

References

- ANDERSON, G. M., KOLLMAN, P. A., DOMELSMITH, L. N. & HOUK, K. N. (1979). *J. Am. Chem. Soc.* **101**, 2344–2352.
- FRENZ, B. A. (1978). In *Computing in Crystallography*, edited by H. SCHENK, R. OLTJOF-HAZEKAMP, H. VAN KONINGSVELD & G. C. BASSI, pp. 64–71. Delft Univ. Press.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht, The Netherlands.)
- JOHNSON, C. K. (1976). ORTEPII. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- KNUUTINEN, J. (1984). Research Report No. 18 (Thesis), Department of Chemistry, Univ. of Jyväskylä, Finland.
- KNUUTINEN, J. & KORHONEN, I. O. O. (1987). *Org. Mass. Spectrom.* **22**, 70–74.
- KOLEHMAINEN, E. & KNUUTINEN, J. (1983). *Org. Magn. Reson.* **21**, 388–390.
- MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1982). *MULTAN*11/82. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
- PAASIVIRTA, J., KNUUTINEN, J., TARHANEN, J., KUOKKANEN, T., SURMA-AHO, K., PAUKKU, R., KÄÄRIÄINEN, H., LAHTIPERÄ, M. & VEIJANEN, A. (1983). *Water Sci. Technol.* **15**, 97–104.
- SAKURAI, T. (1962). *Acta Cryst.* **15**, 1164–1173.
- WALKER, N. & STUART, D. (1983). *Acta Cryst.* **A39**, 158–166.

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Structure of Two Isomers of Perhydro-5,8-epoxy-6,7-dimethoxynaphthalene-1,4-dione

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Abstract. $C_{12}H_{16}O_5$, $M_r = 240.26$. *cis-transoid* form: triclinic, $P\bar{1}$, $a = 9.14$ (2), $b = 9.70$ (2), $c = 7.80$ (1) Å, $\alpha = 110.5$ (3), $\beta = 109.5$ (3), $\gamma = 101.7$ (3)°, $V = 569$ (3) Å³, $Z = 2$, $D_x = 1.402$ (7) g cm⁻³, $\lambda = 0.7107$ Å, $\mu(\text{Mo } K\alpha) = 1.021$ cm⁻¹, $F(000) = 256$, 1172 unique observed reflections. *cis-cisoid* form: orthorhombic, $P2_12_12_1$, $a = 7.808$ (10), $b = 8.840$ (7), $c = 16.662$ (11) Å, $V = 1150$ (2) Å³, $Z = 4$, $D_x = 1.388$ (2) g cm⁻³, $\lambda = 0.7107$ Å, $\mu(\text{Mo } K\alpha) = 1.010$ cm⁻¹, $F(000) = 512$, 1039 unique observed reflections. Room temperature. The structures were solved by direct methods. The final R factors were 0.051 and 0.066 for the *cis-transoid* and *cis-cisoid* forms, respectively.

Introduction. Eugster *et al.* (Hofmann, Wyrsh-Walraf, Iten & Eugster, 1979) have reported that thermal Diels–Alder reaction between 3,4-dimethoxyfuran (1) and benzoquinone (2) leads exclusively to the *endo*-

adduct (3). Under high-pressure conditions (10–20 kbar), both *endo*- and *exo*-adducts (3) and (4) are formed (Jurczak, Koźluk, Tkacz & Eugster, 1983). Hydrogenation of this mixture afforded the tetrahydro derivatives (5) and (6) which were separated by column chromatography to give pure, stable crystals of both title compounds.

