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ANALYSIS OF THE CONFORMATIONAL COMPOSITION OF 5-NITRO-1,3,2-DIOXABORINANES

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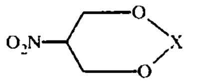
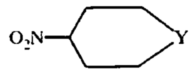
Empirical MM2 and semiempirical AM1, MNDO, and MINDO/3 calculations were carried out to determine the energy with complete geometrical optimization of 5-nitro-1,3,2-dioxaborinanes as well as of model 5-nitro-1,3-dioxanes, 4-nitroborinane, and nitrocyclohexane. Comparison of the experimental and calculated coupling constants and the energy data indicates that the sofa conformation with an axial nitro group perpendicular to the plane of molecular symmetry predominates for cyclic borate esters.

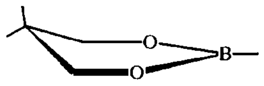
The electron-withdrawing nature of the trigonal boron atom dictates the partial double bond character of the B–O bonds. As a consequence, most six-membered cyclic borate esters exist in the sofa conformation or in an equilibrium between sofa invertomers [1]. In previous work [2, 3], we showed that the sofa conformation with an equatorial substituent at $C_{(5)}$ is characteristic for 2,5-dialkyl-1,3,2-dioxaborinanes. On the other hand, NMR [2], dipole [4], and X-ray diffraction structural data [5] unequivocally indicated predominant axial orientation of the nitro group in 5-nitro-1,3,2-dioxaborinanes. In the present work, we analyzed the conformational composition of these compounds and calculated the energy and three-dimensional structure of possible conformers of nitro esters I and II as well as of model 5-nitro-1,3-dioxanes III and IV, 4-nitroborinane V, and nitrocyclohexane VI by the MM2 molecular mechanics method [6] and LCAO MO SCF methods AM1 [7, 8], MNDO [9, 10], MINDO/3 [11] and, for cyclic carbonate IV, PM3 [12] with complete geometrical optimization.



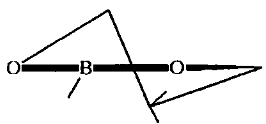


X = B–H (I), B-CH_3 (II), CH_2 (III), C=O (IV);
Y = B–H (V), CH_2 (VI)

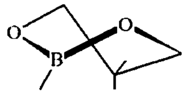
As a result, a number of minima were discovered corresponding to the sofa (S), half-chair (HC), and 1,4- and 2,5-twist (1,4- and 2,5-T) conformers with equatorial (e) and axial (a) orientation of the nitro group.



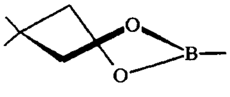
S



HC



1,4-T



2,5-T

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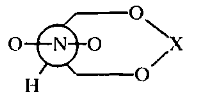
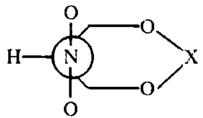
In light of the possibility of rotating the nitro group relative to the heterocycle ring, the number of such forms is doubled due to canonical rotamers with bisectral (B) and orthogonal (O) orientation of the substituent. The orthogonal orientation is perpendicular to the plane of molecular symmetry.


B


O

All the forms except the sofa were obtained in the MM2, AM1, and MNDO calculations with fixed C^4OBO and C^6OBO torsion angles. Otherwise, we obtain isomerization of these conformers to the sofa. During minimization in the MINDO/3 calculation, the SaB form (ester II) is also isolated due to fixation of the torsion angles in the heteroatomic part of the ring. On the other hand, conformers SaB, HCaO, 1,4-T, and 2,5-T (ester I) and also chair CaB and CaO (borinane V) also convert to the symmetrical boat even with these restrictions.

