J. Am. Chem. Soc. **1994**, *116*, 3543–3547

Crystal Structure Determination from Powder Diffraction Data by Monte Carlo Methods

Kenneth D. M. Harris,*,† Maryjane Tremayne, Philip Lightfoot, and Peter G. Bruce*

Contribution from the Department of Chemistry, University of St. Andrews,
St. Andrews, Fife KY16 9ST, Scotland

Received June 22, 1993. Revised Manuscript Received December 7, 1993®

Abstract: Many important crystalline solids cannot be prepared in the form of single crystals of sufficient size and quality for single-crystal X-ray diffraction studies, and in such cases it is essential that structural information can be extracted from powder diffraction data. In this paper, a method employing a Monte Carlo algorithm for crystal structure determination from powder diffraction data is developed and applied. In this method, a series of structural models is generated by random movement of a collection of atoms within the unit cell, and the acceptance or rejection of each trial structure is based upon the Metropolis importance sampling technique—in employing this technique, the agreement between the experimental powder diffraction pattern and the powder diffraction pattern calculated for the structural model is considered. The success of this method for *ab initio* crystal structure determination from powder X-ray diffraction data is demonstrated by its application to determine the known crystal structure of p-$CH_3C_6H_4SO_2NHNH_2$ and the previously unknown crystal structure of p-$BrC_6H_4CH_2CO_2H$. In view of the successful application of the methodology reported here, we predict that this Monte Carlo technique will have an important future role in *ab initio* crystal structure determination from powder diffraction data.

Introduction

A knowledge of crystal and molecular structure is the foundation upon which an understanding of the properties of chemical systems is based. The most powerful method of structure determination is single-crystal X-ray diffraction, and this technique is now applied widely and routinely. However, many important crystalline solids cannot be prepared in the form of single crystals of sufficient size and quality for conventional single-crystal X-ray diffraction studies. In such cases, it is essential that structural information can be extracted from powder diffraction data. In this paper, we present a method, employing a Monte Carlo algorithm, for crystal structure determination from powder diffraction data. In this approach, a series of structural models is generated by random movement of a collection of atoms within the unit cell, with the acceptance or rejection of each trial structure based on the agreement between the experimental powder diffraction pattern and the powder diffraction pattern calculated for the trial structure. The success of this approach is demonstrated by its application to determine the known crystal structure of p-$CH_3C_6H_4SO_2NHNH_2$ and the previously unknown crystal structure of p-$BrC_6H_4CH_2CO_2H$.

The determination of crystal structures from powder diffraction data is a major scientific challenge. Essentially the same information is contained in single-crystal and powder diffraction data, but in the former case the diffraction maxima are distributed in three-dimensional space whereas in the latter case the three-dimensional diffraction data are "compressed" into one dimension. As a consequence, individual peaks in the powder diffraction pattern generally overlap appreciably, leading to ambiguities in determining the intensities of the individual diffraction maxima, with consequent difficulties in structure determination. Methods are now being developed to enable more information to be extracted from powder diffraction patterns containing extensive peak overlap. These include methods based on maximum entropy algorithms,[1–3] which we have recently applied, for the first time, to determine two unknown crystal structures.[4,5] If peak overlap in the powder diffraction pattern is not too severe, or if the structure contains a dominant scatterer, it is often possible to solve the structure by assigning arbitrary intensities to overlapping diffraction maxima,[6–9] despite the severe assumptions involved. However, this is not satisfactory as a general strategy and is limited in its applicability. Other approaches for crystal structure determination from powder diffraction data include techniques based upon energy minimization[10] and simulated annealing;[11] and recently, molecular dynamics simulation has been combined with Rietveld refinement techniques to extract structural information from powder diffraction data.[12] In this paper, we present a Monte Carlo technique for the determination of structural information from powder X-ray diffraction data.

In its general philosophy, the technique presented here differs considerably from the normal approach for structure determination from diffraction data. In particular, rather than extracting structural information directly from the diffraction data, the general strategy here is to postulate initial structural models *independently* of the diffraction data, and then to assess the suitability of these models on the basis of their agreement with the experimental diffraction data. This type of approach avoids the problems (highlighted above) associated with extracting information directly from the powder diffraction data. Once an adequate starting model for the crystal structure has been obtained, it can then be developed and refined by fitting it to the experimental powder diffraction pattern *via* Rietveld refinement

---

* Authors to whom all correspondence should be addressed.

