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Letters to the Editor

THIS section will accept reports of new work, provided these are terse and contain few figures, and especially few halftone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section should not exceed 600 words in length and must reach the office of the Managing Editor not later than the 15th of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual publication charge ($3.00 per page) will not be made and no reprints will be furnished free.

Synthetic Patterson Maps

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July 11, 1946

THE customary test of excellence of a structure is the agreement between the observed and the calculated values of the structure factors $F(h,k,l)$. The mere agreement is not, in itself, a *sufficient* condition for the validity of the postulated structure and it is, in general, only when considerations of chemical plausibility are added that the solution can be considered to be established. This has been shown, in the one-dimensional case, by Patterson[1] who remarks that, when the treatment is extended to three dimensions, the probability of more than one structure giving agreement, is negligible.

However satisfactory the numerical comparison, envisaged above, may be in the case of small molecules, it seems probable that, as the examination of large molecules proceeds, this computation of individual F values for each proposed structure will be difficult or impossible. The reasons for this are twofold: first, the mere labor of calculation will be severe and secondly, the finer details of atomic arrangement may be unknown. It is thus desirable that some method be made available whereby an assessment of the compatibility of any given molecular structure with the experimental observations may be made.

A solution of the problem lies in the construction of synthetic Patterson syntheses. The essence of the method is to determine the general lie of the Patterson map of the proposed structure, since it can be shown that, as the number of scattering centers increases, the appearance of the Patterson map becomes, for the most part, more and more dependent on the broad features of the structure. In order to test the plausibility of a proposed structure, a synthetic Patterson map may be constructed and compared with that obtained from the experimental data. If the two maps agree in sufficient detail, there is a high probability that the proposed structure is correct. Evidently any measure of agreement between the two is exactly equivalent to the same measure of agreement between the observed and calculated structure factors.

To make this technique capable of rapid application, it is desirable that the Patterson maps of various types of structure be constructed and recorded. A beginning has been made on this by Patterson[2] and by Wrinch[3] and it is hoped to publish a detailed study later.

A further application of the technique is possible, for if the phase angles of the structure factors be calculated from these functions, the standard process of Fourier refinement could be applied to the experimental data and finer details obtained.

One technical point in the construction of synthetic Patterson maps may be dealt with here. There is evidently no theoretical difficulty in constructing the three-dimensional Patterson map of the atomic centers of any proposed structure, though the procedure may be complicated and intricate when the number of atoms is large. The "sharpened" version of the Patterson synthesis[4] which has been found by Booth[5] to be of considerable utility may well prove inapplicable to large molecules since, whereas the number of available F values increases at most with the first power of the unit cell volume, the complexity in the Patterson map (i.e., the number of peaks) increases as the square of the same quantity. Thus it becomes questionable whether the sharpened Patterson, with only a limited number of terms, has any physical significance in such cases. It follows that we should study, not only the Patterson map of the atomic centers, but also the map of the electron density distribution of the atoms. The question therefore arises as to how to represent an atom in Patterson space. This question can be answered formally, whatever the electron density distribution may be, by the use of transforms,[6] since the Patterson distribution g_P corresponding to any distribution g is derivable from the transform of T^2, where T is the transform of g in reciprocal space. Thus for a radially symmetric distribution $g(r)$ for example, we have

$$NT(R)=4\pi\int_0^\infty r^2g(r)(\sin 2\pi rR/2\pi rR)dr,$$

where N is the total number of electrons in the distribution. It then follows that

$$g_P(r)=4\pi N^2\int_0^\infty R^2T^2(R)(\sin 2\pi rR/2\pi rR)dR.$$

It has been found by Booth[7] that the distributions of atoms obtained by synthesis are closely represented by expressions of the form

$$g(r)=A\exp(-pr^2).$$

To verify this, the cases of carbon, nitrogen, oxygen, chlorine, and sulphur were studied and the wide applicability of this expression was seen, even when a common p value is used for several different atomic types. The value suggested by the data is

$$p=4.69.$$

If we adopt this representation of the electron density distribution of an atom, the actual form of the distribu-

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tion in Patterson space can be deduced. Thus with

$$g(r)=N(p/\pi)^{\frac{3}{2}}\exp(-pr^2),$$

$$T(R)=(p/\pi)^{\frac{3}{2}}\int_0^\infty r^2\,(\sin 2\pi rR/2\pi rR)dr\,\exp(-pr^2),$$

$$=2(p/\pi)^{\frac{1}{2}}\int_0^\infty \cos 2\pi rRdr\,\exp(-pr^2)=\exp(-PR^2),$$

where $Pp=\pi^2$. From the expression for $g_P(r)$ given above, it then follows that

$$g_P(r)=N^2(\pi/2P)^{\frac{3}{2}}\exp(-\tfrac{1}{2}pr^2)=N^2(p/2\pi)^{\frac{3}{2}}\exp(-\tfrac{1}{2}pr^2).$$

With the help of this expression, it is evidently possible to pass directly from the Patterson map of a pattern of atomic centers to the continuous map of the corresponding pattern of atoms, when the electron density distribution of the atoms is represented as described above.