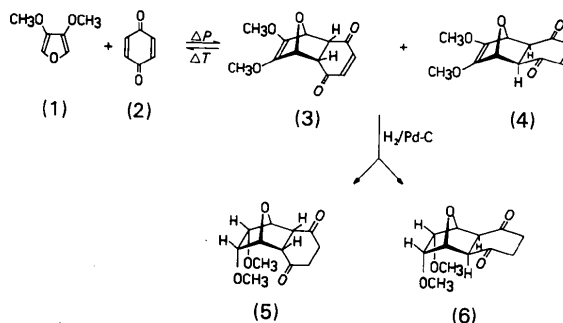


Table 1. Collection and reduction of the intensity data, and the least-squares refinement

	<i>cis-transoid</i>	<i>cis-cisoid</i>
Crystal size (mm)	0.3 × 0.2 × 0.2	0.2 × 0.2 × 0.1
θ interval (°)	3–24	3–24
No. of measured independent reflections	1797	1451
<i>h,k,l</i> range		
<i>h</i>	–11–11	0–8
<i>k</i>	–10–9	0–10
<i>l</i>	0–8	–18–18
No. of reflections used in the final refinements ($I \geq 2\sigma(I)$)	1172	1039
No. of parameters refined	218	176
No. of reflections/parameter	5	6
<i>R</i>	0.051	0.066
<i>wR</i>	0.034	0.067
<i>k</i> , parameter in weight	0.633	9.656
Ratio of maximum shift/e.s.d. in final refinement cycle	0.12	0.82
Maximum height in final difference Fourier synthesis (e Å ⁻³)	0.21	0.28

This study was aimed at unequivocal determination of the configurations of the unstable preliminary adducts (3) and (4) *via* X-ray analyses of their tetrahydro derivatives *cis-cisoid* (5) and *cis-transoid* (6).

Experimental. Numerical information concerning the collection and reduction of the intensity data and the structure refinement are given in Table 1.

The unit-cell dimensions were refined by a least-squares treatment of 20 reflections. A four-circle single-crystal diffractometer (Philips PW1100) was used for the collection of X-ray data. After every 50 measurements, the intensity of a standard reflection was checked but no systematic change was observed. The values of *I* were corrected for Lorentz and polarization effects but not for absorption or extinction. Both structures were solved by direct methods (SHELX; Sheldrick, 1975). All non-hydrogen atoms were located on *E* maps. Blocked full-matrix refinement minimizing $\sum w^{1/2} | |F_o| - |F_c| |$ with weights $w = k/\sigma^2(F_o)$ was performed. Hydrogen atoms of the *cis-transoid* form were located from difference Fourier maps and refined with isotropic thermal parameters; those of the *cis-cisoid* form were located at geometrically calculated positions (C–H distance equal to 1.08 Å) and only thermal parameters were refined.

In Table 2 the positional parameters for non-hydrogen atoms are given. Bond distances and angles are shown in Fig. 1. The scattering factors were taken from *International Tables for X-ray Crystallography* (1974).*

Discussion. *The cis-transoid form.* The molecular conformation, as obtained from the crystal-structure

* Lists of structure factors, H-atom coordinates, torsion angles and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 44068 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Atomic fractional coordinates for non-hydrogen atoms ($\times 10^4$) and isotropic thermal parameters (Å² × 10⁴) with e.s.d.'s in parentheses