† Present address: Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, England.

® Abstract published in *Advance ACS Abstracts*, March 15, 1994.

(1) David, W. I. F. *Nature* **1990**, *346*, 731.

(2) Bricogne, G. *Acta Crystallogr.* **1991**, *A47*, 803.

(3) Gilmore, C. J.; Henderson, K.; Bricogne, G. *Acta Crystallogr.* **1991**, *A47*, 830.

(4) Tremayne, M.; Lightfoot, P.; Mehta, M. A.; Bruce, P. G.; Harris, K. D. M.; Shankland, K.; Gilmore, C. J.; Bricogne, G. *J. Solid State Chem.* **1992**, *100*, 191.

(5) Tremayne, M.; Lightfoot, P.; Glidewell, C.; Harris, K. D. M.; Shankland, K.; Gilmore, C. J.; Bricogne, G.; Bruce, P. G. *J. Mater. Chem.* **1992**, *2*, 1301.

(6) Cheetham, A. K.; David, W. I. F.; Eddy, M. M.; Jakeman, R. J. B.; Johnson, M. W.; Torardi, C. C. *Nature* **1986**, *320*, 46.

(7) McCusker, L. B. *J. Appl. Crystallogr.* **1988**, *21*, 305.

(8) Lightfoot, P.; Glidewell, C.; Bruce, P. G. *J. Mater. Chem.* **1992**, *2*, 361.

(9) Morris, R. E.; Harrison, W. T. A.; Nicol, J. M.; Wilkinson, A. P.; Cheetham, A. K. *Nature* **1992**, *359*, 519.

(10) Freeman, C. M.; Catlow, C. R. A. *J. Chem. Soc. Chem. Commun.* **1992**, 89.

(11) Deem, M. W.; Newsam, J. M. *Nature* **1989**, *342*, 260.

(12) Kaszkur, Z. A.; Jones, R. H.; Waller, D.; Catlow, C. R. A.; Thomas, J. M. *J. Phys. Chem.* **1993**, *97*, 426.

0002-7863/94/1516-3543$04.50/0

procedures.[13] Thus, the major problem in crystal structure determination from powder diffraction data is to obtain a sufficiently good starting structural model.

Development of Methodology

The Monte Carlo method used here is based on the standard Metropolis importance sampling algorithm,[14] but rather than considering the energy of the system as the basis for constructing a Markov chain of structures ("configurations"), we consider the crystallographic R factor (agreement factor):

$$R_{wp} = 100 \times \sqrt{\frac{\sum w_i (y_i - y_{ci})^2}{\sum w_i y_i^2}}$$

where y_i is the intensity of the ith observed point in the experimental powder diffraction profile, y_{ci} is the intensity of the corresponding point in the calculated powder diffraction profile, and w_i is a weighting factor for the ith point in the powder diffraction profile.

The method invokes random numbers to generate a series of configurations $\{x_i;\ i = 1, ..., N\}$ which represent potential structural models for subsequent use in Rietveld refinement calculations. The first configuration (x_1) is chosen at random and may comprise a randomly positioned atom or group of atoms within the unit cell. Each new configuration (x_{i+1}) is ***not*** produced "from scratch" but is derived from the previous configuration (x_i) in Markovian fashion. The process for converting x_i to x_{i+1} (termed a "Monte Carlo move") is as follows.

(i) Starting from configuration x_i, each atom is displaced by a random amount (subject to a user-specified maximum displacement) in a random direction, to generate a *trial* configuration x_{trial} [As is evident from the specific examples discussed below, the exact form of this "displacement" will depend on the particular system under investigation.] The powder diffraction pattern corresponding to the trial configuration x_{trial} is calculated. The scale factor for this powder diffraction pattern is optimized *via* a least-squares fit of the calculated diffraction pattern to the experimental diffraction pattern (essentially, this is a Rietveld refinement calculation in which *only* the scale factor is refined). The agreement factor for the trial configuration is denoted $R_{wp}(x_{\text{trial}})$.

