Effect of *ortho* substituents on the internal rotation processes and conformational preferences of 1,2-diaryl-1,1,2,2-tetrachloroethanes: a ^1H and ^{13}C NMR variable temperature and X-ray structural study

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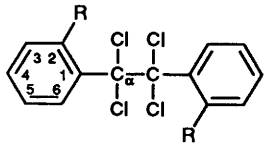
The conformational behaviour of 1,2-diaryl-1,1,2,2-tetrachloroethanes, *ortho,ortho'*-disubstituted with CN (**1**), F (**2**) and CO_2CH_3 (**3**), and of the mesityl derivative (**4**), has been studied in solution by variable temperature ^1H and ^{13}C NMR spectroscopy. The internal rotation processes around the exocyclic C–C and central C–C bonds appear to have similar energy barriers and thus behave differently from the compounds without *ortho* substituents, studied previously, which have a higher barrier for the interconversion of *anti/gauche* conformers. At low temperature, compounds **1–3** exist as mixtures of *gauche* and *anti* conformers with the former prevailing; compound **4** is almost exclusively in the *gauche* form. The solid state crystal and molecular structure has been determined for compounds **2** and **3**. The molecule of compound **2** has point symmetry $\bar{1}$, which defines perfect staggering around the central C–C bond with the aromatic rings *anti*. The structure is affected by statistical disorder due to two alternate orientations of the phenyl rings. The crystal structure of compound **3** indicates one asymmetrical molecule in a *gauche* conformation. Statistical disorder involves both the methoxycarbonyl substituents at the phenyl rings; these latter display almost the same orientation with respect to the $C(sp^3)$ carbons, in both compounds.

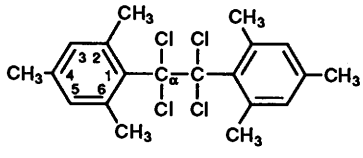
Coupling products of the type $ArCCl_2CCl_2Ar$ are usually obtained in the reaction of $ArCCl_3$ derivatives with iron(II) chloride in anaerobic conditions.[1] This reaction has been tested[2] on several $ArCCl_3$ derivatives, where Ar is a substituted phenyl ring, and reductive coupling produces the main product.

The 1,2-diaryl-1,1,2,2-tetrachloroethanes with a *meta* and *para* CO_2CH_3 substituent exhibit[3] a temperature-dependent ^1H NMR spectrum originating in slow internal rotation processes around the exocyclic $C(sp^2)$–$C(sp^3)$ and the central $C(sp^3)$–$C(sp^3)$ bonds. The rotational barriers of these processes have been measured[3] by means of a ^1H DNMR study. The rotation with the higher barrier is that occurring around the central $C(sp^3)$–$C(sp^3)$ bond, which is nearly 5 kcal mol^{-1} more hindered than that around the $C(sp^2)$–$C(sp^3)$ bond.† The *gauche* conformer has been found[3] to be the more abundant, although theoretical calculations at the semiempirical level indicate that the *anti* conformer is more stable: conformer polarity seems to be responsible for the change in the relative conformer stability of the unperturbed molecules in polar solvents. The *anti* conformation characterizes[3] the solid-state structure of these compounds with the ring in the perpendicular[4] orientation (being the two α-chlorine atoms on the same side of the phenyl ring).

The presence of *ortho* substituents contributes further to the overcrowding of these compounds. In *ortho,ortho'*-dialkyl-substituted benzylidene dichlorides[5] the internal rotation of the dichloromethyl group is fairly restricted with respect to the unsubstituted derivative[6] yet the ground-state conformation retains a nearly planar-type orientation even with *ortho* substituents. In the 1,2-diaryl-1,1,2,2-tetrachloroethanes the presence of *ortho* substituents can modify their conformational behaviour and influence the barrier for internal rotation around the two C–C bonds. Accordingly, we compared the conformational behaviour of the compounds in question with that of the *meta* and *para* substituted derivatives and of the unsubstituted molecule to determine, (*i*) whether the *ortho* substituents influence the *anti/gauche* conformer ratio and the corresponding interconversion barrier, (*ii*) the type of conformer preference involved in the rotation around the exocyclic $C(sp^2)$–$C(sp^3)$ bond and the effect on the interconversion barrier and (*iii*) what structural implications, if any, affect the conformational equilibria of these molecules in solution with respect to the solid state.



1 R = CN
2 R = F
3 R = CO_2CH_3



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The experimental techniques used were: variable temperature ^1H and ^{13}C NMR spectroscopy for the conformational study of molecules **1–4** in solution and X-ray crystal and molecular structure determination for the compounds available in a suitable crystalline form.

Experimental

General procedures for the synthesis of 1,2-diaryl-1,1,2,2-tetrachloroethanes

The appropriate aryltrichloromethane (10 mmol) was dissolved in CH_3CN (40 cm^3) (previously distilled from P_2O_5 in Ar atmosphere); Ar was then continuously bubbled into the solution in order to obtain an inert atmosphere in the reaction

† 1 cal = 4.184 J.

apparatus. $FeCl_2 \cdot 4H_2O$ (30 mmol) was introduced and the mixture stirred for 22 h at room temperature. The reaction was quenched by dilution with water (50 cm^3) and the precipitated organic material was collected by filtration, washed with water and dried. Purification was achieved by crystallization from the solvent. The yields reported below refer to pure isolated products and no attempt was made to maximize the yields by adopting longer reaction times or higher reaction temperatures.

2,2'-(1,1,2,2-Tetrachloroethane-1,2-diyl)bis(benzonitrile) (1). 36%, mp 188–190 °C (benzene) (Found: C, 52.1; H, 2.1; N, 7.6. $C_{16}H_8Cl_4N_2$ requires C, 51.93; H, 2.18; N, 7.57%).

1,1'-(1,1,2,2-Tetrachloroethane-1,2-diyl)bis(2-fluorobenzene) (2). 12%, mp 145–148 °C (ethyl acetate) (Found: C, 47.3; H, 2.1. $C_{14}H_8Cl_4F_2$ requires C, 47.23; H, 2.26%).

Dimethyl 2,2'-(1,1,2,2-tetrachloroethane-1,2-diyl)bis(benzoate) (3). 16%, mp 162–164 °C (ethanol) (Found: C, 49.5; H, 3.2. $C_{18}H_{14}Cl_4O_4$ requires C, 49.57; H, 3.24%).

1,1'-(1,1,2,2-Tetrachloroethane-1,2-diyl)bis(2,4,6-trimethylbenzene) (4). 82%, mp 137–139 °C (decomp.) (acetonitrile) (Found: C, 59.3; H, 5.5. $C_{20}H_{22}Cl_4$ requires C, 59.43; H, 5.49%).

Crystal data and X-ray structure analysis

Intensity data were collected at room temperature on a CAD4 diffractometer, using graphite monochromated Mo-Kα radiation and the ω–2θ scan mode.

