ring is shorter than expected for a single bond (1.552–1.560 Å) and hence may be inferred to show partial double-bond character. The angle C(7)—C(8)—C(9) [138.5 (6)°] is an indication of strain imposed at the junction between the furan ring and the ten-membered ring.

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References

Appendino, G., Calleri, M. & Chiari, G. (1986). *J. Chem. Soc. Perkin Trans.* 2, pp. 205–209.

Bovill, M. J., Cox, P. J., Cradwick, P. D., Guy, M. H. P., Sim, G. A. & White, D. N. J. (1976). *Acta Cryst.* **B32**, 3203–3208.

Calleri, M., Chiari, G. & Viterbo, D. (1983). *Acta Cryst.* **C39**, 758–761.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Koyama, H. & Okada, K. (1975). *Acta Cryst.* **A31**, S18.

Motherwell, W. D. S. & Clegg, W. (1978). *PLUTO*. Program for plotting molecular and crystal structures. Univ. of Cambridge, England.

Okada, K. & Koyama, H. (1991). *J. Appl. Cryst.* **24**, 1067–1070.

Okada, K., Okada, S. & Koyama, H. (1990). *Acta Cryst.* **A46**, C-70.

Sim, G. A. (1987). *Acta Cryst.* **C43**, 1306–1307.

Takeda, K., Horibe, I., Teraoka, M. & Minato, H. (1968). *Chem. Commun.* p. 637.

Takeda, K., Horibe, I., Teraoka, M. & Minato, H. (1969). *J. Chem. Soc. C*, pp. 1491–1495.

Takeda, K., Minato, H. & Horibe, I. (1963). *Tetrahedron*, **19**, 2307–2316.

Watson, W. H., Zabel, V., Mabry, T. J. & Yabuta, G. (1982). *Acta Cryst.* **B38**, 511–514.

Acta Cryst. (1993). **C49**, 343–345

Structure of 3-Benzoylamino-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydrocoumarin

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Abstract. $C_{18}H_{17}NO_4$, $M_r = 311.34$, monoclinic, $P2_1/n$, $a = 6.782\ (2)$, $b = 18.496\ (3)$, $c = 12.439\ (3)$ Å, $\beta = 99.34\ (1)°$, $V = 1539.7\ (8)$ Å^3, $Z = 4$, $D_x = 1.343$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 0.890$ cm^{-1}, $F(000) = 656$, $T = 293\ (2)$ K, final $R = 0.044$ and $wR = 0.063$ for 1821 observed reflections. The overall shape of the molecule is planar. The dihedral angle between the phenyl ring and the planar part of the coumarin group is 6.0 (7)°. The bond lengths and angles agree with expected values. This derivative of coumarin is a valuable material in the synthesis of the novel heterocyclic system 2*H*,-5*H*-pyrano[3,2-*c*]azepine and its derivatives.

Experimental. Plate-like colourless single crystal, 0.45 × 0.35 × 0.20 mm, sealed in glass capillary. Cell dimensions were determined from the angular settings of 25 reflections with $10 < \theta < 12°$ measured on an Enraf–Nonius CAD-4 diffractometer. Space group $P2_1/n$ was determined from the systematic absences. Intensity data were collected in the range $1 < 2\theta < 56°$ with variable-speed ω–2θ scans using graphite-monochromated Mo $K\alpha$ radiation; max. scan time 60 s, scan width $(0.8 + 0.3\tan\theta)°$, background measured for 0.25 of scan time at each scan limit. Three reflections were monitored every 300 reflections. Orientation was checked every 2 h. Data were corrected for intensity variation (−3.4%) and Lp effects; absorption was ignored. 7421 reflections ($\pm h$, $\pm k$, $+l$) were collected. On averaging ($R_{\rm int} = 2.8\%$), 1821 reflections were considered observed [$I > 3\sigma(I)$; $\sigma(I)$ based on counting statistics] out of 3481 unique reflections; range of *hkl*: h −8 to 8, k 0 to 24, l 0 to 16. The structure was solved with *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). The initial structural model was refined by full-matrix least squares, minimizing the function $\sum w(|F_o| - |F_c|)^2$ with *SHELX*76 (Sheldrick, 1976). Final R and wR values were 0.044 and 0.063, respectively, with $w = 1.0/[\sigma^2(F_o) + 0.0094(F_o)^2]$ and 209 variables; H-atom positions were found in the final difference synthesis and included in the refinement with constraint imposed only on the C—H bonds. A common isotropic displacement parameter U for all H atoms was 0.077 (2) Å^2. A final difference Fourier map showed residual electron density within +0.18 and −0.31 e Å^{-3}. $(\Delta/\sigma)_{\rm max}$ at convergence was 0.011 (overall scale factor). Scattering factors for C, N and O atoms were taken from *International Tables for*

