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# MOLECULAR STRUCTURE AND CONFORMATIONS OF A STERICALLY HINDERED ARYL DERIVATIVE OF 1,3,4-OXADIAZOLE CONTAINING AN o,o′-BIPHENYL RING SYSTEM

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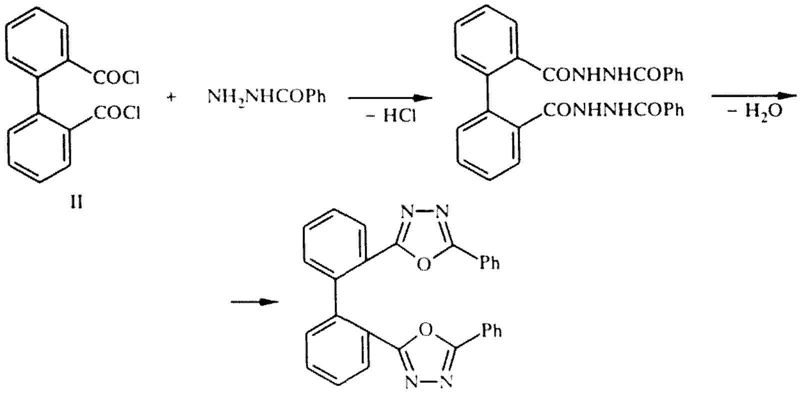
*The structure of sterically hindered molecules of 2,2′-bis(5-phenyl-1,3,4-oxodiazol-2-yl)biphenyl has been studied. Crystals that are suitable for x-ray diffraction analysis can be obtained for the different conformers of this compound. It has been found that during synthesis the molecule of this compound is obtained in an energetically less favorable conformation. On the basis of model calculations using the AM1 method with geometry optimization it has been proposed that during synthesis there are no changes in conformation of either the intermediates or the final product and the conformation of the resulting oxadiazole system is governed by the conformation of the initial 2,2′-diphenic acid dichloride.*

In the unsubstituted biphenyl molecule the planes of the benzene rings, as a result of the repulsion between the hydrogen atoms at the ortho position, are at an angle to each other, with a value, according to different calculations, that ranges from ~10 to 50° [1-5]. The introduction of bulky aryloxazole or aryloxadiazole residues at the o-position of biphenyl has the effect of increasing this angle to 90° [6]. At the same time there is the possibility of the azole residues turning to a certain extent about the single bonds joining them to the biphenyl ring.

In the present publication the results of a theoretical and experimental study of the structure and conformation of symmetric 2,2′-bis(5-phenyloxadiazol-2-yl)biphenyl molecules (I) are presented. The latter is synthesized by a route involving acylation of benzhydrazide with diphenic acid dichloride (II) followed by cyclization of the resulting *N,N′*-diaroylhydrazine in the presence of dehydrating agents ($POCl_3$) [7]:



Product I was purified by chromatography of its solution in chloroform on alumina followed by recrystallization from ethanol.

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Khar'kov State University, Khar'kov 310077. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 7, pp. 984-991, July, 1996. Original article submitted April 23, 1996.

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TABLE 1. Main Crystallographic Data for Conformations A and B of the 2,2′-Bis(5-phenyloxadiazol-2-yl)biphenyl Molecule I

| Parameters | Structure A | Structure B |
|---|---|---|
| Empirical formula | $C_{28}H_{18}N_4O_2$ | |
| Color and shape of crystals | Colorless plates | |
| Crystal dimensions, mm | 0,6 × 0,6 × 0,2 | 0,6 × 0,6 × 0,2 |
| Space group | Pccn | Pbcn |
| Cell parameters, Å | | |
| $a$ | 9,950(2) | 11,337(2) |
| $b$ | 14,147(2) | 10,083(2) |
| $c$ | 15,523(2) | 18,951(4) |
| Cell volume, Å$^3$ | 2185,0(7) | 2165,3(8) |
| $Z$ | 4 | |
| $Mr$, amu | 442,5 | |
| $\rho$x, mg/cm$^3$ | 1,345 | 1,347 |
| $\mu$ (MoK$\alpha$), mm$^{-1}$ | 0,087 | 0,088 |
| F (000) | 920 | |
| $T$, K | 290 | 288 |
| Recorded reflections | | |
| total | 1766 | 1247 |
| independent | 1111 | 1169 |
| observed | 866 ($F > 6\sigma$) | 779 ($F > 4\sigma$) |
| $R_{int}$, % | 1,80 | 1,29 |
| Number of refined parameters | 191 | 190 |
| $R$ and $R_w$ | | |
| from observed reflections, % | 3,11, 2,31 | 3,43, 2,27 |
| from whole body | 6,52, 10,76 | 4,44, 2,31 |
| S (goodness of fit) | 1,89 | 2,01 |
| $(\Delta/\sigma)_{max}/(\Delta/\sigma)_{av}$ | 0,051, 0,004 | 0,209, 0,024 |
| $N/m$ | 4,5 | 4,1 |
| greatest maximum/minimum difference (e·Å$^{-3}$) | 0,10/-0,08 | 0,13/-0,13 |