Compound **2**: $C_{14}H_8Cl_4F_2$, M = 356.065. Monoclinic, a = 7.648(2), b = 12.539(3), c = 7.657(1) Å, β = 111.58(1)°, V = 682.8(4) $Å^3$ (by least-squares refinement on diffractometer angles for 25 automatically centred reflections, λ = 0.710 69 Å), space group $P2_1/a$ (n° 14), Z = 2, D_x = 1.731 g cm^{-3}, $F(000)$ = 356. Colourless, air stable plates. Crystal dimensions 0.28 × 0.21 × 0.14 mm, μ(Mo-Kα) = 7.94 cm^{-1}.

For data collection, ω scan width was (0.50 + 0.35 tan θ)°, ω scan speed 0.78–4.12° min^{-1}. Of 1859 measured reflections ($2 \leqslant \theta \leqslant 26°$) 874 had $I \geqslant 3\sigma(I)$ and 738 were unique (R_{int} = 0.015), and were used in the structure analysis. An empirical absorption correction based on the Ψ scan [7] was applied to intensities ($0.900 \leqslant T_{factor} \leqslant 0.998$).

The structure was solved by direct methods (SHELX86),[8] and refined through full-matrix least-squares calculations (SHELX76).[9] The structure is affected by statistical disorder due to two opposite orientations of the phenyl ring, which differ by a rotation of about 180° around the C(1)–C(2) bond (Fig. 1) [primed atoms are related to unprimed ones by an inversion centre at the midpoint of the C(1)–C(1') bond]. Disordered atoms at major sites [F(a) and H(7)] have an occupation factor = 0.816(6). Non-H atoms with full or major site occupancy were refined anisotropically, F atoms at minor sites isotropically, but with constraint to bond distance, and H atoms isotropically with a common temperature factor [except H(3) which was placed in a calculated position at a bond distance of 1.0 Å]. The weighting scheme, $1.35/[\sigma^2(F_o) + 0.000\,277\,F_o^2]$, with $\sigma(F_o)$ from counting statistics, gave satisfactory agreement analyses. During refinement, zero weight was assigned to the (040) reflection, which may be affected by secondary extinction. Final R and R_w values are 0.028 and 0.029.

Compound **3**: $C_{18}H_{14}Cl_4O_4$, M = 436.117. Monoclinic, a = 11.359(2), b = 11.176(2), c = 14.840(2) Å, β = 102.79(2)°, V = 1837.2(8) $Å^3$ (by least-squares refinement on diffractometer angles for 25 automatically centred reflections, λ = 0.710 69 Å), space group $P2_1/n$ (n° 14), Z = 4, D_x = 1.576 g cm^{-3}, $F(000)$ = 888. Colourless, air stable prisms. Crystal dimensions 0.22 × 0.17 × 0.15 mm, μ(Mo-Kα) = 5.98 cm^{-1}.

For data collection ω scan width was (0.55 + 0.35 tan θ)°, ω scan speed 0.88–3.30° min^{-1}. Of 4138 measured reflections ($2 \leqslant \theta \leqslant 26°$) 1997 had $I \geqslant 3\sigma(I)$ and 1729 were unique (R_{int} = 0.022), and were used in the structure analysis. Linear and approximate isotropic crystal decay (5.0% during 47.9 h of exposure time) was corrected during processing. Absorption correction was deemed unnecessary.

The structure was solved by direct methods (SHELX86),[8] and refined through full-matrix least-squares calculations (SHELX76).[9] The structure (Fig. 2) is affected by statistical disorder arising from two different orientations for the methoxycarbonyl groups, which differ by a rotation of about 180° around the bonds to the phenyl rings. A value of 0.5 for the site occupation factors of all disordered atoms was found to be satisfactory on the basis of atomic peak heights in Fourier maps and of some attempts at least-squares refinement. All non-H atoms were refined anisotropically, whereas the H atoms were constrained to ride in an ideal position on their bonded atoms, at a bond distance of 1.0 Å with common isotropic B for phenyl or methyl hydrogens. Final R and R_w values are 0.048 and 0.050, respectively.

Scattering factors were from SHELX76.[9] Major calculations were carried out on a VAX 6310 computer. Tables of final fractional coordinates and full lists of bond distances and bond angles have been deposited at the Cambridge Crystallographic Data Centre.‡

NMR Measurements

^1H and ^{13}C NMR spectra were recorded at 400.13 MHz and 100.61 MHz on a Bruker AMX-400 spectrometer equipped with a computer-controlled variable temperature unit (accuracy ± 1 K) in 5 mm probes. [$^2H_6$]Acetone solutions (≈0.05 mol dm^{-3}) and, for compounds **1** and **3**, also [$^2H_1$]chloroform solutions (~ 0.01 mol dm^{-3}) were employed. The solutions were close to the saturation limit. Chemical shifts δ are given relative to Me_4Si. Spectral parameters are: pulse width 90°, 10 ppm spectral width, 32 K data points for ^1H and pulse-width 45°, relaxation delay 0.5 s, 80–160 ppm spectral width, 32 K data points for ^{13}C. ^{13}C NMR data were also obtained from ^1H-detected chemical shift correlation *via* heteronuclear multiple-quantum coherence (HMQC)[10] and ^1H-detected heteronuclear multiple-bond correlation (HMBC)[11] experiments with standard pulse sequences. HMQC parameters: 1–2 ppm spectral width (f2), 512–1024 complex points, 60–100 ppm spectral width (f1), 128–256 t1 increments with 32 scans per t1 value, relaxation and evolution delays 0.5 s and 3.07 ms, respectively. Zero filling in f1 and f2, sine function in f1 and sensitivity function in f2 (LB = 1–2) were applied before Fourier transformation. HMBC parameters: the same as for HMQC but 16–64 scans per t1 value, at 180 and 300 K, respectively, and delay for long-range coupling constants evolution 50 ms.

The nuclear Overhauser effect and exchange spectroscopy with time-proportional phase incrementation (NOESY-TPPI)[12] spectra were obtained with a standard pulse sequence. The parameters were: 0.5 s relaxation delay, 80 ms mixing time, 2.5–4 ppm spectral width, 1024 complex points, 128–256 t1 increments with 8–16 scans per t1 value. A sine function (SSB = 8) was applied in f1 and f2 before Fourier transformation.

Results

Crystal structures

Table 1 contains selected interatomic distances and bond and torsion angles, for both structures: atom numbering refers to Figs. 1 and 2. The molecule of compound **2** has point symmetry $\bar{1}$, which defines perfect staggering around the C(1)–C(1') bond with aromatic rings *anti*. The latter are closely perpendicular to

‡ For details of the CCDC deposition scheme, see 'Instructions for Authors (1995)', *J. Chem. Soc., Perkin Trans. 2*, 1995, issue 1.

