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^{1}H and ^{13}C NMR study of some polychlorobuta-1,3-diene derivatives

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ABSTRACT: Because of the upsurge of interest in polychlorobuta-1,3-diene derivatives as uncommon contaminants in underground water, seven congeners, the three pentachloro- and four tetrachloro- [(*Z*)- and (*E*)-1,1,3,4-tetrachloro-, 1,1,4,4-tetrachloro- and (*Z*,*Z*)-1,2,3,4-tetrachloro]buta-1,3-dienes, were synthesized and their ^{1}H and ^{13}C NMR chemical shifts, $^nJ(^1H,^1H)$ and $^nJ(^{13}C,^1H)$ coupling constants were measured. The ^{13}C NMR spectra were recorded in perdeuteroacetone with and without proton decoupling. In addition, to assign the ^{13}C NMR spectrum of 1,1,2,4,4-pentachlorobuta-1,3-diene, a 2D-INADEQUATE ^{13}C experiment was performed. The present results were compared with literature data on organochlorine compounds and possible conformations are discussed. © 1998 John Wiley & Sons, Ltd.

KEYWORDS: NMR; ^{1}H NMR; ^{13}C NMR; chlorinated organic compounds; polychlorobutadienes

INTRODUCTION

During the last few years in Italy[1] and other western countries,[2,3] a number of cases of underground water pollution by manufacturing by-products or by treatment wastes of chlorinated solvents have been observed. The synthetic reactions follow free radical routes; thus, at the bottom fraction of the rectification column chlorinated unsaturated and aromatic organic compounds accumulate. Although a fraction of them can be recycled, their largest part has to be discarded.[4,5] On the other hand, such compounds, at the ppm level, are allowed to remain as contaminants of the chlorinated solvents. Hence, when they are collected as wastes and rectified for recycling, again an accumulation of pollutants occurs. As a result of these unsatisfactory disposal practices, we now have to manage an undesired legacy of chemicals resistant to biodegradation, whose toxic effects are still unknown.

The composition of the raw mixtures is variable, dependent upon the reaction conditions; in addition to the target compounds there are polychlorobuta-1,3-diene and polychlorobenzene congeners. Our attention was attracted by the former, as they could be used as tracers of pollution. Actually, they are uncommon contaminants and data on their toxicity and environmental behavior are scarce. In addition, not being commercially available, even structural information on the individual congeners is lacking.

Although many ^{1}H and ^{13}C NMR spectra of organochlorine compounds have been published,[6–11] we could not find a systematic approach to the tetra- and pentachlorobuta-1,3-dienes, except for 1,1,2,4,4-pentachlorobuta-1,3-diene.[12]

In this paper, we present the NMR spectra of the three pentachlorobuta-1,3-dienes [(*Z*)- and (*E*)-1,1,2,3,4-pentachlorobuta-1,3-diene and 1,1,2,4,4-pentachlorobuta-1,3-diene] and of four tetrachlorobuta-1,3-dienes [(*Z*)- and (*E*)-1,1,3,4-tetrachlorobuta-1,3-dienes, 1,1,4,4-tetrachlorobuta-1,3-diene and (*Z*,*Z*)-1,2,3,4-tetrachlorobuta-1,3-diene] (Fig. 1). These congeners were synthesized in our laboratory according to published methods. For comparison, NMR spectra of hexachlorobuta-1,3-diene were also collected.

EXPERIMENTAL

Sample preparation

1,1,2,4,4-Pentachlorobuta-1,3-diene (**1**) was prepared by dehydrochlorination on iron(III) trichloride of 1,1,3,3,4,4-hexachlorobut-1-ene.[13] It was purified by rectification and preparative gas chromatography (96%, GC).

The (*Z*)- and (*E*)-1,1,2,3,4-pentachlorobuta-1,3-dienes (**2** and **3**) were isolated and purified by preparative GC, starting from a raw bottom fraction from a trichloroethene plant. The purity of the *Z*- and *E*-isomers was 92% and 98%, respectively. Their identity was confirmed by GC–MS and FTIR spectra.

The (*Z*)- and (*E*)-1,1,3,4-tetrachlorobuta-1,3-dienes (**4** and **5**) were obtained, according to Ol'dekop *et al.*,[14] by dechlorination of hexachlorobut-1-ene, prepared by trichloroethene dimerization.[15] The two resulting isomers were separated by preparative GC. Their purity was 97% and 95% respectively.

