

Data collection: *SMART* (Siemens, 1996). Cell refinement: *SMART*. Data reduction: *SAINT* (Siemens, 1996). Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997a). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997b). Molecular graphics: *SCHAKAL88* (Keller, 1988) and *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 1990).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1312). Services for accessing these data are described at the back of the journal.

References

- Görbitz, C. H. & Dalhus, B. (1996). *Acta Cryst.* **C52**, 1756–1759.
 Harding, M. M. & Long, H. A. (1968). *Acta Cryst.* **B24**, 1096–1102.
 Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138, Oak Ridge National Laboratory, Tennessee, USA.
 Keller, E. (1988). *SCHAKAL88. Fortran Program for the Graphic Representation of Molecular and Crystallographic Models*. University of Freiburg, Germany.
 Kerr, K. A. & Ashmore, J. P. (1973). *Acta Cryst.* **B29**, 2124–2127.
 Kerr, K. A., Ashmore, J. P. & Koetzle, T. (1975). *Acta Cryst.* **B31**, 2022–2026.
 Schomaker, V. & Trueblood, K. N. (1968). *Acta Cryst.* **B24**, 63–77.
 Sheldrick, G. M. (1997a). *SHELXS97. Program for the Solution of Crystal Structures*. University of Göttingen, Germany.
 Sheldrick, G. M. (1997b). *SHELXL97. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
 Siemens (1996). *SMART and SAINT. Area Detector Control and Integration Software*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
 Spek, A. L. (1990). *Acta Cryst.* **A46**, C-34.

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1:1 Adducts of 4-picoline with methylcatecholborane and phenylcatecholborane

WILLIAM CLEGG,^a ANDREW J. SCOTT,^a FÁBIO E. S. SOUZA^b AND TODD B. MARDER^c

^aDepartment of Chemistry, University of Newcastle upon Tyne, Newcastle upon Tyne NE1 7RU, England, ^bDepartment of Chemistry, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1, and ^cDepartment of Chemistry, University of Durham, Durham DH1 3LE, England. E-mail: w.clegg@ncl.ac.uk

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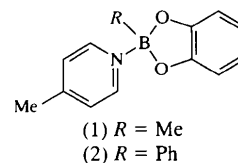
Abstract

In the title compounds, 2-methyl-2-(4-methylpyridine)-1,3,2-benzodioxaborole, C₁₃H₁₄BNO₂, and

2-(4-methylpyridine)-2-phenyl-1,3,2-benzodioxaborole, C₁₈H₁₆BNO₂, boron has a distorted tetrahedral coordination geometry, the two O—B—C angles being greater and all other angles at boron smaller than the ideal tetrahedral value. Both structures contain two crystallographically independent molecules, and all corresponding geometrical parameters in them are essentially the same, except for minor torsional variations. Bond lengths involving boron are similar to those of related adducts of phenylcatecholborane, and longer than those in the parent compound itself and related compounds with trigonal planar boron.

Comment

In conjunction with our recent work on coordination of phosphines and amines to diborane(4) compounds (Nguyen *et al.*, 1995; Clegg *et al.*, 1997), we have also investigated the formation of adducts between Lewis bases and organoboranes containing the catecholboronyl unit bound to alkyl and aryl groups. Because of their facile preparation (Wieber & Künzel, 1974), methyl- and phenylcatecholboranes were chosen as model substrates. NMR studies of these three-coordinate boron compounds have been reported by Goetz *et al.* (1981). Our findings show a similar Lewis acidity to that observed for the diborane(4) compound B₂(cat)₂ (cat = 1,2-O₂C₆H₄). Thus, no evidence for adduct formation was observed in reactions between the catecholboronyl derivatives and phosphines, even with the highly basic PMe₃, and only amines were capable of coordinating to the B atom. We report here the structures of the adducts 2-methyl-2-(4'-methylpyridine)-1,3,2-benzodioxaborole, (1), and 2-phenyl-2-(4'-methylpyridine)-1,3,2-benzodioxaborole, (2), formed between these organoboranes and 4-picoline. These adducts have been discussed previously (Wieber & Künzel, 1974), but only very limited data were reported for them.



