# Conformational Effects in 2,3-Cycloalkyl-2,3-diazabicyclic Tetraalkylhydrazines

**Stephen F. Nelsen,* William C. Hollinsed, Loretta A. Grezzo, and William P. Parmelee**

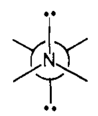
*Contribution from the Samuel M. McElvain Laboratories of Organic Chemistry, Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706.*

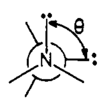
*Received April 6, 1979*

**Abstract:** Bicyclo[2.2.2]octyl (**6**), -[2.2.2]oct-5-enyl (**7**), and -[2.2.1]heptyl (**8**) fused hexahydropyridazines are trans fused. Although the nitrogens are probably little flattened in **6** compared to other hydrazines, considerable flattening is geometrically imposed in **7** and **8**. Their values for $\Delta G^{\ddagger}$ for double nitrogen inversion are 15.0 (+22 °C), 10.3 (−43 °C), and 9.6 (−89 °C) kcal/mol, respectively, and unusual effects on both $^{13}C$ NMR chemical shifts and PE spectral data are reported. The $E°'$ values for **6–8** are similar. Bicyclo[2.2.2]oct-5-enyl-fused 4,4-diethylpyrazolide (**10**) is in the endo cis-fused conformation.

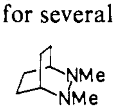
## Introduction

Electronic interactions involving the nitrogen lone pair electrons result in the sterically most favorable anti conformation I ($\theta$ = 180°) not being significantly populated for acyclic tetraalkylhydrazines, which exist overwhelmingly in gauche conformations with $\theta$ near 90°.[1] The size of the dihedral angle $\theta$ has been found to be of considerable importance in determining the rate of nitrogen inversion[2] and of electron transfer to a solid electrode.[3] These studies employ 1,2-dialkylhexahydropyridazine derivatives so that the requirement for a near 60° internal CNNC ring dihedral angle generates conformations separated by substantial barriers in which the external alkyl substituents are diequatorial ($\theta$ = 180°), axial equatorial ($\theta$ ca. 60° [4]), or diaxial (unpopulated at equilibrium, $\theta$ ca. 60°). Another experimentally accessible set of hydrazine conformations with quite different $\theta$ values is generated by linking two alkyl substituents in a bicyclic system, forcing them to be (nearly) eclipsed. Anderson and Lehn[5] showed in important $^1H$ NMR work that only the mirror image anti (trans alkyl) conformations are detectably occupied for **1–4** (as well as for several analogous bicyclic compounds[6]).

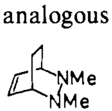

I ($\theta$=180°)



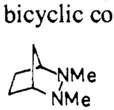
I ($\theta$=90°)



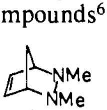
1



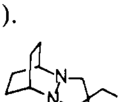
2



3



4



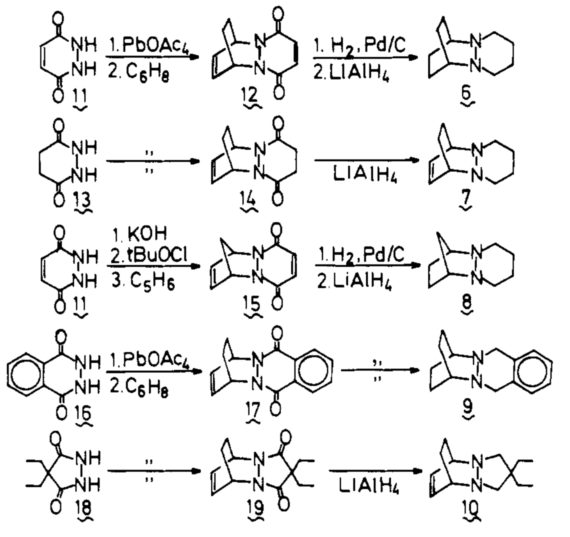
5

An interesting chemical consequence of the bicyclic requirement for $\theta \sim 0°$, $\theta \sim 120°$ conformation set was suggested[7] to be responsible for **4** giving more *cis*- than *trans*-azomethane upon pyrolysis.

When the exocyclic nitrogen substituents of **1–4** are linked in a third ring, the trans-fused conformation should be destabilized, because five- and six-membered rings cannot accommodate an internal torsional angle anywhere near 120°. The five-membered ring linked example **5** exists in the cis-fused conformation,[8a] which was indicated by photoelectron (PE) spectroscopy data to have $\theta$ near 0°.[9]

We report here the preparation of five additional tricyclic hydrazine derivatives, **6–10.** Pitting the $\theta \sim 180°$, 60° preference for six-membered rings against the 120°, 0° preference for bicyclic rings in **6–9** must cause geometric adjustment, the results of which have been studied using $^{13}C$ NMR and PE spectroscopy and cyclic voltammetry (CV) for measurement of the formal potential for electron removal, $E°'$. Compound **10** was expected to be in the $\theta$ = 0° conformation by analogy with **5**, and provide the first example of a cis-fused tetrahydropyridazine derivative. Its properties are compared with trans-fused analogues.

Scheme I

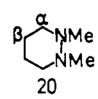


## Compound Preparation

The tricyclic hydrazines **6–10** were prepared by obvious modifications of the method Stetter and Woernle[10] used in preparing **5** (see Scheme I). Diels-Alder addition of cyclohexadiene or cyclopentadiene to the appropriate cyclic diacyl diimide, formed in situ by oxidation of the appropriate bishydrazide, gave tricyclic diketo compounds. The carbonyl groups were successfully reduced by lithium aluminum hydride in the cases of **6–10.** Carbonyl reduction to give the unsaturated analogues of **8** and **9** failed, in our hands.

