The Influence of Steric Constraints on the Conformational Properties and on the ^{17}O NMR Shielding of *ortho*-Substituted Perbenzoates

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The ^{17}O chemical shifts and band widths for *tert*-butyl peresters of *ortho*-substituted benzoic acids have been measured in benzene solution. Two signals are observed, of different line-width, and that at higher field is broader. The two signals shift to lower field with an increase in the number and size of *ortho* substituents (methyl and *tert*-butyl groups were chosen), and the signal at lower field is the one more significantly affected. Correlations with a fair degree of linearity are found for each set of chemical shifts with the twist angle of the carbonyl group from the phenyl plane. Twist angles were calculated from molecular mechanics. From the screening constants estimated theoretically at a semi-empirical level with the Karplus–Pople formula and from line-width arguments based on quadrupole relaxation, it is possible to advance the reasonable conclusion that the signal at lower field of these molecules represents two oxygen nuclei [those of the C(O)–O group] and the other the remaining peroxidic oxygen. For the 2,4,6-tri-Bu^t derivative which is solid at room temperature and can be obtained in a suitable crystal form, the crystal and molecular structure has been determined by X-ray diffraction. The structure is built up of one crystallographically independent molecule, affected by statistical disorder due to two alternative orientations of all the *tert*-butyl groups bonded to the ring. The peroxycarboxyl group is planar and nearly perpendicular (80.8°) to the benzene ring plane.

Chemical and structural properties of organic peroxides have been studied in view of the importance of these molecules in several branches of chemistry.[1] Among them, organic peresters are widely used as initiators of free radical reactions.[2] A commonly accepted interpretation[2] of this reactivity assumes a rate-determining step in which O–O bond cleavage occurs, followed by reactions before and after radical diffusion. Substituted *tert*-butyl perbenzoates decompose[2] in cumene at 100 °C yielding the corresponding acid as one of the products: a large rate enhancement is caused by *ortho* substituents. Destabilization of the ground-state due to the twisting of the carboxyl group out of conjugation with the ring should be at the origin[2] of the increase in rate constants.

The degree of twist of the carboxyl group out of the phenyl plane caused by *ortho* substituents has been monitored by ^{17}O NMR measurements[3,4] in substituted benzoic acids, esters and amides. Almost linear correlations were found to hold between the ^{17}O chemical shifts and the twist angle determined either experimentally or from calculations.

Among organic peroxides, peroxyesters have been least investigated as regards their structural properties.[5] Esters generated from primary and secondary alkyl hydroperoxides have proved to be particularly unstable, yet tertiary alkyl hydroperoxides are comparatively stable.[6] Up to now, only two structure determinations of perbenzoic acid derivatives have been performed[7] and only a few structures of other organic peroxy acids or esters are known.[8] This is undoubtedly due to the chemical and thermal instability of such compounds, and to the intensity decay which often occurs when their crystals are exposed to the X-ray radiation.[8] As regards ^{17}O NMR measurements, organic cyclic and acyclic peroxides have been investigated[9–11] and conformational behaviours derived. A relatively smaller number of ^{17}O NMR measurements for *tert*-butyl esters of carboxylic acids can be found in the chemical literature[12] and systematic studies are lacking. In the spectra of these molecules only two oxygen nuclei are detected and this recalls a peculiarity of dibenzoyl[13] and diacetyl[12] peroxides which show only one ^{17}O resonance, assigned[13] to the carbonyl oxygen.

The effects of bulky *ortho* substituents on the ^{17}O chemical shifts of the different oxygen nuclei of peroxyesters of benzoic acid seem to have been neglected hitherto. These studies may provide, however, useful information on the conformational properties of these molecules. In this paper we report a conformational study on a number of *ortho*-substituted *tert*-butyl perbenzoates, based on ^{17}O NMR measurements and on geometrical features derived from empirical (MM2)[14] calculations and estimated screening constants from semi-empirical MO (AM1/MNDO)[15] wave functions. For the 2,4,6-tri-Bu^t-perbenzoate, which is solid at room temperature, an X-ray crystal and molecular structure determination was also carried out. Rather surprisingly, this compound is very stable to the X-rays, thus enabling a satisfactory accuracy in structure determination, although its crystal structure is affected by statistical disorder problems.

Experimental

Compounds.—Commerical *tert*-butyl perbenzoate (**1**) (Aldrich, 98%), di-*tert*-butyl peroxide (**8**) (Aldrich, 98%), and *tert*-butyl peracetate (**10**) (K & K Lab., 75% soln. in benzene) were used without purification. Dibenzoyl peroxide (**6**) (Aldrich, 97%) was purified by a literature method.[16] *m*-Chloroperbenzoic acid (**7**) (Merck, *ca.* 70%), containing water (*ca.* 25%) and *m*-chlorobenzoic acid (*ca.* 5%), was purified as follows. A CH_2Cl_2 solution of product (10 g) was washed with water containing a few drops of 10% NaOH and then with water. After drying ($MgSO_4$) the solution was reduced to *ca.* 50 cm^3 and subjected to crystallization at 0 °C. The precipitate was filtered and left overnight in a vacuum desiccator in the presence of P_2O_5, affording 3.41 g of peroxyacid, m.p. 90–92 °C (decomp.) [lit.,[16] m.p. 92–94 °C (decomp.)].

