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Synthesis, purification and spectral analysis of mononitrocyclopenta[*cd*]pyrenes

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Abstract. The synthesis, purification and characterization of seven isomeric nitrocyclopenta[*cd*]-pyrenes (nitroCPPs) are described. Nitration of partially hydrogenated CPPs affords mixtures of nitro derivatives, which, after separation, are aromatized with DDQ. The resulting nitroCPPs are characterized by their ^{1}H NMR, ^{13}C NMR, UV-vis, IR and mass spectra. The interaction between the nitro group and the aromatic system of CPP is discussed.

Introduction

Nitrated polycyclic aromatic hydrocarbons (nitro-PAH) constitute a class of widely distributed environmental contaminants[1-3]. Nitro-PAH can be formed directly by incomplete combustion processes or indirectly via thermal or photochemical reactions of their parent hydrocarbons[4,5]. Some of the nitro-PAH are potent mutagens and carcinogens[6,7,8]. The position of the nitro group in the PAH is an important factor in determining the biological activity[9,10]. Numerous papers[11,12] have appeared, in which the omnipresence of nitro-PAH is reported. It is clear that these compounds pose a significant hazard to human health. In order to identify the nitro-PAH and to obtain a better understanding of their chemical and biological properties, it is necessary to have pure reference materials available.
Cyclopenta[*cd*]pyrene (CPP), a ubiquitous environmental carcinogen[13-15], has been the subject of our ongoing studies[16,17]. In a preliminary report, we described the preparation of 4-nitroCPP[17] and hitherto none of the other isomers has been described. In order to study the structure-dependent properties of isomeric nitrocyclopenta[*cd*]-pyrenes, new synthetic routes to other isomers are needed. We now wish to report the synthesis, purification and characterization of a series of seven isomeric nitroCPPs. The biological properties of these compounds will be the subject of a subsequent paper.

Synthesis

Synthetic strategy

A common method for the introduction of a nitro group into a PAH is direct nitration of the parent hydrocarbon. Direct nitration of cyclopenta[*cd*]pyrene (CPP) (**1**) affords 4-nitroCPP (**6**)[17]. To functionalize the ring positions, which are not susceptible to direct electrophilic substitution, partially hydrogenated CPP derivatives containing a pyrene, phenanthrene or biphenyl system are required (Fig. 1). The preferred position of substitution in the hydrogenated derivatives can be predicted by comparison of their structure with that of a simple PAH such as pyrene, phenanthrene and biphenyl. Nitration of these CPP derivatives and subsequent aromatization will afford the various isomers of nitroCPP.
3,4-Dihydrocyclopenta[*cd*]pyrene (DHCPP) (**2**) containing a pyrene system is expected to be reactive at positions 1, 6 and 8. 3,4,4a,5-Tetrahydrocyclopenta[*cd*]pyrene [THCPP(I)] (**3**) and 3,4,9,10-tetrahydrocyclopenta[*cd*]-pyrene [THCPP(II)] (**4**) both contain a phenanthrene system. Upon nitration with nitric acid in acetic anhydride, phenanthrene gives a complex mixture of 1-(26%), 2-(7%), 3-(22%), 4-(5%) and 9-(36%)nitrophenanthrene[18]. **3** and **4** can also be considered as derivatives of 4,5-dihydropyrene, which is reactive towards nitration at positions 1 and 9[19]. Considering these results for phenanthrene and 4,5-dihydropyrene, we expect the reactive positions in THCPP(I) to be 1, 8, 9 and 10, while in THCPP(II), the highest reactivity

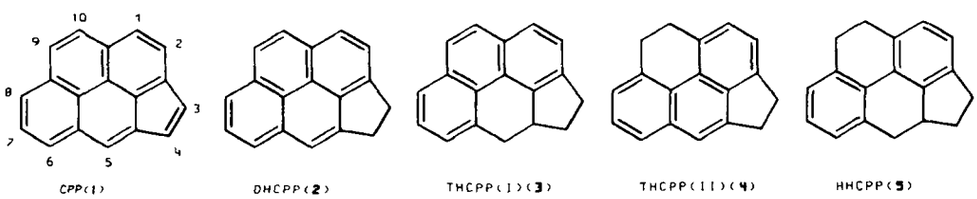
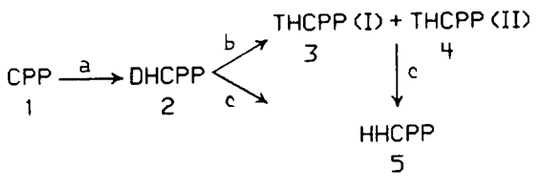


Fig. 1. Cyclopenta[cd]pyrene and four partially hydrogenated CPPs.

will be found at positions 5 and 6. 3,4,4a,5,9,10-Hexahydrocyclopenta[*cd*]pyrene (HHCPP) (**5**) is a biphenyl derivative and is therefore expected to be reactive at positions 2 and 7.

Partial hydrogenation

Cyclopenta[*cd*]pyrene (CPP) (**1**) is converted almost quantitatively (98%) into DHCPP (**2**) by reduction of the 3,4-double bond with hydrazine and Raney nickel as described by *Tintel* et al.[16]. DHCPP is used for the preparation of compounds **3**, **4** and **5**. For this purpose, its pyrene system has to be further hydrogenated. The photochemical reduction as described for pyrene[20] is very suitable for small-scale reduction of alkyl-substituted pyrenes. In this reaction, the aromatic compound is irradiated in acetonitrile with triethylamine as the electron donor and triphenyltin hydride as the hydrogen donor. Alternatively, diethylamine in acetonitrile may serve as electron- and proton-donating reagent. Only the K-region bonds, in which the electrons are more localized than in other aromatic bonds, are hydrogenated. Since the starting material and the product usually have different electronic absorption spectra, a judicious choice of the radiation source and the filter can control the reaction. With a high-pressure mercury arc and a Pyrex filter, only wavelengths above 300 nm are present and the pyrene moiety is hydrogenated to the dihydropyrene system. When no filter (quartz) is used, the reaction will continue to the biphenyl (tetrahydropyrene) system. Upon irradiation through a pyrex filter, **2** was converted into an equimolar mixture of THCPP(I) (**3**) and THCPP(II) (**4**) (Scheme 1). Compounds **3** and **4** were isolated and separated by means of HPLC in an overall yield of 64%. When no filter was used, HHCPP (**5**) was isolated in 42% yield. THCPP(I) was easily identified since it has earlier been described as an intermediate in the synthesis of CPP[16]. THCPP(II) and HHCPP, on the other hand, are novel compounds, which were identified by means of ^{1}H NMR and mass spectrometry.



a) H_2NNH_2, Ra-Ni
b) Et_2NH/CH_3CN; $\lambda > 300$ nm
c) Et_3N, $(C_6H_5)_3SnH/CH_3CN$; $\lambda > 213$ nm

*Scheme 1. Partial hydrogenation of cyclopenta[*cd*]pyrene.*

Nitration

A number of nitrating agents can be used in the preparation of nitro-PAH[12,21]. The reactivity of the PAH, the selectivity of the nitration method, the isomer distribution and the possible side-reactions are important in choosing suitable reaction conditions. Many nitrating agents have oxidative capacities and partial oxidation, followed by nitration, can lead to complex mixtures of undesired oxidation and nitration products. Of the many nitration procedures available, nitration in acetic acid or in acetic anhydride is a mild method often used for reactive PAH.

CPP has been classified as one of the highly reactive PAH[22]. On the basis of its electronic structure, nitration is expected to occur at the electron-rich etheno bridge. Mild nitration under acidic conditions (*viz.* nitric acid in acetic anhydride), however, causes degradation of CPP[19,22]. Nitration under non-acidic conditions, *e.g.* with I_2, $AgNO_3$ and $NaNO_2$ in acetonitrile or with N_2O_4 in dichloromethane, leads to 4-nitroCPP (**6**)[17,23].

Nitration of DHCPP (**2**) with slightly less than one equivalent of fuming nitric acid in acetic anhydride (Scheme 2) afforded a product mixture which was separated by means of HPLC. The two major components, 6-nitroDHCPP (**7**) and 8-nitroDHCPP (**8**), were formed in equimolar quantities. The nitration product with the nitro group at position 1 could not be detected.

Treatment of THCPP(I) (**3**) with nitric acid in acetic anhydride or acetic acid resulted in complicated reaction mixtures, in which no nitrated THCPP(I) could be detected. Apart from unreacted starting material, mono- and di-nitration products of DHCPP, 1-nitropyrene, mononitromethylpyrenes together with other unidentified oxidation products were isolated. Copper(II) nitrate in acetic anhydride proved to be a convenient reagent for nitration of the CPP derivatives with a phenanthrene system. With this reagent, oxidation of the starting material prior to nitration hardly occurred and only nitrated products (including small amounts of 1-nitropyrene), in addition to small amounts (<5%) of ac(etox)ylated compounds, were isolated. Treatment of **3** with copper(II) nitrate in acetic anhydride afforded, in addition to ac(etox)ylated products, three nitroTHCPP(I) isomers: 1-nitroTHCPP(I) (**9**) (33%), 9-nitroTHCPP(I) (**10**) (43%) and a small amount of 8-nitroTHCPP(I) (5%). The isomer distribution was estimated from the ^{1}H NMR spectrum of the crude mixture. The compound having a nitro group at position 10 could not be detected. Nitration of THCPP(II) (**4**) with copper(II) nitrate in acetic anhydride afforded mainly (>90%) 5-nitroTHCPP(II) (**11**) together with one other product, presumably THCPP(II) with the nitro group at position 6. The highly unstable major product was purified by means of HPLC. In a clean reaction with $Cu(NO_3)_2$ in acetic anhydride, compound **5** afforded, in addition to ac(etox)ylated products, 2-nitroHHCPP (**12**) as the major (>95%) nitration product. The only other isomer found appeared to have the nitro group at position 1 and no product with the nitro group at position 7 could be detected.

