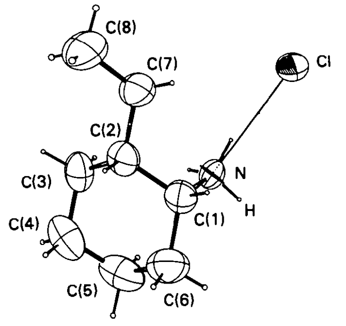

Fig. 1. *ORTEP* drawing (Johnson, 1965) of (–)-(2*b*).HCl.

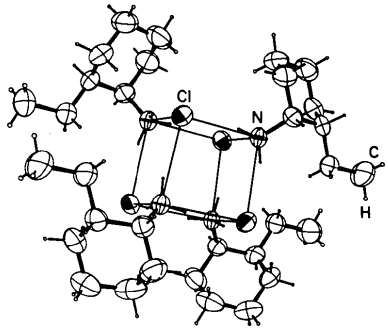

Fig. 2. Salt cluster arrangement of four molecules of (–)-(2*b*).HCl.

Discussion. The atomic coordinates and equivalent isotropic thermal parameters are given in Table 1.* Table 2 summarizes the bond distances and angles. The values vary in the normal range in comparison to literature data (*International Tables for X-ray Crystallography,* 1974). Moreover it is seen that the amino group is in an axial and ethyl group in an equatorial position. This conformation is in contrast to that of the free base in solution (Knupp & Frahm 1984).

An *ORTEP* drawing (Johnson, 1965) of a single molecule of (–)-(2*b*).HCl is depicted in Fig. 1, clearly showing it to possess the (1*R*,2*S*)-*cis* configuration. This is in agreement with the absolute configuration deduced from CD data (Knupp & Frahm, 1984). The cyclohexane ring is in the chair conformation. The packing of the molecules is shown in Fig. 2, with four molecules and four Cl atoms forming a salt cluster *via* $H_2N{\cdots}H{-}Cl$ hydrogen bonds. The somewhat distorted cubic arrangement of the Cl and N atoms is clearly seen. The ethanol molecules between the cubes are omitted.

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, interatomic distances and angles and least-squares-plane data have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39894 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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α-Fluoro-*trans*-cinnamoyl Peroxide, $C_{18}H_{12}F_2O_4$

By Donald Bethell, Derek J. Chadwick, Marjorie M. Harding, Guy Q. Maling and Michael D. Wiley

Departments of Organic and Inorganic Physical and Industrial Chemistry, University of Liverpool, Liverpool L69 3BX, England

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Abstract. $M_r = 330{\cdot}29$, monoclinic, $C2/c$, $a = 18{\cdot}78$ (3), $b = 10{\cdot}91$ (2), $c = 7{\cdot}50$ (1) Å, $\beta = 94{\cdot}4$ (2)°, $U = 1532{\cdot}1$ Å^3, $Z = 4$, $D_x = 1{\cdot}43$ Mg m^{-3}, λ(Cu $K\alpha$) $= 1{\cdot}5418$ Å, $\mu = 1{\cdot}014$ mm^{-1}, $F(000) = 680$, $T = ca$ 293 K, final $R = 0{\cdot}062$ for 607 unique reflexions. As for *trans*-cinnamoyl peroxide, the molecule adopts an extended conformation with the two acyloxy groups in orthogonal planes, *s-cis* stereochemistry in the α,β-unsaturated carbonyl moiety, and unusually short C=O bond lengths [1·185 (11) Å].

Introduction. As part of our program aimed at relating structure and reactivity in diacyl peroxide thermolysis, the structure of the title compound (1) has been

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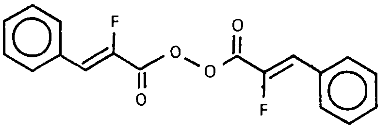
determined. In addition, the molecular geometry of the fluorostyryl moiety was to be used to estimate electron–nuclear hyperfine coupling constants in the corresponding radical. Finally, 3-fluorocoumarin was detected in the products of thermolysis, and it was thought that the molecular geometry might indicate features which would predispose the α-fluorocinnamoyloxy radical to undergo the necessary *cis–trans* isomerization, perhaps by way of a radical containing an α-lactone ring.



