unweighted residual by their equation (4)] is incorrect and that, while the constrained parameters can be obtained from the unconstrained parameters, this requires the minimization of the weighted residual (5) or equivalently, by the application of the usual equations (Hamilton, 1964).

Since there is a procedure for finding the constrained parameters from the unconstrained parameters we have also shown, by counter-example, that Pawley's disproof is incorrect. His argument rests on the lack of an inverse to his equation (1):

$$P_i = f_i(\{p_j\}) .$$

Here the $\{P_i\}$ are the 'usual structure parameters' and the $\{p_j\}$ form 'the set of parameters in the constrained configuration'. There are two interpretations we can give this equation: firstly, that any constrained configuration (specified by the parameters $\{p_j\}$) can be described in terms of the original parameters $\{P_i\}$; and secondly, that for any given set of data, if a constrained refinement results in parameters $\{p_j\}$, then an unconstrained refinement will result in parameters $\{P_i\}$ as given by the function f_i. The first interpretation is a true statement, but in fact there is an inverse to the equation since it is generally 1–1. The inverse is defined only on a subspace (the range of the function), of parameter space. It is apparent from Pawley's arguments subsequent to his equation (1), however, that he intends the second interpretation. Now in this case the equation is patently incorrect, as there does not exist such a function f, even in the linear least-squares, linear-constraints case. There are many different sets of data which will result in the same set of constrained parameters but different values for the unconstrained parameters. This is because of the dimensionality of the two parameter spaces. However, as we have shown above (and as shown by Hamilton, 1964) the *inverse* to the equation does exist for the case of linear least squares with linear constraints.

When the function to be fitted is non-linear in the parameters we cannot rule out the possibility of an inverse to Pawley's equation (1) from dimensionality arguments. However, since fit-space is no longer flat, we cannot say that the projection of **y** into constrained fit-space is necessarily the same as the result obtained by first projecting **y** into the unconstrained fit-space and then projecting this projection into the constrained fit-space. In addition we cannot equate expressions (4) and (5), *i.e.* we cannot even do the latter projection in parameter space. Thus the C & D method [with their equation (4) replaced with (5) above] is invalid for non-linear problems. (The P1 method does not, of course, suffer from these restrictions.)

Aside from these rigorous objections we suspect that the C & D method is likely to be slowly convergent. Algorithms for non-linear least-squares generally only become rapidly convergent when the parameters approach the final values. The C & D method results in the starting parameters for every cycle being held some distance away from the final values. It is not obvious that true convergence will ever be reached.

With reference to P2, we would also like to point out that the many different methods of minimizing a sum of squares generally lead to different parameter shifts even when converging to the same minimum. The argument that two procedures with differing parameter shifts must converge to different minima is incorrect.

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The effect of bonding electrons on molecular dimensions as determined by X-rays.*

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(*Received* 23 *January* 1978; *accepted* 12 *May* 1978)

The central-bond shortening in disubstituted benzenes having an electron-withdrawing group and an electron-releasing group in *para* positions is well known. However, even in several disubstituted benzenes having electron-withdrawing groups in both *para* positions, X-ray analysis shows a central-bond shortening. In monosubstituted benzenes, the middle bonds and the bonds farthest from the substituent show bond shortenings which cannot be accounted for by librational motion alone. It is pointed out that these apparent shortenings are caused by the asymmetry of the charge distribution around the C atoms bonded to the H atoms. This charge asymmetry is to a large extent an artifact of the refinement procedure.