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Table 1. *Final fractional coordinates with e.s.d.'s in parentheses and equivalent isotropic temperature factors* (Å^2)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
O1	0.1893 (2)	0.1561 (1)	−0.0090 (1)	0.043
C2	0.3481 (3)	0.1152 (1)	−0.0323 (2)	0.039
O2	0.4193 (2)	0.0712 (1)	0.0342 (2)	0.049
C3	0.4130 (3)	0.1285 (1)	−0.1357 (2)	0.040
C4	0.3167 (3)	0.1777 (1)	−0.2061 (2)	0.046
C4*A*	0.1522 (3)	0.2172 (1)	−0.1771 (2)	0.041
C5	0.0397 (3)	0.2689 (1)	−0.2554 (2)	0.049
O5	0.0922 (3)	0.2808 (1)	−0.3424 (1)	0.080
C6	−0.1440 (4)	0.3028 (1)	−0.2226 (2)	0.050
C7	−0.1314 (3)	0.3152 (1)	−0.1002 (2)	0.046
C71	−0.3356 (4)	0.3393 (1)	−0.0750 (2)	0.067
C72	0.0235 (4)	0.3745 (1)	−0.0626 (2)	0.061
C8	−0.0712 (3)	0.2442 (1)	−0.0384 (2)	0.048
C8*A*	0.0942 (3)	0.2062 (1)	−0.0799 (2)	0.040
N	0.5759 (3)	0.0847 (1)	−0.1510 (1)	0.045
C	0.6909 (3)	0.0953 (1)	−0.2304 (2)	0.042
O	0.6580 (3)	0.1442 (1)	−0.2962 (1)	0.063
C11	0.8647 (3)	0.0452 (1)	−0.2317 (2)	0.041
C12	0.9680 (3)	0.0514 (1)	−0.3187 (2)	0.053
C13	1.1366 (4)	0.0095 (1)	−0.3231 (2)	0.061
C14	1.2011 (3)	−0.0390 (1)	−0.2412 (2)	0.054
C15	1.0994 (4)	−0.0462 (1)	−0.1552 (2)	0.059
C16	0.9309 (3)	−0.0041 (1)	−0.1502 (2)	0.054

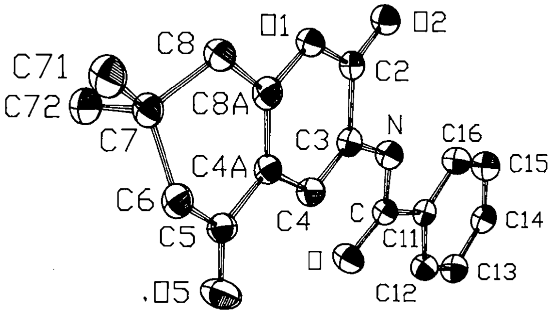

Fig. 1. *ORTEP* (Johnson, 1965) view of the molecule with the atomic numbering scheme. Thermal ellipsoids are drawn at the 50% probability level.

X-ray Crystallography (1974, Vol, IV) and for H atoms from Stewart, Davidson & Simpson (1965). All calculations were performed on the VAX 8550 cluster at University Computer Centre, Ljubljana. The *GX* package (Mallinson & Muir, 1985) was used for data processing and final interpretation of molecular geometry. The final atomic parameters are in Table 1.* Bond lengths and angles are given in Table 2. Views of the molecule with the atomic numbering scheme and of the molecular packing are presented in Figs. 1 and 2.

