bonds in ACC and ACD. A measure of the strength of the N—H···X hydrogen bonds (X=S,O) discussed here is the shortening of the N···X distance below the sum of the van der Waals radii involved (Schuster, Zundel & Sandorfy, 1976). The N—H···O hydrogen bond in the crystal structure of ACC has an N···O distance of 2·668 (4) Å which is 0·26 Å shorter than the sum of the van der Waals radii [2·93 Å; van der Waals radii given by Kitaigorodskii (1971) were used]. The N—H···S hydrogen bond in the crystal structure of ACD with an N···S distance of 2·998 (3) Å is 0·6 Å shorter than the sum of the van der Waals radii (3·59 Å). Furthermore, in N—H···S the H atom is closer to the N···X connection line than in the case of N—H···O. Both suggest the surprising feature that a hydrogen bond of type N—H···S is stronger than that of type N—H···O. The ability of thiocarboxy S to form such an unusually strong hydrogen bond is in agreement with IR and NMR measurements. Correlation between the different hydrogen bonds and the reaction behaviour of ACC and ACD is possible.

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The Structure of 1-(Tetracyclo[5.4.0.0^{3,8}.0^{4,8}]undec-5-en-9-yl)ethanol, $C_{13}H_{18}O$

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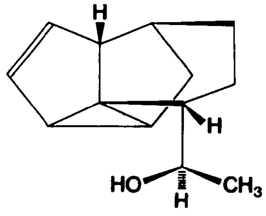
Abstract. $M_r = 190·3$, rhombohedral, $R\bar{3}$, $a = 26·371$ (3), $c = 8·374$ (2) Å (hexagonal axes, obverse setting), $U = 5043$ (2) Å^3, $Z = 18$, $D_m = 1·13$ (flotation), $D_x = 1·128$ (1) g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0·75$ cm^{-1}, $F(000) = 1872$, $T = 295$ K, $R = 0·038$, $R_w = 0·033$ for 1160 counter reflections. The outstanding feature in this highly strained molecule is a C—C—C bond angle of 140·2 (2)°.

Introduction. The *meta*-photocycloaddition of olefins to arenes first reported by Wilzbach & Kaplan (1966) and by Bryce-Smith, Gilbert & Orger (1966) finds extensive application in five-membered ring synthesis. The intramolecular version of this reaction in bichromophoric molecules discovered by Morrison & Ferree (1969) serves to provide cycloadducts that could be used to synthesize a variety of natural products. The title compound (I) appeared as one of several photoproducts from photolysis of *threo*-3-phenyl-6-hepten-2-ol in spectroscopic-grade *n*-hexane with a high-pressure Hg lamp.



(I)

Experimental. Single crystals grown by slow evaporation of a solution in hexane/dichloromethane/*tert*-butyl methyl ether mixture were provided by Dr R. Astik. Cell parameters obtained from diffractometer settings. Crystals showed a tendency to decay rapidly and four had to be used to collect the full data set; $2\theta_{max} = 50°$, ω scans of variable scan rate, Nonius CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$ radiation. Three standard reflections monitored every hour and measurements with a crystal stopped when the intensity of any of them dropped to below 85% of the starting value; decay of the intensity check

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reflections is a linear function of time and is equal to within ~1% for all three standards. Data from the four crystals scaled together through the standard reflections and corrected for decay but not for absorption. 2013 unique reflections measured, 1635 non-zero intensities, 1160 with $I \geq 2{\cdot}5\sigma(I)$ used for structure solution and refinement. Direct methods [*SHELX*76 (Sheldrick, 1976)] with user-specified starting reflections. Positions and isotropic temperature factors of the non-H atoms refined to $R = 0{\cdot}09$ and H atoms located in two successive difference Fourier syntheses. Final refinement on F of all atoms with non-H treated anisotropically and H isotropic led to $R = 3{\cdot}8\%$, $R_w = 3{\cdot}3\%$, with $w = (\sigma^2 + 10^{-5}F^2)^{-1}$, $(\Delta/\sigma)_{\max} = 0{\cdot}038$, final $\Delta\rho$ excursions $\pm 0{\cdot}15$ e Å^{-3}. Complex neutral-atom scattering factors (Cromer & Mann, 1968; Cromer & Liberman, 1970) used for all atoms; diagrams prepared with *ORTEP* (Johnson, 1971).

