Semi-empirical calculation of electronic absorption wavelengths of polyynes, monocyano- and dicyanopolyynes. Predictions for long chain compounds and carbon allotrope carbyne

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Abstract

Absorption wavelengths and oscillator strengths have been calculated using the ZINDO method for the allowed low-energy electronic transition $^1\Sigma^+ \leftarrow {}^1\Sigma^+$ of monocyanopolyynes (HC_yN, $y = 1$–13), $^1\Sigma_u^+ \leftarrow {}^1\Sigma_g^+$ of polyynes and dicyanopolyynes (HC_yH and NC_yN, $y = 1$–40). For $y > 18$, the geometries were extrapolated from DFT optimization of the shortest members. Extrapolation formulas have been drawn up for longer chains, the asymptotic values of those yield an estimation of the absorption wavelength (ca. 400 nm) of the hypothetical carbon allotrope carbyne. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

Except their first members, polyynes $H(C \equiv C)_n H$, monocyanopolyynes $H(C \equiv C)_n CN$ and dicyanopolyynes $NC(C \equiv C)_n CN$ are highly reactive under terrestrial conditions and thus are very difficult to synthesize. Nevertheless, polyynes have been obtained up to $n = 5$ in solution or gas phase [1] and to $n = 12$ in neon matrices [2], and a synthesis with spectroscopic characterization of dicyanopolyynes ($n = 2$–8) has been published [24]. On the other hand, monocyano compounds have been detected since the 1970s [3–6] in interstellar clouds; the other two series should also be present since the derived radicals C_yH and C_yN have been detected [7–10]. The atmosphere of Titan, mainly composed of H, C and N elements contains polyynes already characterized. Photochemically reactive in the UV range, these compounds constitute precursors to the visible absorbing haze materials present in Titan and many of the outer planet atmospheres [11] (and references therein). In addition, as recently recalled by Hirsch and co-workers [12], long polyynes are model units of the hypothetical dico-ordinated carbon allotrope 'carbyne' $(-C \equiv C)_\infty -$.

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Beside IR frequencies, UV data are an alternative way for the detection and determination of the concentration of long polyynes, especially thanks to their low energy allowed transition, $^1\Sigma_u^+ \leftarrow\ ^1\Sigma_g^+$ in $D_{\infty h}$ polyynes and dicyanopolyynes, $^1\Sigma^+ \leftarrow\ ^1\Sigma^+$ in $C_{\infty v}$ monocyanopolyynes. We present here semi-empirical calculations of the energy of this transition up to $C_{40}H_2$, $C_{40}N_2$ and $HC_{13}N$, and an evaluation of its value in infinite chain compounds.

2. Calculation methods

The GAUSSIAN 98 series of programs [13] has been used throughout this work. The energy of electronic transition and the corresponding oscillator strengths have been obtained using the ZINDO method [14]. The geometrical parameters have been obtained by two different ways, as detailed in a previous Letter [15]. For the shortest compounds up to $C_{16}H_2$, $C_{16}N_2$ and $C_{13}HN$, the geometry was optimized at the B3LYP [16,17] level with Dunning's triple zeta basis set (cc-pVTZ) [18]. The accuracy of this method in the calculation of geometries of long chain carbon compounds has been already reported [19,20]. From these data and additional calculation of the geometries of $C_{30}H_2$ and $C_{30}N_2$, extrapolation formulas were stated for both centrosymmetric series. As a final result, in C_yH_2 the length of the xth $C\equiv C$ bond is given by

$$d(x,y) = 1.2289 - 0.06294\,e^{-0.2318y}$$
$$- 0.1041\,e^{-0.3613y}|x - 0.5$$
$$+ 0.25y|^{1.7+0.1y} \qquad (1)$$

and the length of the xth $C-C$ bond is given by

$$d'(x,y) = 1.3290 + 0.1096\,e^{-0.2401y}$$
$$+ 0.2169\,e^{-0.3634y}|x - 0.25y|^{1.6+0.098y}. \quad (2)$$