Table 2. *Bond distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

O1—C2	1.385 (3)	C7—C72	1.538 (4)
O1—C8*A*	1.367 (3)	C7—C8	1.543 (3)
C2—O2	1.204 (3)	C8—C8*A*	1.486 (3)
C2—C3	1.446 (4)	N—C	1.368 (3)
C3—C4	1.355 (3)	C—O	1.216 (3)
C3—N	1.408 (3)	C—C11	1.501 (3)
C4—C4*A*	1.428 (3)	C11—C12	1.386 (4)
C4*A*—C5	1.485 (4)	C11—C16	1.383 (4)
C4*A*—C8*A*	1.346 (4)	C12—C13	1.390 (4)
C5—O5	1.213 (3)	C13—C14	1.375 (4)
C5—C6	1.509 (4)	C14—C15	1.370 (4)
C6—C7	1.528 (4)	C15—C16	1.393 (4)
C7—C71	1.535 (4)		

C2—O1—C8*A*	122.5 (2)	C71—C7—C8	108.7 (2)
O1—C2—O2	117.7 (2)	C72—C7—C8	110.1 (2)
O1—C2—C3	116.9 (2)	C7—C8—C8*A*	112.5 (2)
O2—C2—C3	125.4 (2)	O1—C8*A*—C4*A*	120.4 (2)
C2—C3—C4	120.3 (2)	O1—C8*A*—C8	113.6 (2)
C2—C3—N	112.4 (2)	C4*A*—C8*A*—C8	126.0 (2)
C4—C3—N	127.3 (2)	C3—N—C	124.5 (2)
C3—C4—C4*A*	119.7 (2)	N—C—O	121.9 (2)
C4—C4*A*—C5	120.2 (2)	N—C—C11	117.4 (2)
C4—C4*A*—C8*A*	120.2 (2)	O—C—C11	120.7 (2)
C5—C4*A*—C8*A*	119.5 (2)	C—C11—C12	117.0 (2)
C4*A*—C5—O5	120.5 (2)	C—C11—C16	124.1 (2)
C4*A*—C5—C6	116.7 (2)	C12—C11—C16	118.8 (2)
O5—C5—C6	122.7 (2)	C11—C12—C13	120.5 (2)
C5—C6—C7	114.6 (2)	C12—C13—C14	120.0 (2)
C6—C7—C71	109.9 (2)	C13—C14—C15	120.1 (2)
C6—C7—C72	109.6 (2)	C14—C15—C16	120.1 (2)
C6—C7—C8	109.6 (2)	C11—C16—C15	120.5 (2)
C71—C7—C72	109.0 (2)		

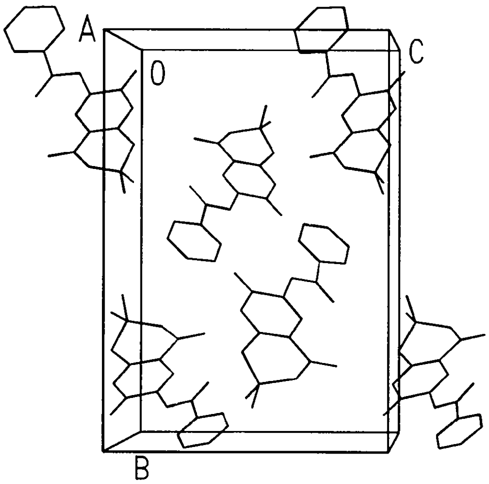

Fig. 2. View of the molecular packing.

Related literature. The title compound represents an example of an α,β-didehydroamino acid derivative and was prepared by a general one-pot synthesis (Kočevar, Polanc, Tišler & Verček, 1989; Kepe, Kočevar, Polanc, Verček & Tišler, 1990; Kočevar, Polanc, Verček & Tišler, 1990).

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and selected torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55397 (16 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AB1004]

References

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

Kepe, V., Kočevar, M., Polanc, S., Verček, B. & Tišler, M. (1990). *Tetrahedron*, **46**, 2081–2088.

Kočevar, M., Polanc, S., Tišler, M. & Verček, B. (1989). *Synth. Commun.* **19**, 1713–1719.

Kočevar, M., Polanc, S., Verček, B. & Tišler, M. (1990). *Justus Liebigs Ann. Chem.* pp. 501–503.

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.