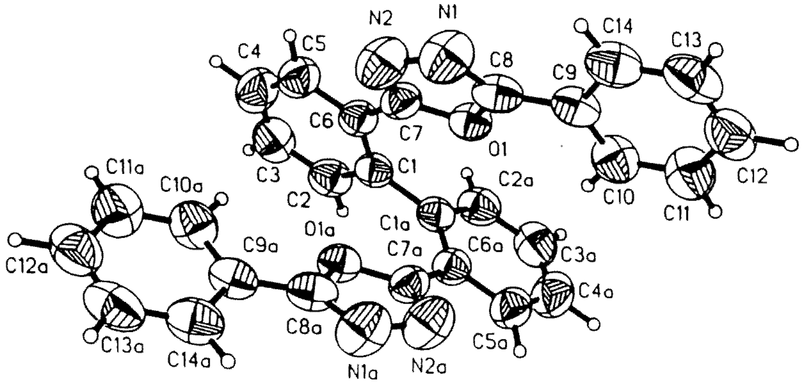


Fig. 1. Diagram for numbering of atoms and thermal vibration ellipsoids of a molecule of compound I in conformation A.

It was established by x-ray diffraction analysis, the main results of which are given in Tables 1-4 and in Fig. 1, that the molecule of the substituted biphenyl synthesized has the conformation IA.

We also studied the possibility of converting compound I into a 1,2,5-triaryl-1,3,4-triazole derivative by reaction with aniline according to the literature method [8]. The substance isolated after a 10-hour period of refluxing these reagents was different from the initial compound, but the x-ray diffraction results (see Tables 1, 5-7 and Fig. 2) showed that it was not a reaction product but another conformer (1B). Our attempts to convert molecules of I from conformation B to the initial confor-

TABLE 2. Atomic Coordinates (Å × $10^4$) and Equivalent Thermal Corrections (Å$^2$ × $10^3$) of 2,2′-Bis(5-phenyl-1,3,4-oxadiazol-2-yl)biphenyl in Conformation A

| Atom | $x$ | $y$ | $z$ | $U(eq)$ |
|---|---|---|---|---|
| $O_{(1)}$ | 1677(1) | 6345(1) | 4890(1) | 58(1) |
| $N_{(1)}$ | 2451(2) | 5715(2) | 6076(1) | 89(1) |
| $N_{(2)}$ | 3553(2) | 5992(1) | 5556(1) | 90(1) |
| $C_{(1)}$ | 3212(1) | 7332(1) | 3514(1) | 55(1) |
| $C_{(2)}$ | 4046(2) | 7621(1) | 2838(1) | 71(1) |
| $C_{(3)}$ | 5363(2) | 7331(1) | 2787(1) | 84(1) |
| $C_{(4)}$ | 5888(2) | 6731(1) | 3393(1) | 88(1) |
| $C_{(5)}$ | 5094(2) | 6414(1) | 4047(1) | 73(1) |
| $C_{(6)}$ | 3768(2) | 6715(1) | 4126(1) | 57(1) |
| $C_{(7)}$ | 3043(2) | 6351(1) | 4868(1) | 59(1) |
| $C_{(8)}$ | 1377(2) | 5936(1) | 5662(1) | 61(1) |
| $C_{(9)}$ | -13(2) | 5821(1) | 5904(1) | 60(1) |
| $C_{(10)}$ | -1015(2) | 6291(1) | 5471(1) | 76(1) |
| $C_{(11)}$ | -2338(2) | 6201(1) | 5730(1) | 90(1) |
| $C_{(12)}$ | -2683(2) | 5630(1) | 6400(1) | 90(1) |
| $C_{(13)}$ | -1691(2) | 5154(1) | 6828(1) | 89(1) |
| $C_{(14)}$ | -356(2) | 5243(1) | 6586(1) | 77(1) |
| $H_{(2)}$ | 3642(5) | 8035(4) | 2402(4) | 83(1) |
| $H_{(3)}$ | 5854(5) | 7581(4) | 2345(4) | 86(1) |
| $H_{(4)}$ | 6839(4) | 6505(4) | 3341(4) | 102(1) |
| $H_{(5)}$ | 5433(5) | 5925(4) | 4455(4) | 101(1) |
| $H_{(10)}$ | -734(5) | 6705(4) | 5013(4) | 84(1) |
| $H_{(11)}$ | -3038(5) | 6557(4) | 5406(4) | 108(1) |
| $H_{(12)}$ | -3684(5) | 5552(4) | 6592(4) | 129(1) |
| $H_{(13)}$ | -1841(5) | 4795(4) | 7269(4) | 106(1) |
| $H_{(14)}$ | 399(5) | 4939(4) | 6870(4) | 71(1) |

