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

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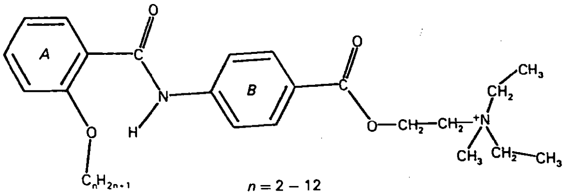
Abstract. $C_{31}H_{47}N_2O_4^+.I^-$, $M_r = 638{\cdot}63$, monoclinic, $P2_1/n$, $a = 40{\cdot}200\,(10)$, $b = 16{\cdot}328\,(4)$, $c = 9{\cdot}975\,(3)$ Å, $\beta = 95{\cdot}72\,(5)°$, $V = 6515\,(3)$ Å^3, $Z = 8$, $D_x = 1{\cdot}302$ g cm^{-3}, Cu $K\alpha$, $\lambda = 1{\cdot}5418$ Å, $\mu = 80{\cdot}2$ cm^{-1}, $F(000) = 2656$, $T = 293$ K, final conventional R is 0·065 for 3695 unique observed reflections. The title compound is present, in the crystalline state, as two molecules which differ in all main conformational features: the relative conformations of the benzoylanilide moieties (in one molecule the departure from planarity is greater than in the other), the relative orientations of the quaternary N-atom side chains and also the decyloxy side chains show remarkable differences in their relative conformations.

Introduction. The substance presented here [$n = 10$ in formula (1)] is part of a series of synthetized molecules which show smooth-muscle relaxant activity (Ghelardoni, Pestellini, Pisanti & Volterra, 1973). The activity is strongly affected by both position and length of the alkyloxy side chain: the pharmacological effect increases when the alkyloxy chain is *ortho* to the amide group and reaches a maximum for the octyloxy derivative ($n = 8$). The 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 (Maggi, Grimaldi, Volterra & Meli, 1983; Maggi & Meli, 1983; Maggi, Manzini & Meli, 1983).

Extensive NMR studies carried out in dimethyl sulfoxide on the propyloxy ($n = 3$), butyloxy ($n = 4$), octyloxy ($n = 8$) and decyloxy ($n = 10$) derivatives have shown that substantial conformational and dynamical changes occur with the increase in length of the alkyloxy chain (Sega, Ghelardoni, Pestellini, Pogliani & Valensin, 1984; Valensin, Pogliani, Ghelardoni, Pestellini & Sega, 1984; Sega, Gaggelli & Valensin, 1985; Valensin, Gaggelli, Lepri & Sega, 1986). In the octyloxy derivative internal motions within the benzoanilide moiety and along the two side chains are the most restricted; this loss of conformational freedom could explain the dipolar connectivity between the H atoms of the terminal methyl of the octyloxy chain and the methyls of the ethyl groups bonded to the quaternary N atom. The crystalline structure of the same compound also shows a conformation with a clear bending of the ends of the two side chains toward each other (Dapporto & Sega, 1986).

In the decyloxy derivative the motional freedom is far greater and the dipolar connectivity between the protons of the terminal methyls is completely absent. The connections found between some key features for the octyloxy derivative in the solid state and in solution prompted us to determine the crystalline structure of the decyloxy derivative. We were interested, above all, in seeing how the remarkable differences presented in solution by these two compounds were reflected in their crystalline structures.



(1)

Experimental. Prismatic crystals obtained by slow crystallization from dimethyl sulfoxide. Philips PW1100 diffractometer; lattice parameters determined using 25 reflections (θ range: 15·8–22·8°); 6782 measured reflections, $2\theta \leq 96°$, θ–2θ scan technique, $-38 \leq h \leq 38$, $0 \leq k \leq 15$, $0 \leq l \leq 9$; 3695 unique observed reflections with $I \geq 3\sigma(I)$ out of a total of 6782 unique reflections; three standard reflections ($\bar{6}31$, $8\bar{2}0$, 530), no significant variation of their intensity; Lp correction, absorption correction with numerical method of *SHELX*76 program (Sheldrick, 1976), transmission factor between 0·36 and 0·53 for a parallelepipedal crystal of dimensions 0·12 × 0·10 × 0·08 mm delimited by (100), (010) and (001) and their

