Struct Chem (2007) 18:87–93
DOI 10.1007/s11224-006-9130-1

ORIGINAL PAPER

Conformational analysis and crystal structure of (*E*)-3-methyl-4-(*p*-tolyldiazenyl)phenol

Hasan Karabıyık · Nazan Ocak İskeleli · Çiğdem Albayrak · Erbil Ağar

Received: 15 September 2006 / Accepted: 26 October 2006 / Published online: 8 December 2006

Abstract The single crystal X-ray diffraction analysis of the title compound, $C_{14}H_{14}N_2O$, reveals that an interesting intermolecular or extended structure (hydrogen-bonded polymeric zigzag chains) is formed by linking its monomer units with O–H · · · N type intermolecular hydrogen bonds. The compound crystallizes in the monoclinic space group $P2_1/n$ with $a = 5.8151(5)$ Å, $b = 18.106(1)$ Å, $c = 11.515(1)$ Å and $\beta = 96.891(7)^\circ$. In order to understand better its structural aspects in solid state, quantum chemical (PM3) calculations were performed on a part of the extended structure of the title compound containing ten monomers. To determine in vacuo conformational flexibility of the compound, molecular energy profile of the title compound was obtained with respect to a selected torsional degree of freedom and the pedal angle varied from -180° to $+180^\circ$ in every 10°. The results from the computational study suggest that hydrogen-bonding properties in the crystal lattice is fundamental in determining the crystallographically observed conformation of the title compound.

Keywords Azobenzene · Pedal motion · Hydrogen bond · PM3 · Crystal structure

H. Karabıyık (✉)
Department of Physics, Dokuz Eylül University,
35160 Buca, İzmir, Turkey
e-mail: hasan.karabiyik@deu.edu.tr

N. O. İskeleli
Department of Science Education,
Ondokuz Mayıs University,
57000 Sinop, Turkey

Ç. Albayrak · E. Ağar
Department of Chemistry,
Ondokuz Mayıs University,
55139 Samsun, Turkey

Introduction

Azo compounds are the most widely used class of dyes because of their versatile applications in various fields. In particular, azo-containing photochromic organic compounds and azo-conjugated metal complexes have received much attention due to their possible applications in the area of photon-mode high-density information storage, photoswitching devices and optical computing [1–4]. On the other hand, azobenzene is one of the representative photochromic compounds with two geometric isomers, a *trans* form and a *cis* form [5–7]. All azo compounds may occur in one of the isomeric forms: *trans* and *cis*. The *trans*-to-*cis* isomerization occurs by photoirradiation with UV light and *cis*-to-*trans* isomerization proceeds with blue-light irradiation or by heating. It is generally accepted that their *trans* forms are thermodynamically more stable than their *cis* forms [8, 9].

Ogawa and Harada have discovered a common motion in crystals of stilbene- and azobenzene-type compounds, which is named as pedal motion [10]. The orientational disorder observed in azo group for some azobenzenes is dynamic and is ascribed to an interconversion between the two conformers in the crystals [10–12]. The conformational interconversion arises from the pedal motion: a pair of aromatic rings moves like the pedals of a bicycle. In fact, the low occupancy factor of the minor pedal conformer makes the disorder invisible in most crystals. However, the absence of the disorder should be mainly attributable to the destabilization of the minor conformer and does not mean that the pedal motion is inhibited. For this reason, Ogawa and Harada reported that the pedal motion takes place even in non-disordered crystals [10].

In the present paper, details of *trans* stereochemistry of the title compound by single crystal X-ray diffraction technique as a part of general study of the crystal chemistry of dyes and PM3 semi-empirical quantum mechanical method in

order to provide templates for molecular modeling studies are examined. The results obtained from both methods were compared and the crystal packing effects on the exact *trans* configuration of the title compound was revealed. In addition, the pedal motion of the title compound was computationally modeled with the aid of two selected torsion angles, and then molecular energy profile against the pedal angle was calculated.

