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On the Trimerization of Cyanoacetylene: Mechanism of Formation of Tricyanobenzene Isomers and Laboratory Detection of Their Radio Spectra

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Abstract: In support of a deeper understanding of the chemistry of cyanoacetylene—a known constituent of planetary atmospheres and interstellar space—theoretical and experimental studies address the chemical mechanism of dimerization and trimerization, and provide high-resolution rotational spectra of two of the trimeric products, 1,2,3- and 1,2,4-tricyanobenzene. Analysis of the rotational spectra is particularly challenging because of quadrupolar coupling from three ^{14}N nuclei. The laboratory rotational spectra provide the basis for future searches for these polar aromatic compounds in interstellar space by radio astronomy.

Keywords: astrochemistry · cyanoacetylene · density functional calculations · quantum chemistry · rotational spectroscopy

Introduction

Cyanocarbons are highly unsaturated organic molecules, the chemistry of which is largely determined by the presence of the polarizing cyano substituents.[1] Recently studied representatives of this class of compounds are the cyanoacetylenes, a group of cyanocarbons known to be quite abundant in the interstellar medium (ISM)[2] and also in the atmosphere of Titan.[3] Ion–molecule reactions have been shown to be the most likely pathways for the formation of molecules such as acetylene in the dense cores of molecular clouds (densities of $10^4\,cm^{-3}$ and temperatures as low as 10 K).[2] HCN is presumably formed by molecular N_2 photodissociation as shown by Equations (1) and (2).[3–4]

$$N_2 \xrightarrow{h\nu} {}^{\bullet}N + N^{\bullet} \quad (1)$$

$${}^{\bullet}N + {}^{\bullet}CH_3 \rightarrow HCN + H_2 \quad (2)$$

Cyanoacetylene (**1**) is subsequently produced through photolysis of HCN followed by a radical reaction between the cyano radical and acetylene [Eqs. (3), (4), and (5)]:[5]

$$HCN \xrightarrow{h\nu} {}^{\bullet}H + {}^{\bullet}CN \quad (3)$$

$${}^{\bullet}CN + HCN \rightarrow NCCN + H^{\bullet} \quad (4)$$

$$C_2H_2 + {}^{\bullet}CN \rightarrow HC{\equiv}C{-}CN + H^{\bullet} \quad (5)$$

Similar reactions can occur with longer alkynes to give larger cyanopolyynes, of which the longest presently known in the interstellar medium is $HC_{11}N$.[6]

Many of these molecules have been discovered by the use of radio and optical spectroscopy, all with the assistance of rotational and vibrational (microwave and infrared, respectively) experiments conducted here on Earth. Both experimental work in which molecules are synthesized or photochemically obtained and then studied spectroscopically, and computational work in which reaction pathways, molecular dipoles, and rotational constants can be computed are extremely helpful in interpreting spectra of the ISM.

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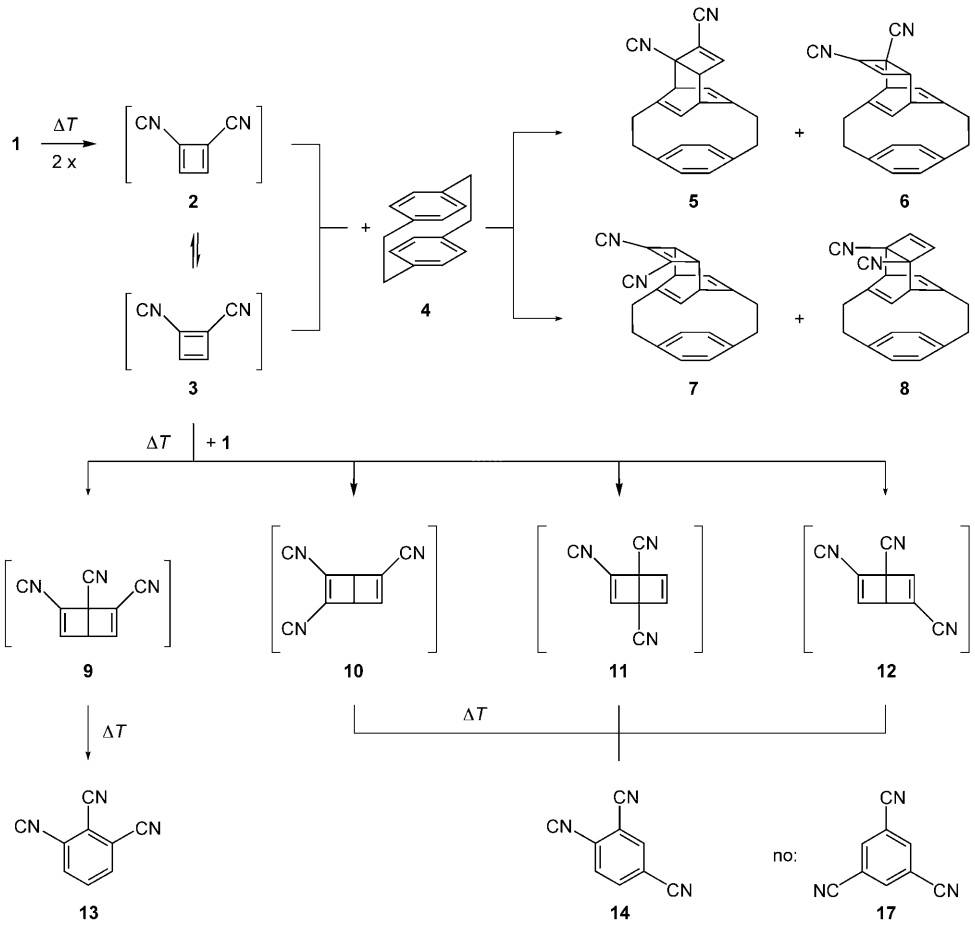
Preparative cyanocarbon chemistry is a field that was heavily researched at du Pont in the 1950s and 1960s. However, further exploration has been limited. Due to the strong electron-withdrawing capability and the cylindrical shape of the nitrile group, cyanocarbons provide some interesting reactivity, especially with electron-rich molecules. Much of this reactivity has been nicely reviewed by one of the lead researchers at du Pont, Owen W. Webster.[7]

