4-(2,5-Dioxo-2,5-dihydro-1H-pyrrol-1-yl)benzoic acid: X-ray and DFT-calculated structure

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In the title compound, $C_{11}H_7NO_4$, there is a dihedral angle of 45.80 (7)° between the planes of the benzene and maleimide rings. The presence of O—H$\cdots$O hydrogen bonding and weak C—H$\cdots$O interactions allows the formation of $R_3^3(19)$ edge-connected rings parallel to the (010) plane. Structural, spectroscopic and theoretical studies were carried out. Density functional theory (DFT) optimized structures at the B3LYP/6–311 G(d,p) and 6–31++G(d,p) levels are compared with the experimentally determined molecular structure in the solid state. Additional IR and UV theoretical studies allowed the presence of functional groups and the transition bands of the system to be identified.

Comment

The structure determination of 4-carboxyphenylmaleimide [systematic name: 4-(2,5-dioxo-2,5-dihydro-1H-pyrrol-1-yl)-benzoic acid], (I), is part of a series of structure determinations on phenylmaleimide derivatives (Moreno-Fuquen et al., 2003, 2006, 2008). There is considerable interest in the development of N-substituted maleimides as photoionizers for free radical polymerization, where the maleimide can produce the initiating radical species (Andersson et al., 1996; Teerenstra et al., 2000). Miller et al. (2001) synthesized a good number of N-arylmaleimides to evaluate their utility as free radical photoinitiators. As a result of this evaluation they found that the photochemical properties of N-arylmaleimide systems depend on the values of the dihedral angle between the benzene and imidic rings (Miller et al., 2000). Even with good crystallographic information on N-phenylmaleimide derivatives reported in the literature, the search for new related systems remains important for the analysis of polymerization processes in which they are involved. Calculations by density functional theory (DFT) on N-phenylmaleimide compounds, modelling the torsional deformation between the

rings and showing the energy barrier to planarity, are also reported (Miller et al., 1999). The present work describes structural, spectroscopic and theoretical studies on 4-carboxyphenylmaleimide.

(I)
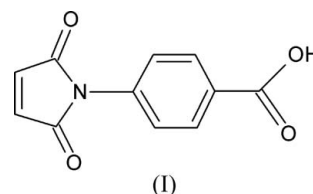
The title compound shows a dihedral angle of 45.80 (7)° between the mean planes of the benzene and maleimide rings (see Fig. 1). This structural behaviour is repeated in similar systems, e.g. p-nitrophenylmaleimide [42.98 (5)°; Moreno-Fuquen et al., 2003], p-chlorophenylmaleimide [47.54 (9)°; Moreno-Fuquen et al., 2008] and 2-p-toluidino-N-p-tolyl-maleimide [42.6 (1)°; Watson et al., 2004], where the interplanar angles of these systems are close to that observed in (I), and their bond distances and angles are very similar. O—H$\cdots$O hydrogen bonds of moderate character (Emsley, 1984) and weak intermolecular C—H$\cdots$O interactions are observed in (I) (see Table 1; Nardelli, 1995). Although C—H$\cdots$O interactions appear to be very weak, these contacts may have a determining effect on the formation of different packing motifs (Desiraju et al., 1993), they can play significant roles in molecular conformation (Saenger & Steiner, 1998) and they are essential in molecular recognition processes (Shimon et al., 1990). With regard to the structure (I), atom O2 acts as a hydrogen-bond donor to carboxyl atom O1 in the molecule at $(x − \frac{1}{2}, −y + \frac{1}{2}, −z + 2)$. At the same time, atom C3 acts as a donor to atom O3 in the molecule at $(x − 1, y, z)$. The molecules of (I) form an infinite chain of edge-connected $R_3^3(19)$ rings (Etter, 1990) running parallel to the (010) plane (see Fig. 2). Neighbouring chains interact through very weak C—H$\cdots$O contacts in which atom C6 acts as a hydrogen-bond donor to carbonyl atom O4 in the molecule at $(x + \frac{1}{2}, −y + \frac{1}{2}, −z + 1)$, forming $R_2^2(12)$ rings, completing the two-dimensional array.

