de l'oxaphénalène est tout a fait cohérent avec une forte activité génotoxique des dérivés α-nitrés de cette série. Il apparaît aussi que, d'une manière générale, les liaisons C—C sont assez différentes de celles observées dans des molécules polycycliques connues.

References

AJANA, A. (1987). Thèse, Bordeaux, France.
AJANA, A., BIDEAU, J.-P., COTRAIT, M., BUISSON, J.-P., DEMERSEMAN, P., EINHORN, J. & ROYER, R. (1988). *Eur. J. Med. Chem.* **23**, 341–346.

BUISSON, J.-P. & ROYER, R. (1988). *J. Heterocycl. Chem.* **25**, 539–542.
GILMORE, C. J. (1984). *J. Appl. Cryst.* **17**, 42–46.
JOHNSON, C. K. (1965). *ORTEP.* Rapport ORNL-3794. Oak Ridge National Laboratory, Tennessee, EU.
PLATZER, N., BUISSON, J.-P. & DEMERSEMAN, P. (1991). *Org. Magn. Reson.* Sous presse.
ROYER, R. & BUISSON, J.-P. (1986). *Ann. Pharm. Fr.* **44**, 177–189.
ROYER, R., BUISSON, J.-P., VLEMINCKX, C. & MOENS, W. (1986). *Eur. J. Med. Chem.* **21**, 352–354.
STEWART, J. J. P. (1988). QCPE Program No. 455. Department of Chemistry, Indiana Univ., Indiana, EU.
STEWART, J. J. P. (1989). *J. Comput. Chem.* **10**, 209–222.
STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

The Rearrangement of Coumarin-4-acethydrazides. Structure of 1-Amino-4-(2-hydroxy-4-methoxyphenyl)-2,6(1*H*,3*H*)-pyridinedione*

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Abstract. $C_{12}H_{12}N_2O_4$, $M_r = 248\cdot2$, triclinic, $P\bar{1}$, $a = 6\cdot793$ (2), $b = 7\cdot209$ (11), $c = 11\cdot405$ (4) Å, $\alpha = 88\cdot77$ (7), $\beta = 89\cdot06$ (2), $\gamma = 74\cdot62$ (6)°, $V = 538\cdot35$ Å^3, $Z = 2$, $D_x = 1\cdot531$ g cm^{-3}, λ(Mo $K\alpha$) = $0\cdot71069$ Å, $\mu = 0\cdot73$ cm^{-1}, $F(000) = 260\cdot0$, $T = 293$ K, $R = 0\cdot0452$ for 1011 observed reflections. A substituted 4-phenyl-2,6(1*H*,3*H*)-pyridinedione crystallizes with coplanar rings [angle between ring planes $2\cdot3$ (3)°]. No π delocalization between the rings is present [ring to ring bond length $1\cdot481$ (4) Å] and the double bond is localized within the heterocycle [bond length $1\cdot356$ (5) Å]. The heterocyclic moiety is planar (r.m.s. deviation from plane = $0\cdot013$ Å).

Introduction. Baker, Haksar & McOmie (1950) have described the synthesis of acyl hydrazides derived from coumarin-carboxylic acids and their use as fluorescent reagents in chromatographic separations of carbonyl compounds.

While reinvestigating the synthesis of 7-hydroxycoumarin-4-acethydrazide, a base-catalyzed rearrangement of the ring system was observed. The rearranged compound was difficult to work with due to its very low solubility in solvents other than dimethyl sulfoxide (DMSO). In order to further understand the rearrangement the analogous 7-

methoxy-4-acethydrazide (I) was prepared and similarly rearranged.

