$C_{12}H_{15}IO_6$

C(11)—O(1)	1.385 (4)		O(5)—C(5)	1.435 (4)
O(2)—C(2)	1.419 (4)		C(6)—C(5)	1.509 (5)
C(3)—C(2)	1.510 (4)		O(6)—C(6)	1.430 (5)
C(2)—C(1)—O(1)	105.4 (3)		C(5)—C(4)—C(3)	108.2 (3)
O(5)—C(1)—O(1)	106.8 (3)		C(5)—C(4)—O(4)	107.8 (3)
O(5)—C(1)—C(2)	110.7 (3)		O(5)—C(5)—C(4)	111.1 (3)
C(11)—O(1)—C(1)	118.7 (3)		C(6)—C(5)—C(4)	113.3 (3)
O(2)—C(2)—C(1)	110.0 (3)		C(6)—C(5)—O(5)	104.5 (3)
C(3)—C(2)—C(1)	108.7 (3)		C(5)—O(5)—C(1)	112.4 (2)
C(3)—C(2)—O(2)	111.0 (3)		O(6)—C(6)—C(5)	110.1 (4)
O(3)—C(3)—C(2)	111.6 (3)		C(12)—C(11)—O(1)	115.7 (3)
C(4)—C(3)—C(2)	112.1 (3)		C(16)—C(11)—O(1)	124.0 (3)
C(4)—C(3)—O(3)	109.8 (3)		C(11)—C(12)—I	120.1 (3)
O(4)—C(4)—C(3)	111.8 (3)		C(13)—C(12)—I	120.0 (3)

D—H···A	D···A	D—H···A
O(2)—H(O2)···O(3^i)	2.742 (4)	170 (1)
O(3)—H(O3)···O(2^{ii})	2.925 (4)	173 (1)
O(4)—H(O4)···O(6^{iii})	2.892 (5)	160 (2)

Symmetry codes: (i) $1 - x, y - \frac{1}{2}, 1 - z$; (ii) $1 - x, \frac{1}{2} + y, 1 - z$; (iii) $2 - x, y - \frac{1}{2}, 1 - z$.

The structure was solved by direct methods using *MULTAN*11/84 (Main, Germain & Woolfson, 1984) and refined using *SHELX*76 (Sheldrick, 1976b). Friedel pairs were not merged. The reported configuration refined to a lower value of *R* than its enantiomorph. Complex scattering factors were used for iodine. High peaks in the residual electron density appear only in the vicinity of the heavy I atom. The figures were prepared using *PLUTO* (Motherwell & Clegg, 1978).

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Formation and Identification of Rotameric 9-Pivaloylfluorene Oximes. Structure of ap-(Z)-9-Pivaloylfluorene Oxime

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Abstract

Reaction of hydroxylamine with sterically hindered *ap*-9-pivaloylfluorene (I) produced the rotameric antiperiplanar (*ap*) and synperiplanar (*sp*) oximes (40% yield) as determined by ^{1}H NMR (CDCl$_3$ or DMSO-d_6). Their *E/Z* configurations (substituent geometry in C=N) could not be ascertained this way. Evaporation of solutions containing both rotamers consistently provided only *one* solid oxime which was shown to be the *ap*-(*Z*) oxime (IIa) [*ap*-(*Z*)-9-pivaloylfluorine oxime, C$_{18}$H$_{19}$NO] by single-crystal X-ray diffraction. When crystalline (IIa) was redissolved (CDCl$_3$ or DMSO-d_6) *both* rotamers were present in ratios dependent on the concentration. The proximity of the oxime O atom to the fluorene-ring plane in (IIa), 2.598 Å, results in a repulsion which raises the ground-state energy, thereby lowering the rotational barrier leading to the isomeric *sp*-(*Z*) oxime (IIIa). This repulsion is reflected in the larger angle, 123.9 (2)° (C9—C10—N1), in *ap* oxime (IIa), compared with 119.2 (4)° (C9—C10—O1) in the *ap* ketone (I). The rotational barrier (IIIa) → (IIa) is also low because of the proximity of the *tert*-butyl group in (IIIa) to the fluorene-ring plane. Together these results demonstrate that rotational interconversion of (IIa) and (IIIa) occurs in solution at ambient temperatures at a rate which is slower than the NMR timescale, and that the crystal packing for (IIa) is more favorable than for (IIIa).
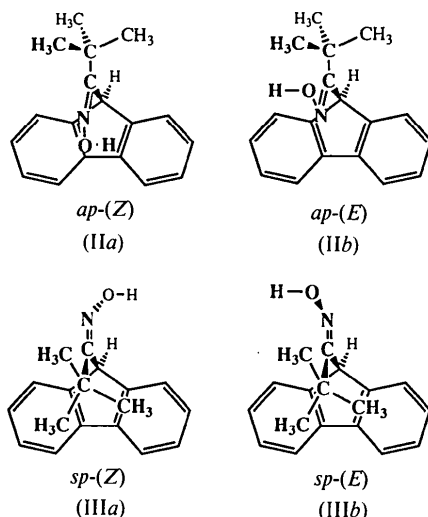
Comment

