The distance O(1)—O(2) of 1·46 (1) in (I) and 1·49 (2) Å in (II) falls in the range typical for organic peroxo compounds (Pedersen, 1972; Glidewell, Liles, Walton & Sheldrick, 1979). The nitro, benzene and peroxycarboxyl parts of the molecules are essentially planar. Full details have been deposited.

There are no unusually short contacts between the molecules.

The financial support of the Research Council of Slovenia is gratefully acknowledged.

References

Belitskus, D. & Jeffrey, G. A. (1965). *Acta Cryst.* **18**, 458–463.

Colapietro, M. & Domenicano, A. (1977). *Acta Cryst.* B**33**, 2240–2243.

Dhaneshwar, N. N., Tavale, S. S. & Pant, L. M. (1974). *Acta Cryst.* B**30**, 583–587.

Glidewell, C., Liles, D. C., Walton, D. J. & Sheldrick, G. M. (1979). *Acta Cryst.* B**35**, 500–502.

Hamilton, W. C. (1959). *Acta Cryst.* **12**, 609–610.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

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

Kim, H. S., Chu, S. & Jeffrey, G. A. (1970). *Acta Cryst.* B**26**, 896–900.

Klyne, W. & Prelog, K. (1960). *Experientia*, **16**, 521–523.

Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

Pedersen, B. F. (1972). *Acta Cryst.* B**28**, 1014–1016.

Sax, M., Beurskens, P. & Chu, S. (1965). *Acta Cryst.* **18**, 252–258.

Sheldrick, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

Acta Cryst. (1984). C**40**, 450–452

Structure of the Adduct between 7,8-Diacetoxybicyclo[4.2.0]octa-2,4-diene and 2,3-Dihydronaphthazarin:* $C_{22}H_{20}O_8$

By P. Rubio, F. Florencio, P. Smith-Verdier and S. García-Blanco

Departamento de Rayos X, Instituto 'Rocasolano', CSIC, Serrano 119, Madrid, Spain

and J. G. Rodriguez

Departamento de Química Orgánica de la Universidad Autónoma de Madrid, Spain

(*Received* 11 *May* 1983; *accepted* 8 *November* 1983)

Abstract. $M_r = 412{\cdot}4$, monoclinic, $P2_1/c$, $a = 7{\cdot}744\,(1)$, $b = 27{\cdot}419\,(2)$, $c = 9{\cdot}449\,(1)$ Å, $\beta = 113{\cdot}16\,(2)°$, $V = 1844{\cdot}6$ Å^3, $Z = 4$, $D_x = 1{\cdot}485$, $D_m = 1{\cdot}50$ Mg m^{-3}, $\mu(\text{Cu } K\alpha) = 0{\cdot}91264$ mm^{-1}, $\lambda = 1{\cdot}5418$ Å, room temperature, $F(000) = 864$, final $R = 0{\cdot}052$ for 2944 observed reflections. The structure was solved by direct methods and refined by least-squares procedure. It was verified that there is no charge-transfer interaction in spite of the presence of a 2,3-dihydronaphthazarin nucleus in the molecule.

Introduction. The present compound is the result of the Diels–Alder reaction between 7,8-diacetoxybicyclo[4.2.0]octa-2,4-diene and naphthazarin. Generally the naphthazarin nucleus forms a charge-transfer self-complex (Rodriguez, Florencio, Smith-Verdier & García-Blanco, 1983). The quinonoid ring in the naphthazarin acts as a dienophile in the Diels–Alder reaction. In the title compound there is a dihydronaphthazarin ring which has less acceptor character than the naphthazarin ring from the point of view of the formation of a charge-transfer complex. Verification of this and elucidation of the stereochemistry of the molecule required the resolution of the crystal structure.

