A Conformational Analysis of The Six Isomers of Oxybispyridine

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Conformational energy contour maps of the six isomers of oxybispyridine have been constructed using the ab initio STO-3G molecular orbital method. The calculations (employing a partial rigid rotor) for all six isomers indicate that the minimum energy conformers are not planar and that energy barriers between 70-1000 kJ mol^{-1} restrict interconversion to planar structures, thereby preventing conjugation between the *p*-electrons of the oxygen atom with the π system of the pyridine rings. It is postulated that of the three mechanisms used to explain conformer interconversion about the C-O bond, the disrotatory one-ring flip mechanism is the most appropriate, since the "Morino's" structures are all within 2.5 kJ mol^{-1} of the minimum. Furthermore, room temperature accessibility of the "Morino's" structures suggests that the Smiles rearrangement would be possible for suitably substituted derivatives of these isomers.

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1. Introduction.

There are six isomers of oxybispyridine, all of which have been prepared. A recent review by Summers [1] has been devoted to these compounds, several of which are of practical interest. For example, partly hydrogenated 2,2'-oxybispyridines have been patented as brighteners in electroplating processes [2], 2,3'-oxybispyridine is claimed to have psychotropic and antibacterial properties [3], derivatives of 2,4'-oxybispyridine were converted to a number of insecticidally active esters and ethers [4] and 3,3'-oxybispyridine is found to influence the learning or memory in mice [5].

The uv absorption spectra of 2,2' and 2,3'-oxybispyridine, in a 1:1 ethanol-water solution, have been interpreted by Trovato *et al.* [6] using the Longuet-Higgins and Murrell [7] molecule-in-molecule (MIM) method. For both molecules, the higher absorption bands at 216 and 214 nm respectively were assigned to a perturbed p-band with moderate charge transfer contributions, whereas the lower absorption band at 264 nm was assigned to a perturbed α-band. The uv spectra of 2,4'- and 3,3'- and 4,4'-oxybispyridine have also been recorded [1].

While there have been no experimental investigations of the conformation of the oxybispyridines, there have been a number of investigations with respect to the related diphenyl ether. Four different models for diphenyl ether have been proposed and are shown in Figure 1: **A** a planar structure; **B** the "Morino's" structure which is based upon electron diffraction [9], dielectric relaxation [10] and infrared spectroscopy [11-12] studies; **C** a structure in which both rings are rotated at various angles to each other relative to the C-O-C plane which is based upon investigations of molar Kerr constants [13-14], optical anisotropy [15], dielectric relaxation [16], uv spectroscopy [16] and vibrational spectroscopy [17]; **D** the "butterfly" structure with the phenyl rings orthogonal to the C-O-C plane.

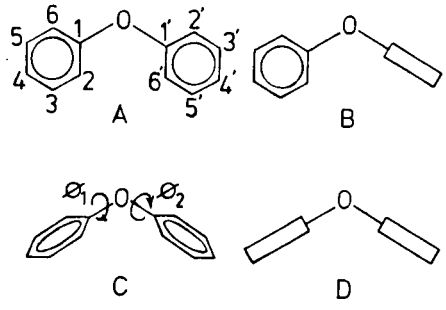

Figure 1. Conformations of oxybispyridine: **(A)** Planar Structure; **(B)** "Morino's" structure; **(C)** Minimum geometry structure with both rings rotated and denoted by torsional coordinates ($\emptyset_1$,$\emptyset_2$); **(D)** "Butterfly" structure.

More important for this investigation is the gas phase electron diffraction study of 2,2'-thiobispyridines [18]. The analysis yielded a R_{s-c} bond distance of 1.786 Å and a C-S-C bond angle of 104.4° with low R-factors for a range of dihedral angles. Hence, the interpretation of the data is consistent with the structure **C**; that is, the pyridine rings undergo large amplitude torsional motion. This notion is also consistent with semi-emprical calculations which predict a broad potential energy minimum for interconversion from one conformer into another [19].

