Perutz (1953) has shown that the birefringence and dichroism of crystalline haemoglobin is dominated by the intrinsic birefringence and dichroism of the haemoglobin molecule. In all the forms he studied, the orientation of the haem groups resulted in the strongest absorption being in the plane perpendicular to the length of the molecule. The dichroism of the three new forms has been studied and is in agreement with this result. In pig haemoglobin I dichroism appears to be weak or absent owing to the large tilt of the molecules relative to each other; in rabbit haemoglobin I there is strong dichroism, and the direction of maximum absorption corresponds closely with the orientation of the molecule deduced above. When looking down *b* the optical extinction direction is almost parallel to the direction of maximum absorption. It was possible to observe the thin plates of pig haemoglobin II only perpendicular to (001). In this orientation strong dichroism was observed with maximum absorption when the vibration direction was parallel to *a*.

These results are in agreement with the general hypotheses referred to above about the molecular shape, birefringence and dichroism of the mammalian haemoglobins.

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Calculation of atomic scattering factors using Slater wave functions: sodium to calcium.

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Following McWeeny's suggestion (1951), we have calculated the atomic scattering factors for the spherically averaged atoms from sodium to calcium, inclusive, by his method using Slater wave functions. The formulae used in our calculation were:

$$f(1s) = \frac{1}{(1+x_1^2)^2},$$

$$\bar{f}(2p) = \frac{1-x_2^2}{(1+x_2^2)^4},$$

$$f(2s) = (1-\alpha_{12}^2)^{-1}\left[\frac{1-x_2^2}{(1+x_2^2)^4}-\frac{2\alpha_{12}^2}{3}\,\frac{3-x_{12}^2}{(1+x_{12}^2)^3}+\frac{\alpha_{12}^2}{(1+x_1^2)^2}\right],$$

$$\bar{f}(3p) = (1-\alpha_{23}^2)^{-1}$$

$$\left[\frac{3-10x_3^2+3x_3^4}{3(1+x_3^2)^6}-\frac{2\alpha_{23}^2}{5}\,\frac{5-10x_{23}^2+x_{23}^4}{(1+x_{23}^2)^5}+\alpha_{23}^2\,\frac{1-x_2^2}{(1+x_2^2)^4}\right],$$

$$f(3s) = \bar{f}(3p)\,,$$

$$x_1 = \frac{4\pi X}{2c_1},\; x_2 = \frac{4\pi X}{2c_2},\; x_3 = \frac{4\pi X}{2c_3},$$

$$x_{12} = \frac{4\pi X}{c_1+c_2},\; x_{23} = \frac{4\pi X}{c_2+c_3},\; X = \sin\theta/\lambda\,,$$

$$\alpha_{12} = 8\times 3^{\frac{1}{2}}c_1^{\frac{3}{2}}c_2^{\frac{5}{2}}/(c_1+c_2)^4\,,$$

$$\alpha_{23} = 160\left(\frac{2}{15}\right)^{\frac{1}{2}}c_2^{\frac{5}{2}}c_3^{\frac{7}{2}}/(c_2+c_3)\,.$$

$\bar{f}(2p)$ and $\bar{f}(3p)$ are the averaged contributions of $2p$ and $3p$ electrons, respectively, to the scattering factor. Although $f(3s) = \bar{f}(3p)$ is not strictly correct†, the influence of this approximation is found to be negligibly small for the final results: for example, the maximum difference due to this approximation for Ca^{2+} is only 0·005. This may not be the case for atoms heavier than Ca. α_{12} and α_{23} are the overlap integrals between $1s$ and $2s$, and $2s$ and $3s$ unorthogonalized Slater wave functions, respectively. c_1 is the effective nuclear charge for the $1s$ electrons, c_2 one-half that for the $2s$ and $2p$ electrons and c_3 one-third that for the $3s$ and $3p$ electrons; the numerical values of these can easily be obtained from Slater's rules (1930). The results are given in Table 1.