In experiments designed to investigate the behavior of cyanoacetylene (**1**) as an addend to strained aromatic compounds,[8] we made the interesting observation that, when [2.2]paracyclophane (**4**) and **1** were heated in benzene, cycloadducts were indeed formed, but that these did not have the structure expected if **4** reacts as a diene and **1** as a dienophile.[9] Rather than the expected 1:1 adduct, we isolated different 2:1 adducts of **1** to **4**, the structures of which were determined by spectroscopic methods and X-ray structural analysis to be the dinitriles **5**–**8** (Scheme 1).[8]

To rationalize this result, we proposed that **1** dimerizes thermally to a cyclobutadiene intermediate, which can exist in two valence-tautomeric forms, **2** and **3**. The products **5**–**8** are then the expected 2:1 adducts if the highly reactive cyclobutadiene is intercepted by the strained aromatic hydrocarbon **4**. That a 1,2- rather than a 1,3-difunctionalized cyclobutadiene is generated in the initial step we have rationalized by the following: a radical mechanism in which the diradical formed in the presumably rate-determining step is more stable with two unsaturated substituents in vicinal position than in 1,3-orientation with opposing nitrile moieties.

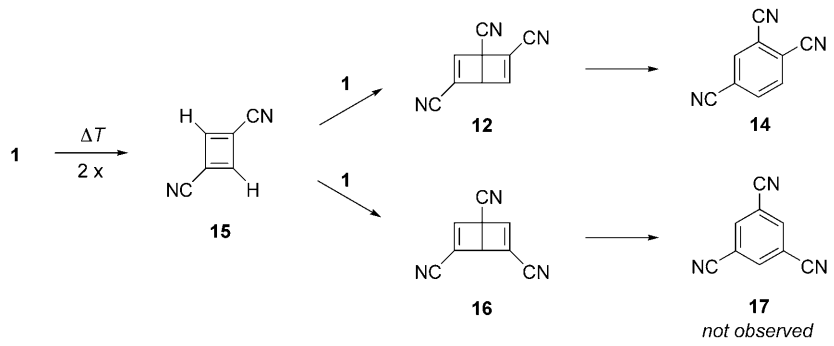
Interestingly, in all our cycloadditions there were also obtained two isomeric trimers of cyanoacetylene (**1**): 1,2,3-tricyanobenzene (**13**) and its 1,2,4-isomer, **14**. In no experiment did we observe the formation of 1,3,5-tricyanobenzene (**17**) (Scheme 1, Scheme 2).

This result agrees with the putative formation of **2**/**3** in the first step. If these isomeric cyclobutadienes are intercepted not by **4** but by an excess amount of **1** in a competitive route, the four isomeric Dewar benzene derivatives **9**–**12** could be produced. These highly strained adducts (trimers) would not be expected to survive under the drastic reaction conditions (reaction temperature: 160 °C, sealed ampoule) and would isomerize by thermal cleavage of one of their four-membered rings. As can be derived from Scheme 1, only the two (observed) trimers **13** and **14**, but never **17**, could be produced by this route. A conceivable route to **17** could involve the head-to-tail dimer **15**, which by addition of a third equivalent of **1** could yield **17** through the intermediate Dewar benzene **16**. Of course, **15** could also furnish **14** through **12** (Scheme 2).



Scheme 1. Observed dimerization, trimerization, and trapping chemistry involving 1,4- and 1,2-dicyano-1,3-cyclobutadiene (**2** and **3**) according to reference [8].

The present paper has two major aims. First, we wished to support or refute the above mechanistic considerations for the formation of **2**/**3**, **13**, and **14** through computational studies of the potential energy surfaces. Second, we sought to obtain laboratory rotational spectra of the two aromatic products **13** and **14**, thus establishing the prerequisite to identify these cyanoacetylene derivatives in interstellar space. Although cyanoacetylene and the family of larger cyanopolyynes are known constituents of interstellar space, cyano-substituted aromatic compounds are not. The rotational spectroscopy of **13** and **14** is of considerable interest in its own right because of the spectral complexity that arises in these highly polar compounds as a consequence of three quadrupolar ^{14}N nuclei. Our combined computational/spectroscopic studies also set

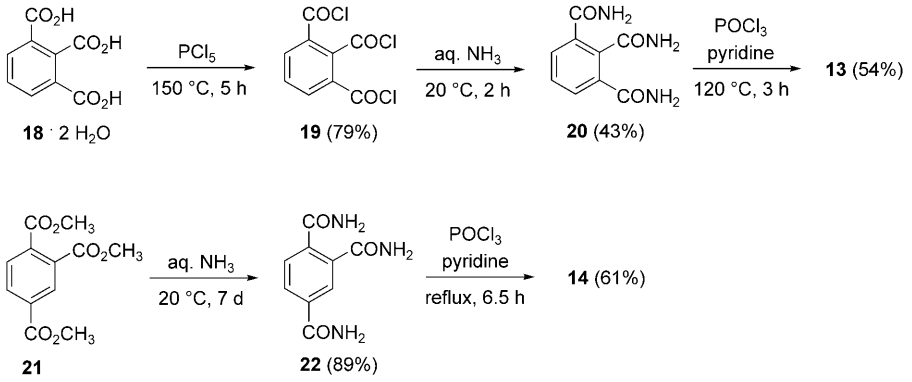


Scheme 2. Hypothetical dimerization and trimerization chemistry involving 1,3-dicyano-1,3-cyclobutadiene (**15**).

the stage for subsequent experimental investigations of the dicyanocyclobutadiene isomers (**2** and **3**).[10]

