head-to-head and tail-to-tail approaches. The sugar ends of the molecules are extensively linked through hydrogen bonding, while the hydrophobic alkene ends are held together by weak van der Waals interactions. There are four symmetry-independent hydrogen bonds in the structure: O(2′)—H···O(6′) ($x,y,z-1$) = 2·729 (10), O(3′)—H···O(6′) ($1·5-x$, $2-y$, $-0·5+z$) = 2·839 (10), O(4′)—H··· O(6′) ($1·5-x$, $2-y$, $-0·5+z$) = 2·908 (10) and O(6′)—H···O(2′) ($x,y,z+1$) = 2·729 (10) Å, all of which involve atom O(6′). Besides, there are two short non-bonding O···O contacts: O(3′)···O(4′) ($1·5-x$, $2-y$, $-0·5+z$) = 2·884 (10) and O(3′)···O(*D*) ($0·5+x$, $1·5-y$, $2-z$) = 2·653 (9) Å. There is no hydrogen bonding between the layers and there is very little overlap of molecules in adjacent layers. Lack of interlayer hydrogen bonding and the presence of hydrophobic regions in the crystal structure may very well explain the rather large crystal mosaic.

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References

ALTONA, C., GEISE, H. J. & ROMERS, C. (1968). *Tetrahedron*, **24**, 13–32.

AVENEL, D., OHANESSIAN, J., GILLIER-PANDRAUD, H. & BOULLANGER, P. (1982). *Acta Cryst.* B**38**, 225–231.

BALLANTINE, J. A., WILLIAMS, K. & BURKE, B. A. (1977). *Tetrahedron Lett.* pp. 1547–1550.

BANDURRAGA, M. M. & FENICAL, W. (1985). *Tetrahedron*, **41**, 1057–1065.

DICKINSON, C. & HOLDEN, J. R. (1978). *Acta Cryst.* B**34**, 2361–2364.

DUAX, W. L., GRIFFIN, J. F. & ROHRER, D. C. (1981). *J. Am. Chem. Soc.* **103**, 6705–6712.

DUAX, W. L. & NORTON, D. (1975). *Atlas of Steroid Structure*, Vol. I. New York: Plenum Press.

DUAX, W. L., WEEKS, C. M. & ROHRER, D. C. (1976). In *Topics in Stereochemistry*, edited by E. L. ELIEL & N. ALLINGER. Vol. 9, pp. 271–283. New York: John Wiley.

FENICAL, W. (1979). In *Marine Natural Products*, Vol. II, edited by P. J. SCHEUER. New York: Academic Press.

FOCES-FOCES, C., CANO, F. H. & GARCÍA-BLANCO, D. (1976). *Acta Cryst.* B**32**, 964–966.

LINDBERG, K. B. (1976). *Acta Cryst.* B**32**, 645–647.

MAIN, P., LESSINGER, L., WOOLFSON, M. M., GERMAIN, G. & DECLERCQ, J.-P. (1976). *MULTAN76. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

MOLDOWAN, J. M., TAN, W. L. & DJERASSI, C. (1975). *Steroids*, **26**, 107–128.

SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

TAKAGI, S. & JEFFREY, G. A. (1978). *Acta Cryst.* B**34**, 2006–2010.

THOMAS, R., SHOEMAKER, C. B. & ERIKS, K. (1966). *Acta Cryst.* **21**, 12–20.

TURSCH, B., HOOTELE, C., KAISIN, M., LOSMAN, D. & KARLSSON, R. (1976). *Steroids*, **27**, 137–142.

VISWAMITRA, M. A. & KANNAN, K. K. (1966). *Nature (London)*, **209**, 1016–1017.

WASYLYK, J. M., ALAM, M., MARTIN, G. E., WEINHEIMER, A. J., HOSSAIN, M. B. & VAN DER HELM, D. (1987). *J. Org. Chem.* In the press.

