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Quantum Calculation of the Intrinsic Torsional Barrier of C—C and C—O Bonds

Camillo Tosi

Istituto Ricerche "G. Donegani", Via G. Fauser 4, I-28100 Novara, Italy

Rolf Hilgenfeld

Institut für Kristallographie, Freie Universität Berlin, Takustrasse 6, D-1000 Berlin 33, Federal Republic of Germany

PCILO and *ab initio* calculations have been performed to investigate the energies associated to rotation about the central bond in *n*-butane and methyl ethyl ether. Quantum mechanical energies have been fit to a classical intramolecular force field, containing torsional and nonbonded (Lennard-Jones 6–12 plus Coulomb) contributions, with a standard deviation comprised between 0.03 and 0.09 kcal mol^{-1}. Two conditions have proved indispensable to reach such level of accuracy: (a) the use of a torsional potential with threefold periodicity, which corrects for the part of the rotation barrier not covered by van der Waals repulsions and may be interpreted as bond–bond repulsion; (b) the introduction in the force field for ethers of terms accounting for orbital interaction effects of different nature than the normal molecular mechanics nonbonded interactions; these terms are represented either by low order rotational potential functions or preferably by interactions of atoms simulating lone-pair orbitals and bonded to oxygen in such a way as to render it sp^3-hybridized. According to *ab initio*, the height of the threefold torsional potential about C—C and C—O bonds is comparable and is of the order of 3 kcal mol^{-1}. According to PCILO, it is larger for C—C (ca. 1.5 kcal mol^{-1}) than for C—O (ca. 0.5 kcal mol^{-1}).

Key words: *n*-butane – Internal rotation in ~ – Methyl ethyl ether – Internal rotation in ~.

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1. Introduction

Molecular mechanics are nowadays one of the most powerful tools in conformational analysis, and there are good hopes that an accurate consideration of all intramolecular forces and their role in determining quantities which are amenable to experiment will lead, in a near future, to the development of reliable force fields for any kind of molecules. Many problems, however, are still open, and the success in answering them will be a decisive factor in the fulfilment of the aforementioned hopes.

One of these problems is the insufficiency of the model of molecular mechanics – according to which the intramolecular force field can be expressed as a sum of contributions from bond stretching, bond angle bending, torsional strain and nonbonded (van der Waals plus Coulomb) interactions – when orbital interaction effects of a different nature play a nonnegligible role. This is true, e.g. for ethers, where the results of force fields calculations are by no means as satisfactory as those for hydrocarbons, or even for carbonyl compounds. In particular, the presence in ethers of an oxygen atom bound to two sp^3-carbon atoms leads to the question, of how high the barrier to rotation about the C—O bond is, as compared to the one about the C—C bond in hydrocarbons.

The present study attempts to give an answer to this question.

2. Energy Calculations

We chose for our comparison *n*-butane (NB) and methyl ethyl ether (MEE). For both molecules we constructed a starting set of cartesian coordinates *with standard valence geometry* (C—C = 1.541 Å, C—O = 1.426 Å, C—H = 1.09 Å; C—C—C = C—O—C = C—C—H = O—C—H = tetrahedral) and all-*anti* torsional geometry (H—C—C—C = C—C—C—C = H—C—C—O = C—C—O—C = C—O—C—H = 180°). Afterwards we computed the energies corresponding to rotation φ about the central bond. Because of the molecular symmetry, the range taken into account was limited to 0°–180°.

The assumption of constant bond lengths and angles may, and in many cases does, lead to unrealistic torsional barriers: indeed, if flexible rotation is permitted, i.e. if these parameters are varied, perhaps to an extent related to the torsional angles' variation, agreement with experiments is much improved. However, the introduction of stretching and/or bending degrees of freedom entails a number of additional parameters to describe our systems, and this would require a large increase of the number of determinations of the dependent variable (calculations of intramolecular energy) in the subsequent evaluation (*vide infra*) of a parameter set in best agreement with quantum mechanical energies.

