Effects of CNN Bond Angle Restriction in 2,3-Diazabicyclo[2.1.1]hexane Derivatives on Nitrogen Inversion Barrier, Ease of Oxidation, and Acidity

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Restriction of the CNN angle of triazolidinedione **3** by the presence of the diazabicyclo[2.1.1]hexyl system causes the nitrogens to be more pyramidal than tetrahedral (α(av) for crystalline **3** is 109.2°) and produces a double nitrogen inversion barrier of 8.7 kcal/mol at −72 °C in CD_2Cl_2. Although the pyramidality at N in tricyclic triazolidinedione derivatives experimentally lies near the prediction by PM3 semiemprical calculations, such calculations give barriers to double nitrogen inversion that are considerably too high. The effect of enlarging the size of the fused bicyclic system on ease of oxidation was determined: **3**, $E^{\circ\prime}$ + 1.77 V [VIP = 8.77 eV]; **5**, 1.53 [8.68]; **6**, 1.32 [8.60]; **7**, 1.32 [8.15]; **8**, 1.31 [7.90]. VIP values for azo compound **4** from PE spectroscopy are 9.3, 11.1, and 12.1 eV. The acidity of protonated bicyclic azo compounds varies 5.1 pK units between **4** (pK_a −2.1) and **12** (pK_a +3.0).

Introduction

Dougherty and co-workers[1] showed that bicyclobutane (**1**) and 4-methyl-1,2,4-triazoline-3,5-dione (**2**) react in hexane to produce the diazabicyclo[2.2.1]hexane-fused triazolidinedione **3** and converted **3** to diazabicyclohexene **4**. The diazabicyclohexyl units of **3** and **4** restrict their NNC bond angles significantly. In this paper the structure of **3** and the effects of NNC bond angle restriction upon the nitrogen inversion barrier and ease of oxidation of bicyclic fused triazolidinediones and upon the basicity and ease of oxidation of bicyclic azo compounds are studied by comparison of the properties of **3** and **4** with compounds having larger diazabicyclic systems.


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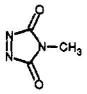

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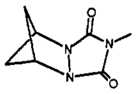

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Results and Discussion

Diazabicycloalkyl-Fused Triazolidinediones. The heavy atom bond lengths and bond angles determined for **3** by X-ray crystallography are shown in Figure 1, and an ORTEP drawing of the structure is given as Figure 2. The bridgehead nitrogens are strongly pyramidal, with the average of the heavy atom bond angles at the bridgehead nitrogens, α(av), being 109.2° and the dihedral angle between the (H)CN,NC(H) and (O)CN,NC(O) planes being 53.9°. Although the bridgehead nitrogens of **3** are acylated, they are strongly pyramidal and are bent past the 109.5° α(av) for tetrahedral geometry at nitrogen.

The ^{13}C NMR spectrum of **3** shows two CH_2 signals at low temperature, as expected when double nitrogen inversion is slow on the NMR time scale. Dynamic NMR experiments in CD_2Cl_2 at 12 temperatures between −104 and −44 °C gave a double nitrogen inversion barrier, which we shall call $\Delta G^{\ddagger}$(N) (at −72 °C, the coalescence temperature) of $8.7_2 \pm 0.05$ kcal/mol, $\Delta H^{\ddagger}(N) = 7.8 \pm 0.5$ kcal/mol, $\Delta S^{\ddagger}(N) = -4.2 \pm 2.4$ cal/deg-mol (eu), extrapolated $\Delta G^{\ddagger}(+25\ °C) = 9.2 \pm 0.3$ kcal/mol.

Table I. Observed and Calculated Geometries for Bicyclic-Fused Triazolidinediones and Calculated Inversion Barriers

compound	3	5[a]	6U[a]
fused bicyclic ring	[2.1.1]	[2.2.1]	[2.2.2]
α(av), deg; X-ray	109.2	110.7	113.2
MNDO	111.0	111.4	114.5
AM1	107.9	108.9	111.2
MNDO-PM3	109.7	110.6	112.9
d(NN), Å; X-ray	1.469	1.467	1.433
MNDO	1.412	1.404	1.397
AM1	1.449	1.434	1.417
MNDO-PM3	1.540	1.519	1.498
d(HC–N), Å; X-ray[b]	1.487/6	1.492/2	1.493/1
MNDO	1.516	1.510	1.501
AM1	1.512	1.513	1.492
MNDO-PM3	1.512	1.511	1.498
d(OC–N), Å; X-ray[b]	1.392/5	1.391/2	1.389/6
MNDO	1.448	1.449	1.447
AM1	1.477	1.480	1.481
MNDO-PM3	1.454	1.455	1.455
ΔH_f,[c] MNDO	−1.9	−35.6	−51.5
AM1	+72.1	+20.2	−8.4
MNDO-PM3	−6.1	−44.6	−61.2
$\Delta H^{\ddagger}$ (N),[c] MNDO	12.4	10.6	6.1
AM1	23.9	21.3	15.8
MNDO-PM3	15.5	13.5	9.9

[a] X-ray data from ref 5. [b] Average of two chemically equivalent bond lengths. The number after the slash is the difference between the two, in the third place. [c] Units, kcal/mol.