The presence of substituents in the benzene ring forces the system to produce several conformations between the benzene and maleimide rings (Miller et al., 2000). The position of the substituent on the benzene ring, the volume of the substituent and its intra- and intermolecular interactions are
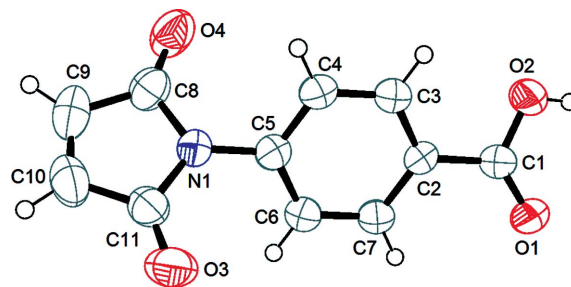

Figure 1
An ORTEP-3 (Farrugia, 1997) plot of (I), showing the atom-labelling scheme. Ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of arbitrary radius.
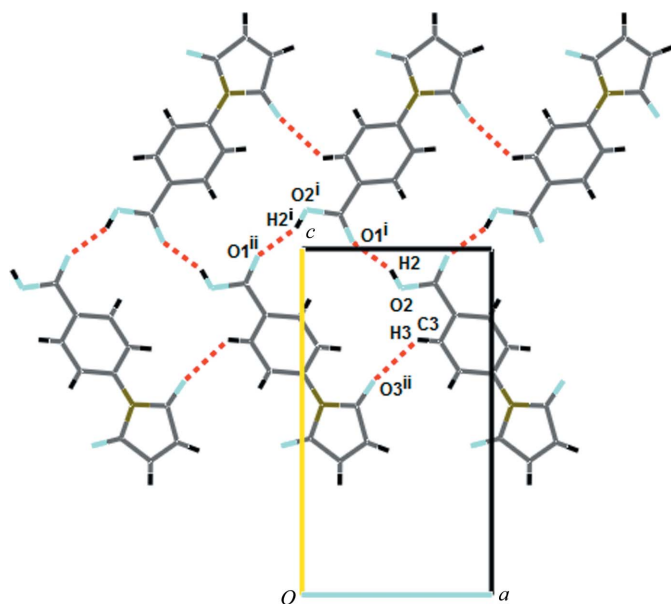
Figure 2
The packing in the unit cell of (I) parallel to the (010) plane, showing the $R_3^3(19)$ edge-fused rings. Dashed lines denote the intermolecular O—H···O hydrogen bonds and the intermolecular C—H···O contacts. [Symmetry codes: (i) $x - \frac{1}{2}, -y + \frac{1}{2}, -z + 2$; (ii) $x - 1, y, z$.]

essential factors when analysing the structural behaviour of these systems. The presence of the carboxyl group in the *para* position allows the analysis of the influence of the substituent on the inter-ring torsion angle along N1—C5. To gain a better understanding of the properties of compound (I), we further explored the stability of this compound in the gaseous state, calculating the harmonic frequencies and comparing the results with those observed in the fundamental vibrational frequencies. Additionally, theoretical studies of the UV spectra were undertaken. Previous studies on similar systems (Miller *et al.*, 1999) showed that calculations at the DFT-B3LYP level were consistently close to experimental values.

Calculations by density functional theory DFT-B3LYP, with basis sets 6–31++G(d,p) and 6–311 G(d,p), of bond lengths and angles were performed. These values were compared with experimental values of the title system (see Table 2). From these results we can conclude that basis set 6–311 G(d,p) is better suited in its approach to the experimental data.

Calculations using basis set 6–311(d,p) modelled torsional deformations between the aryl and maleimide rings, showing different conformations with different energy barriers. Calculations on isolated 4-carboxyphenylmaleimide showed a minimum rotational energy for a rotamer with an inter-ring dihedral angle of 35.11°. This result shows a significant correlation with the experimental value of 45.80 (7)°.