Computations were done with a recent version [1] of the semi-rigorous quantum mechanical method PCILO, this choice being dictated not only by the reliability of the method in angular conformational analysis [2], but also by our aim at getting results of use to elucidate a critical point in the conformational study of

Table 1. PCILO and *ab initio* energy differences (kcal mol^{-1}) for rotation about the central bond in *n*-butane and methyl ethyl ether

Rotation	NB		MEE		Rotation	NB		MEE	
(deg)	PCILO	*ab initio*[a]	PCILO	IBMOL	(deg)	PCILO	*ab initio*[a]	PCILO	IBMOL
0	4.374	7.643	7.095	17.885	95	0.998		1.196	
5	4.249		6.912		100	1.310		1.247	2.673
10	3.910		6.422	16.416	105	1.595		1.300	
15	3.443		5.871		110	1.833		1.337	3.174
20	2.945		5.162	13.226	115	2.008		1.353	
25	2.498		4.690		120	2.107	3.536	1.336	3.336
30	2.113	4.311	4.392	10.152	125	2.125		1.286	
35	1.792		4.220		130	2.064		1.206	3.052
40	1.498		4.083	7.874	135	1.935		1.089	
45	1.192		3.883		140	1.740		0.952	2.408
50	0.873		3.573	5.808	145	1.501		0.798	
55	0.556		3.149		150	1.232	1.751	0.631	1.572
60	0.280	1.062	2.660	3.842	155	0.958		0.470	
65	0.084	0.821	2.177		160	0.700		0.313	0.764
70	0.000[b]	0.824	1.766	2.406	165	0.476		0.183	
75	0.027	0.918	1.461	2.010	170	0.302		0.087	0.205
80	0.169	1.140	1.273	1.859	175	0.191		0.023	
85	0.394		1.179	1.899	180	0.154	0.000[c]	0.000[d]	0.000[e]
90	0.680	1.851	1.165	2.097					

[a] From Table 1 of [8]. [b] Absolute energy = −22784.85 kcal mol^{-1}. [c] Absolute energy = −98176.91 kcal mol^{-1}. [d] Absolute energy = −28896.32 kcal mol^{-1}. [e] Absolute energy = −120719.59 kcal mol^{-1}

nucleic acids, viz. the flexibility of the furanose ring, which is being dealt with by us employing this technique [3]. Recent calculations by Levitt [4] have shown that the height of the barrier between C2′-*endo* and C3′-*endo* ring conformations depends crucially on the relative heights of the intrinsic torsional barrier of the C—C and C—O bonds. Computations on MEE were also carried out with an *ab initio* method, by using Clementi's IBMOL-VI program; a minimal basis set of Gaussian orbitals (three s-functions, contracted to one, for H, and seven s- plus three p-functions, contracted to two s plus one p, for C and O) was used. Our results are collected in Table 1.

According to PCILO results, the *gauche* conformation of NB is more stable than the *anti*, with a free energy difference $\Delta G^{\circ}(a-g) = 0.154$ kcal mole^{-1}. Taking into account the statistical weights of the two conformations ($g = 2$ and $a = 1$), this implies a population of the *anti* conformer of 27.9% at 300°K (if, instead of the energy difference in the minima, the summation over all states belonging to the two regions is considered, this fraction raises to 34.4%). Vapour-phase electron diffraction measurements by Bradford et al. [5] indicate a mole fraction of the *anti* conformer of 54±9%, from which a free energy difference $\Delta G^{\circ}(g-a) = 0.497 \pm 0.22$ kcal mol^{-1} is inferred. Slightly different results had been found by Szasz et al. [6], who established that $\Delta G^{\circ}(g-a)$ amounts to 0.77 ± 0.09 kcal mol^{-1} (% *anti* conformer $= 64.5 \pm 3.5$). Recent ^{1}H-NMR studies revealed that the *anti* conformer of NB is more stable than the *gauche* forms in solution as well [7]. Also *ab initio* computations predict the greater stability of the *anti* conformer, as shown in Table 2.

The PCILO barrier for transformation from the *gauche* to the *anti* conformation is 2.1 kcal mol^{-1}, about half that computed with *ab initio* (Table 2). Experimental values are 3.6 kcal mol^{-1} from entropy data [12], 3.7 kcal mol^{-1} from the heat of formation of cyclopentane [13], and 4.2 ± 0.4 kcal mol^{-1} from ultrasonic

