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The Structures of *syn*- and *anti*-2,3;4,5-Diepoxy-12-oxa[4.4.3]propellane

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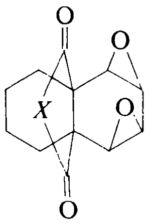
Abstract

syn-2,3:4,5-Diepoxy-12-oxa[4.4.3]propellane (DIUP) ($C_{12}H_{16}O_3$, M_r = 208·25) is monoclinic, $P2_1/n$, a = 11·144 (5), b = 12·305 (6), c = 7·685 (4) Å, β = 102·27 (2)°, Z = 4, D_x = 1·344 Mg m^{-3}. The *anti* isomer (DIDN) is monoclinic, $P2_1/c$, a = 14·174 (7), b = 11·564 (6), c = 14·457 (7) Å, β = 119·55 (3)°, Z = 8, D_x = 1·341 Mg m^{-3}. The final R values are 0·057 (DIUP) and 0·073 (DIDN). The conformations of the *syn* isomer and the two crystallographically independent molecules of the *anti* isomer are similar. The substituted six-membered ring has a twist-boat conformation; the unsubstituted one adopts the chair conformation while the hetero five-membered ring has an envelope shape.

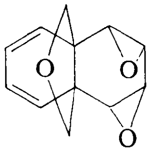
Introduction

In a series of publications dealing with the crystal structures of the similar compounds (I), (II), (III) (Kaftory, 1978, 1979*a*,*b*) a 'significant deviation from the mirror symmetry expected from the formula' has been observed. The distortion was attributed to an attractive intramolecular O···C=O interaction (Bürgi, Dunitz & Shefter, 1974). The distortion described by the torsion angle on the bridged C(1)–C(6) bond (~40°) was observed in the compounds of type (I) where the central five-membered ring was an amide or anhydride, both containing carbonyl groups, and in (II) where the unsubstituted six-membered ring was unsaturated.

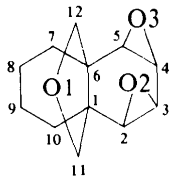


(I)

X = NCH_3, O



(II)



(III)

The distortion in (II) can hardly be explained in terms of a secondary orbital-overlap interaction.

The crystal structures of the two isomers, *syn* and *anti*, of (III) have been determined in the hope that the structure of a saturated compound and the absence of carbonyl groups will clarify the previous observations.

Experimental

Intensities from colourless prismatic crystals [0·3 × 0·3 × 0·4 mm (DIUP) and 0·25 × 0·25 × 0·2 mm (DIDN)] were collected on a Philips PW 1100 four-circle computer-controlled diffractometer with graphite-monochromated Cu $K\alpha$ radiation (λ = 1·5418 Å).

Crystallographic data and details of intensity measurements are given in Table 1. The structures were solved with *MULTAN* (Main, Woolfson, Lessinger, Germain & Declercq, 1977) and refined by least

Table 1. *Crystallographic data and experimental details*

	DIUP	DIDN
Formula	$C_{12}H_{16}O_3$	$C_{12}H_{16}O_3$
a (Å)	11·144 (5)	14·174 (7)
b (Å)	12·305 (6)	11·564 (6)
c (Å)	7·685 (4)	14·457 (7)
β (°)	102·27 (2)	119·55 (3)
Z	4	8
Space group	$P2_1/n$	$P2_1/c$
D_x (Mg m^{-3})	1·344	1·341
λ (Å)	1·5418	1·5418
Scan mode	ω/θ	ω/θ
$\Delta\omega$ (°)	1·0 + 0·1 tan θ	1·0
Scan speed (° s^{-1})	0·05	0·05
Background time* (s)	20·0	20·0
θ_{max} (°)	63·0	63·0
Reflections measured	1743	3363
Significant†	1640	2477
Weighting coefficients‡ (k; g)	0·3974; 0·0244	1·5197; 0·0029
R_w	0·082	0·076
R	0·057	0·073

* Total background counting time.
† $F_o > 0·0$; $F_o > 1·5\sigma(F_o)$.
‡ $W = k/[\sigma^2(F_o) + gF_o^2]$.