There is a lack of ab initio calculations on large-sized molecules in the literature. However, recently von Nagy-Felsobuki [20-22] and Hofmann *et al.* [23-24] in a series of investigations used the all-electron STO-3G calculations in order to study the conformations of the isomers of bipyridinium dication. Using flexible rotor calculations, von Nagy-Felsobuki [20-22] showed that the lowest energy conformers of 2,2'-, 2,3'-, 2,4'-, 3,3'-, 3,4'- and 4,4'-bipyridinium dication yielded (torsion angles, inter-ring bond distance) of (133.2°, 0.1530 nm), (131.6°, 0.1525 nm), (44.9°, 0.1523 nm), (48.9°, 0.1523 nm), (43.4°, 0.1519 nm)

and (45.4°, 0.1522 nm) respectively. For the 2,2′- and 4,4′-bipyridinium dications the more extensively optimized STO-3G calculations of Hofman *et al.* [23-24] yielded (138.1°, 0.1516 nm) and (44.7°, 0.1522 nm) respectively, in excellent agreement with the previous calculations [20-22] and with experiment [25].

In the case of the oxybispyridines, only empirical MIM calculations have been performed, using a flexible rotor approximation; that is, with the C-O-C angle (120°), R_{C-C} (1.395 Å), R_{C-N} (1.360 Å) and R_{C-O} (1.30 Å) bond distances being fixed [6]. The calculations suggest that the lowest energy conformers are of geometric structure C, with both rings twisted by 30° about the C-O-C bond.

It is the purpose of this study to analyse theoretically the ab initio conformational structures of the oxybispyridines, thereby extending the previous empirical theoretical work [6]. Moreover, a thorough investigation of the conformation of these isomers is of interest, since it would provide information on: the most likely lowest energy conformer (vis-a-vis structures A-D); why the p-electrons of the oxygen atom are unable to conjugate with the pyridine rings; which one of the three possible rotational mechanisms is the most viable with respect to conformer interconversion about the C-O bond [26]; possible pathways for intramolecular cyclization rearrangements, such as the Smiles rearrangement [27].

2. Details of the Calculations.

The all-electron energies were computed using the LCAO MO SCF restricted Hartree-Fock method within the GAUSSIAN 86 suite of programmes [28] and using the internal STO-3G (s = p) basis set. This level of the theory has been shown to be moderately successful in reproducing the experimental geometries of closed-shell molecules [29-30]. Moreover, in the case of the mono-substituted benzenes, it is even more successful in predicting rotational barriers than the more flexible split valence basis [31].

A partial flexible rotor model was used in order to reduce the number of degrees of freedom in the optimization procedure. The geometry of the pyridine ring was fixed and due to the electronegativity of the inter-ring oxygen, was based on the pyridine ion. The pyridine moiety geometry (used in subsequent calculations) is given in Table 1. The bond angles and bond lengths differ little from the corresponding STO-3G optimization of the pyridine cation [23] (*i.e.* agree to within 0.2° and 0.02 Å respectively).

Table 1
Geometry of Pyridine Moiety[a)]

Bond Length (/Å)	STO-3G	Bond Angle(/Deg.)	STO-3G
R_{N1-C2}	1.351	<C5-N1-C2	122.4
R_{C1-C2}	1.392	<N1-C2-C3	119.5
R_{C2-C3}	1.387	<C2-C3-C4	119.2
R_{C-H}	1.088[b)]	<C3-C4-C5	120.6
		<N1-C2-H	116.6
		<C2-C3-H	119.5
		<C3-C4-H	119.7

a) Geometry optimized within C_{2v} symmetry with E_{SCF} = -243.633214 E_h. b) Fixed during the course of the optimization.

