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Pyrolysis of annelated hexa- and heptamethylene-tetrazoles. 
Formation of 9- and 10-membered cyclic carbodiimides

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Highlights:

• Flash vacuum pyrolysis of 8- and 9-membered polymethylenetetrazoles is reinterpreted.
• The products are 9- and 10-membered cyclic carbodiimides rather than cyanamides.
• FVP of tetrazolo[1,5-a]azocine yields transient 9-membered cyclic carbodiimide.
• FVP of tetrazolo[1,5-a]azonine yields transient 10-membered cyclic carbodiimide.
Abstract: A reinterpretation of the spectroscopic data for the products of flash vacuum pyrolysis (FVP) of 8- and 9-membered polymethylenetetrazoles 1, 3, 5, and 7 with aneled benzene rings indicates that these are not cyanamides 2, 4, 6, and 8, but 9- and 10-membered cyclic carbodiimides 9, 10, 11, and 12. FVP of the corresponding tetrazolo[1,5-a]azocine and tetrazolo[1,5-a]azonine derivatives 13 and 17 was investigated by isolation of the products in cryogenic matrices and by matrix photolysis and found to yield 9- and 10-membered cyclic carbodiimides 14 and 18 as transient intermediates en route to indolo[2,3-b]quinoline 15 and dibenzo[b,f]naphthyridine 19.

Keywords: Flash vacuum pyrolysis, matrix isolation, matrix photolysis, nitrenes. imidoylnitrenes
1. Introduction
One of the most surprising results emerging from a research programme on flow or flash vacuum pyrolysis (FVP) led by the late professor Mircea D. Banciu [1-4] was the reported formation of cyclic cyanamides 2, 4, 6 and 8 on FVP of suitably annelated tetrazoles 1, 3, 5, and 7 as indicated in Scheme 1 [4-8]. Key spectroscopic data for the alleged cyanamides were $\nu_{\text{CN}} = 2100$-$2150$ cm$^{-1}$ and $\delta_{13\text{C}} = 138$-$142$ ppm.

However, cyanamides do not absorb in the 2100 cm$^{-1}$ range. Instead, they absorb strongly in the 2200 cm$^{-1}$ range [9,10,11]. They also do not absorb at 138-140 ppm in the $^{13}$C NMR spectra; like other nitriles they give rise to resonances at $\sim$115-120 ppm [9]. In contrast, carbodiimides give rise to strong IR bands in the 2100 cm$^{-1}$ range [10,12] and $^{13}$C NMR resonances at 138-140 ppm [12,13]. Cyclic carbodiimides with 9-, 10- and 14-membered rings are stable and absorb at $\sim$2120 cm$^{-1}$ in the IR [14]. Even the 8-membered pentamethylenecarbodiimide is stable for days at room temperature and absorbs at $\sim$2100 cm$^{-1}$ in the IR [14].

In view of these facts, and based on the reported IR and $^{13}$C NMR data, we reassign the “cyanamides” 2-8 (Scheme 1) described by the Banciu group [4-8] as carbodiimides 9-12 as shown in Scheme 2.

The mis-assignment of the carbodiimides as cyanamides is reminiscent of the story of the natural product kinamycin C, which was first characterized as a cyanamide derivative with unusual spectroscopic data for the “cyanamide” group, which turned out to be in fact a diazo compound [15].

The fully unsaturated cyclic carbodiimides corresponding to 9 and 11 have been postulated to occur as reactive intermediates in cyclization reactions [4,5]. In this paper we set out to attempt their direct observation using low temperature IR spectroscopy, and we are pleased to report the results herein.

