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Structure and conformation of 2,3,4-triphenyl-1-oxa-4-azabutadiene

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Abstract

2,3,4-triphenyl-1-oxa-4-azabutadine (C20H15NO) has been studied by X-ray analysis and AM1 molecular orbital methods. It crystallises in the triclinic space group *P*-1 with a = 9.414(3), b = 10.479(3), c = 8.385(2) Å, $\alpha = 103.31(3)^{\circ}$, $\beta = 97.10(3)^{\circ}$, $\gamma = 74.09(1)^{\circ}$, V = 772.5(4) Å³, Z = 2, $D_c = 1.227$ g cm⁻³, and μ (MoK α) = 0.075 mm⁻¹ and $F_{000} = 300$. The structure was solved by direct methods and refined to R = 0.043 for 2672 reflections [$I > 2\sigma(I)$]. The conformational analysis of the title compound were investigated by semi-empirical quantum mechanical AM1 calculations. The minimum conformation energies were calculated as a function of the three torsion angles $\theta_1(O(1)C(7)C(8)N(1))$, $\theta_2(C(8)N(1)C(15)C(16))$ and $\theta_3(C(14)C(9)C(8)N(1))$. The results are compared with the X-ray results. C=O and C=N groups are twisted about each other by 95.5(2)°. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: X-ray; AM1; Schiff base; Benzil monoanil; Conformation; 1-Oxa-4-azabutadiene

1. Introduction

Dienes containing nitrogen atoms have attracted the attention of chemists in recent years because of their importance in natural products synthesis [1-3]. Heterodiene cycloaddition reactions ([4 + 2] and/or [2 + 2]) represent a versatile synthetic methodology for the construction of a variety of heterocyclic compounds [4,5].

Elucidation of the molecular structure and conformational behaviour of 2,3,4,-triphenyl-1-oxa-4azabutadine as α , β -conjugated imine can play a significant role toward a better understanding of the correlation between its molecular structure and periselectivity in cyclo-addition reactions. Steric and electronic effect of substitution on the carbon skeleton affects peri-selectivity [6,7]. While cinnamylideneaniline prefer [4 + 2] cyclo-addition with dichloroketene, β -phenylcinnamylideneaniline give [2 + 2] ones [6]. Molecular conformations of *N*-benzilideneanilines have been studied, using semi-empirical molecular orbital calculations [8–13]. However, there is no study about α , β -conjugated imine in the literature.

In this paper we investigated the structure of 2,3,4triphenyl-1-oxa-4-azabutadiene, benzil monoanil, in order to help in analysing and predicting the properties of other similar systems.

2. Experimental

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The suitable crystals were obtained from the

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synthesis of the compound. A solution of 10 g of desylaniline in 8 ml of dimethylaniline was heated at $150-160^{\circ}$ C in metal bath for 6 h while bubbling oxygen through the solution. The dark solution was taken up in ether and washed repeatedly with 2% hydrochloric acid to remove the dimethylaniline. Some resinous material was present. The ethereal layer was further washed with water, dilute sodium hydroxide and water. The dark syrup remaining after the removal of solvent from the dried solution crystallized from methanol. Recrystallized solid from methanol was obtained as yellow crystals (m.p. = $162-164^{\circ}$ C).

A crystal of dimensions $0.85 \times 0.60 \times 0.25 \text{ mm}^3$ was mounted on a RIGAKU AFC7S diffractometer equipped with a graphite monochromator. Cell constants were determined by least-squares refinement of diffractometer angles for 23 reflections collected in the range $15.04 < 2\theta < 22.43$. Three standard reflections were monitored after every 150 reflections, but no considerable intensity variations were recorded (0.82%). A total number of 4766 reflections (independent reflections were 4515 [$R_{\text{int}} = 0.018$]) were recorded with Miller indices $h_{\text{min}} = 0$, $h_{\text{max}} = 13$, $k_{\text{min}} = -14$, $k_{\text{max}} = 14$, $l_{\text{min}} = -11$ and

 $l_{\text{max}} = 11$ [14]. The structure was solved by the direct methods [15]. The E-map computed form the phase set with the best combined figure of merit revealed the positions of all the non-hydrogen atoms with anisotropic atomic displacement parameters was performed using SHELX97 program package [16]. Positions of H atoms were generated from the assumed geometries and not refined during the refinement process. Final $R(F^2)$ and $\omega R^2(F^2)$ factors were found to be 0.043 and 0.118, respectively, for 200 parameters using the *I* values of $2672 [I > 2\sigma(I)]$ reflections. A weighting scheme was used during refinement as $\omega = 1/[\sigma^2(F_0^2) +$ $(0.0528P)^2 + 0.1202P]$, where $P = (F_0^2 + 2F_c^2)/3$. The highest and lowest electronic charge peaks in the final difference map are 0.23 and -0.14 e Å⁻³.

