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Second-Derivative UV Spectra of Polyacetylene Chromophores: Fingerprints of their Geometrical Isomers

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Second-derivative UV spectra of C₁₅-polyacetylenes are useful for the complete structural identification of their chromophores, stereoisomerism of double bonds included. A series of naturally occurring compounds (1–11) is characterized by this new and rapid method.

Zweite-Ableitung-UV-Spektren der Chromophore von Polyacetylenen:

Fingerabdrücke ihrer geometrischen Isomeren

Die Zweite-Ableitung-UV-Spektren von C₁₅-Polyacetylenen werden zur vollständigen Identifizierung ihrer Chromophore sowie der Stereoisomerie ihrer Doppelbindungen genutzt. Es werden entsprechende Spektren der Naturstoffe 1–11 vorgestellt, die einen neuen Weg zur raschen und substanzsparenden Charakterisierung von Polyacetylenen eröffnen.

Since the early forties ultraviolet spectroscopy has been considered one of the most powerful tools in elucidating the structure of the chromophores of naturally occurring polyacetylenes. In fact, this is one of the rare cases in which UV spectra have a decisive diagnostic value, due to a marked vibrational structure in their lower-frequency zone. This sharply characterizes each chromophore with regard to the number and sequence of the triple and double bonds involved^{1,2}. On the other hand little or no attention has been drawn so far to the possibility of identifying polyacetylene chromophores differing only in the geometry of their double bonds by their UV spectra, most likely because of isolation and purification problems of the corresponding authentic samples. When these samples become available, the resulting profiles of the UV spectra show some slight but significant differences in the high-frequency region related to *cis*–*trans* stereoisomerism. These differences, enhanced by the second-derivative technique (D²), are reproducible and can be explained in terms of different electronic transitions which can be assigned on the basis of their vibrational structure. It is interesting to note that each electronic transition mainly involves a specific conjugated olefinic part of the chromophore. In this way the full second-derivative UV spectra account for all the structural characters of a certain sequence of triple and double bonds (stereoisomerism included), providing a complete fingerprint of the polyacetylene chromophores.

A collection of the UV and their D^2 spectra may then represent a new tool for routine structural identification of the chromophores of this class of compounds, eventually bypassing sample-consuming spectroscopies as NMR.

Here we report a series of D^2 UV spectra of C_{15} -hydrocarbonic and oxygenated polyacetylenes, which demonstrate the usefulness of this approach and prove the above considerations. The following naturally occurring compounds have been investigated: (2*E*,8*E*,10*E*)- and (2*E*,8*Z*,10*E*)-2,8,10-pentadecatriene-4,6-diyne (1) and (2), respectively, (2*E*,9*Z*)-2,9-pentadecadiene-4,6-diyne (3), (5*E*,7*E*,13*E*)- and (5*E*,7*Z*,13*E*)-5,7,13-pentadecatriene-9,11-diyne-4-ol (4) and (5), respectively, (7*E*,13*E*)-7,13-pentadecadiene-9,11-diyne-6-ol (6), (5*E*,7*E*,13*E*)- and (5*E*,7*Z*,13*E*)-5,7,13-pentadecatriene-9,11-diyne-4-one (7) and (8), respectively, (7*E*,13*E*)-7,13-pentadecadiene-9,11-diyne-4-one (9), (13*E*)-13-pentadecene-9,11-diyne-6-one (10), and (7*E*,13*E*)-7,13-pentadecadiene-9,11-diyne-6-one (11).

