Fig. 2. A view of the molecule parallel to the anthraquinone ring showing the disposition of the vanillyl rings.

Discussion. The vanillyl substituents do indeed adopt positions above and below the plane of the anthrone ring (Fig. 2) which explains the NMR shielding effect. The planes of the vanillyl groups are tilted with respect to the anthrone ring, the methoxy group being nearest to the anthrone ring in both cases. Unlike 10-bromoanthrone (Destro, D'Alfonso & Simonetta, 1973), the anthrone ring in the present compound has a minimum amount of puckering, the angle between the planes of the outer phenyl rings being only 1·6°. However, as in 10-bromoanthrone, the central ring adopts a boat-like conformation, the O atom being 0·21 Å out of the plane through C(2), C(7), C(9) and C(14).

The molecules form hydrogen-bonded spirals parallel to *b*. The H atom on O(35) is hydrogen bonded to the carbonyl O atom of a screw-related molecule [H(35)···O(15) = 1·91 Å, O(15)···H(35)—O(35) = 151·6°]. There is no other intermolecular bonding.

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The Structure of 2-(5'-Chloro-2'-hydroxybenzoyl)benzoic Acid

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Abstract. $C_{14}H_9ClO_4$, $M_r = 276\cdot7$, monoclinic, $P2_1/c$, $a = 14\cdot724$ (2), $b = 7\cdot104$ (1), $c = 13\cdot439$ (3) Å, $\beta = 113\cdot60$ (1)°, $Z = 4$, $V = 1288$ Å^3, $D_x = 1\cdot426$, $D_m = 1\cdot425$ Mg m^{-3}, $F(000) = 568$. The structure was solved by direct methods, using three-dimensional photographic data, and refined to an R value of 0·069 for 1088 observed reflexions. In the crystal structure the molecules exist as hydrogen-bonded centro-symmetric dimers. The O—H···O bond is 2·623 (7) Å.

Introduction. This work is a continuation of the studies on the structures of substituted 2-aroylbenzoic acids.

Crystals of $C_{14}H_9ClO_4$ grown from aqueous acetic acid solution were well formed colourless transparent plates. The unit-cell dimensions and the space group were determined from oscillation and Weissenberg photographs. (The unit-cell dimensions were confirmed by measurements on a Syntex $P2_1$ diffractometer.) According to systematic absences the space group was $P2_1/c$. The diffraction data were collected on equi-inclination Weissenberg photographs, with Cu $K\alpha$ radiation, for the layers $h0l$ to $h6l$. The $hk0$ zonal data were also recorded for scaling purposes. The intensities of 1088 independent reflexions were visually estimated by comparison with calibrated strips. The data were corrected for Lorentz and polarization factors and for spot shape, but not for absorption.

After an unsuccessful attempt to solve the structure by the Patterson method, it was solved by direct methods using the Σ_2 and *PHASE* programs of the XRAY 70 system (Stewart, Kundell & Baldwin, 1970). An E map computed with 203 signs for $E > 1\cdot5$ clearly revealed the positions of all 19 non-hydrogen atoms in the structure ($R = 0\cdot337$). The structure was refined by the full-matrix least-squares program *CRYLSQ* first isotropically and then anisotropically to an R value of 0·082. At this stage the positions of eight of the nine H atoms were found on a difference Fourier map. The H

Table 1. *Fractional atomic coordinates* ($\times 10^4$, H atoms $\times 10^3$) *with estimated standard deviations in parentheses*

	x	y	z	B_{eq}* (Å^2)
Cl	401 (2)	5291 (3)	3868 (2)	7·0
O(1)	4211 (3)	3473 (5)	4213 (3)	4·8
O(2)	4951 (4)	3395 (6)	6021 (4)	5·9
O(3)	2253 (4)	2667 (8)	1002 (4)	7·2
O(4)	3230 (4)	342 (7)	2456 (4)	6·2
C(1)	2122 (4)	2485 (7)	2719 (5)	3·9
C(2)	1855 (5)	3272 (10)	1675 (5)	5·4
C(3)	1152 (6)	4730 (12)	1360 (6)	6·7
C(4)	714 (6)	5341 (10)	2030 (7)	6·4
C(5)	978 (5)	4516 (8)	3044 (6)	5·0
C(6)	1687 (4)	3104 (8)	3410 (5)	4·1
C(7)	2886 (4)	989 (8)	3079 (5)	4·4
C(8)	3176 (4)	123 (7)	4170 (5)	4·0
C(9)	3898 (4)	870 (7)	5136 (5)	3·9
C(10)	4142 (5)	−47 (8)	6113 (5)	4·8
C(11)	3705 (5)	−1754 (9)	6169 (6)	5·7
C(12)	2994 (6)	−2499 (9)	5228 (6)	6·1
C(13)	2741 (5)	−1600 (8)	4247 (6)	5·6
C(14)	4361	2712 (8)	5072 (5)	4·2
H(1)	192	244	426	
H(2)	238	−203	345	
H(3)	95	553	49	
H(4)	277	−388	546	
H(5)	383	−248	691	
H(6)	470	44	689	
H(7)	523	475	593	
H(8)	4	641	177	

* $B_{eq} = 8\pi^2 U_{eq}$; $U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33} + 2U_{13}\cos\beta)$.

