Configuration of Diels–Alder Adducts.
IV.* Structures of Configuration-Controlled Monoadducts between Certain Propellanes and Dienophiles

By M. Kaftory

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

Abstract

Results of crystal structure analyses of six mono-adducts of the Diels–Alder reaction between propellanes and dienophiles show that the configuration of the products depends upon the central ring of the propellane and the kind of atoms, in the dienophiles, which participate in the reaction. The configuration *syn* to the central five-membered ring was observed in the monoadduct where the central five-membered ring contained carbonyls and the dienophile contained the $-\ddot{N}=\ddot{N}-$ group. The configuration *anti* to the central five-membered ring was observed whenever the dienophile contained the $-HC=CH-$ group, or when the dienophile contained the $-\ddot{N}=\ddot{N}-$ group but the central ring of the propellane was lacking carbonyl groups.

Introduction

Much work has been done in recent years in the investigation of the Diels–Alder reaction and the
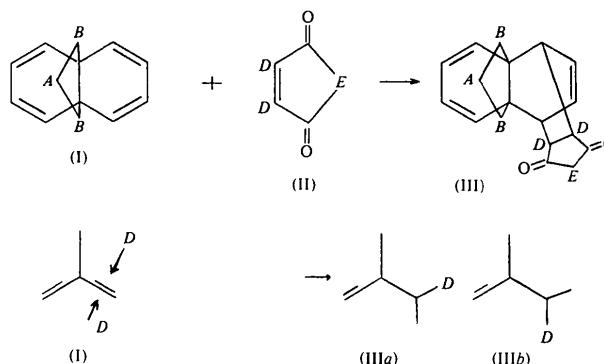
	A	B	D	E
(a)†	N–CH$_3$	C=O	N	N–φ
(b)	N–CH$_3$	C=O	C	N–φ
(c)	O	C=O	C	HC=CH
(d)	CH$_2$	O	N	N–CH$_3$
(e)	O	CH$_2$	C	N–CH$_3$
(f)	O	CH$_2$	C	O

† This compound is slightly different from that which appears in the scheme. For the complete formula see text.

* Part III: *Acta Cryst.* (1978), B**34**, 306–308.

Table 1. *Crystallographic and experimental details*

	(a)	(b)	(c)	(d)	(e)	(f)
Formula	C$_{23}$H$_{24}$N$_4$O$_5$	C$_{23}$H$_{18}$N$_2$O$_4$	C$_{18}$H$_{12}$O$_5$	C$_{14}$H$_{13}$N$_3$O$_4$	C$_{17}$H$_{17}$NO$_3$	C$_{16}$H$_{14}$O$_4$
M_r	436·45	386·39	308·28	287·27	283·39	270·27
a (Å)	12·410 (6)	18·909 (9)	14·190 (7)	6·903 (3)	7·440 (4)	19·489 (9)
b (Å)	13·537 (7)	11·589 (6)	7·562 (4)	11·194 (6)	23·261 (11)	8·625 (4)
c (Å)	13·609 (7)	8·572 (4)	7·203 (4)	17·596 (9)	8·709 (4)	7·495 (4)
α (°)	–	–	117·56 (2)	–	–	–
β (°)	108·19 (2)	–	95·14 (2)	104·51 (2)	110·86 (2)	–
γ (°)	–	–	85·85 (2)	–	–	–
Z	4	4	2	4	4	4
Space group	$P2_1/c$	$P2_12_12_1$	$P\bar{1}$	$P2_1/c$	$P2_1/n$	$P2_12_12_1$
D_x (Mg m^{-3})	1·335	1·367	1·502	1·450	1·337	1·425
Scan mode	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$
$\Delta\omega$ (°)	1·4	1·2	1·2	1·2	1·2	1·2
Scan time (s)	28	24	24	24	30	30
Background time* (s)	20	20	24	24	20	20
θ_{max} (°)	24	24	24	24	24	24
Reflections measured	3580	1724	2148	2059	2215	1174
Significant [$F_o > 1\cdot5\,\sigma(F_o)$]	2647	1675†	2127†	1973†	1571	975
Weighting coefficients (k, g)	1·4560, 0·0017	0·3724, 0·0041	0·4800, 0·0007	0·5567, 0·0	1·4226, 0·0003	1·448, 0·0007
R_w	0·070	0·073	0·056	0·057	0·061	0·061
R	0·066	0·072	0·055	0·082	0·070	0·059

* Total background counting time.
† $F_o > 0\cdot0$.

Table 2. *Positional parameters for non-hydrogen atoms* ($\times 10^4$) *and for hydrogen atoms* ($\times 10^3$) *for* (a) (*e.s.d.'s in parentheses*)

	x	y	z		x	y	z
O(1)	5546 (2)	−601 (2)	8731 (2)	C(20)	−819 (5)	2567 (6)	8623 (9)
O(2)	6000 (2)	2683 (2)	8389 (2)	C(21)	−796 (9)	2114 (7)	9516 (11)
O(3)	2029 (2)	−53 (2)	5416 (2)	C(22)	−17 (10)	1460 (6)	10003 (9)
O(4)	1727 (2)	−234 (2)	8171 (2)	C(23)	875 (5)	1255 (4)	9593 (5)
O(5)	2254 (2)	3101 (2)	8011 (3)	H(2)	336 (2)	−47 (2)	715 (2)
N(1)	5868 (2)	1061 (2)	8791 (2)	H(4)	235 (2)	192 (2)	546 (2)
N(2)	3168 (2)	712 (2)	7918 (2)	H(5)	369 (2)	268 (2)	690 (2)
N(3)	1796 (2)	1485 (2)	8314 (2)	H(71)	474 (2)	173 (2)	556 (2)
N(4)	3329 (2)	1756 (2)	7860 (2)	H(72)	537 (3)	255 (2)	624 (2)
C(1)	4699 (3)	419 (2)	7210 (2)	H(81)	656 (3)	141 (3)	563 (3)
C(2)	3445 (3)	179 (2)	7073 (2)	H(82)	703 (3)	161 (3)	687 (3)
C(3)	2697 (3)	604 (2)	6069 (2)	H(91)	686 (3)	3 (2)	721 (2)
C(4)	2791 (3)	1576 (3)	5997 (3)	H(92)	662 (3)	−17 (2)	601 (3)
C(5)	3643 (3)	2017 (2)	6926 (3)	H(101)	521 (3)	−84 (2)	665 (2)
C(6)	4818 (3)	1557 (2)	7099 (2)	H(102)	456 (3)	−10 (2)	575 (2)
C(7)	5295 (3)	1839 (2)	6233 (3)	H(131)	676 (4)	185 (4)	1001 (4)
C(8)	6396 (3)	1303 (3)	6306 (3)	H(132)	719 (4)	76 (3)	1000 (3)
C(9)	6331 (3)	196 (3)	6515 (3)	H(133)	612 (4)	78 (4)	1028 (4)
C(10)	5152 (3)	−159 (2)	6455 (3)	H(141)	71 (3)	75 (2)	467 (2)
C(11)	5395 (3)	199 (2)	8312 (3)	H(142)	170 (3)	76 (2)	414 (2)
C(12)	5615 (3)	1869 (2)	8139 (3)	H(151)	25 (4)	−22 (4)	303 (4)
C(13)	6534 (3)	1115 (3)	9873 (3)	H(152)	34 (4)	−92 (3)	416 (3)
C(14)	1264 (3)	364 (3)	4478 (3)	H(153)	133 (4)	−87 (4)	363 (4)
C(15)	706 (4)	−461 (3)	3782 (3)	H(19)	17 (6)	260 (6)	752 (5)
C(16)	2166 (3)	554 (3)	8129 (2)	H(20)	−132 (5)	305 (4)	820 (4)
C(17)	2426 (3)	2221 (3)	8047 (3)	H(21)	−154 (5)	236 (5)	964 (4)
C(18)	873 (4)	1688 (3)	8710 (4)	H(22)	−9 (7)	125 (6)	1058 (6)
C(19)	28 (4)	2351 (4)	8165 (5)	H(23)	155 (3)	89 (2)	1005 (2)

