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Conformation and Structure of (1*R*,6′*R*)- and (1*S*,6′*S*)-3-Iodo-2,2-dimethyl-1-[6′-(3′-methyl-1′-oxocyclohex-2′-enylpropyl)] *p*-Nitrobenzoate[*]

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Abstract. $C_{19}H_{22}INO_5$, $M_r=470{\cdot}9$, monoclinic, $P2_1/n$, $a = 6{\cdot}682\,(1)$, $b = 22{\cdot}635\,(3)$, $c = 13{\cdot}316\,(2)$ Å, $\beta = 97{\cdot}46\,(1)°$, $V = 1997{\cdot}1\,(5)$ Å^3, $Z = 4$, $D_x = 1{\cdot}566$, D_m (flotation in CCl_4/CH_2Cl_2)$=1{\cdot}55\,(2)$ Mg m^{-3}, Mo $K\alpha$ radiation ($\lambda K\alpha_1 = 0{\cdot}70926$ Å, $\lambda K\alpha_2 = 0{\cdot}71354$ Å), $\mu = 1{\cdot}583$ mm^{-1}, $F(000) = 944$, $T = 295$ K, $R = 0{\cdot}0436$, $wR = 0{\cdot}0452$ for 1886 data. The configurations at the two asymmetric centers are both *S* (or both *R*), there being an equal distribution of *SS* and *RR* forms in this centrosymmetric cell. The cyclohexenone ring is a very flattened half-chair, and approximates well an envelope conformation with five atoms coplanar and one out of the plane.

Introduction. The generation of carbon asymmetry in carbon—carbon bond forming reactions has emerged as a fundamental cornerstone of modern synthetic organic chemistry and continues to be the subject of intense research and application. In this capacity, the aldol addition reaction has attracted extensive investigation in efforts to elucidate important control elements responsible for simple diastereoselection in the concomitant formation of two adjacent centers of carbon asymmetry. Exhaustive studies have documented aspects of stereochemical control in addition reactions of aldehydes and ketones with metal enolates and silyl enol ethers derived from saturated ketones (Heathcock, 1984). However, little information has appeared addressing the analogous process using α,β-unsaturated ketone kinetic enolates (Stork, Kraus & Garcia, 1974) or the corresponding dienylsilyl ethers (Brown, Campbell, Taylor & Zhang, 1987). We therefore set out to investigate the degree of diastereoselection in the $TiCl_4$-catalyzed crossed-aldol addition reaction of dienylsilyl ethers with aldehydes to ascertain the control effects, if any, the double bond imparts upon stereoselectivity.

Initial studies have focused upon a series of six-membered cyclic enones owing to the geometric homogeneity of the corresponding *E*-enolsilanes, an important consideration in aldol chemistry (Heathcock, 1984; Evans, 1984). $TiCl_4$-mediated reaction of the dienylsilyl ethers with a series of aldehydes provided good yields of the addition products, which were analyzed for direction and degree of diastereoselectivity by ^{1}H NMR spectroscopy. In most cases studied, *erythro*/*threo* assignment of the major isomer produced was readily elucidated from vicinal proton coupling constants and correlation with known magnitudes in saturated systems ($J_{\text{H-1,6}'}$). However, the reaction of the dienylsilane derived from 3-methyl-2-cyclohexenone and 2-iodomethyl-2-methylpropanal provided a 78:22 mixture of isomers, the vicinal coupling constants of which were identical. A crystalline derivative (*p*-nitrobenzoate) of the major aldol product was therefore prepared, to discern the sense of diastereoselectivity in this example.

Experimental. Colorless needles from ethyl acetate/hexane (90:10) solution at room temperature. Crystal 0·8 × 0·2 × 0·1 mm. Nicolet *R*3*m*/V diffractometer. Systematic absences $h0l$ for $(h+l)$ odd, $0k0$ for k odd. Cell constants by least squares using 34 reflections with $20 < 2\theta(\text{Mo}) < 25°$ measured on the diffractometer. Intensity data collected using θ scans. 4623 unique reflections, $2\theta < 55°$, $0 \le h \le 9$, $0 \le k \le 30$, $-18 \le l \le 18$. Lorentz–polarization and absorption corrections applied. No systematic fluctuations in 193, 333, $1,10,\bar{4}$, $36\bar{1}$ measured at the beginning and after every 100 reflections (53 times). Programs from *SHELXTL-PLUS* (Sheldrick, 1987).