Experimental. The title compound, prepared from α-fluoro-*trans*-cinnamic acid by the method of Greene & Kazan (1963), was recrystallized from diethyl ether at 268 K. The resultant crystals [m.p. 365–369 K (dec.)], although showing no deterioration over a period of weeks at room temperature, decomposed slowly in the X-ray beam. Data could be collected from any one crystal for some 72 h whereafter rapidly accelerating decomposition led to loss of the diffraction pattern. Four different crystals from the same batch, each having dimensions 0·3 × 0·3 × 0·3 mm, were therefore used to collect the data. D_m not determined. Reflexion intensities measured by the SERC Microdensitometer Service, Daresbury Laboratory, from Weissenberg photographs of layers *hk*0 to *hk*5; equivalents merged ($R_{\text{int}} = 0{\cdot}057$) giving 607 data; cell dimensions and interlayer scale factors obtained from precession photographs; structures solved by direct methods (*MULTAN*, Germain, Main & Woolfson, 1970) with space group *C*2/*c* (no indication that the lower-symmetry space group *Cc* should be considered); structure refined on *F* using full-matrix least squares (*XRAY* system, Stewart, Kruger, Ammon, Dickinson & Hall, 1972); in final refinement cycle $(\Delta/\sigma)_{\max} = 0{\cdot}0000$; at an intermediate stage in the refinement, the majority of the H atoms located from a difference map and subsequently refined using isotropic thermal parameters; no absorption or extinction corrections applied; final $R = 0{\cdot}062$; max. and min. peak heights in final difference map 0·24 and −0·17 e Å^{-3} respectively.

Discussion. Positional and mean thermal parameters are in Table 1,* and the molecular and crystal structures are in Figs. 1 and 2 respectively. The atomic numbering, bond lengths, bond angles and torsion angles (not involving H) are in Fig. 3.

Table 1. *Atomic coordinates and mean temperature factors* ($\tilde{U}$) ($\times 10^4$) *with e.s.d.'s in parentheses*

$$\tilde{U} = (U_{11} + U_{22} + U_{33})/3.$$

	x	*y*	*z*	$\tilde{U}$ (Å^2)
O(1)	4392 (3)	1983 (6)	8859 (8)	733 (44)
O(2)	4655 (3)	474 (5)	6997 (9)	746 (41)
C(3)	4217 (4)	1282 (8)	7699 (12)	573 (62)
C(4)	3496 (4)	1086 (7)	6914 (10)	467 (50)
F(5)	3448 (2)	178 (4)	5676 (7)	696 (32)
C(6)	2937 (4)	1726 (7)	7338 (10)	501 (51)
C(7)	2193 (4)	1565 (7)	6686 (10)	468 (48)
C(8)	1713 (4)	2363 (7)	7319 (10)	586 (57)
C(9)	1010 (4)	2301 (8)	6830 (12)	667 (63)
C(10)	753 (4)	1425 (9)	5665 (12)	677 (63)
C(11)	1225 (5)	618 (8)	5025 (12)	663 (62)
C(12)	1942 (4)	674 (7)	5509 (11)	565 (55)

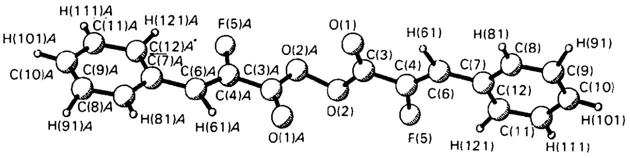


Fig. 1. A view of (1) drawn by *PLUTO* (Motherwell & Clegg, 1978).

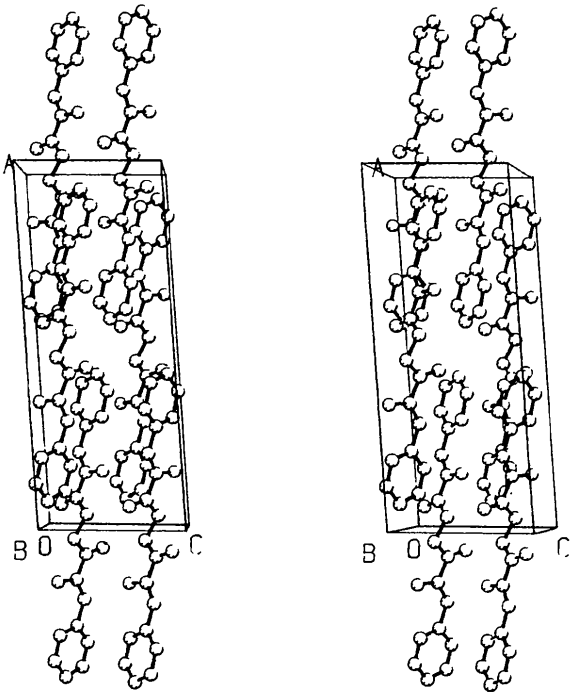


Fig. 2. Stereoscopic view of the crystal structure of (1) (drawn by *PLUTO*).

