

References

- Jacobson, E. N. (1993). *Catalytic Asymmetric Synthesis*, edited by I. Ojima, pp. 159–202. New York: VCH.
- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- Sheldrick, G. M. (1991). *SHELXTL-Plus*. Release 4.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Stoe & Cie (1991a). *DIF4. Diffractometer Control Program*. Version 7.08. Stoe & Cie, Darmstadt, Germany.
- Stoe & Cie (1991b). *REDU4. Data Reduction Program*. Version 7.08. Stoe & Cie, Darmstadt, Germany.
- Vankelecom, I. F., Tas, D., Parton, R. F., Vyver, V. V. & Jacobs, P. A. (1996). *Angew. Chem. Int. Ed. Engl.* **35**, 1346–1348.

Acta Cryst. (1997). **C53**, 1673–1675

Pseudosymmetry in 2,5-Dimethyl-1,4-benzenediol

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(Received 23 January 1996; accepted 13 May 1997)

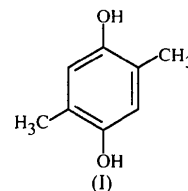
Abstract

The title compound, C₈H₁₀O₂, was prepared from diacetyl by a high temperature and pressure reaction. Pseudosymmetry in the structure results in diffraction symmetry enhancement for half the reflections and the possibility of twinning and stacking faults. The structure consists of two independent but pseudosymmetrically-related *P*₂₁/*c* substructures, each having centrosymmetric molecules on centres of inversion which are strongly hydrogen bonded to symmetry-related molecules to form layers perpendicular to *c**. The structure may be described as an occupancy modulation, ordering a disordered parent structure in *Pnma* symmetry to form, upon change of axes, the *P*₂₁/*c* structure reported. The hydroxyl H atoms have two site options corresponding to alternative hydrogen-bonding patterns and the methyl H atoms in one substructure are rotationally disordered.

Comment

High temperature and pressure reactions utilizing indigenous materials led to a study of the reaction chemistry

of diacetyl, resulting in the title compound, (I). A full quadrant of data was collected using a nearly orthorhombic *B*-centred cell [*a*' = 13.211 (4), *b*' = 4.518 (1), *c*' = 23.655 (8) Å and β' = 89.50 (3)°]. A check on the Laue symmetry led to the observation that the structure is monoclinic (*R*_{int} for 2/*m* symmetry is 0.027), but reflections with *l* even define a pseudo-orthorhombic parent structure (*R*_{int} for pseudosymmetry operations is 0.075). Reflections with *l* odd have an *R*_{int} for pseudosymmetry operations of 0.91 and are clearly monoclinic. A primitive cell was then chosen and reflections re-indexed, so as to describe the *P*₂₁/*c* structure as reported.



The *B*-centred cell is described as *a*' = 2*a* + *c*, *b*' = *b*, *c*' = *c* relative to the reported cell for *P*₂₁/*c* and the pseudo-orthorhombic reflections describe an apparent scattering density with a primitive unit cell *a*'' = *a*'/2, *b*'' = *b*', *c*'' = *c*'/2. Thus, *a*'' = *a* + *c*/2, *b*'' = *b* and *c*'' = *c*/2, and the structure can be thought of as an occupancy modulation [modulation vector *q* = (*a*''* + *c*''*)/2], ordering and distorting a disordered parent structure of *P*₂₁/*n*₂₁/*m*₂₁/*a* symmetry. Absence conditions *h*''*k*''0, *h*'' odd and 0,*k*''*l*'', *k*'' + *l*'' odd of *Pnma* become pseudo-absence conditions *h,k*,0, *h* odd and *h,k*,−2*h*, *h* + *k* odd for the re-indexed reflections and the pseudo-equivalence of intensities relates reflections *h,k,l* and −*h*−*l*,*k,l* with *l* even.

