

Maleic anhydride, redetermination at 130 K

Martin Lutz

Bijvoet Center for Biomolecular Research,
Department of Crystal and Structural Chemistry,
Utrecht University, Padualaan 8, 3584 CH
Utrecht, The Netherlands

Correspondence e-mail: m.lutz@chem.uu.nl

Key indicators

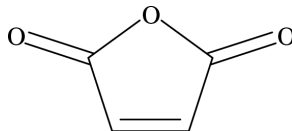
Single-crystal X-ray study
 $T = 130$ K
Mean $\sigma(\text{C}-\text{C}) = 0.001$ Å
 R factor = 0.027
 wR factor = 0.070
Data-to-parameter ratio = 21.4For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

The X-ray crystal structure of the title compound (2,5-furandione), $\text{C}_4\text{H}_2\text{O}_3$, was redetermined at 130 (2) K. The $\text{C}=\text{C}$ double bond, previously reported to be unusually short, was accurately measured as 1.3322 (9) Å and thus proved to be fairly standard. The relatively high melting point of the compound is attributed to the intermolecular dipole–dipole interactions between carbonyl groups.

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Comment

The room-temperature structure of maleic anhydride, (I), was first reported by Marsh *et al.* (1962) with X-ray intensities from Weissenberg photographs. The authors found an unusually short $\text{C}=\text{C}$ double bond of 1.303 (5) Å. The $\text{C}-\text{H}\cdots\text{O}$ distances were found to be the shortest intermolecular contacts, but these did not fulfill the requirements for hydrogen bonding and were therefore described as normal van der Waals interactions.



(I)

The short $\text{C}=\text{C}$ double bond could not be confirmed by a recent neutron study (Parker *et al.*, 2001), which was also performed at room temperature. With a distance of 1.328 (9) Å, it is in a much more normal range. Based on the very accurate H-atom positions from this study, the absence of $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds was confirmed. As an explanation for the difference in the melting points of maleic anhydride (M_r 98.06, m.p. 328 K) and heptane (M_r 100.21, m.p. 182 K), the authors suggested dipole–dipole interactions of maleic anhydride molecules in the crystal. The difficulty in this neutron study was the substantial intensity decay in the course of the experiment, probably owing to sublimation of the crystal at room temperature.

In the present X-ray study, a measurement temperature of 130 (2) K was chosen to avoid the sublimation of the crystal and to minimize thermal motion, which could influence the determination of bond geometries. For a more accurate determination of atomic positions, the X-ray intensities were measured up to a resolution of $(\sin\theta/\lambda)_{\text{max}} = 0.93$ Å⁻¹. This experimental set-up led to a significant decrease in the discrepancy factors, not only for the crystal structure refinement but also for the thermal-motion analysis. The displacement-ellipsoid plot of the molecule is shown in Fig. 1.

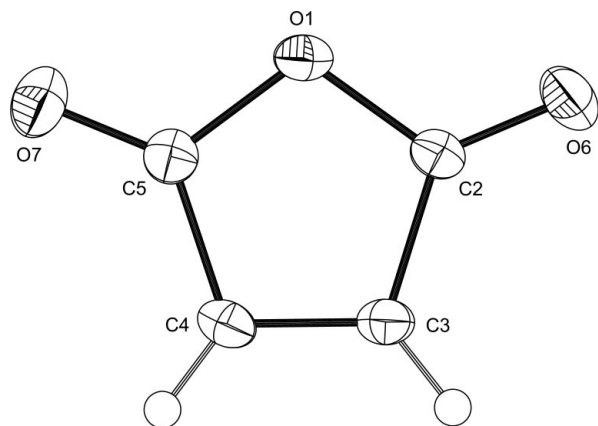


Figure 1
Displacement-ellipsoid plot of maleic anhydride, drawn at the 50% probability level.

The C3=C4 double-bond length, as determined in the present study, is 1.3322 (9) Å. Thermal-motion analysis using the *THMA11a* program (Schomaker & Trueblood, 1998) results in a weighted *R* of 0.024 for all *U*'s, indicating that the maleic anhydride molecule behaves as a rigid body. A rigid-body correction of the intramolecular distances is therefore applicable, and leads to a corrected C3=C4 bond length of 1.337 Å. The effect of thermal motion on the bond lengths is much smaller than in the case of the room-temperature neutron study, where the measured value of 1.328 (9) Å for C3=C4 is corrected to 1.344 Å with a rigid-body correction based on non-H atoms. In the latter case, the weighted *R* for all *U*'s is 0.053.

A closer inspection of the intermolecular interactions in the crystal of the title compound shows that there are short contacts of the negatively charged O6 and O7 atoms with the positively charged C2 and C5 atoms. This type of interaction has been systematically investigated by Allen *et al.* (1998) for ketones. The stabilizing effect of C=O...C=O interactions is expected to be even higher for anhydrides than for ketones, because of the more positive charge on the anhydride-C atoms. The geometrical details of these interactions in maleic anhydride are shown in Fig. 2. According to the nomenclature of Allen *et al.*, the arrangement at O6 (Fig. 2a) is called a perpendicular motif, whereas the arrangement at O7 (Fig. 2b) exemplifies a sheared parallel motif. In conclusion it can be stated that the crystal structure may be stabilized not only due to the significant dipole moment of the whole molecule, but also due to substantial dipole moments of its functional groups.