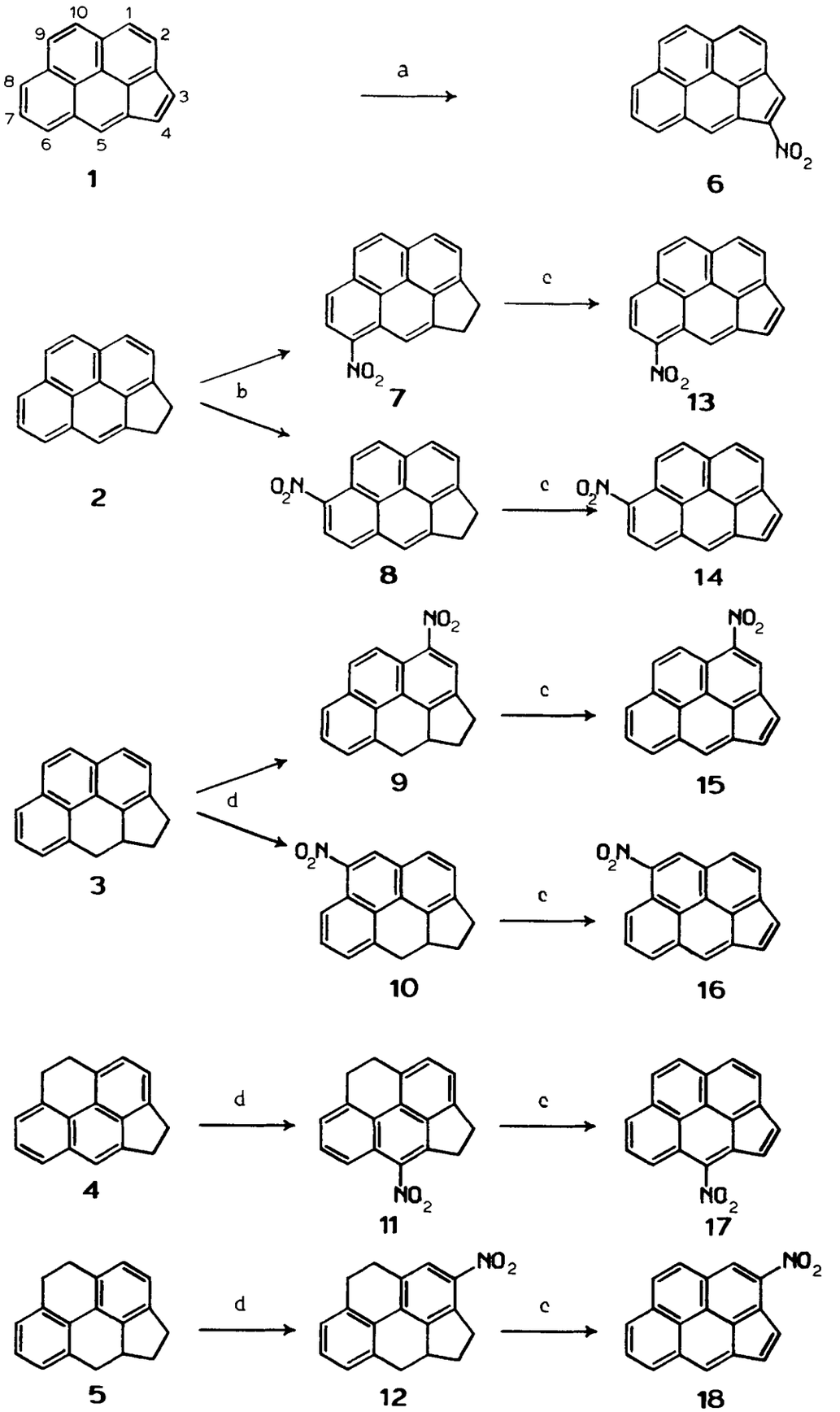
After purification, the nitro compounds were identified by means of mass spectrometry and ^{1}H NMR spectroscopy.

Oxidation

Hydrocarbons such as DHCPP, which contain five-membered rings, are resistant to catalytic dehydrogenation and to oxidation with sulfur[24]. With 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), they are smoothly converted into the corresponding aromatic compounds[24]. Dehydrogenation of nitro-substituted PAH with DDQ turned out to be difficult in some cases[20,25]. Attempts to oxidize the partially hydrogenated nitroCPP derivatives with DDQ in toluene failed. With short reaction times, no aromatization took place and, upon prolonged treatment with DDQ, only decomposition of the starting material was observed. In nitrobenzene, compounds **7** (70%), **8** (49%), **9** (90%), **10** (84%), **11** (56%) and **12** (61%) were aromatized with DDQ by refluxing for half an hour; yields are given in parentheses.

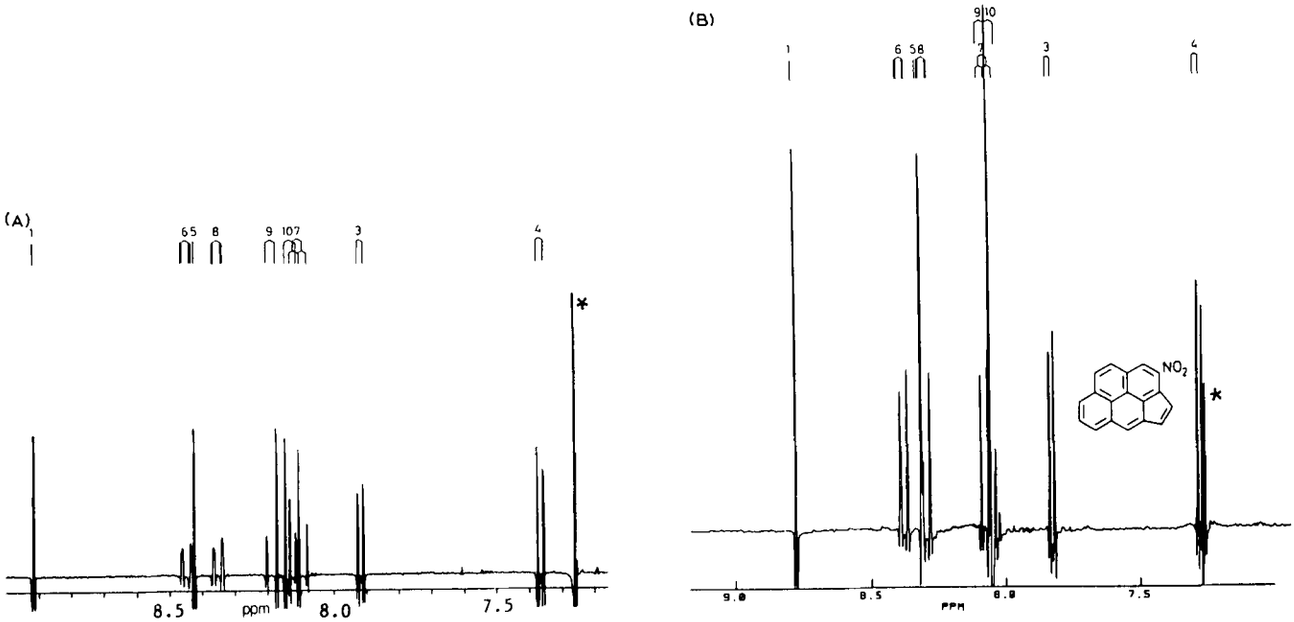
Purification

The nitration products were separated from unreacted starting material and ac(etox)ylated products by chromato-



a) $NaNO_2$, $AgNO_3$, I_2/CH_3CN c) $DDQ/C_6H_5NO_2$
b) $HNO_3/(CH_3CO)_2O$ d) $Cu(NO_3)_2.3H_2O/(CH_3CO)_2O$

Scheme 2. Synthesis of nitrocyclopenta[cd]pyrenes.



(a) 1 mg/ml (b) 5 mg/ml

Fig. 2. ^1H *NMR spectra of 2-nitroCPP;* * $CHCl_3$.

graphy on silica. Since the nitro compounds generally have a low solubility in the eluent, the compounds were adsorbed on silica before being loaded onto the column. The product was dissolved in dichloromethane, a small amount of silica was added to the solution and the mixture was evaporated to dryness. It was then placed on the top of the column and the elution started. Nitro compounds which eluted in the same fraction were separated on a preparative HPLC column. For most compounds, separation on a normal-phase column (10–20% dichloromethane in hexane) proved to be the best method. The best resolutions were obtained with eluents in which the nitro compounds were hardly soluble. When a high flow (30–40 ml/min) was applied, the compounds were separated within 10 min with a loading of about 1 mg per run. Using the same eluent at the more usual flow of 20 ml/min, elution times increased 2–3 fold and the resolution was less satisfactory due to diffusion. Reproducibility on normal-phase (silica) was poor due to the varying quality of dichloromethane, which is stabilized with about 0.1% methanol. Methanol deactivates the silica and, with the varying concentrations of methanol in dichloromethane, the percentage of dichloromethane in hexane necessary to obtain the same resolution can vary considerably. Compounds having the nitro group *ortho* or *peri* to an alkyl side-chain (*e.g.* 2-nitroCPP) were more easily separated on a reversed-phase column using 10% water in acetonitrile as the mobile phase at a normal flow rate.

The separation of the nitro compounds was more successful in the partially hydrogenated state. 6- And 8-nitroDHCPP could be separated on silica, whereas 6- and 8-nitroCPP coeluted under the same conditions. The product mixture of THCPP(I) was also separated at this stage into its main components 1- and 9-nitroTHCPP(I). Separation after aromatization yielded 1-nitroCPP in pure form, although 9-nitroCPP remained contaminated with the by-product 8-nitroCPP. In some of the nitrations of hydrogenated CPP derivatives, small amounts of 1-nitropyrene were formed. On normal-phase HPLC, the removal of this compound is somewhat difficult, whereas on reversed-phase HPLC it is quite simple.

As a consequence of the use of dichloromethane in the preparative HPLC apparatus, considerable amounts of the plasticizer dioctyl phthalate are introduced into the samples. Unfortunately, this compound seems to form a complex with the nitro compounds which does not dissociate in mixtures of hexane and dichloromethane. For the final purification of the nitro compounds, we used hexane containing 0.2% acetonitrile on a short silica column. Despite its low R_f value, the nitro compound eluted before the plasticizer.

Spectroscopy

All nitrocyclopenta[*cd*]pyrenes were characterized by analysis of their NMR, mass, IR and UV-vis-absorption spectra.

^1H *NMR spectra*

The ^1H NMR spectra, recorded at 300 MHz in $CDCl_3$, are sensitive to concentration variations. In order to obtain reliable spectra, we had to use concentrations as low as 1 mg/ml $CDCl_3$. In the spectra of more concentrated solutions, the signals are shifted upfield and they tend to overlap, as is illustrated by the ^1H NMR spectra of 2-nitroCPP shown in Figs. 2a and 2b with concentrations of 1 mg/ml and 5 mg/ml, respectively.

Application of simple NMR techniques (homonuclear decoupling and NOE experiments) and comparison with the nitro-induced chemical shift values of the mononitropyrenes lead to the assignment as presented in Table I. The position of the nitro group in the molecule was unambiguously established. Protons in the vicinity of the nitro group are shifted downfield from those in the parent hydrocarbon due to the strong deshielding effect; *ortho* protons 0.6–1.0 ppm and *peri* protons 0.5–0.8 ppm. In all of the spectra, the 3,4-etheno bridge is marked by the small coupling constant of 5.2 Hz. Unless sited vicinal or *peri* to a nitro group, the protons H-3 and H-4 resonate upfield from the other aromatic protons. In Table II, the coupling con-

Table I ^1H *chemical shifts (300 MHz, $CDCl_3$, 297 K) δ (ppm, relative to TMS) of CPP and mononitroCPPs (conc. 1 mg/ml).*

NitroCPP	H(*n*)									
	1	2	3	4	5	6	7	8	9	10
CPP[26]	8.09	8.06	7.40	7.22	8.33	8.36	7.98	8.24	8.06	7.98
1-nitroCPP	–	8.80	7.35	7.27	8.36	8.44[a]	8.07	8.33[a]	8.19	8.90
2-nitroCPP	8.91	–	7.92	7.36	8.43	8.45	8.10	8.35	8.19[b]	8.13[b]
4-nitroCPP	8.28[c]	8.21[c]	8.39	–	9.12	8.66	8.13	8.46	8.23[d]	8.17[d]
5-nitroCPP	8.11[e]	8.04[e]	7.45	7.27	–	8.79	8.11	8.32	8.02[f]	7.99[f]
6-nitroCPP	8.16[g]	8.06[g]	7.35	7.19	8.99	–	8.63	8.27	7.93[h]	8.13[h]
8-nitroCPP	8.08[i]	8.02[i]	7.32	7.09	8.16	8.31	8.60	–	8.63	8.14
9-nitroCPP	8.31[j]	8.17[j]	7.42	7.32	8.38	8.48	8.14	9.05	–	9.01

[a-j] Resonances indicated with the same character may have to be interchanged.