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Table 2. DIUP–*atomic coordinates* ($\times 10^4$; *for* H $\times 10^3$) *with e.s.d.'s in parentheses*

	x	*y*	*z*		*x*	*y*	*z*
O(1)	4692 (1)	1545 (1)	5667 (2)	H(3)	26 (3)	314 (2)	618 (4)
O(2)	1795 (2)	3721 (1)	5436 (2)	H(4)	117 (3)	250 (2)	882 (4)
O(3)	2979 (1)	2494 (1)	8434 (2)	H(5)	255 (2)	92 (2)	888 (3)
C(1)	2587 (2)	1889 (1)	4590 (2)	H(71)	199 (2)	−49 (2)	650 (3)
C(2)	1538 (2)	2676 (2)	4549 (3)	H(72)	98 (2)	35 (2)	581 (3)
C(3)	1085 (2)	2928 (2)	6162 (3)	H(81)	113 (3)	−99 (2)	360 (4)
C(4)	1669 (2)	2399 (2)	7869 (3)	H(82)	251 (3)	−76 (2)	368 (3)
C(5)	2473 (2)	1454 (2)	7821 (2)	H(91)	62 (3)	81 (2)	250 (4)
C(6)	2698 (2)	1014 (1)	6094 (2)	H(92)	136 (3)	18 (3)	107 (4)
C(7)	1796 (2)	64 (2)	5620 (3)	H(101)	233 (3)	186 (2)	184 (4)
C(8)	1714 (3)	−409 (2)	3772 (3)	H(102)	321 (3)	107 (2)	249 (3)
C(9)	1440 (3)	474 (2)	2370 (3)	H(111)	413 (3)	276 (2)	404 (4)
C(10)	2448 (2)	1329 (2)	2757 (3)	H(112)	391 (2)	294 (2)	604 (4)
C(11)	3856 (2)	2412 (2)	5046 (3)	H(121)	418 (2)	0 (2)	570 (3)
C(12)	4061 (2)	689 (2)	6341 (3)	H(122)	442 (3)	60 (2)	772 (4)
H(2)	92 (3)	277 (2)	344 (4)				

Table 3. DIDN–*atomic coordinates* ($\times 10^4$; *for* H $\times 10^3$) *with e.s.d.'s in parentheses*