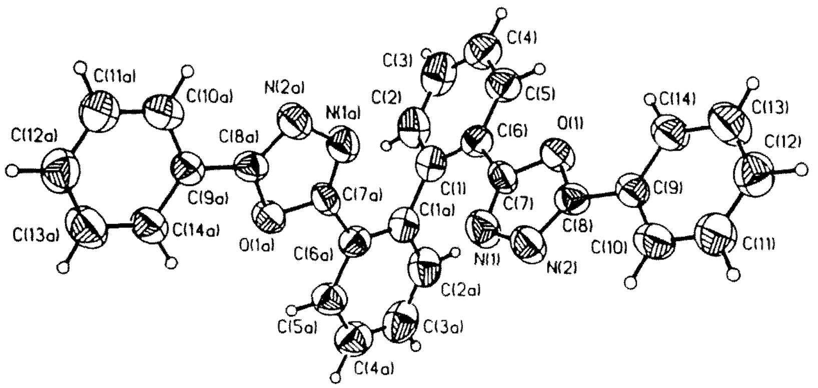


Fig. 2. Diagram for numbering of atoms and thermal vibration ellipsoids of the molecule of compound I in conformation B.

mation A were unsuccessful. The most significant difference between conformers 1A and 1B is the configuration of the aryloxadiazole residues relative to the biphenyl ring system. In the former the oxygen atoms of the heterocycles face each other while in the latter they are on opposite sides. In both cases the molecules have axial symmetry. Thus, half the molecule is a basis for x-ray diffraction calculations. It should also be noted that conformer 1A crystallizes in space group Pccn, which is fairly uncommon.

The angles between the planes of the biphenyl ring ($P_1$), oxadiazole ring ($P_2$) and benzene ring ($P_3$) (the average deviations of the individual atoms from the plane of $P_1$, $P_2$, $P_3$ is 0.008, 0.002, and 0.004 Å respectively for structure A and 0.002, 0.003, and 0.005 Å for structure B).

TABLE 3. Bond Lengths (Å) of 2,2'-Bis(5-phenyl-1,3,4-oxadiazol-2-yl)biphenyl in Conformation A

