carbazole rings are 3.83 and 3.86 Å, respectively. The nitrocarbazole ring of (II) also associates closely with the nitrocarbazole ring of a neighboring molecule (4.00 Å between centers). Interactions which occur between the π systems of two neighboring unnitrated carbazole rings of (II) are much less extensive (5.13 Å between centers). This can be ascribed to dipolar effects which will be stronger for nitrocarbazole than for carbazole moieties.

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{2-[*p*-(*o*-Butoxybenzamido)benzoyloxy]ethyl}diethylmethylammonium Iodide

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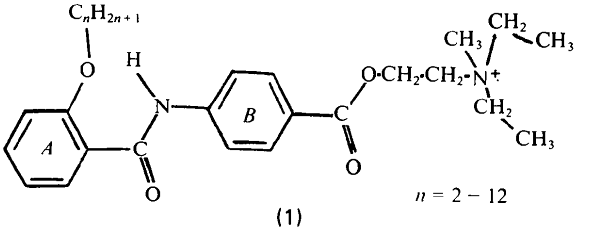
Abstract. $C_{25}H_{35}N_2O_4^+.I^-$, $M_r = 554.47$, orthorhombic, *Pbca*, $a = 13.331\,(3)$, $b = 13.797\,(5)$, $c = 28.179\,(6)$ Å, $V = 5183\,(2)$ Å^3, $Z = 8$, $D_x = 1.42$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 12.51$ cm^{-1}, $F(000) = 2272$, $T = 298$ K, $R = 0.065$ for 1734 unique observed reflections. A comparison of the title compound with other compounds belonging to the same homologous series is offered. It appears that van der Waals interactions are responsible for the differences in conformation found in the solid state of this series of compounds.

Introduction. Compounds of the series {2-[*p*-(*o*-alkyloxybenzamido)benzoyloxy]ethyl}diethylmethylammonium halide (1) show smooth-muscle relaxant activity which is strongly influenced by the length of the alkyloxy side chain and its position on the aromatic ring (Ghelardoni, Pestellini, Pisanti & Volterra, 1973; Maggi, Grimaldi, Volterra & Meli, 1983; Maggi, Manzini & Meli, 1983). This pharmacological effect increases when the alkyloxy chain is *ortho* to the amide group and reaches a maximum with the octyloxy ($n = 8$) derivative. This octyloxy derivative is almost completely devoid of central, ocular and cardiovascular atropine-like side effects when administered in doses that produce spasmolytic effects comparable with those of *N*-butylscopolammonium bromide.



(1)

The solid-state conformations of the propoxy ($n = 3$), octyloxy and decyloxy ($n = 10$) derivatives, as previously determined by X-ray structural analysis, show differences which may explain their different biological behaviour (Dapporto & Sega, 1986, 1987). To obtain information on the conformational features of these compounds in polar solution, NMR investigations have been carried out in dimethyl sulfoxide (DMSO) (Sega, Ghelardoni, Pestellini, Pogliani & Valensin, 1984; Valensin, Pogliani, Ghelardoni, Pestellini & Sega, 1984; Sega, Gaggelli & Valensin, 1985; Valensin, Gaggelli, Lepri & Sega, 1986). These studies have shown that the conformational freedom of the alkyloxy side chain changes

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with its length. In the octyloxy derivative a dipolar connection between the protons of the terminal methyl of the octyloxy chain and the methyls of the ethyl groups bonded to the quaternary N atom exists, thus reducing internal motion. In the decyloxy derivative this dipolar connection is absent allowing greater freedom of movement within the molecule. The solution conformations of these derivatives show some significant differences with respect to the solid-state conformations.

To better understand the influence of the alkyloxy chain length on the overall conformation of this series of compounds, the X-ray crystal structure of the butoxy ($n = 4$) derivative was determined.

