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Acta Cryst. (1993). **B49**, 726–729

A Lattice-Dynamical Calculation of Atomic Displacement Parameters in Oxahydrocarbons

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(Received 30 October 1992; accepted 26 January 1993)

Abstract

A lattice-dynamical calculation of atomic displacement parameters for oxahydrocarbons has been carried out using empirical atom–atom potential functions and estimates of the atomic charge from the literature and considering Coulombic interactions. The Born–von Kármán formalism in terms of molecular translations and rotations has been used. The performances of the different parameter sets are assessed by comparison with experimental data.

Introduction

Lattice-dynamical calculations of atomic displacement parameters in hydrocarbon crystals, made using semiempirical atom–atom potential functions (Pertsin & Kitaigorodski, 1987), have been carried out for many years with considerable success using either rigid-molecule models (Filippini, Gramaccioli, Simonetta & Suffritti, 1973) or, more recently, allowing for molecular flexibility (Bonadeo & Burgos, 1982; Gramaccioli & Filippini, 1983, 1985; Filippini & Gramaccioli, 1986, 1989; Filippini, 1990). Also,

the calculated infrared and Raman frequencies, phonon dispersion curves and thermodynamical quantities are in very good agreement with experiment. An interesting extension of the method to silicates has also been proposed recently (Pilati, Bianchi & Gramaccioli, 1990).

Very little work has been performed on heteroatom molecules, mainly because in this case the semiempirical potential parameter sets are scarcer and have not been thoroughly tested. Moreover, for these compounds, the different electronegativities of the constituent atoms give rise to non-negligible multipolar electrostatic moments, which must be accounted for by the use of an appropriate Coulombic potential model.

In an attempt to extend the range of applicability of the available semiempirical force fields, we have previously applied the method to azahydrocarbons (Criado, 1990) and chloro- and fluorohydrocarbons (Muñoz & Criado, 1992). In both cases, the use of 6-exp potential functions for van der Waals forces and an atomic point-charge model to account for electrostatic forces proved to be fruitful. In the present work, we consider oxahydrocarbons. Closely

Table 1. Potential parameter sets used in this work

$$V(r) = -A/r^6 + B \exp(-Cr).$$

	Reference	A (kJ mol ⁻¹ Å ⁶)	B (kJ mol ⁻¹)	C (Å ⁻¹)
O—O	(a)	1001.6	428843.3	4.06
	(b)	1085.3	325096.8	4.18
	(c)	1123.6	230064.0	3.96
C—C	(d)	2378.0	350142.0	3.60
	(d)	144.0	11112.0	3.74

References: (a) Derissen & Smit (1978); (b) Kitaigorodski, Mirskaya & Nauchitel (1970); (c) Cox, Hsu & Williams (1981); (d) Williams (1967).

related to this work, research on heteroatom molecules has recently been performed using atom-atom potentials for the prediction of molecular packing properties for a large database of oxahydrocarbon (Gavezzotti, 1991) and azahydrocarbon (Gavezzotti & Filippini, 1992) compounds.

The method of calculation is standard and has been explained in detail elsewhere (Criado, Conde & Márquez, 1984). The calculations were made using the Born-van Kármán formalism in terms of molecular rotations and translations to calculate the rigid-body thermal tensors and the individual atomic displacement parameters. An energy-minimization process with respect to molecular coordinates was

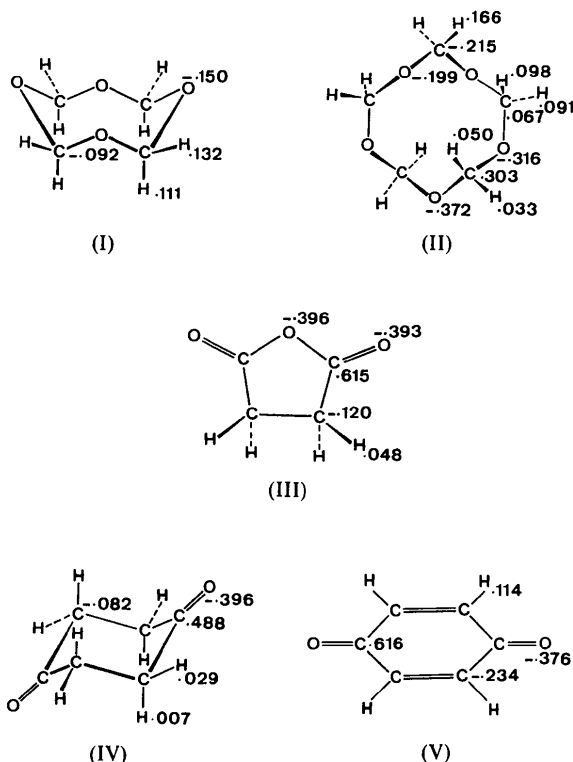


Fig. 1. Molecular structure and charge distribution (electronic units) of the chosen compounds: (I) tetraoxecane, (II) pentaioxecane, (III) succinic anhydride, (IV) 1,4-cyclohexanedione, (V) diglycolic anhydride.