(*Z*,*Z*)-1,2,3,4-Tetrachlorobuta-1,3-diene (**6**) was prepared by dechlorination on zinc powder of 1,1,2,2,4,4-octachlorobutane, obtained by dimerization of 1,1,2,2-tetrachloroethane. It is a white crystalline solid (m.p. 53 °C), which was purified by sublimation (99%, GC).

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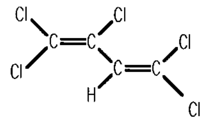

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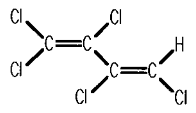

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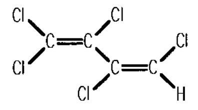

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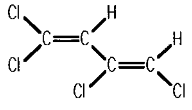

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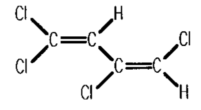

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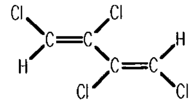

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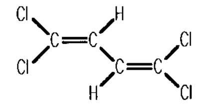

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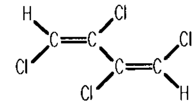

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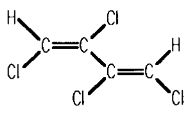

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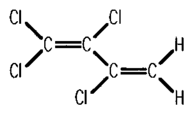

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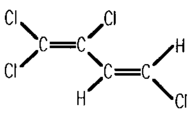

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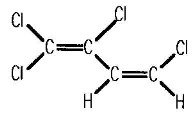

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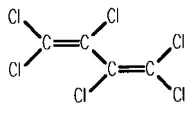

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Figure 1. Molecular structures of the tetra-, penta- and hexachlorobuta-1,3-dienes: 1,1,2,4,4-pentachlorobuta-1,3-diene (**1**), (*Z*)-1,1,2,3,4-pentachlorobuta-1,3-diene (**2**), (*E*)-1,1,2,3,4-pentachlorobuta-1,3-diene (**3**), (*Z*)-1,1,3,4-tetrachlorobuta-1,3-diene (**4**), (*E*)-1,1,3,4-tetrachlorobuta-1,3-diene (**5**), (*Z*,*Z*)-1,2,3,4-tetrachlorobuta-1,3-diene (**6**), 1,1,4,4-tetrachlorobuta-1,3-diene (**7**), 1,1,2,3,4,4-hexachlorobuta-1,3-diene (**8**), (*E*,*E*)-1,2,3,4-tetrachlorobuta-1,3-diene (**a**), (*E*,*Z*)-1,2,3,4-tetrachlorobuta-1,3-diene (**b**), 1,1,2,3-tetrachlorobuta-1,3-diene (**c**), (*E*)-1,1,2,4-tetrachlorobuta-1,3-diene (**d**) and (*Z*)-1,1,2,4-tetra chlorobuta-1,3-diene (**e**). Compounds **1**–**8** were analyzed in the present work.

1,1,4,4-Tetrachlorobuta-1,3-diene (**7**), the sole isomer with this type of substitution, was obtained by thermal decomposition of the sulfolane adduct with copper(II) dichloride in the presence of lithium chloride.[16] The yield was very low (<20%) and the expected compound was purified by rectification and preparative GC (98%, GC).

Hexachlorobuta-1,3-diene (**8**), Merck Uvasol for spectroscopy (98%, GC), was used as received.

Measurements

A 300 μl volume of the liquid congeners were added to 0.5 ml of perdeuteroacetone (Merck). In the case of the solid congener, **6**, 108.45 mg were weighed and dissolved in 0.5 ml of the same solvent. All NMR experiments were performed on a Bruker AM-270 spectrometer, operating at 67.9 MHz for ^{13}C, and equipped with an Aspect-3000 computer. The ^{13}C NMR spectra were obtained with and without proton decoupling using standard pulse sequences. The ^{13}C spectral parameters were as follows: spectral width, 12.8 kHz; recycle delay, 32 s; 128 transients were recorded by using 16K data points, with a spectral resolution of 1.5 Hz; a 1.5 Hz line-broadening factor was applied before Fourier transformation. For sample **1**, the ^{13}C spectral parameters were: spectral width 10.8 kHz, 64K data points for acquisition, zero filled to 128K before Fourier transformation, with a final resolution of 0.166 Hz per point.

The 2D-INADEQUATE ^{13}C experiment was performed with quadrature detection in both dimensions, using an extended Ernst-type phase cycle[17] in order to suppress single quantum peaks and a 120° conversion pulse to maximize the double quantum signals. The spectrum was acquired with a sweep width of 679 Hz over 1K data points, with $\tau = 3.0$ ms, corresponding to $^{1}J(^{13}C,^{13}C) = 83$ Hz. In the t_1 domain 128 traces were acquired (256 scans each) and zero filled to 512 before Fourier transformation; the relaxation delay was 8 s. The spectrum was resolution enhanced with a sine-bell in both dimensions. Chemical shifts were measured from TMS.

