from conformation-stability arguments rather than due to the attractive interaction of the O atom lone-pair electrons.

The author thanks Professor D. Ginsburg and Dr I. J. Landheer for providing samples of the compounds.

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Configuration of Diels–Alder Adducts.
V.* Structures of the Monoadducts Between [4.2.1]-, [4.3.1]- and [4.4.1]Propella-2,4-dienes and 4-Substituted 1,2,4-Triazoline-3,5-diones

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Abstract

Crystal structure analyses of three monoadducts of the Diels–Alder reaction between [4.2.1]-, [4.3.1]- and [4.4.1]propella-2,4-dienes with 4-substituted 1,2,4-triazoline-3,5-diones ([4.2.1]P, [4.3.1]P and [4.4.1]P) show that in the absence of carbonyl groups at the central ring, steric repulsion towards the dienophile would control the direction of attack. It is shown that the overlap of the H atom of the central cyclopropane with the centre of the diene moiety exerts the most steric repulsion leading towards an attack of the dienophile *anti* to that ring. {Crystal data: [4.2.1]P: $C_{12}H_{13}N_3O_2$, space group $P\bar{1}$, $a = 11{\cdot}873\,(6)$, $b = 11{\cdot}100\,(6)$, $c = 8{\cdot}648\,(4)$ Å, $\alpha = 98{\cdot}54\,(2)$, $\beta = 89{\cdot}40\,(2)$, $\gamma = 105{\cdot}50\,(2)^\circ$, final $R = 0{\cdot}054$; [4.3.1]P: $C_{18}H_{17}N_3O_2$, space group $Pna2_1$, $a = 14{\cdot}267\,(7)$, $b = 10{\cdot}381\,(5)$, $c = 10{\cdot}160\,(5)$ Å, final $R = 0{\cdot}067$; [4.4.1]P: $C_{14}H_{19}N_3O_2$, space group $Pna2_1$, $a = 8{\cdot}711\,(4)$, $b = 13{\cdot}476\,(7)$, $c = 11{\cdot}178\,(5)$ Å, final $R = 0{\cdot}045$.}

Introduction

In a previous publication (Kaftory, 1980 and references cited therein) the connection between the type of dienophiles, dienes and the configuration of the Diels–Alder monoadducts has been shown by X-ray crystallographic results. It was concluded that a 4-substituted 1,2,4-triazoline-3,5-dione as a dienophile will attack the diene moiety *syn* to the central ring whenever that ring contains carbonyl groups, due to secondary orbital overlap. In the absence of carbonyl groups other factors such as steric repulsion will be the

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* Part IV: *Acta Cryst.* (1980). B**36**, 597–606.

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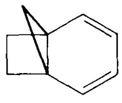
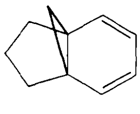
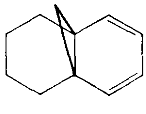
main factor which will govern the direction of attack (Ashkenazi, Kaftory, Grimme, Heger, Vogel & Ginsburg, 1980). The H atoms of cyclopropane as well as cyclobutane, cyclopentane and cyclohexane exert steric repulsions. However, it would be expected that the H atoms of cyclopropane would be the most effective, as they overlap the centre of the diene moiety. The crystal structures of three monoadducts with I, II and III were determined and their geometrical features will be presented here.



(I) [4.2.1]P



(II) [4.3.1]P



(III) [4.4.1]P

Structure determination and refinement

Table 1. *Crystallographic data and experimental details*

	[4.2.1]P	[4.3.1]P	[4.4.1]P
Formula	$C_{12}H_{13}N_3O_2$	$C_{18}H_{17}N_3O_2$	$C_{14}H_{19}N_3O_2$
M_r	231·25	307·34	261·31
a (Å)	11·873 (6)	14·267 (7)	8·711 (4)
b (Å)	11·100 (6)	10·381 (5)	13·476 (7)
c (Å)	8·648 (4)	10·160 (5)	11·178 (5)
α (°)	98·54 (2)		
β (°)	89·40 (2)		
γ (°)	105·50 (2)		
Z	4	4	4
Space group	$P1$	$Pna2_1$	$Pna2_1$
D_x (Mg m^{-3})	1·415	1·357	1·323
Scan mode	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$
$\Delta\omega$ (°)	1·2	1·2	1·4
Scan time (s)	24·0	24·0	28·0
Background time (s)*	20·0	20·0	20·0
θ_{max} (°)	25·0	24·0	25·0
Reflections measured	3504	1392	1364
Significant [F_o > 0·0]	3445	1237	1213
Weighting coefficients (k; g)†	0·4591; 0·0052	0·3340; 0·0024	0·3983; 0·0284
R_w	0·068	0·063	0·062
R	0·054	0·067	0·045

* Total background counting time.