The synthesis of *tert*-butyl *o*-methylperbenzoate (**3**),[2,17] *tert*-butyl 2,4,6-trimethylperbenzoate (**3**),[2,18] *tert*-butyl *o-tert*-

butylperbenzoate (**4**),[19] *tert*-butyl 2,4,6-tri-*tert*-butylperbenzoate (**5**),[2] and *tert*-butyl perpivalate (**11**)[20] implies the reaction of an appropriate acyl chloride with *tert*-butyl hydroperoxide in the presence of a base, sometimes under anhydrous conditions.[2,19,20] We found it convenient to perform this reaction in a two phase system (benzene/water) in the presence of a phase transfer catalyst. The yields were generally high, sometimes nearly quantitative, in the pure isolated product. The physical and spectroscopic (IR, ^{1}H NMR) properties were in agreement with the expected structure and with those reported. The following is an example of the experimental conditions used.

tert-*Butyl* o-tert-*butylperbenzoate* (**6**). A solution of NaOH (3.6 g, 90 mmol) in water (39 cm^3) was prepared in an open flask and cooled to 0 °C. *tert*-Butyl hydroperoxide (Merck, 70% soln. in water, 6.38 g, 90 mmol) and methyltricaprylammonium chloride [aliquat 336 (0.67 g, 1.6 mmol)] were added, followed by dropwise addition (*ca.* 30 min) of a solution of *o-tert*-butylbenzoyl chloride[21] (6.5 g, 38 mmol) in dry benzene (90 cm^3) under efficient magnetic stirring at 0 °C. The stirring was continued overnight allowing the mixture slowly to reach room temperature. Diethyl ether was added and the separated organic phase was washed with ice-cold 10% aqueous NaOH, then with cold saturated aqueous NaCl solution. The combined aqueous phases were extracted with diethyl ether before being discarded. After drying ($MgSO_4$), the solvent was removed *in vacuo* from the combined organic solutions. The crude product on TLC [SiO_2, light petroleum (b.p. 30–40 °C)/diethyl ether 90:10] showed a single spot under the UV lamp and a single IR absorption in the 1700–1800 cm^{-1} region.[19] Purification was achieved by column chromatography [SiO_2, light petroleum (b.p. 30–40 °C)/diethyl ether 95:5] (or by high-vacuum distillation in the case of more volatile peroxyesters). The fractions containing the peroxyester were combined and dried ($MgSO_4$). Removal of the solvent *in vacuo* (last traces at 0.05 mmHg) afforded a colourless viscous oil (7.5 g, 91%); n_D^{24} 1.5005; ν_{max}(neat)/cm^{-1} 1770 (C=O) (lit.,[19] 1762); δ_H($CDCl_3$) 1.38 (9 H, s, *o*-Bu^t), 1.41 (9 H, s, O-Bu^t), 7.20–7.50 (4 H, m, ArH).

tert-*Butyl* 2,4,6-*tri*-tert-*butylperbenzoate* (**5**) *for X-ray analysis*. The product obtained after column chromatography (by the procedure described above, from 2,4,6-tri-*tert*-butylbenzoyl chloride)[22] had m.p. 127–128 °C (decomp.) [lit.,[2] 127–128 °C (decomp.)]. A fraction was dissolved in warm light petroleum (b.p. 30–40 °C) and the solvent left to evaporate slowly at room temperature, affording a crystalline residue (m.p. unchanged) from which a suitable crystal for X-ray analysis could be selected.

4,4,5,5-*Tetramethyl*-1,2-*dioxolan*-3-*one* (*tetramethylperoxypropiolactone*) (**9**).[23,24] This was obtained according to a literature method.[23]

X-Ray Structure Determination of Compound **5**.—*Crystal data*. $C_{23}H_{38}O_3$, $M = 362.551$, monoclinic, $a = 10.167(1)$, $b = 10.773(2)$, $c = 10.843(2)$ Å, $\beta = 102.85(1)°$, $U = 1158(1)$ Å^3 (by least-squares refinement on diffractometer angles of 25 automatically centred reflections, $\lambda = 0.710\,69$ Å), space group $P2_1$ (No. 4), $Z = 2$, $D_c = 1.04$ g cm^{-3}, $F(000) = 400$. Colourless, air-stable prisms were obtained. Crystal dimensions 0.35 × 0.30 × 0.15 mm, μ(Mo-Kα) = 0.37 cm^{-1}.

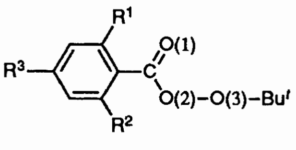
Data collection and processing. CAD4 diffractometer, ω–2θ mode with ω scan width = $(0.70 + 0.35 \tan\theta)°$, ω scan speed 1.1–5.5° min^{-1}, graphite-monochromated Mo-Kα radiation: 2780 reflections measured ($2.0 \leqslant \theta \leqslant 27.0°$, $\pm h$, $+k$, $+l$) giving 1608 with $I \geqslant 3\sigma(I)$; 1527 unique (merging $R = 0.021$) used, after absorption correction based on empirical ψ scan[25] ($0.94 \leqslant T$ factor $\leqslant 0.99$), in the structure analysis. The intensities of two standard reflections measured at 1 h intervals showed no significant changes.