	x	*y*	*z*		*x*	*y*	*z*
Molecule *A*							
O(1)	4601 (2)	2166 (2)	3729 (2)	H(3)	630 (2)	−93 (2)	546 (2)
O(2)	6067 (2)	−1311 (2)	3985 (2)	H(4)	801 (3)	−9 (3)	600 (3)
O(3)	7810 (2)	165 (2)	4526 (2)	H(5)	793 (3)	179 (3)	510 (3)
C(1)	5443 (2)	724 (2)	3216 (2)	H(71)	706 (3)	294 (3)	363 (3)
C(2)	5440 (3)	−290 (3)	3899 (3)	H(72)	585 (3)	297 (3)	285 (3)
C(3)	6399 (3)	−596 (3)	4908 (3)	H(81)	741 (3)	139 (3)	278 (3)
C(4)	7416 (3)	72 (3)	5264 (3)	H(82)	689 (3)	250 (3)	198 (3)
C(5)	7370 (3)	1176 (3)	4755 (3)	H(91)	594 (3)	70 (3)	116 (3)
C(6)	6299 (2)	1648 (3)	3896 (2)	H(92)	517 (3)	163 (3)	132 (3)
C(7)	6489 (3)	2493 (3)	3195 (3)	H(101)	477 (3)	−13 (3)	174 (3)
C(8)	6723 (3)	1903 (4)	2394 (3)	H(102)	615 (3)	−35 (3)	255 (3)
C(9)	5768 (3)	1158 (3)	1648 (3)	H(111)	426 (3)	192 (3)	224 (3)
C(10)	5524 (3)	251 (3)	2259 (3)	H(112)	385 (3)	89 (3)	275 (3)
C(11)	4405 (3)	1417 (3)	2870 (3)	H(121)	595 (3)	312 (3)	456 (3)
C(12)	5732 (3)	2252 (3)	4424 (3)	H(122)	584 (3)	183 (3)	507 (3)
H(2)	469 (3)	−51 (3)	378 (3)				
Molecule *B*							
O(1)	2342 (3)	−285 (3)	9822 (3)	H(3)	267 (4)	173 (4)	730 (4)
O(2)	1930 (2)	2892 (2)	7851 (2)	H(4)	95 (3)	96 (3)	605 (3)
O(3)	6 (2)	1656 (2)	6642 (2)	H(5)	−7 (3)	−8 (3)	666 (3)
C(1)	1509 (2)	1475 (3)	8954 (2)	H(71)	−49 (3)	−42 (3)	810 (3)
C(2)	2269 (3)	1912 (3)	8561 (3)	H(72)	15 (3)	−13 (3)	930 (4)
C(3)	2005 (3)	1775 (3)	7455 (3)	H(81)	−109 (3)	157 (3)	768 (4)
C(4)	972 (3)	1209 (3)	6699 (3)	H(82)	−132 (4)	106 (4)	860 (4)
C(5)	390 (3)	550 (3)	7113 (3)	H(91)	−54 (4)	284 (4)	910 (4)
C(6)	811 (2)	433 (3)	8291 (2)	H(92)	24 (4)	181 (4)	997 (4)
C(7)	−107 (3)	184 (4)	8522 (4)	H(101)	124 (4)	295 (4)	950 (4)
C(8)	−783 (4)	1230 (4)	8433 (4)	H(102)	62 (2)	297 (3)	835 (3)
C(9)	−76 (4)	2146 (4)	9219 (4)	H(111)	179 (3)	88 (4)	1044 (3)
C(10)	848 (4)	2481 (4)	9028 (4)	H(112)	290 (3)	135 (4)	1043 (3)
C(11)	2208 (4)	876 (5)	10027 (3)	H(121)	123 (3)	−132 (4)	861 (3)
C(12)	1652 (4)	−543 (4)	8733 (4)	H(122)	213 (3)	−57 (4)	834 (3)
H(2)	303 (3)	197 (3)	908 (3)				

squares with *SHELX* (Sheldrick, 1976). Both structures were refined with anisotropic thermal parameters for the non-hydrogen atoms, isotropic for H.

Scattering factors for C and O were taken from Cromer & Mann (1968), for H from Stewart, Davidson & Simpson (1965). The final $R = 0{\cdot}057$ (DIUP), $0{\cdot}073$ (DIDN); other details are given in Table 1.

Final positional parameters are listed in Tables 2 and

3.* Bond lengths, bond angles and torsion angles are given in Tables 4, 5 and 6 respectively.

Description of the structures

The molecular structures are shown stereoscopically in Figs. 1 (DIUP) and 2 (DIDN) (for DIDN molecule *B* is shown as both molecules are similar).

Table 4. *Bond lengths* (Å)

For atomic notation see (III). The e.s.d.'s of bond lengths are typically: 0·002–0·004 Å (DIUP), 0·004–0·007 Å (DIDN).

		DIDN	
	DIUP	*A*	*B*
C(1)–C(2)	1·514	1·536	1·530
C(1)–C(6)	1·565	1·552	1·554
C(1)–C(10)	1·546	1·543	1·532
C(1)–C(11)	1·525	1·528	1·533
C(2)–O(2)	1·454	1·446	1·443
C(2)–C(3)	1·467	1·464	1·461
C(3)–O(2)	1·441	1·438	1·438
C(3)–C(4)	1·485	1·485	1·480
C(4)–O(3)	1·437	1·433	1·428
C(4)–C(5)	1·474	1·460	1·453
C(5)–O(3)	1·437	1·439	1·426
C(5)–C(6)	1·503	1·512	1·508
C(6)–C(7)	1·534	1·525	1·523
C(6)–C(12)	1·543	1·524	1·535
C(7)–C(8)	1·519	1·516	1·508
C(8)–C(9)	1·515	1·517	1·516
C(9)–C(10)	1·521	1·518	1·516
C(11)–O(1)	1·430	1·426	1·409
C(12)–O(1)	1·424	1·415	1·417

