Structures of the Radical Cation and Dication from Oxidation of 1,6-Diazabicyclo[4.4.4]tetradecane

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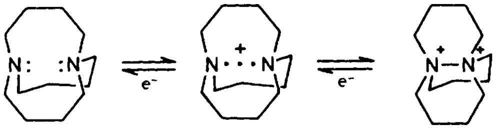
The three-electron σ-bond in 1,6-diazabicyclo[4.4.4]tetradecane radical cation perchlorate is 2.30 Å long; the $\geqq\overset{+}{N}-\overset{+}{N}\leqq$ bond length in 1,6-diazoniatricyclo[4.4.4]tetradecane bistrifluoromethanesulphonate is 1.53 Å.

All three oxidation states in the redox equation (i) are isolable as stable solids, although the diamine (**1**) is destroyed by atmospheric oxygen.[1—3] We have reported[4] the structure of (**1**), which is characterised by an N–N distance of 2.806 Å. We now report *X*-ray structural data for salts of (**2**) and (**3**).

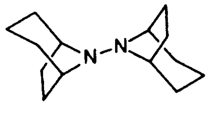
The perchlorate salt of (**2**) was prepared by mixing equivalent quantities of (**1**) and the diperchlorate of (**3**), each dissolved in acetonitrile, followed by removal of the solvent. Dark red (almost black) crystals of (**2**)·ClO_4 were grown by slow diffusion of diethyl ether into a solution in acetonitrile at room temperature. *Crystal data* for (**2**)·ClO_4: $C_{12}H_{24}N_2ClO_4$, $M = 295.78$, monoclinic, space group $P2_1$, $a = 7.708(5)$, $b = 13.194(6)$, $c = 7.898(6)$ Å, $\beta = 114.59(5)°$, $Z = 2$, $U = 730.38(76)$ Å^3, $D_c = 1.35$ g cm^{-3}, $F(000) = 317.95$, Mo-K_α *X*-radiation, $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 2.7 cm^{-1}. The position of the chlorine was located on a Patterson map, and all the atoms including hydrogens were located on difference electron density syntheses. Refinement led to a current R of 0.059 for a total of 852 unique observed $[I > 3\sigma(I)]$ data measured in the range $4 < 2\theta < 50°$ on a Nicolet P3m diffractometer.[†]

Crystals of (**3**)·$2CF_3SO_3$ were grown by slow diffusion of diethyl ether into a solution in acetonitrile at room temperature. *Crystal data* for (**3**)·$2CF_3SO_3$: $C_{14}H_{24}N_2S_2F_6O_6$, $M = 494.49$, monoclinic, space group $P2_1/c$, $a = 7.896(2)$, $b = 22.35(1)$, $c = 12.463(4)$ Å, $\beta = 104.90(3)°$, $Z = 4$, $U = 2125.5(1.3)$ Å^3, $D_c = 1.55$ g cm^{-3}, $F(000) = 1023.88$, Mo-K_α *X*-radiation, $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 3.22 cm^{-1}. The structure was solved using direct methods; all non-hydrogen atoms were located on difference electron density syntheses. The structure[†] was disordered, with the opposite enantiomer of the dication occurring at an occupancy of 0.194(3) on

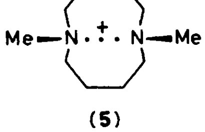


(i)

(**1**) (**2**) (**3**)

