

Concerning the chemical structure of the dicyanogen photopolymer and its presence in certain bodies of the Solar system. Implications on the synthesis of some prebiotic molecules

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Abstract: The chemical structure of the dicyanogen photopolymer $(CN)_x$, also known as paracyanogen, prepared in different solvents from dicyanogen $(CN)_2$ photopolymerization under the action of ultraviolet light, is shown to be very similar to the polymer derived from hydrogen cyanide (HCN) and from certain tholins obtained from a simulated Jovian atmosphere. The implications of dicyanogen and its polymer as a precursor of some organic molecules already detected in cometary comas and tails and in meteorites are discussed. In particular, paracyanogen may be present in the cometary nuclei and in the surface of certain low-albedo objects in the Solar system.

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Introduction

The chemistry of HCN polymerization has been investigated in detail, also in relation to the pre-biological origin of life (Matthews & Moser 1966, 1967; Matthews 1984, 1995; Cruikshank *et al.* 1991; Khare *et al.* 1994). For instance, the water extract of HCN polymers has been hydrolysed (Matthews 1995) to yield alpha-amino acids and polyamides (the polymeric precursors of peptides). According to the fascinating Matthews hypothesis (Matthews 1995), the primitive Earth may have been covered by HCN polymers and other organic products through bolide bombardment or terrestrial synthesis, producing proteinaceous matter and purine and pyrimidine bases, which could have been the basis for the emergence of life. There is experimental evidence which suggests that HCN polymers and CN-bearing molecules and macromolecules are somewhat ubiquitous on planetary bodies and satellites of the Solar system, as well as around other stars and dusty molecular clouds. In relation to these aspects, Cruikshank *et al.* (1991), have already discussed the curious infrared spectral similarities among HCN polymer, spark and ultraviolet (UV) tholins made from methane and ammonia and methane/ammonia/acetylene and the dust of comets, Bowell and Panther, as well as matter from the Uranian rings, D-class asteroids and the low-albedo hemisphere of Japetus. In addition, the mentioned polymers may also be present in the nuclei of comets (Matthews 1995). Thus, HCN and its

polymeric derivatives may be ubiquitous because they are readily produced by corpuscular irradiation of methane and ammonia, as well as from ammonia photolysis in the presence of acetylene (Ferris & Ishikawa 1988; Clarke & Ferris 1997), which is a derivative of methane photolysis and radiolysis.

Direct photolysis of HCN in the gas phase at 185 nm yields dicyanogen $(CN)_2$, H_2 , CH_4 , NH_3 , H_2N-NH_2 , ethane and methylamine as well as polymeric products (Mizutani *et al.* 1975; Becker & Hong 1983). It has already been noted (Khare *et al.* 1994) that some of the HCN polymers may, in reality, be polymers derived from $(CN)_2$, i.e. dicyanogen, which derives from the photolysis of HCN.

The discussion concerning HCN polymeric derivatives has not been limited just to the origins of life, but has also included the colour of certain bodies and satellites. For instance, it has been proposed that the orange colour of Titan, Jupiter and Saturn can be attributed to the formation of a solid aerosol derived from the photopolymerization or radiopolymerization of the nitrile-group-bearing molecules present in the atmosphere of these bodies (Matthews 1995). However, Khare *et al.* (1994) have shown that the aerosol colour in these bodies cannot derive exclusively from HCN polymers. As we had occasion to discuss several times (Cataldo 1994, 1996, 1998; Cataldo & Heymann 1999, 2000, 2001; Heymann & Cataldo 1999; Heymann *et al.* 2000), it is highly probable that the colour of these bodies cannot be a result of the photo- or radiopolymerization of a single species but to the simultaneous

and random polymerization of a plethora of molecules (Cataldo 1998), including acetylene (Cataldo 1994), ethylene (Cataldo 1996), carbon monosulphide (Cataldo & Heymann 1999, 2000, 2001; Heymann & Cataldo 1999; Heymann *et al.* 2000) and many other compounds, yielding copolymers.