## $^{13}C$ NMR Chemical Shifts

Chemical shift data for **6–8** are summarized in Table I, along with those for model compounds, including dimethylhexahydropyridazine **20**. The $C_\beta$ shift for the equilibrating



20

conformational mixture, **20**(**ae**$\rightleftarrows$**ea**), is 5.4 ppm upfield of that for **20ee**,[2] due to the usual upfield shift caused by an axial alkyl group.[11] The site of change in substitution for **6–8** compared to **20** is far enough from $C_\beta$ so that the shifts of **20** conforma-

0002-7863/79/1501-7347$01.00/0

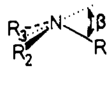
**Table I.** $^{13}C$ NMR Chemical Shifts for **6–8** and Model Compounds[d]

| compd | temp, °C | bridgehead | $C_2H_4$ bridge | $C_\alpha$ | $C_\beta$ | others |
|---|---|---|---|---|---|---|
| **20(ee)**[a] | −68 | | | 58.41 | 25.55 | 44.78 (Me) |
| **20(ae ⇌ ea)**[a] | −68 | | | 48.09 | 20.13 | 35.60 (Me) |
| **1**[b] | amb | 52.16 | 23.83 (br) | | | 43.43 (Me) |
| | −71 | 51.44 | 27.84<br>17.14 | | | 43.55 (Me) |
| **6** | +56 | 54.09 | 24.42 (br) | 52.64 | 25.97 | |
| | −35 | 53.69 | 27.27<br>20.89 | 52.31 | 25.42 | |
| **3**[c] | +76 | 65.1 | 26.6 | | | 43.0 (Me);<br>34.8 ($C_7$) |
| | −40 | 64.6<br>63.1 | 30.2<br>21.0 | | | 45.2 (Me); 33.9 ($C_7$)<br>39.3 (Me) |
| **8** | −34 | 62.01 | 28.48 | 50.47 | 26.33 | 35.81 ($C_7$) |
| | −128 | 61.97<br>61.70 | 34.21<br>21.95 | 52.83<br>47.85 | 26.03<br>25.77 | 36.28 ($C_7$) |
| **2**[b] | amb | 54.57 | 19.22 (br) | | | 43.65 (Me);<br>132.88 (vinyl) |
| | −83 | 54.45<br>53.14 | 22.93<br>15.18 | | | 47.44 (Me);<br>42.25 (Me)<br>135.47 (vinyl)<br>130.25 (vinyl) |
| **7** | amb | 52.98 | 22.86 | 54.93 | 26.04 | 132.00 (vinyl) |
| | −91.4 | 54.73<br>51.69 | 29.76<br>16.20 | 55.52<br>54.42 | 26.45<br>26.14 | 136.25 (vinyl)<br>129.05 (vinyl) |

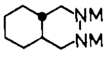
[a] Reference 2. [b] Reference 8a. [c] Reference 8b; no solvent. [d] In parts per million downfield from internal $Me_4Si$.

tions are reasonable models, and the $C_\beta$ shifts for **6–8** are so close to those of **20ee** that it is clear that these compounds must be trans fused.

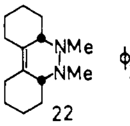
Trans-fused **6–8** ought to differ markedly in the amount of flattening at their nitrogens, and these differences in flattening will be argued later in this paper to cause important differences in their properties. To consider how much flattening occurs at unsymmetrical nitrogens like those of hydrazines, it is convenient to employ $\beta$, the angle of bend of one RN bond from the plane of the other two (see **II**); $\beta$ is 0° for a completely planar nitrogen and 54.7° for a tetrahedral one. X-ray crystal structures[4] have shown that $\beta$ varies with $\theta$ in tetraalkylhydrazines. The diequatorial *N*-methyl compound **21** ($\theta \sim 180°$) has its nitrogens bent somewhat past the tetrahedral value ($\beta_{av}$ = 59°), but the nitrogens of the axial, equatorial *N*-methyl compound **22** ($\theta$ = 70–74°) are significantly less bent. $\beta_{av}$ at the axial methyl N is 51°, and that at the equatorial methyl N 47°. To estimate $\beta$ in **6–8,** it is most convenient to employ Newman projections along the NN bond (see **III**). The dihedral angle $C_3N_2,N_7C_6$ is the torsional angle of the hexahydropyridazine, $\phi_6$, while $\phi_B$ is the corresponding torsional angle in the bicyclic ring. The $C_1N_2C_3$ angle in this projection, $\omega°$, $= 180 - \frac{1}{2}(\phi_6 + \phi_B)$. For the relatively unstrained six-membered rings of **21** and **22,** $\phi_6$ is 65 and 67°, respectively. The value of $\phi_B$ for **1** was estimated from its PE spectrum to be 20°.[9] In the tricyclic **6**, more torsional strains will be applied to both rings, which should increase $\phi_B$ and $\phi_6$. Great flattening at nitrogen is not required for **6**. If $\phi_6$ increased to 75° and $\phi_B$ to 30°, $\omega$ would be 127.5°, corresponding to $\beta_{NN}$ of about 47°,[12] little different from $\beta_{av}$ of a gauche hydrazine. At the other extreme, if no bicyclic torsion were possible in the bicyclic ring ($\phi_B = 0$), and $\phi_6$ were 75°, $\omega$ would be forced to 142.5°, corresponding to $\beta_{NN}$ = 33°. We note that $\beta$ is not a variable which is expected to be linear with energy, strain, or most physical properties. A parameter which we believe will be much more nearly linear with such properties is $f_p$, the fractional p character in the lone-pair orbital ($f_p$ = 0.75 for a tetrahedral nitrogen and 1.00 for a planar one). A $\beta_{av}$ of 59° corresponds to $f_p$ = 0.70, a $\beta_{av}$ = 47° to $f_p$ = 0.83, and a $\beta_{av}$ = 33° to $f_p$ = 0.93.[13] Considered this way, $\beta_{av}$ = 33° corresponds to an effective flattening of (0.93 − 0.75)/0.25 or 72% of the way from a tetrahedral to a planar nitrogen. Since even bicyclo[2.2.1]heptyl systems can twist a few degrees,[14] the actual $\beta_{av}$ even for **8** will presumably be somewhat greater than 33°.



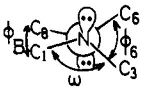
II



21

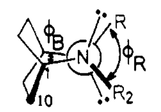


22



III

One property for which we suggest that $\beta_{av}$ for **6–8** has a substantial influence is the chemical shift difference between the two carbons of the $-CH_2CH_2-$ bridge ($\Delta\delta$) at low temperature, where nitrogen inversions are slow, compared with their bicyclic analogues which have the hexahydropyridazine ring replaced by methyl groups. For the saturated bicyclo[2.2.2]octyl pair **1** and **6,** $\Delta\delta$ decreases upon closure of the third ring: $\Delta\delta(\mathbf{1})$ = 10.70, $\Delta\delta(\mathbf{6})$ = 6.38 ppm. This is reasonable sterically. For **1** $\phi_B$ has been estimated at 20° (see **1A**).