(ii) To decide whether to accept or reject the trial configuration x_{trial}, the value of $R_{wp}(x_{\text{trial}})$ is compared with the agreement factor $R_{wp}(x_i)$ (again determined by optimization of the scale factor) for configuration x_i. To do this, the difference

$$Z = R_{wp}(x_{\text{trial}}) - R_{wp}(x_i)$$

is considered. If $Z < 0$, then x_{trial} is accepted as the new configuration (i.e. $x_{i+1} = x_{\text{trial}}$). If $Z > 0$, however, the trial configuration is accepted as the new configuration (i.e. $x_{i+1} = x_{\text{trial}}$) with probability $\exp(-Z/S)$ and rejected with probability $[1 - \exp(-Z/S)]$, where S represents an appropriate scaling of Z and operates in a manner analogous to temperature in conventional Monte Carlo simulation techniques.[15,16] In the case in which x_{trial} is rejected, the new configuration is taken as the previous configuration (i.e. $x_{i+1} = x_i$).

Stages (i) and (ii) are then repeated to generate the Markov chain of configurations $x_{i+2}, x_{i+3}, x_{i+4}, ..., x_N$. The maximum displacements and the value of S are chosen so that about 40% of trial moves are accepted.[17]

After a sufficient number of configurations have been generated *via* this Monte Carlo algorithm (i.e. after a sufficiently extensive range of configuration space has been explored), the best (i.e. lowest R_{wp}) configuration (or configurations) is considered further. This best configuration is then used as the starting structural model for a conventional Rietveld refinement calculation. Note that, in certain cases, structural models generated from the Monte Carlo calculation will only be partially complete structures, and further development through difference Fourier methods may be required. When a complete structural model has been obtained, a full Rietveld refinement calculation is carried out to give the final refined crystal structure.

Experimental Section

For each of the materials considered here, powder diffraction data were collected in transmission mode on a Stoe STADI/P high-resolution powder X-ray diffractometer, employing Ge-monochromatized Cu Kα_1 radiation and a position-sensitive detector covering *ca.* 6° in 2θ. The polycrystalline sample was mounted in a 0.5 mm diameter capillary and data were collected in the range $5° < 2\theta < 85°$ in 0.02° steps. The total data collection time was *ca.* 15 h.

Results and Discussion

To illustrate the successful application of this method, two materials were investigated: (a) *p*-$CH_3C_6H_4SO_2NHNH_2$, the crystal structure of which has been determined previously from X-ray powder diffraction data using the maximum entropy method,[5] and (b) *p*-$BrC_6H_4CH_2CO_2H$, the crystal structure of which was previously unknown.

p-$CH_3C_6H_4SO_2NHNH_2$ crystallizes in space group $P2_1/n$, with $a = 18.6021$ Å, $b = 5.6406$ Å, $c = 8.5356$ Å, $\beta = 106.22°$, and $Z = 4$. The Monte Carlo approach for structure solution was carried out in two stages, though we emphasize that our method is quite general and may be applied in different ways, as appropriate, in the solution of other crystal structures. In the first stage, only the sulfur atom was considered, and this atom was moved within the unit cell from an arbitrary starting position. In each Monte Carlo move, the random displacement of the sulfur atom was constrained such that the *maximum* change in any of the x, y, and z coordinates (in an orthogonal reference frame) was ±0.1 Å; the value of the parameter S was within the range $S = 4$ (in the initial stages of the calculation) to $S = 3$ (in the final stages of the calculation). The Monte Carlo calculation was carried out for 1000 moves, and from this the optimum sulfur atom position (Monte Carlo move number 848) was (0.6690, 0.1610, 0.4161), with $R_{wp} = 43.5\%$. There was a clear discrimination between this position and other positions—the next lowest value of R_{wp} for an unrelated position was greater than 45% and a typical value of R_{wp} for a "random" position of the sulfur atom was 55%. A Rietveld refinement calculation was then carried out for a structural model comprising only the sulfur atom at (0.6690, 0.1610, 0.4161); the final refined position was (0.6692, 0.1486, 0.4031). The sulfur atom was then fixed at this position, and the C_6 ring was introduced as a rigid body in the Monte Carlo calculation and allowed to move around this fixed sulfur atom position; specifically, in each Monte Carlo move, the ring was rotated by a random angular displacement around a random axis which was constrained to pass through the fixed sulfur atom. The random angular displacement was confined within the range ±10°, the parameter S was fixed at $S = 4$ in the initial stages of the calculation and then fixed at $S = 3$ in the final stages of the calculation, and the calculation was run for 1000 moves. The best configuration (Monte Carlo move number 732) generated in this way corresponded to $R_{wp} = 42.4\%$, with no other configuration having R_{wp} below 45%. In Table 1, the coordinates found from the Monte Carlo calculation for the sulfur atom and the atoms of the C_6 ring are compared with the final refined positions[5] of the same atoms. In Figure 1, the positions

---

[13] Rietveld, H. M. *J. Appl. Crystallogr.* **1969**, *2*, 65.

