

(II·5) was calculated for the oxygen f curve, sampled at intervals of 0·1 out to $s'=2·6$. Values of B were taken from 0 to 5 in steps of 1. The summations for $B=0$ and $B=1$ were not very convergent within the range used, but the values for $B=2$ to 5 gave $p=46 \text{ \AA}^{-2}$ from the graph of (II·3). This is the value used in equation (1).

Part of this work forms part of the Ph.D. thesis of one of us (S. F. D.). We are grateful to Prof. N. F. Mott, F. R. S., and Dr W. H. Taylor for the provision of research facilities, Dr M. V. Wilkes for permission to use EDSAC, Mr M. Wells for the use of many of his programmes and several members of the laboratory staff who have greatly assisted in the calculations. One of us (S. F. D.) acknowledges financial support from the Department of Scientific and Industrial Research. We should also like to thank Prof. J. Dunitz, who first drew our attention to this problem.

References

AHMED, F. R. & CRUICKSHANK, D. W. J. (1953). *Acta Cryst.* **6**, 385.

- BERGHUIS, J., HAANAPPEL, IJ. M., POTTERS, M., LOOPSTRA, B. O., MACGILLAVRY, C. H. & VEENENDAAL, A. L. (1955). *Acta Cryst.* **8**, 478.
 BOOTH, A. D. (1946). *Proc. Roy. Soc. A*, **188**, 77.
 CARDWELL, H. M. E., DUNITZ, J. D. & ORGEL, L. E. (1953). *J. Chem. Soc.*, p. 3740.
 COCHRAN, W. (1950). *Acta Cryst.* **3**, 268.
 COCHRAN, W. (1954). *Acta Cryst.* **7**, 503.
 CRUICKSHANK, D. W. J. (1956). *Acta Cryst.* **9**, 757.
 CRUICKSHANK, D. W. J. (1960). *Acta Cryst.* **13**, 774.
 DARLOW, S. F. (1959). *Hydrogen Bonding*, p. 37 (ed. Hadzi). London: Pergamon.
 DARLOW, S. F. (1960). *Acta Cryst.* **13**, 683.
 DARLOW, S. F. (1961). *Acta Cryst.* **14**, 1257.
 JELLINEK, F. (1958a). *Acta Cryst.* **11**, 627.
 JELLINEK, F. (1958b). *Acta Cryst.* **11**, 677.
 LONSDALE, K. & MILLEDGE, J. (1961). *Acta Cryst.* **14**, 59.
 PETERSON, S. W. & LEVY, H. A. (1958). *J. Chem. Phys.* **29**, 948.
 PHILLIPS, D. C. (1956). *Acta Cryst.* **9**, 819.
 SHAHAT, M. (1952). *Acta Cryst.* **5**, 763.
 SKINNER, J. M., STEWART, G. M. D. & SPEAKMAN, J. C. (1954). *J. Chem. Soc.*, p. 180.
 VAND, V. (1955). *J. Appl. Phys.* **26**, 1191.
 VIERVOLL, H. & ØGRIM, O. (1949). *Acta Cryst.* **2**, 277.

Acta Cryst. (1961). **14**, 1257

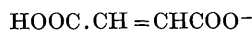
The Configuration of the Strained Hydrogen Maleate Ion

BY S. F. DARLOW

Physics Department, College of Science and Technology, Manchester 1, England

(Received 23 March 1961)

The strained configuration of the hydrogen maleate ion



in the potassium hydrogen maleate structure is investigated. It is shown that the strain energy is approximately 7·5 Kcal./mole, and the corrections to the bond lengths due to the strain are of the order of 0·01 Å. With these corrections, the carbon-carbon bond lengths are equal to the pure single- and double-bond lengths expected between carbons in the sp^2 state of hybridization.

In the preceding paper (Darlow & Cochran, 1961), the three-dimensional refinement of the structure of potassium hydrogen maleate has been described. In this paper the bond-lengths and angles of the hydrogen maleate ion (HM^-) in this structure are discussed. They are shown in Fig. 1 with the oscillation corrections added. The bond-length standard deviations do not include the oscillation correction uncertainties.

The ion is considerably strained in the planar configuration, and in Table 1 the experimentally determined angles are compared with the values expected for the corresponding unstrained angles. The symbols used for them in the following discussion are shown in brackets.

