## APPENDIX *C*

### Expressions for the interaction energy between the various multipoles

$$U_{m-m}=\frac{q^{(1)}\,q^{(2)}}{4\pi\varepsilon_o R}$$

$$U_{m-d}=\frac{R_\alpha}{4\pi\varepsilon_o R^3}\,[q^{(2)}\,\mu_\alpha^{(1)}-q^{(1)}\,\mu_\alpha^{(2)}]$$

$$U_{m-q}=\frac{R_\alpha R_\beta}{4\pi\varepsilon_o R^5}\,[q^{(2)}\,\theta_{\alpha\beta}^{(1)}+q^{(1)}\,\theta_{\alpha\beta}^{(2)}]$$

$$U_{m-o}=\frac{R_\alpha R_\beta R_\gamma}{4\pi\varepsilon_0 R^7}\,[q^{(2)}\,\Omega_{\alpha\beta\gamma}^{(1)}-q^{(1)}\,\Omega_{\alpha\beta\gamma}^{(2)}]$$

$$U_{m-h}=\frac{R_\alpha R_\beta R_\gamma R_\eta}{4\pi\varepsilon_0 R^9}\,[q^{(2)}\,H_{\alpha\beta\gamma\eta}^{(1)}+q^{(1)}\,H_{\alpha\beta\gamma\eta}^{(2)}]$$

$$U_{d-d}=\frac{1}{4\pi\varepsilon_0 R^3}\left[\mu_\alpha^{(1)}\,\mu_\alpha^{(2)}-\frac{3}{R^2}\,(\mu_\alpha^{(1)}\,R_\alpha)\,(\mu_\beta^{(2)}\,R_\beta)\right]$$

$$U_{d-q}=\frac{5R_\alpha R_\beta R_\eta}{4\pi\varepsilon_0 R^7}\,[\mu_\eta^{(1)}\,\theta_{\alpha\beta}^{(2)}-\mu_\eta^{(2)}\,\theta_{\alpha\beta}^{(1)}]+\frac{2R_\alpha}{4\pi\varepsilon_0 R^5}\,[\theta_{\alpha\beta}^{(1)}\,\mu_\beta^{(2)}-\theta_{\alpha\beta}^{(2)}\,\mu_\beta^{(1)}]$$

$$U_{d-o}=-\frac{7R_\alpha R_\beta R_\gamma R_\eta}{4\pi\varepsilon_0 R^9}\,[\mu_\eta^{(2)}\,\Omega_{\alpha\beta\gamma}^{(1)}+\mu_\eta^{(1)}\,\Omega_{\alpha\beta\gamma}^{(2)}]+\frac{3R_\alpha R_\beta}{4\pi\varepsilon_0 R^7}\,[\mu_\gamma^{(2)}\,\Omega_{\alpha\beta\gamma}^{(1)}+\mu_\gamma^{(1)}\,\Omega_{\alpha\beta\gamma}^{(2)}]$$

$$U_{q-q}=\frac{35\theta_{\alpha\beta}^{(1)}\,\theta_{\gamma\eta}^{(2)}}{12\pi\varepsilon_o R^9}\,R_\alpha R_\beta R_\gamma R_\eta-\frac{5\theta_{\alpha\beta}^{(2)}\,.\,\theta_{\alpha\gamma}^{(1)}}{3\pi\varepsilon_0 R^7}\,R_\beta R_\gamma+\frac{\theta_{\alpha\beta}^{(1)}\,\theta_{\alpha\beta}^{(2)}}{6\pi\varepsilon_0 R^5},$$

where summation over repeated subscripts is implied.

## References

ALMLÖF, I., ROOS, B., WAHLGREN, U. & JOHANSEN, H. (1973). *J. Electron. Spectrosc. Relat. Phenom.* **2**, 51–74.

BATS, J. W. & FEIL, D. (1977). *Chem. Phys.* **22**, 175–181.

BUCKINGHAM, A. D. (1959). *Q. Rev. Chem. Soc.* **13**, 183–214.