Experimental. Title compound synthesized by previously reported method (Ghelardoni, Pestellini, Pisanti & Volterra, 1973); colourless crystal 0.50 × 0.25 × 0.15 mm obtained from DMSO. Enraf–Nonius CAD-4 automatic diffractometer; lattice parameters determined using 25 reflections (θ range: 14.25–14.93°); 5077 unique measured reflections, $2\theta < 50°$, θ–2θ scan technique, $0 \leq h \leq 15$, $0 \leq k \leq 16$, $0 \leq l \leq 33$; 1734 unique observed reflections with $I > 3\sigma(I)$; two standard reflections (7,3,12 and 669) measured every 3600 s, no significant variation in intensity; Lp correction, empirical absorption correction with the *DIFABS* program (Walker & Stuart, 1983), $T_{\min} = 0.68$, $T_{\max} = 0.82$; scattering factors for non-H atoms (*International Tables for X-ray Crystallography*, 1974, Vol. IV, p. 99) and for H atoms (Stewart, Davidson & Simpson, 1965), anomalous-dispersion corrections (*International Tables for X-ray Crystallography*, 1974, Vol. IV, p. 149). Patterson and Fourier methods; full-matrix least-squares refinement, $\sum w(|F_o| - |F_c|)^2$ minimized; anisotropic thermal parameters for I, O, N and for the non-aromatic C atoms, isotropic for the other C atoms; H atoms introduced in calculated positions with overall U of 0.1 Å^2 for those bonded to the methyl and ethyl groups of the quaternary N atom, and 0.05 Å^2 for the other H atoms, and not refined; 230 refined parameters; max. $\Delta/\sigma = 0.57$; final $R = 0.065$, $wR = 0.070$, goodness of fit $S = 3.05$, $w = 2.90/[\sigma^2(F) + 0.001(F)^2]$; min. and max. $\Delta\rho$ excursions -0.60 and 0.62 e Å^{-3}, respectively; IBM PS2/80 computer, *SHELX*76 (Sheldrick, 1976) and *PARST* (Nardelli, 1983) programs.

Table 1. *Positional parameters* (× 10^4) *and isotropic or equivalent isotropic thermal parameters* (Å^2 × 10^3)

$U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$. U_{iso} for aromatic C atoms.

	x	y	z	U_{eq}/U_{iso}
I	740 (1)	2178 (1)	2363 (1)	75 (1)
O1	−6040 (7)	1204 (8)	3877 (4)	87 (4)
O2	−6729 (7)	1371 (8)	4578 (4)	84 (4)
O3	−2177 (7)	1223 (8)	5837 (3)	86 (4)
O4	−223 (7)	1292 (6)	4693 (3)	63 (4)
N1	−6930 (8)	136 (8)	2958 (5)	67 (4)
N2	−2026 (8)	1136 (7)	5037 (3)	50 (3)
C1	−6690 (13)	258 (17)	2380 (7)	159 (5)
C2	−6185 (14)	−435 (14)	3226 (7)	105 (5)
C3	−5323 (23)	−232 (26)	3140 (13)	284 (7)
C4	−7864 (16)	−379 (17)	3008 (6)	160 (5)
C5	−8406 (22)	−853 (23)	2829 (9)	262 (6)
C6	−6932 (15)	1188 (13)	3175 (7)	123 (6)
C7	−7021 (12)	1307 (14)	3648 (6)	100 (5)
C8	−5994 (10)	1266 (10)	4348 (6)	61 (4)
C9	−4971 (9)	1207 (9)	4534 (5)	57 (4)
C10	−4797 (9)	1203 (8)	5018 (5)	52 (3)
C11	−3861 (9)	1163 (9)	5192 (5)	56 (4)
C12	−3025 (9)	1132 (9)	4895 (5)	53 (3)
C13	−3206 (10)	1114 (9)	4416 (5)	62 (4)
C14	−4171 (10)	1179 (10)	4224 (6)	71 (4)
C15	−1639 (10)	1209 (8)	5473 (6)	56 (4)
C16	−520 (9)	1251 (9)	5517 (5)	57 (4)
C17	−132 (11)	1285 (10)	5978 (6)	75 (4)
C18	869 (12)	1312 (11)	6060 (7)	87 (5)
C19	1529 (12)	1273 (10)	5693 (6)	77 (4)
C20	1189 (10)	1267 (9)	5223 (5)	63 (4)
C21	153 (9)	1259 (9)	5136 (5)	50 (3)
C22	447 (10)	1392 (11)	4290 (5)	66 (4)
C23	−215 (11)	1554 (12)	3860 (5)	70 (4)
C24	−756 (12)	2523 (12)	3869 (6)	87 (4)
C25	−1443 (14)	2698 (16)	3449 (6)	125 (5)