Experimental

Synthesis of the title compound

A mixture of 4-methylaniline (2 g, 18.7 mmol), water (50 ml) and concentrated hydrochloric acid (4.7 ml, 56 mmol) was stirred until a clear solution was obtained. This solution was cooled to 273–278 K and a solution sodium nitrite (1.8 g, 26 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. 3-Methylphenol (2.02 g, 18.7 mmol) solution (pH 9) was gradually added to a cooled solution of 4-methylbenzenediazonium 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*)-3-methyl-4-(*p*-tolyldiazenyl)phenol. Crystals of (*E*)-3-methyl-4-(*p*-tolyldiazenyl)phenol were obtained after 1 day by slow evaporation from acetic acid (yield 82%, m.p. 398–399 K). Synthesis route of the title compound is shown in Scheme 1.

X-ray crystallography

A suitable sample of size 0.50 mm × 0.40 mm × 0.26 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 room temperature (293 K) using graphite monochromated MoK_α radiation ($\lambda = 0.71073$ Å). The systematic absences and intensity symmetries indicated the monoclinic $P2_1/n$ space group. A total of 17,999 reflections (2682 unique) within the θ range of $[2.11^\circ < \theta < 27.23^\circ]$ for $-7 \le h \le 7$, $-23 \le k \le 23$, $-14 \le l \le 14$ were collected in the rotation mode with $R_{int} = 0.051$. The intensities collected were corrected for Lorentz and polarization factors, absorption correction ($\mu = 0.08$ mm^{-1}) by integration method via X-RED software [13] and cell parameters were determined by using X-AREA software [13]. Extinction correction was not applied. The structure was solved by direct methods using SHELXS-97 [14]. The refinement was carried out by full-matrix least-squares method on the positional and anisotropic temperature parameters of the non-hydrogen atoms, or equivalently corresponding to 155 crystallographic parameters. All H atoms were refined using appropriate riding models, with C–H distances of 0.96 Å for methyl groups, 0.93 Å for aromatic groups and O–H distances of 0.82 Å hydroxyl group. The methyl groups in *ortho* and *para* positions in their parent rings were refined as the idealized disordered methyl groups (two positions). The displacement parameters of H atoms were fixed at 1.2 U_{eq} of their parent carbon atoms for aromatic groups, 1.5 U_{eq} of their parent atoms for methyl and hydroxyl groups. The structure was refined to $R_1 = 0.038$ for observed 1601 reflections which obeyed to the condition of $I > 2\sigma(I)$ and to $R_1 = 0.0637$ for all 2682 data used in refinement process. The maximum peaks and deepest hole observed in the final $\Delta\rho$ map were 0.12 and -0.12 e Å^{-3}, respectively. The scattering factors were taken from SHELXL-97 [14]. Other details of the data collection conditions and parameters of refinement process are summarized in Table 1.