Table 2. Results of *ab initio* computations on *n*-butane

Ref.	Basis set	Geometry	$\Delta G^{\circ}(g-a)$, kcal mol^{-1}	% *anti*	$a-g$, kcal mol^{-1}	$g^{+}-g^{-}$, kcal mol^{-1}
8	(5, 2, 2)	Experimental[a]	0.824	66.6	3.54	6.82
8	(7, 3, 3)	Experimental[a]	0.766	64.4	3.62	6.83
10	STO-3G	Standard, rigid rotation	1.76	90.6	4.00	12.69
10	STO-3G	Experimenal[a], rigid rotation	1.22	79.6	3.50	7.68
10	STO-3G	Optimized CCC angles, flexible rotation	1.13	77.0	3.58	5.72
11	(7, 3, 1) plus one d-orbital on carbon	Standard, optimized CCC angles and C—C torsion	0.575	56.8	3.87	6.22

[a] From [9]

relaxation measurements [14]. The *syn* barrier which hinders the direct interconversion of the two *gauche* forms is 4.4 kcal mol^{-1} from our PCILO computation, while higher values are found with *ab initio* (Table 2). From heat of formation data, Ito [13] estimated a barrier of 5.3 kcal mol^{-1}, and a prediction of 6.5–6.7 kcal mol^{-1} was made by Piercy and Rao [14] on the (indirect) basis of ultrasonic relaxation in 2-methylbutane.

Concerning MEE, PCILO predicts the *anti* conformer as the most stable, and gives a flat minimum at $\varphi = 90°$, whose energy is only 0.19 kcal mol^{-1} lower than in the saddle point at 115°. In addition, a well-pronounced shoulder at ca. 30° is observed. IBMOL computations give a neat *gauche* minimum at 80°, with an energy difference of 1.48 kcal mol^{-1} below the saddle point at 120°, while the shoulder near 30° disappears.

The *ab initio* values correspond well with crystallographic results on a large number of polyether complexes. In these compounds, torsion angles about C—O bonds are usually in the *anti* range; however, if required by ring formation or cation complexation, deviations from this preference may occur resulting in *gauche* torsion angles never being smaller than 70° [15].

For an exhaustive discussion of the large displacement of the *gauche* minimum from the value of 60° normally found for *gauche* rotamers see [16].

The trends of our quantum mechanical computations are very similar to those of a recent work by Jorgensen and Ibrahim [16] on the conformational equilibria of *n*-alkyl ethers, obtained with the GAUSSIAN-76 program, using the minimal STO-3G and split-valence 4-31G basis sets[1].

Experimentally MEE is known, from gas electron diffraction [17], to exist as a mixture of *anti* and *gauche* conformers (dihedral angle for the *gauche* conformer $84 \pm 6°$), the relative abundance in the gas phase at 20°C of the *anti* conformer being $n_a = 0.80 \pm 0.08$. Statistical mechanics simulations [16] show that the distribution in the liquid at 7.35°C is nearly identical, proving the absence of any significant condensed phase effect on the conformational equilibrium. Similar results have been arrived at employing Raman [18] and infrared [19, 20] techniques.

3. Derivation of Potential Energy Functions

Once obtained the quantum mechanical energies, we tried to reproduce them in the usual form of empirical force field calculations, i.e. as the sum of two terms: a term arising from nonbonded interactions, and a torsional term accounting for that part of the rotation barrier, if any, not covered by van der Waals

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[1] The former basis set was applied initially with rigid rotation and standard geometry, then with optimized CCO and COC angles and central CO bond length, while the latter was applied to STO-3G optimized geometries and revealed a significant stabilization of the *syn* rotamer; as predictable, our *ab initio* energies are in close agreement with those of the first kind of GAUSSIAN-76 energies.

Table 3. Net atomic charges in the minimum-energy conformations of *n*-butane and methyl ethyl ether, as resulting from quantum mechanical computations

	n-butane			mehyl ethyl ether	
Atom	PCILO	*ab initio*[a]	Atom	PCILO	IBMOL
C1	−0.0027	−0.4670	C1	−0.0229	−0.5880
H2	−0.0015	0.1528	H2	0.0096	0.2047
H3	−0.0015	0.1528	H3	0.0095	0.2047
H4	−0.0048	0.1532	H4	0.0008	0.1943
C5	0.0320	−0.2979	C5	0.1577	−0.1830
H6	−0.0109	0.1531	H6	−0.0291	0.1768
H7	−0.0109	0.1531	H7	−0.0291	0.1768
C8	0.0319	−0.2979	O8	−0.1755	−0.3630
H9	−0.0108	0.1531			
H10	−0.0108	0.1531			
C11	−0.0030	−0.4670	C9	0.1229	−0.3946
H12	−0.0013	0.1528	H10	−0.0188	0.1815
H13	−0.0013	0.1528	H11	−0.0188	0.1815
H14	−0.0045	0.1532	H12	−0.0063	0.2083

