In both structures the H atoms on N were located from a ΔF synthesis; the positions of these H atoms were allowed to refine with $U_{\rm iso} = 1.2 \times U_{\rm eq}$ of the corresponding N atom. Data collection and cell refinement: *DIF*4 (Stoe & Cie, 1988*a*). Data reduction: *REDU*4 (Stoe & Cie, 1988*b*). Structure solution: *SHELXS*86 (Sheldrick, 1990). Structure refinement: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC* (Sheldrick, 1992).

We thank the SERC for provision of a four-circle diffractometer and Lonza Ltd for a gift of Meldrum's acid.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HA1120). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Blake, A. J., Hunter, G. A. & McNab, H. (1989). *J. Chem. Res.* (*S*), pp. 118–119; *J. Chem. Res.* (*M*), pp. 0921–0943.
Blake, A. J., McNab, H., Morrow, M. & Rataj, H. (1993). *J. Chem. Soc. Chem. Commun.* pp. 840–842.
Concepcion Foces-Foces, M. de la, Cano, F. H., Claramunt, R. M., Sanz, D., Catalan, J., Fabero, F., Fruchier, A. & Elguero, J. (1990). *J. Chem. Soc. Perkin Trans.* 2, pp. 237–244.
Salazar, L., Espada, M., Sanz, D., Claramunt, R. M., Elguero, J., Garcia-Granda, S., Diaz, M. R. & Gomez-Beltran, F. (1993). *J. Chem. Soc. Perkin Trans.* 2, pp. 377–383.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1992). *SHELXTL/PC*. Version 4.3. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* Univ. of Göttingen, Germany.
Stoe & Cie (1988*a*). *DIF*4. *Diffractometer Control Program.* Version 7.09/DOS. Stoe & Cie, Darmstadt, Germany.
Stoe & Cie (1988*a*). *REDU*4. *Data Reduction Program.* Version 7.03/DOS. Stoe & Cie, Darmstadt, Germany.

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α-Pyrone at 150 K

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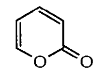
Abstract

We have determined the crystal structure of the low-melting α-pyrone (2-pyrone, $C_5H_4O_2$) at 150 K. The C—C bond distances within the ring exhibit substantial bond-length alternation, indicating that the molecule may be described largely in terms of a localized bond model. The α-pyrone molecules are packed in a herringbone fashion in the unit cell.

Comment

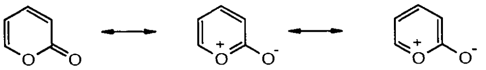
We are involved in determining the structures of fundamental parent compounds which are the simplest representatives of their class. Apart from their inherent interest, these obviously fulfil a valuable role as reference structures, for example in molecular modelling and theoretical studies. The effort required to obtain single crystals from liquid samples such as α-pyrone, (1), is therefore justified.



(1)

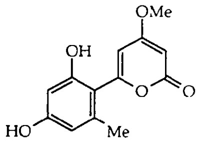
α-Pyrones are valuable synthetic reagents in organic chemistry; for example, they can behave as dienes in Diels–Alder reactions (Boulton & McKillop, 1984). However, inferences regarding their electronic structure have been drawn largely from chemical and spectroscopic data, as the crystal structures of α-pyrones determined so far have been of analogues incorporating π-active functional groups which perturb the pyrone ring.

The crystal structure of α-pyrone consists of discrete $C_4H_5O_2$ molecules (Fig. 1). Although the C—C bond distances within the ring are shorter than formal C_{sp^2}—C_{sp^2} single bonds (typically 1.48 Å), there is substantial bond-length alternation, consistent with C3—C4 and C5—C6 being strongly π-bonded [1.339 (4) and 1.338 (4) Å, respectively] and C2—C3 and C4—C5 being more weakly so [1.439 (4) and 1.424 (4) Å, respectively]. This imples that of the three formal valence canonical forms which define the electronic structure of α-pyrone shown in the scheme below, form I is dominant, with only minor contributions from forms II and III. The electronic structure of α-pyrone is, therefore, essentially localized.

