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N-(3-Cyanoprop-2-ynyl)carbazole: synthesis, crystal structure, and solid-state reactivity

Ulf Drechsler,[a] Daniel J. Sandman[a] and Bruce M. Foxman[b]

[a] *Center for Advanced Materials, Department of Chemistry, University of Massachusetts Lowell, Lowell, Massachusetts, 01854-2881, USA*
[b] *Department of Chemistry, Mail Stop 015, Brandeis University, Waltham, Massachusetts, 02454-9110, USA*

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N-(3-Cyanoprop-2-ynyl)carbazole (**1**) was synthesized in 30% yield by reaction of *N*-(3-bromoprop-2-ynyl)carbazole (**2**) with cuprous cyanide in tetrahydrofuran, or by reaction of lithiated *N*-(prop-2-ynyl)carbazole (**3**) with 1-cyanobenzotriazole in 70% yield. Grown from hexane–dichloromethane solution, compound **1** crystallizes in the orthorhombic space group $P2_12_12_1$, with $a = 6.5553(6)$, $b = 11.3879(25)$, $c = 16.2752(24)$ Å, $V = 1215.0(3)$ Å^3, and $Z = 4$. The title compound undergoes a thermally induced solid-state oligomerization, largely following a 1,2-addition pathway, consistent with the arrangement of molecules observed in the crystal structure.

Introduction

The topochemical and topotactic solid-state polymerization of diacetylenes has stimulated extensive research into the structure and properties of the polydiacetylenes,[1] especially their linear and nonlinear optical properties. In the interest of finding other solid-state reactions analogous to diacetylene polymerization, we have initiated an investigation of cyanoalkynes. Qualitatively, cyanoalkynes (R–C≡C–C≡N) are π-isoelectronic with diacetylenes and are expected to be capable of forming reactive intermediates analogous to the diradicals and dicarbenes[2] involved in diacetylene polymerization. The products of any solid-state reactivity of cyanoalkynes should depend on the details of the reactant crystal structure.

While not structurally analogous to the well-studied symmetrically substituted diacetylenes, such cyanoalkynes present a unique opportunity for examining the solid-state reactivity of a new class of compounds. Cyanoalkynes have not been previously studied with respect to their solid-state reactivity and topochemical polymerization. Monocyanopolyynes (H–(C≡C)$_n$–CN) have been detected as molecules in interstellar space.[3] Vaporization of graphite in the presence of cyanogen has led to the formation of dicyanopolyynes NC–(C≡C)$_n$–CN, n = 3–8.[4] In the solid state, these materials are stable in the dark at low temperatures. At room temperature, they slowly convert to black, insoluble materials presumed to be cross-linked polymers. The solution polymerization[5,6] of the parent cyanoacetylene typically proceeds as a substituted acetylene. Several cyanopolyynes were reported. Initially colorless, they darken in light, but no products were characterized.[7]

The first cyanoalkyne chosen for study is the new compound *N*-(3-cyanoprop-2-ynyl)carbazole (**1**), which was synthesized by reaction of *N*-(3-bromoprop-2-ynyl)carbazole (**2**)[8] with CuCN in tetrahydrofuran (THF), or by the reaction of lithiated prop-2-ynylcarbazole with 1-cyanobenzotriazole.

Experimental

General

Melting points are uncorrected. Ultraviolet–visible solution spectra were obtained on a Perkin-Elmer Lambda 9 UV–VIS–NIR spectrophotometer. Fluorescence spectra were measured on an SLM spectrometer. Fourier transform infrared (FT-IR) spectra were recorded using a Perkin-Elmer 1720 FT-IR spectrometer. The ^{1}H and ^{13}C NMR spectra were recorded on either 200 or 250 MHz Bruker spectrometers. Thin layer chromatography (TLC) was carried out using silica gel as adsorbent.

N-(3-Cyanoprop-2-ynyl)carbazole (1)

