163. *The Crystal Structure of Pentaerythritol Tetranitrate.*

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The crystalline structure of pentaerythritol tetranitrate has been completely elucidated by means of quantitative *X*-ray measurements utilising all those $\{hkl\}$ diffracted beams obtainable with Cu-$K\alpha$ and Mo-$K\alpha$ radiations. The interatomic distances within the molecule are C–C = 1·50, C–O_1 = 1·37, O_1–N = 1·36, N–$O_{2,3}$ = 1·27 A. Two oxygens of the nitrate are equivalent; the third is at the normal single-bond distance from the nitrogen atom. An attempt is made to explain, in terms of resonance, the extraordinary shortness of the C–O bonding.

ALTHOUGH there are many data in the literature concerning the size and shape of the nitro-group, little evidence is available on these features of the nitrate group in organic substances. Admittedly, both fluorine nitrate and methyl nitrate (Pauling and Brockway, *J. Amer. Chem. Soc.*, 1937, **59**, 13) have been examined by electron-diffraction methods from which it has been deduced that the nitrate group is planar; however, probably because of the few compounds available, no determinations of the structure of any solid nitrates have previously been completed.

Pentaerythritol tetranitrate is ideally suited to such a study since the molecule is fairly simple and possesses high symmetry. In addition, it possesses explosive properties (it was used extensively during the war as a high explosive—P.E.T.N.) and therefore it is not unlikely that the molecule might exhibit anomalous bond lengths as evidence of this instability.

Two crystallographic examinations had been made; Knaggs (*Min. Mag.*, 1925, **20**, 346) found that pentaerythritol tetranitrate crystallises in the ditetragonal bipyramidal class exhibiting the forms $\{100\}$ and $\{111\}$; axial ratios determined goniometrically are $a : c$ = 1·000 : 0·506, refractive indices ω = 1·554, ϵ = 1·553, *d* 1·773 g./c.c., imperfect cleavage on (100). *X*-Ray single-crystal photographs obtained by using Co-$K\alpha$ radiation led to the cell dimensions $[a]$ = 13·2 A., $[c]$ = 6·66 A., and the space-group D^7_{4h}. An arrangement of the four molecules in the unit cell was deduced from about twelve qualitative intensity measurements. Later, Gerstacker, Möller, and Reis (*Z. Krist.*, 1927, **66**, 355) obtained large tetragonal crystals exhibiting the forms $\{110\}$ and $\{101\}$ by crystallisation from acetone, and *X*-ray single-crystal rotation photographs and Laue photographs gave the cell dimensions $[a] = 9{\cdot}38$ A., $[c] = 6{\cdot}69$ A., and the space-group $V_d^4 = P\bar{4}2_1c$.

The unit cell reported by Knaggs is centred and contains four molecules; by means of an axial transformation such that $\frac{1}{2}[110]$ (Knaggs) becomes [100], a primitive cell with dimensions $[a] = 9{\cdot}33$ A., $[c] = 6{\cdot}66$ A. is obtained, in fair agreement with the dimensions reported by Gerstacker *et al.* Claringbull (private communication) has redetermined the unit cell and space-group by means of single-crystal rotation and oscillation photographs, using Cu-$K\alpha$ radiation, finding $[a] = 9{\cdot}38$ A., $[c] = 6{\cdot}70$ A., and D_{2d}^4 $(V_d^4) = P\bar{4}2_1c$, respectively.

Preliminary Crystallographic Data.—Well-defined crystals of pentaerythritol tetranitrate exhibiting the forms {110} and {101} were obtained by crystallisation from acetone. It is noteworthy that no modification in the method of crystallisation produced any other forms. *X*-Ray single-crystal photographs confirmed the cell dimensions found by Claringbull, and oscillation photographs revealed the halvings $\{hhl\}$ absent when $l \neq 2n$, $\{h00\}$ absent when $h \neq 2n$, $\{0k0\}$ absent when $k \neq 2n$, whence the space-group is $P\bar{4}2_1c$. The density is 1·773 g./c.c., the calculated value for two molecules in the unit cell being 1·78 g./c.c.

Whilst the crystal as a whole therefore possesses considerable symmetry, the probable accuracy of the structure determination is limited by the absence of a centre. Since the unit cell contains two molecules, the central carbon atom of each molecule must lie in a special position; that of the first molecule is located at the origin of the cell (0, 0, 0) and that of the second at the centre $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. The four $\cdot CH_2\cdot O\cdot NO_2$ groups of each molecule are inter-related by the four-fold alternating axis which passes through the central carbon atom. A determination of the parameters of one of the $\cdot CH_2\cdot O\cdot NO_2$ groups is therefore sufficient to define the molecule located around the origin; the second molecule in the cell, surrounding the carbon atom at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, is derived from the first by the glide planes of symmetry lying in the (110) planes. The complete structure is therefore defined by the parameters of the six atoms $C\cdot C\cdot O\cdot NO_2$ (neglecting the hydrogen atoms whose positions are not revealed directly by *X*-rays).