Experimental. D_m measured by flotation. Orange-red plate crystals 0·2 × 0·15 × 0·05 mm. Nonius CAD-4 automatic diffractometer, Mo $K\alpha$. 3016 independent reflections ($-8 \le h \le 8$, $0 \le k \le 32$, $0 \le l \le 10$), $\theta < 30°$, 2944 with $I > 2\sigma(I)$. Absorption ignored. 30 reflections used for measuring lattice parameters. Direct methods (*MULTAN*80; Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). Anisotropic full matrix; H (from ΔF synthesis) isotropic; $\sum w(\Delta F)^2$ minimized; $w = k/\sigma^2$ (Martínez-Ripoll & Cano, 1975) with $\sigma = a + b(F_o)$ and $k = 0{\cdot}6032$ ($a = 0{\cdot}4141$, $b = 0{\cdot}0143$ for $F_o < 12{\cdot}500$ and $a = 0{\cdot}0815$, $b = 0{\cdot}0373$

---

* 2,3-Dihydronaphthazarin is 2,3-dihydro-5,8-dihydroxy-1,4-naphthoquinone.

0108-2701/84/030450-03$01.50

for $F_o > 12{\cdot}500$). Final $R = 0{\cdot}052$, $R_w = 0{\cdot}069$. $(\Delta/\sigma)_{\rm mean} = 0{\cdot}05$. Maximum excursion in final $\Delta\rho$ map $0{\cdot}22\ {\rm e\ Å^{-3}}$. Scattering factors from *International Tables for X-ray Crystallography* (1974). Univac 1108 computer, programs from XRAY70 system (Stewart, Kundell & Baldwin, 1970) and *PARST* (Nardelli, 1980).

Table 1. *Atomic coordinates and equivalent isotropic thermal parameters*

$$U_{\rm eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i\mathbf{a}_j\cos(\mathbf{a}_i\mathbf{a}_j).$$

	x	y	z	$U_{\rm eq}$(Å^2)
C(1)	0·1377 (3)	−0·10167 (7)	0·7847 (2)	0·0392 (7)
C(2)	0·0203 (3)	−0·05857 (7)	0·7911 (2)	0·0442 (8)
C(3)	0·0548 (3)	−0·01000 (7)	0·7457 (2)	0·0416 (7)
C(4)	−0·0472 (3)	0·02967 (8)	0·7668 (3)	0·0506 (8)
C(5)	−0·0106 (3)	0·07645 (8)	0·7284 (3)	0·0583 (10)
C(6)	0·1173 (3)	0·08411 (8)	0·6643 (4)	0·0538 (9)
C(7)	0·2155 (3)	0·04488 (7)	0·6354 (2)	0·0451 (8)
C(8)	0·1876 (3)	−0·00215 (7)	0·6785 (2)	0·0394 (7)
C(9)	0·2916 (3)	−0·04305 (7)	0·6497 (2)	0·0397 (7)
C(10)	0·2735 (3)	−0·09423 (7)	0·7013 (2)	0·0383 (7)
C(11)	0·4757 (3)	−0·11168 (7)	0·8093 (2)	0·0376 (7)
C(12)	0·4613 (3)	−0·16530 (7)	0·8502 (3)	0·0390 (7)
C(13)	0·3212 (3)	−0·17059 (7)	0·9305 (2)	0·0399 (7)
C(14)	0·2522 (3)	−0·11989 (7)	0·9526 (2)	0·0384 (7)
C(15)	0·4145 (3)	−0·08533 (7)	1·0256 (2)	0·0398 (7)
C(16)	0·5282 (3)	−0·08122 (7)	0·9530 (2)	0·0395 (7)
C(17)	0·4778 (3)	−0·19608 (7)	1·0668 (2)	0·0431 (8)
C(18)	0·6209 (3)	−0·18433 (7)	0·9980 (3)	0·0416 (8)
C(19)	0·4129 (3)	−0·18682 (7)	1·2895 (3)	0·0502 (9)
C(20)	0·4744 (5)	−0·16347 (10)	1·4428 (3)	0·0625 (12)
C(21)	0·8382 (3)	−0·22386 (7)	0·9160 (3)	0·0522 (9)
C(22)	0·9479 (4)	−0·26939 (10)	0·9281 (2)	0·0638 (12)
O(1)	−0·1806 (2)	0·02422 (7)	0·8231 (2)	0·0692 (8)
O(2)	0·3333 (2)	0·05589 (5)	0·5671 (2)	0·0568 (7)
O(3)	−0·1041 (2)	−0·06571 (7)	0·8397 (2)	0·0640 (8)
O(4)	0·3972 (2)	−0·03658 (5)	0·5824 (2)	0·0553 (7)
O(5)	0·5281 (2)	−0·17615 (9)	1·2191 (2)	0·0455 (6)
O(6)	0·2758 (3)	−0·21186 (8)	1·2311 (2)	0·0830 (10)
O(7)	0·7203 (2)	−0·22791 (5)	0·9877 (2)	0·0488 (6)
O(8)	0·8484 (3)	−0·18755 (7)	0·8489 (3)	0·0809 (3)

