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4-(5-Methyl-1,3,4-oxadiazol-2-yl)-1,3-phenylene Diacetate

IVO VENCATO,^a HUGO GALLARDO^b AND EMERSON MEYER^b

^aDepartamento Física, UFSC, 88040-900 Florianópolis, SC, Brazil, and ^bDepartamento Química, UFSC, 88040-900 Florianópolis, SC, Brazil. E-mail: vencato@qmc.ufsc.br

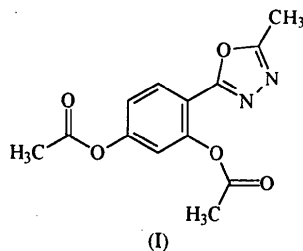
(Received 9 November 1995; accepted 21 March 1996)

Abstract

The title compound, C₁₃H₁₂N₂O₅, is a key intermediate in the synthesis of mesogens, which are derivatives of phenyloxadiazole. The oxadiazole and phenyl rings are planar to within 0.003 (2) and 0.010 (7) Å, respectively. The dihedral angle between the least-squares planes through the rings is 10.9 (1)°.

Comment

As part of an ongoing study of the relationship between molecular structure and mesomorphic behaviour, we have been systematically investigating conventional liquid crystals and metallomesogens which include heterocyclic rings (Gallardo & Favarin, 1993; Gallardo, Meyer & Vencato, 1995). The structure of the title compound, (I), was determined in order to obtain further structural information about substituted phenyl-1,3,4-oxadiazoles (Gallardo & Begnini, 1995; Karamysheva, Torgova, Agafonova & Shiikov, 1995).



The bond lengths and angles of the oxadiazole ring (Table 2) are within the expected ranges (Nygaard, Hansen, Nielsen, Andersen, Sorensen & Steiner, 1972). The phenyl and oxadiazole rings are essentially coplanar with the dihedral angle between their least-squares planes being 10.9 (1)°.

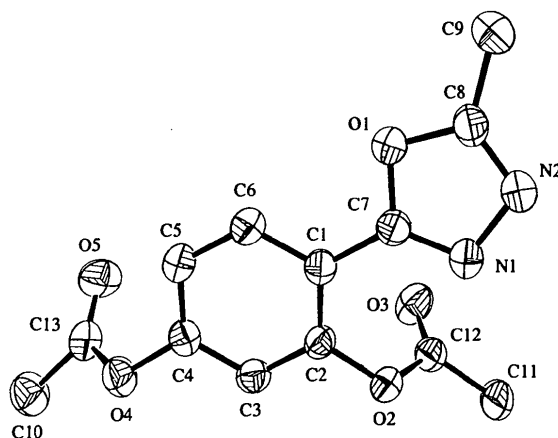


Fig. 1. View of the title compound showing the atomic numbering scheme. Only the positions of the higher occupancy sites of C13, C10 and O5 are shown. Displacement ellipsoids are drawn at the 50% probability level.

The acetoxy group at the C4 position was found to be disordered. While the introduction of a disorder model improved the structure considerably, the bonds lengths between the disordered atoms are unsatisfactory; C10'—C13' of 1.55 (2) Å is too long compared with C10—C13 of 1.493 (4) Å.

Experimental

The reaction mixture of 5-(2,4-dihydroxyphenyl)tetrazole and acetic anhydride was heated and refluxed for 2 h, whereupon it was cooled and poured into water. The crude oxadiazole separated as a solid and was recrystallized from ethanol (m.p. 372–373 K). ¹H NMR (200 MHz, CDCl₃, 298 K): δ (p.p.m.) 7.91 [1H, *d*, *J*_{6–5} = 8.6 Hz, aryl H (C6)], 7.08 [1H, *dd*, *J*_{5–3} = 2.2 Hz, *J*_{5–6} = 8.6 Hz, aryl H (C5)], 6.97 [1H, *d*, *J*_{3–5} = 2.2 Hz, aryl H (C3)], 2.49 [3H, *s*, ArOCOCH₃ (C2)], 2.31 [3H, *s*, ArOCOCH₃ (C4)], 2.21 [3H, *s*, CH₃]. IR (KBr disk): ν_{max} (cm⁻¹) 3028, 2978, 2930, 2854, 1760, 1616, 1556, 1364, 1216.

