clearly in opposite ways. Eventually all possible σ adducts deriving from attack on α and β ring carbon atoms decompose into a single, well-defined, side-chain-substituted product. The results do not indicate the structure of the adduct(s) through which the final product is formed. Furthermore, the mechanism of migration is still to be elucidated in further studies.

Acknowledgments. Professor D. Cordischi (Istituto di Chimica Generale e Inorganica, University of Rome), Dr. A. M. Giuliani (C.N.R., Laboratorio di Teoria e Struttura Elettronica e Comportamento Spettrochimico dei Composti di Coordinazione, Rome), and Mr. G. Frachey are acknowledged for valuable assistance in the ESR and NMR spectral experiments.

Registry No. 1, 2436-79-5; **1a**, 57745-26-3; **2**, 5408-07-1; **2a**, 73018-12-9; **3**, 2199-46-4; **3a**, 73018-13-0; **4**, 2199-47-5; **4a**, 4789-44-0; **5**, 58921-31-6; **5a**, 73018-14-1; ethyl 4-ethyl-5-formyl-3-methylpyrrole-2-carboxylate, 4391-87-1.

Electrophilic Aromatic Substitution in Cyclopropenium Ions

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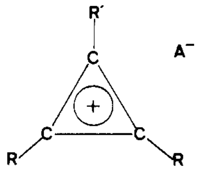
Electrophilic attack by a proton on the cyclopropenium ion is shown by ab initio molecular orbital theory to involve a planar tetracoordinate carbon atom. The process is, however, strongly endothermic, and the protonated cyclopropenium ion ring opens without activation energy. The diaminocyclopropenium ion, on the other hand, can be either C or N protonated exothermically. C protonation can account for the observed H/D exchange in derivatives of the diaminocyclopropenium ion. In this case the protonated ion has a normal tetrahedral carbon atom and is highly stabilized by charge delocalization to nitrogen.

Since the pioneering work of West et al.[1] substitution reactions on cyclopropenium systems of the general form 1 (R = R′ = halogen) have gained an ever increasing importance. Until very recently only substitution reactions on 1 of the classical addition–elimination type were known. The observation of the following reaction types has, however, revealed a complete spectrum of mechanistic possibilities: (a) four-center exchange reactions (R = R′ = halogen),[3] (b) elimination–addition reactions (R = NR_2, R′ = halogen),[4] (c) electrophilic substitutions (R = NR_2, R′ = H).[5] In addition the important influence of the counterion, A^-, on many such substitution reactions has been recognized and exploited synthetically.[6]



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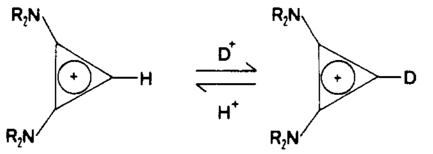
This paper is concerned with the theory of reaction type c. It was stimulated by our observation that donor-stabilized C_3^+ systems are capable of undergoing H/D exchange in strongly acidic media[5] (eq 1).



(1)

1a 1b

This report has aroused considerable interest in electrophilic substitution of positively charged aromatic species.[7] We have chosen to investigate protonation of the parent cyclopropenium ion as a model for this type of reaction. The nature and stability of protonated $C_3H_3^+$ is of particular interest since the resulting dication is isoelectronic with the "anti van't Hoff" BBC ring.[8]

Of all the Hückel aromatic systems, the cyclopropenium ion occupies a special position with respect to electrophilic substitution. This arises because the proximity of high-lying σ (Walsh type) orbitals to the occupied π orbital of cyclopropenium[9] leads to additional possible modes of protonation, one of which involves a planar tetracoordinate carbon atom. Interaction of the proton with the σ system can lead to either in-plane corner or edge attack, whereas out-of-plane corner or face protonation results when the π system acts as the donor.

In this respect electrophilic substitution in the cyclopropenium ion resembles the protonation of cyclo-

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(1) For a review see R. West, *Acc. Chem. Res.*, **3**, 130 (1970).