Intensity Measurements.—Single-crystal oscillation photographs were taken about the [*a*], [*c*], and [110] axes, using both Cu-$K\alpha$ and Mo-$K\alpha$ radiations. The relative intensities of the spots produced by the diffracted beams were estimated by means of standard intensity scales. After correction for angular velocity variations (Cox and Shaw, *Proc. Roy. Soc.*, 1929, *A*, **127**, 71) and polarisation effects by means of the relation $F = k\sqrt{IDp/L}$ (where *D* is the Cox and Shaw factor, *p* the polarisation factor, and *L* the Lorentz factor) these were incorporated in a table of relative structure amplitudes. It is of interest that the photographs obtained with Mo-$K\alpha$ radiation gave no additional diffracted beams, indicating that those planes with spacing less than 0·77 A. (the minimum observable with Cu-$K\alpha$ radiation) do not give rise to diffracted beams of observable magnitude. The structure amplitudes were rendered absolute by comparing the intensities of the orders of (110) (obtained by reflection from a large ground 110 face) with the fourth-order (400) reflection from the ground cleavage face of rock-salt. The effects of extinction were estimated by repeating this procedure after immersing the crystal in liquid air.

Determination of the Structure.—The unit cell contains two molecules, the central carbon atoms being located in the special positions (000) and $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$; of the remaining atoms 8 carbon atoms are in the general positions $(x_1y_1z_1)$, $(\bar{y}_1x_1\bar{z}_1)$, $(\bar{x}_1\bar{y}_1z_1)$, $(y_1\bar{x}_1\bar{z}_1)$, $(\frac{1}{2} - x_1, \frac{1}{2} + y_1, \frac{1}{2} - z_1)$, $(\frac{1}{2} - y_1, \frac{1}{2} - x_1, \frac{1}{2} - z_1)$, $(\frac{1}{2} + x_1, \frac{1}{2} - y_1, \frac{1}{2} - z_1)$, $(\frac{1}{2} + y_1, \frac{1}{2} + x_1, \frac{1}{2} + z_1)$; the eight nitrogen atoms in general positions $(x_2y_2z_2)$, etc., and the three sets of eight oxygens at $(x_3y_3z_3)$, $(x_4y_4z_4)$, and $(x_5y_5z_5)$, etc., respectively. Fifteen parameters, *viz.*, $x_1y_1z_1$, $x_2y_2z_2$, $x_3y_3z_3$, $x_4y_4z_4$, $x_5y_5z_5$, are thus required to define the structure.

Preliminary efforts to elucidate the structure included the use of the Patterson–Harker synthesis (Harker, *J. Chem. Physics*, 1936, **4**, 381) which had proved so useful in determining the structure of pentaerythritol (Llewellyn, Cox, and Goodwin, *J.*, 1937, 887). Patterson (*Z. Krist.*, 1935, **90**, 517) showed that the function $P_{(uvw)}$, where

$$P_{(uvw)} = \frac{1}{V}\sum_{-\infty}^{+\infty}\sum\sum F^2_{(hkl)}\, e^{-2\pi i(hu/a + kv/b + lw/c)}$$

reaches a maximum at those co-ordinates which correspond with interatomic distances in the structure. Harker (*loc. cit.*) extended Patterson's work to include specifically in certain limited evaluations of $P_{(uvw)}$ those interatomic vector distances occasioned by the symmetry of the structure. Thus in pentaerythritol tetranitrate two similar atoms in opposite arms of the molecule having co-ordinates $(x_ry_rz_r)$ and $(\bar{x}_r\bar{y}_rz_r)$ should provide a maximum in the function $P_{(xy0)}$ at the point $2x_r2y_r$. If by chance two atoms, crystallographically dissimilar, have the same z co-ordinate, then their vector distance will also appear. In the same way the function $P_{(x\frac{1}{2}z)}$ should exhibit maxima at $(\frac{1}{2} - 2x_r)$, $(\frac{1}{2} - 2z_r)$, these points representing the vector distance between two crystallographically similar atoms located at $(x_r y_r z_r)$ and $(\frac{1}{2} - x_r, \frac{1}{2} + y_r, \frac{1}{2} - z_r)$.

Both of the Harker–Patterson sections were computed, and when plotted to form a contour map resulted in a large number of somewhat diffuse maxima which could not be correlated satisfactorily with any reasonable atomic model of the pentaerythritol tetranitrate molecule. Further sections, chosen in order to locate particular atoms, were then evaluated. For example, the section at $z = 0{\cdot}13$ should show, near the origin, a maximum in $P_{xy0\cdot13}$ due to the C_0–C_1 separation. If it is assumed that the central carbon atom has a tetrahedral valency arrangement and that the bond length is approximately 1·51 A., then the co-ordinate of C_1 is 0·125 (fractional co-ordinates). Neither this section nor any of the half dozen others computed at various distances along the [c] axis gave any information of value in this structure determination. One reason for this failure of the method may be mentioned. Because of the relatively large number of atoms in the unit cell (as compared with pentaerythritol) the number of vector distances which satisfy, or approximately satisfy, the conditions imposed by restricting one of the variables in $P_{(xyz)}$ in addition to those necessitated by space-group symmetry is probably considerable. Consequently the genuine maxima which could be used in the structure determination are masked by an unknown number of fortuitous maxima.