Discussion. Final atomic parameters are listed in Table 1[*] and distances, angles and torsion angles in Table 2; C—H bond lengths range from 0·91 (3) to 1·02 (2) Å with an average value of 0·98 (3) Å. A view of the molecule is shown in Fig. 1. The molecule has high internal strain at C(1) which is shared by one three-, one six- and two five-membered rings, and to a lesser extent at C(10), C(5), C(6) and C(2). The strain is manifest through the extreme widening of the *exo* angle C(2)—C(1)—C(9) to 140·2 (2)° and of C(2)—C(10)—C(11) to 125·0 (2)°. C(1) is displaced only 0·109 (3) Å towards C(10) from the plane through C(2), C(5) and C(9).

The cyclopentene ring C(1)—C(2)—C(3)—C(4)—C(5) adopts a flattened envelope conformation while the cyclopentane ring C(1)—C(5)—C(6)—C(11)—C(10) is severely puckered into a strongly bent half-chair, the puckering amplitudes being 0·118 (6) and 0·514 (6) Å respectively. The least-squares planes through these rings are inclined 93·0 (2)° to each other and 103·6 (3) and 122·5 (3)° respectively to the cyclopropyl ring. The deviant atom from the best four-atom plane of the first ring is C(1) and from that of the second is C(5). The six-membered ring C(1)—C(9)—C(8)—C(7)—C(6)—C(5) adopts a distorted chair form and its relative orientation to the cyclopentane ring leads to a twisted-boat conformation for the seven-membered ring system C(1)—C(9)—C(8)—C(7)—C(6)—C(11)—C(10).

In the skeleton comprising the cyclopropyl ring and two fused five-membered rings, the angle C(4)—C(5)—C(6) [115·0 (2)°] is considerably larger and C(1)—C(5)—C(6) [98·1 (2)°] slightly smaller than those

Table 1. *Fractional positional* (×10^4) *and isotropic thermal* (×10^3) *parameters with e.s.d.'s in parentheses*

For non-hydrogen atoms, $U_{\rm eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	$U_{\rm eq}/U$ (Å^2)
C(1)	3947 (1)	8912 (1)	2054 (2)	43 (1)
C(2)	4146 (1)	9009 (1)	347 (3)	61 (2)
C(3)	3779 (1)	9205 (1)	−489 (4)	80 (2)
C(4)	3463 (1)	9311 (1)	509 (4)	73 (2)
C(5)	3556 (1)	9186 (1)	2193 (3)	54 (2)
C(6)	3974 (1)	9728 (1)	3179 (3)	60 (2)
C(7)	4014 (1)	9488 (1)	4822 (3)	66 (2)
C(8)	4175 (1)	9000 (1)	4835 (3)	59 (2)
C(9)	3907 (1)	8544 (1)	3473 (3)	45 (1)
C(10)	4538 (1)	9426 (1)	1656 (3)	55 (2)
C(11)	4538 (1)	9979 (1)	2183 (3)	65 (2)
C(12)	4217 (1)	8192 (1)	3300 (3)	51 (2)
C(13)	4182 (2)	7847 (2)	4789 (4)	91 (3)
O(14)	3952 (1)	7811 (1)	1974 (2)	63 (1)
H(C2)	4290 (8)	8786 (8)	−180 (22)	55 (7)
H(C3)	3795 (11)	9272 (11)	−1562 (31)	104 (11)
H(C4)	3209 (10)	9461 (10)	299 (25)	82 (9)
H(C5)	3190 (8)	8940 (8)	2794 (20)	47 (6)
H(C6)	3849 (8)	10017 (9)	3345 (23)	65 (7)
H1(C7)	3622 (10)	9323 (9)	5325 (24)	71 (8)
H2(C7)	4315 (9)	9816 (9)	5489 (24)	71 (7)
H1(C8)	4620 (9)	9193 (9)	4776 (22)	70 (7)
H2(C8)	4055 (9)	8790 (9)	5892 (25)	69 (8)
H(C9)	3490 (8)	8263 (7)	3700 (19)	42 (5)
H(C10)	4886 (9)	9393 (8)	1939 (22)	63 (7)
H1(C11)	4900 (9)	10246 (9)	2821 (23)	74 (8)
H2(C11)	4523 (9)	10215 (10)	1270 (25)	79 (8)
H(C12)	4626 (8)	8456 (8)	3021 (21)	45 (6)
H1(C13)	4324 (10)	7585 (11)	4588 (27)	92 (9)
H2(C13)	4403 (12)	8123 (12)	5686 (35)	119 (13)
H3(C13)	3769 (13)	7594 (13)	5062 (34)	126 (14)
H(O14)	4093 (10)	7610 (10)	1787 (28)	75 (10)

