

## Structure and Stereochemistry of 3-Acetoxy-4-acetyl-4-(*p*-nitrobenzoyloxy)cyclohex-1-ene\*†

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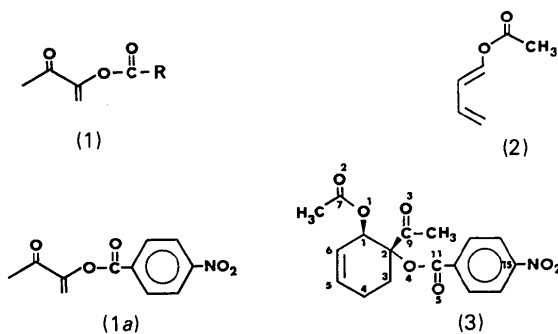
**Abstract.**  $C_{17}H_{17}NO_7$ ,  $M_r = 347.3$ , monoclinic,  $C2/c$ ,  $a = 31.963$  (11),  $b = 5.701$  (2),  $c = 29.859$  (8) Å,  $\beta = 140.63$  (2)°,  $V = 3451$  (1) Å<sup>3</sup>,  $Z = 8$ ,  $D_x = 1.34$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.7107$  Å,  $\mu = 0.098$  mm<sup>-1</sup>,  $F(000) = 1456$ ,  $T = 293$  K, final  $R = 0.056$  for 2173 observed reflections. The X-ray study confirms that in the solid state the structure of the title compound is similar to that inferred from chemical and spectroscopic evidence. The cyclohexene ring adopts a half-chair conformation. Steric hindrance from different chemical groups is minimized by the adoption of a staggered configuration at the C(1)–C(2) and C(2)–C(3) bonds. The molecules in the crystal are packed at normal van der Waals distances. Two C–H...O intermolecular contacts  $< 3.4$  Å are noted.

**Introduction.** Recently there has been great interest in captodative olefins (Viehe, Janousek, Merényi & Stella, 1985) as dienophiles in Diels–Alder reactions (Boucher & Stella, 1985, 1986). As part of our study of captodative dienophiles 1-acetylviny arenecarboxylates  $H_2C=C(COCH_3)OCOR$  with  $R = p$ -nitrophenyl and  $\alpha$ - and  $\beta$ -naphthyl (1) (Tamariz-Mascarúa & Vogel, 1981), we have carried out the Diels–Alder cycloadditions of (1) with 1- and 2-substituted dienes (Aguilar, Reyes-Arellano, Tamariz-Mascarúa & Birbaum, 1987). The adducts obtained from these reactions either under thermal or catalytic ( $ZnCl_2$ ,  $BF_3 \cdot Et_2O$ ) conditions have shown a high regioselectivity. Moreover, the addition of 1-substituted dienes [*i.e.* 1-acetoxy-1,3-butadiene (2)] was also stereoselective. In order to establish the stereochemistry of the major stereoisomer in the addition of 3-(*p*-nitrobenzoyloxy)-3-buten-2-one (1*a*) to the diene (2), we have undertaken the structure determination of the adduct (3: crystallographic numbering shown).

\*IUPAC name: 2-acetoxy-1-acetyl-3-cyclohexen-1-yl *p*-nitrobenzoate.

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**Experimental.** The title compound (3) was prepared from the reaction of (1*a*) and (2) (1:3) with a catalytic amount of hydroquinone in xylene as solvent and under  $N_2$  atmosphere at 403 K for 38 h. The solvent was removed at reduced pressure and the residue was purified by chromatography over florisil with a hexane–ethyl acetate mixture (8:2) as eluent. Subsequent recrystallization from hexane–ethyl acetate gave colourless crystals, m.p. 394–395 K. Composition calculated: C 58.78, H 4.90%; found: C 58.97, H 4.91%. Size of crystal 0.36 × 0.40 × 0.40 mm. Nicolet R3 four-circle diffractometer. Unit-cell parameters by least squares from 25 machine-centred reflections with  $4.2 < 2\theta < 20.5^\circ$ . 3062 unique reflections measured for two octants,  $3 < 2\theta < 50^\circ$ , 2173 with  $I > 2.5\sigma(I)$  used in the analysis, index range  $h \pm 32, k 0 \rightarrow 6, l 0 \rightarrow 34$ ,  $R_{int} = 0.03$ ,  $2\theta/\theta$ -scan mode, variable scan speed, scan width  $1.0^\circ$  ( $\theta$ ). Two standard reflections (204, 311) monitored every 50 measurements, no significant variation. Intensities corrected for Lorentz–polarization but not for absorption. Data adjusted to an approximately absolute scale, overall  $U = 0.057$  Å<sup>2</sup>. Structure solved by combination of direct methods and partial structure expansion by an iterative  $E$ –Fourier procedure using *SHELXTL* (Sheldrick, 1981). Least-squares refinement of all non-H atoms with anisotropic thermal parameters. The H atoms of  $CH$ ,  $CH_2$  and  $CH_3$  groups were allowed to ride on bonded C and

