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# The Dimer of Cyanodiacetylene: Stacking *vs*. Hydrogen Bonding

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**Summary.** The intermolecular energy surface of the cyanodiacetylene dimer was investigated at the MP2 level applying medium to large basis sets. Extensive 2D scans of selected sections of the energy surface were performed. The most stable structure turns out to be an antiparallel stacked dimer. The fully linear structure with a conventional C–H···N≡C hydrogen bond is less stable than the antiparallel stacked arrangement by at least $8\,kJ \cdot mol^{-1}$. The intramolecular geometry relaxations relative to the monomer and the vibrational frequency shifts induced by intermolecular interaction are reported. Moreover, the structural and energetic trends in the series $(HCN)_2$, $(HC_3N)_2$, and $(HC_5N)_2$ are discussed.

**Keywords.** Hydrogen bonding; Cyanodiacetylene; Stacking; MP2 calculations; Theoretical vibrational spectra.

### Das Cyanodiacetylendimer: Stackinganordnung oder Wasserstoffbrückenbindung?

**Zusammenfassung.** Die zwischenmolekulare Energiefläche des Cyanodiacetylendimeren wurde auf MP2-Niveau unter Verwendung von mittleren bis großen Basissätzen untersucht. Ausführliche zweidimensionale punktweise Berechnungen ausgewählter Ausschnitte der Energiefläche wurden durchgeführt. Als stabilste Struktur stellte sich das Dimer mit antiparallel ausgerichteten Monomeren heraus. Die vollständig lineare Struktur mit einer konventionellen C–H···N≡C-Wasserstoffbrücke ist um zumindest $8\,kJ \cdot mol^{-1}$ weniger stabil als die antiparallele Anordnung. Die intramolekularen Geometrierelaxationen bezogen auf das Monomere und die durch die zwischenmolekulare Wechselwirkung induzierten Schwingungsfrequenzverschiebungen werden berichtet. Darüber hinaus werden die strukturellen und energetischen Trends in der Reihe $(HCN)_2$, $(HC_3N)_2$ und $(HC_5N)_2$ diskutiert.

## Introduction

In the last decade, the gas phase structures and vibrational spectra of hydrogen cyanide and cyanoacetylene clusters have been the subject of intense research, both from the experimental side [1–11] and from theory ([12–15] and references therein). In the case of hydrogen cyanide, the only stable dimer configuration is the fully linear arrangement with a conventional C–H···N≡C hydrogen bond [5]. An antiparallel stacked structure with $C_{2h}$ symmetry has recently been found to be a first order saddle point [15]. Similar to the hydrogen cyanide dimer, the experimentally observed cyanoacetylene dimer is also linear [10, 11]. In recent theoretical studies [12, 13], the linear hydrogen-bonded arrangement has indeed

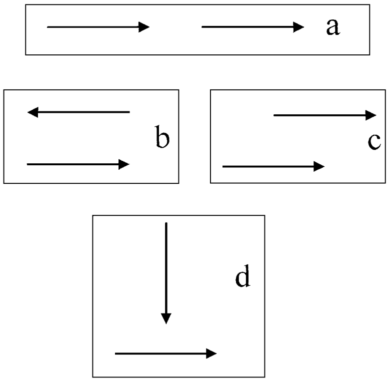

**Fig. 1.** Schematic drawing of conceivable cyanopolyyne homodimer structures: (a) linear hydrogen-bonded (a), antiparallel stacked (b), slipped parallel stacked (c), and $\pi$-type hydrogen-bonded (d)

been found to be the most stable minimum on the cyanoacetylene dimer energy surface. However, in that case an experimentally not yet detected antiparallel stacked structure exhibits also a minimum on the energy surface with a stabilization energy very close to that of the global linear minimum [13].

When comparing the linear and the antiparallel stacked structures sketched in Fig. 1, where the molecules are symbolized simply by arrows, it is immediately evident that the intermolecular interaction energy is dominated mainly by electrostatic contributions in the case of the linear $C–H\cdots N$ hydrogen bond, whereas the dispersion energy plays a much more substantial role in the case of the antiparallel stacked structures. From a purely electrostatic point of view, these two orientations are the most stable ones for two point dipoles, with the linear arrangement twice as stable as the stacked configuration. To argue with point dipoles alone is, however, not valid in this case. With increasing chain length of the cyanopolyyne $H–(C{\equiv}C)_n\text{-}C{\equiv}N$ the stabilization of the stacked structures, which in addition to the electrostatic contribution to the interaction energy are substantially stabilized by dispersion interactions, is expected to grow much faster than the soon converging stabilization energy of the linear hydrogen-bonded arrangement. To date, there are neither gas phase nor matrix investigations available that deal with the structure of the cyanodiacetylene dimer or the dimers of longer cyanopolyynes. Hence, it appeared to be of interest to test from the theoretical side whether the relative stabilities of the linear and the antiparallel stacked structures are already reversed in the dimer of cyanodiacetylene.

To this end, selected sections of the energy surface of the cyanodiacetylene dimer were scanned with the aid of *ab initio* calculations. In analogy to the previously treated case of cyanoacetylene, the 2D energy surfaces for in-plane translational motions of the antiparallel stacked (Fig. 1b), the parallel stacked (Fig. 1c), and the perpendicular (Fig. 1d) dimers were investigated. The structures and the vibrational spectra of the most stable dimer arrangements were then investigated. The structural changes and the shifts of the vibrational frequencies relative to the cyanodiacetylene monomer are discussed. Particular emphasis is laid on a systematic comparison to analogous data as obtained for the hydrogen cyanide dimer and the cyanoacetylene dimer.

