JOURNAL OF PHYSICAL ORGANIC CHEMISTRY
J. Phys. Org. Chem. 2001; **14:** 488–494
DOI:10.1002/poc.397

Probing the influence of stereoelectronic effects on lithium affinity in 1,3- and 1,4-dioxa systems

Bishwajit Ganguly and Benzion Fuchs*

School of Chemistry, Tel-Aviv University, Ramat-Aviv, 69978 Tel-Aviv, Israel

Received 21 February 2001; Revised 17 April 2001; Accepted 17 April 2001

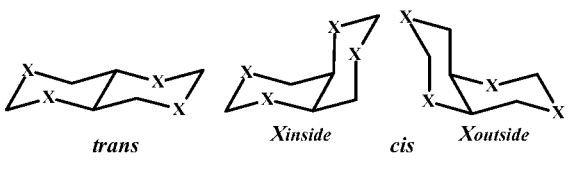
ABSTRACT: A combined computational and structural study of the lithium affinity (LA) of O—C—O systems exhibiting the anomeric effect and of O— C—C—O systems exhibiting the *gauche* effect is presented. QM *ab initio* calculations using the MP2/6–31G* basis set were carried out on the gas-phase lithium affinities of dimethoxymethane (DMOM), dimethoxyethane (DMOE), 1,3-dioxane (DOX) and *cis*- and *trans*-tetraoxadecalin (TOD), along with that of dimethyl ether and of its dimer as reference compounds. Structural parameters were retrieved from the Cambridge Structural Database (CSD) for diethyl ether dimer and O—C—C—O lithium complexes and these agreed well with the calculated data. The computed lithium affinities of dimethoxymethane and dimethoxyethane were found to be conformationally dependent. The LAs are conformationally dependent (wherever applicable) and decrease in the order: $(Me_2O)_2$ > DMOE > DMOM > DOD > DOX > *trans*-TOD, but *cis*-TOD restores the high LA (better than DMOE) by virtue of multiple coordination. Copyright © 2001 John Wiley & Sons, Ltd.

KEYWORDS: lithium affinity; acetals; anomeric effect; *gauche* effect; stereoelectronic effects; tetraoxadecalin

INTRODUCTION

The stereoelectronic behavior of X—C—Y-containing systems (X, Y = OR, NR_2, Hal), known as the anomeric effect, and that of the X—C—C—Y molecular unit, known as the *gauche* effect, have been extensively studied.[1–4] The anomeric effect in an X—C—Y system is due to an Xn_p–$\sigma^*_{C–Y}$ two electron–two orbital interaction[2] (negative hyperconjugation[3] in valence bond terms) and is manifest in[4] (1) structural parameters, e.g. shorter or longer anomeric bonds and larger anomeric bond angles, (2) relative energy, i.e. greater stability of *gauche* (axial) forms over *anti* (equatorial) forms, and (3) stereoselective reactivity. The *gauche* effect consists in the tendency of the X—C—C—Y moiety to alleviate or even revert the preference for the *anti* over the *gauche* conformation, as known for butane (C—C—C—C) and derivatives. This had been observed and calculated,[5,6] but the extent of the phenomenon and its origins are a matter of some debate. Subsequent to Wolfe's *et al.* invocation[5] of prevailing (nuclear–electron) attractive over (nuclear–nuclear and electron–electron) repulsive energy terms, Epiotis *et al.*[7] attributed *gauche* stabilization in O—CH_2—CH_2—O systems to σ–σ^* stabilizing interactions between the best σ-donors (a C—H bond) and the best σ-acceptor (a C—O bond) properly oriented (parallel) only in the *gauche* conformation[7] and later they invoked attractive non-bonded interactions between the oxygen atoms due to the stabilizing (charge withdrawing) interaction between $\sigma^*_{C–C}$ and the bonding and anti-bonding orbitals formed from the interaction between the oxygen's lone pairs.[7c] Wiberg *et al.*[8] concluded (and recent studies endorsed it[9]) that the *gauche* preference in 1,2-difluoroethane is a manifestation of the destabilization of the *anti* form due to bond bending at the carbon nuclei and, hence, poorer overlap between the C—C σ-bond forming orbitals.

Notwithstanding the abundance of research efforts on these stereoelectronic effects, much less attention had been paid to these effects in charged systems and coordination products. We were particularly interested in those, in view of our recent activity on the stereoisomeric tetraheterodecalin systems (Fig. 1) and in



THD

TOD: X = O; TAD: X = NH

Figure 1. The 1,3,5,7-tetraheterodecalin (THD) diastereoisomers

**Correspondence to:* B. Fuchs, School of Chemistry, Tel-Aviv University, Ramat-Aviv, 69978 Tel-Aviv, Israel.
Contract/grant sponsor: Israel Science Foundation.

particular tetraoxadecalin (TOD)[10] new host systems, which are loaded with stereoelectronically controlled fragments.

