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CRYSTAL STRUCTURES OF TWO *SYN* BENT TETRAALKYLHYDRAZINES, THEIR RADICAL CATIONS, AND A DICATION

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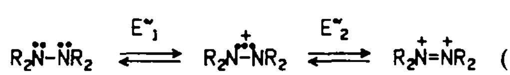
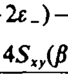
Abstract—The crystal structures of 2,7-diazatetracyclo[6.2.2.2^{3,6}.0^{2,7}]tetradec-4-ene, **2**, its cation radical nitrate salt **2**$^+$, NO$_3^-$, 2,7-diazatetracyclo[6.2.2.2^{3,6}.0^{3,7}]tetradecane, **3**, its dication dihexafluorophosphate salt **3**$^{2+}$(PF$_6^-$)$_2$, and a low quality structure of the monocation radical tosylate salt of **3** are reported and compared with MNDO calculations of these structures. Cations **2**$^+$ and **3**$^+$ are found to be significantly *syn* bent at nitrogen, and the dication **3**$^{2+}$ has a longer N—N distance than its azo analogue, 2,3-diazabicyclo[2.2.2]oct-2-ene (**11**).

The electron transfer which interconverts tetraalkylhydrazines (R_4N_2) and their cation radicals, the $E_1^{\circ\prime}$ equilibrium of Eq. (1), has received a great deal of study. It is one of the only electron transfers which gives a radical cation with a small π system for which the oxidized form is long-lived in the presence of the neutral form, so that the effects of a wide range of saturated alkyl groups on the electron transfer may be studied quantitatively. In contrast to previously studied electron transfer reactions, the thermodynamics of electron transfer are not dominated by the energy of the highest occupied molecular orbital from which an electron is being removed, and both the equilibrium and rate constants involved are very sensitive to the shape of the alkyl groups, especially when they are linked in rings.[1] The reason for this interesting behavior is that there is a significant change in geometry at the nitrogen atoms upon electron removal. The four alkyl groups attached can impose large changes in the geometries available to both the neutral and cation radical forms of R_4N_2. There is significant electronic interaction between the lone pair electrons of neutral hydrazines, which have approximately tetrahedral nitrogens in unstrained examples, and a rather weak electronic preference for perpendicular lone pair axes (lone pair–lone pair dihedral angle $\theta = 90°$). Despite their "lone pair" designation, these orbitals do mix significantly with the σ orbitals of the N—N and C—N bonds and those of the R groups. Photoelectron spectroscopy studies have shown[2] that the energy separation of the molecular orbitals dominated by the symmetric and antisymmetric combination of the lone pair orbitals is dependent upon θ, varying from about 3 eV when θ is near 180 and 0° to about 0.5 eV when θ has its preferred value of near 90°. The interaction of the lone pairs is significantly affected by the hybridization of the lone pair electrons, and hence by how pyramidal the nitrogen atoms are, as well as by θ. The best single-parameter description of the pyramidality of a nitrogen atom is the average of the three bond angles to attached atoms, $\alpha_{(av)}$, which varies almost linearly with lone pair energy and fractional p character.[1] The four electron net destabilization energy ΔE associated with a given hydrazine geometry may be estimated by using Eqs (2) and (3).[3] ΔE is the sum of the lone pair energies obtained in the real system, after mixing, minus their sum in the absence of mixing, as shown schematically in Fig. 1. The size of ΔE may be estimated



$$R_2\ddot{N}-\ddot{N}R_2 \underset{}{\overset{E^{\circ}_1}{\rightleftharpoons}} R_2\overset{+}{N}\!\cdot\!-NR_2 \overset{E^{\circ}_2}{\rightleftharpoons} R_2\overset{+}{N}=\overset{+}{N}R_2 \qquad (1)$$



$$\Delta E = (2\varepsilon_+ - 2\varepsilon_-) - 4\varepsilon_0 = E_1 - E_2 \qquad (2)$$

$$\Delta E = \frac{-4S_{xy}(\beta_{xy} - \varepsilon_0 S_{xy})}{(1 - S_{xy})^2} \qquad (3)$$

from the lone pair overlap integral S_{xy}, their resonance integral, β_{xy}, and the average lone pair energy before mixing, ε_0, according to Eq. (3). Destabilization energies for several conformations of H_4N_2 calculated from semiempirical INDO S_{xy}, β_{xy}, and ε_0 values are shown in Table 1. ΔE is required to be zero for the perpendicular $\theta = 90°$ conformation with planar nitrogens, in which the overlap and resonance integrals both disappear, but in the energy minimized

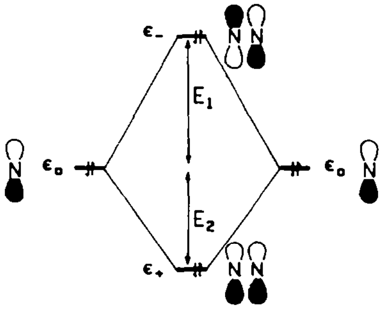


Fig. 1. Schematic representation of the four electron repulsion energy, ΔE, for nitrogen lone pairs.

Table 1. INDO calculated lone pair–lone pair destabilization energies for hydrazine in various conformations

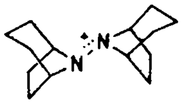
θ (deg.)	α(av) (deg.)	lp hybrid. x in sp^x	S_{xy}	β_{xy} (a.u.)	ε_0 (a.u.)	ΔE (kcal mol^{-1})
0	120	100	0.1707	−0.1568	−0.4913	32.2
0	110.19[a]	1.49	0.1259	−0.1155	−0.6518	10.48
60	110.15[a]	1.70	0.0732	−0.0671	−0.6444	3.68
90	120	100	0	0	−0.4913	0
90	110.23[a]	1.85	0.0232	−0.0212	−0.6356	0.38
180	109.31[a]	1.63	−0.0699	0.0641	−0.6480	3.32

[a] Minimized energy at the given θ value.

