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A Neutron Diffraction Study of 2-Nitrobenzaldehyde and the C–H ··· O Interaction*

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The structure of the stable modification of 2-nitrobenzaldehyde has been redetermined by means of neutron diffraction. Non-hydrogen atom parameters agree with values from the X-ray determination. The parameters of the hydrogen atoms are obtained. C–H ··· O interactions are discussed and it is concluded that the observed geometry of the molecule indicates the absence of an internal hydrogen bond in 2-nitrobenzaldehyde.

Introduction

The previously reported X-ray analysis of the stable modification of *o*-nitrobenzaldehyde (Coppens & Schmidt, 1964) has shown that the two substituents in this compound are not coplanar with the aromatic ring. This suggested that no hydrogen bond exists between the C–H of the aldehyde group and the oxygen of the nitro group, though various authors have interpreted their experimental results as providing evidence for the existence of such a bond. Since the X-ray analysis did not produce a reliable position for the aldehydic hydrogen atom, no definite conclusion could be drawn. In addition the aldehydic hydrogen atom plays a part in the photochemical rearrangement of *o*-nitrobenzaldehyde to nitrosobenzoic acid and its position will throw light on the mechanism of this reaction. Therefore a single-crystal neutron diffraction investigation was undertaken.

Experimental

Small crystals of *o*-nitrobenzaldehyde can be grown from alcohol–water mixtures. When such a crystal is immersed, at the end of a silk thread, in the slightly undercooled melt of *o*-nitrobenzaldehyde it grows slowly. When the melt is kept at 42·5 °C (melting point 43 °C) for about three weeks crystals are obtained of dimensions suitable for neutron diffraction with the flux available at the Brookhaven Graphite reactor (in-pile flux about $2 \cdot 10^{13}$ cm^{-2} sec^{-1}).

Two crystals with dimensions 0·9 × 0·5 × 12·0 mm and 1·1 × 2·1 × 12·5 mm were used to collect *h*0*l* data, the weaker reflections being collected from the larger crystal. (Both crystals were elongated in the direction of the *b* axis, but the smaller one showed the form {101}, while on the larger one the forms {001} and {100} were developed. The first two of the dimensions describing the crystals refer to directions perpendicular to the planes of these forms.) The larger crystal was then cut and a fragment with dimensions 1·1 × 2·1 × 4·0 mm was used to collect *hk*0 and 0*kl* intensities.

The crystals are photosensitive and have a high vapor pressure at room temperature, therefore they were inserted in silica tubes blackened with carbon black. (Both silica and carbon black are sufficiently transparent to neutrons.)

The crystallographic constants as determined by X-rays were used throughout, they are:

$$a = 11{\cdot}37,\ b = 3{\cdot}960,$$
$$c = 7{\cdot}57\ \text{Å};\ \beta = 90^\circ\ 11',$$

space group $P2_1$. In the *h*0*l*, *hk*0 and 0*kl* zones reflections were observable up to 2θ values of 110°, 90° and 80° respectively ($\lambda = 1{\cdot}07$ Å). Within these three ranges there are 319, 69, and 38 non-symmetry-related reciprocal lattice points; 136 *h*0*l*, 40 *hk*0 and 20 0*kl* reflections were strong enough to be observed.

Data reduction and refinement

The data were corrected for absorption with Hamilton's program for the IBM 704 (Hamilton, 1957) ($\mu = 1{\cdot}13$ cm^{-1}). Standard deviations of the intensities were calculated with the formula:

$$\sigma^2(I_{\text{corr}}) = \Delta^2_{\text{stat}} + c_1^2 I^2 + c_2^2 (I_{\text{corr}} - I)^2$$

in which Δ_{stat} is the error due to counting statistics,

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while I and I_{corr} are respectively the observed intensity and the intensity after correction for absorption. The constant c_1 was evaluated by measuring a group of 24 $h0l$ reflections in the medium intensity range once on each of the two crystals used for collecting $h0l$ data. From the 24 ratios thus obtained c_1 was estimated to be 0·04. The constant c_2 was taken to be 0·05, but the influence of this last term is small since the absorption correction fluctuated around 0·15 I and never exceeded 0·3 I.