a. From *N*-(3-bromoprop-2-ynyl)carbazole (2) and cuprous cyanide. To a stirred mixture of **2** (1.14 g, 4.0 mmol) and cuprous cyanide (450 mg, 5.0 mmol) in 15 mL of dry THF was added a solution of anhydrous lithium bromide (180 mg, 2.0 mmol) in 2 mL of THF at 40 °C under an argon atmosphere. After a few minutes the temperature rose to 60–70 °C, and the solids gradually dissolved. Stirring was continued for 1 h at this temperature, followed by a further 8 h under reflux. The dark reaction mixture was cooled to room temperature, and poured into an ice cold solution of KCN (4 g) and NH_4Cl (6 g) in 50 mL of water with vigorous stirring. The resulting mixture was extracted with 3 × 50 mL of diethyl ether; the combined organic layers were washed with 50 mL of saturated NH_4Cl solution and subsequently dried over $MgSO_4$. The ether was evaporated and the residue was purified by column chromatography on normal grade silica gel using hexane–dichloromethane (2:1) as eluent ($R_f = 0.3$). The title compound was obtained in 30% yield as a colorless solid, melting to a yellow–brown liquid at 91–93 °C. The purified product was dissolved in the minimum amount of dichloromethane, and the solution was covered with a layer of a fivefold excess of hexane. Upon standing for 10 days, single crystals were obtained. ν_{max}(KBr)/cm^{-1} 3051, 2915, 2309s, 2241m, 1935w, 1895w, 1599s, 1487, 1465, 1426, 1204, 761. δ_H (250 MHz, $CDCl_3$) 8.15 (2H, d, Ar H), 7.55 (2H, d, Ar H), 7.36 (4H, m, Ar H), 5.16 (2H, s, CH_2). δ_C (62.9 MHz, $CDCl_3$) 139.9 (C_q), 126.8 (CH), 124.1 (C_q), 121.1 (CH), 120.9 (CH), 108.8 (CH), 104.8 (*C*N), 79.6 (C≡*C*–CN), 58.8 (CH_2–*C*≡C), 32.9 (CH_2). λ_{max}(acetonitrile)/nm (log ε) 334 (3.62), 321 (3.61), 289 (4.26), 233 (4.68) (Found: C, 83.1; H, 4.2; N, 12.2. Calc. for $C_{16}H_{10}N_2$: C, 83.4; H, 4.4; N, 12.2%).

b. From *N*-(prop-2-ynyl)carbazole and 1-cyanobenzotriazole. To a stirred solution of *N*-(prop-2-ynyl)carbazole (1.0 g, 5 mmol) in 25 mL of dry diethyl ether was added dropwise 1.6 M *n*-butyllithium in hexane (3.2 mL, 5.2 mmol) at −78 °C under an argon atmosphere. Stirring at this temperature was continued for 30 min. The resulting suspension was then slowly

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Table 1 Crystallographic data[a] for **1**

Chemical formula	$C_{16}H_{10}N_2$
Formula weight	230.27
Crystal system	Orthorhombic
Space group	$P2_12_12_1$ [no. 19]
T/K	294
a/Å	6.5553(6)
b/Å	11.3879(25)
c/Å	16.2752(24)
V/Å^3	1215.0
Z	4
ρ_{calcd}/g cm^{-3}	1.26
ρ_{obs}/g cm^{-3}	1.25(1)
λ/Å	1.54178
μ/mm^{-1}	0.55
Trans. coefficient (empirical correction)	0.85–0.90
Unique reflections; number observed	1499; 1300 [$I > 1.96\sigma(I)$]
R	0.0353
R_w	0.0462

[a] $R = \Sigma||F_o|\Sigma|F_c||/\Sigma|F_o|$; $R_w = \{\Sigma w[|F_o|\Sigma|F_c|]^2/\Sigma w|F_o|^2\}^{1/2}$.

added to a solution of 1-cyanobenzotriazole (940 mg, 6.5 mmol) in 15 mL of dry diethyl ether at −78 °C. After stirring for 1 h at this temperature, the mixture was allowed to slowly warm to room temperature, and was stirred for another 30 min. The dark reaction mixture was poured into 100 mL of ice cold 0.1 M HCl and vigorously shaken. The organic layer was separated and the aqueous phase extracted with 3 × 50 mL of diethyl ether. The combined organic layers were washed with saturated NH_4Cl solution, dried over $MgSO_4$, and the solvent was evaporated. The residue was purified by column chromatography (normal grade silica gel, hexanes–dichloromethane 2 : 1) to give **1** in 70% yield. Melting point and spectroscopic data are the same as reported above.

