Crystal Structure and NMR Spectral Study of (2E,4E)-5-(4-Nitrophenyl)-2,4-pentadienal and (E)-3-(4-Nitrophenyl)propenal

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Rissanen, K., Laihia, K., Pitkänen, M. and Kantolahti, E., 1989. Crystal Structure and NMR Spectral Study of (2E,4E)-5-(4-Nitrophenyl)-2,4-pentadienal and (E)-3-(4-Nitrophenyl)propenal. – Acta Chem. Scand. 43: 787–792.

The structural features of two conjugated aldehydes, (2E,4E)-5-(4-nitrophenyl)-2,4-pentadienal (1, a 'spy dust') and (E)-3-(4-nitrophenyl)propenal (2), have been studied in the solid state and in solution. X-Ray analysis was performed and the crystal data are: (1) space group $P2_1/c$ (No. 14), $a = 3.877(3)$, $b = 11.190(6)$, $c = 27.089$ (9) Å, $\beta = 100.18(5)°$, $V = 1156.8$ Å³, $Z = 4$, $R = 0.066$ for 870 unique observed reflections; (2) space group $P2_1$ (No. 4), $a = 3.847(2)$, $b = 15.046(3)$, $c = 7.422(3)$ Å, $\beta = 94.48(2)°$, $V = 428.3$ Å³, $Z = 2$, $R = 0.047$ for 398 unique observed reflections. According to the X-Ray data, the molecules consist of three planar parts: the slightly deformed aldehyde chain, the benzene ring and the nitro group. The aldehyde chain and the nitro group are coplanar, to within experimental error, while the benzene ring is tilted 8(2)° in compound 1 and 10(2)° in compound 2 toward the aldehyde chain and the nitro group. The ¹H and ¹³C NMR chemical shifts and the J(H,H) and J(H,H) values were determined in CDCl₃ solution making use of 2-D shift correlated spectra (HH- and CH-COSY). The effects of the electronegative nitro group and the formyl oxygen on the E- and Z-vicinal coupling constants are considered and compared with those of nitro- and chloro-benzene and alkyl-substituted propenals.

The light yellow, crystalline solid (2E,4E)-5-(4-nitrophenyl)-2,4-pentadienal (1) or NPPD, was much publicized after it had been used as a spy dust. It strongly absorbs UV light at 333 nm,[1] but does not fluoresce appreciably. The intensity of the light absorption increases markedly after reaction with naphthoresorcinol (1,3-naphthalenediol) so that less than 20 ng 100 cm⁻² of 1 can be detected[2] by spectrometry at 506 nm. This compound was applied in invisible amounts and later the movements of a contaminated person was followed by detecting traces of 1.

We have lately synthesized a number of aromatic conjugated aldehydes, substituted pentadienals and propenals: attention being focused both on synthetic routes and spectroscopic and crystal-structure analysis. In this work we report the crystal structure and ¹H and ¹³C NMR spectral data of (2E,4E)-5-(4-nitrophenyl)-2,4-pentadienal (1) and (E)-3-(4-nitrophenyl)propenal (2), which is an intermediate in the synthesis of 1.

Experimental

Preparation of compounds. The aldehydes 1 and 2 were synthetized by the method of Trippett and Walker,[3] in which the corresponding benzaldehyde is treated with formylmethylenetriphenylphosphorane ylide. This method is particularly suitable for aromatic aldehydes with electron-withdrawing *para*-substituents, as these enhance the reactivity towards the resonance-stabilized ylide.[3] 4-Nitrobenzaldehyde (3.3 mmol) and the ylide (6.6 mmol) were refluxed for 25 h in dry benzene (90 ml). The course of the reaction, which is highly E-stereoselective (about 91 %), was followed by GLC. The two aldehydes were easily separated from each other and from triphenylphosphine oxide by flash chromatography. Ethyl acetate−light petroleum (1:9) was used as the eluent on a 3.5×40 cm silica-gel column (230–400 mesh). Triphenylphosphine oxide, which is sometimes difficult to separate from the products, was adsorbed most strongly, while the aldehydes came through nicely. Recrystallization was carried out from dichloromethane−light petroleum (1:1).