Following this lengthy attempt to utilise the Patterson–Harker syntheses, attention was focused on the projection of the structure on to the c-plane. This projection possesses a centre of symmetry, so the calculation of structure factors for the planes $hk0$ is greatly simplified. Trial and error methods, using reasonable molecular models and molecular orientations, followed by structure-amplitude calculations from approximate (xy) co-ordinates, were not immediately successful; the method led eventually, however, to the correct solution when used in conjunction with the Bragg structure-amplitude charts (*Nature*, 1936, **138**, 362; see also Bragg and Lipson, *Z. Krist.*, 1936, **95**, 323). Following is an outline of the method which illustrates a new application for the structure-amplitude charts in which they prove to be at least as valuable as for the purpose for which they were proposed.

The structure amplitude of a plane ($hk0$) is obtained by summing one of the following functions over each crystallographically different atom in the unit cell:

$$\underset{h+k=2n}{F_{hk0}} = \Sigma\, 4f(\cos 2\pi hx \,.\, \cos 2\pi ky + \cos 2\pi kx \,.\, \cos 2\pi hy)$$

$$\underset{h+k\neq 2n}{F_{hk0}} = \Sigma\, 4f(\sin 2\pi hx \,.\, \sin 2\pi ky + \sin 2\pi kx \,.\, \sin 2\pi hy)$$

where f is the atomic scattering factor of a particular kind of atom for the plane ($hk0$).

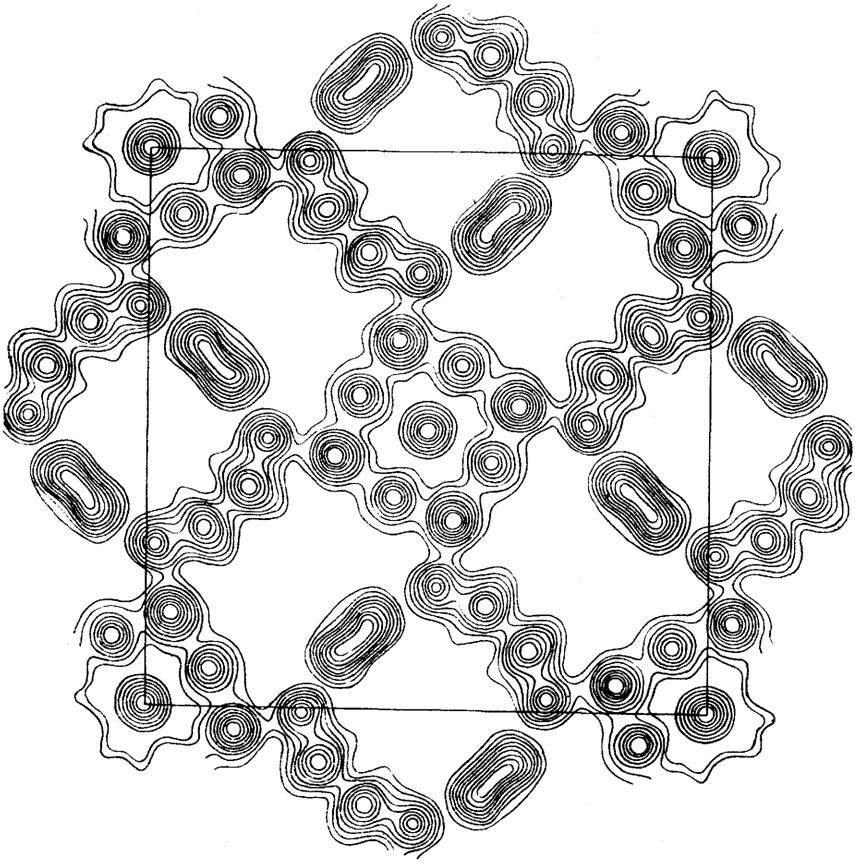
The Bragg chart for the plane $hk0$ is simply a contour map of one of the above functions, depending on $h + k$ being even or odd, plotted at intervals (assuming $f = 1$) over an area whose shape is that of the (c) plane of the crystal. We manufactured a complete set of charts of all the $hk0$ planes up to a complexity corresponding to 730. An atomic model of one arm of the molecule was made up on the same scale as the Bragg charts and held by means of a wall goniometer vertically above a table top on which rested the charts. A shadow of the model was cast on to the charts by means of a suitably arranged parallel beam of light. From the positions of the shadows of the atoms cast on the charts, the structure amplitude is readily obtained by summing the contribution of each atom. (In the preliminary work f_c was taken as unity, $f_N = 7/6$, and $f_0 = 8/6$; the structure amplitude being obtained by multiplying the sum of the contributions of the carbon atoms by unity, the sum of the nitrogen by 7/6, etc., and then the total of all the atoms by f_C.)