Thermal reaction of 1

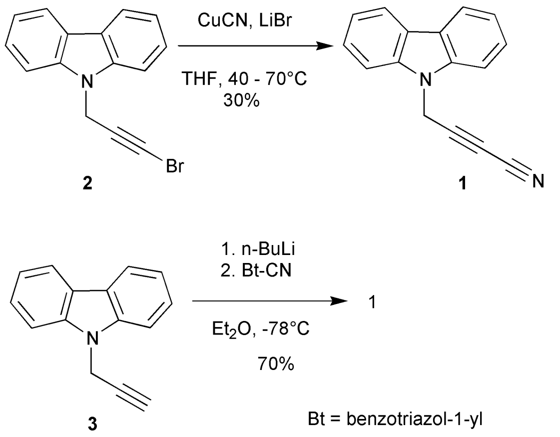
A sealed ampoule containing **1** (230 mg, 1.0 mmol) was heated at 88 °C in the vapor of refluxing triethylamine for 3 days. During the formation of the dark brown reaction product, the initially crystalline sample gradually melted, and then resolidified toward the end of the reaction. After being cooled to room temperature, the crude product was dissolved in 5 mL of dichloromethane, and the solution poured into 30 mL of hexane. The resulting precipitate was removed by centrifugation, and thoroughly washed with hexane. Drying *in vacuo* yielded 160 mg of a dark brown solid. ν_{max}(KBr)/cm^{-1} 3050, 2310w, 2212m, 1935w, 1895w, 1680m, 1625sh, 1597s, 1449vs, 1325vs, 747vs. λ_{max}(THF)/nm (log ε) 290 (3.79), 322 (3.69), 335 (3.70), 370 (3.65). δ_H (250 MHz, $CDCl_3$) 8.23–7.99 (m, Ar H), 7.57–7.16 (m, Ar H), 7.07–7.00 (m, Ar H), 8.23–7.00 (8H), 6.75–6.72 (=CH), 6.28–6.24 (m, =CH), 6.75–6.24 (approx. 0.6H), 5.41–5.31 (m, CH_2), 4.70–4.43 (m, CH_2), 5.41–4.33 (approx. 1.5H). δ_C (62.9 MHz, $CDCl_3$) 161.7, 159.3, 158.5 (C=N), 140.2 (C_q), 127.3, 127.2 (CH), 124.2, 123.9 (C_q), 121.5, 121.2, 121.1, 120.5 (CH), 117.2, 112.1 (C_q), 110.2, 108.4, 108.1 (CH), 92.2, 90.9 (CH), 42.1, 39.6 (CH_2). The assignments in the ^{13}C spectrum follow from a DEPT-135 experiment (Found: C, 83.5; H, 4.4; N, 12.25. Calc. for $(C_{16}H_{10}N_2)_n$: C, 83.4; H, 4.4; N, 12.2%).

Structure determination of *N*-(3-cyanoprop-2-ynyl)carbazole †

Crystallographic data for compound **1** are summarized in Table 1. Data were collected on a Nonius CAD-4U diffractometer (Cu-Kα radiation, $\lambda = 1.54178$ Å).[9] Data were processed using the Nonius MolEN package.[10] The structure was solved by direct methods [SIR-92].[11] Full-matrix least squares refinement was carried out using the Oxford University CRYSTALS system.[12] All non-hydrogen atoms were refined using anisotropic displacement parameters. H atoms were fixed at calculated positions, which were updated following each least-squares cycle. Drawings were produced using the Oxford University graphics program CAMERON.[13]

Results and discussion

Cyanoalkynes can be prepared by numerous synthetic methods, many of which include either the reaction of an acetylenic anion with an electrophilic cyano source, or a formal nucleophilic displacement of a suitable leaving group by a cyanide anion.[5] Since common electrophilic cyanation reagents, such as cyanogen chloride, either are extremely toxic, or cannot be obtained from readily available precursors, *e.g.* phenyl cyanates, we initially chose to prepare the title compound by a copper(I)-promoted bromine–cyano exchange reaction.[14] Starting from *N*-(3-bromoprop-2-ynyl)carbazole (**2**) and cuprous cyanide in THF, the reaction proceeded under fairly mild conditions (Scheme 1). The obtained yield (30%) of the cyanoacetylene, however, was only moderate. A recent report, on the other hand, proposed the general applicability of easily obtainable 1-cyanobenzotriazole in electrophilic cyanations.[15] Reaction of this compound with the lithium salt of *N*-(prop-2-ynyl)carbazole (**3**) in diethyl ether at low temperatures gave **1** in 70% yield as a colorless solid.



Scheme 1 Synthesis of *N*-(3-cyanoprop-2-ynyl)carbazole.