Table II Coupling constants in Hz of CPP and mononitroCPPs.

NitroCPP	H(*n*)									
	1	2	3	4	5	6	7	8	9	10
CPP[26]	7.8	7.8	5.1	5.1		7.8/1.6	7.8	7.8/1.6	9.0	9.0
1-nitroCPP	–		5.2	5.2		7.7/1.0	7.7	7.7/1.0	9.5	9.5
2-nitroCPP		–	5.2	5.2		7.7/1.0	7.7	7.7/1.0	9.1	9.1
4-nitroCPP	8.0	8.0	5.0	–		7.9/0.8	7.9	7.9/0.8	9.0	9.0
5-nitroCPP	7.6	7.6	5.2	5.2	–	8.0/1.0	8.0	8.0/1.0	9.1	9.1
6-nitroCPP	7.6	7.6	5.2	5.2		–	8.4	8.4	9.0	9.0
8-nitroCPP	7.6	7.6	5.2	5.2		8.4	8.4	–	9.5	9.5
9-nitroCPP	7.7	7.7	5.2	5.2		8.0/0.8	8.0	8.0/0.8	–	

stants of CPP and its mononitro derivatives are given. As a consequence of the greater double-bond character of the C(9)–C(10) bond, H-9 and H-10 have a coupling constant of 9.0–9.5 Hz[20,26]. All other aromatic protons have normal *ortho* couplings of 7.5–8.6 Hz.

The spectrum of 4-nitroCPP (Fig. 3) is characterized by two singlets, one ABX and two AB subspectra. The absence of a doublet with a coupling constant of 5.2 Hz and the downfield-shifted singlet at 9.12 ppm indicate the presence of the nitro group at position 4 of the etheno bridge. The singlet at 9.12 ppm is attributable to the 0.79 ppm downfield-shifted H-5, which means that H-3 must be at 8.39 ppm, 0.99 ppm downfield from H-3 in CPP. Irradiation of the double doublets at 8.66 ppm and 8.46 ppm indicates that both protons are coupled with H-7, a triplet at 8.13 ppm, with coupling constants of 7.9 Hz. To distinguish between the double doublets of H-6 (8.66 ppm) and H-8 (8.46 ppm), the nitro-induced chemical shifts were compared: the nitro group is unlikely to exert a greater influence on H-8 than on H-6. Of the four remaining doublets, those of H-9 and H-10 are characterized by their coupling constant of 9.0 Hz, leaving H-1 and H-2 with a coupling constant of 8.0 Hz. The assignment of H-9 (8.23 ppm) and H-10 (8.17 ppm) is based on the assumption that the effects of the nitro group at C-4 on the chemical shift of H-9 and H-10 are similar. The assignment of H-1 (8.28 ppm) and H-2 (8.21 ppm) is based upon comparison with the chemical shifts in the parent hydrocarbon and the nitro-incuded chemical shifts in the structurally related 1-nitroacenaphthylene[6] (Δδ H-4 0.30 ppm and Δδ H-3 0.03 ppm).

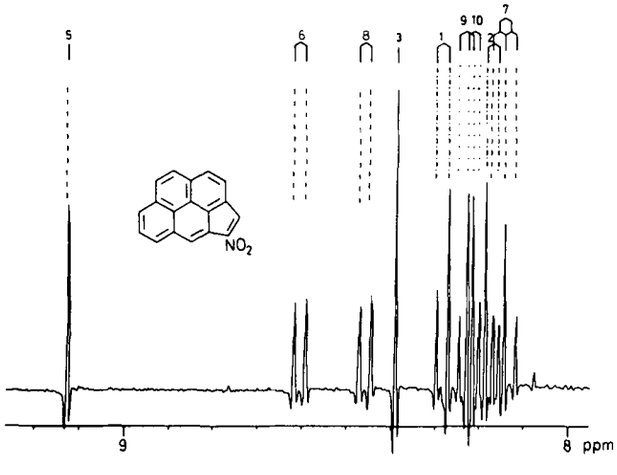


Fig. 3. ^1H *NMR spectrum of 4-nitroCPP.*

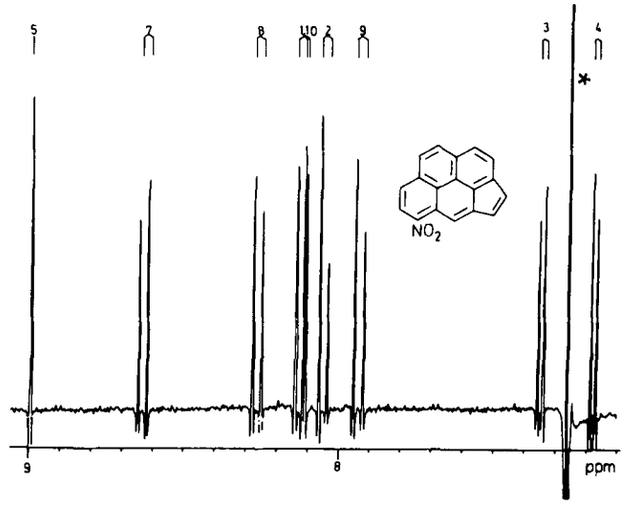


Fig. 4. ^1H *NMR spectrum of 6-nitroCPP; * $CHCl_3$.*

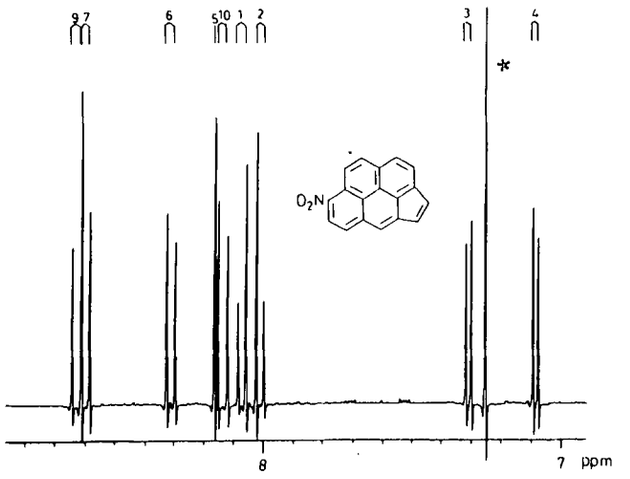


Fig. 5. ^1H *NMR spectrum of 8-nitroCPP; * $CHCl_3$.*

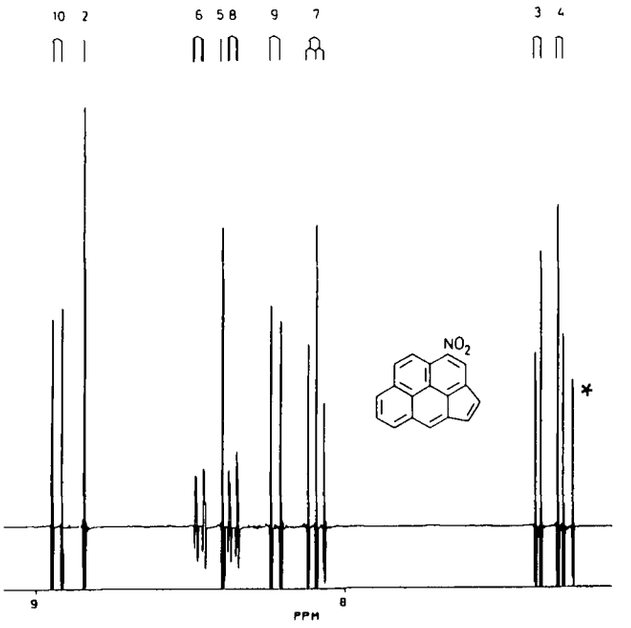


Fig. 6. ^1H *NMR spectrum of 1-nitroCPP; * $CHCl_3$.*

The ^1H NMR spectrum of 6-nitroCPP (Fig. 4) consists of one singlet and four AB subspectra. The singlet must belong to H-5 and the fact that it is shifted 0.66 ppm downfield indicates the presence of the nitro group at position 6. The AB spectrum of the etheno bridge (J 5.2 Hz) was assigned by an NOE experiment on H-5. H-8 was assigned by homonuclear decoupling of the 0.65 ppm downfield-shifted doublet of H-7. The remaining AB spectra were ascribed to H-1/2 and H-9/10, with coupling constants of 7.6 and 9.0 Hz, respectively. H-1 and H-2 were assigned on the basis of the chemical shift changes compared to those of the parent hydrocarbon and they may have to be interchanged. H-9 and H-10 were assigned with the help of the $^{13}C-^1H$-correlated spectrum.

The ^1H NMR spectrum of 8-nitroCPP (Fig. 5) consists of one singlet and four AB subspectra. It is characterized by the partially overlapping downfield-shifted doublets of H-9 (8.63 ppm) and H-7 (8.60 ppm), with coupling constants of 9.5 and 8.4 Hz, respectively. The signals of H-10 and H-6 were found by homonuclear decoupling experiments on H-9 and H-7. Interpretation of the signals of the etheno bridge was accomplished by an NOE experiment: irradiation of H-4 causes enhancement of H-5. The assignment of H-1 and H-2 was based on the same assumptions as stated above and may have to be interchanged.

The ^1H NMR spectrum of 1-nitroCPP (Fig. 6) consists of two singlets, one ABX and two AB subspectra. Downfield from the other aromatic protons are the doublet of H-10 at 8.90 ppm (J 9.5 Hz) and the singlet of H-2 at 8.80 ppm. The protons of the etheno bridge with the small coupling constant of 5.2 Hz at 7.27 and 7.35 ppm are easily recognized and an NOE experiment on H-2 supports the assignment. The singlet at 8.36 ppm must belong to H-5. The remaining ABX subspectrum is assigned on the basis of multiplicities and expected chemical shifts, H-7 giving rise to a triplet at 8.07 ppm, H-6 to a doublet of doublets at 8.44 ppm and H-8 to a doublet of doublets at 8.33 ppm.