[a] From Table 3 of [8]

repulsions. An expression of the form

$$E_0 + \sum_{i>j} \left(-\frac{A}{r_{ij}^6} + \frac{B}{r_{ij}^{12}} + 332.2\frac{q_i q_j}{\varepsilon r_{ij}} \right) + \sum_{k=1}^{3} \tfrac{1}{2} V_k [1 - (-1)^k \cos k\varphi]$$

was fit to both PCILO and *ab initio* energies. E_o accounts for interaction energies of pairs of atoms not involved in the rotation; q_i and q_j are the net atomic charges on atoms, as resulting from quantum mehanical computations (Table 3), and 332.2 is the conversion factor from atomic units to kcal mol^{-1}. The summation is extended over the nonbonded active interactions. By "active" we mean [21] all interactions between those pairs of atoms separated by three or more bonds, whose reciprocal distance changes by virtue of rotation (while the term nonbonded inactive interaction applies when the interatomic distance is not affected by the rotation). In NB, there are 36 active interactions (25 of type H···H, 10 of type C···H, 1 of type C···C), and in MEE 24 (15 H···H, 8 C···H, 1 C···C). However, many authors [22–27] suggest that, in heteroatom containing compounds, hydrocarbon-type force fields show insufficiencies that can be relieved by adding atoms to simulate lone-pair orbitals, or alternatively, by adding torsional energy terms in addition to the term V_3 (where the subscript denotes three-fold periodicity). In particular, a one-fold term was introduced by Burkert [25], who considered it to account for the gauche interactions present in CCCC-, but missing in COCC-fragments. The fictitious atoms L_1 and L_2 were placed at 1.0 Å distance from oxygen, in such a way as to give sp^3 hybridization. With their insertion, the number of active interactions in MEE raises to 36 (in addition to the former, 10 L···H and 2 L···C).

The optimization of parameters was performed with the algorithm STEPIT [28]. For completeness, also the eleven energies computed by Hoyland [8] with the

Table 4. Parameters of the best potentials for *n*-butane and methyl ethyl ether

		n-butane		methyl ethyl ether			
Parameters		Fit to PCILO	Fit to *ab initio*[a]	Fit to PCILO (a)	Fit to PCILO (b)	Fit to IBMOL (a)	Fit to IBMOL (b)
H···H	log A	1.71743	1.67217	0.37688	1.78751	1.44722	1.93461
	log B	3.41772	3.43312	2.96587	3.21834	3.15534	3.31759
C···H	log A	1.90461	1.91452	1.90861	1.24579	2.01295	1.71947
	log B	4.53483	4.59677	4.12429	4.20911	4.35356	4.23467
C···C	log A	2.76703	1.39526	2.24725	2.82312	2.65026	1.53744
	log B	5.26897	4.93381	4.33760	5.00450	5.57997	5.54893
L···H	log A			1.67359		1.91446	
	log B			3.68638		3.73218	
L···C	log A			2.97293		2.92308	
	log B			4.80275		4.75712	
V_1					4.083		3.975
V_2					0.589		1.197
V_3		1.529	2.840	0.613	0.513	2.630	2.960
ε			3.008	1.088	7.002	1.024	1.663
E_0		−22781.28	−98176.91	−28887.79	−28894.80	−120719.60	−120719.61
χ^2		0.055	0.071	0.030	0.085	0.051	0.090

[a] From Table 1 of [8]

(5, 2, 2) basis for NB were taken into account. The values which minimize χ^2, the least-squares difference between quantum mechanical and fit energies, are given in Table 4. The accuracy of our potential is unusually good, since χ^2 never exceeds 0.1 kcal mol^{-1}.

