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Study of Hydrogen Bonding in Nitro Enamides

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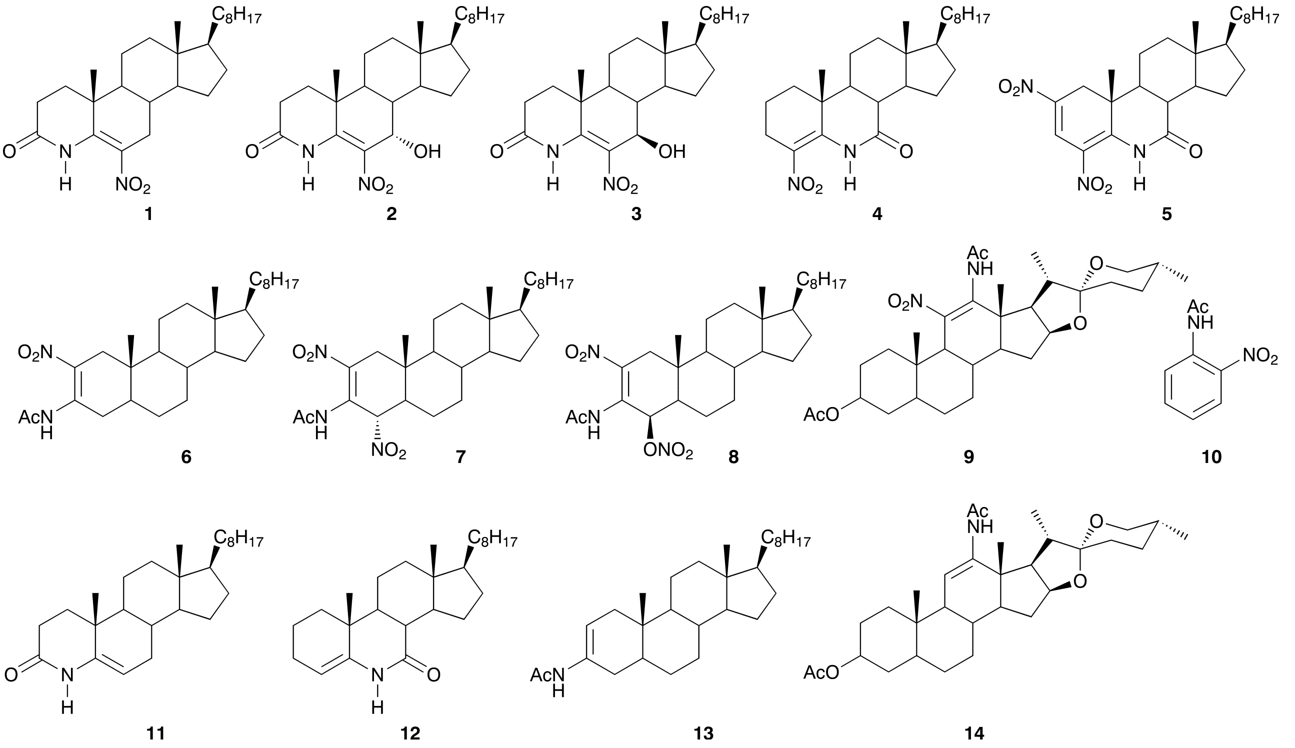
A series of nitro enamides shows the presence of a strong intramolecular hydrogen bond as proved by spectroscopic methods (NMR, IR, UV and MS).

Nitro enamides are a novel class of compounds and their synthesis from the corresponding enamides has been recently described.[1,2] The reagent of choice for this transformation is acetyl nitrate.[3,4] Nitro enamides are stable (more resistant to hydrolysis compared with the parent enamides), crystalline, pale yellow compounds. Their structures are stabilized by intramolecular hydrogen bonds. The spectroscopic properties (NMR, IR, UV and MS) of nitro enamides are discussed in this paper. The molecules in question are those depicted in Scheme 1 (**1**–**10**); the parent enamides (**11**–**14**) are also included for comparison