The new material was purified without difficulty, but the spectral data were ambiguous. Previous workers (Pednekar, Samant & Deodhar, 1984; Peet & Sunder, 1986) have described similar compounds from the condensation of acethydrazides but there is some doubt as to whether a six (II) or a seven (III) membered ring results from the closure of the new heterocycle (see scheme).
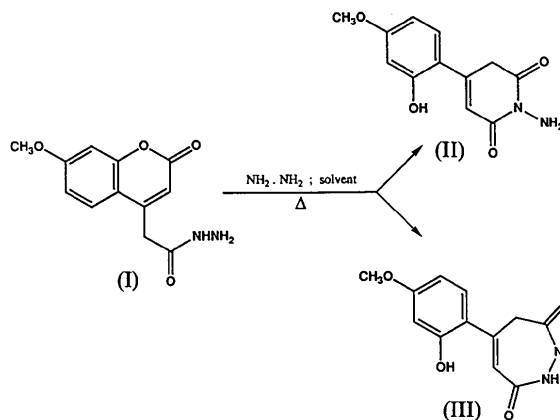
To resolve this question the structure of the rearranged product has been elucidated and shown to be 1-amino-4-(2-hydroxy-4-methoxyphenyl)-2,6-(1*H*,3*H*)-pyridinedione (II).

Experimental. 7-Methoxycoumarin-4-acethydrazide (I) was prepared from methyl 7-methoxycoumarin-4-acetate according to the method of Baker, Haksar & McOmie (1950). The rearrangement was accomplished by refluxing (I) in methanol and 99% hydrazine hydrate (2:3) for 30 min. Acidification with conc. HCl precipitated (II) in 76% yield. Recrystallization from methanol gave yellow elongated prisms, m.p. 506–507 K.

A crystal of the rearrangement product with dimensions $0.4 \times 0.1 \times 0.1$ mm was mounted on an Enraf–Nonius CAD-4 diffractometer; lattice parameters determined from the setting angles of 24 reflections (θ 8 to 19°); intensity data measured with ω–2θ scans in the range $2 < \theta < 27.5°$; index range h −2 to 8, k −9 to 9, l −14 to 14; three standard reflections measured every 2 h showed no significant variation over the period of data collection.

3096 reflections were scanned, of which 2473 were unique ($R_{int} = 0.0231$) and 1011 were considered observed [$F > 5\sigma(F)$] and were used in the analysis. No absorption correction was applied. The structure was solved using direct methods; H-atom positions from a Fourier difference map; coordinates of all atoms refined using full-matrix least squares on F values with weights $w = 1/[\sigma^2(F) + 0.0005F^2]$; non-H atoms were assigned anisotropic thermal parameters and H atoms were refined isotropically. Refinement was terminated when all shifts were less than 0.01σ; $R = 0.0452$, $wR = 0.0502$ and $S = 1.32$ for the 1011 observed reflections; the residual electron density in a final difference map was within the range -0.20 to 0.27 e Å^{-3}.

Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV); computations were carried out with *SHELX*76 (Sheldrick, 1976) and *SHELXS*86 (Sheldrick, 1986). Fig. 1 was drawn using *PLUTO*88 (Motherwell & Clegg, 1988).

Discussion. Atomic coordinates are listed in Table 1,* bond lengths and angles in Table 2. Fig. 1 shows the atomic numbering for the molecule.

The molecule consists of a bicyclic system in which the heterocycle [N(2), C(1), C(2), C(3), C(4) and C(5)] is coplanar with the benzene ring [torsion angles C(2)—C(3)—C(6)—C(7) 179.4 (5)°, C(11)—C(6)—C(3)—C(4) −179.6 (5)°]. However, there is no π stabilization between the C(3)—C(4) double bond [1.356 (5) Å] and the benzene ring [ring to ring bond length 1.481 (4) Å].

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53830 (13 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional atomic coordinates* ($\times 10^4$) *with e.s.d.'s in parentheses and equivalent isotropic temperature factors* (Å$^2 \times 10^3$)