Results and Discussion

Two absorption regions can be recognized in the electronic spectra of simple naturally occurring polyacetylenes with conjugated double bonds. Usually the lower-frequency series bears pronounced vibrational fine structure with a typical band spacing of about 2200 cm^{-1} induced by the stretching frequency of the triple bond. This feature has constantly drawn the attention of spectroscopists involved with polyacetylenes. On the other hand, the higher-frequency absorption region results in a broad band with ill-defined maxima and shoulders. The important information contained in this band has probably been missed because of the less attractive pattern as compared to the low-frequency series. The importance of this band clearly emerges when the spectra of two polyacetylene stereoisomers are compared. In this case the profiles are identical apart from the high-frequency zone, thus leading us to discover that the information relative to the double-bond stereoisomerism is contained there. The D^2 technique in fact enables us to reveal a vibrational fine structure which is responsible for the indistinct shape of the band, where the space of about 1600 cm^{-1} between the peaks is an indubitable evidence that at least two electronic transitions localized in the double bond chromophore region are actually taking place in this zone; the relative intensity of these two transitions changes dramatically on going from the *all-trans* to the *trans-cis-trans* isomers². Consequently, the patterns of the higher-frequency range of D^2 spectra become a fingerprint diagnostic for the stereoisomerism of each double bond involved in each chromophore.

Figures 1 and 2 show the UV and their D^2 spectra of chromophores, ene-diyne-diene and ene-diyne-diene-one, respectively, each of them existing in two different stereoisomers. It can be seen that in all cases there is a very good agreement in the patterns of the chromophores with the same stereoisomerism. In particular the profile in Figure 1 (a) corresponds to compounds 1 and 4 and is thus representative of the ene-diyne-diene chromophore with *trans-trans-trans* isomerism. The profile in Figure 1 (b) matches compounds 2 and 5 and is thus representative of the above-mentioned chromophore but with *trans-cis-trans* isomerism. Profiles of Figures 2 (a) and 2 (b) are representative

of the chromophore with *trans-trans-trans* and *trans-cis-trans* isomerism, respectively, originated from authentic samples 7 and 8. Figure 3 shows the D^2 spectrum of authentic samples of 6 and 9; this pattern is thus representative for the ene-diyne-ene chromophore with *all-trans* configuration. Figure 4 shows the D^2 spectrum of authentic samples 3 and 10, which is representative for the ene-diyne chromophore with *trans* double bond. Finally, the spectrum of the *all-trans* ene-diyne-ene-one chromophore, arising from compound 11 is also reported in Figure 5.

For all these cases it is seen that the higher-frequency absorption band exhibits low intensity for the *all-trans* isomers, while for the *trans-cis-trans* isomers the intensity of this band is comparable with the other ones.