The rather high double nitrogen inversion barrier for **3** is presumably caused by CNN angle restriction imposed by the triazolidinedione and bicyclo[2.1.1]hexyl rings fused at the nitrogens and the necessity of flattening at both nitrogens at once. The barrier for **3** lies between those determined for N-COX substituted aziridines with strongly electron donating X substituents: Anet and Osyany measured $\Delta G^{\ddagger}(T_c)$ values of 7.1 kcal/mol (−138 °C) for N-COOMe and 9.9 (−86 °C) for N-$CONMe_2$ over 20 years ago,[2] although four *N*-benzoyl derivatives including the *p*-methoxy compound had barriers too low to measure, estimated at under 6 kcal/mol.[3] We have considered the question of how angle restriction affects the nitrogen in-

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(1) Chang, M. H.; Jain, R.; Dougherty, D. A. *J. Am. Chem. Soc.* **1984**, *106*, 4211.
(2) Anet, F. A. L.; Osyany, J. M. *J. Am. Chem. Soc.* **1967**, *89*, 352.
(3) Boggs, G. R.; Gerig, T. J. *J. Org. Chem.* **1969**, *34*, 1489.

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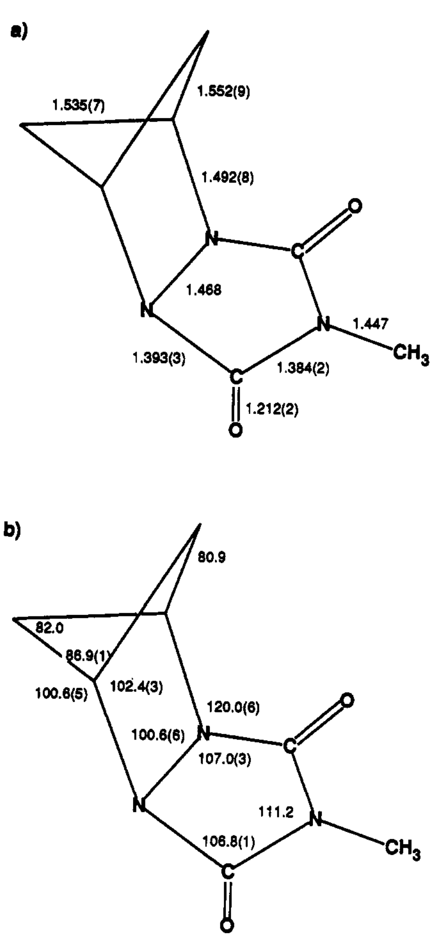
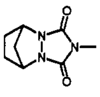


Figure 1. (a) Bond lengths and (b) bond angles for crystalline **3** by X-ray crystallography. Numbers in parentheses are different in the last place quoted for the quantities shown at chemically equivalent positions.

version barriers for diazabicycloalkyl fused triazolidinediones by carrying out semiempirical MO calculations[4] on **3** and the less restricted homologous compounds **5**–**8**.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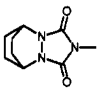
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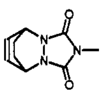
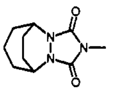

6U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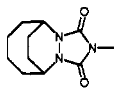
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Amide nitrogen geometries are treated rather poorly by such calculations, as shown by the comparison of the available X-ray data for **3**, **5**,[5] and **6U**[5] with calculated results in Table I. We note that the bond lengths about the bridgehead nitrogen atoms are not very good by any of these methods. The NN bond is too short by MNDO and AM1 (presumably indicating not enough repulsive interaction between the nitrogen lone pairs) but too long by MNDO-PM3 and the N–CO bond too long (presumably indicating too little N,C=O interaction) by all three methods. Nevertheless, the experimental amount of pyramidality at N, measured by α(av), lies between the numbers calculated by MNDO and by AM1 and close to the MNDO-PM3 prediction in all three cases. The calculations at least do get the trends right as the bicyclic ring is contracted. The calculated nitrogen inversion barriers, ΔH^{*}(N), are also far too high. Figure 3 shows a plot of calculated ΔH^{*}(N) versus $\Delta\alpha$(av) = 120 − α(av) for **3** and **5**–**8** all calculated in eclipsed forms with the larger bridge syn to the heterocyclic ring. The calculated points have been arbitrarily connected by lines that are continued to the origin, because ΔH^{*}(N) is by definition zero at $\Delta\alpha$(av) = 0°. The calculated barrier increases as smaller bicyclic ring bridges force $\Delta\alpha$(av) to assume larger values, and the slope of a ΔH^{*}(N) versus $\Delta\alpha$(av) plot is predicted to increase as pyramidality at N increases. The experimental point for **3** is also shown in Figure 3, as an asterisk, along with the X-ray $\Delta\alpha$(av) values for **3**, **5**, and **6U**. A linear extrapolation between the origin and the experimental point for **3**, ΔH^{*}(N) of 7.8 ± 0.5 kcal/mol at the X-ray α(av) of 109.2° leads to a prediction of ΔH^{*}(N) = 4.9 ± 0.3 kcal/mol for **6** at the X-ray $\Delta\alpha$(av) value of **6U**. We expect **6** to be somewhat flatter at nitrogen because the triazolidinedione ring would suffer increased steric interactions when the C_5C_6 double bond is saturated. Figure 3 emphasizes graphically that the barrier observed for **3** leads to the prediction that analogues with larger bicyclic rings are predicted not to "freeze out" by NMR at temperatures available to us, which is our experimental result.