It is quite surprising that until now a large part of the research in this area has been concentrated on HCN, while little attention has been devoted to its parent molecule, dicyanogen (CN)₂ and its photopolymerization (Norrish & Smith 1928; Hogness & Ts'ai 1932; Dresdner *et al.* 1965; Paul & Dalby 1962); also because, as reported previously, the short-wavelength photolysis of HCN produces (CN)₂. In addition, dicyanogen is derived from the association of two cyanogen CN radicals. The photolysis of dicyanogen yields two CN radicals (Hogness & Ts'ai 1932). In this context it is interesting to note that the strength of the C–C bond of dicyanogen (NC–CN) is 128 kcal mol⁻¹, while the H–C bond in gaseous hydrocyanic acid (H–CN) is 123.8 kcal mol⁻¹. This means that approximately the same energy is needed to generate cyanogen radicals from these two molecules. CN radicals have been detected for a long time in the coma and in the tails of comets, and it is believed that cyanogen is trapped in the ice of the cometary nucleus (Kissell & Krueger 1987) and it is present in the interstellar and circumstellar molecular clouds. Dicyanogen is routinely found in sunspots and in the photosphere of cool stars.

Dicyanogen has been detected in the atmosphere of Titan together with many other components (Cousternis *et al.* 1993; Gurwell & Muhleman 1995). Since it is supposed that the haze layers observed on Titan could be a result of the ultraviolet photon-induced and radiation-induced polymerization of the various components of Titan's atmosphere, it would be interesting to know the role played by cyanogen. However, the interest in cyanogen photochemistry is not limited to the atmosphere of Titan, but also involves, for instance, the Jovian atmosphere (McDonald *et al.* 1991).

Recently, we have started an investigation into the synthesis and the structure of dicyanogen photopolymer (Cataldo 1999). The present paper is an account of our earlier results on this matter.

Differences between HCN and dicyanogen (Brun & Fontaine 1956)

Dicyanogen (CN)₂ is a gas at room temperature that has a boiling point of -21 °C and melts at -27.9 °C. Conversely, HCN has a boiling point of +25.6 °C and a melting point of -13.4 °C.

Dicyanogen is very reactive: it changes very quickly into a dark-brown or black mass when it passes into a strong alkaline or ammonia solution. In aqueous solution it is unstable and quickly turns into a black deposit. Among the products detected we mention: azulmic acid, described sometimes as (CONH)₄ and sometimes as C₄N₅H₅O, ammonium oxalate and cyanate, urea, oxamide, ammonia and ammonium formiate (HCOONH₄) (Brun & Fontaine 1956) are formed too. The structure of azulmic acid or azulmine is still controversial: (CONH)₄ suggests a cyclic oligomer of urea, while

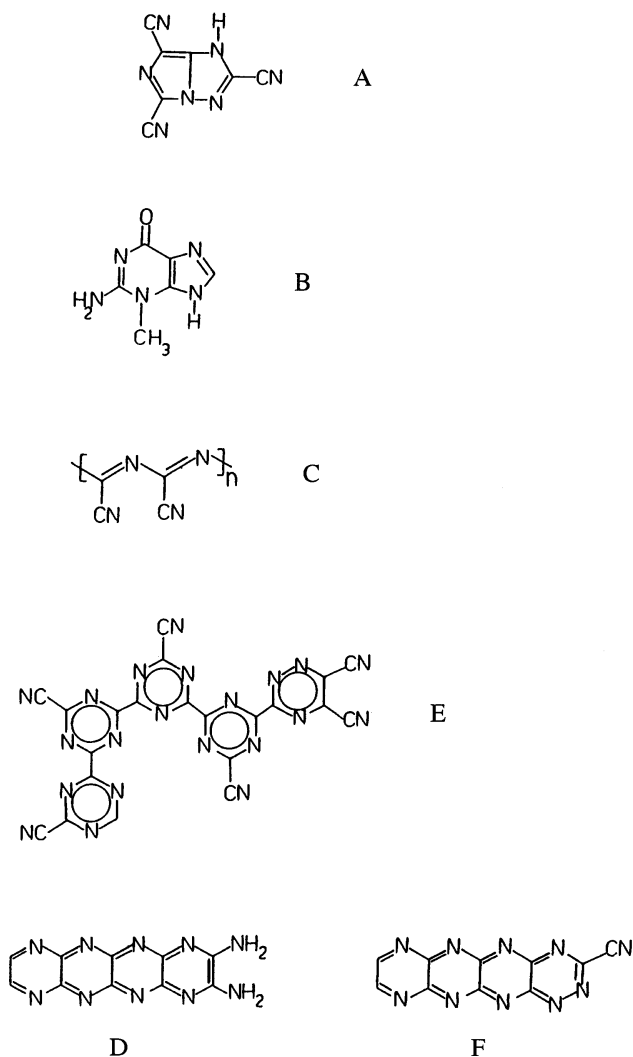
C₄N₅H₅O suggests a heterocyclic structure (two pentagonal condensed rings, for instance). Similar products are obtained when (CN)₂ is dissolved in alcohol and, additionally, it also forms condensation products with the solvent RO–C(=NH)–C(=NH)–OR. In the context of cometary ices, which are essentially made of water and methanol, this polymerization trend of dicyanogen is of particular interest. The polymerization of dicyanogen is also strongly accelerated in solution by UV light irradiation (Cataldo 1999) and by other types of corpuscular or electromagnetic radiation (Brun & Fontaine 1956). In acidic solutions dicyanogen is hydrolysed to oxamide (CONH₂)₂, ammonium oxalate (COONH₄)₂ and ammonia (Brun & Fontaine 1956). Another fascinating aspect of dicyanogen chemistry is its prompt condensation reaction with a cyanide ion (Wiley *et al.* 1976). In addition to an abundant amount of black polymeric product, three dicyanogen molecules react with one cyanide ion giving a very interesting heterocycle (see Scheme 1, structure [A]) C₇N₇H (1H-imidazo[1,5-b]-s-triazole-2,5,7-tricarbonitrile), which is characterized as having two condensed pentagonal rings. The methylation and the hydrolysis of this molecule leads to 3-methylguanine (Scheme 1, structure [B]), a purine base in a reaction where the prebiotic implications are self-explanatory.