The geometry at the positively charged carbonyl-C atoms is not changed by the above-mentioned intermolecular approach of negatively charged O atoms. Atoms C2 and C5 have a planar geometry, with the bond-angle sums equal to 360.00°.

Experimental

Crystals were obtained by evaporation of a solution of maleic anhydride in ethyl acetate at room temperature and subsequent cooling to 277 K.

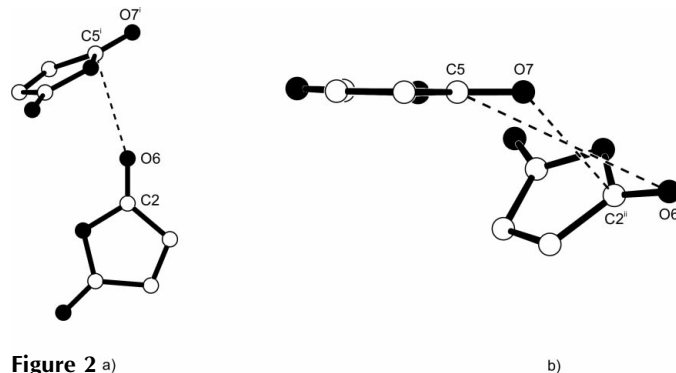


Figure 2 a) b)
Intermolecular carbonyl-carbonyl interactions between the anhydride groups. (a) O6...C5ⁱ 2.9284 (8) Å, C2-O6...C5ⁱ 162.50 (5)° and O6...C5ⁱ-O7ⁱ 100.91 (5)° [symmetry code: (i) 0.5+x, 0.5-y, 1-z]; (b) O7...C2ⁱⁱ 3.0232 (9) Å, C2ⁱⁱ-O6ⁱⁱ...C5 54.80 (4)° and C5-O7...C2ⁱⁱ: 123.13 (5)° [symmetry code: (ii) 0.5-x, -y, z+0.5].

Crystal data

C₄H₂O₃
M_r = 98.06
Orthorhombic, *P*2₁2₁2₁
a = 7.0317 (1) Å
b = 11.0201 (2) Å
c = 5.3323 (1) Å
V = 413.200 (12) Å³
Z = 4
*D*_x = 1.576 Mg m⁻³

Mo *K*α radiation
Cell parameters from 4665 reflections
θ = 1.0–27.5°
μ = 0.14 mm⁻¹
T = 130 (2) K
Needle, colourless
0.50 × 0.24 × 0.24 mm

Data collection

Nonius KappaCCD diffractometer
φ and *ω* scans at three crystal-detector distances
21016 measured reflections
1564 independent reflections
1351 reflections with *I* > 2σ(*I*)

*R*_{int} = 0.049
*θ*_{max} = 41.6°
h = 0 → 13
k = 0 → 20
l = 0 → 9

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.027
wR(*F*²) = 0.070
S = 0.93
1564 reflections
73 parameters
All H-atom parameters refined

w = 1/σ²(*F*_o²)
(Δ/σ)_{max} = 0.002
Δρ_{max} = 0.30 e Å⁻³
Δρ_{min} = -0.19 e Å⁻³
Extinction correction: *SHELXL97*
Extinction coefficient: 0.050 (13)

Table 1

Selected geometric parameters (Å, °).

O1–C5	1.3869 (8)	C3–H8	0.917 (16)
O1–C2	1.3888 (8)	C4–C5	1.4814 (9)
C2–O6	1.1978 (8)	C4–H9	0.900 (19)
C2–C3	1.4764 (9)	C5–O7	1.1975 (8)
C3–C4	1.3322 (9)		
C5–O1–C2	107.56 (5)	C3–C4–C5	107.83 (5)
O6–C2–O1	121.28 (6)	C3–C4–H9	127.4 (12)
O6–C2–C3	130.30 (6)	C5–C4–H9	124.7 (12)
O1–C2–C3	108.42 (5)	O7–C5–O1	120.87 (7)
C4–C3–C2	107.89 (6)	O7–C5–C4	130.85 (7)
C4–C3–H8	127.3 (9)	O1–C5–C4	108.27 (5)
C2–C3–H8	124.0 (9)		

The intensity data were collected in 4 sets. Set 1 was performed as a combination of 0.5 degrees *φ* and *ω* scans with an exposure time of 3 s/frame. Sets 2–4 were 1 degree *φ* and *ω* scans with exposure times of 15, 55, and 120 s/frame, respectively. The detector distances were

35 mm for sets 1 and 2, 45 mm for set 3, and 50 mm for set 4. The absolute structure could not be determined reliably. Friedel pairs were therefore merged in the refinement.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: HKL2000 (Otwinowski & Minor, 1997); data reduction: *EvalCCD* (Duisenberg, 1998) for obtaining the X-ray intensities and *SORTAV* (Blessing, 1997) for scaling and merging of the X-ray intensities; program(s) used to solve structure: coordinates taken from the literature (Marsh, 1962*et al.*); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2001); software used to prepare material for publication: manual editing of *SHELXL97* output.

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