† $w = k/[\sigma^2(F_o) + gF_o^2]$.

Intensities from colourless single crystals (prismatic 0·4 × 0·3 × 0·3 mm of [4.2.1]P, needle 0·3 × 0·1 × 0·2 mm of [4.3.1]P and polyhedron 0·5 × 0·5 × 0·4 mm of [4.4.1]P) were collected on a Philips PW 1100 four-circle computer-controlled diffractometer with graphite-monochromated Mo $K\alpha$ radiation (λ = 0·71069 Å). Crystallographic data and details of intensity measurements are given in Table 1.

The crystal structures were solved with *MULTAN 77* (Main, Woolfson, Lessinger, Germain & Declercq, 1977).

Table 2. [4.2.1]P: *positional parameters for non-hydrogen atoms* (×10⁴) *and for* H *atoms* (×10³) (*e.s.d.'s in parentheses*)

	Molecule (A)				Molecule (B)		
	x	y	z		x	y	z
O(1)	2850 (1)	7753 (2)	304 (2)	O(1)	7230 (1)	8715 (2)	4059 (2)
O(2)	−533 (1)	8618 (2)	−1037 (2)	O(2)	3402 (1)	7538 (2)	5392 (2)
N(1)	953 (1)	7126 (2)	1151 (2)	N(1)	6259 (1)	7402 (2)	5788 (1)
N(2)	1291 (2)	8265 (2)	−781 (2)	N(2)	5217 (2)	8184 (2)	4296 (2)
N(3)	−114 (1)	7412 (2)	748 (2)	N(3)	5054 (1)	7039 (2)	6217 (2)
C(1)	83 (2)	6287 (2)	3391 (3)	C(1)	6835 (2)	6598 (2)	7953 (3)
C(2)	1135 (2)	7238 (2)	2898 (2)	C(2)	7084 (2)	7778 (2)	7193 (3)
C(3)	1086 (2)	8556 (2)	3552 (2)	C(3)	6689 (2)	8793 (2)	8225 (3)
C(4)	123 (2)	8832 (2)	3173 (3)	C(4)	5588 (2)	8472 (2)	8617 (2)
C(5)	−753 (2)	7781 (2)	2170 (3)	C(5)	4923 (2)	7142 (2)	7965 (2)
C(6)	−1044 (2)	6608 (2)	2954 (3)	C(6)	5551 (2)	6225 (2)	8425 (2)
C(7)	−1545 (2)	5246 (2)	2122 (4)	C(7)	5418 (3)	4872 (2)	7581 (3)
C(8)	−413 (2)	4924 (2)	2552 (3)	C(8)	6707 (3)	5252 (2)	7096 (4)
C(9)	−715 (2)	6637 (3)	4634 (3)	C(9)	6524 (2)	6588 (3)	9631 (3)
C(10)	1823 (2)	7732 (2)	243 (2)	C(10)	6346 (2)	8180 (2)	4656 (2)
C(11)	144 (2)	8179 (2)	−411 (2)	C(11)	4437 (2)	7593 (2)	5325 (2)
C(12)	1884 (3)	8923 (3)	−2015 (3)	C(12)	4904 (3)	8808 (3)	3068 (3)
H(2)	190 (2)	708 (2)	305 (3)	H(2)	790 (2)	804 (2)	679 (3)
H(3)	171 (2)	912 (3)	421 (3)	H(3)	720 (3)	956 (3)	845 (4)
H(4)	−7 (2)	967 (3)	348 (3)	H(4)	518 (3)	898 (3)	924 (3)
H(5)	−142 (3)	801 (3)	179 (3)	H(5)	408 (3)	693 (2)	813 (3)
H(71)	−225 (3)	477 (3)	249 (4)	H(71)	522 (3)	425 (3)	836 (3)
H(72)	−165 (2)	521 (2)	90 (3)	H(72)	488 (3)	467 (3)	670 (4)
H(81)	6 (2)	478 (3)	154 (3)	H(81)	676 (3)	527 (3)	601 (4)
H(82)	−49 (2)	425 (3)	327 (3)	H(82)	722 (3)	483 (3)	751 (3)
H(91)	−120 (3)	594 (3)	518 (3)	H(91)	665 (2)	740 (2)	1026 (3)
H(92)	−44 (3)	751 (3)	541 (4)	H(92)	668 (3)	591 (3)	1006 (4)
H(121)	260 (4)	880 (4)	−216 (5)	H(121)	417 (5)	890 (4)	311 (5)
H(122)	183 (4)	975 (4)	−195 (5)	H(122)	501 (4)	835 (4)	208 (5)
H(123)	148 (3)	853 (4)	−302 (5)	H(123)	543 (4)	963 (4)	312 (5)