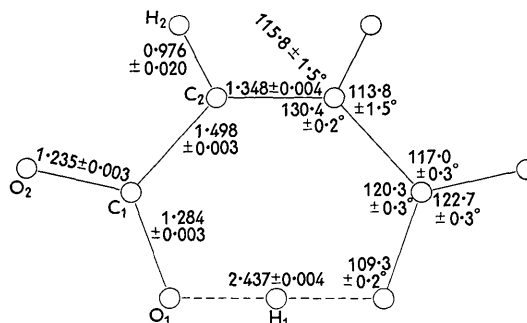


Fig. 1. The bond lengths and angles in the hydrogen maleate ion. The two halves of the ion are related by a mirror plane.

Table 1. Experimentally determined angles compared with the values expected for the corresponding unstrained angles

Angle	Experimental value	Unstrained value	Difference
$C_2-C_2-C_1$	$130.4 \pm 0.2^\circ$ (α)	$121.5 \pm 1.0^\circ$ (α_0)	$8.9 \pm 1.0^\circ$ ($\alpha - \alpha_0$)
$C_2-C_1-O_1$	$120.3 \pm 0.3^\circ$ (β)	$114.2 \pm 0.6^\circ$ (β_0)	$6.1 \pm 0.7^\circ$ ($\beta - \beta_0$)
$O_1-C_1-O_2$	$122.7 \pm 0.3^\circ$ (γ)	$124.5 \pm 0.7^\circ$ (γ_0)	$-1.8 \pm 0.7^\circ$ ($\gamma - \gamma_0$)
$O_2-C_1-C_2$	$117.0 \pm 0.3^\circ$ (ϵ)	$121.3 \pm 0.3^\circ$ (ϵ_0)	$-4.3 \pm 0.4^\circ$ ($\epsilon - \epsilon_0$)

α_0 is the average of five similar angles in unstrained molecules, namely

Diallylsilanediol (120°) (Kasai & Kakudo, 1954),
 Buta-1:3-diene (122°) (Bastiansen, quoted by Allen & Sutton, 1950),
 Vinylacetylene ($123 \pm 2^\circ$) (Morgan & Goldstein, 1952),
 Acraldehyde ($120 \pm 3^\circ$) (Mackle & Sutton, 1951), and
 Vinylocyanide ($121.5 \pm 1^\circ$) (Wilcox, Goldstein & Simmons, 1954).

β_0 and ϵ_0 are derived from the C_1O_1 and C_1O_2 bond lengths (using the relation given by Hahn (1957), see later) and $\gamma_0 (= 360 - \beta_0 - \epsilon_0)$ is consistent with the average value of $125.3 \pm 1.0^\circ$ for 28 carboxyl groups listed by Hahn.

If the $O_1 \cdots O_1'$, C_1O_1 , C_1C_2 and C_2C_2' bond lengths are labelled a , b , c and d respectively, then

$$a = d - 2c \cos \alpha + 2b \cos (\alpha + \beta). \quad (1)$$

With the experimental bond lengths and unstrained angles the value of a would be 1.47 \AA . The strain thus increases the O_1O_1' separation by approximately 0.97 \AA .

This strain is distributed among the bond angles and lengths so that the strain energy is minimized with respect to each variable. An extension of the calculation of Longuet-Higgins (1950) was made, using the expression

$$V = [\frac{1}{2}e(a_0' - a)^2 + f(b - b_0)^2 + g(c - c_0)^2 + \frac{1}{2}h(d - d_0)^2 + 1.5g(\alpha - \alpha_0)^2 + 1.5r(\beta - \beta_0)^2] \quad (2)$$

for the strain energy, where a_0' is the 'unstrained' length for the $O_1H_1O_1'$ bond; e , f , g and h are force constants for the bonds $O_1H_1O_1'$, C_1O_1 , C_1C_2 and C_2C_2' ; g and r are the mean 'couple constants' for the angles at C_2 and C_1 respectively; and the factors of 1.5 assume that the other two angles at each of C_2 and C_1 equally share the strain in α and β respectively, although the factors do not depend critically on this assumption. No terms were included for the straining of close van der Waals contacts such as H_2H_2' .

