

Table 3. Comparison of the bond lengthenings for C, Si and Ge analogues

Bond	Length (Å)	X-C(Ph _{ave}) Å	Difference	Reference
C-C(Ac)	1.555 (3)	X = C, 1.538 (2)	0.017 Å	(1)
C-C(Ph ₁)	1.534 (3)			
C-C(Ph ₂)	1.540 (3)			
C-C(Ph ₃)	1.541 (3)			
Si-C(Ac)	1.926 (14)	X = Si, 1.864 (8)	0.062 Å	(2)
Si-C(Ph ₁)	1.860 (14)			
Si-C(Ph ₂)	1.864 (14)			
Si-C(Ph ₃)	1.867 (14)			
Ge-C(Ac)	2.011 (15)	X = Ge, 1.945 (8)	0.066 Å	(3)
Ge-C(Ph ₁)	1.940 (14)			
Ge-C(Ph ₂)	1.945 (14)			
Ge-C(Ph ₃)	1.950 (14)			

References: (1) Present work; (2) Chieh & Trotter (1969); (3) Harrison & Trotter (1968).

The C(1)—C(Ph) bond distances are 1.534 (3), 1.540 (3), 1.541 (3) Å (Table 2); the mean length of 1.538 (2) Å is somewhat longer than the value of 1.51 Å which might be expected for a C(sp³)—C(sp²) single bond, but is quite close to the 1.53 (1) Å quoted as a mean for C—C₆H₅ bonds (*Molecular Structures and Dimensions*, 1972). The C(1)—C(Ac) bond, 1.555 (3) Å, is 0.017 Å (5σ) longer than the mean C(1)—C(Ph) distance; this lengthening is similar to, but much less prominent, than the lengthenings of about 0.06 Å in the Ge and Si compounds (Table 3). The canonical form (Ic) therefore makes a smaller contribution to the resonance hybrid of the carbon compound, relative to the Ge and Si analogues. This conclusion is in accord with spectroscopic and basicity data (Brook, 1957; Allred & Rochow, 1958; Brook, Quigley, Peddle, Schwartz & Warner, 1960; Yates & Agolini, 1966).

Other molecular dimensions are normal. In the acetyl group C=O is 1.211 (3) and C—CH₃, 1.499 (4) Å; the

C—C distances in the phenyl rings are in the range 1.363–1.392 (4) Å, the shorter distances probably being subject to thermal-libration errors.

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Structure of 5-Benzoyl-4-(p-chlorophenyl)-2,2,5-triphenyl-Δ³-1,3-oxazoline, C₃₄H₂₄ClNO₂

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Abstract. *M_r* = 514.02, orthorhombic, *Pbca*, *a* = 16.354 (7), *b* = 17.464 (9), *c* = 18.599 (9) Å, *V* = 5312 (4) Å³, *Z* = 8, *D_x* = 1.286 Mg m⁻³, *μ*(Mo *Kα*) = 1.721 mm⁻¹, *λ* = 0.71069 Å, *F*(000) = 2144, *T* = 292 K, *R* = 0.054 for 1171 observed reflexions. Bond lengths and angles are normal. The structure analysis confirms that the reaction mechanism leading to the title photoproduct involves a 1,2-acyl migration.

Introduction. The photochemical reactions of enol esters are dominated by 1,3-acyl migration (Bellus, 1971; Muzart & Pete, 1978). Up to the recent work of Armesto, Ortiz, Perez-Ossorio & Horspool (1983) no example of a 1,2-acyl migration has been reported for such systems although 1,2-acyl migrations do occur in the related oxa-di-π-methane systems (Hixson, Mariano & Zimmerman, 1973). The irradiation of 4-benzoyloxy-

3-(*p*-chlorophenyl)-1,1,4-triphenyl-2-aza-1,3-butadiene, a dienol ester, gave a single photoproduct whose structure was difficult to resolve by conventional techniques such as mass, ^{13}C , and ^1H NMR spectroscopy. The product was believed to be a 5-acyl- Δ^3 -1,3-oxazoline, a novel example of a class of compounds difficult, if not impossible, to synthesize by conventional means. Furthermore, the suggested reaction mechanism leading to the photoproduct was thought to involve a novel 1,2-acyl migration and consequently it was of considerable importance to verify the structure by X-ray crystallographic techniques.

