ORIGINAL PAPER

# Anchor Effect on Pedal Motion Observed in Crystal Phase of an Azobenzene Derivative

Hasan Karabıyık • Hande Petek • Nazan Ocak İskeleli • Çiğdem Albayrak • Erbil Ağar

Received: 5 March 2009/Accepted: 9 June 2011/Published online: 7 July 2011 © Springer Science+Business Media, LLC 2011

Abstract Some molecules having a molecular skeleton similar to that of stilbenes and azobenzenes show orientational disorder in the crystals due to pedal motion. Heretofore, the orientational disorder through pedal motion has been observed for the compounds containing only two aromatic rings in the absence of bulky substituent groups. Here we report that the pedal motion can be detected even in the presence of a bulky substituent group to which orientational disorder becomes invisible as a result of anchor effect arising from phenoxyphtalonitrile group. X-ray crystallographic analysis of the compound, C23H18N4O, reveals the existence of partially overlapped two pedal conformers. The compound crystallizes in the monoclinic space group  $P2_1/c$  with a = 12.9429(11) Å, b = 8.5075(5) Å, c = 21.063(2) Å and  $\beta = 123.155(6)^{\circ}$ . Major pedal conformer is stabilized by weak C–H···O type hydrogen bond and C–H··· $\pi$  type edge-to-face interactions in solid state. Quantum chemical

H. Karabıyık (🖂)

H. Petek Department of Physics, Ondokuz Mayıs University, 55139 Samsun, Turkey

N. O. İskeleli

Department of Science Education, Ondokuz Mayıs University, 55139 Samsun, Turkey

Ç. AlbayrakDepartment of Science Education, Sinop University, 57010 Sinop, Turkey

E. Ağar Department of Chemistry, Ondokuz Mayıs University, 55139 Samsun, Turkey calculations at B3LYP/6-311G+(d,p) level suggest that the stabilization of the compound decreases with increasing deviation from the planar geometry of *trans*-azobenzene fragment.

**Keywords** Pedal motion · Azobenzene · Orientational disorder · Conformational interconversion

## 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 sense, molecular motions in crystals are of great importance in determining the effects on their physical properties and in understanding structure-activity relationship. It has been already wellknown that molecules having skeletons similar to those of stilbenes and azobenzenes show orientational disorder in the crystal phase [5-10]. The disorder observed in some azobenzenes is dynamic, and therefore ascribed to an interconversion between the two pedal conformers [11]. The conformational interconversion occurred in crystal phase of such compounds is due to unusual molecular motion referred to as the pedal motion: a pair of benzene rings moving like the pedals of a bicycle [12]. Pedal-like motion (or crankshaft motion) is not only peculiar to stilbene and azobenzene type molecules, it is also one of the key processes in the photochromism of salicylideneanilines [13], the photodimerization of *trans*-cinnamides [14, 15] and photoisomerization of 1,4-diaryl-1,3-butadienes [16]. On the other hand, azobenzene moieties have been recently used in preparation of molecular machines [17, 18], and

Department of Physics, Dokuz Eylül Universitesi, Fen Fakültesi, Fizik Bölümü, Tinaztepe Kampusu, 35160 Buca, Izmir, Turkey e-mail: hasan.karabiyik@deu.edu.tr

pedal motion is of great importance to put them into versatile practise.

The absence of orientational disorder in azobenzene compounds should 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 general, the low occupancy factor (less than 0.1) of the minor pedal conformer makes the disorder invisible in most crystals. Ogawa and Harada [19, 20] reported that the pedal motion takes place even in crystal samples without disorder. As a result of this, orientational disorder arising from dynamical reasons and conformational interconversion through pedal-like motion has been overlooked in most crystal structures of such compounds [19, 20].

Pedal motion in azobenzene-like compounds has been generally observed in the compounds containing two aromatic rings carrying small substituent groups up to the present [19-23]. Since such compounds do not have a bulky substituent group, it is reasonable to consider that the detection of an unfavorable (minor) pedal conformer in their crystal structures is become difficult by anchor effect arising from the presence of a bulky substituent group. Another factor affecting the population of unfavorable minor conformer is also temperature in data collection stage. 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 is detectable only at a high temperature [19, 20]. Under certain circumstances, even if temperature is high enough, the detection of unfavorable conformer is limited by the following reasons. The intensity of diffraction spots at high temperature rapidly drops off at higher scattering angles due to large thermal motion of atoms at lattice sites. In this regard, it is reliable to measure only reflections with low angles. Moreover, structure of the disordered conformers is blurred by the thermal motion of the molecules in crystal phase. Therefore, a high-quality X-ray diffraction analysis of such crystals is needed to detect minor conformer in the presence of bulky substituents.

