

*Acta Cryst.* (1996). **C52**, 2093–2095**Ethyl 3-(2-Cyano-3-phenylazo-2-butenylidene)carbazate at 122 K**CLAUS FLENSBURG,<sup>a</sup> JAN JENSEN,<sup>a</sup> SINE LARSEN<sup>a</sup> AND WIM DEHAEN<sup>b</sup><sup>a</sup>*Department of Chemistry, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen, Denmark, and* <sup>b</sup>*Department of Chemistry, University of Leuven, Celestijnenlaan 200F, B-3001 Heverlee, Belgium. E-mail: claus@laue.ki.ku.dk*

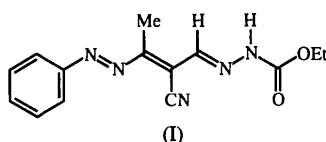
(Received 22 January 1996; accepted 4 March 1996)

**Abstract**

The title compound, C<sub>14</sub>H<sub>15</sub>N<sub>5</sub>O<sub>2</sub>, formed by the opening of a pyrazole ring, contains the three conjugated double bonds in a linear configuration. The phenyl and carbazido ethyl ester groups are virtually coplanar with the remaining molecule. Compared with the pyrazole, the bond lengths in the title compound show a less extensive conjugation.

**Comment**

The title compound (I) was isolated during a study of the ring-opening reaction of 5-azido-4-iminomethylpyrazole. The ethoxycarbonyl hydrazone of 5-azido-4-formyl-3-methyl-1-phenylpyrazole was found to react more readily, but the outcome of the reaction depended strongly on the solvent and reaction time (Dehaen & Becher, 1991).



The present X-ray crystallographic investigation was performed in order to verify the identity of one of the reaction products, assumed to be the *cis* isomer of the ring-opened system. It has further allowed us to study the changes in bond lengths associated with the opening of the pyrazole ring. Fig. 1 and the bond lengths and angles in Table 2 illustrate that the molecular geometry of the reaction product corresponds to the *Z-cis* isomer. In the fragment from C11 to N5, every second bond is a double bond and one could expect that conjugation within this system would be revealed in the bond lengths. A comparison of the bond lengths in Table 2 with those found in the pyrazole ring system with similar substituents (Becher *et al.*, 1995) reveals significant differences. The N1—N2 distance in the

pyrazole ring system, 1.365 (1) Å, is much longer than the N1—N2 bond length of 1.267 (2) Å found in the present structure. Similar discrepancies are observed between the other bond lengths of the pyrazole ring, which are in the range 1.322 (2) to 1.417 (2) Å, and the bond lengths in the ring-opened structure which vary between 1.267 (2) and 1.455 (2) Å. These latter values correspond very closely to the normal values for single and double bonds, which could imply that conjugation is less extensive in the ring-opened structure. Both the phenyl group and the carboxyethyl ester groups are virtually coplanar with the conjugated system. As illustrated by the torsion angles in Table 2, the largest deviation from planarity is found around the C2—C4 bond, as exemplified by the torsion angle C3—C2—C4—N4 of 14.7 (2)°. It seems likely that the lack of conjugation within the moiety C11—N5 is associated with the deviation from planarity.

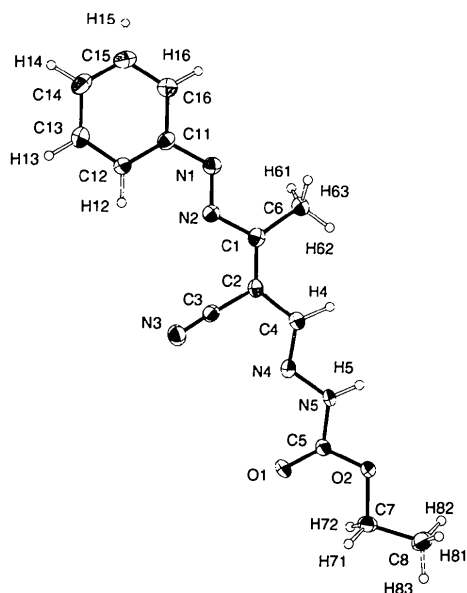


Fig. 1. View of the title compound showing the atomic labelling. The thermal ellipsoids for the non-H atoms are drawn at the 50% probability level, the H atoms are shown as spheres of fixed radius.

An intermolecular hydrogen bond between N5 and O1 connects molecules related by glide planes perpendicular to the *c* axis and translations along the *a* axis, thereby forming infinite hydrogen-bonded chains. The geometry of the hydrogen bond is N5···O1( $\frac{1}{2} + x, -y, \frac{3}{2} - z$ ) 2.820 (2), N5—H5 0.86 (2) Å, N5—H5···O1 163 (2)°. These strong interactions explain why the compound grows as needles along the *a* axis. Fig. 2 illustrates the crystal packing. The molecules are oriented with their longest direction almost parallel to the *b* axis and the molecular planes arranged in a herring-bone pattern.