For the oxybispyridines, the FP algorithm [32] was used to optimize the inter-ring bond distances (denoted by R_{C-O}). Considering the planar (N-inside,N′-inside) conformer as the **A**(0,0) torsional position, then the torsional angles of the oxybispyridine analogs of structures given by **A-D** are denoted by **A**(0,180), **B**(0,90), **C**($\emptyset_1$,$\emptyset_2$) and **D**(90,90) respectively. Here we consider a clockwise rotation of each pyridine moiety (as viewed along the respective inter-ring C-O bond) as being a positive rotation. Hence disrotatory twisting modes are characterized from $(+\emptyset_1, +\emptyset_2)$ or $(-\emptyset_1, -\emptyset_2)$ torsional combinations, whereas conrotatory modes are identified from $(+\emptyset_1, -\emptyset_2)$ or $(-\emptyset_1, +\emptyset_2)$ combinations.

The R_{C-O} bond length was optimized for the **B**(90,90) conformer and held fixed for each 30° torsional rotation.

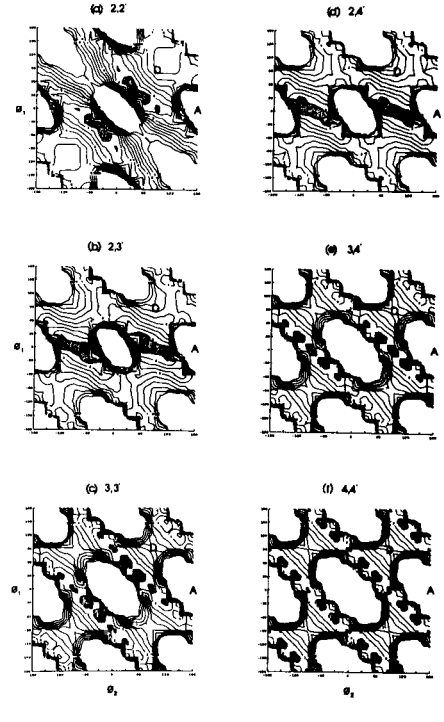

Figure 2. Conformational energy maps of isomers of oxybispyridine; **(a)** 2,2′-oxybispyridine; **(b)** 2,3′-oxybispyridine; **(c)** 3,3′-oxybispyridine; **(d)** 2,4′-oxybispyridine; **(e)** 3,4′-oxybispyridine; **(f)** 4,4′-oxybispyridine. Note: For each isomer the minimum conformer is the **C** structure and a contour step size of 2.5 kJ mol^{-1} was used for each succeeding contour. The shaded area represents conformations accessible because of the ambient temperature. The structure **A-D** are superimposed on each map.

Optimizations of the C-O-C bond angle (denoted by ω) showed little deviation from 120° and so this value was adopted for all subsequent calculations. Figures 2 **(a)-(f)** give two dimensional ($\emptyset_1$,$\emptyset_2$) energy contour plots of the oxybispyridines. The minimum energy conformer is labelled by **C** with **A**, **B** and **D** denoting the oxybispyridine analogs of structures given in Figure 1. Table 2 summarizes various properties of these conformers. For additional comparison we have included the "fully" conjugated conformer in which $R_{C\text{-}O}$ was optimized with ω and ($\emptyset_1$,$\emptyset_2$) fixed at 180° and (0,180) respectively (denoted as **E(0,180)**).

3. Results and Discussion.

In Table 2 the minimum energy conformer of each isomer is denoted as structure **C**. It is only for the 2,4'-oxybispyridine that the "Morino's" structure (*i.e.* structure **B**) is also the minimum energy conformer. Nevertheless, from the energy contour maps (Figure 2) it is clear that for the other isomers the "Morino's" structure is accessible because of the broad potential energy minima for interconversion from one conformer into another. For example,

Table 2. Various Properties of the Conformers of Oxy-Bispyridine[a].