Mallinson, P. R. & Muir, K. W. (1985). *J. Appl. Cryst.* **18**, 51–53.

Sheldrick, G. M. (1976). *SHELX76*. 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.

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Structure of Tri-*p*-tolylphosphine Oxide Hemihydrate, $P(p\text{-}C_6H_4CH_3)_3O.\frac{1}{2}H_2O$

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Abstract. $C_{21}H_{21}OP.\frac{1}{2}H_2O$, $M_r = 329.4$, monoclinic, $C2/c$, $a = 16.192$ (3), $b = 12.382$ (2), $c = 19.353$ (3) Å, $\beta = 104.990$ (10)°, $V = 3748.0$ (10) Å^3, $Z = 8$, $D_x = 1.167$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 0.147$ mm^{-1}, $F(000) = 1400$, $T = 295$ K, $R = 0.0686$, $wR = 0.0429$ for all 1757 unique data and $R = 0.0354$, $wR = 0.0348$ for those 1083 data with $F_o > 6.0\sigma(F_o)$. The central P atom has a distorted tetrahedral environment, with P=O = 1.482 (3) Å and P—C = 1.798 (3)–1.799 (3) Å. Average O—P—C = 112.9° and average C—P—C = 105.8°. The O atom of the water molecule lies on a crystallographic twofold axis and is linked by hydrogen bonds to two tri-*p*-tolylphosphine oxide molecules with O···O(water) = 2.810 (4) Å.

Experimental. A clear crystal with approximate dimensions 0.25 × 0.30 × 0.45 mm was aligned on a Siemens *R*3*m*/*V* diffractometer. Determination of the unit-cell parameters and the orientation matrix and data collection (Mo $K\alpha$; $2\theta = 5.0 \rightarrow 40.0°$; maximum $\sin\theta/\lambda = 0.539$ Å^{-1}) were performed using the *P*3 program package (Siemens Analytical X-ray Instruments, Inc., 1989). Data were collected for the entire sphere by the coupled θ(crystal)–2θ(counter) scan (h $-15 \rightarrow 15$, k $-11 \rightarrow 11$, l $-18 \rightarrow 18$). Three standard reflections were collected after each batch of 97 reflections; no significant fluctuations in their intensities were noted. A total of 7016 data were collected, and were corrected for Lorentz and polarization factors and for the effects of absorption (minimum and maximum transmission factors were 0.8894 and 0.9139, respectively). These data were merged to produce 1757 independent reflections ($R_{\rm int} = 3.30\%$). Axial photographs indicated that the crystal belonged to the *C*-centered subset of the monoclinic system. The systematic absences of hkl for $h + k = 2n + 1$ and $h0l$ for $l = 2n + 1$ indicated the possible space groups as Cc or $C2/c$. Intensity statistics clearly favored the centrosymmetric case. The space group $C2/c$ (C^6_{2h}; No. 15) was assumed and confirmed by the successful solution and refinement of the structure in this higher symmetry space group.

All crystallographic calculations were carried out on a VAX3100 workstation with the use of the Siemens *SHELXTL-Plus* program set (Sheldrick, 1990). The analytical scattering factors for the neutral atoms were corrected for the f' and f'' components of anomalous dispersion using the values compiled in *International Tables for X-ray Crystallography* (1974, Vol. IV, pp. 99–101, 148–150). The structure was solved by a combination of direct methods and difference Fourier techniques. Refinement led to convergence [$(\Delta/\sigma)_{\max} = 0.001$] with $R = 6.86\%$, $wR = 4.29\%$ and GOF = 1.42 for 1757 independent reflections and 239 variables [$R = 3.54\%$, $wR = 3.48\%$ for those 1083 reflections with $F_o > 6.0\sigma(F_o)$]. The quantity minimized was $\sum w(|F_o| - |F_c|)^2$, where $w^{-1} = \sigma^2(F) + 0.0001F^2$.

All non-H atoms were refined anisotropically, and the H atoms of the *p*-tolyl groups were included in calculated positions with C—H = 0.96 Å (Churchill, 1973). The positional and isotropic thermal parameters of the unique H atom of the H_2O molecule were refined. A final difference Fourier synthesis showed features only in the range 0.20 to -0.18 e Å^{-3}. Final

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