Reference to the table of absolute structure amplitudes shows that $F_{120} = 8{\cdot}5$, $F_{220} = 40{\cdot}7$, and $F_{440} = 35{\cdot}8$. The only molecular model and orientation which gives calculated values in approximate agreement with these observed amplitudes is one in which the arm of the molecule zigzags across the [a]. A little experimentation with a molecule of this sort led almost immediately to a set of (xy) co-ordinates which gave reasonable agreement between observed and calculated structure amplitudes up to $\xi = 1{\cdot}0$. A Fourier projection on the c-plane resulted in refinement of these co-ordinates and then, with the inclusion of the remaining $hk0$ planes, the contour map shown in Fig. 1 was produced; from this the xy co-ordinates are :

C_1	0·120	0·061	N	0·285	−0·016	O_3	0·360	0·102
O_1	0·162	−0·048	O_2	0·318	−0·106			

The actual model used in determining these co-ordinates tended continually upwards from the origin to the oxygens of the nitrate group; but it was immediately obvious from the (xy) co-ordinates that other values of the z co-ordinates were possible. Such co-ordinates were then calculated for the various molecular shapes using the following bond lengths : C_0–C_1 = 1·51, C_1–O_1 = 1·41, O_1–N = 1·36, N–$O_{2,3}$ = 1·24 A. The calculation of a few $\{hkl\}$ structure amplitudes soon showed that the original molecule was the correct one. Consequently, the structure amplitudes of all the $\{hkl\}$ planes up to $\xi = 1$ were calculated; fair agreement was obtained and, utilising the calculated phase angles, three-dimensional Fourier line syntheses parallel to the $[c]$ axis and passing through the xy co-ordinates of the atoms were computed.

FIG. 1.



Two-dimensional Fourier projection on (001). *Contours are plotted at intervals of* 1 *electron per* A.^{2}, *the lowest being* 1 *electron per* A.^{2}.

The structure was then refined by means of two complete sets of three-dimensional Fourier sections parallel to the c-plane and three-dimensional Fourier lines parallel to the $[c]$ axis through each of the atoms. Fig. 2 is a composite drawing made from the final set of Fourier sections parallel to the c-plane.

The final atomic co-ordinates, and a list of the principal interatomic distances and bond angles, are given below :

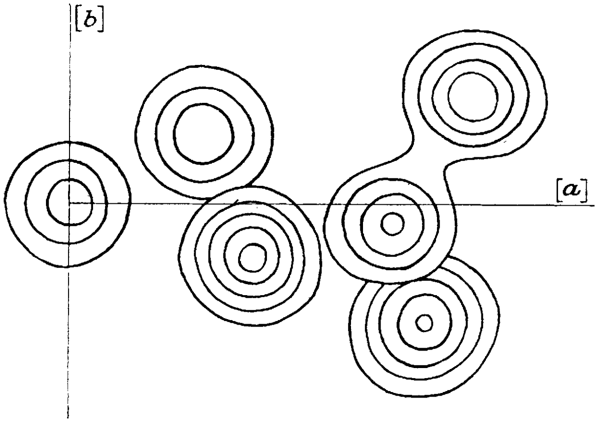
Atom.	x.	y.	z.
C_0	0·000	0·000	0·000
C_1	0·119	0·059	0·124
O_1	0·162	−0·044	0·256
N......................	0·284	−0·015	0·359
O_2	0·318	−0·104	0·494
O_3	0·356	0·099	0·325

C_0–C_1 = 1·50 A.
C_1–O_1 = 1·37 A.
O_1–N = 1·36 A.
O_2–N = 1·27 A.
O_3–N = 1·28 A.

C_1–C_0–C_1 = 112½°
C_0–C_1–O_1 = 108°
C_1–O_1–N = 116°
O_1–N–O_2 = 116°
O_1–N–O_3 = 121°

It is estimated that the accuracy attained is such that the interatomic distances are ± 0·02 A. and the valency angles ± 4°. These limits are somewhat wider than those tolerated in centrosymmetric structures; however, it is not considered practicable to refine the structure further with the present facilities for computation. The average discrepancy between the observed and the calculated structure amplitudes, neglecting 021 which is extinguished, is 22%.

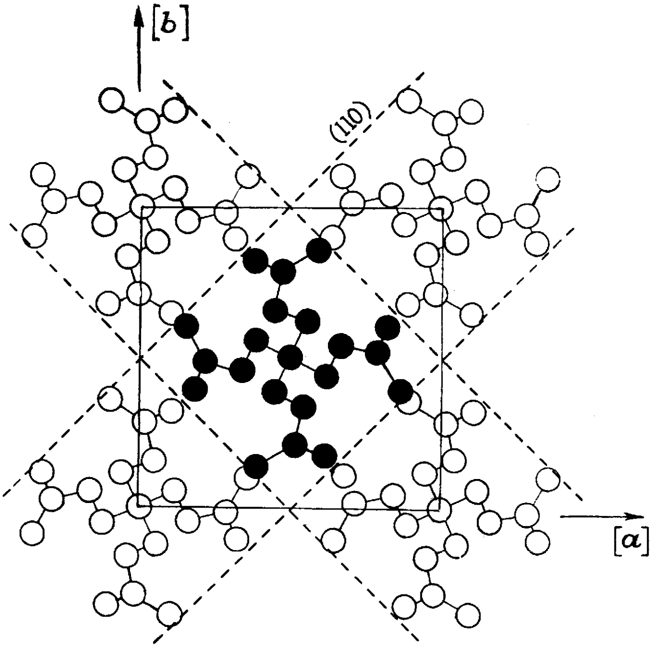
FIG. 2.



