

The Monoadduct Between 8-Oxa-11-thia[4.3.3]propella-2,4-diene and 4-Phenyl-1,2,4-triazoline-3,5-dione*

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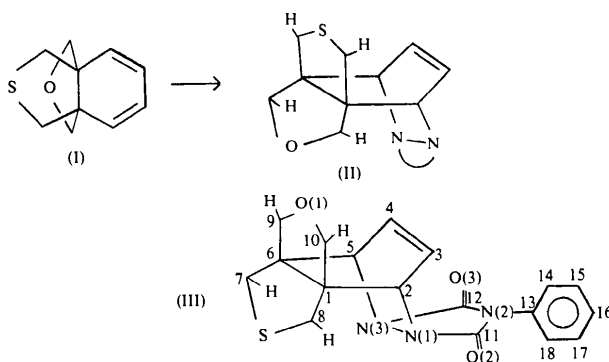
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Abstract. $C_{18}H_{17}N_3O_3S$, monoclinic, $P2_1/c$, $a = 9.250$ (5), $b = 24.914$ (12), $c = 7.176$ (4) Å, $\beta = 100.12$ (3)°, $M_r = 355.04$, $Z = 4$, $D_x = 1.449$ Mg m⁻³. Final $R = 0.07$ for 2689 reflexions. The 4-substituted triazoline-3,5-dione is *syn* to the tetrahydrothiophene moiety, and *anti* to the tetrahydrofuran moiety. Both five-membered rings have envelope shapes, the S atom pointing away from the triazoline group, and the O atom pointing in the same direction. The cyclohexane ring adopts the boat conformation.

Introduction. The configuration of the title compound is of interest in connection with stereochemical studies of the Diels–Alder reaction and the factors which control the direction of dienophile attack on dienes (Ashkenazi, Kaftory, Grimme, Heger, Vogel & Ginsburg, 1980; Kaftory, 1980, and references therein).

The dienophile can attack (I) to obtain (II) or (III). The configuration will therefore depend on the steric repulsion of the H atoms.



* Configuration of Diels–Alder Adducts. VI.

Intensities from a colourless crystal (0.4 × 0.3 × 0.3 mm) were collected on a Philips PW 1100

Table 1. Positional parameters for non-hydrogen ($\times 10^4$) and H atoms ($\times 10^3$) (e.s.d.'s in parentheses)

$$U_{eq} (\text{Å}^2 \times 10^3) = \frac{1}{3} \text{trace } \hat{U}.$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}		<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
S	4286 (1)	2078 (1)	4263 (2)	49	C(15)	3545 (6)	−1308 (2)	−957 (7)	61
O(1)	446 (3)	1853 (1)	5907 (4)	51	C(16)	2954 (6)	−1743 (2)	−195 (8)	65
O(2)	1461 (4)	231 (1)	−554 (4)	46	C(17)	2261 (5)	−1679 (2)	1353 (8)	57
O(3)	3523 (3)	−374 (1)	5359 (4)	40	C(18)	2159 (4)	−1171 (2)	2132 (6)	42
N(1)	2231 (4)	663 (1)	2310 (4)	31	H(2)	47 (4)	112 (1)	113 (5)	
N(2)	2661 (4)	−212 (1)	2139 (4)	37	H(3)	−96 (4)	74 (2)	318 (6)	
N(3)	2915 (3)	476 (1)	4137 (4)	29	H(4)	21 (4)	45 (2)	617 (5)	
C(1)	1740 (4)	1539 (1)	3511 (5)	29	H(5)	283 (4)	60 (2)	696 (5)	
C(2)	1011 (4)	1042 (1)	2440 (5)	30	H(71)	463 (4)	157 (2)	699 (6)	
C(3)	4 (4)	776 (2)	3603 (6)	35	H(72)	479 (4)	118 (2)	522 (5)	
C(4)	672 (4)	619 (1)	5288 (5)	33	H(81)	339 (4)	150 (2)	168 (5)	
C(5)	2287 (4)	732 (1)	5678 (5)	28	H(82)	249 (5)	206 (2)	170 (6)	
C(6)	2560 (4)	1345 (1)	5504 (5)	30	H(91)	242 (5)	195 (2)	743 (6)	
C(7)	4184 (5)	1482 (2)	5717 (6)	42	H(92)	158 (5)	141 (2)	804 (6)	
C(8)	2864 (5)	1803 (2)	2458 (6)	42	H(101)	−36 (5)	190 (2)	322 (6)	
C(9)	1794 (5)	1655 (2)	6909 (5)	39	H(102)	93 (5)	234 (2)	382 (7)	
C(10)	614 (5)	1943 (2)	3987 (6)	41	H(14)	402 (5)	−45 (2)	−66 (6)	
C(11)	2019 (4)	226 (2)	1099 (5)	33	H(15)	401 (7)	−134 (2)	−211 (9)	
C(12)	3069 (4)	−75 (1)	4067 (5)	32	H(16)	306 (6)	−212 (2)	−79 (8)	
C(13)	2772 (4)	−737 (2)	1365 (5)	33	H(17)	186 (6)	−200 (2)	191 (8)	
C(14)	3474 (5)	−793 (2)	−188 (6)	47	H(18)	168 (4)	−111 (2)	325 (6)	

Table 2. Bond lengths (Å)

For atomic notation see (III). The e.s.d.'s are typically 0.004–0.006 Å.

