Guest *R* in region *B*

C111*R*···C61	3.87 (3)	C411*R*···C66^{i}	3.80 (3)
C411*R*···O65*B*	3.74 (4)		

Guest *S* in region *B*

O111*S*···O65*B*	3.55 (4)	O111*S*···C66^{i}	3.48 (3)
C111*S*···O65*B*	3.40 (4)	C111*S*···C65^{i}	3.84 (4)
C321*S*···C53	3.80 (3)	C111*S*···O65*B*^{i}	3.65 (4)
C421*S*···C63	3.83 (3)	C111*S*···C66^{i}	3.58 (3)
C421*S*···C53	3.83 (4)	C411*S*···C67^{i}	3.49 (3)
C421*S*···C62	3.82 (3)		

Guest–guest contact

C221*S*···O112*R*^{ii}	3.62 (4)

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

In the atom-numbering scheme for the guest molecule, a final digit of 1 indicates primary level region *B* and 2 secondary level *A*; the last character (*R* or *S*) indicates the enantiomer.

The positional parameters (except the primary hydroxyl groups) from an isomorphous complex (β-CD benzophenone; Le Bas, 1985) were used as a starting point. Successive full-matrix least-square refinements and difference Fourier syntheses were performed. The difference Fourier maps showed clearly two regions of electron density but the guest molecule could not be located precisely at this stage. The refined coordinates of the *S* enantiomer from the study of overmethylated CD with the same guest (Rysanek, Le Bas & Tsoucaris, 1992) were used. These coordinates were graphically plotted onto the difference Fourier map using *FRODO* (Jones, Bush, Pflugrath & Saper, 1978) and then refined. The next difference Fourier maps still showed some electron density in this region which could be interpreted as the *R* enantiomer. This enantiomer was built up from the *S*-enantiomer coordinates and plotted onto the difference Fourier map. The refinements were performed using *SHELX*76 (Sheldrick, 1976). For β-CD, all non-H atoms were refined anisotropically except the disordered O6 atoms. H atoms were introduced at calculated non-refined positions; H-atom positions were not introduced for the guest molecule, water molecules or hydroxyl groups of the host molecules. The coordinates of the *R*- and *S*-enantiomers of the guest molecule were refined isotropically in a block rigid group with an occupancy factor of 0.25 for each guest enantiomer in the two regions. The O atoms of water molecules were refined with common isotropic displacement parameters. The numerous atoms in disordered positions explain the relative high value of the *R* index; this is usual for cyclodextrin structures.

Data collection: *SDP-Plus* (B. A. Frenz & Associates, Inc., 1983). Cell refinement: *SDP-Plus*. Data reduction: *SDP-Plus*. Program(s) used to refine structure: *SHELX*76 (Sheldrick, 1976). Molecular graphics: *FRODO* (Jones *et al.*, 1978), *SYBYL* (Tripos Associates Inc., 1988), *ORTEP*II (Johnson, 1976).

We thank Dr de Rango for helpful discussions. This work was partially supported by European Value Contract CTT 472.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: PA1216). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

B. A. Frenz & Associates Inc. (1983). *SDP-Plus Structure Determination Package*. College Station, Texas, USA, and Enraf–Nonius, Delft, The Netherlands.

Baker, R., Herbert, R., Howses, P. E., Jones, O. T., Francke, W. & Reith, W. (1980). *J. Chem. Soc. Chem. Commun.* pp. 52–53.

Hamilton, J. A. & Sabesan, M. N (1982). *Carbohydr. Res.* **102**, 31–46.

Hamilton, J. A., Sabesan, M. N. & Steinrauf, L. K. (1981). *Carbohydr. Res.* **89**, 33–53.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory Tennessee, USA.

Jones, T. A., Bush, B. L., Pflugrath, J. W. & Saper, M. A. (1978). *J. Appl. Cryst.* **11**, 268–272.

Le Bas, G. (1985). Doctoral thesis, P. et M. Curie University, Paris, France.