Contours are plotted at intervals of 2 *electrons per* A.^{3}, *the lowest being* 2 *electrons per* A.^{3}.

Discussion of the Structure.—The molecular orientation viewed along the [*c*] axis is illustrated in Fig. 3; the open atoms belong to molecules of which the central carbon is in the plane of the paper, and the black atoms are disposed about a central carbon atom located at $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$. Fig. 4 represents the structure viewed along the [*a*] axis. The broken lines in both figures represent the traces of the naturally occurring faces (110) and (011), respectively. Since there is no

FIG. 3.

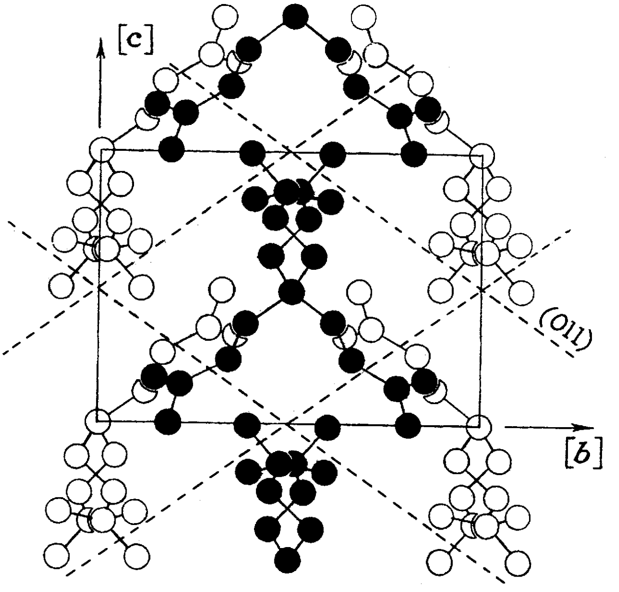


The structure viewed along [c]; *open atoms belong to molecules of which the centre carbon atom is in the plane of the paper.*

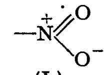
interleaving of groups across the trace of (110) (Fig. 3), cleavage is to be expected in this direction; this was first observed by Knaggs (*loc. cit.*) and we have confirmed it. The (110) face is populated almost entirely by nitrate groups, and it would appear from the separation of the oxygen atoms in neighbouring groups—3·2 A. and 3·4 A.—that the intermolecular forces approximate to the normal van der Waals. The structure viewed along the [*a*] axis is rather more confused (Fig. 4) and there is considerable interleaving of groups across the trace of (011). The arrangement of molecules is such that for any directions other than those represented by the naturally occurring faces very considerable interleaving occurs and this may account for the absence of other forms.

The molecule possesses four-fold alternating symmetry; the tetrahedral valency disposition of the central carbon atom is therefore confirmed. The atoms of each arm lie approximately in a plane inclined at 47½° to (001); the four atoms of the nitrate group are exactly coplanar and the carbon atom, designated C_1, lies slightly above this plane. The two oxygen atoms, O_2 and O_3 are, within the limits of experimental error, equidistant from the nitrogen atom at 1·275 A.; the small difference between this value and those observed (0·005 A.) is almost certainly spurious. The third oxygen atom, O_1 (which links the rest of the molecule to the group), is separated from the nitrogen by 1·36 A., this being the normal N–O single-bond distance. The equivalence of O_2 and O_3 indicates that resonance between the two extreme forms shown in (I) and (II) must take place and that each contributes equally. The bond angles within the group are then as in (III). It has been predicted that the group should have the configuration represented by (IV),

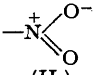
FIG. 4.



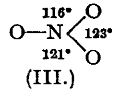
The structure viewed along [a]; *open atoms belong to molecules of which the centre carbon atom is in the plane of the paper.*



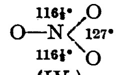
(I.)



(II.)



(III.)



(IV.)

but an examination of the structure shows that the environments of O_2 and O_3 are markedly different and this, taken in conjunction with the fact that bond angles are susceptible to distortion by much smaller external forces than bond distances, makes the observed values quite reasonable. The CH_2–O bond distance of 1·37 A: is considerably shorter than the normal single-bond separation. In pentaerythritol (Llewellyn, Cox and Goodwin, *loc. cit.*) this bond has a value of 1·46 A., and in pentaerythritol tetra-acetate (Goodwin and Hardy, *Proc. Roy. Soc.*, 1938, *A*, **164**, 369) it is 1·41 A. This shortening is undoubtedly significant and is related to the development of negative charges at the extremities of the arms of the molecule (*vide* the series pentaerythritol, pentaerythritol tetra-acetate, pentaerythritol tetranitrate).

Table of calculated and observed F values.