(except for θ) structures, which have approximately tetrahedral nitrogens, ΔE varies from about 0.4 kcal mol^{-1} at $\theta = 90°$ to about 3 kcal mol^{-1} at both *gauche* (60°) and *anti* (180°) conformations, and reaches a maximum of over 10 kcal mol^{-1} at the *syn* (0°) structure, which is the energy maximum. The electron removed from R_4N_2 is calculated to be significantly antibonding, and how antibonding it is depends on the θ and $\alpha_{(av)}$ values imposed by the alkyl groups.

Hydrazine cation radicals $R_4N_2^{\cdot+}$ are known to have high barriers to twisting their lone pair orbitals from coplanarity ($\theta = 180$ or 0°). The rotational barrier calculated by high level *ab initio* methods (MP2-6-31-G*) is 30.2 kcal mol^{-1} for $H_4N_2^{\cdot+}$, and the experimental barrier for rotation of *anti*-1$^+$ to *syn*-$^+$ is $\Delta H = 21.6$ kcal mol^{-1}[4] in acetonitrile solution. A high barrier to twisting about the N—N bond occurs because there are two bonding and only one antibonding π electrons in the two atom π system at the nitrogens; the "three electron π bond" of these systems has a formal π bond order of 0.5. The nitrogens of hydrazine radical cations are flattened compared to those of neutral hydrazines. Whether the equilibrium structure of $H_4N_2^{\cdot+}$ is calculated to have completely planar nitrogens or to be slightly *anti* bent depends on the level of *ab initio* calculation carried out, and bending at nitrogen is calculated to be exceptionally easy. Large spectral changes accompany bending at nitrogen for $R_4N_2^{\cdot+}$[5]. This occurs because σ, π mixing is forbidden when the nitrogens are planar, but occurs increasingly as the nitrogens bend. Furthermore, the different symmetries derived from bending *syn* and *anti* cause σ^*, π^* and σ, π mixing to occur upon bending *syn*, but σ, π^* and σ^*, π mixing to occur upon bending *anti*. The result is a larger ESR nitrogen splitting constant and lower π,π^* transition energy for *syn* hydrazine cations than for *anti* ones at a given amount of bending at nitrogen.

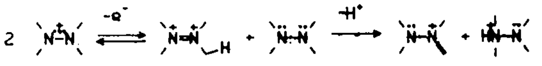
anti1$^+$



syn1$^+$

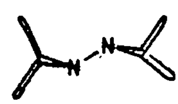
The third oxidation state of R_4N_2, the dication, has the remaining antibonding π electron of the radical cation also removed. Little experimental work has been done on these species because they are kinetically unstable unless special alkyl groups are present.

It is obviously of interest to quantitatively establish the size of the geometry changes which occur upon removal of the antiboding π electrons from R_4N_2. This experimentally requires the isolation of the ions and determination of their structures by X-ray crystallography. Although neutral hydrazines with large enough alkyl groups are easily isolated in crystalline form, most examples of $R_4N_2^{\cdot+}$ prove not to be isolable, despite the fact that they persist for many hours in dilute solution. Electron transfer disproportionation between two $R_4N_2^{\cdot+}$ species leads to neutral, dication pairs, which very rapidly decompose by intermolecular proton transfer, as shown in Eq. (4).

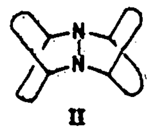


(4)

Although the electron transfer disproportionation is rather endothermic, the proton transfer ordinarily competes with the back electron transfer, leading to decomposition. Special alkyl groups are required to make $R_4N_2^{\cdot+}$ stable enough for isolation; these are bicyclic groups which hold the Cα—H bonds near the nodal plane of the p orbitals in the dication. We believe the first use of the geometrical constraints of bicyclic alkyl groups to kinetically stabilize a radical was that of DePeyre and Rassat,[6] who also pointed out the structural relationship to Bredt's Rule destabilized olefins. The most easily prepared Bredt's Rule protected hydrazines are bi-N,N-bicyclic systems **I**, which are produced in good yield by treatment of the bicyclic chloroamines with t-butyllithium.[4,7,8] In these compounds the four α-branched alkyl groups impose *anti* bent, θ near 180° geometries on both the neutral and radical cationic forms, and the radical cations are isolable. The "proton driven Diels–Alder" addition of protonated bicyclic azo compounds to cyclic dienes makes bi-N,N′-bicyclic hydrazines **II** easily available.[9] Here the substitution tends to hold both internal CNNC angles near 0°, forcing these compounds into the electronically least favorable *syn* bent, θ near 0° geometries.

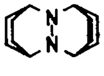


I



II

In this work we report X-ray crystallographic structures for 2, 2^{+}, 3, 3^{+}, and 3^{2+}, providing information on how electron loss affects structure for *syn* bent hydrazines. The isolability of 3^{2+} was an unexpected bonus of the substitution pattern of **II**. Although the



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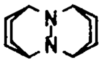


3

hydrazine dications derived from **1** are usually long-lived on the cyclic voltammetry time scale of 1 s, none appear to last minutes. The unsaturated analogue $\mathbf{2}^{2+}$, with its allylic C—N bonds, also proved to be unstable on a time scale of minutes.

