

- ERMER, O. & LIFSON, S. (1973). *J. Amer. Chem. Soc.* **95**, 4121–4132.
- JOHNSON, C. K. (1965). *ORTEP*. Oak Ridge National Laboratory Report ORNL-3794.
- KROGSGAARD-LARSEN, P. & HJEDS, H. (1974). *Acta Chem. Scand.* **B28**, 533–538.
- KROGSGAARD-LARSEN, P. & JOHNSTON, G. A. R. (1975). *J. Neurochem.* **25**, 797–802.
- KROGSGAARD-LARSEN, P., JOHNSTON, G. A. R., CURTIS, D. R., GAME, C. J. A. & MCCULLOCH, R. M. (1975). *J. Neurochem.* **25**, 803–809.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
- X-RAY system (1972). Tech. Rep. TR-192. Computer Science Center, Univ. of Maryland, College Park, Maryland.

*Acta Cryst.* (1976). **B32**, 3339

## Dimethyl 8-*exo*-Phenylbicyclo[5.1.0]octa-2,4-diene-8-phosphonate

BY R. HOGE

*Fachrichtung Kristallographie der Universität des Saarlandes, Im Stadtwald, D-6600 Saarbrücken, Germany (BRD)*

AND G. MAAS

*Fachbereich Chemie der Universität Kaiserslautern, Pfaffenbergstr. 95, D-6750 Kaiserslautern, Germany (BRD)*

(Received 1 June 1976; accepted 12 June 1976)

**Abstract.**  $C_{16}H_{19}O_3P$ , monoclinic,  $P2_1/c$ ;  $a=13.651$  (9),  $b=12.406$  (8),  $c=9.037$  (5) Å,  $\beta=91.25$  (2)°;  $Z=4$ ,  $M=290.28$ ,  $D_x=1.261$  g cm<sup>-3</sup>. The highly strained nature of the bicyclic ring system becomes evident from very short C–C single bonds and a torsion angle around one double bond of 29°.

**Introduction.** The compound is obtained by photolysis or thermolysis of dimethyl (diazobenzyl)phosphonate in excess cycloheptatriene. It is the minor product of the 1:1 addition of the intermediately formed carbene to the solvent. Moreover, there exists a photochemical equilibrium with the analogous *endo*-phenyl isomer

(Maas, 1976) which is the major product of the direct carbene addition to cycloheptatriene. Crystals for X-ray analysis were obtained by sublimation of the crude product and recrystallization from ether (m.p. 129°C).

Systematic extinctions on Weissenberg and precession photographs ( $h0l$  with  $l=2n+1$  and  $0k0$  with  $k=2n+1$ ) indicated space group  $P2_1/c$ . Intensities from a crystal fragment,  $0.24 \times 0.14 \times 0.09$  mm, were collected on a Siemens diffractometer (AED) with Ni-filtered Cu  $K\alpha$  radiation and a scintillation counter. With a  $\theta/2\theta$ -scan and the five-values method, 1688 reflexions in the range  $0 < \theta < 51.45^\circ$  were measured (scan speed  $0.24$  s/ $0.01^\circ$ ). Two control reflexions (900 and 080)

Table 1. Atomic coordinates and thermal parameters of the non-hydrogen atoms (all  $\times 10^4$ , e.s.d.'s are in parentheses)

The thermal ellipsoid is defined by  $\exp [-(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + B_{12}hka^*b^* + \dots)]$ .