The enamide proton signal in the NMR specta of the nitro enamides is at $\delta > 10$ (except for compound **9**). The downfield shift of this signal compared with the parent enamides is larger than would be expected from the electron withdrawing effect of the nitro group.[5] X-Ray analysis of *o*-nitroacetanilide (**10**) has shown the presence of an intramolecular hydrogen bond in the crystals.[6] It is evident that a similar hydrogen bond exists in a solution of **10** and in the steroidal nitro enamides **1**–**8** as well. In the case of compounds **1**–**5**, a conformation appropriate for intramolecular hydrogen bond formation is constrained by their rigid structure. Conjugation of a nitro group with a double bond requires coplanar conformation, which also favours hydrogen bonding. The remaining compounds (**6**–**10**) have more conformational freedom. However, strong intramolecular bonds in **6** and **10** maintain their nitro groups and amide protons close to each other. Such conformation is not allowed in the case of nitro enamide **9** due to steric reasons. The presence of additional functional groups in compounds **7** and **8** causes some steric hindrance and therefore hydrogen bonding in these systems is less efficient. It must be added that an amide proton resonance in compounds **1**–**8** and **10** does not change with concentration unlike the nitro enamide **9** and the parent compounds.

The parent compounds **11**–**12** show a broad IR band of bonded N—H stretching vibrations at 3200–3215 cm^{-1} in concentrated solutions. This band becomes much less significant in dilute solutions in favour of the free N—H band at 3376 cm^{-1}. The influence of a nitro group on the N—H vibration absorption frequency in these systems was examined. A sharp N—H absorption band in **1**, **2**, **4** and **5** in the range 3240–3295 cm^{-1}, unaffected by dilution, proves the existence of an intramolecular hydrogen bond between



Scheme 1

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the nitro group oxygen atom and the amide NH group. Nitro enamides **6**, **7** and **8** also show an absorption band N-H intramolecularly bonded to the nitro group. The N—H bond in **7** and **8**, although unaffected by dilution, is considerably broader than in compounds **1**–**6**. Compound **9** is predominately intermolecularly hydrogen bonded in concentrated solutions (IR spectrum shows a broad absorption band for bonded N-H at 3246 cm^{-1} and a small band for free NH at 3421 cm^{-1}). The complete disappearance of the band for bonded NH stretching and a concomitant increase in the intensity of the free NH absorption was observed on dilution. An intramolecular bonding is unattainable in this case due to steric reasons.

The parent compounds **11**–**13** show strong UV absorption bands at 230–236 nm attributed to $\pi \longrightarrow \pi^*$ transitions. However, coplanarity is required for the most effective overlap of the π orbitals and lower energy of the $\pi \longrightarrow \pi^*$ transition. Enamide **14** is likely to be forced into a nonplanar conformation by steric effects, and therefore a shift of absorption to a shorter wavelength and a decrease in intensity for this compound is observed. Attachment of a nitrogen atom bearing a nonbonded electron pair to the ethylenic linkage brings about a bathochromic shift. The nitro enamides show two bands in the near-UV region resulting from the $\pi \longrightarrow \pi^*$ transitions. The fully conjugated systems, such as **1**–**6**, intensively absorb in the ranges of 210–220 nm and 336–346 nm (at 368 nm for compound **5** with extended conjugation). In contradistinction to that the UV spectrum of compound **9** exhibits only one absorption band at 204 nm proving a non-planar conformation of a chromophore. In the spectra of compounds **7** and **8** a long-wave band underwent a hypsochromic shift and a marked decrease in absorption intensity. This is a result of less effective orbital overlapping in these systems.

The mass spectra of some nitro enamides were also briefly examined. The most characteristic (sometimes the base) peaks come from a loss of NO_2. Nitro enamides with an intramolecular hydrogen bond (as proved by the other methods) show strong M^+–H_2O (or M^+–OH) peaks.

Spectroscopic examination of the nitro enamide series proves their tendency to achieve a planar conformation and to form an intramolecular hydrogen bond, wherever possible.

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Techniques used: ^{1}H and ^{13}C NMR, IR, UV, MS

References: 10

Table 1: ^{1}H and ^{13}C NMR data for compounds **1–14**

Table 2: IR data for compounds **1–14**

Table 3: UV data for compounds **1–14**

Table 4: MS data for selected nitro enamides

Fig. 1: IR band contours in NH stretching region of compounds **1**, **2**, **4**, **5**, **6** and **9**

Fig. 2: UV spectra of compounds **1**, **4**, **6**, **7**, **9** and **10**

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