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

	x	y	z		x	y	z
O(1)	6249 (2)	7740 (3)	3356 (6)	C(19)	3866 (3)	5426 (5)	−3324 (8)
O(2)	7532 (2)	4695 (4)	1618 (7)	C(20)	3441 (4)	5428 (7)	−4660 (9)
O(3)	3737 (2)	5966 (4)	343 (6)	C(21)	2989 (4)	4518 (8)	−4938 (10)
O(4)	5045 (2)	3040 (3)	−1705 (5)	C(22)	2966 (4)	3598 (7)	−3898 (10)
N(1)	7028 (2)	6334 (4)	2558 (6)	C(23)	3399 (3)	3585 (6)	−2622 (8)
N(2)	4294 (2)	4503 (3)	−989 (5)	H(2)	496 (2)	681 (3)	198 (4)
C(1)	5838 (3)	5790 (4)	2829 (6)	H(3)	562 (2)	708 (4)	−39 (5)
C(2)	5251 (3)	6115 (4)	1615 (6)	H(4)	630 (2)	548 (3)	−153 (5)
C(3)	5599 (3)	6360 (5)	94 (6)	H(5)	625 (2)	388 (3)	10 (4)
C(4)	5995 (3)	5504 (5)	−462 (7)	H(7)	651 (2)	311 (4)	275 (5)
C(5)	5990 (3)	4438 (4)	546 (7)	H(8)	597 (2)	299 (4)	511 (5)
C(6)	6268 (3)	4752 (4)	2204 (6)	H(9)	538 (3)	452 (4)	628 (6)
C(7)	6265 (3)	3690 (5)	3232 (8)	H(10)	529 (2)	634 (4)	478 (5)
C(8)	5949 (4)	3684 (5)	4622 (9)	H(131)	810 (3)	659 (5)	229 (7)
C(9)	5577 (4)	4679 (6)	5223 (7)	H(132)	792 (5)	707 (8)	386 (12)
C(10)	5520 (3)	5626 (5)	4423 (7)	H(133)	757 (3)	779 (5)	215 (8)
C(11)	6372 (3)	6761 (5)	2951 (7)	H(14)	458 (2)	486 (3)	244 (5)
C(12)	7015 (3)	5214 (6)	2085 (8)	H(17)	518 (2)	333 (3)	127 (4)
C(13)	7660 (3)	7039 (6)	2623 (10)	H(19)	421 (2)	608 (4)	−322 (5)
C(14)	4775 (3)	5049 (4)	1424 (6)	H(20)	347 (3)	615 (4)	−540 (7)
C(15)	4202 (3)	5242 (5)	258 (7)	H(21)	271 (3)	450 (4)	−591 (6)
C(16)	4862 (3)	3775 (4)	−782 (6)	H(22)	259 (2)	291 (5)	−401 (7)
C(17)	5209 (3)	4052 (4)	762 (6)	H(23)	339 (2)	294 (4)	−170 (5)
C(18)	3850 (3)	4510 (4)	−2330 (7)				

factors that control the direction of attack which establishes the configuration of the adduct (Korat, Tatarsky & Ginsburg, 1972; Ginsburg, 1974a,b; Kalo, Vogel & Ginsburg, 1977; Ashkenazi, Kalo, Rüttimann & Ginsburg, 1978; Kalo & Ginsburg, 1978; Gleiter & Ginsburg, 1979; Kaftory, Peled & Ginsburg, 1979).

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

	x	y	z		x	y	z
O(1)	6908 (1)	−2347 (2)	−510 (2)	C(14)	8510 (1)	5611 (3)	4531 (4)
O(2)	7058 (1)	−783 (3)	−2429 (3)	C(15)	9048 (2)	6471 (4)	6562 (4)
O(3)	6602 (1)	−3105 (2)	2020 (3)	C(16)	9167 (2)	5555 (4)	7763 (4)
O(4)	8654 (1)	6125 (3)	3208 (3)	C(17)	8730 (2)	3631 (3)	7135 (3)
O(5)	9047 (1)	2531 (3)	7871 (3)	C(18)	7865 (2)	3100 (3)	5597 (3)
C(1)	6867 (1)	1216 (3)	1325 (3)	H(2)	774 (1)	299 (3)	82 (3)
C(2)	7778 (1)	2447 (3)	1807 (3)	H(3)	909 (2)	86 (3)	66 (3)
C(3)	8615 (2)	1059 (3)	1615 (3)	H(4)	911 (2)	−78 (4)	286 (3)
C(4)	8630 (2)	184 (3)	2831 (3)	H(5)	787 (1)	9 (3)	511 (3)
C(5)	7828 (1)	804 (3)	4252 (3)	H(7)	605 (2)	70 (4)	540 (5)
C(6)	6852 (1)	378 (3)	2927 (3)	H(8)	480 (2)	267 (4)	495 (5)
C(7)	6027 (2)	1093 (4)	4310 (4)	H(9)	480 (2)	364 (4)	223 (4)
C(8)	5320 (2)	2185 (4)	4043 (5)	H(10)	600 (2)	279 (4)	3 (4)
C(9)	5292 (2)	2838 (4)	2431 (5)	H(13)	720 (2)	483 (3)	428 (3)
C(10)	5992 (2)	2393 (3)	1167 (4)	H(15)	941 (2)	767 (4)	679 (5)
C(11)	6962 (2)	−646 (3)	−748 (4)	H(16)	960 (2)	610 (4)	912 (5)
C(12)	6776 (1)	−1852 (3)	1563 (4)	H(18)	733 (2)	357 (3)	650 (4)
C(13)	7777 (2)	4090 (3)	4110 (3)				