Table 1 Selected bond distances (Å), bond angles (°) and torsional angles (°) for compounds **2** and **3** (atom numbering refers to Figs. 1 and 2)[a]

Compound **2**		Compound **3**	
Cl(1)–C(1)	1.785(3)	Cl(1)–C(1)	1.798(6)
Cl(2)–C(1)	1.790(3)	Cl(2)–C(1)	1.802(6)
C(1)–C(1′)	1.581(6)	Cl(3)–C(2)	1.791(6)
C(1)–C(2)	1.523(4)	Cl(4)–C(2)	1.804(6)
F(a)–C(3)	1.329(4)	C(1)–C(2)	1.590(8)
		C(1)–C(3)	1.517(8)
		C(2)–C(13)	1.544(8)
		C(4)–C(9)	1.489(9)
		C(14)–C(19)	1.489(9)
Cl(1)–C(1)–Cl(2)	104.5(1)	Cl(1)–C(1)–Cl(2)	104.2(3)
Cl(1)–C(1)–C(1′)	108.3(3)	Cl(1)–C(1)–C(2)	107.1(4)
Cl(1)–C(1)–C(2)	111.3(2)	Cl(1)–C(1)–C(3)	112.5(4)
Cl(2)–C(1)–C(1′)	107.0(3)	Cl(2)–C(1)–C(2)	107.4(4)
Cl(2)–C(1)–C(2)	110.5(2)	Cl(2)–C(1)–C(3)	108.9(4)
C(1′)–C(1)–C(2)	114.7(3)	Cl(3)–C(2)–Cl(4)	104.4(3)
C(3)–C(2)–C(7)	115.5(3)	Cl(3)–C(2)–C(1)	108.3(4)
F(a)–C(3)–C(2)	122.7(3)	Cl(3)–C(2)–C(13)	110.8(4)
F(a)–C(3)–C(4)	115.3(3)	Cl(4)–C(2)–C(1)	108.8(4)
		Cl(4)–C(2)–C(13)	108.8(4)
		C(2)–C(1)–C(3)	116.0(5)
		C(1)–C(2)–C(13)	115.3(4)
		C(4)–C(3)–C(8)	117.2(6)
		C(14)–C(13)–C(18)	116.7(6)
		C(5)–C(4)–C(3)	119.4(6)
		C(9)–C(4)–C(5)	113.5(5)
		C(19)–C(14)–C(13)	127.7(6)
		C(19)–C(14)–C(15)	112.1(6)
C(2)–C(1)–C(1′)–C(2′)	180	C(3)–C(1)–C(2)–C(13)	−64.4(7)
Cl(1)–C(1)–C(1′)–C(2′)	−55.1(4)	Cl(1)–C(1)–C(2)–C(13)	62.0(5)
Cl(1)–C(1)–C(1′)–Cl(2′)	67.9(2)	Cl(1)–C(1)–C(2)–Cl(3)	−173.3(3)
Cl(2)–C(1)–C(1′)–C(2′)	57.0(4)	Cl(1)–C(1)–C(2)–Cl(4)	−60.4(5)
Cl(1)–C(1)–C(2)–C(3)	−34.8(4)	Cl(2)–C(1)–C(2)–Cl(3)	−61.9(4)
Cl(1)–C(1)–C(2)–C(7)	145.1(3)	Cl(2)–C(1)–C(2)–Cl(4)	51.0(5)
Cl(2)–C(1)–C(2)–C(3)	−150.5(3)	Cl(2)–C(1)–C(2)–C(13)	173.5(4)
Cl(2)–C(1)–C(2)–C(7)	29.5(4)	Cl(3)–C(2)–C(1)–C(3)	60.2(6)
C(3)–C(2)–C(1)–C(1′)	88.5(5)	Cl(4)–C(2)–C(1)–C(3)	173.1(4)
C(7)–C(2)–C(1)–C(1′)	−91.6(5)	Cl(1)–C(1)–C(3)–C(4)	−23.1(7)
		Cl(1)–C(1)–C(3)–C(8)	152.6(5)
		Cl(2)–C(1)–C(3)–C(4)	−138.1(5)
		Cl(2)–C(1)–C(3)–C(8)	37.7(6)
		C(2)–C(1)–C(3)–C(4)	100.6(7)
		C(2)–C(1)–C(3)–C(8)	−83.6(7)
		C(1)–C(2)–C(13)–C(14)	98.7(7)
		C(1)–C(2)–C(13)–C(18)	−86.0(7)
		Cl(3)–C(2)–C(13)–C(14)	−24.6(8)
		Cl(3)–C(2)–C(13)–C(18)	150.6(5)
		Cl(4)–C(2)–C(13)–C(14)	−138.8(6)
		Cl(4)–C(2)–C(13)–C(18)	36.5(7)
		C(3)–C(4)–C(9)–O(1)	−70.0(8)
		C(3)–C(4)–C(9)–O(2)	115.6(7)
		C(5)–C(4)–C(9)–O(1)	109.8(7)
		C(5)–C(4)–C(9)–O(2)	−64.6(7)
		C(13)–C(14)–C(19)–O(3)	−74.4(9)
		C(13)–C(14)–C(19)–O(4)	110.4(8)
		C(15)–C(14)–C(19)–O(3)	104.8(7)
		C(15)–C(14)–C(19)–O(4)	−70.3(8)

[a] ′ = symmetry transformation $1-x, -y, -z$ of the reference coordinates.

the planar –C(2)–C(1)–C(1′)–C(2′)– moiety (Fig. 1) the dihedral angle between mean planes being 88.6°. Being related by an inversion centre, the phenyl rings lie on parallel planes, and Cl atoms bonded to the same C atom are displaced in the same side (above or below) of these planes. It is of interest to note that the same molecular conformation and symmetry requirements have been previously observed for two *para*-substituted 1,2-diphenyltetrachloroethanes.[3,14] Nevertheless, in the present case, the structure was found to be affected by statistical disorder, which arises from two alternative orientations of the phenyl rings differing by a rotation of 180° around the C(sp^3)–C(sp^2) bonds. Major and minor sites have occupancy factors of 0.816(6) and 0.184(6), respectively. A fairly rare C_{Ar}–H • • • F hydrogen bond interaction could play a role in this type of disorder. In fact, interatomic distances involving the F atom of the molecule with lower occupancy [F(b) • • • C(7) = 3.000 Å; F(b) • • • H(7) = 2.23 Å] and the subtended C–H • • • F angle (144°) are consistent with an attractive intermolecular hydrogen bond.[15] The crystal packing is characterized by only a few intermolecular distances less than 3.60 Å, mainly involving the fluorine atom.