1A

Linking the exocyclic alkyl substituents in closing the third ring of **6** must decrease $\phi_R$ and increase $\phi_B$. These structural changes will increase the $C_{10}C_1,N_2R_2$ dihedral angle, decreasing the $R_2,C_{10}$ gauche interaction and causing a downfield shift at $C_{10}$, resulting in a lower $\Delta\delta$. As expected from these considerations, the upfield $-CH_2CH_2-$ carbon of **6** occurs significantly downfield of the corresponding carbon of **1** (by 3.75 ppm). In contrast, the opposite trend in $\Delta\delta$ is observed for the dimethyl to hexahydropyridazinyl transformation in bicyclo[2.2.1]heptyl ($\Delta\delta(\mathbf{3})$ = 9.23, $\Delta\delta(\mathbf{8})$ = 12.26 ppm) and bicyclo[2.2.2]octenyl ($\Delta\delta(\mathbf{2})$ = 7.75, $\Delta\delta(\mathbf{7})$ = 13.56 ppm) systems, where $\Delta\delta$ is larger in the tricyclic than in the bicyclic systems, and shift of the downfield carbons, not the upfield carbons, is responsible.

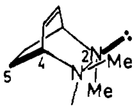
Although the upfield carbon appears slightly downfield in the tricyclic relative to the bicyclic systems again, the change is much smaller, only 0.95 ppm for **8** vs. **3,** 1.02 ppm for **7** vs. **2.** This is accompanied by a substantially larger downfield shift

**Table II.** $^{13}$C NMR Chemical Shifts for **5, 9,** and **10**[b]

| compd | temp, °C | bridgehead | $C_2H_4$ bridge | $C_\alpha$ | other |
|---|---|---|---|---|---|
| **9** | +40 | 54.18 | 23.51 | 52.31 | 135.30, 126.68, 125.67 (arom) |
| | −128 | 53.78 | 26.67<br>19.70 | 52.00 | 134.42, 126.99, 125.74 (arom) |
| **5**[a] | amb | 50.21 | 23.15 (br) | 58.97 | 46.17 (Q), 27.75 (Q, $C$H$_2$), 9.26 (Me) |
| | −69 | 49.63 | 27.51<br>17.91 | 58.80 | 45.18 (Q),<br>27.77<br>25.19 (Q$C$H$_2$),<br>9.84<br>8.98 (Me) |
| **10** | amb | 53.58 | 24.28 | 60.28 | 135.57 (vinyl), 44.68 (Q), 27.54, 26.43 (Q$C$H$_2$), 9.38, 8.75 (Me) |

[a] Reference 8a. [b] In parts per million downfield from internal $Me_4Si$.

for the downfield carbons (4.01 ppm for **8** vs. **3,** 6.83 ppm for **7** vs. **2**). Since bicyclic torsion is much more difficult in **7** and **8** than in **6,** $\phi_B$ will change much less, and the nitrogens will flatten more in **7** and **8.** This suggests to us that an electronic effect associated with flattening the nitrogens may be principally responsible. The origin of such large shift changes for the downfield $-CH_2CH_2-$ carbon is not clear. One possibility would seem to be related to the $\gamma$-antiperiplanar heteroatom upfield shift documented extensively by Eliel, Grant, Wenkert, and co-workers.[15] For **2** and **3,** since $\phi \sim 0°$, the $N_2$ lone pair is nearly parallel with the $C_4C_5$ bond (see **2A**). Flattening at N would tend to disrupt this alignment, which would cause a downfield shift of $C_5$ if the alignment had caused an upfield shift in the methyl compound. The effect postulated is the through-space analogue of the well-documented through-bond upfield shift.[15]



2A

The chemical shifts of **5, 9,** and **10** are summarized in Table II. The cis fusion of the pyrazolidine ring of **5** is proven by the two types of ethyl groups observed at low temperature;[8a] the ethyls of trans-fused **5** would be equivalent. The similarity of the pyrazolidine ring shifts for **10** to those of **5** and downfield shift of the $-CH_2CH_2-$ bridge show that **10** is cis fused with the alkyls cis to the olefin bridge, as expected on steric grounds. Choice of cis vs. trans fusion for **9** is not possible from its $^{13}$C NMR on symmetry grounds, and the similarity of the $-CH_2CH_2-$ shifts for cis- and trans-fused bicyclo[2.2.2]octanes makes a choice difficult, especially because of the apparent sensitivity of $\Delta\delta$ to flattening at nitrogens. We do not believe that one can tell which conformation is occupied for **9** from its $^{13}$C NMR.

## Dynamic NMR Studies

One result of the greater flattening at N which occurs in **7** and **8** relative to **6** should be a lowered activation energy for double nitrogen inversion, $\Delta G^{\ddagger}$(N). Bicyclic hydrazines have been extensively studied, both by dynamic $^1$H[5,6] and $^{13}$C NMR.[8] Lehn[5] has pointed out that sequential nitrogen inversions are involved in conformational interconversion, and that the nitrogen inversion barrier is related (among other factors) to the amount of bending at nitrogen. The results of dynamic $^{13}$C NMR studies on **6–9** are summarized in Table III (**10** has a temperature-invarient spectrum, indicating that only the endo (alkyl cis to vinyl) cis-fused conformation is significantly occupied). The 15.0 kcal/mol $\Delta G^{\ddagger}$(N) for **6** is significantly higher than for the dimethylbicyclic compounds **1** and **2,** an expected result of the presence of the third ring, since inversion of the hexahydropyridazine ring must accompany double N inversion. The barrier observed is comparable to those seen for bridgehead diazadecalin derivatives where similar coupled N inversions and hexahydropyridazine ring reversals are required.[16] When bicyclic ring torsion is made more difficult in **7** and **8,** $\Delta G^{\ddagger}$(N) at the coalescence temperature decreases substantially, by 4.7 kcal/mol for **7** and 5.4 for **8.** This corroborates the expected flattening at nitrogen for the compounds, and seems to suggest flatter nitrogens in **8** than in **7** (especially when the slightly higher barrier for **3** than for **2** is considered) implying that a bicyclo[2.2.2]octenyl system has a lower torsion energy than a bicyclo[2.2.1]heptyl system. The observed barrier for **9** is 2.5 kcal/mol below that of **6.** One does not expect *trans*-**9** to have significantly flatter nitrogens than **6,** since $\phi_6$ is comparable for **21** and **22** (and $\phi_6$ for cyclohexene at 63°[17] is slightly larger than that for cyclohexane). The reduced $\Delta G^{\ddagger}$(N) for **9** could be attributed to the increased ease of the six-ring inversion which must accompany nitrogen inversion, although it should be remembered that we have no evidence that **9** is not cis fused, and the cis barrier for **5** is close enough to that for **9** that the $\Delta G^{\ddagger}$(N) measurement does not help us to decide on the type of fusion for **9.**