In the C_yN_2 series the corresponding formulas are, for the xth $C\equiv C$ bond

$$d(x,y) = 1.2281 - 0.1112\,e^{-0.2947y}$$
$$- 0.1159\,e^{-0.3614y}|x - 0.25y|^{1.6+0.1y} \qquad (3)$$

and for the xth $C-C$

$$d'(x,y) = 1.3295 + 0.1442\,e^{-0.3071y}$$
$$+ 0.2685\,e^{-0.4301y}|x - 0.5$$
$$+ 0.25y|^{2.0+0.115y}. \qquad (4)$$

This way, vertical transition energies at ground state equilibrium geometry are obtained. We can assume that the equilibrium geometry of the excited state is close to that of the ground state, especially for longer chains. As a matter of fact, the experimental spectra exhibit a strong $0 \rightarrow 0$ component, and thus the calculated wavelengths can be compared to those experimentally observed for this transition.

3. Results and discussion

3.1. $C_{\infty v}$ series of monocyano polyynes

The calculated and experimental wavelengths, and the calculated oscillator strengths are given in Table 1. Because accurate extrapolation formulas for the geometrical parameters could not be obtained in this series, we report only results from HCN to $HC_{13}N$. Moreover, due to the high toxicity and reactivity of these compounds, very few experimental data are available, nevertheless in good agreement with the calculated ones. An extrapolation formula for λ (nm) can be proposed

$$\lambda(HC_yN) = 95.167 + 320.532(1 - e^{-0.058y}). \qquad (5)$$

Accordingly, the absorption wavelength reaches a limit for y infinite, which can be evaluated to ca.

Table 1
Wavelengths (nm) and oscillator strengths of the first $^1\Sigma^+ \leftarrow\ ^1\Sigma^+$ transitions in the HC_yN series vs experimental values in the gas phase [26,27]

	λ_{calc}	f_{calc}	λ_{exp}
HCN	113.93	0.0334	112
HC_3N	145.27	1.1129	144.9
HC_5N	175.45	2.3144	–
HC_7N	202.61	3.3196	–
HC_9N	226.14	4.3364	–
HC_1N	246.56	5.3908	–
HC_1N	264.37	6.4641	–

416 nm. The oscillator strength varies according to the fitted function

$$f(HC_yN) = 2.26315 + 0.41820y$$
$$- 2.8349\,e^{-0.06064y} \tag{6}$$

the variation of which becomes rapidly linear as y increases.

3.2. $D_{\infty h}$ series of polyynes and dicyano polyynes

In Tables 2 and 3 we report calculated and experimental data for polyynes and dicyanopolyynes, respectively. Two series of calculated values are displayed corresponding to both methods of determination of the geometrical parameters: from C_2 to C_{18} and for C_{30} compounds we used the optimized geometry at the B3LYP/cc-pVTZ basis set level; from C_2 to C_{40} compounds we used the extrapolation formulas given in the preceding section. For seek of clarity, the variation of λ as a function of the number of carbon atoms is shown

Table 2
Wavelengths (nm) and oscillator strengths of the first $^1\Sigma_u^+(z) \leftarrow {}^1\Sigma_g^+$ transitions in the $HC_{2n}H$ series vs experimental values (experimental conditions: $y = 4 \rightarrow 8$: gas phase [1], $y = 10$: solution [1], $y = 12 \rightarrow 24$: neon matrix [2])

	λ_{calc}[a]	f_{calc}[a]	λ_{calc}[b]	f_{calc}[b]	λ_{exp}
C_2H_2	106.11	0.9572	105.63	0.9466	–
C_4H_2	145.86	2.1436	145.00	2.0976	144.6
C_6H_2	175.81	3.4448	174.75	3.3860	183.1
C_8H_2	201.73	4.6417	200.72	4.5897	207.3
$C_{10}H_2$	225.50	5.7458	223.73	5.7125	251.3
$C_{12}H_2$	244.64	6.7776	244.10	6.7575	256.6
$C_{14}H_2$	262.48	7.7546	262.05	7.7384	274.9
$C_{16}H_2$	278.24	8.6878	277.75	8.6680	292.2
$C_{18}H_2$	292.18	9.5909	291.42	9.5604	307.3
$C_{20}H_2$	–	–	303.27	10.4272	321.4
$C_{22}H_2$	–	–	313.55	11.2772	334.2
$C_{24}H_2$	–	–	322.47	12.1169	345.4
$C_{26}H_2$	–	–	330.23	12.9510	–
$C_{28}H_2$	–	–	336.99	13.7817	–
$C_{30}H_2$	347.55	14.7146	342.91	14.6103	–
$C_{32}H_2$	–	–	348.12	15.4386	–
$C_{34}H_2$	–	–	352.71	16.2662	–
$C_{36}H_2$	–	–	356.78	17.0932	–
$C_{38}H_2$	–	–	360.41	17.9200	–
$C_{40}H_2$	–	–	363.64	18.7458	–