Structure analysis and refinement. Direct methods (SHELX 86)[26] followed by full-matrix least-squares refinement (SHELX 76).[27] During refinement, anomalously large thermal parameters and residual peaks in ΔF maps showed evidence of statistical disorder, as a result of two alternative orientations for all the three *tert*-butyl groups bonded to the benzene ring. Least-squares refinement of their occupancy factors led, for the majority sites, to the values of 0.87(1), 0.83(1) and 0.76(1), which, in the final stage of refinement, were held fixed. Non-hydrogen atoms with full or higher site occupancy were refined anisotropically; those at minor sites, which could only be poorly defined, isotropically. All hydrogen atoms bonded to carbons with full or major occupancy were located in ΔF maps, and then fitted at ideal positions, at a bond distance of 1.0 Å, and treated as fixed contributors. Those bonded to carbons at minor sites were not included in the calculations. The weighting scheme $w = 1.0/[\sigma^2(F_0) + 0.002\,76\ F_0{}^2]$, with $\sigma(F_0)$ from counting statistics, gave satisfactory agreement analyses. Final R and R_w values were 0.046 and 0.055. No attempts were made to determine the chirality of the crystal. Scattering factors from SHELX 76.[27] Calculations carried out on a VAX 6310 computer.

NMR Measurements.—The ^{17}O NMR spectra were recorded on a Bruker AMX 400 WB spectrometer at 54.244 MHz, at a probe temperature of 303 K. The samples were prepared by dissolving the compounds in a mixture of [$^2H_6$]benzene/[$^1H_6$]benzene (1:3) as a solvent: nearly saturated solutions were obtained in the range of concentration 1–1.5 mol dm^{-3}. The reference was D_2O as an external standard. The spectra were obtained with a spin-echo sequence of the type: 90_x–τ–180_x–τ–FID, by choosing a 31 500 Hz spectral width. The acquisition parameters were the following: pulse-width (90°) = 16.4 µs, time domain points = 1024, acquisition time = 16 ms, delay τ = 50 µs, recycle time = 50 ms, number of scans = 64.000. For signal elaboration no line-base correction was introduced and an enhancement multiplication factor LB = 50 Hz was employed. For some of the compounds the spectra were also recorded in solvents other than benzene, such as [$^2H_6$]acetone and [$^2H_1$]chloroform, by employing the same experimental procedure. Calculations were also performed on IBM AIX/RS 6000 and INTEL 80386SX elaborators.

Results

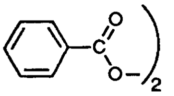
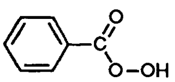
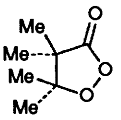
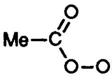
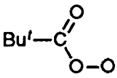
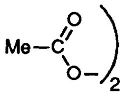
^{17}O *NMR Results*.—Measurements were carried out on compounds **1**–**5**, represented by the general formula:



1; $R^1 = R^2 = R^3 = H$
2; $R^1 = Me$, $R^2 = R^3 = H$
3; $R^1 = R^2 = R^3 = Me$
4; $R^1 = Bu^t$, $R^2 = R^3 = H$
5; $R^1 = R^2 = R^3 = Bu^t$

The chemical shifts of ^{17}O nuclei and line-widths at half height measured at 54.244 MHz are reported in Table 1 and refer to benzene solutions. Two signals are observed for all derivatives except for compound **5**, which shows only one very broad resonance in this solvent: two signals of smaller line-width appear in acetone solutions. The larger molecular size of compound **5**, with respect to the other molecules, slows down molecular reorientation and the resonance lines are broader:[28] by lowering the viscosity of the solvent, on passing from benzene

Table 1 ^{17}O NMR chemical shifts[a] (ppm from external D_2O) measured at 54.244 MHz in benzene solution for a number of *ortho*-substituted *tert*-butyl perbenzoates. Values for reference compounds are also reported.

Molecule	Chemical shifts		
1	344 (540)	297 (1700)	
	330^b (598)	285^b (1296)	
	348^c (488)	298^c (720)	
2	363 (518)	300 (1110)	
3	382 (739)	305 (1232)	
4	382 (776)	303(1800)	
5	395 (very broad)		
	397^c (1200)	310^c (2500)	
Reference compounds			
6 	345 (730) 350^c (480) 339.5^d		
7 	320 (330)	275(1300)	
8 Bu^t—O—O—Bu^t		271^c (490) 269^b (558) 260^e (340)	
9 	345.6^c (400)	328.9^c (125)	322.7^c (240)
10 	365.5 (271)	338.7 (616)	299.7 (407)
11 	352.3 (320)	335.1 (650)	298.8 (580)
12 	327^f (800)		

[a] In parentheses, are reported the line-widths (Hz) of the signals. These contain a 50 Hz component from the data processing. See Experimental section. [b] $[^2H_1]$Chloroform solution. [c] $[^2H_6]$Acetone solution. [d] Ref. 13, $[^2H_1]$chloroform solution. [e] Ref. 9, benzene solution at 36.54 MHz. [f] Ref. 12, at 27.02 MHz.

to acetone, line-width reduction is obtained. From the chemical shifts collected in Table 1, referred to a number of reference compounds and measured in different solvents, it is observed that a shift to lower field occurs (around 10 ppm) on going from benzene to chloroform solution, whereas the values are nearly the same in acetone and benzene solution. In *meta*-dichloroperbenzoic acid, **7**, two signals are observed, as occurs in peresters **1**–**5**. Of the two resonance signals observed for compounds **1**–**5**, that at higher field is broader. In methyl benzoates[29] the two signals observed for the non-equivalent oxygen atoms of the ester group have nearly the same bandwidth at half-height (~175 Hz at 36.5 MHz). From the structural features of peresters one should expect, in principle, three different signals of equal intensity, or, in the case of two signals, one with an intensity twice as great as the other.