The vibrational analysis of the title compound shows the expected IR bands attributed to the constituents of the complex. The spectrum shows several well defined bands: an intense and broad band in the IR spectrum at 1720 cm^{-1} can be assigned to the axial deformation of carbonyl C=O which is also observed in the simulated spectrum at 1793 cm^{-1}. The C=O band of the carboxyl group is masked within the same
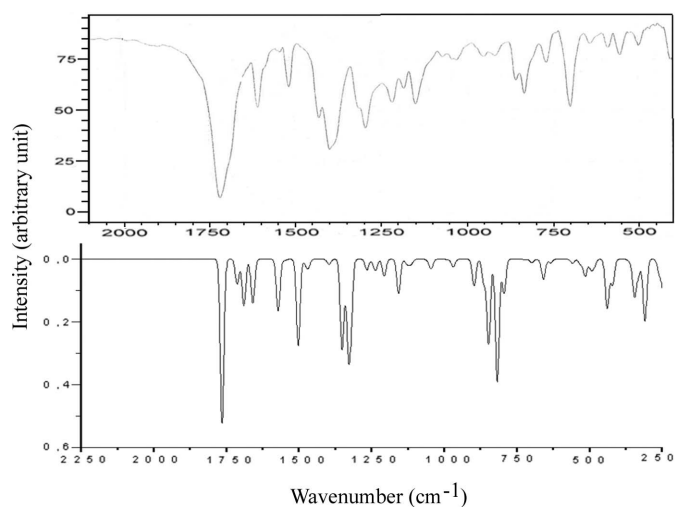

Figure 3
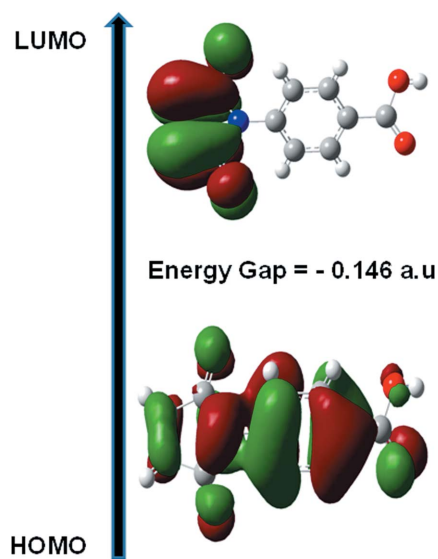Comparison of observed and calculated IR spectra of (I).

Figure 4
Electron distribution of (*a*) the HOMO and (*b*) the LUMO+1 energy levels for (I).

carbonyl C=O band. These and other observed and calculated bands with their assignments are shown in Table 3. The comparison of the observed fundamental frequencies of (I) and the IR spectrum simulated by DFT calculation (B3LYP) showed a good agreement between frequencies (see Fig. 3).

Compound (I) shows an absorption band in the UV region at α = 246.5 nm in methanol. The most intense bands obtained near this region in B3LYP/6–311 G(d,p) calculations for an isolated molecule are around λ = 243 nm [oscillator strength = 0.413 (exp) and 0.330 (calc)]. These bands are attributed to an intramolecular charge transfer (ICT) from the highest occupied molecular orbital (HOMO) to an orbital close to the lowest unoccupied molecular orbital (LUMO+1). The calculations reveal that these are π orbitals, primarily localized in the plane extending from the benzene to the maleimide ring; these orbitals are shown in Fig. 4.

Experimental

Starting materials and reagents were purchased from Aldrich and used as received. The title compound was prepared by mixing equimolar quantities of 4-aminobenzoic acid (1.00 g, 7.3 mmol) and maleic anhydride in N,N-dimethylformamide (20 ml) under a nitrogen atmosphere at ambient temperature for 1 h. Cyclodehydration of the maleamic acid to maleimide was carried out by treating the acid with fused sodium acetate and acetic anhydride for 2 h at 343 K. A yellow–orange precipitate was obtained by adding water to the solution. Crystals were dissolved in methanol and left to evaporate, giving pale-yellow prismatic crystals [m.p. 491 (1) K, 60% yield].