2. Experimental
The apparatus used for preparative FVP with product isolation, IR spectroscopic detection at 50-77 K, and matrix isolation in Ar at 7-22 K have been described previously and correspond to Figures 3b, 5 and 7, respectively, in ref. [16]. The liquid helium cryostat was capable of
reaching an ultimate temperature of 7 K. Vacuum was maintained at $10^{-6}$-10$^{-5}$ hPa with a Balzers Pfeiffer turbomolecular pump. Starting materials were sublimed into the quartz pyrolysis tube (10 cm × 0.8 cm I.D.) at a temperature of 100 °C. Pyrolyses were carried out at the temperatures given in the text (400-900 °C). Preparative pyrolyses were carried out at 500 °C/10$^{-2}$ hPa with isolation of the products on liquid N$_2$ cold fingers. For IR spectroscopy the pyrolysis products were condensed on a KBr target at ~22 K together with Ar in a ratio of roughly 1:1000. A similar procedure was used for isolation of products at 50 K, in which case the Ar gas is not condensed. IR spectra were recorded at 7-10 K with a resolution of 1 cm$^{-1}$. The same cryostat was used for photolyses of Ar matrices at 7-10 K. A 1000 W high-pressure Hg-Xe lamp and a 75 W low-pressure Hg lamp (254 nm) were used. A 10 cm water filter was inserted in the optical path to remove excessive heat radiation.

3. Results

Dibenzo[c,g]tetrazolo[1,5-a]azocine 13 was subjected to FVP at 500 °C/10$^{-2}$ hPa in our apparatus and afforded indolo[2,3-b]quinoline (quinindoline) 15 in ca. 90% yield together with minor, unidentified products in accordance with the previous report [4]. Neither the cyanamide 16 nor the carbodiimide 14 are isolable as pyrolysis products under normal conditions, but it has been proposed that the formation of 15 proceeds via transannular cyclization of the unobserved carbodiimide 14 (Scheme 3) [4]. Similarly, FVP of 17 yielded the dibenzonaphthyridine 19 (25%) in agreement with a previous report [5], but neither carbodiimide 18 nor cyanamide 20 were observable under normal conditions of product isolation. Transannular cyclizations are known in other cumulenes [17], and related cyclizations of open-chain carbodiimides have also been reported [18]. We have investigated the possibility of directly observing the carbodiimides 14 and 18 by FVP and photolysis of 13 and 17 with low-temperature isolation of the products for IR spectroscopic observation.

3.1. Decomposition of 13

FVP of 13 at 450 °C in a steam of Ar with isolation of the products at 50 K (i.e. not a matrix isolation) afforded a new absorption at 2122 cm$^{-1}$ with a weaker companion at 2094 cm$^{-1}$ (Fig. 1a). These absorptions disappeared rapidly on warming the solid film to 284 K (Fig 1b). When the pyrolysis products were deposited with Ar at 7 K to form a matrix, this absorption was observed at 2128 cm$^{-1}$ (a shift to higher wavenumbers is normal for going from the solid to the matrix or gas). It is impossible to obtain a strong spectrum of 14 because
it undergoes a facile pericyclic reaction leading to indoloquinoline 15, which was the main product in all the pyrolyses of 13 between 450 and 900 °C. The identity of 15 was confirmed by isolation and direct spectroscopic comparison with the Romanian sample.

Photolysis of 13 matrix-isolated in Ar at 7 K was very slow, but again a weak band at 2128 cm\(^{-1}\) was observed using the broadband irradiation of the high-pressure Hg-Xe lamp. This absorption in the 2120 cm\(^{-1}\) range could be due to either the azide formed by ring opening of 13 or the carbodiimide 14. However, the absorption is stable to FVP at temperatures up to 800 °C. Usually azides do not survive temperatures above 500 °C in our apparatus. The absorption is also stable to irradiation with either the high-pressure Hg-Xe lamp or a low-pressure Hg lamp (254 nm). Therefore, the absorptions at 2122/2094 cm\(^{-1}\) in Fig. 1 cannot be due to an azide. It can also not be due to the N-cyanamide 16 formed by ring contraction, because this compound is known and absorbs at 2220 cm\(^{-1}\) in CHCl\(_3\) solution [19]. Consequently, the absorptions at 2122/2094 cm\(^{-1}\) are ascribed to the carbodiimide 14. It is common for carbodiimides to show multiple peaks in the 2100 cm\(^{-1}\) range [10].

