$C_{18}H_{17}N_3O_3S$

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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*
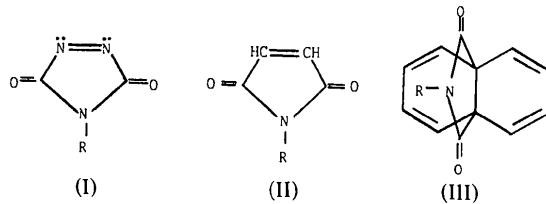
BY M. KAFTORY

Department of Chemistry, Technion–Israel Institute of Technology, Haifa, Israel

Abstract. $C_{33}H_{25}N_3O_6 \cdot H_2O$, monoclinic, $P2_1/n$, $a = 20\cdot340$ (10), $b = 9\cdot111$ (5), $c = 15\cdot149$ (8) Å, $\beta = 105\cdot02$ (4)°, $M_r = 577\cdot60$, $Z = 4$, $D_x = 1\cdot415$ Mg m^{-3}. Final $R = 0\cdot056$ 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 $2\cdot940$ and $3\cdot059$ 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 $-\ddot{N}=\ddot{N}-$ 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).

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 $0\cdot3 \times 0\cdot2 \times 0\cdot2$ mm were collected on a Philips PW 1100 four-circle computer-controlled diffractometer with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0\cdot71069$ 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,


(I)   (II)   (III)
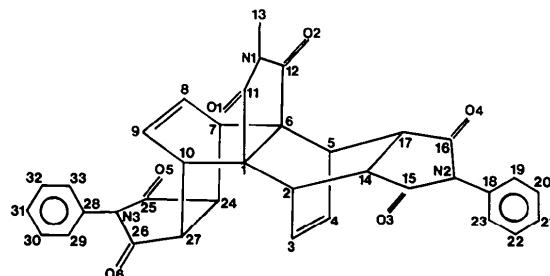
Fig. 1. Schematic drawing of the title compound showing atomic notation.

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* Configuration of Diels–Alder Adducts. VII.