Crystal data for (1), C20H15NO, $Mr = 285 \text{ g mol}^{-1}$, *P*-1 with a = 9.414(3), b = 10.479(3), c = 8.385(2) Å, $\alpha = 103.31(3)^{\circ}$, $\beta = 97.10(3)^{\circ}$, $\gamma = 74.09(2)^{\circ}$, V = 772.5(4) Å, Z = 2, $Dc = 1.240 \text{ g cm}^{-3}$, and $\mu(MoK\alpha) = 0.076 \text{ mm}^{-1}$, $F_{000} = 300$, T = 292 K, $R(F^2) = 0.043$, $\omega R^2(F^2) = 0.118$ for 2672 observed reflections. Flack parameter is found to be 0.028(5) in the refinement [17]. A list of structure factors, H atom fractional atomic co-ordinates and



Fig. 2.



Table 1

Fractional atomic co-ordinates (×10⁴) and equivalent isotropic displacement parameters (Å²×10³). U_{eq} is defined as one third of the trace of orthogonalized U_{ij} tensor

Atom	x	у	z	$U_{ m eq}$
O(1)	8460(1)	6440(1)	1211(1)	67(1)
N(1)	10214(1)	8779(1)	2148(2)	54(1)
C(1)	8225(2)	5927(2)	4287(2)	50(1)
C(2)	8186(2)	5697(2)	5832(2)	64(1)
C(3)	8645(2)	6537(2)	7191(2)	70(1)
C(4)	9126(2)	7619(2)	7027(2)	68(1)
C(5)	9163(2)	7877(2)	5482(2)	53(1)
C(6)	8717(1)	7022(1)	4104(1)	42(1)
C(7)	8712(1)	7250(1)	2429(2)	44(1)
C(8)	8945(2)	8577(1)	2205(2)	46(1)
C(9)	7583(2)	9651(1)	1993(2)	49(1)
C(10)	7602(2)	10695(2)	1247(2)	66(1)
C(11)	6332(2)	11694(2)	1057(3)	81(1)
C(12)	5028(2)	11676(2)	1614(2)	76(1)
C(13)	4985(2)	10651(2)	2345(2)	71(1)
C(14)	6245(2)	9637(2)	2522(2)	61(1)
C(15)	11543(2)	7748(1)	2274(2)	49(1)
C(16)	11872(2)	6536(2)	1135(2)	51(1)
C(17)	13230(2)	5622(2)	1235(2)	57(1)
C(18)	14270(2)	5891(2)	2474(2)	65(1)
C(19)	13951(2)	7092(2)	3613(2)	74(1)
C(20)	12610(2)	8026(2)	3510(2)	66(1)

anisotropic atomic displacement parameters for nonhydrogen atoms has been deposited with the B.L.L.D as supplementary Publications No. SUP (12pp).

Theoretical calculations were carried out with the standard parameters using locally modified versions of the MOPAC 6.0 program package [18] which includes the AM1 Hamiltonian [19]. Geometry optimizations of the crystal structure of the title compound were carried out using the Fletcher–Powell–Davidson algorithm [20,21] implemented in the package and the PRECISE option to improve the convergence criteria. To determine the conformational energy profiles were performed full geometrical optimizations and values of the AM1 total energy were calculated as a function of three torsion angles $\theta 1(O(1)C(7)C(8)N(1))$ from 0 to 180°, $\theta 2(C(8)N(1)C(15)C(16))$ and $\theta 3(C(14)C(9)C(8)N(1))$ from 0 to 90°, varied every 5°. Results are illustrated in Figs. 1–3.

3. Results and discussion

Fractional atomic co-ordinates and equivalent

isotropical thermal parameters for non-hydrogen atoms are given in Table 1. Bond distances, bond angles and torsional angles for X-ray and *gauche* conformations are listed in Table 2. ORTEP [22] view of the molecular structure of the title compound is given in Fig. 4.

The most important contributions to the relative stabilities of *syn*, *trans* and *gauche* forms of 2,3,4-triphenyl-1-oxa-4-azabutadiene are interactions between the n, π , π^* orbitals of the imine and carbonyl fragments.



The planar conformations (1a and 1b) are stabilized by π/π^* interactions. The *syn* conformation (1b) obviously is destabilized due to strong interactions of the lone pair electrons, electrostatic effects, and steric repulsions of the phenyl rings. n/π^* interaction can stabilize the *gauche* conformation (1c).

