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Reaction Pathway in the Photoconversion of a Tetrahydroanthracenedione (I) to its Solid-State Photoproduct (II)

By SARA ARIEL, SYED H. ASKARI, JOHN R. SCHEFFER, JAMES TROTTER AND FRED WIREKO

Department of Chemistry, University of British Columbia, Vancouver, BC, Canada V6T 1Y6

Abstract

$C_{18}H_{20}O_2$, $M_r = 268.36$, $F(000) = 576$, $T = 295$ K, Mo $K\alpha_1$, $\lambda = 0.70930$ Å. (I) 2,3,4aβ,10aβ-Tetramethyl-4a,5,10,10a-tetrahydrobenzo[6,7]naphtho-1,4-quinone (2,3,4a,9a-tetramethyl-cis-4a,9,9a,10-tetrahydro-1,4-anthracenedione), monoclinic, Cc, $a = 6.877$ (2), $b = 22.377$ (3), $c = 9.972$ (3) Å, $\beta = 101.68$ (1)°, $V = 1502.8$ (6) Å^3, $Z = 4$, $D_x = 1.186$ g cm^{-3}, $\mu = 0.71$ cm^{-1}, $R = 0.037$ for 821 observed reflections. The conformation of molecule (I) is twisted such that the bridgehead methyl groups are staggered with a torsion angle of 61.0°. Bond lengths and angles are close to normal values. (II) 1,3,4,6-Tetramethylbenzo[8,9]tricyclo[4.4.0.0^{3,10}]-dec-8-ene-2,5-dione, triclinic, $P\bar{1}$, $a = 9.825$ (2), $b = 12.369$ (3), $c = 12.894$ (3) Å, $\alpha = 107.39$ (1), $\beta = 92.85$ (2), $\gamma = 96.79$ (1)°, $V = 1478.8$ (6) Å^3, $Z = 4$ (two molecules per asymmetric unit), $D_x = 1.205$ g cm^{-3}, $\mu = 0.72$ cm^{-1}, final $R = 0.055$ for 3850 observed reflections. Bond lengths and angles suggest a strained system. Compound (II) is the only solid-state photoproduct of (I). The crystal structures of diketones (I) and (II) allow the proposal of a detailed reaction pathway for the formation of (II). The proposed mechanism involves a γ-H-atom abstraction by an ethylenic C atom to form an intermediate biradical, followed by C–C bonding to generate the tricyclic compound (II). The complete reaction pathway involves a minimum of intramolecular motion, with an accompanying movement of the whole reacting molecule by about 1.0 Å allowing accommodation of the photoproduct in the reactant lattice, in a topochemically favourable process.

Introduction

Photolysis of crystals of (I) gives only product (II), while photolysis in solution gives mainly (II) at high temperature and predominantly (III) at low temperature. The crystal structure of (I) has been determined in an effort to rationalize the observed photochemical behaviour, and that of (II) to provide details of possible reaction pathways.
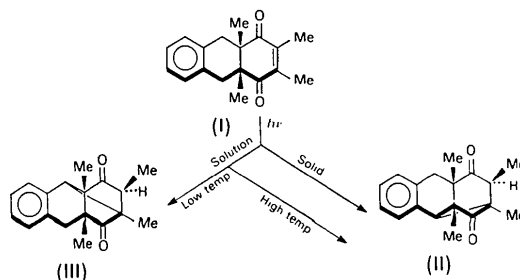
Experimental

Crystal size $0.4 \times 0.4 \times 0.2$ mm for (I) [$0.4 \times 0.4 \times 0.5$ mm for (II)], m.p. 357–358 K [362–363 K], Enraf-Nonius CAD-4 diffractometer, graphite-monochromatized Mo $K\alpha$ radiation, lattice parameters from setting of 25 reflections with $10 \le \theta \le 18°$ [$20 \le \theta \le 23°$]. 1312 unique reflections with $\theta \le 25°$ for (I)