Table 1. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic temperature factors ( $\text{\AA}^2 \times 10^3$ )

	$U_{eq} = (U_{11} \times U_{22} \times U_{33})^{1/3}$			$U_{eq}$
	x	y	z	
C(1)	3541 (1)	4915 (4)	2957 (1)	49 (3)
C(2)	3815 (1)	3375 (4)	2805 (1)	43 (2)
C(3)	3405 (1)	1150 (4)	2432 (1)	53 (2)
C(4)	2693 (1)	1727 (6)	1735 (1)	68 (3)
C(5)	2438 (2)	3733 (6)	1785 (2)	69 (3)
C(6)	2816 (2)	5163 (5)	2338 (2)	62 (3)
O(1)	3725 (1)	3727 (3)	3523 (1)	60 (2)
C(7)	4000 (1)	4990 (5)	4079 (1)	56 (2)
O(2)	4104 (1)	7040 (4)	4132 (1)	85 (3)
C(8)	4137 (2)	3499 (7)	4586 (2)	82 (3)
C(9)	4562 (1)	3061 (5)	3493 (1)	53 (3)
O(3)	4915 (1)	4734 (4)	3730 (1)	71 (2)
C(10)	4817 (2)	784 (6)	3865 (2)	86 (3)
O(4)	3709 (1)	4859 (3)	2325 (1)	47 (2)
C(11)	3976 (1)	4134 (5)	2157 (1)	49 (2)
O(5)	4318 (1)	2425 (4)	2405 (1)	68 (2)
C(12)	3790 (1)	5711 (5)	1624 (1)	47 (2)
C(13)	3328 (1)	7469 (5)	1294 (1)	53 (3)
C(14)	3166 (1)	8914 (5)	801 (1)	56 (3)
C(15)	3474 (1)	8525 (5)	654 (1)	56 (2)
C(16)	3931 (1)	6779 (6)	970 (2)	68 (3)
C(17)	4095 (1)	5366 (6)	1466 (2)	62 (3)
N(1)	3294 (1)	10035 (6)	121 (1)	75 (3)
O(6)	2944 (2)	11710 (5)	-102 (2)	111 (4)
O(7)	3477 (2)	9475 (7)	-94 (2)	134 (4)

Table 2. Molecular geometry of (3)

E.s.d.'s are given in parentheses.

(a) Bond lengths ( $\text{\AA}$ )

C(1)–C(2)	1.535 (6)	C(1)–C(6)	1.478 (4)
C(1)–O(1)	1.457 (5)	C(2)–C(3)	1.520 (3)
C(2)–C(9)	1.539 (3)	C(2)–O(4)	1.461 (5)
C(3)–C(4)	1.514 (3)	C(4)–C(5)	1.479 (7)
C(5)–C(6)	1.329 (5)	O(1)–C(7)	1.340 (4)
C(7)–O(2)	1.192 (4)	C(7)–C(8)	1.475 (7)
C(9)–O(3)	1.203 (4)	C(9)–C(10)	1.477 (4)
O(4)–C(11)	1.345 (6)	C(11)–O(5)	1.201 (4)
C(11)–C(12)	1.494 (5)	C(12)–C(13)	1.381 (4)
C(12)–C(17)	1.386 (8)	C(13)–C(14)	1.391 (6)
C(14)–C(15)	1.373 (8)	C(15)–C(16)	1.372 (5)
C(15)–N(1)	1.480 (6)	C(16)–C(17)	1.385 (6)
N(1)–O(6)	1.207 (5)	N(1)–O(7)	1.197 (8)

(b) Valence angles ( $^\circ$ )