RESULTS AND DISCUSSION

^{1}H NMR spectra

Proton NMR spectra were very simple and not very useful for sample recognition, consisting of a singlet for **1**, **2**, **3**, **6** and **7** (the last two due to the presence of a center of binary symmetry) and of two doublets for **4** and **5**, the splitting being due to the long-range coupling constant through four bonds (C=CH—C=C—H) of 1.15 and 1.45 Hz, respectively. Proton NMR parameters are reported in Table 1. Apparently, the resonances of protons in position 1 or 4, *trans* with respect to chlorine, are deshielded (7.07 and 7.35 ppm for **2** and **6**), whereas those of the remaining samples resonate in the range 6.55–6.74 ppm. For **4** and **5** no specific proton assignment was made.

Table 1. Proton chemical shifts (ppm, relative to TMS = 0.0 ppm) and coupling constants (Hz) of seven chloro-substituted buta-1,3-dienes

Compound	No.	Chemical shift (ppm)		$J(^1H, ^1H)$ (Hz)
		This work	Literature	
$CCl_2{=}CClCH{=}CCl_2$	**1**	6.72	—	—
(Z)-$CCl_2{=}CClCCl{=}CHCl$	**2**	7.07	6.58[18]	—
(E)-$CCl_2{=}CClCCl{=}CHCl$	**3**	6.74	—	—
(Z)-$CCl_2{=}CHCCl{=}CHCl$	**4**	6.57 6.71	H-2 = 6.28; H-4 = 6.65[14]	1.15[a]; 1.1[14]
(E)-$CCl_2{=}CHCCl{=}CHCl$	**5**	6.55 6.70	H-2 = 6.30; H-4 = 6.54[14]	1.45[a]; 1.4[14]
(Z,Z)-$CHCl{=}CClCCl{=}CHCl$	**6**	7.35	7.12[19] 7.05[20] 6.93[21]	—
$CCl_2{=}CHCH{=}CCl_2$	**7**	6.67	6.60[16] 6.59[22]	—

[a] This work; absolute values.

^{13}C NMR spectra

^{13}C NMR spectra were acquired with and without proton decoupling. The latter was necessary for spectral assignment, owing to the presence of direct and long-range couplings. Carbon chemical shifts and coupling constants are given in Table 2. Assignments for each compound are briefly discussed below.

Compound 1. The undecoupled ^{13}C NMR spectrum, acquired with high resolution (0.166 Hz per point), showed the presence of four doublets. The doublet at 123.17 ppm was assigned unambiguously to C-3, this carbon being directly coupled to H-3 with $^1J(^{13}C,^1H) = 172.0$ Hz. A second doublet, indicated shaded in the zoom of Fig. 2(a), was centered at 123.59 ppm: its high-field component appears as a shoulder in the resonances centered at 123.54 ppm. As indicated in the zoom [Fig. 2(a)], a splitting of 6.0 Hz could be read. On the basis of considerations applied to the other six samples, we tentatively assigned this doublet to C-1, being coupled to H-3 through three bonds (see later). The two remaining doublets, centered at 123.54 and 129.65 ppm with a 0.3 and 1.6 Hz splitting, respectively, were assigned not specifically to C-2 and C-4. Figure 2(c) shows the unique carbon–carbon AB correlation, $^1J(^{13}C,^{13}C) = 95$ Hz, observed in the INADEQUATE experiment, i.e. the correlation between C-3, unambiguously assigned, and C-2 or C-4. In order to solve this ambiguity, two possibilities were considered: (i) if the correlation was to be assigned to C-2–C-3 (with C-2 assigned to the resonance at 129.65 ppm), we would also expect the correlation C-1–C-2, which is not present in the spectrum; (ii) if the correlation was to be assigned to C-3–C-4 (with

Table 2. ^{13}C chemical shifts (ppm, relative to TMS = 0.0 ppm) and coupling constants (Hz) of eight chloro-substituted buta-1,3-dienes