[5636 with $\theta \leq 27 \cdot 5°$ for (II)], $h = -8-8$, $k = 0-26$, $l = 0-11$ [$h = -12-12$, $k = -16-16$, $l = 0-16$]; $\omega-2\theta$ [$\omega-(2/3)\theta$] scan, ω-scan width $(0 \cdot 65 + 0 \cdot 3 \tan \theta)°$ [$(1 \cdot 0 + 0 \cdot 3 \tan \theta)°$] extended 25% on each side for background measurement, horizontal aperture $(2 \cdot 0 + \tan \theta)$ mm, vertical aperture 4 mm, Lp corrections, three standard reflections. Both structures were solved by direct methods, (I) with MULTAN80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) and (II) using SHELX76 (Sheldrick, 1976). (I) was refined by full-matrix least squares minimizing $\sum w(|F_o| - |F_c|)^2$ with locally modified versions of standard computer programs. (II) was refined by block-diagonalized least squares using SHELX76. The aromatic H atoms of (I) were placed in calculated positions and the methyl H atoms were idealized in staggered positions by least-squares adjustments to observed positions from a three-dimensional difference Fourier map. All H atoms of (II) were located in a difference synthesis and their temperature factors were refined isotropically. 179 parameters of (I), consisting of 58 positional and 120 anisotropic temperature parameters, and a scale factor; 521 parameters of (II), consisting of 240 positional, 240 anisotropic and 40 isotropic temperature parameters, and a scale factor. Convergence of (I) at $R = 0 \cdot 037$, $wR = 0 \cdot 039$ for 821 observed reflections for which $I \geq 3\sigma(I)$. Convergence of (II) at $R = 0 \cdot 055$, $wR = 0 \cdot 048$ for 3850 reflections for which $F \geq 3\sigma(F)$, where $\sigma^2(I) = S + 2B + [0 \cdot 04(S - B)]^2$, $S = $ scan count, $B = $ time-averaged background count. $R = 0 \cdot 073$, $wR = 0 \cdot 039$ for all data of (I), $R = 0 \cdot 092$, $wR = 0 \cdot 058$ for all data of (II); $w = 1/\sigma^2(F)$, $(\Delta/\sigma)_{max} = 0 \cdot 01$, $\pm 0 \cdot 26$ e Å^{-3} in final difference synthesis of (I), $(\Delta/\sigma)_{max} = 0 \cdot 15$, $\pm 0 \cdot 18$ e Å^{-3} for (II), atomic scattering factors from Cromer & Mann (1968) and Stewart, Davidson & Simpson (1965).

Discussion

Final atomic coordinates are in Table 1, bond distances, bond angles and selected torsion angles in Table 2.*

The conformation of molecule (I) (Fig. 1) is twisted about the C(4a)–C(8a) bond, so that the bridgehead methyl groups are staggered, as in the related compound cis-2,3,4aβ,6,7,8aβ-hexamethyl-4aβ,5,8,8aβ-tetrahydro-1,4-naphthoquinone (IV) (Phillips & Trotter, 1976), the cyclohexenedione and cyclohexene rings both having half-chair conformations.

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* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and bond distances and angles involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44041 (27 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atom coordinates $(\times 10^4)$ and temperature factors $(\text{Å}^2 \times 10^3)$

$$U_{eq} = \tfrac{1}{3} \text{ trace } \tilde{U}.$$

	x	y	z	U_{eq}
Compound (I)				
C(1)	2614 (8)	1604 (2)	−547 (6)	45
C(2)	1055 (9)	1970 (2)	−1428 (6)	54
C(21)	1760 (9)	2553 (2)	−1942 (7)	86
C(3)	−839 (8)	1784 (2)	−1726 (6)	52
C(31)	−2492 (9)	2128 (3)	−2602 (6)	88
C(4)	−1375 (8)	1198 (2)	−1200 (5)	49
C(4a)	0	917 (2)	0	40
C(4a1)	−630 (9)	276 (2)	205 (6)	62
C(5)	−38 (9)	1295 (2)	1280 (6)	52
C(6)	1628 (8)	1161 (2)	2475 (6)	53
C(7)	3382 (8)	905 (2)	2293 (6)	53
C(8)	3643 (8)	698 (2)	907 (6)	52
C(8a)	2134 (7)	953 (2)	−283 (5)	44
C(8a1)	2334 (9)	611 (2)	−1608 (6)	57
C(9)	1444 (9)	1320 (2)	3813 (6)	79
C(10)	2957 (14)	1229 (3)	4902 (6)	98
C(11)	4710 (13)	975 (3)	4718 (7)	99
C(12)	4939 (9)	815 (2)	3419 (7)	69
O(1)	4242 (7)	1819 (1)	−83 (5)	67
O(4)	−2906 (7)	959 (2)	−1767 (5)	78
Compound (II)				
Molecule A				
O(1)	11882 (2)	2852 (1)	9384 (1)	97
O(4)	11432 (1)	305 (1)	5881 (1)	68
C(1)	11167 (2)	2388 (2)	8539 (2)	60
C(2)	10284 (2)	1246 (2)	8381 (1)	54
C(21)	11113 (4)	453 (3)	8772 (3)	89
C(3)	9626 (2)	730 (1)	7198 (1)	48
C(31)	8771 (3)	−430 (2)	6971 (2)	71
C(4)	10711 (2)	914 (2)	6449 (1)	50
C(4a)	10389 (2)	2115 (1)	6562 (1)	46
C(4a1)	10461 (3)	2535 (2)	5574 (2)	67
C(5)	8955 (2)	1674 (1)	6853 (1)	46
C(6)	8216 (2)	2498 (2)	7646 (1)	51
C(7)	8860 (2)	3600 (2)	8198 (1)	59
C(8)	10323 (3)	3967 (2)	8033 (2)	67
C(8a)	11144 (2)	2963 (1)	7631 (2)	56
C(8a1)	12631 (3)	3378 (3)	7474 (3)	94
C(9)	6866 (2)	2174 (3)	7838 (2)	70
C(10)	6174 (3)	2943 (4)	8567 (2)	92
C(11)	6811 (5)	4032 (4)	9084 (2)	104
C(12)	8129 (4)	4357 (2)	8905 (2)	84
Molecule B				
O(1)	5551 (2)	244 (1)	1971 (1)	93
O(4)	3550 (2)	3283 (2)	4103 (1)	98
C(1)	5680 (2)	1254 (2)	2463 (2)	56
C(2)	6191 (2)	1687 (2)	3666 (2)	53
C(21)	5524 (3)	885 (3)	4265 (3)	79
C(3)	6005 (2)	2941 (2)	4175 (1)	50
C(31)	6387 (3)	3415 (3)	5397 (2)	85
C(4)	4620 (2)	3110 (2)	3716 (2)	59
C(4a)	5218 (2)	3275 (2)	2695 (1)	48
C(4a1)	4646 (2)	4130 (2)	2214 (3)	72
C(5)	6596 (2)	3657 (2)	3437 (1)	43
C(6)	7906 (2)	3421 (1)	2926 (1)	44
C(7)	7878 (2)	2776 (2)	1844 (2)	51
C(8)	6529 (2)	2258 (2)	1176 (2)	66
C(8a)	5330 (2)	2106 (2)	1866 (1)	52
C(8a1)	3995 (3)	1593 (3)	1114 (3)	91
C(9)	9167 (2)	3858 (2)	3544 (2)	63
C(10)	10383 (2)	3663 (3)	3083 (3)	85
C(11)	10362 (3)	3059 (3)	2016 (4)	91
C(12)	9136 (3)	2617 (2)	1391 (3)	76