Table II. Comparison of Bicyclic Ring Size Effects on Ease of Electron Removal from Triazolidinediones and Sesquibicyclic Hydrazines

compd	$E^{\circ\prime}$ (ΔE_p), V[a]	$E^{\circ\prime} - E^{\circ\prime}$(**6**)	VIP, eV	VIP − VIP(**6**)
	Triazolidinedione Derivatives			
3	1.77 (0.11)	+0.45	8.77	+0.17
5	1.53 (0.08)	+0.21	8.68	+0.08
6	1.32 (0.06)	[≡0]	8.60	[≡0]
7	1.32 (0.06)	0.00	8.15	−0.45
8	1.31 (0.08)	−0.01	7.90	−0.70
compd	$E°$M, V	$E^{\circ\prime} - E^{\circ\prime}$(**6X**)	VIP, eV	VIP − VIP(**6X**)
	Saturated Sesquibicyclic Hydrazines[b]			
3X	−0.02	+0.51		
5X	−0.26	+0.27	6.81	+0.45
6X	−0.53	[≡0]	6.36	[≡0]
6X	−0.53	[≡0]	6.36	[≡0]
7X	−0.55	−0.02	6.31	−0.05
compd	$E^{\circ\prime}$, V	$E^{\circ\prime} - E^{\circ\prime}$(**6Y**)	VIP, eV	VIP − VIP(**6Y**)
	Unsaturated Sesquibicyclic Hydrazines[b]			
3Y	+0.14	+0.39		
5Y	+0.01	+0.26	7.12	+0.40
6Y	−0.25	[≡0]	6.72	[≡0]
7Y	−0.27	−0.02	6.51	−0.21

[a] Room temperature, acetonitrile containing 0.1 M tetrabutylammonium perchlorate, vs SCE. [b] From ref 6.

Changes in the thermodynamics for electron removal for the series of triazolidinediones were examined by determining their formal oxidation potentials, $E^{\circ\prime}$, by cyclic voltammetry. Only the most strained cation radical $3^{\bullet+}$ showed significant decomposition at a 0.2 V/s scan rate, but it became nearly chemically reversible at an 8 V/s scane rate, where the peak-to-peak potential difference was 0.11 V, so $E^{\circ\prime}$ could be determined reasonably accurately for this compound under the same conditions as the others, see Table II. As shown in the third column, contraction of the fused diazabicyclic ring system from the [2.2.2] system of **6** to the [2.2.1] system of **5** raises $E^{\circ\prime}$ by 0.21 V, and the [2.1.1]-fused compound **3** is 0.45 V harder to oxidize than **6**. Expansion of the fused diazabicyclo ring system to that of the [3.2.2] compound **7** and the [4.2.2] compound **8** does not, however, lead to significantly easier electron loss. Strikingly similar patterns of $E^{\circ\prime}$ changes

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[4] (a) MNDO: Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4889, 4907. (b) AM1: Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *Ibid.* **1985**, *107*, 3902. (c) MNDO-PM3: Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 221.

[5] (a) Agmon, I.; Kaftory, M.; Nelsen, S. F.; Blackstock, S. C. *J. Am. Chem. Soc.* **1986**, *108*, 4477. (b) Krow et al. (Krow, G. R.; Lee, Y. B.; Szczapanski, S. W.; Zacharias, D. E.; Bailey, D. B. *Ibid.* **1987**, *109*, 5744) have reported the X-ray structure of the *N*-phenyltriazolidinedione derivative of dihydrodiazasemibullvalene (a 2,3-diazabicyclo[3.3.2]decane derivative), obtaining essentially planar bridgehead nitrogen atoms (α(av) > 119.6°).

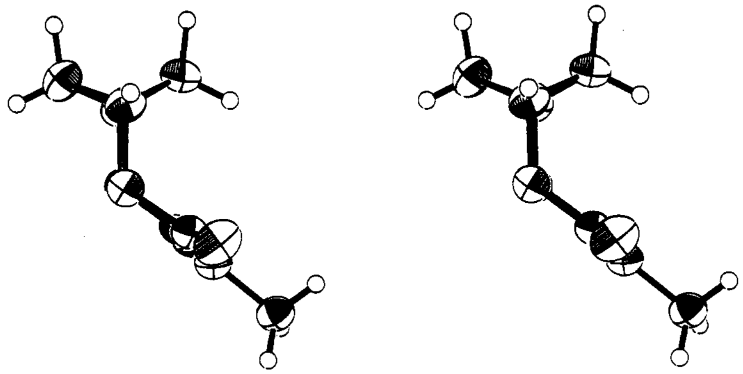


Figure 2. Steroview of the crystal structure of 3.

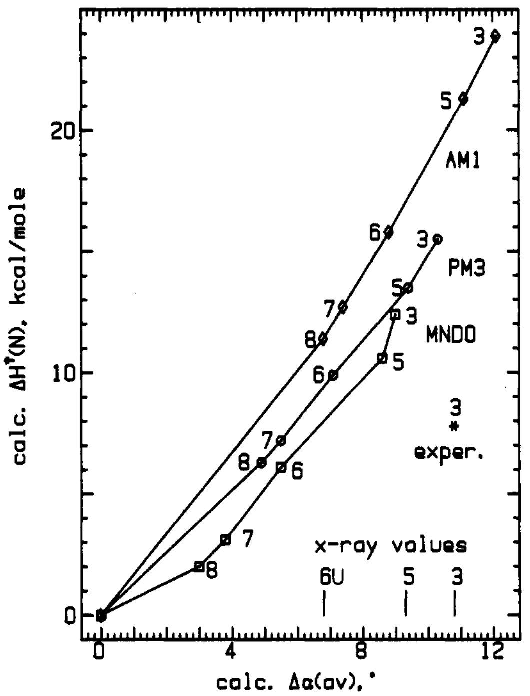


Figure 3. Plot of calculated enthalpies of double nitrogen inversion versus calculated Δα(av) at nitrogen for 3 and 5–8. Diamonds show AM1, circles PM3, and squares MNDO results. The experimenal $\Delta H^{\ddagger}$ of 3 is shown as an asterisk, and values for the X -ray Δα(av) values of 3, 5, and unsaturated 6 are also indicated.