## Methods

All quantum chemical calculations were performed with the Gaussian 94 suite of programs [16]. The standard *Møller-Plesset* second order (MP2) [17] method was used in this work since the inclusion of the dispersion interaction at a sufficiently reliable level is vital in this case. While SCF and density functional methods perform quite well for the hydrogen-bonded structures, they are not at all applicable in the case of the stacked structures [13] where an acceptable description of the dispersion interaction is a necessary prerequisite. Guided by the experience gained from previous investigations on hydrogen cyanide [12, 18–21] and cyanoacetylene [12, 13] clusters and to enable a direct comparison, the same basis sets I–IV as used in Ref. [13] were applied also in this work. Basis set I is the 6–31 G(*d*,*p*) basis [22, 23]. Basis set II is the 10*s*6*p*/6*s* basis set of *Huzinaga* [24, 25] contracted to 6*s*4*p*/4*s* and augmented by a set of *d* functions on nitrogen (0.95) and carbon (1.0) and a set of *p* functions on hydrogen (0.75). Basis set III is the 11*s*7*p*/6*s* *Huzinaga* basis set [24, 25] augmented by two sets of *d* functions on nitrogen (0.95, 0.3) and carbon (1.0, 0.3) and a set of *p* functions on hydrogen (0.75). Basis set IV consists of basis set III plus additional flat *s*, *p*, and *d* functions on nitrogen (0.04/0.03/0.1) and carbon (0.03/0.02/0.1) and flat *s* and 2 sets of *p* functions on hydrogen (0.03/0.2, 0.05), thus representing overall a contracted 8*s*6*p*3*d*/7*s*3*p* basis. Basis set IV was used for monomer calculations only.

The 2D scans of the MP2 energy surface of the cyanodiacetylene dimer were performed with basis sets I and II with monomer structures frozen at the respective monomer equilibrium geometries. At the optimized dimer structures, the MP2 interaction energies were corrected for the basis set superposition (BSSE) effect [26] including geometry relaxation. Zero point energy (ZPE) corrections were taken into account at the MP2 level using basis set I only, since the dimer vibrational analysis with the larger basis sets surpassed the available computing resources by far.

## Results and Discussion

### *The monomer*

The total energies, the optimized structures, the calculated rotational constants, the dipole moments, and the parallel and perpendicular polarizabilities of the cyanodiacetylene monomer as obtained at the MP2 level using basis sets I–IV are compiled in Table 1. For the purpose of evaluation, analogous data as obtained previously [12, 13] for hydrogen cyanide and cyanoacetylene and a comparison to the best available theoretical and experimental data are included as well. It is evident that all errors present in the description of the monomers will be carried over to the dimers.

The best structure available in the case of the cyanodiacetylene monomer stems from the work of *Botschwina et al.* [27] who performed large basis set coupled cluster (CCSD and CCSD(T)) geometry optimizations with subsequent empirical refinement to reproduce the experimental rotational constant. Internally, the computed MP2 structures as obtained with basis sets I–IV are quite similar. They show, however, some systematic deviations from the structures recommended by *Botschwina et al.* [27]. The computed C≡C and C≡N triple bond distances for all three molecules are too large by about 0.01–0.02 Å, whereas the C–C single bond distances are consistently too short by about 0.005 Å. As with hydrogen cyanide and cyanoacetylene, the computed dipole moment of cyanodiacetylene does not depend too sensitively on the quality of the basis set applied. An important quantity for a reliable treatment of the intermolecular interaction for the case in hand is the

**Table 1.** MP2 calculated total energies ($E$), equilibrium structures, rotational constants ($B_e$), dipole moments ($\mu$), and parallel ($\alpha_{\|}$) and perpendicular ($\alpha_{\perp}$) polarizabilities of cyanodiacetylene, cyanoacetylene, and hydrogen cyanide