COPPENS, P., GURU ROW, T. N., LEUNG, P., STEVENS, E. D., BECKER, P. & YANG, Y. W. (1979). *Acta Cryst.* A**35**, 63–72.

HIRSHFELD, F. L. (1971). *Acta Cryst.* B**27**, 769–781.

HIRSHFELD, F. L. & MIRSKY, K. (1979). *Acta Cryst.* A**35**, 366–370.

*International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.

KAY, M. I., OKAYA, Y. & COX, D. E. (1971). *Acta Cryst.* B**27**, 26–33.

KIHARA, T. (1963). *Adv. Chem. Phys.* **4**, 147–188.

MULDER, F. & HUISZOON, C. (1977). *Mol. Phys.* **34**, 1215–1235.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

WITH, G. DE, HARKEMA, S. & FEIL, D. (1976). *Acta Cryst.* B**32**, 3178–3184.

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*Acta Cryst.* (1981). A**37**, 421–425

# Exact Method for the Calculation of Pseudorotation Parameters *P*, $\tau_m$ and Their Errors. A Comparison of the Altona–Sundaralingam and Cremer–Pople Treatment of Puckering of Five-Membered Rings

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## Abstract

A comparison of the two methods available for describing the puckering of five-membered rings – the Altona–Sundaralingam (A–S) [Altona & Sundaralingam (1972). *J. Am. Chem. Soc.* **94**, 8205–8212] pseudorotation parameters $\tau_m$, *P* and the Cremer–Pople (C–P) [Cremer & Pople (1975). *J. Am. Chem. Soc.* **97**, 1354–1358] puckering parameters *q*, $\varphi$ – shows that they are the same for all practical purposes but both have minor shortcomings. In the A–S method, the value of $\tau_m$ is somewhat dependent on the choice of the origin atom, while in the C–P method the normal to the mean plane, rather than being fixed, precesses as the ring puckering changes. We present here an exact procedure for obtaining the A–S parameters $\tau_m$, $P$ that correspond to the amplitude and phase of the Fourier wave of period $4\pi/5$, thus making $\tau_m$ independent of the origin atom. Formulae are also given for the estimation of the standard deivations in the A–S and C–P parameters.

## Introduction

The concept of pseudorotation was introduced by Kilpatrick, Pitzer & Spitzer (1947) to describe the continuum of puckered states attainable by the cyclopentane ring. This concept was applied to five-membered rings by Geise, Altona & Romers (1967) using the endocyclic torsion angles instead of the atomic displacements from the mean plane. Altona & Sundaralingam (1972) (A–S) extended this, with slight modifications, to furanose ring systems. The pseudorotation parameters $P$, $\tau_m$ are obtained from the ring torsion angles so that the phase angle of pseudorotation $P$ describes the state of pucker in the pseudorotation pathway and the amplitude of pseudorotation $\tau_m$ is an upper limit for the endocyclic torsion angle. The method used to obtain the pseudorotation parameters was somewhat empirical and resulted in a minor dependence of $\tau_m$ on the particular atom chosen as the first atom. Cremer & Pople (1975) (C–P) have developed a method for obtaining the puckering parameters $q$, $\varphi$ from the atomic coordinates of the ring atoms. This method requires the definition of a suitable direction (normal to a mean plane); they used an ingenious procedure to find this direction, which appeared to provide an exact parametrization of the ring puckering. But, a closer analysis reveals that this direction is not invariant when the ring pseudorotates (different puckering states), and therefore the C–P method also suffers from inexactitude similar to the A–S method for a comparative study of ring puckerings.

In this paper, we describe an exact method of obtaining the A–S parameters $\tau_m$, $P$ for five-membered rings which correspond to the amplitude and phase of the Fourier wave of period $4\pi/5$. This makes $\tau_m$ independent of the choice of the origin atom. Formulae are also presented to calculate the standard deviations in the A–S and C–P parameters. A comparison of the parameters and their standard deviations for various compounds has been made and it is shown that the two methods provide very similar values and are the same for all practical purposes.