[a] Using B3LYP/cc-pVTZ geometries.
[b] Using geometries given by Eqs. (1) and (2).

Table 3
Wavelengths (nm) and oscillator strengths of the first $^1\Sigma_u^+ \leftarrow {}^1\Sigma_g^+$ transitions in the NC_yN series vs experimental values (experimental conditions: $y = 2$: gas phase [26], $y = 8 \rightarrow 18$: solution [24])

	λ_{calc}[a]	f_{calc}[a]	λ_{calc}[b]	f_{calc}[b]	λ_{exp}
C_2N_2	136.99	0.7480	137.22	0.6423	132
C_4N_2	162.66	2.6352	160.75	2.4846	–
C_6N_2	189.68	4.0674	187.68	3.9354	–
C_8N_2	214.35	5.2216	212.85	5.1357	232
$C_{10}N_2$	236.22	6.2624	235.30	6.2180	259
$C_{12}N_2$	255.55	7.2418	254.99	7.2198	282
$C_{14}N_2$	272.54	8.1776	272.08	8.1609	303
$C_{16}N_2$	287.50	9.0854	286.82	9.0595	322
$C_{18}N_2$	–	–	299.49	9.9307	339
$C_{20}N_2$	–	–	310.38	10.7860	–
$C_{22}N_2$	–	–	319.74	11.6322	–
$C_{24}N_2$	–	–	327.83	12.4763	–
$C_{26}N_2$	–	–	334.82	13.3190	–
$C_{28}N_2$	–	–	340.91	14.1626	–
$C_{30}N_2$	352.24	15.1285	346.23	15.0064	–
$C_{32}N_2$	–	–	350.91	15.8524	–
$C_{34}N_2$	–	–	355.03	16.6987	–
$C_{36}N_2$	–	–	358.68	17.5441	–
$C_{38}N_2$	–	–	361.92	18.3902	–
$C_{40}N_2$	–	–	364.83	19.2344	–

[a] Using B3LYP/cc-pVTZ geometries.
[b] Using geometries given by Eqs. (3) and (4).

graphically in Figs. 1 and 2, respectively, for polyynes and dicyanopolyynes.

Regarding the absorption wavelengths, we first note that both calculation methods give results very close one another since they differ by less than
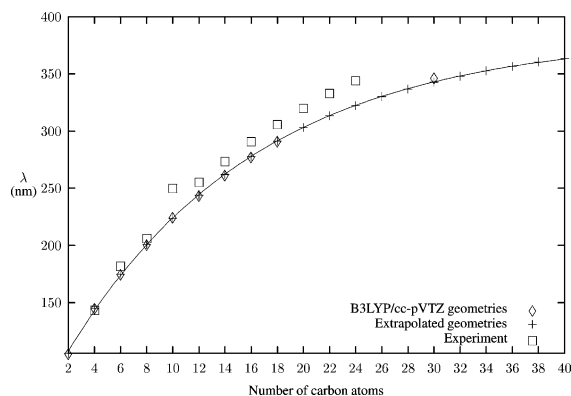