Crystal data

$C_{11}H_7NO_4$	$V = 970.53\ (11)\ \text{Å}^3$
$M_r = 217.18$	$Z = 4$
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation
$a = 7.3326\ (5)\ \text{Å}$	$\mu = 0.12\ \text{mm}^{-1}$
$b = 9.8832\ (5)\ \text{Å}$	$T = 294\ \text{K}$
$c = 13.3922\ (11)\ \text{Å}$	$0.18 \times 0.13 \times 0.10\ \text{mm}$

Data collection

Bruker–Nonius KappaCCD diffractometer	1278 independent reflections
	895 reflections with $I > 2\sigma(I)$
6051 measured reflections	$R_{int} = 0.063$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.049$	145 parameters
$wR(F^2) = 0.128$	H-atom parameters constrained
$S = 1.13$	$\Delta\rho_{max} = 0.19\ \text{e Å}^{-3}$
1278 reflections	$\Delta\rho_{min} = -0.21\ \text{e Å}^{-3}$

Table 1
Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{O2}-\text{H2}\cdots\text{O1}^{i}$	0.82	1.90	2.672 (3)	156
$\text{C3}-\text{H3}\cdots\text{O3}^{ii}$	0.93	2.39	3.103 (4)	134
$\text{C6}-\text{H6}\cdots\text{O4}^{iii}$	0.93	2.68	3.392 (4)	134

Symmetry codes: (i) $x - \frac{1}{2}, -y + \frac{1}{2}, -z + 2$; (ii) $x - 1, y, z$; (iii) $x + \frac{1}{2}, -y + \frac{1}{2}, -z + 1$.

All H atoms were located from difference maps, then their positions were geometrically optimized and refined using a riding model, with C—H = 0.93 Å and O—H = 0.82 Å, and with $U_{iso}(\text{H}) = 1.2U_{eq}(\text{C})$ or $1.5U_{eq}(\text{O})$. Friedel pairs were merged in the data set used for the final structure refinement. The DFT quantum-chemical calculations were performed at the B3LYP/6–311 G(d,p) level (Becke, 1993; Lee *et al.*, 1988). The performance of 6–31++G(d,p) and 6–311 G(d,p) basis functions (Bauschlicher & Partridge, 1995) was checked in these calculations as implemented in *GAUSSIAN03* (Frisch *et al.*, 2004). DFT structure optimization of (I) was performed, starting from the X-ray geometry. The harmonic vibrational analysis at the same level of theory confirmed the stability of the ground state as denoted by the absence of imaginary frequencies.

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and

Table 2
Comparison of selected geometric data for (I) (Å, °) from calculated (DFT) and X-ray data.

	X-ray	B3LYP/6–31++G(d,p)	B3LYP/6–311G(d,p)
O1—C1	1.212 (4)	1.2168	1.2080
O2—C1	1.327 (4)	1.3593	1.3565
C5—N1	1.424 (4)	1.4251	1.4243
C8—O4	1.202 (4)	1.2128	1.2038
C11—O3	1.210 (5)	1.2127	1.2036
C1—C2	1.480 (5)	1.4856	1.4854
O4—C8—N1	124.9 (3)	126.32	126.58
O3—C11—N1	124.8 (3)	126.31	126.57
C11—N1—C5	125.2 (3)	125.31	125.26
N1—C5—C4	119.6 (3)	119.83	119.95
C2—C1—O2	112.6 (3)	113.19	112.90
C2—C1—O1	125.3 (3)	124.97	124.99

Table 3
Comparison of the observed and calculated vibrational frequencies in cm^{-1} for (I).

Assignment	Observed	Calculated
C—H angular deformation out of the aromatic plane	767	717
	831	849
	855	873
C—H scissor deformation at C=C of the maleimide plane	1027	1076
Vibrational axial deformation of C—O of the carboxyl group	1146	1109
Axial deformation of C—N at the maleimidic skeleton	1180	1125
C—H angular deformation in the aromatic plane	1293	1192
	1214	1218
	1312	1226
Axial deformation of C—N between maleimide and benzene rings	1398	1386
Axial deformation of carbonyl C=O	1720	1793

Mercury (Macrae *et al.*, 2006); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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