HCN is much less prone to polymerization. Brown matter is formed when HCN is kept compressed in bombs for several months in the presence of water impurities, Cyanide ions and bases. Among the decomposition products ammonia, carbon monoxide, hydrogen and nitrogen have been detected, together with a brown amorphous polymeric mass. In aqueous solution or in the pure liquid state HCN needs 30 days to polymerize (Khare *et al.* 1994). A catalytic amount of ammonia or other bases is needed. Liquid HCN can polymerize suddenly and violently in the presence of certain impurities (Khare *et al.* 1994).

General aspects of dicyanogen photopolymerization

It was already known that dicyanogen is sensitive to light and is prone to photopolymerization and radiation-induced polymerisation, but only old and sporadic works have covered this subject previously (Norrish & Smith 1928; Hogness & Ts'ai 1932; Lind *et al.* 1961; Paul & Dalby 1962; Dresdner *et al.* 1965). The structure of the photopolymer also called paracyanogen had not been studied using spectroscopic techniques until our recent work (Cataldo 1999).

In 1928 Norrish and Smith published a work where it was reported that dicyanogen undergoes photopolymerization in the gas phase with an initial pressure of 150 torr under irradiation by a high-pressure mercury lamp (with wavelengths between 222 and 366 nm) with an 11% yield of polymer. Hogness and Ts'ai (1932) reported that the dicyanogen absorption spectrum in the gas phase consisted of a series of diffuse bands extending from 224 nm to the limit of transmissivity of quartz (190 nm). Photopolymerization in the gas phase occurred by irradiating dicyanogen with light of wavelength $\lambda \approx 214$ nm with a quantum efficiency of 3 mol einstein⁻¹; this quantum yield was later confirmed (Fabian 1967).



Scheme 1. A, C_7N_7H (1H-imidazo[1,5-b]-s-triazole-2,5,7-tricarbonitrile); B, 3-methylguanidine; C, a linear polymer with a pendant nitrile group; D, ladder (polypyrazinopyrazine) structure for paracyanogen; E, a 1,3,5-triazine polymer; F, a pyrazino-pyrazine ladder structure for paracyanogen photopolymer.

Other researchers have shown that C_2N_2 photopolymerizes even at 1 torr pressure by irradiation with light having $\lambda = 310$ nm (Dresdner *et al.* 1965). Gas-phase, flash-photolysis studies have also been performed (Paul & Dalby 1962).

Treatment with corpuscular radiation of both $(CN)_2$ and HCN yields a heptamer of dicyanogen and an undecamer of HCN (Lind *et al.* 1961).