(2) For a review see Z. Yoshida, *Top. Curr. Chem.*, **40**, 47 (1973).

(3) R. Weiss, *Tetrahedron Lett.*, in press; R. Weiss and P. Maroldt, *Synthesis*, in press.

(4) R. Weiss, C. Priesner, and H. Wolf, *Angew. Chem., Int. Ed. Engl.*, **18**, 472 (1979); R. Weiss, M. Hertel, and H. Wolf, *ibid.*, **18**, 473 (1979).

(5) R. Weiss and C. Priesner, *Angew. Chem., Int. Ed. Engl.*, **17**, 445 (1978).

(6) R. Weiss, H. Kölbl, and C. Schlierf, *J. Org. Chem.*, **41**, 2258 (1976); see also ref 3.

(7) R. M. Pagni and R. J. Smith, *J. Am. Chem. Soc.*, **101**, 506 (1979).

(8) K. Krogh-Jespersen, D. Cremer, D. Poppinger, J. A. Pople, P. v. R. Schleyer, and J. Chandrasekhar, *J. Am. Chem. Soc.*, **101**, 4843 (1979).

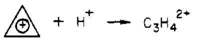
(9) The molecular orbitals of the cyclopropenium ion are shown in W. L. Jorgensen and L. Salem, "The Organic Chemist's Book of Orbitals", Academic Press, New York, 1973. With the 6-31G** basis set (split valence with d functions for carbon and p functions for hydrogen) and the 4-31G optimum geometry for cyclopropenium, the $1a_2''$ orbital is the HOMO at −0.764 652 au, with the 3e′ set lying slightly lower in energy (−0.787 644 au).

0022-3263/80/1945-1790$01.00/0

Table I. Total and Relative Energies and Proton Affinities for Protonated Cyclopropenium

	RHF/STO-3G//STO-3G[a]			RHF/4-31G//STO-3G[a]		
ion	tot energy[b]	rel energy[c]	PA[d]	tot energy[b]	rel energy[c]	PA[d]
2	−113.544 03	8.4	47.9	−114.718 82	17.1	59.5
3	−113.557 37	0.0	39.5	−114.746 13	0.0	42.4
4	−113.534 56	14.3	53.8	−114.728 72	10.9	53.3
5	−113.527 39	18.8	58.3	−114.697 34	30.6	73.0
6	−113.603 56	−29.0	10.5	−114.796 96	−31.9	10.5

[a] The convention for definition of the calculational method is given in ref 21. [b] In au (1 au = 627.49 kcal mol^{-1}). [c] In kcal mol^{-1}. [d] Energy (kcal mol^{-1}) for the reaction



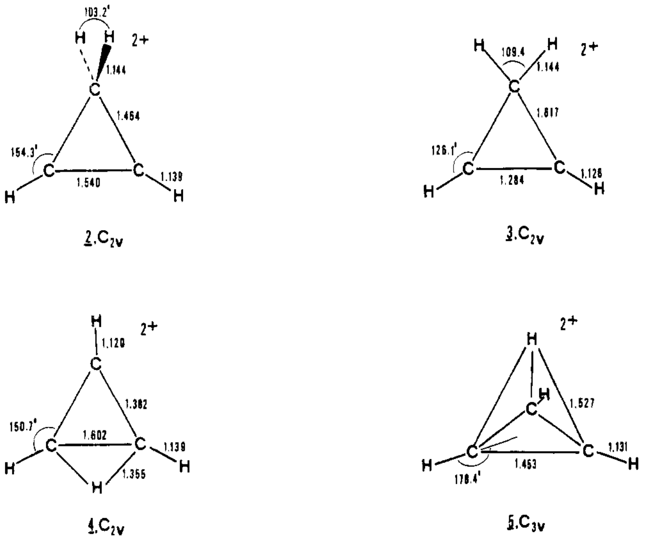


Figure 1. STO-3G optimum geometries for protonated cyclopropenium ions **2–5**. Bond lengths are in angstroms and angles in degrees. The point groups are imposed symmetry constraints.