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

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

	x	y	z	U_{eq}		x	y	z	U_{eq}
O(1)	−413 (1)	4998 (2)	8793 (1)	59	C(26)	1096 (1)	9889 (3)	10181 (2)	34
O(2)	1286 (1)	4829 (2)	7346 (2)	66	C(27)	758 (1)	9257 (3)	9254 (2)	30
O(3)	−1788 (1)	7982 (2)	6220 (1)	47	C(28)	2190 (1)	11212 (3)	10887 (2)	40
O(4)	−65 (1)	7689 (3)	4811 (1)	58	C(29)	2672 (2)	10530 (4)	11554 (2)	62
O(5)	2487 (1)	10113 (2)	9262 (1)	50	C(30)	3106 (2)	11423 (6)	12211 (2)	28
O(6)	858 (1)	10005 (2)	10833 (1)	52	C(31)	3042 (2)	12903 (6)	12186 (3)	94
N(1)	420 (1)	4587 (2)	8052 (2)	51	C(32)	2557 (3)	13559 (5)	11512 (3)	99
N(2)	−1015 (1)	8012 (2)	5351 (1)	35	C(33)	2127 (2)	12704 (4)	10860 (2)	74
N(3)	1745 (1)	10360 (2)	10172 (1)	35	OW	3978 (1)	10613 (3)	10278 (2)	123
C(1)	196 (1)	7049 (3)	8338 (2)	29	H(2)	−80 (1)	788 (3)	800 (2)	
C(2)	−436 (1)	7832 (3)	7704 (2)	29	H(3)	−50 (1)	1018 (3)	747 (2)	
C(3)	−232 (1)	9298 (3)	7400 (2)	32	H(4)	44 (1)	1015 (3)	670 (2)	
C(4)	261 (1)	9254 (3)	6978 (2)	34	H(5)	89 (1)	769 (3)	659 (2)	
C(5)	539 (1)	7745 (3)	6894 (2)	34	H(7)	179 (1)	752 (3)	819 (2)	
C(6)	775 (1)	6998 (3)	7848 (2)	30	H(8)	201 (1)	620 (3)	961 (2)	
C(7)	1448 (1)	7612 (3)	8497 (2)	33	H(9)	111 (1)	630 (3)	1036 (2)	
C(8)	1587 (1)	6753 (3)	9373 (2)	39	H(10)	10 (1)	771 (2)	963 (1)	
C(9)	1088 (1)	6774 (3)	9789 (2)	40	H(131)	42 (2)	288 (3)	753 (2)	
C(10)	478 (1)	7693 (3)	9319 (2)	33	H(132)	18 (2)	264 (5)	850 (3)	
C(11)	17 (1)	5450 (3)	8440 (2)	42	H(133)	80 (2)	260 (5)	801 (3)	
C(12)	883 (1)	5373 (3)	7712 (2)	45	H(14)	−81 (1)	600 (2)	691 (1)	
C(13)	349 (3)	2983 (4)	8022 (4)	102	H(17)	4 (1)	581 (3)	622 (2)	
C(14)	−658 (1)	6915 (3)	6805 (2)	33	H(19)	−148 (1)	1063 (3)	531 (2)	
C(15)	−1233 (1)	7673 (3)	6124 (2)	34	H(20)	−215 (1)	1189 (3)	403 (2)	
C(16)	−359 (1)	7537 (3)	5407 (2)	39	H(21)	−249 (2)	1088 (3)	258 (2)	
C(17)	−79 (1)	6837 (3)	6333 (2)	36	H(22)	−210 (1)	849 (3)	240 (2)	
C(18)	−1417 (1)	8809 (3)	4584 (2)	35	H(23)	−146 (1)	714 (3)	364 (2)	
C(19)	−1608 (1)	10222 (3)	4709 (2)	49	H(24)	121 (1)	984 (2)	821 (1)	
C(20)	−2006 (2)	10986 (3)	3963 (2)	58	H(27)	39 (1)	995 (3)	897 (2)	
C(21)	−2188 (1)	10336 (4)	3121 (2)	36	H(29)	270 (2)	939 (4)	1159 (2)	
C(22)	−1987 (1)	8936 (4)	3005 (2)	52	H(30)	338 (2)	1095 (4)	1266 (3)	
C(23)	−1603 (1)	8146 (3)	3740 (2)	44	H(31)	329 (2)	1352 (4)	1266 (2)	
C(24)	1320 (1)	9213 (3)	8750 (2)	29	H(32)	251 (3)	1452 (6)	1153 (4)	
C(25)	1932 (1)	9911 (3)	9396 (2)	35	H(33)	181 (2)	1318 (4)	1041 (2)	

Table 2. *Bond lengths* (Å)

For atomic notation see Fig. 1. The e.s.d.'s of bond lengths are typically 0·003–0·005 Å.

O(1)–C(11)	1·208	C(6)–C(7)	1·566
O(2)–C(12)	1·208	C(6)–C(12)	1·519
O(3)–C(15)	1·207	C(7)–C(8)	1·503
O(4)–C(16)	1·213	C(7)–C(24)	1·547
O(5)–C(25)	1·210	C(8)–C(9)	1·327
O(6)–C(26)	1·212	C(9)–C(10)	1·513
N(1)–C(11)	1·373	C(10)–C(27)	1·547
N(1)–C(12)	1·385	C(14)–C(15)	1·512
N(1)–C(13)	1·468	C(14)–C(17)	1·531
N(2)–C(15)	1·390	C(16)–C(17)	1·511
N(2)–C(16)	1·385	C(18)–C(19)	1·371
N(2)–C(18)	1·433	C(18)–C(23)	1·376
N(3)–C(25)	1·388	C(19)–C(20)	1·393
N(3)–C(26)	1·392	C(20)–C(21)	1·368
N(3)–C(28)	1·444	C(21)–C(22)	1·365
C(1)–C(2)	1·563	C(22)–C(23)	1·384
C(1)–C(6)	1·546	C(24)–C(25)	1·511
C(1)–C(10)	1·562	C(24)–C(27)	1·530
C(1)–C(11)	1·520	C(26)–C(27)	1·508
C(2)–C(3)	1·506	C(28)–C(29)	1·362
C(2)–C(14)	1·562	C(28)–C(33)	1·364
C(3)–C(4)	1·321	C(29)–C(30)	1·406
C(4)–C(5)	1·505	C(30)–C(31)	1·355
C(5)–C(6)	1·557	C(31)–C(32)	1·360
C(5)–C(17)	1·560	C(32)–C(33)	1·378