We therefore recently performed and reported the results of two systematic computational studies: (i)[11a] of various protonated C—O—C—OH^+—R systems and of their negative C—O—C—O^- counterparts, to assess the anomeric effect on their energies and geometries, and (ii)[11b] of C—O—C—C—OH^+—R and C—O—C—C—O^- systems for the *gauche* effect. These are of considerable interest owing to their mechanistic and synthetic implications in the properties and behavior (viz. relative stability of conformers, structural properties, coordination sites and strength, relative reactivity: acetal formation and hydrolysis, glycosidation, nucleophilic reactions) of molecular systems which are subject to stereoelectronic effects. We had concluded[11] that the anomeric effect in C—O—C—O—C-containing molecules makes them weaker bases then the corresponding simple ethers and differential protonation of O lone pairs in unsymmetrical C—O1—C2—O3—C moieties showed that the one engaged in n–σ^* interaction has a lower proton affinity than the 'free' one, e.g. the preferred site of protonation of 1,3-dioxane is axial, since the equatorial lone pair is hyperconjugatively delocalized. The geometric parameters (mainly bond lengths) are affected by and diagnostic for this stereoelectronic behavior, in line with experimental observations. The COCCOC species, however, are stronger bases then the COCOC (anomeric) species and approach regular ethers in their strength. The *gauche* forms in dimethoxyethane and 1,4-dioxane are altogether stronger bases than the *anti* forms and *anti* (equatorial) protonation is preferred over *gauche* (axial) protonation, unless ditopic protonation is possible. Clearly, both the anomeric and the *gauche* effects play a significant role in the formation, relative stability and reactivity of the charged species.

We then used the same approach to explore the proton affinities of the diastereomeric tetraoxadecalins,[10f] which contain several O—C—O and O—C—C—O moieties. It is in this context and following our keen interest in further cation inclusion properties of the tetraoxadecalins[10] that we undertook and present now the results of a theoretical investigation of the lithium affinity (LA) of such systems, using high-level *ab initio* calculations and comparing the geometric parameters with those of related theoretical and experimental literature results.

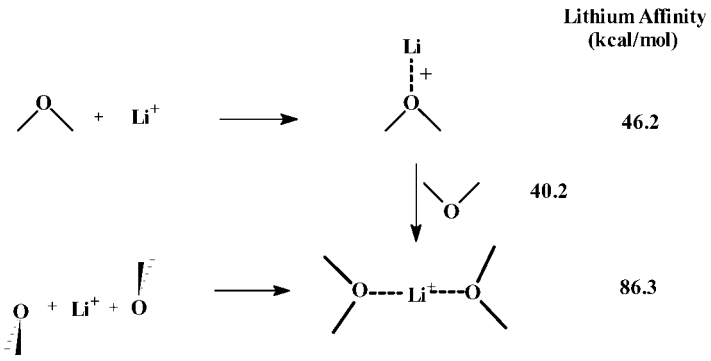
METHODOLOGY

Calculations were performed for dimethoxymethane, dimethoxyethane, 1,3-dioxane, *trans*-1,3-dioxadecalin and *cis*- and *trans*-tetraoxadecalin at the same level of theory, with the lithium affinity of dimethyl ether and of its dimer included within the frame of reference. Gas-phase LAs were calculated by difference from the calculated total energies of the neutral molecule (M) and of the derived ion–molecule complexes LA(M): $M + Li^+ \rightarrow MLi^+$; $LA(M) = E(Li^+) + E(M) - E(MLi^+)$. The geometries of the free and complexed ethers were fully optimized (without any geometric constraints) using the MP2/6–31G* basis set within Gaussian 94,[12] on a Cray J932 supercomputer. The choice of the basis set followed valuable information found in earlier elaborate high-level calculations of basic systems of this kind,[13,14] where RHF/6–31G* calculations provided satisfactory lithium affinities.[13] We deemed it necessary, for the sake of structural adequacy, to include electron correlation, mainly in order to offset the unduly strong C—O bond shortening caused by polarization functions in di- and polyhetero systems,[4,10] since the geometric parameters and their changes as a result of lithium complexation are bound to be of considerable significance in the understanding of the process. To maintain consistency we had to make some concessions, since our ultimate goal was the tetraoxadecalin stereoisomers, each with its 10 heavy atoms; these could be treated at a higher level,[10f,11] except for the additional lithium ion, which made a higher level calculation CPU prohibitive, so we excluded the diffuse functions. Hence our lithium affinities are invariably somewhat higher then available experimental values but, similar to our earlier work,[11] we regard the processes we deal with as isodesmic[15] (e.g. $ROCOLi^+R + Me_2O = ROCOR + Me_2OLi^+$) with internal comparison of energy differences, which should reduce errors caused by the use of differences in total energies instead of heats of formation and by omitting ZPE and other (BSSE) corrections. Some recent relevant high-level studies, which have been reported[16,17] in the course of this investigation, provided valuable collating sources for our own results and we shall refer to them below.