Crystal-structure analysis. The experimental data for the crystal-structure analyses are presented in Table 1.[‡] The lattice parameters were determined by measuring 25 reflections using MoK_α ($\lambda = 0.71073$ Å) radiation at room temperature (296 K). Intensity data were collected on an Enraf−Nonius CAD4 diffractometer using MoK_α radiation and $\omega/2\theta$ scan mode. The intensity data were corrected for Lorenz and polarization effects but not for extinction. Empirical absorption correction according to Stuart and

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‡ Lists of structure factors, anisotropic temperature factors, least-squares planes, Cl- and H-atom coordinates may be obtained from one of the authors (K.R.) on request.

Table 1. Experimental data for the crystallographic analyses.

Compound	1	2
Formula	$C_{11}H_9NO_3 \cdot 0.3CH2Cl_2$	$C_9H_7NO_3$
M_F	228.7	177.2
$a/\text{Å}$	3.877(3)	3.847(2)
$b/\text{Å}$	11.190(6)	15.046(3)
$c/\text{Å}$	27.089(9)	7.422(3)
$\alpha/°$	90	90
$\beta/°$	100.18(5)	98.48(2)
$\gamma/°$	90	90
$V/\text{Å}^3$	1156.8(21)	428.3(4)
Z	4	2
$d_{calc}/\text{Mg m}^{-3}$	1.31	1.37
μ/mm^{-1}	0.22	0.10
$\lambda(\text{Mo}K_\alpha)$	0.71073	0.71073
$F(000)$	467	184
Space group	$P2_1/c$ (No. 14)	$P2_1$ (No. 4)
T/K	296±1	296±1
Crystal size/mm	0.20×0.15×0.20	0.20×0.20×0.15
Refl. for latt. meas.	25	25
θ range for latt. meas./°	2–12	3–11
Scan method	$\omega/2\theta$	$\omega/2\theta$
Scan speed/° min^{-1}	1–17	1–17
Scan width $(\omega)/°$	1.0+0.34tanθ	0.5+0.34tanθ
θ range/°	2–25	2–25
h range	0 → 4	0 → 4
k range	0 → 13	0 → 17
l range	−31 → 31	−8 → 8
Variation of std. refl.	none	none
Refl. measured	2157	797
Condition of obs. refl.	$I > 1.5\sigma(I)$	$I > 2\sigma(I)$
Refl. used in refinement	870	398
Max. shift/error	0.03	0.01
No. of parameters	160	88
Max. in final $\Delta\varrho/e\text{Å}^{-3}$	0.33(4)/−0.15(4)	0.21(4)/−0.21(4)
S	1.53	1.15
R	0.066	0.047
R_w	0.086	0.070
R_w (all refl.)	0.097	0.128
$w = 1/[(\sigma F_o)^2 + (aF_o)^2]$	$a = 0.008$	$a = 0.04$

Walker[4] was done for both data sets, the correction coefficients being max. 1.243 and min. 0.417 for 1 and max. 1.267 and min. 0.796 for 2. The structures were solved by direct methods using the MULTAN11/82 program.[5] Refinements were carried out by the full-matrix least-squares method using the SDP program package,[6] anisotropically for all O, N and C atoms in 1. For compound 2 the benzene ring carbons were refined isotropically in order to reduce the number of parameters; all other non-H atoms were refined anisotropically. No attempts were made to determine the absolute structure of 2. The H-atom coordinates were calculated to their ideal positions (C−H distance 1.00 Å) and used as riding atoms in final refinements with a fixed isotropic temperature factor ($B_{eq} = 5.0$ Å^2). The atomic scattering factors were taken from Ref. 7. The final coordinates are quoted in Tables 2 and 3. During the refinements of compound 1, it was found out that there is a residual electron density (three peaks ca. 2 eÅ^{-3} with no apparent chemical significance) located near to a special position

Table 2. Fractional coordinates and equivalent isotropic temperature factors for 1 with e.s.d.'s in parentheses.