Both crystal structures contain two independent molecules in the asymmetric unit (Figs. 1 and 2). In each case there are no significant differences between the two molecules other than unimportant variations in the orientations of substituents attached to boron as measured by torsion angles around B—C and B—N bonds. Corresponding molecular-geometry parameters for the two compounds are also essentially the same (Tables 1 and 2). There are no particularly short intermolecular contacts. The B atom in each case has distorted tetrahedral coordination; the catecholate chelating group gives an O—B—O angle which is smaller than the ideal tetrahedral angle, and the two

O—B—C angles are several degrees higher than 109.5° in each individual molecule, all other angles at boron being reduced from the ideal value.

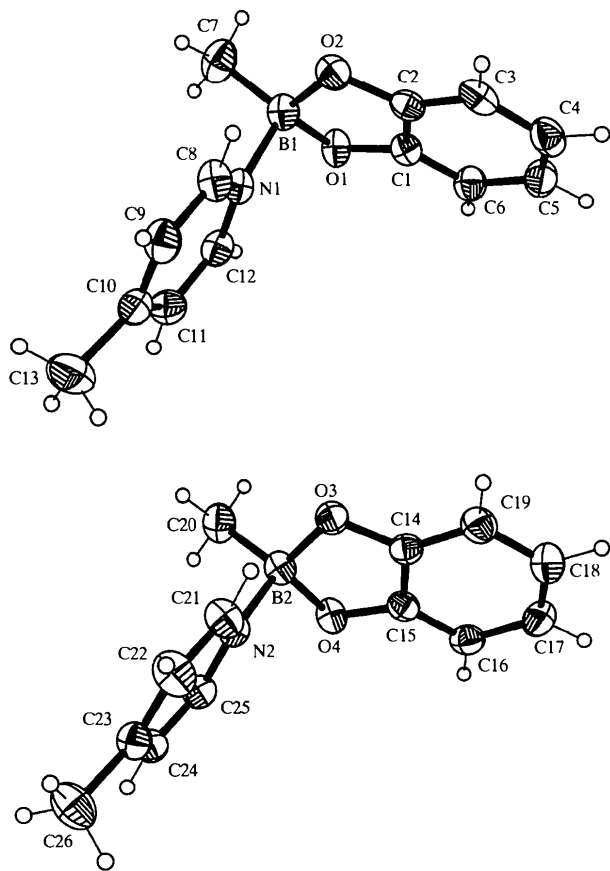


Fig. 1. The two independent molecules of (1) with atom labels and 50% probability ellipsoids for non-H atoms.

The crystal structure of the parent phenylcatecholborane has been reported by Zettler *et al.* (1974). It contains trigonal-planar boron, with B—O bonds of 1.394 and B—C of 1.537 Å. Essentially the same geometry is found in a series of compounds in which the catecholborane unit is bonded to alkenes, resulting from catalytic addition of B₂(cat)₂ to alkynes (Clegg *et al.*, 1996; Lesley *et al.*, 1996); in these, B—C ranges from 1.527 to 1.570 Å, and B—O from 1.380 to 1.393 Å. Marginally shorter bonds are found in an alkyne derivative (Schulz *et al.*, 1993): B—C 1.522, B—O 1.375 and 1.380 Å. Adduct formation with 4-picoline, raising the boron coordination number from 3 to 4 in the title compounds, markedly lengthens these bonds, with B—C 1.581–1.593 Å and B—O 1.464–1.487 Å. A similar effect is seen in two other reported adducts: a benzylamine adduct (Reetz *et al.*, 1992) has B—O 1.465 and 1.473 and B—C 1.623 Å (the phenyl group attached to boron in this case is part of a crown ether, and steric constraints probably lead to additional lengthening), and