Crystallographic results

The details of the data collection and refinement of the structures reported appear in the Experimental. A numbered thermal ellipsoid drawing and line structure with heavy atom bonds lengths and bond angles are given for each structure in Figs 2–6. The numbers in parentheses on these structures are not statistical errors, but instead differences in the indicated bond angle or distance between crystallographically different but chemically identical bonds, which gives a better feeling for the interpretability of the data. Selected dihedral angles appear in Table 2. Tables of bond lengths, bond angles and thermal parameters with errors shown in the usual fashion appear in the thesis, along with packing diagrams,[10] and complete coordinate lists including hydrogens and counterions have been deposited.[11] The structure obtained for **2** is, not surprisingly, disordered at the CH_2CH_2 and CH=CH bridges C(9)C(10) and C(4)C(5). The data listed are for a refinement in which the shorter of these two bonds observed was assigned as the CH=CH bond; the intermediate sizes of the bond lengths between C—C and C=C values show that the cation units are in the crystal lattice both ways, but the *R* value came out to be a respectable 0.044. A disorder model treating the

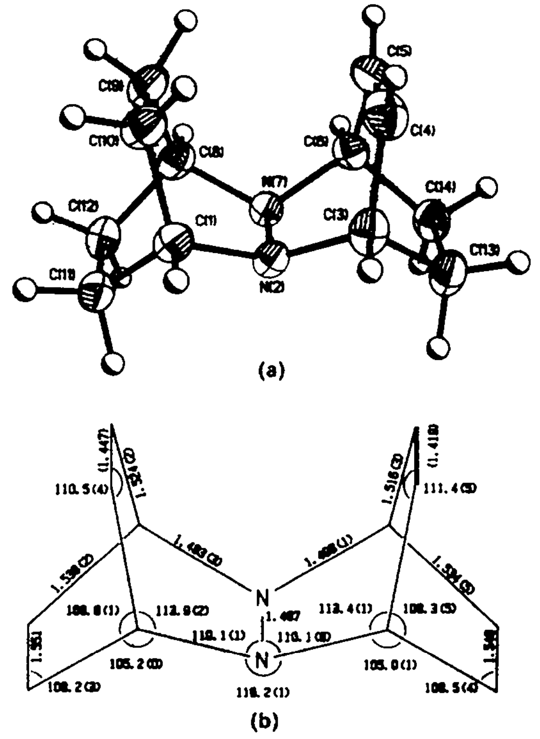


Fig. 2. Thermal ellipsoid plot and bond length bond angle summaries for neutral **2**.

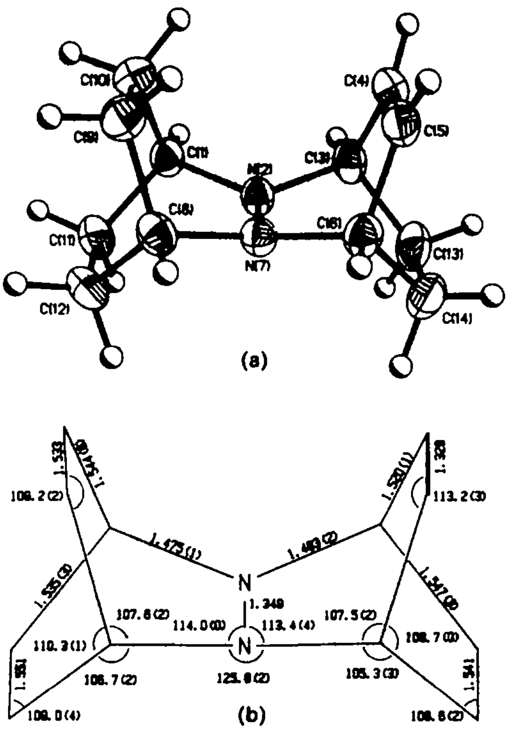


Fig. 3. Thermal ellipsoid plot and bond length bond angle summaries for $2^+NO_3^-$.

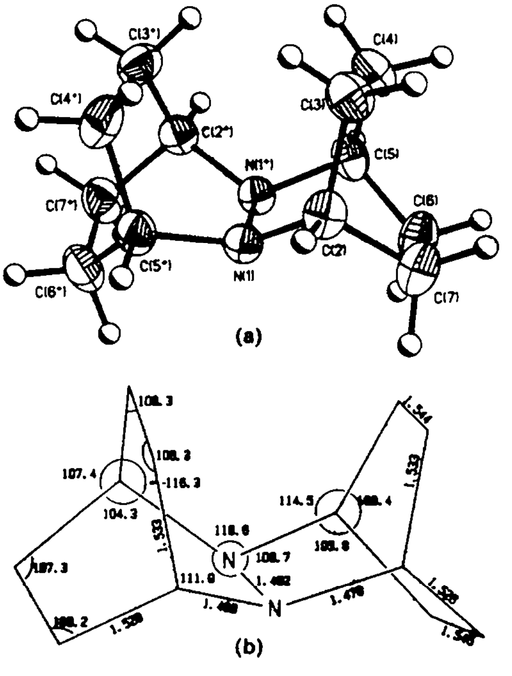


Fig. 4. Thermal ellipsoid plot and bond length bond angle summaries for neutral **3**.

Table 2. Selected dihedral angles (deg.)

	2	2^+	3^a	3^+A	3^+B
C(1)N(2)N(7)C(8)[b]	0.4(3)	1.8(1)	15.0(2)	5.0(14)	−3.6(12)
C(3)N(2)N(7)C(6)[b]	0.0(4)	−0.6(1)	[d]	−1.1(13)	−7.5(11)
C(1)N(2)C(7)C(6)[c]	129.5(3)	−152.3(1)	−117.2(2)	163.4(10)	150.4(9)
C(3)N(2)N(7)C(8)[c]	−129.1(3)	153.6(1)	147.2(2)	−160.4(10)	161.5(8)
C(1)C(10)C(9)C(8)	0.1(4)	2.1(2)	8.8	3.5(13)	−1.2(12)
C(3)C(4)C(5)C(6)	−0.1(5)	−0.3(2)	[d]	1.1(14)	−2.0(15)
C(1)C(11)C(12)C(8)	0.2(5)	2.2(2)	11.9	2.3(15)	−5.8(13)
C(3)C(13)C(14)C(6)	−0.5(3)	−0.5(2)	[d]	−0.8(12)	−1.5(13)

[a] Numbering different because of the C2 axis; see the thermal ellipsoid diagram in Fig. 4 for the proper numbering.