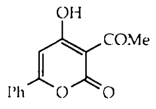


I   II   III

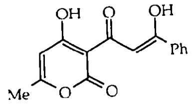
These features are reminiscent of the structure of furan (C—C 1.34 and 1.42 Å; C—O 1.36 Å), for which they have also been interpreted as being symptomatic of rather limited delocalization. These results notwithstanding, there are considerable differences between the bond lengths of the lactone function in α-pyrone and standard values for δ-lactones derived from the analysis of structures in the Cambridge Structural Database (Schweizer & Dunitz, 1982; Norskov-Lauritsen, Bürgi, Hofmann & Schmidt, 1985). The bond lengths in α-pyrone are compared with those observed in three substituted derivatives, 4-methoxy-6-(2,4-dihydroxy-6-methylphenyl)-2-pyrone, (2) (Hirata & Suga, 1978), 3-acetyl-4-hydroxy-6-phenyl-2-pyrone, (3) (Thailambal & Pattabhi, 1985), and 4-hydroxy-3-(3-hydroxy-1-oxo-3-phenyl-2-propenyl)-6-methyl-2-pyrone, (4) (Thailambal, Pattabhi & Gabe, 1986), and the corresponding benzo analogue, coumarin (1-benzopyran-2-one), (5) (Gavuzzo, Mazza & Giglio, 1974), in Table 3. In the substituted pyrones the effect of a $p\pi$–$p\pi$ interaction between the 4-oxy function and C4 is to increase the length of C3—C4, although only in (2) is there a significant concomitant lengthening of the carbonyl bond C2═O2. In (3) and (4) a 4-hydroxy group is conjugated with a 3-(1-carbonyl) group creating a system stabilized by chelation through the formation of an intramolecular hydrogen bond. These systems, like α-pyrone, are also therefore essentially localized. With the exception of the C5═C6 bond, which forms part of the benzene ring, the bond distances in coumarin are very similar to those found in α-pyrone.



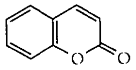
(2)



(3)



(4)



(5)

There are no major variations between the bond angles observed in α-pyrone and those in coumarin, the largest difference being 2.2° in O2—C2—C3. With respect to the lactone function, the difference between the exocyclic O2—C2—C3 and O2—C2—O1 angles in α-pyrone (11.5°) is much larger than expected for standard δ-lactones (3°) (Norskov-Lauritsen, Bürgi, Hofmann & Schmidt, 1985).

The localization of the π system in α-pyrone induces a torsional flexibility absent in perfectly delocalized molecules, and although atoms O1, C3, C4, C5 and C6 define, within error, a perfect plane, C2 and O2 deviate from this plane by 0.042 (4) and 0.099 (5) Å, respectively. The molecule nevertheless librates as a rigid body, and **TLS** fitting of the anisotropic displacement parameters (Dunitz, 1979) carried out using *CRYSTALS* (Watkin, Carruthers & Betteridge, 1985) refined to give a residual of 3.07%.

We sought a comparison between our solid-state results and the gas-phase geometry of α-pyrone. However, no structure has been determined by electron diffraction and the structure based on the interpretation of microwave data (Norris, Benson, Beak & Flygare, 1973), obtained without the benefit of isotopic substitution, contains a number of molecular geometry parameters which do not appear to be reliable.

The results derived from this study and the conclusions drawn regarding the extent of delocalization in α-pyrone are consistent with established trends in heterocyclic chemistry; whereas nitrogen-containing systems are best described as being fully or largely delocalized, oxygen-containing systems are characterized by the dominant contribution of fully localized canonical forms. This has been ascribed to the high electronegativity of oxygen, since the canonical forms which lead to delocalization involve a positive charge on the heteroatom, and for this reason tend to be disfavoured.

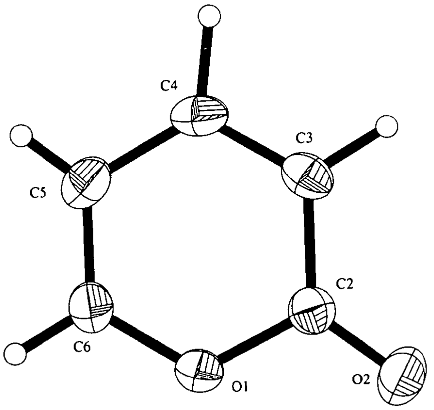


Fig. 1. A view of the molecule showing the atom-numbering scheme. Displacement ellipsoids are shown at the 50% probability level.