3.2. Decomposition of 17.

This compound is very involatile, and consequently it is difficult to obtain good low-temperature spectra of pyrolysis products. A weak absorption at 2130 cm\(^{-1}\) was observed in the Ar matrix IR spectrum following FVP at 450 °C, and this may be due to the carbodiimide 18. An additional band at 2229 cm\(^{-1}\) may be due to the cyanamide 20 formed by ring contraction, but the weakness of the signals make definitive assignments difficult (see Fig. S1, Supplementary Material). Better results were obtained on matrix photolysis at 7 K using the broadband irradiation of the high-pressure Hg-Xe lamp. A strong absorption developed at 2130 cm\(^{-1}\) in the course of 80 min (peak C, Fig. 2). Further irradiation using either the broadband output from the high-pressure Hg-Xe lamp or the low-pressure Hg lamp for 190 min did not cause any significant changes. It is therefore not possible that the compound could be an azide, and it is ascribed to the carbodiimide 18. The 2059 cm\(^{-1}\) band (D, Fig. 2) may also belong to the carbodiimide. Note that a weak absorption at 2229 cm\(^{-1}\) (B, Fig. 2) is also formed in the photolysis, and it may be due to the cyanamide 20. Further IR spectra showing the progress of reaction are available in in the Supplementary Material (Fig. S2).

4. Discussion

Ring expansion, ring opening and ring contraction reactions are ubiquitous in aromatic and heteroaromatic nitrene chemistry [20,21]. Loss of N\(_2\) from 1,5-disubstituted
tetrazoles 21 will in principle lead to (singlet) imidoylnitrenes \( \text{22} \) (Scheme 4), which are known to rearrange to carbodiimides \( \text{23} \) [4,10,22]. The calculated activation energy for the rearrangement \( \text{22} \rightarrow \text{23} \) is low, ca. 17 kcal/mol for a 1,2-H shift and ca. 20 kcal/mol for a 1,2-Ph shift at the B3LYP/6-31+G** level [23]. The imidoylnitrenes can also in principle cyclize to \( 1H \)-diazirines \( \text{22} \) and then rearrange to nitrile imines \( \text{23} \) via a substantially higher barrier [23].

In 2-pyridynitrene \( \text{26} \) the activation barrier for ring expansion to the 7-membered cyclic carbodiimide \( \text{28} \) is \( \sim \)25 kcal/mol at the CASPT2 level [24], but this proceeds via an azirine \( \text{27} \), which cannot be formed from the saturated polymethyleneitetrazole derivatives (Scheme 5). Ring opening of 2-pyridynitrene to a vinylnitrene \( \text{29} \) has a barrier of ca. 10 kcal/mol for the triplet state and 3 kcal/mol for the \( S_1 \) singlet. Ring closure of the vinylnitrene to \( 2H \)-2-cyanopyrrole \( \text{30} \) over a very low barrier leads to 2-cyanopyrrole \( \text{31} \) [24].

A similar scenario is readily formulated for the imidoylnitrenes \( \text{32} \) and \( \text{34} \) derived from polymethyleneitetrazoles (Scheme 6). In principle, they can either undergo ring expansion to carbodiimides \( \text{14} \) and \( \text{18} \) (a 1,2-shift of an aryl or alkyl group) or ring opening/ring contraction leading to cyanamides \( \text{16} \) and \( \text{20} \). Transannular cyclization of the carbodiimides follows a pattern known for many other cyclic cumulenes [17,20] including \( \text{28} \) [24] and leads to \( \text{33} \) and \( \text{35} \), respectively, and then to \( \text{15} \) and \( \text{19} \), in the first case by two consecutive 1,5-H shifts [4], and in the second by thermal 1,4-elimination of \( \text{H}_2 \). The results presented above indicate that the carbodiimides \( \text{14} \) and \( \text{18} \) are observable reactive intermediates. The formation of cyanamides, when it happens at all, may take place via ring opening of either the nitrenes \( \text{32} \) and \( \text{34} \) or the carbodiimides \( \text{14} \) and \( \text{18} \) to biradicals followed by recyclization [20,21].

