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PM3 semiempirical study and its comparison with X-ray crystal structure of 4-[2-Methyl-4-(4-methoxyphenylazo)] phenoxyphtalonitrile

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The molecular and crystal structures of the title compound, $C_{22}H_{16}N_4O_2$, were determined by single crystal X-ray diffraction technique. The title compound crystallizes in monoclinic space group *P1 2₁/n1*, with $a = 12.7811(9)$ Å, $b = 8.2002(4)$ Å, $c = 17.8772(14)$ Å, $Z = 4$, $D_{calc} = 1.3112(1)$ g/cm^3, μ (Mo-K$_\alpha$) $= 0.087$ mm^{-1}. The structure was solved by direct methods and refined to a final $R = 0.056$ for 1891 reflections with $I > 2\sigma$ (I). The asymmetric unit in the crystal structure contains only one neutral molecule. The positions of nitrogen atoms in the azo groups were disordered. There is no classic hydrogen bond in the crystal structure. The molecules in the crystal structure are stacked by π–π stacking and one edge-to-face interactions. In order to determine conformational flexibility and crystal packing effects on the molecules, molecular energy profile of the title compound was obtained with respect to the selected torsion angle, which is varied from -180° to $+180^\circ$ in every 10° via PM3 semi-empirical method.

KEY WORDS: azo compound; phtalonitrile; PM3; crystal structure; conformational analysis.

Introduction

Azo compounds are important due to their versatile applications in many different areas such as polyester fiber,[1] disperse dyes,[2] as well as, their use in many biological reactions and in analytical chemistry.[3] Furthermore, their application as industrial dyes and in biological systems where some may be used as inhibitor for tumor-growth[3] is of great importance.

On the other hand, azobenzene is one of the representative photochromic molecules with two geometric isomers. Moreover, all azocompounds may be in one of the isomeric forms: *trans* and *cis*.[4–6] 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.[7,8] In the present paper, we report details of *trans* arrangement of 4-[2-Methyl-4-(4-methoxyphenylazo)]phenoxyphtalonitrile by single crystal

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X-ray diffraction technique and PM3 semi-empirical quantum mechanical method as a part of general study of the crystal chemistry of dyes. The results obtained from both methods were contrasted and crystal packing effects on the exact *trans* configuration of the title compound comprehensively discussed.

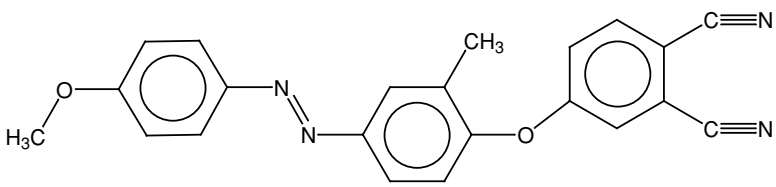
Experimental

Synthesis of the title compound

A mixture of p-anisidine (4 g, 32.4 mmol), water (50 ml) and concentrated hydrochloric acid (8.14 ml, 97.2 mmol) was stirred until a clear solution was obtained. This solution was cooled to 273–278 K and a solution of sodium nitrite (3,13 g, 45.36 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 (3.5 g, 32.4 mmol) solution (pH $\approx$ 9) was gradually added to a cooled solution of 4-methoxybenzenediazonium chloride, prepared as described above, and the resulting mixture was stirred at 273–278 K for 60 min in ice bath, and then it was stirred for 30 min under N_2. 4-Nitrophtalonitrile solution in DMF was added dropwise. The mixture was stirred for 48 h at 323 K under N_2 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-[2-Methyl-4-(4-methoxyphenylazo)]phenoxyphtalonitrile. Crystals of 4-[2-Methyl-4-(4-methoxyphenylazo)] phenoxyphtalonitrile (see Scheme 1) were obtained from ethanol: CCl_4 (1:2) mixture at room temperature via slow evaporation (yield 83%, m.p. 429–430 K).