The asymmetric unit of compound **3** contains one crys-

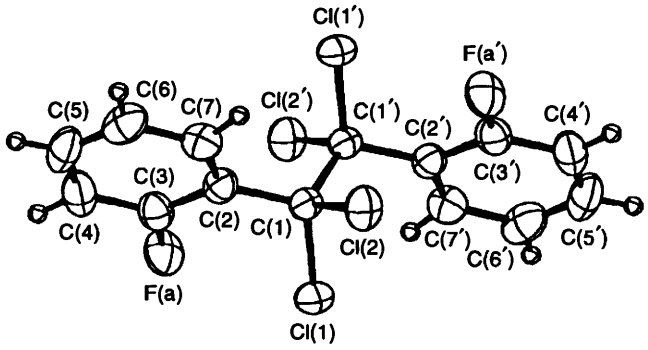


Fig. 1 ORTEP[13] drawing of the molecular structure of compound **2** showing the atom numbering scheme and thermal motion ellipsoids (50%) for non-H atoms

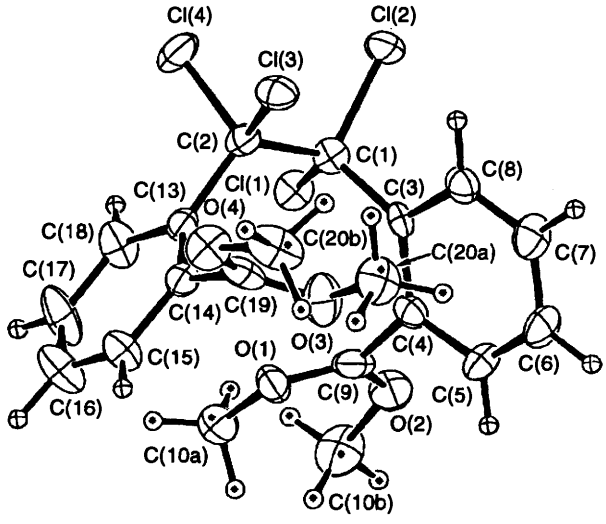


Fig. 2 Atom numbering and thermal ellipsoids (40%) for non-H atoms of compound **3**. Asterisked atoms have alternate half-site occupation factor; oxygen atoms occupy average positions.

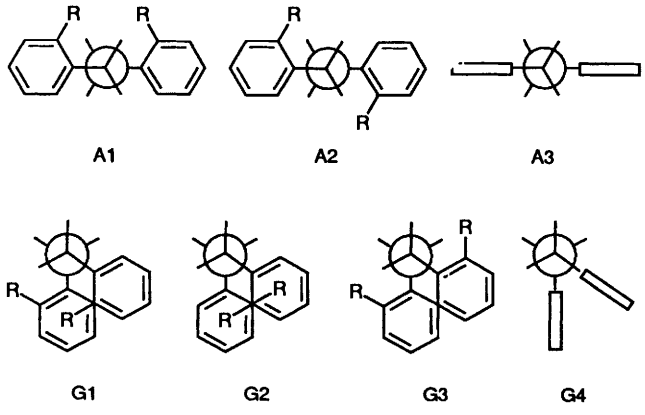
tallographically independent, unsymmetrical molecule. The structure of compound **3**, Fig. 2, is affected by statistical disorder involving both the methoxycarbonyl groups to the same extent. They display two different orientations which arise from a rotation of *ca.* 180° around the bonds to the phenyl rings. As a result, their methyl carbons are equally distributed over two alternative positions (and appear twice in Fig. 2), whereas the carbonyl and MeO oxygens become indistinguishable and their locations are consistent with average positions. Our C–O bond distances are very close to the mean values between C–O and C=O bond lengths in esters.[16] Mean planes through these (disordered) methoxycarbonyl groups make dihedral angles of 62.2° and 70.5° with those of the phenyl rings to which they are bonded. The most interesting structural feature is a *gauche* conformation of the molecule, characterized by a C(3)–C(1)–C(2)–C(13) torsional angle of 64.4(7)°. The existence of *gauche* conformers in 1,2-diaryl derivatives of 1,1,2,2-tetrachloroethane has previously been observed by means of NMR spectra in acetone solution,[3] but never in the solid state. Torsion angles about C(1)–C(3) and C(2)–C(13) show that the phenyl rings have very similar orientations with respect to C(sp^3) carbons. Furthermore, their values compare well with those observed in compound **2** and other 1,2-diaryltetrachloroethanes of known structure.[3,14] The molecular packing of the compounds is characterized by many van der Waals distances of less than 3.60 Å; the shortest ones involve methyl carbons and Cl or O atoms.

As regards bond distances and bond angles involving C(sp^3) carbons, satisfactory agreement between corresponding values in the two compounds is found. Furthermore, the present results confirm the previously observed C–Cl and C–C bond lengthening and bond angle deformations which occur in 1,2-diaryltetrachloroethanes.[3]

NMR spectra and variable temperature results

The ^1H and ^{13}C spectra of the compounds were recorded mostly in [$^2H_6$]acetone solution (owing to the higher solubility compared with [$^2H_1$]chloroform as solvent) and to the lower temperature limit attainable in the former solvent without the samples freezing. Nevertheless, a number of spectra were also recorded in [$^2H_1$]chloroform solution at room temperature. The ^1H and ^{13}C chemical shifts at room temperature were assigned by inspection of the 1D, HMQC[10] and HMBC[11] spectra. The signals were assigned to the different conformers detected at lower temperature by the combined application of several approaches: direct inspection of the spectra, analysis of the integrated areas of the signals, analysis of the NOESY-TPPI spectra, multiplet simulation of parts of the spectra when second-order multiplets are present and by employing the DNMR5 program.[17]

The ^1H and ^{13}C chemical shifts are reported in Tables 2–5 and conformer labelling refers to Scheme 1. For compound **1**, on



Scheme 1 Conformers of compounds **1**–**4** generated in internal rotation around the C(sp^3)–C(sp^3) and C(sp^2)–C(sp^3) bonds (G and A stand for *gauche* and *anti*)

lowering the sample temperature, the ^1H NMR signals became broad, while at 180 K narrow and separate multiplets were observed which correspond to at least four conformers, in different amounts, as can be seen in Fig. 3. Assignments are reported in Table 2. The coalescence temperature is lower than in the corresponding *meta* and *para* isomers of compound **3**, examined previously[3] by us, and freezing of internal rotation around the C(sp^2)–C(sp^3) and C(sp^3)–C(sp^3) bonds seems to occur within the same temperature range.

The ^{13}C spectrum of compound **1** in [$^2H_6$]acetone at 300 K shows the presence of seven signals; that of the CCl_2 carbon is not detected either directly or by the HMBC technique, although, in principle, a cross-peak between 6-H and CCl_2 should be observed owing to the existence of a ^3J(H,C) value of 5 Hz or less. At 180 K the signals of two conformers are clearly evident (Table 2), while those of the other conformers are lost in the noise. A reliable assignment was possible only for the signals appearing between 120 and 114 ppm. In [$^2H_1$]chloroform solution the ^1H and, to a lesser extent, the ^{13}C chemical shifts differ from those in [$^2H_6$]acetone. The most interesting feature in the former solvent is that the signal of CCl_2 was clearly detected at 300 K, conformer interconversion probably being faster in [$^2H_1$]chloroform.