Discussion. The atomic coordinates and isotropic thermal parameters are given in Table 1.* The bond lengths and angles with the atom labels for non-hydrogen atoms are shown in Fig. 1 and the torsion angles in Table 2. The molecule consists of a 2,3-dihydronaphthazarin nucleus ($A+B$) fused to a bicyclo[2.2.2]octene ($C+D$), which is also fused to a cyclobutene ring (E) which bears two acetoxy groups.

Table 2. *Selected torsion angles* (°)

C(3)–C(4)–C(5)–C(6)	2·8 (4)	C(1)–C(10)–C(11)–C(12)	57·4 (3)
C(4)–C(5)–C(6)–C(7)	0·1 (4)	C(10)–C(11)–C(12)–C(13)	−58·4 (3)
C(5)–C(6)–C(7)–C(8)	−2·7 (4)	C(11)–C(12)–C(13)–C(14)	−3·8 (3)
C(6)–C(7)–C(8)–C(3)	2·4 (4)	C(12)–C(13)–C(14)–C(1)	65·7 (3)
C(7)–C(8)–C(3)–C(4)	0·4 (4)	C(13)–C(14)–C(1)–C(10)	−66·1 (3)
C(8)–C(3)–C(4)–C(5)	−3·0 (4)		
		C(12)–C(13)–C(14)–C(15)	−49·7 (3)
C(1)–C(2)–C(3)–C(8)	6·6 (4)	C(13)–C(14)–C(15)–C(16)	54·9 (3)
C(2)–C(3)–C(8)–C(9)	1·3 (4)	C(15)–C(16)–C(11)–C(12)	−55·9 (3)
C(3)–C(8)–C(9)–C(10)	−4·9 (4)	C(16)–C(11)–C(12)–C(13)	55·2 (3)
C(8)–C(9)–C(10)–C(1)	0·7 (3)		
C(9)–C(10)–C(1)–C(2)	6·6 (3)	C(12)–C(18)–C(17)–C(13)	−7·5 (2)
C(10)–C(1)–C(2)–C(3)	−10·4 (4)	C(18)–C(17)–C(13)–C(12)	7·5 (2)
		C(17)–C(13)–C(12)–C(18)	−7·4 (2)
C(1)–C(10)–C(11)–C(16)	−58·6 (3)	C(13)–C(12)–C(18)–C(17)	7·5 (2)
C(10)–C(11)–C(16)–C(15)	59·3 (3)		
C(11)–C(16)–C(15)–C(14)	0·2 (3)	C(17)–O(5)–C(19)–C(20)	−178·3 (2)
C(16)–C(15)–C(14)–C(1)	−58·2 (3)	C(17)–O(5)–C(19)–O(6)	0·7 (3)
C(15)–C(14)–C(1)–C(10)	51·7 (3)		
C(14)–C(1)–C(10)–C(11)	4·7 (3)	C(18)–O(7)–C(21)–C(22)	173·5 (3)
		C(18)–O(7)–C(21)–O(8)	−7·6 (4)