Results and Discussion

Synthesis of 1,2,3- and 1,2,4-tricyanobenzene (13 and 14): Although both compounds could be prepared by trimerization of cyanoacetylene (**1**, see above), this route is rather involved and requires extensive separation work.[8a,b,e] Fortunately, both isomers have been prepared previously by the simple routes summarized in Scheme 3, both of them having been reported in the literature.[11]



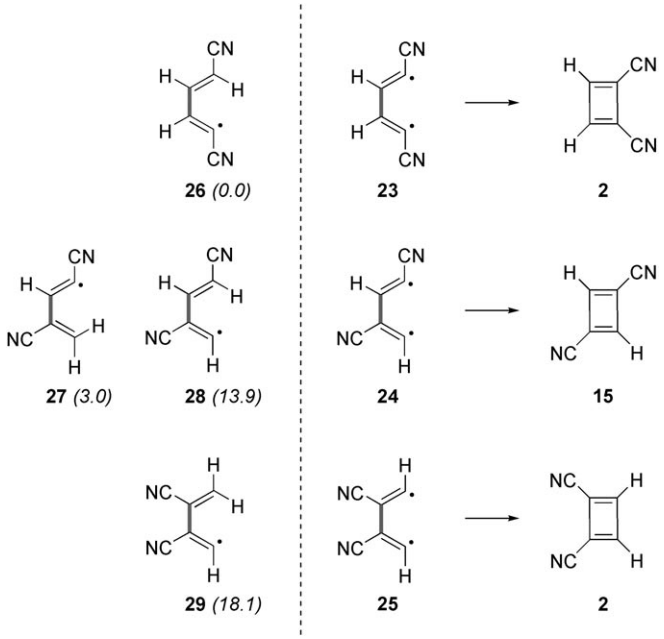
Scheme 3. Syntheses of authentic samples of 1,2,3- and 1,2,4-tricyanobenzene (**13** and **14**) according to reference [11].

As the starting material for **13**, we used the commercially available tricarboxylic acid hydrate **18**. By treatment with phosphorus pentachloride, this was converted into the tris(acid chloride) **19**, which on aminolysis with aqueous ammonia gave the amide **20**. Dehydration to 1,2,3-tricyanobenzene was finally accomplished by treatment with $POCl_3$ in pyridine. The route to the 1,2,4-isomer **14** is essentially the same, except that it starts from the tris(ester) **21** and converts this first to the tris(amide) **22**, the dehydration of which to **14** proceeds without problems in good yields. Both isomers are available in gram quantities by these routes, and their spectroscopic and analytical data are identical with those reported in the literature.[11]

Computations

Dimerization of cyanoacetylene: The thermal [2+2] dimerization of cyanoacetylene to afford dicyano-1,3-cyclobutadiene is forbidden by orbital symmetry. The formation of the dimer, as inferred from trapping with [2.2]paracyclophane (see above), has been rationalized in terms of a stepwise mechanism that involves radical and/or diradical intermediates.[8] In the current study, we sought a deeper understanding of the details of the dimerization mechanism. Stepwise C–C bond formation in the dimerization of cyanoacetylene may proceed through the 1,4-diradicals **23**–**25** depicted in Scheme 4. A key issue involves the relative energies of these diradical intermediates—a direct manifestation of the influence of the cyano substituents.

Computational studies of conjugated radicals and diradicals of this type are challenging for a variety of reasons: 1) the inherent multireference character of diradicals, 2) the inability of perturbation theory to handle spin-contaminated wavefunctions, and 3) the tendency of density functional methods to overestimate delocalization.[12] Nevertheless, the literature provides some general guidance concerning cyano-substituted radicals. The radical stabilization energy of the cyano group in the 1-cyanovinyl radical is estimated to be around 4 kcal mol^{-1}.[13] The 1-cyanovinyl radical ($H_2C{=}C{-}CN$), which bears the cyano substituent at the radical center, is approximately 7 kcal mol^{-1} lower in energy than the isomeric 2-cyanovinyl radical ($H{-}C{=}C(H)CN$).[14] On the basis of these data alone, one may plausibly infer the relative energy of the diradicals as: **23** < **24** < **25**. Although diradicals of this type have been computed for the parent C_4H_4 series,[15] we encountered considerable difficulty in our efforts to optimize structures for the dicyano series (**23**–**25**) using simple DFT methods. (The s-*cis* isomers cyclized during geometry optimization.) We therefore computed the corresponding monoradicals **26**–**29**, which we consider to be suitable surrogates in revealing the influence of the cyano substituents. The structures and relative energies are depicted in Scheme 4. These results clearly depict an influence of cyano stabilization of a vinyl radical intermediate (an effect



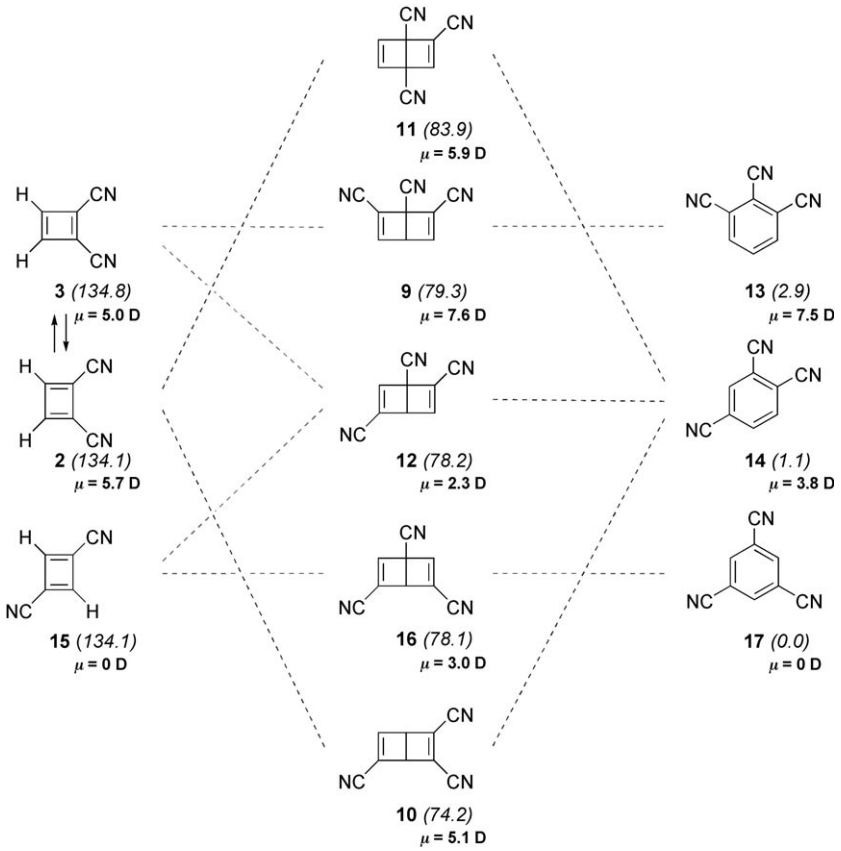
Scheme 4. Diradical intermediates (**23**, **24**, **25**) in the dimerization of cyanoacetylene (**1**), and monoradicals (**26**, **27**, **28**, **29**) that serve as model compounds. Computed relative energies in italics (kcal mol^{-1}; B3LYP/6-31G*, ZPVE included).