The degree of twist is shown by the torsion angles C(5)–C(4a)–C(8a)–C(1), −60·9(4), and C(4a1)–C(4a)–C(8a)–C(8a1), 61·0 (4)°. In (IV), the corresponding values for the two angles are −61·4 (5) and 60·0 (6)°, respectively. Bond lengths and bond angles are not significantly different from those in (IV), except for the increase in C(6)–C(7), 1·380 (6) vs 1·323 (7) Å, resulting from the lower bond order. The

Table 2. Bond lengths (Å), bond angles (°) and selected torsion angles (°)

	Compound (I)	Compound (II) Mol. (A)	Compound (II) Mol. (B)
C(1)-O(1)	1·221 (4)	1·210 (2)	1·207 (3)
C(1)-C(2)	1·487 (6)	1·521 (3)	1·520 (3)
C(2)-C(21)	1·517 (7)	1·524 (4)	1·536 (4)
C(2)-C(3)	1·343 (6)	1·540 (2)	1·530 (3)
C(3)-C(31)	1·499 (6)	1·512 (3)	1·518 (3)
C(3)-C(4)	1·486 (6)	1·516 (3)	1·518 (3)
C(3)-C(5)	—	1·569 (3)	1·570 (3)
C(4)-O(4)	1·214 (5)	1·206 (2)	1·201 (3)
C(4)-C(4a)	1·504 (5)	1·521 (3)	1·527 (3)
C(4a)-C(4a1)	1·524 (6)	1·514 (4)	1·522 (4)
C(4a)-C(5)	1·536 (6)	1·555 (3)	1·556 (2)
C(5)-C(6)	1·506 (6)	1·496 (3)	1·494 (2)
C(6)-C(7)	1·380 (6)	1·392 (3)	1·382 (2)
C(7)-C(8)	1·502 (6)	1·500 (3)	1·505 (3)
C(8)-C(8a)	1·521 (5)	1·535 (3)	1·538 (3)
C(1)-C(8a)	1·527 (5)	1·541 (3)	1·537 (3)
C(4a)-C(8a)	1·552 (5)	1·550 (2)	1·540 (2)
C(8a)-C(8a1)	1·556 (6)	1·534 (4)	1·541 (3)
C(6)-C(9)	1·411 (6)	1·394 (3)	1·396 (2)
C(9)-C(10)	1·359 (8)	1·390 (5)	1·375 (3)
C(10)-C(11)	1·378 (9)	1·369 (6)	1·353 (5)
C(11)-C(12)	1·384 (9)	1·362 (6)	1·372 (4)
C(7)-C(12)	1·401 (6)	1·392 (4)	1·403 (3)
O(1)-C(1)-C(2)	120·2 (4)	119·9 (2)	120·4 (2)
O(1)-C(1)-C(8a)	121·7 (4)	119·9 (2)	119·8 (2)
C(2)-C(1)-C(8a)	118·1 (3)	120·2 (2)	119·8 (2)
C(1)-C(2)-C(3)	120·7 (4)	111·2 (2)	111·4 (2)
C(1)-C(2)-C(21)	115·6 (4)	110·1 (2)	110·2 (2)
C(21)-C(2)-C(3)	123·7 (4)	114·0 (2)	113·8 (2)
C(2)-C(3)-C(4)	119·7 (4)	107·6 (1)	107·8 (1)
C(2)-C(3)-C(31)	123·8 (4)	114·1 (2)	114·8 (2)
C(31)-C(3)-C(4)	116·5 (4)	120·3 (2)	118·9 (2)
O(4)-C(4)-C(3)	118·6 (4)	134·1 (2)	133·3 (2)
O(4)-C(4)-C(4a)	122·2 (4)	133·5 (2)	133·0 (2)
C(3)-C(4)-C(4a)	119·2 (3)	92·0 (1)	92·2 (1)
C(4)-C(4a)-C(4a1)	110·5 (3)	118·3 (2)	117·6 (2)
C(4)-C(4a)-C(5)	108·5 (3)	84·9 (1)	84·1 (1)
