addition of pentane. The reaction conditions are listed in Table I; the physical data of the addition products **5a–e** are listed in Table III.

Addition Products 5f–i. The addition products of *N*-bromophthalimide (**1b**) with the different alkenes **3** were prepared as described above. All reactions were carried out under heterogeneous conditions. Upon completion of the irradiation period (Table II) the volatiles were removed by vacuum distillation, and the solid residue was extracted with CCl_4, in which unreacted *N*-bromophthalimide and phthalimide are virtually insoluble. The CCl_4 washes were collected and filtered, and the solvent was removed under vacuum. The residue was taken up in CCl_4 and chilled, and pentane was added until precipitation began. Crystallization was done twice. The physical properties of the addition products **5f–i** are summarized in Table IV.

Competition Procedure. The competition reactions were carried out as in the syntheses with *N*-bromo-3,3-dimethylglutarimide 1a. The solid residue after evaporation of the volatiles under high vacuum was dissolved in $CDCl_3$ and investigated by NMR, with hexamethyldisiloxane as internal standard.

With the *N*-bromophthalimide (**1b**) the solids were extracted with $CDCl_3$, filtered, and the filtrate was investigated by NMR, with hexamethyldisiloxane as internal standard.

Kinetic Experiments. A mixture of 0.20 mmol of 33DMNBG (**1a**), 0.23 mmol of 2-chloropropene (**3d**), 1 mL of CD_2Cl_2, and 100 μL of a 0.085 M TBPO solution in CH_2Cl_2 was degassed in a NMR tube by using a freeze–pump–thaw technique 5 times. The NMR tube was sealed, and the reaction was monitored by NMR at 35 °C for 2.5 h.

A similar experiment with ethylene (**3a**) was carried out by using 0.14 mmol of 33DMNBG (**1a**), 0.4 mmol of ethene (**3a**), 0.9 mL of CD_2Cl_2, and 0.3 μmol of TBPO. The ethyne concentration in solution was determined by NMR.

The results are summarized in Table XI.

Competition between Cyclohexane and Ethene. A mixture of 550 μmol of 33DMNBG (**1a**), 5 mL of CH_2Cl_2, 4.6 mmol of cyclohexane, and 1.51 mmol of ethene (**3a**) were degassed 5 times in a 30-mL Pyrex pressure tube by freeze–pump–thaw cycles. UV irradiation with a 400-W mercury arc at 11 °C through Pyrex at a distance of 5 cm for 9 min led to 140 μmol of addition product **5a** and 370 μmol of bromocyclohexane. The concentration of ethene (**3a**) in solution (0.15 M, 0.84 mmol) was calculated by Henry's law by using solubilities for similar solvents (0.013 mol fraction per bar). The relative rate constant was calculated to be $k(C_6H_{12}/C_2H_4) = 0.55$.

Acknowledgment. This work was carried out with financial support from the National Science Foundation and the PRF fund of the American Chemical Society. U.L. thanks the Alexander von Humboldt Foundation for a partial stipendium from the Lynen Fund.

Registry No. **1a**, 66393-63-3; **1b**, 2439-85-2; **3a**, 74-85-1; **3b**, 108-05-4; **3c**, 557-98-2; **3d**, 115-11-7; **3e**, 558-37-2; **5a**, 101079-07-6; **5b**, 101079-10-1; **5c**, 101079-11-2; **5d**, 101079-09-8; **5e**, 101079-08-7; **5f**, 101079-12-3; **5g**, 101079-13-4; **5h**, 101079-14-5; **5i**, 101079-15-6; $CH_2{=}CCl_2$, 75-35-4; $Cl_2C{=}CCl_2$, 127-18-4; cyclohexane, 110-82-7; benzene, 71-43-2; fumaronitrile, 764-42-1; maleic anhydride, 108-31-6; neopentane, 463-82-1.

Oxidation of Molecules Containing Two Tetraalkylhydrazine Units

Stephen F. Nelsen* and Mark R. Willi

S. M. McElvain Laboratories of Organic Chemistry, Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706

John M. Mellor and Neil M. Smith

Department of Chemistry, The University, Southampton S09 5NH, U.K.

Received September 10, 1985

Cyclic voltammetry studies have been carried out on several bishydrazines. $Me_2NNMe(CH_2)_nNMeNMe_2$, n = 2–4 (**2–4**), and 1,4-bis(dimethylamino)piperazine (**11**) have only a small separation between their first and second oxidation potentials and give dications which are short-lived in solution (lifetimes below a few milliseconds). In contrast, pentacyclic bishydrazine **14** and tetracyclic bishydrazines **16** and **17** have formal potentials that differ by 0.29, 0.21, and 0.19 V, respectively, and give dications which are long-lived in solution (their lifetimes exceed seconds). Hexacyclic bishydrazines **12** and **13** have a much larger separation in formal potentials for oxidation and give short-lived dications. The shapes of the tetracyclic and pentacyclic compounds are discussed, as is the implication of these results for the consideration of a hydrazine radical cation interacting with a neutral hydrazine.

Considerable study has established that electron loss from tetraalkylhydrazines (R_4N_2) has most unusual thermodynamic and kinetic features.[1] The relative thermodynamics of electron loss may be conveniently established by cyclic voltammetry (CV) for a wide range of R groups because the oxidized form $R_4N_2^+$ is usually long-lived in the presence of the basic neutral form. The effects of changing R groups are notably large; $R_4N_2,R_4N_2^+$ couples covering a $\Delta G°$ range of 30 kcal/mol are known. This occurs because there is a large difference in preferred geometry for the two oxidation states. Neutral R_4N_2 has a strong preference for pyramidal nitrogen atoms (lone pair hybridization about sp^3) and a weak preference for perpendicular lone pairs (lone pair, lone pair dihedral angle $\theta = 90°$). The oxidized form $R_4N_2^+$ has a strong preference for coplanar lone pair orbitals ($\theta = 180°$ or $0°$) and a weak preference for planar nitrogen atoms (lone pair hybridication about pure p). Geometrical demands of the R groups, especially in cyclic systems, can substantially strain either the reduced or oxidized form, leading to the large effects observed on $\Delta G°$. Electron transfer is also unusually slow for $R_4N_2,R_4N_2^+$ couples. The large change in geometry at the hydrazine nitrogens upon electron transfer results in the electron-transfer transition state being considered distorted from the equilibrium geometry of either

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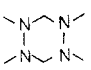
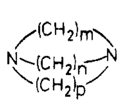
[1] (a) Nelsen, S. F. *Acc. Chem. Res.* **1981**, *14*, 131. (b) Nelsen, S. F. "Hydrazine, Hydrazine Cation Electron Transfer Reactions" *Molecular Structures and Energetics*; Liebman, J. F., Greenberg, A., Eds.; VCH: Deerfield Beach, FL, 1986; Vol. 3, Chapter 1, in press.

0022-3263/86/1951-2081$01.50/0

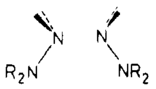
the neutral species or the cation radical. The ESR spectrum of the cation from **1** has shown that its spin is localized on one of the hydrazine units, and that electron transfer between hydrazine units is too slow to observe on the ESR time scale despite the fact that the hydrazine units are held close to each other.[2] The electrochemistry of **1** analogues is complicated because of their high barriers between conformations[3] and the sensitivity of heterogeneous electron-transfer rates in six-membered ring hydrazines to conformational effects.[4]


1

One factor that might slow intramolecular electron transfer for **1** is its inability to achieve geometries in which σ overlap between the nitrogens of the hydrazine units can occur. Alder's group[5] has shown that σ (end on) overlap between the lone pair orbitals of an amine radical cation and an amine is substantially stabilizing. For example, diamines such as I[*mnp*] are much easier to oxidize than monoamine models and give isolable cation radicals in some cases; I[444] has recently been shown by X-ray crystallography to have equivalent nitrogens and a "3e-σ bond" between the nitrogen atoms.[5b] In this work we have studied the electrochemical oxidation of a series of bishydrazines, hoping to use the thermodynamics of electron transfer determined by cyclic voltammetry to probe for through-space stabilizing interaction between two hydrazines units which can approach each other in σ-overlap geometry. In addition to unoriented bishydrazines linked by a polymethylene chain, we have studied examples in which polycyclic structures enforce σ approach of one hydrazine nitrogen on each hydrazine unit as in II, which could lead to a bis-amino-substituted 3e-σ bonded cation radical III, analogous to Alder's bis-monoamine examples, and also cases in which polycyclic structures enforce symmetrical face-on approach of the hydrazine units, as diagrammed in IV.