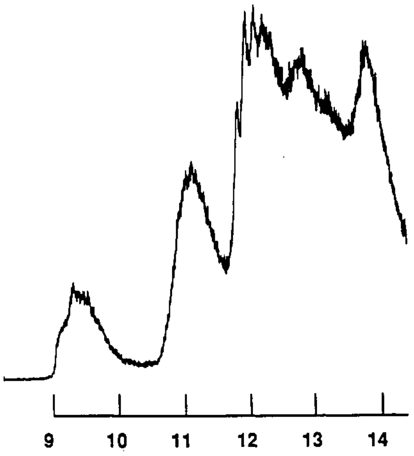
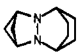


Figure 4. Photoelectron specturm (IP's in eV) of 4.

are exhibited by the two sesquibicyclic hydrazine series previously studied[6] in which the triazolidinedione ring is replaced by a 2,3-diazabicyclo[2.2.2]octane ring (**3X** and homologues) and a 2,3-diazabicyclo[2.2.2]oct-5-ene ring (**3Y** and homologues), respectively, as also shown in Table II. Although replacement of the strongly electron-withdrawing triazolidinedione ring by a hydrocarbon framework has a huge effect on the thermodynamics for electron transfer (electron removal from **6X** 42.7 kcal/mol easier than from **6**, and that from **6Y** is 36.2 kcal/mol easier than from **6**), the effect of changing the fused diazabicycloalkyl system shown on the left side of the structures is remarkably constant.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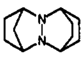
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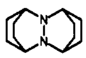
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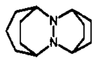
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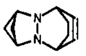
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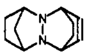
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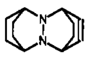
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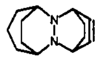
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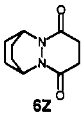
6Z

Photoelectron spectroscopy was used to determine vertical ionization potentials (VIP) for **3** and **5–8**, and results for the first ionization potential are also shown in Table II (see Experimental Section for higher ionization potentials). The large number of lone pair electrons in the triazolidindione rings makes these spectra quite complex, but a broad first ionization band was separated from other bands for these compounds. It is not obvious that this band corresponds to a single ionization in any case, but this band was observed to be rather symmetrical for **3**, **5**, and **6**, although it tailed noticeably on the high IP side for **7** and **8**. We report as VIP in Table II single Gaussian fits to the first ionization band for **3**, **5**, and **6** and the lower IP and larger peak for double Gaussian fits to the tailing bands of **7** and **8**, believing that this procedure determines the first VIP more accurately than attempts at single Gaussian fits. We note that the pattern of VIP values determined by PE spectroscopy does not correspond with the pattern of $E^{\circ\prime}$ values measured; there is clearly a very

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(6) (a) Nelsen, S. F.; Frigo, T. B.; Kim, Y. *J. Am. Chem. Soc.* **1989**, *111*, 5387. (b) We also note that $E^{\circ\prime}$ observed for **6** is the same as that observed for **6Z**, in which the triazolidinedione ring has been replaced by a 2,6-diketo-1,2,4,5-tetrahydropyridazine ring, although VIP for **6Z** is 7.87, 0.73, eV lower than that for **6** (see: Nelsen, S. F.; Blackstock, S. C.; Rumack, D. T. *J. Am. Chem. Soc.* **1983**, *105*, 3115).

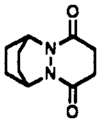

6Z

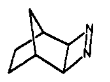
Table III. Comparison of Photoelectron Spectrum of 4 with Those for 9–12

compd	VIP(n_-)[a]	VIP(n_+)[a]	VIP(π)[a,b]	ref
9	8.9_0	10.4_5	11.3_0	7
4	9.3	11.1	12.1 (1070)	this work
10	8.9_0	12.0	11.5_0	7
10	8.82	11.80	11.50 (1050)	8
10	8.96	11.91	11.53 (1300)	9
11	8.32	*c*	10.70 (1200)	9
12	8.07	11.4 ± 0.2	10.60 (1200)	9

[a] Units, eV. [b] Number in parentheses is vibrational fine structure splitting, cm^{-1}. [c] One of two overlapping bands, 11.20/11.37 (two vibrational bands resolved) and 11.45 eV.

significant difference between the vertical ionization potentials and the adiabatic ionization process (plus solvent effects) that determines changes in $E^{\circ\prime}$ for this series of compounds. Previously reported VIP data for the sesquibicyclic hydrazines also are collected in Table II and make it clear that although the $E^{\circ\prime}$ patterns are very similar, the VIP patterns are rather different for the triazolidinediones and the sesquibicyclic hydrazines as bicyclic ring size is changed. VIP only reflects neutral compound geometry effects, while $E^{\circ\prime}$ incorporates both effects of geometry change upon electron loss and solvation change effects. We unfortunately are unable to separate these two effects on the data.