Atom	x	y	z	$B_{eq}/\text{Å}^2$ [a]
O(1)	−0.514(1)	0.7619(4)	0.2585(2)	9.9(1)
O(2)	0.784(1)	−0.1528(4)	0.4555(2)	9.5(1)
O(3)	0.431(1)	−0.2070(4)	0.3897(2)	9.7(1)
N(1)	0.571(1)	−0.1288(4)	0.4170(2)	7.2(1)
C(1)	−0.303(2)	0.7091(6)	0.2890(2)	7.1(1)
C(2)	−0.253(1)	0.5816(5)	0.2914(2)	6.3(1)
C(3)	−0.030(1)	0.5292(5)	0.3288(2)	5.7(1)
C(4)	0.030(1)	0.4039(5)	0.3343(2)	5.6(1)
C(5)	0.247(1)	0.3583(5)	0.3732(2)	5.9(1)
C(6)	0.323(1)	0.2297(5)	0.3824(2)	5.7(1)
C(7)	0.535(1)	0.1972(5)	0.4282(2)	5.8(1)
C(8)	0.614(1)	0.0804(5)	0.4393(2)	5.7(1)
C(9)	0.483(1)	−0.0056(4)	0.4049(2)	5.3(1)
C(10)	0.279(1)	0.0199(5)	0.3598(2)	5.8(1)
C(11)	0.200(1)	0.1372(5)	0.3483(2)	6.1(1)

[a] $B_{eq} = \frac{4}{3}[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

Table 3. Fractional coordinates and equivalent isotropic temperature factors for **2** with e.s.d.'s in parentheses.

Atom	x	y	z	$B_{eq}/Å^{2\,a}$
O(1)	−0.177(2)	0.5135(4)	1.2359(7)	7.2(1)
O(2)	0.569(2)	0.2160(6)	0.1671(7)	8.7(2)
O(3)	0.332(2)	0.1139(4)	0.3167(9)	8.9(2)
N(1)	0.427(2)	0.1921(5)	0.2967(8)	6.3(1)
C(1)	−0.020(2)	0.5134(6)	1.1019(9)	5.8(2)
C(2)	0.021(2)	0.4351(5)	0.9898(9)	5.1(1)
C(3)	0.179(2)	0.4440(5)	0.8407(9)	4.7(1)
C(4)	0.242(2)	0.3758(5)	0.7049(8)	4.1(1)ᵇ
C(5)	0.373(2)	0.4027(5)	0.5452(9)	4.8(1)ᵇ
C(6)	0.434(2)	0.3427(5)	0.4130(9)	5.0(1)ᵇ
C(7)	0.364(2)	0.2542(5)	0.4417(9)	4.5(1)ᵇ
C(8)	0.239(2)	0.2241(5)	0.5968(9)	4.9(1)ᵇ
C(9)	0.183(2)	0.2855(5)	0.7322(9)	4.9(1)ᵇ

$^aB_{eq} = \frac{1}{3}[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$. ᵇAtoms refined isotropically.

(0.50, 0.50, 0.50). Refinement of the structure without the residual electron density gave an *R*-factor of 0.23 with all non-H atoms anisotropic and H-atoms isotropic. From the

recrystallization conditions (dichloromethane−light petroleum) and the size of the free space (the cavity formed by four molecules of **1** around the special position 0.50, 0.50, 0.50 has a diameter about 6 Å) within the unit cell of **1** (Fig. 2) it was deduced that the residual electron density is caused by extremely disordered dichloromethane molecules. After several refinement cycles and difference Fourier calculations (peaks assigned as Cl-atoms with low multiplicity) the residual electron density decreased to 0.33 eÅ^{-3}. Six isotropically refined Cl-atoms with the population parameter 0.10 gave the isotropic temperature factors between 6.3 and 11.4 Å^2. Excluding just one of these Cl-atoms from the refinement changed the *R*-factor from 0.066 to 0.11. Due to the extreme disorder of the CH_2Cl_2 molecules the carbon atoms could not be located and attempts to define the orientations or refinements of the Cl-atom population parameters of the dichloromethane molecules were unsuccessful. The sum of the Cl-atom population parameters gives the overall population of 0.3 CH_2Cl_2 molecules per molecule of **1**. The calculations were performed on a μ-VAX II computer at the Department of Chemistry, University of Jyväskylä. In addition to programs quoted the PLUTO[8] program was used.