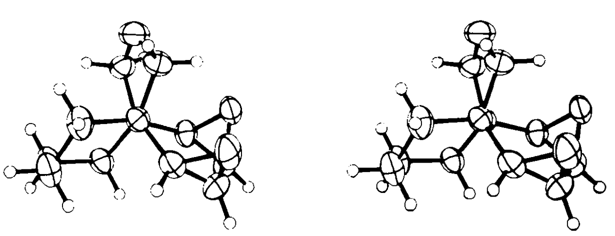

Fig. 1. Stereoscopic view of DIUP down C(1)–C(6), showing vibration ellipsoids at the 50% probability level (Johnson, 1965).

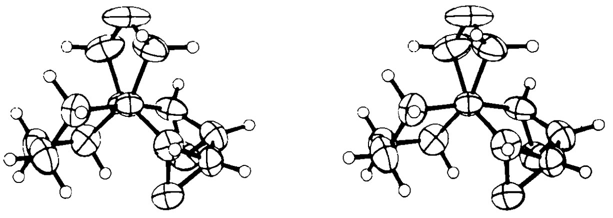

Fig. 2. Stereoscopic view of molecule *B* of DIDN down C(1)–C(6), showing vibrational ellipsoids at the 50% probability level (Johnson, 1965).

The two isomers do not differ in their basic conformation. The substituted six-membered ring adopts the twist-boat conformation while the unsubstituted ring has a chair conformation. The hetero five-membered ring has an envelope shape. In both structures intermolecular distances were not shorter than van der Waals contacts.

Discussion

Although all C atoms in both compounds should be tetrahedral, bond lengths and angles indicate that there are two main types of C atoms. The longer pure $C(sp^3)$–$C(sp^3)$ single bonds (average 1·527 Å) involve all C atoms except those of the oxirane rings. The

Table 5. *Bond angles* (°)

For atomic notation see (III). The e.s.d.'s of bond angles are typically: 0·2–0·3° (DIUP), 0·2–0·4° (DIDN).

		DIDN	
	DIUP	*A*	*B*
C(2)–C(1)–C(6)	113·3	111·6	112·2
C(2)–C(1)–C(10)	109·8	109·3	110·0
C(2)–C(1)–C(11)	114·1	107·7	107·7
C(6)–C(1)–C(10)	110·1	115·6	114·0
C(6)–C(1)–C(11)	101·4	99·9	99·8
C(10)–C(1)–C(11)	107·9	112·2	112·6
O(2)–C(2)–C(1)	118·8	118·9	118·4
C(1)–C(2)–C(3)	121·4	122·0	121·6
O(2)–C(2)–C(3)	59·1	59·2	59·4
O(2)–C(3)–C(2)	60·0	59·8	59·7
O(2)–C(3)–C(4)	117·7	116·1	116·8
C(2)–C(3)–C(4)	119·3	119·0	118·9
C(2)–O(2)–C(3)	60·9	61·0	60·9
O(3)–C(4)–C(3)	117·2	116·7	117·0
C(3)–C(4)–C(5)	118·6	119·1	118·9
O(3)–C(4)–C(5)	59·1	59·6	59·3
C(4)–O(3)–C(5)	61·7	61·1	61·2
O(3)–C(5)–C(4)	59·1	59·2	59·5
O(3)–C(5)–C(6)	118·9	118·6	117·8
C(4)–C(5)–C(6)	121·5	120·5	121·6
C(1)–C(6)–C(5)	113·7	115·2	113·9
C(1)–C(6)–C(7)	113·8	111·1	111·4
C(1)–C(6)–C(12)	100·9	101·1	100·8
C(5)–C(6)–C(7)	105·1	110·1	111·1
C(5)–C(6)–C(12)	109·2	108·6	109·3
C(7)–C(6)–C(12)	114·2	110·4	109·9
C(6)–C(7)–C(8)	114·8	113·4	113·9
C(7)–C(8)–C(9)	110·7	110·1	109·9
C(8)–C(9)–C(10)	109·2	111·0	110·7
C(9)–C(10)–C(1)	114·4	114·6	115·5
O(1)–C(11)–C(1)	105·5	107·0	107·8
O(1)–C(12)–C(6)	108·3	107·8	106·0
C(11)–O(1)–C(12)	109·6	109·1	110·1