Ionization and Protonation of Azo Compounds. Vertical ionization potentials (VIP) determined from the photoelectron spectrum of **4** (shown in Figure 4) are compared with those for other azo compounds **9–12**[7–9] in Table III. The π band of **4** was assigned as that showing vibrational fine structure of the expected size. The PE spectrum of **4** is more analogous to that of diazetidine **9**[10] than those of the homologous bicyclic azo compounds **10–12** both in the relative positions of the π and symmetric lone pair combination (n_+) bands and the size of the n_-,n_+ splitting, 1.8 for **4** and 1.5_5 for **9**,[8] but 3.0–3.1 for **10**, 2.9–3.2 for **11**, and 3.1–3.5 for **12**.[9]



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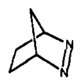

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12

Azo compounds **4** and **9–11** are too weakly basic[11] to allow measurement of their pK_a values of their protonated forms by standard titrimetric methods, and we used the Bunnett–Olsen method,[12] monitoring the difference in bridgehead H chemical shifts from trimethylammonium bisulfate standard as a function of sulfuric acid concentration and relating the difference in bridgehead chemical shifts to the Hammett H_0 values of the solution. **12** proved basic enough to allow its titration versus a glass electrode. The pK_a values for protonated **4** and **9–12** are compared in Table IV.

The principal reason for changes in both VIP and basicity among **4** and **9–12** is presumably the change in CNN angle and NN bond length caused by changing the azo group ring size. Table IV also contains the CNN bond angles from experiment and the molecular mechanics calculations of Kao and Huang[13] and from semiempirical calculations. We note that the pK_a values of protonated **4** and **9** are closer to each other than they are to the larger ring bicyclic azo compounds, in qualitative similarity to the PE spectra. Linear regressions for plots of pK_a versus VIP measured by PE spectroscopy and calculated CNN angle for the data of Table IV show an average residual of 0.6 (VIP) and 0.9 (α by MM1) to 1.0 (α by semiempirical calculation) pK unit on the 5.3 pK unit range covered. Despite the apparently reasonable geometries obtained by semiempirical calculations, the calculated heats of formation are rather poor[14] and not useful for predicting how either VIP or pK_a change with ring size.

Table IV. Acidities of Some Protonated Azo Compounds and Calculated Azo Compound Geometries

			neutral azo compd CNN angle, deg		
compd	pK_a[a]	ϕ[b]	exptl[c]	MM (MM2)[c]	AM1 (PM3)
9	−2.3	+0.20		95.5	97.1 (96.5)
4	−2.1	+0.29		103.6	105.4 (105.4)
10	−1.4[d]	+0.19	108.4	107.6 (107.5)	109.5 (109.2)
11	+0.4[d]	−0.54	115.1	114.0 (114.0)	115.5 (115.4)
12	+3.0[e]			117.2 (117.2)	119.1 (119.2)

[a] For half-protonation. [b] Bunnett–Olsen plot slope.[12] [c] From ref 13a. Numbers in parentheses are calculated by MM2 using the newer constants reported in ref 13b. [d] Reported in ref 11. [e] Determined by titration.

As expected from previous studies on protonated azo compounds,[15] proton NMR indicates that these azo compounds protonate on one nitrogen (presumably at one lone pair), although exchange between the nitrogens is rapid at room temperature in acetonitrile and water. In CD_2Cl_2 $\mathbf{9}H^+BF_4^-$ gives bridgehead hydrogen signals at δ 5.04 and 4.76 and $\mathbf{10}H^+BF_4^-$ shows these signals at δ 5.69 and 5.45 but only an extremely broad peak extending from about δ 5.5 to 5.1 was observed for $\mathbf{4}H^+BF_4^-$.

Conclusion

Although semiempirical calculations do a reasonable job at predicting the changes in pyramidality at nitrogen in triazolidinediones **3** and **5–6** and the geometry at nitrogen in the azo compounds, they are unable to give nitrogen inversion barriers in triazolidinediones, their bond lengths, or ionization potentials and basicity changes in azo compounds at all well. The acidity of protonated azo compounds **4** and **9–12** experimentally varies over a range of 5.3 pK units (corresponding to a 7.2 kcal/mol change in ΔG°), indicating the importance of lone pair hybridization on imino nitrogen basicity.

Experimental Section

All deuterated solvents were commercially purchased, dried over 3A sieves, and used without further purification. ^1H NMR spectra were obtained on a Bruker WP-200, Bruker WP-270, or a Bruker AM-500 spectrophotometer. All chemical shifts are reported in parts per million (ppm) relative to internal tetramethylsilane (TMS). Relaxation delays of at least 5 s were introduced to increase the accuracy of integration. ^{13}C NMR spectra were obtained either on a Bruker AM-360 or a Bruker AM-500 spectrometer at resonance frequencies of 90.136 and 125.76 MHz, respectively. All chemical shifts are reported in ppm relative to

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TMS, and the central line of the deuterated solvent peak was used as the spectral reference. Melting points were obtained on a Hoover Uni-Melt capillary melting point apparatus and are uncorrected. Flash column chromatography was done according to method of Still et al.[16] and except where noted, was done on silica gel. Dichloromethane was distilled either from P_2O_5 or CaH_2. Ethyl acetate and hexane were purchased from Mallinkrodt and used without purification. Palladium on carbon (10%) was purchased from Aldrich chemicals. All other chemicals were purchased from Aldrich chemicals except where noted.

General Procedure for 2 Adducts. A solution of 4-methyltriazoline-3,5-dione (2) dissolved in 15 mL of CH_2Cl_2 was slowly added to a stirred solution of diene dissolved in an additional 5 mL of CH_2Cl_2. The solution was allowed to stir under N_2 for several hours, concentrated under reduced pressure, and flash chromatographed (CH_2Cl_2) to yield analytically pure power. The powder was dissolved in 15 mL of ethyl acetate and 15 mL of hexane and placed in a Parr bottle containing 5 mol % of 10% palladium on carbon. The flask was charged with H_2 at 45 psi unit H_2 uptake ceased. The resulting solution was filtered through Celite and concentrated under reduced pressure to yield a light yellow solid, which was flash chromatographed to yield a white analytically pure powder.