I[mnp]



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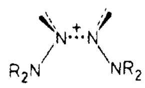

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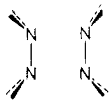
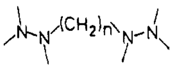


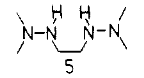
IV

Compound Preparation. The acyclic model compounds **2**–**4** were selected to probe the behavior of unoriented bis(tetraalkylhydrazines). **2** was prepared by Eschweiler–Clarke methylation[6] of bis(trialkylhydrazine) **5**.



2, $n = 2$
3, $n = 3$
4, $n = 4$

The yield of **2** proved remarkably sensitive to conditions (see Experimental Section) and required addition of formalin to a mixture of hydrazine and formic acid. If the reaction mixture was heated, or if the formalin was added before the formic acid, virtually none of the desired product was obtained. We initially tried to prepare **6** as a precursor of **3**, but addition of trimethylhydrazine to methyl acrylate led only to **7**, even upon heating to 200 °C in a sealed tube. In contrast, reaction of trimethylhydrazine with acrylyl chloride gave unsaturated hydrazide **8**, but we could not get the Michael addition to **8** to go in reasonable yield.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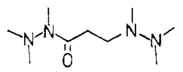
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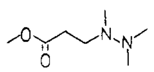
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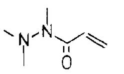
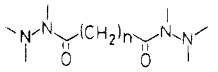
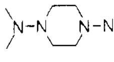

8

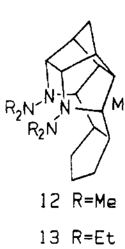
We ended up making **3** and **4** by lithium aluminum hydride reduction of the bishydrazides formed from malonyl and succinyl chloride, **9** and **10**, respectively. The monocyclic bishydrazine **11** was prepared by formalin, sodium cyanoborohydride reductive methylation of *N*,*N*′-diaminopiperidine. We have not observed acceptable yields of dimethylated products from the Eschweiler–Clarke methylation of any *N*,*N*-dialkylhydrazine.



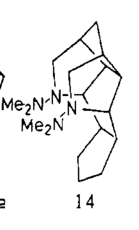
9 n=1
10 n=2


11

Bishydrazines in which the motion of the hydrazine units relative to each other is more restricted because of the presence of polycyclic rings were also studied. Preparations of the hexacyclic compounds **12** and **13** and the pentacyclic hydrazine **14** from the heptacyclic diazetidine **15**, which is conveniently available by the method of Hünig and Bernig,[7] have been previously reported.[8] The hydrocarbon frameworks of these compounds enforce end-on approach of the two hydrazine units with one *N*,*N*′ distance larger than the other, and the *NN*,*N*′*N*′ dihedral angle near 0°, as indicated in II. The tetracyclic com-



12 R=Me
13 R=Et



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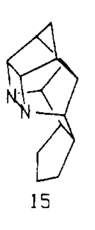

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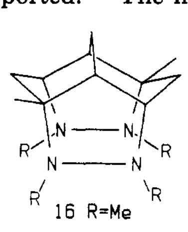

16 R=Me
17 R=Et

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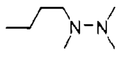
Table I. CV Data for Bishydrazines and Their Models

compd	scan rate, V/s	1st ox. wave $E^{\circ\prime}$ [ΔE_{pp}]^a	2nd wave $E^{\circ\prime}$ [ΔE_{pp}]^{a,b}
2	0.20	0.28 [0.09]	0.41 irrev
	0.50	0.28 [0.09]	0.44 irrev
	20.0	0.29 [0.10]	0.54 irrev
3	0.20	0.28 [0.09]	0.44 [0.08]^c
	0.50	0.28 [0.09]	0.45 [0.09]
	5.0	0.30 [0.13]	0.45 [0.06]
4	0.05	ca. 0.29 [0.09]	0.41 irrev
	0.5		0.43 irrev
18^d	0.20	0.32	
11	0.20	0.42 [0.10]	0.54 irrev
	0.50	0.42 [0.10]	0.55 irrev
	20.0	0.43 [0.10]	0.66 irrev
19^d	0.20	0.36	
12	0.20	0.10 [0.08]	0.88 irrev
13	0.20	0.08 [0.24]	0.90 irrev
14	0.20	0.19 [0.08]	0.48 [0.10]^e
20^d	0.20	0.17	
16	0.10	−0.28 [0.10]	−0.07 [0.15]
	0.20	−0.29 [0.10]	−0.08 [0.16]
	0.50	−0.28 [0.11]	−0.09 [0.19]
17	0.20	−0.16 [0.13]	0.03 [0.11]^f
21^d	0.20	0.07	

[a] Units for potentials, V vs. saturated calomel electrode. Conditions: 2 mM substrate in acetonitrile containing 0.1 M tetra-*n*-butylammonium perchlorate at a planar gold electrode, $\Delta E_{pp} = E_{pa} - E_{pc}$. [b] Waves marked irrev are peak oxidation potentials for totally irreversible waves. [c] A totally irreversible wave was observed at 0.92 V. [d] From: Nelsen, S. F.; Peacock, V. E.; Weisman, G. R. *J. Am. Chem. Soc.* **1976**, *98*, 5269. [e] Totally irreversible waves observed at 0.87 and 1.05 V. [f] A totally irreversible wave was observed at 1.43 V (measured at a planar platinum electrode).

pounds **16** and **17** were prepared from the R = H hydrazine precursor, previously characterized as the tetracetyl derivative[9] (see Experimental Section). The hydrocarbon framework of **16** and **17** encourages face-to-face approach of the hydrazine units as diagrammed in IV.

Acyclic Bishydrazines: Electrochemical Results. Table I summarizes the CV data for the compounds studied. The literature formal potentials for monohydrazines **18–21** are included in Table I as models for the bishydrazines. The electrochemistry of the acyclic bishydrazines **2–4** was found to be disappointingly uninformative because of irreversible decomposition reactions, and this work would almost certainly not have been undertaken if we had examined the acyclic compounds before the polycyclic examples. The first two oxidation waves observed for **2–4** have only a small separation. It is difficult to determine the difference in formal potentials for oxidation quantitatively because the second wave is completely irreversible (no reduction wave is seen for the second oxidation wave even at fast scan rates) for **2** and **4**, and only a tiny reduction wave is observed for **3**. In addition, not even the first oxidation wave shows much reversibility if the oxidation scan includes the maximum of the second oxidation wave. In all three cases, however, the first wave became more reversible if the scan was only carried out just past the maximum of the first wave, and the $E^{\circ\prime}{}_1$ values of Table I are taken from such limited scans. The $E^{\circ\prime}{}_1$ values observed for **2–4** are rather close to that of the monohydrazine model compound **18** (differences in their ΔG° values for electron transfer are under 1 kcal/mol). A bishydrazine with no interaction between the hydrazine units has a statistical factor of 2 for electron loss equilibria relative to a monohydrazine of the same microscopic $E^{\circ\prime}$ value;[10] this will lower the $E^{\circ\prime}$ observed for the bishydrazine by 18 mV (0.4 kcal/mol).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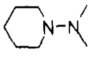
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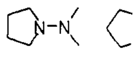
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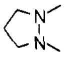
21

Replacing a methylene carbon by a hydrazine nitrogen two or more methylene groups separated from a hydrazine has little effect on the thermodynamics of first electron removal. This result is consistent with little or no thermodynamic stabilization of $R_4N_2^+$ by a nearby unoxidized R_4N_2 unit.

We included bis(dimethylamino)piperazine **11** in the study in the hope that it might show more reversibility in its oxidation behavior. We thought that it might show a bigger difference in standard potential for the oxidations because the oxidized hydrazine unit is linked to the unoxidized one through two two carbon bridges, which might be predicted to increase the electron-withdrawing effect of having the oxidized hydrazine present and raise the second oxidation potential. **11** did prove to be about 60 mV (1.4 kcal/mol) harder to oxidize than its monohydrazine model **19**, which appears to be a small inductive effect, of on the order of 1.8 kcal/mol, because of the statistical factor for **11** vs. **19** oxidation. It is certainly not obvious whether the effect is on the oxidized or reduced forms, or both. Even so, the CV of **11** resembles those of **2** and **4**, and no reversibility was observed for the second oxidation wave.