Crystal data

C₁₃H₁₂N₂O₅
M_r = 276.25
 Triclinic
*P*1
a = 5.6286 (7) Å
b = 10.257 (1) Å
c = 12.0111 (5) Å
 α = 100.924 (7)°
 β = 100.118 (6)°
 γ = 101.45 (1)°
V = 650.7 (1) Å³
Z = 2
D_x = 1.410 Mg m⁻³

Data collection

Enraf–Nonius CAD-4
 diffractometer

Mo Kα radiation
 λ = 0.71073 Å
 Cell parameters from 25
 reflections
 θ = 8.72–13.73°
 μ = 0.110 mm⁻¹
T = 293 (2) K
 Prismatic
 0.60 × 0.45 × 0.40 mm
 Colourless

*R*_{int} = 0.0114
 θ_{max} = 25.02°

$\omega/2\theta$ scans
 Absorption correction: none
 2546 measured reflections
 2294 independent reflections
 1873 observed reflections
 $[I > 2\sigma(I)]$

$h = -6 \rightarrow 0$
 $k = -11 \rightarrow 12$
 $l = -14 \rightarrow 14$
 3 standard reflections
 frequency: 60 min
 intensity decay: -3.6%

| | | | |
|------------|-------------|---------------|------------|
| C7—O1—C8 | 102.85 (15) | C5—C6—C1 | 122.0 (2) |
| C12—O2—C2 | 117.12 (15) | N1—C7—O1 | 112.1 (2) |
| C13'—O4—C4 | 126.9 (5) | N1—C7—C1 | 130.2 (2) |
| C13—O4—C4 | 120.5 (2) | O1—C7—C1 | 117.6 (2) |
| C7—N1—N2 | 106.1 (2) | N2—C8—O1 | 112.4 (2) |
| C8—N2—N1 | 106.5 (2) | N2—C8—C9 | 129.3 (2) |
| C6—C1—C2 | 117.5 (2) | O1—C8—C9 | 118.3 (2) |
| C6—C1—C7 | 119.7 (2) | O3—C12—O2 | 122.2 (2) |
| C2—C1—C7 | 122.7 (2) | O3—C12—C11 | 126.9 (2) |
| C3—C2—O2 | 117.2 (2) | O2—C12—C11 | 110.9 (2) |
| C3—C2—C1 | 121.3 (2) | O5—C13—O4 | 122.9 (2) |
| O2—C2—C1 | 121.4 (2) | O5—C13—C10 | 126.0 (3) |
| C2—C3—C4 | 119.1 (2) | O4—C13—C10 | 111.1 (3) |
| C5—C4—C3 | 121.4 (2) | O5'—C13'—O4 | 120.7 (10) |
| C5—C4—O4 | 121.4 (2) | O5'—C13'—C10' | 130.1 (12) |
| C3—C4—O4 | 117.0 (2) | O4—C13'—C10' | 108.3 (11) |
| C4—C5—C6 | 118.7 (2) | | |

Symmetry code: (i) $1 - x, 3 - y, 1 - z$.

Refinement

Refinement on F^2
 $R(F) = 0.0417$
 $wR(F^2) = 0.1230$
 $S = 1.047$
 2294 reflections
 198 parameters
 H atoms riding, except those on C10 and C10'; U^s refined
 $w = 1/[\sigma^2(F_o^2) + (0.0806P)^2 + 0.1652P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.467$

$\Delta\rho_{\max} = 0.271 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.188 \text{ e } \text{\AA}^{-3}$
 Extinction correction: *SHELXL93* (Sheldrick, 1993)
 Extinction coefficient: 0.0187 (16)
 Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Two unexpected large peaks were found after the isotropic refinement. They were interpreted as O5 and C13 disordered over two positions. The model was improved with C10 disordered over two positions. The occupancy factors for O5 and C10 were constrained to be equal to that of C13; C13', O5' and C10' were constrained in the same way. The occupancy factors for C13 [0.854 (2)] and C13' [0.146 (2)] (also for O5, O5' and C10, C10') were allowed to refine with their sum constrained to 1.0. Anisotropic displacement parameters were used for all except the disordered atoms with occupancy factors less than 0.5. H atoms were added at calculated positions and refined using a riding model. The H atoms of C10 were located from the highest peaks of a difference Fourier map. They were not refined and each was given a site occupancy of 0.854. The H atoms of C10', with site occupancies of 0.146, were not located.