Refinement on the F^2's was carried out with the Busing & Levy least-squares program (1959). Initially, only those observed $h0l$ reflections were refined for which starting coordinates were derived from the X-ray results. All x and z parameters as well as the individual isotropic temperature parameters were varied. After two cycles the information contained in the unobserved reflections was utilized by including them with intensities equal to the theoretical mean value of the intensity in the unobserved intensity range (Hamilton, 1955). After three more cycles, the x and z parameters of the non-hydrogen atoms were compared with the values obtained from the X-ray data. The average of the differences was 0·012 Å, while the average of the ratios of the differences and their standard deviations is 1·2; thus the two sets of positional parameters are essentially equal and henceforth the more accurate X-ray values were used in the calculations. When subsequently the $hk0$ and $0kl$ reflections were added (including those not observed) the X-ray y parameters were used for the heavy atoms, which considerably reduced the amount of information to be extracted from these reflections. In this way it became possible to introduce some anisotropy in the temperature factors; after three isotropic cycles it was decided to refine the three principal elements and the 1–3 cross term of the tensors representing the thermal motion of the 16 atoms. Though keeping the corresponding ellipsoids fixed with one of their principal axes parallel to **b** is obviously not physically justified it was considered a convenient approximation which is not unreasonable, as the mean plane of the molecule is approximately perpendicular to the short b axis. Thus 83 parameters (*i.e.* 4 scale factors, 15 positional parameters and 64 thermal parameters) were determined from the 402 (184 observed and 218 unobserved) reflections which remained after properly scaled averages had been inserted for reflections common to two zones.

After two such cycles refinement was considered complete. Final agreement factors are

$$R = \frac{\Sigma|F_o^2-(kF_c)^2|}{\Sigma(F_o^2)} = 0\cdot14$$

and

$$R_w = \left\{\frac{\Sigma w(F_o^2-(kF_c)^2)^2}{wF_o^4}\right\}^{\frac{1}{2}} = 0\cdot16\,.$$

Table 1(*a*). *Positional parameters of the hydrogen atoms*

H_3	0·0541 ± 0·0014	0·210 ± 0·014	0·0651 ± 0·0020
H_4	0·0066 ± 0·0016	−0·028 ± 0·017	0·3606 ± 0·0025
H_5	0·1637 ± 0·0013	−0·031 ± 0·020	0·5919 ± 0·0021
H_6	0·3596 ± 0·0016	0·168 ± 0·018	0·5276 ± 0·0024
H_7	0·3419 ± 0·0016	0·366 ± 0·018	−0·1090 ± 0·0021

Table 1(*b*). *Temperature factors*

The temperature factors are the coefficients in the expression $\exp\{-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{13}hl)\}$

	β_{11}	β_{22}	β_{33}	β_{13}
O(1)	0·0097	0·10	0·0417	0·0042
O(2)	0·0086	0·18	0·0325	−0·0042
O(3)	0·0122	0·11	0·0206	−0·0010
N	0·0078	0·10	0·0250	−0·0006
C(1)	0·0066	0·07	0·0146	−0·0005
C(2)	0·0056	0·08	0·0136	−0·0011
C(3)	0·0073	0·06	0·0196	0·0000
C(4)	0·0077	0·05	0·0204	0·0015
C(5)	0·0109	0·08	0·0162	0·0016
C(6)	0·0087	0·11	0·0161	−0·0016
C(7)	0·0091	0·10	0·0168	0·0010
H(3)	0·0113	0·16	0·0273	−0·0043
H(4)	0·0113	0·20	0·0383	0·0060
H(5)	0·0161	0·13	0·0224	0·0024
H(6)	0·0141	0·18	0·0258	−0·0034
H(7)	0·0163	0·25	0·0237	0·0048

The positional parameters of the hydrogen atoms and the temperature factors are given in Table 1, while the structure factors of the observed reflections are listed in Table 2. All but 35 of the 218 unobserved reflections were calculated smaller than the estimated threshold value. The b- and c-axis neutron scattering density projections are shown in Fig. 1.