Tetrahydro-2-methyl-5,8-methano-1*H*-[1,2,4]triazolo[1,2-*a*]pyridazine-1,3(2*H*)dione (5). Cyclopentadiene (0.800 g, 12.1 mmol) and 1.36 g (12.1 mmol) of 2 resulted in the formation of 1.67 g (9.22 mmol, 76.2% overall yield) of 5 after column chromatography (CH_2Cl_2): mp 118–119 °C; HRMS for $C_8H_{11}N_3O_2$ 181.0852 (calc), 181.0850 (found); ^1H NMR ($CDCl_3$) 1.6–1.9 (m, 6 H), 3.0 (s, 3 H), 4.5 (br s, 2 H); ^{13}C NMR ($CDCl_3$) 25.11 (CH_3, NCH_3), 27.31 (CH_2, two bridge), 38.05 (CH_2, one bridge), 59.63 (CH, bridgehead), 157.8 (C=O).

Tetrahydro-2-methyl-5,8-ethano-1*H*,5*H*-[1,2,4]triazolo[1,2-*a*][1,2]diazepine-1,3(2*H*)-dione (6). Cyclohexa-1,3-diene (0.400 g, 5.0 mmol) and 0.564 g 95.00 mmol) of 2 resulted in the formation of, after flash column chromatography (CH_2Cl_2), 0.764 g (3.91 mmol, 78.3% overall yield): mp 124–125 °C; HRMS for $C_9H_{13}N_2O_3$ 195.1009 (calc), 195.1007 (found); ^1H NMR ($CDCl_3$) 1.5–2.1 (m, 8 H), 3.03 (s, 3 H), 4.52 (br s, 2 H); ^{13}C NMR ($CDCl_3$) 24.49 (CH_2), 25.06 (NCH_3), 47.79 (CH), 154.03 (C=O).

Tetrahydro-2-methyl-5,9-ethano-1*H*,5*H*-[1,2,4]triazolo-[1,2-*a*][1,2]diazepine-1,3(2*H*)-dione (7). Cyclohepta-1,3-diene (0.5653 g, 6.00 mmol) and 0.6789 g (6.00 mmol) of 2 resulted in, after flash column chromatography (1:1 CH_2Cl_2/Et_2O), 0.284 g (49.4% overall yield) of 7: mp 128–130.5 °C; HRMS for $C_{10}H_{15}N_2O_3$ 209.1165 (calc) 209.1164 (found); ^1H NMR ($CDCl_3$) 1.5–2.1 (m, 10 H), 3.05 (s, 3 H), 4.56 (br s, 2 H); ^{13}C NMR ($CDCl_3$) 19.37 ($CH_2CH_2CH_2$), 22.39 (CH_2), 24.84 (NCH_3), 33.21 (CH_2), 48.51 (CH), 149.96 (C=O).

Hexahydro-2-methyl-5,10-ethano-1*H*-[1,2,4]triazolo[1,2-*a*][1,2]diazocine-1,3(2*H*)-dione (8). Cycloocta-1,3-diene (0.7800 g, 7.21 mmol) and 0.8155 g of 2 (7.21 mmole) resulted in, after flash column chromatography (1:1 CH_2Cl_2/Et_2O), 0.977 g (4.4 mmol, 60.7% overall yield) of 8: mp 131–133 °C; HRMS for $C_{11}H_{17}N_3O_2$ 223.1322 (calc), 223.1319 (found); ^1H NMR ($CDCl_3$) 1.5–2.1 (m, 12 H), 3.08 (s, 3 H), 4.60 (br s, 2 H); ^{13}C NMR ($CDCl_3$) 19.37 (CH_2), 22.82 (CH_2), 23.24 (CH_2) 25.00 (NCH_3), 34.70 (CH_2), 47.92 (CH), 149.52 (C=O).

4-Methyl-1,2,4-triazoline-3,5-dione (2). A modification of the procedure of Cookson et al.[17] was used. A slurry of 4-methylurazole (5 g, 43.4 mmol) in 100 mL of CH_2Cl_2 was cooled to 0 °C. With rapid stirring, 4.71 g (43.4 mmol) of pre-cooled *tert*-butyl hypochlorite[18] was slowly added to the solution over the course of 3 h and allowed to stir an additional hour after addition was complete. The solution was concentrated to yield 4.87 g (43.1 mmol, 99% yield) of crmine red crystals of near analytical purity.

Inversion Barrier of 4-Methyl-2,4,5-triazatricyclo-[5.1.1.0^{2,6}]nonane-3,5-dione (3). ^{13}C NMR δ (CD_2Cl_2, −104 °C) 61.9 (CH), 37.6 and 42.2 (CH_2), 25.5 (CH_3); *T* °C (double nitrogen inversion rate constant, s^{-1}, determined by digital simulation[19]) $-104._2$ (35), $-99._2$ (59), $-94._7$ (96), $-88._6$ (202), $-81._9$ (450), $-77._1$ (840), $-71._9$ (1020), $-66._5$ (2000), $-62._2$ (4000), $-57._1$ (8000), $-51._9$ (11 000), $-43._8$ (16 000). These data give an Eyring plot with a correlation coefficient of −0.9958. Analysis of these data by Program DEEJAY[20] at the 95% confidence level with a transmission coeffficient of 1 gave the statistical errors in activation parameters quoted in the text.

