stituted cyclohexene was carefully distilled from the reaction mixture under vacuum and collected in a trap cooled at −78 °C. The optical rotation was determined in chloroform.

4-Methylcyclohexene (6): IR ($CHCl_3$) 3020 ($\nu_{\mathrm{C-H}}$), 2940, 2920, 2860, 2780 ($\nu_{\mathrm{C-H}}$), 1600, 1450 cm^{-1} ($\nu_{\mathrm{C=C}}$); NMR ($CDCl_3$) δ 0.7–2.2 (m, 10 H), 5.6 (2 H, m, vinylic H).

4-*tert*-Butylcyclohexene (5): IR ($CHCl_3$) 3020 ($\nu_{\mathrm{C-H}}$), 2980–2840, 2870 ($\nu_{\mathrm{C-H}}$), 1660, 1480, 1470 cm^{-1} ($\nu_{\mathrm{C=C}}$); NMR ($CDCl_3$) δ 0.7–2.2 (m, 7 H), 0.9 (s, 9 H, *t*-Bu), 5.65 (2 H, m, vinylic H).

***N,N,N*-Trimethylcyclooctylammonium Hydroxide.** By ion exchange on Amberlite IRA 400 (HO^-), *N,N,N*-trimethylcyclooctylammonium iodide, $F = 267°$,[19] gave quantitatively the corresponding oily quaternary ammonium salt: NMR ($CDCl_3$) δ 1.5–2 (15 H, m), 3.3 (9 H, S, $^+NMe_3$).

Pyrolysis of *N,N,N*-Trimethylcyclooctylammonium Hydroxide in Cholesteric Liquid Crystals. The cholesteric material (10 g) was intimately mixed with the quaternary ammonium salt (5–10% by weight). The cholesteric domain of this mixture was then determined with a microscope. After the mixture was heated at the required temperature for 6 h, cyclooctene was carefully distilled from the reaction mixture under vacuum and collected in a trap cooled at −78 °C. The purity of the product was checked by NMR. The optically active contaminant could only be the substituted cholestadiene used as solvent (these compounds are stable at the pyrolysis temperature). A detected optical activity of, for example, −12.7 or −32.3° (Table IV) would correspond to 10–25% of pollutant which would have been easily detected by NMR. Cyclooctene shows a high intensity signal at 1.5 ppm; meanwhile, the substituted cholestadienes are characterized by high-intensity signals below 1.1 ppm and aromatic protons: IR (CCl_4) 3010 ($\nu_{\mathrm{C-H}}$), 2920, 2850, 2760 ($\nu_{\mathrm{C-H}}$), 1470, 1450 cm^{-1} ($\nu_{\mathrm{C=C}}$); NMR ($CDCl_3$) δ 1.5 (br s, 12 H), 5.1–6.6 (2 H, m, vinylic H).

The cis and trans stereochemistry of cyclooctene was determined by irradiation of the methylenic protons at 2.3 ppm. The vinylic protons gave two singlets at 5.4 and 5.6 ppm, corresponding respectively to the cis and trans cyclooctene as shown by simulated ^1H NMR spectra.[12]

The cyclooctene cis/trans ratio was determined by VPC: column Triton X 305 (10%); temperature 60 °C; retention time cis, 10 min; trans, 11 min.

The optical rotations were determined in chloroform.

Enantiomeric Equilibration of *trans*-Cyclooctene. The cholesteric phase (10 g) was intimately mixed with a mixture of *cis*- and *trans*-cyclooctene obtained by the usual way[18] (cis/trans ratio = 55/45) and heated at the racemization temperature for several hours (Table IV). Cyclooctene is then recovered and analyzed as in the preceding section.