To find some structural information on systems related to those included in this study, we conducted systematic searches of the Cambridge Structural Database (CSD).[18] It became clear from the beginning that any statistical treatment would be delusive, since in all retrieved complexes, lithium had coordination numbers >2 and therefore only qualitative comparisons could be made. Nevertheless, valuable supporting information became available in this way.

RESULTS AND DISCUSSION

The calculated LAs of dimethyl ether (Me_2O) and of its dimer $(Me_2O)_2$ are shown in Fig. 2. The LA of Me_2O obtained at the MP2/6–31G* level (46.2 kcal mol^{-1}) (1 kcal = 4.184 kJ) is somewhat higher than the reported experimental results[19] and some calculated values (ca 40 kcal mol^{-1}),[13,14,16] but the incremental LA to $(Me_2O)_2 \cdot Li^+$ is (40.2) lower by 6 kcal mol^{-1}, just like in a higher level treatment.[16b] In fact, the total LA of the



Me_2O (C1-O-C2)

	Me_2O [a]	Li^+ [a]	$Me_2O.Li^+$ [a]	$(Me_2O)_2.Li^+$ [a]	$(Me_2O)_2.Li^+$-P [b]
O- Li^+			1.839	1.872	1.953
H_g-C1-O-C2			60.0	60.5/-60.7	66.0/-52.64
Li^+-O-C1			124.3	124.3	113-127
O-Li^+-O				180.0	112.0
C-O-Li^+-O-C				0/180.0	134/62
E(hartree)	-154.498839	-7.235533	-161.807965	-316.370786	

Figure 2. (a) *Ab initio* calculated energies (*E*), lithium affinities (LA) and selected parameters (bond lengths in Å, bond and dihedral angles in degrees) of dimethyl ether (Me_2O) and of its lithiated forms ($Me_2O{\cdot}Li^+$) and ($(Me_2O)_2{\cdot}Li^+$. The bottom process total LA is given in the right column and the incremental LA on the left. (b) Experimental (x-ray) structural parameters in $(Me_2O)_2{\cdot}Li^+$–P (P = 2,4,6-triphenylphenyl) (cf. Fig. 3).[20a]

Me_2O dimer towards the formation of $(Me_2O)_2{\cdot}Li^+$ (see Fig. 2, bottom) is virtually the same as that obtained incrementally, as expected from a calculation devoid of constraints or basis set superposition.

The planar geometry obtained for $Me_2O{\cdot}Li^+$ is in agreement with previously reported results[14] and fits conceptually well the similar and well known trigonal–planar geometry of carbenium ions. The initial C_2 geometry of the $(Me_2O)_2{\cdot}Li^+$ complex converged to a D_{2h} structure (Fig. 2).

The CSD search revealed only diethyl ether (or tetrahydrofuran) lithium complexes, which could be compared with our and previous calculated results. The trigonal planar R_2OLi^+ is generally well reproduced, but not so the computed linear O—Li—O geometry (Fig. 2); the retrieved (CSD) structures show a variation of the O— Li— O angle from 96.0° to 130.0°, with the majority falling in the range 110.0–118.0°. This can easily be understood from the tendency of lithium ion to form tri- and tetrahedral coordination with ligands, as manifest in its ability to engage with more than two ethers. Diether–Li^+ complexes are rare and usually accompany coordination to carbanion ligands (Li^+—C^-), as seen in two recent reports[20] (Fig. 3), with O—Li—O angles of 112°[20a] and 114°.[20b] The respective C—O—C/C—O—C dihedral angles of 134° and 127° are in between our coplanar geometry and the recently calculated[16] orthogonal (D_{2d}) one (see also below).