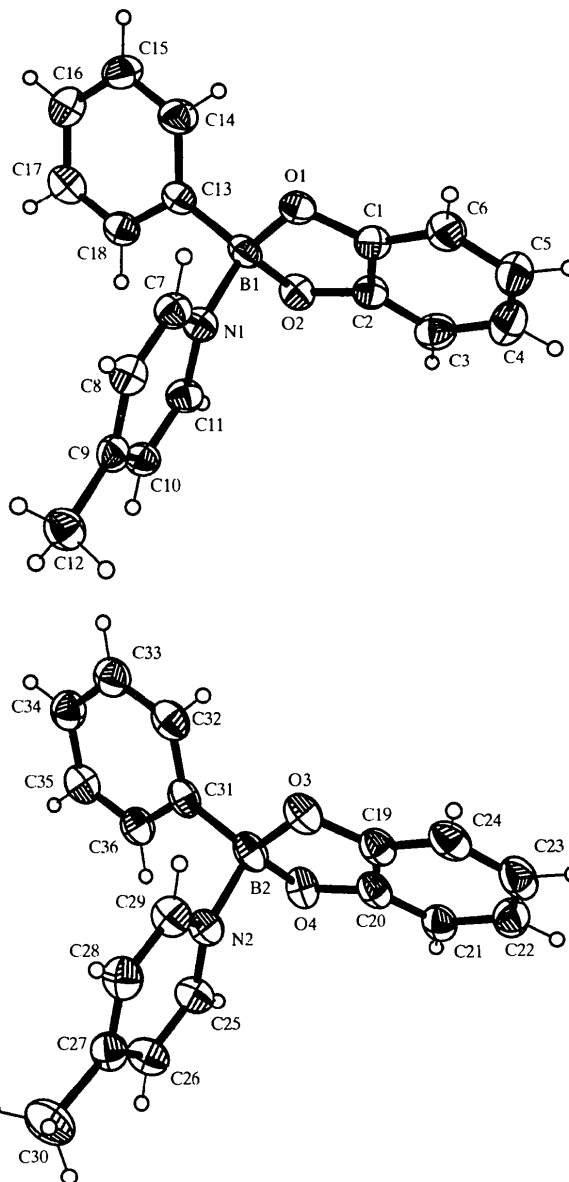


Fig. 2. The two independent molecules of (2) with atom labels and 50% probability ellipsoids for non-H atoms.

an adduct involving chelation by a carbonyl-O atom (Liu *et al.*, 1995) has B—O 1.465 and 1.475 and B—C 1.588 Å. Other geometrical parameters within the BO₂C₂ ring vary much less in these compounds, the major changes being at the B atom itself.

Experimental

The two adducts (1) and (2) were prepared by mixing the appropriate catecholborane (1 mmol) with 4-picoline (93 mg, 1 mmol) in CDCl₃ (1 ml). NMR spectroscopic characterization was carried out *in situ*. Crystals were obtained by slow evaporation of the solvent.

NMR data (CDCl₃ solution, p.p.m.) for (1): ¹H: δ 0.37 (s, 3H), 2.46 (s, 3H), 6.76 (m, 4H), 7.36 (d, *J* = 7 Hz, 2H), 8.57 (d, *J* = 7 Hz, 2H); ¹³C{¹H}: δ 21.3, 110.1, 119.5, 126.1, 142.9, 150.8, 153.6; ¹¹B{¹H}: δ 16.4, and for (2): ¹H: δ 2.36 (s, 3H), 6.81 (m, 4H), 7.17 (d, *J* = 6 Hz, 2H), 7.28 (m, 2H), 7.55 (m, 3H), 8.57 (d, *J* = 7 Hz, 2H); ¹³C{¹H}: δ 21.0, 110.0, 119.1, 125.3, 126.8, 127.3, 127.5, 131.3, 145.9, 151.3; ¹¹B{¹H}: δ 11.9.