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Registry No. Δ^5-Cholesten-3-one, 601-54-7; 3-phenyl-3,5-cholestadiene, 2309-35-5; 3-(*o*–tolyl)-3,5-cholestadiene, 72390-28-4; 3-(*m*-tolyl)-3,5-cholestadiene, 72390-29-5; phenyl bromide, 108-86-1; *o*-tolyl bromide, 95-46-5; *m*-tolyl bromide, 591-17-3; 3-(*p*-tolyl)-3,5-cholestadiene, 72390-30-8; 3-(*o*-anisyl)-3,5-cholestadiene, 72390-31-9; *p*-tolyl bromide, 106-38-7; *o*-anisyl bromide, 578-57-4; 3-(*p*-anisyl)-3,5-cholestadiene, 72390-32-0; 3-(*p*-biphenyl)-3,5-cholestadiene, 72390-33-1; *p*-anisyl bromide, 104-92-7; *p*-biphenyllithium, 1201-71-4; *N*,*N*-dimethyl-4-methylcyclohexylamine *N*-oxide, 72390-34-2; *N*,*N*-dimethyl-4-*tert*-butylcyclohexylamine *N*-oxide, 72390-35-3; trimethylcyclooctylammonium iodide, 72390-36-4; trimethylcyclooctylammonium hydroxide, 13310-46-8; 4-methylcyclohexene, 591-47-9; (+)-4-*tert*-butylcyclohexene, 61062-50-8; (*R*)-(*E*)-cyclooctene, 22770-27-0; (*S*)-(*E*)-cyclooctene, 3958-30-3; (*Z*)-cyclooctene, 931-87-3.

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[19] A. Cope, R. D. Bach, *Org. Synth.*, **49**, 39 (1969).

Notes

Guanidinium Ion: SCF Calculations

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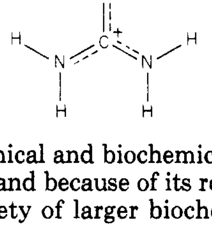
The guanidinium ion $C(NH_2)_3^+$



is of quantum chemical and biochemical interest. This is true both for itself and because of its role as an important fragment in a variety of larger biochemical compounds whose functions are much dependent upon the properties of the ion.[1-8]

The rotational barrier about a single CN bond of the ion has been obtained by an NMR experiment and has a value of 13 kcal mol^{-1}. Two recent quantum mechanical studies in the literature give calculated values for all three rotational barriers associated with this molecule.[6] In the first of these,[4] a MINDO/3 SCF calculation yielded values of 8.9, 15, and 31.0 kcal mol^{-1}, respectively, for single, double, and triple rotational barriers (see Figure 1). By the phrase single (double or triple) barrier we mean the energy difference for the molecule's planar geometry and that cor-

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(1) S. Subramanian, T. S. Sarma, D. Balasubrananian, and J. C. Ahluwalia, *J. Chem. Phys.*, **75**, 815 (1971).

(2) C. A. Swanson, *Arch. Biochem. Biphys.*, **117**, 494 (1966).

(3) S. Katz, *Biochim. Biophys. Acta*, **154**, 468 (1968).

(4) T. Bally, P. Diehl, E. Haselback, and A. Tracey, *Helv. Chim. Acta*, **58**, 2398 (1975).

(5) J. F. Capitani and L. Pedersen, *Chem. Phys. Lett.*, **54**, 547 (1978).

(6) See also the paper of Kollman, McKelvey, and Gund, *J. Am. Chem. Soc.*, **97**, 1640 (1975). The geometry of the guanidinium ion obtained with a STO 431 G basis is essentially the same as that obtained in this work and that obtained by Capitani and Pedersen in ref 5. However, the total optimized energy reported is −204.22345 au, a value higher than ours at −204.44910 au, while the reported single barrier is 14.1 kcal mol^{-1}, to be compared to our value of 14.73 kcal mol^{-1} and to the Capitani and Pedersen value of 14.97 kcal mol^{-1} also obtained with the 4-31 G basis.

(7) H. R. Mahler and E. H. Cordes, "Biological Chemistry", 2nd ed., Harper and Row, New York, p 49.

(8) A. Santoro, *J. Org. Chem.*, submitted.