Table 2 ^1H and ^{13}C chemical shifts[a] (δ) at 300 and 180 K, conformer assignments and populations for derivative **1** in [$^2H_6$]acetone

T/K	Conformer assignment[b] and population	3-H	4-H	5-H	6-H
300		7.82	7.74	7.75	8.01
		7.68[c]	7.54[c]	7.65[c]	8.16[c]
180	G2, 48	7.85	7.84	7.97	8.54
		(7.60)	(7.64)	(7.67)	(8.34)
	G1, 43	7.72–8.14	7.85–7.82	8.00–7.63	8.49–6.98
		(7.47–7.89)	(7.65–7.62)	(7.70–7.33)	(8.29–6.78)
	A2/A1, 5	8.18	7.91	8.04	8.45
		(7.93)	(7.71)	(7.74)	(8.25)
	G3, 4	8.15	7.79	7.50	7.00
		(7.90)	(7.59)	(7.20)	(6.80)

T/K	Conformer assignment[b] and population	C-1	C-2	C-3	C-4	C-5	C-6	CN	CCl_2
300[d]		137.7	115.6	137.8	133.0	133.4	135.6	118.4	*e*
		136.9[c]	114.2[c]	136.3[c]	131.9[c]	131.1[c]	134.6[c]	117.1[c]	96.4[c]
180[d]	G2		114.2					117.3	97.7
	G1		114.8–116.2					117.2–120.5	*f*

[a] ^1H Chemical shifts in parentheses are corrected for the substituent effect: see text. [b] According to Scheme 1. [c] [$^2H_1$]Chloroform solution. [d] Only the signals assigned unambiguously are reported. [e] Not observed. [f] Three signals of similar intensities are present at 98.4, 97.7 and 96.0 ppm, and the two first entries most probably belong to this conformer.

Table 3 ^1H and ^{13}C chemical shifts[a] (δ) at 300 and 180 K, conformer assignments and populations for derivative **2** in [$^2H_6$]acetone

T/K	Conformer assignment[b] and population	3-H	4-H	5-H	6-H
300		7.06	7.56	7.22	7.73
		13.14[c]	4.38[c]	0.41[c]	8.10[c]
180	G2, 31	7.05	7.64	7.42	8.14
		(7.35)	(7.64)	(7.67)	(8.14)
	G1, 57	6.94–7.42	7.64	7.42–7.08	8.11–6.89
		(7.24–7.72)	(7.64)	(7.67–7.33)	(8.11–6.89)
	A2/A1, 9	7.47	7.71	7.42	8.11
		(7.77)	(7.71)	(7.67)	(8.11)
	G3, 3	7.42	7.64	6.97	6.75
		(7.72)	(7.64)	(7.22)	(6.75)

T/K	Conformer assignment[b] and population	C-1	C-2	C-3	C-4	C-5	C-6	CCl_2
300[d]		124.5	161.3	118.5	134.8	124.6	135.0	96.6
		6.0[d]	256.5[d]	25.5[d]	9.7[d]	3.7[d]	<0.5[d]	
180[d]	G2	123.9	160.8	118.6	135.8[e]	125.6	135.9	96.7
		5.5[d]	255.2[d]	25.0[d]				6.0[d]
	G1	123.4–124.0	160.8–161.6	118.3–119.3	135.8[e]	125.4–125.1	135.6–133.8	96.7–96.6
		5.8–4.7[d]	255.2–255.7[d]	24.7–25.1[d]				6.2[d]

[a] ^1H Chemical shifts in parentheses are corrected for the substituent effect: see text. [b] According to Scheme 1. [c] ^nJ(H,F) coupling constants in Hz. [d] ^nJ(C,F) coupling constants in Hz. [e] Two signals separated by a very small chemical shift difference (a few tenths of ppm) are present.

Even for compound **2**, the behaviour at different temperatures indicates that the barriers for internal rotation around the exocyclic C(sp^2)–C(sp^3) and central C(sp^3)–C(sp^3) bonds should not differ significantly. At 180 K the internal rotation processes are slow and at least five sites exist for proton exchange. The NOESY-TPPI reveals the principal exchange pattern, and it appears from the relative intensities of the cross-peaks that the rates of exchange are not the same for all the conformers. Direct acquisition of the ^{13}C spectra does not allow the CCl_2 signal to be detected; it is nevertheless observed by the HMBC technique [Fig. 4(*a*)]. An HMBC experiment run at 180 K enabled the contextual assignment of both proton and carbon signals to be performed for the two major conformers [Fig. 4(*b*)]. The existence of long-range correlations of the type between the 6-H, 4-H, 3-H and C-2 of the same phenyl ring, clearly visible in Fig. 4, allowed identification of the protons belonging to the same molecular framework. A TOCSY experiment[18] run at the same temperature presented exchange as well as bond-correlated cross-peaks and was of no help in further disentangling the complex ^1H spectrum.

The spectral behaviour of compound **3** is more complex. The methyl group ^1H signal at temperatures below room temperature behaves in accordance with the presence of two internal processes of the types occurring in the *meta* and *para* isomers,[3] even though freezing of internal motions occurs at a lower temperature in compound **3**. The signals of the CH_3 group at 180 K indicate the presence of at least two conformers (three-site exchange), one more abundant than the other. The spectral region of the ring protons shows broad signals at 180 K which can be assigned by the NOESY-TPPI technique, as reported in Table 4. Besides the rather large chemical shift difference between the two signals of 6-H, 2.2 ppm, in the more abundant conformer, 4-H also shows two separate signals which could be explained by molecular distortions due to the

Table 4 ^1H and ^{13}C chemical shifts[a] (δ) at 300 and 180 K, conformer assignments and populations for derivative **3** in [$^2H_6$]acetone

T/K	Conformer assignment[b] and population	3-H	4-H	5-H	6-H	CH_3
300		7.25 7.16[c]	7.64 7.40[c]	7.38 7.26[c]	7.52 7.49[c]	3.62 3.65[c]
180	G1, 96	7.25–7.49 (6.55–6.79)	7.69–7.52 (7.59–7.42)	7.78–7.13 (7.58–6.93)	8.43–6.23 (8.33–6.13)	3.15–3.80 (3.83)
	A2/A1, 2				8.30 (8.20)	
	G3, 2				6.59 (6.49)	

T/K	Conformer assignment[b] and population	C-1	C-2	C-3	C-4	C-5	C-6	CH_3	CO	CCl_2
300		133.8	137.2	129.8	131.7	129.6	134.0	53.3	170.7	99.2

[a] ^1H Chemical shifts in parentheses are corrected for the substituent effect: see text. [b] According to Scheme 1. [c] In [$^2H_1$]chloroform.

