

## Phthalimide at 120 K: perforated molecular ribbons containing three different ring motifs

Choudhury M. Zakaria,<sup>a†</sup> John N. Low<sup>b</sup> and Christopher Glidewell<sup>a\*</sup>

<sup>a</sup>School of Chemistry, University of St Andrews, St Andrews, Fife KY16 9ST, Scotland, and <sup>b</sup>Department of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen AB24 3UE, Scotland  
Correspondence e-mail: cg@st-andrews.ac.uk

Received 24 October 2001

Accepted 26 October 2001

Online 14 December 2001

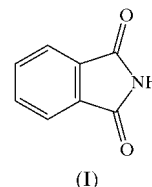
Molecules of phthalimide [*1H*-isoindole-1,3(*2H*)-dione], C<sub>8</sub>H<sub>5</sub>NO<sub>2</sub>, are linked by N—H···O hydrogen bonds [H···O 2.02 Å, N···O 2.8781 (16) Å and N—H···O 167°] and by C—H···O hydrogen bonds [H···O 2.54 and 2.56 Å, C···O 3.3874 (18) and 3.4628 (19) Å, and C—H···O 149 and 159°] into molecular ribbons, which are pierced by three different ring motifs; there are two centrosymmetric  $R_2^2(8)$  rings, each containing a single hydrogen bond, N—H···O in one case and C—H···O in the other, and  $R_2^2(9)$  rings containing all three hydrogen bonds.

### Comment

The structure of phthalimide [*1H*-isoindole-1,3(*2H*)-dione, (I)] was first reported (Matzat, 1972) using data collected from a large crystal of the mineral kladnoite; the structure was refined to  $R = 0.094$  using ambient-temperature data. This report defined a dimeric structure formed by paired N—H···O hydrogen bonds and alluded to some fairly short (less than 3.6 Å) intermolecular C···O distances; however, since at the time of publication (*i.e.* 1972) the notion of C—H···O hydrogen bonds was effectively under anathema (Desiraju & Steiner, 1999), no molecular aggregation beyond dimer formation was discussed. In a later investigation (Ng, 1992), the structure was refined to  $R = 0.038$ , also from ambient-temperature data, but this report made no mention of C—H···O hydrogen bonds.

Following our investigation of intermolecular aggregation *via* hydrogen bonding and  $\pi$ – $\pi$ -stacking interactions in *N,N'*-dithiodiphthalimide (Skakle *et al.*, 2001), we have now re-investigated phthalimide itself at 120 (2) K and have re-refined the structure using a data set rather larger than that employed by Ng (1992), where refinement on  $F$  with 770 reflections labelled observed gave  $R = 0.038$ ,  $\Delta/\sigma = 0.01$  and  $S = 0.54$  for

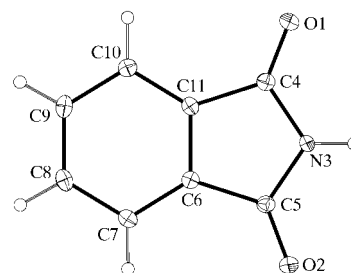
120 variables ( $n/p = 6.4$ ), including isotropic refinement of all H-atom parameters; the present refinement uses 1456 reflections giving an  $n/p$  ratio of 14.4. The intramolecular bonded distances found here are slightly more precise than those reported earlier (Ng, 1992), but show no significant variations from them, and hence will not be discussed further. In addition to the dimeric units generated by the hard hydrogen bonds, as described earlier (Matzat, 1972; Ng, 1992), the structure also contains two significant C—H···O hydrogen bonds which link the dimeric units into perforated molecular ribbons of some complexity.