[b] The average of the absolute values of these angles was used as θ.

[c] The average of the absolute values of these angles was used as ϕ, which is the dihedral angle between the internal CNNC (approximate) planes.

[d] Same as the above entry by symmetry.

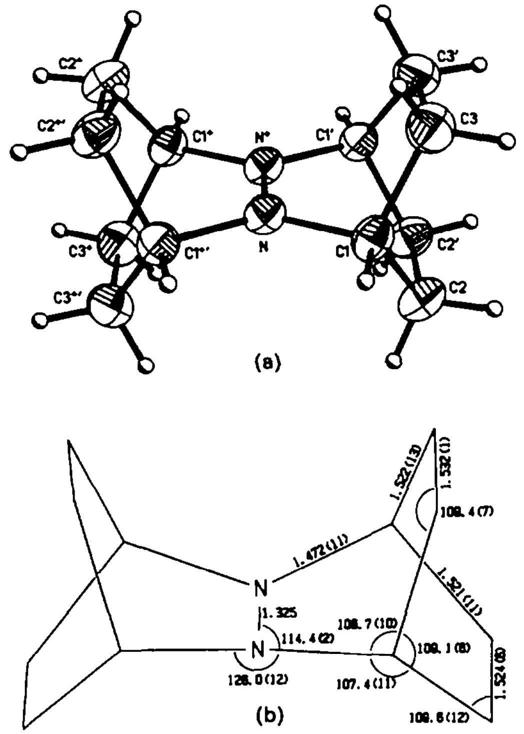


Fig. 5. Thermal ellipsoid plot and bond length bond angle summaries for $3^{2+}(PF_6^-)_2$.

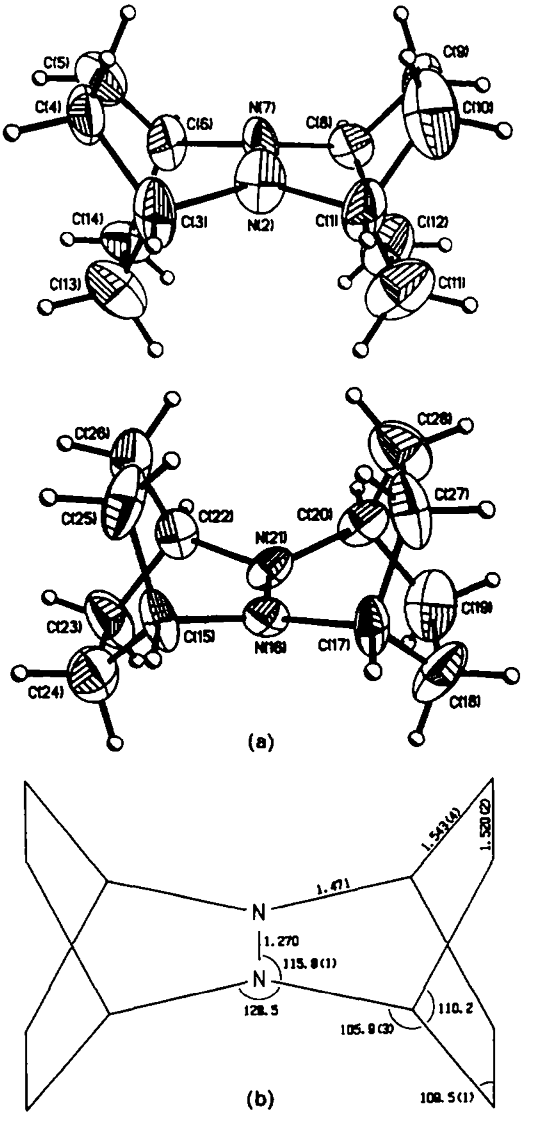


Fig. 6. Thermal ellipsoid plot and bond length bond angle summaries for 3^+TsO^-. Two crystallographically independent 3^+ units are present, and averaged bond angles and bond lengths are shown.

occupancies of these sites as x and $1-x$ gave $x = 0.61$, but R increased to 0.08, so we use the previous structure in our discussion.

The structure obtained for $2^+NO_3^-$ is not detectably disordered at C(4)C(5) and C(9)C(10), but the nitrate anion was found to be disordered and was best refined as one nitrogen with six half-occupied oxygen atoms.

The crystal lattice of 3 possesses a crystallographic C_2 axis perpendicular to the N—N bond, so only half of the molecule is crystallographically unique. The other half was generated by the symmetry transformation $0-x$, $0+y$, $1.5-z$, in accordance with the internal symmetry of the unit cell, and the whole cation is plotted in the pictures.

As reported previously,[9a] $3^{2+}(PF_6^-)_2$ crystallizes

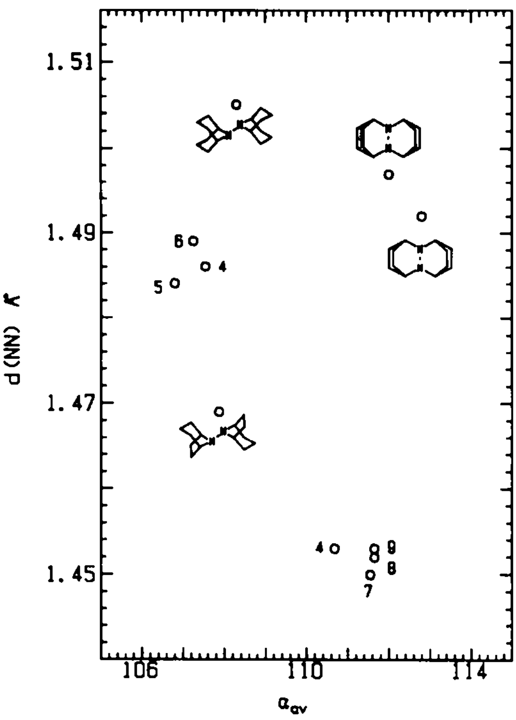


Fig. 7. Plot of N—N distance vs α(av) for six-membered ring tetraalkylhydrazines.