Quantitative measurements of the relative intensity of the signals were problematic owing to experimental difficulties, both because of base line instability and the short, and different, relaxation times of the magnetically different oxygen nuclei. Addition of a known amount of dibutyl ether as internal standard showed that the intensity of the signals of compound **1** is lower than expected for the high field signal if it is assumed to correspond to one oxygen nucleus, and the integrated intensity of that at lower field corresponds to more than one but less than two oxygens. For compound **6** the intensity relative to the same internal standard of the single line detected for this molecule at 345–350 ppm turned out significantly lower than expected for four oxygen nuclei. Thus no direct evidence was acquired for the assignment of ^{17}O resonances to the three oxygen nuclei of compounds **1**–**5** and to the two structurally non-equivalent oxygens of compounds **6** and **12**.

From the ^{17}O NMR spectra of methyl and *tert*-butyl esters of benzoic acid it is found[3,30] that the oxygen nucleus of the C=O group resonates at 340 and 346 ppm: the resonances at 344 ppm in *tert*-butyl perbenzoate **1** and at 345 ppm in dibenzoyl peroxide **6** should represent the carbonyl oxygen of these compounds.

In order to probe more deeply into the possibility of assigning the resonances of the different oxygen nuclei in peroxyesters, we examined the ^{17}O NMR spectra of compounds **9**, **10** and **11**. The results are collected in Table 1: for these compounds three different signals are observed for the three non-equivalent oxygen nuclei. The line-widths of the three signals recorded for these molecules are different, and lower than those of compounds **1**–**5**. The separation of the two signals at lower field in compounds **10** and **11** is of the order of 17–26 ppm and this separation, which may prevent observation of separate signals when the line-width is higher, could become even smaller in the aromatic esters **1**–**5**. In compound **9** a rather small separation is observed for the two signals at higher field: for this compound the signal at lowest field should probably be assigned to the peroxidic oxygen O(3), on the basis of band-width considerations which we shall return to in the discussion.

X-Ray Crystal and Molecular Structure of Compound **5**.—Final fractional coordinates for non-hydrogen atoms are reported in Table 2. Bond distances and bond angles are listed in Table 3. A drawing of the structure, showing the labelling scheme, is presented in Fig. 1. Lists of atomic temperature factors, positional and thermal parameters for hydrogen atoms, bond distances and angles involving atoms at minor sites, torsion angles, and selected least-squares planes have been deposited at the Cambridge Crystallographic Data Centre.*

The structure, made up of one crystallographically independent discrete molecule, is affected by statistical disorder, which involves, to different extents (see Table 3), all the three Bu^t substituents bonded to the benzene ring. In all cases, the methyl carbons of the Bu^t groups are distributed over two alternative positions, which arise from a rotation of *ca.* 60° around the C(ring)–C(Bu^t) bonds. The positions of the atoms at minor sites have been only very poorly defined.

The main interest of our structural investigation was to determine the geometry of the peroxy group. Our results compare well with those reported for the two perbenzoic esters of known structure, namely the *tert*-butyl 3-nitroperbenzoate[8] and the *tert*-butyl 4-nitroperbenzoate.[8] Our O(2)–O(3) bond distance of 1.478(3) Å is in good agreement with the corresponding values of 1.46(1) and 1.49(1) Å observed for the above cited compounds, and with the mean value of 1.482(5) Å retrieved from the Cambridge Crystallographic Data Base.[32]

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* For details of the CCDC deposition scheme, see 'Instructions for Authors' 1992, *J. Chem. Soc., Perkin Trans. 2*, 1992, issue 1.

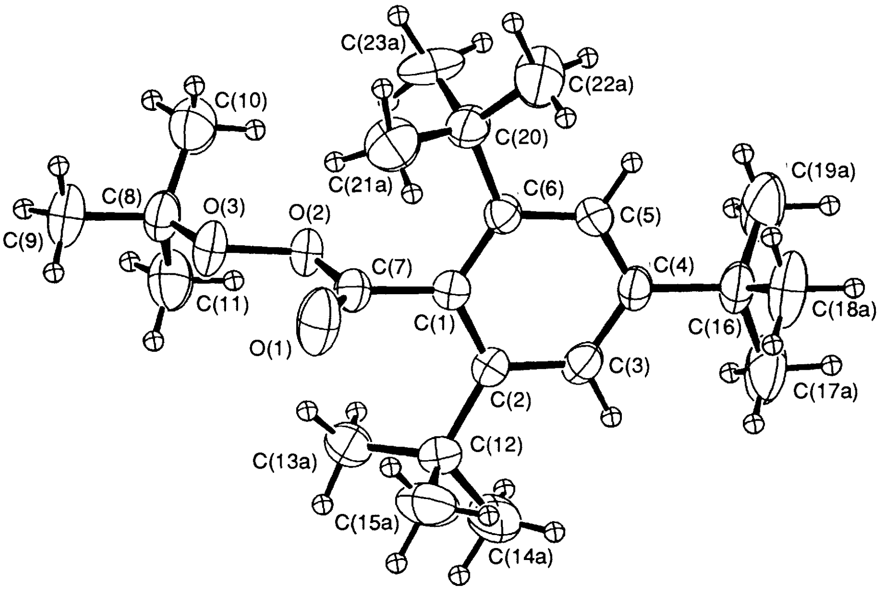

Fig. 1 ORTEP[31] plot of compound **5** with atom numbering scheme. Thermal ellipsoids for non-H atoms enclose 40% probability.