| Bond | Length, Å | Bond | Length, Å |
|---|---|---|---|
| $O_{(1)}-C_{(7)}$ | 1,359(2) | $C_{(5)}-H_{(5)}$ | 0,996(6) |
| $O_{(1)}-C_{(8)}$ | 1,364(2) | $C_{(6)}-C_{(7)}$ | 1,454(2) |
| $N_{(1)}-N_{(2)}$ | 1,418(2) | $C_{(8)}-C_{(9)}$ | 1,443(2) |
| $N_{(1)}-C_{(8)}$ | 1,286(2) | $C_{(9)}-C_{(10)}$ | 1,374(2) |
| $N_{(2)}-C_{(7)}$ | 1,287(2) | $C_{(9)}-C_{(14)}$ | 1,381(2) |
| $C_{(1)}-C_{(2)}$ | 1,399(2) | $C_{(10)}-C_{(11)}$ | 1,382(3) |
| $C_{(1)}-C_{(6)}$ | 1,402(2) | $C_{(10)}-H_{(10)}$ | 0,962(7) |
| $C_{(1)}-C_{(1A)}$ | 1,493(3) | $C_{(11)}-C_{(12)}$ | 1,361(3) |
| $C_{(2)}-C_{(3)}$ | 1,375(3) | $C_{(11)}-H_{(11)}$ | 0,996(6) |
| $C_{(2)}-H_{(2)}$ | 0,981(6) | $C_{(12)}-C_{(13)}$ | 1,366(3) |
| $C_{(3)}-C_{(4)}$ | 1,371(3) | $C_{(12)}-H_{(12)}$ | 1,045(5) |
| $C_{(3)}-H_{(3)}$ | 0,913(6) | $C_{(13)}-C_{(14)}$ | 1,386(3) |
| $C_{(4)}-C_{(5)}$ | 1,363(3) | $C_{(13)}-H_{(13)}$ | 0,865(7) |
| $C_{(4)}-H_{(4)}$ | 1,002(5) | $C_{(14)}-H_{(14)}$ | 0,972(6) |
| $C_{(5)}-C_{(6)}$ | 1,392(2) | | |

TABLE 4. Bond Angles for the 2,2'-Bis(5-phenyl-1,3,4-oxadiazol-2-yl)biphenyl Molecule in Conformation A

| Angle | ω, deg | Angle | ω, deg |
|---|---|---|---|
| $C_{(7)}-O_{(1)}-C_{(8)}$ | 104,1(1) | $N_{(2)}-C_{(7)}-C_{(6)}$ | 126,9(2) |
| $N_{(2)}-N_{(1)}-C_{(8)}$ | 106,9(1) | $O_{(1)}-C_{(8)}-N_{(1)}$ | 111,2(1) |
| $N_{(1)}-N_{(2)}-C_{(7)}$ | 106,1(1) | $O_{(1)}-C_{(8)}-C_{(9)}$ | 119,1(1) |
| $C_{(2)}-C_{(1)}-C_{(6)}$ | 117,1(1) | $N_{(1)}-C_{(8)}-C_{(9)}$ | 129,7(1) |
| $C_{(2)}-C_{(1)}-C_{(1A)}$ | 118,0(1) | $C_{(8)}-C_{(9)}-C_{(10)}$ | 120,9(1) |
| $C_{(6)}-C_{(1)}-C_{(1A)}$ | 124,8(1) | $C_{(8)}-C_{(9)}-C_{(14)}$ | 120,2(1) |
| $C_{(1)}-C_{(2)}-C_{(3)}$ | 121,4(2) | $C_{(10)}-C_{(9)}-C_{(14)}$ | 118,8(2) |
| $C_{(1)}-C_{(2)}-H_{(2)}$ | 116,6(3) | $C_{(9)}-C_{(10)}-C_{(11)}$ | 120,3(2) |
| $C_{(3)}-C_{(2)}-H_{(2)}$ | 121,9(3) | $C_{(9)}-C_{(10)}-H_{(10)}$ | 116,4(3) |
| $C_{(2)}-C_{(3)}-C_{(4)}$ | 120,6(2) | $C_{(11)}-C_{(10)}-H_{(10)}$ | 123,2(3) |
| $C_{(2)}-C_{(3)}-H_{(3)}$ | 116,0(4) | $C_{(10)}-C_{(11)}-C_{(12)}$ | 121,2(2) |
| $C_{(4)}-C_{(3)}-H_{(3)}$ | 123,4(4) | $C_{(10)}-C_{(11)}-H_{(11)}$ | 118,1(4) |
| $C_{(3)}-C_{(4)}-C_{(5)}$ | 119,6(2) | $C_{(12)}-C_{(11)}-H_{(11)}$ | 120,7(4) |
| $C_{(3)}-C_{(4)}-H_{(4)}$ | 120,2(4) | $C_{(11)}-C_{(12)}-C_{(13)}$ | 118,8(2) |
| $C_{(5)}-C_{(4)}-H_{(4)}$ | 120,1(4) | $C_{(11)}-C_{(12)}-H_{(12)}$ | 121,4(4) |
| $C_{(4)}-C_{(5)}-C_{(6)}$ | 121,0(2) | $C_{(13)}-C_{(12)}-H_{(12)}$ | 119,8(4) |
| $C_{(4)}-C_{(5)}-H_{(5)}$ | 120,4(3) | $C_{(12)}-C_{(13)}-H_{(14)}$ | 121,0(2) |
| $C_{(6)}-C_{(5)}-H_{(5)}$ | 118,6(3) | $C_{(12)}-C_{(13)}-H_{(13)}$ | 123,3(4) |
| $C_{(1)}-C_{(6)}-C_{(5)}$ | 120,3(1) | $C_{(14)}-C_{(13)}-H_{(13)}$ | 115,6(4) |
| $C_{(1)}-C_{(6)}-C_{(7)}$ | 124,1(1) | $C_{(9)}-C_{(14)}-C_{(13)}$ | 119,9(2) |
| $C_{(5)}-C_{(6)}-C_{(7)}$ | 115,6(1) | $C_{(9)}-C_{(14)}-H_{(14)}$ | 114,8(4) |
| $O_{(1)}-C_{(7)}-N_{(2)}$ | 111,8(1) | $C_{(13)}-C_{(14)}-H_{(14)}$ | 125,3(4) |
| $O_{(1)}-C_{(7)}-C_{(6)}$ | 121,2(1) | | |