X-ray crystallography

A suitable sample of size $0.380 \times 0.263 \times 0.180$ mm^3 was chosen for the crystallographic study and then carefully mounted on goniometer of a STOE IPDS II diffractometer. All diffraction measurements were performed at room temperature (296 K) using graphite monochromated MoK_α radiation ($\lambda = 0.71073$ Å). The systematic absences and intensity symmetries indicated the monoclinic $P1\,2_1/n1$ space group. A total of 42724 reflections (3657 unique) within the θ range of $[1.60^\circ < \theta < 27.89^\circ]$ were collected in the rotation mode with $R_{int} = 0.0693$. The intensities collected were corrected for Lorentz and polarization factors, absorption correction ($\mu = 0.087$ mm^{-1}) by integration method via X-RED software[9] and cell parameters were determined by using X-AREA software.[9] Extinction correction was not applied. The structure was solved by direct methods using SHELXS-97.[10] 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 273 crystallographic parameters. All non-hydrogen atoms were refined anisotropically, whereas hydrogen atoms were located geometrically and refined as riding with respective C – H distances of 0.93 and 0.96 Å corresponding to the aromatic and methyl C – H bonds. The isotropic displacement parameters $U_{iso}(H)$ were constrained as $1.2U_{eq}(C)$ for aromatic



Scheme 1. Chemical diagram of the title compound.

carbon atoms and $1.5U_{eq}(C)$ for methyl carbon atoms. Throughout the refinement process, two nitrogen atoms (N3 and N4) in the azo bond were treated as a disordered group. The structure was refined to $R_1 = 0.056$ for observed 1891 reflections which obeyed to the condition of $I > 2\sigma(I)$ and to $R_1 = 0.1168$ for all 3657 data used in refinement process. The maximum peaks and deepest hole observed in the final $\Delta\rho$ map were 0.55 and -0.18 e Å^{-3}, respectively. The scattering factors were taken from SHELXL-97.[11] Other details of the data collection conditions and parameters of refinement process are summarized in Table 1.

Computational procedure

The *trans* symmetry imposed geometry optimization of the title molecule leading to energy minima *in vacuo* was performed by using PM3 self-consistent field molecular orbital[12,13] method at the restricted Hartree-Fock (RHF) level[14] with the aid of WinMopac 7.21 package.[15] Non-Linear Least Squares (NLLSQ) gradient minimization routine was used in the optimization procedure with very precise GNorm of 0.01. The crystallographic coordinates of the atoms except for those of the disordered ones (N3 and N4) were used as initial geometry for the calculations. In the initial geometry, probability-weighted coordinates for the disordered atoms were used in the computations. The structure associated with the lowest energy according to the PM3 optimization was compared with the X-ray structure. To elucidate conformational features of the title molecule and crystal packing effects on the molecules, the selected torsion angle [T(N4-N3-C14-C13)] was varied from -180° to $+180^\circ$ in every 10° and the molecular energy profile was obtained by performing single-point calculations on the calculated potential energy surface.

Table 1. Crystal Data and Details of the Structure Refinement for the Title Compound

Deposit Num	CCDC 296239
Color/Shape	Yellow/Prismatic
Chemical formula	$C_{22}H_{16}N_4O_2$
Formula weight	368.39
Crystal system	Monoclinic
Space group	*P1 2$_1$ /n1*
Unit cell dimensions	
a (Å)	12.7811(9)
b (Å)	8.2002(4)
c (Å)	17.8772(14)
Volume (Å^3)	1866.2(2)
Z	4
Density (calculated) (g/cm^3)	1.3112(1)
Absorption coefficient (mm^{-1})	0.087
Calculated T_{min}, T_{max}	0.973, 0.984
F_{000}	768.0
h_{min}, h_{max}	-15, 15
k_{min}, k_{max}	-10, 10
l_{min}, l_{max}	-22, 22
$R_{(int)}$	0.0693
Diffractometer/meas. meth	STOE IPDS II/rotation
Unique reflections measured	3657
Independent/observed reflections	3657/1891
Data/parameters	3657/273
Goodness of fit on F^2	1.043
R indices [$I>2\sigma(I)$]	$R_1 = 0.056$, $wR_2 = 0.1237$
R indices (all data)	$R_1 = 0.1168$, $wR_2 = 0.1405$
Weighting scheme	$w = 1/[\sigma(F_0^2) \pm (0.0625P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