	$x$	$y$	$z$	$B_{11}$	$B_{22}$	$B_{33}$	$B_{12}$	$B_{13}$	$B_{23}$
P	3255 (1)	5788 (1)	6264 (1)	59 (1)	79 (1)	125 (1)	-13 (1)	-29 (2)	-7 (2)
O(1)	4021 (2)	6264 (3)	5195 (4)	99 (3)	104 (3)	204 (5)	-78 (4)	34 (6)	-40 (6)
O(2)	3726 (2)	4674 (2)	6693 (3)	77 (2)	99 (3)	221 (6)	16 (4)	-100 (6)	33 (6)
O(3)	3056 (2)	6474 (3)	7527 (3)	82 (2)	139 (3)	148 (5)	-13 (5)	-41 (5)	-94 (7)
C(1)	1197 (4)	4900 (5)	7461 (5)	86 (4)	146 (5)	163 (8)	-39 (7)	46 (8)	-23 (11)
C(2)	445 (6)	5387 (7)	8079 (7)	210 (8)	248 (10)	193 (10)	11 (15)	162 (15)	-44 (17)
C(3)	-77 (4)	6283 (6)	7675 (6)	81 (4)	270 (10)	224 (10)	10 (10)	-19 (10)	-272 (16)
C(4)	247 (5)	7053 (6)	6775 (8)	140 (6)	173 (7)	324 (13)	99 (11)	-41 (14)	-182 (16)
C(5)	1109 (4)	7045 (4)	5862 (6)	80 (3)	125 (5)	212 (9)	61 (7)	-71 (9)	-99 (11)
C(6)	1292 (3)	6009 (4)	5052 (6)	66 (3)	105 (4)	138 (6)	33 (6)	-49 (7)	-57 (8)
C(7)	1318 (3)	4966 (4)	5822 (5)	73 (3)	107 (4)	136 (7)	-32 (6)	-9 (7)	-52 (9)
C(8)	2249 (3)	5373 (3)	5111 (4)	55 (3)	76 (3)	116 (5)	-2 (5)	-20 (6)	-4 (7)
C(9)	2540 (3)	4847 (3)	3678 (4)	55 (3)	76 (3)	118 (6)	1 (5)	-29 (6)	-17 (7)
C(10)	2626 (3)	5455 (3)	2398 (4)	69 (3)	77 (4)	134 (6)	4 (5)	-13 (7)	1 (7)
C(11)	2861 (3)	4981 (4)	1069 (5)	82 (3)	111 (4)	128 (6)	-19 (6)	-6 (7)	6 (9)
C(12)	3036 (4)	3889 (4)	1010 (5)	96 (4)	109 (4)	152 (7)	1 (7)	16 (8)	-57 (9)
C(13)	2975 (5)	3276 (4)	2265 (5)	106 (4)	77 (4)	207 (8)	27 (6)	0 (9)	-59 (9)
C(14)	2723 (3)	3748 (3)	3606 (5)	91 (4)	71 (4)	168 (7)	26 (6)	-12 (8)	-10 (8)
C(15)	4371 (5)	7341 (4)	5199 (7)	145 (5)	105 (5)	297 (12)	-77 (9)	-42 (13)	12 (13)
C(16)	4635 (4)	4683 (5)	7550 (6)	78 (4)	158 (6)	215 (9)	38 (8)	-82 (9)	53 (12)

were monitored after every 23 reflexions; finally,  $F_{900}$  had diminished by 11% of its original value,  $F_{080}$  by 16%. Therefore, all reflexions were rescaled by a least-squares line based on the 80 values of  $|F_{900}| + |F_{080}|$  obtained in the course of the data collection. The eight strongest reflexions, with a peak maximum  $> 18000$  counts  $s^{-1}$ , were remeasured with Al foil as an attenuator and rescaled. The attenuation factor was determined with the 20 next strongest reflexions. No absorption correction was made [ $\mu(\text{Cu K}\alpha) = 16.25 \text{ cm}^{-1}$ ].

The structure was solved with *MULTAN 74* (Main, Woolfson, Lessinger, Germain & Declercq, 1974). Thirteen peaks from the resulting *E* map were accepted and refined by least squares ( $\sin \theta/\lambda < 0.5$ ). The remaining seven atoms were located on a difference map.