The irreversibility of the second oxidation waves for the acyclic hydrazines makes determination of $E^{\circ\prime}{}_2$ for the species impossible. Only **3** showed any reversibility at all for the second oxidation wave, and its oxidation waves differed in potential by 135 mV. Extensive attempts at digital simulations of the CV of **3** by the Feldberg method[11] failed to fit the experimental curves very well, despite employing complex kinetic schemes for decomposition (see Experimental Section). We were able to fit the observed oxidation peak difference employing $E^{\circ\prime}{}_2 - E^{\circ\prime}{}_1$ differences of 120–140 mV by varying the kinetics for decomposition and have convinced ourselves that the second oxidation is unlikely to be more than 0.15 V positive of the first for **3**.

Polycyclic Bishydrazines: Electrochemical Results and Discussion. The orientation of the hydrazine units with respect to each other is not restricted in **2–4**, except that the dimethylamino-substituted nitrogens cannot get farther apart than their $(CH_2)_n$ "tether" allows. The situation is quite different for the polycyclic bishydrazines, where only a restricted set of conformations is available to the compounds.

The hexacyclic compounds **12** and **13** differ from acyclic model bishydrazine **2** in that the polycyclic ring system forces them to assume conformations in which the NCCN dihedral angle of the tether is held near 0°. This results in very different electrochemical behavior, in that removal of a second electron from the monocations of **12** and **13** is far more difficult than removal of the first. A single one-electron reversible oxidation wave is observed in the region where hydrazine oxidation is expected, and a second oxidation wave is not observed until the potential is increased about 0.8 V past the first wave. Because the second oxidation wave is totally irreversible, we also do not

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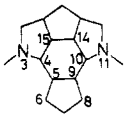
Table II. MM2 Results for Conformations of 22

	conformation		
	22-eclipsed	**22**-closed	**22**-open
rel steric *E*, kcal/mol	2.9	0.4	[0]
NN dist, Å	2.8_3	2.9_1	4.1_8
dihedral angles, deg			
C_6C_5,C_9C_8	0.0	23.7	42.7
$N_3C_4,C_{15}C_{14}$	81.9	79.7	113.5
$N_{11}C_{10},C_{14}C_{15}$	−81.9	−86.8	−102.0

know precisely what the second formal potential is for these compounds, but the decomposition reactions of the dication being so fast suggests that the observed peak potential has been shifted to a value less positive than $E°'_2$, which would mean that $\Delta E°'$ is at least 0.78 V (18 kcal/mol) for **12** and **13**, which is far higher than the approximately 3 kcal/mol observed for **3**, and the difference for the unoriented two carbon bridged analogue **2** may be no larger. Removal of one electron from **12** and **13**, then, substantially "protects" the unoxidized hydrazine from oxidation, which is not observed for the acyclic compounds **2**–**4** or the monocyclic compound **11**. The nitrogens of the two hydrazine units are forced to stay close to each other by the rigid two carbon bridge between the nitrogens of **12** and **13**, and the π-rich oxidized hydrazine spin-bearing orbital is also held in position for good overlap with the C–C bond connecting the hydrazine units. If through-bond interaction of the hydrazine units of the hexacyclic compounds were large enough, one might get a cation radical in which the two hydrazine units have the same geometry and share the positive charge, as is known to occur for the two nitrogens of 1,4-diazabicyclo[2.2.2]octane cation radical.[5a] The ESR spectrum of 12^+, however, shows that this does not occur. The spectrum is not very well resolved but is consistent with nitrogen splittings of 12 and 13 G, six-proton splittings of 13 G (which we assign to the methyl groups on one nitrogen), and a single proton splitting of 15 G, which is only consistent with a structure having the spin and charge localized in one hydrazine unit. The ESR spectrum of 13^+ is even less well resolved but is also consistent with the spin being localized in one hydrazine unit.

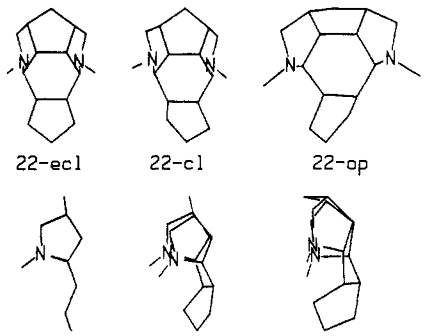
The CV of the pentacyclic compound **14** differs from those of the hexacyclic compounds because of both kinetic and thermodynamic effects. Two completely chemically reversible oxidation waves are seen for **14**. The long lifetime of 14^{2+} provides a great contrast with all bishydrazines previously considered here.

The thermodynamics of **14** oxidation also differ substantially from those of the compounds discussed above. The first and second oxidation potentials of **14** differ by 0.29 V (6.7 kcal/mole). Removal of a second electron is only modestly harder than the first, although $\Delta E°'$ is probably substantially more than in the unoriented four carbon atom bridged bishydrazine **4** (we can only say "probably" because $E°'_2$ is not accurately known for **4**, although the small observed difference in peak potentials of the two oxidation waves is certainly consistent with a $\Delta E°'$ no larger than for **3**). $\Delta E°'$ is much smaller for **14** than it is for the hexacyclic compounds **12** and **13**. As pointed out previously, molecular mechanics calculations on bis(methylamine) **22**, examined as a model for **14**, indicate that conformations with the pyrazolidine nitrogens close together and far apart differ little in energy and interconvert with low barriers. Allinger MM2 calculations[12] on **22** have been redone,[13] and the results appear in Table II, while planar projection of the heavy atom frameworks of two views of each conformation appear in Chart I. The smaller $\Delta E°'$ for **14** than for **12** and **13** is qualitatively expected because the nitrogens in the radical cations will be substantially farther apart in the pentacyclic than in the hexacyclic systems, but we are unable to separate this effect from the lack of the NCCN through bond coupling possible for the hexacyclic systems but not for the pentacyclic compound **14**. We note that $E°'_1$ is 0.09 V (2.1 kcal/mol) lower for **12** than for **14**, which is consistent with some through bond stabilization in 12^+, although possible solvation effects on these potentials and a lack of knowledge of whether the change arises from neutral or cation effects or both make this conclusion less than certain.

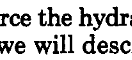


22

Chart I



The ESR spectrum of 14^+ was run, but a satisfactory simulation was not obtained due to the complexity of the spectrum. Oxidizing to the level of the dication led to a sharp decrease in signal intensity, and freezing this solution did not give any lines attributable to a triplet species. We believe that the dication from **14** has a singlet ground state, although it must be admitted that not seeing a spectrum is not as powerful an argument as seeing one. Rassat and co-workers[14] found a triplet ground state for adamantyl dinitroxide **23**, and emphasized that a triplet ground state would only be expected for a diradical with any interaction between the spin-bearing units with the special symmetry properties associated with this symmetrical structure; so our failure to detect triplet 14^{2+} is the espected result.



23

The tetracyclic bishydrazines **16** and **17** resemble the pentacyclic compound **14** in their electrochemical properties, since they show two completely reversible oxidation waves with modest $\Delta E°'$ values of 0.21 and 0.19 V (4.8 and 4.4 kcal/mol), respectively. Molecular models show that like the pentacyclic system, the tetracyclic system is quite flexible. The two six-membered rings can exist in boat conformations which force the hydrazine units close to each other (conformations we will describe as closed) and are easily twisted to allo relief of transannular interactions, or the six-membered rings can be in chair conformations,

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[12] Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 8127. Program 395, Quantum Chemistry Program Exchange, Bloomington, IN.

[13] We only recently found out that we had been using a version of MM2 which had a mistake in the lone pair dipoles used (*QCPE* **1983**, *3*, 36), so the calculations published in ref 8 are incorrect. The conclusions are completely unaltered, but the proper numbers appear in Table II.

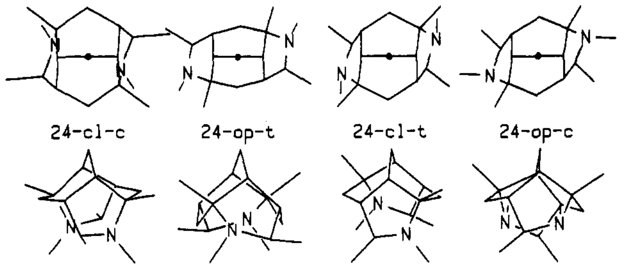
[14] Dupeyre, R.-M.; Rassat, A.; Ronzaud, J. *J. Am. Chem. Soc.* **1974**, *96*, 6559.