We have reported a variety of observations of significant steric effects operating in 9-pivaloylfluorene (Meyers, Lutfi, Varol & Robinson, 1993; Meyers, Tunnell, Robinson, Hua & Saha, 1992; Meyers, Lutfi, Carr, Robinson, Saha & Hua, 1992; Meyers, Wahner, Manohar, Carr, Chan-Yu-King & Robinson, 1991; Meyers, 1990; Mey-

ers, Chan-Yu-King, Wahner, Carr & Robinson, 1989): crystalline 9-pivaloylfluorene is the *ap* rotamer† (I) and this conformation is exclusively maintained in solutions examined between 213 and 375 K; the pK_a value of (I) is much higher than that of other 9-carbonyl-substituted fluorenes; and 9-Li-(I) resists methylation with CH_3I or $(CH_3)_2SO_4$ even at ambient temperatures, although the desired product is obtained rapidly from pivaloylation of 9-lithio-9-methylfluorene with pivaloyl chloride at liquid nitrogen–ethanol temperature. It appeared likely that these steric effects associated with the *tert*-butyl and 9-fluorenyl substituents attached to trigonal C10 (carbonyl) would be even more effective in reducing access to tetrahedral C10 of the transition state and corresponding intermediate required in the formation of carbonyl derivatives. To test this hypothesis we examined the reactivity of (I) with hydroxylamine, one of the least sterically sensitive derivatizing reagents for aldehydes and ketones. Since many unsymmetrical ketones produce *E* and *Z* isomeric ketoximes (*cis*- and *trans*-$R,R'C$=N—OH), this study would not only provide information on the C=O reactivity of (I) but also, if reaction did occur, on the relative hindrance effected by the *tert*-butyl and 9-fluorenyl groups.

5 eq. $NH_2OH \cdot HCl$
4.5 eq. anh. KOAc
EtOH, reflux 2h

(I)
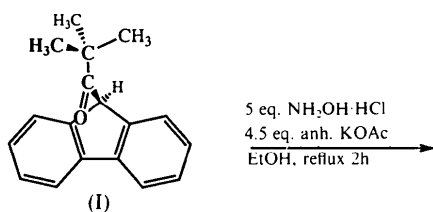
Four theoretically possible isomeric oximes

ap-(*Z*)
(IIa)

ap-(*E*)
(IIb)

sp-(*Z*)
(IIIa)

sp-(*E*)
(IIIb)

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† The designations *ap* (antiperiplanar) and *sp* (synperiplanar) for these conformations are in accordance with Rule E-6.6, *IUPAC Tentative Rules* (IUPAC, 1970).