Plane.	F (obs.).	F (calc.).	α°.
020	23·0	25·1	0
040	35·8	32·9	180
060	12·7	14·0	0
080	<2·5	1·0	0
0, 10, 0	<2·3	2·4	0
011	5·8	10·4	0
021	40·4	83·5	0
031	29·0	26·5	180
041	29·8	31·3	0
051	26·2	26·0	0
061	26·0	17·6	180
071	4·4	1·1	180
081	9·5	6·1	180
091	4·3	6·5	180
0, 10, 1	<2·5	2·8	0
002	17·8	16·5	180
012	32·2	47·5	180
022	9·8	8·0	180
032	15·7	21·4	0
042	9·4	3·3	0
052	8·0	2·8	180
062	4·2	5·4	180
072	7·0	8·4	180
082	4·9	1·5	0
092	11·3	12·7	180
0, 10, 2	11·1	9·2	0
013	6·6	1·2	0
023	2·4	1·6	180
033	19·6	16·0	0
043	7·0	5·0	180
053	18·3	17·5	0
063	11·1	13·9	0
073	3·9	3·8	0
083	2·7	0·9	0
004	8·5	0·4	180
014	13·9	20·1	0
024	3·1	3·6	180
034	3·8	4·0	180
044	8·5	6·9	180
054	4·3	2·3	180
064	7·8	8·4	0
074	3·5	1·9	0
084	4·5	6·7	180
015	10·0	7·9	180
025	7·4	7·7	180
035	6·7	0·4	180
045	<2·5	0·3	180
055	12·5	17·1	0
065	4·5	5·3	180
075	7·7	6·8	0
006	12·0	13·9	0
016	<3·0	0·3	180
026	7·5	1·8	180
036	4·8	1·1	180
046	3·9	5·9	180
056	7·1	4·6	0
066	<2·3	0·0	0
076	3·4	2·7	0
017	5·7	2·2	0
027	7·9	2·9	180
037	6·3	5·5	180
047	4·0	4·4	180
110	10·0	11·6	0
120	8·5	8·1	0
130	27·2	36·1	0
140	8·7	8·4	0
150	8·3	4·7	180
160	13·2	13·4	0
170	10·6	8·0	0
180	4·3	2·3	0
190	8·9	8·8	180
1, 10, 0	8·7	4·1	0
121	35·9	48·3	8
131	24·4	26·2	150
141	8·7	7·7	204
151	13·6	14·0	125
161	16·3	16·0	137
171	10·3	9·9	286
181	17·4	16·7	58
191	6·1	4·4	207
1, 10, 1	4·0	4·1	54
112	15·4	14·1	156
122	30·7	34·7	349
132	20·0	21·7	348
142	14·5	14·3	161
152	12·9	14·0	245
162	14·6	12·3	184
172	8·6	8·3	282
182	9·6	7·9	209
192	9·5	9·1	346
1, 10, 2	3·3	2·5	196
123	13·2	15·8	239
133	17·7	19·3	227
143	7·1	10·1	138
153	9·8	8·5	65
163	11·3	6·4	307
173	17·3	18·0	352
183	5·5	7·1	320
193	6·8	6·0	323
114	8·4	11·3	289
124	14·7	20·0	9
134	5·3	7·8	290
144	10·6	11·8	38
154	14·6	14·1	24
164	5·9	2·6	351
174	4·2	5·7	60
184	3·7	3·5	231
125	8·5	9·1	59
135	9·8	12·3	106
145	10·4	10·2	57
155	7·8	7·2	296
165	5·7	5·3	174
175	5·0	4·6	358
185	3·4	3·4	328
116	9·1	13·7	174
126	2·8	1·0	233
136	10·0	14·0	7
146	10·7	9·7	242
156	2·8	1·5	100
166	3·6	1·7	88
127	8·5	8·1	353
137	5·6	8·3	243
147	3·8	2·7	221
220	40·7	52·1	180
230	21·5	23·5	0
240	9·2	9·4	180
250	4·3	2·5	180
260	17·5	11·9	0

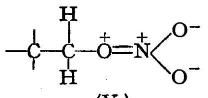
Plane.	F (obs.).	F (calc.).	α°.
270	8·9	11·7	180
280	<2·8	1·6	180
290	6·3	7·9	0
2, 10, 0	2·6	2·4	180
231	9·1	6·7	145
241	7·1	6·4	19
251	13·6	11·8	66
261	18·8	20·1	208
271	5·9	3·3	43
281	3·6	2·6	256
291	10·4	9·8	336
2, 10, 1	6·1	5·8	6
222	30·5	44·6	297
232	28·4	37·2	137
242	21·4	25·1	330
252	8·2	2·7	126
262	5·3	10·0	87
272	6·7	5·3	94
282	<2·8	0·9	151
292	3·6	2·9	312
2, 10, 2	3·7	1·0	6
233	15·4	20·8	273
243	23·9	26·6	349
253	8·9	9·6	233
263	4·4	4·5	92
273	7·6	5·0	279
283	11·0	12·6	202
293	3·5	3·5	222
2, 10, 3	4·8	3·9	269
224	19·7	20·6	73
234	3·9	5·3	272
244	7·7	7·0	6
254	15·9	22·8	1
264	12·7	16·8	337
274	4·6	7·4	350
284	3·5	0·2	214
294	4·4	2·9	5
235	6·8	7·1	91
245	4·5	6·5	51
255	3·4	1·8	180
265	4·4	2·6	210
275	7·6	7·8	86
285	3·8	3·8	75
226	<2·9	2·2	116
236	8·8	6·2	280
246	5·0	6·2	20
256	4·8	6·4	198
266	2·8	0·1	243
237	3·9	1·7	138
247	4·0	2·8	3
257	3·4	2·9	34
330	20·6	27·1	180
340	12·4	11·8	180
350	11·9	19·2	180
360	3·6	5·3	0
370	17·4	17·2	0
380	11·5	8·3	180
390	8·8	8·6	0
3, 10, 0	4·4	0·3	180
341	22·6	22·0	290
351	5·4	5·4	180
361	14·4	16·4	337
371	4·7	5·3	271
381	10·4	9·0	94