that is likely to be overestimated at the B3LYP/6-31G* level).

Closure of the dicyano-1,4-butadienyl diradicals (**23**–**25**) will afford the corresponding dicyanocyclobutadienes. The calculations provide interesting insights concerning the cyclic isomers. Without taking small differences literally, all three isomers are equal in energy (Scheme 5). Thus, the apparent absence of the 1,3-dicyano isomer (**15**) in the trapping experiment cannot be rationalized by an argument that invokes a difference in thermodynamic stability among the dicyanocyclobutadiene isomers. The 1,4- and 1,2-dicyanocyclobutadienes (**2** and **3**), which arise as a consequence of bond-shift isomerism in the rectangular forms of singlet cyclobutadiene, are not equivalent and would not be expected to be equal in energy. The computed energy difference (around 0.7 kcal mol^{-1}) is, however, quite modest (Scheme 5). The 1,2-dicyano isomer, in which both cyano substituents are forced to 'share' the same alkene moiety, is slightly higher in energy than the 1,3- and 1,4-dicyano isomers (and less polar than the 1,4-isomer).

Cycloaddition to produce Dewar benzenes: A common mode of reactivity of cyclobutadienes involves [4+2] cycloaddition.[16] With an alkyne as the dienophile, [4+2] cycloaddition affords a Dewar benzene derivative. In the current investigation, we computed structures for all of the regioisomeric tricyano-Dewar benzene products that may be formed upon [4+2] cycloaddition of 1,2-, 1,3-, and 1,4-dicyanocyclobutadiene with cyanoacetylene (Scheme 5). The computed relative energies of the five Dewar benzenes span a rather wide range, from 74 to 84 kcal mol^{-1}. The tricyano-Dewar benzene derivative that is computed to be the lowest in energy, isomer **10**, has been experimentally isolated as one of the trimerization products of cyanoacetylene.[8e]

Ring opening of Dewar benzenes to tricyanobenzenes: Theoretical analyses[17] and molecular dynamics simulations[17c] reveal that the thermal transformation of Dewar benzene to benzene involves several subtle mechanistic features. Two transition states for ring opening (conrotatory and disrotatory), as well as a *trans*-benzene (Möbius benzene) isomer, lie within 2–4 kcal mol^{-1} of one another at an energy of approx-



Scheme 5. Dimerization and trimerization products of cyanoacetylene (**1**). Computed relative energies in italics (kcal mol^{-1}; B3LYP/6-31G*, ZPVE included). Relative energies reported for dimers are dicyanocyclobutadiene and cyanoacetylene. Computed dipole moments (μ; Debye).

imately 30 kcal mol^{-1} above the Dewar benzene isomer. Although we have not attempted to compute each of these three stationary points for each of the five Dewar benzene isomers shown in Scheme 5, we computed several of the Möbius benzene isomers as surrogates for the lowest energy transition states that connect the Dewar isomers to the ring-opened tricyanobenzene derivatives. As noted recently,[17c] the energies of the Möbius benzene isomers exhibit little dependence on the nature of substituents. We also find this to be the case, as the computed energies for five Möbius tricyanobenzene isomers, relative to 1,3,5-tricyanobenzene (**17**) (Scheme 5), are tightly clustered near (101 ± 1) kcal mol^{-1} (see the Supporting Information).

The tricyanobenzene isomers (**13**, **14**, **17**) lie within 3 kcal mol^{-1} of one another, with the most stable isomer (1,3,5-tricyanobenzene, **17**) being the isomer that is not observed, experimentally, in the trimerization of cyanoacetylene.

Overall mechanism of tricyanobenzene formation: Our computational studies provide no basis to rationalize the observed regioselectivity of cyanoacetylene trimerization in terms of either the formation or destruction of the tricyano-Dewar benzene isomers. If 1,3-dicyano-1,3-cyclobutadiene (**15**) was present as an intermediate, it would reasonably be expected to form a tricyano-Dewar benzene isomer (compound **16**), and this Dewar isomer would reasonably be expected to undergo ring opening to the most stable tricyanobenzene isomer (1,3,5-tricyanobenzene (**17**)). Thus, we are forced to conclude (as we have done previously)[8] that 1,3-dicyano-1,3-cyclobutadiene (**15**) is apparently not formed under the reaction conditions. The basis for this selectivity is not thermodynamic, since the isomeric 1,3- and 1,4-dicyanocyclobutadienes are computed to have the same energy. The rationalization for the experimentally observed regiochemistry rests with the kinetics of cyanoacetylene dimerization. As we described above, the diradical intermediate that leads to 1,4-dicyanocyclobutadiene (diradical **23**) benefits from cyano stabilization of both vinyl radicals, whereas the diradical intermediate that leads to 1,3-dicyanocyclobutadiene (diradical **24**) benefits from cyano stabilization of only one vinyl radical. Estimates for this energy difference range from 7 kcal mol^{-1} (the energy difference between 1-cyanovinyl radical and 2-cyanovinyl radical) to 14 kcal mol^{-1} (the energy difference between model monoradicals **26** and **28**). Even the smaller of these values is sufficient to render the dimerization as virtually regiospecific under the experimental reaction conditions (selectivity >1000 at 160 °C).