isotropic for H. Scattering factors for C, N and O were taken from Cromer & Mann (1968), for H from Stewart, Davidson & Simpson (1965). The final R for 3384 significant reflections $[F_o < 1·5\sigma(F_o)]$ was 0·056, $R_w = 0·058$ $[w = 1·4806/\sigma^2 (F_o) + 0·0009\, F_o^2]$.

Fig. 1 shows the atom numbering. Final positional parameters are given in Table 1.* Bond lengths and angles are given in Tables 2 and 3 respectively; the C–H distances lie in the range 0·79–1·02 Å. The packing is shown in Fig. 2.*

Discussion. The configuration of the monoadduct is *anti* with respect to the hetero-ring (Kaftory, 1980, molecule *b*), that of the bisadduct is *anti,syn*. It is not surprising that the second dienophile molecule attacks *syn*, as the H atoms of the maleimide moiety overlap the cyclohexadiene face *anti* to the central ring, where

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* Lists of structure factors and anisotropic thermal parameters and a stereoview of the molecule down C(1)–C(6) have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35549 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

$$C_{33}H_{25}N_3O_6 \cdot H_2O$$

Table 3. Bond angles (°)

For atomic notation see Fig. 1. The e.s.d.'s of bond angles are typically 0·2–0·3°.

| | | | | | | | | |
|---|---|---|---|---|---|---|---|
| C(11)—N(1)—C(12) | 113·7 | C(4)—C(5)—C(17) | 105·3 | N(1)—C(12)—C(6) | 108·5 | C(7)—C(24)—C(25) | 113·2 |
| C(11)—N(1)—C(13) | 121·3 | C(6)—C(5)—C(17) | 106·6 | C(2)—C(14)—C(15) | 110·4 | C(7)—C(24)—C(27) | 110·1 |
| C(12)—N(1)—C(13) | 125·0 | C(1)—C(6)—C(5) | 110·0 | C(2)—C(14)—C(17) | 110·4 | C(25)—C(24)—C(27) | 105·2 |
| C(15)—N(2)—C(16) | 113·1 | C(1)—C(6)—C(7) | 109·8 | C(15)—C(14)—C(17) | 104·8 | O(5)—C(25)—N(3) | 124·7 |
| C(15)—N(2)—C(18) | 123·8 | C(5)—C(6)—C(7) | 115·8 | O(3)—C(15)—N(2) | 124·2 | O(5)—C(25)—C(24) | 127·0 |
| C(16)—N(2)—C(18) | 123·1 | C(1)—C(6)—C(12) | 104·4 | O(3)—C(15)—C(14) | 127·3 | N(3)—C(25)—C(24) | 108·2 |
| C(25)—N(3)—C(26) | 112·7 | C(5)—C(6)—C(12) | 108·7 | N(2)—C(15)—C(14) | 108·5 | O(6)—C(26)—N(3) | 124·1 |
| C(26)—N(3)—C(28) | 124·8 | C(7)—C(6)—C(12) | 107·5 | O(4)—C(16)—N(2) | 124·9 | O(6)—C(26)—C(27) | 127·6 |
| C(2)—C(1)—C(6) | 109·1 | C(6)—C(7)—C(8) | 107·6 | O(4)—C(16)—C(17) | 126·8 | N(3)—C(26)—C(27) | 108·3 |
| C(2)—C(1)—C(10) | 117·0 | C(6)—C(7)—C(24) | 108·4 | N(2)—C(16)—C(17) | 108·3 | C(10)—C(27)—C(24) | 110·0 |
| C(6)—C(1)—C(10) | 109·2 | C(8)—C(7)—C(24) | 106·1 | C(5)—C(17)—C(14) | 109·3 | C(10)—C(27)—C(26) | 112·2 |
| C(2)—C(1)—C(11) | 108·6 | C(7)—C(8)—C(9) | 114·8 | C(5)—C(17)—C(16) | 109·8 | C(24)—C(27)—C(26) | 104·8 |