The relative energies of the conformers of esters I and II and models III–VI are shown in Table 1. It is readily seen that rotamer B is the most stable for molecules with equatorial orientation of the nitro group. In the case of axial forms, the relative stability of rotamers O and B depends on the calculation method. The sofa is the most stable conformer for 1,3,2-dioxaborinanes. The major minimum corresponds to SeB in the MM2 calculation, to SeB in the AM1 calculation, and to SaB in the MNDO and MINDO/3 calculations (ester II). On the whole, the conformer stability decreases in the series: S > HC > 1,4-T > 2,5-T. Forms HCe (MM2) and HCaO (AM1 and MNDO) correspond to a minimum close in energy to the ground state. However, the actual content of these forms should be negligibly small for symmetrically substituted compounds. Thus, analysis of the conformational state of 5-nitro-1,3,2-dioxaborinanes may be limited to evaluation of the relative stability of the sofa rotamers. The X-ray diffraction structural data indicate that 5-methyl-5-nitro-2-phenyl-1,3,2-dioxaborinane exists in a form close to SaO [5]. This corresponds to the major minimum in the AM1 calculation. Most of the geometric parameters of this form calculated in the AM1 approximation (*r*C–O and the bond and torsion angles) are also in good accord with the experimental results (Table 2). On the other hand, the MNDO calculation provides the best correlation to the experimental *r*B–O value, while the MINDO/3 and MM2 calculations provide the best correlation with the distances between the nitro group oxygen and boron atoms.

The results of the energy calculation for model 1,3-dioxane III from the MNDO and MINDO/3 calculations unequivocally correspond to the experimental data, indicating greatest stability for the axial conformer [13-17] if we assume that the CaB form is the major minimum. The advantageousness of this rotamer was already described in detail in 1972 by Eliel [15]. In the AM1 calculation, the major minimum corresponds to forms CeB, CeO, and CaO, which are almost degenerate in energy. However, the ΔG^0 value depends significantly on the properties of the medium, especially for compounds with polar substituents [18, 19]. The free conformational energy of the nitro group in 1,3-dioxanes varies from 0.38 (CCl_4) to 1.17 kcal/mole (CH_2Cl_2) in favor of the axial orientation [13-16], i.e., a decrease in the solvent polarity destabilizes the axial isomer or conformer. Since all the calculations in the present work were carried out for an isolated molecule in vacuum, we would expect lower calculated ΔE values relative to the experimental ΔG^0 values. Thus, the AM1 calculation data are in qualitative accord with the experimental data. Cyclic carbonate IV has some similarity in structure of the heteroatomic fragment to 1,3,2-dioxaborinanes: the optimal form of the ring of this compound is the sofa (MM2 or MINDO/3) or flattened chair (AM1, PM3, MNDO). For this reason, the conformers corresponding to the major minimum for this molecule in all the calculations are probably analogous to those for esters I and II. We note that the PM3 method, which was not used for calculating the borate esters due to the lack of parameters for the boron atom, gives preference to form CeB. The replacement of the *n*-electron pairs of the oxygen atoms by axial hydrogen atoms in nitroborinane V and nitrocyclohexane VI in most cases leads to the appearance of form CeB as the major minimum. Using the reported ΔG^0 value for the NO_2 group in cyclohexane (CCl_4, 1.1 kcal/mole in favor of Ce [20]), we may assume that the AM1 data are closest to the experimental results.

TABLE 1. Relative Energies of the Conformers of I–VI (kcal/mole)