Computed spectroscopic data for tricyanobenzenes: The computed molecular structures, rotational constants, and dipole moments for 1,2,3- and 1,2,4-tricyanobenzene (**13** and **14**) helped to guide the initial search for rotational transitions in the FT-microwave experiments (see below). In future experiments, we hope to generate and investigate an equilibrating mixture of 1,2- and 1,4-dicyanocyclobutadienes by rotational spectroscopy. Rotational constants are provided for these isomers. We also note that the polarity and structural rigidity of the tricyano-Dewar benzenes make them intriguing candidates for investigation by rotational spectroscopy. In support of future investigations of this type, computed rotational constants are included as Supporting Information.

Spectroscopy

Microwave rotational spectra: The tricyanobenzenes are rigid asymmetric rotors with a single conformation. For 1,2,3-tricyanobenzene (**13**, C_{2v}), the high symmetry of the molecule reduces the observable transitions to only μ_b selection rules. On the other hand, the spectrum benefits from an expected large dipole moment due to the favorable orientation of the three cyano groups. Accordingly, a set of μ_b transitions could be readily assigned by following the initial DFT models (B3LYP/6-311++G(d,p)) collected in the Supporting Information. As observed in Figure 1, each rotational transition is split into a very complicated hyperfine structure (hfs) pattern that arises from the nuclear quadrupole coupling effects originated by the three ^{14}N nuclei of the molecule (spin $I=1$). In these molecules, the electric interaction between the quadrupolar nuclei and the molecular electric field gradient at the quadrupolar site provides a mechanism to couple the spin and rotational angular momenta,[18] and makes the hyperfine analysis a case of considerable difficulty seldom considered.[19]

The analysis of the spectrum was based on a Watson's semirigid-rotor Hamiltonian[20] (A reduction) with a nuclear quadrupole coupling scheme, $I_2+I_3=I_a$, $I_a+I_1=I_T$, $J+I_1=F_1$, $F_1+I_a=J+I_T=F$, which was then directly diagonalized.[21] The rotational constants and quartic centrifugal distortion parameters of 1,2,3-tricyanobenzene, derived from an extensive experimental data set of 245 ^bR- and ^bQ-branch transitions hfs components ($J<15$), are shown in Table 1. The nuclear quadrupole coupling tensors ($\chi=\chi_{\alpha\beta}$; $\alpha, \beta=$ a, b, c) for the three ^{14}N atoms of the molecule are collected in Table 2. Due to the molecular symmetry, the tensors for N(1) and N(3) are identical, and the only nonzero off-diagonal element is χ_{ab} (the *ab* symmetry plane that contain the quadrupolar nuclei). For N(2), no off-diagonal elements (the *ab* and *bc* symmetry planes contain the quadrupolar nucleus) of the coupling tensor are nonzero.

For 1,2,4-tricyanobenzene (**14**, C_s), both μ_a and μ_b selection rules are allowed by symmetry, so the assignment was simplified by the presence of the characteristic patterns of the ^aR-branch transitions. The analysis of the rotational spectrum and hyperfine effects, exemplified in Figure 2, was similar to the previous molecule. The final fit of the rotational and nuclear quadrupole coupling parameters used a data set of 308 transitions ($J<17$) to yield the values shown in Table 1 and Table 3. All experimental measurements and residuals, together with the DFT predictions, are collected in the Supporting Information.

Molecular structure: The standard approach to derive the molecular structure, based on the rotational spectrum of

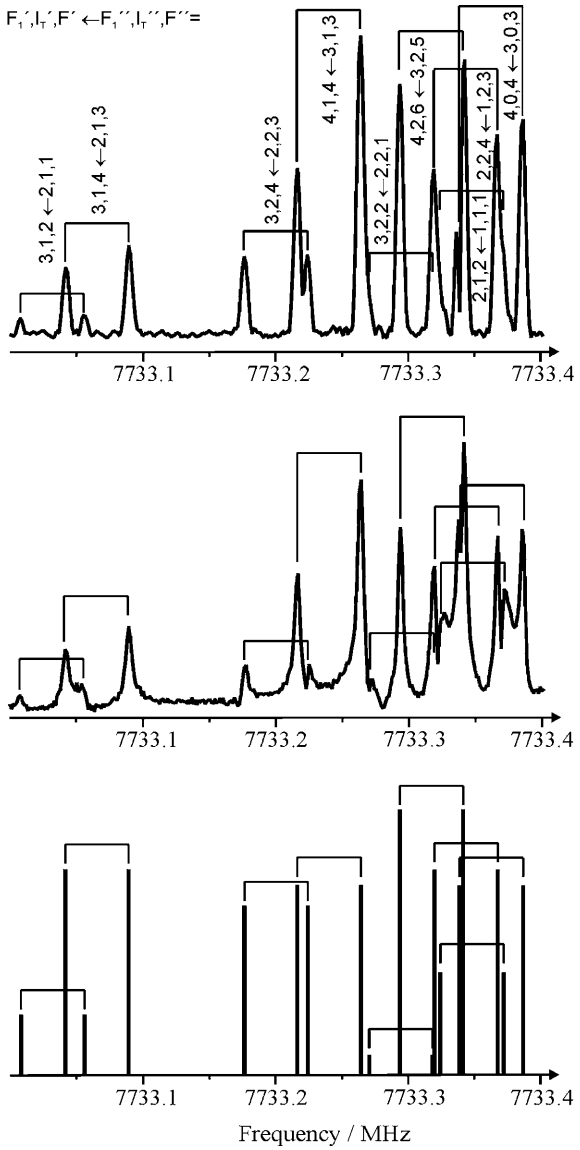


Figure 1. A single rotational transition of 1,2,3-tricyanobenzene (**13**) ($J_{K-1,K1}=3_{3,1}\leftarrow 2_{2,0}$) that illustrates the complex hyperfine pattern due to three-nuclei nuclear quadrupole coupling (each hyperfine component further split into a doublet by the instrumental Doppler effect). The experimental spectrum in the center has been deconvoluted in the upper trace. The hyperfine pattern predicted ab initio is displayed in the lower trace.