Results and discussion

Structure determination

The title complex of which an Ortep[16] view is shown in Fig. 1 crystallizes in the monoclinic space group *P1 2$_1$/n1* with four molecules in the unit cell. The asymmetric unit in the crystal structure contains only one neutral molecule. Crystal packing diagram is shown in Fig. 2.

In the title compound, the aromatic rings, which adopt a distorted *trans* configuration about the N=N double bond, are not exactly coplanar with a dihedral angle of 15.72(14)° between them. The nitrogen atoms in the azo groups were disordered in their positions with the respective site-occupancy factors of 0.561(9) (for N3A and N4A) and 0.439(9) (for N3B and N4B). N3A–N4A and N3B–N4B bond lengths are 1.248(8) and 1.248(10) Å, respectively. These values indicate their double bond character. Corresponding values of these bond lengths mentioned above for similar azo compounds have been of

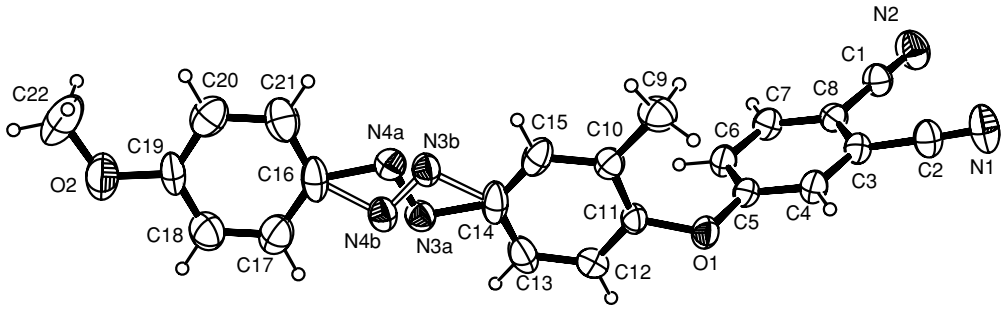


Fig. 1. An ORTEP III drawing of the title molecule with the atomic numbering scheme. Displacement ellipsoids are depicted at the 30% probability level for clarity. Open bonds represent the bonds associated with the part having lower site-occupancy factor in disordered azo group.

consistency with previously reported studies in the literature.[17−20] Phenoxyphtalonitrile ring (ring A) is nearly perpendicular to the ring B formed by C10-····-C15 with the dihedral angle of 87.89(12)° and make a dihedral angle of 78.26(13)° with the average ring plane of C16-····-C21 (ring C). Although N1 atom has maximum deviation from the phenoxyphtalonitrile ring with the perpendicular separation of − 0.166(3) Å, N2 has relatively small deviation from its parent ring than N1 with the perpendicular separation of − 0.025(2) Å. There is no intra-or intermolecular hydrogen bond, but three remarkable π–π stacking and one edge-to-face interactions are observed in the crystal structure. The stacking interaction associated with the ring B (*fractional centroid coordinates: 0.24205(8), − 0.01565(14), 0.16823(6)*) and ring C (*fractional centroid coordinates: − 0.18875(10), 0.25070(17), 0.02459(7)*) has the perpendicular centroid-centroid distance of 3.583 Å and its symmetry code is [$-x$, $-y$, $-z$]. Other two stacking interactions associated with the ring A (*fractional centroid coordinates: 0.58415(7), 0.01462(12), 0.30536(5)*) and ring C have the perpendicular centroid-centroid distance of 3.601 and 3.469 Å and their respective symmetry code are [1/2 − x, − 1/2 + y, 1/2 − z] and [*1/2* − x, 1/2 + y, *1/2* − z]. The molecules are

