Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
C1	1.1717 (5)	0.4038 (3)	0.4717 (2)	0.0283 (7)
C2	1.0257 (5)	0.5179 (3)	0.5150 (2)	0.0221 (6)
C3	1.1089 (4)	0.6005 (3)	0.6143 (2)	0.0224 (7)
C4	0.9445 (5)	0.6944 (3)	0.6659 (2)	0.0246 (7)
C5	0.7488 (5)	0.6099 (3)	0.6939 (2)	0.0269 (7)
C6	0.6782 (5)	0.5328 (3)	0.5906 (2)	0.0275 (7)
O1	1.2212 (4)	0.3049 (2)	0.5570 (2)	0.0359 (6)
O2	0.9834 (4)	0.6152 (2)	0.4303 (2)	0.0284 (6)
O4	1.0342 (4)	0.7627 (2)	0.7595 (2)	0.0397 (7)
O5	0.7820 (4)	0.5146 (2)	0.7834 (2)	0.0345 (6)
O6	0.8403 (3)	0.4428 (2)	0.5469 (2)	0.0243 (5)

Table 2. *Selected geometric parameters (Å, °)*

C1—C2	1.516 (4)	C2—O6	1.438 (3)
C2—C3	1.522 (4)	C1—O1	1.421 (4)
C3—C4	1.511 (4)	C2—O2	1.396 (3)
C4—C5	1.526 (4)	C4—O4	1.419 (4)
C5—C6	1.509 (4)	C5—O5	1.416 (4)
C6—O6	1.441 (3)		
O1—C1—C2	110.6 (2)	C3—C2—O6	109.3 (2)
C1—C2—O2	109.3 (2)	C4—C5—O5	111.8 (2)
C1—C2—C3	114.3 (3)	C4—C5—C6	108.4 (2)
C1—C2—O6	105.1 (2)	C6—C5—O5	111.7 (2)
O2—C2—C3	108.0 (2)	C2—O6—C6	114.3 (2)
O2—C2—O6	110.7 (2)		
O6—C2—C3—C4	−52.8 (3)	C6—O6—C2—C3	57.1 (3)
C2—C3—C4—C5	53.1 (3)	O1—C1—C2—O2	178.7 (2)
C3—C4—C5—C6	−53.7 (3)	O1—C1—C2—C3	57.5 (3)
C4—C5—C6—O6	56.4 (3)	O1—C1—C2—O6	−62.4 (3)
C5—C6—O6—C2	−60.8 (3)		

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···O6^{i}	0.71 (4)	2.04	2.748 (3)	175
O2—H2···O5^{ii}	0.82 (4)	1.95	2.744 (3)	164
O4—H4···O1^{iii}	0.77 (4)	2.03	2.783 (3)	168
O5—H5···O4^{iv}	0.74 (4)	1.98	2.692 (2)	162

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

All H atoms were located in the ΔF maps but due to the low reflection-to-parameter ratio they were allowed for as riding atoms using the appropriate *SHELXL*93 *AFIX* (Sheldrick, 1993) commands (*AFIX* 13 C—H 0.98, *AFIX* 23 C—H 0.97 and *AFIX* 144 with O—H distances refined).

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *Xtal*3.0 (Hall & Stewart, 1990). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93. Molecular graphics: *ORTEP*II (Johnson, 1976) and *PLUTON* (Spek, 1992). Software used to prepare material for publication: *SHELXL*93.

The authors thank the Natural Sciences and Engineering Research Council of Canada for financial support of this work.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1300). Services for accessing these data are described at the back of the journal.

References

Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.

Enraf–Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.

Hall, S. R. & Stewart, J. M. (1990). Editors. *Xtal*3.0 *Reference Manual*. Universities of Western Australia, Australia, and Maryland, USA.

Jeffrey, G. A. & Takagi, S. (1978). *Acc. Chem. Res.* **11**, 264–270.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Kanters, J. A., Roelofsen, G., Alblas, B. P. & Meiners, I. (1977). *Acta Cryst.* B**33**, 665–672.

Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures*. University of Göttingen, Germany.

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Spek, A. L. (1992). *PLUTON92. Molecular Graphics Program*. University of Utrecht, The Netherlands.

Szarek, W. A., Rafka, R. J., Yang, T.-F. & Martin, O. R. (1995). *Can. J. Chem.* **73**, 1639–1644.

Takagi, S. & Jeffrey, G. A. (1977). *Acta Cryst.* B**33**, 3510–3515.