Table 2. Atomic coordinates ( $\times 10^3$ ) and isotropic  $B$ 's ( $\text{\AA}^2$ ) of the hydrogens

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
H(1)	144 (4)	421 (4)	792 (5)	6.6 (1.3)
H(2)	19 (6)	508 (6)	898 (8)	13.8 (2.5)
H(3)	-69 (4)	640 (4)	823 (6)	8.5 (1.6)
H(4)	16 (5)	775 (5)	647 (7)	10.5 (1.9)
H(5.1)	153 (4)	715 (4)	677 (6)	9.1 (1.5)
H(5.2)	136 (4)	764 (5)	526 (6)	7.8 (1.8)
H(6)	104 (3)	602 (3)	400 (4)	3.8 (1.0)
H(7)	95 (3)	437 (3)	534 (4)	3.8 (1.0)
H(10)	254 (3)	622 (3)	242 (4)	3.3 (0.9)
H(11)	288 (2)	547 (3)	23 (4)	2.3 (0.9)
H(12)	325 (3)	359 (4)	91 (5)	5.5 (1.2)
H(13)	308 (3)	249 (3)	224 (5)	4.8 (1.1)
H(14)	254 (3)	330 (4)	458 (5)	4.9 (1.1)
H(15.1)	434 (5)	765 (6)	608 (8)	12.8 (2.2)
H(15.2)	386 (6)	753 (6)	459 (9)	15.7 (2.7)
H(15.3)	500 (6)	725 (6)	493 (8)	13.9 (2.4)
H(16.1)	481 (4)	394 (5)	757 (6)	8.7 (1.6)
H(16.2)	455 (4)	497 (5)	850 (6)	9.6 (1.7)
H(16.3)	523 (4)	500 (5)	688 (6)	10.0 (2.1)

The structure was refined by block-diagonal least-squares with 1268 reflexions with  $F_o > 4\sigma(F_o)$ . Unit weights were used. 16 out of 19 H atoms were found on a  $\Delta F$  map. They were included in the structure factor calculation of two further least-squares cycles for the heavy atoms. The missing H atoms then appeared in a second difference synthesis. The H atoms were now included in the refinement with isotropic  $B$ 's, and a weighting scheme  $w = 1$  if  $F_o < 30.5$ , otherwise  $1/w = F_o/30.5$ . After three cycles,  $R$  was 0.045 and  $R_w$  0.054.

Final positional and thermal parameters are given in Tables 1 and 2, and the molecular geometry in Table 3.\*

**Discussion.** The molecular structure is shown in Fig. 1 (thermal ellipsoids are at the 50% probability level) and Fig. 2.

Apart from the interchange of the C(8) substituents, the overall structure very closely resembles that of the *exo*-phenyl isomer. However, since the steric requirements of the phosphonate group are bigger than those of a phenyl ring, at least one O atom always interacts with C(1), C(5) and H(5.1) of the bicyclic ring, regardless of how the phosphonate group is rotated about the C(7)-P single bond (Fig. 2). The molecule avoids this repulsion by an increase of the angle between the cyclopropane ring and the C(1)-C(7)-C(6)-C(5) plane. C(1)-C(7)-C(8) and C(5)-C(6)-C(8) are enlarged by 3.4 and 2.7° with respect to the *endo*-phenyl isomer, where this kind of steric repulsion does not exist. To a

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31945 (13 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3. Molecular geometry

E.s.d.'s are 0.004-0.009 Å for bond lengths, 0.3-0.7° for bond angles and 0.6-0.9° for torsion angles. Values in parentheses refer to dimethyl 8-*endo*-phenylbicyclo[5.1.0]octa-2,4-diene-8-phosphonate (Maas, 1976).

