

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *DREADD* (Blessing, 1989). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *SHELXL93*, local programs.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1357). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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(+)-(4b*R*,8b*R*,8c*R*,8d*R*)-Tetrahydrodibenzo-[*a,f*]cyclopropano[*cd*]pentalene-8b,8c-bis(di-phenylphosphine)

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Abstract

The title molecule, $C_{40}H_{30}P_2$, is a dibenzosemibulvalene, derived from the enantioselective photolysis of a dibenzobarrelene derivative, and its absolute configuration has been established: it contains one three-membered, two five-membered and two six-membered rings, and has normal geometry and dimensions.

Comment

The title compound (I) was studied in order to determine the absolute configuration of the products of enantioselective photolysis, and to assist in structural/photochemical correlations (Fu, Liu, Scheffer & Trotter, 1993). The molecule (Fig. 1) has a dibenzosemibulvalene ring structure with one three-membered, two five-membered and two six-membered rings. Its molecular geometry and dimensions (Table 2) are similar to those in related compounds.

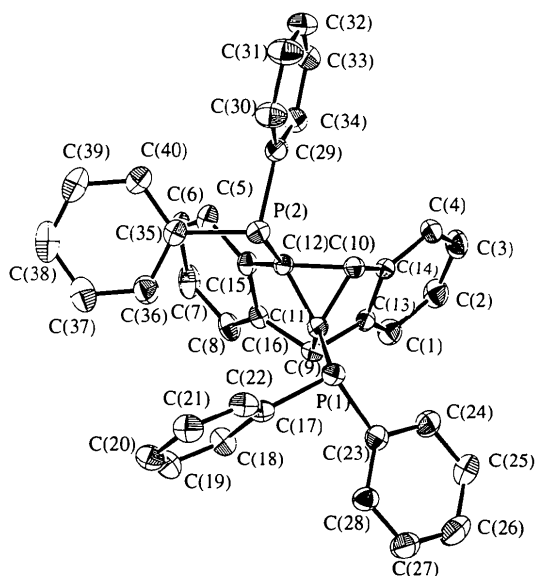
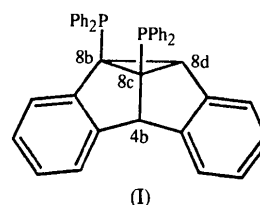


Fig. 1. View of the molecule (30% ellipsoids; crystallographic numbering system based on the dibenzobarrelene precursor).

Experimental

The compound was obtained by reduction of the phosphine oxide product from the photolysis of a dibenzobarrelene-bis(phosphine oxide) (Fu, Liu, Scheffer & Trotter, 1993). The photolysis was performed on a chiral single crystal, yielding a high enantiomeric excess of photoproduct, which was then reduced to an enantiomerically pure sample of the title compound, which has positive optical rotation (Na-D wavelength).

Crystal data

$C_{40}H_{30}P_2$
 $M_r = 572.62$

Cu $K\alpha$ radiation
 $\lambda = 1.5418 \text{ \AA}$

Orthorhombic	Cell parameters from 24 reflections
$P2_12_12_1$	$\theta = 25.2\text{--}39.3^\circ$
$a = 17.381(4) \text{ \AA}$	$\mu = 1.48 \text{ mm}^{-1}$
$b = 18.414(3) \text{ \AA}$	$T = 294 \text{ K}$
$c = 9.591(2) \text{ \AA}$	Needle
$V = 3070(1) \text{ \AA}^3$	$0.30 \times 0.10 \times 0.10 \text{ mm}$
$Z = 4$	Colorless
$D_x = 1.239 \text{ Mg m}^{-3}$	
D_m not measured	

Data collection

Rigaku AFC-6S diffractometer	2878 observed reflections
ω -2 θ scans	$[I > 3.00\sigma(I)]$
Absorption correction:	$\theta_{\max} = 77.59^\circ$
ψ scans (North, Phillips & Mathews, 1968)	$h = 0 \rightarrow 22$
$T_{\min} = 0.896$, $T_{\max} = 1.000$	$k = 0 \rightarrow 23$
3535 measured reflections	$l = 0 \rightarrow 11$
3535 independent reflections	3 standard reflections monitored every 500 reflections
	intensity decay: 0.6%