Compound	No.	Chemical shift (ppm)				Coupling constant $J(^{13}C,^1H)$(Hz)			
		C-1	C-2	C-3	C-4	C-1	C-2	C-3	C-4
$\overset{1}{C}Cl_2{=}\overset{2}{C}Cl\overset{3}{C}H{=}\overset{4}{C}Cl_2$[a]	**1**	123.59	123.54	123.17	129.65	6.0	0.3	172.0	1.6
(Z)-$CCl_2{=}CClCCl{=}CHCl$	**2**	125.51	125.62	127.87	126.24	—	2.9	13.2	200.7
(E)-$CCl_2{=}CClCCl{=}CHCl$	**3**	125.89	123.48	126.42	122.89	—	8.2	1.7	203.2
(Z)-$CCl_2{=}CHCCl{=}CHCl$	**4**	125.68	124.71	128.19	123.31	—	168.7 3.5[d]	13.9[c]	199.1 5.7
(E)-$CCl_2{=}CHCCl{=}CHCl$	**5**	126.01	122.13	128.91	120.22	—	169.0 6.9		201.9 4.4
(Z,Z)-$CHCl{=}CClCCl{=}CHCl$	**6**	123.33	130.12	130.12	123.33	202.0	12.4 3.8	12.4 3.8	202.0
$CCl_2 = CHCH{=}CCl_2$	**7**	125.71	124.03	124.03	125.71	2.5[e]	167.0	167.0	2.5[a]
$CCl_2{=}CClCCl{=}CCl_2$ [b]	**8**	127.17	124.14	124.14	127.17				

[a] In Ref. 12 all chemical shifts (relative to internal chloroform and corrected to carbon disulfide as internal reference) are reported together with $^1J(^{13}C,^1H) = 169.8$ Hz, but only one resonance is unambiguously assigned ($\delta_{C\text{-}3} = 120.1$ ppm), while the other three assignments are doubtful (129.8, 123.7 and 123.4 ppm).

[b] In Ref. 12 chemical shifts are reported without assignment (127.3 and 126.7 ppm), while in Ref. 23 they are assigned via the chlorine isotope effect: C-1 = C-4 = 127.0 ppm and C-2 = C-3 = 124.2 ppm.

[c] ^2J(C-3,H-4).

[d] ^3J(C-2,H-4).

[e] Average value.

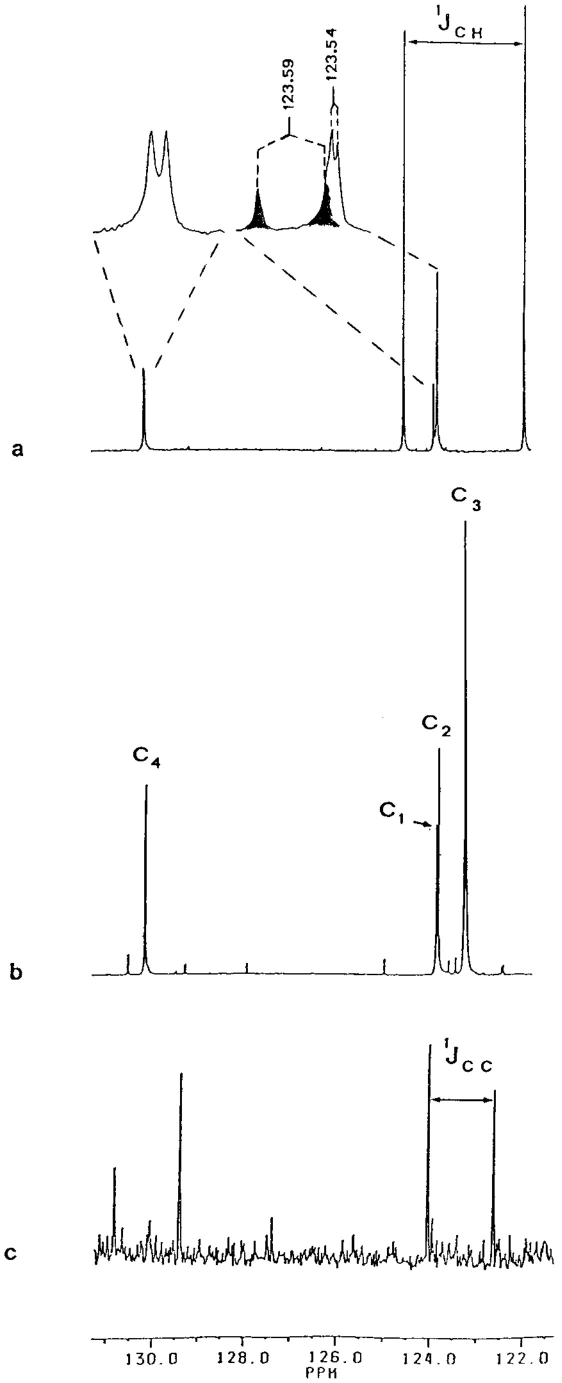

Figure 2. 67.9 MHz ^{13}C NMR spectra of 1,1,2,4,4-pentachlorobuta-1,3-diene in perdeuteroacetone: (a) undecoupled and (b) decoupled spectra are compared with (c) one row of the 2D-INADEQUATE experiment.