Possible effects of various substituent groups on pedal motion in solid-state have not been well-recognized yet. Recently, we have showed that small aryl substituents on the phenyl rings accompany pedal motion synchronously [23]. However, it is not fully understood how pedal motion is affected by the presence of bulky substituents on the phenyl rings. In a continuation of our interest regarding pedal motion, here we report that the effect of a bulky substituent group such as phenoxyphtalonitrile on pedal motion occurred in crystal-phase and *trans* stereochemistry of an azobenzene derivative, 4-[2-Methyl-4-(4-ethyl-phenyldiazenyl)]phenoxyphtalonitrile, are investigated by single crystal X-ray diffraction technique and quantum

chemical calculations by means of Density Functional Theory at B3LYP/6-311+G(d,p) level.

## Experimental

### Synthesis of the 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  $\sim$  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 2-Methyl-4-(4-ethylphenyldiazenyl)phenol (yield 76%, m.p. 398-400 K). To a solution of solid (1 g, 4.1 mmol) in DMF was added potassium carbonato (1.15 g, 8.2 mmol). The mixture was stirred for 30 min under N<sub>2</sub>. 4-nitrophtalonitrile solution in DMF was added. The mixture was stirred for 48 h at 323 K under N<sub>2</sub> and poured into ice-water (150 g). The product was filtered off and washed with water. The product was recrystallized from ethyl alcohol to obtain solid 4-[2methyl-4-(4-ethylphenyldiazenyl)]phenoxyphtalonitrile. Crystals of 4-[2-methyl-4-(4-ethylphenyldiazenyl)]phenoxyphtalonitrile were obtained from ethanol:  $CCl_4$  (1:2) mixture at room temperature via slow evaporation (yield 67%, m.p. 401-403 K) (Scheme 1).

## X-ray Crystallography

A suitable sample of size  $0.60 \times 0.33 \times 0.11$  mm was chosen for the crystallographic study and then carefully mounted on goniometer of a STOE IPDS II diffractometer. All diffraction measurements were performed at 296 K using graphite monochromated MoK<sub>a</sub> radiation ( $\lambda = 0.71073$  Å). The systematic absences and intensity symmetries indicated the monoclinic  $P2_1/c$  space group. A total of 19,409 reflections (3,798 unique) within the  $\theta$  range of [1.88° <  $\theta < 26.00^\circ$ ] for  $-15 \le h \le 15$ ,  $-10 \le k \le 10$ ,  $-25 \le l \le 25$  were collected in the rotation mode with  $R_{int} = 0.072$ . The intensities collected were corrected for Lorentz and polarization factors, absorption correction ( $\mu = 0.08 \text{ mm}^{-1}$ ) by integration method via X-RED software [24] and cell parameters were determined by using X-AREA software [24].



H<sub>2</sub>C



solved by direct methods using SHELXS-97 [25]. 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 347 crystallographic parameters. All H atoms were refined using pertinent riding models, with C-H distances of 0.96 Å for methyl groups, 0.97 Å for methylene groups, 0.93 Å for aromatic groups. 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 methylene groups. The structure was refined to  $R_1 = 0.059$  for observed 2,196 reflections prescribed by the condition of  $I > 2\sigma(I)$  and to  $R_1 = 0.134$  for all 3,798 data used in refinement process. The maximum peaks and deepest hole observed in the final  $\Delta \rho$  map were 0.29 and  $-0.30 \text{ e}\text{\AA}^{-3}$ , respectively. The scattering factors were taken from SHELXL-97 [25]. Other details of the data collection conditions and parameters of refinement process are summarized in Table 1.