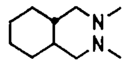
from acetonitrile with two molecules of solvent per dication unit. This solvent of crystallization is lost with frustrating ease, and we were unable to mount crystals which diffracted, even in capillaries containing solvent. Luckily, the dication crystallizes out of water without solvent. Because the internal unit cell symmetry of the $3^{2+}(PF_6^-)_2$ crystals obtained is high, only one-fourth of the dication and one-half of the anion are crystallographically unique. The remainder of the 3^{2+} structure is generated by the symmetry transformations $0+x$, $0-y$, $0+z$ and $1-x$, $0+y$, $1-z$. Some disorder in the PF_6^- anion was observed for the equatorial fluorines, which was treated as the average of an 84 : 16 mixture of two PF_6^- rotamers. The nitrogens and α carbons were found to be coplanar (α(av) = 120, θ = 0, ϕ = 180°).

Despite considerable work, our structure for 3^+X^- remains substantially lower in precision than any of the other four species discussed above. Although crystals of $3PF_6^-$ and $3^+NO_3^-$ which diffracted well were obtained and data were collected, as indicated in the Experimental, the space groups for the unit cells obtained had impossibly high symmetry, indicating internal disorder; the data sets were not solved. The tosylate salt was obtained in a triclinic lattice with two molecules of 3^+TsO^- in the unit cell, but this crystal transformed into one having a monoclinic lattice with eight molecules per unit cell over a period of two days at room temperature. Data collection and refinement on the monoclinic crystal gave a rather low precision structure, $R = 0.123$, $R_w = 0.110$. In spite of the lower precision the 3^+ units fit without expectation by comparison with the much more precise $2^+NO_3^-$ structure. The two unique cation fragments shown as 3^+A and 3^+B, are quite similar. For example, the refinement gives α(av) values of 119.3 at N(2), 118.6 at N(7) of the A cation, and 118.5 at N(16) and 118.0 at N(21) of the B cation. Values averaged over both the A and B cations are used in Fig. 6.

DISCUSSION

Neutral hydrazines 2 *and* 3

Compounds 2 and 3 are the first *syn* bent hydrazines for which X-ray structural data have become available.† The C═C bond of 2 resists bicyclic ring torsion, and θ for 2 is within experimental error of being 0° (see Table 2). When the double bond is saturated in 3, bicyclic torsion twists the N—N bond to θ = 15°. Little lone pair–lone pair electronic interaction would be relieved by such a twist angle [cos (15°) = 0.966], but steric interaction between the hydrogens of the *syn* two carbon bridges is relieved, and the *syn* hydrogen at C(3) may be seen to lie between those on C(4^+) and C(3^+) in the thermal ellipsoid plot. Values of α(av) for 2 and 3 were determined to be 112.1 and 112.8°, respectively. We had expected slightly greater α(av) for 3, which has two (CH_2CH_2) interactions replacing the (CH_2CH_2), (CH═CH) interaction of 2, and is therefore more strained. We compare the N—N bond length and pyramidality at the nitrogens of 2 and 3 with other 6-membered ring hydrazines in Fig. 7. The three diequatorial substituted 6-ring hydrazine structures, 4[13], 5 (diequatorial at both hydrazine units)[14]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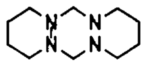
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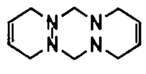
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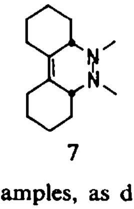
and the diequatorial hydrazine unit of 6 give very similar structures, and have θ values in the range 174.4–180°. Four axial, equatorial hydrazines are plotted, including tetrahydropyridazine 7,[13] the axial, equatorial unit of 6, and benzylated hexahydrotetrazines 8[15] and 9,[14] which have *gauche* lone pairs (θ in the range 60.9–65.4°); they also occur in a small region of the plot (Fig. 7). There is a significant increase in d(NN) (0.03₄ Å, or 2.2%) and decrease in α(av) (4.2°, or 40% of the way from tetrahedral to planar N atoms) comparing the *anti* with the *gauche*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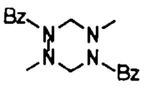

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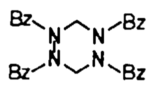

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examples, as discussed previously.[1,13] The *syn* compounds 2 and 3 have only slightly longer N—N bond lengths than the *anti* compounds, but are significantly flatter at nitrogen. The higher α(av) values of the *syn* compounds should put more s character into the N—N bond, tending to decrease the bond length; presumably the larger four electron destabilization for *syn* than for *anti* hydrazines compensates for this tendency. Also included in the plot are the θ = 180°

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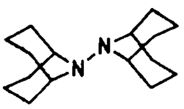
†The electron diffraction structure of 1,5-diazabicyclo [3.3.0]octane[12] has θ = 37.9(33), α(av) 107.7°, d(NN) 1.434 (16) Å.



10

bi-N,N-bicyclic compounds **10**[16] and **1**.[4] They lack NN′ rings, so increasing their N—N distance does not force internal angle distortions as it does in the other compounds shown. Although **10** has the longest N—N distance of this series, that of **1** is a significant 2.4% shorter, despite their structural similarity. The smaller CNC angle of 101.3° for **1**, caused by its 5-membered rings, compared to the 106.7° for **10** is presumably responsible. We note that the shortest R_4N_2 N—N bond length yet reported is for the electron diffraction structure of 1,5-diazabicyclo [3.3.0]octane,[12] which also has α angles restricted by being in 5-membered rings.

Considerably larger steric interactions are clearly present in the tetra-α-branched **2** and **3** than in the other hydrazines, but the α(av) values for **2** and **3** are not significantly larger than for the *gauche* hydrazines **6**–**9**. This probably happens because of the more rapid increase in electronic strain when flattening occurs near $\theta = 0°$ than at *gauche* θ values (Table 1).