C(4a1)-C(4a)-C(5)	110·7 (3)	118·7 (2)	118·8 (2)
C(4)-C(4a)-C(8a)	107·4 (3)	109·6 (2)	110·1 (2)
C(4a1)-C(4a)-C(8a)	112·3 (3)	114·9 (2)	115·2 (2)
C(5)-C(4a)-C(8a)	107·3 (3)	106·6 (1)	107·0 (1)
C(4a)-C(5)-C(6)	114·1 (3)	118·6 (1)	118·5 (1)
C(5)-C(6)-C(7)	121·6 (4)	120·5 (2)	120·4 (1)
C(5)-C(6)-C(9)	119·8 (5)	120·4 (2)	119·9 (2)
C(7)-C(6)-C(9)	118·5 (4)	119·0 (2)	119·7 (2)
C(6)-C(7)-C(8)	121·3 (4)	120·4 (2)	120·5 (2)
C(6)-C(7)-C(12)	120·0 (4)	119·1 (2)	118·2 (2)
C(8)-C(7)-C(12)	118·7 (5)	120·5 (2)	121·2 (2)
C(7)-C(8)-C(8a)	114·3 (4)	113·3 (2)	113·6 (2)
C(1)-C(8a)-C(8)	110·8 (3)	105·8 (2)	107·0 (2)
C(1)-C(8a)-C(4a)	109·1 (3)	110·3 (2)	110·4 (2)
C(4a)-C(8a)-C(8)	111·1 (3)	108·9 (2)	108·4 (2)
C(1)-C(8a)-C(8a1)	105·3 (3)	108·6 (2)	108·7 (2)
C(4a)-C(8a)-C(8a1)	112·2 (3)	111·6 (2)	112·5 (2)
C(8)-C(8a)-C(8a1)	108·3 (3)	111·5 (2)	109·7 (2)
C(6)-C(9)-C(10)	121·1 (6)	120·5 (3)	120·6 (2)
C(9)-C(10)-C(11)	120·3 (5)	119·8 (3)	119·9 (2)
C(10)-C(11)-C(12)	120·0 (5)	120·3 (4)	120·6 (3)
C(7)-C(12)-C(11)	120·0 (5)	121·3 (3)	120·9 (3)
C(2)-C(3)-C(5)	—	108·9 (1)	109·4 (1)
C(31)-C(3)-C(5)	—	117·7 (2)	118·0 (2)
C(4)-C(3)-C(5)	—	84·6 (1)	83·9 (2)
C(3)-C(5)-C(4a)	—	88·7 (1)	89·1 (1)
C(3)-C(5)-C(6)	—	120·5 (2)	120·0 (2)
C(8a)-C(1)-C(2)-C(3)	14·8 (6)	8·8 (3)	11·6 (3)
C(2)-C(1)-C(8a)-C(4a)	-42·6 (5)	-11·4 (3)	-14·5 (2)
C(2)-C(1)-C(8a)-C(8)	-165·2 (4)	106·2 (2)	103·3 (2)
C(1)-C(2)-C(3)-C(4)	-1·6 (6)	41·9 (2)	40·5 (2)
C(2)-C(3)-C(4)-C(4a)	19·8 (6)	-84·5 (2)	-83·7 (2)
C(3)-C(4)-C(4a)-C(5)	68·7 (5)	-23·8 (1)	-24·9 (1)
C(3)-C(4)-C(4a)-C(8a)	-47·1 (4)	81·9 (2)	81·0 (2)
C(4)-C(4a)-C(5)-C(6)	-165·4 (3)	147·5 (2)	148·1 (2)
C(8a)-C(4a)-C(5)-C(6)	-49·7 (4)	38·5 (2)	38·9 (2)
C(4)-C(4a)-C(8a)-C(1)	55·6 (4)	-36·5 (2)	-34·5 (2)
C(4)-C(4a)-C(8a)-C(8)	178·0 (3)	-152·1 (2)	-151·4 (2)
C(5)-C(4a)-C(8a)-C(1)	-60·9 (4)	53·9 (2)	55·4 (2)
C(5)-C(4a)-C(8a)-C(8)	61·5 (4)	-61·7 (2)	-61·6 (2)
C(4a)-C(5)-C(6)-C(7)	23·2 (5)	-6·9 (3)	-6·5 (3)
C(4a)-C(5)-C(6)-C(9)	-159·4 (4)	172·8 (2)	173·3 (2)
C(6)-C(7)-C(8)-C(8a)	17·2 (5)	-23·4 (3)	-22·5 (3)
C(12)-C(7)-C(8)-C(8a)	-165·0 (4)	156·7 (2)	157·3 (2)
C(7)-C(8)-C(8a)-C(1)	75·6 (4)	-62·1 (2)	-63·3 (2)

Table 2 (cont.)

