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A Lattice-Dynamical Comparison of Nonbonded Potential Parameters for Hydrocarbons

BY A. CRIADO AND R. MARQUEZ

Departamento de Optica e Instituto de Ciencia de los Materiales, Universidad de Sevilla, Aptdo 1065, 41080 *Seville, Spain*

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Abstract

The crystallographic thermal parameters have been calculated with a lattice-dynamical procedure for some hydrocarbons in the rigid-body appproximation using some sets of potential parameters taken from the literature. A comparison with experimental data confirms that the well known Williams IV*b* set is very good for describing vibrational properties in polycyclic hydrocarbons.

Introduction

The calculation of crystallographic thermal parameters using a lattice-dynamical approach with empirical potential energy functions has become a routine procedure nowadays. Although some work has been done with heteroatom compounds (Dianez, Criado, Lopez-Castro & Marquez, 1986) the most successful results have been obtained on hydrocarbons because a large number of potential sets have been derived [for a review see Mirsky (1978)] which correctly reproduce the static properties of these compounds. A possible explanation for this success may be that the intermolecular forces in hydrocarbons are well described by r^6 and exp potential models, other interactions, mainly Coulombic, being small in comparison. Evidently, this is not the case for nitrogen (Williams & Cox, 1984) or oxygen (Cox, Hsu & Williams, 1981) compounds where electrostatic interactions are important.

The most extensive contribution in this field has been made by Filippini, Gramaccioli, Simonetta & Suffritti, who made in 1973 a comparison of different potential sets and concluded that the so-called Williams IV*b* set (Williams, 1967)* gives the best agreement with experiment. Since then, this set has been adopted in most calculations, which currently include the contribution of internal modes described by appropriate intramolecular fields (Filippini & Gramaccioli, 1986).

The purpose of this paper is to make an updated comparison of the best potential sets which are available in the literature nowadays. For such a comparison, some particular hydrocarbons have been extensively studied, such as naphthalene and anthracene (Gramaccioli & Filippini, 1983) and for these the results are satisfactory. In order to extend the number of experimental results we consider some additional 'rigid-body' compounds taken from recent literature which gives accurate structure determinations.

Potential sets

Since the only potentials of importance are van der Waals interactions we have selected five different sets of so-called '6-exp' functions which are shown in Table 1. Sets (*a*), (*b*) and (*e*) were derived by Williams (1966, 1967; Williams & Starr, 1977) by fitting crystal structure parameters (non-vibrational). Set (*c*) was derived by Warshel & Karplus (1972) together with an intramolecular potential field to be applied in conformational analysis. Set (*d*) was derived by Mirskaya, Kozlova & Bereznitskaya (1974) (see also Mirsky, 1978). Because of the large number of compounds involved in the fits these sets [except (*d*)] are among the most reliable which can be found in the literature.

Method of calculation

The individual crystallographic thermal parameters (Willis & Pryor, 1975) were obtained from the **T**, **L** and **S** tensors (Schomaker & Trueblood, 1968) calculated by sampling the Brillouin zone and summing the contributions of the allowed vibrational modes. These were found by diagonalization of the dynamical matrix (Born & Huang, 1954) constructed in the quasi-harmonic and rigid-body approximations considering interactions up to a limit of 6 Å. The C–H bond distances were normalized to 1·08 Å, maintaining the experimental bond angles in order to get a better agreement with experiment. A previous energy-minization procedure was necessary in order to achieve the equilibrium configuration. The program *WMIN* (Busing, 1972) was used to perform the Newton-Raphson steps. A more detailed description of the method can be found elsewhere (Criado, Conde & Marquez, 1984).

* This set is indicated by Filippini *et al.* and other authors as IV*a* instead of IV*b*.

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Table 1. *Potential energy parameters*

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

		A(kJ mol^{-1} Å^{-6})	B(kJ mol^{-1})	C(Å^{-1})
(*a*)	C–C	2239·0	311689·0	3·60
	C–H	581·8	39394·4	3·67
	H–H	150·7	16744·0	3·74
(*b*)	C–C	2377·0	350075·0	3·60
	C–H	521·2	36694·5	3·67
	H–H	114·3	11109·6	3·74
(*c*)	C–C	3123·0	386916·0	3·60
	C–H	502·3	47289·2	3·67
	H–H	79·53	6873·41	3·76
(*d*)	C–C	1762·0	299718·0	3·68
	C–H	493·9	77859·6	3·94
	H–H	121·4	20511·4	3·29
(*e*)	C–C	2414·0	367250·0	3·60
	C–H	573·0	65485·0	3·67
	H–H	136·0	11677·0	3·74

(*a*) Williams (1966), set IV*a*; (*b*) Williams (1967), set IV*b*; (*c*) Warshel & Karplus (1972); (*d*) Mirskaya, Kozlova & Bereznitskaya (1974); (*e*) Williams & Starr (1977), set II.