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

C(1)–C(2)	1·411 (10)		C(7)–C(8)	1·486 (10)
C(2)–C(3)	1·404 (12)		C(8)–C(9)	1·411 (12)
C(3)–C(4)	1·372 (16)		C(9)–C(10)	1·378 (10)
C(4)–C(5)	1·388 (12)		C(10)–C(11)	1·389 (9)
C(5)–C(6)	1·388 (9)		C(11)–C(12)	1·383 (13)
C(6)–C(1)	1·395 (11)		C(12)–C(13)	1·375 (11)
C(2)–O(3)	1·332 (11)		C(13)–C(8)	1·405 (9)
C(5)–Cl	1·734 (11)		C(9)–C(14)	1·493 (8)
C(1)–C(7)	1·481 (9)		C(14)–O(1)	1·212 (9)
C(7)–O(4)	1·228 (11)		C(14)–O(2)	1·316 (11)

C(1)–C(2)–C(3)	118·1 (8)		C(8)–C(7)–O(4)	118·9 (5)
C(2)–C(3)–C(4)	121·2 (8)		C(7)–C(8)–C(9)	124·4 (5)
C(3)–C(4)–C(5)	119·3 (7)		C(7)–C(8)–C(13)	118·3 (5)
C(4)–C(5)–C(6)	121·9 (8)		C(13)–C(8)–C(9)	117·2 (6)
C(5)–C(6)–C(1)	118·2 (6)		C(8)–C(9)–C(10)	120·8 (5)
C(6)–C(1)–C(2)	121·1 (5)		C(9)–C(10)–C(11)	121·0 (5)
C(2)–C(1)–C(7)	118·9 (6)		C(10)–C(11)–C(12)	118·8 (7)
C(1)–C(2)–O(3)	121·6 (6)		C(11)–C(12)–C(13)	120·9 (7)
C(3)–C(2)–O(3)	120·3 (7)		C(12)–C(13)–C(8)	121·3 (6)
Cl–C(5)–C(4)	118·4 (6)		C(8)–C(9)–C(14)	118·0 (5)
Cl–C(5)–C(6)	119·6 (6)		C(10)–C(9)–C(4)	121·2 (5)
C(1)–C(7)–C(8)	120·0 (6)		C(9)–C(14)–O(1)	122·2 (5)
C(1)–C(7)–O(4)	120·8 (6)		C(9)–C(14)–O(2)	114·0 (6)
			O(1)–C(14)–O(2)	123·8 (5)

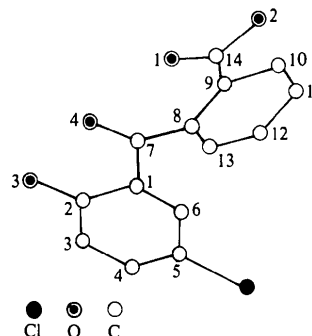Fig. 1. The molecule viewed along *b* with the numbering of the atoms.

atoms were included in the subsequent refinement with the isotropic temperature factors of their adjacent atoms. The final refinement with anisotropic thermal parameters for non-hydrogen atoms and fixed positional and thermal parameters for the H atoms gave $R = 0\cdot069$ and $R_w = 0\cdot089$ for all observed reflexions. The weighting scheme $w = 1/(A + B|F_o| + C|F_o|^2)$ (Cruickshank, Pilling, Bujosa, Lovell & Truter, 1961) was used with $A = 3\cdot62$, $B = 0\cdot0154$, $C = 0$. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962). A final difference map showed no peaks higher than $0\cdot26$ e Å^{-3}. In the final cycle of refinement the maximum shift/error and average shift/error were $0\cdot058$ and $0\cdot014$ respectively. The atomic coordinates are listed in Table 1.*

Discussion. Bond lengths and angles are given in Table 2. A projection of the molecule along the *b* axis with the atomic numbering is shown in Fig. 1. The average C—C bond lengths in the two benzene rings are not significantly different from the expected values; mean