| | $P_1\hat{}P_2$ | $P_2\hat{}P_3$ | $P_1\hat{}P_1'$ | $P_1\hat{}P_3$ |
|---|---|---|---|---|
| conformer IA | 19,1 | 7,4 | 79,6 | 5,6 |
| conformer IB | 9,0 | 14,6 | 66,7 | 11,5 |

These values indicate that the symmetric diaryloxadiazole molecules are more planar in conformer 1B but are rotated relative to each other by a large angle.

It is clear from the data listed in Tables 2-7 that the bond lengths and bond angles have fairly typical values in the oxadiazolylphenyl residues. While for the biphenyl residue, there are substantial distortions of the bonds and angles due to steric hindrance. Thus, the $C_{(1)}'$-$C_{(1)}$-$C_{(6)}$ and $C_{(1)}$-$C_{(6)}$-$C_{(7)}$ angles are increased by 4.8° and 4.1° in conformation IA and by 5.6°

TABLE 5. Atomic Coordinates (Å × $10^4$) and Equivalent Thermal Corrections (Å$^2$ × $10^3$) of 2,2'-Bis(5-phenyl-1,3,4-oxadiazol-2-yl)biphenyl in Conformation B

| Atom | $x$ | $y$ | $z$ | $U(eq)$ |
|---|---|---|---|---|
| $O_{(1)}$ | 7945(2) | 1183(2) | 3583(1) | 54(1) |
| $N_{(2)}$ | 9639(2) | 309(3) | 3897(1) | 62(1) |
| $N_{(1)}$ | 9860(2) | 1326(3) | 3397(1) | 63(1) |
| $C_{(1)}$ | 9353(2) | 3671(3) | 2421(2) | 54(1) |
| $C_{(2)}$ | 8930(3) | 4641(3) | 1961(2) | 69(1) |
| $C_{(3)}$ | 7755(4) | 4791(4) | 1824(2) | 79(2) |
| $C_{(4)}$ | 6949(3) | 3979(4) | 2138(2) | 70(2) |
| $C_{(5)}$ | 7329(3) | 3009(3) | 2596(2) | 60(1) |
| $C_{(6)}$ | 8520(3) | 2851(3) | 2732(2) | 51(1) |
| $C_{(7)}$ | 8842(3) | 1813(3) | 3228(2) | 49(1) |
| $C_{(8)}$ | 8510(3) | 263(3) | 3994(2) | 48(1) |
| $C_{(9)}$ | 7822(3) | -597(3) | 4447(2) | 48(1) |
| $C_{(10)}$ | 8384(3) | -1420(4) | 4916(2) | 65(1) |
| $C_{(11)}$ | 7748(4) | -2262(4) | 5346(2) | 70(2) |
| $C_{(12)}$ | 6556(4) | -2285(4) | 5311(2) | 70(2) |
| $C_{(13)}$ | 5990(3) | -1450(4) | 4851(2) | 77(2) |
| $C_{(14)}$ | 6609(3) | -602(4) | 4420(2) | 64(2) |
| $H_{(2)}$ | 9538(16) | 5252(21) | 1787(10) | 62(7) |
| $H_{(3)}$ | 7529(19) | 5418(21) | 1524(10) | 68(7) |
| $H_{(4)}$ | 6122(18) | 4011(20) | 2051(11) | 80(8) |
| $H_{(5)}$ | 6728(15) | 2447(19) | 2843(9) | 46(7) |
| $H_{(10)}$ | 9193(19) | -1382(25) | 4965(13) | 56(9) |
| $H_{(11)}$ | 8163(25) | -2815(29) | 5691(14) | 87(12) |
| $H_{(12)}$ | 6119(25) | -2881(29) | 5627(15) | 98(13) |
| $H_{(13)}$ | 5192(25) | -1410(28) | 4802(15) | 89(12) |
| $H_{(14)}$ | 6274(26) | -35(29) | 4048(16) | 112(14) |

