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A rotational search procedure for detecting a known molecule in a crystal. Errata.

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(*Received* 17 *February* 1971)

A recently published paper with the above title (Lattman & Love, 1970) contains three errors which require correction:

On page 1855, column 2, fourth line below equation (2), replace **C** by $\tilde{\mathbf{C}}$.

On page 1855, column 2, equation (4), replace $\tilde{\mathbf{C}}$ by **C**.

On page 1856, column 1, equation (6) and following, read:

$$\Delta^2=(1/V)\cdot\int_V[R(\boldsymbol{\theta})-\bar{R}]^2\mathrm{d}V. \qquad (6)$$

Here V is the volume explored in $\boldsymbol{\theta}$ space, $\bar{R}$ is $\cdots$.

Reference

Lattman, E. E. & Love, W. E. (1970). *Acta Cryst.* B**26**, 1854.

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Further refinement of the structure of *p*-nitrobenzoic acid.*

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The structure of *p*-nitrobenzoic acid has been refined further after including hydrogen atoms and using anisotropic temperature factors; final *R* for 744 observed reflexions is 0·074 and the average estimated standard deviation in bond lengths is 0·006 Å. The central aromatic bonds are shortened from the normal value in crystalline benzene, although the shortening is more in *p*-nitroaniline and *p*-aminobenzoic acid; these results probably indicate that cooperative electronic interaction between the *para* substituents in the latter compounds must be only partly responsible for the shortening of the central aromatic bonds.

In the structure of *p*-nitrobenzoic acid reported earlier (Sakore & Pant, 1966; hereinafter referred to as paper I), the central aromatic bonds are of normal length. This result is expected because both the *para* substituents are electron-withdrawing groups and no resonance interaction is expected. However, in view of the shortening of the central aromatic bonds in terephthalic acid (Bailey & Brown, 1967), a molecule which has electron-withdrawing carboxylic groups in *para* positions, it was felt that the structure of *p*-nitrobenzoic acid should be refined thoroughly to decide whether there is in fact central-bond shortening in this molecule. In paper I, hydrogen atoms of the aromatic ring were not included in the structure refinement, and only individual isotropic temperature factors were used.

The refinement was started with the parameters given in paper I. Hydrogen atoms were included in the structure refinement and anisotropic temperature factors were introduced; five cycles of refinement decreased *R* by about

Table 1. *Final atomic and thermal parameters*

Thermal parameters (× 10^4) are of the form $T=\exp\left[-(b_{11}h^2+b_{22}k^2+b_{33}l^2+2b_{12}hk+2b_{23}kl+2b_{13}hl)\right]$.