Little attention, however, has been given to rotational isomerism in ketoximes. Initially, we expected that, because of the steric effects, if any products were formed only *ap* oximes (IIa,b) would be likely. Formation of *sp* oximes (IIIa,b) was deemed improbable: in the *sp* conformation of 9-pivaloylfluorene the *tert*-butyl group impinges upon the π electrons of the fluorene ring, a high-energy situation. However, this conformation may become the thermodynamically favored one when the energy of the *ap* conformation is sufficiently enhanced, as occurs by the steric interaction between the *tert*-butyl group and an additional 9-substituent such as methyl (Meyers, Lutfi, Varol & Robinson, 1993) or hydroxyl (Meyers, Tunnell, Robinson, Hua & Saha, 1992).

Our initial results (NMR, chromatography and melting points; see *Experimental*) showed that (I) indeed underwent reaction with hydroxylamine and that one *ap* oxime (II) and one *sp* oxime (III) were present in solution, and suggested that only one isomer existed in the crystalline form. They did not answer the questions of whether these oximes were *Z* configured (IIa, IIIa) or *E* configured (IIb, IIIb), if the crystalline structure was composed of more than one isomer or, if only one, which one. These questions were resolved by the X-ray structure determination, which showed that the crystals consisted solely of the *ap*-(*Z*) oxime (IIa) (Fig. 1); the unit-cell parameters of ten additional, randomly selected crystals were in agreement, within experimental error, with those of the crystal used for the structure determination, making the presence of an *sp* rotamer very unlikely. These *same* crystals were then dissolved in $CDCl_3$ for NMR analysis; both oximes were again observed. To complete the cycle, this NMR solution was slowly evaporated to dryness leaving crystals which exhibited unit-cell parameters in agreement with those of (IIa), within experimental error. Since *ap–sp* rotational equilibration in solution at ambient temperature has been reported in some instances (reviewed by Ōki, 1985) and *E–Z* equilibration is very unlikely, it is virtually certain that the two oximes observed in solution are the *Z* oximes, (IIa) and (IIIa). Our overall results indicate that the rotational interconversion of these two oximes in solution at ambient temperature is slower than the NMR timescale and that the crystal packing of (IIa) (Fig. 2) is more favorable than that of (IIIa).

These results are rationalized by comparing the crystal structure parameters of (IIa) with those of the related 9-pivaloylfluorenes that we have examined. The high-energy interaction between the *tert*-butyl group and fluorine-ring π electrons of the *sp* conformation of 9-pivaloylfluorene reduces its rotational barrier relative to that of the *ap* conformation so that only the latter rotamer (I) is observed (Meyers, Lutfi, Varol & Robinson, 1993; Meyers, Tunnell, Robinson, Hua & Saha, 1992; Meyers, Lutfi, Carr, Robinson, Saha & Hua, 1992; Meyers, Wahner, Manohar, Carr, Chan-Yu-King & Robinson,
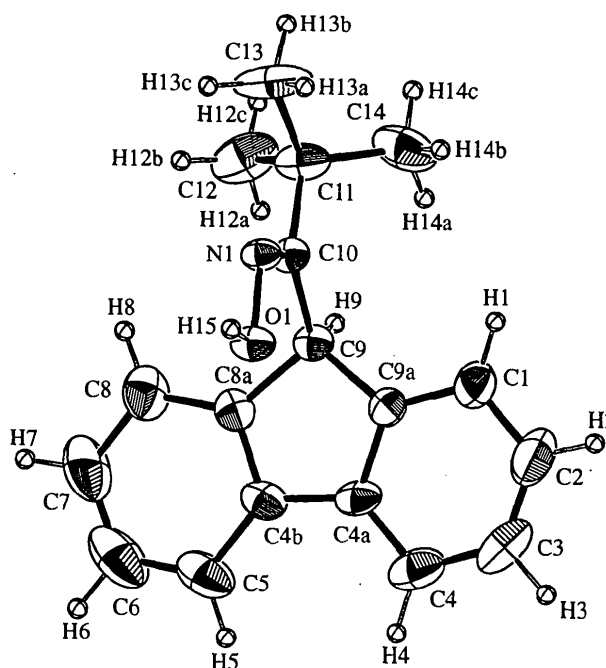
Fig. 1. Molecular configuration and atom-numbering scheme with thermal ellipsoids at the 30% probability level. H atoms are shown as spheres of arbitrary radius.
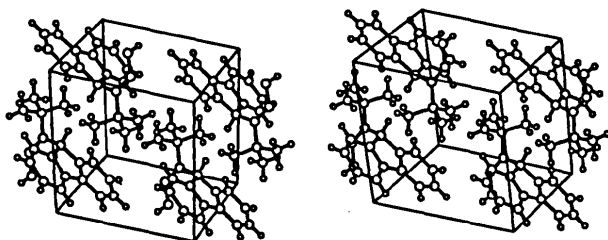