After this paper was submitted, we learnt that Taylor (1980) has also provided a method for calculating the standard deviations in the C–P parameters. Our procedure is the same as that of Taylor if the covariance between atomic coordinates is ignored; a quantity not generally available in the literature.

## Method

In general, any five parameters ($p_i$, $i = 1, 2, 3, 4, 5$) can be exactly expressed in a Fourier series of the form

$$p_i = A_0 + A_1 \cos(\alpha_i + \varphi_1) + A_2 \cos(2\alpha_i + \varphi_2) \quad (1)$$

where

$$\alpha_i = 2\pi(i-1)/5. \quad (2)$$

The parameters $A_0$, $A_1$, $A_2$, $\varphi_1$ and $\varphi_2$ are obtained by Fourier inversion:

$$A_0 = \tfrac{1}{5} \sum_{i=1}^{5} p_i \quad (3)$$

$$A_1 \cos \varphi_1 = \tfrac{2}{5} \sum p_i \cos \alpha_i \quad (4)$$

$$A_1 \sin \varphi_1 = -\tfrac{2}{5} \sum p_i \sin \alpha_i \quad (5)$$

$$A_2 \cos \varphi_2 = \tfrac{2}{5} \sum p_i \cos 2\alpha_i \quad (6)$$

$$A_2 \sin \varphi_2 = -\tfrac{2}{5} \sum p_i \sin 2\alpha_i. \quad (7)$$

For the pseudorotation description of five-membered rings, the $p_i$'s can be either the torsion angles in the range $-\pi$ to $+\pi$ (A–S) or the atomic displacements from the mean plane (Kilpatrick *et al.*, 1947; C–P). $A_2$, $\varphi_2$ denote the pseudorotation amplitude and phase respectively derived from the second-order wave of period $4\pi/5$. The concept as developed for cyclopentane implies that $A_0 = 0$ (by symmetry) and $A_1 = 0$ (no angular momentum); in such a case, the A–S and C–P formalisms are equivalent. This is because the torsion angles transform as atomic displacements (Dunitz, 1972).

In the original A–S formalism, the values of the two parameters $\tau_m$ and $P$ were obtained by an empirical approach [equations (2) and (3) of A–S] from the five endocyclic torsion angles. The zero- and first-order terms are absorbed into the parameters so obtained and even though their effect is small, the values of the parameters do not exactly correspond to the amplitude and phase of the second-order wave. This leads to a small dependence of $\tau_m$ on the choice of the origin atom. One method of overcoming this short-coming is to use the empirically derived parameters as a starting point and perform a least-squares fit for the five equations [equation (1) of A–S]. This procedure separates out the effect of the second-order wave of period $4\pi/5$. An alternative and straightforward method is to obtain directly the two parameters using Fourier inversion as shown in (6) and (7) and described below. In the present treatment, $A_0$ and $A_1$ [equation (1)] will be small but not exactly zero; the departure of these values from zero may be regarded as a measure of the deviation from the ideal pseudorotation description.

The C–P method requires the definition of a suitable direction (normal to a mean plane) so that the atomic displacements along this direction can be used in (1). The plane normal as defined by C–P guarantees that $A_0 = A_1 = 0$. However, the direction of this plane normal is not necessarily fixed as the ring pseudorotates and this lack of coincidence will be reflected as small errors in the parameters $q$ and $\varphi$. Although the C–P parameters provide an exact parametrization of the puckering of a ring in a crystal, for a comparative analysis, the exactness is lost.