**Table III.** Activation Parameters for Conformational Interconversion of Tricyclic Hydrazines **6–9** and Their Bicyclic Analogues

| compd | $\Delta G^{\ddagger}$ [a] [$T$, °C] | $\Delta H^{\ddagger}$ [a] | $\Delta S^{\ddagger}$ [b] | temp range, °C |
|---|---|---|---|---|
| **6** | 15.00 (4) [+22] | 12.0 (6) | −10.2 (21) | +56 to −14 |
| **7** | 10.33 (6) [−43] | 7.5 (6) | −12.5 (27) | −32 to −92 |
| **8** | 9.6 (10) [−89] | 7.9 (15) | −6.0 (85) | −58 to −123 |
| **9** | 12.5 (1) [−3] | 13.2 (16) | +2.6 (59) | +30 to −28 |
| **1**[c] | 12.32 (6) [+25] | 11.7 (2) | −2.1 (10) | |
| **2**[c] | 12.33 (5) [+25] | 11.1 (3) | −4.2 (12) | |
| **3**[d] | 13.0 (2) [−9] | | | |
| **5**[c] | 11.4 [−45] | | | |

[a] In kcal/mol. Number in parentheses is statistical error, in the last digit reported, propagated at the 95% confidence level. [b] In cal/deg·mol. Number in parentheses is statistical error in the last digit reported, calculated at the 95% confidence level. [c] From ref 8b. [d] From ref 5.

## PE Studies

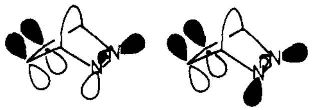
The lone pair and $\pi$ ionization for the PE spectra of **6–10** and model compounds are summarized in Table IV. Both increasing $\theta$ from a value near 120° (that which would occur for

**Table IV.** PE Spectral and $E^{\circ\prime}$ Data for **6–10** and Some Model Compounds

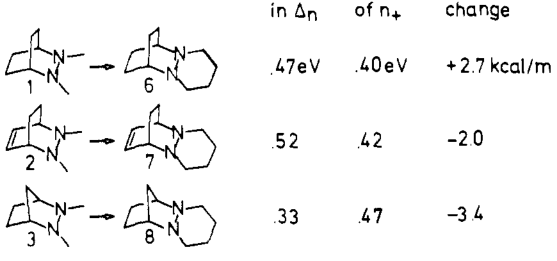
| compd | $IP_1$[a] | $IP_2$ | $IP_3$ | $E^{\circ\prime}$,[b] V |
|---|---|---|---|---|
| **1**[c] | 7.46 ($n_+$) | 9.28 ($n_-$) | | +0.07 |
| **2**[c] | 7.49 ($n_+$) | 9.15 ($\pi$) | 9.49 ($n_-$) | +0.17 |
| **3**[c] | 7.66 ($n_+$) | 9.44 ($n_-$) | | +0.21 |
| **4**[c] | 7.72 ($n_+$) | 9.25 ($\pi$) | 9.63 ($n_-$) | +0.32 |
| **5**[c] | 6.93 ($n_-$) | 9.25 ($n_+$) | | −0.20 |
| **6** | 7.06 ($n_+$) | 9.35 ($n_-$) | | −0.04 |
| **7** | 7.07 ($n_+$) | 9.07 ($\pi$) | 9.59 ($n_-$) | −0.04 |
| **8** | 7.19 ($n_+$) | 9.30 ($n_-$) | | −0,08 |
| **9** | 7.21 (n) | 9.61 (n) | | |
| **10** | 7.04 ($n_-$) | 9.17 ($\pi$) | 9.54 ($n_+$) | −0.01 |

[a] Vertical IPs reported, maxima from least-squares fit of Gaussian curves to the experimental data. [b] In acetonitrile containing 0.1 M tetrabutylammonium perchlorate as supporting electrolyte, vs. SCE. [c] From ref 9.

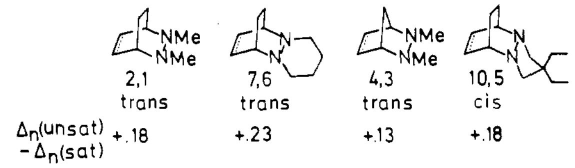
a bicyclic ring with no torsion and tetrahedral nitrogens) toward 180° (the direction which would occur upon increasing bicyclic torsion) and flattening at nitrogen (which both increases $\theta_n$, for a given degree of bicyclic torsion and increases overlap because of rehybridization at N) will increase $\Delta_n$, the difference in IP for the lone pair combination orbitals. Flattening at N should lower the n ionization potentials,[9] because it increases the p character of the lone-pair orbitals. An additional factor which should increase $\Delta_n$ is $\pi$(C=C), lone pair through space overlap when the $\pi$ orbital is higher in energy than the lone-pair combination ($n_-$ in a trans-fused hydrazine) as it is in bi- and tricyclic trans-fused hydrazines. Any $\pi$(C–C),$n_+$ interaction should be smaller because of the opposite signs for the overlap of the orbitals at N, and because the $n_+$,$\pi$ energy separation is larger. Although these factors frequently interact, all have detectable influences on the data of Table IV. Closure of an *N*,*N*′-dimethylbicyclic system to the tricyclic hexahydropyridazine derivative provides some examples; see Scheme II. For the bicyclo[2.2.2]octyl example, **1** → **6**, this structural change increases $\Delta_n$ by 0.47 eV, while $n_+$ is destabilized by 0.40 eV. Part of the changes seen are probably caused by the increase in $\theta$ between **6** and **1**. Relatively little flattening at N is occurring, because of the flexibility of the [2.2.2]octyl system, and $\Delta G^{\ddagger}$(N) is higher for **6** than for **1**. Part of the increase in $n_+$ may be attributed to the increase in size of the alkyl groups attached to N, but this may be estimated to be 0.19 eV from the $IP_1$ for 1,2-dimethyl-1,2-diethylhydrazine (8.08) compared to tetraethylhydrazine (8.27), where $\theta$ does not change significantly. **9** (benzo-**6**) has $\Delta_n$ increased another 0.11 eV. It is not obvious whether **9** is trans or cis fused; both might be expected to show large $\Delta_n$ values. We do not know how to properly assess the 0.21-eV stabilization of $n_+$ in **9** compared to **6**, but the benzo group may be inductively electron withdrawing in this geometry. The bicyclo[2.2.2]octenyl comparison (**2** → **7** in Scheme II) shows comparable $\Delta_n$ increase and $n_+$ destabilization to **1** → **6**, although less $\theta$ change and more flattening at nitrogen must be occurring. For the bicyclo[2.2.1]heptyl comparison (**3** → **8**) the amount of nitrogen flattening is the largest by the $\Delta G^{\ddagger}$(N) comparison, and here the $\Delta_n$ increase is somewhat smaller, but destabilization of $n_+$ is perhaps larger than in the cases with more of a $\theta$ change.