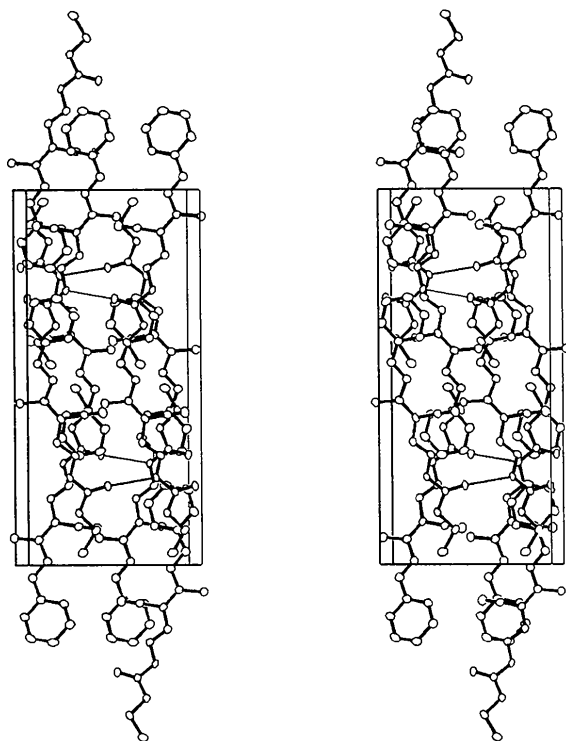


Fig. 2. Stereoscopic view of the crystal packing viewed along the *c* axis. The *a* axis is horizontal and the *b* axis vertical.

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.0350$   
 $wR(F^2) = 0.0829$   
 $S = 1.014$   
 2729 reflections  
 250 parameters  
 All H-atom parameters  
 refined  
 $w = 1/[\sigma^2(F_o^2) + (0.0434P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$   
 $\Delta\rho_{\max} = 0.15(4) \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.20(4) \text{ e } \text{\AA}^{-3}$   
 Extinction correction: none  
 Atomic scattering factors  
 from *International Tables*  
 for *Crystallography* (1992,  
 Vol. C, Tables 4.2.6.8 and  
 6.1.1.4)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}$
O1	0.02157 (10)	0.70917 (5)	0.72765 (8)	0.0284 (3)
O2	0.18682 (10)	0.63720 (5)	0.70109 (8)	0.0250 (2)
N1	0.43351 (12)	1.03455 (6)	0.89663 (9)	0.0239 (3)
N2	0.34697 (12)	0.99036 (5)	0.89969 (9)	0.0226 (3)
N3	0.06272 (13)	0.90326 (6)	0.92816 (10)	0.0309 (3)
N4	0.21515 (11)	0.78948 (5)	0.79430 (9)	0.0235 (3)
N5	0.24270 (12)	0.73105 (5)	0.75703 (10)	0.0255 (3)
C1	0.39211 (14)	0.93349 (7)	0.85753 (10)	0.0223 (3)
C2	0.29804 (14)	0.88668 (7)	0.85345 (10)	0.0212 (3)
C3	0.16700 (14)	0.89756 (7)	0.89498 (10)	0.0227 (3)
C4	0.31883 (15)	0.82450 (7)	0.81076 (11)	0.0238 (3)
C5	0.13868 (14)	0.69351 (7)	0.72905 (10)	0.0215 (3)
C6	0.5317 (2)	0.92796 (8)	0.81982 (12)	0.0264 (3)
C7	0.0860 (2)	0.59193 (7)	0.66745 (11)	0.0255 (3)
C8	0.1612 (2)	0.53213 (8)	0.64245 (13)	0.0308 (4)
C11	0.38964 (15)	1.09292 (7)	0.93712 (10)	0.0231 (3)
C12	0.2608 (2)	1.10372 (7)	0.97350 (11)	0.0262 (3)
C13	0.2312 (2)	1.16235 (7)	1.01263 (12)	0.0318 (4)
C14	0.3280 (2)	1.21023 (8)	1.01489 (12)	0.0338 (4)
C15	0.4545 (2)	1.19956 (8)	0.97833 (13)	0.0348 (4)
C16	0.4861 (2)	1.14088 (7)	0.93901 (12)	0.0293 (3)

### Experimental

Crystals of the title compound were obtained by recrystallization from a CHCl<sub>3</sub>/ether mixture at 253 K.