C-4 assigned to the resonance at 129.65 ppm), we would not expect other AB correlations in the spectrum, since the C-1–C-2 [$\Delta\delta = 3.4$ Hz $\ll {}^{1}J(^{13}\mathrm{C},^{13}\mathrm{C})$] and C-2–C-3 [$\Delta\delta = 27$ Hz $< {}^{1}J(^{13}\mathrm{C},^{13}\mathrm{C})$] pairs form strongly coupled AB systems which are known to give weak double-quantum signals unless the timing interval τ is specially adjusted.[24] Hence the doublet at 129.65 ppm was assigned to C-4 on the basis of the INADEQUATE experiment, and that at 123.54 was assigned to C-2 by exclusion.

Compound 2. The undecoupled ^{13}C NMR spectrum showed three doublets and one singlet. The doublet at 126.24 ppm was assigned to C-4, due to the large splitting of 200.7 Hz, caused by the direct CH coupling. By comparing the values of this coupling in the two samples examined we can deduce that the value of about 200 Hz is typical of —C=CHCl groups, while the value around 170 Hz is characteristic of —CH=CClX groups, where X could be either Cl or H. This rule was verified for all seven samples: in compounds **2**, **3**, **4**, **5** and **6**, $^{1}J(^{13}\mathrm{C},^{1}\mathrm{H})$ for CH moieties in position 1 or 4 is 200.7, 203.2, 199.1, 201.9 and 202.0 Hz, respectively, and in samples **1**, **4**, **5** and **7** the same coupling for CH moieties in position 2 or 3 is 172.0, 168.7, 169.0 and 167.0 Hz, respectively.

Of the remaining doublets, that at 127.87 ppm, exhibiting a splitting of 13.2 Hz, was assigned to C-3 on the basis of the comparison with $^{2}J(^{13}\mathrm{C},^{1}\mathrm{H})$ of 1,2-dichloroethene,[25] 16 Hz for the *cis* and 0.8 Hz for the *trans* isomer.

The doublet at 125.62 ppm was assigned to C-2 due to the small splitting of 2.9 Hz, characteristic of a $^{3}J(^{13}\mathrm{C},^{1}\mathrm{H})$ in a cisoid conformation. In fact, about the same value (3.5 and 3.8 Hz) was observed for $^{3}J(^{13}\mathrm{C}\text{-}2,{}^{1}\mathrm{H}\text{-}4)$ samples **4** and **6**, in which the relationship between C-2 and H-4 is cisoid, while a larger value (8.2 and 6.9 Hz) was found for the same coupling in **3** and **5**, where the conformation is transoid.

C-1 was assigned by exclusion to the singlet at 125.51 ppm. No measurable $^{4}J(^{13}\mathrm{C},^{1}\mathrm{H})$ was observed for this carbon.

Compound 3. By analogy with what observed for the *Z*-isomer, the undecoupled ^{13}C NMR spectrum of the *E*-isomer showed three doublets and one singlet. The doublet at 122.89 ppm was assigned to C-4, due to the large $^{1}J(^{13}\mathrm{C},^{1}\mathrm{H})$ of 203.2 Hz. Of the remaining doublets, that at 126.42 ppm, exhibiting a splitting of 1.7 Hz, was assigned to C-3, most likely due to $^{2}J(^{13}\mathrm{C},^{1}\mathrm{H})$, known to be small (0.8 Hz) in *trans*-1,2-dichloroethene.[25]

The doublet at 123.48 Hz was assigned to C-2, exhibiting a splitting of 8.2 Hz, characteristic of $^{3}J(^{13}\mathrm{C},^{1}\mathrm{H})$ in a transoid conformation.

The singlet at 125.89 ppm was assigned to C-1 and, again, no measurable $^{4}J(^{13}\mathrm{C},^{1}\mathrm{H})$ was observed for this carbon.

Compound 4. On the basis of the direct CH couplings (168.7 and 199.1 Hz) observed in the undecoupled ^{13}C NMR spectrum, the doublet doublets at 124.71 and 123.31 ppm were assigned to C-2 and C-4, respectively. For C-2 and C-4, the second splitting of 3.5 and 5.7 Hz, respectively, seems to be due to the three-bond couplings with H-4 and H-2, respectively.