Scheme 1 Synthesis of the title compound

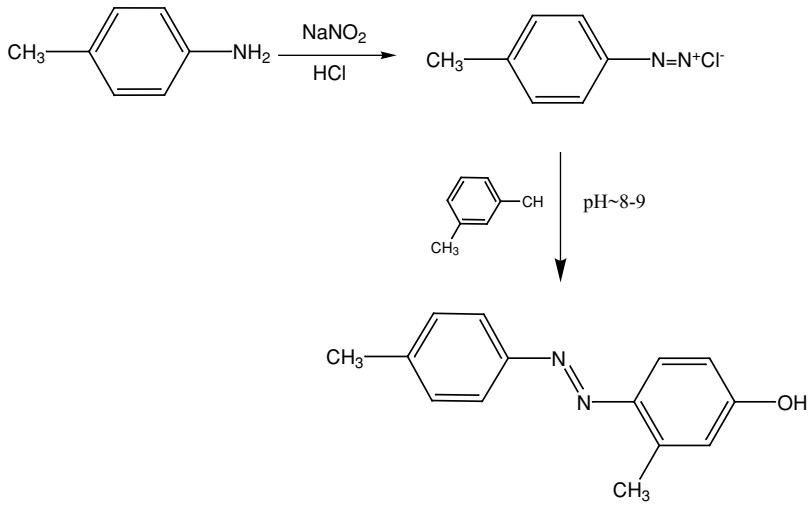

Table 1 Crystallographic data for the title compound

Crystal data	
Chemical formula	$C_{14}H_{14}N_2O$
Color, shape	Yellow, Prism
Formula weight	226.27
Crystal system	Monoclinic
Space group	$P2_1/n$ (No. 14)
Unit cell parameters	$a = 5.8151(5)$ Å
	$b = 18.106(1)$ Å
	$c = 11.515(1)$ Å
	$\beta = 96.891(7)^\circ$
Volume	1203.59(16) Å^3
Z	4
D_x (Mg m^{-3})	1.249
μ (mm^{-1})	0.08
F_{000}	480.0
Crystal size (mm)	$0.50 \times 0.40 \times 0.26$
Data collection	
Diffractometer/meas. meth	STOE IPDS $2/\pi$-scan
Absorption correction	Integration
T_{min}	0.9660
T_{max}	0.9816
No. of measured, independent and observed reflections	17999, 2682, 1601
Criterion for observed reflections	$I > 2\sigma(I)$
R_{int}	0.051
θ_{max} (°)	27.2
Refinement	
Refinement on	F^2
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.038, 0.118, 0.97
No. of relections	2682
No. of parameters	155
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0688P)^2]$
	$P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$	0.001
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.12, −0.12
Extinction coefficient	0.026(4)

Supplementary data

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 621019. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Computational procedures

The *trans* symmetry imposed geometry optimization of the title molecule leading to in vacuo energy minima was performed by using PM3 self-consistent field molecular orbital [15, 16] method with the aid of HyperChem 7.52 package [17]. The optimization was performed by Polak-Ribiere conjugate gradient method [18], RMS gradient of 0.001 kcal/Å mol and convergence criteria of 0.01 kcal/Å mol. The crystallographic coordinates were used as starting geometry for the calculations. The methyl groups having rotational disorder were treated as in one position. The structure associated with the lowest energy according

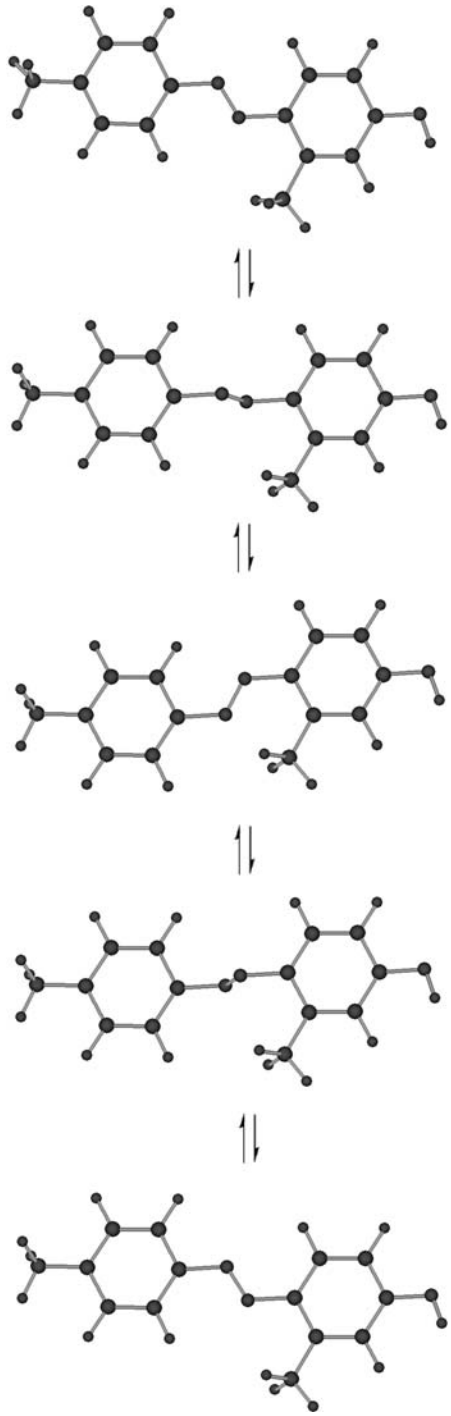

Fig. 1 The stages in the pedal motion of the title compound corresponding to the values of −180°, −90°, 0°, 90° and 180° of the pedal angle ξ