| C(6)—C(1)—C(11) | 104·7 | C(8)—C(9)—C(10) | 114·8 | C(14)—C(17)—C(16) | 105·3 | N(3)—C(28)—C(29) | 120·1 |
| C(10)—C(1)—C(11) | 107·6 | C(1)—C(10)—C(9) | 107·1 | N(2)—C(18)—C(19) | 119·1 | N(3)—C(28)—C(33) | 118·5 |
| C(1)—C(2)—C(3) | 110·2 | C(1)—C(10)—C(27) | 109·6 | N(2)—C(18)—C(23) | 119·6 | C(29)—C(28)—C(33) | 121·4 |
| C(1)—C(2)—C(14) | 107·3 | C(9)—C(10)—C(27) | 105·7 | C(19)—C(18)—C(23) | 121·4 | C(28)—C(29)—C(30) | 117·4 |
| C(3)—C(2)—C(14) | 104·4 | O(1)—C(11)—N(1) | 125·1 | C(18)—C(19)—C(20) | 118·9 | C(29)—C(30)—C(31) | 121·1 |
| C(2)—C(3)—C(4) | 115·1 | O(1)—C(11)—C(1) | 126·3 | C(19)—C(20)—C(21) | 120·0 | C(30)—C(31)—C(32) | 120·3 |
| C(3)—C(4)—C(5) | 114·7 | N(1)—C(11)—C(1) | 108·6 | C(20)—C(21)—C(22) | 120·4 | C(31)—C(32)—C(33) | 119·4 |
| C(4)—C(5)—C(6) | 110·6 | O(2)—C(12)—N(1) | 124·5 | C(21)—C(22)—C(23) | 120·6 | C(28)—C(33)—C(32) | 120·3 |
| | | O(2)—C(12)—C(6) | 127·0 | C(18)—C(23)—C(22) | 118·8 | | |
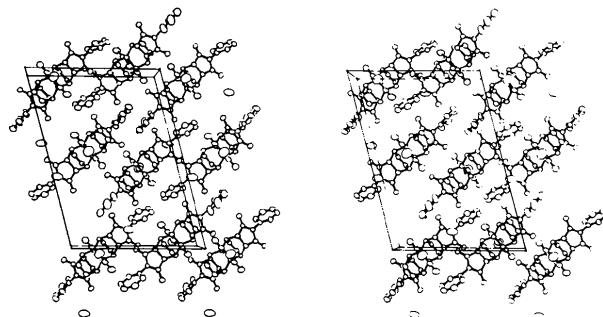
Fig. 2. Stereoview (Johnson, 1965) of the packing of molecules in the cell.

the equivalent H atoms of the second dienophile molecule should approach during an attack. The hetero-ring is planar and exerts less steric repulsion towards the dienophile. The result will be an attack *syn* to that ring.

Bond lengths and angles are in good agreement with those obtained for the monoadduct (Kaftory, 1980, molecule *b*).

The angles between planes may be compared with values obtained for similar compounds (for lettering of planes see Kaftory, 1980, Fig. 13 and Table 10). The opening of the angle between planes L and M (128·8°) compared with the 124·4° in the monoadduct and the 124·9° between L and Q is the result of steric repulsion between H atoms on C(24), C(27) and C(3), C(4) [C(24)···C(3) 3·287, C(27)···C(4) 3·331 Å]. The dihedral angle between the maleimide moiety in the position *syn* to the hetero-ring and the phenyl ring is

63°, in good agreement with values in related compounds (Kaftory, 1980). The other phenyl ring is almost perpendicular to the maleimide portion in the *anti* position. The perpendicular conformation is not so common (Kaftory, 1978) and it seems that packing forces stabilize that conformation in the title compound. Although the H atoms of the water molecule could not be resolved, weak hydrogen bonds can exist between the water O(5) atom (2·940 Å) and the O(4) atom of a molecule related by ($\frac{1}{2} - x$, $\frac{1}{2} + y$, $1\frac{1}{2} - z$) (3·059 Å). The angle O(4)···OW···O(5) is 137·0°.

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