The ^1H NMR spectrum of 9-nitroCPP (Fig. 7) is composed

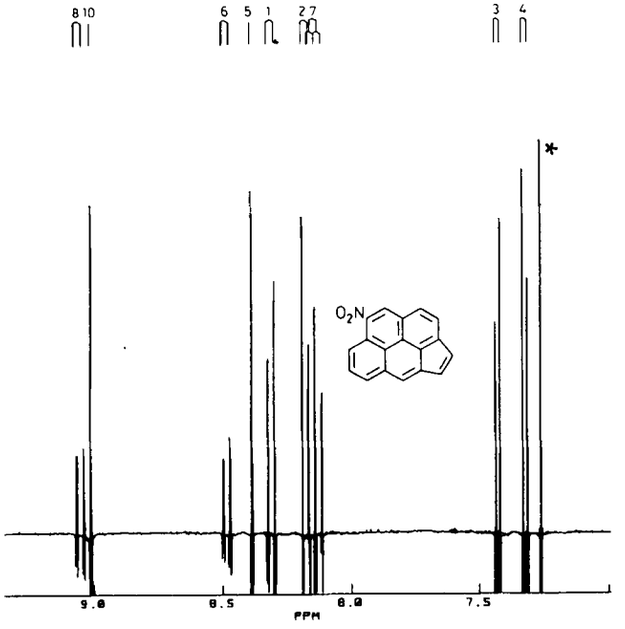


Fig. 7. ^1H *NMR spectrum of 9-nitroCPP; * $CHCl_3$.*

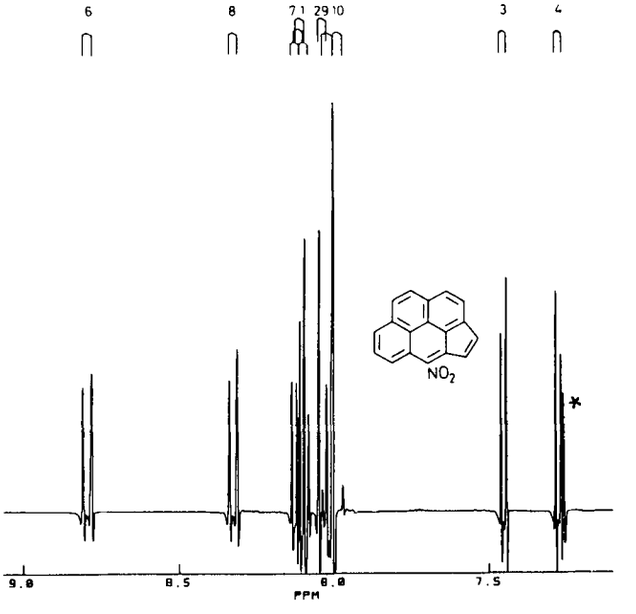


Fig. 8. ^1H *NMR spectrum of 5-nitroCPP; * $CHCl_3$.*

of two singlets, one ABX and two AB subspectra. The signals of protons H-8 and H-10 are found at the lowest field. The doublet of doublets of H-8 at 9.05 ppm has a coupling constant of 8.0 Hz. H-6 and H-7 are found by homonuclear decoupling of H-8. H-1 and H-2 were assigned on the basis of their expected chemical shifts. H-3 and H-4 were assigned after an NOE experiment on the singlet of H-5.

The ^{1}H NMR spectrum of 5-nitroCPP (Fig. 8) is highly characteristic since it lacks the singlet resonance peak of H-5. H-6 and H-8 are easily recognized by the broadening of their peaks due to their *meta* coupling. H-7 is found by means of double resonance experiments. The protons of the etheno bridge are identified after comparison with the ^{13}C–^{1}H correlated experiment. Remarkably, H-4 is found at 7.27 ppm, only 0.05 ppm downfield from H-4 in CPP. This indicates that the nitro group is sterically hindered by the five-membered ring and the *peri* proton H-6, suggesting a rotation of the nitro group out of the aromatic plane[10,27].

The ^{1}H NMR spectrum of 2-nitroCPP (Fig. 2a) consists of two singlets, one ABX and two AB subspectra. At 7.92 ppm, H-3 of the etheno bridge is found, shifted 0.52 ppm downfield from H-3 in CPP. H-3 is coupled to H-4 with J 5.2 Hz. The downfield-shifted singlet at 8.91 ppm must belong to H-1, which means that H-5 resonates at 8.43 ppm. The AB and ABX subspectra were assigned to H-9, H-10, H-6, H-7 and H-8 on the basis of the expected chemical shifts and comparison with the correlated carbon–proton shift experiment.

^{13}C NMR spectra

The ^{13}C NMR spectra were recorded at 75 MHz in $CDCl_3$ at concentrations between 5 and 10 mg/ml. The values of the chemical shifts of the proton-bearing carbon atoms of CPP and seven of its mononitro derivatives are presented in Table III. The assignment was made with the help of broadband homonuclear decoupling ^{13}C–^{1}H shift correlation NMR experiments[28]. Quaternary carbon atoms could not be assigned since the compounds were not available in sufficient quantities. Although all carbon resonances are sufficiently different, the assignment is difficult. In the ^{1}H spectra in the correlated experiments, the resonances are found in a smaller ppm range, due to the higher concentration needed for the ^{13}C measurement. This is especially the case in the spectrum of 4-nitroCPP, where the signals of H-1, H-2, H-7, H-9 and H-10 overlap and interpretation of the carbon spectrum had to be established by comparing the nitro-induced chemical shifts. When the interpretation of the proton spectrum in the correlated experiment was ambiguous, the ^{13}C assignment was based on comparison with shift changes in the mononitropyrenes[20] and consequently some uncertainties still remain. We shall explain this for 1- and 2-nitroCPP. In 1-nitropyrene, the shift changes (relative to pyrene) for C-6 and C-8 are +2.3 and +1.7 ppm, respectively and for 1-nitroCPP we would expect a similar influence of the nitro group on C-6 and C-8; shift changes of +2.7 and +2.3 ppm give a better fit than the alternative +0.3 and +4.7 ppm for C-6 and C-8, respectively. In 2-nitroCPP, H-7, H-9 and H-10 are found at the same frequency (Fig. 2b); the interpretation was therefore based on the most probable shift changes due to the nitro group compared to those reported for 2-nitropyrene[20]. In 2-nitropyrene, $\Delta\delta$ C-6/8: +0.6 ppm; $\Delta\delta$ C-7: +1.5 ppm; $\Delta\delta$ C-9: +1.9 ppm and $\Delta\delta$ C-10: −0.1 ppm. In 2-nitroCPP, the most probable values of $\Delta\delta$ for C-6 and C-8 are +1.5 and +1.8 ppm, respectively, which gives a better fit than the alternative $\Delta\delta$ C-6: −0.2 ppm and $\Delta\delta$ C-8: +3.5 ppm. The assignments of C-7 ($\Delta\delta$ +1.7 ppm), C-9 ($\Delta\delta$ +2.0 ppm) and C-10 ($\Delta\delta$ +0.4 ppm) are in best agreement with the $\Delta\delta$ values in 2-nitropyrene.

UV-vis absorption spectra

The electronic spectra of the nitro derivatives of CPP in methanol are given in Fig. 9. In 2-nitroCPP, the long-wavelength band, characteristic of nitro-aromatic compounds, is very weak. The weak interaction between the nitro group and the aromatic system must be the result of electronic factors, since the nitro-induced chemical shifts in the ^{1}H NMR spectrum do not show an out-of-plane orientation of the nitro group. In 1- and 9-nitroCPP, the interaction is somewhat larger, which is expressed by the value of the extinction coefficient and by the onset of the long-wavelength band. Surprisingly, the absorption spectrum of 5-nitroCPP shows approximately the same normal nitro-aromatic interaction as is observed in the spectra of 6- and 8-nitroCPP. This was not expected since, from the ^{1}H NMR results, it was assumed that the nitro group is rotated out of the aromatic plane of the molecule. In 4-nitroCPP, the intense long-wavelength absorption maximum is found at the high value of 500 nm, resulting in a crimson solution in methanol. In this compound, the nitro group apparently has a very strong interaction with the aromatic system.

IR spectra

In Table IV, the frequencies of the stretching vibrations of the nitro groups in the mononitrocyclopenta[*cd*]pyrenes are presented. For the sake of comparison, the values of the mononitropyrenes[20] are also included. The values of

Table III ^{13}C chemical shifts (75 MHz, $CDCl_3$, 297 K) δ (ppm relative to TMS) of CPP and mononitroCPPs.

NitroCPP	C(n)									
	1	2	3	4	5	6	7	8	9	10
CPP[26]	122.3	124.0	133.1	127.4	126.1	130.1	126.5	128.1	126.5	126.2
1-nitroCPP	–	119.8	132.0	129.6	129.2	132.8[a]	127.5	130.4[a]	131.1	122.9
2-nitroCPP	118.8	–	132.5	130.9	129.1	131.6	128.2[b]	129.9	128.5[b]	126.6[b]
4-nitroCPP	126.2[c]	125.2[c]	135.5	–	131.1	133.1	127.3[c]	131.0	129.4[c]	126.7[c]
5-nitroCPP	124.1[d]	126.7[d]	137.7	125.8	–	126.3	127.6	129.6	126.6[e]	127.7[e]
6-nitroCPP	126.6[f]	123.5[f]	135.0	129.2	120.6	–	122.9	127.2	126.1[g]	130.0[g]
8-nitroCPP	126.1[h]	123.5[h]	135.1	128.3	125.1	129.0	122.5	–	121.5	130.7
9-nitroCPP	127.3[i]	123.2[i]	133.3	129.5	127.5	131.9	127.6[i]	126.0	–	126.9

[a-i] Resonances indicated with the same character may have to be interchanged.