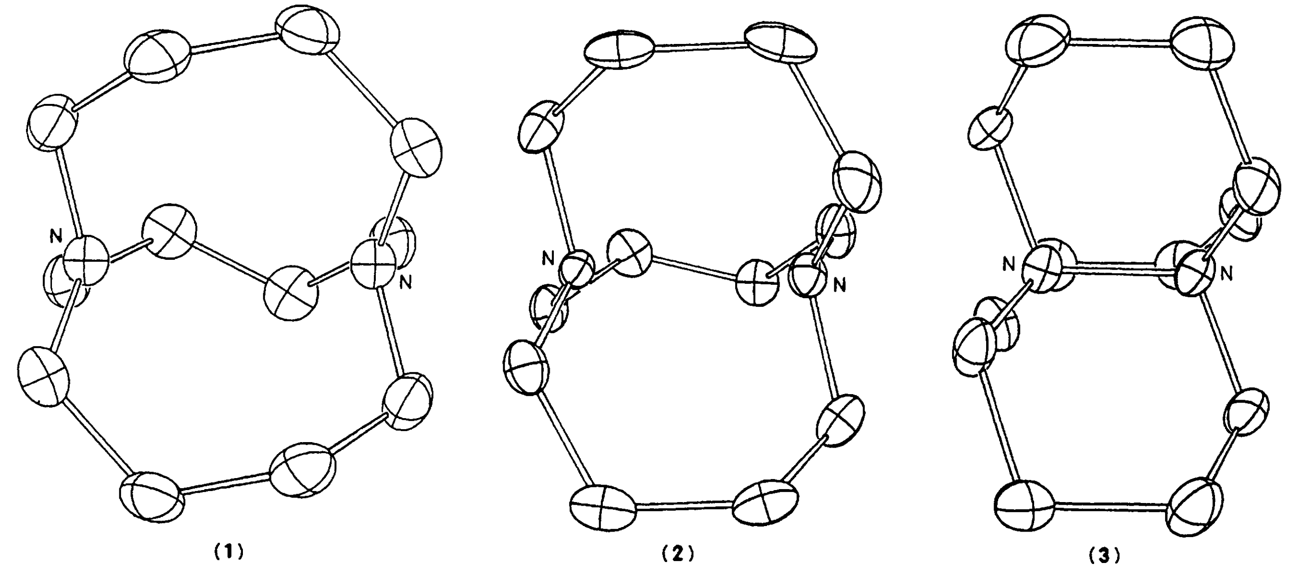


(**4**)



(**5**)

[†] The atomic co-ordinates for the structures reported here are available on request from The Director, Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.



(1) **(2)** **(3)**

Figure 1. Molecular structures of **(1)**, **(2)**, and **(3)**, viewed along an approximate two-fold axis [exact for **(1)**]. Hydrogen atoms have been omitted for clarity.

Table 1. Structural data for **(1)**, **(2)**·ClO_4, and **(3)**·$2CF_3SO_3$ averaged, for **(2)** and **(3)**, to D_3 symmetry.

Interatomic distances/Å	(1)	(2)	(3)
N–N	2.806(3)[a]	2.295(10)	1.532(6)
N–C	1.443(3)	1.466(11)	1.533(6)
C–C[b]	1.521(4)	1.509(12)	1.505(8)
Bond angles/°			
C–N–C	115.5(2)	114.0(6)	109.0(4)
N–C–C	114.1(2)	115.6(7)	114.2(4)
C–C–C	116.3(2)	115.0(8)	111.0(4)
Torsion angles/°			
C–N–N–C[c]	18.2(2)	38.8(7)	52.2(4)
N–N–C–C[c]	−30.6(2)	−44.8(8)	−54.6(5)
N–C–C–C	68.2(2)	63.3(10)	54.8(6)
C–C–C–C	−90.1(2)	−66.9(10)	−53.0(6)

[a] Estimated standard deviation in the least significant digit is given here and throughout. [b] The two types of C–C bond are not significantly different in length. [c] Within one N_2C_4 ring.

essentially the same site. Refinement led to a current R of 0.065 for 2174 unique observed $[I > 3\sigma(I)]$ data measured in the range $4 < 2\theta < 50°$.

Although neither **(2)** nor **(3)** possess any crystallographic symmetry, both are very close to D_3 molecular symmetry, as is found exactly for **(1)**. The geometrical features of **(1)**, **(2)**, and **(3)** are listed in Table 1 and the structures are shown in Figure 1. The relief of strain on proceeding from **(1)** to **(3)** is apparent in both the bond and torsional angle changes, and provides firm structural corroboration for the extreme ease of oxidation of **(1)** to **(2)** and **(2)** to **(3)**.[1] The increased inward pyramidalisation of the nitrogens of radical cation **(2)**, as compared with diamine **(1)**, may be taken as proof of an N · · · N interaction, since simple amine radical cations are flat.