Table III. MM2 Results on Some Symmetrical Conformations of 24

	conformation			
	24-cl-c	**24-op-t**	**24-cl-t**	**24-op-c**
rel steric *E*, kcal/mol	[0]	1.0	1.3	3.3
$N_7C_3{=}N_2C_8$ dist, Å	3.2_2	4.8_4	3.8_3	4.5_4
dihedral angles, deg				
p-N_2,C_3H	40.8	148.9	159.0	37.8
N_2C_3,N_7C_8	11.8	30.9	28.5	5.7
$HC_4,C_{12}H$	17.2	38.6	7.5	8.6
est $^3J_{HH}$, Hz[a]	9.1	6.1	9.8	9.8

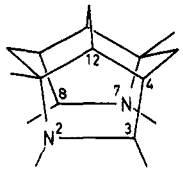
[a] For the adjacent bridgehead hydrogens at the angles given in the above line, using $^3J_{HH} = 20 \cos^2$ (Abraham, R. J.; Loftus, P. *Proton and Carbon-13 NMR Spectroscopy*; Heydon and Son: Bristol, 1979; p 45).

Chart II


24-cl-c 24-op-t 24-cl-t 24-op-c

pulling the hydrazine units apart (open conformations). An additional complexity is that the *N*-alkyl groups can be either cis or trans to each other in the pyrazolidine rings.

To get a more quantitative indication of what the geometries of these molecules might be like, we have again resorted to MM2 calculation on model compounds, which is necessary because a hydrazine force field is not available. The model chosen was diamine 14, in which the nitrogens adjacent to the unmethylated bridgehead positions are replaced by CH groups. We did calculations on four symmetrical conformations of 24, open and closed conformations with cis and trans methyl groups at positions 2,3 and 7,8. The results are shown in Table III., and two views of the frameworks of each conformation are shown in Chart II.



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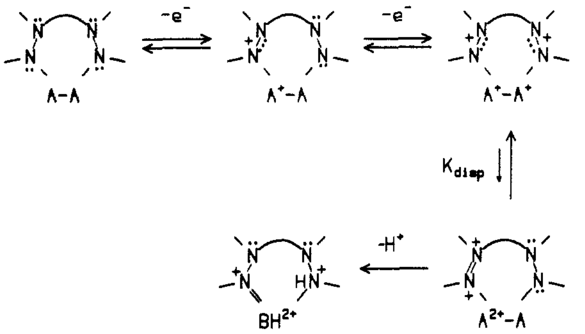
The results of Table III indicate that both open and closed conformations of comparable energy are available. Comparing Tables II and III, the open conformations of the tetracyclic compounds 16/17 are predicted to have larger distances between the hydrazine units than to those of 12/13, which is consistent with the smaller $E^{\circ\prime}$ observed for the tetracyclic than the pentacyclic compounds, although it certainly must be admitted that other factors than closest approach of nitrogens may well be involved in determining $\Delta E^{\circ\prime}$.

We note that 16 is 8.3 kcal/mol easier to oxidize than is the monohydrazine model compound 21. This difference is large and cannot be reasonably explained by solvation or simple substitution differences. Table III suggests a plausible reason. If 16 really exists in a cis conformation, it has a far larger lone pair, lone pair interaction than does the supposed model 21, which has trans methyl groups. Because neutral 16 would be forced into this electronically destabilized conformation by the polycyclic structure, this should destabilize the neutral compound and hence lower the oxidation potential.

Another interesting fact is that the ethyl-substituted compound 17 is 0.13 V (3 kcal/mol) harder to oxidize than is 16. Changing methyl groups for ethyl groups usually does not affect the oxidation potential significantly. For example, the ethyl analogue of 21 was found to have the same oxidation potential as 21 (Table I, footnote d). The difference in behavior of 16 and 17 is readily understood if the two compounds have different preferred conformations. Evidence that this is the case comes from the NMR spectra of 16 and 17. Observation of a 8.7 and a 6.5 Hz coupling in 16 and 17, respectively, for the $^3J_{HH}$ coupling of the two methine hydrogens on adjacent tertiary centers shows that the hydrocarbon framework of 16 is held in a different conformation from that of 17. These values are consistent with 16 adopting a more closed conformation with a cis relationship of the methyl groups and 17 adopting an open-trans conformation. This difference is not unexpected as relief of adverse interactions involving the larger ethyl groups is avoided in an open conformation. In hexahydropyridazines substantial conformational differences between *N*-methyl and *N*-ethyl derivatives have previously been noted.[1,3] The ESR spectrum of 16^+ is quite ill-resolved and complex, but once again it is clear that the spin is localized in one hydrazine unit, for a fair fit was obtained employing $a(2N) = 15$ G, $a(6H) = 12.8$ G, $a(1H) = 14$ G.

Discussion: Structural Effects on Bishydrazine Oxidations. Table I shows that incorporation of a second hydrazine unit into a structure has only a rather small effect on the ease of removal of the first electron. The largest effect seen was for 16 relative 21, which we interpreted as being due to a significant conformational change, so that 21 is not a reasonable model for 16, which receives some support from the fact that the tetraethyl compound 17 is 3 kcal/mol harder to oxidize than is its tetramethyl analogue 16 and is indicated by NMR to exist in a different conformation. There is no indication in the $E^{\circ\prime}{}_1$ values for delocalization of positive charge over both hydrazine units in any of the monocations, and the ESR spectra of 14^+ and 16^+ are also consistent with the odd electron being localized in one hydrazine unit. The difference between the first two oxidation potentials, $\Delta E^{\circ\prime}$, is also small in most cases. The $(CH_2)_3$-bridged acyclic compound 3 has a $\Delta E^{\circ\prime}$ of only 0.13 V, which increases to about 0.20 V for the tetracyclic compounds 16 and 17 and to 0.29 V for the pentacyclic system 14. These polycyclic compounds can assume conformations with the hydrazine units rather far apart (closest approach of N atoms in different hydrazine units estimated at 4.2 Å for 14 and 4.8 Å for 16/17 from MM2 calculations on model compounds). $\Delta E^{\circ\prime}$ is significantly larger, probably at least 0.8 V (18 kcal/mol), for the hexacyclic compounds 12 and 13, where the hydrazine units are constrained to a two carbon bridge held with the NC,CN dihedral angle near 0°. We are unable to address the possible importance of through-bond interaction of the oxidized and unoxidized hydrazine units of these compounds because of our inability to estimate the through-space component of $\Delta E^{\circ\prime}$ reasonably. Two hydrazine cation radicals with d_{NN} 1.32 Å having a charge of 0.5 at each nitrogen restricted to having parallel NN bonds separated by 2.8 Å would have an electrostatic work term of about 56 kcal/mol associated with this geometry, if it were assumed that there were no charge delocalization and if the point charges were in a vacuum. This number drops to 39 kcal/mol at a 4.2-Å separation. We are unable to translate such a simple-minded analysis to real compounds

Scheme I

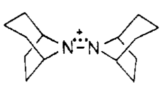


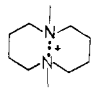
with significant charge delocalized into the attached alkyl groups, with a solvent of dielectric constant 37.5 (that of acetonitrile) partially bathing the hydrazine cations and with counterions around.

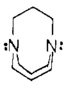
The thermodynamic studies were made difficult by the short lifetimes of most of the bishydrazine dications. Only 14^{2+}, 16^{2+}, and 17^{2+} proved to be long-lived; their lifetimes are seconds at room temperature. Even the polycyclic dications 12^{2+} and 13^{2+} were short-lived (they do not last milliseconds), probably because of CH_2–CH_2 cleavage to two immonium cations, which is formally a Grob fragmentation.[15] 2^{2+} and 11^{2+} may well be undergoing similar fragmentation; we had not expected the short lifetime we observed for 3^{2+} and 4^{2+}, because monohydrazine radical cations are long-lived in solution.[1]

Because removal of a second electron from a hydrazine radical cation is considerably more difficulty than the first, the dication initially formed ought to be A^+–A^+ of Scheme I. We see no reason to expect A^+–A^+ to be inherently unstable unless the bridge between the nitrogens is a two-carbon one. We therefore suggest that a likely pathway for decomposition observed involves intramolecular electron-transfer disproportionation, to A^{2+}–A, which would definitely be unstable to internal proton transfer, shown schematically as giving BH^{2+} (any α proton could be transferred, so several "BH^{2+}" molecules would be formed). Although the electron-transfer conversion of A^+–A^+ to A^{2+}–A is expected to have a thermodynamic barrier, it might be considerably faster in an intramolecular case than in intermolecular cases, and rapid intramolecular proton transfer could follow. All the long-lived examples of bishydrazine dications have strong geometric constraints against intramolecular proton transfer in A^{2+}–A.