S—C(7)	1.827	C(1)—C(6)	1.573
S—C(8)	1.811	C(1)—C(8)	1.536
O(1)—C(9)	1.414	C(1)—C(10)	1.532
O(1)—C(10)	1.431	C(2)—C(3)	1.510
O(2)—C(11)	1.208	C(3)—C(4)	1.317
O(3)—C(12)	1.204	C(4)—C(5)	1.497
N(1)—N(3)	1.430	C(5)—C(6)	1.556
N(1)—C(2)	1.488	C(6)—C(7)	1.522
N(1)—C(11)	1.386	C(6)—C(9)	1.539
N(2)—C(11)	1.394	C(13)—C(14)	1.392
N(2)—C(12)	1.410	C(13)—C(18)	1.381
N(2)—C(13)	1.431	C(14)—C(15)	1.402
N(3)—N(5)	1.481	C(15)—C(16)	1.371
N(3)—C(12)	1.382	C(16)—C(17)	1.386
C(1)—C(2)	1.547	C(17)—C(18)	1.394

Table 3. Bond angles (°)

For atomic notation see (III). The e.s.d.'s are typically 0.2–0.4°.

C(7)—S—C(8)	89.8	C(1)—C(6)—C(5)	108.4
C(9)—O(1)—C(10)	108.0	C(1)—C(6)—C(7)	109.4
N(3)—N(1)—C(2)	111.6	C(5)—C(6)—C(7)	112.5
N(3)—N(1)—C(11)	108.0	C(1)—C(6)—C(9)	103.7
C(2)—N(1)—C(11)	120.9	C(5)—C(6)—C(9)	109.8
C(11)—N(2)—C(12)	110.6	C(7)—C(6)—C(9)	112.4
C(11)—N(2)—C(13)	124.0	S—C(7)—C(6)	105.9
C(12)—N(2)—C(13)	125.2	S—C(8)—C(1)	106.2
N(1)—N(3)—C(5)	112.0	O(1)—C(9)—C(6)	108.0
N(1)—N(3)—C(12)	108.8	O(1)—C(10)—C(1)	107.7
C(5)—N(3)—C(12)	120.8	O(2)—C(11)—N(1)	126.7
C(2)—C(1)—C(6)	107.8	O(2)—C(11)—N(2)	127.0
C(2)—C(1)—C(8)	111.8	N(1)—C(11)—N(2)	106.2
C(6)—C(1)—C(8)	108.6	O(3)—C(12)—N(2)	127.1
C(2)—C(1)—C(10)	112.5	O(3)—C(12)—N(3)	127.5
C(6)—C(1)—C(10)	103.7	N(2)—C(12)—N(3)	105.3
C(8)—C(1)—C(10)	111.9	N(2)—C(13)—C(14)	118.6
N(1)—C(2)—C(1)	105.6	N(2)—C(13)—C(18)	119.9
N(1)—C(2)—C(3)	107.7	C(14)—C(13)—C(18)	121.5
C(1)—C(2)—C(3)	109.6	C(13)—C(14)—C(15)	118.0
C(2)—C(3)—C(4)	113.7	C(14)—C(15)—C(16)	121.1
C(3)—C(4)—C(5)	114.0	C(15)—C(16)—C(17)	120.2
N(3)—C(5)—C(4)	106.8	C(16)—C(17)—C(18)	119.9
N(3)—C(5)—C(6)	105.8	C(13)—C(18)—C(17)	119.4
C(4)—C(5)—C(6)	109.9		

four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å) in the $\omega/2\theta$ scanning mode. 2788 reflections were measured of which 2689 were above background ($F_o > 0.0$). The structure was solved with *MULTAN* 77 (Main, Woolfson, Lessinger, Germain & Declercq, 1977) and refined by least squares with *SHELX* (Sheldrick, 1976) in two blocks, with anisotropic non-hydrogen atoms in one, isotropic H atoms in the other. Scattering factors for C, N, O and S were taken from Cromer &

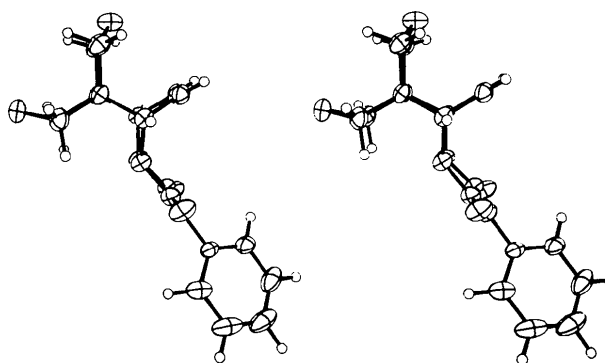


Fig. 1. Stereoview (Johnson, 1965) of a molecule down C(1)—C(6).