Table 2 Final fractional co-ordinates[a]

Atom	*x*	*y*	*z*
C(1)	0.2268(3)	0.5[b]	0.4154(3)
C(2)	0.3312(3)	0.5868(5)	0.4538(3)
C(3)	0.3701(4)	0.6125(5)	0.5826(4)
C(4)	0.3119(4)	0.5576(5)	0.6723(3)
C(5)	0.2109(4)	0.4730(5)	0.6302(3)
C(6)	0.1653(4)	0.4403(4)	0.5038(3)
C(7)	0.1812(4)	0.4696(5)	0.2774(3)
O(1)	0.2351(4)	0.4004(5)	0.2172(3)
O(2)	0.0700(3)	0.5341(4)	0.2285(2)
O(3)	0.0203(3)	0.5004(4)	0.0940(2)
C(8)	−0.0900(4)	0.5826(6)	0.0418(4)
C(9)	−0.1293(5)	0.5362(7)	−0.0953(4)
C(10)	−0.2027(5)	0.5712(7)	0.1085(5)
C(11)	−0.0403(6)	0.7153(6)	0.0444(5)
C(12)	0.4081(4)	0.6530(6)	0.3647(4)
C(13a)	0.3169(7)	0.7050(8)	0.2453(6)
C(14a)	0.4906(9)	0.7646(9)	0.4293(7)
C(15a)	0.5091(7)	0.564(1)	0.3282(8)
C(13b)	0.414(5)	0.578(5)	0.242(5)
C(14b)	0.337(5)	0.787(6)	0.349(5)
C(15b)	0.554(5)	0.675(6)	0.429(5)
C(16)	0.3615(4)	0.5857(5)	0.8153(4)
C(17a)	0.457(1)	0.6979(9)	0.8396(6)
C(18a)	0.4397(9)	0.4752(9)	0.8780(6)
C(19a)	0.2450(7)	0.608(1)	0.8752(7)
C(17b)	0.305(4)	0.488(4)	0.903(3)
C(18b)	0.327(4)	0.708(4)	0.845(3)
C(19b)	0.509(4)	0.576(4)	0.839(3)
C(20)	0.0531(4)	0.3400(5)	0.4723(4)
C(21a)	0.0678(9)	0.2551(8)	0.3580(8)
C(22a)	0.058(1)	0.2500(8)	0.5787(7)
C(23a)	−0.0832(6)	0.4013(8)	0.441(1)
C(21b)	−0.040(2)	0.338(3)	0.593(2)
C(22b)	0.110(2)	0.216(3)	0.451(2)
C(23b)	−0.068(3)	0.372(3)	0.364(2)

[a] a- and b-labelled atoms have alternative occupancy factors; those of major sites are 0.87(1) [C(13)–C(15)], 0.83(1) [C(17)–C(19)], and 0.76(1) [C(21)–C(23)]. [b] The origin of the unit cell was arbitrarily defined by assigning the value 0.5 to the *y* co-ordinate of the C(1) atom.

As previously found,[8] also in this case the peroxycarboxyl group is essentially planar. Its mean plane is nearly perpendicular to the benzene ring (dihedral angle between mean planes = 80.8°) whereas in the nitroperbenzoates dihedral angles of 12.7 and 6.6° indicate a nearly coplanar arrangement. Another conformational difference involves the torsional angle at the O–O bond: values of 129(1) and 120(1)° were found for the nitrobenzoates,[8] whereas our torsional angle of −173.4(4)° is close to that of 170° reported for the 4-nitroperbenzoic acid.[33] The conformation around the O–O bond is not of skew type as occurs in several dialkyl peroxides, yet close to that of the more crowded di-*tert*-butyl peroxide.[34] As regards the conformation around the C(7)–O(2) bond, the molecule assumes an *s-cis* orientation of the oxygen atoms O(1) and O(3), which seems rather characteristic of acyl peroxides.[5] The dimensions of the benzene ring, planar within ±0.006 Å are typical, although some lengthening of the C–C ring bonds adjacent to the peroxy substituent [1.406(5) and 1.411(4) Å] could be significant. There are no short van der Waals contacts between the molecules, with only two interatomic distances being slightly less than 3.60 Å.

Discussion

The applications of ^{17}O NMR chemical shifts stem from their sensitivity in revealing structural dependence in strained and sterically hindered systems. Relationships between ^{17}O chemical shifts and torsional angles of groups containing oxygen atoms have been reported[3] and, as regards the behaviour of compounds **1**–**5**, comparison with aromatic esters[3,4] assumes particular significance.

The existence of such correlations has not been tested in peresters, although it could be of particular interest in preparing a tool for the conformational analysis of these molecules which, in the majority of cases, are not amenable to experimental structural investigations. This test should also help in defining the assignment of experimental resonances of the oxygen nuclei of these molecules.