Fig. 2. Stereoscopic illustration of the molecular packing. The origin is at the lower-right-rear corner, the *a* axis is out of the plane of the paper, the *b* axis is vertical, and the *c* axis is nearly horizontal.

1991; Meyers, 1990; Meyers, Chan-Yu-King, Wahner, Carr & Robinson, 1989). In the *ap* oxime (II*a*), O1 approaches the fluorene-ring plane to within 2.598 Å, which is similar to the distance between the *tert*-butyl H atoms and the fluorene plane in the *sp* rotamer (III*a*), as estimated from the corresponding distances, 2.581 and 2.529 Å, respectively, in *sp*-9-methyl-9-pivaloylfluorene (Meyers, Lutfi, Varol & Robinson, 1993) and *sp*-9-hydroxy-9-pivaloylfluorene (Meyers, Tunnell, Robinson, Hua & Saha, 1992). While the high energy of these two *sp* rotamers reduces their rotational barriers, their *ap* rotamers have even higher energies/lower barriers effected by the additional 9-substituent, and in these cases only the *sp* rotamers are observed. The enhanced steric effect in the *ap* oxime (II*a*) relative to the corresponding

ap ketone (I) is clearly reflected by the substantially larger angle of 123.9 (2)° (C9—C10—N1) of the oxime compared with 119.2 (4)° (C9—C10—O1) in the ketone. This steric effect in *ap* oxime (II*a*) enhances its ground-state energy, reducing its rotational barrier to a level similar to that of *sp* oxime (III*a*), allowing both rotamers to be observed in solution.

Experimental

A mixture of (I) (Meyers, Wahner, Manohar, Carr, Chan-Yu-King & Robinson, 1991) (1.20 g, 4.78 mmol), anhydrous potassium acetate (2.14 g, 21.78 mmol) and hydroxylamine hydrochloride (1.66 g, 23.83 mmol) in absolute ethanol (60 ml) was refluxed for 2 h, after which the ethanol was removed by distillation (atmospheric pressure, then vacuum-rotary evaporator). To the white solid residue ether (70 ml), water (25 ml) and 6 *M* hydrochloric acid (7 ml) were added. Extraction of the organic material was carried out in the usual way, the combined ether solutions were washed with saturated aqueous sodium bicarbonate, then water, dried (anhydrous magnesium sulfate) and evaporated to leave a white solid (1.20 g). The molar composition, 62% of (I), *circa* 30% of oxime (II) and *circa* 8% of oxime (III), was determined by ¹H NMR (300 MHz, CDCl₃): *tert*-butyl protons (sharp singlets); δ 1.46, deshielded *ap* rotamer (II); δ 0.70, shielded, *sp* rotamer (III) (Meyers, Wahner, Manohar, Carr, Chan-Yu-King & Robinson, 1991; Meyers, Tunnell, Robinson, Hua & Saha, 1992; Meyers, Lutfi, Varol & Robinson, 1993). These results were replicated in a second reaction. Flash chromatography (silica gel 60, 230–400 mesh) with hexane and 19:1 hexane–ether removed (I). The residual material was eluted with 9:1 hexane–ether in a single fraction exhibiting one TLC spot. Evaporation provided fine white crystals whose sharp m.p. of 453–455 K (corr.) likewise indicated the presence of one isomer, but whose ¹H NMR spectra in CDCl₃ exhibited resonances from (II) and (III) in ratios between 3:1 and 4:1, depending on the concentration. The resolidified crystals in the melting-point capillary tube again melted sharply at the same temperature. The contents of the capillary were then dissolved in CDCl₃ and subjected to NMR analysis, which again showed (II) and (III) in a ratio in the range noted above. Slow crystallization from ether–dichloromethane provided large white crystals, m.p. 454–456 K (corr.), which were used for the X-ray study.

