There are no intermolecular contacts shorter than 3·35 Å, hence no other interaction but those of the van der Waals type.

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References

Adinolfi, M., Benedetti, E., Di Blasio, B. & Pedone, C. (1975*a*). *Cryst. Struct. Commun.* **4**, 535–538.

Adinolfi, M., Benedetti, E., Di Blasio, B. & Pedone, C. (1975*b*). *Cryst. Struct. Commun.* **4**, 539–542.

Ahmed, F. R., Hall, S. R., Pippy, M. E. & Huber, C. P. (1973). *NRC Crystallographic Programs for the IBM/*360 *System.* Accession Nos. 133–147. *J. Appl. Cryst.* **6**, 309–346.

Albers-Schonberg, G., Joshua, H., Lopez, M., Hensens, O. D., Springer, J. P., Chen, J., Ostrove, S., Hoffman, C. H., Alberts, A. W. & Patchet, A. A. (1981). *J Antibiot.* **34**, 507–512.

Bélanger-Gariépy, F., Beaudoin, S., Hanessian, S. & Brisse, F. (1989). *Acta Cryst.* In preparation.

Bucourt, L. S. & Hainaut, D. (1965). *Bull. Soc. Chim. Fr.* pp. 1366–1378.

Cromer, D. T. & Mann, J. B. (1968). *Acta Cryst.* A**24**, 321–324.

Eguren, L., Fayos, J. & Perales, A. (1981). *Acta Cryst.* B**37**, 2103–2106.

Galdecki, Z. & Glowka, M. L. (1978). *Cryst. Struct. Commun.* **7**, 317–319.

Hirotsu, K., Higuchi, T., Shimada, A., Hayashi, Y. & Sakan, T. (1975). *Bull. Chem. Soc. Jpn*, **48**, 1157–1162.

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

Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1980). *MULTAN*80. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

Prangé, T., Babin, D., Fourneron, J. D. & Julia, M. (1979). *C. R. Acad. Sci. Sér. C*, **289**, 383–386.

Riche, P. C. (1973). *Acta Cryst.* B**29**, 2147–2153.

Sheldrick, G. M. (1976). *SHELX*76. 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.

Acta Cryst. (1989). C**45**, 148–150

Crystal Structure of 3,8aβ-Diethyl-2,4aβ,6,7-tetramethyl-4aβ,5,8,8aβ-tetrahydro-1,4-naphthoquinone

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Abstract. $C_{18}H_{26}O_2$, $M_r = 274{\cdot}40$, monoclinic, $P2_1/n$, $a = 21{\cdot}557$ (3), $b = 7{\cdot}9317$ (4), $c = 9{\cdot}525$ (1) Å, $\beta = 95{\cdot}790$ (7)°, $V = 1620{\cdot}3$ (3) Å^3, $Z = 4$, $D_x = 1{\cdot}125$ g cm^{-3}, Mo $K\alpha_1$, $\lambda = 0{\cdot}70930$ Å, $\mu = 0{\cdot}7$ cm^{-1}, $F(000) = 600$, $T = 295$ K, $R = 0{\cdot}039$ for 1307 reflections. The molecule exists in the solid state in one conformation with the usual twisted geometry [bridgehead torsion angle = −60·9 (4)°], and with the ring-junction methyl and ethyl groups pseudo-axial and pseudo-equatorial, respectively, with respect to the cyclohexene ring. Bond lengths and angles are normal, with no significant asymmetry in the ring skeleton resulting from the asymmetric substitution pattern. The observed photochemical behaviour can be rationalized on the basis of the observed molecular and crystal structure.

Introduction. Solution and solid state photochemical reactions of tetrahydro-1,4-naphthoquinone derivatives [Fig. 1, (1*a*)] proceed by two major reaction pathways (Trotter, 1983): β-hydrogen abstraction by carbonyl oxygen, and γ-hydrogen abstraction by ethylenic C atom. These compounds can exist in two different conformations [Fig. 1, (*A*) and (*B*)], which, for symmetrical quinones such as (1*a*), are enantiomeric and of equal energies. For the related naphthoquin-4-ols the two conformations are diastereomeric, and the lower energy conformation, which is invariably found in the solid state, is that which has the bulkier C4 substituent (usually OH) in the more favourable pseudo-equatorial site of the half-chair six-membered enone ring (Trotter, 1983). For asymmetric naphthoquinones, such as (1*b*) (Fig. 1), the conformers (*A*) and (*B*) are again diastereomeric. (*A*) has the ring-junction methyl (R_1) and ethyl (R_2) groups pseudo-equatorial and pseudo-axial, respectively, with respect to the ene-dione ring (and pseudo-axial and pseudo-equatorial, respectively, with respect to the cyclohexene ring); (*B*) has the opposite orientations. Since methyl and ethyl groups are usually considered to have similar