Discussion. Final atomic coordinates are given in Table 1;* bond lengths and angles in Table 2. Short intramolecular and intermolecular contacts are reported in Table 3. An *ORTEP* (Johnson, 1976) plot of the molecule is shown in Fig. 1. Table 4 lists the dihedral angles responsible for determining the relative solid-state arrangement of the alkyloxy and quaternary ammonium side chains of the butoxy derivative and of the other homologous compounds so far investigated. In the title compound the benzamide moiety is nearly planar, the angles between the A and B rings (1) and the amide plane being 177 (1) and 173 (1)°, respectively. A strong intramolecular hydrogen bond [N—H···O 1.72 (1) Å] occurs between the amide H2 atom and the O4 atom of the butoxy chain; this has already been found in the other compounds of the series. The quaternary ammonium side chain in the butoxy derivative strongly resembles that of procaine hydrochloride and related compounds (Kashino, Ikeda & Haisa, 1982) with a *trans–trans–gauche* 'pharmacophoric pattern' of the dihedral angles τ_3, τ_4 and τ_5 (Table 4), as found in the propoxy, octyloxy and decyloxy-(II) compounds.

NMR measurements performed on all derivatives in DMSO solution showed some significant differences with respect to the solid state: (i) the N—H···O hydrogen bond disappears since the amide group is oriented so that the carbonyl group points toward O4, and (ii) the τ_3 dihedral angle changes its *trans* conformation so as to allow interaction between protons of the C7 and C14 atoms.

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55374 (13 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond lengths* (Å) *and angles* (°)

O1—C7	1.47 (2)	C9—C10	1.38 (2)
O1—C8	1.33 (2)	C9—C14	1.38 (2)
O2—C8	1.18 (2)	C10—C11	1.34 (2)
O3—C15	1.25 (2)	C11—C12	1.40 (2)
O4—C21	1.35 (2)	C12—C13	1.37 (2)
O4—C22	1.45 (2)	C13—C14	1.40 (2)
N1—C1	1.67 (2)	C15—C16	1.50 (2)
N1—C2	1.47 (2)	C16—C17	1.40 (2)
N1—C4	1.44 (2)	C16—C21	1.40 (2)
N1—C6	1.58 (2)	C17—C18	1.35 (2)
N2—C12	1.39 (2)	C18—C19	1.36 (2)
N2—C15	1.34 (2)	C19—C20	1.40 (2)
C2—C3	1.21 (4)	C20—C21	1.40 (2)
C4—C5	1.10 (4)	C22—C23	1.52 (2)
C6—C7	1.35 (3)	C23—C24	1.52 (2)
C8—C9	1.46 (2)	C24—C25	1.52 (2)

C7—O1—C8	118 (1)	N2—C12—C11	126 (1)
C21—O4—C22	120 (1)	C11—C12—C13	117 (1)
C4—N1—C6	114 (1)	N2—C12—C13	117 (1)
C2—N1—C6	107 (1)	C12—C13—C14	123 (1)
C2—N1—C4	106 (1)	C9—C14—C13	118 (1)
C1—N1—C6	107 (1)	O3—C15—N2	122 (2)
C1—N1—C4	108 (1)	N2—C15—C16	188 (1)
C1—N1—C2	115 (1)	O3—C15—C16	120 (1)
C12—N2—C15	129 (1)	C15—C16—C21	125 (1)
N1—C2—C3	114 (2)	C15—C16—C17	117 (1)
N1—C4—C5	145 (2)	C17—C16—C21	118 (1)
N1—C6—C7	120 (2)	C16—C17—C18	122 (2)
O1—C7—C6	110 (1)	C17—C18—C19	120 (2)
O1—C8—O2	121 (1)	C18—C19—C20	121 (1)
O2—C8—C9	126 (1)	C19—C20—C21	119 (1)
O1—C8—C9	113 (1)	C16—C21—C20	120 (1)
C8—C9—C14	120 (1)	O4—C21—C20	122 (1)
C8—C9—C10	121 (1)	O4—C21—C16	118 (1)
C10—C9—C14	120 (1)	O4—C22—C23	106 (1)
C9—C10—C11	121 (1)	C22—C23—C24	113 (1)
C10—C11—C12	122 (1)	C23—C24—C25	114 (1)