multiple isotopic species,[18] is not convenient in this case because of the signal intensity being distributed among the components of the complicated hfs pattern. Nevertheless, the orientation of the three cyano groups can be established by using the nuclear quadrupole coupling tensors. For this calculation, we assume that the principal axis of the coupling tensors, obtained by diagonalization of the inertial axis coupling tensor, is coincident with each of the CN bonds. Thus, the angle α that transforms the inertial axis tensor into its principal axis system, gives the orientation of the CN bond with respect to the inertial axis. The values of the coupling tensors in their principal axis are given in Table 2. Assuming colinearity with the CC bond axes, the orientations

Table 1. Rotational and centrifugal distortion parameters of 1,2,3-tricyanobenzene (**13**) and 1,2,4-tricyanobenzene (**14**).

	1,2,3-Tricyanobenzene (**13**)	
	Experiment	Theory
A [MHz][a]	1413.898772(14)[b]	1421.7[c]
B [MHz]	893.252893(12)	888.0
C [MHz]	547.3164030(58)	546.6
Δ_J [kHz]	0.033883(71)	0.029
Δ_{JK} [kHz]	0.06505(34)	0.061
Δ_K [kHz]	−0.01586(44)	−0.015
δ_J [kHz]	0.014295(39)	0.012
δ_K [kHz]	0.10160(27)	0.089
	1,2,4-Tricyanobenzene (**14**)	
	Experiment	Theory
A [MHz]	1891.26820366(43)	1872.3
B [MHz]	631.74808224(29)	634.1
C [MHz]	473.47493138(11)	473.7
Δ_J [kHz]	0.00904190(34)	0.0084
Δ_{JK} [kHz]	0.0321118(83)	0.033
Δ_K [kHz]	0.856939(16)	0.72
δ_J [kHz]	0.00320496(21)	0.0029
δ_K [kHz]	0.056081(16)	0.055

[a] Rotational constants (A, B, C) and Watson's quartic centrifugal distortion constants (Δ_J, Δ_{JK}, Δ_K, δ_J, δ_K). [b] Standard error in parentheses in units of the last digit. [c] B3LYP/6-311++G(d,p).

Table 2. Nuclear quadrupole coupling parameters for 1,2,3-tricyanobenzene (**13**).

	1,2,3-Tricyanobenzene (**13**)			
	Experiment		Theory	
	N(1), N(3)	N(2)	N(1), N(3)	N(2)
χ_{aa} [MHz][a]	−2.93716(20)[h]	2.28913(31)	−3.25[i]	2.46
χ_{bb} [MHz]	0.80706(57)	−4.47658(90)	0.97	−4.82
χ_{cc} [MHz]	2.13010(37)	2.18745(59)	2.29	2.29
χ_{ab} [MHz]	2.79(12)	0	2.93	0.03
χ_{xx} [MHz][b]	2.29(10)	2.28913(31)		
χ_{yy} [MHz]	2.13010(37)	2.18745(59)		
χ_{zz} [MHz]	−4.42(10)	−4.47658(90)		
$\chi_{xx}-\chi_{yy}$ [MHz]	0.16(10)	0.10168(90)		
η[c]	−0.037(23)	−0.02271(20)		
$\pi_x-\pi_y$[d]	−0.0098(64)	−0.00605(16)		
α [°][e]	28.06(60) 61.94(60)	0		
i_π[f]	0.2279(92)	0.2228(40)		
i_c[g]	0.701(18)	0.691(8)		

[a] Nuclear quadrupole coupling constants $\chi_{\alpha\beta}$ refer to the principal inertial axis system (α, β = a, b, c). [b] Nuclear quadrupole coupling constants in their principal axis system. [c] Asymmetry parameter $(\chi_{xx}-\chi_{yy})/\chi_{zz}$. [d] Double-bond character $2\chi_{zz}\eta/3eQq_{210}$, $eQq_{210}=-11.2(2)$ MHz. [e] Orientation of the principal axis of the nuclear quadrupole coupling tensor with respect to the principal inertial axis. [f] Ionic π character of the CN bond. [g] Total ionic character of the CN bond. [h] Standard error in parentheses in units of the last digit. [i] B3LYP/6-311++G(d,p).

of the CN bonds within the inertia principal axes system are used in Figure 3 to derive bond angles with respect to the coordinates of the aromatic ring C atoms as predicted by the ab initio calculations. For 1,2,3-tricyanobenzene (**13**), we note that the bond angles of the 1,3-cyano groups deviate by about 1.5° from 120°, which can be rationalized by steric or electrostatic repulsion from the neighboring 2-cyano group.