Table V. Atomic Coordinates for Non-Hydrogen Atoms (×10^4) and Hydrogen Atoms (×10^3)[a]

atom	*x*	*y*	*z*	U_{eq}
O(1)	−557 (2)	5883 (3)	3868 (3)	48 (1)
O(2)	2840 (2)	6105 (3)	3592 (3)	51 (1)
N(1)	549 (2)	5416 (3)	2168 (3)	37 (1)
N(2)	1134 (2)	6305 (3)	3972 (3)	36 (1)
N(3)	1641 (2)	5503 (3)	2073 (3)	38 (1)
C(1)	413 (3)	4144 (4)	1852 (4)	44 (1)
C(2)	1115 (3)	4028 (5)	667 (5)	51 (1)
C(3)	1909 (3)	4280 (4)	1734 (4)	43 (1)
C(4)	1254 (3)	3561 (4)	2692 (5)	44 (1)
C(5)	274 (3)	5857 (3)	3398 (4)	36 (1)
C(6)	1974 (3)	5981 (3)	3265 (4)	34 (1)
C(7)	1154 (3)	6874 (4)	5251 (5)	43 (1)
				U_{iso}
H(1)	−27 (4)	390 (4)	193 (5)	5 (1)
H(21)	122 (3)	325 (5)	31 (5)	5 (1)
H(22)	106 (3)	452 (4)	−4 (5)	3 (1)
H(3)	257 (3)	418 (3)	168 (4)	3 (1)
H(41)	125 (4)	270 (5)	260 (5)	6 (1)
H(42)	130 (3)	376 (4)	363 (5)	5 (1)
H(71)	129 (4)	630 (5)	583 (6)	6 (1)
H(72)	129 (4)	761 (6)	525 (5)	6 (2)
H(73)	39 (6)	705 (6)	561 (7)	10 (2)

[a] $U_{eq} = {}^1/_3$ trace U (Å × 10^3), U_{iso} (Å × 10^2).

Tablve VI. Bond Lengths (Å) and Angles (deg)

Bond Lengths			
O(1)–C(5)	1.210 (4)	N(2)–C(7)	1.447 (5)
O(2)–C(6)	1.214 (4)	N(3)–C(3)	1.484 (5)
N(1)–N(3)	1.469 (3)	N(3)–C(6)	1.395 (4)
N(1)–C(1)	1.500 (5)	C(1)–C(2)	1.528 (6)
N(1)–C(5)	1.390 (4)	C(1)–C(4)	1.560 (6)
N(2)–C(5)	1.387 (4)	C(2)–C(3)	1.542 (6)
N(2)–C(6)	1.382 (4)	C(3)–C(4)	1.543 (6)
Bond Angles			
N(3)–N(1)–C(1)	100.0 (2)	C(1)–C(2)–C(3)	82.0 (3)
N(3)–N(1)–C(5)	107.3 (2)	N(3)–C(3)–C(2)	99.8 (3)
C(1)–N(1)–C(5)	120.6 (3)	N(3)–C(3)–C(4)	102.7 (3)
C(5)–N(2)–C(6)	111.2 (3)	C(2)–C(3)–C(4)	86.9 (3)
C(5)–N(2)–C(7)	123.7 (3)	C(1)–C(4)–C(3)	80.9 (3)
C(6)–N(2)–C(7)	124.5 (2)	O(1)–C(5)–N(1)	127.1 (3)
N(1)–N(3)–C(3)	101.1 (2)	O(1)–C(5)–N(2)	126.2 (3)
N(1)–N(3)–C(6)	106.7 (2)	N(1)–C(5)–N(2)	106.7 (2)
C(3)–N(3)–C(6)	119.4 (3)	O(2)–C(6)–N(2)	127.3 (3)
N(1)–C(1)–C(2)	100.1 (3)	O(2)–C(6)–N(3)	125.8 (3)
N(1)–C(1)–C(4)	102.1 (3)	N(2)–C(6)–N(3)	106.9 (2)
C(2)–C(1)–C(4)	86.8 (3)		

Crystallography of 3: orthorhomic, space group *Pccn*, a = 13.392 (7), b = 11.433 (6), and c = 10.098 (5) Å, the calculated density for $Z = 8$ is 1.437 g/cm^3. The structure was solved by MULTAN80[21] and refined by SHELX.[22] The refinement was performed by a full-matrix least-squares procedure anisotropically for the heavy atoms, isotropically for the H atoms. The agreement factors are $R = 0.082$ and $R_w = 0.096$ for the 1078 observed reflection [$F_o > 1.5\sigma(F_o)$] (out of 1322 unique reflections). {$w = 1.0[\sigma(F_o + 0.0787(F_o)^2$}. Atomic coordinations and heavy atom

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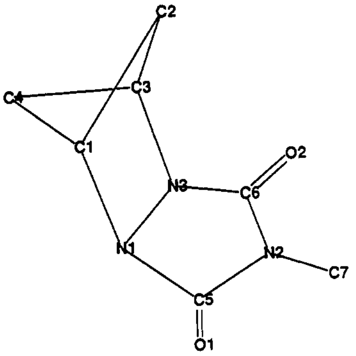
Table VII. Photoelectron Spectroscopic Data for Bicyclic Fused Triazolidinediones

compd	VIP, eV (width at half height, eV) [rel intensity][a]
3	{8.60 (0.50) [1.0], 9.00 (0.40) [1.0]} {10.15 (0.60) [1.0], 11.00 (0.70) [1.0]}
5	{8.48 (0.50) [1.0], 8.90 (0.55) [1.0]} {10.12 (0.60) [1.0], 11.07 (0.45) [1.0]}
6	{8.42 (0.45) [1.0], 8.78 (0.53) [1.2]} {10.15 (0.50) [1.0], 11.05 (0.35) [0.7]}
7	{8.15 (0.55) [1.0], 8.55 (0.55) [0.25]} {9.81 (0.45)}
8	{7.90 (0.50) [1.0], 8.25 (0.60) [0.5]} {9.64 (0.50)} {10.85 (0.30) [1.0], 11.25 (0.40) [1.9]}