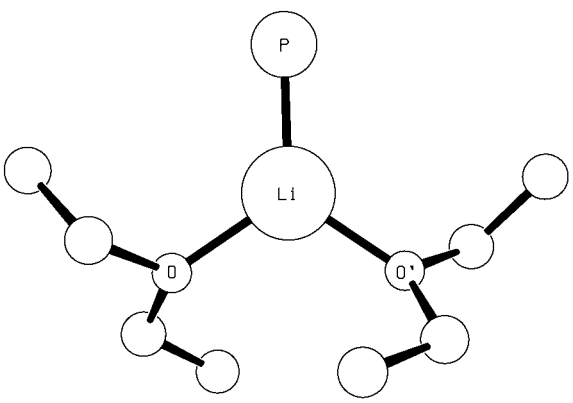
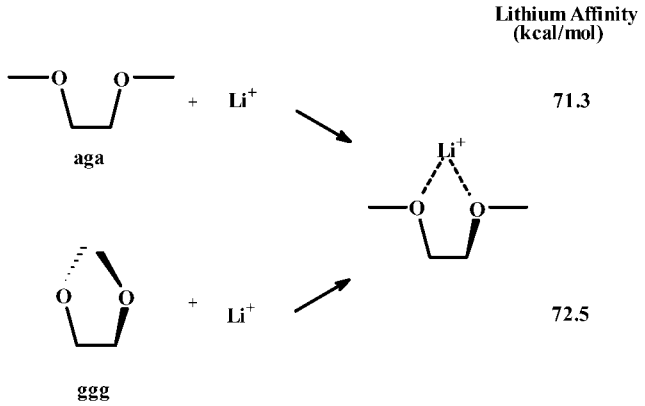


Figure 3. The $(Me_2O)_2{\cdot}Li^+$ moiety C-coordinated to a P ligand [P = 1-(2,4,6-triphenylphenyl)[20a] or 9-fluorenyl[20b]]

Turning to dimethoxyethane (DMOE), of its 10 possible conformations (*aaa, aga, aag*, *agg′*, *agg, ggg, gag*, *gag′*, *gg′g*, *ggg′*, *a* = *anti*, *g* = *gauche*),[4g,11b] only those with *gauche* central bond are formally able to bear ditopic coordination. Thus, of the two lowest conformers (within 0.1 kcal), *aaa* and *aga*, the former binds lithium with similar energy and geometry to ordinary ethers, whereas the latter is perfectly aligned for Li^+ chelation (Fig. 4). Of the other DMOE forms, we chose the (1.2 kcal) higher symmetric form, *ggg*, and these two conformers, ag^+a and $g^+\ g^+\ g^+$ and their lithium ion complexation product were calculated. Both lead to the same $ag^+a{\cdot}Li^+$ complex (the $g^+\ g^+\ g^+$ form after extensive conformational reorganization). The net LA is again higher than the experimental value (61 kcal mol^{-1}) and the matching calculated value (using an MP2/6–31 + G* hybrid basis set) in a remarkably detailed and high-level study.[17] Indeed, there are serious problems in attaining consistent matches of calculated with experimental energies within series of complexes and we are



DMOE (C-O1-C2-C3-O4-C)

	ggg[a]	*aga*[a]	*aga*.Li$^+$[a]	DMOE.Li$^+$[b]
O1-C2	1.416	1.416	1.445	1.432
C2-C3	1.529	1.508	1.510	1.494
O1- Li$^+$			1.896	2.036
O1- Li$^+$-O4			88.9	81.3
O1-C2-C3-O4	-40.8	-71.3	51.1	57.2
C-O1-C2-C3	-59.6	176.3	168.7	177.5
Li$^+$-O1-C2-C3			-38.3	-36.45
E(hartree)	-307.84937	-307.85123	-315.20039	

Figure 4. (a) *Ab initio* calculated energies (*E*), lithium affinities (LA) and selected parameters (bond lengths in Å, torsion angles in degrees) of dimethoxyethane (DMOE) *ggg* and *aga* conformers and the lithiated form (*aga*·Li$^+$). (b) Experimental (x-ray) structural parameters in the DMOE moiety of $(DMOE)_2$·LiI (cf. Fig. 5)

concerned with the mainly relative consistency throughout our results and with the evaluation of the stereoelectronic effects.

Crystal structures of dimethoxyethane–lithium complexes retrieved from the CSD[18] are of varied coordination and ligand assortment and, notwithstanding that, the *aga*·Li$^+$ form prevails and the geometric parameters are in surprisingly good agreement with our calculated results. The Li—O—C—C torsion angle observed is mostly around 40°, the O—C—C—O torsion angle is in the range 55.0–60.0° and the C—O—C—C torsion angle is mainly around 176°. In this case too, the best examples, featuring the lowest coordination and ionic Li$^+$, are the halides, bis(1,2-dimethoxyethane-*O*,*O*′)lithium bromide[21a] and iodide.[21b] The conformation of DMOE in the latter is shown in Fig. 5. C_2OLi^+ is no longer trigonal–planar and O—Li—O is, of course, not linear. In fact, this loss of ideal geometry is reasonably to blame for the lower lithium affinities of dimethoxyethane than the comparable dimethyl ether couple (Fig. 2).