| | Basis set | | | | Previous theoretical |
|---|---|---|---|---|---|
| | I | II | III | IV | and experimental data[a] |
| Cyanodiacetylene | | | | | |
| $E$ (hartree) | −245.01404 | −245.11301 | −245.18362 | −245.18610 | – |
| $r$(H–C$_1$)(Å) | 1.0641 | 1.0629 | 1.0653 | 1.0654 | 1.0626 |
| $r$(C$_1$≡C$_2$) (Å) | 1.2270 | 1.2160 | 1.2205 | 1.2208 | 1.2091 |
| $r$(C$_2$–C$_3$) (Å) | 1.3659 | 1.3588 | 1.3608 | 1.3608 | 1.3661 |
| $r$(C$_3$≡C$_4$) (Å) | 1.2334 | 1.2217 | 1.2266 | 1.2268 | 1.2127 |
| $r$(C$_4$–C$_5$) (Å) | 1.3659 | 1.3626 | 1.3650 | 1.3653 | 1.3710 |
| $r$(C$_5$≡N) (Å) | 1.1901 | 1.1778 | 1.1818 | 1.1818 | 1.1613 |
| $B_e$ (GHz) | 1.3063 | 1.3257 | 1.3184 | 1.3181 | 1.3301 |
| $\mu$ (D) | 4.337 | 4.329 | 4.428 | 4.417 | 4.407 |
| $\alpha_{\|}$ (Å$^3$) | 19.026 | 19.818 | 20.839 | 21.001 | – |
| $\alpha_{\perp}$ (Å$^3$) | 2.776 | 3.508 | 4.664 | 5.473 | – |
| Cyanoacetylene[b] | | | | | |
| $E$ (hartree) | −169.08633 | −169.15923 | −169.20460 | −169.20614 | – |
| $r$(H–C$_1$)(Å) | 1.0640 | 1.0629 | 1.0652 | 1.0652 | 1.0624 |
| $r$(C$_1$≡C$_2$) (Å) | 1.2236 | 1.2116 | 1.2159 | 1.2162 | 1.2058 |
| $r$(C$_2$–C$_3$) (Å) | 1.3770 | 1.3701 | 1.3728 | 1.3729 | 1.3764 |
| $r$(C$_3$≡N) (Å) | 1.1875 | 1.1752 | 1.1789 | 1.1789 | 1.1605 |
| $B_e$ (GHz) | 4.454 | 4.524 | 4.499 | 4.498 | 4.549 |
| $\mu$ (D) | 3.712 | 3.723 | 3.778 | 3.769 | 3.724[c] |
| $\alpha_{\|}$ (Å$^3$) | 8.902 | 9.484 | 9.901 | 9.975 | 9.715[d] |
| $\alpha_{\perp}$ (Å$^3$) | 1.980 | 2.469 | 3.258 | 3.816 | 3.722[d] |
| Hydrogen cyanide[e] | | | | | |
| $E$ (hartree) | −93.16617 | −93.21234 | −93.23288 | −93.23364 | – |
| $r$(H–C)(Å) | 1.0653 | 1.0647 | 1.0666 | 1.0666 | 1.0650 |
| $r$(C≡N) (Å) | 1.1778 | 1.1655 | 1.1686 | 1.1686 | 1.1532 |
| $B_e$ (GHz) | 42.949 | 43.730 | 43.509 | 43.509 | 44.278 |
| $\mu$ (D) | 2.898 | 2.990 | 3.019 | 3.013 | 3.012 |
| $\alpha_{\|}$ (Å$^3$) | 2.869 | 3.174 | 3.262 | 3.308 | 3.283[d] |
| $\alpha_{\perp}$ (Å$^3$) | 1.133 | 1.377 | 1.793 | 2.084 | 2.034[d] |

[a] Theoretical structural data from Refs. [27–29]; [b] data from Refs. [12, 13]; [c] Ref. [30]; [d] MBPT2 data from Ref. [31]; [e] data partially from Ref. [12]

polarizability and in particular, the anisotropy of the polarizability. The variation of the computed parallel component of the polarizability, *i.e.* the polarizability along the long molecular axis, is modest only. For cyanodiacetylene and cyanoacetylene, using the smallest basis set, a value for $\alpha_{\|}$ is obtained which is only about 10 percent lower than the basis set IV result. In case of hydrogen cyanide, the corresponding deviation amounts to about 15 percent. Of decisive importance for a correct description of the energetics of the stacked structures is, however, the

**Table 2.** MP2 calculated harmonic vibrational frequencies ($\mathrm{cm}^{-1}$) and infrared intensities ($\mathrm{km \cdot mol^{-1}}$) of the cyanodiacetylene monomer.

| Basis set | I | III | IV | CCSD (T)[a] | CCSD (T)[a, b] |
|---|---|---|---|---|---|
| Stretching modes | | | | | |
| $\omega_1$ | 3527 (104)[c] | 3456 (106) | 3453 (104) | 3455 (91) | 3349 (49) |
| $\omega_2$ | 2250 (50) | 2209 (49) | 2208 (48) | 2318 (66) | 2319 (39) |
| $\omega_3$ | 2164 (4.1) | 2132 (1.4) | 2130 (1.1) | 2225 (3.9) | 2198 (5.5) |
| $\omega_4$ | 2039 (0.2) | 2013 (0) | 2013 (0.01) | 2090 (0.03) | 2067 (0.08) |
| $\omega_5$ | 1185 (0.02) | 1164 (0.01) | 1159 (0.02) | 1157 (0.13) | 1147 (0.1) |
| $\omega_6$ | 618 (0.6) | 608 (0.5) | 606 (0.5) | 606 (0.34) | 602 (0.34) |
| Bending modes | | | | | |
| $\omega_7$ | 590 (70) | 595 (89) | 566 (77) | – | – |
| $\omega_8$ | 503 (12) | 409 (7.3) | 407 (8.5) | – | – |
| $\omega_9$ | 460 (5.3) | 312 (3.0) | 274 (1.3) | – | – |
| $\omega_{10}$ | 263 (11) | 209 (7.4) | 207 (8.2) | – | – |
| $\omega_{11}$ | 115 (1.4) | 99 (0.6) | 94 (0.7) | – | – |

[a] Ref. [27]; [b] fundamental frequencies; [c] infrared intensities in parentheses

accurate value of the perpendicular component of the polarizability, $\alpha_\perp$. Comparing basis sets I and IV, it is obvious that for all three molecules only about 50 percent of $\alpha_\perp$ are obtained when using basis set I. MP2 structure optimizations of the cyanodiacetylene dimer with basis set IV are unfortunately prohibitively time consuming. However, the trends in the computed polarizability data shown in Table 1 should allow a reasonable estimate of the errors still present when comparing the relative energetics of the different minima.

Computed harmonic vibrational frequencies of the cyanodiacetylene monomer are collected in Table 2 and compared to the CCSD(T) results on the stretching modes reported by *Botschwina et al.* [27]. In line with the already observed too large triple bond distances, the MP2 frequencies for the triple bond stretches ($\omega_2$, $\omega_3$, and $\omega_4$) are all too low.

## *The dimer*

### *1) 2D scans*

For a first exploration of the conceivable non-hydrogen bonded configurations, three different 2D sections of the energy surface of the cyanodiacetylene dimer have been scanned. These correspond to the molecular orientations shown schematically in Figs. 1b–d. Contour plots as computed from the MP2/II energies obtained on a regular mesh with $\Delta z$ increments of 0.5 Å and $\Delta x$ increments of 0.25 Å are shown in Figs. 2–4. Non-planar orientations were not considered and no BSSE corrections were computed.