Compound (1)*Crystal data*

C₁₃H₁₄BNO₂
M_r = 227.06
 Orthorhombic
Pbca
a = 16.3206 (7) Å
b = 15.6683 (7) Å
c = 19.3267 (9) Å
V = 4942.1 (4) Å³
Z = 16
D_x = 1.221 Mg m⁻³
D_m not measured

Data collection

Siemens SMART CCD
 diffractometer
 ω rotation with narrow
 frames
 Absorption correction: none
 28 685 measured reflections
 5939 independent reflections

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.047
wR(*F*²) = 0.118
S = 1.062
 5939 reflections
 312 parameters
 H-atom parameters
 constrained
w = 1/[σ²(*F*_o²) + (0.0472*P*)²
 + 1.8759*P*]
 where *P* = (*F*_o² + 2*F*_c²)/3

Table 1. Selected geometric parameters (Å, °) for (1)

B1—O1	1.4816 (18)	B2—O3	1.4804 (18)
B1—O2	1.4716 (19)	B2—O4	1.4865 (18)
B1—C7	1.587 (2)	B2—C20	1.588 (2)
B1—N1	1.660 (2)	B2—N2	1.6444 (19)
O1—C1	1.3668 (16)	O3—C14	1.3655 (16)
O2—C2	1.3637 (17)	O4—C15	1.3633 (16)
O2—B1—O1	105.88 (11)	O3—B2—O4	105.55 (11)
O2—B1—C7	115.83 (14)	O3—B2—C20	115.87 (13)
O1—B1—C7	116.38 (12)	O4—B2—C20	114.71 (12)
O2—B1—N1	104.95 (11)	O3—B2—N2	106.27 (10)
O1—B1—N1	105.98 (11)	O4—B2—N2	105.94 (11)
C7—B1—N1	106.82 (12)	C20—B2—N2	107.77 (11)
C1—O1—B1	104.98 (10)	C14—O3—B2	105.91 (10)
C2—O2—B1	105.30 (10)	C15—O4—B2	106.13 (10)
C7—B1—N1—C8	-89.16 (15)	C20—B2—N2—C21	-104.60 (15)
C7—B1—N1—C12	82.67 (15)	C20—B2—N2—C25	70.25 (16)

Compound (2)*Crystal data*

C₁₈H₁₆BNO₂
M_r = 289.13
 Triclinic
P1
a = 9.7290 (13) Å
b = 10.3311 (14) Å
c = 15.589 (2) Å
 α = 91.087 (3)°
 β = 106.477 (3)°
 γ = 94.123 (3)°
V = 1497.4 (3) Å³
Z = 4
D_x = 1.283 Mg m⁻³
D_m not measured

Data collection

Siemens SMART CCD
 diffractometer
 ω rotation with narrow
 frames
 Absorption correction: none
 9343 measured reflections
 6486 independent reflections

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.064
wR(*F*²) = 0.167
S = 0.872
 6486 reflections
 400 parameters
 H-atom parameters
 constrained
w = 1/[σ²(*F*_o²) + (0.0772*P*)²]
 where *P* = (*F*_o² + 2*F*_c²)/3
 (Δ/σ)_{max} < 0.001

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

B1—O1	1.481 (3)	B2—O3	1.478 (3)
B1—O2	1.464 (3)	B2—O4	1.477 (4)
B1—C13	1.593 (4)	B2—C31	1.581 (4)
B1—N1	1.651 (3)	B2—N2	1.654 (4)
O1—C1	1.366 (3)	O3—C19	1.367 (3)
O2—C2	1.384 (3)	O4—C20	1.371 (3)
O2—B1—O1	106.0 (2)	O4—B2—O3	105.8 (2)
O2—B1—C13	117.3 (2)	O4—B2—C31	116.2 (2)
O1—B1—C13	113.9 (2)	O3—B2—C31	116.2 (2)
O2—B1—N1	105.25 (19)	O4—B2—N2	106.3 (2)
O1—B1—N1	105.17 (19)	O3—B2—N2	104.91 (19)
C13—B1—N1	108.21 (19)	C31—B2—N2	106.4 (2)
C1—O1—B1	105.18 (19)	C19—O3—B2	105.6 (2)
C2—O2—B1	105.22 (19)	C20—O4—B2	105.58 (19)
C13—B1—N1—C11	92.6 (3)	C31—B2—N2—C25	95.7 (3)
C13—B1—N1—C7	-83.8 (3)	C31—B2—N2—C29	-77.6 (3)
N1—B1—C13—C14	126.7 (2)	N2—B2—C31—C32	114.4 (2)
N1—B1—C13—C18	-52.4 (3)	N2—B2—C31—C36	-64.1 (3)