C—C distances in rings C(1)–C(6) and C(8)–C(13) are $1\cdot393$ (12) and $1\cdot390$ (11) Å, respectively. Both benzene rings are planar, with mean deviations of $0\cdot008$ and $0\cdot006$ Å respectively, and make a dihedral angle of $82\cdot6°$. The Cl and O(3) substituents are approximately coplanar with their benzene ring. The C—Cl bond has a length of $1\cdot734$ (11) Å, typical of values reported for this bond (Rudman, 1971). The grouping around C(7), including the carbonyl oxygen O(4), C(1) and C(8), forms a plane with mean deviation $0\cdot02$ Å [the maximum deviation is for C(7), $-0\cdot03$ Å]. The strictly planar carboxyl group is rotated around the C(9)—C(14) bond, making an angle of $6\cdot0°$ with the plane through the aromatic ring to which it is attached.

The molecules, related by the symmetry operation $1-x$, $1-y$, $1-z$, form dimers through intermolecular hydrogen bonds between the carboxyl groups. The O(2)—H(7)$\cdots$O(1') hydrogen bond has O(2)$\cdots$O(1') = $2\cdot623$ (7) Å.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35582 (29 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Intermolecular distances* (Å) *less than* 3·5 Å
between the non-hydrogen atoms

$C(6)\cdots O(3^i)$	3·286 (12)	$C(11)\cdots O(4^{ii})$	3·308 (10)
$C(10)\cdots O(3^i)$	3·206 (9)	$O(2)\cdots C(11^{iii})$	3·493 (23)
$C(9)\cdots O(3^i)$	3·248 (13)		

Symmetry code: (i) $x, \frac{1}{2} - y, \frac{1}{2} + z$; (ii) $x, -\frac{1}{2} - y, \frac{1}{2} + z$; (iii) $1 - x$, $\frac{1}{2} + y, \frac{3}{2} - z$.

In addition, there is a close contact of 2·523 (13) Å between the phenolic O(3) atom and the O(4) carbonyl atom, which no doubt represents an intramolecular hydrogen bond. In spite of several attempts, the position of the H atom, as in 2-(4'-chloro-2'-hydroxybenzoyl)benzoic acid (Skrzat, 1980), could not be determined from a difference map.

The packing of dimers in the crystal is achieved by van der Waals forces. There are some short contacts but none is significantly different from the sum of the van der Waals radii (Table 3).

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2'-Acetamido-2-chloro-4'-diethylamino-4-mesylazobenzene and
2-Chloro-4'-diethylamino-4-mesyl-2'-propionamidoazobenzene

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Abstract. $C_{19}H_{23}ClN_4O_3S$: $M_r = 422·9$, monoclinic, $P2_1/c$, $a = 4·913$ (1), $b = 16·139$ (2), $c = 25·485$ (3) Å, $\beta = 93·25$ (2)°, $V = 2017·5$ Å³, $Z = 4$, $D_x = 1·392$, $D_m = 1·37$ Mg m⁻³. $C_{20}H_{25}ClN_4O_3S$: $M_r = 437·0$, monoclinic, $P2_1/c$, $a = 8·994$ (2), $b = 17·039$ (3), $c = 14·610$ (3) Å, $\beta = 109·89$ (2)°, $V = 2105·4$ Å³, $Z = 4$, $D_x = 1·379$, $D_m = 1·35$ Mg m⁻³. For both crystals the densities were measured by flotation at 298 K, the structures were solved by the heavy-atom method, and refinement was carried out by block-diagonal least-squares methods using diffractometer-measured intensity data. For the first compound 3114 observed independent reflections gave a final $R = 0·077$ and $R_w = 0·082$; for the second compound 1429 observed reflections led to $R = 0·048$, $R_w = 0·050$. No major structural differences were observed between the geometries of the two molecules.

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Introduction. The title compounds, designated ACLSA and CLSPA, are two members of a group of disperse dyes. Their formulas are shown in (I), where R is CH_3 for ACLSA and C_2H_5 for CLSPA. These dyes actually dissolve in polyester fibres, but their affinities for the fibers are markedly different, that of ACLSA being much greater than that of CLSPA. A theory of solubility has been proposed (Gerber, 1976), in which the dye–fiber affinity is a critical function of the dye's molecular volume. In order to test this theory, the above compounds and also 2'-acetamido-6-bromo-2-cyano-4'-diethylamino-4-nitroazobenzene (ABRCA) and 6-bromo-2-cyano-4'-diethylamino-4-nitro-2'-propionamidoazobenzene (BRCPA) were synthesized and studied (Gerber, Moriconi, Groeke & Altermann, 1976). The second pair also differ by one CH_2 group, but the situation is reversed, *i.e.* the larger molecule has the greater fiber affinity. X-ray investigations of all four compounds have been carried out, in order to