Recent results concerning dicyanogen polymerization

Studies of dicyanogen photopolymerization in solution have not been performed previously and in our work (Cataldo 1999) we have selected four different solvents to study C_2N_2 photopolymerization. We used tetrahydrofuran, hexane, methanol and ethanol. Dicyanogen is very soluble in polar organic solvents and photopolymerization of dicyanogen in these solvents can be considered to be equivalent to a polymerization under pressure due to this large solubility and to the related 'solvent cage effect'. In fact dicyanogen gas has a

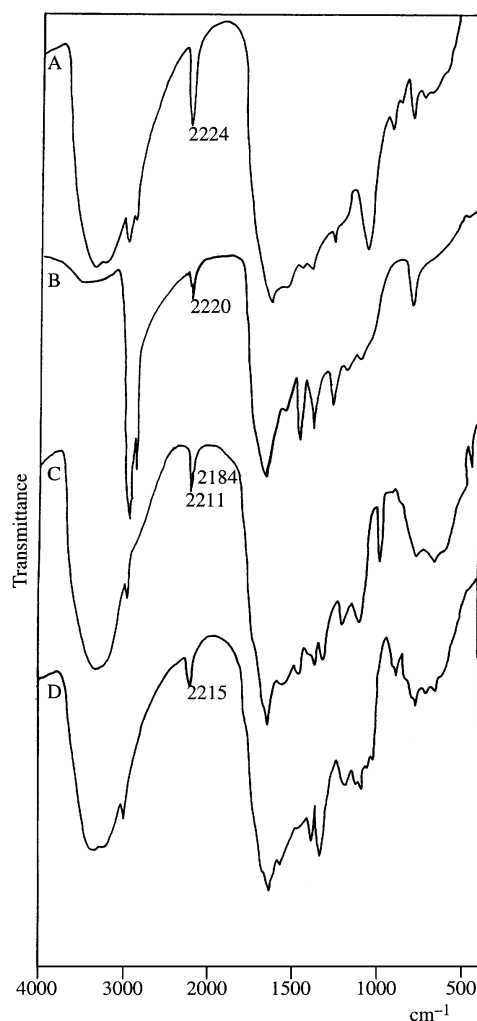


Fig. 1. FT-IR spectra of: (a) C_2N_2 photopolymer obtained in THF by UV irradiation; (b) C_2N_2 photo-oligomer obtained in n-hexane by UV lamp irradiation; (c) C_2N_2 photopolymer obtained in methanol by UV lamp irradiation; (d) C_2N_2 photopolymer obtained in ethanol by sunlight irradiation.

density of 2.321 g l^{-1} , while in organic solvents it is possible to dissolve a relatively high amount of dicyanogen per litre of solvent ($\sim 10 \text{ g l}^{-1}$) at room temperature (Cataldo 1999).

Irradiation of dicyanogen solution at room temperature with UV light from a high-pressure mercury lamp causes quick polymerization, which can be followed spectroscopically by an increase in the optical density of some key absorption bands (Cataldo 1999).

The resulting infrared spectra of dicyanogen photopolymers (see Fig. 1) agree very well with the infrared spectrum of paracyanogen $(CN)_x$ produced by anionic polymerization of cyanogen (Peska *et al.* 1966) and with that produced by electrochemical polymerization of dicyanogen (Chen & Labes 1985). In both cases, previous researchers have assigned mainly a linear conjugated structure to their polymers with pendant nitrile groups from the main chain (see Scheme 1, structure C). Pendant CN groups are suggested by the band at 2220 cm^{-1} , while for azomethine the chains $-C=N-$ are suggested by the intense and broad band in the range between 1650 and

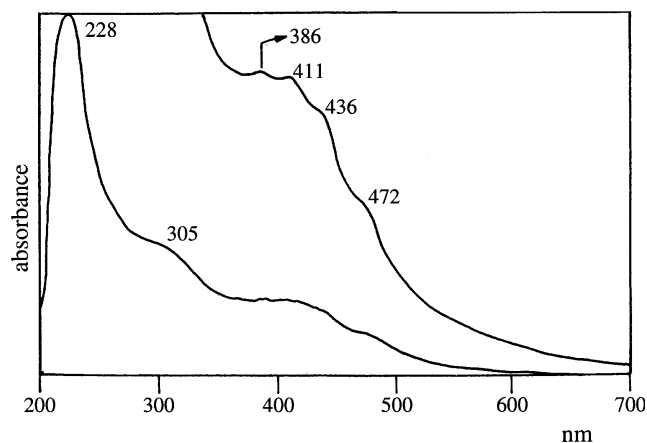


Fig. 2. Electronic spectrum of the cyanogen photopolymer in THF solution.