Refinement

Refinement on F	$\Delta\rho_{\max} = 0.29 \text{ e \AA}^{-3}$
$R = 0.031$	$\Delta\rho_{\min} = -0.15 \text{ e \AA}^{-3}$
$wR = 0.033$	Extinction correction: Zachariasen (1967)
$S = 1.90$	Extinction coefficient: 0.0000034 (1)
2878 reflections	Atomic scattering factors from <i>International Tables for Crystallography</i> (1992), Vol. C, Tables 4.2.6.8, 6.1.1.1 and 6.1.1.2)
500 parameters	
All H-atom parameters refined	
$w = 1/[\sigma^2(F_o) + 0.00001 F_o ^2]$	
$(\Delta/\sigma)_{\max} = 0.0004$	

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)
$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	U_{eq}
P(1)	0.81384 (5)	0.40118 (4)	-0.01480 (8)	0.0427 (2)
P(2)	0.74782 (4)	0.22411 (4)	0.02457 (8)	0.0412 (2)
C(1)	1.0095 (2)	0.3571 (2)	0.3785 (4)	0.0487 (9)
C(2)	1.0792 (2)	0.3204 (2)	0.3697 (4)	0.057 (1)
C(3)	1.0902 (2)	0.2679 (2)	0.2675 (4)	0.060 (1)
C(4)	1.0321 (2)	0.2497 (2)	0.1742 (4)	0.0490 (9)
C(5)	0.7787 (2)	0.1959 (2)	0.3848 (3)	0.0474 (9)
C(6)	0.7772 (2)	0.2006 (2)	0.5285 (4)	0.0569 (10)
C(7)	0.7992 (2)	0.2633 (2)	0.5974 (3)	0.057 (1)
C(8)	0.8255 (2)	0.3227 (2)	0.5233 (3)	0.0481 (8)
C(9)	0.8696 (2)	0.3678 (2)	0.2777 (3)	0.0381 (7)
C(10)	0.8945 (2)	0.2801 (2)	0.0941 (3)	0.0381 (7)
C(11)	0.8417 (2)	0.3429 (1)	0.1310 (3)	0.0364 (7)
C(12)	0.8125 (2)	0.2646 (1)	0.1548 (3)	0.0361 (7)
C(13)	0.9525 (2)	0.3405 (1)	0.2849 (3)	0.0383 (7)
C(14)	0.9627 (2)	0.2858 (1)	0.1853 (3)	0.0377 (7)
C(15)	0.8046 (2)	0.2555 (2)	0.3084 (3)	0.0378 (7)
C(16)	0.8288 (2)	0.3179 (2)	0.3784 (3)	0.0378 (7)
C(17)	0.7160 (2)	0.4316 (1)	0.0219 (3)	0.0430 (7)
C(18)	0.6905 (2)	0.4591 (2)	0.1486 (3)	0.0529 (10)
C(19)	0.6138 (2)	0.4764 (2)	0.1682 (4)	0.060 (1)
C(20)	0.5612 (2)	0.4668 (2)	0.0613 (4)	0.057 (1)
C(21)	0.5855 (2)	0.4404 (2)	-0.0652 (4)	0.062 (1)
C(22)	0.6629 (2)	0.4223 (2)	-0.0844 (4)	0.0522 (10)
C(23)	0.8720 (2)	0.4816 (2)	0.0242 (3)	0.0478 (8)
C(24)	0.9515 (2)	0.4734 (2)	0.0430 (4)	0.060 (1)
C(25)	0.9984 (3)	0.5337 (2)	0.0543 (4)	0.070 (1)