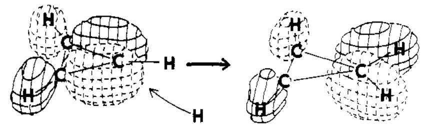


Figure 2. Orbital interactions in the planar corner protonation of cyclopropenium. The charges have been omitted.

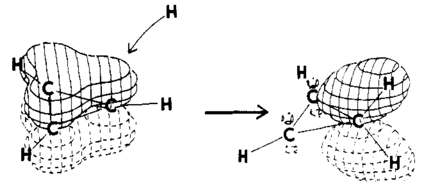


Figure 3. Orbital interactions in the perpendicular corner protonation of cyclopropenium.

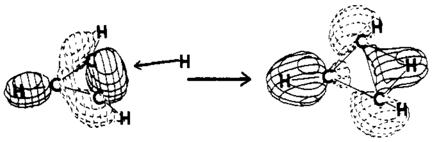


Figure 4. Orbital interactions in the edge protonation of cyclopropenium.

propane,[10] rather than the electrophilic substitution in benzenoid aromatics, where the separation between σ and π energy levels is large enough to ensure that only the latter are high enough to act as donors. As a model for the reaction shown in eq 1 we have also investigated protonation of the diaminocyclopropenium ion, in which the π orbitals are strongly perturbed by the amino groups.

Quantum Mechanical Method

Single-determinant Hartree–Fock theory was used throughout. All calculations employed the Gaussian 70 series of programs[11] modified to include Fletcher–Powell[12] multiparameter geometry optimization via analytical evaluation of the atomic forces.[13] Geometry optimizations were performed at the minimal STO-3G[14] basis-set level, with further single-point calculations on the STO-3G optimum geometry at the split-valence 4-31G[15] level. The molecular orbital plots were made by using Jorgensen's program[16] and the STO-3G wave functions.

Results and Discussion

Protonation of the Cyclopropenium Ion. Four possible modes of protonation of the cyclopropenium ion were considered, giving structures **2–5**. These were optimized at the STO-3G level within the given symmetry constraints. Figure 1 shows the optimum geometries thus obtained. For comparison, the STO-3G C–C and C–H bond lengths in the cyclopropenium ion are 1.377 and 1.095 Å, respectively.[17] The total and relative energies and calculated proton affinities are shown in Table I. At both the STO-3G and 4-31G levels the all-planar species **3** is predicted to be the most stable form of the protonated cyclopropenium ion. The proton affinity of $C_3H_3^+$ is, however, calculated to be of the order of +40 kcal mol^{-1} at both levels of theory, so that electrophilic substitution in the parent cyclopropenium ion is very unlikely to be observed. The "normal" corner-protonated cyclopropenium, **2**, is 17 kcal mol^{-1} less stable than the planar isomer **3** (4-31G). This is due to the fact that the highest occupied orbitals of the cyclopropenium ion [the 3e′ (Walsh σ) set and the $1a_2''$ (symmetrical π)][9] are very close in energy, so that the site of protonation is largely controlled

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(10) L. Radom, J. A. Pople, V. Buss, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **93**, 1813 (1971); P. C. Hariharan, L. Radom, J. A. Pople, and P. v. R. Schleyer, *ibid.*, **96**, 599 (1974).

(11) W. J. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newton, and J. A. Pople, "Quantum Chemistry Program Exchange", Indiana University, Bloomington, IN, program no. 236.

(12) R. Fletcher and M. D. Powell, *Comput. J.*, **6**, 163 (1963); W. C. Davidson, *ibid.*, **10**, 406 (1968); D. Poppinger, *Chem. Phys. Lett.*, **34**, 332 (1975).