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geometrical requirements (Allinger & Freiberg, 1966), it is difficult to predict the conformation adopted by (1*b*), although solid state ^{13}C NMR spectra indicate that only one conformer is present in the solid state. Photolysis of solutions of (1*b*) results in four photoproducts, (2*b*), (2*b*′), (3*b*), (3*b*′) (Fig. 1), while solid state photolysis gives a single photoproduct, (2*b*) (Ariel, Evans, Hwang, Jay, Scheffer, Trotter & Wong, 1985). The present crystal structure analysis was undertaken to provide detailed molecular structural information for (1*b*), as an aid to interpretation of the photochemical behaviour.

Experimental. Colourless crystals, dimensions $\simeq 0{\cdot}3$ mm, Enraf–Nonius CAD-4F diffractometer, lattice parameters from 25 reflections with $\theta = 12$–$18°$. Intensities for $\theta \le 25°$, *hkl*: 0 to 25, 0 to 9, −11 to 11, ω–2θ scan, ω scan width $(0{\cdot}80 + 0{\cdot}35\tan\theta)°$ at 1·1–6·7° min^{-1}, extended 25% on each side for background measurement, three standard reflections (7% decay, appropriate corrections applied), Lp but no absorption corrections, 2850 independent reflections measured, 1307 with $I \ge 3\sigma(I)$, where $\sigma^2(I) = S + 4(B_1 + B_2) + (0{\cdot}04I)^2$, S = scan, B_1 and B_2 = background counts. Structure by direct methods, refined by full-matrix least squares on ΔF^2 using data with $I > 3\sigma(I)$, H atoms from a difference map, $w = 1/\sigma^2(F)$, scattering factors from *International Tables for X-ray Crystallography* (1974), locally written, or locally modified versions of standard computer programs (Evans & Trotter, 1988), final $R = 0{\cdot}039$, $wR = 0{\cdot}044$ for 1307 reflections, $S = 1{\cdot}6$, extinction parameter $g = 2{\cdot}7 \times 10^4$. 182 parameters (non-H atoms, plus 104 H parameters), $R = 0{\cdot}121$ for all 2850 reflections, $\Delta/\sigma = 0{\cdot}02$ (mean), 0·20 (maximum, for *z* of H61a), maximum final difference density −0·11 to +0·17 e Å^{-3}.

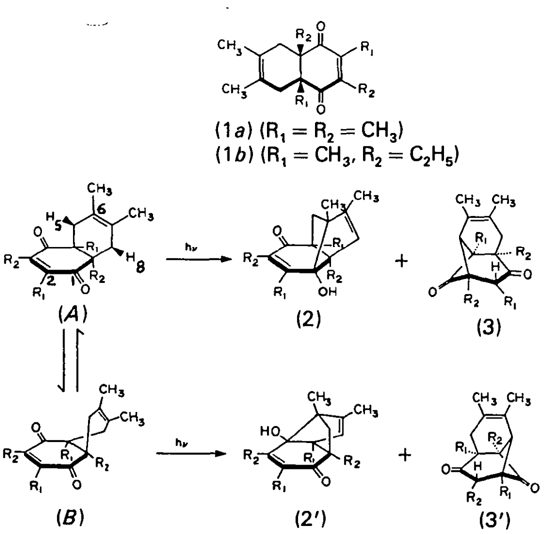

Fig. 1. Photolysis of tetrahydronaphthoquinones.

Table 1. *Positional (fractional,* × 10^4*) and equivalent isotropic thermal parameters* (Å^2 × 10^3), *with e.s.d.'s in parentheses*

	x	*y*	*z*	U_{eq}
O1	6912 (1)	3722 (3)	1892 (3)	62
O4	5824 (1)	−2214 (3)	1727 (3)	78
C1	6619 (2)	2419 (4)	1680 (3)	44
C2	6914 (2)	951 (4)	1037 (4)	47
C21	7503 (2)	1318 (7)	382 (6)	71
C3	6668 (2)	−608 (4)	1106 (4)	47
C31	6931 (2)	−2148 (5)	457 (4)	61
C32	6656 (3)	−2410 (8)	−1058 (5)	82
C4	6097 (2)	−867 (4)	1840 (4)	52
C4a	5869 (2)	544 (4)	2738 (4)	48
C4a1	5196 (2)	208 (7)	3046 (6)	67
C5	6296 (2)	564 (5)	4137 (4)	59
C6	6250 (2)	2147 (5)	5003 (4)	58
C61	6517 (3)	1948 (9)	6529 (5)	88
C7	6000 (2)	3552 (5)	4458 (4)	54
C71	5915 (3)	5140 (8)	5291 (7)	81
C8	5761 (2)	3694 (5)	2923 (4)	54
C8a	5942 (2)	2253 (4)	1985 (3)	43
C8a1	5540 (2)	2306 (5)	541 (4)	51
C8a2	5678 (2)	3776 (6)	−406 (4)	62