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centrosymmetric faces; scattering factors for non-H atoms (*International Tables for X-ray Crystallography,* 1974, p. 99) and for H atoms (Stewart, Davidson & Simpson, 1965), anomalous-dispersion corrections (*International Tables for X-ray Crystallography,* 1974, p. 149), $R_{\text{int}} = 0{\cdot}061$. Patterson and Fourier methods; full-matrix least-squares refinement, $\sum w(|F_o| - |F_c|)^2$ minimized; anisotropic thermal parameters for I, O and N atoms, isotropic for other atoms; H atoms (except those of the decyloxy chain because of high thermal factors) introduced in calculated positions with overall U of 0·05 Å^2 and not refined; 376 refined parameters; max. $\Delta/\sigma = 0{\cdot}82$; final $R = 0{\cdot}065$, $wR = 0{\cdot}066$, goodness of fit $S = 2{\cdot}45$, $w = 1/\sigma^2$; max. and min. $\Delta\rho$ excursions $-0{\cdot}45$ and $0{\cdot}91$ e Å^{-3} respectively; Gould-SEL 32/70 computer; *SHELX76* (Sheldrick, 1976) and *PARST* (Nardelli, 1983) programs.

Discussion. Final atomic coordinates are given in Table 1;* bond lengths and angles in Table 2. The *ORTEP* (Johnson, 1976) plots of molecules (I) and (II) are shown in Fig. 1.

The interactions between the organic cation and the anion occur through H atoms; I···H interactions are shorter than the sum of the van der Waals radii [3·42 Å from $f_{\text{H}} = 1{\cdot}20$ and $f_{\text{I}} = 2{\cdot}22$ Å; Pauling (1960)] and have average values of 3·19 (range: 3·00–3·37) and 3·21 (range: 2·87–3·44 Å) for molecules (I) and (II), respectively. Intermolecular hydrogen bonds involving the most electronegative atoms (N and O) as donors and acceptors are not present.

The decyloxy derivative crystallizes as two molecules, (I) and (II), which differ significantly in all main conformational features.

In molecule (I), the largest displacements of the atoms defining the two benzene planes are −0·014 (12) and 0·011 (12) Å for rings *A* and *B*, respectively. The conformation of the benzoylanilide moiety departs from planarity in both molecules but more significantly in (I); in (I) the angles between rings *A* and *B* and the amide plane are 10 (1) and 22 (1)° respectively; in (II) the same angles are 4 (1) and 14 (1)° respectively. In the propyloxy ($n = 3$) and octyloxy ($n = 8$) derivatives the benzoylanilide moieties are close to planarity. An intramolecular hydrogen bond is present between O(4) and the amide N(2) atom in both molecules: (I) O(4)···H—N (2) = 1·79 (1) Å; (II) O(4)···H—N (2) = 1·76 (2) Å.