Differentiating (2) and equating to zero gives

$$\delta V = [-E \delta a + 2f(b - b_0) \delta b + 2g(c - c_0) \delta c + h(d - d_0) \delta d + 3g(\alpha - \alpha_0) \delta \alpha + 3r(\beta - \beta_0) \delta \beta] = 0, \quad (3)$$

where $E = e(a_0' - a)$ is the strain force in the $O_1H_1O_1'$ bond.

Differentiating (1) and substituting for δa in (3) then leads to

$$\left. \begin{aligned} (b - b_0) &= [\cos (\alpha + \beta)/f] E, \\ (c - c_0) &= [-\cos \alpha/g] E, \\ (d - d_0) &= [1/h] E, \\ (\alpha - \alpha_0) &= [2\{c \sin \alpha - b \sin (\alpha + \beta)\}/3g] E, \\ (\beta - \beta_0) &= [-2b \sin (\alpha + \beta)/3r] E. \end{aligned} \right\} \quad (4)$$

Values of $f = 8 \times 10^5$, $g = 5 \times 10^5$ and $h = 9.6 \times 10^5$ erg.cm.⁻², and $q = r = 0.8 \times 10^{-11}$ erg.radian⁻² were estimated from a few force and couple constants quoted by Westheimer (1956), but they can only be approximate. The parameter E was taken as 8.3×10^{-5} dynes, giving

$$\begin{aligned} (b - b_0) &= -0.003 \text{ \AA}, & (\alpha - \alpha_0) &= 9.4^\circ, \\ (c - c_0) &= 0.011 \text{ \AA}, & (\beta - \beta_0) &= 4.8^\circ, \\ (d - d_0) &= 0.009 \text{ \AA}, \end{aligned}$$

and

$$a_0 = d_0 - 2c_0 \cos \alpha_0 + 2b_0 \cos (\alpha_0 + \beta_0) = 1.45 \text{ \AA},$$

equal to the expected value of 1.47 \AA with the bond length increases allowed for. The calculated values of 9.4° and 4.8° for $(\alpha - \alpha_0)$ and $(\beta - \beta_0)$ compare reasonably with the expected values of $(8.9 \pm 1.0^\circ)$ and $(6.1 \pm 0.7^\circ)$ in Table 1 (although $a_0 = 1.45 \text{ \AA}$ and hence $E = 8.3 \times 10^{-5}$ dynes were effectively determined from these two expected values only), and the bond length changes $(b - b_0)$, $(c - c_0)$ and $(d - d_0)$ due to the strain are probably accurate to within 30%, say. With the above values equation (2) gave 5.1×10^{-15} ergs per HM^- ion or 7.5 Kcal./mole for the strain energy, which must therefore equal an appreciable fraction of the hydrogen-bond energy. Assuming $a_0' = 2.68 \text{ \AA}$ for the unstrained $O_1H_1O_1'$ bond length in the equation $E = e(a_0' - a)$ gave $e = 3.5 \times 10^4$ erg.cm.⁻² for the force constant of the strained hydrogen bond compared with the value 2.7×10^4 erg.cm.⁻² derived from the infrared spectrum of liquid formic acid (Owston, 1951) for a normal OHO hydrogen bond.

Subtracting the calculated strains from the bond lengths gave

$$\begin{aligned} C_2C_2' &= 1.339 \pm 0.005 \text{ \AA}, & C_1O_1 &= 1.287 \pm 0.003 \text{ \AA}, \\ C_2C_1 &= 1.487 \pm 0.004 \text{ \AA}, & C_1O_2 &= 1.235 \pm 0.003 \text{ \AA} \end{aligned}$$

for the unstrained values. The double bond characters of C_1O_1 and C_1O_2 were then calculated as 0.24 ± 0.02 and 0.70 ± 0.04 respectively, the standard deviations including the uncertainties in the end values given by Hahn (1957) for the two types of bond. The sum of these double bond characters is 0.95 ± 0.04 , which is not significantly different from unity, so that the

possible double bond character of C_1C_2 is at most 0.05 ± 0.04 .

The C_1C_2 and C_2C_2' bonds are between carbons in the sp^2 state of hybridization and are close to the expected values for pure single and double bonds of 1.48 and 1.337 Å (Cruickshank & Sparks, 1960).