Crystal data

C₁₈H₁₉NO	Mo *K*α radiation
*M*ᵣ = 265.35	λ = 0.71069 Å
Triclinic	Cell parameters from 25
*P*1̄	reflections
a = 10.275 (6) Å	θ = 10.1–10.9°
b = 11.073 (4) Å	μ = 0.66 cm⁻¹
c = 8.292 (3) Å	*T* = 296 K
α = 71.94 (3)°	Irregular fragment
β = 66.57 (3)°	0.49 × 0.40 × 0.16 mm
γ = 64.41 (3)°	Colorless
V = 770 (1) Å³	
Z = 2	
*D*ₓ = 1.145 Mg m⁻³	

Data collection

Rigaku AFC-5S diffractometer	$R_{int} = 0.012$
$\omega/2\theta$ scans (rate $6°$ min^{-1} in ω)	$\theta_{max} = 25°$
	$h = 0 \rightarrow 12$
Absorption correction:	$k = -13 \rightarrow 13$
none	$l = -9 \rightarrow 9$
2877 measured reflections	3 standard reflections
2713 independent reflections	monitored every 100
1338 observed reflections	reflections
[$I > 3.0\sigma(I)$]	intensity variation: -0.5%

Refinement

Refinement on F	Extinction correction:
$R = 0.040$	Zachariasen (1967),
$wR = 0.046$	type II, Gaussian,
$S = 1.62$	isotropic
1338 reflections	Extinction coefficient:
185 parameters	$0.117(8) \times 10^{-4}$
H-atom parameters not refined	Atomic scattering factors from International Tables
$w = 4F_o^2/\sigma^2(F_o^2)$	for X-ray Crystallography
$(\Delta/\sigma)_{max} = 0.0009$	(1974, Vol. IV, Table
$\Delta\rho_{max} = 0.13$ e Å^{-3}	2.3.1)
$\Delta\rho_{min} = -0.13$ e Å^{-3}	

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
O1	0.6257 (2)	0.0405 (2)	0.3163 (2)	0.052 (1)
N1	0.4828 (2)	0.1360 (2)	0.3852 (3)	0.046 (1)
C1	0.7615 (4)	0.3094 (3)	0.2332 (4)	0.077 (1)
C2	0.9120 (5)	0.2860 (5)	0.2047 (6)	0.107 (2)
C3	1.0240 (4)	0.2220 (5)	0.0683 (7)	0.109 (2)
C4	0.9922 (4)	0.1773 (4)	−0.0436 (5)	0.087 (1)
C4a	0.8411 (3)	0.2022 (3)	−0.0183 (4)	0.058 (1)
C4b	0.7729 (4)	0.1681 (3)	−0.1142 (3)	0.062 (1)
C5	0.8383 (5)	0.1057 (4)	−0.2634 (5)	0.095 (1)
C6	0.7471 (8)	0.0847 (5)	−0.3261 (5)	0.127 (2)
C7	0.5942 (7)	0.1220 (5)	−0.2446 (6)	0.121 (2)
C8	0.5261 (4)	0.1873 (4)	−0.0964 (4)	0.085 (1)
C8a	0.6166 (4)	0.2112 (3)	−0.0336 (3)	0.054 (1)
C9	0.5738 (3)	0.2867 (2)	0.1146 (3)	0.047 (1)
C9a	0.7275 (3)	0.2670 (3)	0.1199 (3)	0.050 (1)
C10	0.4600 (3)	0.2529 (2)	0.2885 (3)	0.046 (1)
C11	0.3085 (3)	0.3631 (3)	0.3547 (4)	0.071 (1)
C12	0.2267 (4)	0.4211 (4)	0.2132 (5)	0.107 (1)
C13	0.2076 (4)	0.3069 (4)	0.5287 (5)	0.122 (1)
C14	0.3366 (4)	0.4759 (3)	0.3891 (5)	0.105 (1)
H15	0.619 (3)	−0.032 (3)	0.398 (3)	

