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Structure of 6-Acetoxycoumarin: Topochemical Photodimerization and Analysis of Acetoxy···Acetoxy Interactions in the Solid State

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Abstract. $C_{11}H_8O_4$, $M_r = 204{\cdot}2$, monoclinic, $P2_1/n$, $a = 3{\cdot}900\,(1)$, $b = 37{\cdot}530\,(6)$, $c = 6{\cdot}460\,(1)$ Å, $\beta = 103{\cdot}7\,(1)°$, $V = 918{\cdot}5\,(5)$ Å^3, $Z = 4$, $D_m = 1{\cdot}443$, $D_x = 1{\cdot}476$ Mg m^{-3}, Cu $K\alpha$, $\lambda = 1{\cdot}5418$ Å, $\mu = 0{\cdot}86$ mm^{-1}, $F(000) = 424$, $T = 293$ K, $R = 0{\cdot}075$ for 1019 significant reflections. Molecules pack in β-type stacking mode which is characterized by the close packing of parallel and nearly planar reactive double bonds with a separation of 3·900 Å along the *a* axis. The *syn* head–head dimer obtained is the direct consequence of this packing arrangement. Molecular packing is stabilized by intermolecular C—H···O hydrogen bonding. Analysis of acetoxy···acetoxy interactions in the acetoxy compounds retrieved from the Cambridge Structural Database reveal that the majority of them are anti-dipolar.

Introduction. The utility of photoreactions in the solid state as a synthetic tool is limited by the difficulty in achieving the desired type of crystal structure in any given case, for the factors that control the crystal packing are not fully understood. The search for functional groups which may be valuable for steering olefinic molecules was initiated by Cohen & Schmidt (1964), Cohen, Schmidt & Sonntag (1964) and Schmidt (1964, 1971). Photochemical investigations of substituted coumarins in the solid state have been undertaken in our laboratory with a view to identification of functional groups which could be used as steering groups. Coumarin, which is photostable in the solid state, appeared to be a good candidate for such a study. Chloro, methyl, methoxy, hydroxy and acetoxy groups were used as functional groups and 28 substituted coumarins were investigated (Gnanaguru, Ramasubbu, Venkatesan & Ramamurthy, 1985). Of these, 12 underwent photodimerization. An analysis of the reactivity pattern of these compounds revealed that chloro and acetoxy groups are outstanding in their steering abilities; all the five chlorocoumarins investigated were photoreactive, while three (6-acetoxy-, 7-acetoxy- and 4-methyl-7-acetoxycoumarin) out of five acetoxycoumarins investigated dimerized upon irradiation yielding *syn* head–head dimers. The crystal structure of 7-acetoxycoumarin (Ramasubbu, Gnanaguru, Venkatesan & Ramamurthy, 1982) revealed that the reactive molecules pack with the reactive double bonds separated by 3·833 (2) Å along the *a* axis. To investigate further the details of the molecular packing of the other acetoxycoumarins, crystallographic investigations of 6-acetoxy- and 4-methyl-7-acetoxycoumarins were undertaken.

In this paper we discuss the packing mode of 6-acetoxycoumarin. The systematics in the mode of packing of acetoxy groups in crystal structures containing this group are also presented.

Experimental. 6-Acetoxy- and 4-methyl-7-acetoxycoumarins were prepared as reported by Pechmann & Welsh (1884) and Borsche (1907). Crystallization of 6-acetoxy- and 4-methyl-7-acetoxycoumarins was attempted in different solvents, *e.g.* acetone, ethyl acetate, methanol, chloroform, benzene and dichloromethane, and good needle-like crystals were obtained for 6-acetoxycoumarin. 4-Methyl-7-acetoxycoumarin did not yield crystals suitable for X-ray crystallographic investigations.