Table 5. *Positional parameters for non-hydrogen atoms* ($\times 10^4$) *and for hydrogen atoms* ($\times 10^3$) *for* (d) (*e.s.d.'s in parentheses*)

	x	y	z		x	y	z
O(1)	7349 (3)	−1557 (2)	3765 (1)	C(11)	9362 (5)	−1277 (3)	4098 (2)
O(2)	9939 (3)	−419 (2)	3621 (1)	C(12)	3087 (4)	189 (3)	1421 (2)
O(3)	1522 (3)	−350 (2)	1279 (1)	C(13)	5724 (5)	1276 (3)	1244 (2)
O(4)	6809 (3)	1825 (2)	929 (1)	C(14)	2733 (5)	1104 (3)	100 (2)
N(1)	4476 (3)	264 (2)	2149 (1)	H(2)	396 (3)	−133 (2)	262 (2)
N(2)	3819 (3)	879 (2)	911 (1)	H(3)	619 (4)	−238 (2)	200 (1)
N(3)	6154 (3)	957 (2)	2036 (1)	H(4)	890 (4)	−115 (2)	180 (2)
C(1)	6417 (4)	−488 (3)	3388 (2)	H(5)	916 (4)	83 (2)	230 (1)
C(2)	5146 (4)	−872 (3)	2576 (2)	H(7)	948 (5)	193 (3)	357 (2)
C(3)	6469 (5)	−1522 (3)	2157 (2)	H(8)	732 (4)	261 (3)	434 (2)
C(4)	7980 (4)	−885 (3)	2060 (2)	H(9)	474 (5)	144 (3)	458 (2)
C(5)	8070 (4)	340 (3)	2389 (2)	H(10)	405 (4)	−51 (3)	395 (2)
C(6)	8192 (4)	281 (3)	3273 (2)	H(111)	1015 (4)	−199 (3)	411 (2)
C(7)	8364 (6)	1494 (3)	3660 (2)	H(112)	947 (4)	−82 (3)	466 (2)
C(8)	7166 (8)	1833 (3)	4104 (2)	H(141)	325 (7)	164 (4)	−13 (3)
C(9)	5559 (7)	1102 (4)	4218 (2)	H(142)	136 (8)	143 (5)	8 (3)
C(10)	5176 (5)	48 (4)	3885 (2)	H(143)	240 (6)	40 (4)	−17 (2)

The model used for the investigation was propellanes of type (I) and the dienophiles of type (II). The dienophile may attack from the same side of the central ring (*syn*) (IIIa) or from the other side of that ring (*anti*) (IIIb). The crystal structures of six monoadducts (a–f) have been studied and used for the interpretation of the factors which control the configuration of the adducts.

Crystal structure analyses

Crystallographic data, and details of intensity measurement and structure refinement are given in Table 1 for all six compounds. The intensities were collected on a Philips PW 1100 four-circle computer-controlled diffractometer with graphite-monochromated Mo $K\alpha$

radiation ($\lambda = 0.71069$ Å). The crystal structures were solved by *MULTAN* 77 (Main, Woolfson, Lessinger, Germain & Declercq, 1977), and refined by full-matrix least squares (*SHELX*, Sheldrick, 1976) with anisotropic thermal parameters for C, N and O atoms, isotropic for H. Scattering factors for C, N, and O were taken from Cromer & Mann (1968), for H from Stewart, Davidson & Simpson (1965). Final positional parameters for (a)–(f) are given in Tables 2–7.* In the

* Lists of structure factors and thermal parameters for the six compounds have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34884 (70 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 6. *Positional parameters for non-hydrogen atoms* $(\times 10^4)$ *and for hydrogen atoms* $(\times 10^3)$ *for* (e) (*e.s.d.'s in parentheses*)

	x	y	z		x	y	z
O(1)	5577 (4)	2655 (1)	5114 (4)	C(16)	162 (5)	3896 (2)	3781 (5)
O(2)	1837 (5)	5338 (1)	3674 (4)	C(17)	−1833 (7)	5177 (2)	1077 (6)
O(3)	−2870 (4)	4020 (1)	1486 (4)	H(2)	471 (7)	439 (2)	476 (6)
N	−738 (5)	4763 (1)	2341 (4)	H(3)	383 (6)	417 (2)	187 (6)
C(1)	4230 (5)	3556 (2)	5356 (5)	H(4)	136 (8)	345 (2)	75 (7)
C(2)	3655 (5)	4116 (2)	4316 (5)	H(5)	−11 (6)	309 (2)	253 (5)
C(3)	3187 (6)	3968 (2)	2539 (5)	H(7)	65 (8)	258 (2)	548 (6)
C(4)	1794 (6)	3587 (2)	1930 (5)	H(8)	186 (5)	284 (2)	821 (5)
C(5)	945 (5)	3369 (2)	3148 (5)	H(9)	450 (8)	354 (2)	932 (6)
C(6)	2568 (5)	3098 (2)	4655 (5)	H(10)	582 (7)	397 (2)	762 (6)
C(7)	1726 (6)	2884 (2)	5878 (6)	H(111)	729 (6)	333 (2)	612 (5)
C(8)	2361 (7)	3027 (2)	7433 (6)	H(112)	611 (7)	337 (2)	406 (6)
C(9)	3911 (7)	3436 (2)	8106 (5)	H(121)	335 (7)	260 (2)	294 (6)
C(10)	4735 (5)	3683 (2)	7155 (5)	H(122)	305 (8)	222 (3)	433 (7)
C(11)	5970 (6)	3250 (2)	5128 (5)	H(13)	203 (5)	440 (2)	567 (4)
C(12)	3589 (6)	2595 (2)	4133 (5)	H(16)	−35 (6)	377 (2)	464 (5)
C(13)	1773 (6)	4340 (2)	4488 (5)	H(171)	−109 (9)	552 (3)	132 (9)
C(14)	1045 (6)	4876 (2)	3511 (5)	H(172)	−312 (9)	523 (3)	114 (8)
C(15)	−1345 (6)	4206 (2)	2414 (5)	H(173)	−199 (9)	503 (3)	2 (8)

Table 7. *Positional parameters for non-hydrogen atoms* $(\times 10^4)$ *and for hydrogen atoms* $(\times 10^3)$ *for* (f) (*e.s.d.'s in parentheses*)

	x	y	z		x	y	z
O(1)	4663 (2)	4510 (6)	−1959 (7)	C(14)	2239 (4)	1483 (9)	197 (10)
O(2)	2339 (2)	−52 (6)	−229 (7)	C(15)	3006 (4)	−472 (9)	109 (10)
O(3)	1681 (3)	2057 (7)	5 (9)	C(16)	3405 (3)	883 (7)	830 (8)
O(4)	3187 (3)	−1748 (6)	−188 (9)	H(2)	280 (2)	438 (5)	−42 (6)
C(1)	3823 (3)	4170 (7)	326 (8)	H(3)	305 (2)	327 (5)	−324 (5)
C(2)	3140 (3)	3522 (7)	−437 (8)	H(4)	393 (2)	106 (5)	−314 (6)
C(3)	3275 (3)	2754 (8)	−2216 (8)	H(5)	431 (2)	59 (4)	−28 (4)
C(4)	3736 (3)	1657 (8)	−2185 (8)	H(7)	497 (2)	164 (5)	231 (7)
C(5)	4020 (3)	1339 (7)	−359 (9)	H(8)	468 (3)	300 (6)	497 (8)
C(6)	4356 (3)	2810 (7)	415 (8)	H(9)	391 (2)	512 (6)	465 (6)
C(7)	4627 (3)	2466 (9)	2274 (9)	H(10)	337 (3)	588 (7)	199 (8)
C(8)	4461 (3)	3271 (9)	3690 (9)	H(111)	442 (3)	620 (8)	−33 (9)
C(9)	3991 (4)	4540 (8)	3602 (9)	H(112)	382 (3)	578 (6)	−182 (8)
C(10)	3683 (3)	4957 (7)	2073 (9)	H(121)	516 (3)	245 (7)	−136 (8)
C(11)	4156 (3)	5308 (8)	−984 (8)	H(122)	523 (3)	406 (7)	−18 (9)
C(12)	4952 (3)	3382 (9)	−786 (10)	H(13)	281 (2)	258 (5)	207 (6)
C(13)	2888 (3)	2213 (8)	832 (9)	H(16)	355 (2)	69 (5)	206 (6)

stereoviews (Figs. 2, 4, 6, 8, 10 and 12) vibration ellipsoids are drawn at the 50% probability level (Johnson, 1965). In no cases were intermolecular distances shorter than van der Waals contacts observed.