Four compounds were chosen to perform the present study: (i) 1,4,5,8-tetramethylnaphthalene (Shiner, Noordik, Fisher, Eckley, Bodenhamer & Haltiwanger, 1984), (ii) 6b,8a-dihydrocyclobut[*a*]acenaphthylene (Hazell, 1976), (iii) fluorene (Belsky, Zavodnik & Vozzhennikov, 1984) and (iv) 1,2,3,4,5,6,7,8-octahydroanthracene (van Koningsveld & Baas, 1984). All these compounds show good agreement with rigid-body behaviour in a Schomaker–Trueblood fit of experimental thermal parameters (Table 2).

Table 2. *Relevant data for the chosen compounds*

	Space group	Z	Formula	T(K)	R(%)
(i)	$P2_1/n$	2	$C_{14}H_{16}$	293	12
(ii)	*Pnma*	4	$C_{14}H_{10}$	293	5
(iii)	*Pnma*	4	$C_{13}H_{10}$	293	7
(iv)	$P2_1/c$	2	$C_{14}H_{18}$	110	6

Z is the number of molecules per unit cell. R is the agreement factor of a Schomaker–Trueblood fit of experimental thermal parameters. T is the structure-determination temperature.

Table 3. *Results of the calculations*

		Δt(Å)	$\Delta\theta$(°)	E(kJ mol^{-1})	R(%)
(i)	(*a*)	—	2·1	81·2	30·6
	(*b*)	—	1·3	80·8	20·4
	(*c*)	—	0·1	90·8	23·8
	(*d*)	—	0·1	80·4	20·0
	(*e*)	—	0·2	69·9	50·9
(ii)	(*a*)	0·02	0·6	76·2	15·9
	(*b*)	0·03	0·7	76·6	9·4
	(*c*)	0·02	0·6	90·4	13·4
	(*d*)	0·01	0·6	71·2	30·4
	(*e*)	0·01	0·6	64·9	37·3
(iii)	(*a*)	0·07	1·6	70·7	17·2
	(*b*)	0·08	1·0	70·3	11·6
	(*c*)	0·10	0·1	81·2	12·4
	(*d*)	0·12	0·3	64·0	33·1
	(*e*)	0·11	0·1	59·9	40·9
(iv)	(*a*)	—	0·7	76·6	39·2
	(*b*)	—	0·3	77·4	21·0
	(*c*)	—	0·1	86·2	13·6
	(*d*)	—	0·7	80·8	21·9
	(*e*)	—	0·4	63·6	44·4

The first and second columns are the Newton–Raphson shifts. The third column is the calculated packing energy at a 6 Å cut-off. The fourth column is the agreement factor between calculated and experimental thermal factors.

Results and discussion

Table 3 shows the results of the Newton–Raphson minimization. The first and second columns are the translational and rotational shifts to get the equilibrium configuration from the experimental structure. The third column is the calculated packing energy. The Ewald–Bertaut–Williams method (Williams, 1971) cannot be used here to evaluate the long-range contribution because some potentials do not fulfil the geometric rule for C–H interactions; therefore we used an integration over an effective continuum.

As we can see, the results are quite similar for the different potential sets. As far as the equilibrium configuration is concerned all the sets are equally good, they reproduce the experimental structure with great accuracy and the packing energies are rather similar. Therefore we can conclude that all the sets considered are suitable for describing the static properties. Static properties depend mainly on the potential-curve minimum position whereas dynamical properties depend on the curvature about the minimum. Therefore, the thermal parameters are expected to be more sensitive to the different sets. We have used an agreement factor defined as

$$R = \sum_i \sum_j |U_{ij}(\text{exp}) - U_{ij}(\text{cal})| / \sum_i \sum_j |U_{ij}(\text{exp})|$$

and the results for the different sets are shown in column four. Sets (*b*) and (*c*) are the best by far and their agreement is rather good. Therefore, in spite of its 'oldness', Williams's IV*b* set continues to be a very good choice for calculating thermal parameters in hydrocarbons.

