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Crystal structure of (7a′*SR*)-7a′-prop-2-ynyl-1′,2′,4′,6′,7′,7a′-hexahydrospiro[1,3-dioxolan-2,5′-indene], $C_{14}H_{18}O_2$

N. T. Tzvetkov[I,II], B. Neumann[III], H.-G. Stammler[III] and J. Mattay*,[I]

[I] Universität Bielefeld, Fakultät für Chemie, Organische Chemie I, Postfach 100131, 33501 Bielefeld, Germany
[II] Universität Bonn, Pharmazeutisches Institut, An der Immenburg 4, 53121 Bonn, Germany
[III] Universität Bielefeld, Fakultät für Chemie, Abteilung für Röntgenstrukturanalyse AC III, Universitätsstr. 25, 33615 Bielefeld, Germany

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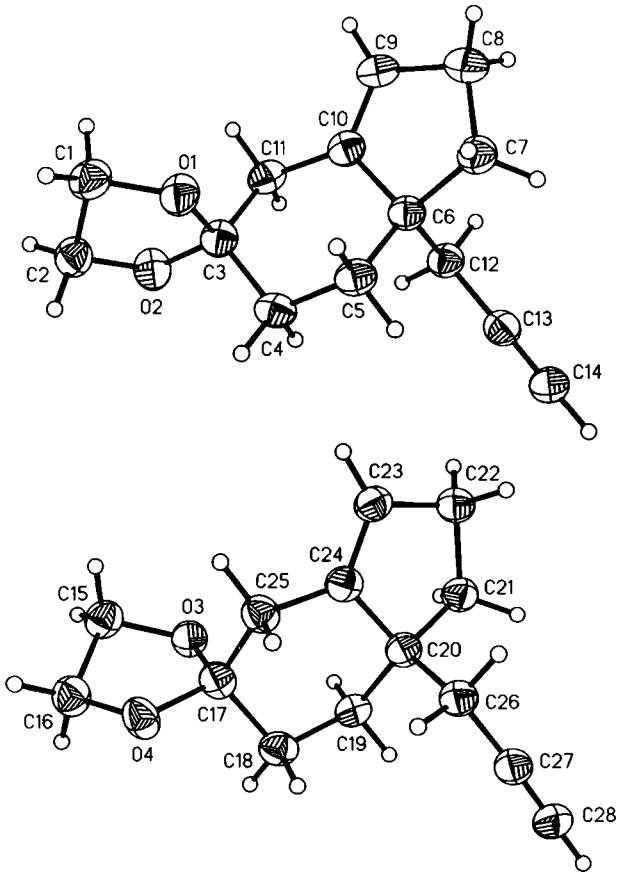

Abstract

$C_{14}H_{18}O_2$, monoclinic, $P12_1/c1$ (no. 14), a = 15.399(1) Å, b = 11.646(1) Å, c = 14.849(1) Å, β = 117.659(4)°, V = 2358.7 Å^3, Z = 8, $R_{gt}(F)$ = 0.068, $wR_{ref}(F^2)$ = 0.206, T = 100 K.

Source of material

The title compound has been obtained by ketalization of (7a*SR*)-7a-prop-2-ynyl-1,2,3,6,7,7a-hexahydro-5*H*-inden-5-one with freshly distilled ethylene glycol in dry benzene under reflux over 6 h and in the presence of *p*-toluenesulfonic acid monohydrate as an acid catalyst [1]. Purification of the crude product by column chromatography (cyclohexane/ethyl acetate, 80:20) and recrystallization from chloroform and petroleum ether (1:2, *v*/*v*) gave the ketal product as colorless crystals suitable for X-ray structure analysis (m.p. 353-354 K, R_f = 0.49).

* Correspondence author (e-mail: oc1jm@uni-bielefeld.de)

Discussion

The title compound was prepared as part of our study of diastereoselective cyclopropanization of centrosymmetric substituted indenones [2]. We introduced a series of new tricyclic α-cyclopropyl indenone structures [3] as suitable intermediates in propellane synthesis.

The racemic compound crystallizes centrosymmetrically and the asymmetric unit contains two independent molecules, which have no significant differences. The enantiomeric molecules show an antiparallel orientation. The significant shorter C9—C10 (1.328(5) Å) and C23—C24 (1.328(5) Å) bonds indicate the localization of the double bond of the five-membered ring. The simultaneous migration of the double bond during ketalization has also been observed in other systems and is best known phenomenon in the steroidal synthesis [4,5]. The crystal packing is conditioned by π-π interactions of the propynyl substituents d(C13···C27) = 5.042 Å and additionally stabilized by weak intermolecular C–H···O hydrogen bonds between identical enantiomeric molecules. The shortest intermolecular distances are d(O2···H4A–C4) = 2.501 Å, d(O3···H23–C23) = 3.509 Å and d(O1···H9–C9) = 3.522 Å. The five-membered cyclopentane ring of the tricycles has a twist conformation whereas the six-membered cyclohexane ring has a chair conformation.