	Compound (I)	Compound (II) Mol. (A)	Compound (II) Mol. (B)
C(7)-C(8)-C(8a)-C(4a)	-45·8 (4)	56·4 (2)	55·8 (2)
C(4a)-C(4)-C(3)-C(5)	—	23·6 (1)	24·7 (1)
C(5)-C(3)-C(2)-C(1)	—	-48·4 (2)	-49·2 (2)
C(4)-C(3)-C(5)-C(6)	—	-145·9 (2)	-147·0 (2)
C(4)-C(3)-C(5)-C(4a)	—	-23·1 (1)	-24·2 (1)
C(2)-C(3)-C(5)-C(6)	—	-39·1 (2)	-40·2 (2)
C(2)-C(3)-C(5)-C(4a)	—	83·7 (2)	82·6 (2)
C(7)-C(6)-C(5)-C(3)	—	100·1 (2)	100·5 (2)
C(9)-C(6)-C(5)-C(3)	—	-80·3 (3)	-79·7 (2)
C(3)-C(5)-C(4a)-C(4)	—	23·0 (1)	24·0 (1)
C(3)-C(5)-C(4a)-C(8a)	—	-86·0 (2)	-85·2 (2)

$C(sp^3)-C(sp^3)$ bond distances (Table 2) are in the range 1·521 (5)–1·556 (6) Å, mean 1·538 Å.
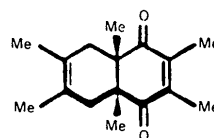
(IV)

Irradiation of tetrahydronaphthoquinone derivatives with UV light[†] results in photoproducts whose formation can be rationalized on the basis of two principal reaction mechanisms (Scheffer, 1980; Trotter, 1983): (i) abstraction of a β-H atom on C(8) by O(1) via an n, π^* singlet excited state, to form a biradical such as (Ia) (Fig. 2); (ii) abstraction of a γ-H atom on C(5) by C(2), via a π, π^* triplet excited state, to form biradical (Ib); both biradicals then form tricyclic products. The twist conformations which are observed in such derivatives have geometries which are ideal for these H-atom abstractions, with $H_\beta\cdots O$ and $H_\gamma\cdots C$ distances of the order of van der Waals separations (2·7 and 2·9 Å, respectively). Other relevant parameters are τ (the angle by which H is dis-

† The solid-state photolyses were carried out at room temperature on single-crystal samples using a nitrogen laser ($\lambda = 337$ nm) as the light source. At low conversions (<5%), the samples remained solid, and the only photoproduct detectable by gas chromatography was cyclobutanone (II); recrystallization was required to obtain single crystals of (II). At higher conversions, the crystals of (I) began to melt, and a second photoproduct, identical to the solution-phase photoproduct (III), was formed in small amounts (Ariel, Askari, Scheffer, Trotter & Wireko, 1987).
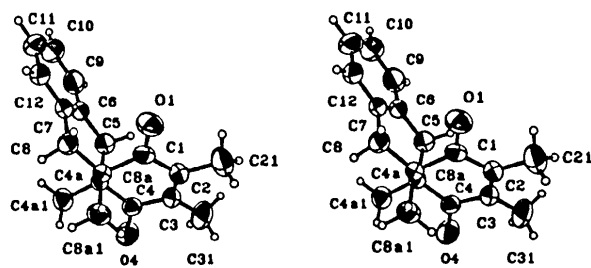

Fig. 1. ORTEP stereoview of compound (I).

placed from the carbonyl or ethylenic plane) and Δ (C=O···H and C=C···H). In addition, the biradical intermediates have ideal geometries for the formation of new C–C bonds with minimum atomic movement, the C···C distances being again of the order of normal van der Waals separations, 3·4 Å. For (Ia), C(1)–C(6) bond formation takes place and/or (after conformational inversion and hence topochemically forbidden in the solid state) C(3)–C(8) bonding; for (Ib), C(3)–C(5) bonding.

In (I), the relevant parameters for β-H abstraction by O are H(8)···O(1) = 2·43 Å, $\tau_O = 3°$, $\Delta_O = 85°$, the corresponding values for (IV) being 2·47 Å, 0°, 85°. Both molecules therefore have geometries which allow such H abstraction, and formation of biradical intermediates of the type (Ia). For (IV), photoproduct (V) results from C(1)–C(6) bond formation [C(1)···C(6) = 3·35 Å] in solution and in the solid state (Scheffer, Trotter, Gayler & Bear, 1973; Dzakpasu, Phillips, Scheffer & Trotter, 1976). In (I), however, C(6) is part of an aromatic-ring system, and hence such a process is unlikely, since it would destroy the aromatic character of the ring. The photoproduct from (I) involves formation of a C(3)–C(8) bond; since C(3)···C(8) is 4·36 (6) Å, such bond formation involves a conformational ring flip (via eclipsed bridgehead substituents) to a conformation in which C(3) and C(8) are in closer proximity [the distance may be approximated by the C(2)···C(5) distance in (I) of 3·31 Å]. The formation from (I) of such a photoproduct (III) occurs in solution, but is topochemically forbidden in the solid state, since the conformational change is prevented by the constraints of the crystal lattice.