2,2'-Oxybispyridine

	A (0,180)	B (0,90)	C (60,30)	D (90,90)	E (0,180)[b]
$R_{C\text{-}O}$(/Å)	1.3970	1.3970	1.3970	1.3970	1.3255
q_{C1}(/e)	0.2381	0.2378	0.2407	0.2280	0.3067
$q_{C1'}$(/e)	0.2180	0.2410	0.2401	0.2280	0.3067
q_O(/e)	-0.2324	-0.2466	-0.2481	-0.2498	-0.3315
q_{N2}(/e)	-0.2848	-0.2808	-0.2631	-0.2633	-0.2781
$q_{N2'}$(/e)	-0.2666	-0.2546	-0.2750	-0.2633	-0.2781
μ(/D)	3.4738	1.8332	0.6939	2.3113	0.0000
Energy(/E_h)	-559.9534	-559.9799	-559.9807	-559.9735	-559.9192

2,3'-Oxybispyridine

	A (0,180)	B (0,90)	C (0,60)	D (90,90)	E (0,180)[b]
$R_{C\text{-}O}$(/Å)	1.4002	1.4002	1.4002	1.4002	1.3308
q_{C1}(/e)	0.2407	0.2310	0.2299	0.2246	0.3028
$q_{C1'}$(/e)	0.1137	0.1400	0.1371	0.1271	0.2057
q_O(/e)	-0.2394	-0.2510	-0.2481	-0.2544	-0.3421
q_{N2}(/e)	-0.2844	-0.2825	-0.2819	-0.2617	-0.2749
$q_{N3'}$(/e)	-0.2521	-0.2427	-0.2435	-0.2437	-0.2372
μ(/D)	5.0511	2.7693	2.5138	2.2559	3.6656
Energy(/E_h)	-559.9311	-559.9752	-559.9753	-559.9679	-559.9111

Table 2. (cont.)

3,3'-Oxybispyridine

	A (0,180)	B (0,90)	C (60,30)	D(90,90)	E (0,180)[b]
$R_{C\text{-}O}$(/Å)	1.4052	1.4052	1.4052	1.4052	1.3336
q_{C1}(/e)	0.1263	0.1296	0.1232	0.1238	0.2024
$q_{C1'}$(/e)	0.1185	0.1212	0.1275	0.1238	0.2024
q_O(/e)	-0.2388	-0.2476	-0.2478	-0.2584	-0.3528
q_{N3}(/e)	-0.2357	-0.2371	-0.2396	-0.2416	-0.2364
$q_{N3'}$(/e)	-0.2394	-0.2406	-0.2379	-0.2416	-0.2364
μ(/D)	2.0739	2.1359	1.8708	0.3783	0.0000
Energy(/E_h)	-559.7168	-559.9669	-559.9674	-559.9621	-559.9039

2,4'-Oxybispyridine

	A (0,180)	B (0,90)	C (0,90)	D (90,90)	E (0,180)[b]
$R_{C\text{-}O}$(/Å)	1.4026	1.4026	1.4026	1.4026	1.3300
q_{C1}(/e)	0.2384	0.2303	0.2303	0.2240	0.3041
$q_{C1'}$(/e)	0.1219	0.1498	0.1498	0.1371	0.2168
q_O(/e)	-0.2395	-0.2508	-0.2508	-0.2540	-0.3396
q_{N2}(/e)	-0.2832	-0.2823	-0.2823	-0.2608	-0.2767
$q_{N4'}$(/e)	-0.2651	-0.2538	-0.2538	-0.2547	-0.2662
μ(/D)	4.6682	3.0245	3.0245	3.0607	3.1574
Energy(/E_h)	-559.9304	-559.9726	-559.9726	-559.9651	-559.9087

3,4'-Oxybispyridine

	A (0,180)	B (0,90)	C (-30,120)	D (90,90)	E (0,180)[b]
$R_{C\text{-}O}$(/Å)	1.4078	1.4078	1.4078	1.4078	1.3341
q_{C1}(/e)	0.1241	0.1288	0.1269	0.1232	0.2054
$q_{C1'}$(/e)	0.1294	0.1312	0.1332	0.1337	0.2154
q_O(/e)	-0.2387	-0.2474	-0.2475	-0.2579	-0.3476
q_{N3}(/e)	-0.2365	-0.2372	-0.2381	-0.2412	-0.2358
$q_{N4'}$(/e)	-0.2616	-0.2516	-0.2543	-0.2533	-0.2661
μ(/D)	2.5523	2.0779	2.1318	1.8144	1.8616
Energy(/E_h)	-559.7302	-559.9644	-559.9647	-559.9594	-559.9011