The position of the iodine atom was located from a three-dimensional Patterson function, the remaining non-hydrogen atoms being located in a subsequent difference Fourier map. Isotropic refinement (on *F*) of all 26 non-hydrogen atoms gave $R = 0{\cdot}102$. Subsequent anisotropic refinement gave $R = 0{\cdot}053$. All 22 hydrogen atoms were located in a difference Fourier synthesis. The final cycle of least squares involved anisotropic refinement of non-hydrogen atoms and isotropic refinement of hydrogen atoms; weights $1/[\sigma^2(F) + gF^2]$, g refined to 0·00043 (1). Final cycle gave $R = 0{\cdot}0436$, $wR = 0{\cdot}0452$, $S = 1{\cdot}237$ using 1886 observations with $F > 5\sigma(F)$ and 323 variables. No

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[*] 3-Iodo-2,2-dimethyl-1-(4-methyl-2-oxo-3-cyclohexen-1-yl)-propyl *p*-nitrobenzoate.

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Table 1. *Atomic coordinates* (× 10^4) *and equivalent isotropic displacement parameters* (Å^2 × 10^3)

	x	y	z	U_{eq}*
I	9214 (1)	−843 (1)	8158 (1)	74 (1)
O(1)	8280 (8)	−2900 (3)	7371 (5)	79 (3)
O(2)	12596 (6)	−1783 (2)	6783 (3)	45 (2)
O(3)	9843 (8)	−1801 (3)	5608 (4)	65 (2)
O(4)	17864 (11)	−211 (3)	3624 (6)	111 (3)
O(5)	15099 (10)	138 (3)	2881 (5)	91 (3)
N	16033 (13)	−187 (3)	3495 (5)	69 (3)
C(3)	12221 (13)	−1199 (4)	8580 (7)	58 (3)
C(2)	12396 (10)	−1878 (3)	8548 (5)	44 (2)
C(5)	14667 (13)	−2009 (5)	8792 (8)	62 (4)
C(4)	11194 (17)	−2160 (4)	9339 (7)	61 (4)
C(1)	11563 (11)	−2120 (3)	7499 (5)	42 (3)
C(6′)	11858 (10)	−2781 (3)	7346 (5)	42 (2)
C(1′)	9838 (12)	−3100 (3)	7129 (5)	51 (3)
C(2′)	9862 (14)	−3684 (3)	6637 (6)	55 (3)
C(3′)	11523 (14)	−3929 (3)	6354 (6)	61 (3)
C(10)	11500 (25)	−4530 (5)	5894 (10)	88 (5)
C(4′)	13492 (13)	−3614 (4)	6502 (8)	63 (3)
C(5′)	13243 (13)	−2950 (4)	6581 (7)	54 (3)
C(13)	11562 (12)	−1648 (3)	5872 (5)	46 (3)
C(14)	12821 (11)	−1298 (3)	5249 (5)	43 (3)
C(15)	11810 (13)	−1003 (4)	4418 (6)	63 (3)
C(16)	12871 (14)	−638 (4)	3835 (7)	66 (3)
C(17)	14904 (13)	−586 (3)	4095 (6)	54 (3)
C(18)	15945 (13)	−887 (4)	4888 (6)	66 (3)
C(19)	14877 (13)	−1244 (4)	5473 (6)	56 (3)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

evidence for extinction. Final difference Fourier map contained no peak higher than 0·46 e Å^{-3}. $(\Delta/\sigma)_{max} = 0·018$. Atomic scattering factors taken from *International Tables for X-ray Crystallography* (1974).

Discussion. The positional parameters, along with their standard deviations as estimated from the inverse least-squares matrix, are presented in Table 1.* The geometry of a single molecule of the title compound is depicted in Fig. 1.