Table 3. *Intramolecular and intermolecular* I···H (< 3.5 Å) *interactions and* C—H···O (< 2.5 Å) *contacts*

$\mathrm{I\cdots H253^{i}}$	3.24 (2)	$\mathrm{I\cdots H32^{ii}}$	3.08 (4)
$\mathrm{I\cdots H11^{ii}}$	3.25 (2)	$\mathrm{I\cdots H61^{iii}}$	3.04 (2)
$\mathrm{I\cdots H12^{iii}}$	3.39 (2)	$\mathrm{I\cdots H62^{ii}}$	3.04 (2)
$\mathrm{I\cdots H21^{iv}}$	3.23 (2)	$\mathrm{I\cdots H18^{v}}$	3.38 (2)

$\mathrm{H22\cdots O1^{i}}$	2.27 (2)	$\mathrm{H17\cdots O3^{i}}$	2.39 (2)
$\mathrm{H32\cdots O1^{i}}$	2.36 (4)	$\mathrm{H242\cdots O4^{i}}$	2.60 (2)
$\mathrm{H10\cdots O2^{i}}$	2.60 (2)	$\mathrm{H42\cdots O3^{vi}}$	2.47 (2)
$\mathrm{H111\cdots O3^{i}}$	2.23 (2)	$\mathrm{H20\cdots O2^{iii}}$	2.31 (2)
$\mathrm{H14\cdots O1^{i}}$	2.34 (2)		

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

Table 4. *Selected dihedral angles* (°) *of the compounds of the series*

	$n = 3$	$n = 4$	$n = 8$	$n = 10$(I)	$n = 10$(II)
τ_1(O4—C22—C23—C24)	178	68 (1)	−72	−62	−177
τ_2(C10—C9—C8—O1)	175	−176 (1)	−177	−168	0
τ_3(C9—C8—O1—C7)	−175	−177 (1)	−179	176	174
τ_4(C8—O1—C7—C6)	132	−178 (1)	157	91	170
τ_5(O1—C7—C6—N1)	89	84 (2)	84	81	75
τ_6(C7—C6—N1—C1)	−55	−174 (2)	174	−55	169

The τ_1 dihedral angle is principally responsible for determining the different solid-state conformations of the aklyloxy chain, all the other angles being *trans* except for C23—C24—C25—C26 (−101°) of the decyloxy-(I) derivative (Dapporto & Sega, 1987). When τ_1 has a *gauche* conformation the alkyloxy and quaternary ammonium side chains point toward each other (as found in the butoxy derivative), reaching a 'loop' shape for the octyloxy derivative which has just the right alkyloxy chain length to achieve this peculiar conformation. In the decyloxy-(I) derivative, the second *gauche* dihedral angle causes the two side chains to point in different directions. This, coupled with an angle between the two benzene rings of 30.4°, allows the alkyloxy chain to lie over the benzamide moiety. To verify the rotational freedom around the τ_1 angle we have evaluated the rotational energy barrier using the rigid-rotor approximation for each compound of the series. In the case of the propoxy and butoxy derivatives, minima were found corresponding to *gauche* and *trans* conformations of τ_1. For both compounds, each conformation minimized using the *MMX* force field [derived from *MM*2 (Allinger, 1980)] exhibits a similar energy content. Therefore, the different conformations adopted by τ_1 in the propoxy and butoxy compounds seem to result from the packing forces. On the other hand, the τ_1 *gauche* conformation in the octyloxy derivative has a smaller energy content than the *trans* conformation, the only remarkable difference being in the van der Waals energy-term contributions. Therefore, we can ascribe the stabilization of the *gauche* conformation to the attractive interactions between the H atoms on the terminal C atoms of the octyloxy chain and those linked to a C atom of one of the ethyl groups of the quaternary N atom. This interaction, which is responsible for the 'loop' shape of the cation, also exists in DMSO solution as shown by the NMR studies already reported. The low conformation freedom of the octyloxy derivative, which has the highest pharmacological activity, suggests that its shape is the most suited to inducing a biological response.