The structures were refined by least squares by means of *SHELX* (Sheldrick, 1976) with, for [4.2.1]P, each of the two crystallographically independent molecules in a separate block, anisotropic for non-hydrogen, isotropic for H atoms; for [4.3.1]P and [4.4.1]P in two separate blocks: anisotropic for non-hydrogen, isotropic for H atoms.

Scattering factors for C, N and O were taken from Cromer & Mann (1968), for H from Stewart, Davidson & Simpson (1965). The final agreement factors and weighting schemes are given in Table 1. Final positional parameters are listed in Tables 2, 3 and 4.* Bond lengths and angles are shown in Figs. 1, 2 and 3.

The C–H distances (not shown) lie in the range 0·85–1·11 Å. Stereoscopic drawings down C(1)–C(6) are given in Figs. 4, 5, 6 {molecule (*A*) of [4.2.1]P is

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35477 (38 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. [4.3.1]P: *positional parameters for non-hydrogen atoms* $(\times 10^4)$ *and for* H *atoms* $(\times 10^3)$ (*e.s.d.'s in parentheses*)

	x	*y*	*z*		*x*	*y*	*z*
O(1)	2859 (3)	−851 (4)	6968 (0)	C(16)	4781 (6)	1232 (6)	3211 (10)
O(2)	2126 (3)	3289 (4)	5839 (7)	C(17)	4972 (4)	819 (6)	4478 (10)
N(1)	1615 (3)	477 (4)	7498 (6)	C(18)	4253 (4)	793 (6)	5399 (8)
N(2)	2632 (3)	1164 (4)	6001 (6)	H(2)	181 (3)	−69 (4)	916 (4)
N(3)	1381 (3)	1772 (4)	7136 (7)	H(3)	268 (4)	105 (5)	1020 (7)
C(1)	487 (4)	508 (5)	9216 (8)	H(4)	218 (4)	314 (6)	965 (7)
C(2)	1516 (4)	262 (6)	8963 (7)	H(5)	96 (4)	343 (5)	801 (5)
C(3)	2116 (5)	1255 (8)	9594 (8)	H(71)	−102 (5)	250 (7)	827 (9)
C(4)	1886 (5)	2429 (9)	9272 (9)	H(72)	−47 (3)	189 (5)	709 (6)
C(5)	1086 (5)	2545 (5)	8306 (9)	H(81)	−153 (4)	64 (7)	913 (7)
C(6)	219 (4)	1856 (5)	8802 (9)	H(82)	−145 (3)	18 (6)	756 (6)
C(7)	−657 (5)	1787 (7)	7994 (10)	H(91)	−9 (4)	−89 (6)	791 (7)
C(8)	−1083 (5)	462 (8)	8327 (11)	H(92)	−48 (4)	−104 (5)	928 (6)
C(9)	−254 (5)	−396 (6)	8688 (9)	H(101)	63 (4)	172 (5)	1092 (6)
C(10)	162 (5)	1480 (7)	10222 (9)	H(102)	−42 (5)	127 (6)	1059 (6)
C(11)	2426 (4)	143 (5)	6853 (7)	H(14)	248 (4)	203 (5)	358 (6)
C(12)	2055 (4)	2207 (5)	6275 (7)	H(15)	378 (4)	193 (5)	196 (6)
C(13)	3365 (3)	1164 (5)	5035 (7)	H(16)	528 (4)	130 (5)	256 (6)
C(14)	3176 (4)	1577 (6)	3782 (8)	H(17)	564 (3)	62 (4)	465 (5)
C(15)	3888 (6)	1596 (6)	2857 (8)	H(18)	438 (3)	37 (5)	622 (7)