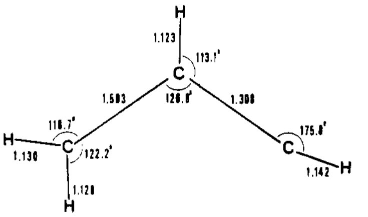
(13) The analytic force evaluation routines [H. B. Schlegel, S. Wolfe, and F. Bernardi, *J. Chem. Phys.*, **63**, 3632 (1975)] were incorporated into the earlier Fletcher–Powell program[12] by Dr. J. Chandrasekhar.

(14) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969); W. J. Hehre, R. Ditchfield, R. F. Stewart, and J. A. Pople, *ibid.*, **52**, 2769 (1970).

(15) R. Ditchfield, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, **54**, 724 (1971); W. J. Hehre and J. A. Pople, *ibid.*, **56**, 4233 (1972); J. D. Dill and J. A. Pople, *ibid.*, **62**, 2921 (1975).

(16) All molecular orbital plots employed Jorgensen's program,[9] using the STO-3G wave functions.

(17) J. A. Pople, *Int. J. Mass Spect. Ion Phys.*, **19**, 89 (1976); L. Radom, P. C. Hariharan, J. A. Pople, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **98**, 10 (1976); L. Radom and H. F. Schaefer, III, *ibid.*, **99**, 7522 (1977).



6, C_s

Figure 5. STO-3G optimum geometry for the ring-opened dication **6** (units as for Figure 1).

by the overlap between the donor and acceptor orbitals. In this respect, one of the 3e′ orbitals,[18] with a large concentration of electron density at the relevant carbon atom, is ideally suited, allowing strong overlap with the attacking acceptor (see Figure 2).

The "classical" protonated cyclopropenium ion, **2**, is the result of interaction of the proton with the $1a_2''$ (π) cyclopropenium donor orbital, as shown in Figure 3. The above arguments are specifically based on fragment analyses for the interaction of the cyclopropenium ion with a proton (i.e., they are conceptually related to the protonation reaction itself). Schleyer et al.[8] have given alternative analyses of the relative stabilities and also the geometry changes in the diboracyclopropanes corresponding to **2** and **3**, so that we will not discuss them in further detail for the isoelectronic $C_3H_4^{2+}$ species.

The edge-protonated cyclopropenium ion, **4**, is the result of interaction between the proton and the 3e′ orbital which shows the largest concentration of electron density between two carbon atoms,[18] as shown in Figure 4.

The face-protonated cyclopropenium ion, **5**, can be considered to result from interaction of the proton with the $1a_2''$ (π) cyclopropenium orbital.

Although overlap should be good for the C_{3v} species, electrostatic repulsion is high, resulting in this being the least stable of the $C_3H_4^{2+}$ ions investigated. The protonated cyclopropenium ions **3** and **4**, which formally result from proton interaction with the 3e′ (σ) orbitals, are calculated to be relatively more stable at 4-31G than at STO-3G (see Table I). This is a result of the well-known tendency[19] of STO-3G to underestimate the strain in three-membered rings. This tendency actually means that the σ orbitals are relatively too low in energy and hence poorer donors.

As the structures **2**–**5** were all optimized within the given symmetry constraints, it is not clear that they represent local minima on the $C_3H_4^{2+}$ potential surface. We have therefore investigated the ring opening of the most stable protonated cyclopropenium ion, **3**, to the dication **6**, whose STO-3G optimum geometry is shown in Figure 5.

Dication **6** is calculated to be about 30 kcal mol^{-1} more stable than **3** (see Table I), and the STO-3G reaction-path calculations for the ring opening show this process to occur without activation energy and with retention of planarity. The calculated proton affinity for the cyclopropenium ion to give **6** is still, however, +10.5 kcal mol^{-1}.