Table 1. Data collection and handling.

Crystal:	colorless fragment, size 0.15 × 0.30 × 0.30 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	0.80 cm^{-1}
Diffractometer, scan mode:	Nonius KappaCCD, φ/ω
$2\theta_{max}$:	50°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	19404, 4147
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 3094
$N(param)_{refined}$:	290
Programs:	SHELXS-97 [6], SHELXL-97 [7], SHELXTL-plus [8]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(1A)	4*e*	0.1143	0.1460	−0.0488	0.052
H(1B)	4*e*	0.2224	0.1592	0.0463	0.052
H(2A)	4*e*	0.2218	0.3551	0.0290	0.048
H(2B)	4*e*	0.1632	0.3168	−0.0886	0.048
H(4A)	4*e*	0.0209	0.4527	0.0998	0.041
H(4B)	4*e*	0.1309	0.4066	0.1638	0.041
H(5A)	4*e*	0.0413	0.3718	0.2548	0.042
H(5B)	4*e*	0.0751	0.2524	0.2276	0.042

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(7A)	4e	−0.0422	0.1516	0.2553	0.044
H(7B)	4e	−0.1381	0.2243	0.2360	0.044
H(8A)	4e	−0.1509	0.0208	0.1494	0.048
H(8B)	4e	−0.2377	0.1145	0.1007	0.048
H(9)	4e	−0.1605	0.0677	−0.0181	0.043
H(11A)	4e	−0.1000	0.3313	−0.0607	0.042
H(11B)	4e	−0.0613	0.2072	−0.0722	0.042
H(12A)	4e	−0.1381	0.4328	0.0649	0.042
H(12B)	4e	−0.2153	0.3560	0.0821	0.042
H(14)	4e	−0.1005	0.5509	0.3364	0.047
H(15A)	4e	0.2729	0.1625	0.3254	0.046
H(15B)	4e	0.3837	0.1590	0.3405	0.046
H(16A)	4e	0.3285	0.3296	0.2541	0.048
H(16B)	4e	0.2651	0.3593	0.3122	0.048

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(18A)	4e	0.3614	0.4088	0.5455	0.042
H(18B)	4e	0.4708	0.4556	0.5846	0.042
H(19A)	4e	0.4202	0.2501	0.6569	0.041
H(19B)	4e	0.4584	0.3662	0.7211	0.041
H(21A)	4e	0.6362	0.2110	0.8612	0.042
H(21B)	4e	0.5387	0.1411	0.7871	0.042
H(22A)	4e	0.7314	0.1083	0.8110	0.045
H(22B)	4e	0.6454	0.0139	0.7771	0.045
H(23)	4e	0.6452	0.0683	0.6157	0.042
H(25A)	4e	0.5472	0.2185	0.4757	0.041
H(25B)	4e	0.5875	0.3399	0.5300	0.041
H(26A)	4e	0.7115	0.3469	0.7845	0.041
H(26B)	4e	0.6350	0.4289	0.6974	0.041
H(28)	4e	0.6059	0.5420	0.9385	0.049