The hydrogen atom positions

The bond lengths and angles are given in Table 3 and Fig. 2. The displacements of the aromatic hydrogen atoms from the plane of the benzene ring and of the aldehyde hydrogen from the plane through C(2), C(7) and O(3) are given in Table 3. Since these displacements are not significant, the hydrogen atoms were subsequently put in these planes by moving them parallel to the b axis. C–H distances calculated with these new positions are listed in the last column of Table 3(*a*); they are only slightly different from those obtained from the least-squares results. The average of the aromatic C–H distances is 1·08 Å; this compares well with the length of similar bonds in other compounds (Hamilton, 1962). The aldehydic C–H distance (1·12 ± 0·02 Å) agrees with the observed distance in formaldehyde of 1·097 Å (microwave spectroscopy, taking the electron diffraction value of 1·213 Å for the C=O bond length; Davidson, Stoicheff & Bernstein, 1954).

The intramolecular non-bonding distances between the aldehydic hydrogen atom H(7) and the atoms C(2) and O(3) are respectively 2·04 and 2·22 Å. With

Table 2. *Observed and calculated values of structure factors*

	h	k	l	F_o^2	$(kF_c)^2$	A	B
I	1	0	2	280	283	3.51	
	1	0	3	162	160	-2.63	
	1	0	4	111	99	2.07	
	2	0	5	113	121	2.29	
	2	0	7	163	168	-2.70	
	3	0	1	323	326	-3.76	
	3	0	2	59	61	-1.62	
	3	0	6	438	393	-4.12	
	4	0	2	375	363	3.97	
	5	0	1	79	94	2.02	
	5	0	3	34	38	-1.28	
	5	0	4	34	36	1.26	
	6	0	1	50	49	1.46	
	7	0	3	93	91	-1.99	
	7	0	6	90	74	-1.79	
	8	0	1	269	229	3.15	
	9	0	1	419	330	3.78	
	9	0	2	282	265	-3.39	
	10	0	1	425	392	-4.12	
	10	0	2	162	155	-2.59	
	1	0	-1	318	405	4.19	
	2	0	-2	562	693	-5.48	
	2	0	-3	60	58	1.59	
	2	0	-5	56	62	-1.65	
	3	0	-1	44	40	1.31	
	3	0	-2	39	41	1.34	
	3	0	-4	147	137	2.43	
	4	0	-6	118	111	-2.19	
	5	0	-2	178	192	2.88	
	5	0	-3	433	457	-4.45	
	6	0	-1	452	431	-4.32	
	6	0	-4	211	184	2.83	
	7	0	-5	381	383	4.08	
	8	0	-4	163	142	-2.48	
	10	0	-2	122	115	2.23	
II	0	0	1	318	311	1.52	
	0	0	2	1762	1902	-3.76	
	0	0	3	705	727	-2.32	
	0	0	5	63	48	- .60	
	0	0	7	235	243	1.34	
	0	0	10	167	175	-1.14	
	1	0	0	814	848	-2.51	
	1	0	1	3495	3588	-5.16	
	1	0	5	253	243	-1.34	
	1	0	6	3075	2894	4.63	
	1	0	7	207	198	1.21	
	1	0	10	51	48	- .60	
	2	0	0	960	1014	-2.74	
	2	0	1	37	36	.52	
	2	0	2	107	65	- .70	
	2	0	4	105	84	.79	
	2	0	6	197	187	1.18	
	2	0	9	34	45	.58	
	3	0	0	3740	3743	-5.27	
	3	0	3	1673	1619	3.47	
	3	0	4	164	178	1.15	
	3	0	5	641	599	2.11	
	3	0	7	102	95	- .84	
	4	0	0	427	438	1.80	
	4	0	3	85	102	.87	
	4	0	4	156	94	- .83	
	4	0	8	98	98	- .85	
	5	0	0	950	942	-2.64	
	5	0	5	416	356	1.63	
	5	0	7	85	98	.85	
	5	0	8	99	101	.87	
	5	0	10	100	86	- .80	
	6	0	0	1028	1046	-2.79	
	6	0	2	52	39	.54	