C(2)–C(1)–C(6)	112.7 (3)	C(2)–C(1)–O(1)	105.4 (2)
C(6)–C(1)–O(1)	109.3 (4)	C(1)–C(2)–C(3)	109.1 (3)
C(1)–C(2)–C(9)	108.8 (3)	C(3)–C(2)–C(9)	116.8 (2)
C(1)–C(2)–O(4)	101.9 (2)	C(3)–C(2)–O(4)	110.5 (2)
C(9)–C(2)–O(4)	108.7 (3)	C(2)–C(3)–C(4)	110.8 (2)
C(3)–C(4)–C(5)	112.9 (3)	C(4)–C(5)–C(6)	123.8 (3)
C(1)–C(6)–C(5)	122.4 (4)	C(1)–O(1)–C(7)	118.6 (2)
O(1)–C(7)–O(2)	122.5 (4)	O(1)–C(7)–C(8)	110.6 (3)
O(2)–C(7)–C(8)	126.8 (4)	C(2)–C(9)–O(3)	118.3 (2)
C(2)–C(9)–C(10)	119.3 (3)	O(3)–C(9)–C(10)	122.3 (2)
C(2)–O(4)–C(11)	117.0 (2)	O(4)–C(11)–O(5)	124.0 (4)
O(4)–C(11)–C(12)	111.6 (3)	O(5)–C(11)–C(12)	124.5 (5)
C(11)–C(12)–C(13)	121.4 (4)	C(11)–C(12)–C(17)	118.2 (3)
C(13)–C(12)–C(17)	120.4 (4)	C(12)–C(13)–C(14)	120.1 (5)
C(13)–C(14)–C(15)	118.1 (3)	C(14)–C(15)–C(16)	122.9 (4)
C(14)–C(15)–N(1)	118.1 (3)	C(16)–C(15)–N(1)	119.0 (5)
C(15)–C(16)–C(17)	118.6 (5)	C(12)–C(17)–C(16)	119.9 (3)
C(15)–N(1)–O(6)	118.5 (5)	C(15)–N(1)–O(7)	118.4 (4)
O(6)–N(1)–O(7)	123.1 (5)		

(c) Endocyclic torsion angles ( $^\circ$ ) in the cyclohexene ring

C(1)–C(2)–C(3)–C(4)	61.1 (5)	C(4)–C(5)–C(6)–C(1)	1.7 (9)
C(2)–C(3)–C(4)–C(5)	-43.4 (6)	C(5)–C(6)–C(1)–C(2)	16.6 (7)
C(3)–C(4)–C(5)–C(6)	12.1 (8)	C(6)–C(1)–C(2)–C(3)	-47.0 (4)

assigned a fixed isotropic temperature factor,  $U = 0.06 \text{\AA}^2$ .  $\sum w(\Delta F)^2$  minimized,  $w = [\sigma^2(F_o) + 0.004(F_o)^2]^{-1}$ , where  $\sigma$  is the standard deviation of observed amplitudes, based on counting statistics; isotropic extinction parameter  $X = 0.0015$ . In the last cycle  $(\Delta/\sigma)_{\max} = 1.0$ , mean = 0.21;  $\Delta\rho$  from -0.27 to 0.21 e  $\text{\AA}^{-3}$ ; final  $R = 0.056$ ,  $wR = 0.085$ ,  $S = 1.09$ ; scattering factors from *International Tables for X-ray Crystallography* (1974).

All computations performed on a Nova 4S computer and plots drawn on a Tektronix plotter with the *SHELXTL* system of programs.

**Discussion.** Atomic coordinates are in Table 1.\* Fig. 1 shows the molecular conformation of the title compound (3). The bond lengths and angles for non-H atoms, together with endocyclic cyclohexene torsion angles, are listed in Table 2.

The cyclohexene ring exhibits an almost perfect half-chair conformation [Table 2(c)]. The torsional angles that define the conformation of the three

\* Lists of structure amplitudes, anisotropic thermal parameters, H-atom coordinates and least-squares-planes' calculations have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44766 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