An interesting aspect of the spectral properties of **1** is its infrared spectrum (see Experimental). Of particular significance are the strong absorption at 2309 cm^{-1} and the medium intensity absorption at 2241 cm^{-1}, assigned to the acetylenic and cyano stretches, respectively. While dialkylacetylenes exhibit low intensity triple bond stretching between 2230 and 2240 cm^{-1}, substituents on a triple bond that are strongly electron attracting can move the triple bond stretch into the region discussed here.[16] For example, cyano(isocyano)acetylene has its acetylene stretch at 2295.72237 cm^{-1}.[17] Cyanoacetylene's triple bond stretch is reported at 2273.996 cm^{-1},[18] that of dicyanoacetylene at 2267 cm^{-1} [16] and that of hexafluorobut-2-yne at 2305 cm^{-1}.[16]

In order to grow single crystals, the chromatographically purified material was dissolved in the minimum amount of dichloromethane, and the solution was cautiously covered with a layer of excess hexane. Upon standing for ten days, the compound crystallized as colorless single crystals suitable for X-ray diffraction analysis.

Fig. 1 shows the molecular structure of **1**; bond lengths and angles lie in normal ranges. The C(14)–C(15) and C(16)–N(2) distances are 1.183(3) and 1.141(3) Å, respectively, while the angles subtended at C(14), C(15) and C(16) are 178.1(3), 177.0(3) and 177.9(3)°, respectively. The shortest contacts in the

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† CCDC reference number 188/286. See http://www.rsc.org/suppdata/p2/b0/b007807g/ for crystallographic files in .cif format.

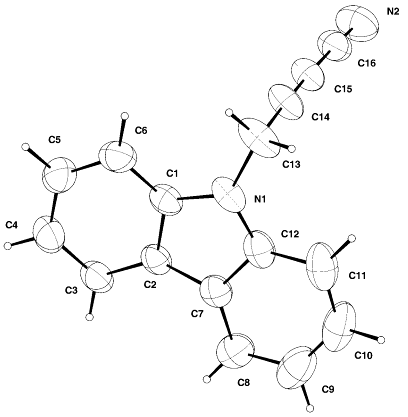


Fig. 1 Molecular structure of **1**, showing labelling scheme and 40% probability ellipsoids for atoms refined using anisotropic displacement parameters.

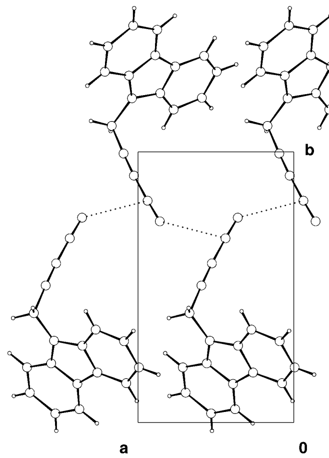


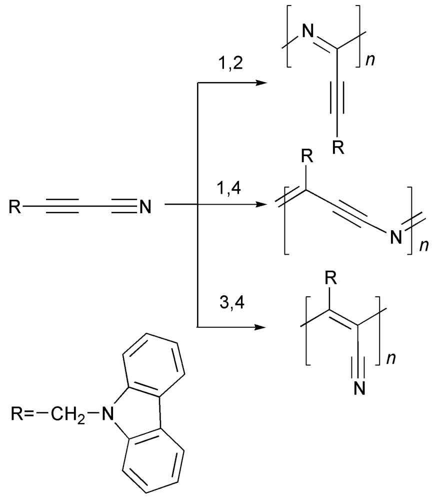
Fig. 2 View of molecules in the crystal structure of **1**, showing interleaving of cyanoalkyl groups and short N(2)–C(16) contacts of 3.339 Å.

crystal structure are between cyano groups. Fig. 2 shows part of a set of infinite contacts, N(2)–C(16) [$x - 1/2$, $3/2 - y$, $2 - z$], at 3.339 Å. The arrangement shown in Fig. 2 suggests that a 1,2-addition might be possible, if topochemical effects were responsible for at least the onset of reactivity.[19,20] The unit cell translation of *ca.* 4.9 Å common for *symmetrical* diacetylenes is not present in this structure; thus a 1,4-addition is not a likely event.

In order to investigate the solid-state reactivity of **1**, samples of the substance were exposed to UV light at 254 and 370 nm, as well as to 500 kGy of ^{60}Co γ-radiation. After 10 days, the sample irradiated at 254 nm turned slightly brown, possibly indicating the presence of a conjugated π-electron system. However, TLC analysis revealed that most of the starting material remained unchanged. The sample exposed to 370 nm light showed practically no change, even after a prolonged period of time. Exposure to γ-radiation, on the other hand, led to a somewhat more intensely colored product. Nevertheless, TLC confirmed only poor conversion, which, in turn, made it impractical to isolate the reaction products. Given the additional observation that **1** shows no sensitivity to Cu-Kα X-rays, we conclude that solid-state reactivity may only be driven thermally.