H atoms were placed geometrically and refined with a riding model (including free rotation about C—C bonds), and with *U*_{iso} constrained to be 1.2 (1.5 for methyl groups) times *U*_{eq} of the carrier atom.

For both compounds, data collection: SMART (Siemens, 1995); cell refinement: local programs; data reduction:

Mo *K*α radiation
 λ = 0.71073 Å
 Cell parameters from 17 365
 reflections
 θ = 2.09–28.32°
 μ = 0.081 mm⁻¹
T = 160 (2) K
 Block
 0.70 × 0.42 × 0.32 mm
 Colourless

4863 reflections with
I > 2σ(*I*)
*R*_{int} = 0.029
 θ_{max} = 28.52°
h = -21 → 21
k = -20 → 19
l = -25 → 17
 Intensity decay: none

(Δ/σ)_{max} < 0.001
 Δρ_{max} = 0.23 e Å⁻³
 Δρ_{min} = -0.25 e Å⁻³
 Extinction correction:
 SHELXTL (Sheldrick,
 1994)
 Extinction coefficient:
 0.00133 (19)
 Scattering factors from
 International Tables for
 Crystallography (Vol. C)

Mo *K*α radiation
 λ = 0.71073 Å
 Cell parameters from 4970
 reflections
 θ = 1.97–27.81°
 μ = 0.082 mm⁻¹
T = 160 (2) K
 Block
 0.34 × 0.18 × 0.16 mm
 Colourless

3266 reflections with
I > 2σ(*I*)
*R*_{int} = 0.045
 θ_{max} = 28.43°
h = -10 → 12
k = -13 → 13
l = -20 → 16
 Intensity decay: none

Δρ_{max} = 0.31 e Å⁻³
 Δρ_{min} = -0.47 e Å⁻³
 Extinction correction:
 SHELXTL (Sheldrick,
 1994)
 Extinction coefficient:
 0.017 (2)
 Scattering factors from
 International Tables for
 Crystallography (Vol. C)

SAINT (Siemens, 1995); program(s) used to solve structures: *SHELXTL* (Sheldrick, 1994); program(s) used to refine structures: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and local programs.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1357). Services for accessing these data are described at the back of the journal.

References

- Clegg, W., Dai, C., Lawlor, F. J., Marder, T. B., Nguyen, P., Norman, N. C., Pickett, N. L., Power, W. P. & Scott, A. J. (1997). *J. Chem. Soc. Dalton Trans.* pp. 839–846.
- Clegg, W., Scott, A. J., Lesley, G., Marder, T. B. & Norman, N. C. (1996). *Acta Cryst. C52*, 1991–1995.
- Goetz, R., Nöth, H., Pommerening, H., Sedlak, D. & Wrackmeyer, B. (1981). *Chem. Ber.* **114**, 1884–1893.
- Lesley, G., Nguyen, P., Taylor, N. J., Marder, T. B., Scott, A. J., Clegg, W. & Norman, N. C. (1996). *Organometallics*, **15**, 5137–5154.
- Liu, X.-C., Hubbard, J. L. & Scouten, W. H. (1995). *J. Organomet. Chem.* **493**, 91–94.
- Nguyen, P., Dai, C., Taylor, N. J., Power, W. P., Marder, T. B., Pickett, N. L. & Norman, N. C. (1995). *Inorg. Chem.* **34**, 4290–4291.
- Reetz, M. T., Niemeyer, C. M., Hermes, M. & Goddard, R. (1992). *Angew. Chem. Int. Ed. Engl.* **31**, 1017–1019.
- Schulz, H., Gabbert, G., Pritzkow, H. & Siebert, W. (1993). *Chem. Ber.* **126**, 1593–1595.
- Sheldrick, G. M. (1994). *SHELXTL*. Version 5.0. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Siemens (1995). *SMART and SAINT. Area Detector Control and Integration Software*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Wieber, V. M. & Künzel, W. (1974). *Z. Anorg. Allg. Chem.* **403**, 107–115.
- Zettler, F., Hausen, H. D. & Hess, H. (1974). *Acta Cryst. B30*, 1876–1878.