Examples of three-electron σ-bonds in cation and anion radicals are now widespread,[5] but we believe that the only established bond lengths are those in **(2)** and in $He_2^{+\cdot}$ (1.081 Å).[6] The corresponding dication, He_2^{2+}, recently detected experimentally,[7] has a bond length of 0.704 Å, according to definitive (James–Coolidge) calculations.[8] Bouma and Radom[9] report 6–31G calculations on the parent ions of **(2)** and **(3)**; $N_2H_6^{+\cdot}$ has a bond length of 2.164 Å, and $N_2H_6^{2+}$ 1.442 Å, the latter agreeing well with crystal structure data (1.41—1.44 Å).[10] It is interesting that in all three examples the 3-electron/2-electron bond length ratio is close to 3/2; $He_2^{+\cdot}/He_2^{2+}$ 1.536, $N_2H_6^{+\cdot}/N_2H_6^{2+}$ 1.501; **(2)**/**(3)** 1.498. Nevertheless, we are surprised the N–N distance in **(2)** is so long. There is no doubt that any reduction in the N–N distance towards ~1.5 Å relieves strain within the $[CH_2]_4$ bridges, and the bond length ratio for **(2)**/**(3)** might be expected to be less than in an unconstrained case. Furthermore delocalisation of the σ* electron in **(2)** into the hydrocarbon framework[11] might be expected to lead to bond *shortening* as compared to $N_2H_6^{+\cdot}$.

The two-electron N–N bond in **(3)** is also longer than in the model $N_2H_6^{2+}$. In this case however the increase could be due to the relief of non-bonded interactions within the compact propellane structure. The geometrical parameters for dication **(3)** are almost identical to those of the hydrocarbon [4.4.4]propellane,[12] even down to the surprisingly large N–C–C angle; the corresponding C–C–C angle in the propellane averages to 114.3°. The N–C bond length in **(3)** is 0.09 Å longer than in **(1)**, with **(2)** intermediate. A major part of this change can be ascribed to changes in nitrogen hybridisation.

Finally, it is interesting to compare the bond length changes in the σ/σ* redox system **(1)** ⇌ **(2)** ⇌ **(3)** with those in the π/π* systems $R_2\ddot{N}{-}\ddot{N}R_2 \rightleftharpoons R_2N\overset{+}{\overset{\cdot\cdot\cdot}{-}}NR_2 \rightleftharpoons R_2\overset{+}{N}{=}\overset{+}{N}R_2$ studied by Nelsen and co-workers. The N–N bond lengths for **(4)** and its radical cation (3-electron π-bond) are 1.469 and 1.323 Å.[13] Data for the dication are unavailable but it is highly unlikely that the $R_2\overset{+}{N}{=}\overset{+}{N}R_2$ bond length is <1.18 Å; known R–N=N–R bonds lie in range 1.22—1.26 Å.[14] The 3-electron π-bonded radical cation therefore lies more than half the way from **(4)** to its dication. Three-electron σ-bonded ion **(2)** however lies nearer to **(1)** than to **(3)**. It is interesting that the 3-electron π-bond in the radical cation of **(4)** has a dissociation energy[15] of 22.5 kcal mol^{-1}, whereas the 3-electron σ-bond strength in **(5)** is about [16] 14.5 kcal^{-1} mol^{-1} (1 cal = 4.184 J).

We thank the S.E.R.C. for support of this work, and Dr. Graham Taylor and Dr. Peter Woodward for their earlier efforts to solve the structure of (**2**)·CF_3SO_3, which were frustrated by disorder problems. We thank Professor S. F. Nelsen for a preprint of ref. 13.

Received, 1st April 1985; Com. 434

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