Mann (1968), for H from Stewart, Davidson & Simpson (1965). The final R for 2689 reflections was 0.07. Final positional parameters are listed in Table 1.* Bond lengths and angles are given in Tables 2 and 3. C—H distances lie in the range 0.87–1.10 Å.

Discussion. A stereoview of the molecule is shown in Fig. 1.* The configuration of the monoadduct indicates that the dienophile attacks *anti* to the ether ring, *syn* to the thioether ring. As a result of the shorter C—O compared with C—S bonds in the five-membered rings, the angles C(1)—C(6)—C(7), C(6)—C(1)—C(8) (in the thioether ring) (109.4, 108.6°) are larger than the equivalent ones in the ether ring (103.7, 103.7°). The opening of those angles prevents the methylenic H atoms from overlapping with the diene moiety, and enables a dienophile attack from that side of molecule (I).

Both five-membered rings have an envelope shape. The S atom of the thioether ring is displaced by 0.842 Å from the mean plane, away from the triazoline moiety; the O atom of the ether ring is displaced by 0.046 Å from the plane away from the thioether ring.

Bond lengths and angles are in good agreement with those in similar compounds (Kaftory, 1978, 1980). There are no intermolecular distances shorter than van der Waals contacts.

The author thanks Professor D. Ginsburg and Dr P. Ashkenazi for providing a sample of the compound.

* Lists of structure factors and anisotropic thermal parameters and a stereoview of the packing of molecules have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35548 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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The Bisadduct Between 12-Methyl-12-aza[4.4.3]propella-2,4,7,9-tetraene-11,13-dione and *N*-Phenylmaleimide*

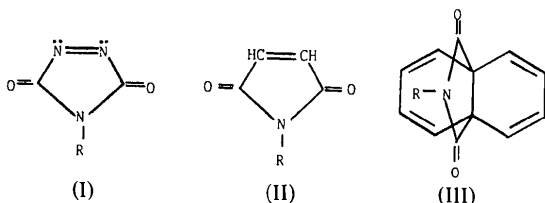
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(Received 21 June 1980; accepted 2 September 1980)

Abstract. C₃₃H₂₅N₃O₆·H₂O, monoclinic, *P*2₁/*n*, *a* = 20·340 (10), *b* = 9·111 (5), *c* = 15·149 (8) Å, β = 105·02 (4)°, *M_r* = 577·60, *Z* = 4, *D_x* = 1·415 Mg m⁻³. Final *R* = 0·056 for 3384 reflections. One of the *N*-phenylmaleimide molecules reacts *anti* to the central hetero-ring, the other *syn* to it. The title compound crystallizes with a molecule of water which is surrounded by carbonyl groups. The H atoms of the water molecule have not been located but the presence of hydrogen bonding is seen by the distances 2·940 and 3·059 Å between the O atom of the water molecule and carbonyl O atoms.

Introduction. 4-Substituted 1,2,4-triazoline-3,5-diones (I) attack the *syn* face of a cyclohexadiene with respect to the hetero-ring in propellanes of type (III). When —N=N— in the dienophile is replaced by —CH=CH— (II) the attack will take place on the face *anti* to the hetero-ring (Kaftory, Peled & Ginsburg, 1979; Kaftory, 1980, molecule *b*).



* Configuration of Diels–Alder Adducts. VII.

The structure of the monoadduct of the title compound has been determined (Kaftory, 1980) and shows that the first molecule of the dienophile attacks *anti*; the second can attack the other cyclohexadiene *syn* or *anti* to the hetero-ring.

As no secondary orbital overlap is available the configuration of the bisadduct is determined by the difference in the steric repulsions of the central hetero-ring and the mono substituent *anti* to that ring.

Intensities from a colourless crystal 0·3 × 0·2 × 0·2 mm were collected on a Philips PW 1100 four-circle computer-controlled diffractometer with graphite-monochromated Mo *K*α radiation (λ = 0·71069 Å).

The crystal structure was solved by *MULTAN 77* (Main, Woolfson, Lessinger, Germain & Declercq, 1977), and refined by full-matrix least squares (*SHELX*, Sheldrick, 1976) in three separate blocks, with anisotropic thermal parameters for C, N and O,

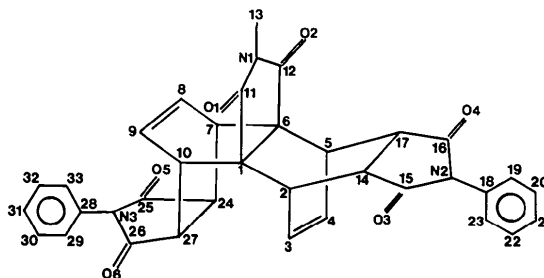


Fig. 1. Schematic drawing of the title compound showing atomic notation.