$U_{eq} = \frac{1}{3} \times$ trace of diagonalized U tensor.

Discussion. Positional parameters are given in Table 1, and other data have been deposited.* The molecule (Fig. 2) adopts the usual twisted conformation, with staggered bridgehead substituents, C4a1—C4a—C8a—C8a1 torsion angle = −60·9 (4)° (for the molecule in Table 1 and Fig. 2; the crystals are racemic). Both six-membered rings have half-chair conformations, with quite similar deviations from planarity, mean ring torsion angles (Table 2) being 28·9 and 30·1°, respectively, in the ene-dione and cyclohexene rings. The molecule adopts conformation (*A*) in the solid state, *i.e.* with the C4a1 methyl group pseudo-axial and the C8a1—C8a2 ethyl group pseudo-equatorial with respect to the slightly less planar cyclohexene ring (Fig. 2). Conformation (*B*) (Fig. 1), which is present together with (*A*) in solution media, probably has an energy rather similar to that of (*A*), with an energy barrier for (*A*)/(*B*) interconversion of about 40 kJ mol^{-1} (Ariel & Trotter, 1988).

Bond lengths and angles in the molecule (Table 2) are close to normal values (Phillips & Trotter, 1977); there is no significant asymmetry in the ring skeleton dimensions resulting from the asymmetric substitution pattern, so that the electronic and steric influences of the methyl and ethyl substituents appear to be fairly similar. The observed solid state molecular conformation (*A*) (Figs. 1 and 2) has an H atom on C8 favourably situated for abstraction by O1 to form a biradical on

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* Lists of anisotropic thermal parameters, hydrogen positions, bond lengths and angles involving hydrogen, torsion angles, and structure factors, and a packing diagram have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51369 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

solid state photolysis. The relevant parameters are O···H8a = 2·44 (3) Å, τ_O (displacement of O···H vector from carbonyl plane) = 5 (3)°, and Δ_O (C—O···H) = 83 (1)°, in comparison with ideal values of ≤2·72 Å, 0°, and 90°, respectively (Trotter, 1983). The C1···C6 distance of 3·347 (5) Å is also favourable for subsequent bond formation to give the only observed solid state photoproduct, (2*b*) (Fig. 1). The molecule also has a C5 hydrogen atom suitably oriented for abstraction by C2, with C2···H5b = 2·89 (3) Å, τ_C (displacement of C···H from the C=C plane) = 47 (3)°, Δ_C (C=C···H) = 75 (1)°, with subsequent C3···C5 [3·212 (6) Å] bond formation leading to photoproduct (3*b*) (Fig. 1) (ideal values ≤2·9 Å, 90°, 90°, ≤3·4 Å); however, no (3*b*) is formed in the solid state photolysis.

The absence of (3*b*) can be attributed to unfavourable steric compression energies during the required hydrogen abstraction step. The pyramidalization at C2 which accompanies hydrogen transfer would produce unfavourable intramolecular methyl···methyl interactions between methyl group C21 and the terminal methyl groups, C32 and C8a2, of the ethyl substituents; at full pyramidalization, H···H distances would become as short as 1·6 Å (Ariel *et al.*, 1985). Hence only (2*b*) is formed in the solid state photolysis. For compound (1*a*), where all the substituents are Me, no unfavourable contacts are developed and both (2*a*) and (3*a*) [and their enantiomers, (2*a*′) and (3*a*′)] are produced in solid state photolysis. In solution, conformational interconversion occurs, so that both conformers (*A*) and (*B*) are present, and in addition the rotations of the ethyl groups are less restricted than in the solid state, and all four diastereomeric photoproducts (Fig. 1) are formed for (1*b*).