Protonation of the Diaminocyclopropenium Ion. The STO-3G optimum geometries for the di- and triaminocyclopropenium ions, **7** and **8**, are shown in Figure 6. **8** has been included in order to compare the STO-3G

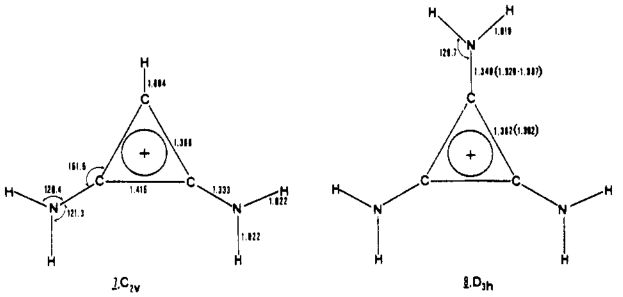


Figure 6. STO-3G optimum geometries for di- and triaminocyclopropenium ions **7** and **8** (units as for Figure 1).

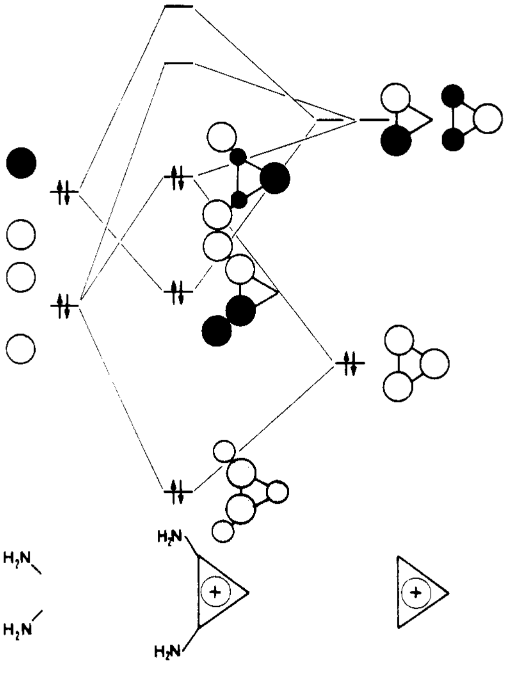
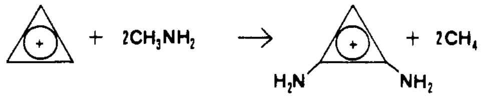


Figure 7. π molecular orbital interaction diagram for the interaction of two amino groups with the cyclopropenium ion.

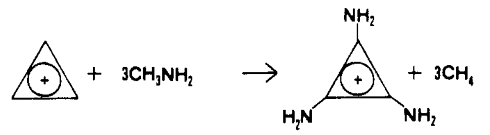
geometry with that obtained in X-ray studies of the perchlorate and SbF_6^- salts of tris(dimethylamino)cyclopropenium.[20] The X-ray C–C and C–N bond lengths are shown in parentheses in Figure 6.

The isodesmic exchange reactions 2 and 3 illustrate the strength of the stabilization gained by substituting the cyclopropenium ion with amino groups.



(2)

$\Delta H(4\text{-}31G//STO\text{-}3G)^{21} = -83.0$ kcal mol^{-1}



(3)

$\Delta H(4\text{-}31G//STO\text{-}3G)^{21} = -109.9$ kcal mol^{-1}

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[18] Strictly speaking there are an infinite number of representations of a set of doubly degenerate orbitals, so that they cannot be discussed as a discrete pair. In this case, however, the approach of the proton lowers the symmetry and lifts the degeneracy. We have retained the orbital symmetry designations for D_{3h} cyclopropenium throughout the discussion, for simplicity.

[19] L. Radom, W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Am. Chem. Soc.*, **93**, 5339 (1971).

[20] A. T. Ku and M. Sundaralingam, *J. Am. Chem. Soc.*, **94**, 1688 (1972); G. Huttner and U. Schubert, personal communication.

[21] The 4-31G//STO-3G energy for the cyclopropenium ion is taken from ref 17 and those for CH_3NH_2 and CH_4 from W. A. Lathan, L. A. Curtiss, W. J. Hehre, J. B. Lisle, and J. A. Pople, *Prog. Phys. Org. Chem.*, 11, 1 (1974). The "double slash" notation indicates that the calculation was performed by using the first basis set on the optimum geometry obtained by using the second basis set (e.g., 4-31G//STO-3G denotes a 4-31G calculation on the STO-3G optimum geometry).