	6	0	7	69	44	.57	
	7	0	0	491	480	1.89	
	7	0	1	201	193	1.20	
	7	0	2	213	177	1.15	
	7	0	4	379	439	1.81	
	7	0	5	555	583	-2.08	
	8	0	0	344	356	-1.63	
	8	0	2	1640	1289	3.09	
	8	0	3	299	316	1.53	
	8	0	4	77	81	- .78	
	8	0	5	500	487	-1.90	
	8	0	8	77	92	- .82	
	9	0	0	437	451	1.83	
	9	0	3	455	313	-1.52	
	9	0	5	474	352	1.62	
	10	0	0	117	123	.95	
	10	0	3	296	310	1.52	
	10	0	7	134	119	.94	
	11	0	8	227	169	-1.12	
	12	0	4	26	31	.48	
	12	0	5	93	117	- .93	
	12	0	7	154	186	-1.17	
	13	0	1	63	76	.75	
	14	0	1	275	210	-1.25	
	15	0	0	244	179	-1.15	
	18	0	3	29	75	- .74	
	1	0	- 3	90	96	- .84	
	1	0	- 4	2251	2403	-4.22	
	2	0	- 1	500	532	-1.99	
	2	0	- 4	34	39	.54	
	2	0	- 6	158	160	1.09	
	2	0	- 7	116	114	.92	
	3	0	- 3	247	242	1.34	
	3	0	- 5	310	302	1.50	
	3	0	- 6	65	53	- .63	
	3	0	- 7	287	246	1.35	
	4	0	- 1	160	175	1.14	
	4	0	- 2	37	36	.52	
	4	0	- 3	126	148	-1.05	
	4	0	- 4	81	78	.76	
	4	0	- 5	732	707	-2.29	
	4	0	- 8	157	125	.96	
	4	0	-11	91	96	- .84	
	5	0	- 1	960	1050	2.79	
	5	0	- 4	88	78	- .76	
	5	0	- 5	820	751	-2.36	
	5	0	- 7	157	140	-1.02	
	5	0	-10	108	84	.79	
	6	0	- 7	178	172	1.13	
	7	0	- 3	440	341	-1.59	
	7	0	- 4	232	202	1.22	
	7	0	- 6	166	179	-1.15	
	7	0	- 7	48	57	- .65	
	8	0	- 1	88	82	.78	
	8	0	- 2	88	92	- .83	
	8	0	- 5	264	279	1.44	
	8	0	- 6	201	192	1.19	
	8	0	- 9	98	98	- .85	
	9	0	- 4	194	183	-1.16	
	9	0	- 5	317	312	-1.52	
	9	0	- 8	75	73	.73	
	10	0	- 5	31	37	- .53	
	11	0	- 1	64	59	- .66	
	11	0	- 2	140	136	1.01	
	11	0	- 3	86	103	.87	
	14	0	- 1	112	110	.90	
	17	0	- 3	174	100	- .86	
III	1	1	0	765	706	-3.83	-1.85
	1	2	0	193	199	.26	2.24
	1	3	0	21	18	- .62	.29
	1	4	0	25	31	.01	.90
	2	1	0	253	241	-1.50	1.99
	2	3	0	18	18	- .28	- .62
	2	4	0	21	18	- .09	- .67
	3	1	0	175	177	2.09	.42
	3	2	0	86	77	- .73	-1.20
	3	3	0	34	35	- .84	- .45
	3	5	0	12	13	- .58	.05
	4	1	0	404	399	-1.34	2.91
	4	2	0	171	183	- .52	-2.10
	5	1	0	229	218	- .08	-2.36
	5	2	0	154	159	1.84	- .82
	5	3	0	96	89	-1.45	.43
	6	1	0	162	159	2.01	- .19
	6	2	0	99	101	-1.25	1.01
	6	3	0	42	32	- .13	.90
	7	1	0	125	135	1.81	- .46
	7	2	0	18	27	- .55	.62
	7	4	0	39	46	.13	-1.07
	8	1	0	18	22	- .13	- .74
	8	2	0	64	62	-1.05	- .70
	8	3	0	40	22	.12	- .74
	9	1	0	65	83	1.23	- .78
	10	1	0	207	194	-1.79	-1.33
	10	2	0	89	66	- .78	1.04
	11	1	0	120	101	- .49	1.53
	12	2	0	18	26	.73	- .36
	14	1	0	23	22	- .68	- .32
IV	0	1	1	1122	1230	-5.28	- .48
	0	1	2	189	175	.85	-1.81
	0	1	3	494	475	.73	3.21
	0	1	4	164	205	2.06	- .67
	0	1	6	192	180	1.98	- .45
	0	1	7	164	162	.04	1.92
	0	2	0	30	32	- .46	.72
	0	2	1	118	120	.30	-1.63
	0	2	2	192	128	1.34	1.07
	0	2	3	22	11	.21	- .44
	0	2	4	290	238	1.17	-2.02
	0	2	6	46	47	.27	1.00
	0	2	7	74	87	-1.28	.61
	0	2	8	31	30	- .49	- .67
	0	3	1	65	62	- .66	.99
	0	3	2	81	82	.97	.96
	0	4	5	37	30	.16	- .82