Conclusion. Even for polycyclic bishydrazines having easily available conformations which push the hydrazine units into each other, there is no experimental evidence for delocalized structures in which both hydrazines units share the positive charge. At the time we started this work, we hypothesized that the bis(dialkylamino) three-electron σ-bonded cation III might well form from some of these compounds, but it rather clearly does not happen. In retrospect, this is not surprising. To go from $R_4N_2^+$ and R_4N_2 to III, the three-electron π bond of $R_4N_2^+$ is broken, and the three-electron σ bond of III is formed. The strength of the three-electron π bond of a tetraalkylhydrazine cation may be estimated from the rotational barrier for such a species, since the π bond is broken in this process. $\Delta H^{\ddagger}$ for conversion of *syn*-8,8′-bi(8-azabicyclo[3.2.1]octane) (**25**) radical cation to the anti isomer has been recently measured at 20 kcal/mol,[16] giving a reasonable experimental estimate of the three-electron π-bond strength for a tetraalkylhydrazine radical cation.


25^+


26^+


27

The strength of the three-electron σ bond for hexaalkylhydrazine cation radicals has been estimated at about 14.5 kcal/mol from the lifetime of 26^+ in solution,[17] and similar values are also obtained from differences of vapor phase N^+–H bond strengths of protonated **27** and its monoaza analogue.[18] Unless substitution of dialkylamino groups for two of the alkyl groups of a hexaalkylhydrazine cation radical had a large stabilizing effect on the strength of the three-electron σ bond, then, it would cost energy to go from $R_4N_2^+$ and R_4N_2 to III. Experimentally, we have not observed it. In keeping with the above, our MNDO calculations of III constrained to an NN,NN dihedral angle of 0° gave an energy of 9 kcal/mol higher than isolated $R_4N_2^+$ and R_4N_2 and nearly parallel NN bonds, with essentially no covalent bonding between the hydrazine units (interunit NN bond distances of 3.06 and 3.12 Å were obtained). At the MNDO level, the H_4N_2 dimer cation radical prefers to minimize with the charge localized on one nearly planar hydrazine unit if hydrogen bonding is not permitted (it cannot be present in the compounds of interest here), although the lack of diffuse orbitals in MNDO makes the geometry and stabilization energy of the species calculated meaningless. Higher level ab initio calculations on H_4N_2 dimer radical cation[19] also give the result that the charge is localized on one hydrazine unit and that III is an energy maximum, which is consistent with our experimental results.

Experimental Section

General. Unless otherwise noted, all reactions were run under dry nitrogen and were magnetically stirred. The term in vacuo means removal of solvents under reduced pressure on a rotary evaporator followed by evacuation to 0.2 torr to remove the last traces of solvents. Hexane, benzene, and methylene chloride were purified by repeated washing with concentrated sulfuric acid, washing with aqueous sodium bicarbonate, washing with water, and preliminary drying with calcium chloride, followed by drying over and distilling from calcium hydride. Toluene was purified similarly, except that the final drying and distillation were from sodium. Ether used as a reaction solvent was purified by washing with 10% ferrous sulfate and preliminary drying with magnesium sulfate followed by drying over and distillation from sodium immediately before use. THF was distilled from sodium/benzophenone ketyl immediately before use. All reactions involving LAH were carried out in glassware which had been flame-dried and cooled under dry nitrogen. Nonreferenced compounds were obtained from commercial sources and were used as received.

Melting points were obtained on a Hoover Uni-Melt capillary apparatus and are uncorrected. Infrared spectra were taken on a Beckman Acculab 7 spectrometer and, unless otherwise noted, are dilute solutions in carbon tetrachloride. Mass spectra were run on an AEI MS-902 or Kratos MS-30 (for **16** and **17**) mass spectrometer at ionizing potentials of 40 and 70 V, respectively. All ^{1}H NMR spectra were recorded in deutriochloroform solution, unless otherwise noted, by using tetramethylsilane (Me_4Si) as an internal standard. All peaks were expressed as parts per million (ppm, δ) downfield from Me_4Si. Routine spectra were taken on a JEOL JNM MH-100, IBM WP-200, Bruker WP-270, or Bruker

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[15] Grob, C. A. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 1; **1969**, *8*, 535.

[16] Nelsen, S. F.; Cunkle, G. T.; Evans, D. H.; Haller, K. J.; Kaftory, M.; Kirste, B.; Kurreck, H.; Clark, T. *J. Am. Chem. Soc.* **1985**, *107*, 3829.

[17] Nelsen, S. F.; Alder, R. W.; Sessions, R. B.; Asmus, K.-D.; Hiller, K.-O.; Göbl, M. *J. Am. Chem. Soc.* **1980**, *102*, 1429.

[18] Alder, R. W.; Arrowsmith, R. J.; Casson, A.; Sessions, R. B.; Heilbronner, E.; Kovac, B.; Huber, H.; Taagepera, M. *J. Am. Chem. Soc.* **1981**, *103*, 6137.

[19] Clark, T. Universität Erlangen-Nürnberg, private communication.

360-AM (for **16** and **17**) spectrometer. Splitting patterns are designated as follows: s, singlet; d, doublet; t, triplet; m, complex multiplet; br, broad. ^{13}C NMR spectra were run in deuteriochloroform solution on a JEOL FX-60, JEOL FX-200, or Bruker 360-AM (for **16** and **17**) spectrometer. Peaks are expressed in ppm (δ) downfield from Me_4Si, with the center resonance of the solvent pattern (δ 77.000 for $CDCl_3$) as a reference. Off-resonance spectra on the FX-60 were obtained by moving the ^{1}H decoupler 1.2 kHz upfield from Me_4Si and lowering the decoupling power. All polarization transfer experiments were done on the FX-200 spectrometer. A phasing time of 6.3 μs ($3/4J$) were used to give a spectrum in which methine and methyl carbon signals appear upright, but methylene carbon signals are inverted. A phasing time of 4.2 μs ($2/4J$) was used to suppress methyl carbon signals and leave the methine carbon signals enhanced.

Glyoxal Bis(dimethylhydrazone). Aqueous glyoxal (14.5 g, 0.1 mol, 40%), 15 g (0.25 mol) of dimethylhydrazine, and 250 mL of benzene were refluxed with a Dean–Stark trap for 18 h. The benzene was removed by distillation at atmospheric pressure, and the residue was distilled (0.2 torr), yielding a pale yellow oil that solidified on standing. The low-melting solid was sublimed under a static vacuum of 0.1 torr and 35 °C to yield 11.36 g (80%) of product as large colorless crystals.

2,7-Dimethyl-2,3,6,7-tetraazaoctane (5) was prepared in 88% yield by an LAH reduction of glyoxal bis(dimethylhydrazone): bp 78–81 °C (16 torr); ^{1}H NMR δ 2.55 (s, 4 H), 2.3 (br s, 2 H), 2.35 (s, 6 H); ^{13}C NMR δ 46.5 (CH_3), 45.9 (CH_2).

2,3,6,7-Tetramethyl-2,3,6,7-tetraazaoctane (2). **5** (2.0 g, 13.68 mmol) was added to 4.44 mL (54.72 mmol of H_2CO) of 37% formalin solution and cooled to 0 °C in an ice bath. Formic acid (4.67 mL, 88%) was added in one portion and the mixture stirred while warming to room temperature 18 h, followed by heating to 85 °C for 18 h. The mixture was then cooled to 0 °C and poured into 70 mL of 15% sodium hydroxide solution. The solution was extracted with five portions of 25 mL of ether, the ether dried with potassium carbonate, and the ether removed by distillation. The product was distilled at reduced pressure and the fraction boiling at 95–96 °C (16 torr) collected to yield 1.7 g (78%) of **2**; the empirical formula was established as $C_8H_{22}H_2$ by high-resolution mass spectroscopy: ^{1}H NMR δ 2.61 (s, 4H), 2.36 (s, 12 H), 2.30 (s, 6 H); ^{13}C NMR δ 51.7 (CH_2), 38.1 (2 CH_3), 34.1 (CH_3).

Trimethylhydrazine was prepared from 1,1-dimethylhydrazine by the method of Beltrami and Bissell[20] in 68% yield (lit. 52%).