Cation radicals $\mathbf{2}^+$ *and* $\mathbf{3}^+$

Only the structure of $\mathbf{2}^+$ is really of sufficient precision to make discussion of the detailed structure particularly meaningful, although the similarity in both gross structure and the parameters derived by X-ray crystallography encourage us to believe the structure given above for $\mathbf{3}^+$ is also essentially correct. The only accurate structure previously reported for a tetraalkylhydrazine cation radical is that for $\mathbf{1}^+NO_3^- \cdot H_2O$.[4b] Rather different structural constraints are present in the cations of **1** and **2**. The alkyl groups force *anti* bending for $\mathbf{1}^+$, but electronically less favored *syn* bending for $\mathbf{2}^+$. For $\mathbf{1}^+$, the CNC angles are restricted by the bicyclic rings (obs 105.5°), while the CNN angles are unconstrained (obs 120.7°), while for $\mathbf{2}^+$ the CNC angles are unrestricted (obs 125.8°) and the CNN angles are constrained in 6-membered rings (obs 113.7°). The average increase in bond angle at nitrogen for $\mathbf{2}^+$ compared to $\mathbf{1}^+$ corresponds to 20% of the way from tetrahedral to planar nitrogen atoms, but despite the large alkyl groups, $\mathbf{2}^+$ has nitrogen atoms which are bent 22% of the way from being planar to being tetrahedral. The N—N distance obtained for $\mathbf{2}^+$ is 0.024 Å (1.8%) longer than that of $\mathbf{1}^+$. The X-ray structure obtained for $\mathbf{3}^+$ indicates that it is also significantly nonplanar at nitrogen, and its spectroscopic data show that this is not an artifact of the lower precision of our structure; $\mathbf{3}^+$ is clearly somewhat bent at nitrogen,[5] but less bent than $\mathbf{2}^+$.

Dication $\mathbf{3}^{2+}$

As expected, the N atoms of $\mathbf{3}^{2+}(PF_6^-)_2$ are planar in the structure we obtained. It is of interest to compare the structure of $\mathbf{3}^{2+}$ with that for the monocyclic azo compound analogue 2,3-diazabicyclo[2.2.2]oct-2-ene **11**, whose gas phase electron diffraction structure[17a] is shown in Fig. 8. Except for the N—N bond length and bond angles about the methine carbons, they are very similar. The N—N bond length of $\mathbf{3}^{2+}$ is about 0.03 Å longer than that of **11**, despite the fact that **11** has eclipsed nitrogen lone pairs. One might expect the covalent radius for a formally positive nitrogen, as in $\mathbf{3}^{2+}$, to be somewhat shorter than that for a neutral nitrogen. Alder *et al.*[18] have reported a similar increase in N—N bond length for a bis-alkylated R_4N_2 dication. As Fig. 7 shows, the d(NN) range for 6-membered ring neutral hydrazines is 1.45–1.50 Å, depending on θ, but that for the hexa-alkylhydrazine dication $\mathbf{12}^{2+}$ is significantly longer, at 1.53 Å.

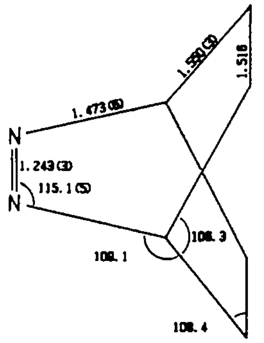
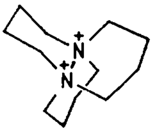


Fig. 8. Electron diffraction bond lengths and bond angles[17a] for azo compound **11**.



12²⁺

The other noteworthy difference between the structures of **11** and $\mathbf{3}^{2+}$ involves the bond angles at the methine carbons. The $NCHCH_2$ angles contract from 109.1° in **11** to 105.9° in $\mathbf{3}^{2+}$, while the CH_2CHCH_2 angles expand from 106.3 to 110.2°. Any residual steric interaction between the bridges in $\mathbf{3}^{2+}$ would cause the opposite change in angles, so an electronic effect is presumably involved. We suggest that a likely explanation is an enhanced σ,π^* hyperconjugative interaction between the hydrocarbon σ bonds and the exceptionally low-lying N—N π^* orbital of $\mathbf{3}^{2+}$, which is centered at positive nitrogens. The observed angle changes seen in $\mathbf{3}^{2+}$ compared to **11** would increase σ,π^* overlap. Such interaction might also be the reason for the increased N—N bond length. As previously noted,[9a] $\mathbf{3}^{2+}$ has strong near UV absorptions, λ (m) nm 317 (ε 2600), 227 (ε 8400), for both $(BF_4^-)_2$ and $(PF_6^-)_2$ counterions, which we suggest are therefore unlikely to involve ion pair phenomena. The π,π^* absorption would certainly be expected to occur at much shorter wavelength, and we suggest that the transition involved might well be σ,π^*.

Geometry change upon electron loss

The sizes of the geometry changes upon electron loss from R_4N_2 now available are compared in Table 3. The N—N bond length changes upon electron removal from *syn*-hydrazine **2** and *anti*-hydrazine **1** are within experimental error of being the same size. The observed α(av) change is greater for **1** (7.7° increase) than for **2** (5.6° increase), but since neutral-

Table 3. Comparison of structural changes upon one electron removal observed by X-ray and calculated by MNDO