scale factors:

group I : 15.19
II : 36.72
III : 19.74
IV : 20.94

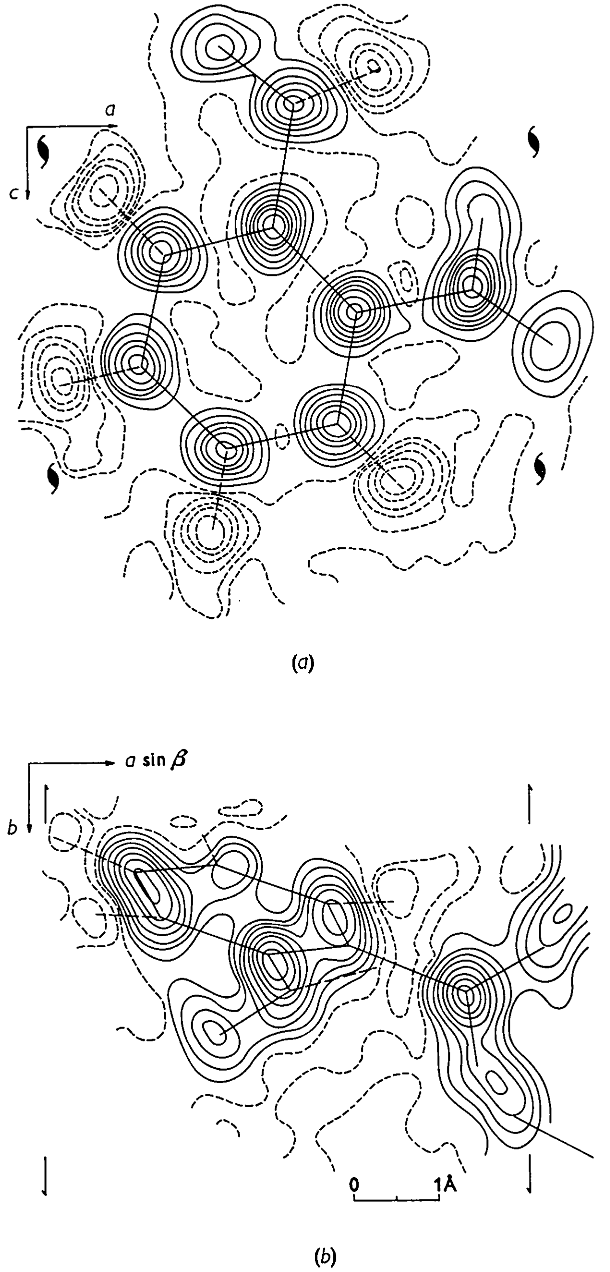

Fig. 1. Neutron scattering density projections along (*a*) the **b** direction and (*b*) the **c** direction. Zero contour and negative contours shown by dashed lines. Contour lines in negative regions at half the interval.

the Bartell 'hard sphere' radii (Bartell, 1960) (O, 1·13; C, 1·25; H, 0·92 Å) we calculate C(2) · · · H(7) as 2·05 and O(3) · · · H(7) as 2·17 Å. The calculated distance between C(2) and O(3) of 2·38 Å is equal to the observed value; thus, the shape of the aldehyde group conforms within the experimental errors with the hard sphere model.