C(26)	0.9685 (3)	0.6026 (2)	0.0459 (5)	0.076 (1)
C(27)	0.8904 (3)	0.6116 (2)	0.0273 (4)	0.069 (1)
C(28)	0.8422 (2)	0.5517 (2)	0.0180 (4)	0.0538 (9)
C(29)	0.7850 (2)	0.1314 (2)	0.0044 (3)	0.0469 (8)
C(30)	0.7548 (2)	0.0917 (2)	-0.1043 (4)	0.065 (1)
C(31)	0.7798 (3)	0.0210 (2)	-0.1315 (5)	0.079 (1)
C(32)	0.8329 (2)	-0.0095 (2)	-0.0468 (5)	0.070 (1)
C(33)	0.8637 (2)	0.0286 (2)	0.0634 (4)	0.057 (1)
C(34)	0.8404 (2)	0.0991 (2)	0.0881 (4)	0.0506 (9)
C(35)	0.6587 (2)	0.2099 (2)	0.1228 (3)	0.0450 (8)
C(36)	0.6206 (2)	0.2707 (2)	0.1727 (4)	0.059 (1)
C(37)	0.5499 (2)	0.2651 (3)	0.2372 (5)	0.075 (1)
C(38)	0.5157 (2)	0.1980 (3)	0.2539 (5)	0.081 (2)
C(39)	0.5523 (3)	0.1371 (3)	0.2042 (5)	0.078 (1)
C(40)	0.6234 (2)	0.1427 (2)	0.1402 (4)	0.061 (1)

Table 2. Selected geometric parameters (\AA , $^\circ$)

P(1)—C(11)	1.828 (3)	C(9)—C(16)	1.510 (4)
P(1)—C(17)	1.825 (3)	C(10)—C(11)	1.518 (4)
P(1)—C(23)	1.832 (3)	C(10)—C(12)	1.565 (4)
P(2)—C(12)	1.839 (3)	C(10)—C(14)	1.477 (4)
P(2)—C(29)	1.835 (3)	C(11)—C(12)	1.546 (4)
P(2)—C(35)	1.832 (3)	C(12)—C(15)	1.489 (4)
C(9)—C(11)	1.557 (4)	C(13)—C(14)	1.400 (4)
C(9)—C(13)	1.528 (4)	C(15)—C(16)	1.395 (4)
C(11)—P(1)—C(17)	106.2 (1)	P(2)—C(12)—C(10)	112.2 (2)
C(11)—P(1)—C(23)	99.9 (1)	P(2)—C(12)—C(11)	118.6 (2)
C(17)—P(1)—C(23)	103.2 (1)	P(2)—C(12)—C(15)	124.7 (2)
C(12)—P(2)—C(29)	103.5 (1)	C(10)—C(12)—C(11)	58.4 (2)
C(12)—P(2)—C(35)	103.0 (1)	C(10)—C(12)—C(15)	118.2 (2)
C(29)—P(2)—C(35)	102.7 (1)	C(11)—C(12)—C(15)	106.3 (2)
C(11)—C(9)—C(13)	103.7 (2)	C(1)—C(13)—C(9)	129.6 (3)
C(11)—C(9)—C(16)	104.6 (2)	C(1)—C(13)—C(14)	121.0 (3)
C(13)—C(9)—C(16)	102.3 (2)	C(9)—C(13)—C(14)	109.0 (2)
C(11)—C(10)—C(12)	60.2 (2)	C(4)—C(14)—C(10)	128.4 (3)
C(11)—C(10)—C(14)	107.0 (2)	C(4)—C(14)—C(13)	120.6 (3)
C(12)—C(10)—C(14)	121.6 (2)	C(10)—C(14)—C(13)	110.7 (2)
P(1)—C(11)—C(9)	126.9 (2)	C(5)—C(15)—C(12)	129.6 (3)
P(1)—C(11)—C(10)	115.4 (2)	C(5)—C(15)—C(16)	119.5 (3)
P(1)—C(11)—C(12)	125.0 (2)	C(12)—C(15)—C(16)	110.9 (2)
C(9)—C(11)—C(10)	104.3 (2)	C(8)—C(16)—C(9)	128.1 (3)
C(9)—C(11)—C(12)	104.1 (2)	C(8)—C(16)—C(15)	121.3 (3)
C(10)—C(11)—C(12)	61.4 (2)	C(9)—C(16)—C(15)	109.6 (2)

The absolute configuration was determined by inclusion of anomalous dispersion terms; the opposite chirality refined to a higher R value (0.038).