For γ-H abstraction by C in (I), H(5)···C(2) = 2·75 Å, $\tau_C = 51°$, $\Delta_C = 74°$; the parameters for (IV) are 2·80 Å, 52°, 73°. Formation of biradicals of type (Ib) is therefore feasible, and furthermore the geometry of (Ib) is ideal for direct C(3)–C(5) bonding, C(3)···C(5) = 3·13 (6) Å in (I), 3·17 Å in (IV),

resulting in products (II) in solution and in the solid state.

Hence, the photochemistry of (I) results in formation of (II) in solution and in the solid state via γ-H abstraction by C, and of (III) in solution via β-H abstraction by O, the formation of (III) in the solid state being topochemically forbidden. The temperature dependence of the photoproduct ratio in solution can be rationalized in terms of two competing first-order processes with different activation energies (Ariel et $al.$, 1987).

The conformation of photoproduct (II) (Fig. 3) is twisted about the C(4a)–C(8a) bond, so that the bridgehead methyl groups are staggered in the two independent molecules (A) and (B). The degree of twist is shown by the torsion angles C(5)–C(4a)–C(8a)–C(1), −53·9 (2), −55·4 (2)°, for molecules (A) and (B), respectively, and C(4a1)–C(4a)–C(8a)–C(8a1), 51·7 (3), 48·7 (3)°. Bond distances and angles (Table 2) suggest a strained system, as a result of the presence of the four-membered ring. This ring is puckered, torsion angles about 24°, with normal C(sp^2)–C(sp^3) bonds of 1·516, 1·521 Å [1·518, 1·527 (3) Å] for molecule (A) [and (B)], long C(sp^3)–C(sp^3) distances of 1·569, 1·555 Å [1·570, 1·556 (3) Å], and deviations of up to 25° from normal tetrahedral angles at C(3), 84·6–120·3° [83·9–118·9 (2)°], and at C(5), 88·7–120·5° [89·1–120·0(2)°]. O(4) deviates by 0·122 (2), 0·202 (2) Å from the C(3), C(4), C(4a) plane in molecules (A) and (B), respectively; O(1) is coplanar with the C(1), C(2), C(8a) plane [corresponding deviations 0·016 (2), 0·002 (2) Å, respectively]. The distortion from planarity of the O(4) carbonyl is probably induced by the strain of the four-membered ring. The C(sp^2) nature of C(4) is highly strained as its bond angles range from 92·0 (1) to 134·1 (2)° for molecule (A), 92·2 (1)–133·3 (2)° for molecule (B), deviations of up to 28° from normal trigonal angles. No such strain exists for C(1).

The two crystallographically independent molecules of (II) are related roughly by a non-crystallographic centre of symmetry (at 0·82, 0·25, 0·53), and adopt similar conformations. Intermolecular
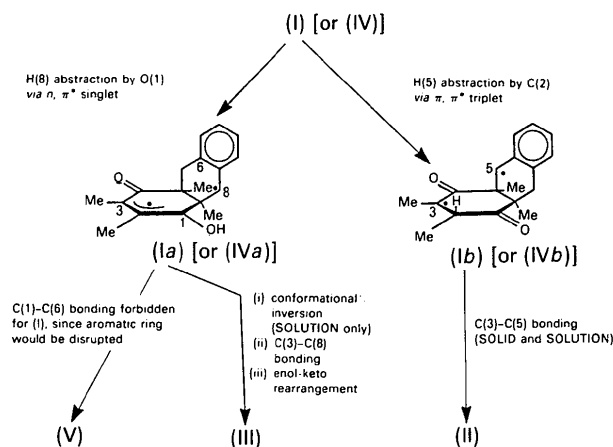

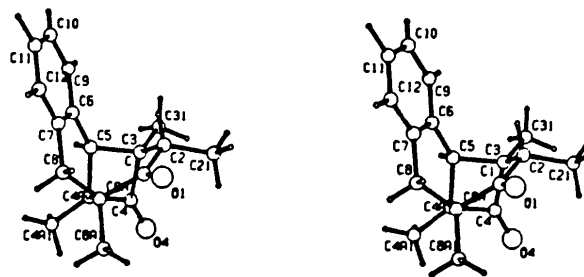Fig. 2. Mechanisms of H-abstraction reactions.

Fig. 3. $PLUTO$ stereoview of molecule (A) of compound (II). The mirror image is shown for comparison with compound (I).

contacts for both compounds (I) and (II) correspond to van der Waals distances.

