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A priori, for estriol, $\varphi_{200}=0$ or π . By RICHARD D. GILARDI, *Laboratory for the Structure of Matter, Naval Research Laboratory, Washington D.C., U.S.A.*

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The determination of $\varphi_{200}=0$ for estriol is re-examined. It is easy to show, from a consideration of the structure-factor equations or by test calculation, that $\varphi_{200}=\pi$ is also consistent with the data. Therefore, the method of determination should not be considered definitive.

In a recent note by Hauptman (1972) entitled 'For estriol, $\varphi_{200}=0$ ', a rationale was presented for the choice $\varphi_{200}=0$ rather than $\varphi_{200}=\pi$ in the solution of the estriol structure (Hauptman, Fisher, Hancock & Norton, 1969). The argument was based upon the following: (a) the estriol molecules are approximately planar; (b) $|E_{200}|=5.40$, which is very large, but not near the theoretical maximum (~ 9.2); (c) $|E_{100}|=0.00$. If the two molecules of the asymmetric unit were lying near the $x=0$ and $x=\frac{1}{2}$ planes, respectively, ensuring a large modulus and a zero phase for E_{200} , the atoms which were off the planes would make only small, second-order contributions to E_{100} , as expressed by Hauptman's equation (9):

$$E_{100} \simeq -\frac{1}{\sqrt{84}} \left\{ \sum_{\mu=1}^{21} \varepsilon_{\mu}^2 - \sum_{\mu=22}^{42} \varepsilon_{\mu}^2 \right\}. \quad (1)$$

Moreover, the above structure-factor equation expresses the difference between two summations of small positive quantities, and they could cancel one another.

Alternatively, if the molecules are almost coincident with the planes $x=\frac{1}{4}$ and $x=-\frac{1}{4}$ (which would give $\varphi_{200}=\pi$), the atoms would be lying near nodes of the trigonometric portion of the E_{100} structure-factor equation, and any deviations of atoms from the planes would contribute in a linear fashion to $|E_{100}|$. Hauptman's equation (10) expresses this hypothetical situation:

$$E_{100} \simeq \frac{2}{\sqrt{84}} \left\{ \sum_{\mu=1}^{21} \varepsilon_{\mu} - \sum_{\mu=22}^{42} \varepsilon_{\mu} \right\}. \quad (2)$$

The individual contributors are first-order quantities, and are thus larger than the terms in the first equation. However, the ε_{μ} 's are independent and have varying signs, in contrast to the ε_{μ}^2 in equation (1) which must all be positive; the ε_{μ}

may cancel one another within the summations and this can overrule the argument that the ε_{μ} are larger quantities. Thus, it is not 'clear' (as Hauptman states) that the right-hand side of equation (1) is more consistent with a value of zero than that of equation (2). One could not have said, given this situation, that φ_{200} was definitely zero.

To check this analysis of the problem, a test calculation was performed on estriol. Using the published coordinates for the non-hydrogen atoms from Table 2a of Cooper, Norton & Hauptman (1969) and the point-atom structure formulae for E_{200} and E_{100} given by Hauptman (1972), structure factors were calculated with the estriol molecules at varying positions in the unit cell. With no shift, $E_{200}=+6.46$ and $E_{100}=+0.05$; these values agree well with the experimentally derived moduli. If molecule I is shifted by $r=-0.24a$, and molecule II is shifted by $r=-0.265a$, the resultant values are $E_{200}=-6.51$ and $E_{100}=+0.00$. No *a priori* packing arguments could rule out this possible trial structure; it is possible that other available structure-factor information might do so. There are many other possible combinations of shifts which yield a similar result, namely, $\varphi_{200}=\pi$.