TABLE 6. Bond Lengths (Å) of 2,2'-Bis(5-phenyl-1,3,4-oxadiazol-2-yl)biphenyl in Conformation B

| Bond | Length, Å | Bond | Length, Å |
|---|---|---|---|
| $O_{(1)}—C_{(7)}$ | 1,374(4) | $C_{(5)}—H_{(5)}$ | 1,002(18) |
| $O_{(1)}—C_{(8)}$ | 1,371(3) | $C_{(6)}—C_{(7)}$ | 1,454(4) |
| $N_{(2)}—N_{(1)}$ | 1,419(4) | $C_{(8)}—C_{(9)}$ | 1,447(4) |
| $N_{(2)}—C_{(8)}$ | 1,295(4) | $C_{(9)}—C_{(10)}$ | 1,373(5) |
| $N_{(1)}—C_{(7)}$ | 1,295(4) | $C_{(9)}—C_{(14)}$ | 1,376(5) |
| $C_{(1)}—C_{(2)}$ | 1,395(5) | $C_{(10)}—C_{(11)}$ | 1,379(5) |
| $C_{(1)}—C_{(6)}$ | 1,387(4) | $C_{(10)}—H_{(10)}$ | 0,922(22) |
| $C_{(1)}—C_{(1A)}$ | 1,498(5) | $C_{(11)}—C_{(12)}$ | 1,353(6) |
| $C_{(2)}—C_{(3)}$ | 1,366(5) | $C_{(11)}—H_{(11)}$ | 0,980(28) |
| $C_{(2)}—H_{(2)}$ | 0,981(20) | $C_{(12)}—C_{(13)}$ | 1,371(6) |
| $C_{(3)}—C_{(4)}$ | 1,363(5) | $C_{(12)}—H_{(12)}$ | 0,982(29) |
| $C_{(3)}—H_{(3)}$ | 0,889(21) | $C_{(13)}—C_{(14)}$ | 1,376(6) |
| $C_{(4)}—C_{(5)}$ | 1,376(5) | $C_{(13)}—H_{(13)}$ | 0,911(29) |
| $C_{(4)}—H_{(4)}$ | 0,953(21) | $C_{(14)}—H_{(14)}$ | 0,983(30) |
| $C_{(5)}—C_{(6)}$ | 1,384(4) | | |

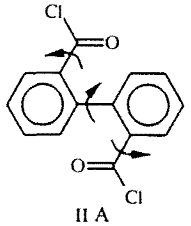
and 2.2° in conformation IB respectively compared to the distortion-free value of the bond angle in an $sp^2$-hybridized carbon atom. In addition, the $C_{(1)}'$-$C_{(1)}$-$C_{(2)}$ angle in both conformers is appreciably smaller (by 2.0-2.5°), with the result that the biphenyl residue on the whole appears bent, so that the intramolecular distances for $C_{(2)}$-$C_{(2)}'$ and $C_{(6)}$-$C_{(6)}'$ are 3.09 and 3.36 Å respectively for conformer IA and 3.17 and 3.47 Å for conformer IB. The fact that in both conformers the $C_{(6)}$-$C_{(7)}$ bond is appreciably longer than the $C_{(8)}$-$C_{(9)}$ bond, which relative to the oxadiazole ring is "symmetric" to it, is consistent with the occurrence of considerable steric hindrance.