There are three hydrogen bonds, one of the N—H···O type and two of the C—H···O type (Table 1), each of which alone generates a specific motif. The N—H···O hydrogen bond, where N3 at ( $x, y, z$ ) (Fig. 1) acts as donor to O2 at ( $1 - x, 2 - y, -z$ ), generates a centrosymmetric  $R_2^2(8)$  ring centred at ( $\frac{1}{2}, 1, 0$ ); C7 at ( $x, y, z$ ) similarly acts as hydrogen-bond donor to O2 at ( $-x, 1 - y, -z$ ), generating a second  $R_2^2(8)$  ring centred at ( $0, \frac{1}{2}, 0$ ). The combination and propagation of these two motifs thus generates a chain of fused rings running parallel to the [110] direction, in which the rings formed by the hard hydrogen bonds are centred at ( $n - \frac{1}{2}, n, 0$ ) ( $n$  is zero or an integer) and those formed by the soft hydrogen bonds are centred at ( $n, n + \frac{1}{2}, 0$ ) (Fig. 2). Finally C8 at ( $x, y, z$ ) acts as hydrogen-bond donor to O1 at ( $-1 + x, -1 + y, z$ ), generating by translation a  $C(7)$  chain which serves to reinforce the chain of fused rings by the addition of peripheral  $R_2^3(9)$  rings (Fig. 2), so generating a broad ribbon pierced by three types of ring.

It is striking how closely the  $R_2^3(9)$  ring observed in (I) resembles that observed in the structure of 1,4-benzoquinone, where this motif links molecular chains built from  $R_2^2(8)$  rings into a sheet (Trotter, 1960; Thalladi *et al.*, 1998); in (I), this motif links  $R_2^2(8)$  dimers into a ribbon.

There are two ribbons passing through each unit cell in (I), one in the domain  $-0.24 < z < 0.24$  (Fig. 2), and the other in the domain  $0.26 < z < 0.74$ . The only direction-specific interaction between adjacent ribbons is a very weak C—H···O contact having a C—H···O angle of 129° (Table 1), probably

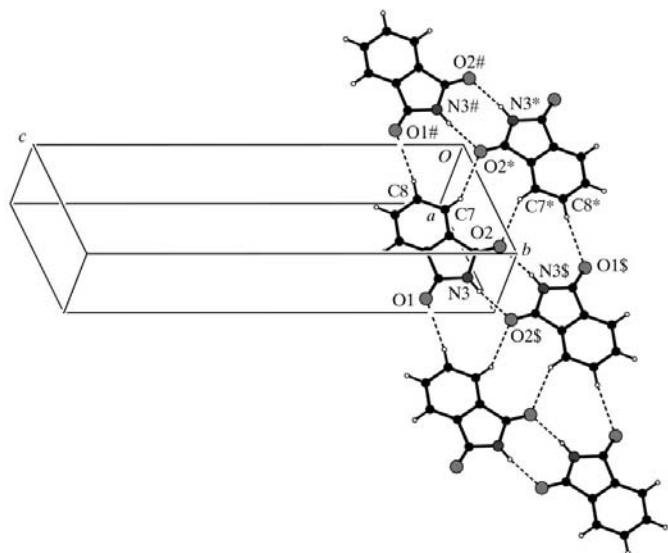


**Figure 1**

The molecule of (I) at 120 (2) K, showing the atom-labelling scheme and displacement ellipsoids drawn at the 30% probability level.

<sup>†</sup> On leave from the Department of Chemistry, University of Rajshahi, Rajshahi, Bangladesh.

too small to be structurally significant. There are no aromatic  $\pi$ - $\pi$ -stacking interactions in the crystal structure of (I). It is interesting to note that the three C—H...O interactions in Table 1 correspond to three of the four shortest intermolecular C...O contacts noted by Matzat (1972), although their



**Figure 2**  
Part of the crystal structure of (I) showing the formation of a perforated molecular ribbon parallel to [110]. The atoms marked with an asterisk (\*), hash (#) or dollar sign (\$) are at the symmetry positions  $(-x, 1 - y, -z)$ ,  $(-1 + x, -1 + y, z)$  and  $(1 - x, 2 - y, -z)$ , respectively.

significance was obscured, both by the historical context, and by the emphasis on C...O distances at the expense of H...O distances and C—H...O angles. The fourth of Matzat's short C...O contacts (Matzat, 1972) is between C9 in the molecule at  $(x, y, z)$  and O1 at  $(\frac{3}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z)$ , but this has a C...O distance of 3.3722 (19) Å associated with a very long H...O distance (2.82 Å) and a narrow C—H...O angle (118°).

## Experimental

Crystals of (I) were obtained following an attempt to crystallize *N,N'*-dithiodipthalimide from hot pyridine.

