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258. The Bond-Rotational Mobility of Guanidinium Ion

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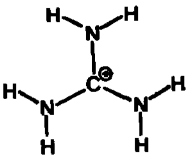
Summary. The NMR. spectrum of guanidinium ion **1** is studied in anisotropic liquid crystalline nematic solution. Assuming an HNH-angle of 120°, the distance ratio $\overline{NH}/\overline{NC} = 0.784$ is obtained, from which using $\overline{NC} = 1.330$ Å (from X-ray data) $\overline{NH} = 1.043$ Å results. An upper bound for the free energy of activation for bond rotation of $\Delta G^{\neq} \leq 13$ kcal/mol is deduced. The bond-rotational mobility of **1** is also investigated using the MINDO/3-SCF-procedure. The results obtained for the three conceivable consecutive activation energies for bond-rotation indicate that the observed bond-rotational mobility of **1** does not involve cooperative two- or three-bond rotations. The 'conjugative stabilization' of **1** has been estimated to be of the order of 24–26 kcal/mol.

Introduction. – Guanidine is the strongest organic base known, having a base-strength similar to that of the hydroxide ion. According to resonance theory the strong basicity results from the additional resonance energy liberated when guanidine is protonated, yielding guanidinium ion **1**. The remarkable stability of this and other Y-shaped systems containing 6 π-electrons has led to the creation of a new class of chemicals, the 'Y-aromatics' [1]. This is in line with *Erlenmeyers* early proposal [2],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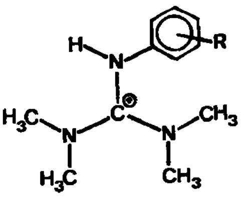
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that non-benzenoid compounds with extraordinary chemical stability might also be termed 'aromatic'.

Insight into the resonance stabilization of **1**, the 'leader' among the Y-aromatics, could be obtained if barriers to rotation about the C–N bonds were accessible. In an elegant study using N, N'-tetramethyl-N''-phenyl-guanidinium ions **2** carrying various substituents R in the aromatic ring, *Kessler & Leibfritz* [3] provided NMR. evidence that the free energy of activation for rotation of the (non-equivalent!) C–N bonds lies around 10–13 kcal/mol.

Unfortunately the chemical equivalence of the N–H protons in the parent system **1** precludes standard NMR. studies using isotropic conditions. It was therefore decided to investigate the guanidinium ion **1** in an anisotropic liquid crystalline nematic solution, the general applicability of this method for the investigation of ionic structures in solution having been demonstrated [4] [5].

Experimental. *Apparatus.* NMR. spectra were obtained using a *Varian* HA-100 spectrometer operating in the HR-mode at 27°, and their calibration achieved by use of an external frequency synthesizor.

Chemicals. Sodium decylsulfate (2.5 gm) was refluxed with a mixture of guanidinium chloride (1.1 gm), water (1 ml) and chloroform/ethanol 9:1 (100 ml) until solution was completed. The water was removed by codistillation with chloroform/ethanol, additional solvent being added as required. The precipitated NaCl was removed, the resultant solution evaporated to dryness and the product crystallized from acetone to yield quantitatively the guanidinium decylsulfate.

The nematic phases were prepared in test tubes by alternately stirring and centrifuging the combined components until a clear anisotropic solution was formed. The proportions of the various components of the phases studied are given below.

I	sodium decylsulfate	38.5 wt %	II	guanidinium decylsulfate	9.8 wt %
	guanidinium chloride	6.3 wt %		sodium decylsulfate	30.1 wt %
	decanol	3.4 wt %		guanidinium chloride	6.3 wt %
	H_2SO_4/H_2O, pH = 1	51.8 wt %		decanol	3.8 wt %
				H_2SO_4/H_2O, pH = 1	50.0 wt %

Guanidinium decylsulfate was not sufficiently soluble for a higher concentration at the operating temperature of the magnet.

Analysis of the Spectra. The NMR. spectra obtained from the nematic phases I and II above were virtually identical. The spectra did not have sharp transitions but the spectral width of approximately 3 kHz allowed a reasonable analysis. The most interesting feature of the spectra was their relative simplicity compared to that expected for a six-spin system with chemical but not magnetic equivalence. On attempting to analyse the spectra it became obvious that they correspond to an $A_2A_2'A_2''$ spin system. The best resolved spectrum (phase II) gave the parameters $D_{HNH} = 586 \pm 1$ Hz and $D_{H_2NCNH_2} = 121 \pm 1.5$ Hz.