[14] Metropolis, N.; Rosenbluth, A. W.; Rosenbluth, M. N.; Teller, A. H.; Teller, E. *J. Chem. Phys.* **1953**, *21*, 1087.

[15] Allen, M. P.; Tildesley, D. J. *Computer Simulation of Liquids*; Oxford University Press: Oxford, 1987.

[16] Ciccotti, G.; Frenkel, D.; McDonald, I. R. *Simulation of Liquids and Solids*; North-Holland: Amsterdam, 1987.

[17] Rao, M.; Pangali, C.; Berne, B. J. *Mol. Phys.* **1979**, *37*, 1773.

Table 1. Final Refined Coordinates (First Line) and the Corresponding Coordinates Obtained from the Monte Carlo Calculation (Second Line) for the Sulfur Atom and the Atoms of the C_6 Ring in *p*-$CH_3C_6H_4SO_2NHNH_2$

atom	*x*/*a*	*y*/*b*	*z*/*c*	Δ^a/Å
S	0.6835(3)	0.1583(9)	0.4085(7)	
	0.6692	0.1486	0.4031	0.26
C1	0.596(1)	0.332(2)	0.329(2)	
	0.585	0.306	0.330	0.26
C2	0.595(1)	0.531(2)	0.223(2)	
	0.578	0.478	0.209	0.43
C3	0.528(1)	0.648(2)	0.166(2)	
	0.510	0.603	0.151	0.41
C4	0.457(1)	0.613(2)	0.201(2)	
	0.450	0.556	0.215	0.38
C5	0.466(1)	0.392(3)	0.289(2)	
	0.457	0.384	0.336	0.47
C6	0.528(1)	0.244(2)	0.352(2)	
	0.525	0.259	0.394	0.39

[a] Δ represents the distance between the final refined position of the atom (see ref 5) and the position obtained from the Monte Carlo calculation.

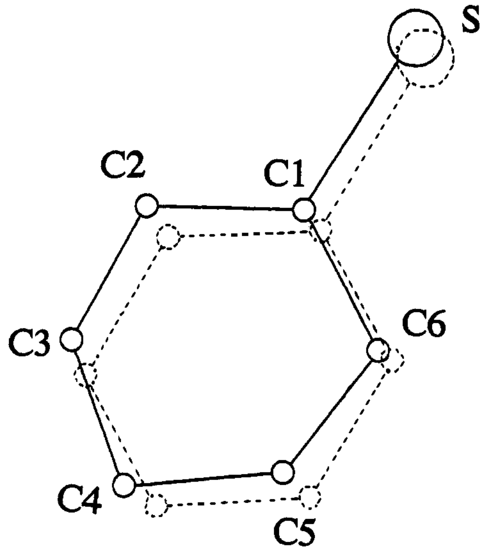

Figure 1. View of the structure of *p*-$CH_3C_6H_4SO_2NHNH_2$ (sulfur atom and the C_6 ring) obtained from the Monte Carlo calculation (dotted lines) overlayed on the positions of the corresponding atoms in the final refined crystal structure (solid lines).

Table 2. Atomic Coordinates Obtained from the Monte Carlo Calculation for the Bromine Atom and the Atoms of the C_6 Ring in *p*-$BrC_6H_4CH_2CO_2H$

atom	*x*/*a*	*y*/*b*	*z*/*c*	Δ^a/Å
Br	0.0723	0.0570	0.1830	0.19
C1	0.1679	0.1982	0.1800	0.53
C2	0.1710	0.3241	0.0732	0.70
C3	0.2481	0.4626	0.0711	0.95
C4	0.3221	0.4753	0.1757	1.05
C5	0.3189	0.3494	0.2826	0.97
C6	0.2418	0.2108	0.2847	0.71
C7	0.4046	0.6238	0.1734	1.32

[a] Δ represents the distance between the final refined position of the atom (see Table 3) and the position obtained from the Monte Carlo calculation.