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

	x	y	z	U_{eq}
N(1)	3605 (9)	6665 (8)	818 (4)	58
N(2)	4038 (4)	6885 (4)	2018 (2)	36
O(1)	7319 (4)	5289 (4)	1709 (2)	59
O(5)	730 (4)	8428 (4)	2322 (2)	45
O(7)	1837 (4)	9264 (4)	6188 (2)	49
O(9)	6758 (4)	8445 (4)	9123 (2)	46
C(1)	6005 (6)	6119 (5)	2394 (3)	35
C(2)	6481 (6)	6383 (6)	3639 (3)	32
C(3)	4778 (5)	7381 (5)	4426 (3)	29
C(4)	2892 (6)	7995 (6)	3955 (3)	36
C(5)	2455 (6)	7799 (5)	2735 (3)	32
C(6)	5268 (5)	7649 (5)	5662 (3)	27
C(7)	3816 (5)	8585 (5)	6510 (3)	31
C(8)	4383 (6)	8819 (6)	7638 (3)	35
C(9)	6387 (6)	8124 (5)	7984 (3)	32
C(10)	7858 (6)	7174 (6)	7185 (3)	37
C(11)	7271 (5)	6967 (5)	6055 (3)	34
C(12)	8817 (7)	7781 (8)	9529 (4)	50

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

N(1)—N(2)	1.426 (5)	C(3)—C(4)	1.356 (5)
N(2)—C(1)	1.375 (4)	C(3)—C(6)	1.481 (4)
N(2)—C(5)	1.370 (4)	C(4)—C(5)	1.444 (5)
O(1)—C(1)	1.216 (4)	C(6)—C(7)	1.417 (4)
O(5)—C(5)	1.237 (4)	C(6)—C(11)	1.396 (5)
O(7)—C(7)	1.357 (4)	C(7)—C(8)	1.375 (5)
O(9)—C(9)	1.363 (4)	C(8)—C(9)	1.381 (5)
O(9)—C(12)	1.434 (5)	C(9)—C(10)	1.390 (5)
C(1)—C(2)	1.489 (5)	C(10)—C(11)	1.378 (5)
C(2)—C(3)	1.487 (5)		

|			
N(1)—N(2)—C(1)	118.1 (3)	O(5)—C(5)—C(4)	122.7 (3)
N(1)—N(2)—C(5)	118.0 (4)	C(3)—C(6)—C(7)	124.3 (3)
C(1)—N(2)—C(5)	123.9 (3)	C(3)—C(6)—C(11)	120.1 (3)
C(9)—O(9)—C(12)	118.0 (3)	C(7)—C(6)—C(11)	115.6 (3)
N(2)—C(1)—O(1)	120.1 (3)	O(7)—C(7)—C(6)	118.6 (3)
N(2)—C(1)—C(2)	118.4 (3)	O(7)—C(7)—C(8)	120.1 (3)
O(1)—C(1)—C(2)	121.5 (3)	C(6)—C(7)—C(8)	121.3 (3)
C(1)—C(2)—C(3)	118.1 (3)	C(7)—C(8)—C(9)	120.9 (3)
C(2)—C(3)—C(4)	117.4 (3)	O(9)—C(9)—C(8)	115.4 (3)
C(2)—C(3)—C(6)	117.8 (3)	O(9)—C(9)—C(10)	124.8 (3)
C(4)—C(3)—C(6)	124.8 (3)	C(8)—C(9)—C(10)	119.8 (3)
C(3)—C(4)—C(5)	124.1 (3)	C(9)—C(10)—C(11)	118.6 (3)
N(2)—C(5)—O(5)	119.5 (3)	C(6)—C(11)—C(10)	123.8 (3)
N(2)—C(5)—C(4)	117.9 (3)		
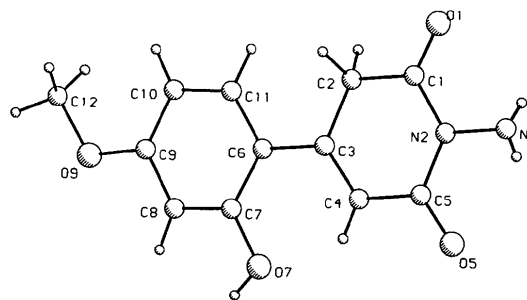
Fig. 1. View of the molecule showing the atomic numbering scheme.