The expectations, which were based on the orbital interactions, regarding conformation are confirmed by the X-ray analysis: the molecule has a *gauche* conformation and the $\theta 1(O(1)C(7)C(8)N(1)$ torsional angles is $-95.5(2)^{\circ}$. In 2,3-4-triphenyl-1-oxa-4-azabutadiene the phenyl rings introduce two important factors into O=C-C=N system which are bulky and could be sterically important interactions, and the π -orbitals in the phenyl ring can interact within the O=C-C=N system.

During the change in the torsional angles $\theta_2(C(8)N(1)C(15)C(16))$ and $\theta_3(C(14)C(9)C(8)N(1))$ from 0 to 90°, which are varied every 5° could be affected from several factors and controlled by the geometry: (i) steric interaction between the anilino hydrogen atom and a substituent at the azomethine carbon atom, hence increasing the dihedral angle [23]; (ii) the interactions between the azomethine nitrogen lone pair electrons (which posses electron donating character) and the π -system upon twisting. The importance of the nitrogen lone-pair electrons in the anilino group for non-planar conformations was indicated that the planarities of hydrogen bonded

Table 2 Bond distances (Å) and angles (°) of X-ray form of molecule with esds in parenthesis

	X-ray	X-opt.		X-ray	X-opt.	
O(1)–C(7)	1.214(2)	1.24	C(8)-N(1)-C(15)	121.7(1)	124.1	
N(1)-C(8)	1.278(2)	1.29	C(2)-C(1)-C(6)	120.0(1)	120.2	
N(1)-C(15)	1.422(2)	1.41	C(3)-C(2)-C(1)	120.0(2)	120.1	
C(1)–C(2)	1.379(2)	1.39	C(4)-C(3)-C(2)	120.5(1)	120.0	
C(1)–C(6)	1.395(2)	1.40	C(3)-C(4)-C(5)	120.4(2)	120.2	
C(2)–C(3)	1.373(3)	1.39	C(6) - C(5) - C(4)	119.3(2)	120.1	
C(3)–C(4)	1.370(3)	1.40	C(5)-C(6)-C(1)	119.7(1)	119.5	
C(4)–C(5)	1.390(2)	1.39	C(1)-C(6)-C(7)	118.3(1)	118.9	
C(5)-C(6)	1.386(2)	1.40	C(5)-C(6)-C(7)	122.0(1)	121.6	
C(6)-C(7)	1.477(2)	1.48	O(1)-C(7)-C(6)	122.3(1)	122.6	
C(7)–C(8)	1.522(2)	1.51	O(1)-C(7)-C(8)	118.1(1)	120.0	
C(8)-C(9)	1.478(2)	1.48	C(6)-C(7)-C(8)	119.5(1)	117.1	
C(9)-C(10)	1.385(2)	1.40	N(1)-C(8)-C(7)	124.0(1)	126.6	
C(9)-C(14)	1.391(2)	1.40	N(1)-C(8)-C(9)	120.2(1)	120.1	
C(10)-C(11)	1.376(2)	1.39	C(9)-C(8)-C(7)	115.7(1)	113.3	
C(11)-C(12)	1.373(3)	1.40	C(10)-C(9)-C(8)	120.8(1)	120.0	
C(12)-C(13)	1.366(3)	1.39	C(10)-C(9)-C(14)	118.1(1)	120.4	
C(13)-C(14)	1.377(2)	1.39	C(14)-C(9)-C(8)	121.1(1)	119.6	
C(15)-C(16)	1.386(2)	1.41	C(11)-C(10)-C(9)	120.6(2)	120.1	
C(15)-C(20)	1.390(2)	1.41	C(12)-C(11)-C(10)	120.5(2)	120.2	
C(16)-C(17)	1.378(2)	1.39	C(13)-C(12)-C(11)	119.8(2)	119.9	
C(17)-C(18)	1.372(2)	1.39	C(12)-C(13)-C(14)	120.2(2)	120.3	
C(18)-C(19)	1.378(2)	1.39	C(13)-C(14)-C(9)	120.9(2)	120.0	
C(19)-C(20)	1.376(2)	1.39	C(16)-C(15)-C(20)	118.8(1)	123.1	
			C(20)-C(15)-N(1)	118.1(1)	118.1	
			C(17)-C(16)-C(15)	120.4(1)	120.4	
			C(18)-C(17)-C(16)	120.5(2)	120.5	
			C(17)-C(18)-C(19)	119.4(2)	119.7	
			C(20)-C(19)-C(18)	120.7(2)	120.7	
			C(19)-C(20)-C(15)	120.1(2)	120.5	

o-salicylideneanilines in which lone pair electrons are available [24]. In the benzylideneanilines twisting of the π -system originates from a steric interaction of the azomethine proton (-CH=N) and the *ortho* positioned protons in the aniline ring and lone-pair interaction with phenyl ring. In benzylideneanilines $\theta 2$ is 40–55° [25–30]. In this molecule, there is a benzoyl group instead of imine moiety H.





