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Concerning the Mechanism of Reaction of Simple Conjugated Olefin Triplet States with Oxygen

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Abstract: The quenchings by oxygen in benzene of the triplet states of a series of simple conjugated olefins (1,3-cyclopentadiene, 1,3-cyclohexadiene, ergosterol, 1,3,5-cycloheptatriene, neoalloocimene, and vitamin D_3) have been examined. Of specific concern was the relationship between the efficiency of singlet oxygen, $O_2(^1\Delta_g)$, formation and triplet properties, lifetimes, energies, geometries, and oxygen quenching rate constants. The key finding is that high-energy triplet states with a single accessible geometry do not yield $O_2(^1\Delta_g)$ with unit efficiency in situations where oxygen-induced intersystem crossing does not play a role. It would appear that efficiency of $O_2(^1\Delta_g)$ formation *decreases* as deviation from planarity *increases*. These facts, together with essential uniformity of oxygen quenching rate constants, lead us to propose tentatively that the consumation of quenching results from a branching of the singlet encounter complex to give either $O_2(^1\Delta_g)$ or a 1,4-biradical. The formation of the latter is favored for nonplanar triplets which involve a greater degree of uncoupled electron localization.

1. Introduction

Characterization of flexible olefin (Ol) triplet states in terms of energy and geometry has proved a major challenge to the mechanistic photochemist, as exemplified by the vast literature devoted to the stilbene problem alone. Although fast, time-resolved techniques now allow routine determination of lifetimes in the nanosecond time regime, there are still considerable difficulties associated with work in this area. These are principally concerned with the relationship between triplet lifetimes and energy-donating properties and the relative dispositions of S_0 and T_1 surfaces as a consequence of relaxation within T_1.

In the above respect, oxygen quenching and an analysis of the products thereof could, in principle, provide significant information[1] since reaction may take place via either electron or spin exchange as summarized in eq 1 and 2, respectively. Reaction

$$^3\mathrm{Ol}^* + O_2(^3\Sigma_g^-) \rightleftharpoons {}^1[\mathrm{Ol}\cdots O_2]^* \rightarrow \mathrm{Ol} + O_2(^1\Delta_g) \quad (1)$$

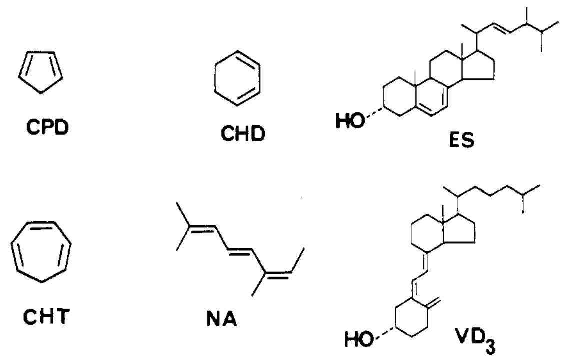
$$^3\mathrm{Ol}^* + O_2(^3\Sigma_g^-) \rightleftharpoons {}^3[\mathrm{Ol}\cdots O_2]^* \rightarrow \mathrm{Ol} + O_2(^3\Sigma_g) \quad (2)$$

$$^3\mathrm{Ol}^* + O_2(^3\Sigma_g^-) \rightleftharpoons {}^5[\mathrm{Ol}\cdots O_2]^* \quad (3)$$

via the quintet encounter complex, eq 3, is forbidden on spin and energy grounds. The operation of reaction channel 1, which has a maximum anticipated rate constant in mobile liquids of $k_D/9$ ($k_D \sim 3 \times 10^{10}$ L mol^{-1} s^{-1}), indicates the "availability", in some accessible geometry of $^3\mathrm{Ol}^*$, of at least the electronic excitation energy requirement of oxygen, 7882 cm^{-1} ($\sim$22 kcal mol^{-1}). The operation of reaction channel 2, having a maximum anticipated rate constant $k_D/3$, should become more important as the S_0 and T_1 surfaces approach each other. Therefore, the determination of oxygen quenching rate constants and measurement of singlet oxygen, $O_2(^1\Delta_g)$, yields provides a means, in principle, of differentiating between contributions from channels 1 and 2 and possibly indicating from where on the T_1 surface reactions are taking place. Recently we have employed such an approach to contribute to the understanding of the factors influencing the reactivity of stilbene triplet.[2]