C-3 was assigned to the doublet at 128.19 ppm, due to the presence of a $^{2}J(^{13}\mathrm{C},^{1}\mathrm{H})$ of 13.9 Hz with H-4, located in a *cis* double bond.[25]

C-1 was assigned by exclusion to the singlet at 125.68 ppm.

Compound 5. For this isomer the same considerations applied as for **4**. On the basis of the direct CH couplings (169.0 and 201.9 Hz), observed in the undecoupled ^{13}C NMR spectrum, C-2 and C-4 were assigned to the double doublets at 122.13 and 120.22, respectively. The second splittings of 6.9 Hz for C-2 and 4.4 Hz for C-4 are most likely due to the three-bond coupling with H-4 and H-2, respectively. In this isomer the C-3 resonance appears as singlet in the undecoupled ^{13}C NMR spectrum, indicating that $^2J(^{13}C,^1H)$ with H-4 (and H-2) is very small, in good agreement with Mooney and Winson,[25] for a *trans*-substituted double bond.

By comparing **4** and **5**, C-1 and C-3 were tentatively assigned to the singlets at 126.01 and 128.91, respectively.

Compound 6. The undecoupled ^{13}C NMR spectrum showed a doublet at 123.33 ppm for C-1 = C-4 [$^1J(^{13}C,^1H) = 202.0$ Hz] and a double doublet at 130.12 ppm for C-2 = C-3. The splittings of 12.4 and 3.8 Hz correspond to the two possible couplings with H-1 (two-bond coupling) and H-4 (three-bond coupling), respectively. We tentatively assigned the value of 12.4 Hz to $^2J(^{13}C\text{-}2,^1H\text{-}1)$.[25] The smaller splitting of 3.8 Hz can only derive from the three-bond coupling with proton in position 4, $^3J(^{13}C\text{-}2,^1H\text{-}4)$.

Compound 7. The undecoupled ^{13}C NMR spectrum showed a doublet at 124.03 ppm for C-2 = C-3 [$^1J(^{13}C,^1H) = 167.0$ Hz] and a pseudo-triplet (average splitting of about 2.5 Hz) at 125.71 ppm for C-1 = C-4.

Compound 8. The ^{13}C NMR spectrum showed two singlets at 124.14 and 127.17 ppm which were assigned to C-2 = C-3 and C-1 = C-4, respectively, following the results of Buchner and Scheutzow.[23]

In comparison with previous data, analogies and differences appear and they deserve some discussion.

First, qualitatively, proton chemical shifts are as expected from comparison with assignments of other chlorinated buta-1,3-dienes, which, for convenience, are collected in Table 3.

Compared with buta-1,3-diene,[27] as a general rule, the more substituted the compound the larger is the deshielding of the protons, probably caused by the large electronegativity of the chlorine atom. For instance, in tetra- and pentachloro derivatives, δ_H ranges between 6.55 and 7.35 ppm (Table 1), whereas in mono-, di- and trichloro-substituted compounds it lies between 5.07 and 6.88 ppm (Table 3).

The large proton chemical shifts of **2** and **6** are the most evident anomalies and, in our opinion, may be explained by a strong attractive intramolecular interaction between H and Cl (2,4-interaction in **2**, 1,3- and 2,4-interactions in **6**, according to the numbering scheme of **15** in Fig. 3). Following this line of reasoning, for example, Viehe and Franchimont[28] showed that the *Z*-isomer of 1-chlorobuta-1,3-diene is more stable than the *E*-isomer. As a consequence, this hypothesis would imply that **2** and **6** were all predominantly in a planar *s-trans* conformation ($\theta = 180°$), which minimizes the 1,3- or 2,4-distance, or, at most, in a skew conformation with a small dihedral angle (see Fig. 4).