Table 5 ^1H and ^{13}C chemical shifts[a] (δ) at 300 and 180 K, for derivative **4** in [$^2H_6$]acetone

T/K	2,6-CH_3	3-H/5-H	4-CH_3
300	2.34	6.88	2.21
180	2.97–1.46	7.05–6.77 (7.45–7.22)	2.15

T/K	2,6-CH_3	4-CH_3	C-1	C-2/C-6	C-3/C-5	C-4	CCl_2
300	28.2	20.6	134.0	142.2	135.0	140.6	103.3

[a] ^1H Chemical shifts in parentheses are corrected for the substituent effect: see text.

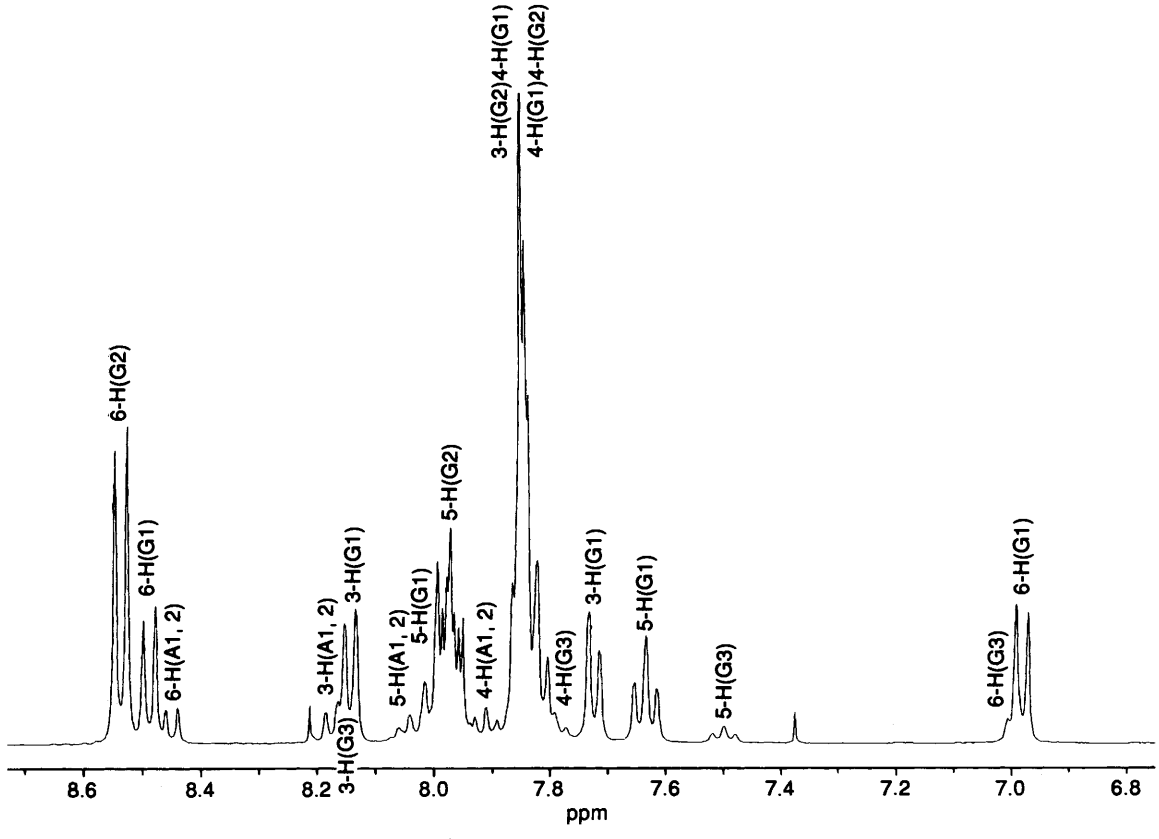


Fig. 3 ^1H Spectrum of derivative **1** at 180 K

severe overcrowding caused by *ortho* substituents. In the X-ray structure of this compound it is observed that the phenyl ring axis through the C(1)–C(4) atoms is not coincident with the axis of rotation of the ring about the C(1)–C(α) bond, and a significant degree of deformation of the ring from planarity is also present. The spectral changes as a function of temperature are qualitatively similar in [$^2H_1$]chloroform solution, at least in the temperature range where it could be followed, and the 6-H signal moves to a higher field as sample temperatures are lowered, as in [$^2H_6$]acetone. This behaviour might be

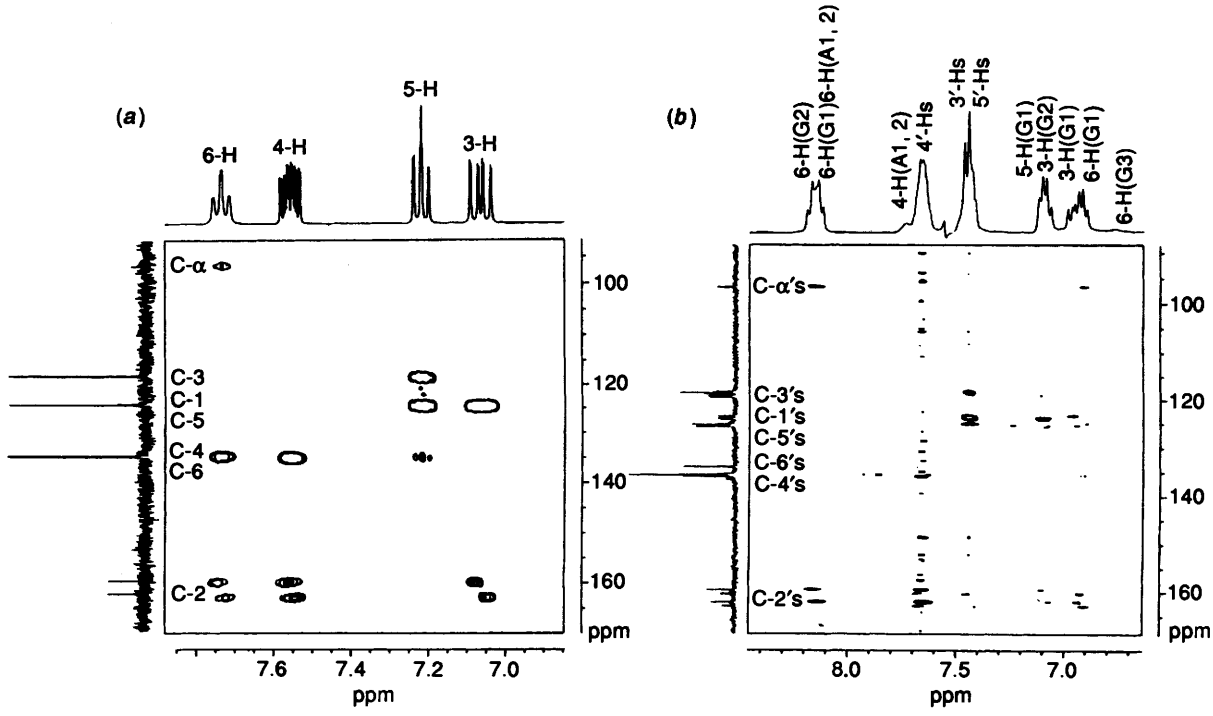


Fig. 4 HMBC Spectra of derivative **2** at (*a*) 300 and (*b*) 180 K

associated with an increase in the population of G1 and G3 conformers at lower temperatures.