Le Bas, G. & Rysanek, N. (1987). *Cyclodextrins and Their Industial Uses*, ch. III, edited by D. Duchene, p. 105. Paris: Editions de Santé.

Le Bas, G. & Tsoucaris, G. (1994). *Supramolecular Chem.* **4**, 13–14.

Mazomenos, B. E. & Haniotakis, G. E. (1981). *J. Chem. Ecol.* **7**, 437–443.

Mazomenos, B. E. & Haniotakis, G. E. (1985). *J. Chem. Ecol.* **11**, 397–405.

Mazomenos, B., Kondilis, P., Moustakali, I., Hadjoudis, E. & Tsoucaris, G. (1989). *Proc. Int. Symp. Control Rel. Bioact. Mater.* pp. 239–240. Chicago.

Rysanek, N., Le Bas, G., Villain, F. & Tsoucaris, G. (1992). *Acta Cryst.* C**48**, 1466–1471.

Sheldrick, G. M. (1976). *SHELX*76. *Program for Crystal Structure Determination*. University of Cambridge, England.

Szejtli, J (1989). In *Cyclodextrin Technology*. Dordrecht: Kluwer Academic Publishers.

Tripos Associates, Inc. (1988). *SYBYL*. Version 5.10. Tripos Associates, Inc., Missouri, USA.

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cis-4,5-Dihydroxy-2,3,4,5-tetraphenylcyclopent-2-enone

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Abstract

The title compound, $C_{29}H_{22}O_3$, was prepared by the oxidation of tetraphenylcyclopentadienone with tetranitromethane. The cyclopentenone ring has a C5-envelope conformation, with an elongated C_{sp^3}—C_{sp^3} bond length of 1.569 (2) Å. One hydroxyl group takes part in a bifurcated hydrogen bond involving an intra- and intermolecular bond to adjacent hydroxyl

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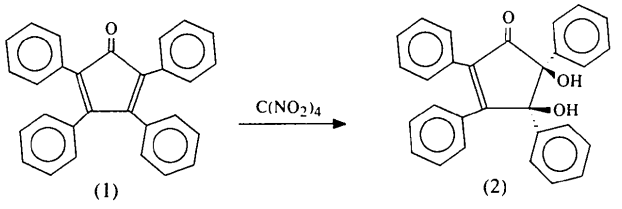
groups [O···O 2.6299 (16) and 2.9279 (15) Å], while the second hydroxyl group forms an intermolecular hydrogen bond to an adjacent carbonyl O atom [O···O 2.8441 (18) Å].

Comment

The present study was undertaken as part of a systematic investigation into the reactions of tetranitromethane with functionalized arenes and alkenes (Masnovi & Kochi, 1986; Masnovi, Sankararaman & Kochi, 1989). The products obtained depend upon the ability of the latter compounds to serve as electron donors. The reaction of tetraphenylcyclopentadienone, (1), and $C(NO_2)_4$ in CH_2Cl_2 was found to afford the title compound, (2).



Extensive studies have been performed on the static and dynamic stereochemistry of organic molecules containing rotating aryl rings. For example, none of the phenyl rings of compound (1) lie in the plane of the central five-membered ring. Instead, compound (1) assumes a four-bladed propeller-like structure with the blades alternately above and below the central ring. The dihedral angles of the four phenyl substituents with the central five-membered ring of (1) are 35.3 (2), 47.3 (4), 61.1 (3) and 28.0 (2)° (Barnes, Horspool & Mackie, 1991).