It is known that buta-1,3-diene and most of its simple derivatives exist principally in the planar *s-trans* conformation, i.e. compounds **10–15**, but it is also recognized that steric interactions between bulky substituents in positions 1–3 and 2–4 destabilize this conformation in favor of a skew one, as happens[8] in **8** and **9** (see Fig. 4). Nevertheless, a highly electronegative substituent can generate an attractive interaction with the hydrogen, which would tend to stabilize the planar form. For instance, (*Z*,*Z*)-1,2,3,4-tetrachlorobuta-1,3-diene (**6**), in the solid state,[19] assumes the *s-trans* conformation, but the *E*,*E*-isomer possesses a skew conformation as a consequence of the steric 1,3- and 2,4-repulsions between chlorine atoms,[29] and consistently, in the former the proton chemical shift resonates at 7.35 ppm and in the latter at 6.47 ppm.[22] NMR data on the *Z*,*E*-isomer, if available, would be of help because, according to this reasoning, one proton should be much more deshielded than the other; in fact, in this molecule two competing factors appear: the repulsive 1,3-interaction (Cl···Cl) and the attractive 2,4-interaction (H···Cl). However, it should be noted that the same happens in **2** and the

Table 3. Proton chemical shifts (ppm, relative to TMS = 0.0 ppm) and coupling constants (Hz) of buta-1,3-diene and of some chloro-substituted derivatives (Fig. 3) collected from the literature

		Proton chemical shift (ppm)[b]							
Compound[a]	Ref.	1	1′	2	3	4′	4	^4J_c (Hz)	^4J_t (Hz)
9	8	—	—	6.33	—	5.62	5.69	−1.05	0.0
10	6	—	6.14	6.69	6.69	6.14	—	—	−1.17
11	6	6.17	—	6.33	6.33	—	6.17	−0.69	—
12	6	6.37	—	6.88	6.25	6.03	—	−0.71	−1.19
13	26	6.00	5.59	—	—	5.59	6.00	—	—
14	8	5.07	5.20	—	6.18	5.09	5.59	−0.60	−0.18
15	27	5.14	5.03	6.27	6.27	5.03	5.14	−0.79	−0.86

[a] Compounds are numbered according to Fig. 3.

[b] Proton positions follow the scheme relative to **15** in Fig. 3.

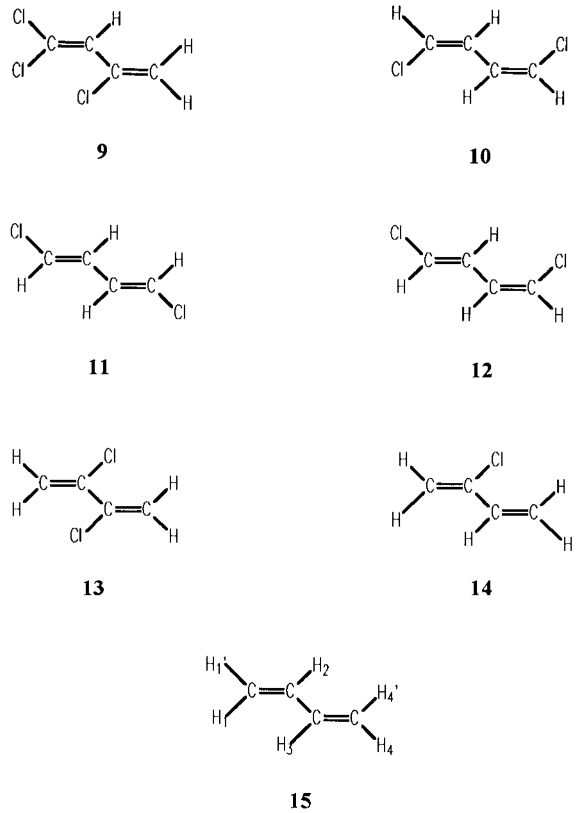

Figure 3. Molecular structures of some chloro-substituted buta-1,3-dienes: 1,1,3-trichlorobuta-1,3-diene (**9**), (*Z*,*Z*)-1,4-dichlorobuta-1,3-diene (**10**), (*E*,*E*)-1,4-dichlorobuta-1,3-diene (**11**), (*E*,*Z*)-1,4-dichlorobuta-1,3-diene (**12**), 2,3-dichlorobuta-1,3-diene (**13**), 2-chlorobuta-1,3-diene (**14**) and buta-1,3-diene (**15**). Numbering scheme of proton positions is illustrated in the structure of buta-1,3-diene.

proton is significantly deshielded ($\delta_H = 7.07$ ppm). Unfortunately, experimental evidence on the favored conformations of molecules such as **2** is lacking, at least to our knowledge, and theoretical results,[30] which would attribute a skew conformation to both **2** and 1,1,2,3-tetrachloro-buta-1,3-diene, may not be conclusive.