For Na, Mg^{2+}, Al^{3+}, Si^{4+}, Cl^-, A, K^+ and Ca, revised atomic scattering factors have been given by Berghuis *et al.* (1955), calculated from self-consistent-field electron-density data. Comparison with our results shows the following points:

(*a*) Ca^{2+}, K^+, A and Cl^-.—Good agreement is obtained in the region of $\sin\theta/\lambda < 0·5$. (For calcium, comparison cannot be made in the region of $\sin\theta/\lambda < 0·15$ as Berghuis

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† The exact formula of $f(3s)$ is

$$f(3s) = N^2\left[\frac{3-10x_3^2+3x_3^4}{3(1+x_3^2)^6}+Q_1^2\,\frac{1-x_2^2}{(1+x_2^2)^4}+Q_2^2\,\frac{1}{(1+x_1^2)^2}\right.$$

$$-\frac{2}{5}\,Q_1\alpha_{23}\,\frac{5-10x_{23}^2+x_{23}^4}{(1+x_{23}^2)^5}-2Q_2\alpha_{13}\,\frac{1-x_{13}^2}{(1+x_{13}^2)^4}$$

$$\left.+\frac{2}{3}\,Q_1Q_2\alpha_{12}\,\frac{3-x_{12}^2}{(1+x_{12}^2)^3}\right],$$

$$N = (1-\alpha_{12}^2)^{\frac{1}{2}}/(1-\alpha_{12}^2-\alpha_{13}^2-\alpha_{23}^2+2\alpha_{12}\alpha_{13}\alpha_{23})^{\frac{1}{2}}\,,$$

$$Q_1 = (\alpha_{23}-\alpha_{12}\alpha_{13})/(1-\alpha_{12}^2),\; Q_2 = (\alpha_{13}-\alpha_{12}\alpha_{23})/(1-\alpha_{12}^2),$$

$$\alpha_{13} = 32\left(\frac{2}{5}\right)^{\frac{1}{2}}c_1^{\frac{3}{2}}c_3^{\frac{7}{2}}/(c_1+c_3)^5\,.$$

Table 1. *Atomic scattering factors calculated by the use of Slater atomic wave functions*

X is sin θ/λ in atomic units

X	0·000	0·025	0·050	0·075	0·100	0·125	0·150	0·175	0·200	0·250	0·300	0·400	0·500	0·600	0·700	0·800
Na^+	10·00	9·91	9·66	9·26	8·74	8·13	7·46	6·77	6·08	4·80	3·76	2·40	1·77	1·50	1·37	1·28
Na	11·00	10·56	9·81	9·23	8·71	8·11	7·45	6·77	6·08	4·81	3·76	2·40	1·77	1·50	1·37	1·27
Mg^{2+}	10·00	9·93	9·74	9·43	9·02	8·52	7·97	7·38	6·77	5·58	4·52	2·96	2·09	1·66	1·45	1·34
Mg	12·00	11·48	10·42	9·55	8·95	8·45	7·93	7·36	6·77	5·59	4·53	2·96	2·09	1·66	1·45	1·34
Al^{3+}	10·00	9·95	9·80	9·55	9·22	8·81	8·35	7·84	7·31	6·23	5·21	3·55	2·49	1·89	1·58	1·41
Al	13·00	12·47	11·27	10·11	9·27	8·69	8·23	7·77	7·28	6·24	5·23	3·57	2·49	1·90	1·58	1·41
Si^{4+}	10·00	9·96	9·83	9·63	9·36	9·02	8·63	8·20	7·74	6·77	5·81	4·14	2·94	2·19	1·76	1·52
Si	14·00	13·51	12·26	10·89	9·77	9·20	8·47	8·04	7·63	6·75	5·84	4·17	2·96	2·20	1·77	1·52
P	15·00	14·53	13·31	11·82	10·47	9·46	8·77	8·27	7·88	7·13	6·33	4·75	3·46	2·57	2·01	1·67
S	16·00	15·56	14·38	12·84	11·34	10·10	9·19	8·55	8·10	7·40	6·72	5·27	3·96	2·98	2·30	1·87
S^{2-}	18·00	17·26	15·37	13·10	11·13	9·74	8·88	8·37	8·03	7·43	6·71	5·26	3·95	2·96	2·29	1·86
Cl	17·00	16·58	15·46	13·92	12·31	10·88	9·76	8·94	8·36	7·60	7·00	5·72	4·45	3·41	2·64	2·11
Cl^-	18·00	17·48	16·07	14·22	12·35	10·77	9·60	8·80	8·27	7·59	7·01	5·73	4·45	3·40	2·63	2·11
A	18·00	17·61	16·54	15·02	13·35	11·78	10·47	9·46	8·72	7·80	7·21	6·09	4·91	3·84	3·00	2·39
K^+	18·00	17·70	16·85	15·60	14·15	12·68	11·35	10·22	9·32	8·13	7·41	6·38	5·31	4·27	3·39	2·70
Ca^{2+}	18·00	17·76	17·07	16·03	14·78	13·45	12·15	10·99	10·01	8·57	7·68	6·60	5·56	4·64	3·77	3·04