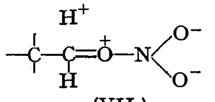
Plane.	F (obs.).	F (calc.).	α°.
391	12·8	12·8	104
3, 10, 1	3·8	3·9	350
332	13·6	14·5	0
342	19·9	22·4	143
352	3·6	8·6	292
362	3·9	1·6	99
372	6·8	5·3	159
382	6·6	7·7	333
392	3·5	4·1	60
3, 10, 2	4·2	3·1	193
343	10·0	15·0	4
353	7·9	12·7	113
363	3·7	3·1	354
373	6·2	6·4	6
383	6·0	5·0	233
393	2·7	2·5	245
334	12·8	16·7	203
344	3·5	6·8	297
354	5·1	6·2	60
364	10·0	9·2	351
374	3·3	3·3	175
384	3·2	3·8	36
245	11·8	11·9	22
355	5·4	7·1	293
365	4·0	7·3	21
375	3·0	3·5	34
336	5·1	5·7	48
346	4·6	6·1	174
356	2·9	4·4	180
366	2·8	4·8	16
347	1·9	1·4	121
440	24·8	27·5	0
450	8·9	8·0	180
460	12·3	8·4	0
470	14·7	16·5	180
480	13·2	8·4	0
490	6·4	4·1	0
4, 10, 0	5·9	3·8	0
451	7·5	6·9	220
461	14·2	14·0	119
471	7·2	6·0	110
481	8·2	8·0	72
491	8·1	8·2	350
442	4·9	2·5	304
452	11·3	13·8	385
462	8·4	8·5	134
472	7·0	7·7	106
482	7·5	7·8	315
492	1·7	0·7	311
4, 10, 2	3·2	2·6	248
453	11·2	12·4	92
463	11·1	13·1	23
473	8·3	10·8	15
444	9·6	8·7	211
454	6·2	9·3	62
464	3·9	2·5	198
474	8·8	10·3	193
455	9·9	12·2	246
465	5·6	8·6	289
475	3·3	3·8	247

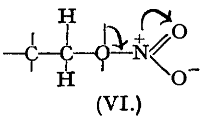
Plane.	F (obs.).	F (calc.).	α°.
446	7·5	10·6	16
456	2·7	2·2	124
550	8·1	6·7	0
560	5·3	4·9	180
570	8·5	9·9	0
580	10·6	9·7	180
590	8·5	8·0	180
561	12·9	13·1	333
571	10·4	10·1	249
581	5·3	3·3	11
591	3·2	2·9	88
552	12·5	16·5	10
562	6·2	7·6	10
572	5·6	6·2	101
582	10·6	10·0	18
592	2·1	0·8	197
563	10·7	10·5	124
573	5·1	5·2	169
583	4·3	5·1	163
554	9·9	14·5	359
564	4·0	1·3	167
574	4·3	3·3	231
584	2·3	2·2	135
565	3·6	3·7	299
660	13·4	12·7	180
670	3·9	1·6	0
680	2·4	0·0	—
690	1·9	3·1	180
671	5·5	6·7	91
681	2·7	1·0	108
691	2·7	1·0	43
662	10·9	5·9	88
672	11·1	10·9	50
682	6·6	6·9	1
673	6·6	5·9	349
683	5·6	2·5	100
664	2·1	2·2	147
674	4·0	4·2	298
770	7·2	4·7	0
780	2·4	3·1	180
781	5·7	4·3	116
782	3·8	3·5	196

No entirely satisfactory explanation for the shortening of this C–O bond is forthcoming; an interpretation, which is attempted below, in terms of resonance leads to the existence of canonical forms which appear somewhat "exotic," and since the arguments are general, should apply also to other nitrates; the fact that the corresponding atomic separation in methyl nitrate (Pauling and Brockway, *loc. cit.*) is normal militates against the probability of the resonance explanation. However, for the moment this electron-diffraction evidence is laid aside because the authors cannot overlook the possibility that, since no abnormality of the sort was expected in methyl nitrate, a model incorporating a short C–O bond was probably not examined in much detail.

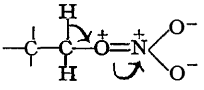
If one assumes that the negative charges on O_2 and O_3 and the resulting positive charge on the N produce a tendency for electrons in the remainder of the arm to drift towards the nitrogen, then two possible resonance forms (neglecting the resonance in the $\cdot NO_2$) may be considered,

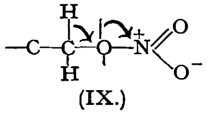

(V.)

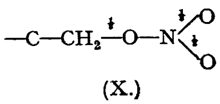

(VII.)


(VI.)

viz., (V), derived from the unexcited molecule by the electromeric shift (VI), and (VII), derived either from (V) by the shift (VIII) or from the unexcited molecule as in (IX).