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(1)	4e	0.1142(2)	0.2115(2)	0.0765(2)	0.044(1)	0.031(1)	0.047(2)	0.010(1)	0.025(1)	0.009(1)
O(2)	4e	0.0755(2)	0.3672(2)	−0.0296(2)	0.043(2)	0.035(1)	0.048(2)	0.010(1)	0.025(1)	0.014(1)
C(1)	4e	0.1566(3)	0.1946(3)	0.0101(3)	0.054(2)	0.033(2)	0.050(2)	0.004(2)	0.029(2)	0.002(2)
C(2)	4e	0.1625(3)	0.3156(3)	−0.0223(3)	0.038(2)	0.036(2)	0.047(2)	0.005(2)	0.022(2)	0.003(2)
C(3)	4e	0.0483(3)	0.3078(3)	0.0379(3)	0.040(2)	0.026(2)	0.038(2)	0.008(1)	0.020(2)	0.009(2)
C(4)	4e	0.0614(3)	0.3826(3)	0.1259(3)	0.030(2)	0.026(2)	0.040(2)	0.002(1)	0.010(2)	0.003(2)
C(5)	4e	0.0320(3)	0.3199(3)	0.1982(3)	0.035(2)	0.031(2)	0.035(2)	0.002(1)	0.012(2)	−0.001(2)
C(6)	4e	−0.0759(2)	0.2797(3)	0.1433(3)	0.033(2)	0.027(2)	0.034(2)	0.002(1)	0.014(2)	0.002(2)
C(7)	4e	−0.1022(3)	0.1886(3)	0.2026(3)	0.040(2)	0.032(2)	0.039(2)	0.003(2)	0.019(2)	0.001(2)
C(8)	4e	−0.1673(3)	0.1000(3)	0.1227(3)	0.040(2)	0.030(2)	0.045(2)	−0.001(2)	0.015(2)	0.001(2)
C(9)	4e	−0.1429(3)	0.1193(3)	0.0372(3)	0.037(2)	0.027(2)	0.035(2)	0.002(1)	0.010(2)	−0.003(2)
C(10)	4e	−0.0939(2)	0.2164(3)	0.0470(3)	0.032(2)	0.030(2)	0.033(2)	0.005(1)	0.012(2)	0.002(2)
C(11)	4e	−0.0576(3)	0.2662(3)	−0.0225(3)	0.044(2)	0.029(2)	0.030(2)	0.004(2)	0.015(2)	0.000(2)
C(12)	4e	−0.1468(3)	0.3842(3)	0.1148(3)	0.036(2)	0.030(2)	0.038(2)	0.003(2)	0.017(2)	0.001(2)
C(13)	4e	−0.1301(3)	0.4537(3)	0.2033(3)	0.034(2)	0.030(2)	0.045(2)	0.002(1)	0.020(2)	0.002(2)
C(14)	4e	−0.1137(3)	0.5077(3)	0.2772(3)	0.045(2)	0.030(2)	0.044(2)	−0.001(2)	0.023(2)	−0.002(2)
O(3)	4e	0.3740(2)	0.2187(2)	0.4634(2)	0.038(1)	0.030(1)	0.036(1)	−0.005(1)	0.015(1)	0.001(1)
O(4)	4e	0.4099(2)	0.3802(2)	0.3985(2)	0.038(1)	0.033(1)	0.036(1)	−0.005(1)	0.009(1)	0.006(1)
C(15)	4e	0.3369(3)	0.2025(3)	0.3559(3)	0.041(2)	0.034(2)	0.040(2)	−0.006(2)	0.018(2)	−0.004(2)
C(16)	4e	0.3270(3)	0.3248(3)	0.3199(3)	0.039(2)	0.038(2)	0.037(2)	−0.003(2)	0.013(2)	−0.001(2)
C(17)	4e	0.4401(2)	0.3147(3)	0.4897(3)	0.032(2)	0.026(2)	0.036(2)	−0.006(1)	0.012(2)	0.002(2)
C(18)	4e	0.4306(3)	0.3852(3)	0.5708(3)	0.031(2)	0.028(2)	0.044(2)	−0.002(1)	0.016(2)	−0.001(2)
C(19)	4e	0.4639(3)	0.3171(3)	0.6696(3)	0.037(2)	0.029(2)	0.037(2)	−0.000(2)	0.018(2)	−0.003(2)
C(20)	4e	0.5700(2)	0.2755(3)	0.7112(3)	0.034(2)	0.027(2)	0.035(2)	−0.003(1)	0.013(2)	−0.001(2)
C(21)	4e	0.5981(3)	0.1793(3)	0.7918(3)	0.040(2)	0.029(2)	0.036(2)	−0.000(2)	0.017(2)	0.001(2)
C(22)	4e	0.6606(3)	0.0942(3)	0.7675(3)	0.042(2)	0.028(2)	0.040(2)	0.002(2)	0.016(2)	0.001(2)
C(23)	4e	0.6314(3)	0.1181(3)	0.6581(3)	0.035(2)	0.032(2)	0.037(2)	−0.001(2)	0.017(2)	−0.005(2)
C(24)	4e	0.5840(2)	0.2172(3)	0.6273(3)	0.028(2)	0.029(2)	0.038(2)	−0.003(1)	0.013(2)	−0.002(2)
C(25)	4e	0.5455(2)	0.2736(3)	0.5256(3)	0.032(2)	0.031(2)	0.036(2)	−0.001(1)	0.013(2)	0.002(2)
C(26)	4e	0.6439(3)	0.3775(3)	0.7541(3)	0.037(2)	0.028(2)	0.037(2)	−0.000(2)	0.016(2)	0.000(2)
C(27)	4e	0.6316(3)	0.4444(3)	0.8312(3)	0.039(2)	0.026(2)	0.039(2)	−0.003(2)	0.013(2)	0.002(2)
C(28)	4e	0.6173(3)	0.4987(3)	0.8908(3)	0.049(2)	0.028(2)	0.040(2)	0.000(2)	0.017(2)	−0.002(2)

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