Figs. 1–4 show the energy partitioning into its nonbonded (Lennard-Jones plus Coulomb) and torsional components. *Ab initio* energies for NB are more repulsive than PCILO energies. The potentials reproducing the two kinds of computations are not too dissimilar in the nonbonded part, except for the attractive part

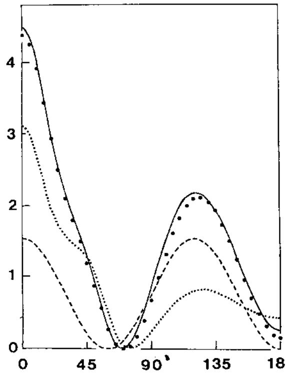

Fig. 1. PCILO energies (kcal mol^{-1}, full circles), and the fitting potential for rotation about the central bond in *n*-butane (solid line), partitioned into nonbonded (dotted line) and torsional (dashed line) contributions

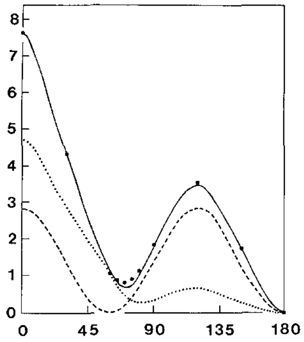

Fig. 2. As for Fig. 1, *ab initio* energies

of the C···C interaction, whose value in the fit to PCILO, approx. 20 times as large as in the fit to *ab initio*, explains the preference of PCILO for the *gauche* conformer. Thus, the difference is mainly accounted for by the torsional term, and this indicates a stronger bond–bond repulsion with *ab initio* than with PCILO. We note that in a force field like ours, derived from *ab initio* computations and containing also a bending term [11], the parameter V_3 amounts to 3.40 kcal-mol^{-1}. All attempts to drop the torsional contribution failed, in the sense that a consistent loss of accuracy (about one order of magnitude) was observed, and even the qualitative reproduction of quantum mechanical energies was bad. The conformer population evaluated with the potential fit to *ab initio* ($a = 66.6\%$, $g = 33.4\%$) is obviously in much closer agreement with experiments than that evaluated with the potential fit to PCILO ($a = 34.3\%$, $g = 65.7\%$).

In case of MEE, the potentials containing lone-pair interactions explicitly (labelled with *a* in Table 4 and Figs. 3 and 4) are more accurate than those where these interactions are simulated by one-fold and two-fold torsional terms (labelled *b*). Here again the C···C potential is much softer with PCILO than *ab initio*, and the torsional term V_3 is sizably smaller, whereas the lone-pair interactions are of comparable magnitude.

We also tried to reproduce both PCILO and IBMOL energies with the Fourier expansion used by Jorgensen and Ibrahim [16]: $V = \frac{1}{2}V_1(1+\cos\varphi)+\frac{1}{2}V_2(1-\cos 2\varphi)+\frac{1}{2}V_3(1+\cos 3\varphi)$. The resultant V_1, V_2 and V_3

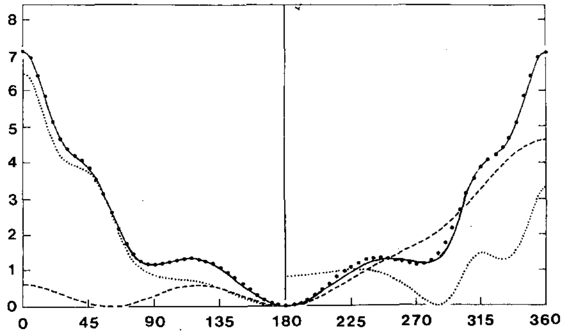

Fig. 3. PCILO energies (kcal mol^{-1}, full circles), and the fitting potential for rotation about the central bond in methyl ethyl ether (solid line), partitioned into nonbonded (dotted line) and torsional (dashed line) contributions. Left, potential *a*; right, potential *b*

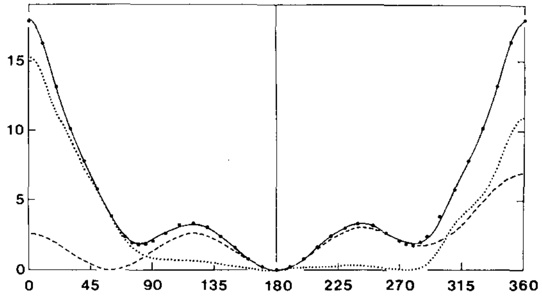

Fig. 4. As for Fig. 3, IBMOL energies

are 5.04, 1.93, 1.40 kcal mol^{-1} (PCILO) and 10.87, 5.85, 5.26 (IBMOL) and the standard deviations are 0.27 and 0.38 kcal mol^{-1}, resp. The main differences from the potential of ref. [16], which refers to flexible rotation, ($V_1 = 4.744$, $V_2 = -1.398$, $V_3 = 2.193$, $\chi^2 = 0.10$ kcal mol^{-1}) are the positive value of V_2 and the consistently worse accuracy.