0022-3263/80/1945-0719$01.00/0

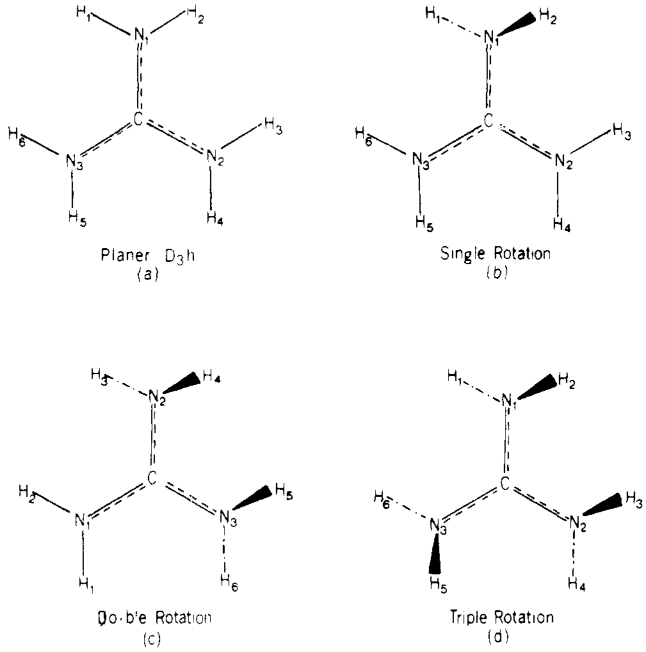

Figure 1. Geometry of the guanidinium ion.

responding to a 90° rotation of one (two or three) of the NH_2 groups about the CN bonds. The second study[5] involved an ab initio SCF calculation. The results include an optimized geometry for the planar D_{3h} configuration of the molecule's ground state, a population analysis of the electron density, and magnitudes for the rotational barriers. Their best numbers are 14.97, 50.21, and 115.20 kcal mol^{-1}, respectively, for the analogous barriers.

We have calculated properties of the guanidinium ion within the Hartree–Fock approximation, using the GAUSSIAN-70 computer program[9] with an STO-6-31G basis set. The calculations in this paper differ from those just mentioned in that the basis used is slightly larger. In this respect they might be expected to be slightly more reliable, and as one shall see they do in fact agree more closely with the experimentally available barrier for single rotation. They also differ from the previous calculations in that all of the results refer to optimized geometries, including those for the double and triple rotational barriers. Experience shows that results associated with the theoretical model used here can be interpreted quite reliably. In particular, it gives a good representation of a closed shell molecular ground state, such as that of guanidinium. The bond distances associated with the minimum in the Hartree–Fock energy surface are fairly accurate, although tending to be somewhat longer than experimental results indicate. Importantly qualitative changes induced in the geometry of one part of a molecule by geometrical changes elsewhere in the molecule are well represented. The correlation error, i.e., the error inherent in the Hartree–Fock approximation, for all practical purposes cancels out in the calculation of some property differences. Thus, for example, rotational barriers should be well predicted for guanidinium ion. Cancellation of errors aside, considering the expected size of the successive barriers for this molecule, we cannot expect the difference of correlation errors to change the qualitative trends associated with the barriers. The electron charge density may also be reliably predicted by the Hartree–Fock model. On general grounds, one knows that the Hartree–Fock density will be accurate to second order.[10] We display our numerical results for the guanidinium ion in Table I.

Table I. Calculated Rotational Barriers (kcal mol^{-1}), Bond Distances (Å), and Net Atomic Charges (eu)

	planar	single rotation	double rotation	triple rotation
E, kcal mol^{-1}	0	14.73	45.34	111.63
C-N, Å	1.33	1.31	1.29	1.38
	1.33	1.31	1.38[a]	1.38
	1.33	1.38[a]	1.38[a]	1.38
N-H, Å	1.00	1.00	1.00	1.00
	1.00	1.00	1.00	1.00
	1.00	1.00	1.00	1.00
C	1.141	0.999	0.913	1.041
N_1	−0.918	−0.952[a]	−0.727	−0.929
N_2	−0.918	−0.850	−0.934[a]	−0.929
N_3	−0.918	−0.850	−0.934[a]	−0.929
H_1	0.435	0.440	0.461	0.458
H_2	0.435	0.440	0.461	0.458
H_3	0.435	0.430	0.440	0.458
H_4	0.435	0.456	0.440	0.458
H_5	0.435	0.456	0.440	0.458
H_6	0.435	0.430	0.440	0.458

[a] Rotated nitrogens.