(VIII.)


(IX.)


(X.)

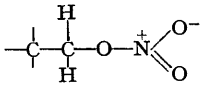
Although it is recognised that both mechanisms are novel, these possibilities must be entertained if an explanation in terms of resonance is attempted.

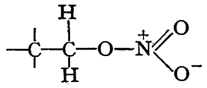
Using the expression

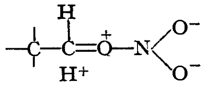
$$B = (k_s x_s S + k_d x_d D)/(k_s x_s + k_d x_d)$$

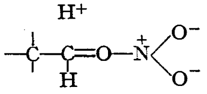
(where B = length of the resonating bond, S = length of the single bond, x_s and x_d represent the extent of single- and double-bond character, respectively, and k_s and k_d are the force constants of single and double bonding), we can calculate x_s and x_d for all bonds in the structure. Such a calculation leads to a molecule (X), where the fractions represent the extent of double-bond character in the various bonds.

Four canonical forms of the molecule may therefore be postulated, *viz.*, (*a*)—(*d*). The

(*a*) 
$-C-\overset{H}{\underset{H}{C}}-O-\overset{+}{N}(O^-)=O$

(*b*) 
$-C-\overset{H}{\underset{H}{C}}-O-\overset{+}{N}(=O)O^-$

(*c*) 
$-C-\overset{H}{\underset{H^+}{C}}=\overset{+}{O}-N(O^-)O^-$

(*d*) 
$-C-\overset{H^+}{\underset{H}{C}}=O-\overset{+}{N}(O^-)O^-$

contributions of these forms are 1/3, 1/3, 1/6, and 1/6, respectively.

These simple calculations, in which it is recognised that no account is taken of the formal charges on the various atoms, lend support to the postulated resonance mechanism. Sutherland (private communication, to be published elsewhere) has observed the infra-red spectrum of pentaerythritol tetranitrate. He finds anomalies both in the nitrate group and in the CH_2 vibrations. The highest characteristic frequency of the NO_2 group (at 6 mμ) is abnormally high; this would indicate that the force constant for the N–O bond is higher than usually exists in nitro-paraffins, and consequently that this bond would be relatively shortened. These deductions are not in accordance with the crystallographic results, but it must be remembered that comparison is being made between the nitro-group of a nitro-paraffin and that of a nitrate. The CH_2 stretching vibrations are shown by Sutherland to be exceptionally weak, indicating that the charge distributions of the CH_2 group is considerably different from that of a CH_2 group in a paraffin chain. Unfortunately, no definite information could be obtained concerning the state of the C–O bond.

Whilst the infra-red work does not directly help in elucidating the structural riddle of the short C–O bond in pentaerythritol tetranitrate, it does lend support to the suggestion that the electronic configuration of the CH_2 grouping has been considerably modified. The resonance mechanism suggested earlier calls for a considerable alteration in the charge distribution on the CH_2 group, but whether such modification would result in a weaker band at 6·8 mμ is not certain.

The observation that the C_0–C_1 distance in pentaerythritol tetranitrate is 1·50 A.—considerably shorter than the value 1·54 A. found in diamond (Bragg and Bragg, *Proc. Roy. Soc.*, 1913, *A*, **89**, 277) and in the paraffins, ethane and *neo*pentane (Pauling and Brockway, *J. Amer. Chem. Soc.*, 1937, **59**, 1233)—is not inconsistent with this postulated modification of the CH_2 grouping. Similar values have been reported in a number of other organic compounds (see table below), so now it appears probable that the single-bond C–C separation in substances other than the paraffins and diamond approximate more nearly to 1·51 A. than to 1·54 A.

Carbon–Carbon Bond Lengths (A.) *in Various Organic Compounds.*

Succinic acid (Verweel and MacGillavry, *Nature*, 1938, **142**, 161)	1·52
Acetamide (Senti and Harker, *J. Amer. Chem. Soc.*, 1940, **62**, 2008)	1·51
Pentaerythritol (Llewellyn, Cox, and Goodwin, *loc. cit.*)	1·50
Pentaerythritol tetra-acetate (Goodwin and Hardy, *loc. cit.*)	1·52
Glycine (Albrecht and Corey, *J. Amer. Chem. Soc.*, 1939, **61**, 1087)	1·52
s-Bisnitroaminoethane (Llewellyn and Whitmore, unpublished)	1·52

The remaining bond distance within the molecule, O_1–N, is 1·36 A. in agreement with the normal single-bond separation reported in methyl nitrate and fluorine nitrate (Pauling and Brockway, *loc. cit.*). This excludes the possibility that the excited form of the molecule (V) contributes appreciably to the stability of the structure.

There are then three remarkable features in the structure of pentaerythritol tetranitrate: (1) The shortness of the C_0–C_1 bond, *viz.*, 1·50 A.; (2) the short C_1–O_1 bond; (3) the normal O_1–N bond. No entirely satisfactory explanation for (2) and (3) can yet be given. It is obviously necessary to examine in detail the structures of additional solid nitric acid esters in order to decide whether these bond lengths are peculiar to pentaerythritol tetranitrate or whether they are representative of these atomic separations in this type of compound.

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