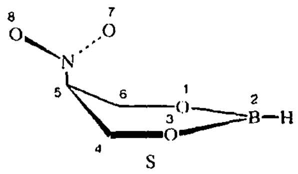
Compound	Conformer	MM2		AM1		MNDO		MINDO/3	
		E	Δ*E*	-*E*	Δ*E*	-*E*	Δ*E*	-*E*	Δ*E*
1	2	3	4	5	6	7	8	9	10
I	SeB	12.8	0.0	1449.6	0.4	1430.3	0.0	1497.2	0.0
	SeO	13.5	0.7	1449.4	0.6	1428.9	2.0	1495.1	2.1
	SaB	14.2	1.4	1448.7	1.3	1430.9	0.0	—	—
	SaO	14.2	1.4	1450.0	0.0	1428.5	2.4	1496.5	0.7
	HCeB	13.0	0.2	1449.4	0.6	1430.1	0.8	1496.9	0.3
	HCaO	14.5	1.7	1449.7	0.3	1430.6	0.3	—	—
	1,4-TeB	14.8	2.0	1447.5	2.5	1427.6	3.3	—	—
	1,4-TaO	16.3	3.5	1448.0	2.0	1428.0	2.9	—	—
	2,5-TB	19.9	7.1	1445.9	4.1	1427.3	3.6	—	—
II	SeB	11.4	0.0	1735.2	0.3	1721.6	0.6	1799.0	3.6
	SeO	12.1	0.7	1735.0	0.5	1720.3	1.9	1796.8	5.8
	SaB	12.6	1.2	1734.2	1.3	1722.2	0.0	1802.6	0.0
	SaO	12.7	1.3	1735.5	0.0	1719.9	2.3	1798.2	4.4
III	CeB	15.9	0.0	1496.2	0.0	1471.8	0.2	1493.0	1.8
	CeO	16.2	0.3	1496.0	0.2	1470.5	1.5	1491.8	3.0
	CaB	16.7	0.8	1493.8	2.4	1472.0	0.0	1494.8	0.0
	CaO	17.3	1.4	1496.1	0.1	1470.2	1.8	1492.9	1.9
IV	CeB	12.5	0.0	1476.7	0.6	1458.5	1.1	1493.4	1.8
	CeO	12.8	0.3	1476.7	0.6	1457.4	2.2	1492.1	3.1
	CaB	13.4	0.9	1475.8	1.5	1459.6	0.0	1495.2	0.0
	CaO	13.3	0.8	1477.3	0.0	1459.6	0.0	1492.9	2.3
V	CeB	14.5	0.0	1763.5	0.0	1757.7	0.0	1782.3	0.0
	CeO	15.9	1.4	1763.3	0.2	1755.2	2.5	1779.4	2.9
	CaB	16.9	2.4	1762.7	0.8	1756.9	0.8	—	—
	CaO	15.9	1.4	1763.1	0.4	1754.8	2.9	—	—

TABLE 1 (continued)

Compound	Conformer	MM2		AM1		MNDO		MINDO/3	
		E	ΔE	$-E$	ΔE	$-E$	ΔE	$-E$	ΔE
1	2	3	4	5	6	7	8	9	10
VI	CeB	16.3	0.0	1867.0	0.0	1846.1	0.0	1865.6	0.1
	CeO	17.0	0.7	1866.8	0.2	1844.1	2.0	1863.4	2.3
	CaB	18.6	2.3	1866.1	0.9	1845.1	1.0	1865.7	0.0
	CaO	17.5	1.2	1866.4	0.6	1843.1	3.0	1862.7	3.0

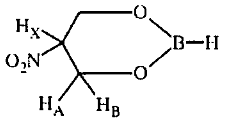
Results of the PM3 calculation for carbonate IV (kcal/mole): $-E = 1481.0$, $\Delta E = 0.0$ for CeB, $-E = 1480.4$, $\Delta E = 0.6$ for CeO, $-E = 1479.7$, $\Delta E = 1.3$ for CaB, $-E = 1480.3$, $\Delta E = 0.7$ for CaO.