Table 4. [4.4.1]P: *positional parameters for non-hydrogen atoms* $(\times 10^4)$ *and for* H *atoms* $(\times 10^3)$ (*e.s.d.'s in parentheses*

	x	*y*	*z*		*x*	*y*	*z*
O(1)	6229 (4)	−2565 (2)	9458 (0)	H(2)	626 (4)	−66 (3)	1031 (4)
O(2)	9389 (4)	−1570 (2)	6422 (4)	H(31)	892 (7)	−108 (5)	1037 (6)
N(1)	6777 (3)	−1017 (2)	8662 (4)	H(32)	878 (4)	−1 (3)	1076 (4)
N(2)	7759 (3)	−2336 (2)	7782 (4)	H(41)	1024 (6)	56 (4)	919 (6)
N(3)	7750 (3)	−708 (2)	7687 (4)	H(42)	1038 (5)	−59 (4)	879 (4)
C(1)	6424 (4)	663 (2)	9288 (5)	H(5)	922 (4)	44 (3)	720 (4)
C(2)	6944 (4)	−357 (3)	9727 (5)	H(71)	729 (6)	194 (4)	682 (5)
C(3)	8624 (5)	−384 (3)	10111 (5)	H(72)	662 (6)	91 (4)	658 (5)
C(4)	9654 (4)	−31 (3)	9068 (6)	H(81)	462 (5)	213 (4)	669 (5)
C(5)	8640 (4)	206 (3)	7978 (5)	H(82)	506 (5)	248 (4)	785 (6)
C(6)	7405 (4)	994 (3)	8244 (5)	H(91)	303 (7)	127 (5)	793 (7)
C(7)	6676 (6)	1444 (3)	7152 (5)	H(92)	407 (5)	45 (4)	750 (5)
C(8)	5065 (6)	1863 (3)	7386 (6)	H(101)	408 (5)	19 (3)	956 (4)
C(9)	4089 (5)	1087 (3)	8016 (6)	H(102)	445 (6)	141 (4)	986 (5)
C(10)	4673 (4)	832 (3)	9268 (6)	H(111)	848 (4)	145 (3)	994 (4)
C(11)	7479 (5)	1538 (2)	9416 (5)	H(112)	709 (4)	219 (3)	947 (4)
C(12)	6854 (4)	−2044 (3)	8735 (5)	H(141)	887 (7)	−338 (4)	678 (6)
C(13)	8440 (5)	−1536 (2)	7212 (5)	H(142)	735 (7)	−367 (5)	728 (6)
C(14)	8137 (5)	−3372 (3)	7535 (6)	H(143)	867 (8)	−368 (5)	830 (8)