In this work we report the crystal structure of the title compound.

Experimental. A clear, colourless, prismatic crystal, $0.4 \times 0.3 \times 0.3$ mm, prepared by Armesto *et al.* (1983), Nonius CAD-4F automatic diffractometer, cell dimensions refined by least-squares fitting of the θ values of 24 reflexions; intensities of 5745 unique reflexions, $1^\circ < \theta < 27^\circ$, hkl 0,0,0 to 20,22,23, monochromatic Mo $K\alpha$ radiation, $\omega/2\theta$ scans; three reflexions monitored periodically during data collection showed no crystal decomposition; intensities corrected for Lorentz and polarization effects; 1171 considered as observed [$I > 2\sigma(I)$]; no absorption corrections ($\mu R =$

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

$$U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Cl	-491 (2)	1255 (2)	5414 (2)	81 (1)
N	966 (4)	509 (5)	2114 (4)	48 (3)
O	2314 (3)	162 (4)	1862 (3)	43 (2)
O(7)	1788 (4)	-951 (4)	3225 (4)	59 (3)
C(2)	1502 (5)	281 (6)	1531 (5)	42 (4)
C(4)	1334 (6)	445 (5)	2714 (5)	38 (3)
C(5)	2244 (5)	175 (5)	2636 (4)	39 (3)
C(6)	2353 (6)	-644 (5)	2906 (5)	42 (3)
C(8)	3130 (5)	-1062 (6)	2758 (5)	44 (4)
C(9)	3233 (7)	-1789 (6)	3052 (6)	58 (4)
C(10)	3954 (8)	-2184 (6)	2949 (7)	76 (5)
C(11)	4584 (8)	-1856 (8)	2551 (8)	85 (6)
C(12)	4493 (7)	-1143 (8)	2258 (7)	75 (5)
C(13)	3755 (6)	-748 (6)	2347 (6)	59 (4)
C(14)	1173 (6)	-440 (5)	1191 (5)	43 (4)
C(15)	1626 (6)	-1116 (7)	1163 (5)	57 (4)
C(16)	1285 (8)	-1784 (6)	865 (6)	69 (5)
C(17)	487 (8)	-1770 (7)	622 (6)	68 (5)
C(18)	30 (7)	-1107 (8)	653 (6)	68 (5)
C(19)	375 (6)	-447 (6)	925 (6)	60 (4)
C(14')	1620 (6)	938 (5)	1003 (5)	44 (4)
C(15')	2144 (6)	841 (6)	412 (5)	61 (4)
C(16')	2292 (7)	1445 (7)	-56 (6)	74 (5)
C(17')	1906 (7)	2138 (7)	47 (7)	69 (5)
C(18')	1390 (8)	2246 (6)	617 (7)	71 (5)
C(19')	1229 (6)	1647 (6)	1085 (6)	57 (4)
C(20)	896 (6)	641 (5)	3401 (5)	34 (3)
C(21)	76 (6)	868 (6)	3350 (6)	55 (4)
C(22)	-345 (6)	1063 (7)	3979 (6)	63 (5)
C(23)	59 (7)	1017 (6)	4633 (5)	47 (4)
C(24)	859 (8)	780 (7)	4690 (6)	68 (5)
C(25)	1270 (6)	592 (6)	4066 (6)	54 (4)
C(26)	2843 (5)	776 (6)	2940 (5)	39 (4)
C(27)	2933 (6)	1459 (6)	2589 (6)	55 (4)
C(28)	3443 (7)	2014 (7)	2877 (8)	82 (6)
C(29)	3848 (7)	1885 (8)	3520 (9)	82 (6)
C(30)	3768 (7)	1190 (9)	3851 (7)	79 (5)
C(31)	3270 (6)	617 (6)	3578 (5)	56 (4)