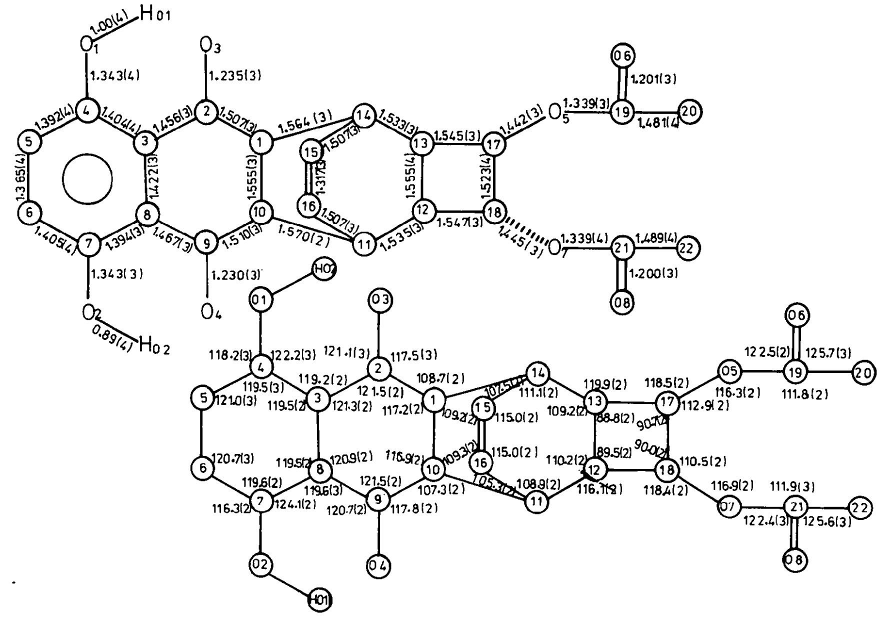

Fig. 1. Bond lengths (Å) and bond angles (°).

---

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, short intermolecular contacts and least-squares-planes' data have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38969 (26 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

2,3-Dihydronaphthazarin. Ring *A* has a benzene character and the shortest [C(5)—C(6) = 1·365 (4) Å] and longest [C(3)—C(8) = 1·422 (3) Å] bonds have values in good agreement with those found in diacetylnaphthazarin (Rodriguez, Cano & García-Blanco, 1977). In ring *B* the bond distances C(1)—C(10) = 1·555 (3), C(1)—C(2) = 1·507 (3) and C(9)—C(10) = 1·510 (3) Å have single-bond character and C(2)—C(3) = 1·456 (3) and C(8)—C(9) = 1·467 (3) Å are hybrid bonds with predominant single-bond character. The O(1)···O(3) = 2·526 (3) and O(2)···O(4) = 2·572 (2) Å distances seem to indicate the presence of intramolecular H bonds with O(1)—H(O1) = 1·00 (4), H(O1)···O(3) = 1·57 (4) Å, O(1)—H(O1)···O(3) = 157 (4)° and O(2)—H(O2) = 0·89 (4), H(O2)···O(4) = 1·75 (4) Å, O(2)—H(O2)···O(4) = 153 (4)°.

Ring *A* is near to planarity; O(1) and O(2) deviate 0·081 (3) and 0·061 (2) Å from the plane through the ring. Ring *B* adopts a slight boat conformation as can be seen from the torsion angles (Table 2). O(3) and O(4) deviate 0·171 (3) and 0·093 (2) Å from the plane through ring *B*. The dihedral angle between the mean planes through the atoms of the rings is 3·0 (5)°.

Bicyclo[2.2.2]*octene*. The torsion angles C(11)—C(10)—C(1)—C(14), C(11)—C(12)—C(13)—C(14) and C(11)—C(16)—C(15)—C(14) are 4·7 (3), −3·8 (3) and 0·2 (3)° respectively. Consequently only two wings of the bicyclic system are slightly twisted and so deviate from planarity, so that C(1) and C(10) lie to either side of the plane through C(1),C(10),C(11),C(14), and C(12) and C(13) are also on opposite sides of the plane through C(11),C(14),C(12),C(13). The value of 0·2° for the torsion angle involving C(11),C(16),C(15),-C(14) results from the constraint of the sp^2 atoms.