Experimental

Crystal data

$C_5H_4O_2$
$M_r = 96.08$
Orthorhombic
$Pna2_1$
$a = 19.263\ (10)$ Å
$b = 3.886\ (3)$ Å
$c = 5.902\ (3)$ Å
$V = 441.9\ (5)$ Å^3
$Z = 4$
$D_x = 1.444$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 21 reflections
$\theta = 14$–$16°$
$\mu = 0.113$ mm^{-1}
$T = 150.0\ (2)$ K
Cylinder
0.8 × 0.5 × 0.5 mm
Colourless

Data collection

Stoe Stadi-4 diffractometer
ω–2θ scans
Absorption correction: none
703 measured reflections
703 independent reflections
660 observed reflections [$I > 2\sigma(I)$]

$\theta_{\max} = 30.07°$
$h = 0 \rightarrow 27$
$k = 0 \rightarrow 5$
$l = 0 \rightarrow 8$
3 standard reflections
frequency: 60 min
intensity variation: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0470$
$wR(F^2) = 0.1535$
$S = 1.251$
698 reflections
81 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0978P)^2 + 0.0994P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = -0.006$
$\Delta\rho_{\max} = 0.327$ e Å^{-3}
$\Delta\rho_{\min} = -0.273$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.04 (2)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Absolute configuration: Flack (1983) (not identified)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{\text{eq}} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
O1	0.31953 (9)	0.2080 (5)	0.2260 (3)	0.0305 (5)
C2	0.38637 (12)	0.0882 (6)	0.2600 (5)	0.0273 (5)
O2	0.39611 (12)	−0.0760 (6)	0.4306 (4)	0.0405 (6)
C3	0.43614 (11)	0.1769 (6)	0.0879 (5)	0.0286 (6)
C4	0.41688 (13)	0.3492 (6)	−0.0982 (5)	0.0309 (6)
C5	0.34675 (15)	0.4558 (7)	−0.1286 (5)	0.0339 (6)
C6	0.30114 (14)	0.3809 (7)	0.0352 (5)	0.0324 (6)

Table 2. *Selected geometric parameters* (Å, °)

O1—C6	1.358 (3)	C3—C4	1.339 (4)
O1—C2	1.384 (3)	C4—C5	1.424 (4)
C2—O2	1.207 (4)	C5—C6	1.338 (4)
C2—C3	1.439 (4)		
C6—O1—C2	122.0 (2)	C4—C3—C2	121.0 (2)
O2—C2—O1	116.3 (2)	C3—C4—C5	120.8 (2)
O2—C2—C3	127.8 (2)	C6—C5—C4	117.9 (3)
O1—C2—C3	115.9 (2)	C5—C6—O1	122.4 (2)
C6—O1—C2—O2	−176.6 (2)	C2—C3—C4—C5	1.4 (4)
C6—O1—C2—C3	3.8 (4)	C3—C4—C5—C6	0.5 (4)
O2—C2—C3—C4	177.1 (3)	C4—C5—C6—O1	−0.2 (4)
O1—C2—C3—C4	−3.4 (4)	C2—O1—C6—C5	−2.1 (4)

Table 3. *A comparison of the bond lengths* (Å) *in α-pyrone and substituted α-pyrones*

	α-Pyrone	(2)[a]	(3)[b]	(4)[c]	(5)[d]
O1—C2	1.384 (3)	1.378 (4)	1.398 (8)	1.394 (7)	1.367 (4)
C2═O2	1.207 (4)	1.233 (4)	1.200 (7)	1.205 (7)	1.204 (4)
C2—C3	1.439 (4)	1.404 (5)	1.438 (8)	1.438 (8)	1.448 (5)
C3═C4	1.339 (4)	1.372 (5)	1.398 (8)	1.400 (8)	1.344 (5)
C4—C5	1.424 (4)	1.427 (5)	1.413 (9)	1.406 (8)	1.431 (5)
C5═C6	1.338 (4)	1.343 (5)	1.321 (9)	1.348 (8)	1.395 (4)
C6—O1	1.358 (3)	1.376 (4)	1.362 (7)	1.364 (7)	1.378 (4)
C4—O4		1.340 (4)	1.316 (8)	1.322 (7)	
C3—C7			1.456 (9)	1.452 (9)	
C7═O7			1.277 (9)	1.245 (8)	

References: (*a*) Hirata & Suga (1978); (*b*) Thailambal & Pattabhi (1985); (*c*) Thailambal, Pattabhi & Gabe (1986); (*d*) Gavuzzo, Mazza & Giglio (1974).