0.69); scattering factors for neutral atoms from *International Tables for X-ray Crystallography* (1974). Structure solved with *MULTAN* (Main, Lessinger, Woolfson, Germain & Declercq, 1977), best E map revealed all the non-hydrogen atoms; anisotropic full-matrix least-squares refinement, $\sum(|F_o| - |F_c|)^2$ minimized, $R = 0.07$; difference synthesis calculated with reflexions having $\sin \theta/\lambda < 0.5 \text{ \AA}^{-1}$ showed all H atoms as highest peaks of the map; final refinement with fixed isotropic temperature factors and coordinates for H atoms, and unit weights led to $R = 0.054$; maximum and average Δ/σ in final LS cycle 0.98 and 0.28; final difference synthesis had no electron density $> 0.21 \text{ e \AA}^{-3}$ and $< -0.19 \text{ e \AA}^{-3}$. No correction for secondary extinction. Most of the calculations carried out with XRAY70 (Stewart, Kundell & Baldwin, 1970); LS planes computed with *PARST 5* (Nardelli, Musatti, Domiano & Andreotti, 1965).

Table 2. Bond lengths (\AA) and angles ($^\circ$)

E.s.d.'s are ca 0.015 \AA for lengths and ca 0.9 $^\circ$ for angles.

N-C(2)	1.450	C(17)-C(18)	1.380
-C(4)	1.273	C(18)-C(19)	1.380
O-C(2)	1.479	C(14')-C(15')	1.405
-C(5)	1.444	-C(19')	1.401
O(7)-C(6)	1.221	C(15')-C(16')	1.389
C(2)-C(14)	1.508	C(16')-C(17')	1.379
-C(14')	1.523	C(17')-C(18')	1.368
C(4)-C(5)	1.568	C(18')-C(19')	1.387
-C(20)	1.503	C(20)-C(21)	1.402
C(5)-C(6)	1.526	-C(25)	1.382
-C(26)	1.544	C(21)-C(22)	1.399
C(6)-C(8)	1.492	C(22)-C(23)	1.387
C(8)-C(9)	1.393	C(23)-Cl	1.759
-C(13)	1.389	-C(24)	1.376
C(9)-C(10)	1.380	C(24)-C(25)	1.381
C(10)-C(11)	1.392	C(26)-C(27)	1.367
C(11)-C(12)	1.368	-C(31)	1.404
C(12)-C(13)	1.399	C(27)-C(28)	1.388
C(14)-C(15)	1.394	C(28)-C(29)	1.385
-C(19)	1.396	C(29)-C(30)	1.367
C(15)-C(16)	1.406	C(30)-C(31)	1.387
C(16)-C(17)	1.381		
C(2)-N-C(4)	110.3	C(14)-C(15)-C(16)	120.5
C(2)-O-C(5)	109.9	C(15)-C(16)-C(17)	119.3
N-C(2)-O	105.7	C(16)-C(17)-C(18)	120.8
O -C(14')	105.1	C(17)-C(18)-C(19)	119.7
O -C(14)	112.2	C(14)-C(19)-C(18)	121.3
C(12)-C(14)-C(19)	110.6	C(2)-C(14)-C(19)	122.6
N -C(14)	109.2	C(2)-C(15)-C(16)	119.4
N -C(14)	113.8	C(15')-C(16)-C(17)	118.0
C(14)-C(15)-C(16)	120.0	C(14')-C(15)-C(16)	120.4
N -C(5)	113.2	C(15')-C(16)-C(17)	120.0
C(5)-C(2)-C(1)	126.9	C(16')-C(17)-C(18')	120.8
O-C(5)-C(4)	100.0	C(17)-C(18)-C(19')	120.0
C(4)-C(2)-C(1)	111.3	C(14')-C(19)-C(18')	120.8
C(4)-C(6)	111.2	C(4)-C(20)-C(25)	122.3
O -C(26)	109.0	C(4) -C(21)	117.6
O -C(6)	107.8	C(21) -C(25)	120.1
C(6) -C(26)	116.3	C(20)-C(21)-C(22)	118.8
O(7)-C(6)-C(5)	118.9	C(21)-C(22)-C(23)	119.1
C(5) -C(8)	119.8	Cl-C(23)-C(22)	117.8
O(7) -C(8)	121.3	C(22) -C(24)	122.5
C(6)-C(8)-C(13)	122.4	Cl -C(24)	119.6
C(6) -C(9)	118.4	C(23)-C(24)-C(25)	118.0
C(9) -C(13)	119.2	C(20)-C(25)-C(24)	121.5
C(8)-C(9)-C(10)	120.3	C(5)-C(26)-C(31)	119.4
C(9)-C(10)-C(11)	120.1	C(5) -C(27)	119.1
C(10)-C(11)-C(12)	120.4	C(27) -C(31)	121.5
C(11)-C(12)-C(13)	119.7	C(26)-C(27)-C(28)	119.3
C(8)-C(13)-C(12)	120.3	C(27)-C(28)-C(29)	120.4
C(2)-C(14)-C(19)	119.3	C(28)-C(29)-C(30)	119.2
C(2) -C(15)	122.3	C(29)-C(30)-C(31)	121.1
C(15) -C(19)	118.4	C(26)-C(31)-C(30)	117.3