Table 4. Bond distances (Å) and angles (°) in **1** and **2** with e.s.d.'s in parentheses.

| 1		2	
O(2) −N(1)	1.240(6)	O(2)−N(1)	1.199(9)
O(3) −N(1)	1.210(6)	O(3)−N(1)	1.243(9)
O(1) −C(1)	1.207(7)	O(1)−C(1)	1.202(9)
N(1) −C(9)	1.444(7)	N(1)−C(7)	1.460(10)
C(1) −C(2)	1.440(9)	C(1)−C(2)	1.457(10)
C(2) −C(3)	1.344(7)	C(2)−C(3)	1.311(10)
C(3) −C(4)	1.424(8)	−	−
C(4) −C(5)	1.329(7)	−	−
C(5) −C(6)	1.481(8)	C(3)−C(4)	1.471(10)
C(6) −C(7)	1.409(7)	C(4)−C(5)	1.385(9)
C(6) −C(11)	1.414(7)	C(4)−C(9)	1.395(10)
C(7) −C(8)	1.365(8)	C(5)−C(6)	1.366(10)
C(8) −C(9)	1.372(7)	C(6)−C(7)	1.379(10)
C(9) −C(10)	1.365(7)	C(7)−C(8)	1.359(10)
C(10)−C(11)	1.371(7)	C(8)−C(9)	1.395(10)
O(2)−N(1) −O(3)	121.1(5)	O(2)−N(1)−O(3)	122.4(7)
O(2)−N(1) −C(9)	119.5(4)	O(2)−N(1)−C(7)	120.7(7)
O(3)−N(1) −C(9)	119.4(4)	O(3)−N(1)−C(7)	116.8(6)
O(1)−C(1) −C(2)	125.9(5)	O(1)−C(1)−C(2)	123.9(8)
C(1)−C(2) −C(3)	122.1(5)	C(1)−C(2)−C(3)	118.6(7)
C(2)−C(3) −C(4)	125.4(5)	C(2)−C(3)−C(4)	128.3(7)
C(3)−C(4) −C(5)	122.0(5)	−	−	−
C(4)−C(5) −C(6)	125.9(5)	−	−	−
C(5)−C(6) −C(7)	117.8(5)	C(3)−C(4)−C(5)	118.3(6)
C(5)−C(6) −C(11)	124.5(4)	C(3)−C(4)−C(9)	122.9(6)
C(7)−C(6) −C(11)	117.6(5)	C(5)−C(4)−C(9)	118.8(6)
C(6)−C(7) −C(8)	121.0(5)	C(4)−C(5)−C(6)	121.1(7)
C(7)−C(8) −C(9)	118.7(5)	C(5)−C(6)−C(7)	118.7(7)
N(1)−C(9) −C(8)	118.2(4)	N(1)−C(7)−C(6)	117.4(6)
N(1)−C(9) −C(10)	118.6(4)	N(1)−C(7)−C(8)	120.0(6)
C(8)−C(9) −C(10)	123.2(5)	C(6)−C(7)−C(8)	122.6(7)
C(9)−C(10)−C(11)	118.3(5)	C(7)−C(8)−C(9)	118.3(7)
C(6)−C(11)−C(10)	121.1(4)	C(4)−C(9)−C(8)	120.4(6)
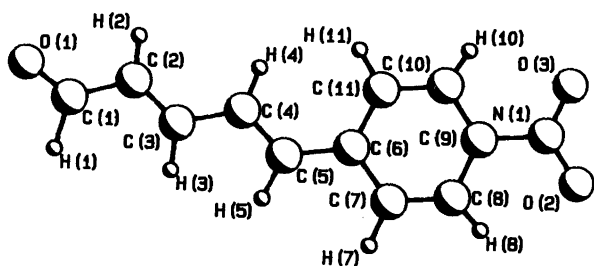
Fig. 1. PLUTO plot and the numbering scheme for 1.