There is no evidence of enolization in the molecule; C(1)—O(1) [1·216 (4) Å] and C(5)—O(5) [1·237 (4) Å] are typical of carbonyl bond lengths as described by Amorese, Gavuzzo, Mazza, Casini & Ferappi (1982) and by Onan, Rao & Parry (1985). This is noteworthy because proton NMR spectroscopy suggests that in DMSO solution there exists a pair of keto–enol tautomers, the more dominant being the enol form (approx. 60%). Also typical are the bond lengths N(2)—C(1) and N(2)—C(5) of 1·375 (4) and 1·370 (4) Å, respectively, implying some delocalization across the imide system. Such delocalization explains why N(2) is trigonal, with the O(1)–C(1)–N(2)–N(1)–C(5)–O(5) system being planar (r.m.s. deviation 0·008 Å).

The C(11)—C(6)—C(7) angle in the benzene ring is unusually small [115·6 (3)°], probably due to a number of factors: the repulsions between the H atom on C(11) and those on C(2), the repulsion between ring and alkene π clouds and the inductive effect caused by the release of electrons along the C(3)—C(6) bond towards C(6) may all contribute.

With such repulsive interactions and without any ring–ring stabilization, it is perhaps surprising that the molecule adopts such a planar conformation. It is, however, possible to rationalize this on three counts. Firstly there exists the possibility of a hydrogen bond between H(4) and O(7) [2·11 (3) Å], secondly when the symmetry related molecule at $-x$, $2-y$, $1-z$ is considered it is apparent that the two molecules are oriented such that all four rings are coplanar. The proton on O(7) forms a strong hydrogen bond [1·85 (4) Å] to the carbonyl O(5)′ of the second molecule [angle H(7)—O(7)—O(5)′ 15 (3)°]. Similarly, the O(7)′ H atom on the second molecule bonds to O(5) of the first. Consistent with this hydrogen-bonding model, the C(5)—O(5) bond is some 0·021 (4) Å longer than the C(1)—O(1) bond. The third contribution may arise from packing forces which encourage planar packing within the crystal. It appears that the sum of these effects is strong enough to overcome the steric and electronic repulsions which tend to induce torsional asymmetry.

For comparison, biphenyl is also apparently planar in the solid (Charbonneau & Delugeard, 1977) and the endocyclic angle at the ring to ring bond is 117·3 (2)°.

References

Amorese, A., Gavuzzo, E., Mazza, F., Casini, G. & Ferappi, M. (1982). Acta Cryst. B38, 3145–3147.

Baker, W., Haksar, C. N. & McOmie, J. F. W. (1950). J. Chem. Soc. pp. 170–173.

Charbonneau, G.-P. & Delugeard, Y. (1977). Acta Cryst. B33, 1586–1588, and references therein.

Motherwell, W. D. S. & Clegg, W. (1988). PLUTO88. Program for plotting molecular and crystal structures. Cambridge Structural Database System. Users Manual, Part II. Univ. of Cambridge, England.

Onan, K. D., Rao, H. S. P. & Parry, R. J. (1985). Acta Cryst. C41, 428–431.

Pednekar, S. R., Samant, S. D. & Deodhar, K. D. (1984). Heterocycles, 22, 1979–1984.

Peet, N. P. & Sunder, S. (1986). Heterocycles, 24, 393–399.

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

Sheldrick, G. M. (1986). SHELXS86. Program for the solution of crystal structures. Univ. of Göttingen, Germany.

Structure of exo,exo-9,10,12-Tribromotricyclo[6.3.1.0²,⁷]dodeca-2(7),3,5,10-tetraene

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Abstract. $C_{12}H_9Br_3$, $M_r = 392·915$, orthorhombic, $P2_12_12_1$, $a = 6·979 (4)$, $b = 9·596 (1)$, $c = 18·056 (4)$ Å, $V = 1209·22$ Å^3, $Z = 4$, $D_m = 2·1$, $D_x = 2·158$ g cm^{-3}, λ(Cu $K\alpha$) = 1·54180 Å, μ(Cu $K\alpha$) = 122·24 cm^{-1}, $F(000) = 744$, $T = 293$ K, $R = 0·044$ for 1254 observed reflections. In the title compound, the Br(1)—C(12) [1·966 (9) Å] and Br(3)—C(9) [1·971 (7) Å] distances are almost equal but Br(2)—C(10) [1·892 (7) Å] is shorter. The structural analysis has revealed that the starting compound,