Woods, R. J., Szarek, W. A. & Smith, V. H. Jr (1990). *J. Am. Chem. Soc.* **112**, 4732–4741.

Acta Cryst. (1997). C**53**, 1923–1926

α,α-Difluoro-β-lactone and its Non-Fluorinated Analog

Khalil A. Abboud, Rogelio Ocampo† and William R. Dolbier Jr

Department of Chemistry, University of Florida, PO Box 117200, Gainesville, Florida 32611-7200, USA. E-mail: abboud@chem.ufl.edu

(*Received 22 November 1996; accepted 8 July 1997*)

Abstract

The structures of 4,4-dibenzyloxetan-2-one, $C_{17}H_{16}O_2$, (1), and 4,4-dibenzyl-3,3-difluorooxetan-2-one, $C_{17}H_{14}F_2O_2$, (2), were determined in order to relate their structures to differences in their reactivities towards nucleophiles and thermal decarboxylation. The lactone rings in the two compounds are different, with the former exhibiting a planar ring, while the latter has a bent ring and an average endocyclic torsion angle of 6.8 (2)°. Bond distances of the CO_2 fragment are shorter in compound (2) than in their counterparts in (1).

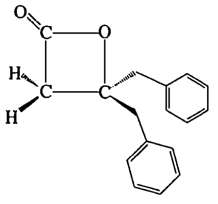
Comment

Although β-lactones (oxetan-2-one) have been known for more than 100 years (Einhorn, 1883; Pommier &

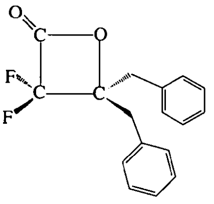
---

† Permanent Address: Departamento de Quimica, Universidad de Caldas, AA 275, Manizales, Colombia.

Pons, 1993), α,α-difluoro-substituted β-lactones have until recently received little attention (England & Krespan, 1968). Fluorine substituents have been observed to strongly influence the structure and reactivity of organic molecules because of their small size and high electronegativity, and also because of their π-donor ability (Smart, 1994). We reported recently a general method for the synthesis of α,α-difluoro-β,β-dialkyl-β-lactones (Dolbier, Ocampo & Paredes, 1995). Consistent with expectations, we have thus far observed that α,α-difluoro-β,β-dialkyl-β-lactones are significantly less reactive than their non-fluorine-containing counterparts with respect to thermal decarboxylation, but are much more reactive with respect to their reaction with nucleophiles (Dolbier *et al.*, 1995). In order for us to fully evaluate the relative significance of electronic and structural features which give rise to these differences in reactivity, it was essential to obtain comparative structural information about fluorinated and non-fluorinated β-lactones. We therefore determined the crystal structures of 4,4-dibenzyloxetan-2-one, (1), and 4,4-dibenzyl-3,3-difluorooxetan-2-one, (2).



(1)



(2)

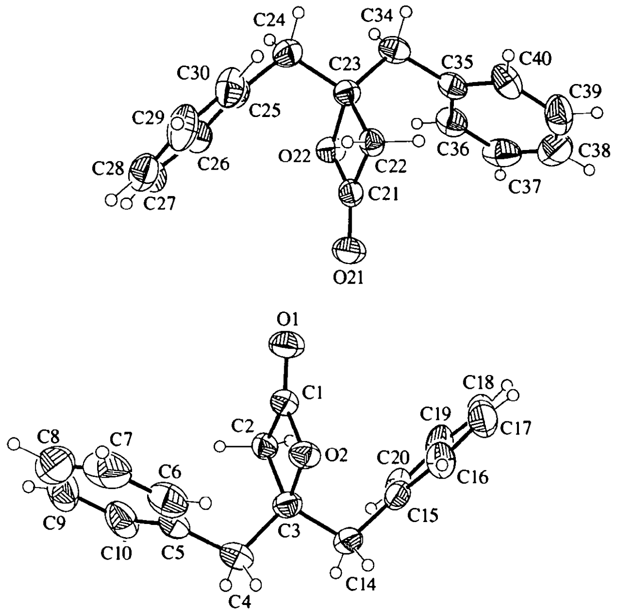


Fig. 1. The molecular structures of molecules (1*A*) and (1*B*) of (1), with 50% probability ellipsoids, showing the atom-numbering schemes.