The lowest energy configuration is the planar geometry of symmetry D_{3h} that is displayed in Figure 1a and corresponds to a total energy of −204.44910 au. The calculated value of the CN bond distance is 1.33 Å. This lies between the values of 1.29 and 1.47 Å respectively for single and double CN bond distances. This partial double bond character associated with the calculated value of the CN bond lengths is consistent with the picture of "Y aromaticity" often attributed to the guanidinium ion. The molecule in a planar geometry is stabilized by delocalized π bonds associated with the p-type atomic orbitals orthogonal to the plane at carbon and at the nitrogens. This delocalization is also undoubtedly responsible for the fact that it is energetically so favorable for guanidine to accept a proton, making it a strong organic base.

The geometries of the guanidinium ion associated with the rotated conformations are displayed in Figure 1b,c,d. One may note the following trend associated with these geometries. Turning an NH_2 group about a CN bond line results in the elongation of that bond distance to 1.38 Å, a movement in the direction of the single bond value of 1.47 Å. At the same time, an accompanying contraction to a value of 1.31 Å occurs in the CN bonds with NH_2 groups remaining in the plane of the molecule. The contraction is in the direction of the CN double bond distance of 1.29 Å.

In Table I we list the calculated magnitude of the barrier associated with the respective single, double, and triple rotation of NH_2 groups about the corresponding CN bond lines. The bond distances are also collected there. Our calculated barrier to single rotation is of magnitude 14.73 kcal mol^{-1}. This compares favorably with the experimental value of 13 kcal mol^{-1}. As expected, this represents a slight improvement over the value of 14.97 kcal mol^{-1} obtained using the smaller STO 4-31 G basis and a considerable improvement in the more limited STO 3G basis value of 20.38 kcal mol^{-1}. The value obtained using the semiempirical method MINDO/3 was 8.9 kcal mol^{-1}. The trend

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[9] W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969).

[10] J. A. Pople and R. Seeger, *J. Chem. Phys.*, **62**, 4566 (1975); C. Møller and M. S. Plesset, *Phys. Rev.*, **44**, 618 (1934).

J. Org. Chem. **1980**, *45*, 721-724

shown by the rotational barriers of Table I is, as expected, that of increasingly higher energy as successive NH_2 groups are twisted to a position standing orthogonally to the molecular plane. Hence twisting one NH_2 requires 14.73 kcal mol^{-1}, twisting two NH_2 requires 45.34 kcal mol^{-1}, and twisting three NH_2 requires 111.63 kcal mol^{-1}. The qualitative features of this trend also show up in each of the other calculations which have been cited. The behavior of these rotational barriers is related to the presence of "Y aromaticity" in the molecule. In the planar configuration, that of lowest energy, each of the equivalent CN bonds has double bond character due to the delocalized orbitals associated with the carbon and nitrogen atoms. The first barriers must in a general way be a measure of the energy required to break the π bonding in the CN group about which the rotation is made. At the same time, the remaining CN bonds not involved in rotation become more strongly π bonded than before. This is consistent with the observed shortening of such CN bonds. Hence a second rotation must be energetically more costly than a first rotation because it involves twisting about a π bond whose strength has been enhanced as a reaction to the first twisting. Similarly, Table I shows that twisting about any two CN bonds has the effect of lengthening these bonds but shortening the remaining CN bond even further than before. This shortening reflects a further increase in bond stability, and hence this must correspond to an even higher rotational barrier when a third NH_2 group is twisted. It is as though twisting successive NH_2 groups corresponded to winding increasingly tighter springs.

One may also notice that the barriers described introduce hysterisis effects so that the energy trajectory of one rotation is not a unique function of rotation angle alone but is affected by the history of twistings inflicted at other barriers as well.