By analogy to the already known case of cyanoacetylene [13], the most stable non-hydrogen bonded configuration should be the antiparallel stacked arrangement

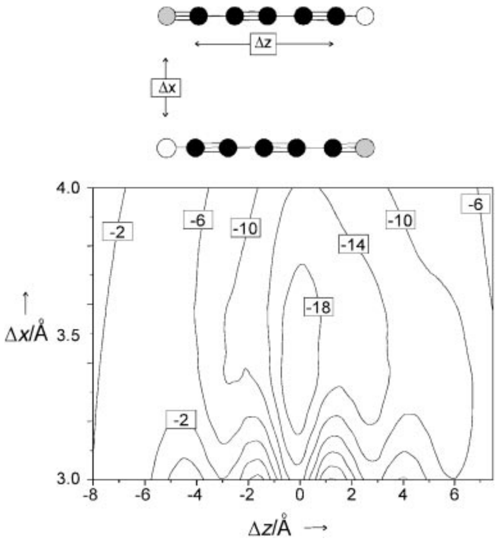

**Fig. 2.** Contour plot for $x,z$ translations of a cyanodiacetylene monomer in antiparallel orientation to a fixed cyanodiacetylene molecule; energy values obtained from MP2 calculations applying basis set II; contour labels in $\mathrm{kJ \cdot mol^{-1}}$ relative to twice the monomer energy; the upper picture indicates $\Delta z = 0$

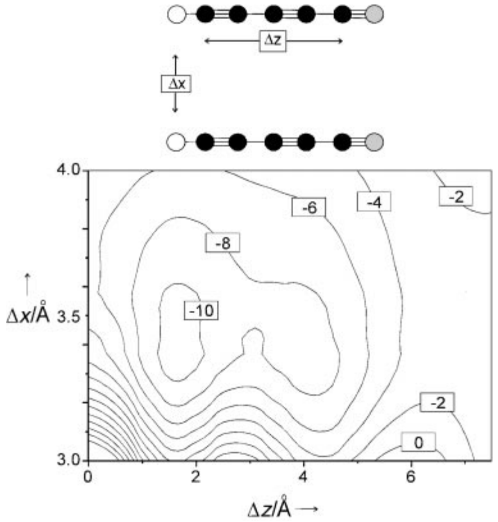

**Fig. 3.** Contour plot for $x,z$ translations of a cyanodiacetylene monomer in parallel orientation to a fixed cyanodiacetylene molecule; energy values obtained from MP2 calculations applying basis set II; contour labels in $\mathrm{kJ \cdot mol^{-1}}$ relative to twice the monomer energy; the upper picture indicates $\Delta z = 0$

in which the two molecular dipoles are oriented such that the hydrogen and nitrogen atoms of different monomers have the closest contact. This results in two strongly distorted, but very weak hydrogen bonds with two nearly 90° bond angles at H and N in the $\mathrm{C{-}H \cdots N{\equiv}C}$ moiety. It is indeed a matter of taste whether this strongly non-linear $\mathrm{C{-}H \cdots N{\equiv}C}$ arrangement is still considered as a hydrogen

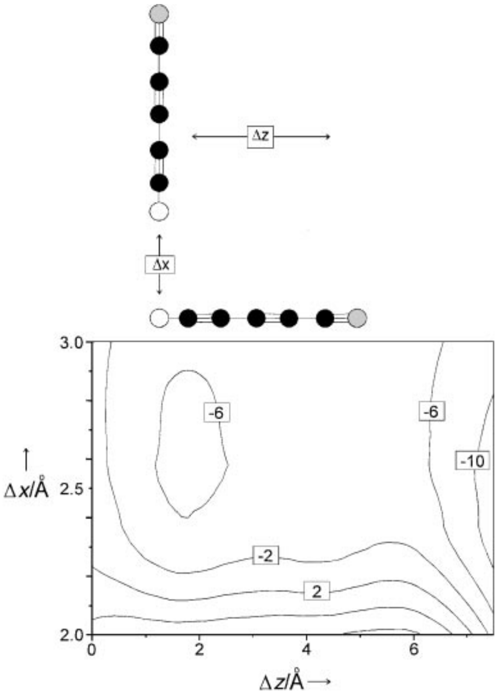

**Fig. 4.** Contour plot for *x*,*z* translations of a cyanodiacetylene monomer in perpendicular orientation to a fixed cyanodiacetylene molecule; energy values obtained from MP2 calculations applying basis set II; contour labels in $\mathrm{kJ \cdot mol^{-1}}$ relative to twice the monomer energy; the upper picture indicates $\Delta z = 0$

bond. Even with frozen monomers the computed contour plot depicted in Fig. 2 shows a deep minimum of about $-20\,\mathrm{kJ \cdot mol^{-1}}$ for a non-slipped antiparallel stacked structure with an intermolecular distance of about 3.4 Å, qualitatively quite similar to the case of cyanoacetylene, but, when viewed quantitatively, distinctly more attractive. This stabilization is already comparable to that of the linear hydrogen-bonded structure for which by analogy to the cyanoacetylene and hydrogen cyanide dimers a stabilization energy close to $-20\,\mathrm{kJ \cdot mol^{-1}}$ could be expected. There are no distinct side minima corresponding to slipped antiparallel stacked conformations.

The contour plot for the parallel stacked case shown in Fig. 3 exhibits two minima, one for a structure in which one monomer is displaced by about 2 Å relative to the other and a second, less stable and shallower minimum for a displacement of about 4 Å. The bare, uncorrected interaction energies for these two structures are in the vicinity of $-10\,\mathrm{kJ \cdot mol^{-1}}$.