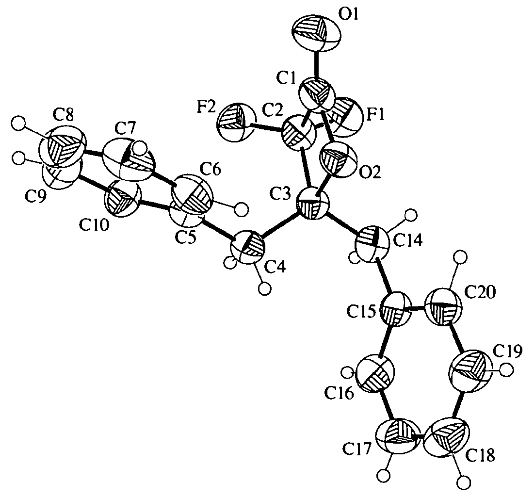


Fig. 2. The molecular structure of (2), with 50% probability ellipsoids, showing the atom-numbering scheme.

There are two independent molecules of (1) in the asymmetric unit, (1*A*) and (1*B*). The molecular structures with the atom-labeling schemes of molecules (1*A*) and (1*B*), and of compound (2) are presented in Figs. 1 and 2, respectively. The two structures differ only in the substituents on C2, where compound (1) has two H atoms, while compound (2) has two F atoms. However, they have two significant structural differences, one in the puckering of the lactone ring and the other in the lactone bond lengths and angles. The lactone rings of (1) are planar, with average atomic deviations of 0.004 (5) and 0.009 (9) Å for molecules (1*A*) and (1*B*), respectively. Atom O1 of (1*A*) and atom O21 of (1*B*) are at distances of 0.034 (6) and −0.034 (6) Å from their respective rings. On the other hand, the lactone ring of (2) is significantly bent as a result of having two F atoms on C2. The average atomic deviation in the lactone ring of (2) is 0.044 (1) Å, with O1 at a distance of −0.154 (3) Å. The average endocyclic lactone ring torsion angles for the three molecules are 0.7 (3) for (1*A*), 1.5 (3) for (1*B*) and 6.8 (2)° for (2).

The F atoms seem to cause a change in the bond lengths and angles of the lactone ring, most noticeably, the shortening of the C1—O2 bond and to a lesser extent the C1═O1 bond. The electron induction effect of fluorine creates a partial positive charge on C1, which is then stabilized by withdrawing electrons from the lone pairs on O2. This leads to the C1—O2 bond acquiring partial double-bond character and thus a shorter bond length. Additionally, a partial positive charge on C1 makes the fluoro derivative more reactive towards nucleophiles. In contrast, the fluoro derivatives can also be less reactive in their thermal decarboxylation than their non-fluoro counterparts for the same reason. Such a decarboxylation reaction involves a partially broken C1—C2 and/or O2—C3 bond, both of which are strengthened by the fluorine substituents, and the formation of a partial positive charge at C2 can occur when the bond breaking is asymmetric. Such charge would be destabilized by the F atoms, leading to a higher potential transition state and slower reaction.

The endocyclic bond angles of C1 and C3 are smaller in compound (2) than in (1), while the endocyclic angles of C2 and O2 are larger in (2) than in (1). The phenyl ring on C14 of (2) has a different orientation than its counterparts in molecules (1*A*) and (1*B*). It occupies a position obtained by a rotation of about 60° about the C3—C14 bond. The phenyl C—C bond distances have averages of 1.380 (7), 1.383 (7) and 1.372 (3) Å in (1*A*), (1*B*) and (2), respectively. A search of the April 1996 release of the Cambridge Structural Database (Allen *et al.*, 1991) revealed the presence of 26 crystal structures containing a β-lactone ring fragment. Of these, only five had two alkyl substituents on C3. Four of these five structures have planar rings while one, (1*R*,6*R*,7*S*)-1-methyl-3,5-dioxo-2,4-diazabicyclo[4.2.0]octane-7-spiro-2′-oxetan-4′-one (refcode BEVLOD; Chiba, Takahashi, Kato, Yoshida & Moroi, 1982), has endocyclic torsion angles of about 4°.

Experimental

4,4-Dibenzyloxetan-2-one, (1), was synthesized by strict adherence to the classical Adam's procedure (Adam, Baeza & Liu, 1972) and crystals were grown from a pentane–hexane mixture. The synthesis of 4,4-dibenzyl-3,3-difluorooxetan-2-one, (2), has been reported previously (Dolbier *et al.*, 1995) and its crystals were grown from hexane. In both cases, slow cooling of a saturated solution successfully gave rise to the desired crystals.