As elucidated in the Introduction and Results sections, the ring expansion to cyclic carbodiimides is the normal course of events in all these reactions. However, a cyanamide appears to have been identified correctly in the case of \( \text{40} \), formed by FVP of tetrahydro-dibenzo[\( d,f \)]tetrazolo[1,5-\( a \)]azocine \( \text{36} \). Again, \( \text{40} \) may form via ring opening/ring contraction of either imidoylnitrene \( \text{37} \) or carbodiimide \( \text{38} \) to a biradical \( \text{39} \) (Scheme 7) in the same way that 9-phenanthridinylnitrene rearranges to dibenzo-1,3-diazacycloheptatetraene and 9-
cyanocarbazole [20,21,25]. This reaction and further discussion of the FVP of 36 are presented in the Supplementary Material (Schemes S1 and S2).

In the cases of tetra- and pentamethylenetetrazoles, FVP results in ring opening accompanied by H-shifts to form alkenylcyanamides as described for pentamethylenetetrazole 41 in Scheme 8 [11]. The ring opening with H-shift leading to 4-pentenylcyanamide 44 may take place either in the imidoylnitrene 42 or in the carbodiimide 43 under the pyrolysis conditions. Notably, 1-cyanopiperidine 45 was not formed [11]. The ring opening may be concerted with the migration of the indicated H atom (Scheme 8), or it may involve nitrene or biradical intermediates as described in Scheme 7. In the light of the results of the present investigation, the previously unidentified “isocyanide” [11] formed from pentamethylenetetrazole 41 under the mildest pyrolysis conditions with low conversion (400 °C/5×10⁻³ hPa) can now be assigned the structure of the known [14] pentamethylenecarbodiimide 43.

5. Conclusion
The normal course of rearrangement of polymethylenetetrazoles on flash vacuum pyrolysis (FVP) is the formation of imidoylnitrenes and ring expansion to cyclic polymethylene-carbodiimides. FVP of tetrazoles 1, 3, 5, 7, 13 and 17, which are dibenzotetrazolo[1,5-a]azocine and dibenzotetrazolo[1,5-a]azonine derivatives, yields 9- and 10-membered cyclic carbodiimides 9, 10, 11, 12, 14, and 18. Ring contraction to cyclic cyanamides is a less common pathway, which however is observed in the case of the N-cyanodihydrodibenzazepine 40 formed on FVP of tetrazole 36 and the open-chain 4-pentenylcyanamide 44 formed on FVP of pentamethylenetetrazole 41.

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Supplementary data: additional IR spectra arising from the pyrolysis and photolysis of 17.
Additional discussion of the FVP of 36. This material can be found in the online version at http://dx.doi.org/10.1016/j.jaap.2015

References


Fig. 1. Product of FVP of 13 at 450 °C. (a) IR spectrum of the product at 50 K, peaks at 2122 and 2094 cm$^{-1}$ are ascribed to carbodiimide 14. (b) IR spectra following warm-up to 274, 281 and 284 K.
Fig. 2. Product of photolysis of 17 in Ar matrix at 7 K. Peak A = CO$_2$ (2342 cm$^{-1}$), B 2229, C 2130, D 2059 cm$^{-1}$. Peaks C and D are ascribed to carbodiimide 18. Peak B may be due to a small amount of cyanamide 20. The majority of absorptions in the fingerprint area are due to the starting material, 17. For further details see Fig. S2.
Scheme 1. Cyclic cyanamides 2, 4, 6, and 8 supposedly formed by FVP of annelated polymethylene tetrazoles 1, 3, 5, and 7 [4].
Scheme 2. Reassigned structures of the products FVP of annelated polymethylenetetrazoles 1, 3, 5, and 7 as carbodiimides 9-12.
Scheme 3. Formation of compounds 15 and 19 by FVP of 13 and 17. Direct observation of carbodiimides 14 and 18 is described in the text.

Scheme 4. Rearrangements of imidoynitrenes.
Scheme 5. Ring expansion, ring opening and ring contraction of 2-pyridylnitrene.

Scheme 6. Rearrangements of imidoylnitrenes 32 and 34.
Scheme 7. Potential formation of cyanamide 40 via ring opening to biradical 39 followed by ring closure, $36 \rightarrow 37 \rightarrow 39 \rightarrow 40$ or $38 \rightarrow 39 \rightarrow 40$. See further discussion of this reaction in the Supplementary Material.
Scheme 8. Rearrangements of pentamethyleneimidoylnitrene 42 in the pyrolysis of 41.