Fig. 1. Wavelength of the first $^1\Sigma_u^+ \leftarrow {}^1\Sigma_g^+$ electronic transition in the HC_yH series as a function of the number of carbons in the chain. For more detail on the experimental conditions, see Table 2 caption.
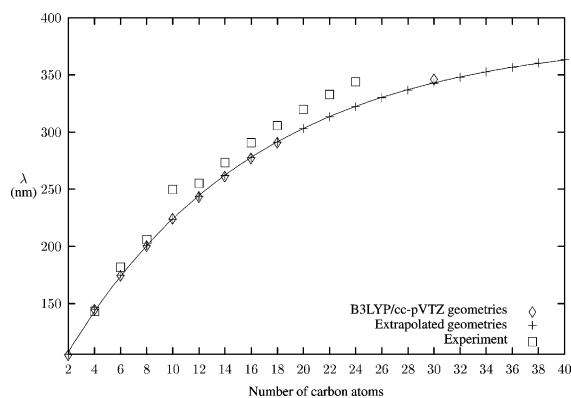
Fig. 2. Wavelength of the first $^1\Sigma_u^+ \leftarrow {}^1\Sigma_g^+$ electronic transition in the NC_yN series as a function of the number of carbons in the chain. For more detail on the experimental conditions, see Table 3 caption.

2 nm in the C_2–C_{18} range and 6 nm for the C_{30} molecules, at any rate less than 1000 cm^{-1} in energy, which indicates the reliability of the extrapolation formulas. As compared to experimental results, we have to take into account the various physical states of the samples. Spectra of polyynes ranging from C_2H_2 to C_8H_2 were obtained in the gas phase whereas in the range $C_{12}H_2$–$C_{24}H_2$, they were obtained in a neon matrix, which is expected to be close to vacuum conditions. For all these compounds, the calculated values appear to be systematically overestimated by ca. 1000–2000 cm^{-1}. This difference is indeed rather small and should be lesser after correction by the difference of ZPEs between the ground state and the excited state of concern. Larger discrepancies between experimental and calculated absorption wavelengths exhibited for other compounds can be partly due to experimental conditions. As a matter of fact, the UV spectrum of $C_{10}H_2$ has been recorded in methanol solution; spectra of the dicyano series were recorded in acetonitrile solution. In the latter series, we note an energy error almost constant ca. 4000 cm^{-1}, which is unfortunately too large to identify a precise molecule in space. The following extrapolation formulas are proposed for wavelengths absorptions as a function of y, the number of carbon atoms:

$$\lambda(HC_yH) = 66.9848 + 316.561(1 - e^{-0.058y}), \quad (7)$$

$$\lambda(HC_yN) = 96.0384 + 290.163(1 - e^{-0.06616y}). \quad (8)$$

Like in the monocyano series the oscillator strengths tend towards a linearly increasing asymptote as the length of the molecule increases according to:

$$f(HC_yH) = 2.20467 + 0.41355y$$
$$- 3.0823\,e^{-0.16048y}, \quad (9)$$

$$f(NC_yN) = 2.32163 + 0.42284y$$
$$- 2.8349\,e^{-0.25667y}. \quad (10)$$

4. Predictions for carbon allotrope carbyne

Long chain polyynes can be regarded as models of infinite linear carbon chains which constitute an hypothetical carbon allotrope. Previous calculations [15,21–25] at various levels indicate that an alternation of shorter 'triple' bond and longer 'single' bonds might persist in an infinite chain, resulting in a HOMO–LUMO gap and insulator properties. As a good index of this gap, the asymptotic absorption wavelength λ_∞ of polyynes was evaluated to 565–570 nm by several experimentalists using various end-cap protected polyynes [12,24,28]. By extrapolation, values of 416 nm, 384 nm and 386 nm are found from Eqs. (5), (7) and (8), respectively. The mean value, ca. 400 nm is rather shorter than those previously published, indicating, if true, that the asymptotic value is reached more rapidly than expected by the preceding authors. Even after correction of 4000 cm^{-1} in energy, which appears as the maximum error of calculated values (in the dicyano series), a value of ca. 480 nm is found, which remains smaller than 565 nm by 3000 cm^{-1}.

Note added in proof

Recent gas phase absorption wavelengths measured by Pino et al. (J. Chem. Phys. 114 (2001) 2208) in the $C_{16}H_2$–$C_{26}H_2$ range differ by less than 10 nm from our calculated values.

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