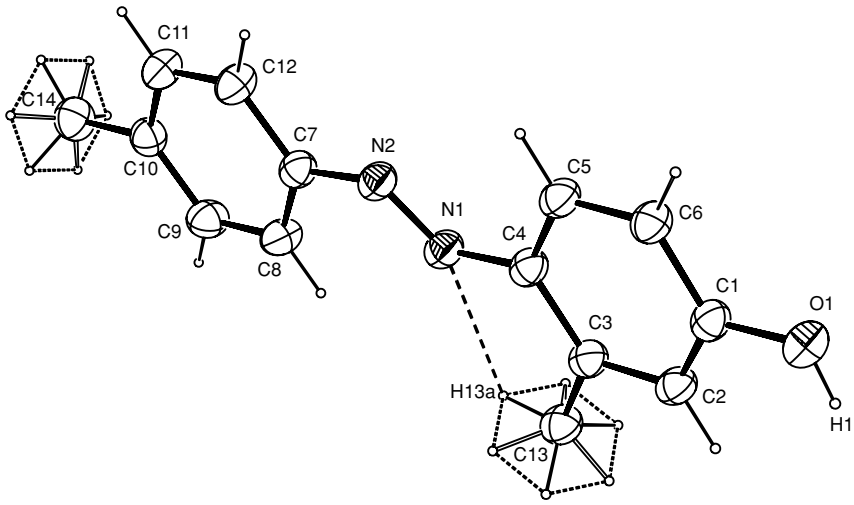

Fig. 2 Ortep drawing of the molecule indicating atom numbering scheme including H-atoms that participate to the formation of inter- and intramolecular hydrogen bonds with 30% probability level. Open methyl C–H bonds represent one of the alternative methyl positions

to the PM3 optimization was compared with the X-ray structure. To clarify conformational preference of the title molecule in solid state and crystal packing effects on the molecules, PM3 quantum chemical calculations were performed on a part of two hydrogen-bonded zigzag chains of the title compound containing ten monomers. We have not employed higher level molecular orbital theory calculations on the part of zigzag chains due to large size of its extended structure containing 170 non-hydrogen atoms (equivalently 820 atomic orbitals). To elucidate conformational preference of the title compound in gas-phase, the selected degree of torsional freedom, T(N2-N1-C4-C3) was varied from -180° to $+180^\circ$ in every 10° and the molecular energy profiles were obtained by performing single-point calculations on the calculated potential energy surface. In addition, a possible pedal motion in the title compound was modeled by PM3 quantum chemical calculations. Pedal motion can be envisaged as two coupled torsional rotations around the single bonds between the azo bridge and the substituted phenyl rings. These rotations around the torsional degrees of freedom T(C12–C7–N2–N1) and T(N2–N1–C4–C3) are coupled with overall motion of the molecule as a whole leads to pedal-like motion in the title compound under the condition prescribing that both torsions are equal in their magnitudes but have opposite signs. The calculations performed to reveal the effect of pedal motion on the conformational flexibility of the title compound involve a set of constrained single-point calculations on the calculated potential energy surface, where the torsion angle ξ_1 for rotation around C7–N2 and ξ_2 for rotation around N1–C4 bond are constrained in such a way that $\xi_1 = -\xi_2$. The pedal angle ξ is also defined by the equation $\xi = \xi_1 = -\xi_2$. Some stages for pedal motion