The molecular conformation and atom-labeling scheme for (2) are shown in Fig. 1. Although the central five-membered ring of (2) is not planar, atoms C1, C2, C3 and C4 are essentially coplanar (plane 1), with the C5 atom out of this plane by 0.377 (3) Å. C3*A*, the *ipso* position of the phenyl ring attached at the C3 position, lies almost in plane 1, with an out-of-plane distance of 0.039 (3) Å. This phenyl ring is also the most coplanar of the four phenyl rings with plane 1 [dihedral angle 36.50 (7)°]. Such a conformation allows the cyclopentenone π system to overlap best with that of the phenyl ring attached to C3, preserving conjugation between them. C2*A*, the *ipso* position of the phenyl ring attached at the C2 position, lies further out of plane 1 [out-of-plane distance 0.198 (3) Å] and the dihedral angle it makes with plane 1 is also larger [48.80 (8)°]. This phenyl ring is conjugated with the double bond but not with the carbonyl group of cyclopentenone. C4*A* and C5*A*, the *ipso* positions of the two phenyl rings attached to the saturated C4 and C5 atoms, lie on the face of the central ring opposite the hydroxyl groups and, as expected, show the least preference to align with the cyclopentenone π system [dihedral angles 84.58 (8) and 57.42 (8)°, respectively]. Bond distances and angles within the phenyl rings are mostly unexceptional (Barnes *et al.*, 1991) and each individual ring is planar (out-of-plane displacements being less than 0.02 Å). It is noteworthy, however, that the internal angles about the substituted C atoms of the phenyl groups are consistently less than 120° [ranging from 118.20 (16) to 118.69 (16)°; Table 2]. Furthermore, the C4—C5 bond of the cyclopentenone ring is slightly elongated [1.569 (2) Å] relative to a typical C—C single-bond length. This is most likely due to steric effects resulting from the high functionality of C4 and C5.

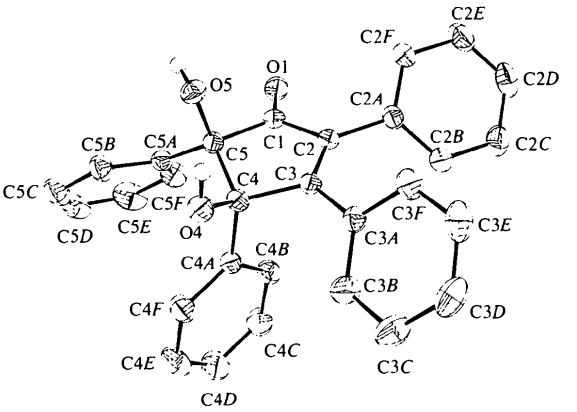


Fig. 1. *ORTEP*II (Johnson, 1976) representation of (2) showing the atom-numbering scheme with displacement ellipsoids at the 30% probability level (aromatic H atoms omitted).

The molecules are linked to form centrosymmetric dimers by O—H···O hydrogen bonds (details are in Table 3). The O4—H4 hydroxyl group takes part in both an intramolecular (to the adjacent O5 atom) and intermolecular (to the O5 atom of an adjacent molecule) O—H···O hydrogen bond. The O5—H5 hydroxyl group only forms an intermolecular O—H···O hydrogen bond to the keto O1 atom of an adjacent molecule.

The ^{13}C NMR spectrum of (2) in solution indicates rapid rotation of the phenyl substituents on the NMR timescale; only 21 resonances are observed (Jedrzejas, 1993), indicating eight pairs of symmetrically equivalent C atoms (the *ortho* and *meta* positions of each phenyl group). Coalescence is approached near 200 K. Studies on the dynamics of cyclopentanediol, cyclopentanone and (1) (Lambert, Johnson & Xue, 1994; Willem, Pepermans, Hoogzand, Hallenga & Gielen, 1981) suggest that a change in conformation about the C4—C5 bond may contribute to the temperature-dependent behavior of (2) in solution. The five-membered ring of crystalline (2) is non-planar, with the C5 phenyl substituent *exo*. In solution, the cyclopentenone ring should be sufficiently

flexible to allow conformations such as placement of this phenyl group in an *endo* orientation or puckering at C4 rather than C5, in correlation with rotations of the phenyl groups.