TABLE 2. Optimal Geometrical Parameters of the SaO Form of 5-Nitro-1,3,2-dioxaborinane



Calculation	Bond lengths, Å		Distances between nonbonded atoms, Å						Bond angles, deg		Torsion angles, deg		
	B–O	C–O	$B–O^7$	$B–O^8$	$O^1–O^7$	$O^3–O^8$	$C^6–O^7$	$C^4–O^8$	OBO	COB	1-2-3-4	2-3-4-5	3-4-5-6
MM2	1.471	1.406	3.88	3.70	3.28	3.13	2.88	2.83	118.9	120.3	-1.2	30.0	-58.9
AM1	1.357	1.422	4.03	4.00	3.43	3.41	2.79	2.78	123.3	120.5	-3.4	26.6	-46.5
MNDO	1.369	1.400	4.23	4.18	3.59	3.55	2.87	2.86	119.5	124.3	-3.9	24.5	-41.7
MINDO/3	1.317	1.338	3.87	3.83	3.37	3.34	2.75	2.74	131.6	117.2	-3.7	-24.5	50.5
Experimental [5]	1.371	1.437	3.89	3.46	3.34	2.95	2.76	2.66	122.4	120.8	-2.8	26.8	-48.7

TABLE 3. Torsion Angles Between Protons and Vicinal Coupling Constants for Ester I*



Conformer	SSCC calculation	MM2					AM1				
		φ_{AX}	φ_{BX}	$^3J_{AX}$	$^3J_{BX}$	$\Sigma\Delta J^{*2}$	φ_{AX}	φ_{BX}	$^3J_{AX}$	$^3J_{BX}$	$\Sigma\Delta J^{*2}$
1	2	3	4	5	6	7	8	9	10	11	12
SeB	A	179.0	55.6	10.7	1.4	8.3	172.5	49.2	10.5	2.1	7.8
	B			10.2	3.7	9.1			10.1	4.5	9.8
	C			10.3	3.2	8.7			10.1	4.0	9.3
SeO	A	177.7	54.1	10.7	1.6	8.1	174.0	51.1	10.6	1.9	7.7
	B			10.2	3.9	9.3			10.1	4.3	9.6
	C			10.2	3.4	8.8			10.2	3.8	9.2
SaB	A	53.2	68.9	1.7	2.3	1.6	46.5	74.6	2.5	1.9	0.4
	B			4.0	2.3	1.5			4.8	1.9	1.9
	C			3.5	2.0	0.7			4.3	1.7	1.6
SaO	A	60.3	61.8	1.1	3.0	2.9	46.2	75.4	2.5	1.8	0.5
	B			3.2	3.0	1.4			4.9	1.9	2.0
	C			2.8	2.6	0.8			4.4	1.6	1.8
SeB	A	157.9	39.2	9.3	3.5	8.0	163.9	49.4	9.9	2.1	7.2
	B			9.0	5.8	10.0			9.6	4.5	9.3
	C			9.1	5.2	9.5			9.6	4.0	8.8
SeO	A	159.0	40.0	9.4	3.3	7.5	162.8	47.2	9.8	2.4	7.4
	B			9.2	5.7	10.1			9.5	4.8	9.5
	C			9.2	5.1	9.5			9.5	4.2	8.9

TABLE 3 (continued)

1	2	3	4	5	6	7	8	9	10	11	12
SaB	A			4.9	1.4	2.5			3.5	2.1	0.8
	B	29.8	86.3	6.9	1.5	4.4	39.1	72.0	5.8	2.1	3.1
	C			6.3	1.4	3.9			5.2	1.8	2.4
SaO	A			3.4	1.8	0.6			3.0	2.3	0.5
	B	39.6	76.6	5.7	1.8	2.9	42.2	69.5	5.4	2.3	2.9
	C			5.2	1.6	2.6			4.8	2.0	2.0

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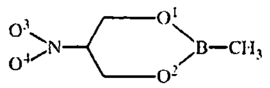
* Differences from the corresponding φ angles in ester II from 0.1 to 2°.

*2 $\Sigma\Delta J = |{}^3J_{AXexp} - {}^3J_{AXcalc}| + |{}^3J_{BXexp} - {}^3J_{BXcalc}|$. Experimental coupling constants [2]: ${}^3J_{AX} = 2.9$, ${}^3J_{BX} = 1.9$ Hz.