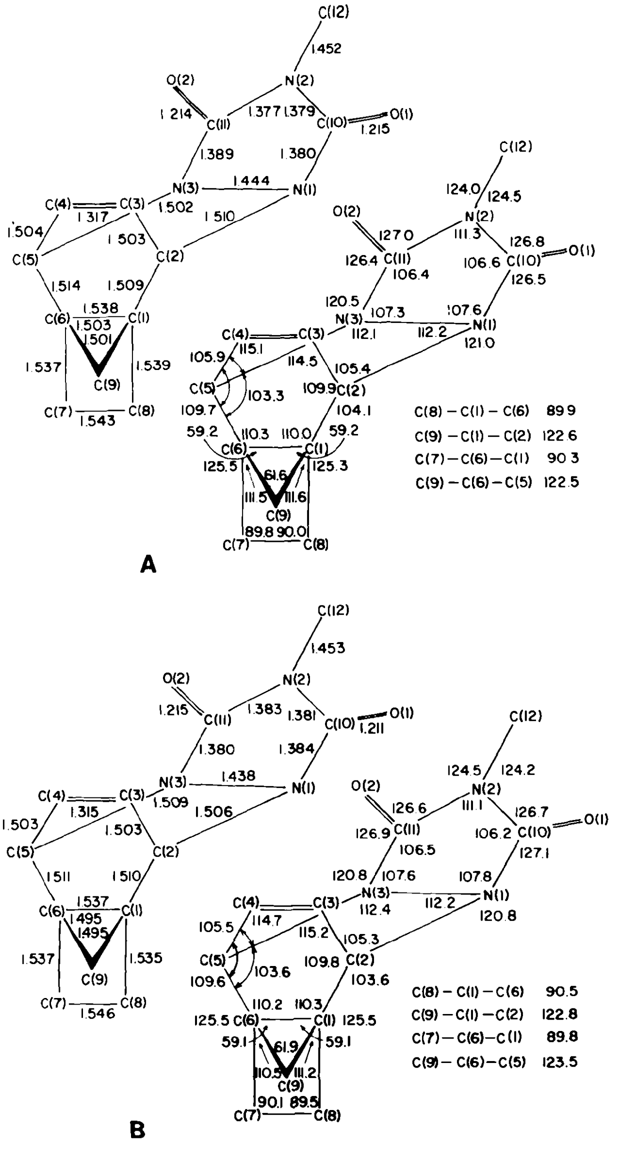


Fig. 1. Bond lengths (Å) and angles (°) in [4.2.1]P. E.s.d.'s of bond lengths are typically 0·003–0·004 Å, of angles 0·1–0·2°.

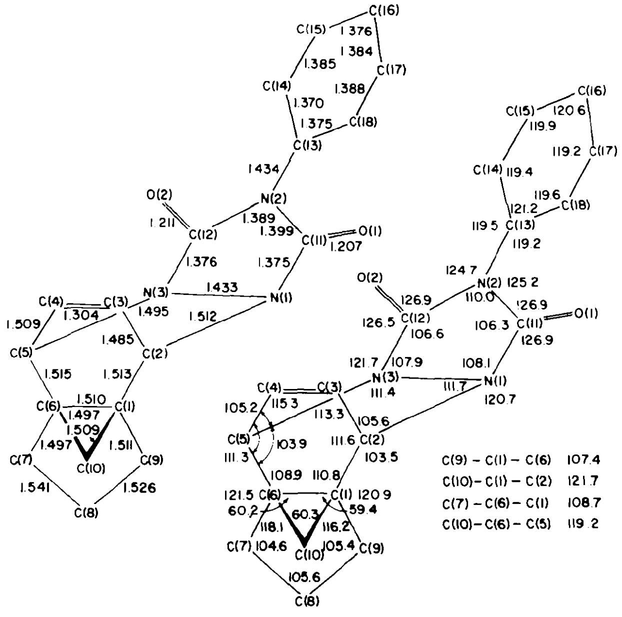


Fig. 2. Bond lengths (Å) and angles (°) in [4.3.1]P. E.s.d.'s of bond lengths are typically 0·006–0·008 Å, of angles 0·4–0·6°.

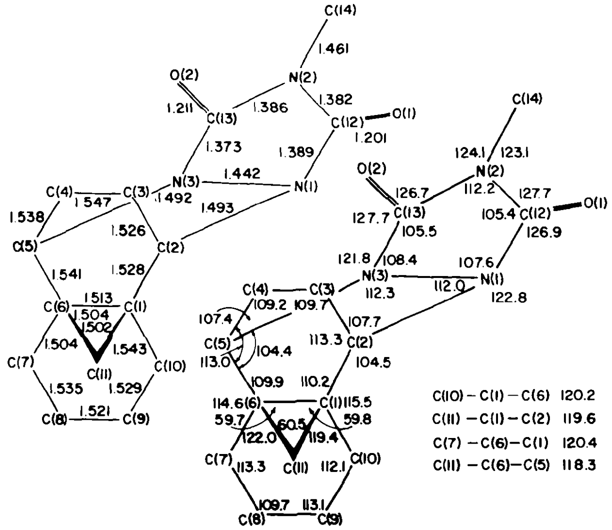


Fig. 3. Bond lengths (Å) and angles (°) in [4.4.1]P. E.s.d.'s of bond lengths are typically 0·005–0·007 Å, of angles 0·3–0·4°.

given in Fig. 4 as the two crystallographically independent molecules are practically the same}.

Discussion

Bond lengths and angles

The bond lengths and angles do not differ significantly among the three title compounds. However, comparison with bond lengths and angles obtained in related compounds (Kaftory, 1980) shows that C(1)–C(2), C(5)–C(6) and the bridging C(1)–C(6) are considerably shorter: 1·509–1·515 Å for the first two types in compounds [4.2.1]P and [4.3.1]P, 1·528–1·541 Å in [4.4.1]P; 1·513–1·537 Å for the third type. The ranges of equivalent bond lengths in related compounds (Kaftory, 1980) are: 1·536–1·574 Å for C(1)–C(2), C(5)–C(6) and 1·552–1·580 Å for C(1)–C(6). The shortening must be caused by the cyclopropane which lowers the hybridization of C atoms from sp^3 towards sp^2 as was found to a greater extent in σ-homobenzenes (Heller, Dreiding, Grieb & Niggli, 1972). Bond angles are in good agreement with those of the related compounds.