Table 4 shows the experimental thermal parameters along with those obtained with set (*b*). In those cases where the agreement with experiment is less good a systematic difference occurs between experimental and calculated values, *i.e.* the former are nearly constantly higher than the latter. Therefore, if an adjustable scale factor is introduced the disagreement would drop drastically. There may be many sources of experimental systematic errors, TDS contributions, absorption *etc.*, and the theoretical model has its own limitations, rigid-body and harmonic approximations. The rigid-body approximation might be a little too drastic for large molecules where internal degrees of freedom might include relatively 'soft modes'. Even for pyrene, a 'classical' example of a rigid molecule because of an excellent TDS fit, inclusion of internal

Table 4. *Experimental and calculated thermal parameters*

$T(H) = \exp[-2\pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* H_i H_j]$, $H = (hkl)(\text{Å}^2 \times 10^4)$

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
(i)						
C1 (exp.)	420	430	370	32	85	94
(cal.)	392	324	344	34	82	91
C2	510	460	420	60	100	50
	487	388	376	49	118	55
C3	460	500	460	−20	90	100
	408	394	427	−6	91	98
C4	480	690	600	−70	210	10
	444	528	509	−1	182	94
C5	590	680	560	0	260	−30
	517	522	460	49	207	54
C6	720	580	540	−10	170	−80
	685	450	438	42	115	−18
C7	610	690	630	−190	150	−40
	499	468	554	−89	50	86
(ii)						
C1	332	551	511	−55	−29	4
	314	471	531	−29	−43	−12
C2	371	453	393	−25	−33	−48
	370	444	364	−10	−50	−34
C3	340	417	335	16	39	−14
	337	408	318	24	16	−12
C4	457	427	466	40	67	−16
	436	434	466	82	37	10
C5	538	503	485	179	57	90
	442	584	510	159	20	92
C6	410	672	381	112	−25	62
	354	715	409	105	−23	71
C7	317	553	308	0	3	0
	296	603	308	0	0	0
C8	298	408	301	0	41	0
	288	443	263	0	23	0
(iii)						
C1	760	700	750	110	20	100
	790	584	783	53	44	121
C2	930	600	1000	40	120	20
	898	532	1034	−27	109	9
C3	810	690	970	−130	70	−190
	847	624	990	−131	11	−158
C4	670	740	680	−30	−30	−30
	642	672	724	−85	−64	−109
C5	370	630	630	−20	70	−10
	451	550	524	−17	31	−16
C6	440	680	580	40	10	30
	542	558	535	15	36	41
C7	650	760	510	0	−140	0
	657	670	510	0	−59	0
(iv)						
C1	126	99	148	−17	78	−11
	102	89	97	−15	52	−8
C2	116	109	123	−6	61	−14
	96	95	83	−7	43	−11
C3	120	151	167	−11	47	0
	101	139	115	−3	32	−11
C4	162	180	143	15	39	6
	137	166	101	28	27	3
C5	172	138	180	31	78	28
	161	133	115	38	58	24
C6	159	117	169	11	91	29
	153	105	115	10	71	21
C7	131	94	126	2	76	−2
	108	87	83	−4	52	−5

modes appreciably increases calculated temperature factors (Gramaccioli & Filippini, 1983).

On the other hand, the calculated thermal parameters are rather sensitive to different normalizations of the C–H bond distances. As a consequence of these facts, we cannot push the comparison beyond the limits (experimental and of the model) and the results obtained can be considered as very good.

As mentioned before, more sophisticated models are currently proposed, such as non-rigidity, which accounts for internal-mode contributions. Another way of improving results might be the use of more complete potential models. In this way we are currently working on the implementation of Coulombic interactions in our computer programs. This will enable us to study the influence of the electrostatic energy on the computed thermal parameters, a point which is essential for heteroatom systems with larger electrostatic interactions.

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A full-symmetry translation function. II. The introduction of positioned fragments.

By JORDI RIUS and CARLES MIRAVITLLES, *Institut de Ciència dels Materials, CSIC, c/. Martí i Franqués, s/n Box* 30102, 08028-*Barcelona, Spain*

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Abstract

A generalization of the full-symmetry τ translation function [Rius & Miravitlles (1986). *Acta Cryst.* A**42**, 402–404] is given that allows the explicit introduction of the positioned part of the structure in its computation. This generalization is useful for the structural expansion of molecular crystals with more than one molecule in the asymmetric unit, specially in those cases where the non-availability of high-resolution diffraction data prevents the use of the tangent-formula recycling of a single positioned fragment, *e.g.* in the determination of crystal structures from powder diffraction data. Its application to four structures is shown.

Rius & Miravitlles (1986) described the reciprocal-space τ translation function which places molecular fragments with respect to all symmetry elements simultaneously using the Fourier expansion of Harada, Lifchitz, Berthou & Jolles (1981). Here a generalization of the τ function is introduced that also considers the positioned part of the structure. This generalization is useful for molecular crystals with more than one molecule in the asymmetric unit, since it allows one to take advantage of the molecular orientations found in the rotation search. If the symmetry-independent molecules are similar, a single rotation search furnishes all correct orientations. Once the first molecular fragment is positioned, another symmetry-independent oriented molecular fragment can be placed with respect to it. This procedure can be repeated iteratively in crystal structures containing more than two independent molecules in the asymmetric unit.