A single crystal of the title compound was obtained from ethyl acetate solution by slow evaporation; D_m by flotation in KI solution. Preliminary oscillation and Weissenberg photographs indicated that the crystal belonged to the monoclinic system in the space group $P2_1/n$. It may be added that the crystals were poorly diffracting, and this could be the reason for the rather poor value of the *R* index reached at the end of the refinement. Intensity data for a crystal of 6-acetoxycoumarin of dimensions 0·3 × 0·18 × 0·55 mm were collected on an Enraf–Nonius CAD-4 diffractometer using graphite-monochromated Cu $K\alpha$ radiation ($\lambda = 1{\cdot}5418$ Å) in $\omega/2\theta$ scan mode with a scan speed of 1° min^{-1}. The lattice parameters were accurately determined by a least-squares fit of 24 centred reflections in the range $30 \leq \theta \leq 40°$. Three reflections were used as standard reflections to monitor the stability and orientation of the crystal during the data collection. These reflections (041, 160 and 142) were remeasured after every 2000 s of exposure time. The intensity of these reflections varied by a maximum of ±1%. A total of 2040 unique reflections was collected ($\theta \leq 70°$, $h = 0$ to 4, $k = 0$ to 42, $l = -7$ to 7), of which 1019 were judged significant $[|F_o| \geq 3\sigma(|F_o|)]$. Data

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were corrected for Lorentz and polarization factors, but not for absorption.

The structure was solved by the direct-methods program *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq and Woolfson, 1980). Full-matrix least-squares refinement (Sheldrick, 1976) of a scale factor, positional and anisotropic thermal parameters of non-hydrogen atoms, positional and isotropic temperature factors of H atoms obtained from a difference map converged at $R = 0{\cdot}075$, $wR = 0{\cdot}067$, $S = 1{\cdot}25$. The function minimized was $\sum w(|F_o| - |F_c|)^2$ where $w = 2{\cdot}55/[\sigma^2(|F|) + 0{\cdot}000016|F|^2]$. The maximum value of Δ/σ for non-hydrogen atoms was 0·01 and for H atoms 0·02; $\Delta\rho_{\max} = +0{\cdot}3$, $\Delta\rho_{\min} = -0{\cdot}3$ e Å^{-3}. The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974).

Discussion. The final positional parameters for the non-hydrogen atoms are given in Table 1.* Bond lengths and angles are recorded in Table 2. A perspective view of the molecule drawn using the program *ORTEP* (Johnson, 1976) is shown in Fig. 1. A packing diagram drawn using the program *PLUTO*78 (Motherwell & Clegg, 1978) is given in Fig. 2.

The observed *syn* head–head dimer is consistent with the short translational axis (*a* axis) of 3·900 (1) Å. In an ideal situation for [2+2] photodimerization reactions the π orbitals of the reactive double bonds would be expected to overlap. The geometrical parameters involved in this process, in addition to centre–centre distance, are θ_1, θ_2 and θ_3 and the displacement of the double bonds D_1 and D_2 with respect to each other (Fig. 3). For the best overlap of π orbitals of the reactive double bonds, the ideal values for θ_1, θ_2 and θ_3 are 0, 90 and 90° respectively. At this orientation D_1 and D_2 will be zero. In the 6-acetoxycoumarin crystal lattice, these parameters for the reactive pair of double bonds are $\theta_1 = 0$, $\theta_2 = 94$ and $\theta_3 = 118{\cdot}3°$, $D_1 = 0{\cdot}28$ and $D_2 = 1{\cdot}92$ Å. Thus, considerable changes in the juxtaposition of the molecules are required to achieve the ideal orientation for dimerization. In this context, lattice-energy calculations were carried out using the program *WMIN* developed by Busing (1981). This revealed that the increase in energy to bring the molecules into the ideal geometry is not very large (35 kJ mol^{-1}). This is consistent with the general observation (Murthy, Arjunan, Venkatesan & Ramamurthy, 1986) that the calculated increase in energy is considerably smaller for the photoreactive molecules than for the photoinert cases in the solid state.

Table 1. *Fractional atomic coordinates* (× 10^4) *and equivalent isotropic temperature factors* (× 10^3) *for non-hydrogen atoms with e.s.d.'s in parentheses*

$$U_{eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}(Å^2)
O(1)	4702 (8)	829 (1)	−388 (4)	43 (1)
C(2)	3122 (12)	498 (1)	−339 (7)	41 (2)
C(3)	934 (12)	368 (1)	−2320 (7)	42 (2)
C(4)	470 (13)	555 (1)	−4121 (7)	40 (2)
C(5)	1644 (11)	1120 (1)	−5944 (6)	37 (1)
C(6)	3301 (11)	1442 (1)	−5778 (6)	35 (1)
C(7)	5453 (12)	1563 (1)	−3880 (7)	40 (2)
C(8)	5879 (12)	1351 (1)	−2084 (7)	40 (2)
C(9)	4205 (11)	1026 (1)	−2238 (6)	35 (1)
C(10)	2083 (11)	902 (1)	−4136 (6)	33 (1)
O(11)	3707 (9)	352 (1)	1377 (5)	59 (1)
O(12)	2973 (8)	1646 (1)	−7648 (4)	42 (1)
C(13)	1644 (12)	1981 (1)	−7684 (7)	41 (2)
O(14)	552 (9)	2102 (1)	−6257 (6)	60 (1)
C(15)	1739 (20)	2166 (2)	−9687 (10)	59 (2)