In Table I we list a population analysis of the electronic charge density for the guanidinium molecule. The numbers shown are net excess charges associated with the various atomic centers. The analysis is shown for the planar ground state of the molecule and for each of its rotated geometries. The charge distribution tends to be somewhat sensitive to scale factor optimization which has not yet been carried out. Therefore we only point to large trends not expected to change qualitatively with later scale factor optimization. Most importantly we see an alternation of charge sign moving outward from the molecular center at the carbon (highly positive) to nitrogens (highly negative) and to hydrogens (highly positive). This efficient distribution of the ion's net positive charge over atomic centers is consistent with the delocalization of the molecule and is conducive to its electrostatic stability. Moreover, this distribution of charge must be important to the ion's ability to enter into hydrogen bonds and to affect the structure of water. As a first approximation, one may suppose that the magnitude of positive charge carried by the hydrogen atoms will be a measure of the efficacy of formation of hydrogen bonds. Table I shows that the hydrogen atoms are very positive with at least +0.435 electron units of charge for the planar ground state. For comparison, we calculated the excess positive charge on hydrogen in a free water molecule, using the same basis as that used for the results listed in Table I. Thus hydrogen on a free water molecule carried +0.394 electron units of charge. Hence the much more positive hydrogens on guanidinium may be expected on energetic grounds to compete favorably with water molecules for hydrogen bonds to water molecules. In this respect, the charge distributions calculated are consistent with the notion that the guanidinium ion is a structure breaker in solution with water.

Acknowledgment. We thank Professor Santoro for bringing the problems of the electronic structure of the guanidinium ion to our attention and for providing us with a copy of his manuscript on rotational barriers in substituted guanidinium ions in advance of publication. It is a pleasure to acknowledge many interesting discussions with him about this molecule. It is also a pleasure to acknowledge discussions with Professor Barrett. We thank Barbara Rubensohn for constructing Figure 1.

Registry No. Guanidinium ion, 43531-41-5.

Synthetic Applications of *N*-Sulfonylamines. 2. Novel Reactions with Ynamines To Form Heterocycles[1]

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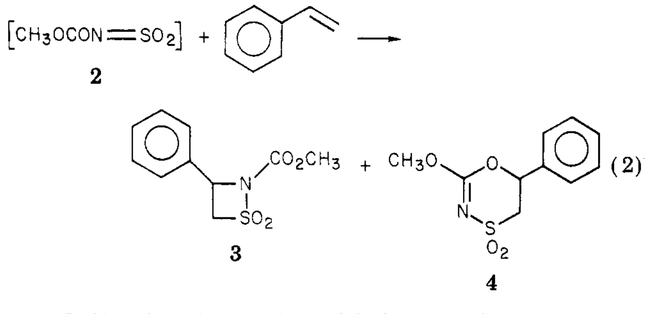
N-Sulfonylamines (**2**) are a class of heterocumulene first characterized by Burgess.[2] While they are not stable to isolation, they are readily generated in situ from the corresponding sulfamoyl chloride (**1**) via dehydrohalogenation (eq 1). These heterocumulenes are reactive electrophiles,

$$\underset{\mathbf{1}}{\mathrm{RNHSO_2Cl}} \xrightarrow{-\mathrm{HCl}} \underset{\mathbf{2}}{[\mathrm{RN{=}SO_2}]} \qquad (1)$$

and Burgess isolated products from their addition reactions with various nucleophiles and olefins.[3]

Of particular interest were the reactions of *N*-sulfonylurethane **2** (R = CO_2CH_3).[4] This heterocumulene was relatively stable in solution and offered the advantage of being capable of cycloaddition-like reactions in both a 2 + 2 and a 4 + 2 sense. For example, reaction of **2** (R = CO_2CH_3) with styrene gave mixtures of the 2-(carbomethoxy)-1,2-thiazetidine **3** and the 5,6-dihydro-2-methoxy-1,4,3-oxathiazine **4** shown in eq 2.[4]



N-Sulfonylurethane **2** (R = CO_2CH_3) has been generated by two methods. The first is simple dehydrohalogenation of the corresponding sulfamoyl chloride (eq 1) using sodium hydride.[4] The second involves in situ fragmentation

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[1] For Part 1, see J. A. Kloek and K. L. Leschinsky, *J. Org. Chem.*, 44, 305 (1979).

[2] G. M. Atkins, Jr., and E. M. Burgess, *J. Am. Chem. Soc.*, **89**, 2502 (1967).

[3] G. M. Atkins, Jr., and E. M. Burgess, *J. Am. Chem. Soc.*, **94**, 6135 (1972).

[4] E. M. Burgess and W. M. Williams, *J. Am. Chem. Soc.*, **94**, 4386 (1972).

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