NMR measurements. ¹H spectra were recorded on Varian VXR 300, Bruker AC 300 or Jeol GSX 270 spectrometers. The samples were dissolved in CDCl₃ and [1] was 1.5 % (w/w) and [2] 2.5 % (w/w) in a 5 mm tube. The digital resolution was 0.04–0.11 Hz/pt. ¹³C Spectra were recorded with a Bruker AC 300 spectrometer at 75.5 MHz (for 1) and a Jeol GSX 270 spectrometer at 67.8 MHz (for 2) for ca. 5 % (w/w) solutions (CDCl₃). The digital resolution was 0.3–0.9 Hz/pt for the decoupled spectra and 0.2–0.3 Hz/pt for the coupled spectra. ¹H and ¹³C chemical shifts are reported relative to internal SiMe₄. The homonuclear two-dimensional shift correlated spectrum (HH-COSY) for 1 was recorded on a Bruker AC 300 spectrometer. The pa-
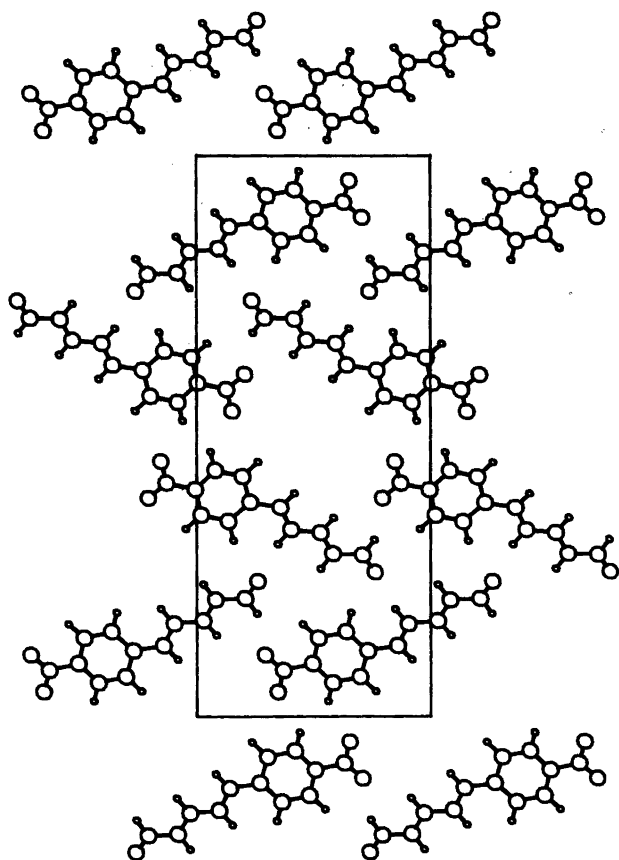
rameters were as follows: spectral width 632.8 Hz (f_2 and 316.4 Hz (f_1), the size of the data matrix for processing was 2048×1024 and the number of scans was four. The heteronuclear two dimensional ¹³C–¹H shift correlated spectrum (CH-COSY) for 1 was recorded on a Bruker AC 300 spectrometer. The parameters were: spectral width 3289.5 Hz (¹³C axis) and 325.0 Hz (¹H axis), the size of the data matrix was 2048×1024 and the number of the scans was 40. For compound 2 CH-COSY was recorded on a Jeol GSX 270 spectrometer and the parameters were: spectral width 8958.3 Hz (¹³C axis) and 1069.2 Hz (¹H axis), the size of the data matrix was 2048×1024 and the number of scans was 40. The CH-COSY spectra were optimized to 170 Hz, 7 Hz (only for 1) and 5 Hz (only for 2) coupling constants.

Results and discussion

The bond distances and angles are presented in Table 4. The views of the molecules are shown in Figs. 1 and 3 and the packing in Figs. 2 and 4.

Conjugated aldehydes, such as 1 and 2, are expected to possess a planar or almost planar structure due to the extensive sp² hybridization. As a result of electron delocalization the single bonds are shorter and the double bonds longer than in non-conjugated systems. Becher et al.[9] confirmed the expected planar all-E structure of 5-hydroxy-2,4-pentadienal by using X-ray data of the acetate derivative. The bond distances in 5-acetoxy-2,4-pentadienal, 1.323(9) [C(2)−C(3)] and 1.317(8) Å [C(4)−C(5)] for double and 1.44(1) [C(1)−C(2)] and 1.464(8) Å [C(3)−C(4)] for single bonds, are slightly different from the values in compounds 1 and 2 (Table 4). The bond angles in 1 and 2 do not markedly deviate from the values observed in 5-acetoxy-2,4-pentadienal. The bond distance between the benzene ring and the aldehyde chain [C(5)−C(6) = 1.481 (8) Å in 1 and C(3)−C(4) = 1.471(10) Å in 2] is comparable to the values observed for the single bond between conjugated sp²-hybridized carbon atoms, values being 1.46 Å for butadiene,[10] 1.44 Å for stilbene[10] and 1.47–1.49 Å for biphenyls with electron-withdrawing substituents.[11a,b]

The molecules of 1and 2 consist of three planar parts: the aldehyde chain, the benzene ring and the nitro group, of