### A–S description: calculation of the parameters $\tau_m$ and $P$

The five parameters $p_i$ in (1) are substituted with the five endocyclic torsion angles $\theta_1$, $\theta_2$, $\theta_3$, $\theta_4$ and $\theta_5$. In the case of the furanose ring in nucleic acids, we follow the convention adopted by A–S whereby $P = 0$ corresponds to the symmetrical twist $^3_2T$ conformation or C(3′)-*endo*-C(2′)-*exo* pucker and the origin atom is C(1′). In such a case, $\theta_1$ is the torsion angle C(1′)–C(2′)–C(3′)–C(4′), $\theta_2$ is the torsion angle C(2′)–C(3′)–C(4′)–O(4′), *etc.* Setting $A_2 = \tau_m$ and $\varphi_2 = P$, we get from (5) and (6)

$$A = \tau_m \cos P = \tfrac{2}{5} \sum_{i=1}^{5} \theta_i \cos 2\alpha_i \qquad (8)$$

$$B = \tau_m \sin P = -\tfrac{2}{5} \sum \theta_i \sin 2\alpha_i, \qquad (9)$$

where $\alpha_i$ is defined in (2). Substitution of the five torsion angles in (8) and (9) gives the values of $A$ and $B$ from which one can readily calculate $\tau_m$ and $P$ with the relations

$$\tau_m^2 = A^2 + B^2 \qquad (10)$$

$$\tan P = B/A. \qquad (11)$$

From (8) and (9), (10) can be easily shown to be

$$\tau_m^2 = \left[\frac{2}{5}\right]^2 \left\{ \sum \theta_i^2 - \left[\frac{1+\sqrt{5}}{2}\right] \sum \theta_i \theta_{i+1} + \left[\frac{-1+\sqrt{5}}{2}\right] \sum \theta_i \theta_{i+2} \right\}, \qquad (12)$$

where $\theta_6 = \theta_1$ and $\theta_7 = \theta_2$. From (12) it is seen that the value of the amplitude of puckering depends on the sum of cyclic products of the torsion angles and is independent of which ring atom is chosen as the first atom. The phase angle $P$, however, is dependent on the choice of origin atom and shifts by 144° each time the origin atom is shifted along the ring, for example from C(1′) to C(2′) *etc.*

### Standard deviations in A–S ($\tau_m$,$P$) and C–P ($q$,$\varphi$) parameters

A–S: The standard deviations ($\theta_i$) in the torsion angles $\theta_i$ can be readily calculated (Shmueli, 1974) from the errors in the atomic coordinates and from (8) and (9) we get

$$\sigma^2(A) = \left[\frac{2}{5}\right]^2 \sum \sigma^2(\theta_i) \cos^2 2\alpha_i \qquad (13)$$

$$\sigma^2(B) = \left[\frac{2}{5}\right]^2 \sum \sigma^2(\theta_i) \sin^2 2\alpha_i. \qquad (14)$$

Now,

$$\sigma^2(\tau_m) = \left[\frac{\partial \tau_m}{\partial A}\right]^2 \sigma^2(A) + \left[\frac{\partial \tau_m}{\partial B}\right]^2 \sigma^2(B) = \left[\frac{1}{\tau_m}\right]^2 [A^2 \sigma^2(A) + B^2 \sigma^2(B)]. \qquad (15)$$

Similarly,

$$\sigma^2(P) = \left[\frac{\partial P}{\partial A}\right]^2 \sigma^2(A) + \left[\frac{\partial P}{\partial B}\right]^2 \sigma^2(B) = \left[\frac{1}{\tau_m}\right]^4 [A^2 \sigma^2(B) + B^2 \sigma^2(A)]. \qquad (16)$$

Notice that $\sigma(P)$ becomes large as $\tau_m \to 0$, *i.e.* the ring becomes flat. Equations (15) and (16) can be used to calculate the standard deviations in the pseudorotation parameters $\tau_m$ and $P$.