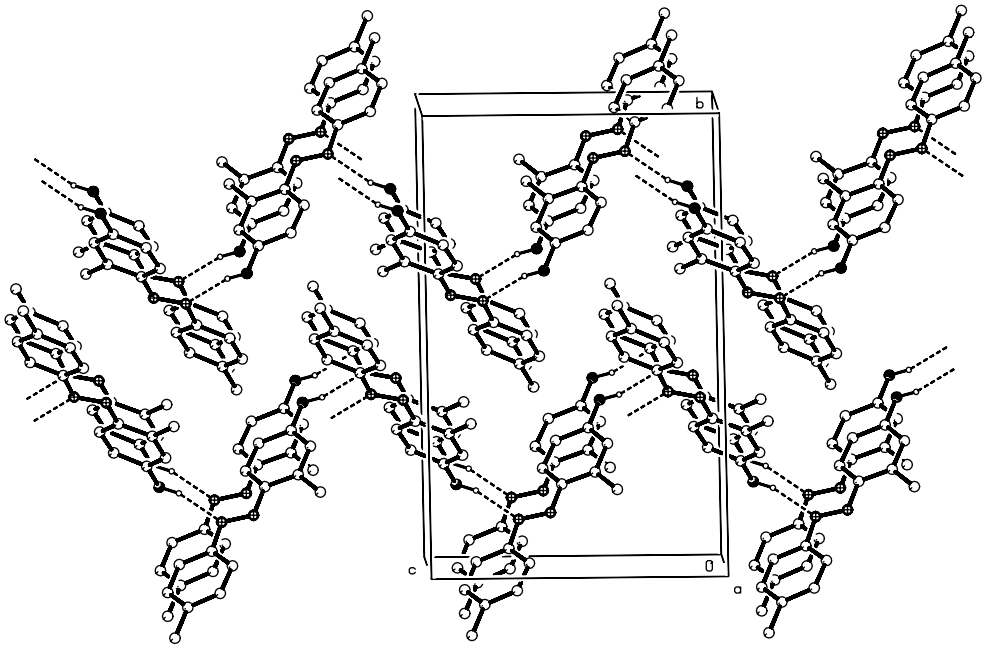

Fig. 3 Hydrogen-bonded zigzag chains along the crystallographic [1 0 1] direction. Dotted lines represent O–H · · · N type intermolecular H-bonds. H atoms except for those participating intermolecular hydrogen bonds are omitted for clarity

Table 2 Atomic coordinates and equivalent isotropic displacement parameters (Å^2) of the non-hydrogen atoms for the title compound

Atom	x	y	z	U_{eq}
O1	−0.17595(16)	0.32799(5)	0.39511(8)	0.0718(3)
N1	0.44627(19)	0.11521(6)	0.58248(9)	0.0633(4)
N2	0.45899(19)	0.10156(5)	0.69023(8)	0.0605(4)
C1	−0.0220(2)	0.27557(7)	0.43923(10)	0.0596(4)
C2	0.1532(2)	0.24934(7)	0.37945(10)	0.0620(4)
C3	0.3051(2)	0.19527(7)	0.42615(10)	0.0593(4)
C4	0.2823(2)	0.16883(6)	0.53888(10)	0.0581(4)
C5	0.1019(2)	0.19477(7)	0.59810(10)	0.0632(4)
C6	−0.0493(2)	0.24710(7)	0.54882(10)	0.0639(4)
C7	0.6295(2)	0.04713(6)	0.72933(10)	0.0595(4)
C8	0.8026(3)	0.02327(8)	0.66496(12)	0.0722(5)
C9	0.9603(3)	−0.02832(8)	0.71154(13)	0.0765(5)
C10	0.9514(2)	−0.05835(7)	0.82136(12)	0.0657(4)
C11	0.7788(3)	−0.03409(8)	0.88406(12)	0.0716(5)
C12	0.6207(3)	0.01844(7)	0.83959(11)	0.0696(5)
C13	0.4883(3)	0.16598(8)	0.35686(12)	0.0718(5)
C14	1.1207(3)	−0.11647(9)	0.87058(14)	0.0847(6)

Note. U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

of the title compound corresponding to principal values of the pedal angle is illustrated in Fig. 1.

Results and discussion

Structure determination

The title compound of which an Ortep [19] view of the monomers in its asymmetric unit is shown in Fig. 2 crystallizes in the monoclinic space group $P2_1/n$ with four monomers in the unit cell. Non-hydrogen atomic coordinates and equivalent isotropic thermal parameters are listed in Table 2.