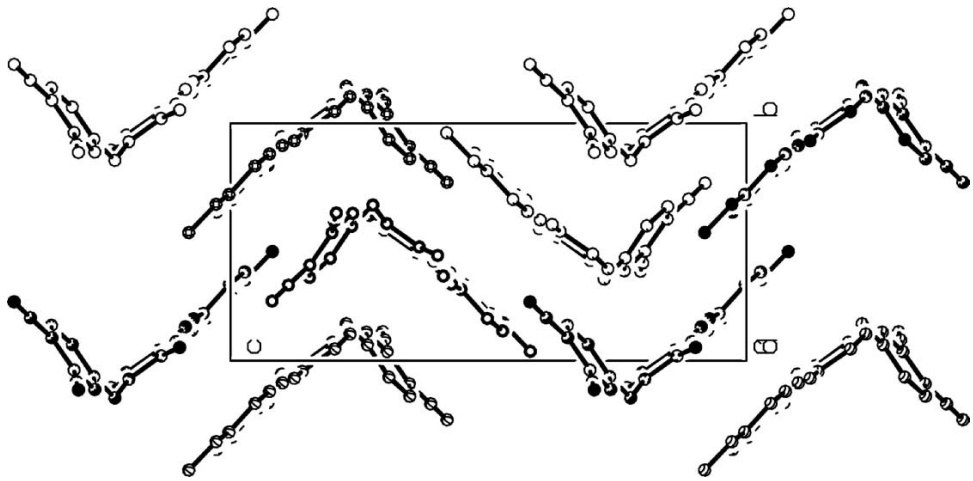


Fig. 2. Orientations of the non-H atoms in the unit cell.

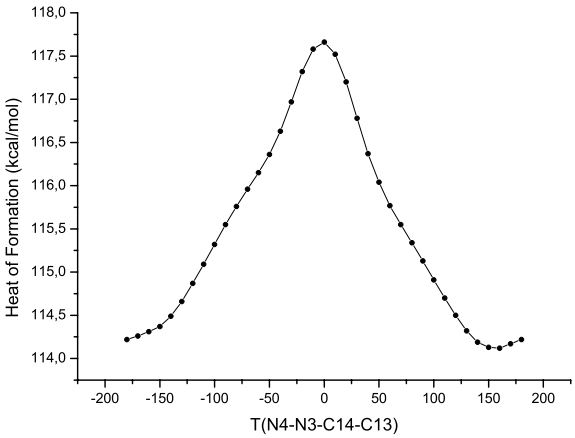


Fig. 3. Variation of heat of formation versus the selected torsion angle.

stacked via weak C – H···π-ring interaction. The perpendicular C12 – H12···ring B contact separation is 3.757(3) Å and C12 – H12···ring B angle is 146°. The perpendicular distance between atom H12 and the ring B is 2.95 Å.

Comparison with the computational modelling

In order to understand better the packing effects on the structure of the title compound in solid state, we have carried out gas-phase quantum chemical PM3 calculation on the monomer structure of the compound. In addition, the *trans* symmetry imposed semi-empirical PM3 molecular orbital calculations were carried out in order to define the conformational flexibility of the title molecule as a function of the selected torsion angle T(N4-N3-C14-C13) (see Fig. 3). Some selected geometrical parameters experimentally obtained and theoretically calculated are listed in Table 2.