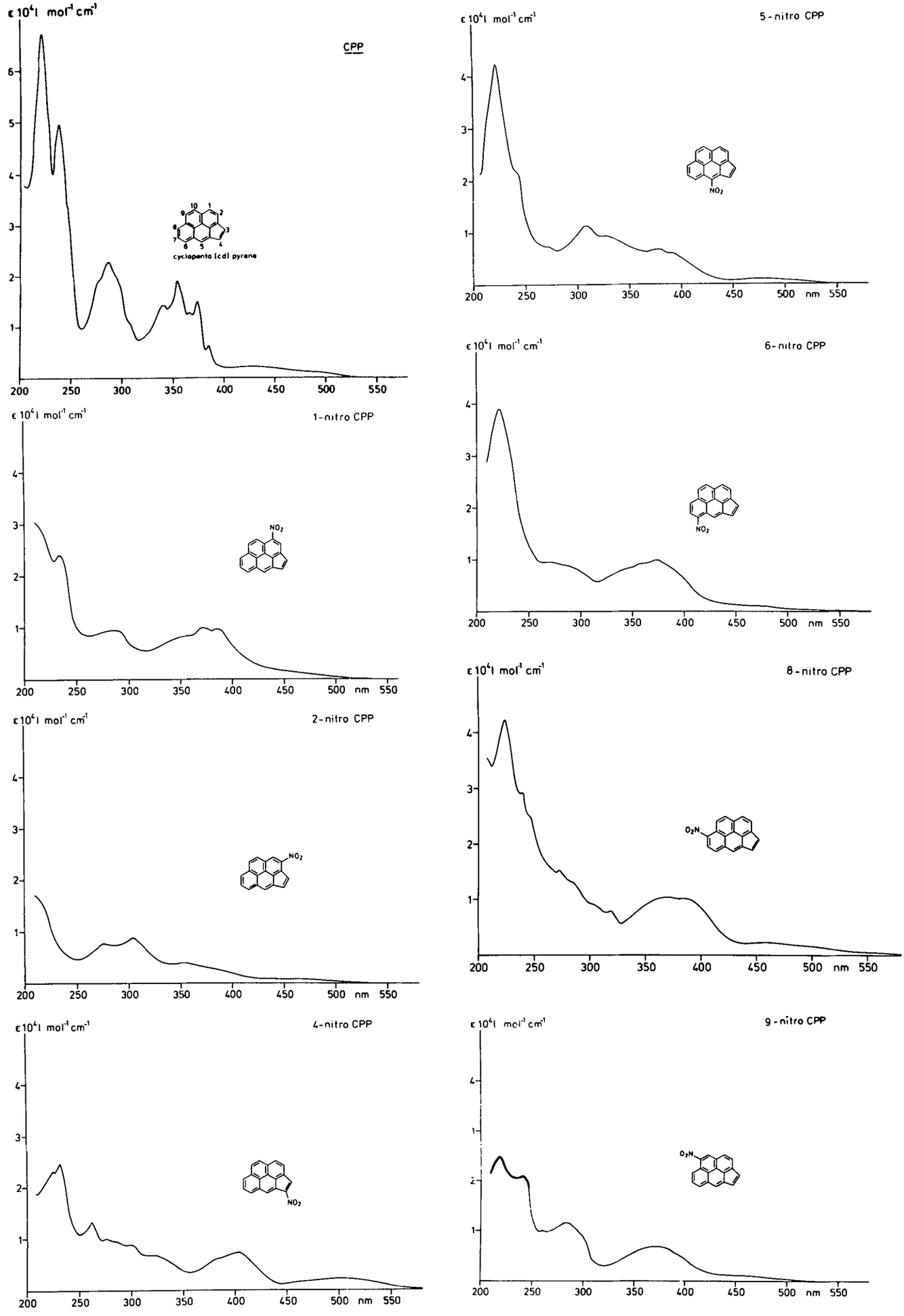


Fig. 9. UV-vis absorption spectra of CPP and seven nitro derivatives.

$\nu_{as}(N-O)$ and $\nu(C-N)$ reflect the degree of conjugation of the nitro group with the aromatic system, while $\nu_s(N-O)$ provides information about the coplanarity of the nitro group with the π-system: the more twisted out of the aromatic plane, the longer the wavenumber $\nu(C-N)$[27]. The measured values are in agreement with the UV and NMR spectra.

Table IV Infrared frequencies of the nitro group in mononitrocyclopenta[cd]pyrenes (in cm^{-1}).

NitroCPP	$\nu(C-N)$	$\nu_s(N-O)$	$\nu_{as}(N-O)$
1-nitroCPP	822	1330	1524
2-nitroCPP	790	1335	1532
4-nitroCPP	831	1341	1500
5-nitroCPP	840	1339	1510
6-nitroCPP	849	1325	1502
8-nitroCPP	844	1325	1510
9-nitroCPP	829	1327	1520
1-nitropyrene	841	1330	1510
2-nitropyrene	795	1340	1535
4-nitropyrene	827	1348	1510

In 5-, 6- and 8-nitroCPP, the values of the frequencies are very close to those found in 1-nitropyrene, with a strong interaction between the nitro group and the π-system[20]. In 5-nitroCPP, $\nu_s(N-O)$ is relatively large, which is in agreement with a deviation from coplanarity. In 1- and 9-nitroCPP, the frequencies of the nitro group are approximately equal, which points to a similar interaction. This interaction is not very strong as can be seen from the relatively low value of $\nu(C-N)$ and the relatively high value of $\nu_{as}(N-O)$, compared to the compounds with a normal interaction. The frequencies of the nitro group as found in 2-nitroCPP are very similar to those found in 2-nitropyrene[20], in which we established the mesomeric interaction between the nitro group and the pyrene system to be only small. The frequencies of the nitro group in 2-nitroCPP suggest a similar small interaction; this is also in agreement with the mass and UV-vis spectra. In 4-nitroCPP, the nitro group is attached to a bond having significant olefinic character[16] and the conjugation is considerable, as can be seen from the UV-vis absorption spectrum. The values of $\nu_{as}(N-O)$ and $\nu(C-N)$ are in agreement with this observation.

Mass spectra

The electron-impact mass spectra of nitro-aromatic compounds show very characteristic fragmentations[29]. The fragmentation process not only gives information about the structure of the compound, but also about the electronic interaction between the nitro group and the aromatic moiety[20,30]. In the case of large interaction, nitro–nitrite isomerisation, followed by loss of NO, is observed $(M-30)^+$. Other fragmentations involve complete loss of the nitro group $(M-46)^+$, loss of HNO_2 $(M-47)^+$ and loss of CO after NO loss $(M-58)^+$.

In all recorded mass spectra, the intensity of the $(M-OH)^+$ fragment is very low, indicating that in none of the compounds the nitro group is severely hindered[31]. 2-NitroCPP is the only compound showing the $(M-NO_2)^+$ fragment as the base peak in the mass spectrum. Furthermore, the $(M-NO)^+$ and $(M-NO-CO)^+$ abundances are low, so that also in this respect there is a strong resemblance between 2-nitroCPP and 2-nitropyrene[20], both compounds having only a small electronic interaction between the nitro group and the aromatic system. This phenomenon was also observed from the IR and UV-vis spectra. The EI mass spectra are insufficiently different to allow a positive identification of the isomers on the basis of only mass spectrometry.

Discussion

The direct nitration of CPP (**1**), leading to 4-nitroCPP, has been discussed in a preliminary report[17]. Direct nitration of DHCPP (**2**) can be performed with nitric acid in acetic anhydride, but this system is unsuitable for the other partially hydrogenated CPP derivatives, due to oxidation reactions, one of which involves removal of the five-membered ring (formation of 1-nitropyrene). In these cases, copper(II) nitrate in acetic anhydride was used successfully. The true identity of the reactive species is unknown, but it has been suggested that acetyl nitrate is in fact the electrophile[21,32]. Unfortunately, not all nitration products predicted on the basis of the expected reactivity of the partially hydrogenated CPPs were formed.

Nitration of DHCPP (**2**) was expected to occur at positions 1, 6 and 8 and we were surprised not to find the isomer with the nitro group at position 1. Considering the intermediate σ-complexes (Fig. 10), the formation of only 6- and 8-nitro-DHCPP is understandable. Attack at positions 6 and 8 gives rise to an arenium ion in which the positive charge is distributed over seven alternating carbon atoms of a phenalenium cation. This phenalenium cation is stabilized by the two methylene groups of the hydrogenated five-membered ring. In the intermediate formed after attack at position 1, the positive charge can also reside in a phenalenium cation, but now the five-membered ring is not attached to positions with a relative positive charge.

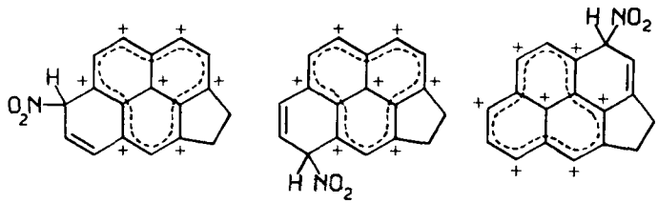


Fig. 10. Intermediate σ-complexes from DHCPP.

Table V Relative abundances (%) of the major peaks in the EI mass spectra of mononitroCPPs.

NitroCPP	Exact mass	M^+	$(M-30)^+$	$(M-46)^+$	$(M-47)^+$	$(M-58)^+$
$nitroCPP_{calc}$	271.0633					
1-nitroCPP	271.0632	100	28	78	48	12
2-nitroCPP	271.0636	84	3	100	38	10
4-nitroCPP	271.0646	100	84	44	60	47
5-nitroCPP	271.0631	100	13	88	49	34
6-nitroCPP	271.0634	100	33	90	74	64
8-nitroCPP	271.0632	100	28	96	45	80
9-nitroCPP	271.0631	100	10	88	50	32

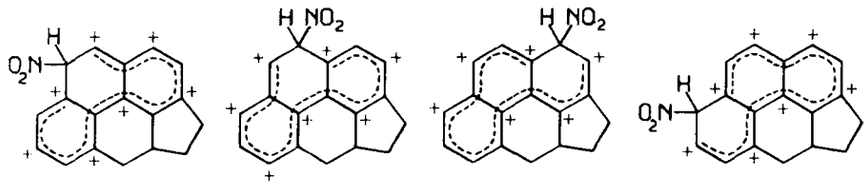


Fig. 11. Intermediate σ-complexes in the nitration of THCPP(I).

The formation of 5-nitro- in preference to 6-nitroTHCPP(II) can be rationalised on the basis of the activating properties of the *ortho* alkyl group in THCPP(II). In the reaction of THCPP(I), the composition of the product mixture was not quite what we had anticipated: only three of the four expected isomers could be detected. Apparently, the formation of the compound with the nitro group at position 10 is disfavoured. Comparison of the intermediates (Fig. 11) shows that more alkyl side-chains are attached to positively charged carbon atoms when the nitro group is at position 9. The formation of the compounds with the nitro group at position 1 or 8 is more difficult to understand. Both intermediates are stabilized by a naphthalenic moiety. However, only the intermediate with the nitro group at position 8 enjoys extra stabilization due to the alkyl groups. The high percentage of product substituted at position 1 indicates that stabilization of the intermediate is not the only factor governing positional reactivity. The electron density in the starting material will also be of importance and attack at the ring with the most alkyl substituents will be favoured. The formation of 2- and 1-nitroHHCPP, in preference to 7-nitroHHCPP, must be ruled by the same effects. Substitution at positions 2 or 7 gives rise to intermediates in which the positive charge is distributed over two phenyl rings. When the nitro group is at position 2, more alkyl groups are attached to carbons bearing a positive charge than when position 7 is attacked. The positive charge in the σ-complex, formed after attack at position 1, is delocalized in only one phenyl ring! It is remarkable that substitution occurs only in one of the two phenyl rings, indicating that also in this case the electron density is an important factor. A crucial step in the preparation is the separation of the nitro-substituted isomers. Owing to the poor solubility in the eluent and the poor resolution with HPLC, pure nitro-substituted partially hydrogenated CPPs could be obtained only on a mg scale. The oxidation reaction therefore has to be practicable on a small scale involving a high yield. DDQ oxidation is the best option for the aromatization of systems containing a five-membered ring, but in the usual solvent (toluene) the desired aromatization is not observed. Aromatization with DDQ has been extensively reviewed by *Fu* and *Harvey*[24] and many examples of successful applications were given. The rate-determining step involves hydride ion transfer from the hydrocarbon to the quinone, followed by rapid proton transfer from the resulting conjugate acid to the phenolate ion:

$$AH_2 + Q \xrightarrow{\text{slow}} AH^{\bullet} + QH^{-} \xrightarrow{\text{fast}} A + QH_2$$

Scheme 3

The reaction is faster in polar (*e.g.* acetonitrile) than in non-polar solvents (*e.g.* benzene)[24]. Apparently, the electron-withdrawing nitro group renders the loss of a hydride ion from the hydrocarbon difficult. We reasoned that a polar solvent at a high temperature should facilitate the formation of the intermediate carbocation and this was indeed found to be the case. The reaction is practicable on a small scale with reasonable to good yields (49–90%).