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

	x	y	z	U_{eq}*/U_{iso}
I(1)	−1845 (<1)	4553 (1)	2885 (1)	88 (1)
I(2)	−2654 (<1)	1950 (1)	−2986 (1)	129 (1)
Molecule (I)				
O(1)	1640 (2)	−1034 (5)	4534 (8)	75 (6)
O(2)	1479 (2)	−2065 (5)	3131 (8)	80 (6)
O(3)	1497 (3)	177 (5)	−2712 (8)	111 (8)
O(4)	1524 (3)	2567 (6)	−1374 (10)	148 (10)
N(1)	2213 (3)	−1500 (6)	6891 (10)	78 (8)
N(2)	1546 (3)	975 (6)	−879 (9)	74 (8)
C(1)	2268 (3)	−680 (7)	6229 (12)	71 (4)
C(2)	2085 (3)	−1358 (9)	8242 (14)	100 (5)
C(3)	2309 (4)	−856 (10)	9235 (16)	147 (6)
C(4)	2542 (4)	−1917 (9)	6977 (16)	120 (5)
C(5)	2554 (4)	−2737 (10)	7666 (17)	157 (7)
C(6)	1952 (3)	−2004 (7)	6024 (12)	77 (4)
C(7)	1626 (3)	−1582 (7)	5669 (12)	75 (4)
C(8)	1557 (3)	−1353 (9)	3297 (14)	67 (4)
C(9)	1557 (3)	−746 (7)	2233 (12)	59 (3)
C(10)	1418 (3)	−948 (7)	948 (12)	69 (4)
C(11)	1412 (3)	−390 (7)	−98 (12)	69 (3)
C(12)	1545 (3)	385 (8)	85 (13)	69 (4)
C(13)	1679 (3)	587 (8)	1407 (13)	83 (4)
C(14)	1687 (3)	39 (7)	2455 (13)	74 (4)
C(15)	1524 (3)	863 (9)	−2214 (15)	77 (4)
C(16)	1544 (3)	1621 (8)	−3081 (13)	70 (4)
C(17)	1577 (3)	1451 (9)	−4430 (13)	89 (4)
C(18)	1619 (4)	2094 (9)	−5303 (17)	118 (5)
C(19)	1624 (3)	2880 (9)	−4855 (16)	105 (5)
C(20)	1584 (3)	3085 (9)	−3578 (13)	88 (4)
C(21)	1543 (3)	2436 (8)	−2695 (15)	80 (4)
C(22)	1429 (4)	3384 (11)	−841 (18)	146 (7)
C(23)	1215 (7)	3293 (15)	269 (27)	226 (11)
C(24)	928 (7)	3018 (16)	580 (28)	229 (11)
C(25)	761 (6)	2745 (15)	1973 (27)	214 (10)
C(26)	772 (6)	1727 (15)	2024 (25)	200 (9)
C(27)	698 (5)	1206 (16)	3141 (24)	194 (9)
C(28)	712 (5)	317 (15)	3097 (24)	183 (9)
C(29)	667 (6)	−83 (18)	4266 (29)	220 (11)
C(30)	627 (7)	−964 (21)	4075 (33)	244 (14)
C(31)	623 (10)	−1314 (25)	5064 (44)	384 (23)
Molecule (II)				
O(1)	3551 (2)	1567 (4)	−5177 (8)	71 (6)
O(2)	3598 (2)	2485 (5)	−3504 (9)	87 (7)
O(3)	4946 (3)	−762 (7)	−3310 (14)	153 (11)
O(4)	5452 (3)	646 (7)	−381 (11)	129 (9)
N(1)	2981 (2)	674 (6)	−6984 (9)	73 (8)
N(2)	4950 (3)	447 (7)	−2251 (12)	104 (10)
C(1)	2802 (4)	503 (9)	−8347 (14)	116 (5)
C(2)	2736 (3)	497 (8)	−6009 (14)	91 (4)
C(3)	2466 (4)	1017 (10)	−5961 (17)	153 (7)
C(4)	3249 (3)	64 (8)	−6636 (14)	95 (5)
C(5)	3515 (4)	97 (10)	−7533 (16)	144 (6)
C(6)	3095 (3)	1557 (7)	−6905 (11)	67 (4)
C(7)	3221 (3)	1885 (7)	−5567 (11)	65 (3)
C(8)	3713 (3)	1912 (9)	−4095 (14)	69 (4)
C(9)	4032 (3)	1516 (7)	−3658 (12)	69 (4)
C(10)	4152 (3)	854 (8)	−4317 (13)	84 (4)
C(11)	4457 (3)	469 (9)	−3883 (14)	97 (4)
C(12)	4642 (4)	778 (8)	−2778 (14)	88 (4)
C(13)	4530 (3)	1456 (8)	−2111 (14)	93 (4)
C(14)	4224 (3)	1814 (8)	−2549 (13)	86 (4)
C(15)	5071 (5)	−274 (13)	−2506 (18)	113 (6)
C(16)	5414 (4)	−520 (10)	−1732 (16)	106 (5)
C(17)	5533 (4)	−1266 (11)	−2119 (18)	138 (6)
C(18)	5844 (5)	−1555 (12)	−1407 (18)	149 (7)
C(19)	5982 (5)	−1069 (11)	−461 (18)	139 (6)
C(20)	5886 (4)	−336 (10)	−58 (17)	127 (6)
C(21)	5572 (5)	−79 (11)	−755 (18)	116 (6)
C(22)	5611 (4)	1174 (10)	566 (18)	141 (7)
C(23)	5395 (4)	1939 (11)	717 (17)	135 (6)
C(24)	5557 (5)	2569 (12)	1682 (20)	158 (7)
C(25)	5348 (5)	3335 (12)	1792 (19)	148 (7)
C(26)	5535 (5)	3946 (13)	2727 (20)	167 (7)
C(27)	5318 (6)	4696 (14)	2883 (22)	183 (8)
C(28)	5499 (6)	5332 (15)	3767 (24)	196 (9)
C(29)	5256 (6)	6034 (16)	3884 (24)	203 (9)
C(30)	5433 (7)	6654 (18)	4889 (28)	237 (11)
C(31)	5172 (8)	7301 (18)	4906 (30)	279 (14)

* $U_{\text{eq}} = \frac{1}{3}\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j$ for I, O, N atoms.

