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ORIGINAL PAPER

Desynchronization of Pedal Motion: Crystallographic and Theoretical Study of (*E*)-4-[(4-ethylphenyl)diazenyl]-2-methylphenol

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Abstract The single crystal X-ray diffraction analysis of the title compound, $C_{15}H_{16}N_2O$, reveals that its molecules exhibit whole-molecule disorder at both crystal lattice sites due to pedal motion in solid state. The compound crystallizes in the monoclinic space group $P\ 2_1/c$ with $a = 20.5504(14)$ Å, $b = 10.8887(5)$ Å, $c = 12.0191(8)$ Å and $\beta = 96.927(5)°$. While major pedal conformers of the compound in solid state are stabilized by intermolecular O–H···N type hydrogen bonds leading to the formation of $C(7)$ chains at Site 1 and $C(8)$ chains at Site 2 along [0 1 0] axis, C–H···π type intermolecular interactions between major and minor conformers also serve to stabilize minor pedal conformers. An interesting feature about the crystal structure is that pedal conformers at Site 1 have two different occupancy factors arising from desynchronization of pedal motion along [2 1 0] direction in crystal phase. Quantum chemical calculations at the B3LYP/6-31++G** level suggest that the desynchronization of pedal motions make more unstable pedal conformers at Site 1 than those at Site 2.

Keywords Pedal motion · Crystal structure · Whole-molecule disorder · Azobenzene · DFT/B3LYP

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Introduction

Solid-state conformational changes have received considerable attention for the past three decades in order to explain the dynamic aspects associated with certain features of the molecules having photoreactivity and photochemical properties [1–4]. In this regard, molecular motions in crystals are of great importance in determining the effects on their physical properties.

Some molecules having molecular skeletons similar to those of (*E*)-stilbenes and azobenzenes show orientational disorder in the crystal phase [5–10]. The disorder observed in some azobenzenes is dynamic and therefore ascribed to a conformational interconversion between major and minor conformers [11]. The conformational interconversion observed in such compounds is due to the pedal (or crankshaft) motion: a pair of benzene rings moving like the pedals of a bicycle. Pedal motion is not only peculiar to stilbene- and azobenzene-type molecules, it is also one of the key processes in the photochromism of salicylideneanilines [12] and the photodimerization of *trans*-cinnamides [13, 14]. The absence of orientational disorder in such compounds can be attributable to the destabilization of the minor conformer and the non-disordered crystal structures of them do not mean that the pedal motion is inhibited. In fact, the low occupancy factor of the minor pedal conformer makes the disorder invisible in most crystals. Ogawa and Harada reported that the pedal motion takes place even in non-disordered crystals [15]. As a result of this, orientational disorder arising from pedal motion has been overlooked in most of crystal structures of such compounds [15]. On the other hand, it is very difficult to determine the structure of the minor conformer whose occupancy factor is very low (generally less than 0.10) as being in most of disordered azobenzenes. The occupancy

factor of the minor conformers of azobenzene-type molecules decreases as the temperature is lowered [15]. According to the Boltzmann distribution law, the population of an energetically unfavorable conformer in equilibrating systems increases as the temperature is raised. Therefore, the population of a minor conformer of such a compound cannot be easily detectable at a low temperature. In agreement with experiment, molecular simulations of solid stilbene show the onset of pedal motion at one of the crystal lattice sites between 150 and 200 K, while such a motion starts at both lattice sites at higher temperatures [16].

The disordered pedal conformers of azobenzene-type molecules are usually located at one of the crystal lattice sites [15, 17]. The single crystal X-ray diffraction method gives us valuable information regarding the populations of major and minor conformers for the structures in which conformational changes occur in solid-state. In the present paper, we report that the wholly disordered molecules of the title azobenzene derivative are located at both crystal lattice sites and desynchronization of pedal motion results in different-site occupancy factors in the crystal phase. Stability levels of crystallographically observed pedal conformers were quantitatively compared by using the results from quantum chemical calculations at level of B3LYP/6-31++G**.