The spectroscopic data of the mononitrocyclopenta[*cd*]-pyrenes provide information about the interaction between the nitro group and the aromatic π-system. If the nitro group is sterically hindered, it will be forced out of the plane of the aromatic molecule. In the ^{1}H NMR spectrum, a perpendicular orientation of the nitro group causes an upfield shift (0.15–0.5 ppm) of the *peri* proton[10,27]. In 5-nitroCPP, H-4 is shifted only 0.05 ppm downfield from the parent compound, whereas the other *peri* proton H-6 has an almost normal downfield shift (0.43 ppm). The nitro group in 5-nitroCPP is sterically hindered by the five-membered ring and is forced out of the plane of the molecule, but not in a perpendicular orientation. The UV-vis spectrum indicates that there is still a rather strong mesomeric interaction. The nitro group in 2-nitroCPP is also situated *peri* to a hydrogen of the five-membered ring. Interestingly, this proton undergoes a normal downfield shift of 0.52 ppm, indicating that the nitro group is not sterically hindered by the neighbouring proton. This can also be explained by the diminished interaction between the nitro group and the aromatic system which causes the C–N bond in 2-nitroCPP to be longer than in 5-nitroCPP.
The interaction between the nitro group and the aromatic system of CPP appears in all cases to be governed by electronic factors. From the spectroscopic data, it can be concluded that the interaction increases in the following order: 2-nitroCPP < 1-nitroCPP, 9-nitroCPP < 5-nitroCPP, 6-nitroCPP, 8-nitroCPP < 4-nitroCPP. From our studies on the nitropyrenes[20], we have learned that strong interaction between the nitro group and the aromatic system renders the product unstable. 4-NitroCPP was indeed found to be very unstable. Even on storing in the dark at −20°C it decomposed. The six other isomers were found to be much more stable, whereas the hydrogenated nitroCPP derivatives were quite unstable. In particular, 5-nitroTHCPP(II) and 8-nitroDHCPP had to be converted with DDQ as soon as possible after synthesis and purification. This is also shown in the yield of the DDQ oxidation.

Conclusion

The synthesis and purification of seven nitro-substituted isomers of cyclopenta[*cd*]pyrene made it possible to study their spectroscopic properties. These compounds have now become available as reference materials for their identification in the environment. In addition, it is now also possible to explore their biological properties and eventually to establish the structure–activity relationship.

Experimental

General

Cyclopenta[*cd*]pyrene (**1**) and 3,4-dihydrocyclopenta[*cd*]pyrene (**2**) were prepared as described by *Tintel* et al.[16]. All solvents were distilled prior to use. Acetonitrile was purified by method A as described by *Walter* et al.[33]. Silica (230–400 Mesh) ASTM was supplied by Merck. All other chemicals were commercial products

and were used without further purification. Irradiations were carried out in well-stirred solutions in a vessel fitted with an inner tube (quartz or pyrex) in which the light source, Hanau TQ-150 or TQ-81 medium-pressure mercury arc, was mounted. The inner tube and the outside of the vessel were cooled with water. The ^1H and ^{13}C NMR spectra were recorded on a Jeol JNM-FX200 and a Bruker WM-300 spectrometer. The routine ^1H NMR spectra were measured on a Jeol PS 100. TMS (δ 0 ppm) was used as internal standard. The coupling constants (*J*) are given in Hz. The IR spectra were recorded on a Pye-Unicam SP3-200 spectrophotometer and the UV spectra on a Varian C-219 spectrophotometer. The mass spectra were determined on a KRATOS MS9/50 or an AEI MS 20 mass spectrometer (source 70 eV, temperature as reported). For HPLC purification, a Du Pont HPLC system (normal phase Zorbax Sil or reversed-phase Zorbax ODS 21.2 mm × 25 cm) was used. **Warning!** All the compounds in the present study are potential carcinogens.

3,4,4a,5-Tetrahydrocyclopenta[cd]pyrene [THCPP(I)] **3** *and 3,4,9,10-tetrahydrocyclopenta[cd]pyrene [THCPP(II)]* **4**

3,4-Dihydrocyclopenta[*cd*]pyrene (**2**) (100 mg, 0.44 mmol) was dissolved in a mixture of acetonitrile (300 ml) and diethylamine (10 ml). Nitrogen was bubbled through the solution $\frac{1}{2}$ h prior to and during the irradiation. The solution was irradiated for 50 min through a pyrex inner tube. The reaction mixture was evaporated to dryness and the resulting dark green residue was adsorbed on silica (35–70 mesh) and chromatographed on silica impregnated with 5% caffein, using hexane as eluent. The resulting mixture of THCPP(I) (**3**) and THCPP(II) (**4**) was separated by means of HPLC (normal phase, hexane), yielding 32 mg **4** (0.14 mmol, 32%) and 32 mg **3** (0.14 mmol, 32%), both as a white solid.
The spectral properties of **3** were identical to those reported by *Tintel* et al.[16].
4: ^1H NMR (200 MHz, $CDCl_3$, TMS) δ: 3.27–3.32 [t, 2H, H(3,3′) and t, 2H, H(4,4′) *J* (3,4) = *J* (3,4′) 5.7]; 3.42 [s, 4H, H(9,9′,10,10′)]; 7.30–7.72 [m, 6H, H(1,2,5,6,7,8)]. MS *m/z* (%): 230 (100); 229 (47); 228 (20); 227 (24); 226 (25); 215 (35); 203 (39); 202 (41).

3,4,4a,5,9,10-Hexahydrocyclopenta[cd]pyrene (HHCPP) **5**

3 (83 mg, 0.36 mmol) was dissolved in a mixture of acetonitrile (300 ml), triethylamine (5 ml) and triphenyltin hydride (0.18 g, 0.5 mmol). Nitrogen was bubbled through the solution $\frac{1}{2}$ h prior to and during the irradiation. The solution was irradiated for 1 h through a quartz inner tube. The resulting white suspension was evaporated to dryness. The residue was dissolved in dichloromethane and extracted with sulfuric acid (M). The water layer was washed with dichloromethane and the combined organic layers were washed with a saturated sodium bicarbonate solution, dried over magnesium sulfate, filtrated and evaporated to dryness, yielding 295 mg of a white crystalline mixture which still contained some organotin compound. Chromatography on silica (hexane) afforded 35 mg (0.15 mmol, 42%) HHCPP (**5**) as a colourless oil.
^1H NMR (300 MHz, $CDCl_3$, TMS) δ: 1.70–1.83 [m, 1H, H(4)]; 2.44–2.53 [m, 1H, H(4′)]; 2.62 [t, 1H, H(5) *J* (5,4a) = *J* (5,5′) 15.0]; 2.81–2.99 [m, 6H, H(3,3′, 9,9′, 10,10′)]; 3.03 [dd, 1H, H(5′) *J* (5′,5) 15.0, *J* (5′,4a) 7.0]; 3.21-3.34 [m, 1H, H(4a)]; 6.97–7.08 [m, 5H, H(1,2,6,7,8)]. MS *m/z* (%): 232 (100); 231 (27); 217 (24); 210 (50); 203 (36); 202 (42).

4-Nitrocyclopenta[cd]pyrene (4-nitroCPP) **6**

$AgNO_3$ (53 mg, 0.31 mmol) and $NaNO_2$ (146 mg, 2.12 mmol) were added to a stirred solution of CPP (**1**) (35 mg, 0.15 mmol) in 50 ml dry acetonitrile. The mixture was cooled to 0 °C and I_2 (78 mg, 0.31 mmol) was added. A precipitate of AgI appeared and the colour of the mixture turned from orange to red. After 10 min, TLC (silica, hexane/dichloromethane 4/1) showed that CPP had disappeared completely, but the nitro substituted product could not yet be detected. After additional stirring for 2 h, during which the red colour intensified, water was added and the remaining I_2 was destroyed with sodium sulfite. The mixture was extracted twice with dichloromethane and the organic layer was dried over sodium sulfate, filtered and evaporated to dryness. The product was chromatographed on silica (25 g, 70–230 mesh) with hexane/dichloromethane 4/1, yielding 18 mg (0.066 mmol, 43%) **6**. Like many other nitro-PAH, the product is sensitive to light, heat and moisture. A considerable amount (30%) of a ketone, cyclopenta[*cd*]pyren-3(4*H*)-one, was also isolated.
6: ^1H NMR (300 MHz, $CDCl_3$, TMS) δ: 8.13 [t, 1H, H(7) *J* 7.9]; 8.17 [d, 1H, H(10 or 9) *J* 9.0]; 8.21 [d, 1H, H(2 or 1) *J* 8.0]; 8.23 [d, 1H, H(9 or 10) *J* 9.0]; 8.28 [d, 1H, H(1 or 2) *J* 8.0]; 8.39 [s, 1H, H(3)]; 8.46 [dd, 1H, H(8) *J* 7.9/0.8]; 8.66 [dd, 1H, H(6) *J* 7.9/0.8]; 9.12 [s, 1H, H(5)]. IR (KBr): 1500, 1451, 1410, 1341, 1325, 1310, 1260, 1215, 1098, 1020, 889, 879, 831, 815, 800, 749, 681 cm^{-1}. UV (methanol) λ_{max} nm (relative ε); 500 (0.10); 403 (0.30); 375 sh (0.25); 324 (0.28); 300 (0.35); 286 sh (0.37); 277 (0.40); 262 (0.54); 232 (1.00); 225 (0.93); log ε (λ 232): 4.39. Exact mass calculated for $C_{18}H_9NO_2$: 271.0633 *m/z*; found: 271.0646 *m/z*. MS (175 °C) *m/z* (%): 271 (100); 241 (84); 226 (78); 225 (44); 224 (60); 213 (47); 202 (6).