Experimental

The purple color of a solution of tetraphenylcyclopentadienone [(1); 1.00 g] and $C(NO_2)_4$ (1.35 g) in 30 ml CH_2Cl_2 bleached over a period of *ca.* two weeks in the dark, during which time a dense almost colorless liquid phase separated. Colorless crystals of (2) (1.07 g, 98%) precipitated spontaneously.

Crystal data

$C_{29}H_{22}O_3$
M_r = 418.49
Orthorhombic
Pccn
a = 24.856 (5) Å
b = 22.041 (5) Å
c = 7.921 (3) Å
V = 4340 (2) Å^3
Z = 8
D_x = 1.281 Mg m^{-3}
D_m = 1.26 Mg m^{-3}
D_m measured by flotation in aqueous NaOH

Mo $K\alpha$ radiation
λ = 0.7107 Å
Cell parameters from 25 reflections
θ = 7.1–12.4°
μ = 0.08 mm^{-1}
T = 293 K
Tetragonal prism
0.36 × 0.35 × 0.30 mm
Colorless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
3815 measured reflections
3815 independent reflections
3815 observed reflections

θ_{max} = 24.92°
h = 0 → 29
k = 0 → 26
l = 0 → 9
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R(F)$ = 0.081
$wR(F^2)$ = 0.058
S = 0.99
3815 reflections
290 parameters
H atoms riding, with C—H 0.94–1.02, O—H 0.88 Å
$w = 1/[\sigma^2(F) + 0.001F^2]$
$(\Delta/\sigma)_{max}$ = 0.0004

$\Delta\rho_{max}$ = 0.26 e Å^{-3}
$\Delta\rho_{min}$ = −0.25 e Å^{-3}
Extinction correction: Zachariasen (1963)
Extinction coefficient: 3.60 (14)
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.3.1)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	B_{eq}
O1	0.06201 (5)	0.46570 (5)	0.00567 (15)	3.84 (6)
O4	0.06147 (4)	0.57199 (5)	0.52881 (14)	3.51 (5)
O5	−0.00172 (4)	0.52413 (4)	0.29818 (13)	3.37 (5)
C1	0.07086 (6)	0.48221 (7)	0.1495 (2)	3.00 (8)
C2	0.10093 (6)	0.44817 (7)	0.2792 (2)	2.90 (7)
C3	0.10888 (6)	0.48358 (7)	0.4153 (2)	2.89 (7)
C4	0.08831 (6)	0.54795 (7)	0.3870 (2)	2.83 (7)
C5	0.04977 (6)	0.54081 (7)	0.2315 (2)	2.83 (7)
C2*A*	0.12133 (7)	0.38627 (7)	0.2452 (2)	3.22 (8)
C2*B*	0.17473 (7)	0.37213 (8)	0.2741 (2)	4.01 (9)
C2*C*	0.19501 (8)	0.31565 (9)	0.2340 (3)	5.28 (11)
C2*D*	0.16163 (10)	0.27271 (8)	0.1648 (3)	5.84 (12)
C2*E*	0.10871 (9)	0.28558 (8)	0.1368 (3)	5.45 (11)
C2*F*	0.08841 (7)	0.34251 (8)	0.1760 (3)	4.39 (10)
C3*A*	0.13600 (6)	0.46655 (7)	0.5741 (2)	3.14 (8)
C3*B*	0.16867 (7)	0.50707 (8)	0.6587 (2)	4.37 (9)
C3*C*	0.19611 (7)	0.49028 (10)	0.8032 (2)	5.02 (11)
C3*D*	0.18996 (8)	0.43337 (11)	0.8667 (2)	5.17 (11)
C3*E*	0.15579 (9)	0.39302 (9)	0.7894 (3)	5.14 (10)
C3*F*	0.12911 (7)	0.40900 (8)	0.6429 (2)	4.08 (9)
C4*A*	0.13470 (6)	0.59099 (7)	0.3439 (2)	2.98 (7)
C4*B*	0.17481 (7)	0.57381 (7)	0.2338 (2)	4.03 (9)
C4*C*	0.21464 (7)	0.61409 (9)	0.1865 (3)	5.09 (11)
C4*D*	0.21557 (8)	0.67129 (9)	0.2527 (3)	6.13 (13)
C4*E*	0.17642 (10)	0.68930 (8)	0.3636 (3)	5.94 (12)
C4*F*	0.13581 (7)	0.64917 (8)	0.4091 (2)	4.24 (9)
C5*A*	0.04609 (7)	0.59702 (7)	0.1241 (2)	3.08 (8)
C5*B*	0.01568 (7)	0.64502 (8)	0.1834 (2)	4.12 (9)
C5*C*	0.01665 (9)	0.70048 (8)	0.1020 (3)	5.61 (11)
C5*D*	0.04739 (11)	0.70807 (9)	−0.0398 (3)	6.46 (13)
C5*E*	0.07598 (10)	0.66041 (10)	−0.1034 (3)	6.28 (12)
C5*F*	0.07550 (8)	0.60476 (8)	−0.0215 (2)	4.49 (10)