The CCl_2 signal is not observed in the ^{13}C spectrum at 300 K and is detected only by the HMBC technique: the signal is stronger at lower temperatures. Signals due to CCl_2 and CO were detected through the long-range correlations with 6-H and 3-H, respectively. In [$^2H_1$]chloroform solution this signal is detected directly at 300 K. The ^{13}C signals at 180 K are broad above coalescence, and faster exchange with respect to compounds **1** and **2** is apparent. The slow exchange already observed in the proton spectrum is nevertheless present. It was not possible in this case to exploit an HMBC experiment at this temperature in order to assign ^1H major signals, nor was a TOCSY experiment any more useful, for the reasons given above. For compound **4**, the ^1H spectrum reveals the presence of only one conformational equilibrium. The *ortho* methyl groups and 3-H, 5-H give only one signal at room temperature: these signals split at low temperatures passing through coalescence (at *ca.* 210 K for the *ortho*-CH_3 groups and 190–200 K for 3-H, 5-H). The signal of 4-Me is not appreciably affected by the temperature being lowered. These results suggest that the internal motion affecting the modification of the observed spectrum is that occurring around the $C(sp^2)$–$C(sp^3)$ bond, and this could occur in either one *gauche* or one *anti* form of a very biased rotation equilibrium around the central bond. The spectral features at low temperature would appear to be consonant with the presence of a predominant *gauche* form.

The complexity of the spectra due to the presence of several multiplets originating from at least three conformers, and the similar magnitudes of the two barriers to internal rotation around the two C–C bonds, did not allow a complete line-shape simulation to be performed at different temperatures in order to estimate the thermodynamic parameters for the internal rotation processes. Simplified procedures were nevertheless applied in order to arrive at approximate estimates of the barriers to conformer interconversion, results being obtained for compounds **3** and **4**. In compound **3**, the spectral behaviour as a function of temperature resembles that found in the corresponding *meta* and *para* isomers,[3] and *anti* $\rightleftharpoons$ *gauche* interconversion appears to affect the observed spectrum. The line-shape of the methyl groups signal at 190–220 K was simulated with the DNMR5 program.[17] A three-site exchange problem was solved: two equally populated sites for the predominant *gauche* conformer and one (7%) for the *anti* form. The aromatic region of the spectrum was also employed to the same end by considering a four-nuclei, two-site exchange within the *gauche* form. The activation energies, E_a, are: for the rotational process around the exocyclic $C(sp^2)$–$C(sp^3)$ bond, 8.5 ± 0.2 kcal mol^{-1}; and for internal rotation around the central $C(sp^3)$–$C(sp^3)$ bond, 8.1 ± 0.6 kcal mol^{-1}. Although these values must be considered rather approximate, the barriers for the two rotational processes are nevertheless very close to each other.

For compound **4**, a two-spin (uncoupled), two-site problem relative to the aromatic protons was solved in the temperature range 180–220 K. The activation energy obtained for rotation around the $C(sp^2)$–$C(sp^3)$ bond is 10.4 ± 0.2 kcal mol^{-1}, the order of magnitude being close to that found[3] in compounds without *ortho* substituents.

Application of the inverse-detection HMBC technique to the systems here studied deserves some comment. It is well known that this technique enhances the relative responses of quaternary carbons with respect to those obtained in a normal ^{13}C one-dimensional spectrum acquired with the same short relaxation delay. A further improvement can be expected on the basis of what has been observed when the inverse-detection HMQC technique is applied to a system undergoing chemical exchange:[19] the relative line-width of ^{13}C resonances, which appears broad in the one-dimensional spectrum, is improved in the HMQC spectrum. The latter effect can play an important role in the detection of the CCl_2 signals at 300 K in derivatives **2** and **3**, yet it is difficult to understand why this signal does not appear in the HMBC spectrum of derivative **1** at the same temperature.

HMBC also yielded better results than a TOCSY experiment[18] when a system was below the coalescence temperature both in the f1 and in the f2 part of the two-dimensional

Table 6 Ranges of substituent independent (see text) ^{1}H chemical shifts (δ) of *gauche* and *anti* rotamers of 1,2-diphenyl-1,1,2,2-tetrachloroethanes[a]

	2-H	3-H	4-H	5-H	6-H
anti	7.89–8.32	7.61–7.81	7.40–7.49	7.61–7.81	7.89–8.32
gauche	7.88–8.33	7.64–7.82	7.36–7.81	7.18–7.46	6.01–6.75

[a] 6-H in the *gauche* form is under the screening influence of the adjacent phenyl ring.

spectrum, as occurs for derivative **2** at 180 K, thus allowing identification of the protons belonging to the same molecular framework.

Discussion

A feature which appears to distinguish the *ortho*-substituted derivatives of 1,2-diaryl-1,1,2,2-tetrachloroethanes from their isomers without *ortho* substituents is the height of the barriers for internal rotation. In the compounds here examined the barriers for rotation around the C(sp^2)–C(sp^3) and C(sp^3)–C(sp^3) bonds are close to each other and of the order of 8–10 kcal mol^{-1}, while in their *meta* and *para* isomers a higher barrier, 13–14 kcal mol^{-1}, was found for the internal rotation around the central C–C bond. Thus, *ortho* substituents lower the barrier for rotation around the central C–C bond and only slightly affect that around the C(sp^2)–C(sp^3) bond, at least between the orientations of the *gauche* conformers that could be observed (from two perpendicular orientations of the phenyl ring with the *ortho* substituents in opposite directions).

Rotation around the two C–C bonds generates a number of ground state conformations, the most significant being depicted in Scheme 1: G1–G3 and A1,A2 of perpendicular type and A3,G4 of planar type. The latter are a series of conformations with different orientations of the *ortho* substituents. The planar type conformations are expected to be of higher energy than the perpendicular ones owing to the coplanarity of the central C(sp^3)–C(sp^3) bond with the phenyl ring. These conformations were found[3] to be insignificant for the *meta* and *para* substituted derivatives. Furthermore, the X-ray solid-state structures of compounds **2** and **3** show that these adopt the perpendicular conformation. Accordingly, conformations A3 and G4 were not considered among the number of significative conformers of compounds **1–4**.