A major potential problem in work of this kind concerns the anticipated exclusive operation of channel 1 for the oxygen quenching of $^3\mathrm{Ol}^*$ conformers which possess vertical triplet energies significantly above 22 kcal mol^{-1}. Although, for instance, an excellent and critical recent review[1] assumes that this is the case, we are unaware of definitive evidence concerning this point.[3] In fact, although the quenchings of high-energy triplets by oxygen were originally concluded, on both theoretical[4] and experimental[5] grounds, to proceed exclusively via channel 1, this is not always the case, in particular for aromatic ketones. Although possible explanations have been put forward,[5-7] the reasons for this are as yet not critically defined. The situation for flexible olefin triplets is further complicated by the subtlety of geometrical factors which influence non-radiative transitions within such molecules.[9]

Chart I



In the work to be described, we have addressed ourselves to problems of the kind outlined above by an examination of the oxygen quenchings of the triplet states of 1,3-cyclopentadiene (CPD), 1,3-cyclohexadiene (CHD), ergosterol (ES), 1,3,5-cycloheptatriene (CHT), neoalloocimene (NA), and vitamin D_3 (VD_3). This set of three dienes and three trienes (Chart I) was chosen specifically because their triplet states in benzene have been fully characterized by pulse radiolysis in terms of their vertical and relaxed triplet energies, lifetimes, and rate constants for oxygen quenching. Equally importantly we have shown that each of the triplets under consideration transfers triplet energy to perylene (E_T = 35.1 kcal mol^{-1}) with essentially optimum efficiency. Therefore, in no case can channel 1 be inefficient as a consequence of energetic factors. In other words, inefficient $O_2(^1\Delta_g)$ formation must reflect competition by an alternative favored process. Were

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(2) Gorman, A. A.; Rodgers, M. A. J. *Chem. Phys. Lett.* **1985**, *120*, 58.

(3) In our stilbene work this problem, although recognized,[2] did not affect the conclusions reached.

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Table I. Vertical (VE), Relaxed (RE), and Relaxation (ΔE) Energies (in kcal mol^{-1}), Triplet Lifetimes (τ) (in μs), and Rate Constants for Quenching of ^{3}Ol* by Perylene (k_{pe}), Oxygen (k_{ox}), and Ol (k_{sq}) and of ^{3}BP* by Ol (k_{ol}) (in L mol^{-1} s^{-1})

Ol	VE[a]	RE[a]	ΔE	τ	k_{pe}	k_{ox}	k_{sq}	k_{ol}
CPD	58[b]	58[b]	0	1.7[b]	1.1×10^{10}	3.0×10^9	1.4×10^7	6.5×10^9
CHD	53[c]	51[d]	2	15[d]	1.0×10^{10}	2.9×10^9	1.0×10^6[d]	8.8×10^9
ES	51[e]	51[e]	0	77[e]	5.0×10^9[e]	3.0×10^9	4.1×10^6[e]	4.5×10^9
CHT	55[f]	38[f]	17	6[f]	6.6×10^9[f]	2.7×10^9[f]	...[g]	4.9×10^9
NA	47[h]	40[h]	7	0.33[i]	9.1×10^9[i]	3.2×10^9	...[g]	7.9×10^9
VD_3	55[j]	38[j]	17	0.28[j]	3.0×10^9[j]	4.2×10^9[j]	...[g]	3.8×10^9[j]

[a] Values quoted to two significant figures. [b] Reference 10. [c] Reference 11. [d] Reference 12. [e] Reference 13. [f] Reference 14. [g] Insignificant. [h] Reference 15. [i] Reference 16. [j] Reference 17.

that process to take place via the triplet encounter complex, (cf. eq 2), a significant increase in the rate constant for oxygen quenching should be observed. In Table I are listed the key parameters for each olefin triplet which have been determined as referenced or as part of this work. Our primary aim was to establish whether or not oxygen quenchings of high-energy olefin triplet state conformers produce $O_2(^1\Delta_g)$ with unit efficiency.

2. Experimental Section

Benzene was either AnalaR grade, purified as described,[18] or MCB Omnisolve, used as received. Benzophenone (Bush) and perylene (Fluka) were recrystallized from ethanol and toluene, respectively. CPD,[10] CHD,[12] ES,[13] CHT,[14] NA,[16] and VD_3[17] were as described.

Pulse radiolysis experiments were performed at the Christie Hospital and Holt Radium Institute, Manchester. Experimental details have been described.[16] Determination of rate constants (cf. Table I) for the quenching of olefin triplets by oxygen (CPD, CHD, and NA) and by perylene (CPD and CHD)[14] and of benzophenone triplet by olefins[18] was as previously described.