There are some conformational discrepancies between the optimized and X-ray geometry of the title compound. Although the dihedral angle between the ring B and C is 15.72(14)° in X-ray structure, in the optimized structure the angle is found as 35.40°. Another difference in the optimized structure is observed in the relative orientation of the ring A and B. In X-ray structure, both rings are nearly perpendicular to one another with the angle of 87.89(12)°, dihedral angle between them in its PM3 optimized counterpart is found as 107.31°. When C16 – N4 – N3 – C14 torsion angle is considered, while distortion from exact *trans* configuration of the title compound is 0.02° in optimized geometry, the average distortion in disordered azo bond from exact

Table 2. Some Selected Geometrical Parameters of the Title Compound (Å, °) Obtained from the X-ray Crystallographic and Theoretical Study

Bond Dist	X-ray	PM3	Bond Ang	X-ray	PM3
C1 – N2	1.137(3)	1.159	C21 – C16 – N4a	104.8(4)	115.30
C2 – N1	1.141(3)	1.159	C21 – C16 – N4b	145.2(4)	
N3a – N4a	1.248(8)	1.232	C13 – C14 – N3a	101.9(4)	115.69
N3b – N4b	1.248(10)		C13 – C14 – N3b	141.4(4)	
C16 – N4a	1.492(6)	1.443	C22 – O2 – C19	119.1(3)	117.66
C16 – N4b	1.489(8)		C5 – O1 – C11	118.44(18)	116.36
C14 – N3a	1.485(6)	1.449	C17 – C16 – N4a	135.6(4)	124.43
C14 – N3b	1.503(7)		C17 – C16 – N4b	95.2(4)	
C11 – O1	1.406(3)	1.397	C15 – C14 – N3a	138.4(4)	123.54
C5 – O1	1.364(3)	1.380	C15 – C14 – N3b	98.8(4)	
Tor. Ang	X-ray	PM3	Tor. Ang	X-ray	PM3
C6 – C5 – O1 – C11	– 27.0(3)	1.16	C9 – C10 – C11 – O1	5.1(3)	6.26
C13 – C14 – N3a – N4a	– 171.7(4)	154.29	C15 – C14 – N3a – N4a	11.8(6)	– 28.18
C13 – C14 – N3b – N4b	18.8(9)		C15 – C14 – N3b – N4b	–165.4(5)	
C21 – C16 – N4a – N3a	– 174.6(4)	175.70	C17 – C16 – N4a – N3a	4.6(7)	– 4.69
C21 – C16 – N4b – N3b	– 2.6(9)		C17 – C16 – N4b – N3b	178.9(5)	
C20 – C19 – O2 – C22	– 1.0(4)	– 179.87	C9 – C10 – C15 – C14	–178.9(2)	– 179.53

trans configuration is 3.5° in X-ray structure. The calculated molecular energy profile with respect to the selected torsion angle is a one-fold rotational potential barrier. Heat of formation values corresponding to the most unfavorable conformer appearing at 0° of the selected torsion angle and the optimized structure of the title compound, which is appeared at 154.29° of the selected torsion angle, are 117.66 kcal/mol and 114.12 kcal/mol, respectively. The substituted rings linked by azo bridge are nearly planar in the unfavorable conformer. In addition, it can be stated that there is no remarkable steric hindrance during the rotation around the selected torsion angle. PM3 method can not consider structural properties of the crystalline materials properly, since this method has some limitations such as partial ignorance of overlap of the atomic orbitals and the fact that the molecule is regarded as isolated (or single) molecule *in vacuo* throughout the computations. For these reasons, the conformation of the molecule in solid state is slightly different from its PM3 optimized geometry. The observed conformational differences in the optimized structure are presumably due to the contributions from the packing of the molecules according to space group symmetry operations. In conclusion, X-ray structure is in general agreement with its PM3 optimized counterpart except for conformational discrepancies mentioned above due to the limitations of PM3 method. The crystal structure is stabilized by π-π stacking and edge to face interactions and crystal packing of the title compound is dominated by these interactions occurred during crystallization process.

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 296239. 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).

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