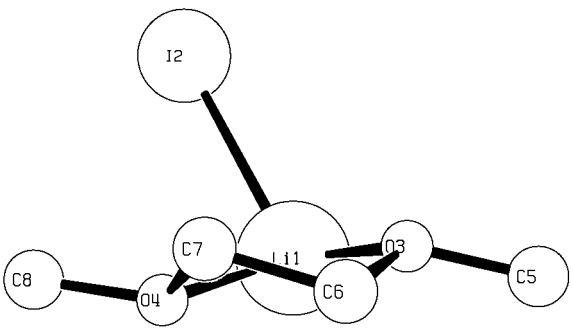
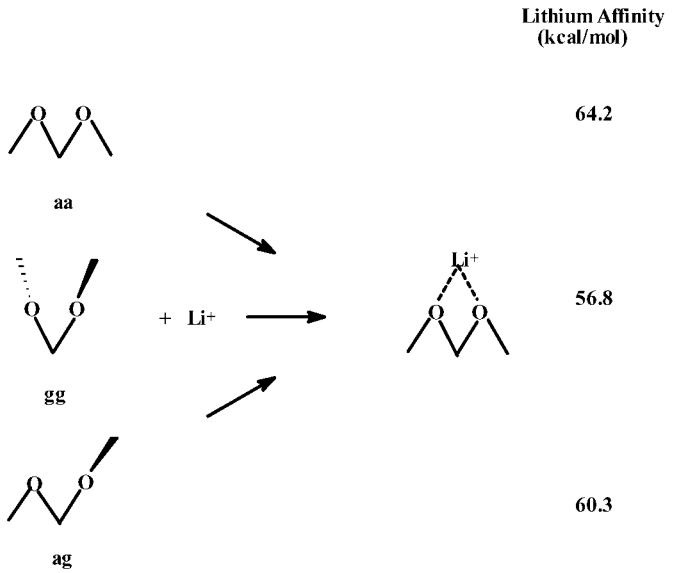


Figure 5. One of the DMOE·Li$^+$ moieties coordinated to I in the C_2 (around the Li—I axis) symmetric $(DMOE)_2$·LiI structure.[21b]

We turn now to the anomeric systems: the LA of dimethoxymethane (DMOM) is given in Fig. 6 and those of 1,3-dioxane and 1,3-dioxadecalin in Fig. 7. As is well known,[1,4g,11a] the relative energies of the DMOM conformers are $gg < ag < aa$ and no minimum has been found for the g^+g^- form (whose hypothetical high energy is due to steric encumbrance). Hence only the first three were considered here and, interestingly, all initial conformations converged in the lithiation process to the same *aa*·Li$^+$ form, in which Li$^+$ is coordinated with both oxygen atoms in a four-membered ring complex (Fig. 6). Thus, the most unstable *aa* form, devoid of any anomeric effect, provides the platform for the most stable lithium complex (*aa*·Li$^+$). The geometry is coplanar again with a very small O—Li—O angle. This is presumably the main reason for the calculated LA of dimethoxymethane, being lower than that of dimethoxyethane and of the dimethyl ether couple. We did not succeed in obtaining a fully optimized monotopic lithium complex of DMOM on one oxygen within a fragment subject to an anomeric effect and, to preserve consistency, we refrained from introducing any geometric constraints.

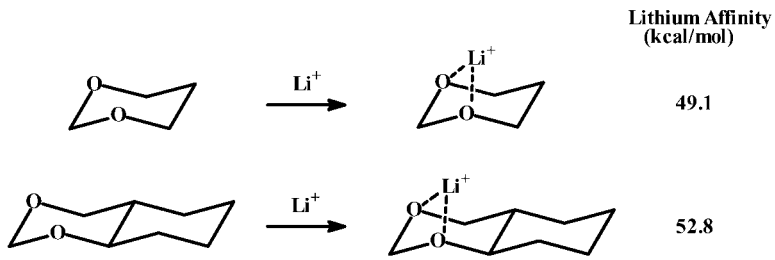
An instructive comparative exercise was performed by



DMOM (C-O1-C2-O3-C)				
	gg	*ag*	*aa*	Li^+.*aa*
O1-C2	1.405	1.415	1.400	1.419
C2-O3		1.390		1.448
O1- Li^+				1.926
O1-C2-O3	113.6	109.6	106.0	101.0
O1- Li^+-O3				69.3
Li^+-O1-C2-O3				0.1
E(hartree)	-268.69866	-268.69300	-268.68678	-276.02466