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* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, C—C bond lengths and C—C—C angles within the decyloxy side chain, I···H distances and C—H···O contacts have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43928 (28 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond lengths* (Å) *and angles* (°) *for molecules* (I) *and* (II)

	(I)	(II)		(I)	(II)
O(1)–C(7)	1·45 (1)	1·44 (1)	C(6)–C(7)	1·49 (2)	1·48 (2)
O(1)–C(8)	1·35 (2)	1·33 (1)	C(8)–C(9)	1·45 (2)	1·47 (2)
O(2)–C(8)	1·21 (2)	1·22 (2)	C(9)–C(10)	1·39 (2)	1·38 (2)
O(3)–C(15)	1·22 (2)	1·20 (2)	C(9)–C(14)	1·39 (2)	1·37 (2)
O(4)–C(21)	1·34 (2)	1·34 (2)	C(10)–C(11)	1·38 (2)	1·41 (2)
O(4)–C(22)	1·50 (2)	1·39 (2)	C(11)–C(12)	1·38 (2)	1·36 (2)
N(1)–C(1)	1·52 (1)	1·51 (2)	C(12)–C(13)	1·41 (2)	1·39 (2)
N(1)–C(2)	1·51 (2)	1·47 (2)	C(13)–C(14)	1·37 (2)	1·39 (2)
N(1)–C(4)	1·48 (2)	1·48 (2)	C(15)–C(16)	1·51 (2)	1·56 (2)
N(1)–C(6)	1·53 (1)	1·51 (2)	C(16)–C(17)	1·39 (2)	1·38 (2)
N(2)–C(12)	1·36 (2)	1·40 (2)	C(16)–C(21)	1·39 (2)	1·32 (2)
N(2)–C(15)	1·34 (2)	1·31 (2)	C(17)–C(18)	1·38 (2)	1·45 (2)
C(2)–C(3)	1·51 (2)	1·38 (2)	C(18)–C(19)	1·36 (2)	1·31 (2)
C(4)–C(5)	1·50 (2)	1·46 (2)	C(19)–C(20)	1·34 (2)	1·33 (2)
			C(20)–C(21)	1·40 (2)	1·44 (2)

	(I)	(II)		(I)	(II)
C(8)–O(1)–C(7)	117 (1)	115 (1)	C(12)–C(11)–C(10)	122 (1)	118 (1)
C(22)–O(4)–C(21)	122 (1)	126 (1)	C(13)–C(12)–C(11)	116 (1)	120 (1)
C(2)–N(1)–C(1)	109 (1)	105 (1)	C(11)–C(12)–N(2)	126 (1)	123 (1)
C(4)–N(1)–C(1)	105 (1)	111 (1)	C(13)–C(12)–N(2)	118 (1)	116 (1)
C(6)–N(1)–C(1)	110 (1)	109 (1)	C(14)–C(13)–C(12)	122 (1)	120 (1)
C(4)–N(1)–C(2)	114 (1)	104 (1)	C(13)–C(14)–C(9)	120 (1)	121 (1)
C(6)–N(1)–C(2)	108 (1)	112 (1)	N(2)–C(15)–O(3)	121 (1)	126 (2)
C(6)–N(1)–C(4)	110 (1)	115 (1)	C(16)–C(15)–N(2)	117 (1)	118 (1)
C(15)–N(2)–C(12)	127 (1)	127 (1)	C(16)–C(15)–O(3)	121 (1)	117 (2)
C(3)–C(2)–N(1)	116 (1)	119 (1)	C(17)–C(16)–C(15)	114 (1)	114 (1)
C(5)–C(4)–N(1)	115 (1)	113 (1)	C(21)–C(16)–C(15)	129 (1)	124 (2)
C(7)–C(6)–N(1)	115 (1)	117 (1)	C(18)–C(17)–C(16)	119 (1)	117 (1)
C(6)–C(7)–O(1)	112 (1)	110 (1)	C(19)–C(18)–C(17)	120 (1)	116 (2)
O(2)–C(8)–O(1)	122 (1)	123 (1)	C(20)–C(19)–C(18)	123 (1)	130 (2)
C(9)–C(8)–O(1)	113 (1)	114 (1)	C(21)–C(20)–C(19)	116 (1)	112 (1)
C(9)–C(8)–O(2)	125 (1)	124 (1)	C(20)–C(21)–C(16)	123 (1)	122 (2)
C(10)–C(9)–C(8)	119 (1)	123 (1)	C(16)–C(21)–O(4)	115 (1)	122 (2)
C(14)–C(9)–C(8)	123 (1)	119 (1)	C(20)–C(21)–O(4)	121 (1)	116 (1)
C(11)–C(10)–C(9)	121 (1)	123 (1)			