WEINHEIMER, A. J., CHANG, C. W. J. & MATSON, J. A. (1979). *Prog. Chem. Org. Nat. Prod.* **36**, 285–387.

Acta Cryst. (1987). C**43**, 2427–2429

Structure of 4-Isopropyl-1,6-dimethyl-7-phenylbicyclo[3.2.1]oct-6-en-8-one (Two Crystalline Forms)

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Abstract. $C_{19}H_{24}O$, $M_r = 268·4$, monoclinic (form I), $P2_1$, $a = 13·853$ (8), $b = 7·893$ (5), $c = 14·855$ (6) Å, $\beta = 95·91$ (3)°, $V = 1615·4$ (6·2) Å^3, $Z = 4$, $D_x = 1·10$ Mg m^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 0·48$ mm^{-1}, $F(000) = 584$, $T = 293$ K. Final $R = 0·091$ for 1546 observed reflections. $C_{19}H_{24}O$, $M_r = 268·4$, orthorhombic (form II), $Pna2_1$, $a = 17·565$ (18), $b = 11·707$ (14), $c = 7·806$ (13) Å, $V = 1605·2$ (6·2) Å^3, $Z = 4$, $D_x = 1·11$ Mg m^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 0·48$ mm^{-1}, $F(000) = 584$, $T = 293$ K. Final $R = 0·051$ for 890 observed reflections. The regiochemistry is established of the cyclopentene double bond with respect to the cyclohexane ring and the isopropyl group in the *exo* configuration with respect to the bicyclo[3.2.1] framework. The six-membered ring has a chair conformation. The five-membered ring exists in an envelope conformation with an angle of pucker in the range 42·5 (1·0)–42·9 (1·0)°.

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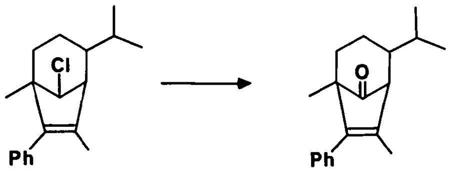
Introduction. During continuing studies into the Lewis-acid-catalyzed [3+2]cycloaddition of allyl halides and alkynes (Miller & Moore, 1980), we found that the reaction of geranyl chloride with 1-phenylpropyne in the presence of zinc chloride gave the unexpected cycloadduct (1).



(1) (2)

This bicyclic chloride was converted to the title compound (2) (Gray & Miller, 1987), the X-ray crystal structure of which was undertaken to establish the regiochemistry of the cyclopentene double bond with respect to the cyclohexane ring and the stereochemistry of the isopropyl group with respect to the bicyclo[3.2.1] framework.

Experimental. Colorless crystals were grown from petroleum ether (b.p. 333–353 K) and found to consist of two types. Preliminary studies showed that form I is monoclinic and II is orthorhombic, and that the cells have similar volumes but are not related by any transformation. Accordingly, the structures of both forms were determined. Data were collected photographically from cleaved fragments approximately 0·15 × 0·15 × 0·15 mm and corrected for Lorentz–polarization effects, absorption ignored. Equi-inclination multi-film Weissenberg exposures of reciprocal-lattice layers *h*0–7*l* and *hk*0–3 (form I) and *h*0–3*l* and *hk*0–7 (form II) were scanned by use of a microdensitometer (SERC Service, Daresbury Laboratory, England). The resolution attainable was limited in both cases by the virtual absence of reflections with $\theta > 50°$ (Cu radiation), up to this limit, *ca* 45% and 52% of reflections were above background for forms I and II respectively. Data reduction gave 1546 independent reflections for form I and 890 independent reflections for form II, with merging R values of 0·045 and 0·039 respectively. The structure was solved and refined using the *SHELX*76 program system (Sheldrick, 1976). The E maps generated by the *TANG* subprogram showed the majority of C and O atoms for both compounds, but only after the inclusion of unobservably weak reflections with $|F_o|$ set at $0{\cdot}2\,|F_o|_{\max}$ and (for form I) a number of strong low-angle reflections (which had been omitted from the data received because of streaking on film) with visually estimated intensities. All subsequent calculations used observed data only. The paucity of data for form I necessitated the retention of isotropic thermal parameters for all atoms. In the case of form II, isotropic refinement to $R = 0{\cdot}108$ (81 parameters) was followed by refinement to $R = 0{\cdot}078$ with anisotropic parameters for all C and O atoms (181 parameters), a decrease in R significant at the 99% confidence level. A number of peaks attributable to H atoms were subsequently located in difference maps for