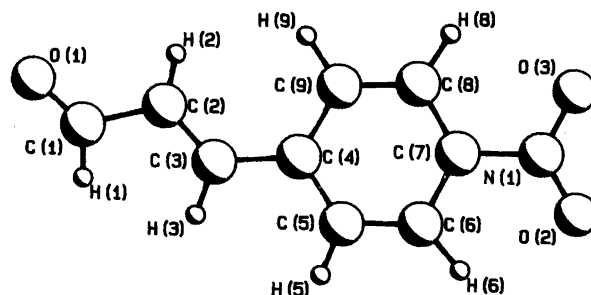Fig. 2. View of the packing for 1 along the a-axis. The disordered CH₂Cl₂ molecule is omitted for clarity.
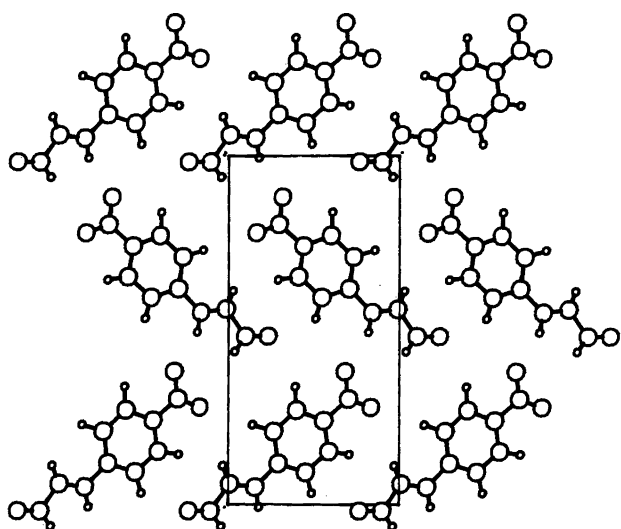

Fig. 3. PLUTO plot and the numbering scheme for 2.

Fig. 4. View of the packing for 2 along the a-axis.

which the aldehyde chain is slightly deformed [maximum displacements from the calculated least-squares plane are $-0.054(5)$ Å for O(1) and $0.031(5)$ Å for C(2)]. Similar small deviations from planarity were also observed for 5-hydroxy-2,4-pentadienal.[9] The aldehyde chain and the nitro group are coplanar, to within experimental error, whereas the benzene ring has a twist angle of $8(2)°$ in compound 1 and $10(2)°$ in compound 2 towards the aldehyde chain and the nitro group. The packing is similar for

the both compounds (Figs. 2 and 4). These molecules form b–c planes, which are stacked along the a-axis with benzene rings above each other. The twist angles, almost equal in 1 and 2, are mainly caused by the packing forces viz. the π-electron overlap between the adjacent phenyl rings. There are no intermolecular contacts shorter than the sums of the van der Waals radii.

The NMR spectral data of 1 and 2 are presented in Tables 5–7. Chemical-shift correlated 2-D spectra were used for the assignments and in elucidating the geminal and vicinal C,H coupling constants. In compound 1 [Table 5(a)], a HH-COSY spectrum verifies the following mutual order of the three close shifts: H-3 (7.30 ppm), H-4 (7.15 ppm) and H-5 (7.06 ppm). The ^{13}C chemical shifts (for C-3, C-4 and C-5) were then assigned from a CH-COSY spectrum (Table 6).

In compound 2 [Table 5(b)], as in 1, the higher-field aliphatic proton shift, 6.78 ppm (6.36 ppm in 1), is that of H-2 as is general in α,β-unsaturated aldehydes. The shift of H-3 is 7.53 ppm. The coupling of H-2 to the formyl proton (7.4 Hz) and H-3 (16.1 Hz) verifies this shift order. The reverse order is given in a paper by Cresp et al.[12b]

Large ^2J(C-2,H) values are characteristic of formyl protons and are thus immediately recognizable. The sign of the coupling has been shown to be positive.[13] Apart from this, the vicinal C,H coupling constants observed are always larger than the geminal ones. The vicinal coupling depends[14] on the substituent electronegativity in the fragment ^{13}C–C=C–H. An oxygen atom (of the formyl group) on

Table 5. ^{1}H Chemical shifts and coupling constants (absolute values) of (a) (2E,4E)-5-(4-nitrophenyl)-2,4-pentadienal (1) and (b) (E)-3-(4-nitrophenyl)propenal (2).