		(I)	(II)
Decyloxy chain			
C–C	average	1·44	1·52
	range	1·14–1·66	1·49–1·55
C–C–C	average	121	109
	range	106–144	101–114

The quaternary ammonium side chain strongly resembles that of procaine hydrochloride and related compounds (Kashino, Ikeda & Haisa, 1982); in these molecules the sequence of torsional angles is *trans–trans–gauche* and the same pharmacological pattern is shown by the propyloxy and octyloxy derivatives. Even in this respect molecules (I) and (II) differ; indeed, the sequence of torsional angles τ_1[C(9)–C(8)–O(1)–C(7)], τ_2[C(8)–O(1)–C(7)–C(6)], τ_3[O(1)–C(7)–C(6)–N(1)], which are 176 (1) (I) and 174 (1)° (II), 90 (1) (I) and 170 (1)° (II), 82 (1) (I) and 75 (1)° (II), respectively, shows that for (II) we have again the *trans–trans–gauche* pattern but for (I) this pattern is *trans–gauche–gauche.*

The orientations of the decyloxy chain in (I) and (II) are once more strikingly different. In (II) the sequence of torsional angles from τ_1[C(21)–O(4)–C(22)–C(23)] to τ_9[C(28)–C(29)–C(30)–C(31)] shows an 'all *trans*' conformation as in the propyloxy derivative. However, in (II) the two side chains extend in opposite directions with respect to the benzoylanilide moiety (see Fig. 1*b*). In (I) the same sequence of torsional angles shows two significant deviations from the 'all *trans*' geometry: τ_2[O(4)–C(22)–C(23)–C(24)] = −62 (5) and τ_4[C(23)–C(24)–C(25)–C(26)] = −101 (4)°. These changes coupled with the angle between the two benzene rings [30·4 (4)°] determine a conformation which significantly differs from both (II) and the octyloxy derivative: in particular, the two side chains do not bend toward each other.

It is worth noting that in going from the octyloxy to the decyloxy chain a noticeable change in the conformation of their respective molecules is brought about: for the octyloxy derivative we have only one conformation with a 'loop structure' (Dapporto & Sega, 1986) while the decyloxy derivative crystallizes in molecular conformations corresponding to (I) and (II), none of which presents or even resembles the peculiar conformation of the most active compound.

So some key features of the octyloxy and decyloxy derivatives as determined by NMR investigations in solution find a correspondence in the conformation(s) adopted by these compounds in the crystalline state.