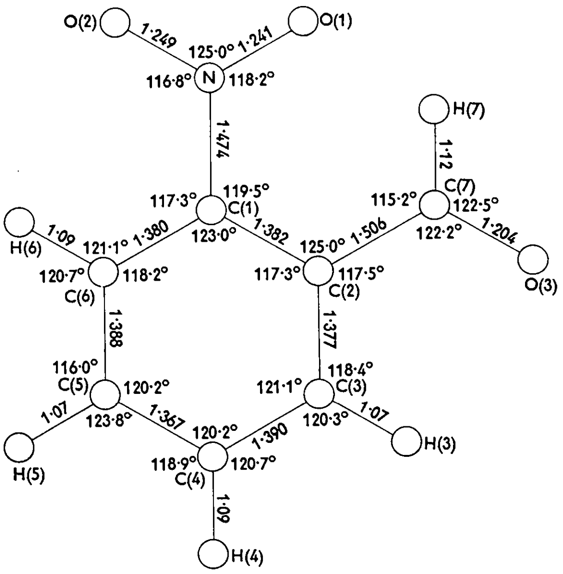

Fig. 2. Bond lengths and angles in *o*-nitrobenzaldehyde. Bond lengths between non-hydrogen atoms in the substituents have been corrected for thermal motion. The X-ray temperature factors were used in the calculation of these corrections.

Table 3(*a*). C–H *bond lengths and distances to planes*

	Plane	Distance	C–H	C–H when H atom is moved along **b** into plane
H(3)	*a*	−0·08 Å	1·07 ± 0·02 Å	1·08 Å
H(4)	*a*	−0·09	1·09 ± 0·03	1·06
H(5)	*a*	+0·02	1·07 ± 0·03	1·08
H(6)	*a*	+0·05	1·09 ± 0·02	1·10
H(7)	*b*	−0·08	1·12 ± 0·02	1·10

a = plane through ring carbons.
b = plane through atoms C(2), C(7) and O(3).

Table 3(*b*). *Bond angles involving hydrogen atoms*

Angle	
H(3)–C(3)–C(2)	118·4 ± 1·4°
H(3)–C(3)–C(4)	120·3 ± 1·6
H(4)–C(4)–C(3)	120·7 ± 1·3
H(4)–C(4)–C(5)	118·9 ± 1·5
H(5)–C(5)–C(4)	123·8 ± 1·1
H(5)–C(5)–C(6)	116·0 ± 1·2
H(6)–C(6)–C(5)	120·7 ± 1·8
H(6)–C(6)–C(1)	121·1 ± 1·8
H(7)–C(7)–O(3)	122·5 ± 1·7
H(7)–C(7)–C(2)	115·2 ± 1·9

The C–H · · · O interaction

The hydrogen atom of a C–H group can participate in a weak hydrogen bond when activated by other groups as in $CHCl_3$ and HCN (Hunter, 1946; Pimentel & McClellan, 1960). If the aldehyde group is capable of hydrogen bonding, *o*-nitrobenzaldehyde could be internally hydrogen bonded, a six-membered ring being formed. A number of workers did find evidence for such a bond: Arshid, Giles & Jain (1956) showed that *m*- and *p*-nitrobenzaldehyde, but not *o*-nitrobenzaldehyde, associate with pyridine. Pinchas (1955, 1957) observed that the aldehyde C–H stretching frequency is *largest* for the *ortho* isomer, which he explained by a weak O · · · H–C hydrogen bond in which the angle at the hydrogen is acute.

A similar increase in frequency was found on solidification of formaldehyde and acetaldehyde but interpreted differently by Schneider & Bernstein (1956). It should also be noted that the ultraviolet spectrum of *o*-nitrobenzaldehyde does not support the existence of an internal hydrogen bond (Lutskii & Alekseeva, 1959; Forbes, 1962).

The present structure analysis shows that the nitro group and the aldehyde group are turned out of the plane of the benzene ring each by about 30°. This distortion enlarges the distances between the oxygen of the nitro group and the C and H atoms of the aldehyde group to, respectively, 2·70 and 2·35 Å. Repulsion between the carbon and the oxygen can explain the rotation of the nitro group, but to explain the rotation of the aldehyde group we must invoke a repulsion between the hydrogen and the oxygen, since the H · · · N distance of 2·76 Å is larger than the sum of the van der Waals radii of these two atoms.