The symmetry operations associated with the *a*'' and *c*'' axes of *Pnma* must be destroyed in the ordered structure as otherwise the extra reflections will not be observed. However, pseudosymmetry operations can be used to describe the relationship between adjacent layers of the ordered structure. Using the cell *a,b,c* with 1 − *x*, 1 − *y*, 1 − *z* chosen as the asymmetric unit for the second molecule, the relationship between layers may be described as: layer at *x* = (2*N* + 1)/2 is obtained from layer at *x* = *N* by operation $\frac{1}{2} + x$, *y*, $\frac{1}{2} + x - z$; layer at *x* = *N* is obtained from layer at *x* = (2*N* − 1)/2 by operation $\frac{1}{2} + x$, *y*, *x* − *z*, any *N*. Both these operations correspond to *a*-glide operations of *Pnma* for the cell *a*'', *b*'', *c*''.

The odd and even layers belong to separate substructures of *P*₂₁/*c* symmetry. A pseudo-*a*-glide that transforms substructure 1 into substructure 2 also transforms substructure 2 into substructure 1 translated by *c*/2. This corresponds to a re-orientation of the total structure. It also allows the possibility of alternative origins for individual layers. The consequence of such stacking faults has negligible effect on *l* even reflections but can be modelled as a scaling and twinning of *l* odd reflections

similar to what is observed for Pb(SPh)₂ (Rae *et al.*, 1997).

The quality of fit for the *l* odd and *l* even reflections separately confirms the correctness of the structure solution, and the lack of stacking faults in the crystal studied.

And so the crystals of 2,5-dimethyl-1,4-benzenediol contain two independent centrosymmetric molecules (Fig. 1) with usual bond lengths and angles [International Tables for Crystallography (1992, Vol. C)]. The molecules are strongly hydrogen bonded, forming layers approximately parallel to the *bc* plane: H1''...O1''(1 - *x*, $\frac{1}{2}$ + *y*, $\frac{1}{2}$ - *z*) 1.81 (4), O1''...O1'' 2.710 (2) Å, O1''—H1''...O1'' 172 (3)°; H1...O1(-*x*, $\frac{1}{2}$ + *y*, $\frac{1}{2}$ - *z*) 1.84 (3), O1...O1 2.722 (1) Å, O1—H1...O1 171 (2)°. The hydrogen bonding can be described as two sets of C₂'(9)[R₄'(18)] (Bernstein, Davis, Shimon & Chang, 1995). Hydrogen bonding can also occur in the reverse directions along *b*, and a 0.85 (5):0.15 (5) ratio was obtained for both substructures after fixing the H atoms of the minor components along the appropriate O...O bond direction. The methyl H atoms on one ring bound to C4'' are rotationally disordered and have been modelled successfully using two linked sets (H41''...H43'' and H44''...H46'').

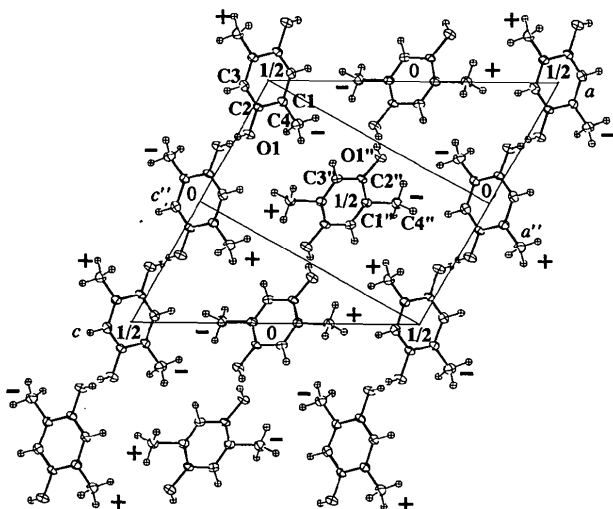


Fig. 1. View (ORTEP; Johnson, 1976) of the unit-cell contents of C₈H₁₀O₂ looking down the *b* axis. Only the unique labels of non-H atoms for the centrosymmetric molecules are shown for clarity. Displacement ellipsoids are shown at 30% probability levels and H atoms are drawn as small circles of arbitrary radii.