Methyl 2,3-Dimethyl-2,3-diazahexanoate (7). Methyl acrylate (2.0 g, 23.23 mmol) and 3.79 g (51.12 mmol) of trimethylhydrazine were combined and refluxed for 24 h. The excess trimethylhydrazine was distilled at atmospheric pressure and the product distilled at reduced pressure. The product boiling at 76–69 °C (15 torr) was collected to yield 7.3 g (73%) of **7**: empirical formula $C_7H_{16}N_2O_2$ (present as *m/e* 160, 3% of the base peak at 44); IR 1750 (C=O stretch) cm^{-1}; ^{1}H NMR δ 3.65 (s, 3 H), 2.66 (t, J = 6.0 Hz, 2 H), 2.44 (t, J = 6.0 Hz, 2 H), 2.30 (s, 9 H); ^{13}C NMR δ 171.7 (C=O), 50.5 (CH_3), 49.2 (CH_2), 37.8 (2 CH_3), 32.8 (CH_3), 32.4 (CH_2).

2,3-Dimethyl-2,3-diaza-4-ketohex-5-ene (8). Acrylyl chloride (0.80 g, 7.51 mmol) was dissolved in 25 mL of dry ether and cooled to −78 °C in a dry ice/ethanol bath. A solution of 1.12 g (15.11 mmol) of trimethylhydrazine, 3.05 g (30.15 mmol) of triethylamine, and 10 mL of dry ether was added dropwise. After the addition was complete, the mixture was warmed to room temperature and stirred 18 h. The solution was poured into 75 mL of 15% sodium hydroxide solution and extracted with five portions of 25 mL of methylene chloride. The methylene chloride was dried with potassium carbonate and removed in vacuo: ^{1}H NMR δ 7.16 (dd, J = 10.55, 17.44 Hz, 1 H), 6.32 (dd, J = 17.44, 2.5 Hz, 1 H), 5.60 (dd, J = 10.55, 2.5 Hz, 1 H), 3.0 (s, 3 H), 2.53 (s, 6 H); ^{13}C NMR δ 127.6, 126.5, 43.0 (double intensity), 22.0 (C=O not seen).

Malonyl dichloride was prepared from malonic acid by the method of McMaster and Ahnmann[21] in 18.5% yield (lit. 60%).

2,3,7,8-Tetramethyl-2,3,7,8-tetraaza-4,6-diketononane. Malonyl dichloride (1.5 g, 10.64 mmol) was dissolved in 30 mL of dry ether and cooled to −78 °C in a dry ice/ethanol bath. A mixture of 1.60 g (21.59 mmol) of trimethylhydrazine, 4.3 g (42.57 mmol) of triethylamine, and 10 mL of dry ether was added dropwise. After the addition was complete, the reaction was allowed to stir and warm to room temperature for 12 h. The white precipitate was filtered off and the filtrate concentrated in vacuo. The resulting white solid was recrystallized from hexane to yield 0.46 g (20%): mp 78–83 °C; empirical formula $C_6H_{20}N_4O_2$ (present at *m/e* 216, 0.1% of base peak at 73); IR 1600 (C=O stretch) cm^{-1}; ^{1}H NMR δ 3.8 (s, 2 H), 2.90 (s, 6 H), 2.56 (s, 12 H); ^{13}C NMR δ 169.8 (C=O), 42.8 (2 CH_3), 39.6 (CH_3), 22.0 (CH_2).

2,3,8,9-Tetramethyl-2,3,8,9-tetraaza-4,7-diketodecane. Succinyl chloride (2.0 g, 12.9 mmol) chloride was dissolved in 25 mL of dry ether and cooled to −78 °C in a dry ice/ethanol bath. A solution of 1.91 g (25.8 mmol) of trimethylhydrazine, 5.30 g (51.7 mmol) of triethylamine, and 10 mL of dry ether was added dropwise. The solution was allowed to stir while warming to room temperature for 1 h. The mixture was poured into 50 mL of 15% sodium hydroxide solution and extracted with five 25-mL portions of methylene chloride. After drying with sodium sulfate, the solvent was removed in vacuo to yield 1.2 g of a brown solid. Recrystallization from ethyl acetate yielded 1.12 g (38%) of a light tan solid: mp 194–197 °C; empirical formula $C_{10}H_{22}N_4O_2$ (present as *m/e* 230, 0.2% of the base peak at 157); IR 1705 (C=O stretch) cm^{-1}. The ^{1}H NMR showed several singlets, indicating that several conformations about the hydrazide CN bonds were populated. The ^{13}C NMR also showed several conformations present: The major conformation has peaks at δ 174.4 (C=O), 42.8 (2 CH_3), 21.9 (CH_2).

2,3,7,8-Tetramethyl-2,3,7,8-tetraazanonane (3). Bishydrazide (0.3 g, 1.39 mmol) was dissolved in 25 mL of dry ether and added dropwise to a suspension of 0.4 g of LAH in 25 mL of dry ether. The mixture was refluxed 18 h and following a 1:1:3 workup,[22] and the resulting pale yellow oil was Kugelrohr distilled to yield 0.10 g (38%) of a clear oil; the empirical formula was established as $C_9H_{24}N_4$ by high-resolution mass spectroscopy: ^{1}H NMR δ 2.49 (t, J = 7.26 Hz, 4 H), 2.31 (s, 12 H), 2.26 (s, 6 H), 1.65 (quintet, J = 7.26 Hz, 2 H); ^{13}C NMR δ 51.6 (2 CH_2), 38.9 (4 CH_3), 34.6 (2 CH_3), 26.5 (CH_2).

2,3,8,9-Tetramethyl-2,3,8,9-tetraazadecane (4) was prepared from 0.15 g (1.65 mmol) of bishydrazide by the same method used in preparing **3**, yielding 0.06 g (81%) of **4** as a clear oil; empirical formula was established as $C_{10}H_{26}N_4$ by high-resolution mass spectroscopy: ^{1}H NMR δ 2.44 (m, 4 H), 2.31 (s, 12 H), 2.26 (s, 6 H), 1.50 (m, 4 H); ^{13}C NMR δ (52.7 CH_2), 38.0 (2 CH_3), 33.5 (CH_3), 25.1 (CH_2).

11,4-Bis(dimethylamino)piperazine (11). 1,4-Diaminopiperazine 1,4-dihydrochloride (0.5 g, 2.64 mmol) (prepared by zinc, acetic acid reduction of the bisnitroso compound using the method of Evans and co-workers[23]) was suspended in 50 mL of acetonitrile, and 8.95 mL (105 mmol of H_2CO) of 37% formalin solution and 3.29 g (50.7 mmol) sodium cyanoborohydride were added. One drop of acetic acid was added, causing the reaction to get very hot. The reaction was allowed to cool to room temperature before adding more acetic acid. The acetic acid was added dropwise, allowing the reaction to cool to room temperature between additions. A total of 15 mL of acetic acid was added over a 3-h period. The reaction was allowed to stir at room temperature an additional 18 h, after which 25 mL of concentrated hydrochloric acid was added, and the solvents were removed in vacuo. The salts were taken up in 50 mL of 15% sodium hydroxide solution and extracted five times with 25-mL portions of ether. The ether was dried with potassium carbonate and removed by distillation through a 12-in. Widmar column. The crude product was distilled at reduced pressure and the fraction boiling at 94–95 °C (14 torr) collected to yield 0.21 g (46%) of **11**: empirical formula $C_8H_{20}N_4$ (present as *m/e* 172, base peak of the spectrum); ^{1}H NMR δ 2.78 (s, 8 H), 2.38 (s, 12 H).