	x	y	z	b_{11}	b_{22}	b_{33}	b_{12}	b_{23}	b_{13}
C(1)	0·4163 ± 0·0003	0·4987 ± 0·0009	0·0896 ± 0·0002	49 ± 2	308 ± 18	16 ± 1	−1 ± 6	6 ± 4	3 ± 1
C(2)	0·4898 ± 0·0003	0·6421 ± 0·0009	0·1293 ± 0·0002	42 ± 2	346 ± 20	20 ± 1	−5 ± 6	−7 ± 4	1 ± 1
C(3)	0·4590 ± 0·0003	0·8345 ± 0·0009	0·1689 ± 0·0002	49 ± 2	368 ± 21	18 ± 1	−11 ± 6	−1 ± 4	1 ± 1
C(4)	0·3536 ± 0·0003	0·8881 ± 0·0009	0·1666 ± 0·0002	54 ± 2	275 ± 17	15 ± 1	−3 ± 6	−2 ± 3	4 ± 1
C(5)	0·2790 ± 0·0003	0·7492 ± 0·0010	0·1281 ± 0·0002	46 ± 2	368 ± 19	19 ± 1	−1 ± 6	−1 ± 4	4 ± 1
C(6)	0·3105 ± 0·0003	0·5525 ± 0·0009	0·0896 ± 0·0002	40 ± 2	338 ± 20	20 ± 1	−9 ± 6	−9 ± 4	4 ± 1
C(7)	0·4525 ± 0·0003	0·2878 ± 0·0009	0·0490 ± 0·0002	47 ± 2	305 ± 18	17 ± 1	−1 ± 6	8 ± 4	2 ± 1
O(1)	0·5464 ± 0·0002	0·2407 ± 0·0007	0·0487 ± 0·0001	49 ± 2	405 ± 14	23 ± 1	9 ± 5	−21 ± 3	3 ± 1
O(2)	0·3798 ± 0·0002	0·1585 ± 0·0006	0·0147 ± 0·0001	48 ± 2	412 ± 15	23 ± 1	2 ± 5	−35 ± 3	2 ± 1
O(3)	0·3821 ± 0·0002	0·1783 ± 0·0007	0·2504 ± 0·0002	66 ± 2	515 ± 18	27 ± 1	−15 ± 6	−46 ± 4	3 ± 1
O(4)	0·2295 ± 0·0002	0·1722 ± 0·0007	0·1983 ± 0·0001	60 ± 2	440 ± 16	28 ± 1	32 ± 5	−4 ± 3	8 ± 1
N	0·3184 ± 0·0003	0·0933 ± 0·0008	0·2085 ± 0·0002	57 ± 2	329 ± 16	22 ± 1	−12 ± 6	−8 ± 4	13 ± 1
H(1)	0·408 ± 0·004	0·034 ± 0·012	−0·007 ± 0·002						
H(2)	0·560 ± 0·004	0·602 ± 0·011	0·131 ± 0·002						
H(3)	0·512 ± 0·004	0·931 ± 0·011	0·200 ± 0·002						
H(5)	0·210 ± 0·004	0·813 ± 0·012	0·130 ± 0·002						
H(6)	0·261 ± 0·004	0·470 ± 0·012	0·064 ± 0·002						

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* Communication No. 1548 from the National Chemical Laboratory, Poona, India.

1·4 %. At this stage, the central aromatic bond lengths were 1·379 and 1·381 Å. A few errors in F_o were detected; therefore, the intensities of all the reflexions were re-estimated. Some faint high-angle reflexions which were left out in paper I were also included. Some extra *h*0*l* reflexions could also be included from a strong photograph. In all, 745 observed reflexions were obtained; of these, reflexion 202 was left out as it appears to suffer from extinction. The scaling was done with the help of F_c. For the refinement, unobserved reflexions having a threshold value less than F_c were also used. Thermal parameters of hydrogen atoms were assumed to be the same as those of the carbon atoms to which they are attached. Five cycles of refinement were given, using Cruickshank's weighting scheme and the block-diagonal approximation. During these cycles, the atomic parameters of the hydrogen atoms were also refined, although their thermal parameters were kept constant. The final *R* for observed reflexions is 0·074. Final atomic and and thermal parameters, along with the e.s.d.'s (obtained from the diagonal terms of the least-squares inverse matrices) are given in Table 1; for brevity, the table of F_o and F_c has been omitted.

Intramolecular bond lengths and angles are shown in Fig. 1 and listed in Table 2. The corrections to C(4)–N, N–O(3), N–O(4), C(7)–O(1) and C(7)–O(2) bond distances, arising from large thermal vibrations, were evaluated in the usual way (Takwale & Pant, 1971) and amounted to 0·006, 0·018, 0·014, 0·010 and 0·011 Å respectively; details of the atomic thermal-vibration ellipsoids have been omitted for the sake of brevity. The observed root-mean-square displacements of atoms C(7), O(1) and O(2) imply an r.m.s. oscillation amplitude, of the carboxylic group about the C(1)–C(7) bond, of about 9°; however, the nitro group does not appear to oscillate as a rigid group. The equations of the various planes referred to the *a*′, *b*, and *c*