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* Lists of structure factors, H-atom positions, and anisotropic thermal parameters (for C, O, and F atoms) have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39920 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

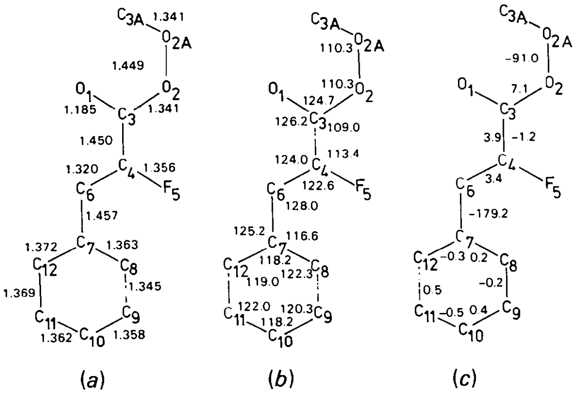

Fig. 3. (*a*) Bond lengths (Å), (*b*) bond angles (°), and (*c*) torsion angles (°) for (1). Torsion angles not shown are: 1—3—4—5, −176·6; 2—3—4—6, 179·3; 2*A*—2—3—4, −168·3; 3—4—6—7, −177·1; 4—6—7—12, 1·3; 6—7—8—9, −179·4; 6—7—12—11, 179·2°. E.s.d.'s are 0·011 Å for bond lengths, 0·7° for bond angles and somewhat larger for torsion angles (excluding H).

In all respects the molecular geometry is closely similar to that reported for *trans*-cinnamoyl peroxide (Bethell, Chadwick, Harding & Maling, 1984). Thus the two α-fluorocinnamoyl groups adopt the *s-cis* conformation and lie in orthogonal planes (torsion angle about the O—O bond, 91·0°) connected through a peroxide bond of length 1·449 (7) Å, somewhat longer than for *trans*-cinnamoyl peroxide, but close to the average of values from diacyl peroxide structures (almost all substituted dibenzoyl peroxides) in the Cambridge Crystallographic Data Base ($R \leq 0{\cdot}14$). The carbonyl bond length of 1·185 (11) Å is again shorter than in unconjugated acyloxy groups, but almost identical with the average in published diacyl peroxide structures, confirming the view that the carbonyl group is affected most by being attached to the peroxide bond, and little by its coplanarity with the conjugated styryl moiety. The presence of the F atom has little discernible effect on the C=C bond length and the C—F bond is almost identical in length to corresponding bonds in two aryl-substituted perfluoro-olefins (Yurchenko, Antipin, Struchkov & Yagupolski, 1978).

The title compound and *trans*-cinnamoyl peroxide show closely similar kinetic behaviour (thermolysis rates and of activation parameters in hexachloro-acetone solution); the fluoro-substituted compound reacts some 30% faster than the unsubstituted peroxide at 373·2 K. It seems surprising that the presence of the highly electronegative F atom in the molecule has such a small effect on both the structural and kinetic characteristics. The present structure provides no clue to the origin of 3-fluorocoumarin in the thermolysis products.

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Structure of 4-Oxopyrido[1,2-*a*]pyrimidin-1-ium-2-olate, $C_8H_6N_2O_2$

By Niels Thorup

Structural Chemistry Group, Chemistry Department B, Technical University of Denmark, DK-2800 Lyngby, Denmark

and Ole Simonsen

Department of Chemistry, University of Odense, DK-5230 Odense M, Denmark

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Abstract. $M_r = 162{\cdot}15$, monoclinic, $P2_1/c$, $a = 8{\cdot}358\,(2)$, $b = 5{\cdot}432\,(1)$, $c = 15{\cdot}153\,(3)$ Å, $\beta = 94{\cdot}11\,(2)°$, $V = 686{\cdot}2\,(6)$ Å^3, $Z = 4$, $D_m = 1{\cdot}57\,(1)$, $D_x = 1{\cdot}569$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71073$ Å, $\mu = 0{\cdot}109$ mm^{-1}, $T = 295$ K, $F(000) = 336$, $R = 0{\cdot}040$ for 1991 observed unique reflections. Different tautomeric forms of the title compound (alias malonyl-α-aminopyridine) have been suggested since 1924. In

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