		$U_{eq} = (U_{11}U_{22}U_{33})^{1/3}$.			
		<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
<i>cis-transoid form</i>					
C(1)	3555 (4)	1967 (3)	5817 (5)	467	
C(2)	5408 (4)	2589 (4)	6416 (5)	535	
C(3)	6132 (4)	2084 (4)	8118 (4)	459	
C(4)	4523 (4)	1207 (4)	8092 (4)	463	
C(5)	2576 (4)	1576 (3)	9710 (4)	523	
C(6)	774 (5)	1242 (5)	8535 (7)	766	
C(7)	475 (5)	2568 (5)	7991 (6)	686	
C(8)	1336 (4)	2759 (3)	6718 (5)	560	
C(9)	3141 (4)	2944 (4)	7495 (5)	400	
C(10)	3825 (4)	2380 (4)	9144 (4)	376	
C(11)	7024 (8)	4659 (6)	6166 (9)	953	
C(12)	8083 (6)	3007 (6)	11496 (7)	672	
O(1)	3358 (2)	494 (2)	5968 (3)	462	
O(2)	3073 (3)	1178 (3)	11037 (3)	934	
O(3)	624 (3)	2794 (3)	5135 (3)	955	
O(4)	6033 (3)	4233 (2)	7054 (3)	646	
O(5)	7239 (2)	3427 (2)	9982 (3)	514	
<i>cis-cisoid form</i>					
C(1)	844 (10)	570 (5)	–1081 (2)	514	
C(2)	913 (9)	–843 (5)	–522 (2)	436	
C(3)	1057 (9)	–2146 (5)	–1149 (2)	472	
C(4)	1216 (9)	–1247 (6)	–1935 (3)	541	
C(5)	4546 (10)	–1316 (6)	–1858 (3)	570	
C(6)	5661 (10)	–1033 (5)	–1130 (3)	543	
C(7)	5778 (11)	649 (6)	–915 (3)	576	
C(8)	4035 (10)	1354 (5)	–817 (2)	475	
C(9)	2604 (8)	963 (5)	–1411 (2)	413	
C(10)	2969 (10)	–394 (5)	–1996 (2)	480	
C(11)	2051 (11)	–46 (6)	732 (3)	573	
C(12)	2282 (11)	–4527 (6)	–1445 (3)	660	
O(1)	2 (6)	–49 (3)	–1784 (2)	619	
O(2)	4951 (8)	–2290 (4)	–3950 (2)	824	
O(3)	3720 (7)	2356 (3)	–322 (2)	624	
O(4)	2378 (5)	–835 (3)	–4 (1)	466	
O(5)	2386 (6)	–3160 (3)	–969 (2)	540	

determination, is shown in Fig. 2. As in norbornane (Alden, Kraut & T aylor, 1968), the C(1)–O(1)–C(4) bridge imposes a boat conformation on the C(1) through C(4), C(9), C(10) ring. The ‘boat’ is symmetric, with a dihedral angle between the planes defined by C(1), O(1) and C(4) (I) and C(2), C(3), C(9) and C(10) (II) equal to 88.8 (6)°, and with practically equal deviations of C(1) and C(4) from plane (II) [0.807 (7) and 0.827 (7) Å, respectively]. C(5), C(8), C(9) and C(10) are almost coplanar [within 0.023 (7) Å; plane (III)] but C(6) and C(7) deviate from this plane by 0.209 (7) and –0.526 (7) Å, respectively. O(2) and O(3) lie below [O(2)] and above [O(3)] the plane with respective distances equal to –0.073 (6) and 0.344 (6) Å. The angle between planes (II) and (III) is equal to 154.0 (3)°. The crystal packing is illustrated in Fig. 3.

The cis-cisoid form. The result of the structure determination is illustrated in Fig. 4. The ring formed by C(1), C(2), C(3), C(4), C(9) and C(10) adopts a boat conformation which is imposed by O(1), bridging C(1) and C(4). The ring formed by carbon atoms C(5) through C(10) is asymmetric: C(6) and C(7) deviate from the plane defined by C(5), C(8), C(9) and C(10) [which are planar within 0.041 (5) Å] by –0.294 (6) and 0.385 (6) Å, respectively, while O(2) and O(3) are

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References

- ALDEN, R. A., KRAUT, J. & TRAYLOR, T. G. (1968). *J. Am. Chem. Soc.* **90**, 74–82.
- HOFMANN, A. A., WYRSCH-WALRAF, I., ITEN, P. X. & EUGSTER, C. H. (1979). *Helv. Chim. Acta*, **62**, 2211–2217.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
- JOHNSON, C. K. (1976). *ORTEP*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- JURCZAK, J., KOŹLUK, T., TKACZ, M. & EUGSTER, C. H. (1983). *Helv. Chim. Acta*, **66**, 218–221.
- SHELDRIK, G. M. (1975). *SHELX*. Program for crystal structure determination. Univ. of Cambridge, England.