Table 3. Atomic Coordinates and Thermal Parameters for *p*-$Br_6C_6H_4CH_2CO_2H$ (Space Group $P2_1/c$; a = 16.0475(4) Å; b = 4.6094(1) Å; c = 11.7397(3) Å; β = 109.336(1)°)

atom	*x*/*a*	*y*/*b*	*z*/*c*	U_{iso}/Å^2
Br	0.0620(1)	0.0677(4)	0.1879(2)	0.075(1)
C1	0.153(1)	0.299(2)	0.162(1)	0.037(2)
C2	0.134(1)	0.420(2)	0.049(1)	0.037(2)
C3	0.200(1)	0.598(3)	0.032(1)	0.037(2)
C4	0.279(1)	0.637(3)	0.125(1)	0.037(2)
C5	0.294(1)	0.521(3)	0.239(1)	0.037(2)
C6	0.228(1)	0.348(3)	0.259(1)	0.037(2)
C7	0.351(1)	0.829(3)	0.110(1)	0.037(2)
C8	0.419(1)	0.669(2)	0.072(1)	0.037(2)
O1	0.496(1)	0.729(2)	0.102(1)	0.091(3)
O2	0.396(1)	0.484(2)	0.009(1)	0.091(3)
H21	0.066(1)	0.449(9)	−0.007(3)	0.05
H51	0.358(2)	0.529(9)	0.307(3)	0.05
H31	0.186(2)	0.703(9)	−0.055(3)	0.05
H61	0.245(2)	0.205(9)	0.336(3)	0.05
H71	0.385(2)	0.928(7)	0.197(2)	0.05
H72	0.322(2)	0.994(5)	0.045(3)	0.05

of these atoms are compared—it is clear from this plot that the Monte Carlo approach has successfully located, and discriminated, a position for the rigid fragment (sulfur atom and the C_6 ring) close to the true position of this fragment in the crystal structure.

Taking the positions of the sulfur atom and the atoms of the C_6 ring as the starting structural model, the structure was then developed in a straightforward manner *via* conventional Rietveld refinement and difference Fourier techniques to locate the remaining non-hydrogen atoms. After all non-hydrogen atoms had been located, the structure was refined (the final refined structure was within experimental error of the previously published structure).[5] No attempt was made to locate or to refine the positions of the hydrogen atoms.

For *p*-$BrC_6H_4CH_2CO_2H$, the powder diffraction pattern was indexed using the program of Visser[18] on the basis of the first 20 observed maxima in the powder diffraction pattern. This generated a monoclinic unit cell with a = 16.020 Å, b = 4.607 Å, c = 11.715 Å, and β = 109.33°. On the basis of systematic absences, the space group was determined unambiguously as $P2_1/c$. The structure was solved in two stages, both employing the Monte Carlo approach. The first stage considered only the bromine atom, whereas the second stage considered the bromine atom *plus* a rigid body comprising a C_6 ring with an additional carbon atom in the position *para* to the bromine atom. In each stage, the calculation was carried out for 1000 Monte Carlo moves. In the first stage, the maximum change in any of the x, y, and z coordinates (in an orthogonal reference frame) of the bromine atom position was ±0.1 Å, and the parameter S was fixed at 3 throughout the calculation. The best bromine atom position (Monte Carlo move number 324) was (0.0723, 0.0570, 0.1830) with R_{wp} = 45.2%. A typical value for a "random" position of the bromine atom was R_{wp} = 55%. The only configurations with R_{wp} less than 48% were the optimum position given above and symmetry-related positions— the ability of R_{wp} to discriminate successfully the optimum position is clear. In the second stage, the bromine atom was fixed at the optimum position and the rigid body was rotated by a random angular displacement around a random axis passing through the fixed bromine atom position. The angular displacement was confined to ±9° and the value of the parameter S was fixed at 3. Most positions of the rigid fragment gave $R_{wp} \approx 52\%$, and only two configurations were found with R_{wp} less than 45%—Monte Carlo move number 38 with R_{wp} = 42.1% and Monte Carlo move number 317 with R_{wp} = 43.0%. Examination of the structure obtained in Monte Carlo move number 38 revealed that the C_6 rings of neighboring molecules were too close to be structurally plausible, and hence this configuration was discarded. In Table 2, the coordinates found (Monte Carlo move number 317) from the Monte Carlo calculation for the bromine atom and the atoms of the C_6 ring are compared (see also Table 3) with the final refined positions of the same atoms.