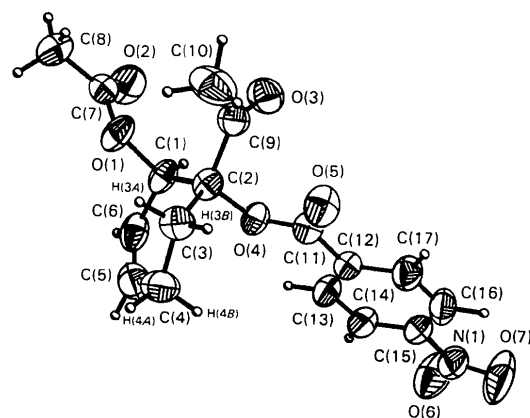
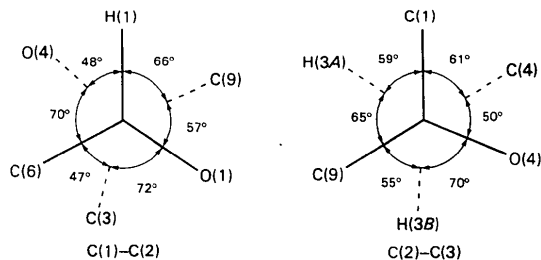


Fig. 1. The molecular conformation of (3), showing atom numbering. The thermal ellipsoids are drawn at the 50% probability level.

Fig. 2. Newman projections of selected C–C bonds. E.s.d.'s of torsion angles 0.3–0.5 $^\circ$ .

substituents about the C(1)–C(2) and C(2)–C(3) bonds of the ring are illustrated in Fig. 2. The acetoxy and *p*-nitrobenzoyloxy groups at C(1) and C(2) are axial; the acetyl group at C(2) is equatorial. The torsion angle involving the acetoxy and acetyl groups, O(1)–C(1)–C(2)–C(9), is  $-56.3(3)^\circ$ , which minimizes the *gauche* interaction between these two substituents. Both acetoxy and acetyl groups are planar, maximum deviations  $0.009(7)$  and  $-0.029(7)$  Å for O(1) and C(9), respectively. The dihedral angles between the mean planes through the acetoxy and acetyl groups with respect to the cyclohexene ring are  $77.2(7)$  and  $129.6(7)^\circ$ , respectively.

The Newman projection along the C(2)–C(3) bond (Fig. 2) shows that the projected angle between the acetyl and *p*-nitrobenzoyloxy groups at C(2) is  $125^\circ$  which helps to reduce the *gauche* interactions between these two groups.

The phenyl ring of the *p*-nitrobenzoyloxy substituent shows normal geometry,  $1.381(6)$  Å and  $120(4)^\circ$  for the mean C–C bond distance and the mean internal angle, respectively. The *p*-nitrobenzoyloxy substituent forms a dihedral angle of  $80.0(7)^\circ$  with the mean plane of the cyclohexene ring. The nitro group is bent out of the plane of the phenyl ring by  $10.0(7)^\circ$ .

There are two intermolecular approaches  $< 3.4$  Å involving non-H atoms: C(16)···O(3)( $1-x, y, 0.5-z$ )

$3.27(1)$  and C(8)···O(7)( $x, 1-y, -0.5+z$ )  $3.37(1)$  Å. The molecules are held in the crystal by van der Waals forces.

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## Structure of the Smectogenic Compound 4-(2-Cyanoethyl)cyclohexyl 4-*n*-Pentylcyclohexanecarboxylate

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**Abstract.**  $C_{21}H_{35}NO_2$ ,  $M_r = 333.5$ , triclinic,  $P\bar{1}$ ,  $a = 5.611(1)$ ,  $b = 12.827(1)$ ,  $c = 14.348(2)$  Å,  $\alpha = 93.07(1)$ ,  $\beta = 89.15(1)$ ,  $\gamma = 95.762(8)^\circ$ ,  $V = 1025.9(2)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.079$  g cm<sup>-3</sup>,  $\lambda(\text{Cu } K\alpha) = 1.54178$  Å,  $\mu = 5.0$  cm<sup>-1</sup>,  $F(000) = 368$ ,  $T = 293$  K, final  $R = 0.062$  ( $wR = 0.064$ ) for 2266 observed reflections. The linearity of the almost fully stretched molecule is only distorted by the *gauche* conformation of the cyanoethyl group [torsion angle  $-57.7(4)^\circ$ ]. The crystal packing is characterized by an antiparallel arrangement of neighboring molecules.

**Introduction.** In a series of previous publications (Hartung, Baumeister, Jaskólski, Mädicke & Wiegeleben, 1986, and references therein) we have described the results of our structural investigations on mesogenic cyano-substituted phenyl benzoates and phenyl cyclohexanecarboxylates in their crystalline state. This type of compound is of potential importance for practical use in liquid-crystal displays. The title compound, here abbreviated as CECPC, is one such material. It was studied to examine the influence of the dimethylene spacer between the polar cyano group and