	X-ray			MNDO		
	Reduced	Oxidized	Difference	Reduced	Oxidized	Difference
$\mathbf{2}(\theta = 0°)/\mathbf{2}^+(\theta = 0°)$						
d(NN), Å	1.497	1.349	−0.148(9.9%)	1.406	1.325	−0.081(5.8%)
α(CNN), deg.[a]	110.1	113.7	+3.6	112.4	114.1	+1.7
α(CNC), deg.	116.2	125.8	+9.6	119.6	130.2	+10.6
α(av), deg.	112.1	117.7	+5.6(53%)[b]	114.8	119.5	+4.7(45%)[b]
ϕ, deg.	129.5	152.6	+23.1(39%)[b]	138.6	168.2	+29.6(49%)[b]
ΔH_f,[c]				55.8	213.2	157.4
$\mathbf{3}(\theta = 15°)/\mathbf{3}^+(\theta = 4°)$						
d(NN), Å	1.492	1.325	−0.167(11.2%)	1.396	1.315	−0.081(5.8%)
α(CNN), deg.	108.7	114.4	+5.7	112.6	114.7	+2.1
α(CNC), deg.	118.6	126.0	+7.4	121.6	130.6	+9.0
α(av), deg.	112.8	118.3	+6.3(60%)	115.6	120.0	+4.4(42%)
ϕ, deg.	132.2	155.9	+23.7(40%)	142.1	180.0	+39.7(66%)
ΔH_f,[c]				27.8	179.6	151.8
$\mathbf{1}(\theta = 180°)/\mathbf{1}^+(\theta = 180°)$[d]						
d(NN), Å	1.469	1.323	−0.146(9.9%)		1.302	
α(CNN), deg.	111.1	120.7	+9.6		125.9	
α(CNC), deg.	101.3	105.5	+4.2		104.1	
α(av), deg.	107.9	115.6	+7.7(73%)		118.6	
β(NN), deg.[d]	55.3	32.5	−27.8(42%)		17.3	
ΔH_f,[c]					117.1	
$\mathbf{3}^+(\theta = 0°)/\mathbf{3}^{2+}(\theta = 0°)$						
d(NN), Å	1.325	1.270	−0.055(4.2%)	1.315	1.263	−0.052(4.0%)
α(CNN), deg.	114.4	115.8	+1.4	114.7	115.4	+0.7
α(CNC), deg.	126.0	128.5	+2.5	130.6	129.0	−1.6
α(av), deg.	118.3	120.0	+1.7(16%)	120.0	120.0	0
ϕ, deg.	155.9	180.0	+24.1(40%)	180.0	180.0	0
ΔH_f,[c]				179.6	479.1	299.5

[a] Averaged for the two types of C—N bonds.

[b] Percentage of the change from tetrahedral to planar nitrogens (10.53° for α(av), 60° for ϕ).

[c] kcal mol^{-1}.

[d] From Ref. 4. β(NN) is the angle the N—N bond makes with the CNC plane, and changes 57.7° between tetrahedral and planar nitrogen.

2 has a 4.2° higher α(av) value than **1**, the nitrogens of $\mathbf{2}^+$ end up with a 2.1° higher α(av) value than those of $\mathbf{1}^+$. The geometry change for the slightly more hindered $\mathbf{3},\mathbf{3}^+$ pair came out a little bit larger than that for $\mathbf{2},\mathbf{2}^+$, but the low precision of the $\mathbf{3}^+$ structure makes this somewhat uncertain. It is certainly plausible that α(av) of $\mathbf{3}^+$ would be a little higher than that of $\mathbf{2}^+$.

Even given the lower precision of the $\mathbf{3}^+$ structure, it is clear that the geometry change upon removal of the second electron from **3** is smaller than that for removal of the first. The N—N bond length shortening observed is about 11% for removal of the first electron, and 4% for the second, and α(av) increases about 6° when the first electron is removed and 2° when the second is removed. Cation $\mathbf{3}^+$ is flat enough at nitrogen that flattening completely upon removal of the second π^* electron only can cause a small increase in α(av).

It is interesting to compare the geometry changes upon first and second electron loss from the nitrogens of tetraalkylhydrazine **3** with those for diamine **12**. The lone pair–lone pair interactions are considerably different in these two cases. The lone pairs interact in π fashion for **3** (N—N axis perpendicular to the lone pair axes in the dication form), but in σ fashion for **12** ("lone pair" axis is coincident with the N—N axis in the dication form). Alder *et al.*[18] have found that the N—N distance decreases from 2.806(3) Å in neutral **12** to 2.295(10) Å in $\mathbf{12}^+$, an 18.2% decrease, while it is 1.532(6) Å in $\mathbf{12}^{2+}$, corresponding to a 33.2% decrease upon removal of the second electron. Bonding differs substantially in the π and σ lone pair interaction geometries, of course. Compound **3** maintains a σ bond between the nitrogens in all three oxidation states, while the formal π bond order changes from 0 to 1/2 to 1 as the electrons are removed; **12** has a formal σ bond order between the nitrogens which increases from 0 to 1/2 to 1 as the electrons are removed. In both cases the formal bond orders of 0 actually correspond to significant antibonding, because the lone pair orbitals overlap and are both filled, leading to a four electron repulsion term (see Table 1 for calculations on the π overlap situation).

Because we are also interested in using molecular orbital calculations to examine both electron transfer and spectral phenomena involving these species, we have determined structures using MNDO calculations[19] and include these results in Table 3 as well. The semiempirical MNDO method represents the highest level calculations for which geometry optimized structures can be obtained presently for molecules as large as the ones in which we are interested. The shortcomings of the MNDO method for hydrazine structures are well known. MNDO does not treat lone pair–lone pair interactions properly, giving too