The fact that the spectrum corresponds to an $A_2A_2'A_2''$ spin system establishes that on the NMR. time scale rotation about the C–N< bonds is rapid. The broadness of the resonances probably originates from two mechanisms:

1) The ^{14}N-nuclei are not completely decoupled from the protons by the quadrupolar relaxation of the nitrogen. This leaves a residual coupling which appears as a line broadening, already observed in other systems [5]; 2) rotational exchange is sufficiently slow to prevent complete averaging of the dipole coupling; some evidence

for this latter mechanism was provided from the spectrum. Two transitions are given by the sum of all the couplings and are therefore virtually independent of rotation; these, although not sharp, appeared sharper than the remaining transitions.

An attempt to clarify this point by experiments at higher temperature was not successful. The nematic solution was heated to near the nematic/isotropic transition temperature (∼45°). The transitions still did not become sharp although there was no longer an apparent difference in line widths. Lower temperatures were impossible since the guanidinium decylsulfate crystallized from solution.

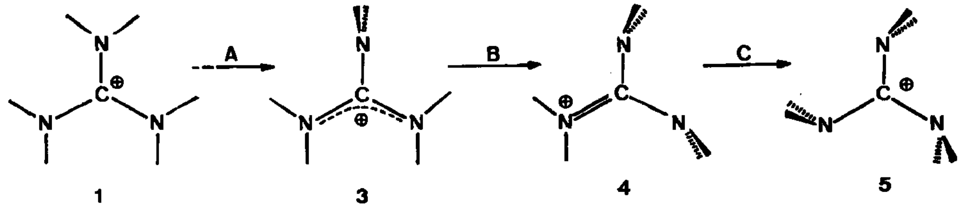
Even though only two dipole couplings are observed for this ion, the symmetry of the system allows some structural interpretations from the spectrum if it is assumed that the time spent in nonplanar configurations is negligibly small compared to that in the planar configuration. With this assumption, the symmetry of the ion allows a determination of the distance ratio $\overline{NH}/\overline{NC} = 0.784 \pm 0.004$ if the HNH-angle is 120°. This angle could be determined by ^{15}N-substitution but it is unlikely to be significantly different from 120°. If the value $\overline{NC} = 1.330$ Å obtained from X-ray data is used, then $\overline{NH} = 1.043 \pm 0.005$ Å and $|S_{C_3}| = 0.0574$. With these values of $\overline{NC}$ and $\overline{NH}$ rotation must occur more than about two thousand times per second to average the dipolar couplings which would be observed in a static situation (*i.e.* 5 × the maximum difference in the dipole interaction between NH_2 groups); hence k (bond rotation) $\geqslant 2 \times 10^3$ s^{-1}. This value is virtually independent of the assumed HNH-angle.

Discussion. – Inserting the value k (bond rotation) $\geqslant 2 \times 10^3$ s^{-1} into the *Eyring* equation yields an upper bound for the corresponding free energy of activation: $\Delta G^{\neq} \leqslant 13$ kcal/mol. This value is close to that found in [3] for the substrate **2**, in particular with respect to that C–N bond which is least affected by steric crowding ($\Delta G^{\neq} = 12$–13 kcal/mol).

Alkyl substitution is not likely to alter the barrier in such systems to a large extent since the positive charge in both the ground and the transition state is well distributed. Hence, we conclude that our upper bound value is not far from the true one.

As indicated in the introduction, the great base-strength of guanidine is generally considered to be a reflection of the high resonance stabilization due to extensive charge delocalization in the conjugate acid **1**. On this basis the above deduced upper limit $\Delta G^{\neq} \leqslant 13$ kcal/mol for C–N< bond rotation in **1** seems – from a chemist's intuitive standpoint – rather low.

In order to shed more light on this problem we have embarked on some theoretical calculations using the MINDO/3-SCF-procedure [8]. The minimum energy geometry of **1** was calculated without any constraints, and turned out to be virtually planar with D_{3h}-symmetry. For the transition states **3**, **4** and **5** of the three conceiv-



able consecutive bond rotation processes A, B and C, the NH_2-plane(s) was (were) assumed to be perpendicular to the CN_3-plane, allowing however for pyramidalization of the rotated NH_2-group(s). The NH-bondlengths were also optimized; they turned out to approximate always 1.01 Å.