The principal application of this function lies in those problems where only low-resolution data are available, *i.e.* when the tangent-formula recycling of a single positioned fragment is not possible. One example of this potential application is the crystal-structure determination from powder diffraction data only, since, as is well known, the better resolved and consequently the more reliable indexed reflections of a powder spectrum are those appearing at low 2θ angles.

The τ function is defined as

$$\tau(\mathbf{r}) = (1/V)\sum_{\mathbf{h}} |\mathbf{F}'_o(\mathbf{h})|^2 |\mathbf{F}'_c(\mathbf{h},\mathbf{r})|^2 \quad (1)$$

$$= \mathrm{Re}\,(2/V)\sum_{\mathbf{h}} \Big[\sum_j |\mathbf{F}'_o(\mathbf{h})|^2 \mathbf{F}_p(\mathbf{h}) \mathbf{S}_j^*(\mathbf{h}) \times \exp(-i2\pi\mathbf{h}\mathbf{t}_j) \exp(-i2\pi\mathbf{h}_j\mathbf{r})$$

$$+ \sum_j \sum_{k>j} |\mathbf{F}'_o(\mathbf{h})|^2 \mathbf{S}_j(\mathbf{h}) \mathbf{S}_k^*(\mathbf{h}) \times \exp(-i2\pi\mathbf{h}\mathbf{t}_{kj}) \exp(-i2\pi\mathbf{h}_{kj}\mathbf{r}) \Big] \quad (2)$$

with

$$|\mathbf{F}'_o(\mathbf{h})|^2 = |\mathbf{F}_o(\mathbf{h})|^2 - |\mathbf{F}_p(\mathbf{h})|^2 - \sum_l |\mathbf{S}_l(\mathbf{h})|^2 - \sum_m^q f_m(\mathbf{h})^2, \quad (3)$$

where $\boldsymbol{r}$ = shift vector applied to the input oriented molecule (hereafter called search fragment); $\mathbf{F}_o(\mathbf{h})$ = observed structure factor; $\mathbf{S}_j(\mathbf{h})$ = molecular structure factor computed with the atomic coordinates obtained after applying the rotation matrix R_j to the search fragment, referred to a fixed local origin in the fragment; $\mathbf{t}_j$ = translation of the jth space-group symmetry operation; $\mathbf{t}_{kj} = \mathbf{t}_k - \mathbf{t}_j$; $\mathbf{h}_{kj} = \mathbf{h}(R_k - R_j)$; $\mathbf{h}_j = \mathbf{h}R_j$; $\mathbf{F}_p(\mathbf{h})$ = structure factor computed with the positioned atoms; q = number of atoms in the unit cell not included in the calculation of $\mathbf{F}_p(\mathbf{h})$ or $\mathbf{S}_j(\mathbf{h})$.

$|\mathbf{F}'_o(\mathbf{h})|^2$ are the Fourier coefficients of the observed Patterson function without the Patterson function of the positioned part and without the self-Patterson function of the search fragment (and symmetry-related ones). The last term in (3) subtracts the contribution from the q atoms to the Patterson origin peak (Beurskens, Gould, Bruins Slot & Bosman, 1987).

$|\mathbf{F}'_c(\mathbf{h},\mathbf{r})|^2$ are the Fourier coefficients of the calculated cross-Patterson function without those cross-Patterson peaks due to interactions between the atoms in the positioned part. $|\mathbf{F}'_o(\mathbf{h})|^2$ and $|\mathbf{F}'_c(\mathbf{h},\mathbf{r})|^2$ are equal only for $q = 0$ and if $\mathbf{r}$ is the correct shift vector. The correct shift vector is always characterized by a strong positive maximum in τ.

The generalization of the τ function to consider the positioned part of the structure is reflected in the appearance of the double summation in (2),

$$\mathrm{Re}\,(2/V)\sum_{\mathbf{h}}\sum_j |\mathbf{F}'_o(\mathbf{h})|^2 \mathbf{F}_p(\mathbf{h}) \mathbf{S}_j^*(\mathbf{h}) \times \exp(-i2\pi\mathbf{h}\mathbf{t}_j) \exp(-i2\pi\mathbf{h}_j\mathbf{r}) \quad (4)$$

which nearly represents the convolution of the inverted search fragment with the modified α function (Ramachandran & Srinivasan, 1970) and vanishes when no part of the structure is known. This is an automated interpretation of the modified α function when the geometry of the molecular search fragment is known. If a fragment is already positioned, the τ asymmetric unit will be, in general, the whole unit cell (except for non-primitive lattices).

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