N1 and N2 atoms are nearly in the same planes of 1-methyl-3-hydroxyphenyl and 3-methyl phenyl rings with the respective deviations of 0.028(1) and 0.012(1) Å. In the title compound, the aromatic rings, which adopt a distorted *trans* configuration around the N=N double bond, are not coplanar with the value of −166.69(10)° for the pedal angle. In the azo groups, C7–N2 and C4–N1 bond lengths, which reflect their single bond character, are found as 1.432(2) and 1.410(2) Å, respectively; whereas N1–N2 bond length is 1.259(1) Å. This value obviously indicates its double bond character. Corresponding values of these bond lengths mentioned above for similar compounds are of consistence with the previously reported studies in the literature [20–28]. N2–C7 and N1–C4 bond distance are of remarkable difference due to a possible through-resonance effect between the electron-donating hydroxyl group and the two-electron-accepting N atom.

Table 3 Hydrogen-bonding geometries (Å, °) for the title compound

D–H···A	D–H	H···A	D···A	∠D–H···A
C13–H13a···N1	0.96	2.31	2.794(2)	110
O1–H1···N2[a]	0.82	2.08	2.873(1)	164

Note. D: donor, A: acceptor.

[a] Symmetry transformations used to generate equivalent atoms: −1/2 + x, 1/2 − y, −1/2 + z.

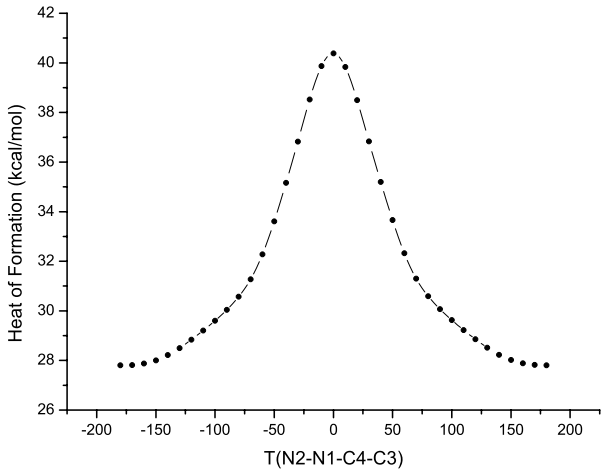

Fig. 4 Molecular energy profile of the PM3 optimized counterpart of the title compound against the selected degree of torsional freedom

We have used PARST [29] to analyze the intra- and intermolecular hydrogen bonds in the crystal structure. There is only one C–H···N type intramolecular hydrogen bond in the structure, C13–H13a···N1. The C13···N1 distance is shorter than the sum of the van der Waals radii of C and N (3.25 Å). The intramolecular hydrogen bond supplies leading contribution to the stabilization of the crystallographically observed conformation of the title compound. Further details about the hydrogen-bonding geometries observed in the crystal structure can be found in Table 3. It is worth noting that the intermolecular hydrogen-bonding interactions in the crystal packing are the most important feature in terms of supramolecular environment of the title compound. When the monomers are interconnected with the O–H···N type intermolecular H-bonds, polymeric chains are formed in the crystal structure. The axis of the hydrogen-bonded zigzag chains runs co-linear with the crystallographic [1 0 1] direction (Fig. 3). The primary hydrogen-bonded motif in the crystal structure can be described as a graph-set motif of $C(8)$ [30].

Computational study

The *trans* symmetry imposed semi-empirical PM3 molecular orbital calculations were carried out in order to define