The above data undoubtedly indicate that the molecules of both conformers of compound I are sterically hindered to a considerable degree. From a comparison of the results of x-ray diffraction analysis for conformers IA and IB, it may be assumed that the latter is hindered to a slightly greater extent. However, calculations carried out by the AM1 method [9] using

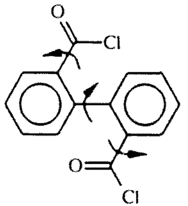
TABLE 7. Bond Angles for the 2,2'-Bis(5-phenyl-1,3,4-oxadiazol-2-yl)biphenyl Molecule in Conformation B

| Angle | ω, deg | Angle | ω, deg |
|---|---|---|---|
| $C_{(7)}-O_{(1)}-C_{(8)}$ | 104,2(2) | $N_{(1)}-C_{(7)}-C_{(6)}$ | 131,1(3) |
| $N_{(1)}-N_{(2)}-C_{(8)}$ | 107,2(2) | $O_{(1)}-C_{(8)}-N_{(2)}$ | 110,9(2) |
| $N_{(2)}-N_{(1)}-C_{(7)}$ | 106,4(2) | $O_{(1)}-C_{(8)}-C_{(9)}$ | 119,4(2) |
| $C_{(2)}-C_{(1)}-C_{(6)}$ | 116,7(3) | $N_{(2)}-C_{(8)}-C_{(9)}$ | 129,7(3) |
| $C_{(2)}-C_{(1)}-C_{(1A)}$ | 117,5(3) | $C_{(8)}-C_{(9)}-C_{(10)}$ | 119,7(3) |
| $C_{(6)}-C_{(1)}-C_{(1A)}$ | 125,6(3) | $C_{(8)}-C_{(9)}-C_{(14)}$ | 121,2(3) |
| $C_{(1)}-C_{(2)}-C_{(3)}$ | 122,1(3) | $C_{(10)}-C_{(9)}-C_{(14)}$ | 119,1(3) |
| $C_{(1)}-C_{(2)}-H_{(2)}$ | 114,1(12) | $C_{(9)}-C_{(10)}-C_{(11)}$ | 120,8(3) |
| $C_{(3)}-C_{(2)}-H_{(2)}$ | 123,5(12) | $C_{(9)}-C_{(10)}-H_{(10)}$ | 120,0(16) |
| $C_{(2)}-C_{(3)}-C_{(4)}$ | 120,3(3) | $C_{(11)}-C_{(10)}-H_{(10)}$ | 119,1(16) |
| $C_{(2)}-C_{(3)}-H_{(3)}$ | 118,8(15) | $C_{(10)}-C_{(11)}-C_{(12)}$ | 120,3(4) |
| $C_{(4)}-C_{(3)}-H_{(3)}$ | 120,9(15) | $C_{(10)}-C_{(11)}-H_{(11)}$ | 119,5(17) |
| $C_{(3)}-C_{(4)}-C_{(5)}$ | 119,5(3) | $C_{(12)}-C_{(11)}-H_{(11)}$ | 120,2(17) |
| $C_{(3)}-C_{(4)}-H_{(4)}$ | 124,3(13) | $C_{(11)}-C_{(12)}-C_{(13)}$ | 119,2(4) |
| $C_{(5)}-C_{(4)}-H_{(4)}$ | 116,2(13) | $C_{(11)}-C_{(12)}-H_{(12)}$ | 119,0(17) |
| $C_{(4)}-C_{(5)}-C_{(6)}$ | 120,3(3) | $C_{(13)}-C_{(12)}-H_{(12)}$ | 121,8(17) |
| $C_{(4)}-C_{(5)}-H_{(5)}$ | 118,9(10) | $C_{(12)}-C_{(13)}-H_{(14)}$ | 121,4(4) |
| $C_{(6)}-C_{(5)}-H_{(5)}$ | 120,7(10) | $C_{(12)}-C_{(13)}-H_{(13)}$ | 123,8(18) |
| $C_{(1)}-C_{(6)}-C_{(5)}$ | 121,1(3) | $C_{(14)}-C_{(13)}-H_{(13)}$ | 114,8(18) |
| $C_{(1)}-C_{(6)}-C_{(7)}$ | 122,2(3) | $C_{(9)}-C_{(14)}-C_{(13)}$ | 119,3(3) |
| $C_{(5)}-C_{(6)}-C_{(7)}$ | 116,7(3) | $C_{(9)}-C_{(14)}-H_{(14)}$ | 114,3(17) |
| $O_{(1)}-C_{(7)}-N_{(1)}$ | 111,3(3) | $C_{(13)}-C_{(14)}-H_{(14)}$ | 126,1(17) |
| $O_{(1)}-C_{(7)}-C_{(6)}$ | 117,6(3) | | |