## Computational Details

All quantum chemical calculations for the compound was performed by utilizing DFT computation with the use of Becke's three-parameters hybrid exchange-correlation functional B3LYP [26] incorporating B88 gradient-corrected exchange [27] and Lee-Yang-Parr non-local correlation functional [28] by means of 6-311+G(d,p) basis set implemented in Gaussian 03W program package [29]. Geometry optimization of the compound was achieved by the application of Berny optimization algorithm [30]. Instead of conventional SCF iterations, quadratically convergent SCF [31] routine was used to guarantee to reach a stationary point on the potential energy surface. The values of the convergence criteria for geometry optimization are below  $4.5 \times 10^{-4}$  hartree/bohr for maximum force,  $3 \times 10^{-4}$  hartree/bohr for RMS force,  $1.8 \times 10^{-3}$  Å for maximum displacement, and  $1.2 \times 10^{-3}$  Å for RMS displacement. To be able to compare stabilization levels of the

#### Table 1 Crystallographic data for the compound

Crystal data	
Crystal size	$0.60 \times 0.33 \times 0.11 \text{ mm}$
Color, shape	Orange, prism
Chemical formula	$C_{23}H_{18}N_4O$
Formula weight	366.41
Crystal system	Monoclinic
Space group	$P2_{1}/c$
Unit cell parameters	a = 12.9429 (11)  Å
	b = 8.5075 (5) Å
	c = 21.063 (2) Å
	$\beta = 123.155 \ (6)^{\circ}$
Volume	1941.7 (3) Å <sup>3</sup>
Ζ	4
$D_{\rm x} ~({\rm Mg}~{\rm m}^{-3})$	1.253
<i>F</i> (000)	768
Data collection	
Diffractometer/meas. meth.	STOE IPDS 2/m-scan
Absorption correction type	Integration
$T_{\min}, T_{\max}$	0.960, 0.985
No. of measured, independent and observed reflections	19,409, 3,798, 2,196
Criterion for observed reflections	$I > 2\sigma(I)$
R <sub>int</sub>	0.072
$\theta_{\max}$ (°)	26.00
Refinement	
Refinement on	$F^2$
$R[I > 2\sigma(I)], \text{ GoF}(S)$	0.059, 0.923
Weighting scheme	w = 1/ $[\sigma^2(F_o^2) + (0.1223P)^2]$
	$P = (F_{\rm o}^2 + 2 F_{\rm c}^2)/3$
$(\Delta/\sigma)_{\rm max}$	< 0.001
$\Delta \rho_{\rm max}, \ \Delta \rho_{\rm min} \ ({\rm e}{\rm \AA}^{-3})$	0.29, -0.30

crystallographically observed pedal conformers, their total energies were calculated at the same level of theory on the crystallographically observed geometries with the aid of single-point calculations.

#### **Results and Discussion**

X-ray crystallographic analysis of the compound reveals that two pedal conformers partially overlapped coexist in the same crystal lattice at 296 K. A thermal ellipsoid view [32] of them is shown in Fig. 1. The compound crystallizes in the monoclinic space group  $P2_1/c$ . Minor conformer (B) of the compound having 44% site occupancy factor coexist with stable major pedal conformer (A) 56% site occupancy factor in crystal phase. Selected geometrical parameters for both conformers obtained from crystallographic analysis and the computational study are listed in Table 2.

Pedal motion is essentially related to the molecular fragments around azo-bridge, and therefore conformational interconversion through pedal motion is primarily observed in the orientations of two aromatic rings lying at opposite sides of azo-bridge in such compounds. It is worth noting certain differences in relative orientations of the molecular fragments around azo-bridge (N=N). Although the difference between the orientations of the major and minor component in 4-ethylphenyl ring is evident, the orientations of the major and minor component of the other ring participating to pedal motion are slightly different. While dihedral angle between the mean planes through major and minor component of 2-methylphenyl ring is  $4.4(1)^{\circ}$ , dihedral angle between the mean planes through major and minor component of 4-ethylphenyl ring is 20.2(6)°. The difference between relative orientations of the major and minor components of the substituted rings linked by azobridge is due to the presence of bulky substituent group, i.e., phenoxyphtalonitrile. It is inferred from these results that the difference in atomic positions of the major and minor components is reduced to being more negligible toward bulky substituent and therefore residual peaks corresponding to phenoxyphtalonitrile fragment of the minor conformer can not be appeared independently. Thus, positional separations of certain atom pairs such as C9A/B, C10A/B, C14A/B and C15A/B on 2-methylphenoxy fragment are not sufficiently distinguishable. In particular, C9A and C9B (nearest atoms to phenoxyphtalonitrile fragment) have almost coincident atomic positions with interatomic separation of 0.127 Å. Therefore, phenoxyphtalonitrile fragments belonging to major and minor pedal conformers of the compound are properly overlapped and the crystal structure of the compound can not be completely refined as a superposition of two pedal conformers.