The contour plot for the perpendicular configuration shown in Fig. 4 displays an extremely shallow minimum corresponding to a $\pi$-type hydrogen bond to the $C_1{\equiv}C_2$ triple bond with an interaction energy of about $-6\,\mathrm{kJ \cdot mol^{-1}}$. There are no corresponding minima for $\pi$-type hydrogen bonds to the $C_3{\equiv}C_4$ and $C_5{\equiv}N$ triple bonds, since the nitrogen atom creates a too attractive basin. Even the configuration where the hydrogen bond donating monomer is rotated by 90° out of its optimal linear structure is more attractive than any of the $\pi$-type hydrogen-bonded alternatives. Thus, the two latter configurations, slipped parallel stacked and $\pi$-type hydrogen-bonded, cannot compete in stability with the non-slipped antiparallel stacked and the conventional linear hydrogen-bonded structures. This situation is entirely analogous to the cyanoacetylene dimer energy surface [13].

**Table 3.** MP2/I and MP2/III optimized geometrical parameters of the linear hydrogen-bonded $C_{\infty v}$ and the antiparallel $C_{2h}$ stacked structures of the cyanodiacetylene, cyanoacetylene, and hydrogen cyanide homodimers[a]

| | $C_{\infty v}$ | | | $C_{2h}$ | | |
|---|---|---|---|---|---|---|
| | | I | III | | I | III |
| $(HC_5N)_2$ | $H{-}C_1$ | 1.0644 | 1.0656 | $H{-}C_1$ | 1.0650 | 1.0665 |
| | $C_1{\equiv}C_2$ | 1.2271 | 1.2205 | $C_1{\equiv}C_2$ | 1.2283 | 1.2224 |
| | $C_2{-}C_3$ | 1.3648 | 1.3598 | $C_2{-}C_3$ | 1.3638 | 1.3580 |
| | $C_3{\equiv}C_4$ | 1.2337 | 1.2269 | $C_3{\equiv}C_4$ | 1.2348 | 1.2288 |
| | $C_4{-}C_5$ | 1.3674 | 1.3631 | $C_4{-}C_5$ | 1.3675 | 1.3626 |
| | $C_5{\equiv}N$ | 1.1888 | 1.1808 | $C_5{\equiv}N$ | 1.1908 | 1.1831 |
| | $N\cdots H'$ | 2.2478 | 2.2525 | $N\cdots H'$ | 3.1862 | 3.1357 |
| | $H'{-}C_1'$ | 1.0697 | 1.0712 | $C_1\cdots C_5'$ | 3.3289 | 3.2592 |
| | $C_1'{\equiv}C_2'$ | 1.2285 | 1.2222 | $C_2\cdots C_4'$ | 3.4115 | 3.3463 |
| | $C_2'{-}C_3'$ | 1.3645 | 1.3597 | $C_3\cdots C_3'$ | 3.4456 | 3.3747 |
| | $C_3'{\equiv}C_4'$ | 1.2341 | 1.2274 | $\angle HC_1C_2$ | 177.6 | 179.1 |
| | $C_4'{-}C_5'$ | 1.3685 | 1.3643 | $\angle C_1C_2C_3$ | 179.5 | 178.6 |
| | $C_5'{\equiv}N'$ | 1.1905 | 1.1821 | $\angle C_2C_3C_4$ | 178.3 | 178.6 |
| | | | | $\angle C_3C_4C_5$ | 178.8 | 179.1 |
| | | | | $\angle C_4C_5N$ | 177.9 | 178.2 |
| | | | | $\angle C_5NH'$ | 91.9 | 91.5 |
| | | | | $\angle NH'C_1'$ | 95.4 | 94.9 |
| $(HC_3N)_2^b$ | $H{-}C_1$ | 1.0645 | 1.0656 | $H{-}C_1$ | 1.0649 | 1.0661 |
| | $C_1{\equiv}C_2$ | 1.2235 | 1.2159 | $C_1{\equiv}C_2$ | 1.2243 | 1.2170 |
| | $C_2{-}C_3$ | 1.3754 | 1.3712 | $C_2{-}C_3$ | 1.3757 | 1.3712 |
| | $C_3{\equiv}N$ | 1.1869 | 1.1776 | $C_3{\equiv}N$ | 1.1878 | 1.1794 |
| | $N\cdots H'$ | 2.2433 | 2.2532 | $N\cdots H'$ | 3.2800 | 3.2222 |
| | $H'{-}C_1'$ | 1.0694 | 1.0710 | $C_1\cdots C_3'$ | 3.3661 | 3.3161 |
| | $C_1'{\equiv}C_2'$ | 1.2249 | 1.2175 | $C_2\cdots C_2'$ | 3.4041 | 3.3747 |
| | $C_2'{-}C_3'$ | 1.3762 | 1.3720 | $\angle HC_1C_2$ | 178.6 | 179.3 |
| | $C_3'{\equiv}N'$ | 1.1878 | 1.1792 | $\angle C_1C_2C_3$ | 178.7 | 177.7 |
| | | | | $\angle C_2C_3N$ | 177.8 | 177.2 |
| | | | | $\angle C_5NH'$ | 92.0 | 91.8 |
| | | | | $\angle NH'C_1'$ | 92.2 | 93.0 |
| $(HCN)_2^c$ | $H{-}C$ | 1.0655 | 1.0673 | $H{-}C$ | 1.0655 | 1.0674 |
| | $C{\equiv}N$ | 1.1758 | 1.1670 | $C{\equiv}N$ | 1.1776 | 1.1685 |
| | $N\cdots H'$ | 2.2203 | 2.2342 | $N\cdots H'$ | 3.2842 | 3.2711 |
| | $H'{-}C'$ | 1.0706 | 1.0729 | $C\cdots C'$ | 3.3216 | 3.3013 |
| | $C'{\equiv}N'$ | 1.1779 | 1.1692 | $\angle HCN$ | 178.6 | 178.7 |
| | | | | $\angle CNH'$ | 95.1 | 93.8 |
| | | | | $\angle NH'C'$ | 86.3 | 87.6 |