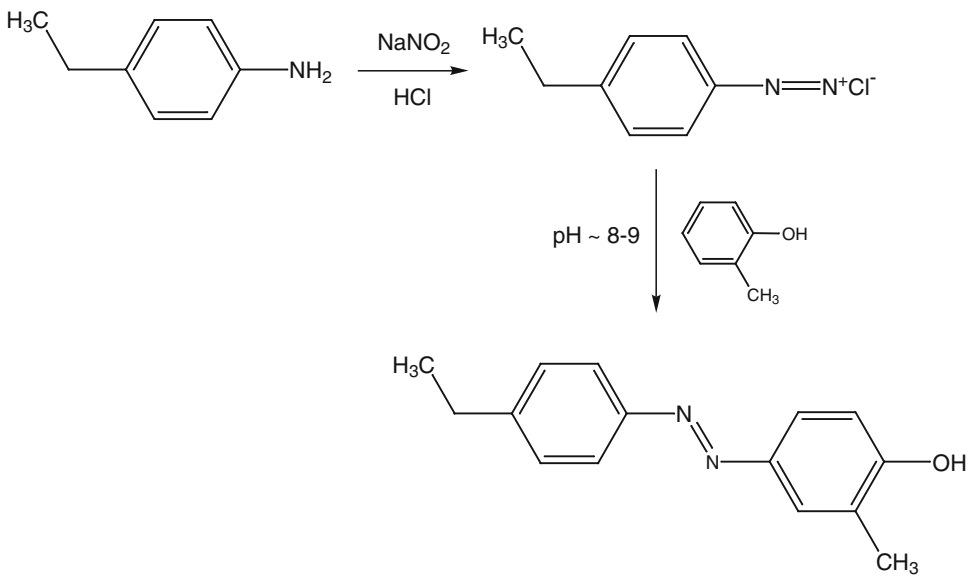
Experimental

Synthesis of the Title Compound

A mixture of 4-ethylaniline (2.5 g, 20.6 mmol), water (50 mL) and concentrated hydrochloric acid (5 mL, 61.8 mmol) was stirred until a clear solution was obtained. This solution was cooled to 273–278 K and a solution sodium nitrite (1.42 g, 29.2 mmol) in water was added dropwise while the temperature was maintained below 278 K. The resulting mixture was stirred for 30 min in an ice bath. *o*-Cresol (2.23 g, 20.6 mmol) solution (pH ~ 8–9) was gradually added to a cooled solution of 4-ethylbenzenediazonium chloride, prepared as described above, and the resulting mixture was stirred at 273–278 K for 60 min in ice bath. The product was recrystallized from ethyl alcohol to obtain solid (*E*)-4-[(4-ethylphenyl)diazenyl]-2-methylphenol. Crystals of (*E*)-4-[(4-ethylphenyl)diazenyl]-2-methylphenol were obtained from ethyl alcohol at room temperature via slow evaporation (yield 76%, m.p. 398–400 K). Synthesis route of the title compound is shown in Scheme 1.

X-ray Crystallography

A suitable sample of size 0.60 × 0.33 × 0.11 mm was chosen for the crystallographic study and then carefully mounted on goniometer of a STOE IPDS 2 diffractometer. All diffraction measurements were performed at 300 K using graphite monochromated MoK$_\alpha$ radiation ($\lambda = 0.71073$ Å). The systematic absences and intensity symmetries indicated the monoclinic $P\,2_1/c$ space group. A total of 36,045 reflections (5,240 unique) within the θ range of [2.00° $< \theta <$ 26.00°] for $-24 \le h \le 25$, $-13 \le k \le 13$, $-14 \le l \le 14$ were collected in ϖ-scan mode with $R_{int} = 0.0802$. The intensities collected were corrected for Lorentz and polarization factors, absorption correction ($\mu = 0.076$ mm^{-1}) by integration method via X-RED software [18]. Extinction correction was not applied. Cell parameters were determined by using X-AREA software [18]. The structure was solved by direct methods using SHELXS-97 [19]. The refinement was