The shortening of the central bonds in disubstituted benzenes having an electron-withdrawing group and an electron-releasing group in *para* positions is well known. However, the central-bond shortening has also been observed, although generally to a lesser extent, in several disubstituted benzenes having electron-withdrawing groups in both *para* positions, *e.g.* in *p*-nitroacetophenone (Kim, Boyko & Carpenter, 1973), α-*p*-nitrobenzaldoxime (Bachechi & Zambonelli, 1973), *anti*-4-nitro-*N*-methylbenzaldoxime (Bachechi & Zambonelli, 1975) and in several other structures; these structures were all determined at room temperature by X-

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* Communication No. 2228 from the National Chemical Laboratory, Poona, India.

rays. The pattern of observed ring deformation in monosubstituted benzene derivatives (determined by X-rays) is described by Domenicano, Vaciago & Coulson (1975); the two bonds which are farthest from the molecular centre are generally about 1·36–1·38 Å while the middle bonds are around 1·385 A irrespective of the nature of the substituent. In fluorobenzene and cyanobenzene, whose structures are determined by microwave spectroscopy, the corresponding bond lengths are normal (1·395–1·397 Å).

The errors in the bond lengths of the aromatic ring due to molecular librations are generally less than 0·015 Å and these errors cannot account for shortenings of about 0·02–0·03 Å. The residual error is in fact caused by the charge asymmetry around the C atoms bonded to the H atoms; the asymmetry is to a large extent artificially created by the assumption that the H atom position is at the centroid of the charge distribution around it instead of at the nuclear position. When the H atom is taken at its true nuclear position, the centroid of the charge density of the attached C atom coincides with its nuclear position (if the charge distribution in the C–C and the C–H bonds is assumed to be similar). But when the H atom is assumed to be at the centroid of the charge distribution (this is the position that is obtained by refinement of X-ray data), the electron density peak in the C–H bond is eliminated and the centroid of the C atom shifts towards the centre of the aromatic ring leading to a shortening of the observed bond lengths.

An estimate of the correction to the bond lengths owing to charge asymmetry can be made from the very precise structure analyses of sodium sulphanilate dihydrate at room temperature (Bats & Coppens, 1975) and at 78 K (Bats, 1977). The room-temperature study was performed with the help of all the reflexions and H atoms were included in the refinement; the final low-temperature refinement was performed with the help of high-angle reflexions only, thereby ensuring that molecular dimensions are not significantly affected by bonding electrons. The bond lengths after correction for thermal motion are as follows.

	78 K	295 K	Difference	Mean
a	1·405 (1) Å	1·398 (2) Å	0·007 Å	0·007 Å
	1·399 (1)	1·392 (2)	0·007	
c	1·407 (1)	1·403 (2)	0·004	
	1·404 (1)	1·396 (2)	0·008	
b	1·389 (1)	1·374 (2)	0·015	0·017 .
	1·399 (1)	1·380 (2)	0·019	

a and *c* are the bonds near the substituents and *b* are the central bonds; as expected, the correction for the central bonds is nearly double that for the other four bonds. The deformation density in the aromatic plane at 78 K shows very little electron density in the C–H bonds whereas there are peaks of about 0·5 e Å^{-3} in the C–C bonds; the measured C–H bond lengths [0·95–0·98 (1) Å] are, as expected, smaller than the neutron diffraction value of 1·08 Å.

It is interesting to recall that in the structure of *p*-nitrobenzoic acid refined without including H atoms (Sakore & Pant, 1966), the central bonds were nearly of normal length [1·389 (8) and 1·396 (8) Å]. When H atoms were included in an effort to improve the refinement, the central bonds shortened to 1·381 (6) and 1·384 (6) Å (Tavale & Pant, 1971); in the light of the preceding discussion this shortening is only to be expected. A more precise structure analysis using a larger number of structure factors reduced the bond shortening; the observed bond lengths became 1·387 (2) and 1·390 (2) Å (Colapietro & Domenicano, 1977); presumably the inclusion of many high-angle reflexions has reduced the systematic error in bond lengths.

In conclusion, it may be said that for accurate structure analysis, work should be carried out at low temperature in order to reduce the effect of thermal motion and the refinement of nonhydrogen atoms should be carried out with high-angle reflexions only in order to eliminate the errors caused by bonding electrons. If the analysis is carried out with room-temperature data, proper correction should be applied not only for the librations of the molecule but also for any asymmetry of the charge distribution.

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