[a] Bond distances in Å, bond angles in degrees; [b] taken from Refs. [12, 13]; [c] data for the linear structure taken from Ref. [12]

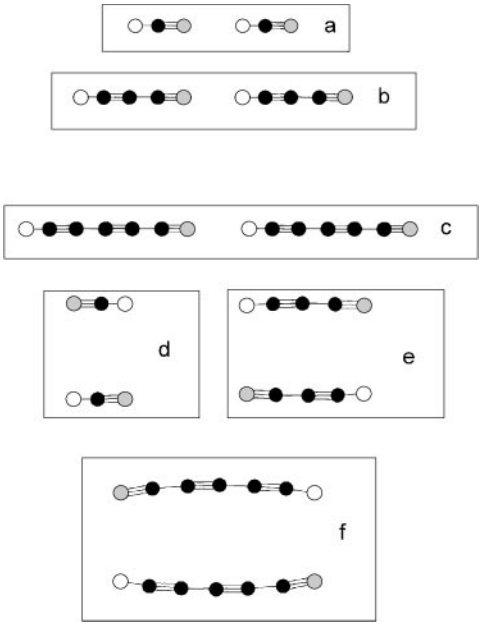

**Fig. 5.** Schematic drawing of linear hydrogen-bonded (a–c) and antiparallel stacked (d–f) structures of hydrogen cyanide, cyanoacetylene, and cyanodiacetylene dimers

### *2) Optimized dimer structures*

As a consequence of the relative stabilities just discussed, only the two most stable configurations are considered for more detailed structural and vibrational analysis. The optimized geometrical parameters of the linear hydrogen-bonded configuration and of the antiparallel stacked structure of the cyanodiacetylene dimer as obtained with basis sets I and III are compiled in Table 3, where a comparison is also made to the corresponding cyanoacetylene dimer and hydrogen cyanide dimer structures. The structures of these dimers are sketched in Fig. 5. With the exception of the antiparallel stacked hydrogen cyanide dimer, which is a first order saddle point, all other structures are true minima. Comparing the linear hydrogen-bonded structures of the three dimers, it can be observed that, with increasing size of the cyanopolyyne, the local hydrogen bond geometry does not change very much and appears to be very soon converged. A slight, almost insignificant widening of the $H\cdots N$ distance by almost 0.02 Å occurs upon going from the hydrogen cyanide dimer to the cyanoacetylene dimer. The $H\cdots N$ distance in the cyanodiacetylene dimer is already practically identical to that in the cyanoacetylene dimer.

In the equilibrium structure of the stacked antiparallel cyanodiacetylene dimer the interacting monomers deviate significantly from linearity. Whereas the MP2/III computed $H\cdots N'$ distance amounts to 3.13 Å, the distance between the two central carbon atoms $C_3\cdots C'_3$ is 3.37 Å, very close to the expected *van der Waals* distance of about 3.4 Å. Again, this structure is very similar to its counterpart in the antiparallel stacked cyanoacetylene dimer and even to the saddle point structure in the stacked hydrogen cyanide dimer.

**Table 4.** Computed MP2 stabilization energies ($\Delta E$), BSSE-corrected stabilization energies ($\Delta E$(BSSE)), and ZPE-corrected stabilization energies ($\Delta E$(ZPE)), for the linear $C_{\infty v}$ and antiparallel stacked $C_{2h}$ structures of the cyanodiacetylene, cyanoacetylene, and hydrogen cyanide dimers; all values in $\mathrm{kJ \cdot mol^{-1}}$

| | | | Basis set | | |
|---|---|---|---|---|---|
| | | | I | II | III |
| $(HC_5N)_2$ | $C_{\infty v}$ | $\Delta E$ | −20.3 | −16.5 | −18.0 |
| | | $\Delta E$(BSSE) | −16.6 | −14.9 | −17.2 |
| | | $\Delta E$(ZPE) | −17.1 | −13.3[a] | −14.8[a] |
| | | $\Delta E$(BSSE+ZPE) | −13.4 | −11.8 | −14.0 |
| | $C_{2h}$ | $\Delta E$ | −21.9 | −23.5 | −25.7 |
| | | $\Delta E$(BSSE) | −11.9 | −12.3 | −22.9 |
| | | $\Delta E$(ZPE) | −21.0 | −22.6[a] | −24.8[a] |
| | | $\Delta E$(BSSE+ZPE) | −11.0 | −11.5 | −22.0 |
| $(HC_3N)_2$[b] | $C_{\infty v}$ | $\Delta E$ | −20.6 | −18.0 | −18.2 |
| | | $\Delta E$(BSSE) | −16.9 | −16.5 | −17.5 |
| | | $\Delta E$(ZPE) | −17.2 | −15.9 | −15.9 |
| | | $\Delta E$(BSSE+ZPE) | −13.6 | −14.4 | −15.2 |
| | $C_{2h}$ | $\Delta E$ | −15.3 | −15.9 | −16.8 |
| | | $\Delta E$(BSSE) | −8.7 | −9.3 | −15.2 |
| | | $\Delta E$(ZPE) | −14.0 | −14.8 | −15.5 |
| | | $\Delta E$(BSSE+ZPE) | −7.4 | −8.2 | −13.9 |
| $(HCN)_2$[c] | $\mathrm{C}_{\infty v}$ | $\Delta E$ | −22.1 | −19.4 | −19.3 |
| | | $\Delta E$(BSSE) | −18.0 | −18.0 | −18.7 |
| | | $\Delta E$(ZPE) | −17.5 | −16.2 | −16.1 |
| | | $\Delta E$(BSSE+ZPE) | −13.4 | −14.8 | −15.5 |
| | $C_{2h}$ | $\Delta E$ | −11.3 | −11.0 | −11.6 |
| | | $\Delta E$(BSSE) | −7.7 | −8.5 | −11.0 |
| | | $\Delta E$(ZPE) | −9.8 | −10.1 | −10.7 |
| | | $\Delta E$(BSSE+ZPE) | −6.3 | −7.6 | −10.1 |