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 electrondonating O atom and the two-electron accepting N atom in azo-bridge as being in general agreement with those in previously reported azobenzene compounds [33–38]. N=N bond distances in the disordered azo-bridge are comparable with those of similar compound previously reported [33–38].

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. During these changes, an intermediate crystal phase may be regarded as either mixed crystals in which various conformers are held together in the same crystal lattice or pure crystals in which only one conformer is trapped during the



**Fig. 1** Orientation of thermal ellipsoid views of the major (A) and minor (B) conformers of the title compound with the atom numbering scheme of non-H atoms. Displacement ellipsoids are drawn at the

Table 2 Selected geometrical parameters (Å, °) for the crystallographically observed conformers and optimized geometry of the compound

Bond lengths	X-ray	B3LYP/6-311+G(d, p)
01–C9A	1.400(9)	1.413
O1-C9B	1.40(1)	
N1-C1	1.143(4)	1.172
N2-C2	1.139(4)	1.173
C16A-N4A	1.44(1)	1.406
C16B-N4B	1.43(2)	
N3A–N4A	1.250(6)	1.292
N3B–N4B	1.246(8)	
N3A-C12A	1.53(1)	1.410
N3B-C12B	1.54(3)	
Bond angles	X-ray	B3LYP/6-311+G(d, p)
N3A-N4A-C16A	115(1)	115.00
N3B-N4B-C16B	108.0(2)	
N4A-N3A-C12A	103(1)	114.47
N4B-N3B-C12B	93(1)	
Torsion angles	X-ray	B3LYP/6-311+G(d, p)
C17A-C16A-N4A-N3A	5.5(14)	0.43
C21A-C16A-N4A-N3A	-174.1(9)	-179.57
N4B-N3B-C12B-C11B	171.7(4)	0.26
N4B-N3B-C12B-C13B	-15.4(6)	179.46

molecular motion in solid-state. 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. Two type crystal packing interactions associated with the major conformer of the compound are observed in the crystal structure. Molecular packing arrangement of both pedal conformers of the compound is shown in Fig. 2. The crystal structure is stabilized by C–H…O type weak intermolecular hydrogen bonding

30% probability level. Major and minor conformers are represented by *solid* and *broken lines*, respectively

(C23A-H23B...O1) between the major components and C–H $\cdots\pi$  type edge-to-face interaction involving 2-methylphenyl rings of the major components. Distance of H---Cg1 [at (1 - x, 1/2 + y, 3/2 - z)] and C-H··· $\pi$  angle for the interaction of C10A–H10A··· $\pi$  are found as 2.95 Å and 158°. Donor acceptor distance and the D-H...A angle regarding the weak intermolecular hydrogen bonding are found as 3.460(9) Å and 149.4° with the symmetry code [1 - x, 1 - y, 1 - z]. These intermolecular interactions serve to stabilize major components in crystal structure. According to graph-set notation [39], C-H...O type weak H-bond generates  $R_2^2(14)$  pseudo-cyclic centrosymmetric dimers having symmetry centre at  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$  for major components in the crystal structure as shown in Fig. 2 and C-H··· $\pi$  interactions serve to be strengthened dimeric packing arrangement.

Conformational discrepancies between the optimized molecule and the crystallographically observed geometries of the compound were quantitatively analyzed by r.m.s. overlays including H atoms as shown in Fig. 3. While the r.m.s. fits of the atomic positions of the optimized geometry (green) to their corresponding values in the major (red) and minor (blue) conformer of the compound are obtained as 0.125 Å and 0.139 Å respectively, the r.m.s. fit of the atomic positions in major and minor component is 0.104 Å. These values correlate well with the stabilization levels of the conformers. As far as the results from computational study concerned that, as expected, major pedal conformer is more stable than minor component by 13.297 kcal/mol. Total energy values of the major and minor pedal conformers with respect to the optimized geometry of the compound are 55.420 and 68.717 kcal/ mol, respectively.