O(1)-P	1.556 Å	P-O(1)-C(15)	125.9°	C(7)-C(6)-C(8)	61.1 (61.2)°
O(2)-P	1.570	P-O(2)-C(16)	117.8	C(1)-C(7)-C(8)	123.2 (120.5)
O(3)-P	1.454	O(1)-P-O(3)	113.9	C(1)-C(7)-C(6)	121.0 (120.3)
O(1)-C(15)	1.419	O(2)-P-O(3)	113.8	C(7)-C(1)-C(2)	119.7 (118.4)
O(2)-C(16)	1.448	O(1)-P-O(2)	102.1	C(1)-C(2)-C(3)	131.5 (132.2)
C(1)-C(2)	1.325 (1.374)	O(1)-P-C(8)	105.4	C(2)-C(3)-C(4)	124.6 (122.6)
C(2)-C(3)	1.366 (1.365)	O(2)-P-C(8)	101.4	C(3)-C(4)-C(5)	128.6 (127.0)
C(3)-C(4)	1.336 (1.351)	O(3)-P-C(8)	118.3	C(4)-C(5)-C(6)	115.3 (119.8)
C(4)-C(5)	1.452 (1.413)	C(8)-C(9)-C(10)	120.5	C(5)-C(6)-C(7)	121.7 (119.4)
C(5)-C(6)	1.502 (1.480)	C(10)-C(9)-C(14)	118.5	C(5)-C(6)-C(8)	125.2 (121.8)
C(7)-C(1)	1.496 (1.502)	C(9)-C(10)-C(11)	121.2		
C(7)-C(6)	1.469 (1.484)	C(10)-C(11)-C(12)	119.7	C(7)-C(1)-C(2)-C(3)	-28.9 (-30)
C(8)-C(6)	1.527 (1.531)	C(11)-C(12)-C(13)	120.0	C(1)-C(2)-C(3)-C(4)	-20.9 (-23)
C(8)-C(7)	1.523 (1.536)	C(12)-C(13)-C(14)	120.5	C(2)-C(3)-C(4)-C(5)	10.9 (16)
C(8)-P	1.781 (1.784)	C(13)-C(14)-C(9)	120.0	C(3)-C(4)-C(5)-C(6)	42.4 (41)
C(8)-C(9)	1.511 (1.511)	C(9)-C(8)-P	114.4 (115.0)	C(4)-C(5)-C(6)-C(7)	-51.8 (-55)
C(9)-C(10)	1.388	C(6)-C(8)-P	121.3 (113.6)	C(5)-C(6)-C(7)-C(1)	-2.1 (-2)
C(10)-C(11)	1.382	C(7)-C(8)-P	119.2 (113.4)	C(6)-C(7)-C(1)-C(2)	51.0 (52)
C(11)-C(12)	1.377	C(6)-C(8)-C(9)	115.7 (120.6)		
C(12)-C(13)	1.370	C(7)-C(8)-C(9)	117.1 (124.2)		
C(13)-C(14)	1.395	C(6)-C(8)-C(7)	57.6 (57.9)		
C(14)-C(9)	1.388	C(8)-C(7)-C(6)	61.3 (60.9)		

more marked extent, the C(8)–P bond turns away from the bicyclic skeleton: C(6)–C(8)–P and C(7)–C(8)–P are augmented by 7.7 and 6.8° compared with the *exo*-phosphonate isomer.

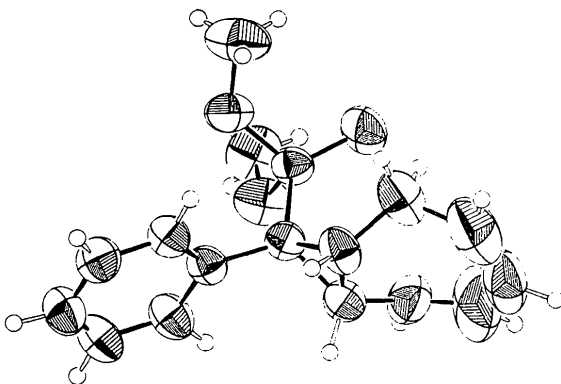


Fig. 1. An ORTEP plot of dimethyl 8-*exo*-phenylbicyclo[5.1.0]octa-2,4-diene-8-phosphonate.