Structure of the monoadduct between 3-ethoxy-12-methyl-12-aza[4.4.3]propella-2,4-diene-11,13-dione and 4-phenyl-1,2,4-triazoline-3,5-dione (a)

Bond lengths and angles involving C, N and O atoms are given in Fig. 1; the C—H distances (not shown) lie in the range 0·88–1·06 Å. The e.s.d.'s of bond distances are typically 0·004–0·006 Å, of bond angles 0·2–0·3°. Torsion angles are given in Table 8. A

stereoview of the molecule is shown in Fig. 2. The 4-phenyl-1,2,4-triazoline-3,5-dione is *syn* to the hetero-ring. The unsubstituted six-membered ring is saturated and an H atom on C(3) was replaced by an OEt group.

The atoms of the phenyl group have high temperature factors (Fig. 2) but no attempt has been made to analyze for thermal motion.

Structure of the monoadduct between 12-methyl-12-aza[4.4.3]propella-2,4,7,9-tetraene-11,13-dione and N-phenylmaleimide (b)

Bond lengths and angles involving C, N and O atoms are given in Fig. 3; the C—H distances (not shown) lie
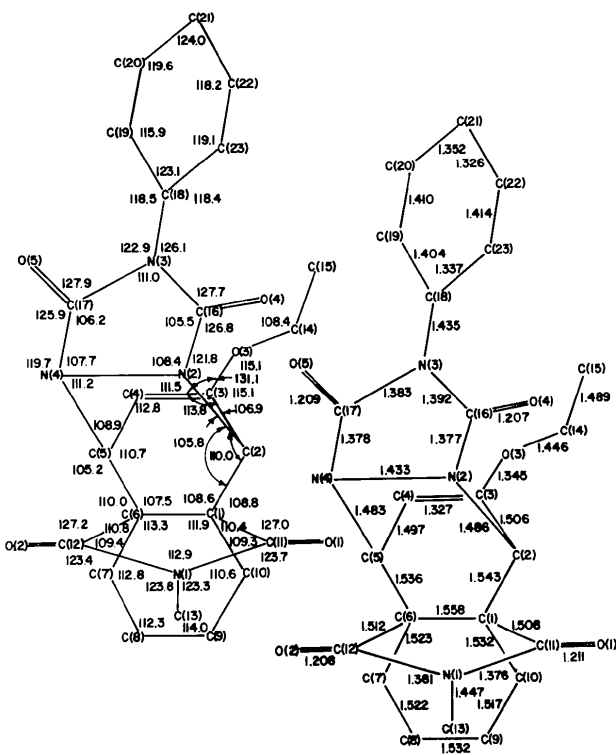
Fig. 1. Bond lengths (Å) and angles (°) in (a). [Angles not shown: C(2)–C(1)–C(10) 112·3; C(6)–C(1)–C(11) 104·5; C(5)–C(6)–C(7) 111·1; C(1)–C(6)–C(12) 103·8°.]
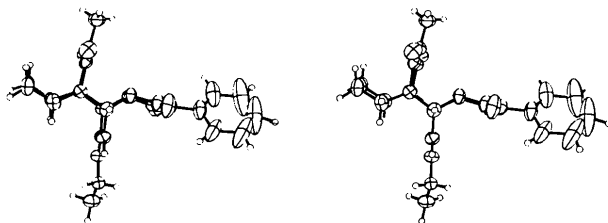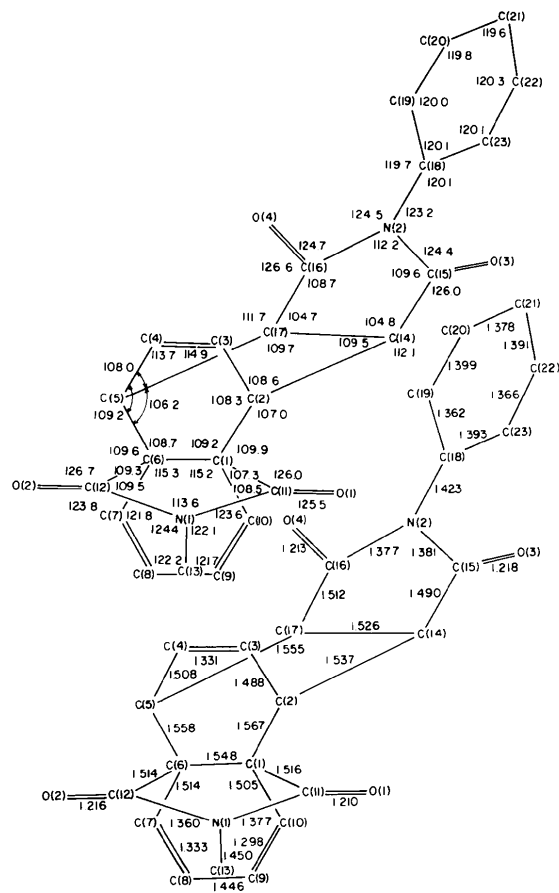

Fig. 2. Stereoview of (a).

Fig. 3. Bond lengths (Å) and angles (°) in (b). [Angles not shown: C(10)–C(1)–C(2) 110·5; C(11)–C(1)–C(6) 104·5; C(7)–C(6)–C(5) 109·9; C(12)–C(6)–C(1) 103·8.]
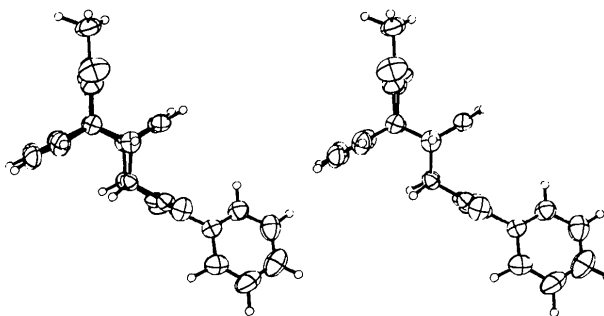

Fig. 4. Stereoview of (b).

in the range 0·89–1·16 Å. The e.s.d.'s of bond distances are typically 0·006–0·010 Å, of bond angles 0·4–0·5°. Torsion angles are given in Table 8. A stereoview of the molecule is shown in Fig. 4. The N-phenylmaleimide is *anti* with respect to the hetero-ring.

The compound crystallizes in a noncentrosymmetric space group $(P2_12_12_1)$ and the two enantiomers are distinguishable by the rotation of the phenyl ring compared to the maleimide ring. No attempt has been made to find the absolute configuration of the compound.

Structure of the monoadduct between 12-oxa[4.4.3]propella-2,4,7,9-tetraene-11,13-dione and p-benzoquinone (c)

Bond lengths and angles involving C and O atoms are given in Fig. 5; the C—H distances (not shown) lie in the range 0·94–1·03 Å. The e.s.d.'s of bond distances are typically 0·003–0·004 Å, of bond angles 0·2–0·3°.