Scheme 1 Synthesis route for the title compound

Table 1 Crystallographic data and the details of refinement process for the title compound

Chemical formula	$C_{15}H_{16}N_2O$
Color, shape	Orange, prism
Formula weight	240.30
Crystal system	Monoclinic
Space group	$P\ 2_1/c$
Unit cell parameters	a = 20.5504(14) Å
	b = 10.8887(5) Å
	c = 12.0191 (8) Å
	β = 96.927(5)°
Volume	2669.8(3) Å^3
Formula Z	8
D_x (Mg m^{-3})	1.196
μ (mm^{-1})	0.076
F_{000}	1024
T_{min}, T_{max}	0.965, 0.990
No. of measured, independent and observed reflections	36045, 5240, 2648
θ_{max} (°)	26.00
Refinement on	F^2
$R[I > 2\sigma(I)]$, S	0.059, 0.974
No. of parameters	640
Weighting scheme	$w = 1/[\sigma^2(F_o^2)+(0.1447P)^2]$
	$P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$	0.012
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.27, −0.45

carried out by full-matrix least-squares method on the positional and anisotropic temperature parameters of the non-hydrogen atoms. All H atoms were refined using appropriate riding models with C–H distances of 0.96 Å for methyl groups, 0.97 Å for methylene groups and 0.93 Å for aromatic CH groups. The displacement parameters of H atoms were fixed at 1.2 U_{eq} of their parent carbon atoms for aromatic groups and methylene groups, 1.5 U_{eq} of their parent atoms for methyl and hydroxyl groups. The disordered N atoms were refined using the *SADI* restraints. In addition, the disordered aromatic rings were adapted to their regular hexagonal geometries by *DFIX* restraints. The structure was refined to $R_1 = 0.059$ for observed 2648 reflections prescribed by the condition of $I > 2\sigma(I)$ and to $wR_1 = 0.148$ for all 5,240 data used in refinement process. The scattering factors were taken from SHELXL-97 [19]. Other details of the data collection conditions and parameters of refinement process are summarized in Table 1.

Computational Procedures

All quantum chemical calculations were performed by DFT calculations with the use of Becke's three-parameters hybrid exchange-correlation functional (B3LYP) [20] incorporating B88 gradient-corrected exchange [21] and Lee–Yang–Parr non-local correlation functional [22] by means of 6-31++G** basis set [23–25] implemented in HyperChem 7.52 program package [26]. Numerical integrations involving the exchange-correlation functional were carried out on 32-point Gauss–Chebyshev radial and 50-point Lebedev angular integration grid by using cut-off for density of 10^{-6} eÅ^{-3}. Geometry optimization of the title compound was achieved by the application of a conjugate gradient method known as Polak-Ribiere optimization algorithm [27] with convergence limit of 10^{-2} kcal/mol and quite precise RMS gradient of 10^{-3} kcal/Åmol. In order to compare stabilization levels of the pedal conformers in solid state, total energies of pedal conformers were also calculated for their crystallographically observed atomic configurations (single-point calculations).

Results and Discussion

X-ray diffraction analysis of the title compound, $C_{15}H_{16}N_2O$, revealed that its thermodynamically unstable minor pedal conformers coexist with stable major components at the same crystal lattice sites. In the asymmetric unit, there are two crystallographically independent molecules (Residue 1 at lattice Site 1 and Residue 2 at lattice Site 2) each of which is refined as a superposition of major and minor pedal conformer of the compound as shown in Fig. 1 [28]. Residue 1 represents the monomer containing O1A and O1B atoms. Other O atoms in the asymmetric unit are included in Residue 2. The major (A) and minor (B) pedal conformers at Site 2 have 0.72 and 0.28 site occupancy factors, respectively, whereas site occupancy factors of the disordered atoms at Site 1 have two different ratios: 0.53:0.47 for atoms C9A/B to C15A/B and 0.72:0.28 for the remaining disordered fragment at Site 1. This interesting feature of the crystal structure is related to a possible displacive phase transition accompanied with conformational interconversion between major and minor conformers at Site 1 along [2 1 0] direction due to desynchronization of the pedal motions and indicates that the compound is probably open to polymorphism.