Table 4. Summary of crystal data and intensity collection

Compound	2	$2^+NO_3^-$	3	$3^{2+}(PF_6^-)_2$	3^+PF_6	$3^+NO_3^-$	3^+TsO^-
Empirical formula	$C_{12}H_{18}N_2$	$C_{12}H_{18}N_3O_3$	$C_{12}H_{20}N_2$	$C_{12}H_{20}N_2F_{12}P_2$	$C_{12}H_{20}N_2F_6P$	$C_{12}H_{20}N_3O_3$	$C_{19}H_{27}N_2O_3S$
Formula wt, g m^{-1}	190.29	252.30	192.31	482.24	337.27	254.31	363.50
Crystal dimensions, mm	0.3 × 0.35 × 0.4	0.2 × 0.4 × 0.75	0.3 × 0.3 × 0.4	0.15 × 0.15 × 0.2	0.3 × 0.4 × 0.4	0.2 × 0.25 × 0.5	0.2 × 0.25 × 0.4
Temperature, K	105	128	294	294	294	105	294
Cell parameters							
a	14.862(5)	6.322(1)	15.918(7)	12.700(2)	7.571(2)	7.763(1)	9.572(3)
b	—	13.431(2)	6.239(3)	9.271(1)	—	—	39.444(20)
c	—	14.333(3)	10.919(4)	8.142(1)	13.189(3)	10.317(1)	10.301(4)
α	116.66(3)	—	—	—	—	—	—
β	—	92.98(1)	107.93(3)	116.76(1)	—	—	111.68(3)
Space group	R_3	$P_{2_1/c}$	$C_{2/c}$	$C_{2/m}$	[a]	[b]	$P_{2_1/n}$
Z	6	4	4	2	2	2	8
Density, calc, g cm^{-3}	1.24	1.38	1.24	1.87	1.48	1.36	1.34
Absorpt coeff μm cm^{-1}	0.393	0.610	0.386	3.137	1.908	0.596	1.568
Scan range deg. below 20 MoKα	0.7	0.8	0.6	0.65	0.86	0.6	[c]
deg above 20 MoKα	0.7	0.8	0.6	0.65	0.85	0.6	—
Scan speed, deg. min^{-1}	3.0–24.0	2.5–24.0	3.5–20.3	2.0–24.0	2.0–24.0	2.0–24.0	3.5–24.0
Scan type	θ–2θ	θ–2θ	θ–2θ	θ–2θ	θ–2θ	θ–2θ	ω
2θ limits, deg.	3.5–58.7	3.5–58.7	3.5–58.2	3.5–54.9	3.5–62.1	3.6–63.7	3.5–45.77
sin θ/λ_{max}, Å^{-1}	0.690	0.690	0.684	0.649	0.726	0.742	0.547
Unique data, theoretical	2790	3340	1417	1956	1210	1066	4960
$F_0 > 3\sigma(F_0)$	1490	2661	1082	818	—	—	2675
Discrepancy index,							
R	0.044	0.050	0.051	0.043	—	—	0.123
R_w	0.048	0.052	0.051	0.044	—	—	0.110
Goodness of fit	1.408	1.783	1.577	1.515	—	—	1.436
Data, variable ratio	7.4	10.1	10.3	7.3	—	—	5.9

[a] Tetragonal lattice with I space group.

[b] P_{4_2nm}, $P_{4_2/mnm}$, or P_{4_n2}.

[c] 1.5° wide omega scan centered on 2θ MoKα.

short N—N bond lengths and the $\theta = 180^\circ$ instead of the correct $\theta = 90^\circ$ structure as the energy minimum for hydrazine itself.[20] Nevertheless, we have shown that MNDO calculations are very useful for considering how alkyl group structural changes affect $R_4N_2^+$ spectral properties,[5] and will in the near future apply such calculations to electron transfer barriers for these species. It is convenient to compare the experimental and calculated geometries here. The restricted Hartree–Fock option (RHF) has been used for the singlet species, but unrestricted Hartree–Fock (UHF) has been used for the doublet radical cations. In all cases θ has been held at 0° (our attempts at twisting **3** in these calculations led to an inability to achieve self-consistency), and C_s and C_{2v} symmetry has been enforced for species based on **2** and **3**, respectively. The HCCC and HCCN dihedral angles of the species based on **2** which are near 180° were held at 180° artificially, but otherwise, all bond lengths, angles, and dihedral angles are allowed to vary to minimize the energy in these calculations.

It will be noted in Table 3 that the calculated N—N bond lengths are systematically too short, with the greatest error (*ca* 0.1 Å) for the neutral hydrazines and the least (0.007 Å) for the dication. The C—N and C—C bonds are calculated to be too long, usually by 0.01–0.03 Å. The largest error found was for the C—N bonds of $\mathbf{3}^{2+}$, which MNDO predicts at 1.546 Å, 0.075 Å longer than that observed. The MNDO structures of **2** and **3** as well as their cation radicals are significantly flatter at nitrogen than is observed, which probably results from MNDO overestimating steric interactions, a well-established fact for amino nitrogen compounds in the MNDO approximation. Much of the error in the calculated N—N bond lengths may result from the structures being calculated as too flat, because these structural features interact. Despite its errors, the MNDO method successfully predicts both the N—N bond length decreases and flattening at nitrogen which are observed upon electron removal, although the changes are calculated to be rather smaller than actually observed.

EXPERIMENTAL

Details of the preparations of the compounds studied here have been published.[9] Crystals of **2** and **3** were grown by slow cooling of dilute ether solutions to −78°, and radical cation salts by vapor diffusion of ether into acetonitrile solns at −20°. This technique gave solvent inclusion for $\mathbf{3}^{2+}(PF_6^-)_2$, which was obtained solvent free by slow supercooling of aqueous solns. All crystals were mounted on glass fibers and coated with cyanoacrylate glue for the X-ray studies. Measurements were carried out on Nicolet diffractometers equipped with monochromated MoK_α radiation sources. Structure amplitudes and their standard deviations were calculated from the intensity data by procedures similar to those described previously,[21] and all structures were solved and refined using SHELXTL direct methods and least squares refinement procedures.[22] Final refinement cycles assumed all non-hydrogen atoms to vibrate anisotropically and included the hydrogens as isotropic atoms. Hydrogen atoms were not refined for $\mathbf{3}^+TsO^-$. Crystal data and details of the intensity collection are given in Table 4.

The calculations of Table 1 employed Weinhold's BONDO modification of INDO.[23]

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