The structure consists of monomeric units which are well separated from each other. In the absence of any potential donor, there is no hydrogen bonding in the structure. The principal bond lengths and bond angles in the structure are given in Table 2. The C(3)—I bond length of 2·171 (8) Å is normal (Singh & Hodgson, 1974), as are the other distances in the structure. The bond lengths in the cyclohexenone ring show the expected pattern of five nominally single bonds of lengths 1·477 (1) to 1·524 (10) Å [average 1·50 (2) Å] and one [C(2′)—C(3′)] nominally double bond of 1·338 (11) Å. As expected, the substituted phenyl ring is planar, with an average deviation of less than 0·009 Å from the six-atom mean plane. The conformation of the cyclohexenone ring is always of interest. Robinson and co-workers have demonstrated that highly substituted cyclohexen-2-ones adopt a flattened half-chair conformation (Hartshorn, Martyn, Robinson & Vaughan, 1986), with atoms C(1′), C(2′), C(3′) and C(4′) in a plane and C(6′) and C(5′) approximately equally disposed above and below the plane. In the present case the degree of flattening is extreme. If the ring is viewed as a flattened half-chair, the in-plane atoms C(1′), C(2′), C(3′) and C(4′) form

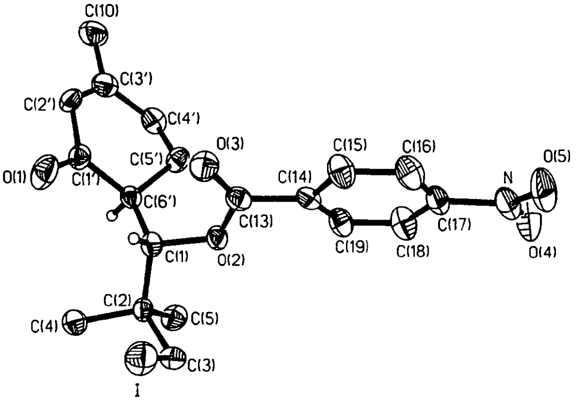

Fig. 1. View of a single molecule of the compound. Hydrogen atoms are omitted for clarity. The molecule shown here is the (1*S*, 6′*S*) enantiomer, but in this centrosymmetric crystal there are an equal number of (1*R*,6′*R*) forms.

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

I—C(3)	2·171 (8)	O(1)—C(1′)	1·216 (8)
O(2)—C(1)	1·461 (8)	O(2)—C(13)	1·350 (8)
O(3)—C(13)	1·208 (8)	O(4)—N	1·214 (8)
O(5)—N	1·210 (8)	N—C(17)	1·477 (10)
C(3)—C(2)	1·541 (10)	C(2)—C(5)	1·539 (11)
C(2)—C(4)	1·544 (10)	C(2)—C(1)	1·535 (9)
C(1)—C(6′)	1·527 (9)	C(6′)—C(1′)	1·524 (10)
C(6′)—C(5′)	1·511 (10)	C(1′)—C(2′)	1·477 (10)
C(2′)—C(3′)	1·338 (11)	C(3′)—C(10)	1·491 (12)
C(3′)—C(4′)	1·488 (11)	C(4′)—C(5′)	1·518 (11)
C(13)—C(14)	1·486 (9)	C(14)—C(15)	1·390 (10)
C(14)—C(19)	1·373 (10)	C(15)—C(16)	1·390 (11)
C(16)—C(17)	1·363 (11)	C(17)—C(18)	1·368 (11)
C(18)—C(19)	1·383 (10)		

C(13)—O(2)—C(1)	118·3 (5)	O(5)—N—O(4)	123·0 (8)
C(17)—N—O(4)	118·1 (7)	C(17)—N—O(5)	118·8 (8)
C(2)—C(3)—I	115·8 (5)	C(5)—C(2)—C(3)	105·2 (6)
C(4)—C(2)—C(3)	110·2 (7)	C(4)—C(2)—C(5)	111·2 (7)
C(1)—C(2)—C(3)	111·1 (6)	C(1)—C(2)—C(5)	110·8 (6)
C(1)—C(2)—C(4)	108·3 (6)	C(2)—C(1)—O(2)	105·2 (5)
C(6′)—C(1)—O(2)	110·1 (6)	C(6′)—C(1)—C(2)	115·6 (6)
C(1′)—C(6′)—C(1)	111·3 (6)	C(5′)—C(6′)—C(1)	116·0 (6)
C(5′)—C(6′)—C(1′)	110·9 (6)	C(6′)—C(1′)—O(1)	122·7 (7)
C(2′)—C(1′)—O(1)	120·6 (7)	C(2′)—C(1′)—C(6′)	116·6 (7)
C(3′)—C(2′)—C(1′)	123·6 (7)	C(10)—C(3′)—C(2′)	122·0 (9)
C(4′)—C(3′)—C(2′)	121·0 (7)	C(4′)—C(3′)—C(10)	117·0 (9)
C(5′)—C(4′)—C(3′)	112·4 (7)	C(4′)—C(5′)—C(6′)	112·3 (7)
O(3)—C(13)—O(2)	123·6 (6)	C(14)—C(13)—O(2)	111·2 (6)
C(14)—C(13)—O(3)	125·2 (7)	C(15)—C(14)—C(13)	116·7 (7)
C(19)—C(14)—C(13)	123·3 (7)	C(19)—C(14)—C(15)	119·9 (7)
C(16)—C(15)—C(14)	120·0 (8)	C(17)—C(16)—C(15)	118·2 (8)
C(16)—C(17)—N	118·5 (7)	C(18)—C(17)—N	118·6 (8)
C(18)—C(17)—C(16)	122·9 (8)	C(19)—C(18)—C(17)	118·5 (8)
C(18)—C(19)—C(14)	120·4 (8)		