Some selected geometrical parameters for both conformers obtained from crystallographic analysis are listed in Table 2. It is worth noting some conformational differences between the orientations of the major and minor components at both crystal sites. The most remarkable difference in the disordered orientations is observed in the dihedral angle between the mean planes through major and minor part of the 4-ethylphenyl ring at Site 1 with the angle of 11(1)°, while the dihedral angle between the mean

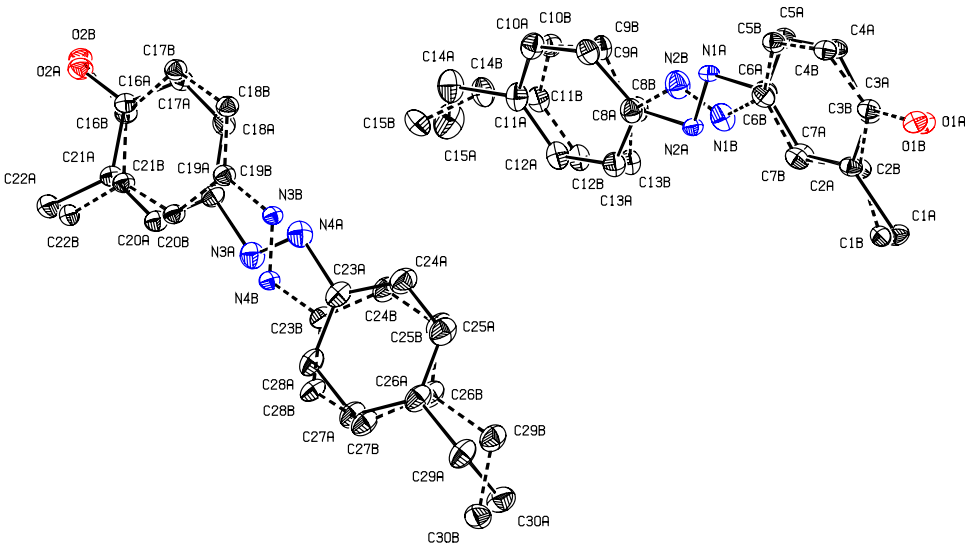


Fig. 1 Superposition of thermal ellipsoid views of the major (full lines) and minor (broken lines) pedal conformers of the title compound with the atom numbering scheme of non-H atoms in the asymmetric unit. Displacement ellipsoids are depicted at the 30% probability level

Table 2 Some geometrical parameters (Å, °) for the crystallographically observed conformers of the title compound

Bond lengths			
O1A–C3A	1.36(2)	O2A–C16A	1.38(1)
O1B–C3B	1.37(6)	O2B–C16B	1.32(2)
N1A–N2A	1.283(4)	C19A–N3A	1.472(9)
N1A–C6A	1.446(8)	C19B–N3B	1.41(3)
N1B–C6B	1.43(1)	N3A–N4A	1.219(5)
N1B–N2B	1.233(9)	N3B–N4B	1.240(8)
N2A–C8A	1.428(8)	N4A–C23A	1.467(7)
N2B–C8B	1.37(1)	N4B–C23B	1.402(9)
Bond angles			
N2A–N1A–C6A	110.6(4)	N1A–N2A–C8A	110.5(4)
N2B–N1B–C6B	125(2)	N1B–N2B–C8B	123(2)
N4A–N3A–C19A	109.7(6)	N4B–N3B–C19B	122(1)
N3A–N4A–C23A	108.7(5)	N3B–N4B–C23B	119.3(8)
Torsion angles			
C6A–N1A–N2A–C8A	−179(1)	C19A–N3A–N4A–C23A	180.0(5)
C6B–N1B–N2B–C8B	−167(4)	C19B–N3B–N4B–C23B	176(2)
C10A–C11A–C14A–15A	159(1)	C10B–C11B–C14B–C15B	−97(1)
C25A–C26A–C29A–C30A	−97(1)	C25B–C26B–C29B–C30B	−158(2)