4. Conclusions

At the beginning of this paper we raised the question of the relative hindrance to rotation around C—C and C—O bonds. The energy partitioning shown in Figs. 1–4 proves that an intrinsic rotational potential is indispensable to reproduce quantum mechanical results with good accuracy; the V_3 term is always higher in the fit to *ab initio* than in the fit to PCILO, and in MEE it is scarcely sensitive to the presence of lone-pair interaction terms coupled with the absence of one-fold and two-fold rotational terms, or *vice versa*; while, according to PCILO, V_3(C—C) is 2.5–3 times as large as V_3(C—O), according to *ab initio* the V_3 terms for NB and MEE are very similar.

Another conclusion to be drawn is that *ab initio* results on both NB and MEE correspond with experimental data much better than do PCILO results.

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References

1. Fantucci, P. C., Tosi, C.: XVI National Congress of the Italian Association of Chemical Physics, Abano Terme (Padova), 1981, Abstracts of papers, p. 33
2. Pullman, B., Courrière, Ph.: Proc. Jerusalem Symposia Quantum Chem. Biochem., Vol. V (Eds. E. D. Bergmann and B. Pullman), Jerusalem Academic Press, Jerusalem, 1972, p. 547
3. Tosi, C., Sänger, W.: Chem. Phys. Letters, in press
4. Levitt, M.: personal communication
5. Bradford, W. F., Fitzwater, S., Bartell, L. S.: J. Mol. Struct. **38**, 185 (1977)
6. Szasz, G. J., Sheppard, N., Rank, D. H.: J. Chem. Phys. **16**, 704 (1948)

7. Schrumpf, G.: Angew. Chem. **94**, 152 (1982); Angew. Chem. Int. Ed. **21**, 146 (1982)
8. Hoyland, J. R.: J. Chem. Phys. **49**, 2563 (1968)
9. Kuchitsu, K.: Bull. Chem. Soc. Jpn. **32**, 748 (1959)
10. Radom, L., Pople, J. A.: J. Am. Chem. Soc. **92**, 4786 (1970)
11. Giunchi, G., Barino, L.: Gazz. Chim. Ital. **110**, 395 (1980)
12. Pitzer, K. S.: J. Chem. Phys. **8**, 711 (1940)
13. Ito, K.: J. Am. Chem. Soc. **75**, 2430 (1953)
14. Piercy, J. E., Rao, M. S. G.: J. Chem. Phys. **46**, 3951 (1967)
15. Hilgenfeld, R., Saenger, W.: Topics Curr. Chem. **101**, 1 (1982)
16. Jorgensen, W. L., Ibrahim, M.: J. Am. Chem. Soc. **103**, 3976 (1981)
17. Oyanagi, K., Kuchitsu, K.: Bull. Chem. Soc. Jpn. **51**, 2237 (1978)
18. Kitigawa, T., Kusaki, K., Miyazawa, T.: Bull. Chem. Soc. Jpn. **46**, 3685 (1973)
19. Kitigawa, T., Ohno, K., Sugeta, H., Miyazawa, T.: Bull. Chem. Soc. Jpn. **45**, 969 (1972)
20. Durig, J. R., Compton, D. A. C.: J. Chem. Phys. **69**, 4713 (1977)
21. Tosi, C., Lipari, G.: Theoret. Chim. Acta **60**, 41 (1981)
22. Allinger, N. L., Chung, D. Y.: J. Am. Chem. Soc. **98**, 6798 (1976)
23. Burkert, U.: Tetrahedron **33**, 2237 (1977)
24. Tvaroska, I., Bleha, T.: Biopolymers **18**, 2537 (1979)
25. Burkert, U.:Tetrahedron **35**, 1945 (1979)
26. Burkert, U.: J. Comput. Chem. **1**, 285 (1980)
27. Platt, E., Robson, B., Hillier, I. H.: J. Theor. Biol. **88**, 333 (1981)
28. Chandler, J. P.: QCPE Program No. 66, 1973

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