Pulsed laser experiments for determining singlet oxygen yields were performed at the Center for Fast Kinetics Research. Experimental details have been described.[2] Quoted rate constants have confidence limits of ±10%.

3. Results

For $O_2(^1\Delta_g)$ production which occurs exclusively via channel 1, the quantum yield of formation, Φ_Δ, is simply a product, eq 4, of the triplet yield, Φ_T, and the fraction of the oxygen quenchings

$$\Phi_\Delta = \Phi_T S_\Delta \tag{4}$$

which actually yield $O_2(^1\Delta_g)$, the S_Δ value.[19] We have previously shown that Φ_Δ, and therefore S_Δ, for benzophenone (BP) in benzene is 0.29.[20,21] Therefore, in order to establish S_Δ for individual olefins (Ol), it was only necessary, in principle, to perform parallel laser excitation experiments of the types summarized in eq 5 and 6. A plot of the $O_2(^1\Delta_g)$ luminescence

$$\mathrm{BP} \xrightarrow{355\ \mathrm{nm}} {}^3\mathrm{BP}^*(\Phi_T = 1.0) \xrightarrow{O_2} O_2(^1\Delta_g) \tag{5}$$

$$\mathrm{BP} \xrightarrow{355\ \mathrm{nm}} {}^3\mathrm{BP}^* \xrightarrow{\mathrm{Ol}} {}^3\mathrm{Ol}^* \xrightarrow{O_2} O_2(^1\Delta_g) \tag{6}$$

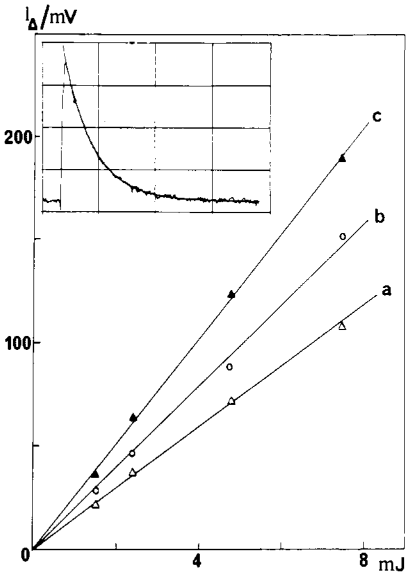

Figure 1. Emission intensity at 1270 nm extrapolated to time zero, I_Δ, against laser energy for benzene solutions of BP (7×10^{-3} mol L^{-1}; $OD_{355} = 0.7$) containing (a) oxygen (2×10^{-3} mol L^{-1}; aerated), (b) CHD (10^{-2} mol L^{-1}) and oxygen (8.7×10^{-4} mol L^{-1}; 9% oxygen in nitrogen), and (c) CHT (10^{-1} mol L^{-1}) and oxygen (2×10^{-3} mol L^{-1}). Inset: Time dependence of emission at 270 nm after absorption of a 7.5-mJ pulse by a CHD solution; 40 mV/division, 26 μs/division, τ_Δ = 13.5 μs.

Table II. Olefin and Oxygen Concentrations (mol L^{-1}) Present During Laser Excitation of Benzophenone (7×10^{-3} mol L^{-1}) at 355 nm Together with Resulting Φ_{obs} and Corrected S_Δ Values

Ol	[Ol]	[oxygen]	Φ_{obs}[a]	$S\Delta$[b]
CPD	10^{-2}	8.7×10^{-4}	0.58	0.75
CHD	10^{-2}	8.7×10^{-4}	0.38	0.40
ES	10^{-2}	8.7×10^{-4}	0.81	0.83
CHT	10^{-1}	2×10^{-3}	0.51	0.66
NA	10^{-1}	1×10^{-2}	0.41	0.45
VD_3	2×10^{-2}	2×10^{-3}	0.18	0.25

[a] Values were reproducible to ±3%. [b] Confidence limits are ±10%.

intensity extrapolated to time zero, I_Δ,[20] as a function of the laser energy,[21] should then give a straight line passing through the origin with a slope proportional to Φ_Δ and hence S_Δ in these cases.[22] Use of the known value for BP would then give S_Δ for individual olefins on an absolute basis.