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1993). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1995). Program(s) used to solve structure: *MITHRIL* (Gilmore, 1984). Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: FG1181). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Unusual Hetarynic Condensation of 3-Bromo-2-ethoxypyridine with Diisopropyl Ketone Enolate in the Presence of a Complex Base

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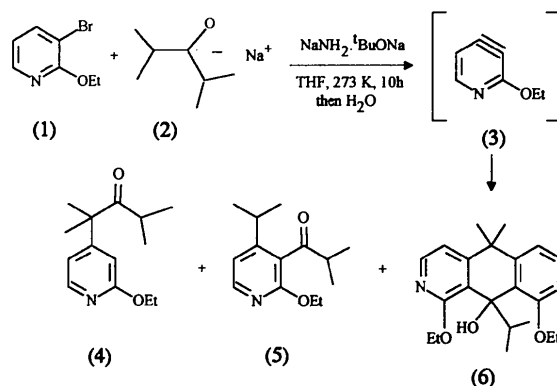
Abstract

The crystal structure analysis of 1,8-diethoxy-9,10-dihydro-9-isopropyl-10,10-dimethyl-2,7-diaza-9-anthrol, C₂₁H₂₈N₂O₃, obtained from the condensation of 3-bromo-2-ethoxypyridine with diisopropyl ketone enolate in the presence of the complex base NaNH₂·tBuONa, shows the tricyclic nature of the compound and allows interpretation of the reaction mechanism. The structure and conformation of the two independent molecules present in the asymmetric unit are compared with molecular modelling results.

Comment

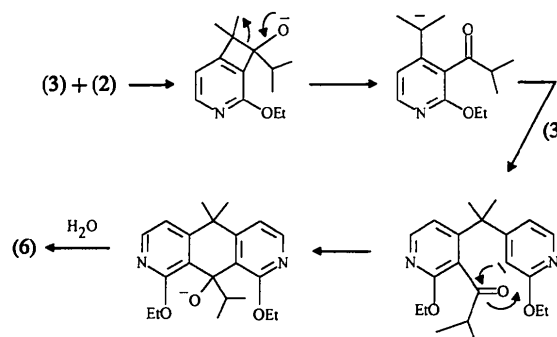
In a preceding short communication (Jamart-Grégoire, Léger & Caubère, 1990), it was established for the first time that ketone enolates are capable of condensation with 3,4-dihydropyridines generated from 3-bromopyridines and appropriate complex bases (Caubère, 1991, 1993) to give pyridinyl ketones and pyridinocyclobutenols. In a continuation of our exploration of this new route to pyridine derivatives, we undertook the study of the chemical behaviour of 3-bromo-2-ethoxypyridine in such reactions and found that during its condensation with isopropyl ketone enolate in the

presence of the complex base NaNH₂·tBuONa, an unusual result was observed (see scheme below).



Taking into account the results obtained from the aryne condensation of ketone enolates (Caubère, 1974, 1978, 1991, 1993), the formation of compounds (4) and (5) was expected. The formation of compound (6) was also observed, however, and this is rather unusual. Interestingly, we once observed such a reaction during the aryne condensation of diisopropyl ketone enolate with bromobenzene (Caubère & Guillaumet, 1972).

Compounds (4) and (5) were easily identified from spectroscopic data, but characterization of compound (6) required X-ray analysis. The results show that, as in aryne chemistry, the alkoxy groups direct the nucleophilic attack in the *meta* position relative to the carbon bearing the O atom. We can thus propose the mechanism given in the scheme below for the formation of compound (6).



One of the two independent molecules is shown in Fig. 1. The geometric parameters were compared with those calculated for the free molecule by the TRIPOS molecular-modelling optimization procedure of the SYBYL package (Tripos Associates Inc., 1992) using default parameters. From the results of this comparison it was noticed that the largest differences were observed for: (i) bond distances in the isopropyl and ethyl groups, probably caused by the high thermal motion (or disorder) affecting these groups, (ii) bond angles at the junction of the isopropyl substituent on the central