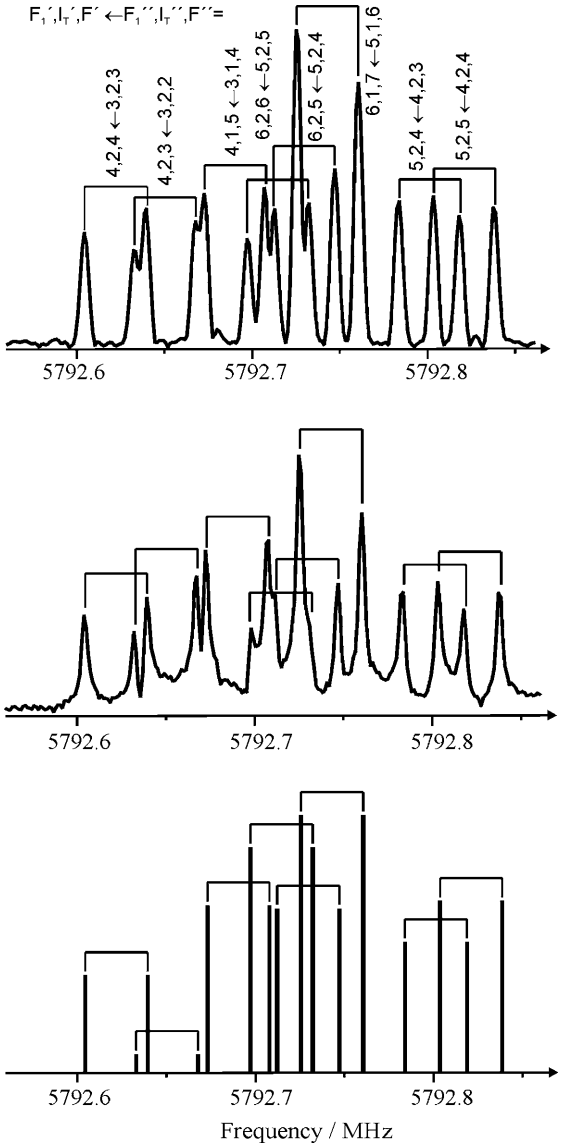


Figure 2. The $J_{K-1,K+1}=5_{1,5}\leftarrow4_{0,4}$ rotational transition of 1,2,4-tricyanobenzene (**14**), with the experimental signal (center), the deconvoluted spectrum (upper trace), and the ab initio (lower trace) hyperfine patterns due to the three-nuclei nuclear quadrupole coupling (additional doubling caused by the instrumental Doppler effect).

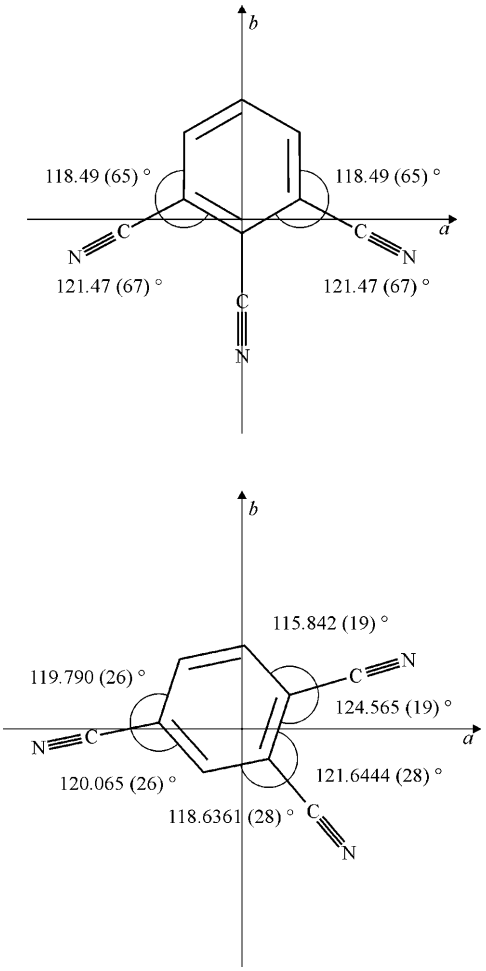


Figure 3. Molecular orientation of the cyano groups in 1,2,3- and 1,2,4-tricyanobenzene. The structural angles reflect the orientation of the CN bond axis derived from the quadrupole coupling tensor with respect to the coordinates of the aromatic ring C atoms from the quantum chemical calculation. See text for details.

A similar situation is found for 1,2,4-tricyanobenzene (**14**). Here the 4-cyano group, which has no immediate neighbors, exhibits deviations of less than 1°.

Electronic structure: The ionic character i_σ of the CN σ bond can be calculated as $i_\sigma=|\Delta EN/2|=0.245$ from the electronegativity difference ΔEN between the carbon (EN(C)=2.52) and nitrogen atom (EN(N)=3.01), with the values of the latter being obtained from the number of valence electrons n and the covalent radius r of the homonuclear single bond as $EN=0.31(n+1)/r+0.50$, which was empirically found to be surprisingly accurate.[22] The total ionic character i_c of the CN bond, formed by one σ and two π orbitals, consists of a σ contribution (i_σ) and a π contribution (i_π and, accordingly, $i_c=i_\sigma+mi_\pi$, $m=2$). The limiting case of a complete ionization leads to a spherical charge distribution at the nuclei, which corresponds to a vanishing electric field gradient that results from all p electrons, at the nuclei's position. Thus, the z component of the field gradient q_z also vanishes, itself being directly proportional to the principal value χ_{zz} of the quadrupole coupling tensor [Eq. (6)]:

$$\chi_{zz}=eQq_z=eQ[-(U_p)_zq_{n10}]=eQ\{-[(n_x+n_y)/2-n_z]q_{n10}\} \quad (6)$$

Therefore, the quadrupole coupling constant eQq_z is a direct probe for properties of the chemical bond. The molecular value χ_{zz}(N) is related to the atomic constant q_{210}(N)=−11.2(2) MHz[23] and denotes the coupling of the N nucleus to the electrons in the p orbitals of all spatial directions in its valence shell $n=2$, weighed by the occupations n_x, n_y, and

Table 3. Nuclear quadrupole coupling parameters for 1,2,4-tricyanobenzene (**14**).