The structure obtained in Monte Carlo move number 317 was then developed using difference Fourier analysis and Rietveld refinement to locate the remaining non-hydrogen atoms. Hydrogen atoms were then placed on the ring and the positions of

---

(18) Visser, J. W. *J. Appl. Crystallogr.* **1969**, *2*, 89.

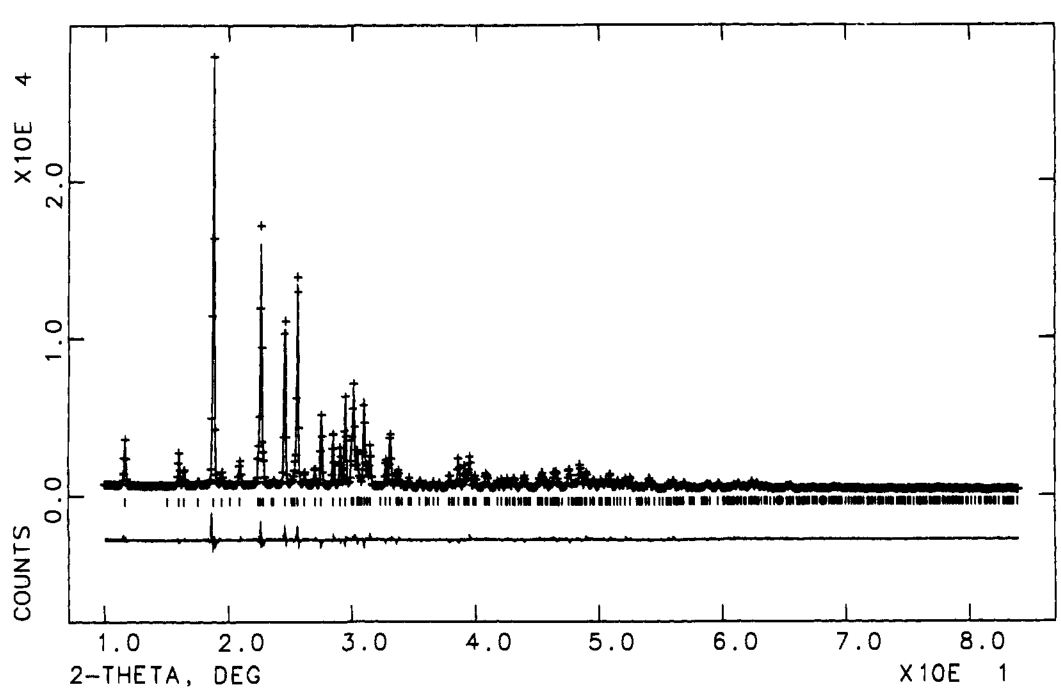

Figure 2. Experimental (+ marks), calculated (solid line), and difference (below) powder diffraction profiles for the Rietveld refinement of p-$BrC_6H_4CH_2CO_2H$. Reflection positions are marked. The calculated powder diffraction profile is for the final refined crystal structure, details of which are given in Table 3.

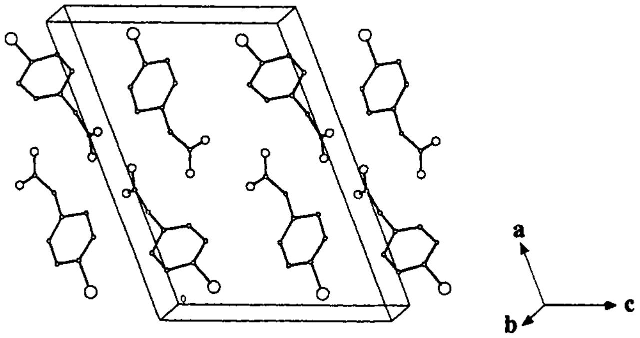

Figure 3. Final refined crystal structure of p-$BrC_6H_4CH_2CO_2H$ (hydrogen atoms are not shown). Full details of this crystal structure are given in Table 3.

these atoms were refined using soft constraints. The final refined structure had $R_{wp} = 6.66\%$ and $\chi^2 = 4.24$, distributed over 3769 points ($10° < 2\theta < 85°$) in the powder diffraction pattern (Figure 2). The final refined crystal structure is shown in Figure 3. Atomic coordinates in the final refined crystal structure are reported in Table 3, and interatomic distances and angles in this structure are reported in Table 4.