Data collection: *CAD-4 EXPRESS* (Enraf-Nonius, 1993). Cell refinement: *MolEN* (Fair, 1990). Data reduction: *MolEN*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEX* (McArdle, 1994). Software used to prepare material for publication: *SHELXL93*. Calculations were performed on DEC3000 AXP and PC 486 computers.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1339). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

$$U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i \cdot a_j$$

| | x | y | z | U_{eq} |
|-------|-------------|--------------|--------------|------------|
| O1 | 0.3075 (2) | 0.96308 (14) | 0.75367 (12) | 0.0507 (4) |
| O2 | 0.9839 (2) | 1.22200 (15) | 0.73524 (11) | 0.0507 (4) |
| O3 | 0.8497 (3) | 1.3526 (2) | 0.87090 (15) | 0.0753 (5) |
| O4 | 0.5759 (3) | 1.31382 (14) | 0.38984 (12) | 0.0542 (4) |
| O5† | 0.2521 (4) | 1.4055 (2) | 0.4051 (2) | 0.0726 (6) |
| O5'‡ | 0.7681 (15) | 1.5173 (8) | 0.4832 (7) | 0.041 (2) |
| N1 | 0.7104 (3) | 1.0160 (2) | 0.8235 (2) | 0.0590 (5) |
| N2 | 0.5954 (3) | 0.9231 (2) | 0.8821 (2) | 0.0603 (5) |
| C1 | 0.5437 (3) | 1.1164 (2) | 0.6617 (2) | 0.0417 (4) |
| C2 | 0.7621 (3) | 1.2041 (2) | 0.6555 (2) | 0.0428 (4) |
| C3 | 0.7700 (3) | 1.2708 (2) | 0.5660 (2) | 0.0456 (5) |
| C4 | 0.5557 (4) | 1.2514 (2) | 0.4823 (2) | 0.0447 (5) |
| C5 | 0.3356 (4) | 1.1681 (2) | 0.4866 (2) | 0.0467 (5) |
| C6 | 0.3316 (4) | 1.1020 (2) | 0.5765 (2) | 0.0467 (5) |
| C7 | 0.5337 (3) | 1.0357 (2) | 0.7495 (2) | 0.0437 (4) |
| C8 | 0.3636 (4) | 0.8963 (2) | 0.8394 (2) | 0.0504 (5) |
| C9 | 0.1593 (5) | 0.8073 (3) | 0.8696 (2) | 0.0696 (7) |
| C10† | 0.4990 (8) | 1.4635 (4) | 0.2703 (3) | 0.0716 (9) |
| C10'‡ | 0.615 (4) | 1.467 (2) | 0.2714 (19) | 0.068 (6) |
| C11 | 1.2428 (4) | 1.2988 (3) | 0.9226 (2) | 0.0713 (7) |
| C12 | 1.0059 (4) | 1.2977 (2) | 0.8453 (2) | 0.0532 (5) |
| C13† | 0.4235 (5) | 1.3940 (2) | 0.3614 (2) | 0.0538 (6) |
| C13'‡ | 0.657 (2) | 1.4440 (11) | 0.3963 (10) | 0.035 (2) |

† Occupancy of 0.854 (2). ‡ Occupancy of 0.146 (2).

Table 2. Selected geometric parameters (\AA , $^\circ$)

| | | | |
|---------------------|------------|-----------|-----------|
| O1—C7 | 1.356 (2) | N2—C8 | 1.269 (3) |
| O1—C8 | 1.366 (2) | C1—C6 | 1.393 (3) |
| O2—C12 | 1.371 (3) | C1—C2 | 1.395 (3) |
| O2—C2 | 1.390 (2) | C1—C7 | 1.460 (3) |
| O3—C12 | 1.187 (3) | C2—C3 | 1.381 (3) |
| O4—C13' | 1.305 (11) | C3—C4 | 1.382 (3) |
| O4—C13 | 1.346 (3) | C4—C5 | 1.373 (3) |
| O4—C4 | 1.393 (2) | C5—C6 | 1.380 (3) |
| O5—C13 | 1.191 (3) | C8—C9 | 1.464 (3) |
| O5—O5' ¹ | 1.458 (8) | C10—C13 | 1.493 (4) |
| O5'—C13' | 1.155 (14) | C10'—C13' | 1.55 (2) |
| N1—C7 | 1.287 (3) | C11—C12 | 1.482 (3) |
| N1—N2 | 1.411 (3) | | |

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4,4'-Bis(2,4,6-trimethylbenzenesulfonamido)diphenylmethane