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* ($Å^2 \times 10^3$) *with e.s.d.'s in parentheses* (*form* I)

	x	y	z	U_{iso}
O(1)	0·4506 (6)	0·0722 (16)	0·1122 (6)	76 (2)
C(1)	0·2853 (7)	0·1780 (18)	0·0988 (7)	48 (3)
C(2)	0·2735 (8)	0·3140 (19)	0·1708 (8)	58 (3)
C(3)	0·3058 (8)	0·4882 (18)	0·1432 (8)	61 (3)
C(4)	0·4062 (8)	0·4889 (19)	0·1077 (7)	55 (3)
C(5)	0·4091 (7)	0·3430 (17)	0·0375 (7)	48 (3)
C(6)	0·3182 (8)	0·3400 (20)	−0·0293 (8)	57 (3)
C(7)	0·2490 (7)	0·2470 (18)	0·0040 (7)	45 (3)
C(8)	0·3927 (7)	0·1823 (18)	0·0874 (7)	49 (3)
C(9)	0·2456 (9)	0·0089 (19)	0·1232 (9)	70 (4)
C(10)	0·4900 (8)	0·4797 (20)	0·1848 (8)	59 (3)
C(11)	0·5870 (9)	0·4507 (21)	0·1508 (9)	75 (4)
C(12)	0·4940 (10)	0·6383 (22)	0·2445 (10)	93 (5)
C(13)	0·3131 (9)	0·4461 (20)	−0·1117 (8)	70 (4)
C(14)	0·1489 (7)	0·2202 (17)	−0·0406 (7)	45 (3)
C(15)	0·0682 (8)	0·2635 (19)	0·0062 (8)	63 (3)
C(16)	−0·0231 (11)	0·2388 (22)	−0·0398 (10)	89 (4)
C(17)	−0·0378 (9)	0·1825 (20)	−0·1247 (8)	66 (3)
C(18)	0·0387 (8)	0·1428 (19)	−0·1701 (8)	61 (3)
C(19)	0·1328 (8)	0·1593 (18)	−0·1266 (8)	57 (3)
O(1′)	0·0151 (6)	0·4820 (17)	0·4478 (5)	68 (2)
C(1′)	0·1899 (7)	0·4866 (18)	0·4693 (7)	50 (3)
C(2′)	0·2275 (8)	0·6261 (18)	0·5388 (7)	54 (3)
C(3′)	0·2271 (7)	0·5682 (18)	0·6385 (7)	46 (3)
C(4′)	0·1337 (7)	0·4769 (17)	0·6559 (7)	42 (2)
C(5′)	0·1054 (6)	0·3497 (17)	0·5800 (6)	39 (2)
C(6′)	0·1903 (7)	0·2432 (17)	0·5609 (6)	39 (2)
C(7′)	0·2373 (7)	0·3152 (17)	0·4968 (6)	39 (2)
C(8′)	0·0928 (7)	0·4468 (18)	0·4934 (7)	49 (3)
C(9′)	0·1967 (9)	0·5474 (20)	0·3712 (8)	68 (3)
C(10′)	0·0530 (7)	0·6050 (18)	0·6719 (7)	53 (3)
C(11′)	−0·0469 (9)	0·5262 (20)	0·6665 (9)	72 (4)
C(12′)	0·0715 (11)	0·6956 (24)	0·7621 (10)	94 (5)
C(13′)	0·2169 (8)	0·0849 (18)	0·6137 (7)	56 (3)
C(14′)	0·3212 (7)	0·2466 (18)	0·4557 (7)	48 (3)
C(15′)	0·4039 (8)	0·3447 (22)	0·4490 (8)	69 (3)
C(16′)	0·4843 (11)	0·2753 (22)	0·4080 (9)	83 (4)
C(17′)	0·4781 (10)	0·1184 (21)	0·3732 (9)	78 (4)
C(18′)	0·3976 (10)	0·0228 (23)	0·3785 (9)	85 (4)
C(19′)	0·3209 (9)	0·0840 (20)	0·4183 (8)	65 (3)