	1,2,4-Tricyanobenzene (**14**)					
	Experiment			Theory		
	N(1)	N(2)	N(3)	N(1)	N(2)	N(3)
χ_{aa} [MHz][a]	−4.048847(40)	−0.566751(20)	−4.093065(37)	−4.33	−0.48	−4.41
χ_{bb} [MHz]	1.891201(80)	−1.565488(45)	1.991751(77)	1.99	−1.80	2.15
χ_{cc} [MHz]	2.157646(40)	2.132239(26)	2.101315(40)	2.34	2.28	2.25
χ_{ab} [MHz]	−1.9283(30)	3.0087 (16)	−1.3114(32)	−1.71	3.56	1.42
χ_{xx} [MHz]	2.4623(16)	1.9837(17)	2.2624(13)			
χ_{yy} [MHz]	2.157646(10)	2.132239(26)	2.101314(39)			
χ_{zz} [MHz]	−4.6199(15)	−4.1160(17)	−4.3637(13)			
$\chi_{xx}-\chi_{yy}$ [MHz]	0.3046(16)	−0.1485(17)	0.1610(14)			
η	−0.06594(32)	0.03608(42)	−0.03690(13)			
$\pi_x-\pi_y$	−0.01813(42)	0.008840(58)	−0.00959(25)			
α [°]	16.497(19) 73.503(19)	40.2881(28) 49.7119(28)	11.659(26) 78.341(26)			
i_π	0.2100(38)	0.2250(47)	0.2329(42)			
i_c	0.665(8)	0.755(10)	0.711(8)			

[a] Parameter definition as in Table 2.

n_z. The latter numbers can be collected to give a measure $(U_p)_z$ for the occupation state of the p orbitals along the bond axis. The occupations n_x and n_y of the respective p orbitals depend on the ionic character i_π. Assuming the same degree of ionization for both π bonds, we have $n_x = n_y = 1 + i_\pi$. The occupation n_z is given by $n_z = (1+i_\sigma)(1-a_s^2) + 2a_s^2$; it depends on the ionic character i_σ of the σ bond that exhibits a p character of $(1-a_s^2)$ and the free s-electron pair that exhibits a p character of a_s^2 due to hybridization. Assuming $a_s^2 = 0.5$, that is, sp hybridization for the CN bond, we can calculate the ionic character i_π of the CN bond [Eq. (7)]:

$$i_\pi(\mathrm{CN}) = (1 + i_\sigma(\mathrm{CN}))/2 - \chi_{zz}(\mathrm{N})/eQq_{210}(\mathrm{N}) \quad (7)$$

Thus, an increase of the ionic character i_π of the π bonds correlates with a decrease of the quadrupole coupling constant χ_{zz}(N). The ionic characters of the CN bonds are compiled in Tables 2 and 3. The total ionic character denotes the partial charge at the nitrogen atom of the cyano group that arises from the polarizations of the participating σ bond and two π bonds. As seen, the three bonds contribute almost equally to the total polarization of the CN group. One should note, however, that due to the assumptions that have been made by such a model, the results should be taken with care. An asymmetry $\eta = (\chi_{xx}-\chi_{yy})/\chi_{zz}$ of the coupling tensor indicates a deviation from the cylindrical charge distribution of a triple bond, that is, a partial double-bond character, which corresponds to an uneven occupation of the p orbitals. Tables 2 and 3 also give the derived values for the double-bond character $\pi_x - \pi_y = n_x - n_y$. We note that the charge distribution is rather symmetric and shows a deviation from a pure triple-bond character on the order of about 1%. This indicates the minor importance of the mesomeric structures to the conjugated π system that exhibit a CN double bond.

Conclusion

As known from earlier studies, cyanoacetylene undergoes dimerization and trimerization in sealed-tube experiments (benzene, 160 °C). Our computational studies rationalize the observed regioselectivity of these processes in terms of selectivity in the initial dimerization event, which likely proceeds through a radical mechanism. Most of the cyanoacetylene dimers and trimers are computed to possess large molecular dipole moments, which will confer strong rotational transitions. Laboratory rotational spectra for two of the trimers, 1,2,3- (**13**) and 1,2,4-tricyanobenzene (**14**), have been acquired using FT-microwave spectroscopy and analyzed to reveal the effects of quadrupolar coupling from three ^{14}N nuclei. The laboratory rotational spectra provide the basis for future searches for these polar aromatic compounds in interstellar space by radio astronomy.

Experimental Section

Preparative methods: The tricyanobenzenes **13** and **14** were prepared by the routes described in reference [11] and characterized by the usual spectroscopic and analytical methods as summarized in reference [8a,b].

Computational methods: Optimized structures, harmonic vibrational frequencies, and infrared intensities were computed using the B3LYP density functional[24] with the 6-31G* or the 6-311++G(d,p) basis sets,[25] as implemented in Gaussian 03.[26] Harmonic vibrational frequencies were computed to verify that all geometries were energy minima (no imaginary frequencies) and to obtain zero-point vibrational energies (ZPVE). Unless otherwise noted, relative energies have been corrected for ZPVE (B3LYP/6-31G* level).

Microwave spectroscopy: The study of the microwave spectrum of the two tricyanobenzenes was conducted in a supersonic jet. The preparation of the sample as a supersonic expansion of a highly diluted gas mixture entrained in a noble carrier gas provides a virtually collision-free environment in which the molecular properties can be determined under conditions of effective isolation.[27] The solid compounds were vaporized in situ by using a heating nozzle (110–120 °C). Neon (1–2 bar) was used as carrier gas. The jet species were probed with the Balle–Flygare-type[28] Fourier transform microwave (FTMW) spectrometer in Hannover, which uses a coaxial arrangement of the supersonic beam and resonator axis (COBRA).[29] The experimental coherence technique is described elsewhere.[30] Briefly, a short (1 μs) MW excitation pulse polarizes the molecular ensemble, and the subsequent free-induction decay (FID) of the polarization is recorded in the time domain. After Fourier transform, the spectrum in the frequency domain is obtained, from which the resonance frequencies of the rotational transitions can be extracted. All transitions appear as doublets by the Doppler effect of the jet transiting though the resonator. The accuracy of the frequency measurements is on the order of 1 kHz. Transitions separated more than 6 kHz are resolvable.

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