.

---

(3) F. W. Vierhapper and E. L. Eliel, *J. Org. Chem.*, **44**, 1081 (1979).

(4) (a) K. D. Hargrave and E. L. Eliel, *Tetrahedron Lett.*, 1987 (1979). (b) K. D. Hargrave and E. L. Eliel, *Isr. J. Chem.*, in press. (c) The major distortions of 4 are a twisting (~14°) of the *tert*-butyl group from the ideal staggered form and a slight bending of the group away from the piperidine nitrogen. In 3 the axial group is also twisted from the staggered conformation and bent ~16° outward from the ideal cyclohexane geometry. The *N*-methyl group of **2m** exhibits a bending of ~10° from the ideal geometry and a slight bending of the *C*-methyl away from the piperidine nitrogen.

(5) (a) Shift parameters for the following groups are from ref 1: axial *N*-methyl, -20.2 ppm; equatorial *N*-methyl, +2.2 ppm; γ-gauche methyl, -10.3 ppm; γ-anti methyl, +3.7 ppm. Because of the small number of examples available to obtain the average, these parameters can only be considered as approximations. (b) These approximations do not take into account possible effects of the interactions between C-8 and the *N*-methyl carbon, for which no satisfactory models exist.

(6) P. R. Srinivasan and R. L. Lichter, *J. Magn. Reson.*, **28**, 227 (1977).