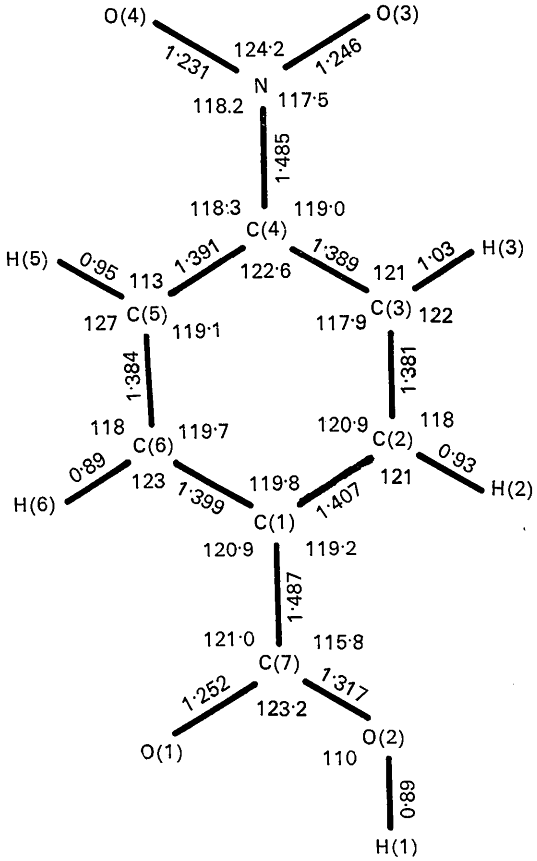

Fig. 1. Bond lengths and angles.

Table 2. *Intramolecular bond lengths and angles*

	Lengths				Angles
	Uncorrected	Corrected	E.s.d.		
C(1)–C(2)	1·407 Å		0·006	C(1)–C(2)–C(3)	120·9 ± 0·4°
C(2)–C(3)	1·381		0·006	C(2)–C(3)–C(4)	117·9 ± 0·4
C(3)–C(4)	1·389		0·006	C(3)–C(4)–C(5)	122·6 ± 0·4
C(4)–C(5)	1·391		0·006	C(4)–C(5)–C(6)	119·1 ± 0·4
C(5)–C(6)	1·384		0·006	C(5)–C(6)–C(1)	119·7 ± 0·4
C(6)–C(1)	1·399		0·006	C(6)–C(1)–C(2)	119·8 ± 0·4
C(1)–C(7)	1·487		0·006	C(7)–C(1)–C(2)	119·2 ± 0·4
C(4)–N	1·479	1·485 Å	0·006	C(7)–C(1)–C(6)	120·9 ± 0·4
N——O(3)	1·228	1·246	0·005	O(1)–C(7)–O(2)	123·2 ± 0·4
N——O(4)	1·217	1·231	0·005	C(1)–C(7)–O(2)	115·8 ± 0·3
C(7)–O(1)	1·242	1·252	0·005	C(1)–C(7)–O(1)	121·0 ± 0·4
C(7)–O(2)	1·306	1·317	0·005	C(3)–C(4)–N	119·0 ± 0·4
O(2)–H(1)	0·89		0·05	C(5)–C(4)–N	118·3 ± 0·4
C(2)–H(2)	0·93		0·05	C(4)–N——O(3)	117·5 ± 0·4
C(3)–H(3)	1·03		0·05	C(4)–N——O(4)	118·2 ± 0·4
C(5)–H(5)	0·95		0·05	O(3)–N——O(4)	124·2 ± 0·4
C(6)–H(6)	0·89		0·05		

Table 3. *Equations of planes*

(1) Benzene ring	$-0{\cdot}0618x-0{\cdot}6759y+0{\cdot}7344z+1{\cdot}0690=0$
(2) Nitro group	$-0{\cdot}2921x-0{\cdot}6872y+0{\cdot}6652z+2{\cdot}3421=0$
(3) Carboxylic group	$-0{\cdot}0422x-0{\cdot}6603y+0{\cdot}7498z+0{\cdot}9126=0$
(4) Plane through O(1), O(2) and dimer centre	$-0{\cdot}0627x-0{\cdot}6045y+0{\cdot}7941z+0{\cdot}9803=0$

Table 3 (*cont.*)

Angles between different planes (°)

	(2)	(3)	(4)
(1)	13·8	1·6	5·3
(2)	—	—	—
(3)	—	—	4·4

Deviations of atoms from different planes (Å)