Table 2. *Bond lengths* (Å), *angles* (°) *and torsion angles* (°) *involving non-hydrogen atoms, e.s.d.'s in parentheses*

C(1)—C(2)	1·500 (3)	C(6)—C(7)	1·539 (3)
C(1)—C(5)	1·531 (3)	C(6)—C(11)	1·535 (3)
C(1)—C(9)	1·504 (3)	C(7)—C(8)	1·545 (3)
C(1)—C(10)	1·506 (3)	C(8)—C(9)	1·548 (3)
C(2)—C(3)	1·483 (4)	C(9)—C(12)	1·520 (3)
C(2)—C(10)	1·531 (3)	C(10)—C(11)	1·524 (3)
C(3)—C(4)	1·307 (4)	C(12)—C(13)	1·518 (4)
C(4)—C(5)	1·497 (3)	C(12)—O(14)	1·424 (3)
C(5)—C(6)	1·536 (3)		
C(2)—C(1)—C(5)	104·7 (2)	C(5)—C(6)—C(11)	101·5 (2)
C(2)—C(1)—C(9)	140·2 (2)	C(7)—C(6)—C(11)	114·4 (2)
C(2)—C(1)—C(10)	61·2 (1)	C(6)—C(7)—C(8)	116·8 (2)
C(5)—C(1)—C(9)	113·4 (2)	C(7)—C(8)—C(9)	115·7 (2)
C(5)—C(1)—C(10)	103·2 (2)	C(1)—C(9)—C(8)	102·9 (2)
C(9)—C(1)—C(10)	117·6 (2)	C(1)—C(9)—C(12)	115·6 (2)
C(1)—C(2)—C(3)	105·9 (2)	C(8)—C(9)—C(12)	111·6 (2)
C(1)—C(2)—C(10)	59·6 (1)	C(1)—C(10)—C(2)	59·2 (1)
C(3)—C(2)—C(10)	114·2 (2)	C(1)—C(10)—C(11)	107·6 (2)
C(2)—C(3)—C(4)	111·8 (3)	C(2)—C(10)—C(11)	125·0 (2)
C(3)—C(4)—C(5)	111·2 (3)	C(6)—C(11)—C(10)	102·0 (2)
C(1)—C(5)—C(4)	104·8 (2)	C(9)—C(12)—C(13)	113·4 (2)
C(1)—C(5)—C(6)	98·1 (2)	C(9)—C(12)—O(14)	106·4 (2)
C(4)—C(5)—C(6)	115·0 (2)	C(13)—C(12)—O(14)	110·8 (2)
C(5)—C(6)—C(7)	105·3 (2)		
C(1)—C(2)—C(3)—C(4)	8·8 (2)	C(6)—C(7)—C(8)—C(9)	−37·9 (3)
C(2)—C(3)—C(4)—C(5)	−1·6 (2)	C(7)—C(8)—C(9)—C(1)	39·2 (3)
C(3)—C(4)—C(5)—C(1)	−6·1 (2)	C(8)—C(9)—C(1)—C(5)	−66·4 (2)
C(4)—C(5)—C(1)—C(2)	10·9 (2)	C(9)—C(1)—C(5)—C(6)	84·1 (2)
C(5)—C(1)—C(2)—C(3)	−11·8 (2)	C(8)—C(7)—C(6)—C(11)	−57·7 (2)
C(1)—C(5)—C(6)—C(11)	51·7 (2)	C(7)—C(6)—C(11)—C(10)	73·5 (2)
C(5)—C(6)—C(11)—C(10)	−39·1 (3)	C(6)—C(11)—C(10)—C(1)	11·2 (3)
C(6)—C(11)—C(10)—C(1)	11·2 (3)	C(11)—C(10)—C(1)—C(9)	−104·8 (3)
C(11)—C(10)—C(1)—C(5)	21·0 (2)	C(10)—C(1)—C(9)—C(8)	54·2 (3)
C(10)—C(1)—C(5)—C(6)	−44·2 (2)	C(1)—C(9)—C(12)—C(13)	177·8 (2)
C(1)—C(5)—C(6)—C(7)	−67·7 (2)	C(1)—C(9)—C(12)—O(14)	−60·1 (2)
C(5)—C(6)—C(7)—C(8)	52·7 (3)		