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* Lists of structure factors and anisotropic thermal parameters and figures showing the crystal packing for both compounds have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35394 (29 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 6. *Torsion angles* (°)

For atomic notations see (III). The e.s.d.'s in torsion angles are typically: 0·5–0·7° (DIUP), 0·6–0·8° (DIDN). The signs of the torsion angles do not have any absolute significance as both enantiomers are present in the crystals.

	DIUP	DIDN	
		A	*B*
C(1)–C(2)–C(3)–C(4)	0·1	−1·9	0·6
C(2)–C(3)–C(4)–C(5)	−14·4	15·0	−15·6
C(3)–C(4)–C(5)–C(6)	−0·7	1·6	0·2
C(4)–C(5)–C(6)–C(1)	28·2	−30·3	28·7
C(5)–C(6)–C(1)–C(2)	−40·0	40·3	−40·6
C(6)–C(1)–C(2)–C(3)	27·3	−25·5	27·6
C(1)–C(6)–C(7)–C(8)	46·1	−50·9	51·3
C(6)–C(7)–C(8)–C(9)	−53·7	61·1	−60·3
C(7)–C(8)–C(9)–C(10)	58·8	−58·6	57·9
C(8)–C(9)–C(10)–C(1)	−60·0	49·3	−50·6
C(9)–C(10)–C(1)–C(6)	51·4	−41·0	42·7
C(10)–C(1)–C(6)–C(7)	−43·0	40·5	−41·3
C(1)–C(11)–O(1)–C(12)	−24·7	17·4	−9·7
C(11)–O(1)–C(12)–C(6)	1·6	7·9	−15·9
O(1)–C(12)–C(6)–C(1)	21·2	−29·1	34·1
C(12)–C(6)–C(1)–C(11)	−34·1	37·1	−37·5
C(6)–C(1)–C(11)–O(1)	36·9	−34·4	30·3

C—C—C angles on those atoms are tetrahedral. The shorter bond lengths (average 1·470 Å) are between C atoms of the oxirane rings and are close to the typically $C(sp^2)$—$C(sp^2)$ single bond. The bond angles are close to 120° (Table 5). The geometrical parameters of the second type of C atoms are due to multiconjugated interactions (for comparisons see Kaftory, 1979*b*, Table 7 and references cited therein).

Mean-plane calculations show that the five-membered ring has an envelope shape with one of the bridging atoms [C(1) or C(6)] as the flap. Departures from planarity are: C(1) −0·583 (DIUP), C(1) 0·581, C(6) −0·601 Å (DIDN) in molecules *A* and *B* respectively.

The dihedral angles between oxirane rings and the plane through the neighbouring atoms are: 106·7, 107·0° (DIUP) and 105·9, 106·4, 106·2, 105·9° (DIDN), in good agreement with similar compounds (Kaftory, 1979*b*, Table 7). The intramolecular non-bonded distances between the O atoms and the methylene C(11), C(12) of the *syn* isomer should be compared with the distances to the carbonyl C atoms of (I) (Kaftory, 1978, 1979*a*). The distances are O(2)···C(11) 2·872, O(2)···C(12) 4·475, O(3)···C(11) 2·970, O(3)···C(12) 3·130 Å compared with 2·852–2·900, 4·396–4·449, 2·797–2·865, 2·942–2·981 Å respectively.