6-Nitro- and 8-nitro-3,4-dihydrocyclopenta[cd]pyrene (6-nitro-DHCPP **7** *and 8-nitroDHCPP* **8***)*

DHCPP (**2**) (125 mg, 0.55 mmol) was dissolved in 25 ml of acetic anhydride. A solution of 50 mg nitric acid in 2.8 g acetic anhydride was added dropwise over 2 min. The solution of nitric acid was prepared as follows: 0.5 ml nitric acid (65%, d 1.39) was dissolved in 10 g acetic anhydride; 1.1 g of this solution was added to 1.7 g acetic anhydride. The solution was freshly prepared half an hour prior to use. The colour of the reaction mixture rapidly turned orange. After stirring at room temperature for 1 h 45 min, TLC (silica, hexane/dichloromethane 1/1) showed that almost all the starting material had disappeared. The mixture was poured onto 100 g of ice containing 2 ml sulfuric acid (M) to hydrolyse the acetic anhydride. The mixture was extracted three times with dichloromethane, washed with water and with a saturated sodium bicarbonate solution and dried over magnesium sulfate. After filtration and evaporation of the solvent, the mixture was chromatographed on silica (100 g) with hexane/dichloromethane (4/1) as eluent, yielding 30 mg of the starting material DHCPP and 99 mg of a mixture of nitrated DHCPP, containing two main components. The mixture was separated with HPLC (normal phase, hexane/dichloromethane 4/1. 22 ml/min) yielding, in the following order, 6-nitroDHCPP (**7**) 43.6 mg (0.160 mmol, 51%) and 8-nitroDHCPP (**8**) 41.6 mg (0.152 mmol, 49%).
7: ^1H NMR (300 MHz, $CDCl_3$, TMS) δ: 3.68–3.74 [m, 4H, H(3,3′,4,4′)]; 8.01 [d, 1H, H(2) *J* 7.6]; 8.05 [d, 1H, H(8) *J* 8.7]; 8.06 [d, 1H, H(9 or 10) *J* 8.9]; 8.24 [d, 1H, H(10 or 9) *J* 8.9]; 8.29 [d, 1H, H(1) *J* 7.6]; 8.68 [d, 1H, H(7) *J* 8.7]; 8.74 [t, 1H, H(5) *J* 1.5]. UV (hexane) λ_{max} nm (relative ε): 422 (0.25); 405 (0.32); 371 (0.31); 354 (0.23); 320 (0.23); 288 (0.42); 239 (0.91); 235 (1.00). MS (125 °C) *m/z* (%): 273 (100); 243 (42); 227 (58); 226 (96); 225 (27); 224 (27); 215 (14); 213 (15).
8: ^1H NMR (300 MHz, $CDCl_3$, TMS) δ: 3.62–3.66 [m, 2H, H(4,4′)]; 3.71–3.75 [m, 2H, H(3,3′)]; 7.83 [t, 1H, H(5) *J* 1.8]; 8.01 [d, 1H, H(2 or 1) *J* 7.7]; 8.04 [d, 1H, H(6) *J* 8.7]; 8.27 [d, 1H, H(1 or 2) *J* 7.7]; 8.32 [d, 1H, H(10) *J* 9.5]; 8.71 [d, 1H, H(7) *J* 8.7]; 9.01 [d, 1H, H(9) *J* 9.5]. UV (hexane) λ_{max} nm (relative ε): 420 (0.29); 400 (0.36); 380 (0.33); 362 (0.20); 334 (0.13); 318 (0.12); 290 (0.37); 272 (0.28); 235 (1.00). MS (125 °C) *m/z* (%): 273 (100); 243 (60); 227 (62); 226 (90); 225 (24); 224 (28); 215 (20); 213 (13).

6-Nitrocyclopenta[cd]pyrene (6-nitroCPP) **13**

DDQ (25 mg, 0.11 mmol) was dissolved in 30 ml of nitrobenzene. The solution was heated until reflux and 6-nitroDHCPP (8 mg, 0.03 mmol) dissolved in 10 ml of nitrobenzene was added over 15 min. The reaction was performed under nitrogen. The yellow reaction mixture immediately turned red. After refluxing for $\frac{1}{2}$ h, the reaction mixture was left to cool down overnight. At room temperature, a saturated aqueous sodium sulfite solution was added to destroy unreacted DDQ. The mixture was filtered over hyflo and the organic layer was separated. The solvent was evaporated and the residue chromatographed on silica with hexane containing 0.2% acetonitrile yielding 5.6 mg of the red-brown solid 6-nitroCPP (**13**) (0.02 mmol, 70%).
13: ^1H NMR (300 MHz, $CDCl_3$, TMS) δ: 7.19 [d, 1H, H(4) *J* 5.2]; 7.35 [d, 1H, H(3) *J* 5.2]; 7.93 [d, 1H, H(9 or 10) *J* 9.0]; 8.06 [d, 1H, H(2 or 1) *J* 7.6]; 8.13 [d, 1H, H(10 or 9) *J* 9.0]; 8.16 [d, 1H, H(1 or 2) *J* 7.6]; 8.27 [d, 1H, H(8) *J* 8.4]; 8.63 [d, 1H, H(7) *J* 8.4]; 8.99 [s, 1H, H(5)]. IR (KBr): 1549, 1520, 1502, 1478, 1348, 1325, 1260, 1202, 1100, 1025, 925, 890, 849, 800, 768, 739, 710, 686 cm^{-1}. UV

(methanol) λ_{max} nm (relative ε): 470 (0.04); 396 sh (0.19); 374 (0.26); 284 sh (0.24); 272 sh (0.26); 222 (1.00); log ε (λ 224): 4.59. Exact mass calculated for $C_{18}H_9NO_2$: 271.0633 *m/z*; found: 271.0634 *m/z*. MS (175°C) *m/z* (%): 271 (100); 241 (33); 225 (90); 224 (74); 223 (20); 213 (64); 202 (13),

8-Nitrocyclopenta[cd]pyrene (8-nitroCPP) **14**

DDQ (76 mg, 0.33 mmol) was dissolved in 10 ml of nitrobenzene. The solution was heated until reflux and 8-nitroDHCPP (37 mg, 0.14 mmol) dissolved in 15 ml of nitrobenzene was added dropwise over 10 min. The reaction was performed under nitrogen. The colour of the solution immediately turned from yellow to red. After refluxing for 45 min, the nitrobenzene was removed by evaporation. The resulting brown solid was dissolved in dichloromethane and a saturated sodium sulfite solution was added to destroy unreacted DDQ. The organic layer was separated and washed with the sodium sulfite solution, a saturated sodium bicarbonate solution and water. After drying over magnesium sulfate and filtration, the solvent was removed by evaporation. The residue was chromatographed on silica with hexane/dichloromethane (4/1) as eluent yielding 18 mg of the red-brown solid (>95% pure) 8-nitroCPP (0.07 mmol, 49%). The compound was further purified by HPLC (normal phase, hexane/dichloromethane 9/1).
^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ: 7.09 [d, 1H, H(4) *J* 5.2]; 7.32 [d, 1H, H(3) *J* 5.2]; 8.02 [d, 1H, H(2 or 1) *J* 7.6]; 8.08 [d, 1H, H(1 or 2) *J* 7.6]; 8.14 [d, 1H, H(10) *J* 9.5]; 8.16 [s, 1H, H(5)]; 8.31 [d, 1H, H(6) *J* 8.4]; 8.60 [d, 1H, H(7) *J* 8.4]; 8.63 [d, 1H, H(9) *J* 9.5]. IR (KBr): 1510, 1455, 1380, 1325, 1305, 1290, 1260, 889, 844, 829, 795, 769, 738, 648 cm^{-1}. UV (methanol) λ_{max} nm (relative ε): 460 (0.04); 375 sh (0.29); 360 (0.30); 318 (0.19); 304 sh (0.21); 284 sh (0.31); 272 (0.36); 240 sh (0.69); 224 (1.00); log ε (λ 224): 4.62. Exact mass calculated for $C_{18}H_9NO_2$: 271.0633 *m/z*; found: 271.0632 *m/z*. MS (175°C) *m/z* (%): 271 (100); 241 (28); 225 (96); 224 (45); 213 (80); 201 (5).

1-Nitro- and 9-nitro-3,4,4a,5-tetrahydrocyclopenta[cd]pyrene [1-nitroTHCPP(I) **9** *and 9-nitroTHCPP(I)* **10***]*

THCPP(I) (40 mg, 0.17 mmol) was dissolved in 20 ml of acetic anhydride. At room temperature, a solution of copper(II) nitrate trihydrate (25.7 mg, 0.10 mmol) in 30 ml of acetic anhydride was added dropwise over one hour. The reaction was performed under nitrogen. After stirring at room temperature for 24 h, the reaction mixture was poured onto ice (300 g) containing 6 ml sulfuric acid (M) and worked up as described under **7** and **8** yielding 50 mg of a yellow-orange solid. After chromatography on silica (hexane/dichloromethane 4/1), three fractions could be isolated: 21 mg of the starting material THCPP(I) (54%); 28 mg of a mixture containing nitrated THCPP(I) and 5 mg of a mixture probably containing acylated THCPP(I). The mixture containing nitro-THCPP(I) was separated with HPLC (normal phase, hexane/dichloromethane 4/1, 30 ml/min) into the two main components in the following order: 9-nitroTHCPP(I) (**10**) (13.6 mg, 64%) and 1-nitroTHCPP(I) (**9**) (7.6 mg, 36%).
9: ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ: 1.96–2.10 [m, 1H, H(4)]; 2.65–2.73 [m, 1H, H(4')]; 2.95 [t, 1H, H(5) *J* (5,4a) = *J* (5,5') 14.7]; 3.11–3.17 [m, 2H, H(3,3')]; 3.48 [dd, 1H, H(5') *J* (5',5) 14.7, *J* (5',4a) 7.0]; 3.55–3.65 [m, 1H, H(4a)]; 7.45 [d, 1H, H(6 or 8) *J* 7.3]; 7.56 [dd, 1H, H(7) *J* 7.3/7.9]; 7.74 [d, 1H, H(8 or 6) *J* 7.9]; 7.86 [d, 1H, H(9) *J* 9.5]; 8.25 [s, 1H, H(2)]; 8.47 [d, 1H, H(10) *J* 9.5]. UV (hexane) λ_{max} nm (relative ε): 420 (0.01); 367 (0.13); 338 (0.17); 301 (0.25); 278 (0.45); 265 (0.54); 257 (0.59); 242 (0.62); 233 (0.60); 222 (1.00). Exact mass calculated for $C_{18}H_{13}NO_2$: 275.0946 *m/z*; found: 275.0943 *m/z*. MS (125°C) *m/z* (%): 275 (100); 258 (5); 245 (11); 229 (20); 227 (100); 217 (10); 214 (7); 202 (20).
10: ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ: 2.00–2.08 [m, 1H, H(4)]; 2.67–2.71 [m, 1H, H(4')]; 3.03 [t, 1H, H(5) *J* (5,4a) = *J* (5,5') 14.1]; 3.15–3.19 [m, 2H, H(3,3')]; 3.54 [dd, 1H, H(5') *J* (5',5) 14.1, *J* (5',4a) 6.7]; 3.63 [m, 1H, H(4a)]; 7.51 [dd, 1H, H(6) *J* 7.3/1.0]; 7.57 [d, 1H, H(2 or 1) *J* 8.1]; 7.64 [dd, 1H, H(7) *J* 8.4/7.3]; 7.80 [d, 1H, H(1 or 2) *J* 8.1]; 8.42 [dd, 1H, H(8) *J* 8.4/1.0]; 8.59 [s, 1H, H(10)]. UV (hexane) λ_{max} nm (relative ε): 334 (0.26); 290 (0.30); 277 (0.50); 268 (0.57); 250 (0.82); 242 (0.98); 234 (1.00); 225 (0.77). Exact mass calculated for $C_{18}H_{13}NO_2$: 275.0946 *m/z*; found: 275.0947 *m/z*. MS (125°C) *m/z* (%): 275 (100); 258 (28); 245 (5); 229 (17); 228 (30); 227 (42); 226 (39); 217 (5); 214 (19); 202 (17).