There are some noteworthy geometrical discrepancies between the optimized and crystallographically observed geometries, in particular orientations of aryl ( $-C_2H_5$ ) and phenoxyphtalonitrile fragment. In the optimized geometry, *trans*-azobenzene fragment is planar as expectedly [40, 41], whereas crystallographically observed azobenzene **Fig. 2** Packing of the dimers formed by C–H···O type weak H-bonds and C–H··· $\pi$ interactions. Minor pedal conformers and H atoms not involved in the motif have been ignored for the sake of clarity. Symmetry operations used to generate equivalent atomic positions: (1) 1 - *x*, 1 - *y*, 1 - *z* and (2) 1 - *x*, 1/2 + *y*, 3/2 - z





Fig. 3 Superimpositions of **a** the major conformer (*red*) and the optimized geometry (*green*), **b** the minor conformer (*blue*) and the optimized geometry (*green*) and **c** the major (*red*) and minor conformer (*blue*) (Color figure online)

fragments are not planar due to pedal motion. Dihedral angle between the mean planes through planar azobenzene fragment and phenoxyphtalonitrile fragment is  $74.20^{\circ}$  in the optimized geometry. Dihedral angles between substituted aromatic rings lying at opposite sides of azo-bridge are  $12.6(9)^{\circ}$  for major component and  $23.3(8)^{\circ}$  for minor component. Considering these, it can be stated that deviation from the planar geometry of *trans*-azo benzene fragment has an adverse effect on the stabilization of the compound. Therefore, co-planarity of aromatic rings participating in pedal motion supplies primary contribution to stabilization of the compound. On the other hand, C23A and C23B are out of plane with deviations of -0.42(2) Å and -0.19(3) Å from their related ring planes. It can be inferred from these results that the stabilities of pedal conformers are proportional to the amount of the out-of-plane separation of ethyl group, and their stability is increased as the amount of deviation of ethyl group from the related ring plane increases.

## Conclusion

In conclusion, X-ray crystallographic study of the compound reveals that detection of pedal conformers becomes difficult by anchor effect accompanying pedal motion from the presence of bulky substituent group. Quantum chemical calculations suggest a guiding rule of how far breaking the planarity of trans-azobenzene moiety decreases the stabilization level of whole molecule. Intermolecular interactions and weak H-bonds supply leading contribution to the stabilization of the major pedal conformers. More interestingly, an important effect on the pedal motion in terms of molecular motions occurred in solid state have been firstly recognized and examined in this study. As known, some of recent technological advances have based on the tools to manipulate and measure the properties of single molecules. After this study was submitted to publish, Kim et al. [42] have reported that molecular rotors based on

azobenzene derivatives can be controlled by the presence of anchoring sites on Au(111) surface. Therefore, our results are of great importance in designing novel molecular machines and engineering crystal structure.

## **Supplementary Data**

Crystallographic data (excluding structure factors) for the structure re-ported in this article have been deposited with the Cambridge Crystallo-graphic Data Centre as supplementary publication number CCDC 625922. 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: data\_request@ccdc.cam.ac.uk).

Acknowledgments The authors wish to acknowledge Ondokuz Mayıs University for the use of the STOE IPDS II diffractometer purchased under Grants F.279 and F.377.

#### References

- 1. Paul IC, Curtin DY (1973) Acc Chem Res 6:217–225
- 2. Gavezzotti A, Simonetta M (1982) Chem Rev 82:1-13
- 3. Bürgi HB (2000) Annu Rev Phys Chem 51:275–296
- 4. Bürgi HB (2002) Faraday Discuss 122:41-63
- 5. Finder CJ, Newton MG, Allinger NL (1974) Acta Cryst B 30: 411–415
- 6. Bernstein J (1975) Acta Cryst B 31:1268-1271
- 7. Hoekstra A, Meertens P, Vos A (1975) Acta Cryst B 31: 2813–2817
- 8. Bouwstra JA, Schouten A, Kroon J (1983) Acta Cryst C 39: 1121–1123
- 9. Bouwstra JA, Schouten A, Kroon J (1984) Acta Cryst C 40: 428–431
- 10. Brown CJ (1966) Acta Cryst 21:146-152
- 11. Harada J, Ogawa K, Tomoda S (1997) Acta Cryst B 53:662-672
- 12. Harada J, Ogawa K (2009) Chem Soc Rev 38:2244-2252
- Harada J, Uekusa H, Ohashi Y (1999) J Am Chem Soc 121: 5809–5810
- 14. Ito Y, Hosomi H, Ohba S (2000) Tetrahedron 56:6833-6844
- 15. Ohba S, Hosomi H, Ito Y (2001) J Am Chem Soc 123:6349–6352
- Saltiel J, Krishna TSR, Laohhasurayotin S, Fort K, Clark RJ (2008) J Phys Chem A 112:199–209
- McCullagh M, Franco I, Ratner MA, Schatz GC (2011) J Am Chem Soc 133:3452–3459
- Choi B-Y, Kahng S-J, Kim S, Kim H, Kim HW, Song YJ, Ihm J, Kuk Y (2006) Phys Rev Lett 96:156106