Table 8. *Comparison of torsion angles* (°) *in the six compounds* (a)–(f)

The signs of the torsion angles in the table do not have any absolute significance as both enantiomers are present in the crystals (except for b and f, but their absolute configurations have not been found).

E.s.d.'s (°)	(a) 0·4–0·6	(b) 0·6–0·8	(c) 0·4–0·6	(d) 0·5–0·7	(e) 0·5–0·7	(f) 0·7–0·9
C(1)–C(2)–C(3)–C(4)	−58·8	56·8	−56·9	−59·1	58·1	56·2
C(2)–C(3)–C(4)–C(5)	1·4	1·9	−2·5	0·4	−0·4	2·2
C(3)–C(4)–C(5)–C(6)	58·5	−59·1	57·9	58·2	−57·3	−59·2
C(4)–C(5)–C(6)–C(1)	−57·3	52·8	−48·2	−54·0	53·7	53·2
C(5)–C(6)–C(1)–C(2)	1·7	3·0	−8·1	−1·9	0·7	2·4
C(6)–C(1)–C(2)–C(3)	53·9	−56·8	59·8	56·6	−54·5	−55·2
C(1)–C(6)–C(7)–C(8)	−52·2	−4·0	6·7	4·3	−4·1	−3·1
C(6)–C(7)–C(8)–C(9)	46·1	1·3	−1·9	−3·3	3·0	1·4
C(7)–C(8)–C(9)–C(10)	8·1	1·4	−1·3	0·0	0·5	1·4
C(8)–C(9)–C(10)–C(1)	−57·0	−0·9	−1·0	2·1	−2·5	−2·2
C(9)–C(10)–C(1)–C(6)	50·0	−1·9	5·8	−0·8	1·0	0·3
C(10)–C(1)–C(6)–C(7)	3·1	4·2	−8·2	−2·2	2·0	2·1
*C(1)–C(6)–B(2)–A	−3·7	0·0	10·0	−16·9	24·2	−22·5
C(6)–B(2)–A–B(1)	3·7	−2·5	−6·8	30·7	−42·0	35·0
B(2)–A–B(1)–C(1)	−2·1	3·9	0·4	−32·0	42·3	−33·5
A–B(1)–C(1)–C(6)	−0·3	−3·6	5·8	20·0	−25·0	17·8
B(1)–C(1)–C(6)–B(2)	2·3	2·0	−9·1	−1·9	0·3	3·0
D(1)–D(2)–C(2)–E	−6·7	−2·7	†	−4·4	−1·6	−2·7
D(2)–C(2)–E–C(1)	10·6	2·5	†	7·6	0·9	1·8
C(2)–E–C(1)–D(1)	−10·3	−1·1	†	−7·7	0·2	0·0
E–C(1)–D(1)–D(2)	5·7	0·7	†	4·6	−1·2	−1·6
C(1)–D(1)–D(2)–C(2)	0·6	2·0	†	−0·1	1·7	2·5

* Atomic notation is as in (III). The first five lines belong to the central hetero-ring while the next five lines belong to the dienophile moiety.

† C(13)–C(14)–C(15)–C(16) 23·2; C(14)–C(15)–C(16)–C(17) −2·1; C(15)–C(16)–C(17)–C(18) −23·0; C(16)–C(17)–C(18)–C(13) 25·8; C(17)–C(18)–C(13)–C(14) −5·9; C(18)–C(13)–C(14)–C(15) −17·7.
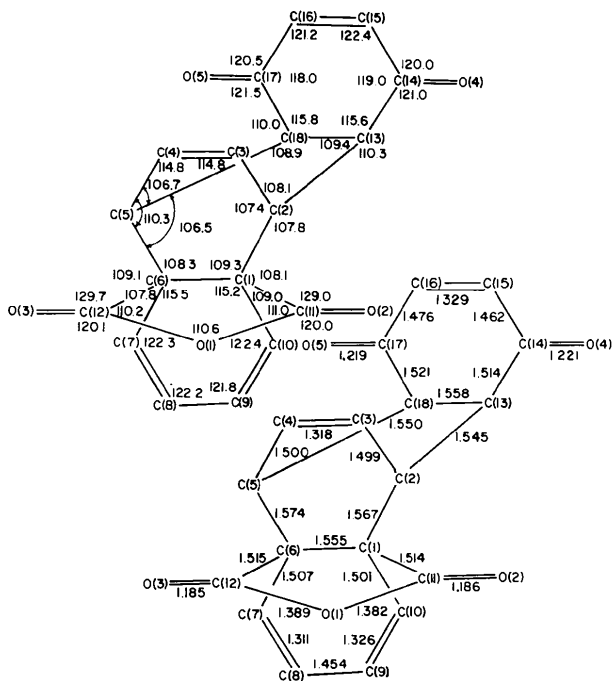

Fig. 5. Bond lengths (Å) and angles (°) in (c). [Angles not shown: C(2)–C(1)–C(10) 111·4; C(6)–C(1)–C(11) 103·3; C(5)–C(6)–C(7) 111·8; C(1)–C(6)–C(12) 103·9.]
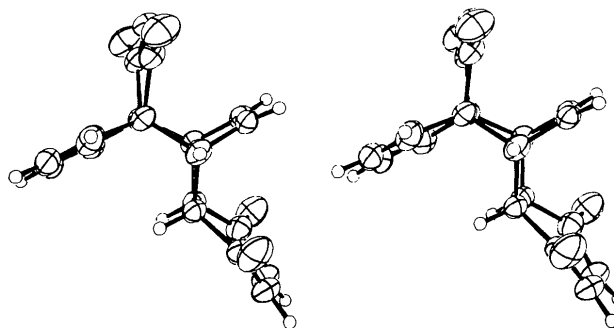

Fig. 6. Stereoview of (c).

Torsion angles are given in Table 8. A stereoview of the molecule is shown in Fig. 6.

The cyclohexene-1,4-dione is *anti* to the hetero-ring. The molecule deviates slightly from mirror symmetry [torsion angles on C(1)–C(6) are ~8°]; the cyclohexene-1,4-dione is non-planar (see *Discussion*).