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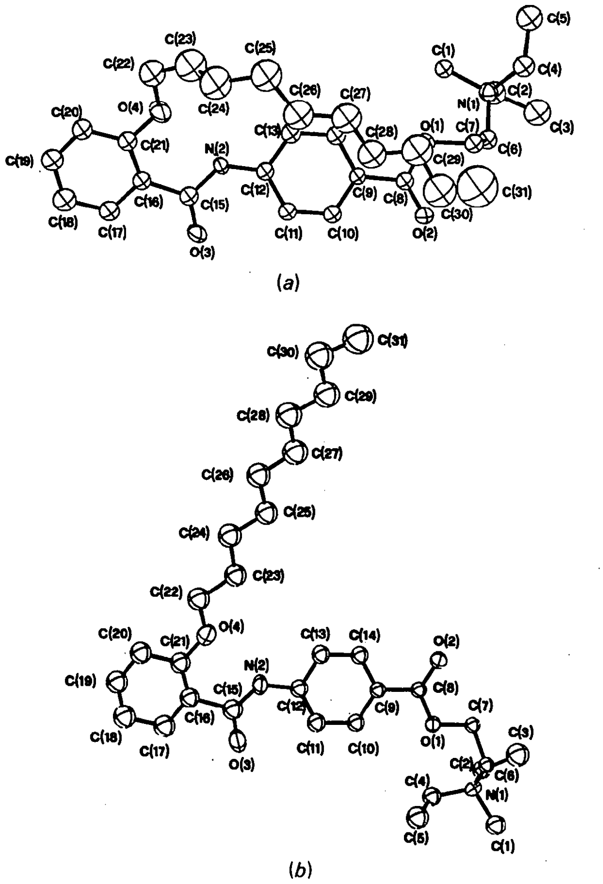

Fig. 1. View of the decyloxy derivative (ellipsoids at 30% probability level) with the atomic labelling system: (*a*) molecule (I), (*b*) molecule (II).

of Florence for collection of the intensity data and for computer time.

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Studies in Nonlinear Optical Materials: Structure of 3-Menthyl 2-[Bis(dimethylamino)methylene]-3-oxobutyrate Hemihydrate

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Abstract. $C_{19}H_{34}N_2O_3.\frac{1}{2}H_2O$, $M_r = 347{\cdot}5$, monoclinic, $C2$, $a = 15{\cdot}473\,(3)$, $b = 6{\cdot}963\,(2)$, $c = 20{\cdot}708\,(4)$ Å, $\beta = 108{\cdot}2\,(2)°$, $V = 2119\,(2)$ Å^3, $Z = 4$, $D_x = 1{\cdot}089$ Mg m^{-3}, $\lambda(\mathrm{Cu}\,K\alpha) = 1{\cdot}5418$ Å, $\mu = 0{\cdot}523$ mm^{-1}, $F(000) = 760{\cdot}0$, $T = 293$ K, $R = 0{\cdot}068$ for 1967 unique reflections. The C=C bond length is 1·447 (6) Å, significantly longer than in ethylene, 1·336 (2) Å. The crystal structure is stabilized by O—H···O hydrogen bonding. Explanation for the observed low second-harmonic-generation efficiency (0·5 times that of urea) is provided.

Introduction. Among the various driving forces stimulating interest in nonlinear optical materials is the development of 'all-optical devices' suitable for optical communication or optical signal processing components which permit longer band width or shorter switching times than are achieved with their electronic counterparts (Williams, 1984). In the search for new nonlinear optical materials, organic molecular crystals are of particular interest due to the extremely large variety of compounds that can be investigated for practical applications satisfying the stringent requirement (Tweig & Jain, 1983; Zyss, 1982). Systematic studies have shown that substituted aromatic molecules may exhibit very large optical nonlinearities especially if suitable donors and acceptors are bonded to the molecular framework. For example, 2-methyl-4-nitroaniline shows exceptionally large second-harmonic nonlinear optical susceptibility (Lipscomb, Garito & Narang, 1981). Of the many potential applications of organic materials to optics technology, the one aspect the present authors have chosen to concentrate upon is the development of systems exhibiting large second-harmonic generation (SHG). In this phenomenon, light with large intensity, as with laser light, with a fundamental frequency ω interacts with the material in such a way that efficient conversion to 2ω takes place. The necessary conditions to be satisfied are (i) the crystals must be noncentrosymmetric and (ii) the molecule should have loosely bound electrons that can be displaced by the optical field. Earlier crystallographic studies on the structures of a large number of push–pull ethylenes with donor and acceptor groups in the vicinal positions of the ethylene have shown considerable delocalization of π electrons from the donor to the acceptor across the ethylene bond (Adhikesavalu, Kamath & Venkatesan, 1983). Indeed the C=C bond length in one case is observed to be as large as 1·468 (3) Å (Adhikesavalu & Venkatesan, 1983*a*). It appeared to us that push–pull ethylenes could be a promising system for second-order nonlinear effects. A programme of research has been initiated by us to develop suitably substituted push–pull

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