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p- and *o*-Bis(*N,N*-diacetylamino)benzene

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Abstract. *p*-C₁₄H₁₆N₂O₄ (I): $M_r = 276.29$, monoclinic, $C2/m$, $a = 13.883$ (8), $b = 6.967$ (3), $c = 7.720$ (1) Å, $\beta = 112.42$ (3)°, $V = 690.26$ Å³, $Z = 2$, $D_x = 1.329$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.106$ mm⁻¹, $F(000) = 292$, $T = 293$ K, $R = 0.044$ for 797 reflexions with $F > 3\sigma(F)$. *o*-C₁₄H₁₆N₂O₄ (II): $M_r = 276.29$, monoclinic, $C2/c$, $a = 29.546$ (9), $b = 9.626$ (2), $c = 16.126$ (5) Å, $\beta = 113.37$ (3)°, $V = 4210.13$ Å³, $Z = 12$, $D_x = 1.307$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.105$ mm⁻¹, $F(000) = 1752$, $T = 293$ K, $R = 0.057$ for 2488 reflexions with $F > 3\sigma(F)$. All of the diacetylamino groups in (I) and (II) adopt the usual *syn-anti* configuration. Structure (I) displays crystallographic C_{2h} symmetry with the diacetylamino functions lying in a mirror plane at right angles to the benzene ring. Structure (II) is composed of two conformers, one of which is bisected by a crystallographic twofold axis and the other, although similar, is asymmetric.

Introduction. Several structures are known in which a diacetylamino (DAA) group is bound to an sp^2 C, e.g. amino sugars (Ruzić-Toroš, Rogić & Kojić-Prodić, 1980), but it is only in 6-(*N,N*-diacetylamino)chrysene (Wieckowski & Krygowski, 1981) that the bonded C atom forms part of a delocalized hydrocarbon. The present work offers several opportunities to study this type of system, of which (I) is the first example where both ring substituents flanking the DAA groups are H atoms.

Experimental. The tetraacetyl compounds were prepared by treating the respective diamines with excess

acetic anhydride under reflux for 2h; residual acetic anhydride and acetic acid were removed *in vacuo*, and the acetylation procedure repeated twice. The resultant mixtures of tri- and tetraacetyl derivatives were extracted with 60–80° petroleum ether and evaporated to give the tetraacetyl derivatives, which were recrystallized from aqueous ethanol.

(I): Colourless 0.2 × 0.2 × 0.4 mm; CAD-4 diffractometer, graphite-monochromatized Mo $K\alpha$ radiation; lattice parameters from 25 reflexions ($10.0 < \theta < 10.9^\circ$); ω - 2θ scan; $-18 < h < 18$, $0 < k < 9$, $0 < l < 10$ with $0 < \theta < 25^\circ$; no systematic variations in intensities of standards (330, 603, 711); 1107 reflexions, 797 with $F > 3\sigma(F)$; $R_{\text{int}} = 0.013$; Lp correction applied but absorption ignored; direct methods, *MULTAN80* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980); anisotropic full-matrix refinement on F , *SHELX76* (Sheldrick, 1976), H (from ΔF synthesis) isotropic; empirical extinction correction applied where $F_c^* = F_c(1 - 0.00000825F_c^2/\sin\theta)$; final $R = 0.044$, $wR = 0.050$, $w = 4.127/[\sigma^2(F_o) + 0.00004F_o^2]$; max. $\Delta/\sigma = 0.04$ for x of O(12); all features in final ΔF synthesis between -0.25 and $+0.25$ e Å⁻³.

(II): Colourless 0.2 × 0.3 × 0.4 mm; CAD-4 diffractometer, graphite-monochromatized Mo $K\alpha$ radiation; lattice parameters from 25 reflexions ($8.3 < \theta < 9.3^\circ$); ω - 2θ scan; $-31 < h < 31$, $0 < k < 11$, $0 < l < 18$ with $0 < \theta < 25^\circ$; no systematic variation in intensities of standards (822, 12,0,0,623); 4011 reflexions, 2488 with $F > 3\sigma(F)$; $R_{\text{int}} = 0.023$; Lp correction applied but absorption ignored; direct methods, *MULTAN80*; anisotropic full-matrix refinement on F , *SHELX76*, H