In order to examine the thermally induced solid-state reactivity, a sample was heated below the melting point at 80 °C for one week. The colorless solid turned light brown, and the product, obtained in extremely low yield, was isolated by preparative TLC. The amount of material obtained allowed only a mass spectral analysis. The FAB mass spectrum indicated the presence of a dimeric species.

In order to gain information on the behavior of **1** at or near the melting point, a sample was heated just below the melting point for several days. This experiment was carried out knowing *a priori* that the lattice would not control the products formed. Nevertheless, this would allow us to obtain sufficient material for characterization. After having reached the final temperature, the color of the material turned to light brown, and the compound gradually melted, indicating a contamination of the reactant crystal by newly formed reaction products. Toward the end of the reaction, the dark brown material slowly solidified. The UV–VIS spectrum of the product in THF solution shows—besides the strong absorption of the carbazole units—a relatively intense, broad absorption band peaking at 372 nm and tailing to 500 nm, indicating the presence of a conjugated π-electron system, presumably composed of different types of oligomerized –C≡C–C≡N subunits (see Scheme 2 for an illustration of products that would arise from 1,2-addition at cyano groups, 1,4-addition, and 3,4-addition at the acetylene). When excited at 389 nm in THF solution, the material shows a relatively strong fluorescence, peaking at 526 nm. The gel permeation chromatogram indicated a dimer and, additionally, showed a weak signal possibly arising from a trimer, as well as a tailing into the higher molecular weight range.



Scheme 2 Possible reaction pathways for the thermal reaction of **1**.

Since the product consists of a mixture of inseparable components with the same elemental composition as the reactant (elemental analysis), it is not described in terms of a simple composition. The interpretation of both the ^{1}H and the ^{13}C NMR spectra appears to be complex. The most prominent features of the ^{1}H NMR spectrum are the carbazole resonances as three complex multiplets centered at 8.1, 7.5 and 7.0 ppm (area 8H), respectively, accompanied by two signal groups at 6.7 and 6.3 ppm (area about 0.6H), which can be assigned to vinylic protons. Furthermore, different types of methylene groups appear as complex multiplets at 5.4 and 4.6 ppm (total area about 1.5H, in a 7:6 ratio, respectively). The ^{13}C NMR spectrum supports the presence of –C=N– subunits, exhibiting resonances between 161 and 158 ppm. The signal groups centered at 140, 127, 123, 121, and 109 ppm, respectively, arise from the carbazole substituents. As confirmed by comparison with the ^{13}C DEPT-135 spectrum, a group of quaternary carbons show signals between 117 and 111 ppm, which can be assigned to cyano and double bond units, presumably arising from 3,4-linked subunits. Furthermore, the ^{13}C DEPT-135 spectrum shows CH resonances at 92.2 and 90.9 ppm, consistent with the observation of vinylic or allenylic protons in the ^{1}H NMR spectrum. Finally, the ^{13}C DEPT-135 spectrum features CH_2 signals at 42 and 39 ppm. The infrared spectrum exhibits a weak acetylene triple bond stretch at 2310 cm^{-1} and a C≡N stretching vibration at 2212 cm^{-1}. The presence of conjugated –C=N– units is demonstrated by an absorption at 1680 cm^{-1}.

Supported by the obtained infrared and NMR spectral information, the most likely oligomerization process appears to be a 1,2-addition, accompanied, to a lesser extent, by a 3,4-addition.

Conclusions

N-(3-Cyanoprop-2-ynyl)carbazole (**1**) has been synthesized by two different methods for the purpose of studying its crystal structure and potential solid-state reactivity. Inspection of the crystal structure shows no short acetylene–acetylene contacts: rather, the shortest contacts involve only cyano groups. The intermolecular arrangement precludes a 1,4-addition reaction under topochemical control. However, the presence of short 1,2-contacts between cyano groups in the crystal structure suggests that a topochemical product would be produced; accordingly, dimer formation is observed at 80 °C. This information provides an entry to the understanding of structure–reactivity relationships for the thermal reactions of cyanocarbon moieties in the solid state.

While **1** is effectively inert to ultraviolet and ionizing radiation, its thermal reactivity at temperatures near the melting point leads to a complex material that appears to be chemically inhomogeneous. We will continue to pursue solid-state reactivity of cyanoalkynes *via* synthesis of monomers whose programmed assembly promises to lead to structures that permit the desired 1,4-addition reaction.

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