Compound (1)

Crystal data

$C_{17}H_{16}O_2$
$M_r = 252.30$
Orthorhombic
$Pna2_1$
$a = 21.3183\ (5)$ Å
$b = 5.6751\ (2)$ Å
$c = 22.5050\ (4)$ Å
$V = 2722.7\ (1)$ Å^3
$Z = 8$
$D_x = 1.231$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 4673 reflections
$\theta = 3.0$–25.0°
$\mu = 0.08$ mm^{-1}
$T = 173\ (2)$ K
Needle
0.38 × 0.18 × 0.15 mm
Colorless

Data collection

SMART platform diffractometer
ω scans
Absorption correction: none
9301 measured reflections
3113 independent reflections
2768 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.040$
$\theta_{\rm max} = 25°$
$h = 0 \rightarrow 25$
$k = 0 \rightarrow 6$
$l = -26 \rightarrow 20$
Intensity decay: <1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.048$
$wR(F^2) = 0.113$
$S = 1.08$
3108 reflections
344 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.0244P)^2 + 2.1047P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.18$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.16$ e Å^{-3}
Extinction correction: *SHELXTL5*
Extinction coefficient: 0.0049 (6)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °) for (1)*

O1—C1	1.190 (5)	O21—C21	1.198 (5)
O2—C1	1.392 (5)	O22—C21	1.387 (5)
O2—C3	1.491 (5)	O22—C23	1.514 (5)
C1—C2	1.509 (5)	C21—C22	1.499 (5)
C2—C3	1.558 (5)	C22—C23	1.558 (5)
C1—O2—C3	91.4 (3)	C21—O22—C23	90.7 (3)
O2—C1—C2	94.9 (3)	O22—C21—C22	95.8 (3)
C1—C2—C3	84.6 (3)	C21—C22—C23	85.0 (3)
O2—C3—C2	89.1 (3)	O22—C23—C22	88.5 (3)

Compound (2)

Crystal data

$C_{17}H_{14}F_2O_2$
$M_r = 288.28$
Orthorhombic
$P2_12_12_1$
$a = 6.154\ (1)$ Å
$b = 13.484\ (2)$ Å
$c = 17.732\ (3)$ Å
$V = 1471.4\ (4)$ Å^3
$Z = 4$
$D_x = 1.301$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 32 reflections
$\theta = 10$–11°
$\mu = 0.10$ mm^{-1}
$T = 293\ (2)$ K
Needle
0.47 × 0.27 × 0.23 mm
Colorless

Data collection

Siemens *P*3/*PC* diffractometer
ω scans
Absorption correction: none
4168 measured reflections
3055 independent reflections
1816 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.021$
$\theta_{\rm max} = 27.50°$
$h = -7 \rightarrow 7$
$k = 0 \rightarrow 17$
$l = 0 \rightarrow 23$
4 standard reflections every 100 reflections intensity decay: 3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.070$
$S = 1.05$
3052 reflections
191 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.0245P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = -0.02$

$\Delta\rho_{\rm max} = 0.09$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.08$ e Å^{-3}
Extinction correction: *SHELXTL5*
Extinction coefficient: 0.035 (2)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 2. *Selected geometric parameters (Å, °) for (2)*

F1—C2	1.352 (2)	O2—C3	1.506 (2)
F2—C2	1.349 (2)	C1—C2	1.514 (3)
O1—C1	1.187 (2)	C2—C3	1.526 (2)
O2—C1	1.352 (2)		
C1—O2—C3	93.92 (12)	C1—C2—C3	86.96 (13)
O2—C1—C2	92.3 (2)	O2—C3—C2	86.03 (12)

For (1), a hemisphere of data was collected (1321 frames, 0.3° scan in ω). The first 50 frames were remeasured at the end of data collection to monitor instrument and crystal stability. The full data set has a 97.1% coverage and a range of 2.7 to 3.8 redundancy. For (2), data were collected by ω scans over 1.2° using 3–6° min^{-1} scan speeds depending on intensity. Attempts were made to solve the structure of (1) in both centrosymmetric and non-centrosymmetric space groups *Pnma* and *Pna*2_1. A solution, followed by successful refinement, was only obtained in space group *Pna*2_1. Examination of the crystal packing revealed the presence of a pseudo-center of inversion in the lattice but no mirror-plane symmetry which is a requirement for the centrosymmetric space group *Pnma*. Since *XL* in *SHELXTL5* (Sheldrick, 1995) automatically generates origin restraints for polar space groups (floating origin restraint), no *z* coordinate of an atom has to be fixed for space group *Pna*2_1. The H atoms were placed in idealized positions and were refined riding on their parent atoms. C—H distances of 0.97 and 0.93 Å were used for methylene and aromatic C atoms, respectively. The displacement parameters of the H atoms were set at $1.2U_{eq}$ of the parent C atoms. The absolute configuration of the title compounds is undetermined.