α-Pyrone, a clear liquid, was purified by Kugelrohr distillation and sealed in a fine Pyrex capillary tube using epoxy adhesive. The tube was fixed in a thermally insulating Tufnol pip which was then mounted in a standard arcless goniometer head. The sample was mounted on a Stoe Stadi-4 four-circle diffractometer with χ set to −90°, 10 mm from the outlet nozzle of an Oxford Cryosystems low-temperature device (Cosier & Glazer, 1986). The melting-point range of pyrone under these conditions was established as 268–276 K. Accordingly, the liquid sample was cooled from 277 K at a rate of 60 K h^{-1} until solidification began at 273.5 K. At least two competing growth fronts were observed on cooling to 268 K at a rate of 15 K h^{-1}, by which temperature the sample had completely solidified. The presence of a single crystal was not immediately obvious, although the observation of extinction on χ-rotation of the sample in a beam of plane-polarized light indicated an area of crystallinity. A random search generated a list of reflections which could not be indexed automatically and was likely to have resulted from diffraction by more than one crystal within the sample. However, a plausible unit cell was obtained by indexing a judiciously selected sample of reflections. Data collection and cell refinement: *DIF*4 (Stoe & Cie, 1990*a*). Data reduction: *REDU*4 (Stoe & Cie, 1990*b*). Structure solution: *SHELXS*86 (Sheldrick, 1990). Structure refinement: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL*/*PC* (Sheldrick, 1992).

We thank the SERC for provision of a four-circle diffractometer.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HA1121). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Boulton, A. J. & McKillop, A. (1984). *Comprehensive Heterocyclic Chemistry*, Vol. 3, ch. 2.22–2.24. Oxford: Pergamon Press.
Cosier, J. & Glazer, A. M. (1986). *J. Appl. Cryst.* **19**, 105–107.
Dunitz, J. D. (1979). *X-ray Analysis and the Structure of Organic Molecules*, p. 244. Ithaca, New York: Cornell Univ. Press.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Gavuzzo, E., Mazza, F. & Giglio, E. (1974). *Acta Cryst.* B**30**, 1351–1357.
Hirata, T. & Suga, T. (1978). *Bull. Chem. Soc. Jpn*, **51**, 842–849.
Norris, C. L., Benson, R. C., Beak, P. & Flygare, W. H. (1973). *J. Am. Chem. Soc.* **95**, 2766–2772.
Norskov-Lauritsen, L., Bürgi, H.-B., Hofmann, P. & Schmidt, H. R. (1985). *Helv. Chim. Acta*, **68**, 76–82.
Schweizer, W. B. & Dunitz, J. D. (1982). *Helv. Chim. Acta*, **65**, 1547–1554.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1992). *SHELXTL*/*PC*. Version 4.3. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* Univ. of Göttingen, Germany.
Stoe & Cie (1990*a*). *DIF*4. *Diffractometer Control Program.* Version 7.09/DOS. Stoe & Cie, Darmstadt, Germany.
Stoe & Cie (1990*b*). *REDU*4. *Data Reduction Program.* Version 7.03/DOS. Stoe & Cie, Darmstadt, Germany.
Thailambal, V. G. & Pattabhi, V. (1985). *Acta Cryst.* C**41**, 802–804.
Thailambal, V. G., Pattabhi, V. & Gabe, E. J. (1986). *Acta Cryst.* C**42**, 1017–1019.
Watkin, D. J., Carruthers, J. R. & Betteridge, P. W. (1985). *CRYSTALS User Guide*. Chemical Crystallography Laboratory, Univ. of Oxford, England.