Table 2. *Selected geometric parameters* (Å, °)

O1—N1	1.403 (3)	C6—C7	1.365 (6)
N1—C10	1.272 (3)	C7–-C8	1.397 (5)
C1—C2	1.384 (5)	C8—C8a	1.375 (4)
C1—C9a	1.380 (4)	C8a—C9	1.514 (4)
C2—C3	1.365 (5)	C9—C9a	1.514 (4)
C3—C4	1.370 (5)	C9—C10	1.513 (3)
C4—C4a	1.392 (5)	C10—C11	1.520 (4)
C4a—C4b	1.457 (4)	C11—C12	1.532 (5)
C4a—C9a	1.383 (4)	C11—C13	1.535 (4)
C4b—C5	1.388 (4)	C11—C14	1.524 (5)
C4b—C8a	1.391 (4)	O1—H15	0.88 (3)
C5—C6	1.362 (6)		

O1—N1—C10	113.3 (2)	C8—C8a—C9	130.0 (3)
C2—C1—C9a	118.3 (3)	C8a—C9—C9a	102.1 (2)
C1—C2—C3	120.8 (4)	C8a—C9—C10	116.7 (2)
C2—C3—C4	121.5 (4)	C9a—C9—C10	117.6 (2)
C3—C4—C4a	118.2 (3)	C1—C9a—C4a	120.8 (3)
C4—C4a—C4b	130.8 (3)	C1—C9a—C9	129.1 (3)
C4—C4a—C9a	120.2 (3)	C4a—C9a—C9	110.1 (3)
C4b—C4a—C9a	108.9 (3)	N1—C10—C9	123.9 (2)
C4a—C4b—C5	130.7 (3)	N1—C10—C11	116.8 (2)
C4a—C4b—C8a	108.9 (2)	C9—C10—C11	119.3 (2)
C5—C4b—C8a	120.4 (3)	C10—C11—C12	109.6 (3)
C4b—C5—C6	118.7 (4)	C10—C11—C13	111.1 (2)
C5—C6—C7	121.6 (4)	C10—C11—C14	108.9 (3)
C6—C7—C8	120.4 (4)	C12—C11—C13	109.1 (3)
C7—C8—C8a	118.6 (4)	C12—C11—C14	109.4 (3)
C4b—C8a—C8	120.3 (3)	C13—C11—C14	108.7 (3)
C4b—C8a—C9	109.7 (2)	N1—O1—H15	100 (2)

Weak reflections [$I < 10 \sigma(I)$] were rescanned (maximum of three rescans) and the counts were accumulated to improve accuracy. The positional parameters of the H15 atom were refined. All other H atoms were placed at calculated positions with C—H = 0.95 Å and $U = 1.2 \times U_{eq}$ of the associated C atom and were fixed. Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1985). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *TEXSAN LS*. Molecular graphics: *TEXSAN, ORTEP* (Johnson, 1965). Software used to prepare material for publication: *TEXSAN FINISH*.

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representing the amido group (C1, N1, C7, O7 and C8). The angles between the best planes for A and B are 40.0 (1) in (I) and 33.8 (1)° in (II). The angle between the COO group and the amide group is similar for the two structures, *i.e.* 23.2 (3) for (I) and 31.5 (1)° for (II).