Table II. Total and Relative Energies and Proton Affinities for Aminocyclopropenium Ions and Protonated Diaminocyclopropenium

	RHF/STO-3G//STO-3G[a]			RFH/4-31G//STO-3G		
ion	tot energy[b]	rel energy[c]	PA[d]	tot energy[b]	rel energy[c]	PA[d]
7	−222.342 54			−224.796 38		
8	−276.678 42			−279.764 38		
9	−222.500 60	0.0	−99.2	−224.902 18	0.0	−66.4
10	−222.322 51	111.7	12.6	−224.764 69	86.3	19.9
11	−222.346 56	96.7	−2.5	−224.783 79	74.3	7.9
12	−222.531 41	−19.3	−118.5	−224.919 76	−11.0	−77.4
13	−222.540 44	−25.0	−124.1	−224.964 75	−39.3	−105.5
14	−222.245 89	(60.6[e])		−224.686 12	(69.2[e])	
15	−222.455 60	28.2	−70.9	−224.818 71	52.4	−14.0

[a-d] Footnotes as for Table I. [e] Energy relative to 6.

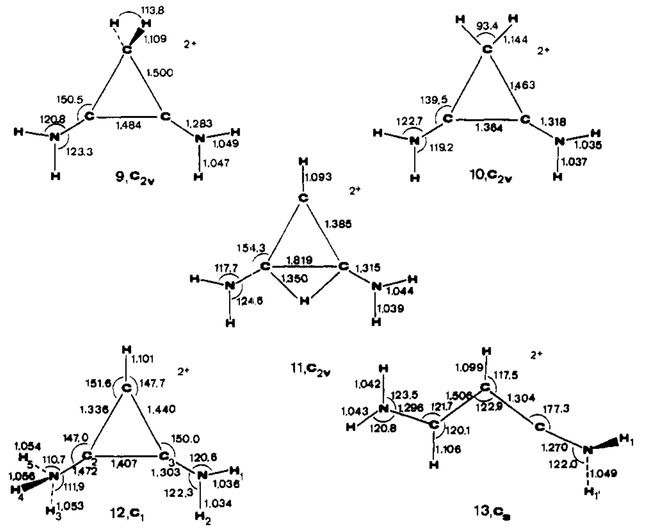


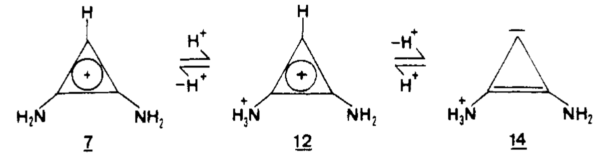
Figure 8. STO-3G optimum geometries for the protonated diaminocyclopropenium ions 9–13 (units as in Figure 1). Dihedral angles for 12 are as follows: $C_2C_3NH_1$, 179.9° (H_1 below the plane as drawn); $C_2C_3NH_2$, 0.2° (H_2 above the plane as drawn); $C_3C_2NH_4$, 86.8°; $C_3C_2NH_5$, 205.7°; $C_3C_2NH_3$, 327.8°. The C_2NH_4 angle is 111.4°. The $CCNH_1$ and $CCNH_{1'}$ dihedral angles in 13 are ±90.8°.

The σ molecular orbitals of the cyclopropenium ring are perturbed relatively little by the amino substituents, whereas the π system is drastically altered. The interaction diagram (Figure 7) shows that the highest occupied π orbital of diaminocyclopropenium is an antibonding combination of the cyclopropenium $1a_2''$ orbital with the symmetric combination of the nitrogen p orbitals. This orbital is much higher in energy than the highest occupied Walsh orbitals, and, therefore, the site of protonation is controlled by the energy gap between the donor and acceptor orbitals, rather than by the overlap as for the parent cyclopropenium ion.