1450 cm^{-1} (Peska *et al.* 1966; Chen & Labes 1985) (see Fig. 1). However, other authors (Birkumshaw *et al.* 1954) proposed a ladder (polypyrazinopyrazine) structure for paracyanogen obtained by thermal decomposition reactions of inorganic salts (see Scheme 1, structure [D]). Very recent reinvestigation of the structure of paracyanogen (Jenneskens *et al.* 1994) has substantially confirmed early spectroscopic results (Birkumshaw *et al.* 1954), with the product showing essentially three bands: 2200 cm^{-1} owing to $-\text{CN}$ groups, an intense and broad azomethine band with a maximum at $\sim 1500\text{ cm}^{-1}$ and another broad band in the $700\text{--}800\text{ cm}^{-1}$ region (Jenneskens *et al.* 1994).

If we compare the spectra of Fig. 1 with those reported by Khare *et al.* (1994) for HCN polymers prepared under different conditions, we can observe striking similarities. This may lead us to formulate the conclusion that the final brown or black products formed from both HCN and $(\text{CN})_2$ polymerization, having substantially the same infrared spectrum, should have substantially the same chemical structure.

Another curious aspect is that the infrared spectrum of the dicyanogen photopolymer prepared in this work (Fig. 1a, c, d) shows a surprising similarity with the spectrum of unfractionated Jupiter tholin prepared by McDonald *et al.* (1991) (by sparking methane, ammonia and water) having a CN stretching at 2200 cm^{-1} and a broad band with transmittance minima at 1663 , 1560 and 1456 cm^{-1} .

A feature of the spectra of the dicyanogen photopolymer reported in Fig. 1 is the C–H stretching appearing in the range $2850\text{--}2980\text{ cm}^{-1}$; this absorption band is not expected in the photopolymerization of dicyanogen, but since it is present in all cases, it is clear that the solvent participates in the polymerization and is incorporated into the polymer structure. If the mechanism of dicyanogen photopolymerization involves free radicals, then from the C–H stretching intensity we can conclude that the maximum chain transfer to solvent occurs with n-hexane (Fig. 1b), causing in this case the formation of aliphatic nitriles by hydrogen abstraction from hexane and addition of CN radicals. The degree of chain transfer is also significant in THF (Fig. 1a), while this phenomenon can be considered less important in the case of ethanol and methanol

(Fig. 1c, d) since in these cases the C–H stretching band is very weak. Elemental analysis confirms the spectroscopic indications completely. In fact, the dicyanogen photopolymer prepared in THF can be described by the formula $[(\text{C}_2\text{N}_2)(\text{CH}_2\text{CH}_2\text{O})]_x$, showing that THF copolymerizes with dicyanogen, while in the case of methanol as the solvent, elemental analysis suggests the following formula $[(\text{C}_3\text{N}_3)(\text{OH})]_x$, hence incorporation of a fragment of the methanol molecule or partially, from other sources (e.g. moisture or air) seems to occur (it may be that the oxygen detected is a result of the moisture present in the sample). Elemental analysis and the calculated minimal formulae show in any case that the C/N ratio is equal to unity as was expected (after correction for foreign monomeric units).

Concerning the chemical structure of the dicyanogen polymer

Based on the above results and considerations, it is quite a difficult task to assign an unequivocal structure to the cyanogen photopolymer. General guidelines could be deduced as follows:

- cyanogen photopolymerization involves a free-radical mechanism advocating C–C bond homolysis of the molecule;
- these CN free radicals are responsible for the chain transfer reaction to solvent molecules involving hydrogen abstraction in the case of hexane, ring opening in the case of THF and, finally, some minor interaction with methanol;
- cyanogen radicals can recombine to form the dicyanogen molecule, could trimerize to form a 1,3,5-triazine polymer (see Scheme 1, structure [E]), could interact with the dicyanogen molecule to form a 1,2,4-triazine polymer (also shown as part of the schematic structure [E]) and could promote radical polymerization of cyanogen to give a linear polymer with a pendant nitrile group (Scheme 1, structure [C]). Linear polymers with an azomethine structure, although already proposed in the case of chemical paracyanogen, are unusual because they should only be stable at low temperatures. Hence, if formed, on standing at room temperature or during work-up they should undergo cyclization to form a ladder structure (Scheme 1, structure [D]). This kind of cyclization reaction is well known and has already been reported for the considerably more stable polyacrylonitrile when it is heated at $160\text{--}300\text{ }^\circ\text{C}$, forming a ladder polymer known as ‘black orlon’ (Klimenko *et al.* 1991).