Comparison of C—C and C=C distances and angles in the bicyclo[2.2.2]octene skeleton with similar fused-ring compounds (Cameron, Ferguson & Morris, 1968; Ermer & Dunitz, 1969; Destro, Filippini, Gramaccioli & Simonetta, 1971) reveals no significant differences. Only C(1)—C(14), C(1)—C(10) and C(10)—C(11) are longer than the sp^3—sp^3 bond; it may be steric interactions between the bridge C(14),C(15),C(16),-C(11) and the acetoxy group O(7),C(21),C(22),O(8) that cause the decrease in the bond angles C(1)—C(14)—C(15) and C(10)—C(11)—C(16), and consequently increase the bond lengths.

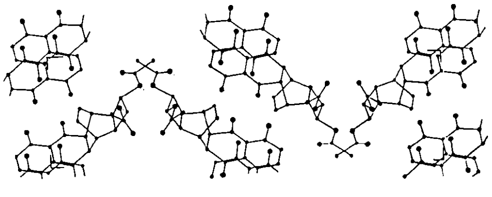

Fig. 2. Packing of the compound along the *c* axis.

Cyclobutane. The ring is slightly puckered with a dihedral angle of 7·5 (5)°, similar to those found by Andersen & Srinivasan (1972) and Andersen & Fernholt (1970). It is reasonable to assume that the differences involving the dihedral angles in several four-membered rings are the result of the different ring systems fused to the cyclobutane and they are relatively independent of how the molecules pack in the crystal. The torsion angles in the ring are ±7°. Each C atom deviates ±0·20 Å from the ring. The bond lengths and angles are similar to those found in other fused cyclobutane compounds (Cotton & Frenz, 1974).

Acetoxy groups. The two acetoxy groups are *trans* and are nearly planar, the more planar being C(17)—O(15)—C(19)—O(6)—C(20).

Molecular packing. There are no ring overlaps which could give rise to charge-transfer interactions.

The crystal packing, shown in Fig. 2, is through short C···O, C—H···O and O···O contacts. The O(2)···O(4) contact of 2·992 (3) Å could be a weak hydrogen bond.

The authors thank the Centro de Proceso de Datos, MEC, Madrid, Spain, for providing facilities for the use of the 1108 Univac computer.

References

Andersen, B. & Fernholt, L. (1970). *Acta Chem. Scand.* **24**, 445–452.

Andersen, B. & Srinivasan, R. (1972). *Acta Chem. Scand.* **26**, 3468–3474.

Cameron, A. F., Ferguson, C. & Morris, D. G. (1968). *J. Chem. Soc. B*, pp. 1249–1253.

Cotton, F. A. & Frenz, B. A. (1974). *Tetrahedron*, **30**, 1587–1594.

Destro, R., Filippini, G., Gramaccioli, G. M. & Simonetta, M. (1971). *Acta Cryst.* B**27**, 2023–2028.

Ermer, D. & Dunitz, J. D. (1969). *Helv. Chim. Acta*, **52**, 1861–1886.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

Martínez-Ripoll, M. & Cano, F. H. (1975). *PESOS. A Computer Program for the Automatic Treatment of Weighting Schemes.* Instituto 'Rocasolano', CSIC, Madrid, Spain.

Nardelli, M. (1980). *PARST.* Instituto di Chimica Generale, Univ. Parma, Italy.

Rodriguez, J. G., Cano, F. H. & García-Blanco, S. (1977). *Acta Cryst.* B**33**, 491–494.

Rodriguez, J. G., Florencio, F., Smith-Verdier, P. & García-Blanco, S. (1983). *J. Mol. Struct.* In the press.

Stewart, J. M., Kundell, F. A. & Baldwin, J. C. (1970). The XRAY70 system. Computer Science Center, Univ. of Maryland, College Park, Maryland.