#### Crystal data

C<sub>14</sub>H<sub>15</sub>N<sub>5</sub>O<sub>2</sub>

$M_r = 285.31$

Orthorhombic

*Pbca*

$a = 9.9456(9) \text{ \AA}$

$b = 21.0106(11) \text{ \AA}$

$c = 14.1793(14) \text{ \AA}$

$V = 2962.9(4) \text{ \AA}^3$

$Z = 8$

$D_x = 1.279 \text{ Mg m}^{-3}$

$D_m$  not measured

Cu *K*α radiation

$\lambda = 1.54184 \text{ \AA}$

Cell parameters from 22

reflections

$\theta = 32.9\text{--}39.8^\circ$

$\mu = 0.740 \text{ mm}^{-1}$

$T = 122(1) \text{ K}$

Needle

$0.50 \times 0.08 \times 0.08 \text{ mm}$

Reddish

#### Data collection

CAD-4 diffractometer

Profile data from  $\omega$ - $2\theta$  scans

Absorption correction:

none

4905 measured reflections

2729 independent reflections

2203 observed reflections

$[I > 2\sigma(I)]$

$R_{\text{int}} = 0.0139$

$\theta_{\text{max}} = 74.86^\circ$

$h = 0 \rightarrow 12$

$k = -26 \rightarrow 26$

$l = 0 \rightarrow 17$

3 standard reflections

frequency: 166.7 min

intensity decay: 2.8%

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

O1—C5	1.210 (2)	N4—N5	1.364 (2)
O2—C5	1.336 (2)	N5—C5	1.360 (2)
O2—C7	1.462 (2)	C1—C2	1.359 (2)
N1—N2	1.267 (2)	C1—C6	1.492 (2)
N1—C11	1.423 (2)	C2—C3	1.448 (2)
N2—C1	1.410 (2)	C2—C4	1.455 (2)
N3—C3	1.145 (2)	C7—C8	1.505 (2)
N4—C4	1.288 (2)		
C5—O2—C7	115.28 (11)	C3—C2—C4	116.03 (13)
N2—N1—C11	114.18 (12)	N3—C3—C2	176.9 (2)
N1—N2—C1	112.98 (12)	N4—C4—C2	118.33 (13)
C4—N4—N5	115.05 (12)	O1—C5—O2	125.49 (13)
C5—N5—N4	118.82 (12)	O1—C5—N5	125.38 (13)
C2—C1—N2	114.36 (13)	O2—C5—N5	109.11 (11)
C2—C1—C6	124.68 (14)	O2—C7—C8	106.22 (13)
N2—C1—C6	120.95 (13)	C16—C11—N1	114.87 (13)
C1—C2—C3	119.22 (13)	C12—C11—N1	124.69 (13)
C1—C2—C4	124.75 (13)		
C11—N1—N2—C1	178.86 (12)	C3—C2—C4—N4	14.7 (2)
N1—N2—C1—C2	-175.37 (12)	C7—O2—C5—N5	-179.09 (12)
C6—C1—C2—C3	178.41 (14)	N4—N5—C5—O2	-175.73 (12)
N2—C1—C2—C4	178.02 (13)	C5—O2—C7—C8	-178.56 (13)
N5—N4—C4—C2	-177.99 (13)	N2—N1—C11—C12	-3.2 (2)
C1—C2—C4—N4	-166.07 (15)		

Reflections measured only in the prescan were omitted from the data because they have been shown to suffer from systematic errors (Seiler, Schweizer & Dunitz, 1984).

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.

We thank Mr Flemming Hansen for technical assistance with the data collection.

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*]cyclopropa[*cd*]pentalene-8b,8c-bis(di-phenylphosphine)

TAI YU FU, JOHN R. SCHEFFER AND JAMES TROTTER

*Department of Chemistry, University of British Columbia, Vancouver, BC, Canada V6T 1Z1. E-mail: james.trotter@mtsg.ubc.ca*

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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.

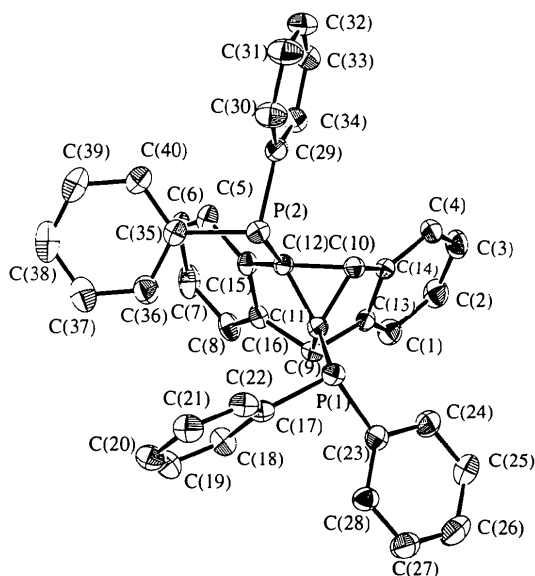
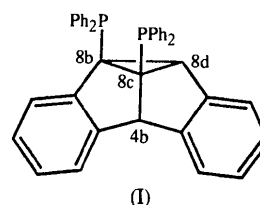


Fig. 1. View of the molecule (30% ellipsoids; crystallographic numbering system based on the dibenzobarrelene precursor).

## 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  
 $\lambda = 1.5418 \text{ \AA}$