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* Lists of structure amplitudes, H-atom positional parameters and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51513 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

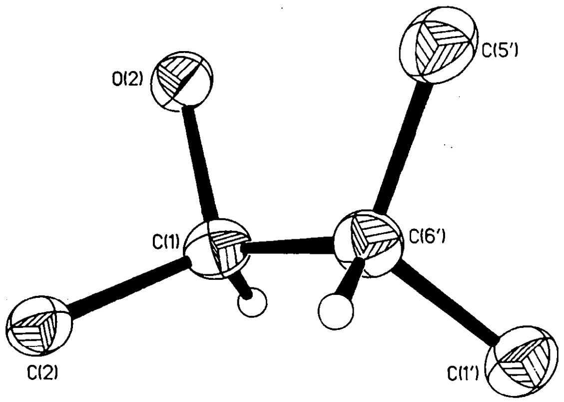

Fig. 2. The stereochemistry at the asymmetric centers C(1) and C(6′).

an excellent plane (maximum deviation 0·005 Å), with C(5′) lying 0·570 Å out of the plane. Atom C(6′), however, sits only 0·075 Å above this four-atom plane. Alternatively, if we view the ring as an envelope conformation we calculate a plane through the five atoms C(6′), C(1′), C(2′), C(3′) and C(4′); the maximum deviation from this plane is 0·022 Å, and C(5′) lies 0·617 Å below the plane.

Our principal interest in the title compound is in the configuration at the asymmetric carbon centers C(1) and C(6′), since we were unsure with which diastereomer we were dealing. The geometry at C(1) and C(6′) is shown in Fig. 2. As can be seen in that figure, the configuration in the molecule shown is C(1)*S*, C(6′)*S*; naturally, in this centrosymmetric crystal there are an equal number of the enantiomeric C(1)*R*, C(6′)*R* species, but no other diastereomers.

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Structure of Elsinochrome A: a Perylenequinone Metabolite

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Abstract. *trans*-1,2-Diacetyl-1,2-dihydro-5,10-dihydroxy-3,7,8,12-tetramethoxybenzo[*ghi*]perylene-4,11-dione, $C_{30}H_{24}O_{10}$, $M_r = 544{\cdot}51$, orthorhombic, $P2_12_12_1$, $Z = 4$, $a = 12{\cdot}428$ (3), $b = 13{\cdot}048$ (3), $c = 14{\cdot}933$ (3) Å, $V = 2421{\cdot}5$ (9) Å^3, $D_x = 1{\cdot}494$, D_m (by flotation) $= 1{\cdot}48$ g cm^{-3}, λ(Mo $K\alpha$) $= 0{\cdot}71069$ Å, $\mu = 1{\cdot}057$ cm^{-1}, $F(000) = 1136$, $T = 293$ K, $R = 0{\cdot}046$ (2065 observed reflections). Elsinochrome A is shown to exist in the solid state as a non-planar quinone tautomer; the pigment adopts a helical conformation, in analogy with the related cercosporin, but the perylenequinone moiety in elsinochrome A appears to be significantly less skewed.

Introduction. Perylenequinones form a group of chemically interesting biologically active (especially photosensitizing) pigments obtainable from natural sources (Weiss, Merlini & Nasini, 1987); almost all the

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