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

O1—C1	1.216 (2)	C2—C2*A*	1.480 (2)
O4—C4	1.410 (2)	C3—C4	1.525 (2)
O5—C5	1.4325 (18)	C3—C3*A*	1.476 (2)
C1—C2	1.475 (2)	C4—C5	1.569 (2)
C1—C5	1.538 (2)	C4—C4*A*	1.532 (2)
C2—C3	1.346 (2)	C5—C5*A*	1.506 (2)
O1—C1—C2	126.29 (15)	C3—C4—C5	103.10 (12)
O1—C1—C5	125.82 (15)	C3—C4—C4*A*	110.90 (13)
C2—C1—C5	107.80 (14)	C5—C4—C4*A*	110.28 (13)
C1—C2—C3	109.73 (14)	O5—C5—C1	104.17 (12)
C1—C2—C2*A*	121.02 (15)	O5—C5—C4	106.35 (12)
C3—C2—C2*A*	129.06 (15)	O5—C5—C5*A*	111.42 (12)
C2—C3—C4	111.89 (14)	C1—C5—C4	101.99 (12)
C2—C3—C3*A*	127.06 (14)	C1—C5—C5*A*	118.26 (14)
C4—C3—C3*A*	120.99 (14)	C2*B*—C2*A*—C2*F*	118.57 (15)
O4—C4—C3	113.06 (13)	C3*B*—C3*A*—C3*F*	118.20 (16)
O4—C4—C5	111.98 (12)	C4*B*—C4*A*—C4*F*	118.48 (15)
O4—C4—C4*A*	107.54 (12)	C5*B*—C5*A*—C5*F*	118.69 (16)

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H···A	D—H	H···A	D···A	D—H···A
O4—H4···O5	0.88	2.26	2.6299 (16)	105
O4—H4···O5^i	0.88	2.16	2.9279 (15)	145
O5—H5···O1^{ii}	0.88	1.99	2.8441 (18)	165

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

The space group was determined uniquely as *Pccn* from the systematic absences.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *SET4* and *CELDIM* (Enraf–Nonius, 1989). Data reduction: *DATRD2* in *NRCVAX* (Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to solve structure: *SOLVER* in *NRCVAX*. Program(s) used to refine structure: *LSTSQ* in *NRCVAX*. Molecular graphics: *ORT* in *NRCVAX*. Software used to prepare material for publication: *TAB* in *NRCVAX*.

The authors thank the CSU College of Graduate Studies for support.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: FG1122). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Barnes, J. C., Horspool, W. M. & Mackie, F. I. (1991). *Acta Cryst.* C**47**, 164–168.

Enraf–Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.

Gabe, E. J., Le Page, Y., Charland, J.-P., Lee, F. L. & White, P. S. (1989). *J. Appl. Cryst.* **22**, 384–387.