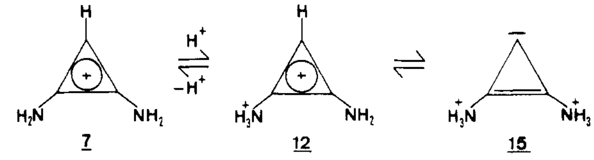
Again we have considered four modes of protonation for the diaminocyclopropenium ion: the two corner-protonated species **9** and **10**, the edge-protonated form **11**, and the N-protonated isomer **12**. Their STO-3G optimum geometries are shown in Figure 8, and their relative and total energies and the corresponding proton affinities for the diaminocyclopropenium ion are given in Table II.

The most stable form of the protonated diaminocyclopropenium ion is the N-protonated species **12**, which naturally does not lead to exchange at the ring CH. The perpendicular C-protonated species **9** is, however, only 11.0 kcal mol^{-1} less stable than **12** (4-31G), so that C protonation may compete with the more favorable N protonation to give H/D exchange. Both **9** and **12** are formally derived from interaction of the proton with the π HOMO of **7**, the largest coefficients in this orbital being at the CH carbon and at nitrogen. The planar C-protonated isomer **10** and the edge-protonated **11** are not competitive in energy, as they result from protonation of the low-lying σ orbitals. The ring-opened ion **13**, whose STO-3G optimum geometry is also shown in Figure 8 and which may possibly be produced via **11**, is calculated to be 25–40 kcal mol^{-1} more stable than **12**. The fact that ring opening is not observed[5] probably is a result of the relatively high energy of structures like **11**, which may intervene in such a process.

We have also investigated other possible mechanisms by which **12** can give H/D exchange on the ring. Equations 4 and 5 are two alternatives.



(4)



(5)

In the first case (eq 4) **12** may deprotonate at carbon to give carbene **14**, which may then reprotonate to give exchange. In the second case (eq 5) **12** may isomerize to give the carbene dication **15** via a simultaneous protonation/deprotonation step. Calculations[22] (see Table II) show that any path involving **14** or **15** is higher in energy than direct C-protonation via **9**, so that, not surprisingly, these possibilities can be discounted.

Our calculations suggest, therefore, that the observed H/D exchange occurs via the protonated ion **9**, which is in competition with its N-protonated isomer, **12** (eq 6).

Our calculated proton affinities for **7** to give either **12** or **9** are, however, very low, and **7** would not normally be expected to give exchange in sulfuric acid.[23] The previously calculated proton affinities apply to neutral molecules,[24] so that charge repulsion does not play a significant

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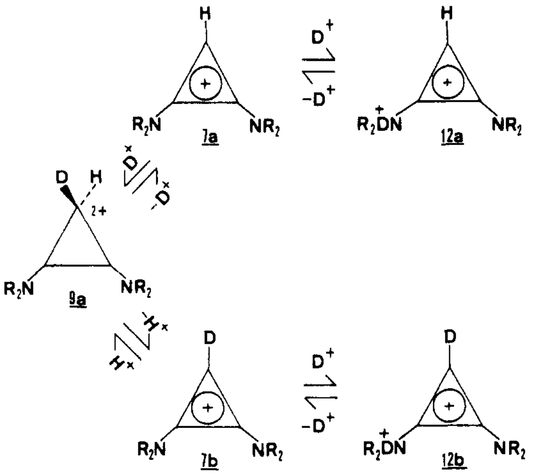
(22) The STO-3G-optimized geometries for **14** and **15** are available from the authors.

(23) The 4-31G calculated proton affinity for methane, which does not exchange in D_2SO_4, is, for instance, −117.6 kcal mol^{-1}: W. A. Lathan, W. J. Hehre, L. A. Curtiss, and J. A. Pople, *J. Am. Chem. Soc.*, **93**, 6377 (1971); J. B. Collins, P. v. R. Schleyer, J. S. Binkley, and J. A. Pople, and L. Radom, *ibid.*, **98**, 3436 (1976).