Table 2. *R* disagreement factors obtained for the thermal parameters with the different potential sets
$$R = \frac{\sum_i \sum_j |U_{ij}(\text{exp.}) - U_{ij}(\text{calc.})|}{\sum_i \sum_j |U_{ij}(\text{exp.})|}.$$

	(a)	(b)	(c)
Tetraoxecane	0.143	0.506	0.337
Pentaioxecane	0.209	0.192	0.140
Succinic anhydride	0.154	0.354	0.236
1,4-Cyclohexanedione	0.360	0.268	0.294
Diglycolic anhydride	0.279	0.276	0.221

References: (a) Derissen & Smit (1978); (b) Kitaigorodski, Mirskaya & Nauchitel (1970); (c) Cox, Hsu & Williams (1981).

carried out first, to obtain the equilibrium configuration. Coulombic interactions were handled by the Ewald method.

Potential parameters

Potential functions $V(r) = -A/r^6 + B \exp(-Cr)$, with parameters taken from the literature, have been adopted. For interactions involving C and H atoms, Williams IVa parameters (Williams, 1967) have been taken because they have in the past widely proved to be the best for lattice-dynamical calculations. For oxygen-involving interactions, three different potential sets have been selected from the literature and are shown in Table 1. Sets (a) (Derissen & Smit, 1978, set III) and (c) (Cox, Hsu & Williams, 1981) were derived from the crystal structures and heats of sublimation, when available, of a wide number of compounds, whereas set (b) (Kitaigorodski, Mirskaya & Nauchitel, 1970) was derived from O₂ crystal data. Mixed interactions were obtained by the usual combination rules (Criado, Conde & Márquez, 1984).

In calculating Coulombic interactions, we have used atomic point charges available in the literature, obtained from *ab initio* molecular quantum-mechanical calculations.

Results

For our purposes, five oxahydrocarbons with well determined crystal structures have been selected from the literature, according to two criteria: that there are no hydrogen bonds present in the crystal packing and that there are reliable experimental atomic displacement parameters.

The chosen compounds are: tetraoxecane (Chatani, Yamauchi & Miyake, 1974), pentaioxecane (Chatani & Kitahama, 1973), succinic anhydride (Ehrenberg, 1965), 1,4-cyclohexanedione (Mossel & Romers, 1964) and diglycolic anhydride (Brisse & Sygusch, 1975). Fig. 1 shows their molecular structures and the point-charge Coulombic model obtained from quantum-mechanical calculations (Cox, Hsu & Williams, 1981). A TLS rigid-body fit (Schomaker & Trueblood, 1968) of the experimental

Table 3. Calculated (set of Derissen & Smit, 1978) and experimental thermal parameters (10^{-4} \AA^2) of some selected atoms

$$T(\mathbf{H}) = \exp(-2\pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* H_i H_j); \quad \mathbf{H} = (h, k, l).$$

		U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Tetraoxecane							
C(1)	Exp.	484	632	497	73	104	-11
	Cal.	511	783	481	70	65	-25
C(2)		623	524	452	1	239	-12
		678	654	423	-13	237	-12
O(1)		599	621	466	-32	148	-141
		663	727	384	-2	99	-105
O(2)		545	520	564	-70	204	8
		530	689	573	-70	211	-32
Pentaoxecane							
C(1)	Exp.	423	387	440	0	74	0
	Cal.	361	315	400	0	66	0
O(1)		383	509	390	22	67	2
		287	388	349	-41	72	-13
C(2)		340	514	511	-36	-28	-49
		261	465	411	-13	-15	-79
O(2)		406	504	614	76	-16	-58
		324	457	464	96	-76	-72
Succinic anhydride							
C(1)	Exp.	432	555	479	16	19	-65
	Cal.	380	551	544	7	-53	-75
C(2)		506	590	365	-22	-81	-9
		412	608	485	-19	-79	43
O(5)		417	639	397	22	-3	-43
		404	647	462	84	-9	-77
O(6)		709	694	785	-152	-7	-107
		619	626	897	-109	-12	-122
1,4-Cyclohexanedione							
C(1)	Exp.	216	163	210	-24	24	0
	Cal.	158	88	127	0	23	-2
C(2)		193	245	201	-24	68	-11
		134	112	169	-23	51	-10
O(1)		253	247	219	-24	-8	-14
		234	136	150	-7	-18	-6
O(2)		301	445	226	-96	33	-74
		257	242	155	-37	-18	-26
Diglycolic anhydride							
Molecule 1							
O(1)	Exp.	562	325	511	32	51	-10
	Cal.	301	263	438	16	116	-27
O(4)		480	514	485	49	100	-9
		341	425	404	102	138	-29
C(2)		425	377	463	-16	64	24
		281	314	364	15	58	47
C(3)		569	414	392	4	71	-9
		388	356	321	10	83	-46
Molecule 2							
O(1)	Exp.	501	335	567	24	115	26
	Cal.	274	265	383	-8	65	61
O(4)		492	558	425	56	55	49
		347	395	336	71	47	92
C(2)		419	392	428	-22	73	-28
		265	299	372	-27	95	-14
C(3)		589	457	462	13	117	39
		396	340	331	-23	129	57

atomic thermal parameters has been carried out as a test of the molecular rigidity; the resulting disagreement factors are 1.5, 6.7, 7.2, 6.9 and 6.1%, for the fits of the five compounds, respectively, indicating that they behave fairly well as rigid bodies.