1,2,3,6,7,8-Hexamethyl-2,3,7,8-tetraazatetracyclo-[7.3.1.0^{4,12}.0^{6,10}]tridecane (16). Formic acid (6 mL, 159 mmol) was added to acetic anhydride (12.5 mL, 127 mmol) at 0 °C with constant stirring over 15 min. The solution temperature was raised to 60 °C and maintained at this temperature for 2 h. After the

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mixture cooled to room temperature, tetrahydrofuran (10 mL) was added, and the resulting solution was added dropwise to a suspension of 1,6-dimethyl-2,3,7,8-tetraazatetracyclo-$[7.3.1.0^{4,12}.0^{6,10}]$tridecane (**28**)[8] (500 mg, 2.4 mmol) in tetrahydrofuran (20 mL). A white precipitate formed immediately, but the reaction mixture was stirred at room temperature for a further 3 h. Removal of solvent under reduced pressure afforded as a white solid crude 2,3,7,8-tetraformyl-1,6-dimethyl-2,3,7,8-tetraazatetracyclo$[7.3.1.0^{4,12}.0^{6,10}]$tridecane (**29**) (0.66 g, 87%). A portion of **29** (588 mg, 1.8 mmol) was dissolved in tetrahydrofuran and cooled to 0 °C. Borane–dimethyl sulfide complex (5 mL of 10 M solution, 50 mmol) was added at 0 °C over 15 min, and the solution was heated under reflux for 20 h. The resulting suspension was cooled to room temperature and solvent (60 mL) removed by distillation at atmospheric pressure. To the residual solution at room temperature hydrochloric acid (50 mL, 4 M solution) was added carefully, and the solution was then evaporated to dryness under reduced pressure. To the residue was added hydrochloric acid (40 mL, 4 M solution), and this solution was heated under reflux for 1 h, cooled to room temperature, and neutralized by addition of sodium hydroxide (solid). The basic solution was extracted with methylene chloride (50 mL × 3) and then saturated with sodium chloride (50 mL). The combined organic layers were dried, filtered, and evaporated to give an oil (387 mg). Bulb-to-bulb distillation afforded as a low-melting solid 1,2,3,6,7,8-hexamethyl-2,3,7,8-tetraazatetracyclo$[7.3.1.0^{4,12}.0^{6,10}]$-tridecane (**16**) (243 mg, 50%): bp 130 °C (0.5 mmHg); ^{1}H NMR δ 2.75 (dt, J = 8, 6 Hz, H-4 and H-9, 2 H), 2.44 and 2.36 (2 s, NCH_3, 12 H), 2.11 (dt, J = 8, 6 Hz, H-10 and H-12, 2 H), 1.99 (dd, J = 15, 5 Hz, H-5 and H-13, 2 H), 1.70 (t, J = 3 Hz, H-11, 2 H), 1.34 (dd, J = 15, 8 Hz, H-5 and H-13, 2 H), 1.50 (s, CH_3, 6H); ^{13}C NMR 62.6 (C-4 and C-9), 62.1 (C-1 and C-6), 43.15 (NCH_3), 40.7 (C-10 and C-12), 34.4 (NCH_3), 32.7 (C-5 and C-13), 27.3 (CH_3), 19.3 (C-11); MS (70 eV), 264.2368, $C_{15}H_{28}N_4$ requires 264.2314.

2,3,7,8-Tetraethyl-1,6-dimethyl-2,3,7,8-tetraazatetracyclo-$[7.3.1.0^{4,12}.0^{6,10}]$tridecane (17). 2,3,7,8-Tetraacetyl-1,6-dimethyl-2,3,7,8-tetraazatetracyclo$[7.3.1.0^{4,12}.0^{6,10}]$tridecane[9b] (100 mg, 0.3 mmol) and lithium aluminum hydride (300 mg, 8 mmol) in ether (40 mL) were heated under reflux with stirring for 5 h. Addition of aqueous sodium hydroxide solution (4 M) to the cooled ethereal solution gave a white precipitate, which was removed by filtration. The residue was washed with methanol (100 mL) and then chloroform (100 mL). The combined filtrates and washings were concentrated under reduced pressure, and the residue was dissolved in chloroform (100 mL). The resulting solution was dried, filtered, and evaporated under reduced pressure to give a residual yellow oil (78 mg). Bulb-to-bulb distillation afforded as a colorless oil 2,3,7,8-tetraethyl-1,6-dimethyl-2,3,7,8-tetraazatetracyclo$[7.3.1.0^{4,12}.0^{6,10}]$tridecane (**17**) (64 mg, 75%): bp 127 °C (0.5 mmHg); ^{1}H NMR δ 2.9–2.5 (complex, H-4, H-9, CH_2CH_3, 10 H), 2.10 (dt, J = 6, 3 Hz, H-10 and H-12, 2 H), 1.98 (dd, J = 15, 9 Hz, H-5 and H-13, 2 H), 1.81 (t, J = 3 Hz, H-11, 2 H), 1.53 (dd, J = 15, 9 Hz, H-5 and H-13, 2 H), 1.14 (s, CH_3, 6 H), 1.10 and 1.01 (t, J = 7 Hz, CH_2CH_3, 12 H); ^{13}C NMR δ 62.8 (C-1 and C-6), 60.7 (C-4 and C-9), 55.4 and 46.2 (CH_2CH_3), 40.8 (C-10 and C-12), 37.9 (C-5 and C-13), 28.6 (CH_3), 19.7 (C-11), 16.2 and 13.95 (CH_2CH_3); MS (70 eV), 320.3088, $C_{19}H_{36}N_4$ requires 320.2932.

Electrochemistry. All electrochemistry was run at ambient temperature at 2×10^{-3} M in acetonitrile (Burdick and Jackson "Distilled in Glass", used as received). Tetra-*n*-butylammonium perchlorate (TBAP) used as supporting electrolyte was obtained from Eastman and was recrystallized from 1:1 water/ethanol and dried in vacuo prior to use. The gold and platinum planar electrodes used for CV have been previously described.[1] The electrode was polished to a mirror finish and used directly. Cyclic voltammetry was performed in a standard three-electrode cell. The counter electrode was a ca. 1 in. length coil of platinum wire, and the reference electrode was a Corning ceramic junction SCE, which was isolated from the main compartment by a cracked glass bead. Voltammograms were obtained in static solution, stirring between scans being accomplished by bubbling nitrogen via a syringe needle through the solution. The instrument consisted of a Princeton Applied Research (PAR) 173 potentiostat/galvanostat, a PAR 179 digital coulometer, and a PAR 175 universal programmer. Scans ≤1 V/s were recorded on a Houston Instruments "Omnigraphic 2000"$^{1}/_{4}$ X–Y recorder, while those at faster scan rates were photographed from a Tektronix 5000 storage oscilloscope.

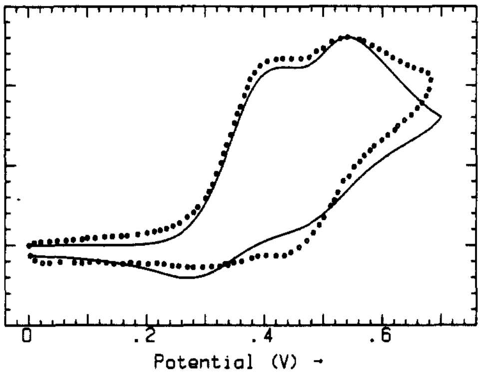

Figure 1. Observed (○) and simulated (—) CV data for **3** at a scan rate of 0.5 V/s. See Experimental Section for the simulation parameters.

Scheme II. Reactions Used for Feldburg Simulation of the CV of 3

$A \rightleftharpoons A^+$	$1 \rightleftharpoons 2 + e^-$	Rxn 1
$A^+ \rightleftharpoons A^{++}$	$2 \rightleftharpoons 3 + e^-$	Rxn 2
$A^{++} \longrightarrow BH^{++}$	$3 \longrightarrow 4$	Rxn 3, Rate3
$A + BH^{++} \rightleftharpoons AH^+ + B^+$	$1 + 4 \rightleftharpoons 5 + 6$	Rxn 4, K_{eq} 4
$A + A^{++} \rightleftharpoons 2A^+$	$1 + 3 \rightleftharpoons 2 + 2$	Rxn 5, K_{eq} 5
$B^+ \rightleftharpoons B^{++} + e^-$	$6 \rightleftharpoons 7 + e^-$	Rxn 6
$A + BH^{++} \longrightarrow A\text{-}BH^{++}$	$1 + 4 \longrightarrow 8$	Rxn 8, Rate8
$A + B^+ \longrightarrow A\text{-}B^+$	$1 + 6 \longrightarrow 9$	Rxn 9, Rate9