Structure of the monoadduct between 11,13-dioxa[4.4.3]propella-2,4,7,9-tetraene and 4-methyl-1,2,4-triazoline-3,5-dione (d)

Bond lengths and angles involving C, N and O atoms are given in Fig. 7; the C–H distances (not shown) lie
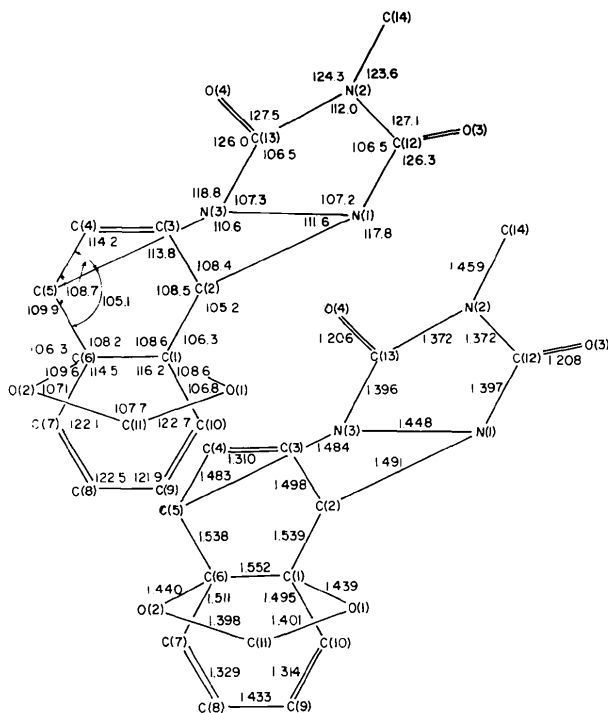
Fig. 7. Bond lengths (Å) and angles (°) in (d). [Angles not shown: C(6)–C(1)–O(1) 104·2; C(10)–C(1)–C(2) 112·2; C(1)–C(6)–O(2) 104·3; C(7)–C(6)–C(5) 113·3.]
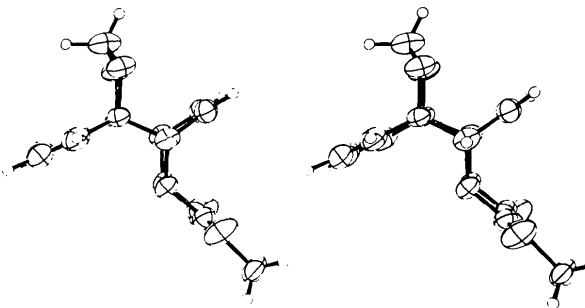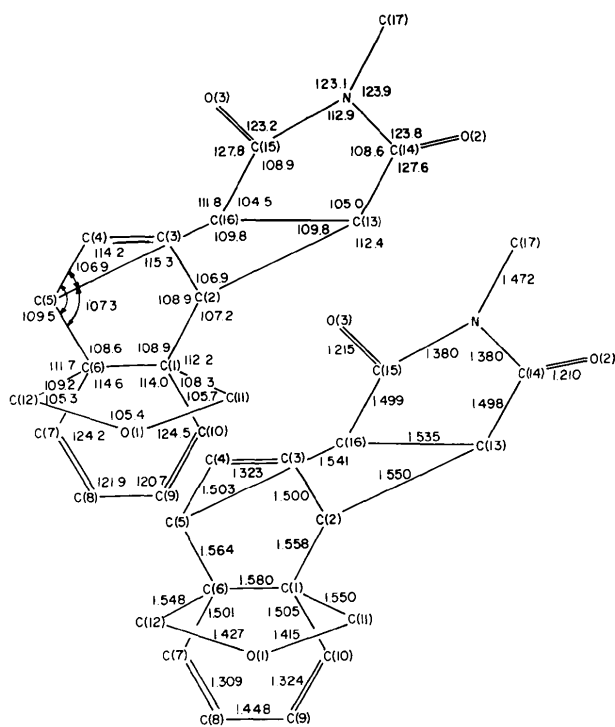

Fig. 9. Bond lengths (Å) and angles (°) in (e). [Angles not shown: C(10)–C(1)–C(2) 110·8; C(11)–C(1)–C(6) 102·5; C(7)–C(6)–C(5) 109·6; C(12)–C(6)–C(1) 102·9.]
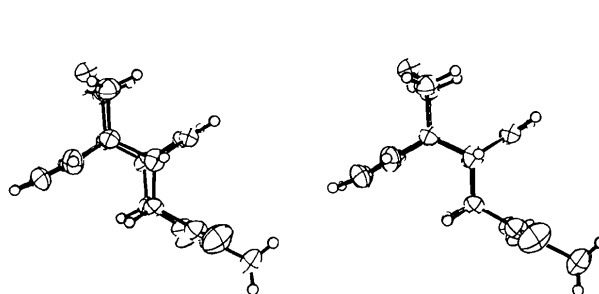

Fig. 8. Stereoview of (d).

Fig. 10. Stereoview of (e).

in the range 0·86–1·11 Å. The e.s.d.'s of bond distances are typically 0·003–0·007 Å, of bond angles 0·2–0·4°. Torsion angles are given in Table 8. A stereoview of the molecule is shown in Fig. 8.

The 4-methyl-1,2,4-triazoline-3,5-dione is *anti* to the hetero-ring; the latter has an envelope shape, the methylene group flipping towards the unsubstituted six-membered ring.

Structure of the monoadduct between 12-oxa[4.4.3]propella-2,4,7,9-tetraene and *N*-methyl-maleimide (*e*)

Bond lengths and angles involving C, N and O atoms are given in Fig. 9; the C—H distances (not shown) lie

in the range 0·94–1·09 Å. The e.s.d.'s of bond distances are typically 0·003–0·006 Å, of bond angles 0·3–0·4°. Torsion angles are given in Table 8. A stereoview of the molecule is shown in Fig. 10.

The *N*-methylmaleimide is *anti* to the hetero-ring; the latter has an envelope shape, the O atom flipping towards the unsubstituted six-membered ring.

Structure of the monoadduct between 12-oxa[4.4.3]propella-2,4,7,9-tetraene and maleic anhydride (*f*)

Bond lengths and angles involving C and O atoms are given in Fig. 11; the C—H distances (not shown) lie in the range 0·86–1·08 Å. The e.s.d.'s of bond distances are typically 0·008–0·009 Å, of bond angles 0·5–0·6°.
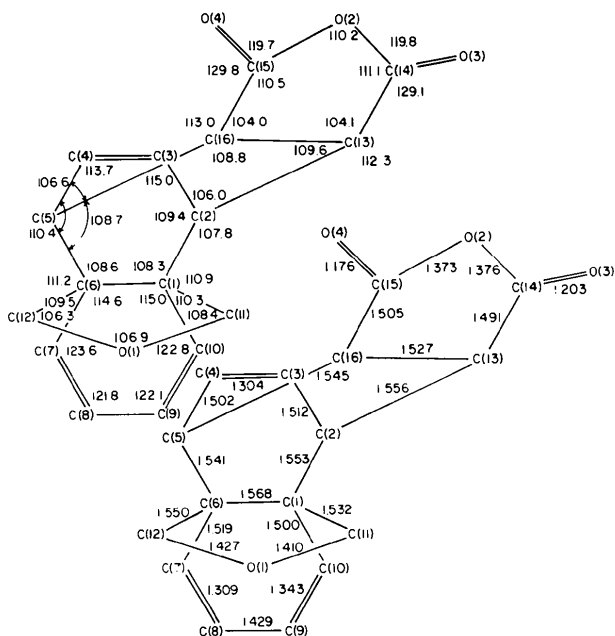
Fig. 11. Bond lengths (Å) and angles (°) in (*f*). [Angles not shown: C(10)–C(1)–C(2) 109·1; C(11)–C(1)–C(6) 103·1; C(7)–C(6)–C(5) 109·4; C(12)–C(6)–C(1) 103·5.]
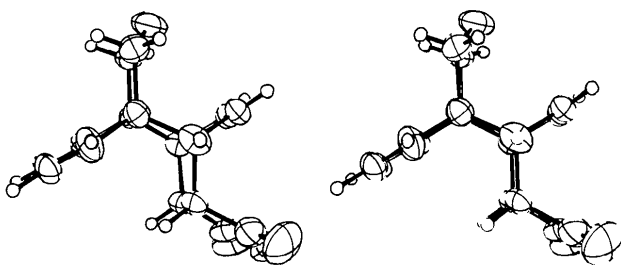

Fig. 12. Stereoview of (*f*).