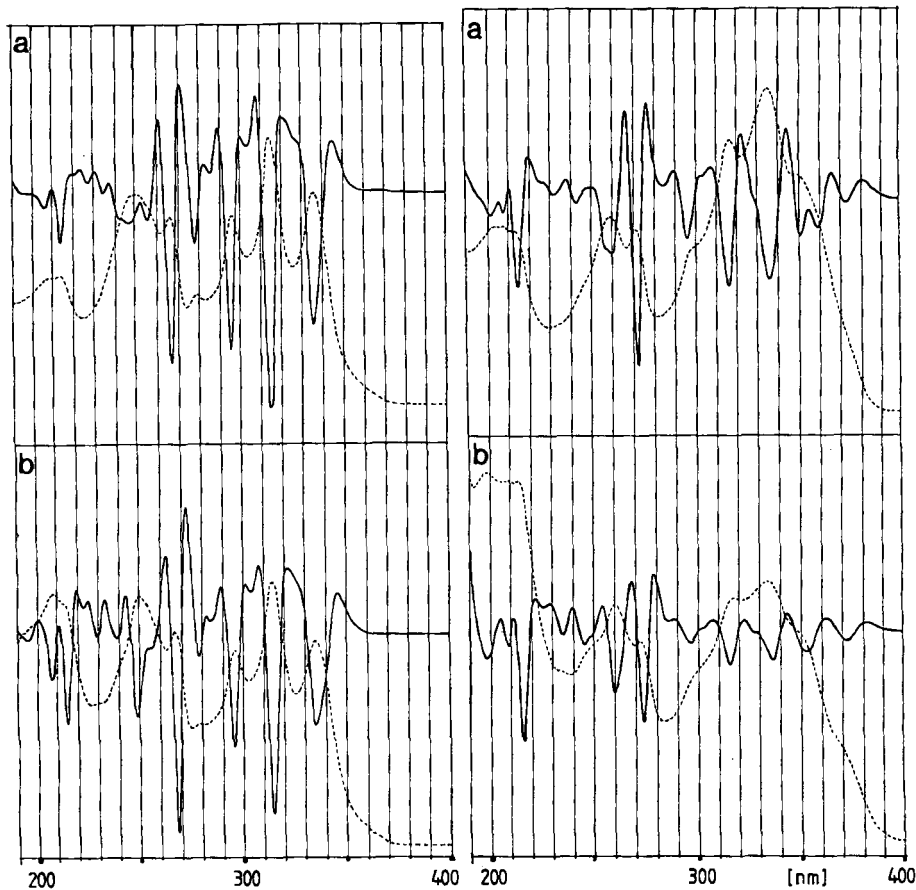


Figure 1. UV (dotted line) and corresponding D^2 (solid line) spectra of the chromophores $-t-t-t-$ (a) from 1 and 4 and

$-t-c-t-$ (b) from 2 and 5

Figure 2. UV (dotted line) and corresponding D^2 (solid line) spectra of the chromophores

$-t-t-CO-$ (a) from 7 and $-t-c-t-CO-$ (b) from 8

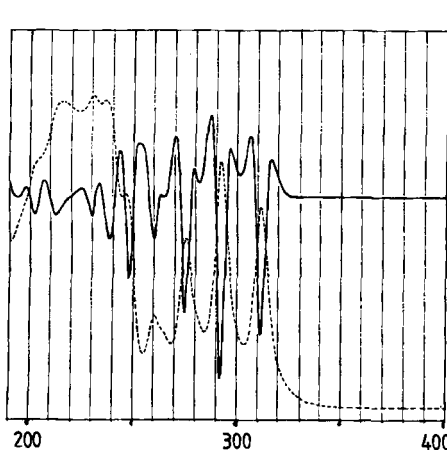


Figure 3. UV (dotted line) and corresponding D^2 (solid line) spectra of the chromophore $-\overset{t}{C}\equiv C-\equiv C-\equiv C-\overset{t}{C}-$ from **6** and **9**

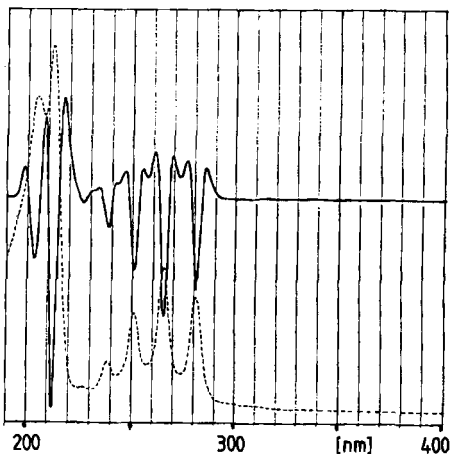


Figure 4. UV (dotted line) and corresponding D^2 (solid line) spectra of the chromophore $-\overset{t}{C}\equiv C-\equiv C-$ from **3** and **10**

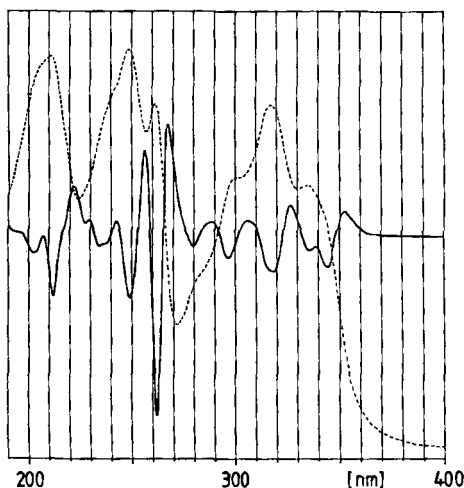


Figure 5. UV (dotted line) and corresponding D^2 (solid line) spectra of the chromophore $-\overset{t}{C}\equiv C-\equiv C-\overset{t}{C}-CO-$ from **11**

Further work is currently in progress on the theoretical aspects of these findings.