(24) For reviews of carbocation calculations, see: L. Radom, D. Poppinger, and R. C. Haddon in "Carbonium Ions", Vol. V, G. A. Olah and P. v. R. Schleyer, Eds., Wiley-Interscience, New York, 1976, p 2303; W. J. Hehre in "Methods of Electronic Structure Theory", H. F. Schaefer III, Ed., Plenum, New York, 1977, p 277. The 4-31G basis set appears to underestimate proton affinities slightly in comparison with larger basis sets and with experiment. Correlation has little effect on calculated hydrocarbon proton affinities (see Radom et al., p 2324, for instance).

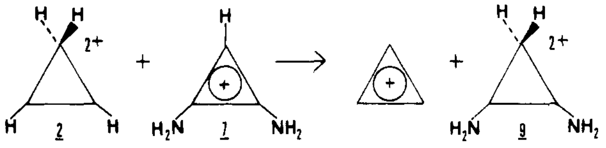


(6)

role in determining the magnitude of the proton affinities. Our calculations for the protonation of positively charged ions refer to the gas phase and include the full effects of repulsion between the two positive charges. This repulsion will naturally be greatly reduced in solution where both ions, and especially the proton, are heavily solvated. It is, therefore, reasonable to propose that positive ions with relatively low gas-phase (calculated) proton affinities may be protonated in highly acidic media.

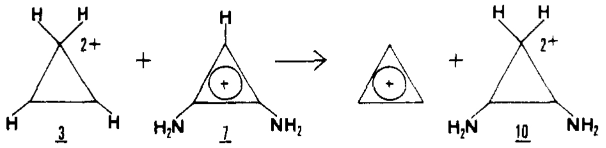
The reverse is, of course, true for the protonation of anions.[25] There is, unfortunately, too little experimental and calculated data on the protonation of cations to further clarify this point.

Finally, we should consider the stabilization of the individual protonated diaminocyclopropenium ions relative to the corresponding $C_3H_4^{2+}$ species. This can be demonstrated via reactions 7, 8, and 9.



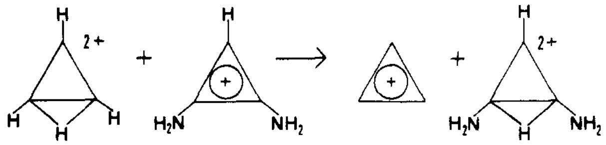
(7)

$\Delta H(4\text{-}31G//STO\text{-}3G)^{21} = -126$ kcal mol^{-1}



(8)

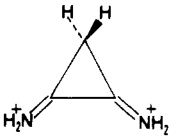
$\Delta H(4\text{-}31G//STO\text{-}3G)^{21} = -23$ kcal mol^{-1}

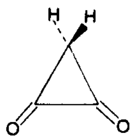


(9)

$\Delta H(4\text{-}31G//STO\text{-}3G)^{21} = -45$ kcal mol^{-1}

The relatively small stabilization energies for 10 and 11 are the result of inductive destabilization of the σ orbitals in 7, making them better donors.[26] The very large stabilization found for 9 is the result of the strong π HOMO destabilization in 7, relative to the parent cyclopropenium ion, as outlined in Figure 7. This is, naturally, equivalent to the structure **9b** in valence-bond terms. Highly strained structures like **9b** can be considered as the first derivates of the hitherto unknown cyclopropane dione 16.


9b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Registry No. 2, 73137-33-4; **6**, 73137-34-5; **7**, 73156-81-7; **8**, 73156-82-8; **9**, 73137-35-6; **12**, 73156-80-6; **13**, 73137-36-7; **14**, 73137-37-8; **15**, 73137-38-9.

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[25] The heats of protonation of aliphatic carboxylate anions in aqueous solution are, for instance, practically zero: K. J. Breslauer, *J. Chem. Thermodyn.*, 11, 527 (1979).

[26] For a discussion of the effects of substituents on ring strain, see: J. D. Dill, A. Greenberg, and J. F. Leibman, *J. Am. Chem. Soc.*, 101, 6814 (1979).