Torsion angles are given in Table 8. A stereoview of the molecule is shown in Fig. 12. The anhydride is *anti* to the hetero-ring; the latter has an envelope shape, the O atom flipping away from the unsubstituted six-membered ring.

No attempt has been made to find the absolute configuration of the compound.

Discussion

Bond lengths and angles

Four types of C–C bonds are present in the common bicyclohexane skeleton: (*a*) single sp^3–sp^3 bonds [C(1)–C(6), C(1)–C(2), C(5)–C(6)]; the mean length of this type of bond is 1·555 (±0·02) Å; (*b*) single sp^3–sp^2 bonds; the mean value of 1·501

(±0·018) Å agrees well with 1·505 Å (Sutton, 1965); (*c*) single sp^2–sp^2 bonds; the mean value of 1·442 (±0·013) Å is shorter, as expected, than the previous single bonds; (*d*) sp^2–sp^2 double bonds; the mean value of this bond is 1·319 (±0·025) Å.

Although there are some discrepancies from the mean values in the different types of C–C bonds, it seems that these are due to differences in the accuracy of the individual values and not to real effects.

There are also two types of C–C bonds involving the bridging C(1), C(6) atoms and those of the central five-membered ring. In (*e*) and (*f*) the bond lengths corresponding to an sp^3–sp^3 single bond [C(1)–C(11), C(6)–C(12)] are longer (1·532–1·550 Å) than in (*a*), (*b*) and (*c*) (1·508–1·516 Å), which correspond to an sp^3–sp^2 single bond due to the C=O groups involved. Similar values for the first type were observed by Kaftory & Dunitz (1976*a,b*) and for the second type by Kaftory (1978*a,b*), and Birnbaum (1972*a,b*).

Three types of C–O bonds exist in (*c*), (*d*), (*e*), and (*f*). The shortest were observed in (*c*) [O(1)–C(11), O(1)–C(12): 1·382, 1·389 Å respectively] and in (*f*) [C(14)–O(2), C(15)–O(2): 1·376, 1·373 Å respectively]. The shortening is ascribed to interaction of the O lone-pair electrons with the two C=O groups attached to it.

Somewhat longer C–O bonds were observed in (*d*) [C(11)–O(1), C(11)–O(2): 1·401, 1·398 Å respectively]. The shortening of these bonds, compared with the normal C–O length, is found when a C is bonded to more than a single O atom (Jeffrey, Pople & Radom, 1972; Lehn, Wipff & Bürgi, 1974).

A longer C–O bond was observed in (*e*) and (*f*) [O(1)–C(11), O(1)–C(12): 1·415, 1·427 Å, 1·410, 1·427 Å respectively] and somewhat longer in (*d*) [C(1)–O(1), C(6)–O(2): 1·439, 1·440 Å respectively]. These distances are close to 1·426 Å (Sutton, 1965).

The C–N bonds may be divided into three main types. The longest is between N and an sp^3 C atom. The mean value obtained from (*a*) and (*d*) is 1·486 Å for C(2)–N(*x*), C(5)–N(*y*) and 1·459, 1·472 Å in (*d*) and (*e*) respectively (to a methyl C atom). The second bond type is N to an sp^2 C atom: 1·435, 1·423 Å in (*a*) and (*b*) respectively (to a phenyl group). The shortest C–N bond is also between N and an sp^2 C atom but with the possibility of lone-pair electron interaction with carbonyls. The mean value for this bond is 1·382 (±0·01) Å.

There are several types of bond angles in the bicyclohexane skeleton. (*a*) Tetrahedral angles were observed for C(1)–C(2)–C(3), C(4)–C(5)–C(6), C(2)–C(1)–C(6), C(5)–C(6)–C(1). The angles lie in the range 107·3–110·7°. (*b*) Somewhat larger angles were observed in (*b*)–(*f*) [C(1)–C(6)–C(7), C(6)–C(1)–C(10)]. The angles lie in the range 114·0–116·2°. The opening of these angles is a result of the

Table 9. *Deviations* (Å) *from mean planes*

E.s.d.'s are between 0·001 and 0·002 Å.

(a)		(b)		(c)		(d)		(e)		(f)	
C(1)	−0·002	C(1)	0·0	C(1)	0·001	C(1)	0·011	C(1)	0·002	C(1)	0·018
C(6)	0·001	C(6)	0·0	C(12)	−0·001	C(6)	−0·011	C(6)	−0·002	C(6)	−0·018
C(11)	0·002	C(12)	0·0	C(11)	−0·002	O(1)	−0·008	C(11)	−0·001	C(11)	−0·013
N(1)	−0·001	N(1)	0·0	O(1)	0·002	O(2)	0·008	C(12)	0·001	C(12)	0·013
*C(12)	−0·054	*C(11)	−0·054	*C(6)	0·160	*C(11)	0·424	*O(1)	0·571	*O(1)	−0·467
C(16)	−0·002	C(14)	0·002	C(14)	0·004	C(12)	0·0	C(14)	−0·001	C(14)	0·0
C(17)	0·002	C(17)	−0·004	C(15)	−0·009	C(13)	0·0	C(15)	−0·001	C(15)	0·0
N(2)	0·003	C(18)	0·004	C(16)	0·009	N(1)	0·0	C(16)	0·001	C(16)	0·0
N(4)	−0·003	N(2)	−0·003	C(17)	−0·004	N(3)	0·0	N	0·001	O(2)	0·0
*N(3)	0·144	*C(15)	−0·037	*C(18)	−0·561	*N(2)	−0·103	*C(13)	−0·028	*C(13)	0·043
				*C(13)	−0·485						
				*O(5)	0·395						
				*O(4)	0·402						

* Atoms which are not included in the mean-plane calculations.

diene moiety bonded to the atoms involved in these angles; in the absence of this effect the angle is smaller, as in (a) (111·9, 113·3°); 111·0, 112·1° (Kaftory, 1978a); 111·1, 112·8° (Kaftory, 1978b). (c) Single to double bond angles on C(7), C(8), C(9), and C(10) (120·7–124·5°). (d) Somewhat smaller angles of type (c) which were found on atoms C(3), C(4) (112·8–115·3°). These may be ascribed to a geometrical constraint imposed by the substituent on C(2)···C(5) which also causes the puckering of that cyclohexene ring (see also torsion angles in Table 8).

The C—O—C bond angles are 105·4–107·1° in (d)–(f) (compared with 105·2°; Birnbaum, 1972a) while this angle is opened when the O atom is bonded to carbonyls [110·6 (c); 110·2° (f)].