2,3,4-triphenyl-1-oxa-4-azabutadiene

Therefore, in the title molecule, $\theta 2(C(8)N(1))$ C(15)C(16)) is $-62.6(2)^{\circ}$ and the steric effects are more effective than in the benzylideneanilines. Conjugation of the lone pair electrons of the nitrogen atom with the π -system of aniline ring and steric effect are more effective than *N*-benzylideneanilines. Due to steric effects between lone pair electrons of oxygen and hydrogens of benzylidene rings the title molecule is more stable at the $-19.4(1)^{\circ}$ of the $\theta 3$ (C(14)C(9)C(8)N(1)) torsional angle. In benzylideneanilines $\theta 3$ is $0-10^{\circ}$.

The bond length of C(7)–C(8) [1.522(2) Å] which is clearly greater than the standard bond distance between two sp² hybridized carbon atoms (1.466 Å) is of special interest. The central C–C bond length in the buta-1,3-diene [31], acrolein, glyoxal, benzyl [32]



are 1.465, 1.484, 1.526 and 1.542, respectively. The C(7)–C(8) bond length of 2,3,4-triphenyl-1-oxa-4azabutadiene is between that of glyoxal and benzil, which seems to be reasonable. The C(8)–N(1) bond length [1.278(2) Å] is well within the range of 1.23– 1.29 Å which was found in the previous X-ray crystallographic determinations for the C=N bond in simple conjugated imines [33] or 1.29 Å in C-aryl-substituted imines [34–36]. The two phenyl rings are twisted with respect to each other. The plane angles between A(C(1),C(2), C(3),C(4),C(5),C(6)) and B(C(9), C(10),C(11),C(12)C(13),C(14)) and C(C(15),C(16), C(17), C(18), C(19), C(20)) planes are 87.58(6), 81.28(6) and 79.32(5)°, respectively.

The semi-empirical calculations using the AM1 molecular orbital method were carried out in order to define the conformational flexibility of the title molecule as a function of $\theta 1$, $\theta 2$, $\theta 3$.

Bond distances and angles are normal in X-ray structure and in the AM1 calculated structures. Except that the $\theta 1$, $\theta 2$ and $\theta 3$ torsional angles are 94.01, -47.97, -37.27, respectively, in the AM1 calculation

whereas the $\theta 1$, $\theta 2$ and $\theta 3$ torsional angles are 95.5(2), -62.6(2), -19.6(1) in the X-ray structures, respectively. $\theta 3$ angle is larger in the crystals than in the calculated structure.

The heat of formation energy profile of the $\theta 1(O(1)C(7)C(8)N(1))$ shows two maxima at 0° (83.58 kcal/mol) and 180° (85.85 kcal/mol) for *syn* and for *anti* conformation. The energy differences among the most stable conformation with *syn* and *anti* conformations are 6.83 and 9.10 kcal/mol, respectively. This energy barrier arises from the steric interactions of the three-phenyl ring atoms and lone-pair electron repulsions. The energy minima was found at -94.01° .

The energy profile function of as a $\theta 2(C(8)N(1)C(15)C(16))$ torsion angle shows one minima at -47.96° . Steric interaction between benzoyl group attached C=N double bond and ortho hydrogen on the anilino, delocalization between the C=N- double bond and the aniline ring and delocalization of nitrogen lone pair increased nonplanarity. This explanation had been suggested by Burgi and Dunitz to explain the non-planarity of N-benzilidenanilines [37]. This idea was proved by our work, because in this molecule the H atom at the azomethine carbon atom was replaced by the benzoyl group which is more steric.

The conformational energy as a function of $\theta 3(C(14)C(9)C(8)N(1))$ shows one minima at -42.27° . Although in benzylideneanilines there is a strong preference for the benzylidene ring to be planar $(0-10^{\circ})$, $\theta 3$ angle is large due to steric effects.

In summary, semi-empirical AM1 calculations show a good agreement with the X-ray structure. The AM1 optimized geometry of the X-ray structure of the title compound corresponding to the nonplanar-*gauche* conformation is the most stable conformation. The results strongly indicate that steric repulsion of three phenyl rings and interaction between the N-lone pair and the π -electrons of the rotated phenyl ring which contribute to the conformational energy of the title compound.

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