Scheme II



Scheme III



To investigate an effect of $\pi$(C=C), lone pair overlap on $\Delta_n$, we compare saturated and unsaturated compounds in Scheme III. There is a larger $\Delta_n$ for the unsaturated compound in each pair, but substantial differences in $\theta$ occur for **2** and **1**, and in flattening at nitrogen for **7** and **6**. Such differences ought to be small in the **4**, **3** and **10**, **5** comparisons, and we suggest that through-space $\pi$(C=C), lone-pair interactions are principally responsible for the $\Delta_n$ increases here. Larger through-space interactions will be seen in [2.2.1]heptyl than in [2.2.2]octyl cases because of greater overlap. For example, the dihedral angle between the planes containing the double bonds in norbornadiene is 115.6°,[18a] while that for bicyclo[2.2.2]octadiene is 123.4°,[18b] and the $\pi$ splittings measured by PE spectroscopy are 0.86 and 0.58 eV, respectively.[19] It is clear that $\pi$(C=C),n interaction is sensitive to stereochemistry because the cis-endo [2.2.2]system **10** experimentally has a larger $\Delta_n$(unsat) − $\Delta_n$(sat) than does the trans [2.2.1] system **10**. The larger interaction by the PE criterion of larger $\Delta_n$(unsat) − $\Delta_n$(sat) for **10** than **4** (Scheme III) is corroborated by consideration of $\lambda_{max}$ for the n→$\pi^*$ UV band of these compounds.[20] Lehn and co-workers report an n→$\pi^*$ band at 266 nm ($\epsilon$ 680) for **4** in cyclohexane,[20] whereas **2** only shows an inflection point near 270 nm.[5] The n→$\pi^*$ band for **10** appears as a distinct maximum, $\lambda_{max}$ 300 nm ($\epsilon$ 710) in hexane.

## Cyclic Voltammetry $E^{\circ\prime}$ Measurements

The formal potential for one-electron oxidation, $E^{\circ\prime}$, was measured for **6–8** and **10** by cyclic voltammetry, and is reported in Table IV. The difference in $E^{\circ\prime}$ for two compounds under the same experimental conditions is the difference in $\Delta G^{\circ}$ for the two electron transfer reactions. Because there is a large difference in preferred geometry for a neutral hydrazine and its radical cation,[21] $E^{\circ\prime}$ measurements have provided useful insight into strain energy effects on the free energy of hydrazine radical cations.[22] The energy of the highest occupied MO has an effect on $E^{\circ\prime}$, and considerable work on tetraalkylhydrazines indicates that using $IP_1$ is a good way of estimating this effect. The combination of loss of alkyl group polarization effects in going to solution[23] and solvation changes as the alkyl group is lengthened in acetonitrile[22] results in a nearly linear change in $E^{\circ\prime}$ as $IP_1$ changes with alkyl group structure in the absence of steric effects. Steric effects relative to those present in the tetramethylhydrazine couple may be usefully estimated by considering $E^{\circ\prime}$ deviations from a line of slope 0.15 through tetramethylhydrazine in an $IP_1$ vs. $E^{\circ\prime}$ plot;[22b] dev (kcal/mol) = 23.06 [$E^{\circ\prime}$ (obsd) − $E^{\circ\prime}$ (correl)], where $E^{\circ\prime}$ (correl) = 0.15($IP_1$) − 0.91, with the 0.1 M tetrabutylammonium perchlorate supporting electrolyte used in this work ($E^{\circ\prime}$ ($Me_2NNMe_2$) is 0.33 V with tetrabutylammonium perchlorate supporting electrolyte, compared with 0.28 V with sodium perchlorate[22]). Dev is negative for all bi- and tricyclic compounds in Table IV, as qualitatively expected on the basis of strain relief when the electron is removed and the preferred nearly tetrahedral geometry at N for the neutral compound is replaced by a preferred planar geometry at N in the radical cation. One Me,Me eclipsing interaction present in tetramethylhydrazine radical cation is also relieved by having a bicyclic structure. We had expected **7** and **8**, which are constrained to be unusually flat at nitrogen in the neutral form, to show lower $E^{\circ\prime}$ values than **1** and **6**. The dev values observed are **1** (−3.2), **6** (−4.4), **7** (−4.4), **8** (−6.7 kcal/mol), much less sensitive than the $\Delta G^{\ddagger}$(N) changes. We conclude that the structural constraints forcing the nitrogens to bend in the radical cations (and **3–5** are known to be substantially bent from ESR work[24]) and constraining the NNC angles to unusual values cause changes in the neutral and radical cation energies which tend to cancel each other. The extent to which solvation changes might affect $E^{\circ\prime}$ for these compounds is not experimentally clear, but we would not expect large effects based on previous work,[22] except possibly for unsaturated compounds, which have received less study. There is a rather large dev difference for **5** (−7.6 kcal/mol) and **10** (−3.6 kcal/mol). The $E^{\circ\prime}$ for **5** at −0.25 V[22a] ($NaClO_4$ supporting electrolyte, −0.20 V with the $Bu_4NClO_4$ employed in this work) was the most negative $E^{\circ\prime}$ in a series of over 70 tetraalkylhydrazines. Although **10** shares the 0° dihedral angle of **5**, its dev value is close to that for the trans-fused compounds. We note that **10** is less strained in the neutral form because the cis alkyl groups are opposed to a vinyl bridge rather than a dimethyl bridge as those of **5** must be. No exo conformation was observed for **10**, or for 2-methyl-2-azabicyclo[2.2.2]oct-5-ene,[8a] which has only one alkyl interaction. The steric factor alone could account for a 2 kcal/mol or more positive increment in dev for **10** relative to **5**. Poorer solvation for the olefinic groups may well account for much of the rest of the observed dev difference, but we lack quantitative information on this rather subtle point.