Data collection: *SMART* (Siemens, 1995) for (1); *P3/PC Diffractometer Program* (Siemens, 1989) for (2). Cell refinement: *SMART* and *SAINT* (Siemens, 1995) for (1); *P3/PC Diffractometer Program* for (2). Data reduction: *SHELXTL5* (Sheldrick, 1995) for (1); *SHELXTL-Plus* (Sheldrick, 1990) for (2). For both compounds, program(s) used to solve structures: *SHELXTL5*; program(s) used to refine structures: *SHELXTL5*; molecular graphics: *SHELXTL5*; software used to prepare material for publication: *SHELXTL5*.

KAA wishes to acknowledge the National Science Foundation and the University of Florida for funding allowing the purchase of the X-ray equipment.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BS1033). Services for accessing these data are described at the back of the journal.

References

Adam, W., Baeza, J. & Liu, J.-C. (1972). *J. Am. Chem. Soc.* **94**, 2000–2006.
Allen, F. H., Davies, J. E., Galloy, J. J., Johnson, O., Kennard, O., Macrae, C. F., Mitchell, E. M., Mitchell, G. F., Smith, J. M. & Watson, D. G. (1991). *J. Chem. Inf. Comput. Sci.* **31**, 187–204.
Chiba, T., Takahashi, H., Kato, T., Yoshida, A. & Moroi, R. (1982). *Chem. Pharm. Bull.* **30**, 544–551.
Dolbier, W. R. Jr, Ocampo, R. & Paredes, R. (1995). *J. Org. Chem.* **60**, 5378–5379.
Einhorn, A. (1883). *Ber. Dtsch Chem. Ges.* **16**, 2208–2216.
England, D. C. & Krespan, C. G. (1968). *J. Org. Chem.* **33**, 816–819.
Pommier, A. & Pons, J.-M. (1993). *Synthesis*, pp. 441–459.
Sheldrick, G. M. (1990). *SHELXTL-Plus*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1995). *SHELXTL5*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Siemens (1989). *P3/PC Diffractometer Program*. Version 3.13. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Siemens (1995). *SMART* and *SAINT*. *Data Collection and Processing Software for the SMART System*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Smart, B. E. (1994). *Organofluorine Chemistry: Principles and Commercial Applications*, edited by R. E. Banks, B. E. Smart & J. C. Tatlow, pp. 57–88. NewYork/London: Plenum Press.

Acta Cryst. (1997). **C53**, 1926–1927

2-Acetyl-3-(5-cyano-2-furyl)propenenitrile

Viktor Vrábel,[a] Július Sivý[b] and Štefan Marchalín[a]

[a]*Faculty of Chemical Technology, Slovak University of Technology, Radlinského 9, 812 37 Bratislava, Slovakia, and* [b]*Faculty of Pharmacy, Comenius University, Odbojarov 10, 832 32 Bratislava, Slovakia. E-mail: vrabel@cvt.stuba.sk*

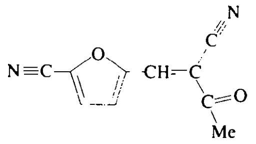
(*Received 26 March 1997; accepted 31 July 1997*)

Abstract

The crystal structure of the title compound, $C_{10}H_6N_2O_2$, consists of relatively isolated molecules, the shortest intermolecular contacts [C—H···O 2.51 (2); C—H···N 2.50 (1) and 2.60 (2) Å] indicate the presence of weak hydrogen bonding. As indicated by the planarity of the molecule and the pattern of bond lengths, the π-electron delocalization extends over the whole molecule.

Comment

The title compound, (I), belongs to a series of large conjugated molecules with potential use as organic dyes (Vrábel *et al.*, 1994; Lokaj *et al.*, 1990). The molecules absorb in the near ultraviolet and visible regions of the spectrum and exhibit pronounced colour changes depending on the nature of the substituents attached to the ethylene C atom and the furan ring. We report here on the crystal structure on the cyano–acetyl derivative, (I).



(I)

Acta Crystallographica Section C
ISSN 0108-2701 © 1997