4,4'-Oxybispyridine

	A (0,180)	B (0,90)	C (60,30)	D (90,90)	E (0,180)[b]
$R_{C\text{-}O}$(/Å)	1.4062	1.4062	1.4062	1.4062	1.3346
q_{C1}(/e)	0.1321	0.1394	0.1377	0.1342	0.2148

Table 2. (cont.)

$q_{C1'}$(/e)	0.1321	0.1325	0.1341	0.1342	0.2148
q_O(/e)	-0.2395	-0.2481	-0.2483	-0.2587	-0.3481
q_{N4}(/e)	-0.2615	-0.2628	-0.2600	-0.2533	-0.2655
$q_{N4'}$(/e)	-0.2614	-0.2518	-0.2545	-0.2533	-0.2655
μ(/D)	0.7658	0.7539	0.6833	0.4965	0.0000
Energy(/E_h)	-559.6396	-559.9609	-559.9616	-559.9568	-559.8983

a) Optimized R_{C-O} bond length at ω =120°.
b) Optimized R_{C-O} bond length at ω=180°.

the difference in energy between structures **C** and **B**(0,90) for 2,2′-, 2,3′-, 3,3′-, 3,4′- and 4,4′-oxybispyridines is 2.2, 0.2, 1.3, 0.8 and 1.8 kJ mol^{-1} respectively, all within the 2.5 kJ mol^{-1} available from the ambient surroundings.

From the **A**(0.0) position, the **D**(90,90) conformers are obtained *via* a conrotatory twisting mode. The energy differences between the **C** and "butterfly" (or **D**) conformers for 2,2′-, 2,3′-, 3,3′-, 2,4′-, 3,4′- and 4,4′-oxybispyridines are 19, 19, 14, 20, 14 and 13 kJ mol^{-1} respectively. The disrotatory twisting mode yields the cisoid conformer; that is, the **D**(−90,90) structure. For the unsymmetrical isomers these two conformers are distinct. For 2,2′-, 2,3′- and 3,3′-oxybispyridine the transoid conformer is more stable by 9.7, 1.6 and 0.7 kJ mol^{-1} respectively.

For all the isomers, the planar **A** structure is the least favourable conformer. The energy difference from the minimum energy conformer and the **A**(0,180) structure for the 2,2′-, 2,3′-, 3,3′-, 2,4′-, 3,4′- and 4,4′-oxybispyridines is 72, 116, 658, 111, 616 and 845 kJ mol^{-1} respectively. For the unsymmetrical isomers, the **A**(0,0) conformers are energetically distinct from the **A**(0,180) and **A**(180,180) structures. For 2,3′-, and 3,3′-oxybispyridines the **A**(0,0) structure is more stable by 32 and 183 kJ mol^{-1} respectively, whereas for the 2,2′-oxybispyridine the **A**(0,180) is more stable by 12 kJ mol^{-1}. In the case of the former two oxybispyridines, the increasing trend in the barrier height is indicative of the decrease in the respective $R_{N\cdot N'}$ distances, whereas the dominant interaction for 2,2′-oxybispyridine is the destabilizing effect of the nitrogen "through space" steric interaction. The (N-outside,N′-outside) or **A**(180,180) conformer for 2,2′-, 2,3′ and 3,3′-oxybispyridine is 296, 467 and 305 kJ mol^{-1} above the **A**(0,180) energy. Hence, an important conclusion from this analysis is that there are no apparent low energy pathways to the planar **A** structures.