1-Nitro- and 9-nitrocyclopenta[cd]pyrene (1-nitroCPP **15** *and 9-nitroCPP* **16***)*

A mixture of nitrated THCPP(I)s, consisting mainly of 1-nitro-THCPP(I) and 9-nitroTHCPP(I) (37 mg, 0.13 mmol), was dissolved in 40 ml of nitrobenzene. The solution was heated until reflux and a solution of DDQ (71 mg, 0.31 mmol) in 10 ml of nitrobenzene was added over 15 min. The reaction was performed under nitrogen. The yellow reaction mixture turned red immediately after the yellow DDQ solution had been added. After the DDQ was added, the reaction mixture was left to cool under constant stirring and worked up as described under **13** yielding a red-brown solid. Column chromatography (silica 50 g, hexane/dichloromethane 4/1) yielded 39 mg of an orange-red solid mixture of nitroCPPs. Using HPLC (normal phase, hexane/dichloromethane 4/1), the mixture was separated into two main fractions. The first fraction, 17.4 mg (0.06 mmol, 48%), a mixture of 9-nitroCPP (**16**) 90% and 8-nitroCPP (**14**) 10%, could not be further separated. The second fraction, 12.1 mg (0.04 mmol, 33%), consisted solely of 1-nitroCPP (**15**).
15: ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ: 7.27 [d, 1H, H(4) *J* 5.2]; 7.35 [d, 1H, H(3) *J* 5.2]; 8.07 [t, 1H, H(7) *J* 7.7]; 8.19 [d, 1H, H(9) *J* 9.5]; 8.33 [dd, 1H, H(8 or 6) *J* 7.7/1.0]; 8.36 [s, 1H, H(5)]; 8.44 [dd, 1H, H(6 or 8) *J* 7.7/1.0]; 8.80 [s, 1H, H(2)]; 8.90 [d, 1H, H(10) *J* 9.5]. IR (KBr): 1524, 1501, 1330, 1294, 1275, 1262, 1133, 1074, 810, 822, 789, 760 cm^{-1}. UV (methanol) λ_{max} nm (relative ε): 404 sh (0.19); 386 (0.32); 371 (0.32); 354 sh (0.30); 287 (0.31); 274 sh (0.30); 234 (0.80); 212 (1.00); log ε (λ 212): 4.48. Exact mass calculated for $C_{18}H_9NO_2$: 271.0633 *m/z*; found: 271.0632 *m/z*. MS (175°C) *m/z* (%): 271 (100); 241 (28); 225 (78); 224 (48); 213 (12).
9-NitroTHCPP(I) (**10**) (8 mg, 0.03 mmol) was dissolved in 10 ml of nitrobenzene and added over 10 min to a refluxing solution of DDQ (13 mg, 0.06 mmol) in 10 ml of nitrobenzene. The yellow reaction mixture immediately turned red after the yellow DDQ solution was added. After refluxing for 15 min, the solvent was removed by evaporation. The mixture was dissolved in dichloromethane and a saturated sodium sulfite solution was added to destroy unreacted DDQ. The organic layer was separated and washed with sodium sulfite and with a saturated sodium bicarbonate solution. The combined aqueous layers were washed with ether. The organic layers were dried over sodium sulfate, filtered and evaporated to dryness yielding an orange-red solid. Column chromatography (silica 50 g, hexane/dichloromethane 4/1) yielded 6 mg of an orange solid containing (>95% pure) 9-nitroCPP (**16**) (0.025 mmol, 84%). The compound was further purified by HPLC (normal phase, hexane/dichloromethane 9/1).
16: ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ: 7.32 [d, 1H, H(4) *J* 5.2]; 7.42 [d, 1H, H(3) *J* 5.2]; 8.14 [t, 1H, H(7) *J* 8.0]; 8.17 [d, 1H, H(2 or 1) *J* 7.7]; 8.31 [d, 1H, H(1 or 2) *J* 7.7]; 8.38 [s, 1H, H(5)]; 8.48 [dd, 1H, H(6) *J* 8.0/0.8]; 9.01 [s, 1H, H(10)]; 9.05 [dd, 1H, H(8) *J* 8.0/0.8]. IR (KBr): 1649, 1520, 1499, 1378, 1327, 910, 882, 845, 829, 819, 791, 758, 676, 638 cm^{-1}. UV (methanol) λ_{max} nm (relative ε): 374 (0.28); 278 (0.41); 298 (0.41); 260 (0.40); 241 (0.85); 218 (1.00); log ε (λ 218): 4.40. Exact mass calculated for $C_{18}H_9NO_2$: 271.0633 *m/z*; found: 271.0631 *m/z*. MS (175°C) *m/z* (%): 271 (100); 241 (10); 225 (88); 224 (50); 213 (32).

5-Nitrocyclopenta[cd]pyrene (5-nitroCPP) **17**

THCPP(II) (44 mg, 0.19 mmol) was dissolved in 15 ml acetic compound (30 mg, 57%) was chromatographed on silica (hexane/dichloromethane 1/1), followed by HPLC (reversed phase, acetonitrile/water 9/1), yielding 21 mg (0.08 mmol, 40%) 5-nitro-THCPP(II) (**11**) as a yellow solid.
11: ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ: 3.28 [t, 2H, H(9,9' or 10,10') *J* 6.8]; 3.36 [t, 2H, H(10,10' or 9,9') *J* 6.8]; 3.49 [t, 2H, H(3,3') *J* 5.7]; 3.79 [t, 2H, H(4,4') *J* 5.7]; 7.45 [dd, 1H, H(8) *J* 8.5/1.0]; 7.47 [d, 1H, H(1 or 2) *J* 8.0]; 7.53 [d, 1H, H(2 or 1) *J* 8.0]; 7.62 [t, 1H, H(7) *J* 8.5]; 7.83 [dd, 1H, H(6) *J* 8.5/1.0]. MS (50°C) *m/z* (%): 275 (0); 258 (100); 245 (2); .243 (34); 228 (6); 227(8).
11 (20 mg, 0.07 mmol) was dissolved in 25 ml of nitrobenzene and added to a refluxing solution of DDQ (37 mg, 0.16 mmol) in 25 ml of nitrobenzene. The reaction was performed under nitrogen. After refluxing for ½ h, the dark brown solution was left to cool, filtered over hyflo and evaporated to dryness and worked up as described under **15** yielding a red-brown solid. Column chromatography (silica 50 g, hexane/dichloromethane 4/1) yielded 11 mg (0.04 mmol, 56%) of an orange-red solid consisting, for more than 95%,

of 5-nitroCPP (**17**). By means of HPLC (reversed phase, acetonitrile/water 9/1), the product was further purified, yielding 5.4 mg (0.02 mmol, 27%) 5-nitroCPP (**17**) as a red-brown solid.
17: ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ: 7.27 [d, 1H, H(4) *J* 5.2]; 7.45 [d, 1H, H(3) *J* 5.2]; 7.99 [d, 1H, H(10 or 9) *J* 9.1]; 8.02 [d, 1H, H(9 or 10) *J* 9.1]; 8.04 [d, 1H, H(2 or 1) *J* 7.6]; 8.11 [t, 1H, H(7) *J* 8.0]; 8.11 [d, 1H, H(1 or 2) *J* 7.6]; 8.32 [dd, 1H, H(8) *J* 8.0/1.0]; 8.79 [dd, 1H, H(6) *J* 8.0/1.0]. IR (KBr): 1510, 1351, 1339, 840, 770, 748 cm^{-1}. UV (methanol) λ_{max} nm (relative ε): 470 (0.02); 394 sh 0.11); 380 (0.13); 326 (0.21); 309 (0.25); 241 sh (0.51); 222 (1.00); log ε (λ 222): 4.63. Exact mass calculated for $C_{18}H_9NO_2$: 271.0633 *m/z*; found: 271.0631 *m/z*. MS (175°C) *m/z* (%): 271 (100); 241 (13); 225 (88); 224 (49); 213 (34).

2-Nitrocyclopenta[cd]pyrene (2-nitroCPP) **18**

HHCPP (21 mg, 0.09 mmol) was dissolved in 20 ml of acetic anhydride. At room temperature, copper(II) nitrate trihydrate (61 mg, 0.25 mmol) was added. After stirring at room temperature for 24 h, the reaction mixture was poured onto ice (500 g) and the acetic anhydride was hydrolysed with sodium hydroxide. After stirring for 2 h, the mixture was worked up as described under **7** and **8**. The resulting yellow oil was chromatographed on silica (hexane/dichloromethane 4/1) and two fractions could be isolated: 9 mg of the starting material HHCPP (39%) and 16 mg of 2-nitroHHCPP (**12**) (61%).
12: ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ: 1.75–1.90 [m, 1H, H(4)]; 2.53–2.71 [m, 2H, H(4',5)]; 2.85–3.00 [m, 4H, H(9,9',10,10')]; 3.15 [dd, 1H, H(5') *J* (5',5) 15.0, *J* (5',4a) 6.0]; 3.21–3.38 [m, 1H, H(4a)]; 3.57 [dd, 2H, H(3,3') *J* (3,4') 17.0, *J* (3,4) 8.0]; 7.10–7.24 [m, 3H, H(6,7,8)]; 7.90 [s, 1H, H(1)].
2-NitroHHCPP (15 mg, 0.06 mmol) was dissolved in 15 ml of nitrobenzene and added dropwise over 10 min to a refluxing solution of DDQ (51 mg, 0.22 mmol) in 10 ml of nitrobenzene. The reaction was performed under nitrogen. After refluxing for $\frac{1}{2}$ h, the dark brown solution was evaporated to dryness and worked up as described under **15**, yielding a red-brown solid. Column chromatography (silica 50 g, hexane/dichloromethane 4/1) yielded 9 mg (0.03 mmol, 61%) of solid orange 2-nitroCPP (**18**) (>95% pure). By means of HPLC (reversed phase, acetonitrile/water 9/1), the product was further purified.
18: ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ: 7.36 [d, 1H, H(4) *J* 5.2]; 7.92 [d, 1H, H(3) *J* 5.2]; 8.10 [t, 1H, H(7) *J* 7.7]; 8.13 [d, 1H, H(10 or 9) *J* 9.1]; 8.19 [d, 1H, H(9 or 10) *J* 9.1]; 8.35 [dd, 1H, H(8) *J* 7.7/1.0]; 8.43 [s, 1H, H(5)]; 8.45 [dd, 1H, H(6) *J* 7.7/1.0]; 8.91 [s, 1H, H(1)]. IR (KBr): 1532, 1465, 1453, 1425, 1386, 1335, 1300, 1285, 1279, 1250, 1135, 1125, 1073, 895, 880, 832, 818, 790, 769, 680 cm^{-1}. UV (methanol) λ_{max} nm (relative ε): 440 (0.05); 352 (0.24); 304 (0.53); 275 (0.46); 212 (1.00); log ε (λ 212): 4.21. Exact mass calculated for $C_{18}H_9NO_2$: 271.0633 *m/z*; found: 271.0636 *m/z*. MS (175°C) *m/z* (%): 271 (84); 241 (3); 225 (100); 224 (38); 213 (10).

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