Experimental

Diacetyl was dissolved in water containing 2% (w/w) of zinc chloride and subjected to heat and pressure (493 K and 4137–8274 kPa) under a nitrogen atmosphere. After heating for 30 min and cooling for 2 h, the tarry mixture was dissolved in diethyl ether and partitioned in water. The product was isolated from the ether phase by distillation at 473 K and 26.6 kPa, and recrystallized from diethyl ether/dichloromethane.

Crystal data

C₈H₁₀O₂
M_r = 138.16
 Monoclinic
*P*2₁/*c*
a = 13.497 (5) Å
b = 4.5178 (11) Å
c = 13.211 (4) Å
 β = 118.80 (2)°
V = 705.9 (4) Å³
Z = 4
D_x = 1.300 Mg m⁻³
D_m not measured

Data collection

Siemens-Nicolet P3 four-circle diffractometer
 ω scans
 Absorption correction: none
 1325 measured reflections
 1232 independent reflections
 882 reflections with *I* > 2σ(*I*)

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.037
wR(*F*²) = 0.094
S = 0.975
 1232 reflections
 139 parameters
 H atoms not refined
w = 1/[σ²(*F_o*²) + (0.0558*P*)²]
 where *P* = (*F_o*² + 2*F_c*²)/3

Mo *K*α radiation

λ = 0.71069 Å
 Cell parameters from 20 reflections
 θ = 3.5–18.8°
 μ = 0.092 mm⁻¹
T = 133 (2) K
 Needle
 0.65 × 0.18 × 0.08 mm
 Colourless

*R*_{int} = 0.015
 θ_{max} = 25°
h = -16 → 13
k = 0 → 5
l = 0 → 15
 3 standard reflections
 every 97 reflections
 intensity decay: none

(Δ/σ)_{max} = -0.007
 $\Delta\rho_{\text{max}}$ = 0.141 e Å⁻³
 $\Delta\rho_{\text{min}}$ = -0.154 e Å⁻³
 Extinction correction: none
 Scattering factors from International Tables for Crystallography (Vol. C)

Table 1. Selected geometric parameters (Å, °)

O1—C2	1.390 (2)	O1''—C2''	1.391 (2)
C1—C2	1.391 (2)	C1''—C3'''	1.391 (2)
C1—C3'	1.391 (2)	C1''—C2''	1.394 (2)
C1—C4	1.502 (3)	C1''—C4''	1.502 (2)
C2—C3	1.385 (2)	C2''—C3''	1.380 (2)
C2—C1—C3'	117.2 (2)	C3'''—C1''—C4''	121.3 (2)
C2—C1—C4	121.2 (2)	C2''—C1''—C4''	121.8 (2)
C3'—C1—C4	121.6 (2)	C3''—C2''—O1''	121.02 (15)
C3—C2—O1	121.4 (2)	C3''—C2''—C1''	121.38 (15)
C3—C2—C1	121.24 (15)	O1''—C2''—C1''	117.59 (15)
O1—C2—C1	117.39 (15)	C2''—C3''—C1'''	121.7 (2)
C3'''—C1''—C2''	116.9 (2)		
C4—C1—C2—O1	-1.7 (2)	C4''—C1''—C2''—O1''	2.0 (2)

Symmetry codes: (i) -*x*, 1 - *y*, -*z*; (ii) 1 - *x*, 1 - *y*, 1 - *z*.

Data collection: *R3M Software* (Siemens, 1983). Cell refinement: *R3M Software*. Data reduction: *R3M Software*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEP* (Johnson, 1976). Software used to prepare material for publication: *CIFTAB* in *SHELXL93*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1089). Services for accessing these data are described at the back of the journal.