The torsion angle of ~40° on the bridging atoms C(1) and C(6), though there is no secondary type of interaction available, led to the conclusion that the explanation given in previous publications (Kaftory, 1978, 1979*a*,*b*) is incorrect. The deviations from mirror symmetry imposed by the non-zero torsion angle on the bridging atoms was attributed to an attractive interaction of the epoxy O atom lone pair to the carbonyl C atom of the central ring. The structures of the title compounds show the same type of deviation although no carbonyl groups are present.

The geometrical resemblance between a three-membered ring and unsaturated bonds was observed in a variety of compounds. In some σ-homobenzene compounds the cyclohexane ring is planar (Kabuto, Yagihara, Asao & Kitahara, 1973; Littke & Drück, 1974); bond lengths tend to be shortened from a $C(sp^3)$—$C(sp^3)$ single bond (see comparison in Table 7, Kaftory, 1979*b*). On the basis of these observations it would be reasonable to compare the conformation of the oxa-substituted cyclic skeleton with the parent structures. 2,3;4,5-Diepoxycyclohexane should therefore be compared with 2,4-cyclohexadiene which, in its stable conformation, is not planar, in spite of the conjugated diene system. Microwave spectroscopy, electron diffraction and molecular-mechanics calculations show a torsion angle of 12–18° on the C(3)—C(4) bond and one of 45° on C(1)—C(6), leading to a twist-boat conformation (Trætteberg, 1968; Oberhammer & Bauer, 1969; Allinger & Sprague, 1973). The torsion angles obtained in the title compounds are in good agreement with those of the parent compound [−14·4° on C(3)—C(4) (DIUP); 15·0, −15·6° (DIDN); −40·0° on C(1)—C(6) (DIUP); 40·3, −40·6° (DIDN)]. Similar values were observed in tripdiolide and triptolide (Gilmore & Bryan, 1973) (−14·6, −37·8°; −16·2, −39·5°), and by Kaftory (1978, 1979*a*,*b*) (18·0, 41°; mean values −18, −42°). The most stable conformation of cyclohexane is the chair form. When cyclohexane is fused to another ring it can be either a *trans* or a *cis* fusion. The propellanes are *cis* fused; hence, the conformation of one ring is transmitted to the others. The conformation of [4.4.4]-propellane (Ermer, Gerdil & Dunitz, 1971) is all-chair (D_3 virtual symmetry); the most stable chair conformation is transmitted to the other two cyclohexane rings. The torsion angle [C(1)—C(6)] in the substituted ring of the title compounds (mean value 40·3°) is transmitted to the unsubstituted six-membered ring, leading to a somewhat flattened chair conformation. The five-membered ring, which is a puckered flexible ring and characterized by pseudorotation, has no energy barriers (During & Wertz, 1968; Adams, Geise & Bartell, 1970). Hence, the conformation of this ring (an envelope conformation in the title compounds) has no influence on the stability of the overall molecular conformation.

Conclusion

The evidence from this analysis leads to the conclusion that the deviations from mirror symmetry are inherent from conformation-stability arguments rather than due to the attractive interaction of the O atom lone-pair electrons.

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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 $P\bar{1}$, $a = 11.873\,(6)$, $b = 11.100\,(6)$, $c = 8.648\,(4)$ Å, $\alpha = 98.54\,(2)$, $\beta = 89.40\,(2)$, $\gamma = 105.50\,(2)°$, final $R = 0.054$; [4.3.1]P: $C_{18}H_{17}N_3O_2$, space group $Pna2_1$, $a = 14.267\,(7)$, $b = 10.381\,(5)$, $c = 10.160\,(5)$ Å, final $R = 0.067$; [4.4.1]P: $C_{14}H_{19}N_3O_2$, space group $Pna2_1$, $a = 8.711\,(4)$, $b = 13.476\,(7)$, $c = 11.178\,(5)$ Å, final $R = 0.045$.}

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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