[a] ZPE corrections taken over from MP2/I; [b] data taken from Ref. [13]; [c] data taken from Ref. [12]

### *3) Dimer stabilization energies*

The raw dimer stabilization energies and the corresponding BSSE and ZPE corrected values are collected in Table 4. Turning first to the linear $C_{\infty v}$ structures, we observe a slight increase of the stabilization energy upon increasing the length of the cyanopolyyne. The MP2/III results lead to uncorrected stabilization energies ranging from $-19.3$ to $-18.0\,\mathrm{kJ \cdot mol^{-1}}$ and to BSSE and ZPE corrected values from $-14.0$ to $-15.5\,\mathrm{kJ \cdot mol^{-1}}$. With basis set III the BSSE error amounts only to about $0.6$–$0.8\,\mathrm{kJ \cdot mol^{-1}}$.

As expected, in the case of the antiparallel stacked $C_{2h}$ structures the stabilization energy is substantially lowered upon going from the hydrogen cyanide dimer *via* the cyanoacetylene dimer to the cyanodiacetylene dimer. The BSSE and ZPE corrected stabilization energies as obtained at the MP2/III level are $-10.1$, $-13.9$, and $-22.0\,\mathrm{kJ \cdot mol^{-1}}$, respectively. Because of the still large BSSE error when using basis sets I and II and because of the still significantly underestimated perpendicular component of the monomer polarizability when using these two smaller basis sets, the naive routine application of the BSSE correction is not advisable in this case. The result would be a wrong energetic order of the two alternative structures.

Overall, the BSSE corrections tend to favor the linear structures, a consequence of the smaller molecular overlap in the case of the linear structures. The ZPE corrections, on the other hand, tend to favor the stacked structures, a consequence of the larger intermolecular distance and hence smaller perturbations of the intermolecular structure and vibrational frequencies in the stacked structures. Whereas in case of the cyanoacetylene dimer the linear $C_{\infty v}$ structure is still slightly more stable than the $C_{2h}$ configuration, the relative stabilities are clearly reversed in the case of cyanodiacetylene. With about $-22.0\,\mathrm{kJ \cdot mol^{-1}}$, the antiparallel stacked structure is about $8\,\mathrm{kJ \cdot mol^{-1}}$ lower than the stabilization of the linear cyanodiacetylene dimer. Based on the still sizeable error in the perpendicular monomer polarizability at the MP2/III level, it is to be expected that with still more extended basis sets the antiparallel stacked structure is energetically even more preferred.

### *4) Dimer vibrational frequencies*

The MP2/I computed vibrational frequencies of the linear cyanodiacetylene dimer are compiled in Table 5, that of the antiparallel stacked structure are reported in Table 6. More important than the absolute frequency values are the frequency shifts relative to the monomer vibrations. The latter are expected to be quite reliable within a few wavenumbers.

In the case of the hydrogen cyanide dimer and of larger hydrogen cyanide clusters, mainly the spectral region of the C–H stretching frequencies has been investigated from the experimental side [1–6, 8, 9], with the exception of CARS and PARS studies in the region of the C≡N stretching frequency [1, 2]. For the cyanoacetylene clusters only the C–H stretching region has been scanned so far by infrared spectroscopic experiments [10–11]. However, for both cases the two dimer C–H stretching frequencies, one corresponding to the non-hydrogen-bonded C–H group, the other to its hydrogen-bonded counterpart, have been accurately determined. As already mentioned, to date no experimental data are available for the case of the cyanodiacetylene dimer.

For the C–H stretching frequencies of the linear cyanodiacetylene dimer we compute shifts of $-3\,\mathrm{cm^{-1}}$ for the non-hydrogen-bonded C–H group and $-73\,\mathrm{cm^{-1}}$ for the hydrogen-bonded C–H group. At the same methodical level the corresponding shifts in the linear hydrogen cyanide and cyanoacetylene dimers [12] are $-1$ and $-74\,\mathrm{cm^{-1}}$, and $-4$ and $-72\,\mathrm{cm^{-1}}$, respectively, which may be compared to the corresponding experimental shifts of $-4$ and $-70\,\mathrm{cm^{-1}}$ in the case of the hydrogen cyanide dimer, and $-3$ and $-66\,\mathrm{cm^{-1}}$ for the cyanoacetylene dimer. Thus, the C–H stretching frequency shifts for the linear cyanodiacetylene dimer should be almost identical to that observed in the linear cyanoacetylene dimer, provided that this configuration can be observed experimentally. Compared to the infrared intensity of the monomer C–H stretch, the intensity of the lower-