### Crystal data

$C_8H_5NO_2$   
 $M_r = 147.13$   
Monoclinic,  $P2_1/n$   
 $a = 3.7303$  (2) Å  
 $b = 7.6638$  (4) Å  
 $c = 22.6435$  (13) Å  
 $\beta = 90.369$  (2)°  
 $V = 647.33$  (6) Å<sup>3</sup>  
 $Z = 4$

$D_x = 1.510$  Mg m<sup>-3</sup>  
Mo  $K\alpha$  radiation  
Cell parameters from 1456 reflections  
 $\theta = 3.2$ – $27.5^\circ$   
 $\mu = 0.11$  mm<sup>-1</sup>  
 $T = 150$  (2) K  
Prism, colourless  
 $0.15 \times 0.05 \times 0.05$  mm

### Data collection

Nonius KappaCCD diffractometer  
 $\varphi$  scans, and  $\omega$  scans with  $\kappa$  offsets  
Absorption correction: multi-scan (DENZO-SMN; Otwinowski & Minor, 1997)  
 $T_{\min} = 0.984$ ,  $T_{\max} = 0.995$   
4750 measured reflections

1456 independent reflections  
1061 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.054$   
 $\theta_{\text{max}} = 27.5^\circ$   
 $h = -4 \rightarrow 4$   
 $k = -9 \rightarrow 8$   
 $l = -29 \rightarrow 25$

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.043$   
 $wR(F^2) = 0.103$   
 $S = 1.02$   
1456 reflections  
101 parameters  
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0485P)^2 + 0.0173P]$   
where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 0.22$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.22$  e Å<sup>-3</sup>  
Extinction correction: SHELXL97  
Extinction coefficient: 0.037 (7)

**Table 1**

Hydrogen-bond parameters and short intermolecular contacts (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$N3-H3 \cdots O2^i$	0.88	2.02	2.8781 (16)	167
$C7-H7 \cdots O2^{ii}$	0.95	2.54	3.3874 (18)	149
$C8-H8 \cdots O1^{iii}$	0.95	2.56	3.4628 (19)	159
$C10-H10 \cdots O1^{iv}$	0.95	2.55	3.2303 (18)	129

Symmetry codes: (i)  $1 - x, 2 - y, -z$ ; (ii)  $-x, 1 - y, -z$ ; (iii)  $x - 1, y - 1, z$ ; (iv)  $\frac{3}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$ .

Compound (I) crystallized in the monoclinic system; space group  $P2_1/n$  was uniquely assigned from the systematic absences. H atoms were treated as riding atoms with distances C—H = 0.95 Å and N—H = 0.88 Å.

Data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2001); software used to prepare material for publication: *SHELXL97* and *PRPKAPPA* (Ferguson, 1999).

X-ray data were collected at the EPSRC X-ray Crystallographic Service, University of Southampton. CMZ thanks the Association of Commonwealth Universities for the award of a Commonwealth Fellowship 2000–2001.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1520). Services for accessing these data are described at the back of the journal.

## References

- Desiraju, G. R. & Steiner, T. (1999). *The Weak Hydrogen Bond*, pp. 32–38. Oxford: OUP/IUCr.
- Ferguson, G. (1999). *PRPKAPPA*. University of Guelph, Canada.
- Matzat, E. (1972). *Acta Cryst.* **B28**, 415–418.
- Ng, S. W. (1992). *Acta Cryst.* **C48**, 1694–1695.
- Nonius (1997). *KappaCCD Server Software*. Windows 3.11 Version. Nonius BV, Delft, The Netherlands.
- Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter & R. M. Sweet, pp. 307–326. London: Academic Press.
- Sheldrick, G. M. (1997). *SHELXL97* and *SHELXS97*. University of Göttingen, Germany.
- Skakle, J. M. S., Wardell, J. L., Low, J. N. & Glidewell, C. (2001). *Acta Cryst.* **C57**, 742–746.
- Spek, A. L. (2001). *PLATON*. October 2001 Version. University of Utrecht, The Netherlands.
- Thalladi, V. R., Weiss, H.-C., Bläser, D., Boese, R., Nangia, A. & Desiraju, G. R. (1998). *J. Am. Chem. Soc.* **120**, 8702–8710.
- Trotter, J. (1960). *Acta Cryst.* **13**, 86–95.