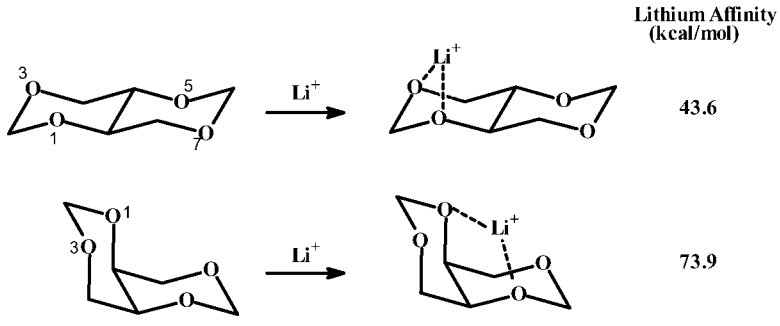
Figure 6. *Ab initio* calculated energies (*E*), lithium affinities (LA) and selected parameters (bond lengths in Å, torsion angles in degrees) of the 1,2-dimethoxymethane (DMOM) *aa, gg* and *ag* conformers, which converge to the same complex

calculating the lithium affinity of the g^+g^- conformer in frozen form, present in 1,3-dioxane (DOX) and in its bicyclic relative, 1,3-dioxadecalin (DOD) (Fig. 7). The C—O—C—O—C fragments in these systems are subject to a second-order anomeric effect, i.e. an On_{σ}–σ^*_{C-O} two electron–two orbital mixing. The LA of 1,3-dioxane is the lowest in the dioxa series and that of DOD is somewhat higher, presumably owing to its relative rigidity and to the electron-donating character of the fused ring. The O—Li—O angles are even smaller than in the *aa*·Li^+ complex and the O— Li bonds are longer (Fig. 6). We found, unfortunately, no experimental probe



	DOX	**DOX. Li^+**	**DOD**	**DOD. Li^+**
O1-C2	1.409	1.428	1.411	1.430
C2-O3			1.410	1.429
O3-C	1.430	1.466	1.431	1.467
O1- Li^+		2.042		2.022/2.043
O1-C2-O3	113.0	106.6	113.2	107.0
O1- Li^+-O3		68.2		68.8
Li^+-O1-C2-O3		37.5		35.3
E(hartree):	-306.70275,	-314.01652;	-462.21210,	-469.53175

Figure 7. *Ab initio* calculated energies (*E*), lithium affinities (LA) and selected parameters (bond lengths in Å, torsion angles in degrees) of 1,3-dioxane (DOX) and 1,3-dioxadecalin (DOD)



	t-TOD	Li^+.*t*-TOD	*c*-TOD	Li^+.*c*-TOD
O1-C2	1.418	1.435	1.412	1.435
C2-O3	1.410	1.429	1.406	1.410
O3-C	1.432	1.466	1.424	1.445
O1(3)- Li^+		2.065(2.048)		2.023
O1-C2-O3	113.1	106.9	112.9	107.8
O1- Li^+-O3		68.0		92.4
Li^+-O1-C2-O3		-38.2		-33.4
E(hartree):	-533.91893,	-541.22378;	-533.91809,	-541.27140

Figure 8. *Ab initio* calculated energies (*E*), lithium affinities (LA) and selected parameters (bond lengths in Å, torsion angles in degrees) of *trans*- and *cis*-1,3,5,7-tetraoxadecalin (TOD)

of the behavior of lithium ions with either 1,3-dioxane or dimethoxymethane.

We come now to the *raison d'être*, in a way, of this study, namely the calculated lithium affinities of *cis*- and *trans*-1,3,5,7-tetraoxadecalin (TOD). The latter's LA is even lower than that of 1,3-dioxane and we attribute this to the electron-withdrawing character of the oxygens of the fused dioxane ring, not involved in the complexation process. The effect is opposite to that caused by the electron-donating cyclohexane ring in 1,3-dioxadecalin.

Finally, we calculated the lithium affinity of *cis*-1,3,5,7-TOD and it optimized with the lithium ion binding with O1 and O5 (2.02 Å). Its LA is considerably higher than that of its *trans* isomer and of the other 1,3-dioxa systems and even than that of dimethoxyethane. This suggests that there is some degree of additional coordinative bonding to the other two oxygens. In fact, we were anticipating the possibility of a 1,3,5-double *gauche* bonding, but it seems that the latter is delocalized over both (symmetrical) sites, with Li—O3(7) distances of 2.40 Å. At this point, we wish to highlight a general feature of such di- and poly-oxa systems,[10] namely that high concentrations of lone-pair electrons cause bond order enhancement (shortening) in adjacent C—C and C—O bonds and coordination, in the present study with lithium ions brings about a depletion (lengthening) of these bonds. This is well illustrated in all above cases.