In Figure 1 are shown plots of the type described above for experiments with a typical diene (CHD) and triene (CHT). Plots were linear and the ratio of slopes to that of the plot for BP alone gave observed $O_2(^1\Delta_g)$ yields, Φ_{obs}, for each olefin (Table II). These were converted to absolute S_Δ values on the basis of the criteria outlined below.

(a) The small S_1–T_1 energy gap for aromatic ketones with lowest n,π* states makes them ideal sensitizers for work of the type in question. Benzophenone has a high triplet energy, 68.6 kcal mol^{-1},

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(22) In order to ensure the accuracy of the extrapolation procedure it is necessary, in experiments of this kind, that the lifetime of $O_2(^1\Delta_g)$, τ_Δ, be >5 μs, an order of magnitude greater than the detection system risetime of ~0.5 μs. The formation time of $O_2(^1\Delta_g)$ should be no greater than the latter value.

but an $S_0 \rightarrow S_1$ absorption band well to the red of those for simple diene/trienes. Even at the high olefin concentrations required in this work (10^{-1} - 10^{-2} mol L^{-1}), only CHT (10^{-1} mol L^{-1}) competed with BP (7×10^{-3} mol L^{-1}; $OD_{355} = 0.7$) for the 355-nm laser light (~18%). To ensure identical distributions of emitting states within the reaction cell, experiments corresponding to eq 5 and 6 were performed with solutions optically matched at 355 nm. A simple correction for the light absorbed by CHT was then applied. This is an accurate procedure only because $S_1 \rightarrow T_1$ nonradiative transitions have efficiencies of zero for such molecules.

(b) All six olefins quenched ^{3}BP* efficiently with rate constants between 3.8 and 8.8×10^9 L mol^{-1} s^{-1} (Table I).[23] These values together with the known value for quenching of ^{3}BP* by oxygen, 1.8×10^9 L mol^{-1} s^{-1},[19] and the olefin/oxygen concentrations given in Table II showed that for experiments corresponding to channel 6 only minor (<3%) corrections were necessary for competitive $O_2(^1\Delta_g)$ formation via channel 5.

(c) In all cases except VD$_3$ a very minor correction was required for the small amount of ^{3}Ol* not scavenged by oxygen.

(d) Only in the case of CPD was the correction for self-quenching significant.

It can be seen from Table II that conversion of Φ_{obs} to S_Δ only required significant correction in the cases of CPD (mainly for self-quenching), CHT (mainly for competitive absorption), and VD$_3$ (mainly for incomplete triplet quenching).

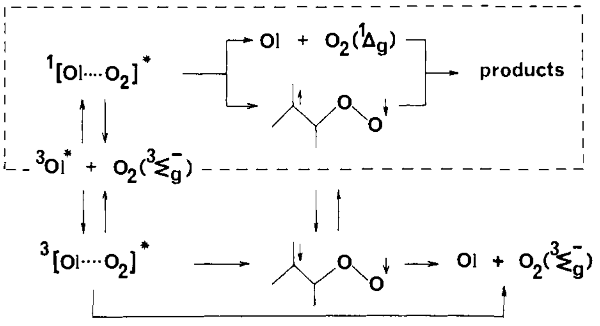
4. Discussion

Each olefin triplet examined in this work has an "available" triplet energy which is a minimum of 13 kcal mol^{-1} above the electronic excitation energy of $O_2(^1\Delta_g)$. This is witnessed by the close-to-optimum rate constants for triplet energy transfer to perylene ($E_T = 35.1$ kcal mol^{-1}; Table I). As already mentioned,[23] the "low" value of 3.0×10^9 L mol^{-1} s^{-1} for VD$_3$ reflects steric as opposed to energetic factors. In no case therefore can a situation reminiscent of the stilbenes exist where an activation barrier to the requisite conformational change lowers the measured rate constant for energy transfer from a less favored geometry. However, S_Δ values are clearly very different from unity, varying from 0.83 to 0.25.

4.1. Quenching via the Triplet Complex. Values of S_Δ significantly below unity are consonant with a situation in which channel 2 competes with channel 1. However, this would mean that in the cases under consideration k_{ox} should vary by almost a factor of 4. This is clearly not so.[24] In addition one would expect lower S_Δ values to be associated with lower triplet energies[25] and shorter lifetimes since the factors which promote the operation of channel 2 should also favor non-oxygen-induced $T_1 \rightarrow S_0$ intersystem crossing. Consideration of the data in Tables I and II shows that this is not the case and lends support to the conclusion, generated by the fact that $k_{ox} \approx k_D/9$, and that quenching does not occur via the triplet encounter complex.