For compounds **1**–**4** the torsional angle of the acyl group with respect to the phenyl plane is not known and cannot be determined experimentally, at least with X-ray diffraction, since they are not solid at room temperature. The relevant twist angles can be obtained from theoretical methods, and we employed the molecular mechanics approach[14] with the MM2 computer software.[35] Calculations with this approach were found to reproduce quite satisfactorily the structural features of methyl esters of substituted benzoic acids. The calculated twist angles between the carbonyl group and the plane of the aromatic ring give linear correlations with the ^{17}O chemical

Table 3 Bond distances (Å) and bond angles (°)[a] of compound **5** from X-ray analysis

C(2)–C(1)	1.406(5)	C(6)–C(1)	1.411(5)
C(7)–C(1)	1.500(5)	C(3)–C(2)	1.392(5)
C(12)–C(2)	1.546(5)	C(4)–C(3)	1.379(5)
C(5)–C(4)	1.373(5)	C(16)–C(4)	1.550(5)
C(6)–C(5)	1.391(5)	C(20)–C(6)	1.553(5)
O(1)–C(7)	1.200(5)	O(2)–C(7)	1.333(4)
O(3)–O(2)	1.478(3)	C(8)–O(3)	1.442(5)
C(9)–C(8)	1.535(6)	C(10)–C(8)	1.490(7)
C(11)–C(8)	1.514(8)	C(13a)–C(12)	1.522(8)
C(14a)–C(12)	1.542(9)	C(15a)–C(12)	1.52(1)
C(17a)–C(16)	1.53(1)	C(18a)–C(16)	1.507(9)
C(19a)–C(16)	1.492(8)	C(21a)–C(20)	1.574(9)
C(22a)–C(20)	1.499(7)	C(23a)–C(20)	1.504(8)
C(6)–C(1)–C(2)	121.4(3)	C(7)–C(1)–C(2)	119.1(3)
C(7)–C(1)–C(6)	119.5(3)	C(3)–C(2)–C(1)	117.2(3)
C(12)–C(2)–C(1)	125.1(3)	C(12)–C(2)–C(3)	117.7(3)
C(4)–C(3)–C(2)	123.4(3)	C(5)–C(4)–C(3)	117.2(3)
C(16)–C(4)–C(3)	121.8(4)	C(16)–C(4)–C(5)	121.0(3)
C(6)–C(5)–C(4)	123.8(3)	C(5)–C(6)–C(1)	116.9(3)
C(20)–C(6)–C(1)	125.6(3)	C(20)–C(6)–C(5)	117.4(3)
O(1)–C(7)–C(1)	126.9(4)	O(2)–C(7)–C(1)	109.2(3)
O(2)–C(7)–O(1)	123.8(3)	O(3)–O(2)–C(7)	109.7(2)
C(8)–O(3)–O(2)	107.5(3)	C(9)–C(8)–O(3)	101.1(4)
C(10)–C(8)–O(3)	111.9(4)	C(10)–C(8)–C(9)	112.3(4)
C(11)–C(8)–O(3)	110.3(4)	C(11)–C(8)–C(9)	109.9(4)
C(11)–C(8)–C(10)	111.0(5)	C(13a)–C(12)–C(2)	113.9(4)
C(14a)–C(12)–C(2)	112.0(4)	C(14a)–C(12)–C(13a)	105.4(5)
C(15a)–C(12)–C(2)	109.8(5)	C(15a)–C(12)–C(13a)	109.2(5)
C(15a)–C(12)–C(14a)	106.1(5)	C(17a)–C(16)–C(4)	112.2(4)
C(18a)–C(16)–C(4)	108.5(4)	C(18a)–C(16)–C(17a)	107.2(5)
C(19a)–C(16)–C(4)	110.8(4)	C(19a)–C(16)–C(17a)	109.2(7)
C(19a)–C(16)–C(18a)	108.8(7)	C(21a)–C(20)–C(6)	112.6(4)
C(22a)–C(20)–C(6)	112.5(4)	C(22a)–C(20)–C(21a)	103.7(6)
C(23a)–C(20)–C(6)	109.8(4)	C(23a)–C(20)–C(21a)	108.7(6)
C(23a)–C(20)–C(22a)	109.4(6)		

[a] Only disordered methyl carbons at major sites were included.

Table 4 Conformational features[a] calculated for the molecules **1**–**5** with molecular mechanics (MM2)

Compound	θ/°
1	14.09 (16.09)
2	43.80 (44.89)
3[b]	60.34 (49.54)
4	69.39 (77.38)
5[b]	80.77 (80.39)

[a] θ is the twist angle between the carbonyl plane and the phenyl ring (in parentheses are the values calculated with the AM1/MNDO approach): the calculated C–O–O–C dihedral angle is 180° for all these molecules. [b] Calculations refer to the molecule with only *ortho* substituents (R^3 = H).

shifts of these molecules.[4] The calculated twist angles θ (between the plane of the carbonyl group and that of the phenyl ring) are collected in Table 4. For compounds **3** and **5** calculations were performed on the derivatives with *ortho* substituents only (R^3 = H) in order to reduce molecular complexity. The angle θ increases with the size and the number of *ortho* substituents and, for a given substituent, is higher than in the corresponding methyl ester.[4] For compound **5** the calculated angle is close to that determined experimentally in this work with X-ray diffraction. The preferred conformation around the O–O bond corresponds to a dihedral angle of 180° which is that found for the molecule in the solid state. Furthermore, comparison of the energies of *s-cis* and *s-trans* conformations, referred to internal rotation around the C(O)–O bond, calculated with the MM2 approach, showed the former to be more stable, in agreement with the solid state structure. The energy difference between these conformations is nevertheless rather small (less than 1 kcal mol^{-1}).* Similar results are also obtained with the MO semi-empirical AM1/MNDO method,[15,36] and the *s-cis* conformation is here decidedly more stable than the *s-trans* one.