The $E^{\circ\prime}$ data of Table IV make it clear that the energy gap between neutral and radical cationic forms is more complex for these strained compounds than we had hoped, and that $E^{\circ\prime}$ does not provide a very useful criterion for flattening at nitrogen in hydrazines.

## Experimental Section

**2,7-Diaza-3,6-diketotricyclo[6.2.2.$0^{2,7}$]dodeca-3,8-diene (12)** was prepared by the method Clement[25] employed for structurally similar compounds. Maleic hydrazide **11**[26] (11.2 g, 100 mmol) and 350 mL of dry methylene chloride were cooled to −50 °C, with stirring, and 45.2 g (102 mmol) of lead tetraacetate and 8.12 g (102 mmol) of 1,3-cyclohexadiene were added. The stirred mixture was allowed to warm to room temperature over a period of 24 h. After washing with 3 × 100 mL of $H_2O$, the organic layer was dried and concentrated to give 14.75 g of greenish-brown solid. Recrystallization from ethyl acetate/hexane gave **12**[27] as light green needles in 47.9% yield: mp 215–216 °C; NMR ($CDCl_3$) $\delta$ 6.80 (s, 2 H), 6.67 (t, 2 H), 5.85 (m, 2 H), 1.93 (AB′BB′, 4 H); IR ($CHCl_3$) 2980, 2950, 1670, 1610, 1570, 1448 $cm^{-1}$.

**2,7-Diaza-3,6-diketotricyclo[6.2.2.$0^{2,7}$]dodecane (tetrahydro-12)** was prepared by catalytic hydrogenation of **12** (1.50 g, 7.89 mmol) in 100 mL of 95% ethanol over 300 mg of 10% Pd/C at 45 psig. Filtration, evaporation, and recrystallization (hexane) gave 1.12 g (73.9%) of tetrahydro-**12**:[27] mp 115–116 °C; NMR ($CDCl_3$) $\delta$ 4.74 (m, 2 H), 2.60 (s, 4 H), 1.95 (AB, $J_{AB}$ = 8 Hz, 8 H); IR ($CHCl_3$) 2995, 2970, 2942, 2905, 2865, 1655, 1458, 1410 $cm^{-1}$.

**2,3-Diazatricyclo[6.2.2.$0^{2,7}$]dodecane (6).** To solution of 1.0 g (5.2 mmol) of **12-$H_4$** in 100 mL of anhydrous ether cooled to 0 °C was added 20 mL of 1 M ethereal $LiAlH_4$ solution via syringe. After stirring at 0 °C for 10 min and warming to room temperature over 25 min, the mixture was refluxed for 24 h. After addition of 1 mL of $H_2O$, 1 mL of 15% NaOH, and 3 mL of $H_2O$ (1:1:3 workup; mL/g $LiAlH_4$), filtering, drying, and concentration, 0.77 g (89%) of **6**[27] was obtained as a colorless oil: NMR ($CDCl_3$) $\delta$ 2.78 (br s, 4 H), 2.46 (br s, 2 H), 2.07 (AA′ of AA′BB′, $J_{AB} \sim$ 7 Hz, 4 H), 1.63 (m, 4 H), 1.41 (BB′ of AA′BB′, 4 H); IR ($CHCl_3$) 2800, 2715, 2660, 1428 $cm^{-1}$.

**2,7-Diaza-3,6-diketotricyclo[6.2.2.$0^{2,7}$]dodec-9-ene (14).** The method used for preparation of **12** was employed, substituting 1.14 g (10 mmol) of **13** (prepared by the method of Feuer and co-workers[26] using aluminum amalgam prepared by the method of Corey and co-workers[28]), 35 mL of methylene chloride, 4.44 g (10 mmol) of vacuum-dried lead tetraacetate, and 0.8 g (10 mmol) of cyclohexadiene. Workup gave an oil, which solidified upon trituration with ether, giving 0.68 g (35%) of **14**[27] as white needles: mp 135–137 °C; NMR ($CDCl_3$) $\delta$ 6.48 (m, 2 H), 5.32 (m, 2 H), 2.48 (m, 4 H), 1.80 (AA′BB′, 4 H); IR ($CHCl_3$) 2995, 2942, 2865, 1660, 1455, 1400 $cm^{-1}$.

**2,7-Diazatricyclo[6.2.2.$0^{2,7}$]dodec-9-ene (7).** The $LiAlH_4$ reduction used was as that for **6**, employing 0.68 g (3.5 mmol) of **14** and 15 mL of $LiAlH_4$ solution, and a 52-h reflux. **7** was obtained as a colorless oil:[27] 0.47 g (82%); NMR ($CDCl_3$) $\delta$ 6.40 (m, 2 H), 3.14 (m, 2 H), 2.68 (AA′BB′, 4 H), 2.08 (AA′ of AA′BB′, 2 H), 1.58 (m, 4 H), 1.20 (BB′ of AA′BB′); IR 3045, 2950, 2675, 1610, 1430 $cm^{-1}$.

**2,7-Diaza-3,6-diketotricyclo[6.2.1.$0^{2,7}$]undecane (Tetrahydro-15).** A solution of 3.17 g (18 mmol) of **15**[29] in 175 mL of 95% EtOH was hydrogenated at 45 psig over 600 mg of 10% Pd/C. Filtration and evaporation gave a brown oil, which solidified upon trituration with hexane as a hygroscopic white solid:[27] 3.36 g (103%); mp 60–62 °C; NMR ($CDCl_3$) $\delta$ 4.95 (br s, 2 H), 2.57 (s, 4 H), 1.61–2.00 (br s overlapping with AB q, 6 H); IR ($CHCl_3$) 2980, 1630, 1400 $cm^{-1}$.

**2,7-Diazatricyclo[6.2.1.$0^{2,7}$]undecane (8).** The reduction of 0.4 g of tetrahydro-**15** was conducted as for tetrahydro-**12** using 10 mL of 1 M $LiAlH_4$ solution and a 93 h reflux. Workup gave 0.36 g (100%) of **8**[27] as a colorless oil: NMR ($CDCl_3$) $\delta$ 3.10 (br s, 2 H), 3.72 (AA′BB′, 4 H), 1.10–2.08 (m, 10 H); IR (neat) 2900, 2680, 2600, 1460, 1450 $cm^{-1}$.