The electronic spectrum reported in Fig. 2 refers to the cyanogen photopolymer prepared in THF. This spectrum is a typical spectrum for an aromatic heterocyclic compound, but not for a polyenic or, which is the same, polyazomethinic compound. In fact, only aromatic compounds display three bands (Silverstein *et al.* 1981) called, respectively, E_1 , E_2 and B that in Fig. 2 appear at 228, 305 and at 411 nm, respectively. The longest wavelength band, the B-band, shows fine vibrational structure, which is a typical phenomenon for aromatic compounds (Silverstein *et al.* 1981), as testified by the small sub-bands at 386, 411, 436 and 472 nm. Therefore the electronic spectrum favours heterocyclic structures [D] and [E]

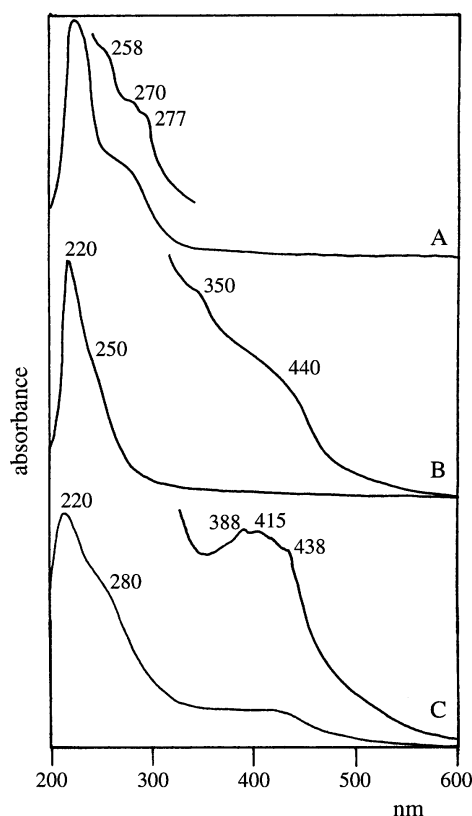


Fig. 3. Electronic spectra of: (a) pure dicyanogen in methanol, (b) C_2N_2 photopolymer obtained in methanol by UV lamp irradiation and (c) C_2N_2 photopolymer obtained in ethanol by sunlight irradiation.

rather than structure [C], but structure [D] cannot explain the presence of the free CN group as indicated by the infrared spectrum of Fig. 1 unless we admit that it contains a nitrile end group owing to the presence of a 1,2,4 triazine end group [E]. Similar reasoning is applicable to the cyanogen photopolymer obtained in methanol (Fig. 3b) and in ethanol and sunlight (Fig. 3c), where in both cases the band at ~ 440 nm is observable and in the case of spectrum 3c a fine vibrational structure is also detectable. The general conclusion is that in polar solvents cyanogen yields a product having structure [E] or [F] (see Scheme 1).

The triazine-based structure [E] should be less conjugated than the pyrazino-pyrazine ladder structure [F], because the triazine rings are necessarily connected in 1,3,5 position, which causes minimum conjugation between the rings. Since s-triazine shows its longest-wavelength maximum at 272 nm and 1,2,4-triazine at 384 nm (Perkampus 1993), structure [E] should show just these two maxima without a bathochromic shift arising from conjugation. The spectra of the cyanogen photopolymer shown in Figs 2 and 3 have longest-wavelength bands at 440–470 nm and hence cannot be represented by structure [E]. On the other hand, structure [F] is highly conjugated and explains well the UV spectra of the cyanogen photopolymer; in fact, tetramethylpyrazino-pyrazine shows its longest-wavelength maximum at 383 nm, while its inferior homologue pyrazine shows this maximum at 330 nm. Hence

by passing from pyrazine (one ring) to pyrazino-pyrazine (two condensed rings) a bathochromic shift of 50 nm should occur. To reach 440–470 nm (Figs 2, 3), we should add at least another two rings and we obtain structure F (Scheme 1), which is a cyanogen pentamer.

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