Table 2. *Selected bond distances* (Å) *and angles* (°) *involving non-hydrogen atoms with e.s.d.'s in parentheses*

O(1)—C(2)	1·390 (5)	C(6)—C(7)	1·388 (6)
O(1)—C(9)	1·379 (5)	C(6)—O(12)	1·410 (5)
C(2)—C(3)	1·445 (6)	C(7)—C(8)	1·384 (6)
C(2)—O(11)	1·209 (5)	C(8)—C(9)	1·376 (6)
C(3)—C(4)	1·334 (6)	C(9)—C(10)	1·387 (5)
C(4)—C(10)	1·447 (6)	O(12)—C(13)	1·358 (5)
C(5)—C(6)	1·363 (6)	C(13)—O(14)	1·193 (6)
C(5)—C(10)	1·403 (5)	C(13)—C(15)	1·477 (8)

C(2)—O(1)—C(9)	121·8 (3)	C(7)—C(8)—C(9)	119·2 (4)
O(1)—C(2)—C(3)	117·0 (4)	O(1)—C(9)—C(8)	116·5 (4)
O(1)—C(2)—O(11)	115·9 (4)	O(1)—C(9)—C(10)	121·2 (4)
C(3)—C(2)—O(11)	127·1 (4)	C(8)—C(9)—C(10)	122·3 (4)
C(2)—C(3)—C(4)	121·6 (4)	C(4)—C(10)—C(5)	124·2 (4)
C(3)—C(4)—C(10)	120·7 (4)	C(4)—C(10)—C(9)	117·7 (4)
C(6)—C(5)—C(10)	119·3 (4)	C(5)—C(10)—C(9)	118·0 (4)
C(5)—C(6)—C(7)	122·4 (4)	C(6)—O(12)—C(13)	118·3 (3)
C(5)—C(6)—C(12)	118·0 (4)	O(12)—C(13)—O(14)	122·9 (4)
C(7)—C(6)—O(12)	119·5 (4)	O(12)—C(13)—C(15)	111·2 (5)
C(6)—C(7)—C(8)	118·7 (4)	O(14)—C(13)—C(15)	125·9 (5)

Geometry of the molecule. Bond lengths and angles in 6-acetoxycoumarin are in good agreement, within experimental error, with those observed in 7-acetoxycoumarin (Ramasubbu *et al.*, 1982). The plane of the acetoxy group makes a dihedral angle of 60·9 (5)° with the plane of the coumarin ring, whereas in 7-acetoxycoumarin this angle is 57·4 (3)°. Schweizer & Dunitz (1982) have observed that the out-of-plane twist of acetoxy groups lies in the range 30–90° for compounds having the fragment C(*sp*)^2—C↕C—Ar. The acetoxy group adopts an extended antiperiplanar conformation. The torsion angle C(6)—O(12)↑C(13)—O(14) = −4·6 (6)°.

C—H···O *hydrogen bonding*. A noteworthy feature of the crystal packing in this structure is the presence of two C—H···O hydrogen bonds, C(3)···O(11$^{\rm i}$) = 3·387 (6), H(3)···O(11$^{\rm i}$) = 2·42 (4) Å, C(3)—H(3)···O(11$^{\rm i}$) = 158 (3)°; C(15)···O(14$^{\rm ii}$) = 3·391 (9), H(152)···O(14$^{\rm ii}$) = 2·58 (8) Å, C(15)—H(152)···

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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 44356 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

$O(14^{ii}) = 143\ (6)°$ [symmetry code: (i) $-x, -y, -z$; (ii) $\frac{1}{2}+x, \frac{1}{2}-y, z-\frac{1}{2}$]. These C—H···O interactions are within the limits specified by Taylor & Kennard (1982). In the present structure, the *d* values as defined by Taylor & Kennard (1982) for the glide-related and centrosymmetrically related C—H···O hydrogen bonds are 0·012 and 0·28 Å respectively. Another parameter suggested by Murray-Rust & Glusker (1984) is the angle C=O···H. The observed values are 123·8 (6) and 150·0 (3)° for the glide-related and centrosymmetrically related hydrogen bonds respectively. From all these considerations we may conclude that the crystal structure is further stabilized by C—H···O hydrogen bonds.