**2,7-Diaza-3,6-diketo-4,5-benzotricyclo[6.2.2.$0^{2,7}$]dodeca-4,9-diene (17).** The procedure used for **12** preparation, employing **16**[30] as dienophile precursor, gave **17**[27] in 80% yield after recrystallization from 95% alcohol: mp 300–302 °C; NMR ($CDCl_3$) $\delta$ 8.29 (AA′ of AA′BB′, 2 H), 7.78 (BB′ of AA′BB′), 6.72 (t, 2 H), 6.05 (m, 2 H), 1.96 (AA′BB′, 4 H); IR ($CHCl_3$) 2980, 2950, 1605, 1480, 1430, 1390 $cm^{-1}$.

**2,7-Diaza-3,6-diketo-4,5-benzotricyclo[6.2.2.$0^{2,7}$]dodec-4-ene (Dihydro-17).** **17** (5.0 g, 21 mmol) in 160 mL of glacial acetic acid was hydrogenated at atmospheric pressure on 5% Pd/C. After filtration, evaporation, and extraction of a methylene chloride solution with 10% $NaHCO_3$, drying and evaporation gave dihydro-**17**[27] as a white solid: 3.43 g (68%); mp 262–265 °C; NMR ($CDCl_3$) $\delta$ 8.40 (AA′ of AA′BB′, 2 H), 7.86 (BB′ of AA′BB′, 2 H), 5.43 (br 2, 2 H), 2.07 (m, 8 H); IR ($CHCl_3$) 2950, 2875, 1600, 1480, 1430, 1385 $cm^{-1}$.

**2,7-Diaza-4,5-benzotricyclo[6.2.2.$0^{2,7}$]dodec-4-ene (9).** A solution of 0.24 g (1 mmol) of dihydro-**17** in 30 mL of methylene chloride was added over 2 min to a slurry of 0.20 g (5.3 mmol) of $LiAlH_4$ in 15 mL of ether which had been cooled to 0 °C. After the mixture was stirred at 0 °C for 2 h, 1:1:3 workup gave 0.22 g of a tan solid. Sublimation at 50 °C (1 mm) gave **9**[33] as a yellow solid: mp 150–156 °C; NMR ($CDCl_3$) $\delta$ 7.00 (s, 4 H), 3.83 (s, 4 H), 2.68 (br s, 2 H), 2.18 (AA′ of AA′BB′), 1.52 (BB′ of AA′BB′); IR ($CHCl_3$) 2930, 2870, 2810, 1450 $cm^{-1}$.

**2,6-Diaza-4,4-diethyltricyclo[5.2.2.$0^{2,6}$]undec-8-ene (10).** A solution of 6.0 g (25.6 mmol) of **19**[10] in 250 mL of ether was added over 30 min to a stirred slurry of 3.90 g (103 mmol) of $LiAlH_4$ in 250 mL of refluxing ether. After 91 h reflux, 1:1:3 workup gave 5.06 g (96%) of a yellow oil, which gave **10**[27] as a colorless oil upon Kugelrohr distillation: NMR ($CDCl_3$) $\delta$ 6.52 (m, 2 H), 3.57 (br s, 2 H), 2.88 (A of AB, $J_{AB}$ = 9.0 Hz, 2 H), 2.67 (B of AB, 2 H), 2.03 (AA′ of AA′BB′, $J_{AB}$ = 9.0 Hz, 2 H), 1.66 (q, $J$ = 8 Hz, 2 H), 1.32 (overlapping of q and BB′ of AA′BB′, 4 H), 0.8 (overlapping triplets, 6 H); IR (neat) 3040, 2962, 2940, 2879, 2860, 2835, 1680, 1455, 1376, 1362 $cm^{-1}$; UV (hexane) 300 nm ($\epsilon$ 710).

**Variable temperature $^{13}$C NMR** data were collected using a Varian XL-100 spectrometer, as previously described.[8a] Activation parameters for dynamic NMR processes were calculated using rate constants derived from total line shape analysis. The program NMRSIM, written by Michael Chen (Department of Chemistry, University of Wisconsin) using the equations of Reeves and Shaw,[31] was used to generate calculated curves, which were visually compared with the experimental ones. NMRSIM allows simulations where nonbroadening peaks overlap with the broadening ones, and the example of the fits for **6**, in which this feature was used, is shown in Figure 1. The statistical analysis of the errors in the activation parameters employed program DEEJAY, written by G. R. Weisman.[32]

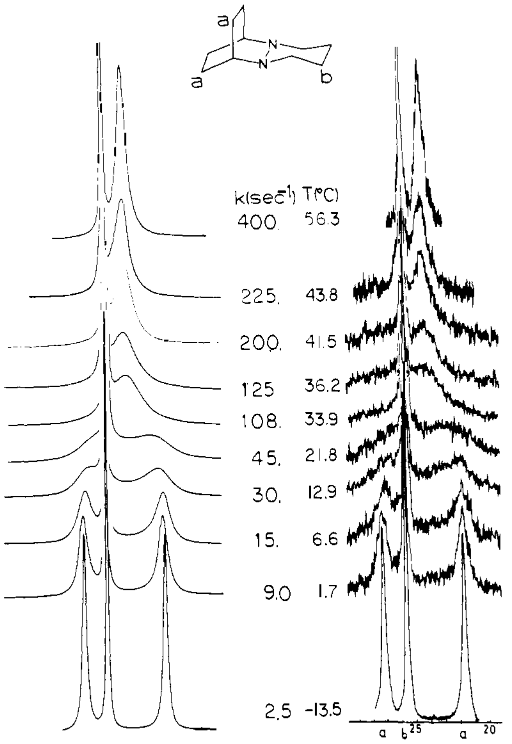


**Figure 1.** Comparison of observed $^{13}$C NMR spectra for carbons A and B of **6** with calculations.

**Photoelectron spectra** were recorded and analyzed as previously reported.[9] **Electrochemical** measurements were made as previously described,[22] employing 0.1 M tetrabutylammonium perchlorate in acetonitrile as the solvent. **Calculations** employed a Harris/7 computer.

**Acknowledgment.** We thank the Advanced Opportunity Fellowship program, the National Science Foundation, and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial financial support of this work. We thank Professor J. W. Taylor for making a copy of MINDO/3 available to us, and Professor P. R. Certain for helping us to reprogram it to the Harris computer. We thank Michael Chen for assistance in using his program, NMRSIM. We thank V. E. Peacock for determination of the PE spectrum of **6**, and E. L. Clennan for the $^{13}$C NMR study of **10**.