(a) Proton	δ/ppm	J_{HH}/Hz	(b) Proton	δ/ppm	J_{HH}/Hz
H-1	9.66	7.8(H-2)	H-1	9.74	7.4(H-2)
H-2	6.36	15.0(H-3) 7.8(H-1)	H-2	6.78	16.1(H-3) 7.4(H-1)
H-3	7.30	15.0(H-2) 9.8(H-4)	H-3	7.53	16.1(H-2)
H-4	7.15	15.4(H-5) 9.8(H-3)			
H-5	7.06	15.4(H-4)			
H-7,11	7.65	9.0(H-8,10) 2.2(H-10,8)	H-5,9	7.73	8.8(H-6,8) 1.9(H-8,6)
H-8,10	8.22	9.0(H-7,11) 2.2(H-11,7)	H-6,8	8.25	8.8(H-5,9) 1.9(H-9,5)

Table 6. ^{13}C Chemical shifts and CH coupling constants (absolute values) of (2E,4E)-5-(4-nitrophenyl)-2,4-pentadienal (1) in CDCl$_3$.

Carbon	δ/ppm	$^1J_{CH}$/Hz	^2J(C,H)/Hz and ^3J(C,H)/Hz	
C-1	193.1	172.5	8.1(H-3)[a]	
C-2	133.4	161.2	25.8(H-1)	3.2(H-4)[a] 1.1(H-3)
C-3	150.0	155.0	7.7(H-5)[a]	1.1–1.5(H-1,H-2,H-4 evidently)
C-4	130.1	159.0	7.1(H-2)[a]	3.4(H-5)[a] 1.0(H-3)
C-5	138.8	157.3		
C-6	141.6	–		
C-7,11	127.8	162.9	7.2(H-11,7)[a]	4.4(H-5)[a] 0.7(H-10,8)
C-8,10	124.0	168.9	4.6(H-8,10)[a]	1.2(H-7,11)[a]
C-9	147.6	–	9.5(H-7,11)[a]	3.5(H-8,10)[a]

[a]From CH-COSY spectrum, optimized to J 7 Hz.

Table 7. ^{13}C Chemical shifts and CH coupling constants (absolute values) of (E)-3-(4-nitrophenyl)propenal (**2**) in CDCl$_3$.

Carbon	δ/ppm	$^1J_{CH}$/Hz	^2J(C,H)/Hz and ^3J(C,H)/Hz	
C-1	192.8	174.6	9.1(H-3)	1.0(H-2)
C-2	131.8	160.8	26.6(H-1)	1.7(H-3)
C-3	148.8	155.1	4.6(H-5,9)[a]	0.8(H-1)
C-4	140.0	–		
C-5,9	129.1	163.8	7.0(H-9,5)[a]	5.0(H-3)[a]
C-6,8	124.4	169.4	4.6(H-8,6)[a]	1.1(H-9,5)[b]
C-7	148.8	–		

[a]From CH-COSY spectrum, optimized to J 5 Hz. [b,a]J(C,H)//Hz.

the terminal carbon (^{13}C) is responsible for the greater Z-vicinal coupling constants, 8.1 Hz in **1** and 9.1 in **2**, compared with 7.1 Hz (C$_4$H$_2$) and 7.7 Hz (C$_3$H$_5$) of similar fragments in compound **1**. These formyl carbon couplings agree well with those reported by Vogeli et al.[14] for propenal and its alkylated derivatives.

In benzene the E-vicinal J(C,H) is 7.6 Hz, but in nitrobenzene and in chlorobenzene the vicinal couplings of substituted carbons are 9.67 and 10.93 Hz, respectively.[15] In compound **1** the corresponding coupling is 9.5 Hz. An opposite effect is observed when the electronegative substituent is on the adjacent carbon on the coupling pathway; vicinal couplings of C-8 (C-10) in **1** and C-6 (C-8) in **2** are both only 4.6 Hz. The corresponding coupling in nitrobenzene is 4.45 Hz and in chlorobenzene is 5.0 Hz.[15] In the former, the coupling between C-3 and H-5 is 8.18 Hz; here the couplings over the olefinic side chain are 7.2 Hz in **1** and 7.0 Hz in **2**.

The ^3J(C,H) coupling of aromatic carbon (C-7, C-11 in **1** and C-5, C-9 in **2**) to the olefinic proton is 4.4 Hz in **1** and 5.0 Hz in **2**. The former is close to the value for styrene,[16] the latter is the same as for toluene.[15]

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