The ^{1}H and ^{13}C chemical shifts measured at low temperature allow a reasonable assignment of the rotational conformers detected in the NMR spectra.

A direct comparison of the ^{1}H chemical shifts of the rotamers is rather tricky owing to the effect of *ortho* substituent(s) on chemical shifts. We have therefore tried to achieve ranges of chemical shift values characteristic of one particular proton in one conformer, independent of substituent effects. The ranges reported in Table 6 are obtained from the ^{1}H chemical shifts[3] of the *anti* and *gauche* conformers of the *meta* and *para* isomers of compounds **1** and **3** and of the 3,3′-bis(pyridine) derivative by employing substituent contributions in an additive fashion.[20] For the protons in position 2 and 6, and those in positions 3 and 5, a clearly different range in the *gauche* conformation is evident and reflects the effect of the ring current contribution of the other phenyl ring. The experimental chemical shifts observed at low temperature for the different rotamers of compounds **1–4**, corrected for the substituent effect and reported in Tables 2–5 in parentheses, can thus be employed for conformational assignments. Allowing for the qualitative character of substituent-effect additivity on chemical shifts, the conformer assignments for compounds **1–4** and the ranges of chemical shift values reported in Table 6 show an acceptable consistency. For the *anti* form, present in small amounts, the A2/A1 configuration cannot be deduced from ^{1}H spectra: in a polar solvent, the more polar A1 form (expected from bond-moment composition) should become more abundant. The rather large amount of conformer G2 in compounds **1** and **2** (Tables 2 and 3), which is apparently the most sterically hindered, is rather surprising. The assignment seems, nevertheless, to be confirmed by the fact that the resonances of C-2 and that of the CN group for compound **1**, in the conformer G1, are split, that at higher field being close to that of the conformer G2: the substituent in one of the phenyl rings of the conformer G1 is oriented like those of the conformer G2. The same conclusion probably applies to the ^{13}C chemical shift of CCl_2 as well.

The presence of the CO_2CH_3 group in derivative **3** should, in principle, lead to further complications owing to the additional conformational requirements of this group. The X-ray structure of this molecule in the solid state shows that the CO_2CH_3 groups are oriented with their planes almost perpendicular to that of the phenyl ring, and this is also likely to be the case in solution since the ^{1}H chemical shifts of compound **3** (Table 4) are systematically at a higher field (particularly that *ortho* to the CO_2CH_3 group) than expected not only from the substituent effect of this group but also by comparison with those of the corresponding *meta* substituted derivative.[3] For this compound, one conformer is predominant and detection of the signals of the other conformers is problematical. The methyl group resonates at 3.62 ppm, *i.e.* at higher field than in the *meta* derivative[3] (3.84 ppm), and this agrees with the predominant presence of the *gauche* form, where one of the methyl groups should be screened by the second phenyl ring.

For compound **4**, the results of NMR spectra point to the almost exclusive presence of one conformer, the different chemical shifts of 3-H and 5-H, and of the *ortho* methyl groups at low temperature, indicating one conformer of the *gauche* type. In benzylidene dichlorides, *ortho*-disubstituted with two methyl groups, the ^{1}H and ^{13}C chemical shifts measured[5] at low temperature are consistent with a frozen conformation of nearly planar type, yet their values show a markedly different trend with respect to those of compound **4**. In the latter, the chemical shift difference between the two *ortho* methyl groups is far higher (1.51 *vs.* 0.35 ppm), as is that between 3-H and 5-H (0.28 *vs.* 0.14 ppm). Furthermore, in compound **4** the ^{13}C chemical shifts of the C-2/C-6 is at 7.5 ppm higher field with respect to C-4, but only 0.6 ppm in the benzylidene dichloride.[5] In compound **4**, the *gauche* conformation of the G1–G3 type, where one methyl group is screened by the second phenyl ring, seems to us to be preferred.

In compounds **1–4** the *gauche* conformations appear to be preferred, in solution, over the *anti* ones. The same kind of conformer preference was found previously[3] for the derivatives of 1,2-diaryl-1,1,2,2-tetrachloroethane without *ortho* substituents. In polar solvents, this preference seems to be due to the more polar character of the *gauche* conformer, since, at least for the derivative without *ortho* substituents, the *anti* conformer is more stable as a free molecule. This conclusion was derived[3] from theoretical semiempirical calculations.

Energy calculations for the molecules in question with the semiempirical AM1/MNDO method[21] have also been performed[22] but the findings do not afford any reliable evidence enabling conclusions regarding conformations to be drawn. A large number of energy minima is found in the potential energy surface calculated as a function of the internal rotation degrees of freedom. Sets of these minima have very similar energy values and correspond to conformers with different dipole moments: an order of stability referring to the molecules in solution and compared with the experimental relative stability of the conformers must therefore be open to question.

Tetrasubstituted ethanes were investigated by Rüchardt and co-workers[23] using force field (MM2) calculations:[24] experimental rotational barriers, conformational equilibria and dipole moments were found to be satisfactorily reproduced by this empirical approach. Information was also obtained[23] on the degree to which internal strain affects the thermal stability of these molecules. From tests carried out on polychlorinated ethanes within the framework of the force-field method[25] we found poor agreement between the calculated and experimental heats of formation of these molecules and concluded that the method was unlikely to afford reliable insight into the complex conformational problems associated with compounds **1–4**. The useful qualitative information obtained from AM1/MNDO and force-field calculations (MM2) is that the *gauche* conformers have dipole moments higher than the *anti* forms and the former should thus be favoured in solution. For compound **3** the CO_2CH_3 group is not coplanar with the aromatic ring and, in the different conformers of this molecule, the dihedral angle between their planes ranges between 60 and 80°, in agreement with the result of the X-ray structure determination and in line with the interpretation of the ^1H chemical shifts. Finally, for compound **4**, the *gauche* conformer of perpendicular type turns out to be 2.5 kcal mol^{-1} more stable than the other conformers, and this form is the one expected to be the most populated even in solution, as in fact concluded from the interpretation of the NMR results.

Comparison of the conformational behaviour of these molecules in solution and their solid-state molecular structure shows the perpendicular orientation of the rings to be a feature in common. The conformation in the solid state is mainly dictated by packing requirements, and the different rotamer found for compounds **2** and **3**, A and G, respectively, should indicate that there is no great energy difference between *gauche* and *anti* conformers: in compound **2** the *anti* form seems to be stabilized by intermolecular H • • • F interactions. A shift of the conformational equilibrium toward the *gauche* forms in polar solutions thus seems quite likely, as is favoured on statistical grounds by their chiral character. In compound **3**, moreover, the disorder characterizing the CO_2CH_3 groups would appear to indicate that different orientations of this group, below and above the phenyl ring, do not differ greatly in energy.

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