The results indicated that the bond angles around the N-atoms in all cases summed up to 360°, *e.g.* the three bonds emerging from the central C-atom were found to lie roughly in the same plane. In addition for **1** D_{3h}-, for **3** and **4** C_{2v}- and for **5** C_{3h}-symmetry was found. The residual geometrical parameters together with the calculated heats of formation (ΔH_f^0) are given in the table below

	$\overline{CN}$	$\overline{CN}$ rot.	∢ NCN a)	∢ CNH	∢ CNH rot.	∢ NCNH b) rot.	ΔH_f^0 kcal/mole
1	1.329 Å	–	120°	125	–	–	103.7
3	1.318	1.357 Å	~120	125	123	~90	112.6
4	1.296	1.368	~120	126	119	69	127.7
5	–	1.358	120	–	118	66	159.6

a) The two N-atoms are those which are symmetry-equivalent.
b) Dihedral angle.

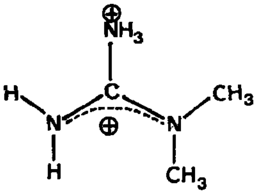
The following points concerning the calculated geometrical features are worth mentioning:

- For ground-state **1** the calculated CN-bond length is in close agreement with that found from X-ray studies ($\overline{CN}$ = 1.330 Å [7]). On the other hand the HNH-angles in **1** and also in **3** seem rather small for the essentially sp^2-hybridized N-atoms of the non-rotated NH_2-groups and too much weight should not be attached to these values. Note also that for **3** the rotated NH_2-group is still trigonal, while for **4** and **5** slight pyramidalization occurs. In the latter case however the barrier to inversion is small, thus rendering this structural possibility rather insignificant.
- The rotated C-N bonds are all around 1.36–1.37 Å, *i.e.* significantly larger than the other C-N bonds with partial π-character, though shorter than an ordinary $\geqslant$C-N$<$ single bond of about 1.47 Å. This is not unexpected given that the length of a C_{sp^2}-N_{sp^2} single bond ought to be smaller than that of a C_{sp^3}-N_{sp^3} single bond due to smaller covalent radii of the N- and C-atoms with higher *s*-character. Indeed the difference of 0.1 Å is close to that between an ordinary C_{sp^3}-C_{sp^3} bond length of 1.54 Å and the C_{sp^2}-C_{sp^2} bond length of 1.451 Å, found for example in butadiene.
- One notes a decrease in length of the non-rotated C-N bonds along the series **1** → **3** → **4**, the second shortening being roughly twice as large as the first. This can easily be accomodated in view of the *Pauling* bond orders for **1** (0.33), **3** (0.5) and **4** (1), the change in bond order for process B being three times as large as that associated with process A.

From the calculated ΔH_f^0-values the following barriers for the assumed consecutive bond rotations are obtained: $E_a(A) = 8.9$ kcal/mol, $E_a(B) = 15.0$ kcal/mol, $E_a(C) = 31.9$ kcal/mol. In view of these values a bond rotation process involving cooperative two- or three-bond rotations seems quite unlikely. Indeed the experimentally observed upper limit $E_a \leqslant 12$ kcal/mol (assuming log A = 12) is in good agreement with E_a(A), which leads us to postulate that the bond rotational mobility of **1** involves consecutive one-bond rotations.

Support for the calculated value $E_a(B) = 15.6$ kcal/mol is obtained from the work of *Olah & White* [8], where it was observed that diprotonated 1,1-dimethylguanidine

(**6**) which is iso-π-electronic to **2** shows a coalescence temperature of 16° for the methyl group signals. Using the reported chemical shift difference of these groups under static conditions at $-60°$ ($\Delta\nu = 7$ Hz) and the above mentioned frequency factor log A = 12, application of the *Gutowsky* and *Arrhenius* equation yields $E_a = 14.3$ kcal/mol for this process which is in good agreement to E_a(B) calculated for the analogous process B in **1**.



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At first sight the total π-energy of **1** could be estimated simply by adding the three calculated barriers for the individual processes A, B and C, leading to $E_\pi =$ 55.9 kcal/mol. However the calculated differences in C–N bond lengths between **1** and **5** suggests that this quantity is not exclusively related to the delocalization of the π-electrons, the two systems also differing in their σ-electron contribution to the total energy. The same is obviously true also for an estimate of the 'resonance energy' E_R of **1** obtained either by adding the calculated barriers of the processes A and B ($E_R = 23.9$ kcal/mol) or by adding the experimental barriers obtained for **1** in this work and for **6** ($E_R = 26.3$ kcal/mol) in [8]. According to [9] this quantity is therefore better termed 'conjugation energy' E_C; it may then be directly compared with $E_C \approx 20$ kcal/mol estimated for benzene relative to classical cyclohexatriene [10]. Clearly guanidinium ion **1** exhibits about the same conjugative stabilization as the prototype aromatic system benzene, justifying thus the creation of the class of 'Y-aromatics' [1].

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