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An *o*-xylyl cross-bridged 5,12-dioxocyclam

TIMOTHY J. HUBIN,^a NICKOLAY TYRYSHKIN,^a
NATHANIEL W. ALCOCK^b AND DARYLE H. BUSCH^a

^aDepartment of Chemistry, University of Kansas, Lawrence, KS 66045, USA, and ^bDepartment of Chemistry, University of Warwick, Coventry CV4 7AL, England. E-mail: msrbb@csv.warwick.ac.uk

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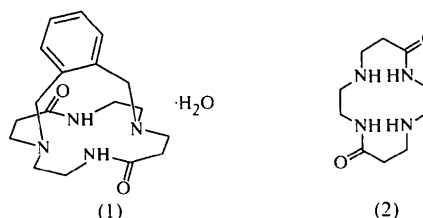
Abstract

The preparation and crystal structure of 1,10,13,18-tetraazatricyclo[8.6.6.0^{3,8}]docosa-3,5,7-triene-11,17-

dione monohydrate, C₁₈H₂₆N₄O₂·H₂O, are described. The molecule has a U-shaped conformation, with the N atoms well oriented for metal complexation.

Comment

The compound 1,10,13,19-tetraazatricyclo[8.6.6.0^{3,8}]docosa-3,5,7-triene-14,20-dione was synthesized during our study of the transition metal complexes of cross-bridged tetraazamacrocycles (Hubin *et al.*, 1998). Initially, our research centred on ethylene cross-bridged tetraazamacrocycles (Weisman *et al.*, 1996), but it has recently expanded to include macrocycles bridged by other groups and macrocycles containing amide groups. Recent work by others (Denat *et al.*, 1997) describes bis-amide macrocycles and corresponding reduced tetraamine species that have been cross-bridged by five-atom groups derived from *m*-xylene and 2,6-dimethylpyridine bis-electrophiles. Although no crystal structures of these molecules were reported, we considered that a four-atom bridged analogue would be more effective as a rigid ligand. 1,10,13,19-Tetraazatricyclo[8.6.6.0^{3,8}]docosa-3,5,7-triene-14,20-dione was synthesized as the monohydrate, (1), by the high-dilution reaction of α,α' -dibromo-*o*-xylene and *trans*-diprotected 5,12-dioxocyclam (Tomalia & Wilson, 1985) and its crystal structure determined.



No other cross-bridged 5,12-dioxocyclams have been structurally characterized to date, although we have recently determined the crystal structure of unbridged unsubstituted 1,4,8,11-tetraazacyclotetradecane-5,12-dione, (2), and its Ni^{II} complex (Hubin *et al.*, 1999). The structures of several bis-linked substituted 5,12-dioxocyclam ligands and their Ni^{II} complexes have been determined (Dumas *et al.*, 1995); these could also be regarded as bridged dioxocyclams.

In (1), the dioxocyclam has a U-shaped conformation, with the C=O groups pointing outwards and with the *o*-xylyl bridge spanning the base of the U (Fig. 1). Compared with the unbridged species, this molecule has a clearly defined cavity in which the nitrogen donors appear to be well oriented for complexation. The bridges in the linked dioxocyclams characterized by Dumas *et al.* (1995) are much longer than that in (1) and the macrocycles have extended rather than U-shaped conformations, similar to those in the unsubstituted complex.

The asymmetric unit of (1) contains one water molecule, which is hydrogen bonded to one of the C=O groups [O11...O001 2.852(2) Å] and to a symmetry-