TABLE 4. Partial Atomic Charges in Ester II



Conformer	AM1						MNDO					
	B	O^1	O^2	N	O^3	O^4	B	O^1	O^2	N	O^3	O^4
SeB	0.2055	-0.2744	-0.2741	0.5233	-0.3420	-0.3535	0.1225	-0.2870	-0.2866	0.4304	-0.3196	-0.3291
SeO	0.2034	-0.2751	-0.2762	0.5262	-0.3497	-0.3498	0.1193	-0.2875	-0.2889	0.4308	-0.3264	-0.3265
SaB	0.2166	-0.2728	-0.2727	0.5169	-0.3330 (closest to boron)	-0.3609	0.1313	-0.2839	-0.2838	0.4251	-0.3195 (closest to boron)	-0.3290
SaO	0.2018	-0.2736	-0.2744	0.5197	-0.3496	-0.3488	0.1203	-0.2839	-0.2846	0.4278	-0.3265	-0.3255

Thus, comparison of the results of the calculations for esters I and II and models III–VI shows that a high concentration of axial conformers relative to dioxane III due to the presence of the cyclic BO_2 fragment is a distinguishing feature of 1,3,2-dioxaborinanes.

In order to obtain an independent evaluation of the conformational composition of esters I and II, we compared the experimental [2] and calculated coupling constants $^3J_{AX}$ and $^3J_{BX}$. These constants were obtained using the torsion angles φ between the corresponding protons (optimal geometry data) by three independent methods: A) using the equation derived by Haasnoot [21], B) using the equation derived by Durette and Horton [22], and C) using the classical Karplus equation [23] with parameters taken from Haasnoot [21]. The data for the electronegativity of carbon, hydrogen, and cyclic oxygen atoms required for equations (A) and (B) were obtained from Huggins [24], while the data for the nitro group were obtained from Sandberg [25]. The results shown in Table 3 unequivocally support the predominance of conformer Sa. According to the value of $\Sigma\Delta J$, the MNDO and MINDO/3 calculations give preference to the SaO form, while rotamers SaO and SaB are difficult to distinguish in the MM2 and AM1 calculations. Conjugation of the *n*-electron pairs of the ring oxygen atoms with the nitro group π-system and electrostatic interaction of the nitro group nitrogen atom and heteroatomic fragment of the ring have been noted as the probable reasons for the predominantly axial orientation of the NO_2 group in dioxanes [14, 16]. The partial charges on the atoms in ester II (Table 4) show that such an interaction in the SaO rotamer for the axial forms should be somewhat stronger than in SaB due to the greater charge on nitrogen. On the other hand, efficient *p*-π electron exchange between the nitro group and ring oxygen atoms is possible only in rotamer SaO. This confirms the nature of the highest occupied molecular orbital (AM1) formed for this form by the combination of the ring oxygen *n*-electron pairs (*p*-orbitals parallel to the plane of molecular symmetry) with the axial and equatorial C–H bonds of two adjacent carbon atoms and the *n*-electrons of the nitro group oxygen atoms. On the other hand, rotation of the nitro group in nitromethane is virtually free ($\Delta G^{\neq} = 6$ kcal/mole [26]; this value is 1 kcal/mole according to our AM1 calculation). Rotation of the NO_2 group for 2-nitropropane, which is the closest aliphatic analog to the systems studied, is also almost free (the barrier is 0.2 kcal/mole in favor of the conformer with NO–CH staggering, which corresponds to the our data for the equatorial forms of I and II, Table 1). The much greater calculated barrier for rotation of the axial nitro group in cyclic borate esters in favor of the SaO form (up to 1.3 kcal/mole, AM1) confirms the existence of additional interactions between the substituent and heteroatomic fragment of the ring.

Hence, the nitro group in 5-nitro-1,3,2-dioxaborinanes has predominant axial orientation and is in an orthogonal position stabilized by electron exchange and electrostatic interactions with the ring oxygen atoms.

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