Concluding Remarks

As described above, both structures were determined with the minimum of user intervention. Conventional methods for structure solution from the powder diffraction data, on the other hand, required considerably more time to develop the structural models. Although the examples presented here considered systems that could be represented by rigid bodies, the principles underlying the approach are completely general, and it could be extended readily to problems involving two or more independent fragments (e.g. atoms or rigid bodies). Indeed, we predict that the relative efficiency of the Monte Carlo approach, in comparison with other techniques for structure solution, may become greater as the structures to be solved become more complex. We stress that this approach for structure solution does not directly *extract* structural information from the powder diffraction pattern, but rather generates, under a Monte Carlo algorithm, a series of structures which can then be compared to the experimental diffraction data. By employing an approach based upon Metropolis importance sampling, the series of structures generated should "converge" toward a structural distribution close to the correct structure. The advantages of the Monte Carlo approach, over alternatives based upon *minimization* of the agreement factor (for which local, rather than global, minimum structures would invariably be found), should be emphasized.

Table 4. Interatomic Distances (Å) and Angles (deg) in the Final Refined Crystal Structure of p-$BrC_6H_4CH_2CO_2H$

Br–C1	1.91(1)	Br–C1–C2	116(1)
		Br–C1–C6	118(1)
C1–C2	1.38(1)	C2–C1–C6	125(1)
C2–C3	1.41(1)	C1–C2–C3	116(1)
C3–C4	1.39(1)	C2–C3–C4	120(1)
C4–C5	1.39(1)	C3–C4–C5	121(1)
C5–C6	1.40(1)	C4–C5–C6	119(1)
C1–C6	1.37(1)	C1–C6–C5	118(1)
C4–C7	1.50(1)	C3–C4–C7	122(1)
		C5–C4–C7	117(1)
C7–C8	1.49(1)	C4–C7–C8	114(1)
C8–O1	1.24(1)	C7–C8–O1	118(1)
C8–O2	1.24(1)	C7–C8–O2	121(1)
		O1–C8–O2	119(1)

C2–H21	1.09(1)	C1–C2–H21	119(1)	C3–C2–H21	120(1)
C3–H31	1.09(1)	C2–C3–H31	118(1)	C4–C3–H31	122(1)
C5–H51	1.08(1)	C4–C5–H51	121(1)	C6–C5–H51	119(1)
C6–H61	1.09(1)	C5–C6–H61	119(1)	C1–C6–H61	120(1)
C7–H71	1.09(1)	C4–C7–H71	108(1)	C8–C7–H71	107(1)
C7–H72	1.07(2)	C4–C7–H72	109(1)	C8–C7–H72	109(1)
		H71–C7–H72	110(1)		
O1–O2[a]			2.14(1)		

[a] Intermolecular distance.

Furthermore, it is important to stress that each trial move in the Monte Carlo calculation is tested by determining the goodness-of-fit of the calculated powder diffraction pattern to the *entire* experimental powder diffraction pattern. No partitioning of the data into a set of "single-crystal-like" intensities is carried out. The avoidance of such arbitrary partitioning is an important strength of the method described here, and it is important to emphasize the advantages of adopting a strategy based upon this philosophy. Indeed, this feature of our Monte Carlo technique is in contrast with all other strategies that have been developed for *ab initio* crystal structure determination from powder diffraction data.

Finally, it is relevant to note that Monte Carlo techniques have become of immense value in many areas of science, and the so-called reverse Monte Carlo (RMC) method has recently been applied successfully in modeling the structural properties of glassy materials by fitting structural models to X-ray and neutron scattering data.[19] A unique feature of this approach has been the use of the entire scattering data to extract the maximum structural information on these materials.

After completion of the work reported here, a related methodology for structure determination from powder diffraction data has been reported,[20] and its successful application to determine the known crystal structure of benzene has been demonstrated.

Acknowledgment. We are grateful to the SERC for financial support.

---

(19) Keen, D. A.; McGreevy, R. L. *Nature* **1990**, *344*, 423.

(20) Newsam, J. M.; Deem, M. W.; Freeman, C. M. *Accuracy in Powder Diffraction II*; NIST Special Publication No. 846, 1992.