planes of major and minor components of 4-ethylphenyl ring at Site 2 is 7.1(7)°. Moreover, the dihedral angles between the mean planes of 2-methylphenol rings of minor and major components at Site 1 and Site 2 are 8(1)° and 3(1)°, respectively. Consequently, the disordered fragment having different occupancy ratio from the remaining part of Site 1, atoms C9A/B to C15A/B, is of evident orientational difference. On the other hand, positional separations of some atom pairs at crystal lattice Site 1 are not sufficiently distinguishable. C6A and C6B have almost coincident atomic positions, as do atoms C8A and C8B. None of the pedal conformers in the asymmetric unit is planar around the azo bridges and each pedal conformer is adapted to *trans* stereo-configuration. Dihedral angles between the aromatic rings of major and minor conformers at Site 1 are found as 11(2)° and 6(2)°, respectively, these angles at Site 2 are 16.3(5)° and 26(1)°. Although the mentioned values for the dihedral angles between the aromatic rings at Site 1 are in agreement with the values of 5°–15° observed for (*E*)-azo benzenes [10], it is inferred from these results that non-planarities of the conformers become more visible at Site 2 than those at Site 1.

The r.m.s. fit of the bond distances of major conformer to those of minor conformer is 1.0742 Å at Site 1 and 0.9417 Å at Site 2. These values indicate that there are remarkable discrepancies between in bond distances of the major and minor conformer at both sites. As far as geometrical parameters of the major and minor components are concerned that the most important differentiation is observed for N=N bonds in both lattice sites and for C–O bonds at Site 2. The unexpected shortenings in N3A–N4A and N1B–N2B bonds and elongations in N1A–N2A and N3B–N4B bonds can be explained by low stabilization levels of the minor conformers during solid-state conformational interconversion and the presence of intermolecular hydrogen bonds in the crystal structure. Pairs of formally single C–N bonds at opposite sides around azo bridges in both pedal conformers of the compound are slightly different from each other due to a possible through-resonance effect between the electron-donating O atom and the two-electron accepting N atom in azo bridge. This tendency is observed for similar azo compounds [29–34].

Solid-state conformational changes are proceeded in a different way from those in gas-phase and coupled with changes in supramolecular environment of the compounds. In this sense, changes in supramolecular environment as well as the conformational changes accompanied with intermolecular interactions are of special importance in terms of conformational stabilities of the conformers. In this sense, there are two remarkable intermolecular hydrogen bonds between hydroxyl groups and azobridges of major pedal conformers. Intermolecular hydrogen bonding geometries and details of C–H$\cdots\pi$ interactions are given in Table 3. According to graph-set notation [35], the major pedal conformers of the title compound at Site 1 and Site 2 are linked into $C(7)$ and $C(8)$ hydrogen-bonded polymeric chains generated by translation along the [0 1 0] direction as shown in Figs. 2 and 3, respectively. Furthermore, there are two remarkable C–H$\cdots\pi$ interactions between methyl groups of minor conformers and 2-methylphenol rings of major conformers at both lattice sites as shown in Fig. 4. It can be inferred from these results that O–H$\cdots$N type intermolecular hydrogen bonds supply leading contribution to the stabilization of major conformers, while minor pedal conformers are stabilized by C–H$\cdots\pi$ type edge-to-face interactions in solid state.

Total energy values for the crystallographically observed geometries of pedal conformers in comparison with total energy value of the optimized geometry of the title compound are listed in Table 4. According to these results, the most stable pedal conformer of the title compound is major conformer at Site 2. As expected, major pedal conformers are more stable than minor conformers at both crystal sites. Furthermore, pedal conformers located at Site 2 are more stable than their counterparts at Site 1. These inferences are reasonable in order that the desynchronization of pedal motions resulting in two different occupancy ratios along [2 1 0] direction makes somewhat unstable pedal conformers at Site 1 than the conformers at Site 2.