[1] A. L. Patterson, Phys. Rev. **65**, 195 (1944).
[2] A. L. Patterson, Phys. Rev. **56**, 972 (1939).
[3] Dorothy Wrinch, "Fourier Transforms and Structure Factors," 1946. (Monograph 2 of the American Society for X-Ray and Electron Diffraction.)
[4] A. L. Patterson, Zeits. f. Krist. **90**, 517 (1935).
[5] A. D. Booth, unpublished.
[6] Dorothy Wrinch, Nature **157**, 226 (1946).
[7] A. D. Booth, Proc. Roy. Soc. in the press.

The O—O Bond Energy in Hydrogen Peroxide

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July 12, 1946

In a recent paper, Skinner[1] amends the value for the O—O bond energy from 34.9 kcal. or 1.51 ev[2] to approximately 52 kcal. or 2.26 ev after assuming that the OH bond energy in H_2O_2 is not similar to the OH bond energy in H_2O, but is more nearly equal to the OH bond energy of the free radical (~100 kcal. or 4.35 ev). As a tentative explanation, a comparison of resonating structures of H_2O and H_2O_2 is offered. It appears to us, however, that the resonance structures discussed by Skinner can equally well be used to argue that the OH bond in hydrogen peroxide is more nearly like the similar bond in water than it is in the free hydroxyl radical, as can be seen from Fig. 1.

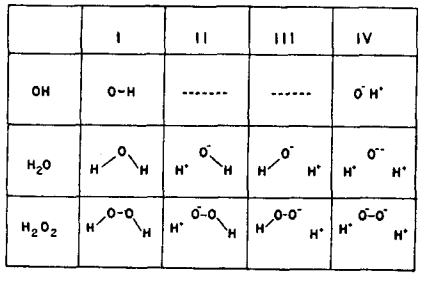

Fig. 1. Resonance structures involving hydroxyl groups.

Table I. Bond energies and interatomic distances of O—O bonds.

Substance	Bond energy (ev)	r_e(A)
$O_2(^3\Sigma_u^-)$	0.97[b]	1.60[a]
H_2O_2	1.51[b]	1.47[c]
O_3	3.06[d]	1.26[e]
$O_2(^1\Delta)$	4.11[b]	1.22[f]
$O_2(^1\Sigma_g^+)$	3.47[a]	1.223[a]
$O_2(^3\Sigma_g^-)$	5.08[g]	1.21[g]

[a] W. Jevons, *Band Spectra of Diatomic Molecules* (The University Press, Cambridge, England, 1932), p. 290.
[b] L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1940), p. 53.
[c] Giguère and Schomaker, J. Am. Chem. Soc. **67**, 2025 (1945).
[d] Glockler and Matlack, J. Chem. Phys. (to be published).
[e] W. Shand and R. A. Spurr, J. Am. Chem. Soc. 65, 177 (1943).
[f] H. Sponer, *Molekülspektren* (Tabellen) (Verlagsbuchhandlung Julius Springer, Berlin, 1935), p. 16.
[g] G. Herzberg, *Molecular Spectra and Molecular Structure, I. Diatomic Molecules* (Prentice-Hall, Inc., New York, 1939).

Skinner states that, in his belief, the completely ionic structure of water (under IV) has no counterpart in the hydroxyl radical or in hydrogen peroxide. It would seem to us that there is quite an analogy between the purely ionic structures of the three molecules, whereas the OH radical has no counterpart to structures II and III in water and hydrogen peroxide. (Fig. 1.) The structures under IV (Fig. 1) are totally ionic configurations. Whether the double charge resides on one oxygen as in water or on the O—O complex as in hydrogen peroxide seems to us immaterial. The point is that in these models (IV) the structures have reached complete ionic character. On the other hand, figures II and III are only partially ionic in makeup, a situation which is impossible in hydroxyl radical. Following this analogy further, it would seem that the OH binding energy in hydrogen peroxide is more simi-

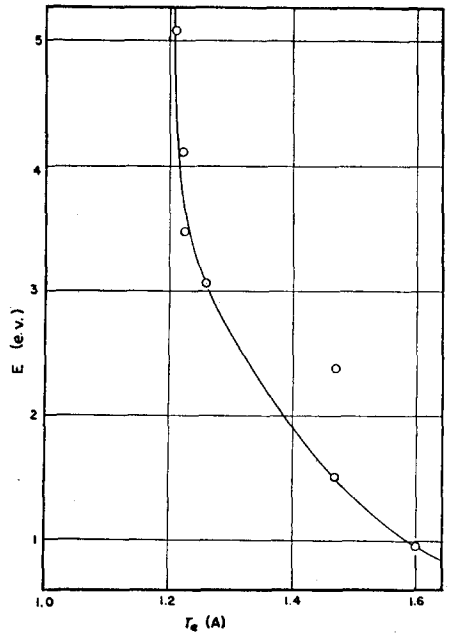

Fig. 2. Dissociation energies of oxygen bonds as a function of interatomic distances.

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