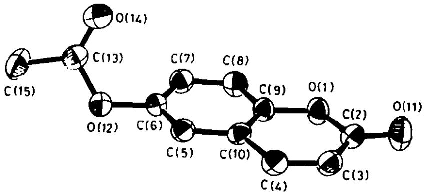

Fig. 1. A perspective view of the molecule with the atomic numbering scheme and the thermal ellipsoids at 50% probability level.

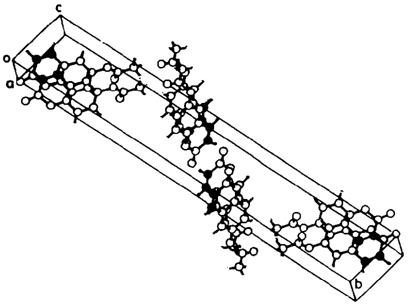

Fig. 2. Packing of the molecules in the unit cell. The filled circles represent the reactive double bonds.

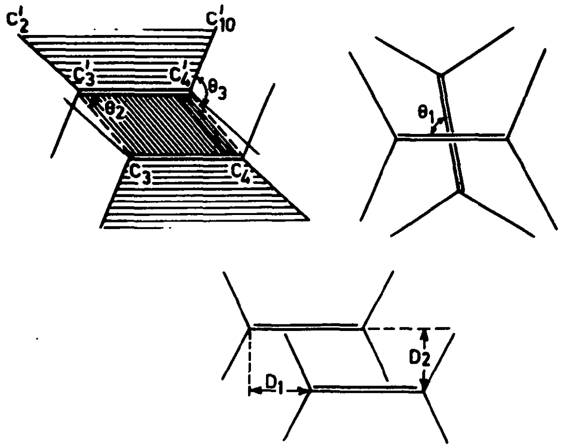

Fig. 3. Geometrical parameters used in the relative representation of the reactive double bonds.

Table 3. OAc···OAc *interactions – summary of statistical analysis*

	Aliphatic	Aromatic	Total
Structures analysed	28	28	56
Structures with no OAc···OAc interactions (≤ 4·2 Å)	12	5	17
Type I	10	11	21
Type II	1	2	3
Type III	1	4	5
Type IV	1	1	2
Only C—H···O short contacts	3	5	8

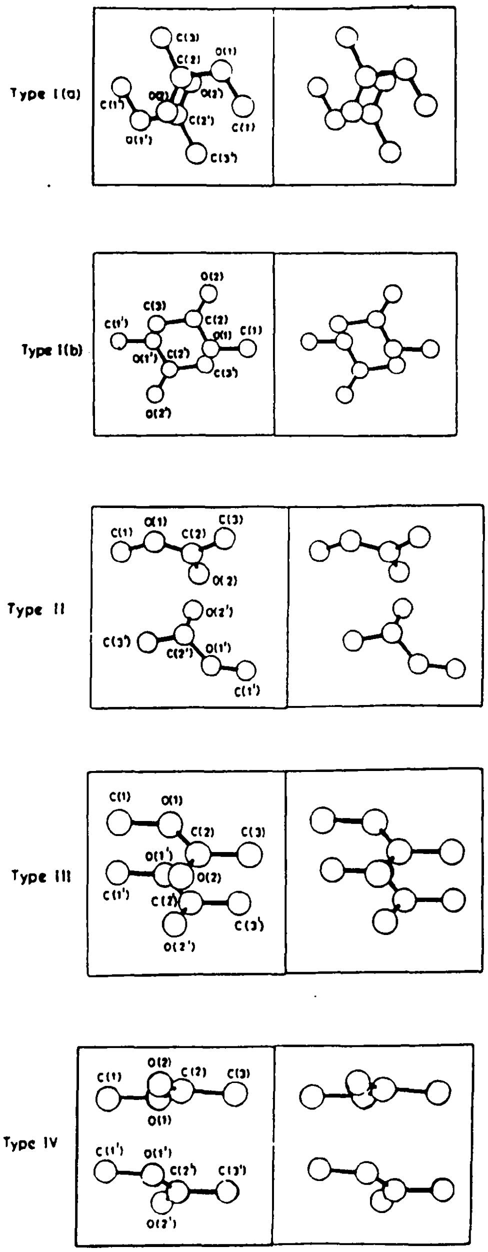

Fig. 4. Type I–IV interactions between the acetoxy groups.