Table 3 Geometrical details of H-bonds and C–H$\cdots\pi$ interactions (Å, °)

D–H···A	D–H	H···A	D···A	∠D–H···A
O1A–H3A···N1A[a]	0.82	2.15	2.97(2)	174.3(3)
O2A–H16A···N4A[b]	0.82	2.01	2.83(2)	172.2(3)
C–H···Cg	C–H	H···Cg	C···Cg	∠C–H···Cg
C1B–H1E···Cg1[c]	0.96	2.51	3.37(2)	150(2)
C22B–H22F···Cg2[d]	0.96	2.69	3.52(3)	145(2)

Note: D: donor, A: acceptor. Cg1 and Cg2 denote the centroids of the rings formed by atoms C2A–C7A and C16A–C21A. Symmetry operations: [a] $1-x, y-1/2, 3/2-z$; [b] $-x, 1/2+y, 1/2-z$; [c] $1-x, 1-y, 2-z$; [d] $-x, 1-y, 1-z$

It is worth noting some conformational discrepancies between the optimized geometry and experimentally observed structures. While N = N bond is optimized geometry is 1.232 Å, it ranges from 1.22 to 1.28 Å in pedal conformers at both sites. The optimized geometry of the compound is exactly planar. The most remarkable conformational discrepancy is observed in the orientations of ethyl groups. Although ethyl group in the optimized geometry lies in the same plane with its parent ring, C15A and C15B atoms are out of plane with r.m.s. deviations of 1.32(5) and −0.56(3) Å from the related ring planes. Similarly, C30A and C30B are also out of plane with r.m.s. deviations of 1.31(2) and 0.73(5) Å from the related ring planes. This result is not surprising because the most flexible part of the molecule in solid state is 4-ethylphenyl fragment participating in neither intra- nor intermolecular interaction according to crystallographic analysis and indicates that orientations of substituent ethyl groups have a primary influence on the stabilization levels of the conformers. The stabilities of pedal conformers at the same lattice site are proportional to the out-of-plane separation. Keeping in mind that the planar geometry of the molecule is the most stable conformation in gas-phase, it can be stated that O–H$\cdots$N and C–H$\cdots\pi$ intermolecular interactions besides crystal packing interactions prescribed by the space group symmetry operations supply leading contribution to the stabilizations of the conformers in solid state.

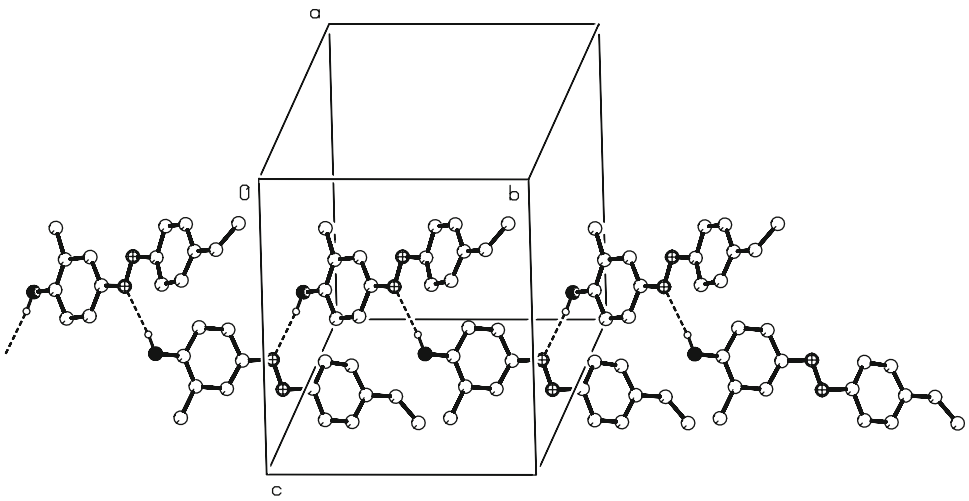


Fig. 2 *C*(7) zigzag chain formed by the major conformer at Site 1. Minor conformers and H atoms not involved in the motif have been omitted for the sake of clarity