## References and Notes

(1) Shvo, Y. In "The Chemistry of Hydrazo, Azo, and Azoxy Groups", Part 2; Patai, S., Ed.; Wiley: New York, 1975; pp 1017–1095.

(2) (a) Nelsen, S. F.; Weisman, G. R. *J. Am. Chem. Soc.* **1976**, *98*, 3281. (b) Nelsen, S. F. *Acc. Chem. Res.* **1978**, *11*, 14.

(3) (a) Nelsen, S. F.; Echegoyen, L.; Evans, D. H. *J. Am. Chem. Soc.* **1975**, *97*, 4930. (b) Nelsen, S. F.; Echegoyen, L.; Clennan,E. L.; Evans, D. H.; Corrigan, D. A. *Ibid.* **1977**, *99*, 1130. (c) Nelsen, S. F.; Clennan, E. L.; Evans, D. H. *Ibid.* **1978**, *100*, 4012.

(4) Nelsen, S. F.; Hollinsed, W. C.; Calabrese, J. C. *J. Am. Chem. Soc.* **1977**, *99*, 4461.

(5) Anderson, J. E.; Lehn, J. M. *J. Am. Chem. Soc.* **1967**, *89*, 81.

(6) Lehn, J. M. *Fortschr. Chem. Forsch.* **1971**, *15*, 311.

(7) Nelsen, S. F. *J. Am. Chem. Soc.* **1974**, *96*, 5669.

(8) (a) Nelsen, S. F.; Weisman, G. R. *J. Am. Chem. Soc.* **1976**, *98*, 1842. (b) Nomura, Y.; Masi, N.; Takeuchi, Y. *J. Chem. Soc., Chem. Commun.* **1974**, 288.

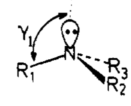
(9) Nelsen, S. F.; Buschek, J. M. *J. Am. Chem. Soc.* **1974**, *96*, 6987.

(10) Stetter H.; Woernle, P. *Justus Liebigs Ann. Chem.* **1969**, *724*, 150.

(11) Dalling, D. K.; Grant, D. M. *J. Am. Chem. Soc.* **1974**, *96*, 1874, and references cited therein.

(12) $\omega = 2 \arctan ((\tan (\alpha_{CNC}/2))/(\sin \beta_{NN}))$, where $\alpha_{CNC}$ is the $C_1N_2C_3$ bond angle and $\beta_{NN}$ is the angle between the $N_2N_3$ bond and the $C_1N_2C_3$ plane.

(13) For calculation of $f_p$, see: Atkins, P. W.; Symons, M. C. R. "The Structure of Inorganic Radicals", American Elsevier: New York, 1967; App. 4. Where $\gamma$ is the lone pair axis, NR bond angle (see IV), and $\alpha_{av}$ the average CNC angle, $\gamma = \arccos(-((2 \cos \alpha + 1)/3)^{1/2})$, $\lambda^2 = ((\cos^2 \gamma)^{-1} - 3)/2$, and $f_p = \lambda^2/(1 + \lambda^2)$.



IV

(14) Altona, C.; Sundaralingam, M. *J. Am. Chem. Soc.* **1970**, *92*, 1995.

(15) Eliel, E. L.; Bailey, W. F.; Kopp, L. D.; Willer, R. L.; Grant, D. M.; Bertrand, R.; Christensen, K. A.; Dalling, D. K.; Durch, M. W.; Wenkert, E.; Schell, F. M.; Cochran, D. W. *J. Am. Chem. Soc.* **1975**, *97*, 322.

(16) Nelsen, S. F.; Clennan, E. L. *J. Am. Chem. Soc.* **1978**, *100*, 4004.

(17) Scharpan, L. H.; Wollrab, J. E.; Ames, D. P. *J. Chem. Phys.* **1968**, *49*, 2368. See also: Lambert, J. B. *Acc. Chem. Res.* **1971**, *4*, 87.

(18) (a) Yokozeki, A.; Kuchitsu, K. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 2356. (b) *Ibid.* **1971**, *44*, 1783.

(19) Bischof, P.; Hashmall, J. A.; Heilbronner, E.; Hornung, V. *Helv. Chim. Acta* **1969**, *52*, 1745.

(20) Wagner, J.; Wajnarowski, W.; Anderson, J. E.; Lehn, J. M. *Tetrahedron* **1969**, *25*, 657.

(21) Nelsen, S. F.; Hollinsed, W. C.; Kessel, C. R.; Calabrese, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 7876.

(22) (a) Nelsen, S. F.; Peacock, V. E.; Weisman, G. R. *J. Am. Chem. Soc.* **1976**, *98*, 5269. (b) Nelsen, S. F.; Peacock, V. E.; Kessel, C. R. *Ibid.* **1978**, *100*, 7017. (c) Nelsen, S. F.; Kessel, C. R.; Brace, H. N. *Ibid.*, in press.

(23) Taft, R. W.; Taagepera, M.; Abbourd, J. L. M.; Wolf, J. F.; DeFrees, D. J.; Hebre, W. J.; Bartness, J. E.; McIver, R. T. Jr. *J. Am. Chem. Soc.* **1978**, *100*, 7765.

(24) Nelsen, S. F.; Weisman, G. R.; Hintz, P. J.; Olp, D.; Fahey, M. R. *J. Am. Chem. Soc.* **1974**, *96*, 2916.

(25) Clement, R. A. *J. Org. Chem.* **1962**, *27*, 115.

(26) Feuer, H.; White, E.; Wyman, J. *J. Am. Chem. Soc.* **1958**, *80*, 3791.

(27) Empirical formula established by mass spectroscopy.

(28) Corey, E. J.; McCaully, R. J.; Sachdev, H. W. *J. Am. Chem. Soc.* **1970**, *92*, 2476.

(29) Kealy, T. J. *J. Am. Chem. Soc.* **1962**, *84*, 966.

(30) Drew, K. D. H.; Hatt, H. H. *J. Chem. Soc.* **1937**, 16.

(31) Reeves, L. W.; Shaw, K. N. *Can. J. Chem.* **1970**, *48*, 3641.

(32) For a listing, see: Weisman, G. R. Ph.D. Thesis, University of Wisconsin, 1976, pp 375–380.