The lattice-dynamical atomic displacement parameters U_{ij} have been calculated for the five chosen compounds using the three different potential

Table 4. Calculated crystal energy (E_T) and Coulombic contribution (E_C) (kJ mol^{-1}) for the different compounds and parameter sets

	(a)	(b)	(c)
Tetraoxecane			
E_T	-69.8	-77.2	-75.4
E_C	-17.3	-17.6	-17.5
Pentaoxecane			
E_T	-78.0	-87.0	-84.8
E_C	-18.0	-18.5	-18.3
Succinic anhydride			
E_T	-67.5	-77.4	-74.4
E_C	-25.5	-25.9	-25.6
1,4-Cyclohexanedione			
E_T	-65.4	-74.8	-71.8
E_C	-17.1	-16.9	
Diglycolic anhydride			
E_T	-69.9	-82.5	-78.8
E_C	-26.1	-26.9	-26.6

References: (a) Derissen & Smit (1978); (b) Kitaigorodski, Mirskaya & Nauchitel (1970); (c) Cox, Hsu & Williams (1981).

parameter sets. As usual, a disagreement factor between calculated and experimental factors, R , has been calculated for each compound and parameter set; the results are shown in Table 2. The experimental and calculated [set (a), Derissen & Smit (1978)] U_{ij} thermal factors for the different compounds are shown in Table 3. Table 4 shows the calculated total lattice energy and its Coulombic contribution at the minimum-energy configuration for the different compounds, obtained using the three potential parameter sets.

Discussion

The calculated values of the atomic displacement parameters are in agreement with the experimental ones; this is similar to the situation for hydrocarbons (Criado & Márquez, 1988) and can be regarded as satisfactory, in view of the uncertainties and systematic errors that usually affect experimental atomic displacement parameter values. The agreements for atomic displacement parameters calculated with both (a) and (c) sets are alike on average and better than those found for set (b), probably because a larger database was considered in their derivation.

As in the case of azahydrocarbons (Criado, 1990), the atomic point charges may attain large values (Fig. 1), indicating that Coulombic interactions play an important role in oxahydrocarbons (see Table 4) and must be accounted for in order to obtain satisfactory lattice-dynamical results.

As a summary of this series of papers, we can conclude that the field of applicability of empirical atom-atom potential functions to the calculation of lattice-dynamical atomic displacement parameters

can be considerably extended to molecules containing nitrogen, chlorine, fluorine or oxygen and that a reliable lattice-dynamical model can be obtained with atom-atom parameter sets taken from the literature, provided that information about the electric charge is available. This last point is not a serious problem nowadays, because quantum-mechanical calculation of atomic point charges, even for complex molecules, is not a forbidding task with modern computers.

It is also stimulating to notice how atom-atom potentials derived from static properties give a good performance in lattice-dynamical calculations.

Future work will be devoted to obtaining more reliable experimental atomic displacement parameters for comparisons. In particular, work is in progress on the correction of experimental atomic displacement systematic parameters for systematic thermal diffuse scattering (TDS) errors with lattice-dynamical models.

We acknowledge the financial support given to this work by the Spanish CICYT through project PB 89-0540.

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Acta Cryst. (1993). **B49**, 729–738

Solid-State and Solution Conformations of Isotiazofurin: Crystallographic, Computational and ¹H NMR Studies

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(Received 28 May 1992; accepted 27 January 1993)

Abstract

Isotiazofurin (C₉H₁₂N₂O₅S, NSC363223) is a thiazole nucleoside analogue of the antitumour agent tiazofurin. The conformation of this analogue has been studied using a variety of experimental and computational techniques. The crystal and molecular structure of isotiazofurin has been determined using single-crystal X-ray diffraction techniques and refined to a conventional *R* value of 0.030 for all data. Conformational features conserved in other thiazole nucleoside structures are also observed in

the solid-state structure of isotiazofurin. The C-glycosidic torsion angle remains in the *anti* conformation and the carboxamide amino group remains *cis*-planar to the ring nitrogen. *Ab initio* calculations at the RHF/321G*/321G* level and natural bond orbital analysis of the results suggest that the carboxamide *cis*-planar conformation observed in the solid state is maintained in solution. However, semi-empirical calculations suggest that a *syn* conformation about the C-glycosidic bond is energetically favored. This is supported by ¹H nuclear Overhauser enhancement (NOE) studies. Analyses of NOE results using both slow- and rapid-exchange models

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