C–P: In this formalism, the parameters $p_i$ in (1) are the atomic displacements from a suitable mean plane. The plane is so chosen as to guarantee $A_0 = A_1 = 0$. If $\mathbf{r}_i$ are the position vectors of the five ring atoms in a certain Cartesian system of coordinates, then the steps involved are:

(*a*) Shift the origin to $\mathbf{r}_0$ where

$$\mathbf{r}_0 = \tfrac{1}{5} \sum_{i=1}^{5} \mathbf{r}_i \qquad (17)$$

and define

$$\mathbf{r}'_i = \mathbf{r}_i - \mathbf{r}_0. \qquad (18)$$

(*b*) Define two vectors $\mathbf{R}_1$ and $\mathbf{R}_2$ such that

$$\mathbf{R}_1 = \sum \mathbf{r}'_i \sin \alpha_i \qquad (19)$$

and

$$\mathbf{R}_2 = \sum \mathbf{r}'_i \cos \alpha_i \qquad (20)$$

and a direction $\mathbf{n}$

$$\mathbf{n} = (\mathbf{R}_1 \times \mathbf{R}_2)/|(\mathbf{R}_1 \times \mathbf{R}_2)|. \qquad (21)$$

This direction defines the normal to the mean plane which passes through $\mathbf{r}_0$. It may be noted that this normal is very close to, but not coincident with, the normal to the least-squares plane through the five ring atoms.

(*c*) Compute the atomic displacements $z_i$ along the direction $\mathbf{n}$ from the point $\mathbf{r}_0$ from

$$z_i = \mathbf{r}'_i . \mathbf{n}. \tag{22}$$

Using $z_i$'s as parameters in (6) and (7) and setting $A_2 = q$ and $\varphi_2 = \varphi$, one gets

$$q \cos \varphi = [\tfrac{2}{5}]^{1/2} \sum z_i \cos 2\alpha_i \tag{23}$$

and

$$q \sin \varphi = - [\tfrac{2}{5}]^{1/2} \sum z_i \sin 2\alpha_i. \tag{24}$$

Note the factor is $[\frac{2}{5}]^{1/2}$ and not $\frac{2}{5}$ [equations (6), (7)] and hence $q$ denotes $[\frac{2}{5}]^{1/2}$ times the maximum displacement of any atom from the mean plane. In this description, the origin atom has been chosen as O(4′). The standard deviations in $z_i$ can be readily calculated from the errors in the atomic coordinates and the manipulations in steps (*a*), (*b*) and (*c*). Then, from these errors on $z_i$, the standard deviations in the parameters $q$, $\varphi$ can be estimated from (23) and (24) with the procedure outlined earlier [equations (13) to (16)].

## Relationship between the A–S and C–P parameters

The relationship between $\tau_m$,$P$ (A–S) and $q$,$\varphi$ (C–P) can be written as

$$P = \varphi + 90° \; (= \varphi^*) \tag{25}$$

and

$$\tau_m(°) = 102{\cdot}5 \, q(\text{Å}) \; (= q^*). \tag{26}$$

Equation (26) was derived by Dunitz (1972) for small atomic displacements from the mean plane.

## Comparison between the two descriptions

In Table 1, we have compiled the pseudorotation parameters given by the two descriptions together with their derived standard deviations for some structures solved or refined in this laboratory. An analysis of this table yields:

(i) For unsubstituted furanose rings or for furanose rings belonging to nucleosides and nucleotides in their preferred conformations [(*a*) through (*g*) in Table 1], the differences between $P$ and $\varphi^*$ and $\tau_m$ and $q^*$

Table 1. *Pseudorotation and puckering parameters of furanoid rings in a variety of nucleoside derivatives*

The average standard deviations (Å) in the bond lengths for the compounds are given below the name of the compound. The standard deviations refer to the least significant digit. $\varphi^* = \varphi + 90°$ and $q^* = 102{\cdot}5\,q$ where $\varphi$ and $q$ are the C—P parameters. $P$ is to be compared with $\varphi^*$ and $\tau_m$ with $q^*$.