Plane	(1)	(2)	(3)	(4)
C(1)	0·004	—	−0·005	—
C(2)	0·007			
C(3)	−0·014			
C(4)	0·010	0·049	—	—
C(5)	0·001			
C(6)	−0·008			
C(7)	−0·013	—	—	−0·045
O(1)	0·005			
O(2)	−0·051			
O(3)	−0·261			
O(4)	0·254			
H(1)	−0·08	—	—	0·04
H(2)	−0·03			
H(3)	−0·08			
H(5)	0·07			
H(6)	0·02			
Dimer centre	−0·139	—	−0·099	—
N	−0·012			

orthogonal axes, the angles between them and deviations of the atoms from the different planes are shown in Table 3.

The maximum change in bond length (uncorrected) from the structure reported in paper I is 0·020 Å in the C(7)–O(1) bond; the maximum difference between the lengths of the equivalent bonds in the aromatic ring is now 0·008 Å. The central aromatic bonds are 1·381 and 1·384 Å long. These bond lengths are smaller than the C–C bond lengths in crystalline benzene (1·393 Å), but they compare well with the corresponding bond lengths in *p*-toluic acid, 1·379 and 1·379 Å (Takwale & Pant, 1971), and in *p*-nitrotoluene, 1·382 and 1·383 Å (Barve & Pant, 1971). However, the central bonds are still shorter in *p*-nitroaniline, 1·373 and 1·377 Å (Trueblood, Goldish & Donohue, 1961), and in *p*-aminobenzoic acid (average length of four central bonds in two crystallographically independent molecules, 1·375 Å; Lai & Marsh, 1967). These results probably imply that cooperative electronic interaction between the *para* substituents in the latter compounds must be only partly responsible for the shortening of the central bonds of the benzene ring.

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Book Review

Works intended for notice in this column should be sent direct to the Book-Review Editor (M. M. Woolfson, Physics Department, University of York, Heslington, York YO1 5DD, England). As far as practicable books will be reviewed in a country different from that of publication.

Perspectives in structural chemistry. Vol. III. Edited by J. D. DUNITZ and J. A. IBERS. Pp. ix + 259. London: John Wiley, 1971. Price £ 7·00.

The third volume in *Perspectives in Structural Chemistry* maintains the standard of earlier volumes and amply justifies the editor's claim that this series is filling a genuine need. Four articles are included. The first, by A. D. Wadsley and S. Andersson, is concerned with the investigation by X-ray diffraction, electron diffraction, and electron microscopy of the microstructure of complex oxides and oxide fluorides based on Nb_2O_5. The authors first establish the structural principles and observe that the large unit cells encountered imply the existence of long-range ordering forces in these inorganic materials. They then go on to discuss crystal defects and the interrelation between crystallographic shear on the one hand and diffusion and reaction mechanisms on the other. The article is of great value to inorganic chemists, solid state physicists, and materials scientists who are interested in understanding old or designing new structures.

The second article, by R. Mason, deals with the problem of intermolecular forces in non-ionic crystals. Until recently it has been generally accepted that it is not possible to predict a crystal structure, except for very simple ionic substances. Kitajgorodskij has shown how the structures of known molecular crystals can be rationalized, and we have now reached the stage, largely due to the efforts of crystallographers in Italy, at which crystal structures are being successfully solved by means of potential energy calculations. Starting from a consideration of the interatomic potential between two hydrogen atoms, Mason treats the various attractive and repulsive forces that need to be taken into account, comparing the magnitudes of the different contributions, and illustrating his arguments by discussions of lattice energies, lattice dynamics, and solid state dimerizations.

The third article, by M. R. Churchill, gives a comprehensive survey of transition-metal complexes containing σ-bonded carbon atoms. Perhaps the most immediately useful information that can be gained from a review of this type is concerned not so much with the compounds that have been investigated as with those that have not, and Churchill draws attention to several large gaps in our knowledge that need to be filled or explained. In addition his survey enables conclusions to be drawn about the lengthening of a bond *trans* to a σ-bonded carbon atom, and also about the high sensitivity of metal–carbon bond lengths to small changes in bond order.

The final article on organophosphorus compounds is by J. J. Daly who has contributed so much to our knowledge