CONCLUSIONS

We have calculated *ab initio* (full optimization at the MP2/6–31G* level) the LAs of dimethyl ether (Me_2O), its dimer $(Me_2O)_2$, dimethoxyethane (DMOE), dimethoxymethane (DMOM), 1,3-dioxane (DOX), 1,3-dioxadecalin (DOD) and the diastereomeric *trans*- and *cis*-1,3,5,7-tetraoxadecalins (TOD). In all cases (except Me_2O), the lithiated species converged to structures with ditopic coordination. The natural tendency of lithium ion is to form linear O—Li and trigonal coplanar C(C)O—Li coordination and departure from this geometry lowers the LA. Indeed, the strain introduced by the coordination with both oxygens (forming five- or four-membered ring complexes) largely overshadows the stereoelectronic effects, but the molecules exhibiting the anomeric effect have the lowest LA, just as they showed the lowest basicity on protonation.[11] The LAs are conformationally dependent (wherever applicable) and decrease in the order $(Me_2O)_2$ > DMOE > DMOM > DOD > DOX > *trans*-TOD, but *cis*-TOD restores the high LA (better than DMOE) by virtue of multiple coordination.

Acknowledgements

This work was supported in part by a research grant from the Israel Science Foundation, by a postdoctoral fellowship from the National Council for Higher Education (to B.G.) and by generous Supercomputer CPU allocation by the Inter-University Computation Center.

REFERENCES

1. (a) Thatcher GRJ (ed). *The Anomeric Effect and Associated Stereoelectronic Effects ACS Symposium Series* No. 539. American Chemical Society: Washington, DC, 1993; (b) Juaristi E,

Cuevas G. *Tetrahedron* 1992; **48**: 5019; (c) Kirby AJ. *The Anomeric Effect and Related Stereoelectronic Effects at Oxygen*. Springer: Berlin, 1983; (d) Szarek WA, Horton D. (eds). *Anomeric Effect. Origins and Consequences*. *ACS Symposia Series* No. 87. American Chemical Society: Washington, DC, 1979; (e) Deslongchamps P. *Stereoelectronic Effects in Organic Chemistry*. Wiley: New York, 1983; (f) Lemieux RU. *Pure Appl. Chem*. 1971; **25**: 527; (g) Romers C, Altona C, Buys HR, Havinga E. *Top. Stereochem*. 1969; **4**: 39.