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Experimental

Oenanthe aquatica L. fruits were collected in Po valley by A. Minardi & Figli, Ravenna, Italy, in June 1984. A voucher specimen has been preserved at the Dipartimento di Scienze Farmaceutiche, University of Florence, Italy.

Gas chromatographic macropreparative work-up was performed with a Perkin-Elmer (mod. F 21) instrument fitted with glass columns. The operative conditions were described^{3,4}. — GC micropreparative work-up utilized a Perkin-Elmer (mod. F 30) analytical instrument especially modified for the collection of pure samples in small glass capillaries⁴.

Infrared spectra were run on a Perkin-Elmer (mod. 983) spectrophotometer equipped with a microcell-beam condenser arrangement.

Mass spectra were obtained by GC-MS with a Perkin-Elmer (mod. 270/B) instrument at 70 eV and 170 °C source temperature.

Normal and D² UV spectra, in hexane, were recorded with a Perkin-Elmer (mod. 552/S) spectrophotometer in 1-cm-path low-volume cells. D² spectra were run at 120 nm/min scan speed, 2 nm slit and 0.5 s response. Short-path distillations were performed with a Leybold-Heraeus KDL1 glass apparatus.

Extraction and Isolation: Ground *Oenanthe aquatica* fruits (2 kg) were extracted by percolation with light petroleum (40–60 °C) (15 l). The solvent was removed under vacuum (30–35 °C). The residue was submitted to column chromatography on silica gel 60 (Merck, 70–230 mesh) using stepwise light petroleum (40–60 °C)/Et₂O (95:5) to elute hydrocarbons (fraction A) and light petroleum (40–60 °C)/Et₂O (1:1) to elute oxygenated compounds (fraction B).

Fraction A: The solvent was removed under vacuum and the residue submitted to a trap-to-trap distillation at 1.3 Pa (evaporator at room temperature and condenser at –190 °C) to separate the high-boiling from the low-boiling hydrocarbons⁹. The high-boiling fraction contained mainly the polyacetylene hydrocarbons; the combined use of macro- and micro-preparative GC gave pure individual components **1**, **2**, **3** which were immediately submitted to spectroscopic measurements.

Fraction B: The solvent was removed under vacuum and the residue distilled in a short-path still apparatus (5.3 Pa, evaporator 55 °C, condenser –5 °C, rotational speed of wiper 400 r. p. m.). The oxygenated polyacetylenes were contained in the high-boiling fraction. Two-step column chromatography on silica gel 60 (Merck, 70–230 mesh), eluent light petroleum and light petroleum/Et₂O (1:1) afforded two fractions containing carbonyl and alcoholic polyacetylenes, respectively. A further combination of preparative TLC (silica gel 60 F₂₅₄ Merck, eluent CH₂Cl₂) with macro- and micro-preparative GC gave pure individual components **4**–**11** for immediate spectroscopic measurements. The structures of all compounds were unambiguously verified by comparison of their GC and spectroscopic data with those obtained previously by us^{3,4}.

CAS Registry Numbers

1: 19812-23-8 / 2: 77093-85-7 / 3: 19812-24-9 / 4: 20311-66-4 / 5: 97915-40-7 / 6: 20311-64-2 / 7: 20311-67-5 / 8: 97915-37-2 / 9: 32768-92-6 / 10: 97915-38-3 / 11: 102588-17-0

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