The two sets of ^{17}O chemical shifts obtained for compounds **1**–**5** are plotted against the calculated θ (MM2) in Fig. 2. The correlations are well approximated by the linear eqns. (1) and (2), (r is the correlation coefficient) which have different slopes.

$$\delta(^{17}O) = 0.76\theta + 332.41 \qquad (1)$$
$$r = 0.9984$$

$$\delta(^{17}O) = 0.17\theta + 293.62 \qquad (2)$$
$$r = 0.9157$$

By employing the twist angles calculated with the AM1 method, correlations similar to eqns. (1) and (2) were obtained but the scattering was higher. The slope of eqn. (1), which refers to the signals at lower field, is in the range of those found[4] for the oxygen nuclei of carbonyl functions (esters, ketones and amides) and the same holds for the intercept. Assuming that this signal embodies both the carbonyl oxygen O(1) and the peroxidic oxygen O(2), their nuclei are affected to a comparable extent by twisting of the phenyl ring. In the esters of benzoic acid the dicoordinated oxygen is less affected than the carbonyl oxygen.[4] The slope of eqn. (2) is smaller than that found[4] for the dicoordinated oxygen of esters. This signal is assigned to the oxygen O(3) of peresters, which is less affected by ring twisting than the dicoordinated oxygen of esters.

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* 1 cal = 4.184 J.

The chemical shifts of ^{17}O nuclei can be estimated, for a qualitative interpretation of the molecular structural factors which can determine their behaviour, at a semi-empirical level. It is widely accepted[13-28] that variations of ^{17}O chemical shifts are dominated by the local paramagnetic term, $\sigma^P(O)$, which can be calculated with the Karplus–Pople formula[37] by employing density matrix elements from MO calculations. We have employed the wave function from AM1 semi-empirical calculations[15,36] and, as a measure of the average excitation energy, the first ionization potential calculated at the same MO level was assumed. The calculated rotationally averaged screening constants show different ranges of values for the three oxygen nuclei O(1), O(2) and O(3) of the compounds examined. The oxygen O(1) is the most deshielded one. The diamagnetic contribution to the screening constant calculated at the same level of approximation[28] ranges within 4–5 ppm for the different compounds and is not taken into account. The calculated values of $\sigma^P(O)$ are plotted against the experimental $\delta(^{17}O)$ chemical shifts in Fig. 3 where a number of compounds with the peroxidic bond and known values of ^{17}O chemical shifts have also been included. The crude approximation from employing the Karplus–Pope formula, an average excitation energy and a wave function limited to ground-state electron contributions, is the origin of a large scatter in the calculated values of mono- and di-coordinated oxygens and of separate correlations with experimental values.[38] Nevertheless the approximations involved in the formalism for the evaluation of these observables, combined with the large size of some of the molecules to be tackled do not, in our opinion, justify employment of wave functions estimated at higher level, and the comparison between calculated and experimental values will be carried out at the simplest level of application of the Karplus–Pople formula. The correlations of Fig. 3 show trends and qualities no different from those obtained for other oxygen compounds.[13,38] In the correlation (*a*) of Fig. 3 the largest deviation is for compound **10** and amounts to 20 ppm (least-squares treatment). In plot (*b*) the data for the peroxidic oxygen bonded to the carbonyl group are collected. For compounds **1**–**5**, **6** and **12** the chemical shifts assigned to the carbonyl oxygen are employed: the agreement is of the same order of magnitude as that of plot (*a*). The data of plot (*c*) refer to the peroxidic oxygen O(3): the result relative to di-*tert*-butyl peroxide has been included as well and fits this correlation.

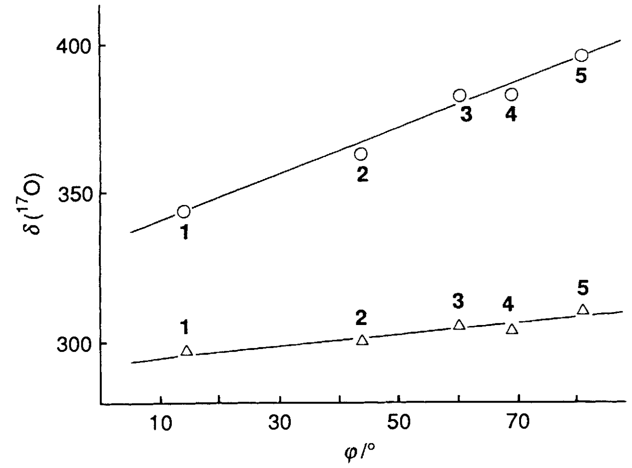

Fig. 2 Plots of the two sets of ^{17}O chemical shifts (ppm) obtained for compounds **1**–**5** against the calculated (MM2) twist angle θ (○ low-field signal; △ high-field signal).

It thus seems reasonable to conclude that the oxygen nuclei O(1) and O(2) in compounds **1**–**5**, **6** and **12** have close chemical shifts, not experimentally resolved. The shielding constants calculated for the three oxygen nuclei were also correlated with the torsional angles θ of Table 4. The plots show approximately linear behaviour and the highest slope is found for O(1),