Table 4. *Geometrical parameters of possible* C—H···O *hydrogen bonding in compounds with acetoxy substitution retrieved from the Cambridge Structural Database*

For atomic numbering see Fig. 4.

	O2···C3	O2···H3*X**	C3—O2···H3*X*	H3*X*—C3···O2	O2···H3*X*—C3	C2=O2···H3*X*	*d*=(*r*O+*r*H—*d*OH)	References
1	3·349 (3) Å	2·64 (4) Å	11 (1)°	35 (1)°	134 (1)°	157 (1)°	0·05 Å	(*a*)
2	3·557 (3)	2·62 (3)	2 (2)	5 (3)	173 (3)	120 (2)	0·07	(*b*)
3	3·559 (4)	2·59 (4)	6 (2)	16 (1)	158 (1)	131 (2)	0·11	(*c*)
4	3·390 (6)	2·42 (4)	7 (3)	16 (3)	158 (3)	124 (1)	0·28	(*a*)
5	3·390 (9)	2·58 (8)	10 (5)	27 (6)	144 (6)	150 (3)	0·12	(*d*)
6	3·485 (6)	2·58 (6)	11 (5)	27 (6)	142 (3)	126 (4)	0·12	(*e*)
7	3·270 (2)	1·99 (2)	9 (1)	14 (1)	157 (1)	129 (1)	0·71	(*f*)
8†	3·534 (7)	2·74	3	10	168	125	—0·05	(*g*)
9	3·489 (5)	2·97 (4)	13 (5)	48 (5)	119 (8)	117 (7)	—0·27	(*h*)
10	3·479 (9)	2·82 (6)	7 (2)	27 (4)	145 (3)	134 (2)	—0·12	(*i*)
11	3·450 (4)	2·76 (5)	5 (3)	20 (3)	154 (3)	109 (3)	—0·06	(*j*)
12	3·300 (3)	2·75 (3)	14 (2)	50 (3)	120 (3)	149 (4)	—0·05	(*b*)
13	3·498 (3)	2·74 (3)	11 (3)	32 (2)	138 (3)	120 (2)	—0·05	(*b*)
14	3·404 (3)	2·80 (3)	13 (3)	42 (2)	125 (3)	113 (2)	—0·10	(*k*)
15	3·485 (6)	2·78 (6)	14 (3)	39 (1)	127 (1)	117 (1)	—0·08	(*e*)
Ideal	<3·30	<2·70	0·0	0·0	180·0	120·0	<0·0	

References: (*a*) Precigoux, Busetta, Courseille, Hospital & Miquel (1978); (*b*) Ramasubbu, Gnanaguru, Venkatesan & Ramamurthy (1982); (*c*) White, Carnduff, Guy & Bovil (1977); (*d*) Murthy, Arjunan, Venkatesan & Ramamurthy (1986); (*e*) Moriski, Furukama, Nozoe, Itai & Iitaka (1980); (*f*) Kurutova, Potekhim, Struchkov & Zefirov (1979); (*g*) Rodriguez, Vilcher, Verdir & Blanco (1983); (*h*) Brassy, Bodo & Molho (1977); (*i*) Rodriguez, Cano & Blanco (1979); (*j*) Jurd & Wong (1980); (*k*) Van Remortere & Flynn (1974).

* H3*X* indicates hydrogen on C3; *X* = 1, 2, 3.
† E.s.d.'s of H's were not given in literature.

From the photobehaviour of acetoxycoumarins it appears that the acetoxy group may be a reasonably good steering group. In this connection, it was considered worthwhile to examine the systematics of the mode of packing in crystal structures containing an acetoxy group on an aromatic ring.

Analysis of OAc···OAc *interactions in the crystalline state*. Experimental data for the analysis were extracted from the Cambridge Structural Database (December, 1983). Metal complexes and molecules carrying charges were eliminated from the analysis. The structures retrieved were divided into two categories: (i) aromatics in which the acetoxy group is directly connected to an aromatic ring, and (ii) non-aromatics in which the acetoxy group is attached to a carbon which is not part of an aromatic ring. An analysis of intermolecular short contacts was carried out and only the structures which showed acetoxy···acetoxy contact distances of less than 4·2 Å were used for further analysis.