Table 2. *Fractional atomic coordinates and equivalent isotropic thermal parameters* ($Å^2 \times 10^3$) *with e.s.d.'s in parentheses* (*form* II)

	x	y	z	U_{eq}*
O(1)	0·2575 (2)	−0·1685 (3)	0·3270 (12)	75 (1)
C(1)	0·2938 (3)	−0·0032 (4)	0·4997 (11)	46 (1)
C(2)	0·2206 (3)	0·0682 (5)	0·5428 (11)	57 (1)
C(3)	0·1987 (3)	0·1480 (5)	0·3976 (11)	61 (1)
C(4)	0·1974 (3)	0·0935 (5)	0·2200 (10)	52 (1)
C(5)	0·2716 (3)	0·0218 (5)	0·2010 (11)	53 (1)
C(6)	0·3407 (3)	0·0867 (4)	0·2545 (10)	45 (1)
C(7)	0·3547 (3)	0·0718 (4)	0·4210 (10)	44 (1)
C(8)	0·2714 (3)	−0·0678 (4)	0·3417 (12)	49 (1)
C(9)	0·3181 (4)	−0·0778 (5)	0·6505 (12)	71 (2)
C(10)	0·1254 (3)	0·0248 (6)	0·1808 (11)	65 (2)
C(11)	0·1287 (4)	−0·0304 (7)	0·0020 (12)	86 (2)
C(12)	0·0540 (3)	0·0960 (8)	0·1925 (15)	102 (3)
C(13)	0·3819 (4)	0·1622 (6)	0·1299 (11)	67 (2)
C(14)	0·4194 (3)	0·1191 (4)	0·5178 (10)	44 (1)
C(15)	0·4938 (3)	0·0962 (5)	0·4678 (10)	56 (1)
C(16)	0·5547 (3)	0·1407 (5)	0·5565 (11)	61 (2)
C(17)	0·5435 (3)	0·2102 (5)	0·6960 (12)	59 (1)
C(18)	0·4697 (3)	0·2339 (5)	0·7476 (11)	61 (1)
C(19)	0·4091 (3)	0·1902 (5)	0·6608 (11)	52 (1)

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

both forms, but as these were of similar intensity to the stronger 'noise' peaks the H atoms were included at calculated 'riding' positions in the last cycles. Full-matrix least squares refinement (on F) rapidly converged (maximum Δ/σ in last cycle was 0·082 for form I and 1·000 for form II) at $R = 0{\cdot}092$, $wR = 0{\cdot}109$ for form I, and at $R = 0{\cdot}051$, $wR = 0{\cdot}066$ for form II. The function minimized was $\sum w(|F_o| - |F_c|)^2$. The weighting scheme used was of the type $w = k[\sigma^2(F) + gF^2]^{-1}$ with $\sigma(F)$ set at unity as recommended for photographic data (Sheldrick, 1976); final values of k, g were 5·14, 0·00022 for form I, and 0·477, 0·00509 for form II. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974). The final difference maps were flat to within $\pm 0{\cdot}2$ e Å^{-3} (form I) and $\pm 0{\cdot}4$ e Å^{-3} (form II) and showed no evidence of disorder or of the presence of lattice solvent molecules.