Reaction pathway

The reaction pathway for (I) → (II) involves a reduction of the C(3)···C(5) non-bonded distance of 3·133 (6) Å to a bonded C(3)–C(5) length of 1·570 (3) Å, which can be achieved with minimum total atomic movement (of about 1·5 Å). The pyramidalization at C(2) and movement of C(3) towards C(5) causes a change in the dione ring from an initial half-chair conformation to a final boat shape, but the overall conformations of the other two six-membered rings are relatively unaffected (compare Figs. 1 and 3).
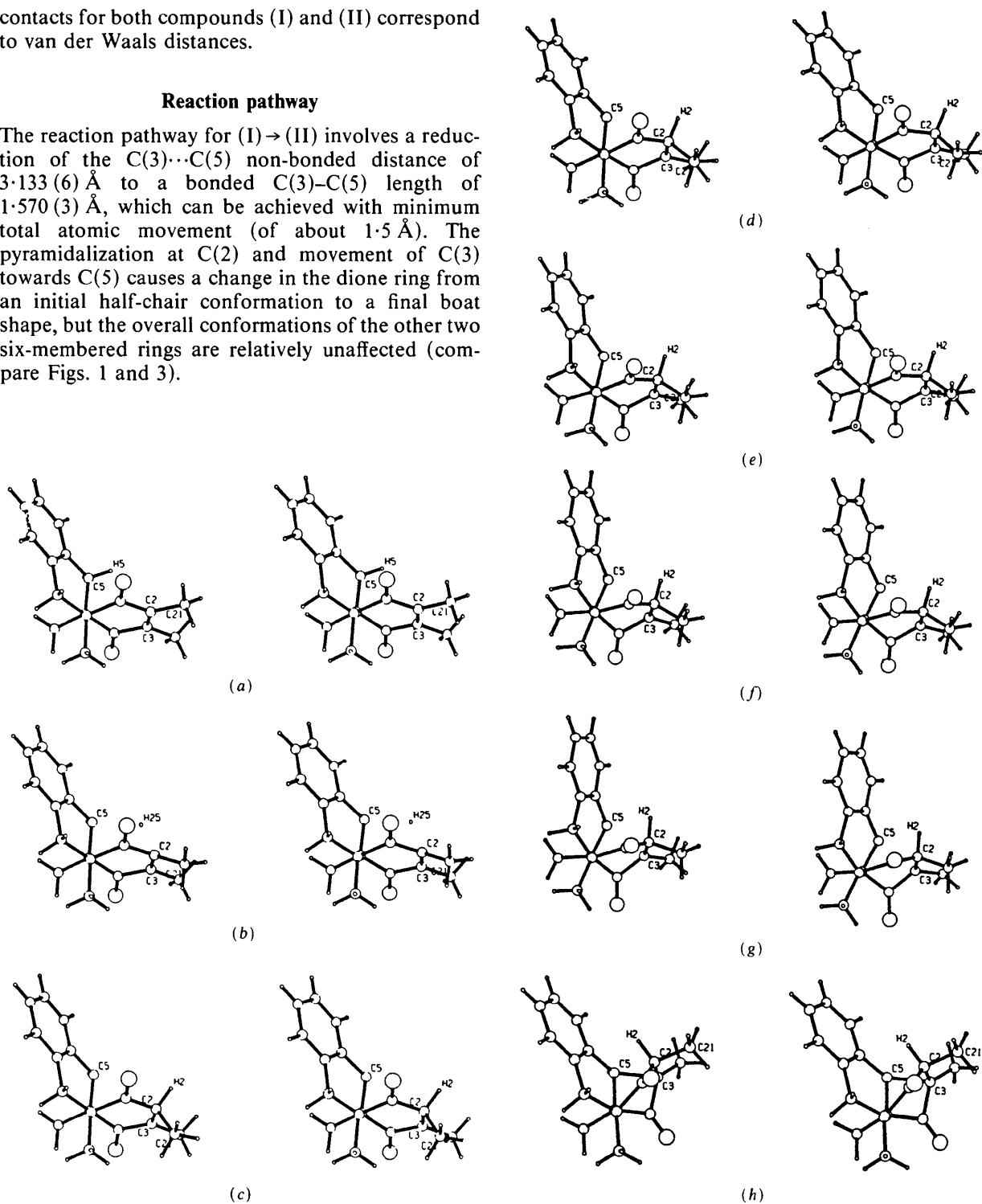

Fig. 4. Reaction pathway. Step (i): Transfer of H(5) to C(2) to form a biradical, with accompanying pyramidalization at C(2): (a) starting material, compound (I); (b) half-way through H transfer [partial pyramidalization at C(2)]; (c) biradical [change of hybridization at C(5), from sp^3 to sp^2, is ignored - see text]. Step (ii): Stepwise reduction of the C(3)···C(5) distance of 3·133 (6) Å (Fig. 1) to a final bonded distance of 1·570 (3) Å (Fig. 3) via: folding about C(4a)–C(8a) by 20°, folding about C(1)···C(4) by 50°, partial pyramidalization at C(3) [C(31) is 20° out of plane of C(2), C(3), C(4)], and maintaining approximate planarity of carbonyl functions: (d) 20% of motions applied [C(3)···C(5) = 2·896 Å]; (e) 40% [2·633 Å]; (f) 60% [2·347 Å]; (g) 80% [2·044 Å]; (h) 100% [1·729 Å]. Step (iii): MMP2 minimization of the energy of the simulated photoproduct (4 h, 100%) results in minor adjustments of the conformation, with C(3)–C(5) adjusting to 1·563 Å, compared with measured values of 1·569, 1·570 Å.