Table 2 also gives results for the "fully" conjugated **E**(0,180) conformer. Predictably, the calculations for all **E**(0,180) conformers yield optimized R_{C-O} bond lengths significantly shorter (by ~0.07 Å) than for the **C** structures. Remarkably, the energy difference between the **C** and **E**(0,180) structures for all the isomers is ~170 kJ mol^{-1}. For the unsymmetrical isomers the difference in energy between the **E**(0,0) and **E**(0,180) conformers is less than 8 kJ mol^{-1}. From these barrier heights it is clear that the p-electrons of the oxygen atom do not conjugate with the π system of the pyridine rings, thereby complicating the interpretation of the photoelectron spectra of the oxybispyridines [33].

Gust and Mislow [26] have suggested that there are three possible rotational mechanisms of conformer interconversion about the C-O bond for diphenyl ethers. In the case of the isomers of the oxybispyridines interconversion from one **C** structure to another may occur *via* the following mechanisms: a conrotatory rotation of both rings through structure **A**(0,0) involving zero-ring flip; a disrotatory rotation *via* structure **B**(0,90) involving a one-ring flip; a conrotatory rotation through structure **D**(90,90) involving a two-ring flip. Since the **A**(0,0) structures are between 80 and 845 kJ mol^{-1} above the minimum the first mechanism is not likely. It is clear from the energy contour maps given in Figure 2 and barrier heights given above, that the second mechanism is the most viable, since for all the isomers studied here the **B**(0,90) structure is within 2.5 kJ mol^{-1} of the minimum. Furthermore, due to the symmetry of the oxybispyridines, various potential energy minima exist for each isomer so that at room temperature the geometries may be best described in terms of time-average structures of the **C** conformers.

Table 2 highlights, for all isomers and **A-E** structures, the redistribution of electron density centered on the ipso carbons, inter-ring oxygen and ring nitrogens. For all conformers, the oxygen atom and ring nitrogens are electron rich sites, whereas the ipso carbons are electron deficient sites. As expected, for the "fully" conjugated conformers (**E**) the oxygen atom has a greater accumulation of electronic charge (~0.1 e) when compared with the ring nitrogens. However, for the **A-D** structures the accumulation of electronic charge on the oxygen atom is comparable to that of the ring nitrogens. The ipso carbons are more electron deficient for the **E** structures (by ~0.1 e) than for the **A-D** conformers. Clearly the ring positions of the nitrogen atoms determine the extent of electron deficiency on the ipso carbons.

Table 2 also gives the calculated dipole moments for the oxybispyridines. The dipole moments vary significantly within the family and also as a function of geometry for each isomer. For example, the dipole moment of 2,2′-oxybispyridine varies 1.6 **D** from the **C** to **D** structures, whereas the barrier height between these conformers is 20 kJ mol^{-1}. For the **C** structures, the smallest dipole moment is 0.68 **D** (4,4′-oxybispyridine) whereas the largest is 3.02 **D** (2,4′-oxybispyridine). The dipole moments of the 2,3′-, 2,4′-, 3,3′- and 3,4′-oxybispyridine are of the same order of

magnitude, which is almost one order of magnitude different from the 2,2′- and 4,4′-oxybispyridine.

The Smiles rearrangement [27] has so far not been observed for derivatives of the oxybispyridines. One factor which is important for this intramolecular cyclization rearrangement is the stabilization of structure **B** (0,90) since, for this geometry the distance between the entering group on one ring and the ipso carbon on the other is at a minimum, thereby facilitating a nucleophilic attack at the ipso carbon. The ipso carbons are electron deficient sites for all the oxybispyridines (as shown in Table 2). Furthermore, for *ortho* substituents that are electron withdrawing the ipso carbons would be even more electron deficient. For all these isomers, structure **B** is accessible at room temperature (*i.e.* within 2.5 kJ mol^{-1} of the minimum). While for substituted oxybispyridines variations to these barrier heights would occur (especially for bulky substituents) [33], nevertheless from these calculations it would be expected that the Smiles rearrangement is likely for the oxybispyridine family (provided that an appropriate entering group is available that can weaken the ether bond).

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