et al. give the data for neutral calcium.) For higher sin θ/λ the differences are somewhat larger but do not exceed 4%. The positions of maximum difference, which are out of the range of Cu $K\alpha$ radiation, gradually shift towards larger sin θ/λ as the atomic number increases.

(*b*) Na, Mg^{2+} and Si^{4+}.—The maximum difference is 5% for Na and decreases as the atomic number increases. The positions of maximum difference are now in the range of Cu $K\alpha$ radiation and again gradually shift towards larger sin θ/λ with increasing atomic number.

(*c*) Al^{3+}.—The maximum difference is somewhat larger (7%). This can be accounted for by the fact that in the electron distribution for Al^{3+} used by Berghuis *et al.*, exchange has been neglected. (Compare for instance the old James–Brindley values for Na (Hartree) in *Internationale Tabellen* (1935) and the revised ones (Hartree–Fock) of Berghuis *et al.*)

(*d*) P and S.—No data are given by Berghuis *et al.* The differences between our values and the self-consistent-field results for Na to Si^{4+} on the one hand and for Cl^- to Ca^{2+} on the other, suggest that for P and S the differences would be small for lower sin θ/λ and less than 4% for higher sin θ/λ.

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Zur Kristallographie einiger Organophosphate.

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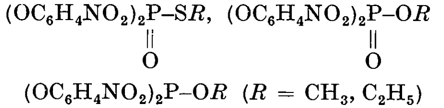
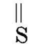
Wir haben Strukturveränderungen, die durch die Substitution des Sauerstoffs durch ein Schwefelatom verursacht werden, bei den Verbindungen vom Typ



$$(OC_6H_4NO_2)_2\underset{\underset{O}{\|}}{P}\text{–}SR, \quad (OC_6H_4NO_2)_2\underset{\underset{O}{\|}}{P}\text{–}OR$$

und



$$(OC_6H_4NO_2)_2\underset{\underset{S}{\|}}{P}\text{–}OR \quad (R = CH_3, C_2H_5)$$

untersucht. Bei diesen Verbindungen ist auch ihre biologische Wirkung bekannt. Die vorläufigen Resultate sind in Tabelle 1 zusammengestellt. Aus Drehaufnahmen (Kalibration mit Al, Cu$K\alpha$ = 1538,7 Å) und Präzessionsaufnahmen wurden die Gitterkonstanten ermittelt. Die Untersuchung der systematischen Auslöschungen wurde auf Präzessions- und Weissenbergaufnahmen bei Reflexionen vom Typ $hk0$, $h0l$ und $0kl$ durchgeführt. Die Messwerte für die Dichte $\varrho_{\text{exp.}}$ wurden mit Hilfe der Schwebemethode erhalten. Die nadelförmigen O-aethyl- und S-aethyl-O,O-di-(*p*-nitrophenyl)-Phosphate existieren nur in der Form von Zwillingskristallen. Die Zwillingsfläche ist (100).

Aus der Tabelle 1 ist der Einfluss der Substitution des Sauerstoffs durch eine Schwefelatom ersichtlich. Wenn diese Substitution in der Aethoxy-Gruppe eintritt, ändert sich die Symmetrie der Struktur nicht, und die Gitterkonstanten ändern sich nur sehr wenig. Die Substitution des am Phosphoratom liegenden Sauerstoffatoms durch ein Schwefelatom jedoch, sowie auch die Substitution in