| | A—S | | C—P | |
|---|---|---|---|---|
| Compound | $P(\sigma_p)$ | $\tau_m(\sigma_{\tau_m})$ | $\varphi^*(\sigma_{\varphi^*})$ | $q^*(\sigma_{q^*})$ |
| 5′-GMP (*a*)<br>$\sigma(l)$ 0·003 | 4·7 (5)° | 35·7 (2)° | 4·7 (4)° | 35·8 (3)° |
| 3′-DHUMP (*b*)<br>0·005 | 159·0 (7) | 39·7 (4) | 160·8 (8) | 39·5 (6) |
| 5′-dCMP (*c*)<br>0·003 | 213·4 (4) | 32·8 (2) | 211·2 (5) | 32·0 (3) |
| K.ADP (*d*)<br>0·012 | 163 (2) | 38 (1) | 165 (2) | 38 (1) |
| Ara-A (*e*)<br>0·003 | 24·6 (4) | 42·1 (2) | 22·6 (4) | 42·1 (3) |
| Ba.5′-CMP (*f*)<br>0·05 | 147 (6)<br>146 (6) | 43 (3)<br>45 (3) | 150 (9)<br>149 (9) | 42 (7)<br>43 (7) |
| CpA.PF (*g*)<br>0·02 | 10 (3)<br>153 (2) | 35 (1)<br>43 (1) | 10 (3)<br>154 (3) | 35 (2)<br>42 (2) |
| 2′,3′-A (*h*)<br>0·008 | 27 (10)<br>214 (1)<br>75 (1)<br>148 (1) | 3·9 (5)<br>31·6 (5)<br>25·4 (8)<br>35·4 (6) | 25 (11)<br>212 (1)<br>74 (2)<br>149 (1) | 3·8 (8)<br>30·7 (8)<br>22·7 (9)<br>36·2 (7) |
| Cyclo Ara-O (*i*)<br>0·003 | 132·8 (4) | 42·1 (3) | 135·2 (5) | 39·9 (4) |
| Cyclo Ara-C (*j*)<br>0·005 | 231 (1) | 27·7 (4) | 228 (1) | 26·2 (5) |
| 8,5′-cyclo A (*k*)<br>0·004 | 288·6 (3) | 47·6 (4) | 288·8 (6) | 44·3 (4) |
| 3′,5′-cIMP (*l*)<br>0·003 | 27·5 (3) | 43·4 (2) | 25·0 (4) | 43·0 (3) |

References: (*a*) Guanosine 5′-monophosphate.$3H_2O$ (Emerson & Sundaralingam, 1980*a*); (*b*) potassium dihydrouridine 3′-monophosphate.$5H_2O$ (Emerson & Sundaralingam, 1980*b*); (*c*) deoxycytidine 5′-monophosphate.$H_2O$ (Viswamitra, Reddy, Lin & Sundaralingam, 1971); (*d*) potassium adenosine 5′-disphosphate.$2H_2O$ (Swaminathan & Sundaralingam, 1980); (*e*) 9-*β*-D-arabinofuranosyl-8-morpholinoadenosine.$2H_2O$ (Swaminathan, Sundaralingam, Chattopadhyaya & Reese, 1980); (*f*) barium cytidine 5′-monophosphate.8·$5H_2O$ (Hogle, Sundaralingam & Lin, 1980), the first and second lines correspond to the first and second molecules in the asymmetric unit; (*g*) proflavine cytidine-3′,5′-adenosine monophosphate (Westhof, Rao & Sundaralingam, 1980), the first and second lines correspond to the cytidine ribose and adenosine ribose, respectively; (*h*) 2′,3′-*O*-isopropylideneadenosine (Sprang, Rohrer & Sundaralingam, 1978), the first two lines correspond to the two ribose fragments present in the asymmetric unit and the last two to the two oxolane rings; (*i*) 7,2′-anhydroarabinosylorotidine (Smith, Chwang & Sundaralingam, 1980); (*j*) 2,2′-anhydroarabinosylcytidine.HCl (Brennan & Sundaralingam, 1973); (*k*) 8,5′-cycloadenosine (Haromy, Raleigh & Sundaralingam, 1980); (*l*) 3′,5′-cyclic inosine monophosphate.$H_2O$ (Sundaralingam, Haromy & Prusiner, 1980).

respectively, are within twice the combined standard deviations.

(ii) Larger deviations are observed when the furanose ring is involved in extracyclic structure, or when the nucleo*side*,-*tide* adopts a less preferred conformation [(*h*) through (*l*)]. In such cases, one parameter (either $P$ or $\tau_m$) usually absorbs most of the discrepancy. It is not clear why one or the other of the two parameters differ in a given case.