Discussion. Atomic coordinates and equivalent isotropic thermal parameters for the two crystal forms are given in Tables 1 and 2.* An *ORTEP*II (Johnson, 1976) view of the molecule with atom numbering is shown in Fig. 1. The two independent molecules in form I have the same chirality and are in general very similar to one another and to the molecule in form II. The C(4) isopropyl group is in the *exo* configuration with respect to the bicyclo[3.2.1] framework confirming our previously postulated steric-approach-control argument in the [3+2]cycloaddition reaction (Gray & Miller, 1987). The phenyl ring is on the vinyl C atom adjacent to the quaternary bridgehead C atom indicating that the regiochemistry of the [3+2]cycloaddition reaction giving the bicyclo[3.2.1] structure is the same as that observed for the formation of simple cyclopentenes (Miller & Moore, 1980). The six-membered ring has a chair conformation. As expected, the C(2)—C(1)—C(8) and C(4)—C(5)—C(8) angles observed in the title compound are slightly larger than the corresponding angles in 4-isopropyl-6-methoxymethyl-1-methyl-7-phenylthiobicyclo[3.2.1]oct-6-en-8-ol (Gray, Miller & Weakley, 1987) owing to an increased flattening at this end of the cyclohexane ring by the sp^2-hybridized bridge carbonyl. The cyclopentene ring adopts an envelope conformation. The angle of pucker between the planes defined by atoms [C(1), C(5), C(7), C(6)] and [C(1), C(5), C(8)] is 42·9 (1·0) and 42·5 (1·0)° for the molecules in form I, and 42·7 (1·0)° in form II. The angle between atoms C(1), C(8) and C(5) forming the ketone bridge is 106·0 (9) and 107·0 (8)° for the molecules in form I and 104·2 (4)° in form II. These values are similar to values of 44·1 and 104·2° observed in 2,3-dihydroxy-1-methylbicyclo[3.2.1]-octan-8-one (Gillon, Ovadia, Kapon & Bien, 1982), and 41·0 and 106·6° in 2-(2,6-dimethoxyphenyl)-2,5-dimethylbicyclo[3.2.1]octane-6,8-dione (Murthy, Venkatesan, Reddy & Kasturi, 1982).

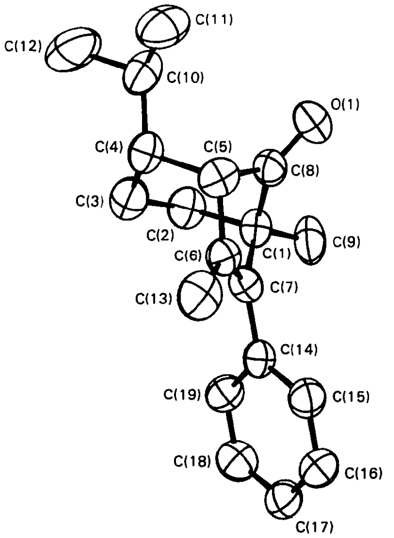


Fig. 1. *ORTEP*II diagram (Johnson, 1976) for the structure of crystal form II, illustrating the numbering scheme. Non-H-atom ellipsoids at 50% probability level.

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References

Gillon, A., Ovadia, D., Kapon, M. & Bien, S. (1982). *Tetrahedron*, **38**, 1477–1484.

Gray, B. D. & Miller, J. A. (1987). *J. Chem. Res.* (*S*), pp. 206–207.

Gray, B. D., Miller, J. A. & Weakley, T. J. R. (1987). *Acta Cryst.* C**43**, 1434–1435.

International Tables for X-ray Crystallography (1974). Vol. IV, pp. 99, 149. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

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

Miller, J. A. & Moore, M. (1980). *Tetrahedron Lett.* **21**, 577–580.

Murthy, P. S., Venkatesan, K., Reddy, S. M. & Kasturi, T. R. (1982). *Acta Cryst.* B**38**, 2055–2057.

Sheldrick, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

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* Lists of structure factors, bond lengths and angles, H-atom coordinates and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44318 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.