A total of 56 structures were retrieved and the results of the analysis are summarized in Table 3. Five aromatic and 12 non-aromatic structures did not reveal any contact less than 4·2 Å between the acetoxy groups. Of the remaining 39 structures, in about 21 (11 aromatic and 10 non-aromatic) the acetoxy groups of the neighbouring molecules are close to either a crystallographic centre of inversion (17 cases) or a noncrystallographic inversion centre (four cases) (type I). Further analysis of these 21 structures reveals that in 16 cases (Fig. 4) the C=O groups lie close to the centre of inversion with C(2)···O(2′) distances varying from 3·14 to 4·2 Å and in four others (Fig. 4) the disposition of the carbonyl groups is such that the C(3)···O(1′) contacts are closer and lie in the range 3·46–3·90 Å. In one case the centre of symmetry is close to the C(1)—O(1) bond with a C(1)···O(1′) distance of 3·34 Å. Thus, in the 16 structures mentioned above, the dipole–dipole interactions of the partially charged carbonyl groups seem to be the important stabilizing factor.

A total of eight structures exhibited arrangements of the kinds (types II and III) shown in Fig. 4 with C(2)···O(2′) distances in the range of 3·15–4·04 Å. The crystal structures of 6- and 7-acetoxycoumarins belong to type III. It seems likely that 4-methyl-7-acetoxycoumarin, which gives a *syn* head–head dimer, may also belong to type III. This pattern could be due to electrophile–nucleophile interactions between C(2) and O(2) of the two carbonyl groups.

Only in two structures was the arrangement (type IV, depicted in Fig. 4) observed in which the C(1)—O(1) bond is *syn* to the C(1′)—O(1′) bond, with distances 3·71 and 4·03 Å C(1)···C(1′) and 3·62 and 3·57 Å O(1)···O(1′), and the other atoms of the acetoxy group are oriented in an *anti* fashion.

In the remaining eight structures, no patterns of types I to IV (Table 3) were observed. However, the methyl carbon C(3) and the carbonyl oxygen of the acetoxy groups of symmetry-related molecules come close, to lie within 3·24–3·66 Å.

The possibility of hydrogen bonding of the type C—H···O was examined in all the 39 structures. However, hydrogen positions were available for only 12 structures. The geometrical parameters involved in those 12 compounds (14 interactions) are given in

Table 4. In seven cases there is definite evidence for a C—H···O bond, as they fulfil the criteria proposed by Taylor & Kennard (1982) as well as by Murray-Rust & Glusker (1984).

Statistical analyses of the Cl···Cl (Gnanaguru, Murthy, Venkatesan & Ramamurthy, 1984) and OAc···OAc interactions show that, in general, there is a definite propensity for both chloro and acetoxy groups of symmetry-related molecules to come closer. While there is a significant directionality in the case of Cl···Cl interactions (Gnanaguru *et al.*, 1984), acetoxy interactions are not so specific for crystal engineering. Unlike chloro-substituted compounds, in the acetoxy compounds there is no preponderance for the β-type of packing. There exists a greater preference in acetoxy interactions to align with C=O groups in an antiparallel orientation (Fig. 4) indicative of dipole–dipole interactions. It may be mentioned that only types III and IV would bring the parent molecules into a packing orientation similar to β type (Schmidt, 1964).

It is noteworthy that all the three acetoxy compounds which are photoreactive prefer the β type of packing. This indicates that not only the interaction between the functional groups (in this case acetoxy) but also the total interactions between the parent molecules are of crucial importance in reaching a packing suitable for reactivity.

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2-Aminopyridinium Salicylate

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Abstract. $C_5H_7N_2^+.C_7H_5O_3^-$, $M_r = 232{\cdot}2$, orthorhombic, *Pbca*, $a = 15{\cdot}928\,(5)$, $b = 11{\cdot}830\,(5)$, $c = 11{\cdot}768\,(6)$ Å, $V = 2217\,(2)$ Å^3, $Z = 8$, $D_m = 1{\cdot}40$, $D_x = 1{\cdot}391$ g cm^{-3}, graphite-monochromated Cu $K\alpha$, $\lambda = 1{\cdot}54178$ Å, $\mu = 8{\cdot}04$ cm^{-1}, $F(000) = 976$, $T = 295$ K, final $R = 0{\cdot}050$ for 1116 reflections. Both

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