2. (a) Altona C. PhD Thesis, University of Leiden, 1964; 2(b) David S, Eisenstein O, Hehre WJ, Salem L, Hoffmann R. *J. Am. Chem. Soc*. 1973; **95**: 3806.
3. (a) Reed AE, Schleyer PvR. *Inorg. Chem*. 1988; **27**: 3969; (b) Salzner U, Schleyer PvR. *J. Org. Chem*. 1994; **59**: 2138, and references cited therein.
4. (a) Schleifer L, Senderowitz H, Aped P, Tartakovsky E, Fuchs B. *Carbohydr. Res.* 1990; **206**: 21; (b) Fuchs B, Schleifer L, Tartakovsky E. *Nouv. J. Chim.* 1984; **8**: 275; (c) Fuchs B, Ellencweig A, Tartakovsky E, Aped P. *Angew. Chem., Int. Ed. Engl.* 1986; **25**: 287; (d) Aped P, Apeloig Y, Ellencweig A, Fuchs B, Goldberg I, Karni M, Tartakovsky E. *J. Am. Chem. Soc.* 1987; **109**: 1486; (e) Aped P, Fuchs B, Schleifer L, Wolfe S. *J. Comput. Chem.* 1989; **10**: 265; (f) Senderowitz H, Aped P, Fuchs B. *Helv. Chim. Acta* 1990; **73**: 2113; *J. Comput. Chem.* 1993; **14**: 944; *Tetrahedron*, 1993; **49**: 3879; (g) Senderowitz H, Fuchs. B. *J. Mol. Struct. THEOCHEM* 1997; **395/396**: 123.
5. (a) Wolfe S, Tel LM, Haines WJ, Robb MA, Csizmadia IG. *J. Am. Chem. Soc*. 1973; **95**: 4863; (b) Wolfe S. *Acc. Chem. Res.* 1972; **5**: 102.
6. (a) Zefirov NS. *J. Org. Chem. USSR* 1974; 1147; (b) Zefirov NS, Gurvich LG, Shashkov AS, Krimer MZ, Vorob'eva EA. *Tetrahedron* 1976; **32**: 1211.
7. (a) Epiotis ND, Yates RL, Larson JR, Kirmaier CR, Bernardi FJ. *J. Am. Chem. Soc.* 1977; **99**: 8379; (b) Epiotis ND, Cherry W. *Chem. Commun.* 1973; 278; (c) Epiotis ND. *J. Am. Chem. Soc.* 1973; **95**: 3087.
8. Wiberg KB, Murcko MA, Laiding KE. *J. Phys. Chem.* 1990; **94**: 6956.
9. (a) Craig NC, Chen A, Suh KH, Klee S, Mellau GC, Winnewisser BP, Winnewisser M. *J. Am. Chem. Soc.* 1997; **119**: 4789; (b) Engkvist O, Karlstrom G, Widmark PO. *Chem. Phys. Lett.* 1997; **265**: 19.
10. (a) Senderowitz H, Linden A, Golender L, Abramson S, Fuchs B. *Tetrahedron* 1994; **50**: 9691; (b) Senderowitz H, Golender L, Fuchs B. *Tetrahedron* 1994; **50**: 9707; (c) Abramson S, Ashkenazi E, Goldberg I, Greenwald M, Jatzke H, Vardi M, Weinman S, Fuchs B. *J. Chem. Soc., Chem. Commun*. 1994; 1611; (d) Frische K, Greenwald M, Ashkenazi E, Lemcoff NG, Abramson S, Golender L, Fuchs B. *Tetrahedron Lett.* 1995; **36**: 9193; (e) Jatzke H, Frische K, Greenwald M, Golender L, Fuchs B. *Tetrahedron*, 1997; **53**: 4821; (f) Linden A, Beckhaus H-D, Verevkin SP, Rüchardt C, Ganguly B, Fuchs B. *J. Org. Chem.* 1998; **63**: 8205; (g) Grabarnik M, Abramson S, Lemcoff NG, Madar R, Weinman S, Fuchs B. *J. Org. Chem.* 2000; **65**: 1636.
11. (a) Ganguly B. Fuchs B. *J. Org. Chem.* 1997; **62**: 8892; (b) Ganguly B, Fuchs B. *J. Org. Chem.* 1999; **65**: 558.
12. Frisch MJ, Trucks GW, Schlegel HB, Gill PMW, Johnson BG, Robb MA, Cheeseman JR, Keith T, Petersson GA. Montgomery JA, Raghavachari K, Al-Laham MA, Zakrzewski VG, Ortiz JV, Foresman JB, Cioslowski J, Stefanov BB, Nanayakkara A, Challacombe M, Peng CY, Ayala PY, Chen W, Wong MW, Andres JL, Replogle ES, Gomperts R, Martin RL, Fox DJ, Binkley JS, Defrees DJ. Baker J, Stewart JP, Head-Gordon M, Gonzalez C, Pople JA. Gaussian 94. Gaussian: Pittsburgh, PA, 1995.
13. Smith SF, Chandrasekhar J, Jorgensen WL. *J. Phys. Chem.* 1982; **86**: 3308.
14. (a) Hay BP, Rustad JR. *J. Am. Chem. Soc.* 1994; **116**: 6316; (b) Hay BP, Rustad JR, Hostetler CJ. *J. Am. Chem. Soc.* 1993; **115**: 11158.
15. Ponomaraev DA, Takhistov VV. *J. Chem. Educ.* 1997; **74**: 201.
16. (a) Hill SE, Glendening ED, Feller D. *J. Phys. Chem. A* 1997; **101**: 6125; (b) More MB, Glendening ED, Ray D, Feller DF, Armentrout PB. *J. Phys. Chem. A* 1996; **100**: 1605; (c) Smith GD, Jaffe RL, Partridge H. *J. Phys. Chem.* 1997; **101**: 1705.
17. (a) Hill SE, Feller D, Glendening ED. *J. Phys. Chem. A* 1998; **102**: 3813; (b) Ray D, Feller DF, More MB, Glendening ED, Armentrout PB. *J. Phys. Chem. A* 1996; **100**: 16116.
18. (a) Allen FH, Kennard O. *Chem. Des. Autom. News* 1993; **8**: 31; (b) Allen FH, Kennard O, Taylor R. *Acc. Chem. Res.* 1983; **16**: 146.
19. (a) Staley RH, Beauchamp JL. *J. Am. Chem. Soc.* 1975; **97**: 5920; (b) Woodin RL, Beauchamp JL. *J. Am. Chem. Soc.* 1978; **100**: 501; *Chem. Phys.* 1979; **41**: 1.
20. (a) Olmstead MM, Power PP. *J. Organomet. Chem.* 1991; **408**: 1; (b) Hikansson M, Ottosson C-H, Boman A, Johnels D. *Organometallics* 1998; **17**: 1208.
21. (a) Rogers RD, Bynum RV, Atwood JL. *J. Cryst. Spectrosc.* 1984; **14**: 29; (b) Riffel H, Neumuller B, Fluck EZ. *Anorg. Allg. Chem.*, 1993; **619**: 1682.