The strain for the isolated anion would be completely relieved if the ion became non-planar with the carboxyl groups tilted by 46° about their C–C bonds so that O_1 and O_1' lay on opposite sides of the plane of the carbons at distances of 0.85 Å from the plane. The C=C bond prevents the carbons becoming appreciably non-planar. Such a configuration would require a different structural arrangement and packing.

O_1 and O_2 have much larger temperature parameters in a direction perpendicular to the molecular plane, although C_1 and C_2 have not. These extra temperature factors suggest either a r.m.s. oscillation of the carboxyl groups of approximately 15° with a r.m.s. displacement for O_1 and O_1' of 0.3 Å out of the plane, or a random distribution throughout the structure of non-planar ions with O_1 either above or below the carbon plane by 0.3 Å. With O_1 and O_1' on opposite sides of the plane H_1 would still be in the plane so

that it would not have a larger temperature parameter perpendicular to the anion plane. This is exactly the result obtained, although the shape of the H_1 sections in Fig. 6 of the previous paper may not be very significant.

References

- ALLEN, P. W. & SUTTON, L. E. (1950). *Acta Cryst.* **3**, 46.
 CRUICKSHANK, D. W. J. & SPARKS, R. A. (1960). *Proc. Roy. Soc. A*, **258**, 270.
 DARLOW, S. F. & COCHRAN, W. (1961). *Acta Cryst.* **14**, 1250.
 HAHN, T. (1957). *Z. Kristallogr.* **109**, 4.
 KASAI, N. & KAKUDO, M. (1954). *Bull. Chem. Soc. Japan*, **27**, 605.
 LONGUET-HIGGINS, H. C. (1950). *Acta Cryst.* **3**, 76.
 MACKLE, H. & SUTTON, L. E. (1951). *Trans. Farad. Soc.* **47**, 691.
 MORGAN, H. W. & GOLDSTEIN, J. H. (1952). *J. Chem. Phys.* **20**, 1981.
 OWSTON, P. G. (1951). *Quart. Rev.* **5**, 344.
 WESTHEIMER, F. H. (1956). *Steric Effects in Organic Chemistry*, p. 525 (ed. Newman). New York: Wiley.
 WILCOX, W. S., GOLDSTEIN, J. H. & SIMMONS, J. W. (1954). *J. Chem. Phys.* **22**, 516.

Acta Cryst. (1961). **14**, 1259

The Temperature Dependence of the Debye Temperature Θ of Silver by X-ray Diffraction Measurements

By M. SIMERSKÁ

Institute of Technical Physics, Czech. Acad. Sci., Cukrovarnická 10, Prague 6, Czechoslovakia

(Received 14 February 1961)

The study of the temperature dependence of the characteristic temperature Θ for silver in the temperature range from 18 to 760 °C. is presented. The determination of Θ -values from measured X-ray data was carried out by three procedures. Comparison with previous measurements is given.

1. Introduction

Several authors have presented experimental data of the temperature variation of the Debye characteristic temperature Θ of silver obtained by X-ray diffraction methods (Andriessen, 1935; Boskovits *et al.*, 1958; Spreadborough & Christian, 1959a). Their results differ considerably so that the experimental redetermination of the dependence of Θ_{Ag} on T seems desirable. This work is a part of a detailed X-ray diffraction study of the atomic vibrations in Al–Ag equilibrium solid solutions.

2. Experimental technique

The finely grained powder of silver used for our diffraction measurements was prepared by the reduction of a 5% solution of silver nitrate (p.a.) in the

presence of ammonia with a dilute solution of formaldehyde. The sample was a compressed platelet ($10 \times 10 \times 2$ mm.) of this powder. A diffraction photograph showed the absence of any preferred orientation. The sample was annealed for 10 hr. at 650 °C. in vacuum before the measurements were carried out. A series of diffraction photographs was taken in a Unicam high-temperature vacuum camera in the temperature range 18 to 760 °C. A bent quartz crystal of the Johansson type was used for monochromatization of Cu $K\alpha$ radiation. The semifocusing method was applied, the inclination of the flat sample surface to the direct beam being 29° and the distance from the focus to the centre of the cylindrical camera of the diameter 190 mm. being 52 mm. In this way we have obtained the optimum resolution of the last eight diffraction lines (Simerská & Syneček, 1959). The