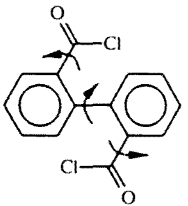
x-ray geometry of the molecules showed that conformation IB is energetically more favorable by almost 7 kcal/mole. The gain in energy is most likely achieved through the greater degree of planarity of the diphenyloxadiazole residues of conformer IB, while conjugation of these residues with each other has a much smaller effect. The lower polarity of conformer IB is also conducive to the greater stability of its crystals. The calculated dipole moment of molecule I in conformation A is almost twice that for conformation B (information is available on the trend of a more favorable formation of crystals from molecules of less polar conformers [10]). It may be concluded from the results of calculation and from the fact that the conversion of conformer A to conformer B on prolonged boiling in sufficiently high-boiling solvents is irreversible that compound I is formed during synthesis in an energetically less favorable form.



II A



II B



II C

In order to elucidate the possible reasons for this not very common behavior, we performed calculations with geometry optimization by the AM1 method on three possible rotamers of dichloride II (A, B, and C), which is the starting material in the synthesis of compound I. It transpired that in all three conformations the molecule of compound II is considerably nonplanar — the angles between the planes of the benzene rings amount to ~80-85° and the COCl group is rotated by an angle of up to 60° relative to the plane of the ring. Conformer IIA proved to be the most favorable energetically and also the least polar ($\mu_A$ = 3.5 D, $\mu_B$ = 4.3 D, $\mu_C$ = 5.0 D), although the difference in energy on changing to another conformer in this case is not more than a few kcal/mole. It should, however, be noted that despite the small differences in energy between the calculated rotamers, it cannot be concluded from the results obtained that the interconversions A $\rightleftarrows$ B $\rightleftarrows$ C occur readily, as we did not determine the respective energy barriers, and they could, in fact, prove to be quite significant. An analysis of the synthesis route for compound I shows that its molecular conformation A can only be formed from conformer IIA. The slightly greater steric accessibility of the chlorine atoms of the latter compared to conformers IIB and IIC may be an additional factor that assists in the formation of product IA from it.

Thus, it may be concluded from the results of this study that in the preparation of sterically hindered aromatic oxadiazole systems the conformation of the final cyclization product is governed by the conformation of the initial carboxylic acid chloride, since it is likely that there are no changes in conformation of the resulting azole system on ring closure.

## EXPERIMENTAL

Crystals of the conformers of compound I for x-ray diffraction analysis were obtained by recrystallization from octane. Initial x-ray diffraction analysis of the crystals was carried out photographically in a Waisenberg RGNS-2 chamber in filtered out copper radiation. Final determination of the lattice parameters and selection of data for structure interpretation were carried out on an automated four-circle Siemens P3/PC diffractomer ($\lambda(\mathrm{MoK}\alpha) = 0.71073$ Å, graphite monochromator, $T = 290$ deg K, $2\theta/\theta$-scanning, where $2\theta \leq 50°$, scanning rate ranging from 4 to 20°/min for the crystal of conformer IA and from 4 to 20°/min for the crystal of conformer IB, scanning interval 2°, ratio of time for recording background to time for recording reflex 0.30, 2 control reflexes after every 98 recordings of reflections). In conversion of intensities to $F_{\mathrm{hkl}}$ absorption was not taken into account, while the Lorentz factors and polarization were taken into account. For the crystal of conformer IA an extinction correction of the form $F^* = F(1 + 0.002\chi F^2 \sin(2\theta))^{-1/4}$, $\chi = 0.0045(3)$ was introduced. The structures were resolved directly and refined by a least-squares full-matrix method using the weight scheme $I/w = \sigma^2(F)$ in an anisotropic approximation for the nonhydrogen atoms and an isotropic approximation for the hydrogen atoms. The SHELXTL PLUS program system was used in the interpretation and refining of the structures [11].

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