The proposed detailed pathway can be analysed in terms of the following motions:

(i) Transfer of H(5) to C(2) to form a biradical, with accompanying pyramidalization at C(2). [Initial sp^3 hybridization at C(5) probably changes to sp^2 in the biradical, but in the photoproduct C(5) again becomes 4-coordinate.]

(ii) Reduction of the C(3)$\cdots$C(5) distance of 3·133 (6) Å to a final bonded distance of 1·570 (3) Å; the motion can be analysed as:

(a) folding about C(4a)–C(8a) by 20°;

(b) folding about C(1)$\cdots$C(4) by 50°;

(c) partial pyramidalization of C(3);

(d) minor movements of O atoms to maintain approximate planarity of carbonyl functions [the C(4)–O(4) carbonyl group in (II) shows deviations from planarity as described above].

(iii) Minor adjustments of the resulting photoproduct conformation and dimensions to minimize the molecular energy.

The pathway was mapped (Fig. 4) by H-atom transfer [step (i) above, shown in Figs. 4(a), (b), (c)], followed by reduction of the C(3)$\cdots$C(5) distance [step (ii), with all the motions applied concurrently; intermediate steps at 20, 40, 60, 80, 100% of the motions are shown in Figs. 4(d), (e), (f), (g), (h)]. A local computer program was designed to perform the various motions. Finally, MMP2 adjustment of the energy of the photoproduct (Allinger & Flanagan, 1983) was carried out.

The topochemical implications of the reaction were determined by examining intermolecular interactions developed between the reacting molecule and surrounding unreacting molecules in the lattice of the reactant. Movement of C(3) towards C(5) produces unfavourable H$\cdots$H intermolecular contacts, which, in the absence of any overall movement of the reacting molecule, become as short as 1·226 Å (Figs. 5a,b). However, the motion results in some free space becoming available in the lattice (Fig. 5b), and the short H$\cdots$H contacts can be relieved by a movement of the whole reacting molecule by about 1·0 Å along the $-z$ axis (Fig. 5c); the process is thus topochemically favourable.
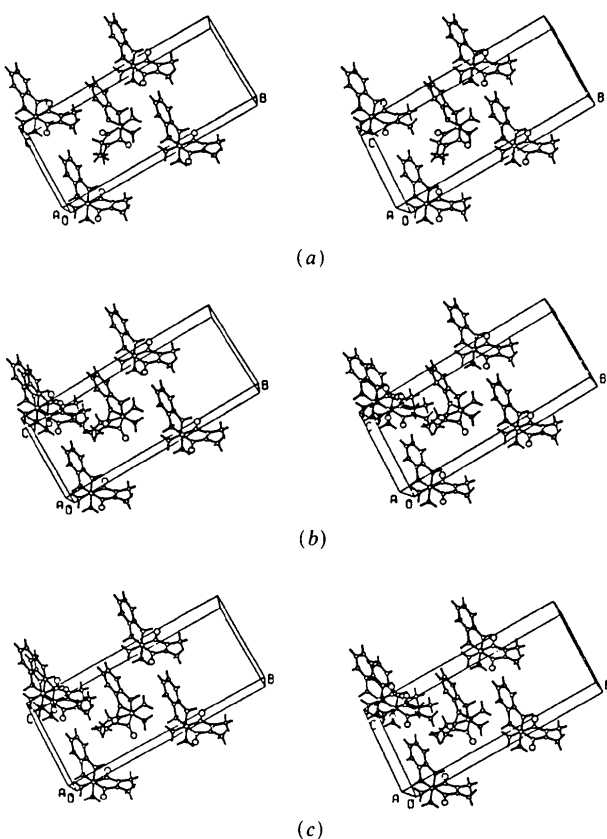
Fig. 5. Stereoview of the reacting molecule (centre) in the surrounding unreacting molecules in the lattice of the reactant. (a) Centre - simulated photoproduct at 40% reaction occupying a lattice position of the reactant. Shortest intermolecular H$\cdots$H contact = 1·884 Å [H(2)40%(x, y, z)$\cdots$H(312)reactant (1/2 + x, 1/2 − y, 1/2 + z)]. No other intermolecular H$\cdots$H contact <2·0 Å. (b) Centre - simulated photoproduct at 100% reaction occupying a lattice position of the reactant. Shortest intermolecular H$\cdots$H contact = 1·226 Å [H(213)100%(x, y, z)$\cdots$ H(312)reactant (1/2 + x, 1/2 − y, 1/2 + z)]. Six other intermolecular H$\cdots$H contacts < 2·0 Å. Free space becoming available below centre molecule. (c) All short intermolecular contacts are relieved by a movement of the reacting molecule [centre, the same as (b)] by 0·997 Å (c/10) along the $-z$ axis.

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