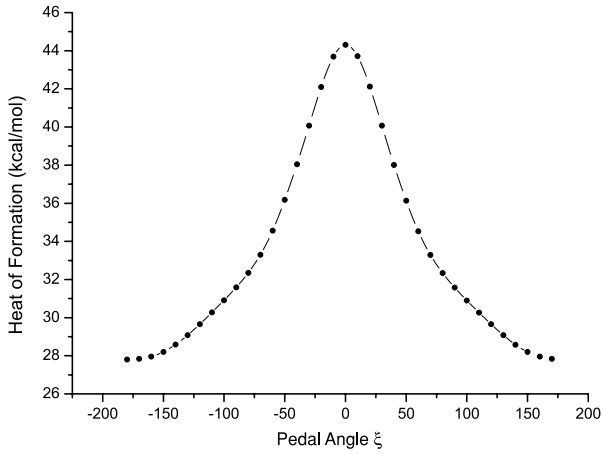

Fig. 5 Molecular energy profile against the pedal angle

the gas-phase conformational flexibility of the title molecule as a function of the selected degree of torsional freedom, T(N2–N1–C4–C3). According to the results (Fig. 4), there is an evident increase in molecular energy in vicinity of 0° due to the steric hindrance between the methyl group in *ortho* position and azo bridge in the compound. Energy difference between the most favorable and unfavorable gas-phase conformer of the title compound, which arises from rotational potential barrier calculated with respect to the selected torsion angle, is calculated as 12.6 kcal/mol. On the other hand, to properly define in vacuo conformational flexibility of the compound, the pedal motion in addition to the rotation around the torsional degree of freedom T(N2–N1–C4–C3) should be also incorporated into the discussion. Molecular energy profile against the pedal angle is shown in Fig. 5. There is an evident maximum in the profile for $\xi = 0°$. Pedal barrier defined as energy difference between the most favorable and unfavorable pedal conformer of the compound is 16.5–kcal/mol in gas-phase. According to the Fig. 5, it can be stated that the planar geometry of the title compound ($\xi = \pm 180°$) is the most stable pedal conformer in gas-phase and the crystallographically observed conformation of the title compound is slightly different from the global minimum on the potential energy surface of the compound. As far as these results are concerned that the crystallographically observed conformation of the compound is near to the global energy minimum in gas-phase. However, the most important fact remains that the experimentally observed conformation of the compound in the absence of the crystal lattice environment is not the lowest-energy conformation for this system.

In solid state, hydrogen bonds are practically never in optimal geometry, and are always influenced by their environment. For this reason, to recognize crystal packing effects on the molecular conformation, a series of quantum chemical PM3 calculations were performed on both the isolated

Table 4 Some geometrical parameters (Å, °) for X-ray and PM3 optimized structure in the part involving ten monomers of the title compound

	X-ray	PM3
Bond lengths		
O1–C1	1.360(2)	1.358
C13–C3	1.502(2)	1.490
C14–C10	1.505(2)	1.483
C7–N2	1.432(2)	1.453
N2–N1	1.259(1)	1.236
C4–N1	1.410(2)	1.436
Bond angles		
N1–N2–C7	113.69(10)	117.30
N2–N1–C4	116.32(11)	121.10
C3–C4–N1	115.39(11)	116.88
C9–C10–C14	121.63(14)	120.29
Torsion angles		
C12–C7–N2–N1	− 167.02(11)	− 160.08
C7–N2–N1–C4	− 179.58(9)	178.40
N2–N1–C4–C3	166.37(10)	159.08

structure and the structure surrounded by nine molecules in two neighbor chains in the crystal lattice. When the X-ray structure of the title compound is contrasted with its in vacuo PM3 optimized counterpart, it is seen that there is a conformational discrepancy between them, especially observed in the relative orientation of the substituted rings in the title compound. Although the PM3 optimized geometry of a single monomer is essentially planar as different from the X-ray structure, the PM3 optimized geometry of the title compound in the hydrogen-bonded extended structure is non-planar. In this sense, the structure obtained from the geometry optimization considering ten hydrogen-bonded monomers in solid state is more similar to the crystallographically observed monomer units than the PM3 optimized geometry of a single monomer. The r.m.s. (root-mean square) fit of the PM3 optimized gas-phase conformation of the title compound to the crystallographically observed conformation is well (r.m.s.d. = 0.1757 Å), but the r.m.s. fit of the PM3 optimized conformation calculated by considering ten monomers in two neighbor zigzag chains to the experimentally observed conformation is better than the former fit (r.m.s.d. = 0.1238 Å). The selected geometrical parameters for the PM3 optimized counterpart of the title compound in its hydrogen-bonded extended structure and the crystallographically observed conformation are given in Table 4. The optimized geometry in the hydrogen-bonded extended structure is the pedal conformer with the angle ($\xi = -160.08°$). The experimentally observed and the optimized structure in its extended structure indicate two different pedal conformers of the compound, but these pedal conformers corresponding to $\xi = -166.69(10)°$ and $\xi = -160.08°$ are of no remarkable difference in energy. It is obvious that when all neighbor