Few remarks can be made about H,H coupling constants of **4** and **5**. The $^4J(^1H,^1H)$ values are in good agreement with those in the literature (Table 1) and are qualitatively consistent with data relating to other chlorinated derivatives of buta-1,3-diene (Table 3); for instance, $^4J(^1H,^1H)_t$ is generally greater than $^4J(^1H,^1H)_c$. However, $^4J(^1H,^1H)_c$ in **4** and $^4J(^1H,^1H)_t$ in **5** are substantially larger than analogous couplings in chloroprene (**14**) and dichlorosubstituted butadiene derivatives (**10**–**13**), as appears from Table 3; in contrast, the comparison with **9** gives good agreement in the case of $^4J(^1H,^1H)_c$ values, but a large discrepancy appears in the values of $^4J(^1H,^1H)_t$. At this point, it is worth observing that whereas compounds **10**–**14** are all predominantly in the *s-trans* conformation,[8,28,29] it seems reasonable to assume that **4**, **5** and **9** are all non-planar due to the steric repulsion of chlorine atoms, in analogy with (*E*,*E*)-1,2,3,4-tetrachlorobuta-1,3-diene. Then it is likely that the $^4J(^1H,^1H)_c$ and $^4J(^1H,^1H)_t$ differences among chloro-substituted buta-1,3-dienes stem from both substituent effects, i.e. different numbers of chlorine atoms, and a peculiar dependence of the couplings, and in particular of $^4J(^1H,^1H)_t$, on the dihedral angle.

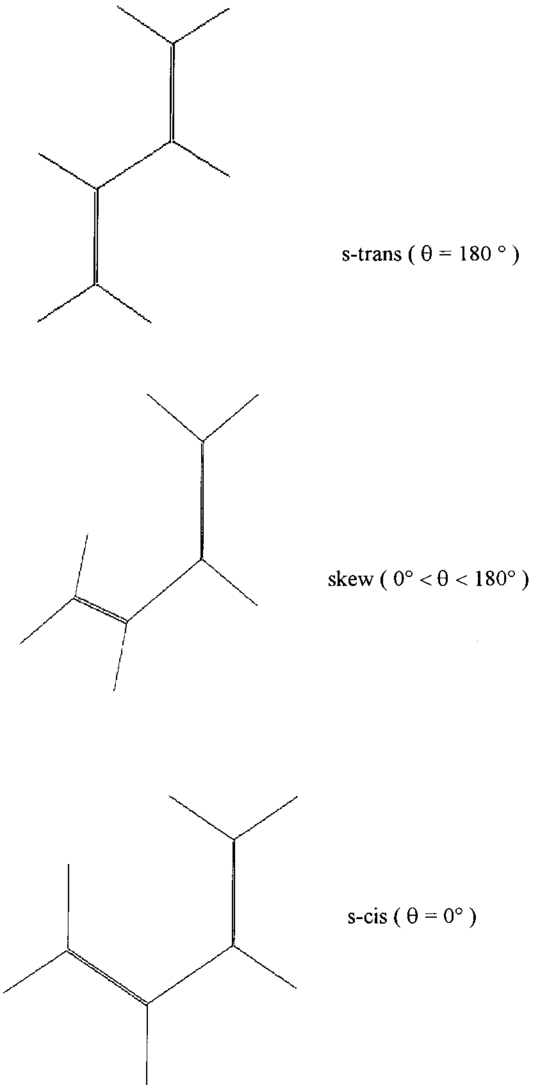

Figure 4. The planar (a) *s-trans* and (b) *s-cis* conformations of buta-1,3-dienes and (c) a possible skew (non-planar) conformation.

Carbon chemical shifts results were available in the literature[12] only for **1** and **8**, among which it is worth noting that chemical shifts of C-3 in **1** and C-2 = C-3 in **8** show a difference of about 3 ppm with respect to our data, probably due to the different solvents used, chloroform in Ref. 12 and acetone in our experiment. The values of the chemical shifts lie in a narrow range, 120–130 ppm, which makes it difficult to find possible correlations among them. It is worth noting that in chlorinated derivatives, C-1 and C-4 are deshielded and C-2 and C-4 shielded, with respect to buta-1,3-diene ($\delta_{C\text{-}1} = \delta_{C\text{-}4} = 117.53$ and $\delta_{C\text{-}2} = \delta_{C\text{-}3} = 137.78$).

More interesting is the regularity, already observed by Hawkes *et al.*,[12] in the values of one-bond ^{13}C–^1H couplings; mean values of terminal (=CHCl) and internal (=CH—) carbon couplings, as calculated from present data (Table 2), are 201.4 ± 1.6 and 169.2 ± 2.1 Hz, respectively, close to the values found by Hawkes *et al.* (202 ± 7 and 174 ± 6 Hz) for a number of compounds different from those analyzed here.

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