(iii) For well-refined structures, the standard deviations derived for the two sets of parameters are the same.

(iv) For less-well-refined structures, the A–S description gives somewhat lower standard deviations than the C–P description.

## Summary

The two-parameter description of the puckered state of the furanoid ring system provided by the A–S and C–P formalisms is the same in the first order of approximation. Inherent to the C–P formalism is the shortcoming that, when comparing the puckering parameters of equivalent five-membered rings in the same crystal (*i.e.* two independent molecules) or different crystals, the plane normals for the different rings do not necessarily coincide. The precession of the plane normal as the ring puckering changes (*i.e.* the ring pseudorotates) would be very small. Thus, it is seen that both the original A–S and C–P methods suffer from similar shortcomings; the absorption of the parameter $A_1$ in the puckering parameters. In the A–S case, this leads to a small dependence of $\tau_m$ on the choice of origin atom and in the C–P case to a precession of the plane normal.

With the improved method proposed here, the A–S parameters $\tau_m$ and $P$ now correspond to the amplitude and phase of the second-order Fourier wave of period $4\pi/5$. This makes $\tau_m$ independent of the choice of the origin atom and overcomes the shortcoming of the earlier A–S formalism. The C–P method still has the problem of definition of a suitable direction (normal to a mean plane) that can be regarded as invariant (in the molecular system) under pseudorotation and about which the currently defined plane normal precesses.

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## References

ALTONA, C. & SUNDARALINGAM, M. (1972). *J. Am. Chem. Soc.* **94**, 8205–8212.

BRENNAN, T. & SUNDARALINGAM, M. (1973). *Biochem. Biophys. Res. Commun.* **52**, 1348–1351.

CREMER, D. & POPLE, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.

DUNITZ, J. D. (1972). *Tetrahedron*, **28**, 5459–5463.

EMERSON, J. & SUNDARALINGAM, M. (1980*a*). *Acta Cryst.* B**36**, 1510–1513.

EMERSON, J. & SUNDARALINGAM, M. (1980*b*). *Acta Cryst.* B**36**, 537–543.

GEISE, H. J., ALTONA, C. & ROMERS, C. (1967). *Tetrahedron Lett.* pp. 1383–1386.

HAROMY, T., RALEIGH, J. & SUNDARALINGAM, M. (1980). *Biochemistry*, **19**, 1718–1722.

HOGLE, J., SUNDARALINGAM, M. & LIN, G. H. (1980). *Acta Cryst.* B**36**, 564–570.

KILPATRICK, J. E., PITZER, K. S. & SPITZER, R. (1947). *J. Am. Chem. Soc.* **64**, 2483–2488.

SHMUELI, U. (1974). *Acta Cryst.* A**30**, 848–849.

SMITH, J., CHWANG, A. & SUNDARALINGAM, M. (1980). *Acta Cryst.* B**36**, 833–837.

SPRANG, S., ROHRER, D. C. & SUNDARALINGAM, M. (1978). *Acta Cryst.* B**34**, 2803–2810.

SUNDARALINGAM, M., HAROMY, T. & PRUSINER, P. E. (1980). Unpublished.

SWAMINATHAN, P. & SUNDARALINGAM, M. (1980). *Acta Cryst.* B**36**, 2590–2597.

SWAMINATHAN, V., SUNDARALINGAM, M., CHATTOPADYAYA, J. B. & REESE, C. B. (1980). *Acta Cryst.* B**36**, 828–832.

TAYLOR, R. (1980). *Acta Cryst.* A**36**, 828–829.

VISWAMITRA, M. A., REDDY, B. S., LIN, Y. & SUNDARALINGAM, M. (1971). *J. Am. Chem. Soc.* **93**, 4565–4570.

WESTHOF, E., RAO, S. T. & SUNDARALINGAM, M. (1980). *J. Mol. Biol.* **142**, 331–361.