The decyloxy derivative has greater conformational freedom as demonstrated by X-ray solid-state and NMR solution studies, and it crystallizes as two molecules [(I) and (II)] having a very different overall shape, but with comparable energy content. The (II) isomer shows an all-*trans* conformation (τ_1 = −177°) of the decyloxy chain which points in the

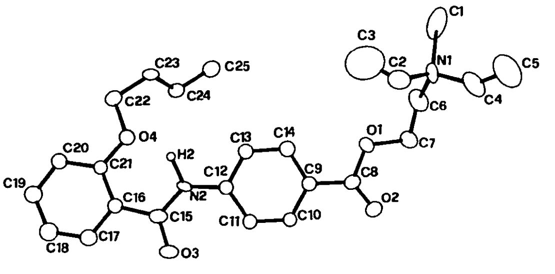

Fig. 1. View of the butoxy derivative with the atomic labelling system.

opposite direction to the quaternary N side chain ($\tau_2 = -3°$). In (I), the arrangement of the alkyloxy chain over the benzamide moiety allows the H atoms of the terminal C atoms to interact favourably with some of the H atoms of the *B* phenyl ring and with the O atoms of the ester group. This favourable interaction is supported by the lower van der Waals contribution to the total steric energy of this isomer with respect to the second isomer, which shows smaller bending and torsional energy values. On this basis we can assume that the van der Waals interactions involving the alkyloxy side chain are responsible for establishing the overall structure of the cation and its freedom of motion.

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Structure of a New C_{13}-Norisoprenoid

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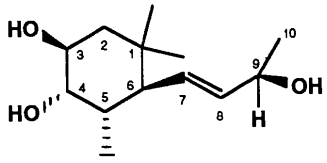
Abstract. (3*S*,4*S*,5*S*,6*S*,9*R*)-3,4-Dihydroxy-5,6-dihydro-β-ionol, $C_{13}H_{24}O_3$, $M_r = 228.3$, monoclinic, $P2_1$, $a = 6.746$ (1), $b = 7.712$ (1), $c = 12.620$ (10) Å, $\beta = 102.86$ (1)°, $V = 640.1$ (5) Å^3, $Z = 2$, $D_x = 1.18$ g cm^{-3}, λ(Cu $K\alpha$) = 1.5418 Å, $\mu = 6.21$ cm^{-1}, $F(000) = 252$, $T = 298$ K, $R = 0.055$, $wR = 0.058$ for 622 reflections with $I \geq 3\sigma(I)$. The ring adopts a slightly distorted chair conformation, and the side chain is in an extended configuration. The structure is stabilized by two intermolecular O—H···O hydrogen bonds [2.846 (1) and 2.860 (1) Å]. Bond lengths and angles are in the usual range.

Introduction. The compound (I) was isolated from the leaves of *Apollonias barbujana* (Lauraceae) which were collected in the Canary Islands. A large number of the ionone-related compounds have been found mainly in the tobacco leaf (Enzell, Wahlberg & Aasen, 1977; Wahlberg, Eklund, Enzell & Berg, 1987; Ohloff, 1978; Wahlberg & Enzell, 1987), *Vitis vinifera* grapes (Nykänen & Suomalainen, 1983; Marais, 1983) and quince fruit (Winterhalter, Harmsen & Trani, 1991; Ishihara, Tsuneya, Shiota, Shiga & Nakatsu, 1986).



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