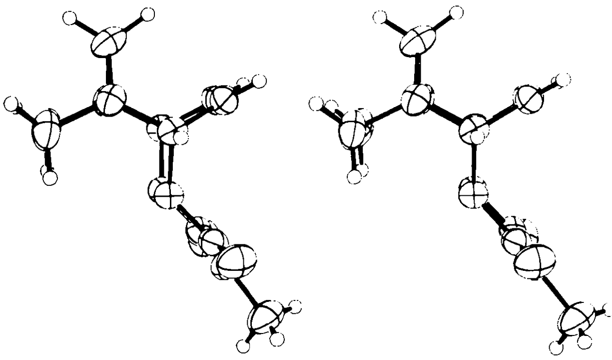


Fig. 4. Stereoview of [4.2.1]P molecule (*A*) (Johnson, 1965).

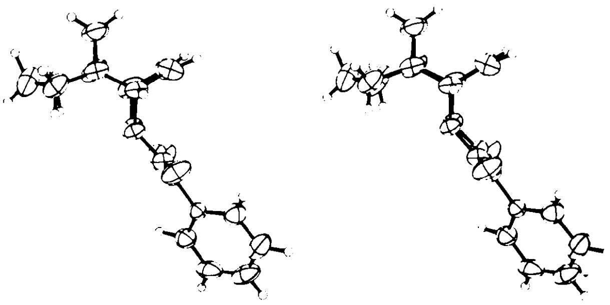


Fig. 5. Stereoview of [4.3.1]P.

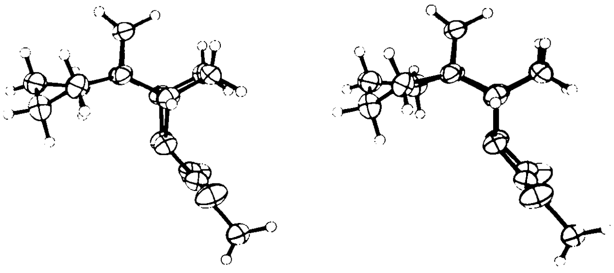


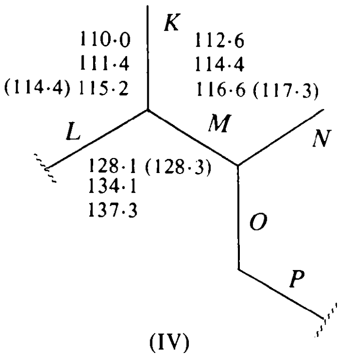
Fig. 6. Stereoview of [4.4.1]P.

Configuration and conformation

As was expected the H atoms of the cyclopropane govern the direction of attack by the substituted triazoline leading to a configuration *anti* to the cyclopropane. The same configuration was observed previously (Kaftory, 1978, 1980).

The saturated and unsaturated substituted six-membered rings have the same boat conformation imposed by the rigid substituent on C(2)···C(5). The four-membered ring in [4.2.1]P is planar (mean-plane displacements are within ±0·003 Å). The five-membered ring in [4.3.1]P has an envelope shape, C(8) flapping towards the cyclopropane [mean-plane displacement of C(8) is 0·388 Å]. The unsubstituted six-membered ring in [4.4.1]P has a half-chair conformation, while in other related compounds (Kaftory, 1978, 1980 compound *a*) that ring adopted the boat conformation. As a half-chair is expected to be more stable than a boat conformation it must be concluded that in the other related compounds one should not exclude packing forces in explaining the relative stability of different conformations.

The angles between planes described in (IV) may be compared with those given by Kaftory (1980) (Table 10 and Fig. 13). The angles between planes O···P are in a good agreement with those observed in similar compounds with triazoline as the substituent (135·0, 135·4° in [4.2.1]P; 135·6° in [4.3.1]P and 137·6° in [4.4.1]P). Significant differences have been observed in angles involved with the planes *K*, *L* and *M*. Angles between *L*···*M* increase in going from [4.2.1]P to [4.4.1]P, angles between *K*···*M* and *K*···*L* decrease. As the change in the angle between *K*···*L* is the least significant it seems reasonable to conclude that the order of increasing steric hindrance between the triazoline moiety and the rings *syn* to it is from four- to six-membered rings.



(IV)

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