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[*] Lists of structure factors, anisotropic thermal parameters and least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38900 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

found in other similar structures, where they range from 93·1 (2) to 107·9 (3)° and 102·3 (5) to 102·9 (5)° respectively (Lindgren, 1978; Becker, Ruge, Skelton & White, 1979; Christoph & Beno, 1978; Bartlett, Kimura, Nakayama & Watson, 1979; Miller, Grohmann, Dannenberg & Todaro, 1981). Further the cyclopropane bond lengths in the present study are inequivalent and the ring is more scalene than in the first two references quoted above but far less so than in the next three that contain two cyclopentene rings.

A stereoview of the molecular packing is shown in Fig. 2. The molecules are linked together by O—H···O hydrogen bonds [O—H = 0·80 (2), O···O = 2·667 (5) Å, ∠O—H···O = 176 (3)°] across the $\bar{3}$ axes, the six-membered ring of such linkages thus exhibiting a perfect chair configuration. Other than a separation of 2·30 (6) Å between symmetry-related atoms H(O14), the shortest H···H intermolecular contact is 2·44 (2) Å.

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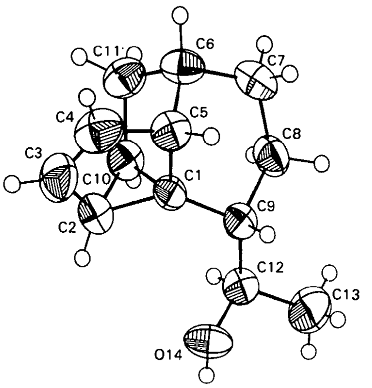

Fig. 1. View of the molecule showing thermal ellipsoids of 50% probability. H atoms are depicted as 0·1 Å radius spheres.

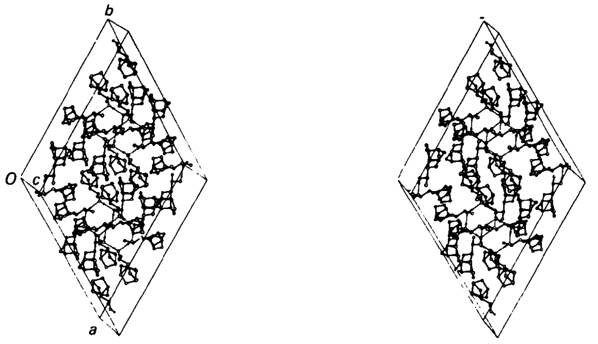

Fig. 2. Molecular packing. Hydrogen bonds are shown by thin lines and H atoms except H(O14) are omitted.

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Structure of Azomycin (2-Nitroimidazole), $C_3H_3N_3O_2$, at 105 K

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Abstract. $M_r = 113{\cdot}08$, monoclinic, $P2_1/c$, $a = 7{\cdot}319\,(4)$, $b = 9{\cdot}802\,(3)$, $c = 6{\cdot}754\,(2)$ Å, $\beta = 115{\cdot}70\,(4)°$, $V = 436{\cdot}6\,(4)$ Å^3 at 105 K, $Z = 4$, $D_x = 1{\cdot}720\,(1)$, $D_m(293\text{ K}) = 1{\cdot}646\,(5)$ Mg m^{-3}, $\lambda(\text{Mo }K\alpha) = 0{\cdot}71069$ Å, $\mu = 0{\cdot}137$ mm^{-1}, $F(000) = 232$. Final $R = 0{\cdot}040$ for 1028 unique observed reflections. The molecules are planar and connected in the **b** direction by NH···N hydrogen bonds.

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