Note added in proof: The intent of this note is to demonstrate that Hauptman's (1972) analysis was not definitive and to imply that the probability of the alternative conclusion ($\varphi_{200}=\pi$) may be significant. Hauptman has since provided me with an *a posteriori* calculation on estriol which, although quite approximate, estimates this probability to be in the 10 to 20% range. This estimate is not directly related to the point in question, namely, the *a priori* probability, since it is based on known structural parameters. Moreover, because the calculation explores only a limited number of packing arrangements, its applicability to the estriol case is difficult to assess. However, even accepting these estimates as correct, they support the conten-

tion that the probability that $\phi_{200} = \pi$ is not insignificant. It seems reasonable to insist that a probabilistic argument be labelled as such, particularly when the probabilities involved cannot be evaluated readily and rough estimates are not overwhelmingly conclusive; the argument presented by Hauptman certainly falls in this category, but no indication of this was given in the original article.

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Comments on Gilardi's paper 'A priori, for estriol, $\phi_{200} = 0$ or π '. By HERBERT HAUPTMAN, Medical Foundation of Buffalo, Buffalo, New York, U.S.A.

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Gilardi's thesis [*Acta Cryst.* (1973). **B29**, 1739–1740] is certainly correct. However, his work is based on a misunderstanding of the intent of the earlier paper which it purports to criticize so that it is, in reality, a valid criticism of his misinterpretation.

First, it is surely true that there exist *a priori* acceptable structures with E_{200} large and negative and $E_{100} = 0$, as Gilardi (1973) demonstrates by his example. However, he has misconstrued the essential point of the earlier paper (Hauptman, 1972) which is not that there are no acceptable structures with $\phi_{200} = \pi$ but that such structures are relatively rare. The proof of this contention lies in the comparison (apparently too concise in the earlier paper) of Gilardi's equations (1) and (2). First, since the ε_μ are small, it is clear that the magnitude of each contributor to (1) is, in general, significantly less than the magnitude of the corresponding contributor to (2). Next, 21 of the contributors to (1) are positive and 21 are negative, a distribution of signs most conducive to complete or nearly complete annihilation. A situation as favorable as this is quite unlikely (but admittedly not impossible) in (2) since the ε_μ are, *a priori*, just as likely to be positive as negative so that the probability of equal numbers of positive and negative signs is only 0.1, approximately. (In fact, the probability that the difference between the number of positive contributors to (2) and the number of negative contributors be less than four is still

only about 0.3. A similar comparison may be made if one chooses to invoke the one-dimensional random walk.) Finally, the numerical factor in (1), $1/\sqrt{84}$, is just half the corresponding factor in (2), $2/\sqrt{84}$. For these three reasons then, while it may not have been 'clear' in the earlier paper, it is nevertheless true that the 'right-hand side of equation (1) is more consistent with a value of zero (for E_{100}) than that of equation (2)', in the probabilistic sense.

In correspondence with Professor David Templeton it has been pointed out that several factors 2π following equation (6) have been lost. This error is most easily corrected by replacing the ε_μ of equations (4) and (5) of the original paper by $\varepsilon_\mu/2\pi$. I wish to thank Professor Templeton for noting this error and also for other constructive criticism.

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The crystal structure and X-ray diffraction data for anhydrous gadolinium bromide. By HENRY H. THOMAS, Goodyear Atomic Corporation, P.O. Box 628, Piketon, Ohio 45661, U.S.A. and W. A. BAKER JR, University of Texas, Arlington, Texas, U.S.A.

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The X-ray diffraction data for GdBr_3 are reported. The crystal structure of GdBr_3 is the monoclinic AlCl_3 type belonging to space group $C2/m$. The unit-cell parameters are: $a = 7.224 \pm 0.005$, $b = 12.512 \pm 0.005$, $c = 6.84 \pm 0.01$ Å, and $\beta = 110.6 \pm 0.2^\circ$. The results of pycnometer density measurements are reported.

Introduction

In the course of a general investigation of the properties of some anhydrous rare-earth halides, an X-ray study of several

of the compounds was carried out and the lattice parameters determined. The result of the X-ray investigation of GdBr_3 is reported herein.

Though nearly all the lanthanide trifluoride, trichloride,