[a] Regions fit together are enclosed in braces.

bond lengths and bond angles are listed in Tables V and VI, respecitvely, using the crystallographic numbering system shown below:



pK_a Determination of Azo Compounds. Reagent-grade concentrated sulfuric acid was standardized by titration with standardized NaOH solution and diluted by weight with triply distilled water to make solutions of lesser concentration. Azo compounds (0.1 mmol) and 80 mg of $Me_3NH^+HSO_4^-$ as reference were dissolved in 10 mL of each concentration of aqueous H_2SO_4, and proton NMR spectra were obtained on the solutions. A Bunnett-Olsen[12] analysis was used, in which pK_a is the intercept of plot of log (I) + (H_0 versus H_0 + log (C_H+), where H_0 is the Hammett acidity function, C_{H^+} the concentration of H$^+$, and I is the ionization ratio, assumed to be $(\delta_n - \delta_o)/(\delta_o - \delta_{nH^+})$, where δ_n is the observed chemical shift of neutral azo compound, δ_{nH^+} that of fully protonated azo compound, the δ_o the chemical shift observed in a given solution. Percentages of sulfuric acid required for half-protonatin were found to be 47 (**9**), 42 (**4**), 29 (**10**), and 4 (**11**). **12** was too basic to use the NMR method, and it was titrated potentially in 0.1 M tetraethylammonium perchlorate using 0.01 M $HClO_4$, on an Orion 811 meter with an Orion 917002 glass electrode.

Photoelectron spectra were run on a Varian IEE-15 spectrometer, modified as previously described.[23] Peak potentials were estimated by superimposing sums of Gaussian curves of adjustable position, width, and intensity over the unsmoothed data points on the screen of an IBM-PC-XT, using locally written software by P.A.P.) based on ASYST programming. The first ionization bands of **3**, **5**, and **6**, although broad, are quite symmetrical, and the VIP values quoted for these compounds in Table II are 0.65–0.7 eV wide single Gaussian fits. For comparison, two Gaussian fits to these data are included in Table VII, along with fits for the other bands up to 11 eV for **3** and **5**–**8**.

Acknowledgment. We thank the National Science foundation for partial support of this work under grants CHE-84-15077 and CHE-88-10588 and the National Institutes of Health under grant GM-29549. We also thank Jocelyn C. Schultz for recording the photoelectron spectrum of **6**. We thank Timothy Clark and James Stewart for supplying the semiempirical programs employed.

Registry No. **2**, 13274-43-6; **3**, 78715-55-6; **3x**, 121574-11-6; **3y**, 121574-10-5; **4**, 72192-13-3; **4** H$^+$, 130408-52-5; **4** H$^+$BF$_4^-$, 121574-09-2; **5**, 54168-24-0; **5x**, 90046-50-7; **5y**, 90046-47-2; **6**, 54168-25-1; **6u**, 78790-57-5; **6x**, 90046-49-4; **6y**, 90046-42-7; **7**, 54168-26-2; **7x**, 121574-15-0; **7y**, 121574-13-8; **8**, 54168-19-3; **9**, 117066-41-8; **9** H$^+$, 130466-86-3; **9** H$^+$BF$_4^-$, 121652-16-2; **10**, 2721-32-6; **10** H$^+$, 90046-46-1; **10** H$^+$BF$_4^-$, 106875-41-6; **11**, 3310-62-1; **11** H$^+$, 106875-40-5; **12**, 43195-77-3; **12** H$^+$, 130408-53-6; cyclopentadiene, 542-92-7; 1,3-cyclohexadiene, 592-57-4; 1,3-cycloheptadiene, 4054-38-0; 1,3-cyclooctadiene, 1700-10-3; 4-methylurazole, 16312-79-1.

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The Structure of 7,12-Dilithio-7,12-dihydropleiadene: An Investigation by ^{13}C NMR Spectroscopy and MNDO Calculations

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MNDO calculations have been carried out on 7,12-dihydropleiadene dianion, disparkle (point positive charges), and dilithio derivatives. Calculations predict a planar geometry for the dianion in contrast to the neutral hydrocarbon where ring folding results in an angle of ϕ = 122° between the planes containing the two aromatic ring systems. The disparkle derivative, where sparkle represents a point positive charge, is also predicted to be planar with the sparkles located symmetrically over and under the central ring. The dilithio derivative, on the other hand, is predicted to be folded (ϕ = 153°) with significant pyramidalization at the anionic centers. However, when three waters of solvation are included for each lithium, the calculations predict a significantly flatter structure. The ^{13}C NMR spectrum of the dilithio derivative shows alternating upfield shifts, characteristic of highly delocalized anions, with somewhat greater shifts observed in the naphthalene moiety. A slightly nonplanar geometry with sp^2 hybridization is proposed for the dilithio species in solution, with one or both lithiums positioned more closely to the naphthalene ring. Comparison of the ^{13}C NMR data for both the dilithium and dipotassium salts suggests the presence of ion triplets.

The structure of organolithiums, as well as other organometals and carbanions, is of great importance due to the intermediacy of these species in numerous chemical reactions.[2,3] We have been interested in benzannelated,

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