4.2. Quenching via the Singlet Encounter Complex. (i) Geminate Quenching. Olefins react with $O_2(^1\Delta_g)$. If such interaction were to take place within the unseparated Ol/$O_2(^1\Delta_g)$ product pair (geminate quenching), an S_Δ value below unity would be observed. However, under normal diffusion-controlled conditions, the most effective $O_2(^1\Delta_g)$ quencher of the six olefins, CPD, only undergoes reaction once in ~750 collisions,[26] hence making geminate quenching unlikely. However, reactions of this type are entropy-controlled,[26,27] and it could be argued that the Ol/$O_2(^1\Delta_g)$ pair is produced fortuitously in just the correct orientation for reaction. However, this could not possibly hold for a whole series of molecules with differing modes of reaction with $O_2(^1\Delta_g)$. In addition, in contrast to the anticipated situation for geminate reaction, the $O_2(^1\Delta_g)$ quenching rate constant for one of the best sensitizers, CPD (3.9×10^7 L mol^{-1} s^{-1}),[26] is more than two orders of magnitude greater than that of the worst sensitizer, VD$_3$ (2.0×10^5 s^{-1}).[17]

Scheme I



(ii) Competitive Chemistry. As a consequence of the above considerations, we conclude that the low S_Δ values herein determined reflect reaction from the singlet encounter complex which competes with $O_2(^1\Delta_g)$ formation. Although, as already emphasized (section 4.1), the physical parameters listed in Table I do not provide obvious correlation with the S_Δ values of Table II, a consideration of known facts concerning individual relaxed geometries is illuminating.

Firstly, the three most efficient $O_2(^1\Delta_g)$ sensitizers, CPD, ES, and CHT, all have triplet geometries that are close to planar. It is clear from the lack of relaxation in ^{3}CPD* and ^{3}ES* and the extraordinarily long lifetime of the latter that these triplets are essentially planar.[28] The case of CHT is particularly interesting. Although its ground-state geometry is boat-like and grossly nonplanar, we have presented evidence to show that the large degree of relaxation (~17 kcal mol^{-1}) corresponds to the adoption of a close-to-planar equilibrium conformation for ^{3}CHT*.[14]

The least efficient sensitizer, VD$_3$, will clearly have the most nonplanar triplet geometry of the molecules examined. The triene moiety is already twisted in the ground state[30] owing to steric factors, and this should become more pronounced within the triplet. The shorter lifetime and lower triplet energy relative to ^{3}NA* are in agreement with this.

The two sensitizers of intermediate efficiency are CHD and NA. That deviation from planarity occurs in the case of ^{3}CHD* is best shown by comparison with ^{3}ES* which contains the same basic six-membered diene unit. The latter (a) does not relax, (b) exhibits longer wavelength $T_1 \rightarrow T_n$ absorption, and (c) has a much longer lifetime. Evidence that ^{3}NA* is only slightly twisted has already been presented.[15,16]

The available information is therefore consistent with a situation in which planarity of the π system of ^{3}Ol* optimizes the S_Δ value. Conversely, lack of planarity promotes an alternative non-energy-transfer step. Since nonplanarity leads effectively to localization of uncoupled electron density, we propose that high-energy olefin triplets of the type examined here are quenched via a mechanism which is adequately summarized by the framed upper portion of

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[23] The lowest value of 3.8×10^9 L mol^{-1} s^{-1} for VD$_3$ results from a steric factor associated with this molecule.[17] This also influences the rate constant for transfer to perylene ($E_T = 35.1$ kcal mol^{-1}; cf. Table I) as witnessed by a similarity "low" value determined[17] for transfer to β-carotene ($E_T \sim 22$ kcal mol^{-1}).

[24] Five of the k_{ox} values in Table I are typical of processes which proceed exclusively via the singlet encounter complex ($<3 \times 10^9$ L mol^{-1} s^{-1}). Only in the case of VD$_3$ does a slightly higher value indicate a possible contribution from oxygen-induced intersystem crossing, channel 2. The corresponding k_{ox} value for stilbene is 5.8×10^9 L mol^{-1} s^{-1}.[2]

[25] Although this is generally true, it would clearly depend in individual cases on the exact vertical and horizontal dispositions of S_0 and T_1 close to the favored T_1 geometry.