monomers in the crystal lattice are included in the calculation, the PM3 optimized conformation of the title compound closely matches the crystallographically observed structure. Consequently, it can be stated that hydrogen-bonding properties and packing effects in the crystal lattice as well is fundamental in determining the experimentally observed pedal conformer of the compound and supply leading contribution to its stabilization, presumably to optimize the formation of its hydrogen-bonded polymeric zigzag chains.

Acknowledgment Hasan Karabıyık would like to thank TÜBİTAK (The Scientific and Technical Research Council of Turkey) for partial financial support.

References

1. Nishihara H (2004) Bull Chem Soc Jpn 77:407
2. Joachim C, Gimzewski JK, Aviram A (2000) Nature 408:541
3. Nishihara H, Kurashina M, Murata M (2003) Macromol Symp 196:27
4. Kurashina M, Murata M, Watanab T, Nishihara H (2003) J Am Chem Soc 125:12420
5. Lee M-J, Yoo BW, Shin ST, Keum SR (2001) Dyes Pigments 51:15
6. Aramaki S, Atkinson GH (1992) J Am Chem Soc 114:438
7. Tamai N, Miasaka H (2000) Chem Rev 100:1875
8. Azuki M, Morihashi K, Watanabe T, Taskahashi O, Kikuchi O (2001) J Mol Struct THEOCHEM 542:255
9. Grebenkin SY, Bolshakov BV (1999) J Photochem Photobiol A Chem 122:205
10. Harada J, Ogawa K (2001) J Am Chem Soc 123:10884
11. Harada J, Ogawa K, Tomoda S (1997) Acta Crystallogr B 53:662
12. Ocak-İskeleli N, Karabıyık H, Albayrak Ç, Petek H, Ağar E (2006) J Chem Cryst 36:709
13. Stoe Cie (2002) X-ARAEA (Version 1.18) and X-RED32 (Version 1.04), Darmstadt, Germany
14. Sheldrick GM (1997) SHELXS-97 and SHELXL-97, Programs for the solution and refinement of crystal structures. University of Göttingen, Germany
15. Stewart JJP (1989) J Comput Chem 10:209
16. Stewart JJP (1989) J Comput Chem 10:221
17. Hypercube (2003) HyperChem, Version 7.52. Hypercube Inc., 1115 NW 4th Street, Gainsville, FL 32601-4256, USA
18. Fletcher P (1990) Practical Methods of Optimization. Wiley, New York
19. Farrugia LJ (1997) J Appl Cryst 30:565
20. Albayrak Ç, Odabaşoğlu M, Büyükgüngör O, Lönnecke P (2004) Acta Cryst C60:o318
21. Şahin O, Albayrak Ç, Odabaşoğlu M, Büyükgüngör O (2005) Acta Cryst E61:o4154
22. Deveci Ö, Işık Ş, Albayrak Ç, Ağar E (2005) Acta Cryst E61:o3226
23. Deveci Ö, Işık Ş, Albayrak Ç, Ağar E (2005) Acta Cryst E61:2878
24. Özdemir G, Işık Ş, Albayrak Ç, Ağar E (2006) Acta Cryst E62:o342
25. Kocaokutgen H, Gür M, Soylu MS, Lörnnecke P (2004) Acta Cryst E60:o1756
26. Yazıcı S, Albayrak Ç, Ağar E, Şenel İ, Büyükgüngör O (2006) Acta Cryst E62:o521
27. Ocak-İskeleli N, Karabıyık H, Albayrak Ç, Petek H, Ağar E (2006) Struc Chem 17:393
28. Yatsenko AV, Paseshnichenko KA (2001) Acta Cryst C57:961
29. Nardelli M (1995) J Appl Cryst 28:659
30. Bernstein J, Davis RE, Shimoni L, Chang N-L (1995) Angew Chem Int Ed Engl 34:1555