- 19. Harada J, Ogawa K (2001) J Am Chem Soc 123:10884–10888 and references therein
- 20. Harada J, Ogawa K (2009) Chem Soc Rev 38:2244-2252
- 21. Harada J, Ogawa K (2004) J Am Chem Soc 126:3539-3544
- Adams H, Allen RWK, Chin J, O'Sullivan B, Styring P, Sutton LR (2004) Acta Cryst E 60:o289–o290
- 23. Ocak-Iskeleli N, Karabiyik H, Albayrak C, Agar E (2008) J Chem Cryst 38:671–677
- 24. Stoe & Cie (2002) X-ARAEA (Version 1.18) and X-RED32 (Version 1.04), Darmstadt, Germany
- 25. Sheldrick GM (2008) Acta Cryst A 64:112-122
- 26. Hertwig RH, Koch W (1997) Chem Phys Lett 268:345-351
- 27. Becke AD (1988) Phys Rev A 38:3098–3100
- 28. Lee C, Yang W, Parr RG (1988) Phys Rev B 37:785-789
- 29. Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Montgomery JA, Vreven T Jr, Kudin KN, Burant JC, Millam JM, Iyengar SS, Tomasi J, Barone V, Mennucci B, Cossi M, Scalmani G, Rega N, Petersson GA, Nakatsuji H, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Klene M, Li X, Knox JE, Hratchian HP, Cross JB, Adamo C, Jaramillo J, Gomperts R, Stratmann RE, Yazyev O, Austin AJ, Cammi R, Pomelli C, Ochterski JW, Ayala PY, Morokuma K, Voth GA, Salvador P, Dannenberg JJ, Zakrzewski VG, Dapprich S, Daniels AD, Strain MC, Farkas O, Malick DK, Rabuck AD, Raghavachari K, Foresman JB, Ortiz JV, Cui Q, Baboul AG, Clifford S, Cioslowski J, Stefanov BB, Liu G, Liashenko A, Piskorz P, Komaromi I, Martin RL, Fox DJ, Keith T, Al-Laham MA, Peng CY, Nanayakkara A, Challacombe M, Gill PMW, Johnson B, Chen W, Wong MW, Gonzalez C, Pople JA (2003) Gaussian 03 W Revision E.01. Gaussian Inc, Pittsburgh
- 30. Schlegel HB (1982) J Comput Chem 3:214-218
- 31. Bacskay GB (1981) Chem Phys 61:385-404
- 32. Spek AL (2009) Acta Cryst D65:148-155
- Iskeleli NO, Karabiyik H, Albayrak C, Petek H, Agar E (2006) J Chem Cryst 36:709–714
- Atalay S, Petek H, Iskeleli NO, Albayrak C, Agar E (2006) Acta Cryst E 62:o3092–o3093
- Iskeleli NO, Karabiyik H, Albayrak C, Petek H, Ağar E (2006) Struct Chem 17:393–399
- Karabiyik H, Iskeleli NO, Albayrak C, Agar E (2007) Struct Chem 18:87–93
- Iskeleli NO, Karabiyik H, Albayrak C, Agar E, Gumrukcuoglu IE (2008) Struct Chem 19:565–570
- Karabiyik H, Petek H, Iskeleli NO, Albayrak C (2009) Struct Chem 20:903–910
- Bernstein J, Davis RE, Shimoni L, Chang N-L (1995) Angew Chem Int Ed Engl 34:1555–1573
- 40. Biswas N, Umapathy S (1997) J Phys Chem A 101:5555-5566
- Tsuji T, Takashima H, Takeuchi H, Egawa T, Konaka S (2001) J Phys Chem A 105:9347–9353
- 42. Kim HW, Han M, Shin H-J, Lim S, Oh Y, Tamada K, Hara M, Kim Y, Kawai M, Kuk Y (2011) Phys Rev Lett 106:146101