References

- Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
- Johnson, C. K. (1976). *ORTEP*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Rae, A. D., Craig, D. C., Dance, I. G., Scudder, M. L., Dean, P. A. W., Kmetz, M. A., Payne, N. C. & Vital, J. J. (1997). *Acta Cryst.* **B53**, 457–465.
- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
- Siemens (1983). *R3M Software*. Version 4.11. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Acta Cryst. (1997). **C53**, 1675–1676

3-Diazo-1-benzoyloxycarbonylpyrrolidin-2-one†

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(Received 7 April 1997; accepted 27 May 1997)

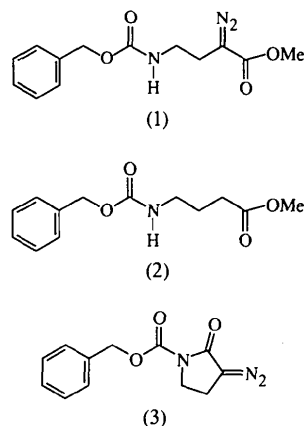
Abstract

The title compound, $C_{12}H_{11}N_3O_3$, was an unexpected reaction product. It is a rare example of a cyclic diazo amide and is a potential precursor for important azetidine derivatives *via* Wolff rearrangement.

Comment

In an attempt to prepare 2-diazo-4-benzoyloxycarbonylaminobutyric acid methyl ester, (1), from 4-benzoyloxycarbonylaminobutyric acid methyl ester, (2), according to a modified Danheiser diazo-transfer procedure (Danheiser, Miller, Brisbois & Park, 1990) described below, we isolated as a by-product 3-diazo-1-benzoyloxycarbonylpyrrolidin-2-one, (3), presumed to be the *in situ* product of cyclization of (1). A search of the Cambridge Structural Database (Allen, Kennard & Taylor, 1983) revealed that, of the 22 recorded crystal and molecular structures of diazocarbonyl compounds, five are cyclic molecules but none is a diazopyrrolidinone. As cyclic diazocarbonyl compounds are of considerable use as intermediates in modern organic synthesis (Ye & McKerver, 1994; Doyle, Ye & McKerver, 1997), especially in Wolff rearrangement, we have determined the crystal and molecular structure of (3) by X-ray diffraction.

† IUPAC name: benzyl 3-diazo-2-oxopyrrolidine-1-carboxylate.



The molecule (Fig. 1) consists of two broadly planar sections (saturated C atoms notwithstanding), with the phenyl ring inclined to the mean plane of the rest of the molecule at $44.69(3)^\circ$. There is evidence of π – π interactions between the phenyl ring and the diazo-carbonyl group of an adjacent molecule at $(\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z)$. The vertical distance between the phenyl plane and that of the diazo group is *ca* 3.2 Å and the two π systems show the expected offset arrangement.

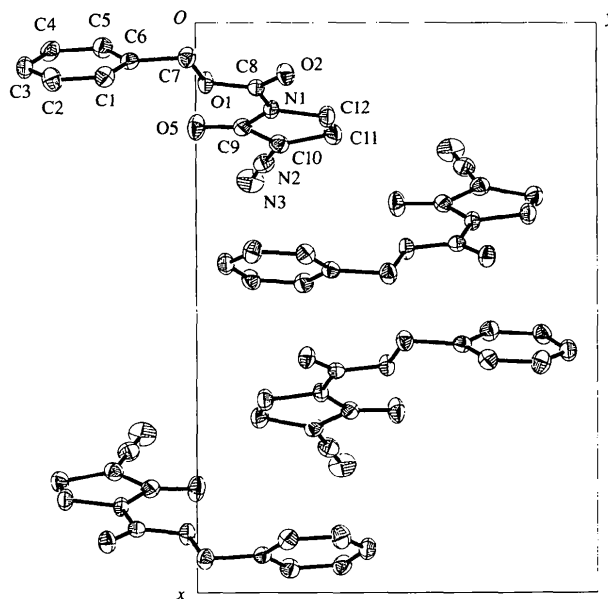


Fig. 1. A view of the unit cell projected along z , showing the disposition of the π systems of the phenyl and diazo groups in adjacent molecules. Atoms are represented by 50% probability displacement ellipsoids and H atoms have been omitted for clarity.

Experimental

A 100 ml two-necked round-bottomed flask equipped with a rubber septum and a 25 ml pressure-equalizing addition funnel containing an Ar atmosphere was charged with a solution of 1,1,1,3,3,3-hexamethyldisilazane (6.69 mmol, 1.079 g, 1.41 ml)