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[28] We have already noted the fact that the lifetime of ^{3}CPD* appears significantly shorter than anticipated on the basis of a comparison with other monocyclic 1,3-dienes[29] although there can be no doubt that significant relaxation does not occur.

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Scheme I. Scheme I can be considered as a general mechanism, without defining individual conformers, which may become significantly simplified by the relative importance of particular rate constants. This mechanism is closely related to that already proposed by us[8] for the oxygen quenching of ketone triplets which themselves have highly localized uncoupled electrons. A putative 1,4-biradical of the type shown in Scheme I will have a lifetime no longer than a few tens of nanoseconds.[9,31] The obvious spin-allowed process is intramolecular reaction to yield products. These latter could of course be allylic hydroperoxides, endoperoxides, etc., typical $O_2(^1\Delta_g)$-derived products. Such species would, in any event, be produced because (a) significant yields of $O_2(^1\Delta_g)$ are also produced, and (b) at the high olefin concentrations necessarily employed most of that $O_2(^1\Delta_g)$ will be chemically quenched. However, there is no reason to believe that the individual biradical products and distribution thereof would be identical with those derived via $O_2(^1\Delta_g)$. Any difference would clearly be dependent on the individual olefin but in the general case would be expected to be more significant with decreasing S_Δ. We are unaware of any steady-state experiments which have addressed this specific problem.

5. Conclusions

Our results have shown that the reaction of olefin triplets with oxygen is an even more complicated function of triplet properties than has hitherto been assumed. In particular, we have provided evidence that the efficiency of the electron-exchange mechanism leading to $O_2(^1\Delta_g)$ is sensitive to the degree of distortion from planarity of the individual reacting conformer. This applies to triplets with "available" triplet energies considerably higher than the electronic excitation energy requirement of $O_2(^1\Delta_g)$. Although we recognize that the mechanistic proposals summarized in Scheme I are of necessity speculative, the key message is absolutely clear. Singlet oxygen quantum yields cannot be assumed to indicate the fraction of oxygen-quenched olefin triplets that lie more than 7882 cm^{-1} above the ground state surface.

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$(C_3H_6N)^+$ Cations in the Gas Phase: Ab Initio Molecular Orbital Calculations and Tandem Mass Spectrometry Experiments

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Abstract: Structures and energies of 26 linear or cyclic $(C_3H_6N)^+$ cations have been examined by ab initio molecular orbital calculations. The geometries of all ions were fully optimized with the 3-21G basis set; energies were improved by inclusion of polarization and electron correlation effects (CI/6-31G*//3-21 G). The seven structures predicted to be the most stable are as follows: **1** $(CH_3NCCH_3)^+$; **2**, $(CH_2CHCHNH_2)^+$; **3**, $(CH_3CH_2CNH)^+$; **4**, $(CH_3CHNCH_2)^+$; **5**, $(CH_2CHNHCH_2)^+$; **6**, (c-$CH_2CH_2NHCH)^+$; **7**, $(CH_3CH_2NCH)^+$. All other isomers have energies greater than that of **1** by ca. 100 kJ mol^{-1}. Experimental generation of five cations (**1–3**, **5** (and/or **6**), and **7**) in the source of a tandem mass spectrometer is also reported. Mass-analyzed ion kinetic energy and collisionally induced dissociation spectra have been used to characterize the five ion structures.

The positive $(C_nH_{2n}N)^+$ ions occur as major fragment ions during dissociation of unsaturated amines or as protonation or alkylation product of cyanides and isocyanides. Ions $(C_2H_4N)^+$ generated by proton transfer to CH_3CN or CH_3NC or from association of CH_3^+ and HCN have been detected by mass spectrometry.[1] The optimized molecular geometries and relative stabilities of isomers of these cations have been determined by semiempirical or ab initio calculations.[2-5] The calculations predict that $(CH_3CNH)^+$, $(CH_3NCH)^+$, $(CH_2CNH_2)^+$, and $(CH_2NCH_2)^+$ ions are the $(C_2H_4N)^+$ isomers of lowest energy.

Although the positive $(C_3H_6N)^+$ ions are present in the electron impact (EI) spectra of cyclic amines,[6] allylamine,[7] and heterocyclic compounds such as aziridine, azetidine, and ethyleneimine derivatives[8] or may be produced by protonation of C_3H_5N isomers, they have not been studied in great details.

In the present study we report first completely optimized geometries, energies, and relative stabilities of isomers **1–23** presented in Chart I. Several of those that are determined to be the most

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