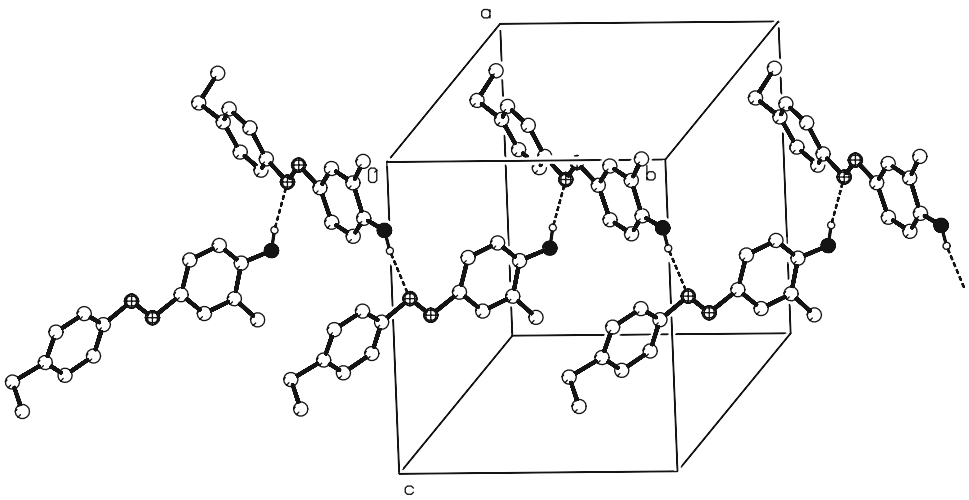


Fig. 3 *C*(8) zigzag chain formed by the major conformers at Site 2. Minor conformers and H atoms not involved in the motif have been omitted for the sake of clarity

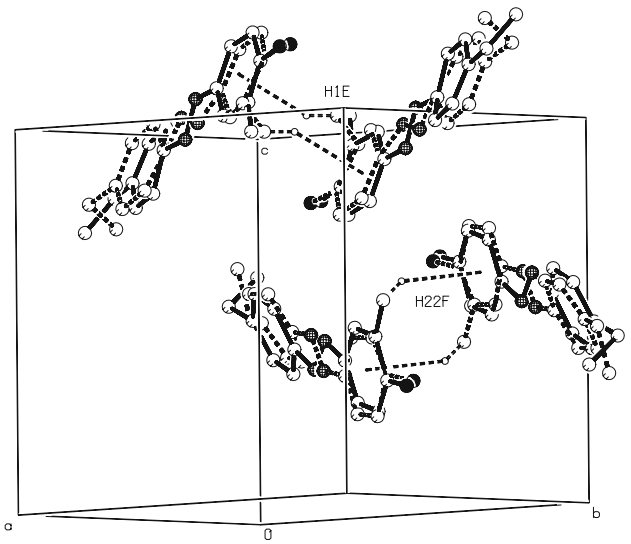


Fig. 4 C–H···π type interactions involving major and minor pedal conformer in the unit cell. Only H atoms involved in the interactions (H1E and H22F) have been plotted for the sake of clarity

Table 4 Total energy values of the crystallographically observed pedal conformers of the title compound in comparison with the most stable in vacuo optimized geometry

Conformer	Site	Energy[a]	Conformer	Site	Energy[a]
Minor	1	0.194	Major	1	0.127
Minor	2	0.149	Major	2	0.102

[a] Energy values related to the pedal conformers are calculated in atomic units (a.u.)

Supplementary Material

Crystallographic data (excluding structure factors) for the structure reported in this article have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 631822. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: data_request@ccdc.cam.ac.uk).

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