Jedrzejas, M. J. (1993). PhD dissertation, Cleveland State University, USA.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Lambert, J. B., Johnson, S. C. & Xue, L. (1994). *J. Am. Chem. Soc.* **116**, 6167–6174.

Masnovi, J. M. & Kochi, J. K. (1986). *Recl. Trav. Chim. Pays-Bas*, **105**, 286–295.

Masnovi, J. M., Sankararaman, S. & Kochi, J. K. (1989). *J. Am. Chem. Soc.* **111**, 2263–2276.

Willem, R., Pepermans, H., Hoogzand, C., Hallenga, K. & Gielen, M. (1981). *J. Am. Chem. Soc.* **103**, 2297–2306.

Zachariasen, W. H. (1963). *Acta Cryst.* **16**, 1139–1144.

Acta Cryst. (1996). C**52**, 2939–2941

A Potential Antiprotozoal Drug Containing Acridine and Thiadiazole Moieties

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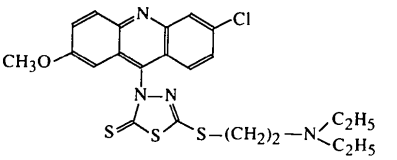
Abstract

The title compound, 3-(6-chloro-2-methoxy-9-acridinyl)-5-[2-(diethylamino)ethylthio]-1,3,4-thiadiazol-2(3*H*)-one, $C_{22}H_{23}ClN_4OS_3$, belongs to a series of new potential antiprotozoal drugs containing the acridine and thiadiazole systems. These two quasi-planar moieties are bonded together and are almost perpendicular to one another because of steric hindrance.

Comment

In the course of our research on antiprotozoal (Bsiri *et al.*, 1995) and antimicrobial drugs (Crèmieux *et al.*, 1994), we synthesized derivatives with two active pharmacophoric moieties in order to produce a heteroaromatic acridine nucleus with a basic [(diethylamino)ethylthio]thiadiazole substituent. The title product, (I), was obtained by the attack of 9-chloroacridine at an unexpected point on the thiadiazole and we have investigated its crystal structure in order to confirm ^{13}C NMR results (Amiel *et al.*, 1995).



(I)

The title molecule can be described in terms of two parts corresponding to the two pharmacophoric moieties (Fig. 1). The heterocyclic nucleus of the 9-substituted acridine is not completely planar and the three unsaturated aromatic rings look like a very flattened boat, with a dihedral angle of 2.5 (3)° between the external rings. This conformation is in agreement with data obtained from the Cambridge Structural Database (Allen & Kennard, 1993) for 51 compounds containing the 9-substituted acridine moiety. The thiadiazole substituent is directly attached to the acridine system *via* the C9′—N3*a* bond. The five-membered heteroatomic ring is almost planar, the largest deviation from the mean plane being only 0.013 (2) Å for the C2*a* atom. The thiadiazole ring is almost perpendicular to the acridine nucleus, forming a dihedral angle of 74.1 (1)° with it.

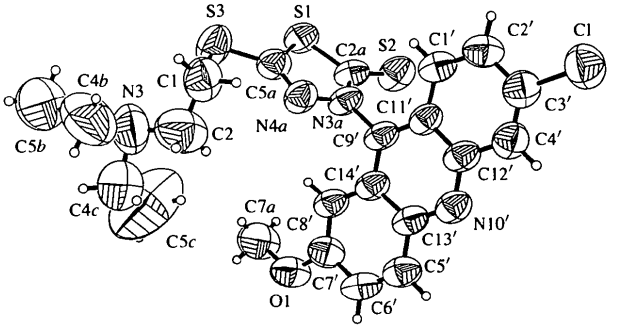


Fig. 1. The molecular structure of (I) showing 50% probability displacement ellipsoids.

The geometry of the diethylaminoethyl substituent on the S3 atom is unreliable because of the high displacement parameters for these atoms, which may be genuinely dynamic or may mask some degree of static disorder. Low-temperature data collection was unfortunately not possible because the crystals cracked on cooling.