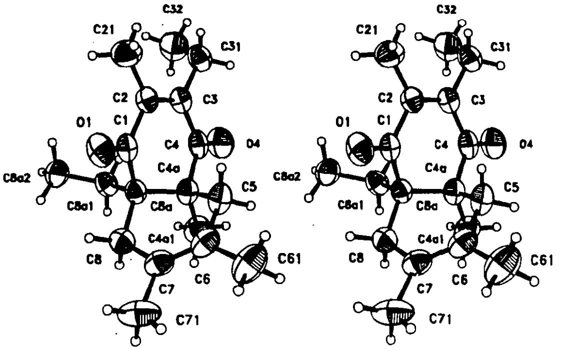

Fig. 2. Stereoview of the molecule.

Table 2. *Bond lengths* (Å), *angles* (°), *and intra-annular torsion angles* (°), *with standard deviations in parentheses*

O1—C1	1·216 (4)	C4a—C5	1·542 (5)
O4—C4	1·220 (4)	C4a—C8a	1·549 (4)
C1—C2	1·489 (4)	C5—C6	1·511 (5)
C1—C8a	1·523 (5)	C6—C61	1·517 (6)
C2—C21	1·498 (5)	C6—C7	1·321 (5)
C2—C3	1·349 (4)	C7—C71	1·509 (6)
C3—C31	1·505 (5)	C7—C8	1·504 (5)
C3—C4	1·490 (5)	C8—C8a	1·526 (5)
C31—C32	1·518 (6)	C8a—C8a1	1·551 (5)
C4—C4a	1·521 (5)	C8a1—C8a2	1·521 (5)
C4a—C4a1	1·530 (6)		
O1—C1—C2	119·8 (3)	C4a1—C4a—C8a	112·6 (3)
O1—C1—C8a	122·2 (3)	C5—C4a—C8a	108·2 (3)
C2—C1—C8a	117·9 (3)	C4a—C5—C6	114·4 (3)
C1—C2—C21	115·8 (3)	C5—C6—C61	113·4 (4)
C1—C2—C3	120·7 (3)	C5—C6—C7	122·2 (3)
C21—C2—C3	123·5 (4)	C61—C6—C7	124·4 (4)
C2—C3—C31	123·9 (3)	C6—C7—C71	124·3 (4)
C2—C3—C4	119·8 (3)	C6—C7—C8	122·1 (3)
C31—C3—C4	116·4 (3)	C71—C7—C8	113·6 (4)
C3—C31—C32	112·0 (4)	C7—C8—C8a	115·5 (3)
O4—C4—C3	119·6 (3)	C1—C8a—C4a	108·0 (3)
O4—C4—C4a	120·9 (3)	C1—C8a—C8	110·7 (3)
C3—C4—C4a	119·5 (3)	C1—C8a—C8a1	106·9 (3)
C4—C4a—C4a1	110·3 (3)	C4a—C8a—C8	109·9 (3)
C4—C4a—C5	107·1 (3)	C4a—C8a—C8a1	111·1 (3)
C4—C4a—C8a	109·2 (3)	C8—C8a—C8a1	110·3 (3)
C4a1—C4a—C5	109·3 (3)	C8a—C8a1—C8a2	114·9 (3)
C8a—C1—C2—C3	−19·4 (4)	C8a—C4a—C5—C6	47·2 (4)
C2—C1—C8a—C4a	47·3 (4)	C5—C4a—C8a—C8	−59·4 (4)
C1—C2—C3—C4	−0·3 (5)	C4a—C5—C6—C7	−17·0 (6)
C2—C3—C4—C4a	−11·5 (5)	C5—C6—C7—C8	−2·1 (6)
C3—C4—C4a—C8a	40·2 (4)	C6—C7—C8—C8a	−11·7 (6)
C4—C4a—C8a—C1	−54·9 (3)	C7—C8—C8a—C4a	42·9 (5)

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References

ALLINGER, N. L. & FREIBERG, L. A. (1966). *J. Org. Chem.* **31**, 894–897.

ARIEL, S., EVANS, S., HWANG, C., JAY, J., SCHEFFER, J. R., TROTTER, J. & WONG, Y.-F. (1985). *Tetrahedron Lett.* **26**, 965–968.

ARIEL, S. & TROTTER, J. (1988). *Acta Cryst.* B**44**, 538–544.

EVANS, S. V. & TROTTER, J. (1988). *Acta Cryst.* B**44**, 63–72.

International Tables for X-ray Crystallography (1974). Vol. IV, pp. 99–102. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

PHILLIPS, S. E. V. & TROTTER, J. (1977). *Acta Cryst.* B**33**, 996–1003.

TROTTER, J. (1983). *Acta Cryst.* B**39**, 373–381.