M. FEIGEL,^{a*†} TH. STRASSNER,^{a‡} J. MANERO^{a§} AND E. WECKERT^b

^a*Institut für Organische Chemie, Universität Erlangen-Nürnberg, Henkestrasse 42, 90154 Erlangen, Germany, and*
^b*Institut für Kristallographie, Universität Karlsruhe (TH), Kaiserstrasse 12, 76128 Karlsruhe, Germany*

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Abstract

The crystal structure of the title compound, C₃₁H₃₂N₂O₄S₂, has been determined at 293 K. The structure of the central diphenylmethane moiety can be described as nearly C₂ symmetrical. The central bond angle at the CH₂ group has a value of 112.1 (8)° and the dihedral angles between the planes of the central aromatic rings and the central plane, defined by C_{ar}—CH₂—C_{ar}, are 53.8 (8) and 57.9 (6)°, respectively.

Comment

The molecular geometry at the central atom of compounds of the type aryl—X—aryl with different X groups [*e.g.* X = O, CH₂, diphenylether (DPE) and diphenylmethane (DPM)] has been discussed for several years now (Le Fèvre & Saxby, 1966; Montaudo, Cacamese & Finocchiaro, 1971; Barnes, Paton, Damewood & Mislow, 1981; Naik, Parsons, McGrail & MacKenzie, 1991). One of the reasons for this interest is the occurrence of the aryl—X—aryl structural unit in many important natural compounds and another arises from the growing importance of polymeric materials, where the aryl—X—aryl unit seems to account for their extraordinary properties (Domininghaus, 1988). There are some published X-ray structures of diphenylmethane compounds, but most are substituted in the *ortho* po-

† Present address: Ruhr-Universität Bochum, Fakultät für Chemie, 44780 Bochum, Germany.

‡ Present address: Institut für Organische Chemie, Technische Universität Dresden, Mommsenstrasse 13, 01062, Dresden, Germany.

§ Present address: Hoechst AG, Geschäftseinheit Forschungsprodukte, LCD-Materialien, 65926 Frankfurt, Germany.

sition and therefore free rotation is restricted. We are looking for *para*-substituted compounds where no steric interaction of substituents influences the conformational behaviour. In the course of an experimental and theoretical study on the usefulness of diphenylmethane compounds as a constituent unit of host–guest compounds, several compounds were synthesized for comparison. During this research, we obtained crystals of the title compound, (I), of suitable quality for diffraction studies and we now report its structure.

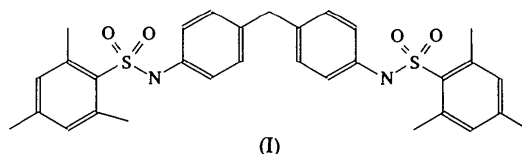


Fig. 1 shows the molecular geometry and atom labelling scheme. The dihedral angles between the planes of the central aromatic rings and the central plane, defined by C13,C16,C17, are 53.8 (8) and 57.9 (6)°, so the structure of the central diphenylmethane moiety is nearly C₂ symmetrical.

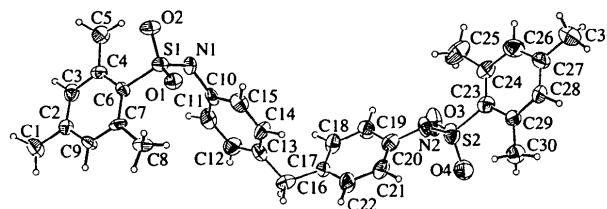


Fig. 1. *CRYSTAN88* (Burszlaff & Rothammel, 1989) plot of (I). Displacement ellipsoids are drawn at the 50% level.

The geometry of compound (I) is similar to the X-ray structure of diphenylmethane (DPM) where the dihedral angles are 63.9 and 71.9°. Significantly larger bond angles have been reported in the crystal structures of other substituted diphenylmethane derivatives (Barnes, Paton, Damewood & Mislow, 1981). The central bond angle of 112.5° in DPM is in good agreement with the value of 112.1 (8)° for the title compound.

Experimental

Compound (I) was prepared by reaction of 4,4'-diaminodiphenylmethane with 2,4,6-trimethylbenzenesulfonyl chloride in pyridine and recrystallization from EtOH following standard procedures for the synthesis of sulfonamides. Crystals suitable for X-ray study were obtained from an EtOH solution by slow evaporation of solvent.

Crystal data

C₃₁H₃₂N₂O₄S₂
M_r = 560.73

Cu Kα radiation
 λ = 1.5418 Å

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