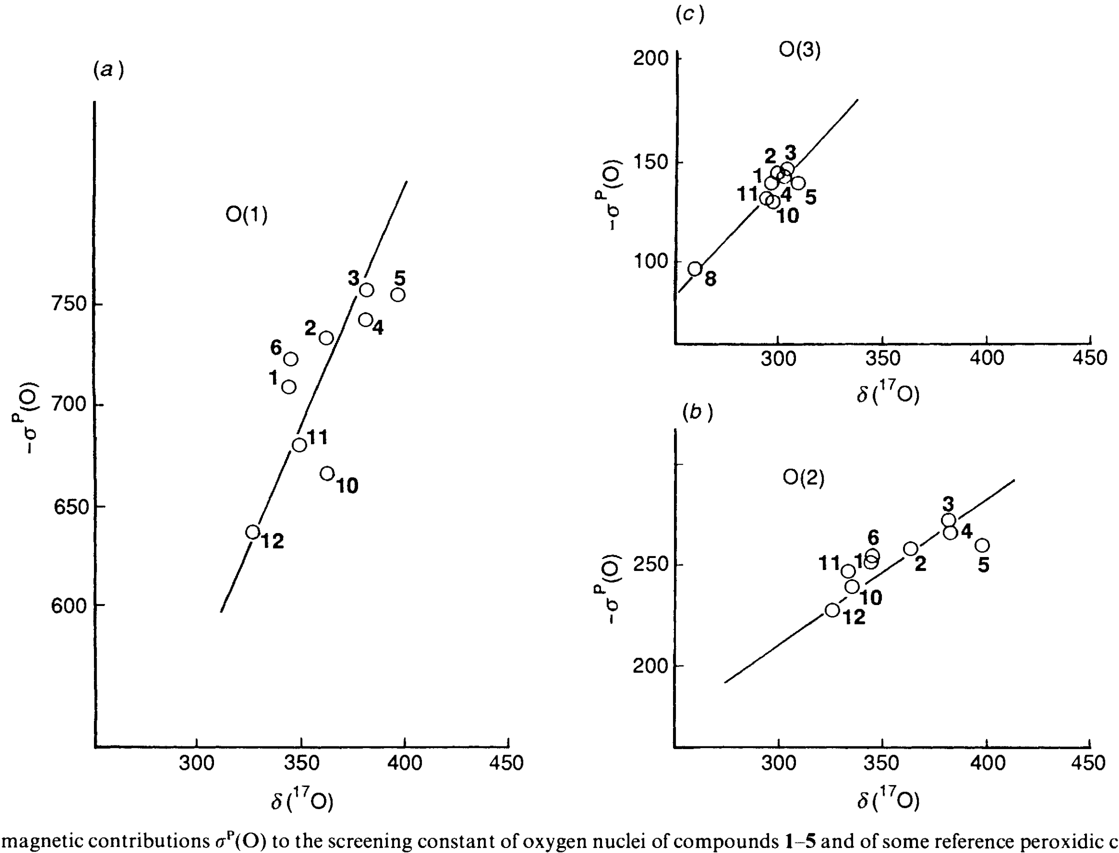

Fig. 3 Paramagnetic contributions $\sigma^P(O)$ to the screening constant of oxygen nuclei of compounds **1**–**5** and of some reference peroxidic compounds *vs.* the experimental chemical shifts $\delta(^{17}O)$. Numbering refers to the compounds reported in Table 1.

followed by O(2) and O(3): for the latter nuclei the slope is close to 0.1. This behaviour appears qualitatively to confirm the experimental finding that the highest sensitivity of ^{17}O chemical shifts to ring twisting is for O(1) and O(2).

A further argument in favour of the assignment of the ^{17}O signals in the molecules examined can be obtained from their nuclear relaxation properties, by assuming that relaxation times T_1 and T_2 for oxygen nuclei are approximately given[28] by the inverse of the line-width at half-height ($W_{\frac{1}{2}}$). For compounds **10** and **11** the signal at lower field should be assigned to the carbonyl oxygen: this signal is the one with the smallest band-width. Thus the assignments also seem justified on the basis of line-width features for the following reasons.

In benzoyl peroxide the peroxidic oxygen has the higher nuclear quadrupole moment: $e^2Qq/h = 8.696$ and 11.916 MHz for the C=O and C–O– oxygens.[39] By assuming that the nuclear quadrupole moments of these two different types of oxygen nuclei do not differ significantly in diacyl peroxides and peresters and that the band-widths for ^{17}O resonances are mostly regulated by nuclear quadrupole relaxation,[40] in the extreme narrowing limit the ratio of band-widths $W_{\frac{1}{2}}$ of the oxygen nuclei should be given by eqn. (3). The terms η and

$$\frac{(W_{\frac{1}{2}})_{\mathrm{C=O}}}{(W_{\frac{1}{2}})_{\mathrm{C-O-}}} = (1 + \eta/3)(1 + \eta'/3)\,\frac{(e^2Qq/h)^2{}_{\mathrm{C=O}}}{(e^2Qq/h)^2{}_{\mathrm{C-O-}}} \qquad (3)$$

η' refer to the asymmetry parameters of the electric field gradient tensor and amount to 0.157 and 0.987 for the C=O and C–O– oxygen atoms of dibenzoyl peroxide.[39] For benzoyl peroxide this ratio amounts to 0.41. The experimental ratio of band-widths for compounds **10** and **11**, referred to the two signals at lower field, is 0.44 and 0.49 and seems in line with the assignments performed for these compounds, taking into account the large errors in band-width measurements. For derivatives **6** and **12** the band-width is much greater than expected if the signal observed for these compounds belonged to the carbonyl resonance alone. The overlapping of two signals of different band-width thus seems a more reasonable assignment for the resonances observed for these compounds.

Incidentally, the assignment of the resonances to the oxygen nuclei of compound **9** reported in Table 1, taking into account the line-width of the signals, should be reexamined. The carbonyl oxygen should not in fact be the one at lowest field but the one resonating at 328.9 ppm (for this molecule the line-widths refer to acetone solution and are thus smaller than those measured in benzene). The low-field shift of the peroxidic oxygen O(3) of this molecule as compared to the other molecules examined should be due to the strained nature of the ring, as occurs in other cyclic peroxides.[9]

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