The cyclohexene-1,4-dione moiety in (c) may be regarded as a geometrical intermediate of p-benzoquinone and cyclohexane-1,4-dione. While p-benzoquinone is planar (Trotter, 1960), cyclohexane-1,4-dione is non-planar; the molecule has a boat-shaped conformation with two planar groups [C(13), C(14), C(15), O(4) and C(16), C(17), C(18), O(5) according to the notation of the present work] (Mossel & Romers, 1964). The cyclohexene-1,4-dione has a flat boat shape with best planes passing through C(14), C(15), C(16), C(17) with C(13), C(18) and O(4), O(5) displaced from this plane in opposite directions (see torsion angles in Table 8 and mean planes in Table 9). The C—C and C=O lengths are in good agreement with the comparable values of the other molecules, except for the C(13)—C(18) single bond which is 1·558 Å, compared with 1·531, 1·540 Å in cyclohexane-1,4-dione. The lengthening might be imposed by the constrained geometry of the substituent on these atoms.

Configuration

All five-membered hetero-rings involved in the structures have an envelope shape but the degree of non-planarity depends on the possibility of conjugation. Whenever such a conjugation is feasible with carbonyl groups, the hetero-rings are much more planar than when this possibility does not exist. Some mean-plane calculations are given in Table 9.

In (d), (e) and (f), where the central ring is lacking in carbonyls, the methylene C atom in (d), and the O atoms in (e) and (f) are flipping. The central C(11) in (d) deviates 0·424 Å out of the plane; O(1) in (e) deviates by 0·571 Å; both are flipping towards the unsubstituted ring as found by Kaftory (1978a,b). O(1) in (f) is flipping away from the unsubstituted ring (0·467 Å from the mean plane). The reason for the difference between the conformation in (e) and (f) is not understood.

The dihedral angles between the phenyl group and the triazoline ring are 52·7 (a) and 68·3° (b), compared with 45 (Kaftory, 1978a), 54 (Kaftory, 1978b) and 75·3° (van der Ende, Offereins & Romers, 1974). Other angles between mean planes are summarized in Table 10 (for explanation of symbols see Fig. 13).

The angle between mean planes O and P depends upon the nature of the atoms of the dienophiles. When the original dienophile contains a —HC=CH— group in a five-membered ring the angle between these planes lies in the range 119·7–120·5°, while in a six-membered ring (cyclohexene-1,4-dione in c) it is 124·8° (Table 10). The values observed when the original dienophile contains an —N̈=N̈— group are 130·6 (d), 134·8 (a), 134·2 (Kaftory, 1978a), 139·5 (Kaftory, 1978b), and 149·3° (van der Ende, Offereins & Romers, 1974). The angle between planes L and Q (Fig. 13) depends on the unsubstituted ring. When this ring is saturated the configuration is that of a boat and the angle in (a) is 128·1°, compared with 130·2° in (g), and 129·8° in (h); in all other compounds where the unsubstituted six-membered ring is unsaturated the ring is practically planar (see torsion angles in Table 8).

Table 10. *Comparison of angles (°) between mean planes in monoadducts between propellanes and dienophiles*

For explanation of symbols see Fig. 13.

	(a)	(b)	(c)	(d)	(e)	(f)	(g)*	(h)†
K,L	119·8	118·5	117·9	119·6	117·6	119·6	121·8	124·5
K,M	116·3	117·0	114·9	112·9	118·8	117·9	117·6	117·7
M,L	123·8	124·4	126·0	127·4	123·6	122·5	120·6	117·6
M,N	122·6	121·9	122·4	121·8	122·6	123·1	123·6	122·8
M,O	115·5	116·3	116·8	115·1	117·0	117·8	116·3	117·1
N,O	121·9	121·8	120·7	123·1	120·4	119·0	120·0	120·1
O,P	134·8	119·7	124·8	130·6	120·5	120·5	139·5	134·2
L,Q	128·1	–	–	–	–	–	130·2	129·8

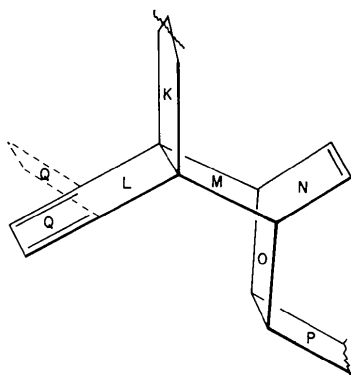* Kaftory (1978a).
† Kaftory (1978b).

Fig. 13. Explanation of symbols used in Table 10. The dotted lines show the configuration in (a), (g) and (h).

The substituted six-membered ring adopts the boat form in all compounds studied; the angles between mean planes M and N lie in the range 121·8–123·1°. The sums of angles between mean planes K, L, M are in the range 359·9–360·2° which indicates the planarity of the projected planes down C(1)–C(6). The sum of these angles in (c) is 358·8° which indicates a slight distortion that can be seen in the torsion angle on C(1)–C(6) (8·2°). The sums of angles between mean planes M, N, O are 359·9–360·0° for all the compounds.

References

ASHKENAZI, P., KALO, J., RÜTTIMANN, A. & GINSBURG, D. (1978). *Tetrahedron*, 34, 2161–2165.

BIRNBAUM, G. I. (1972a). *J. Am. Chem. Soc.* 94, 2455–2459.

BIRNBAUM, K. B. (1972b). *Acta Cryst.* B28, 161–168.

CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* A24, 321–324.

ENDE, C. VAN DER, OFFEREINS, B. & ROMERS, C. (1974). *Acta Cryst.* B30, 1947–1952.

GINSBURG, D. (1974a). *Tetrahedron*, 30, 1487–1497.

GINSBURG, D. (1974b). *Acc. Chem. Res.* 7, 286–293.

GLEITER, R. & GINSBURG, D. (1979). *Pure Appl. Chem.* 51, 1301–1315.

JEFFREY, G. A., POPLE, J. A. & RADOM, L. (1972). *Carbohydr. Res.* 25, 107–116.

JOHNSON, C. K. (1965). *ORTEP.* Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

KAFTORY, M. (1978a). *Acta Cryst.* B34, 300–303.

KAFTORY, M. (1978b). *Acta Cryst.* B34, 303–305.

KAFTORY, M. & DUNITZ, J. D. (1976a). *Acta Cryst.* B32, 617–619.

KAFTORY, M. & DUNITZ, J. D. (1976b). *Acta Cryst.* B32, 619–621.

KAFTORY, M., PELED, M. & GINSBURG, D. (1979). *Helv. Chim. Acta*, 62, 1326–1329.

KALO, J. & GINSBURG, D. (1978). *Tetrahedron*, 34, 2155–2160.

KALO, J., VOGEL, E. & GINSBURG, D. (1977). *Tetrahedron*, 33, 1177–1182.

KORAT, M., TATARSKY, D. & GINSBURG, D. (1972). *Tetrahedron*, 28, 2315–2332.

LEHN, J. M., WIPFF, G. & BÜRGI, H. B. (1974). *Helv. Chim. Acta*, 57, 493–496.

MAIN, P., WOOLFSON, M. M., LESSINGER, L., GERMAIN, G. & DECLERCQ, J. P. (1977). *MULTAN 77. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

MOSSEL, A. & ROMERS, C. (1964). *Acta Cryst.* 17, 1217–1223.

SHELDRICK, G. M. (1976). *SHELX. A program for crystal structure determination.* Univ. of Cambridge, England.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* 42, 3175–3187.

SUTTON, L. E. (1965). *Tables of Interatomic Distances and Configuration in Molecules and Ions.* Spec. Publ. No. 18. London: The Chemical Society.

TROTTER, J. (1960). *Acta Cryst.* 13, 86–95.