**Table 5.** Computed MP2/I harmonic vibrational frequencies ($cm^{-1}$) and infrared intensities ($km \cdot mol^{-1}$) of the linear $C_{\infty v}$ cyanodiacetylene dimer

| Frequencies | Infrared intensities | Frequencies | Infrared intensities |
|---|---|---|---|
| Intramolecular stretchings | | Intramolecular bendings | |
| 3524 (−3)[a] | 110 | 757 (167) | 75 |
| 3454 (−73) | 715 | 594 (4) | 77 |
| 2250 (0) | 62 | 523 (20) | 6 |
| 2247 (−3) | 176 | 499 (−4) | 19 |
| 2168 (4) | 3 | 482 (22) | 2 |
| 2160 (−4) | 37 | 444 (−16) | 1 |
| 2041 (2) | 2 | 282 (19) | 7 |
| 2033 (−6) | 19 | 248 (−15) | 10 |
| 1191 (6) | 0.4 | 130 (15) | 1 |
| 1187 (2) | 2 | 115 (0) | 3 |
| 627 (9) | 0.2 | | |
| 619 (1) | 0.3 | | |
| Intermolecular stretching | | Intermolecular bendings | |
| 71 | 2 | 43 | 4 |
| | | 8 | 0.2 |

[a] Frequency shifts relative to the cyanodiacetylene monomer in parentheses

lying dimer C–H stretch is increased by about a factor of 7, an increase typical for medium-strength hydrogen bonds, whereas that of the higher-lying C–H stretch has essentially the same intensity as that of the monomer since it originates from the non-hydrogen-bonded C–H group.

For the nearly degenerate C–H stretching frequencies of the antiparallel stacked cyanodiacetylene dimer we predict shifts of $-9\,cm^{-1}$. For symmetry reasons, only the $b_u$ mode is infrared-active with an intensity of about twice that of the monomer. This shift of $-9\,cm^{-1}$ is comparable and only slightly larger than the corresponding shift of $-7\,cm^{-1}$ for the hitherto unobserved antiparallel stacked cyanoacetylene dimer, if computed at the same level of approximation [13].

Inspecting the remaining dimer frequency shifts, we observe that the H–C≡C bending modes are also interesting candidates to eventually discern between the two alternatives. For the linear cyanodiacetylene dimer shifts of 167 and $4\,cm^{-1}$ are computed. The larger shift originates again from the hydrogen-bonded C≡C–H group. For the antiparallel stacked dimer the computed shifts of $+19$ and $-12\,cm^{-1}$ lead to a quite different pattern. Although there are sizeable shifts in other spectral regions as well, they are probably less suited to allow for a reliable discrimination between the two structural alternatives.

**Table 6.** Computer MP2/I harmonic vibrational frequencies ($\mathrm{cm}^{-1}$) and infrared intensities ($\mathrm{km \cdot mol^{-1}}$) of the antiparallel stacked $C_{2h}$ cyanodiacetylene dimer

| Frequencies | Infrared intensities | Frequencies | Infrared intensities | Frequencies | Infrared intensities |
|---|---|---|---|---|---|
| Intramolecular stretchings | | In-plane intramolecular bendings | | Out-of-plane intramolecular bendings | |
| 3518 (−9)[a] | 0 | 578 (−12) | 106 | 609 (19) | 0 |
| 3518 (−9) | 202 | 578 (−12) | 0 | 609 (19) | 76 |
| 2245 (−5) | 113 | 499 (−4) | 0 | 511 (8) | 0 |
| 2238 (−12) | 0 | 497 (−6) | 24 | 511 (8) | 14 |
| 2160 (−4) | 0 | 428 (−32) | 7 | 477 (17) | 0 |
| 2160 (−4) | 10 | 418 (−42) | 0 | 477 (17) | 0.4 |
| 2033 (−6) | 0 | 244 (−19) | 0 | 268 (5) | 10 |
| 2033 (−6) | 2 | 242 (−21) | 14 | 266 (3) | 0 |
| 1189 (4) | 0.2 | 125 (10) | 1 | 121 (6) | 0 |
| 1188 (3) | 0 | 121 (6) | 0 | 116 (1) | 1 |
| 620 (2) | 0 | | | | |
| 620 (2) | 0.4 | | | | |
| Intermolecular stretching | | In-plane intermolecular bendings | | Out-of-plane intermolecular bendings | |
| 82 | 0 | 69 | 9 | 25 | 4 |
| | | 43 | 0 | | |

[a] Frequency shifts relative to the cyanodiacetylene monomer in parentheses

## *Conclusions*

A large-scale systematic study of the energy surface of the cyanodiacetylene dimer has been performed with a subsequent structural and vibrational spectroscopic characterization of the two energetically most stable minima. Contrary to the cases of hydrogen cyanide and cyanoacetylene dimers, the most stable cyanodiacetylene dimer has an antiparallel stacked structure with an interaction energy of about −20 to $-24\,\mathrm{kJ\ mol^{-1}}$. The linear hydrogen-bonded structure is less stable by at least $8\,\mathrm{kJ \cdot mol^{-1}}$. The attractive contribution of the dispersion energy which increases with increasing length of the cyanopolyyne chain leads to a reversal of the relative stabilities of linear and stacked structures upon going from cyanoacetylene to cyanodiacetylene. From the trends just discussed in the series of short cyanopolyynes it is to be expected that in larger cyanopolyynes the antiparallel stacked structures will always be more stable and that it will be quite difficult if not impossible to observe the conventional linear hydrogen-bonded configurations experimentally. Other alternatives, like $\pi$-type hydrogen-bonded or slipped parallel stacked arrangements, are energetically definitely unfavorable and, hence, very unlikely to occur.

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