The intermolecular hydrogen bonding for (I) and (II) is similar and results in ribbons, comparable with those found in one form of 6-oxo-6-(phenylamino)hexanoic acid (Feeder & Jones, 1994) and a *p*-amidobenzoic acid

Two ω-Oxo-ω-(phenylamino) Aliphatic Acids

NEIL FEEDER AND WILLIAM JONES

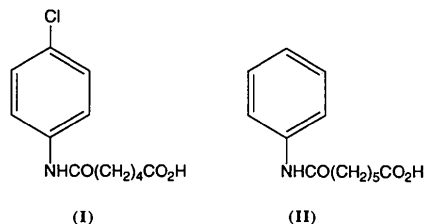*Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, England*

Abstract

The crystal structures of 6-(4-chlorophenylamino)-6-oxohexanoic acid, C₁₂H₁₄ClNO₃ (I), and 7-oxo-7-(phenylamino)heptanoic acid, C₁₃H₁₇NO₃ (II), have been determined. The hydrogen-bond networks found in both structures are very similar to that found in one form of 6-oxo-6-(phenylamino)hexanoic acid previously determined by us [Feeder & Jones (1994). *Acta Cryst.* C50, 816–820].

Fig. 1. Atom-numbering scheme for (*a*) (I) and (*b*) (II).

Comment

These structure determinations are part of a general study of the stability of organic peracids and peracid salts (Kariuki & Jones, 1990), and in particular of the role of hydrogen bonding in controlling the crystal structure of peracid and acid amides (Feeder & Jones, 1992).

The bond lengths and angles found are similar to those found for other ω-oxo-ω-(phenylamino) aliphatic acids (Feeder & Jones, 1994) and *p*-amidobenzoic acids (Feeder & Jones, 1993).

(I)   (II)

Each molecule is considered to contain two planar groups denoted as moiety A, the benzene ring [C1–C6, including Cl for (I)] and moiety B, the atoms
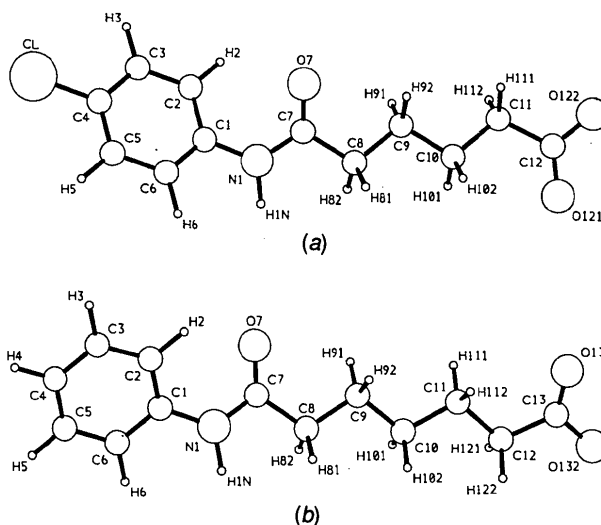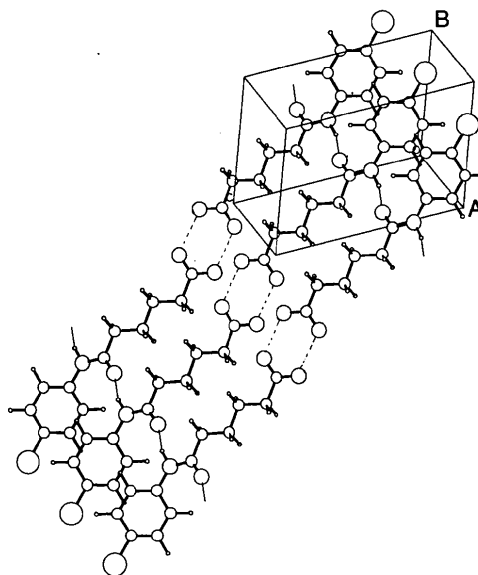

Fig. 2. Packing diagram for (I), viewed perpendicular to the plane of the benzene rings, demonstrating that a Cl-bounded ribbon-type structure is produced through intermolecular hydrogen bonding.