Cyclic Voltammogram Simulations. The voltammogram of **3** was selected for attempted digital simulation because it is the only one that showed any reduction current at all associated with the second oxidation wave. In attempts to fit the observed voltammogram of **3** quantitatively, we kept adding reactions to a Feldburg[11] simulation, finally ending up with the eight reactions shown in Scheme II. In Scheme II A^{2+} is used to represent both the A^+–A^+ and A^{2+}–A dications of Scheme I because they presumably interconvert rapidly, and we cannot separate their chemistry with the data at hand. Reaction 3 therefore represents both the electron-transfer disproportionation and the internal proton transfer of Scheme I. It seems clear that decomposition of A^{2+} destroys the monocation radical reduction wave (reaction 1), which will occur if unoxidized hydrazine diffusing to the electrode is trapped as species which do not oxidize easily. There are several ways that this could happen, and three appear in Scheme II, in which BH^{2+} is shown protonating incoming neutral hydrazine (reaction 4) and A adds to both BH^{2+} and BH^+ (reaction 8 and 9). Also included are two electron-transfer steps, the comproportionation of A and A^{2+} (reaction 5), and oxidation of B^+ (reaction 6). The dimensionless ψ parameter which sets the heterogeneous rate of electron-transfer loss from A^+ affects the shape of the curves simulated substantially, moving the maximum of the second wave to higher potential and broadening it as ψ is decreased. A value near 0.3 gave the best fit. Increasing the rate of A^{2+} (species **3**) decomposition, rate 3, decreases the size of the second oxidation wave and also increases the concentration of BH^{2+} (species **4**), affecting the rates of all reactions consuming **4**; we found it most effective to adjust rate 3 to match the relative oxidation peak heights in the experimental curve and found that rate 3 could have values varying from about 20 to 80 s^{-1} and keep the same relative oxidation peak heights, by varying K_{eq} 4, rate 8, and rate 9. Increasing K_{eq} 4 increases the ratio of the first to second oxidation wave peak heights. The value of K_{eq} 5 is determined by the $E^{\circ\prime}$ separation. The simulated curves proved rather insensitive to $E^{\circ\prime}$ for B^+ (species **6**). We were unfortunately unable to include reactions 8 and 9 as equilibrium processes because of oscillations in the calculated voltammogram (arising from physically unreasonable calculated negative concentrations of species **4** and **6**) and finally had to include these reactions as irreversible decompositions. The kinetic scheme is extremely complicated by this point, and we still are not able to adjust the several parameters to obtain good fit to the experimental curves.

The fit we managed to obtain is shown in Figure 1.

Voltammograms were digitized by using a Textronix 4953 graphics tablet attached to the Chemistry Department HARRIS/7 computer. The experimental CV curve was subtracted from a background scan and the resulting digitized curve transferred to an IBM PC. The simulated curve was matched to the experimental trace by scaling the simulated maximum to the experimental maximum in the current dimension and by offsetting the zero point of the simulation by the voltage offset used in the simulation.[24] For the data simulated, the scan range was 0.7 V and the starting potential was 0.337 V negative of $E^{\circ\prime}_1$, so the starting potential for the simulation was −0.337 V and the switching point 0.363 V. The peak current in the simulation was normalized to that of the experimental data. The ratios of heterogeneous electron-transfer rate from the substrate to the electrode and from the electrode to the substrate were taken to be 1; i.e., α was set at 0.5 for all species. The peaks are both broad, and all ψ values (which describe the broadening of the peaks induced by slow heterogeneous electron transfer rates) were set at 0.3. The parameters used for the simulation in Figure 1 (see Scheme III for the reactions referred to) were $E^{\circ\prime}_2-E^{\circ\prime}_1 = 0.135$ V (reactions 1 and 2), rate 3 = 59 s^{-1}, K_{eq} 4 = 6, $E^{\circ\prime}_1-E^{\circ\prime}(B^+) =$ 0.2 (reaction 6, a larger value did not affect the simulation), rate 8 = 2 $M^{-1}\ s^{-1}$, rate 9 = 0.0001 $M^{-1}\ s^{-1}$.

ESR. Preparation of the ESR samples of 12^+, 14^+, and 16^+ were accomplished by chemical oxidation. A solution of hydrazine (2×10^{-3} M) was made up in butyronitrile and the solution cooled under nitrogen. Nitrogen was bubbled through the solution for at least 15 min, and 1 equiv of tris(*p*-bromophenyl)amminium hexachloroantimonate was added as the oxidant. A portion of this solution was forced through a cooled cannula into a precooled 3-mm (o.d.) Pyrex tube and kept in dry ice/ethanol until ready for use. Spectra were recorded on a Varian E-15 instrument, and simulations were carried out on an IBM PC, plotted on an HP-7047A digital plotter, and visually compared with the experimental curves.

Calculations. MM2 calculations[12] on the hexacyclic and pentacyclic bis(methylamine)s **22** were done on the Chemistry Department HARRIS/7 computer. Calculations on model diamine **24** were done on an IBM PC using a three-part MM2 program supplied by Prof. G. R. Weisman. MNDO calculations[25] were carried out on the Madison Academic Computing Center VAX-780.

Acknowledgment. We thank the National Institutes of Health for partial financial support under Grant GM-29549. We thank SERC for a studentship (N.M.S.). We thank J. T. Ippoliti for obtaining the high-resolution mass spectral data on **2–4**.

Registry No. **2**, 49840-62-2; **3**, 101032-34-2; **4**, 101032-35-3; **5**, 2594-64-1; **7**, 101032-36-4; **8**, 77144-30-0; **11**, 49840-61-1; **12**, 87783-35-5; **13**, 87783-36-6; **14**, 87783-37-7; **16**, 101032-37-5; **17**, 101032-38-6; **18**, 52598-10-4; **19**, 49840-60-0; **20**, 53779-90-1; **21**, 38704-89-1; **22**, 87783-30-0; **24**, 39123-05-2; $Me_2NN{=}CHCHNNMe_2$, 26757-28-8; $Me_2NN(Me)C(O)CH_2C(O)N(Me)NMe_2$, 101032-39-7; $MeNN(Me)C(O)(CH_2)_3C(O)N(Me)NMe_2$, 101054-48-2.

Supplementary Material Available: Observed and simulated ESR spectra for 12^+ and 16^+ (3 pages). Ordering information is given on any current masthead page.

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(24) The effects of changing the simulation parameters on the simulated CV curves are discussed in more detail in the thesis of M. R. Willi (University of Wisconsin, 1985). Our lack of success in quantitatively fitting the experimental curves shows that the simulations done were inadequate, and we do not feel that space describing them here is warranted.

Electrochemical Oxidation and Reduction of a Substituted Alkylidenecyclopropanaphthalene[†]

Kevin Ashley, John K. Foley, Qiu Mei, Jamal Ghoroghchian, Fereshteh Sarfarazi, John Cassidy,
Brian Halton,[‡] Peter J. Stang, and Stanley Pons*

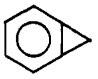
The Department of Chemistry, University of Utah, Salt Lake City, Utah 84112, and Department of Chemistry, Victoria University of Wellington, Private Bag, Wellington, New Zealand

Received December 4, 1985

Electrochemical and spectroelectrochemical investigations of 1-(diphenylmethylene)cycloprop[*b*]naphthalene in dry acetonitrile solutions show the formation of a stable anion radical (λ_{max} 519 nm) and cation radical, the first evidence of stable radicals of a methylenecyclopropene structure. Reaction of the radical anion with oxygen occurs at a rate close to the diffusion-controlled limit.

Highly strained molecules have fascinated chemists for over a century due to their unusual properties and reactivity.[1] There is a great deal of current interest and research activity in cyclopropene chemistry. The parent cyclopropene compound I has a strain energy of 68 kcal/mol, which is one of the highest known.[2]

The even more strained and unusual alkylidene derivatives of I have recently been reported.[3] Although the highly strained methylenecyclopropene parent compound II has not been isolated to date, two of us[3] have reported the successful synthesis of the 1,1-diphenyl (III) and the 1-methyl-1-phenyl (IV) derivatives as well as the corresponding naphthalene analogues V and VI. Compound V is stable in air and in aprotic solvents against rapid oxidation. Our initial spectral characterization indicated the possibility of charge-separated resonance forms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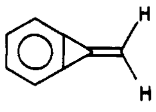

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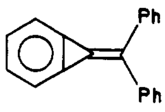
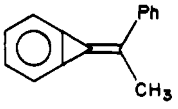


III



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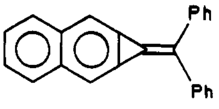
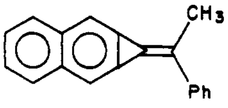


V



VI

[†] Dedicated to Professor Cheves Walling on the occasion of his 70th birthday.

[‡] Victoria University.

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(2) Halton, B. *Ind. Eng. Chem. Prod. Res. Dev.* **1980**, *19*, 349. Billups, W. E. *Acc. Chem. Res.* **1978**, *11*, 245.

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