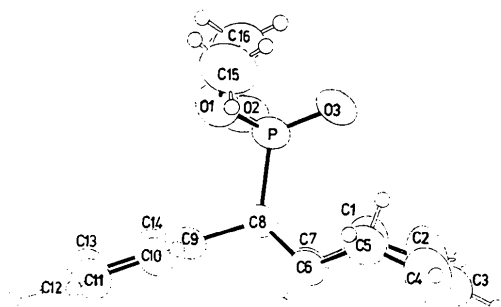


Fig. 2. Possible steric interactions between the phosphonate group and the bicyclic system become evident from this plot.

In the diene moiety of the bicyclic ring, differences between single- and double-bond lengths are more distinct than in the *endo*-phenyl isomer (Table 3). However, a C(2)–C(3) contact of 1.366 Å is again found; even for a  $Csp^2$ – $Csp^2$  single bond, this is a surprisingly short distance: the normal single-bond length between  $Csp^2$  atoms in unsaturated seven-membered rings is 1.40–1.46 Å (for some examples see Bürgi, 1975).

Another uncommon feature concerns the torsion angle of 29° about one of the two double bonds in the cycloheptadiene ring. Dihedral angles about double bonds in cyclic polyenes do not exceed *ca* 18° (*e.g.* Gramaccioni, Mimun, Mugnoli & Simonetta, 1973) and structures with a nearly planar conjugated  $\pi$  system are known, *e.g.* cycloheptatriene–Mo(CO)<sub>3</sub> (Dunitz & Pauling, 1960). The dihedral angle between the two double bonds approaches 21°. This lack of planarity may be one reason why the 1,3-diene system is not prone to a Diels–Alder reaction, even at elevated temperature.

This work was supported by the Deutsche Forschungsgemeinschaft. G. M. thanks the Fonds der Chemischen Industrie for a Liebig fellowship. Computational work was done on the TR 440 computers in Saarbrücken and Kaiserslautern.

#### References

- BÜRGI, H.-B. (1975). *Angew. Chem.* **87**, 461–475.  
 DUNITZ, J. D. & PAULING, P. (1960). *Helv. Chim. Acta*, **43**, 2188–2197.  
 GRAMACCIOLI, C. M., MIMUN, A. S., MUGNOLI, A. & SIMONETTA, M. (1973). *J. Amer. Chem. Soc.* **95**, 3149–3154.  
 MAAS, G. (1976). *Cryst. Struct. Commun.* **5**, 107–111.  
 MAIN, P., WOOLFSON, M. M., LESSINGER, L., GERMAIN, G. & DECLERCQ, J.-P. (1974). *MULTAN* 74. Univ. of York, England.

*Acta Cryst.* (1976). **B32**, 3341

### 3,4-Dihydro-3,4,4-trimethyl-4,3-borazaroisoquinoline

BY CHRISTER SVENSSON

*Division of Inorganic Chemistry 2, Chemical Center, University of Lund, P.O. Box 740, S-220 07 Lund, Sweden*

(Received 1 June 1976; accepted 18 June 1976)

**Abstract.** C<sub>10</sub>H<sub>15</sub>N<sub>2</sub>B, orthorhombic,  $P2_12_12_1$ ,  $a = 13.177(1)$ ,  $b = 12.115(1)$ ,  $c = 6.392(1)$  Å,  $V = 1020.3$  Å<sup>3</sup>,  $Z = 4$ , F.W. 174.05 g mol<sup>-1</sup>,  $D_x = 1.13$  g cm<sup>-3</sup>,  $\mu(\text{Cu } K\alpha) = 4.4$  cm<sup>-1</sup>. The structure was determined from diffractometer data and refined to  $R = 0.037$  for 836 observed reflexions. The B atom has a tetrahedral environment with four approximately equal lengths to three C (1.62 Å) and one N (1.65 Å). The hetero-

atomic ring has a twist conformation with the methyl group on N equatorial.

**Introduction.** Dewar & Dougherty (1964) first synthesized and examined the properties of the heteroaromatic 4-methyl-4,3-borazaroisoquinoline (I). The naming convention used here is that of Dewar & Dietz (1959). The  $\pi$ -bonding is achieved through donation of the N