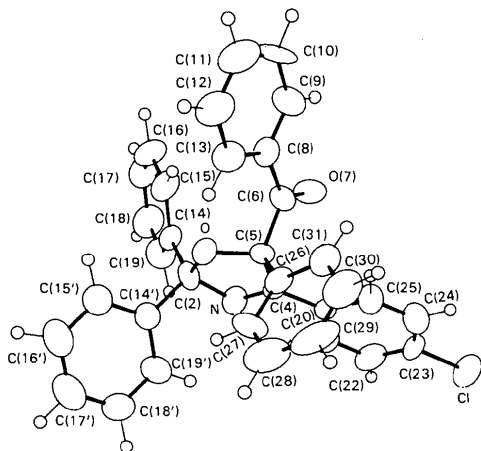


Fig. 1. ORTEP (Johnson, 1965) drawing of the molecule showing the atom numbering.

Discussion. Table 1 shows the final atomic parameters.* Fig. 1 (Johnson, 1965) shows the geometry of the structure and the atom labelling. Bond lengths and angles together with their e.s.d.'s are in Table 2.

* Lists of structure factors anisotropic thermal parameters, H-atom parameters and least-squares-planes' calculations have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38854 (43 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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The Structure of Phyllanthocindiol Methyl Ester, $C_{25}H_{32}O_8$ *

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Abstract. $M_r = 460.52$, monoclinic, $P2_1$, $a = 9.891$ (5), $b = 24.84$ (1), $c = 9.687$ (5) Å, $\beta = 94.82$ (2)°, $V = 2372$ (2) Å³, $Z = 4$, $D_m = 1.21$, $D_x = 1.29$ Mg m⁻³, $\lambda(\text{Cu } K\alpha) = 1.5418$ Å, $\mu(\text{Cu } K\alpha) = 0.71$ mm⁻¹, $F(000) = 984$, room temperature. Final $R = 0.072$ for 3692 reflections. The two independent molecules have similarly folded configurations and a network of inter- and intramolecular hydrogen-bonding obtains.

* The present contribution is part 97 of Antineoplastic Agents. For part 96 refer to Pettit, Kamano & Tozawa (1984).

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The structure analysis confirms that the irradiation of 4-benzoyloxy-3-(*p*-chlorophenyl)-1,1,4-triphenyl-2-aza-1,3-butadiene gives a photoproduct which is derived from the dienol ester through 1,2-acyl migration.

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Introduction. A detailed chemical investigation of the Central American tree *Phyllanthus acuminatus* Vahl (Euphorbiaceae family) led to isolation and structural elucidation (chemical and spectral methods) of the four most prominent anticancer constituents as amorphous glycosides designated phyllanthostatins 1–3 and phyllanthoside (Pettit, Cragg, Gust, Brown & Schmidt, 1982; Pettit, Cragg, Gust & Brown, 1982). One of these potentially important substances will be selected and evaluated for eventual clinical trial by the US National Cancer Institute. Since configuration of the 7-hydroxyl group in phyllanthostatins 1–3 could not be definitely

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