A lower limit for the repulsive force between these atoms can be calculated as follows: Maki & Geske (1962) have given an upper limit of $2{\cdot}8\times10^6$ cps for the rotational frequency of the aldehyde group in *p*-nitrobenzaldehyde. This rotation is hindered because conjugation between the aldehyde group and the ring favors the planar conformation. If we make the plausible assumption that without conjugation the frequency would be $\sim10^{13}$ cps we can find a lower limit for the energy barrier from the equation $\exp(-E/kT)<2{\cdot}8\times10^6/10^{13}$, which gives $E>62\times10^{-14}$ erg $=8{\cdot}9$ kcal.mol^{-1}. We now approximate the resonance energy as a function of the angle θ between the aldehyde group and the benzene ring by the formula: $V=E\sin^2\theta$. Assuming E to be the same in the *ortho* and *para* isomers we find for the restoring force $dV/d\theta$ in *o*-nitrobenzaldehyde ($\theta=31°\,17'$) a lower value of $5{\cdot}5\times10^{-14}$ erg.radian^{-1}, corresponding to $>0{\cdot}55\times10^{-5}$ *dyne* at the position of the hydrogen atom.

This force is to be balanced by the component of the O · · · H repulsion perpendicular to the plane of the aldehyde group, since the molecule is in equilibrium. No potential function is available for the interaction between oxygen and hydrogen, but we shall attempt to get an estimate of the size of the interaction by using the C · · · H potential function given by Bartell (1960), corrected for the difference in van der Waals radii between oxygen and carbon. We will take the O · · · H interaction at the observed distance of 2·38 Å equal to the force between C and H at $2{\cdot}95/2{\cdot}60\times2{\cdot}38=2{\cdot}70$ Å (using van der Waals radii H, 1·20; C, 1·75; O, 1·40 Å). The repulsive force calculated this way is $0{\cdot}9\times10^{-5}$ dyne, its component perpendicular to the aldehyde group being $0{\cdot}7\times10^{-5}$ dyne, only slightly larger than the lower limit of the restoring force calculated above. The extremely good agreement is probably fortuitous, but it seems to justify the conclusion that the interaction between O and H in *o*-nitrobenzaldehyde is of the ordinary van der Waals type. This definitely rules out the existence of an O · · · H–C hydrogen bond in the molecule.

Table 4. *The position of the aldehydic hydrogen atom*

Distance	
C(7)–H(7)	1·12 ± 0·02 Å
H(7) · · · O(1)	2·38 ± 0·04
C(7) · · · O(1)	2·70 ± 0·01
H(7)–plane *b*	−0·08 ± 0·07
Angle	
C(7)–H(7) · · · O(1)	94·1 ± 2·5°
O(1) · · · C(7)–H(7)	61·6 ± 2·1
H(7) · · · O(1)–N	94·5 ± 1·5

Pinchas explained the increase in C–H stretching frequency by assuming a C–H · · · O bond in which the angle at the hydrogen is acute, while we find this angle (Table 4) to be obtuse (94·1°). It is possible to calculate the change of the component of the repulsive force in the H–C direction with a change in the H–C distance, using again the modified Bartell potential function and the observed C–H · · · O angle. The force constant thus calculated is about 0·001 of the stretching force constant of the C–H bond, and ac-

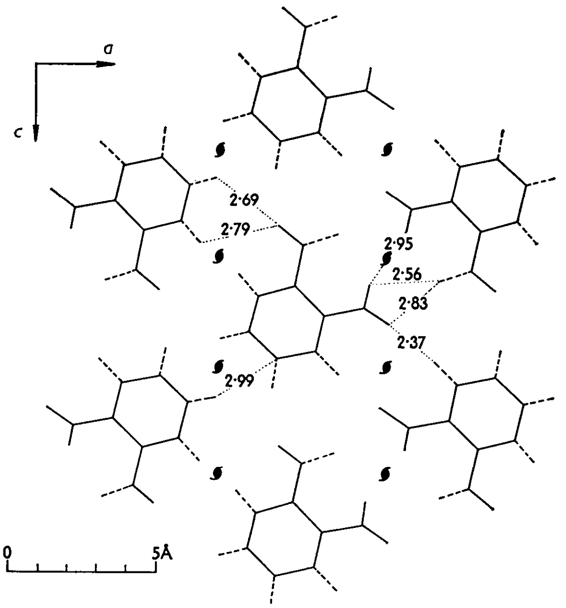

Fig. 3. Intermolecular O · · · H, C · · · H and O · · · O distances smaller than 3 Å (see also Table 5). The intermolecular H · · · H distances are all larger than 2·5 Å.

Table 5. *Intermolecular* H · · · O *distances shorter than* 3 Å

Between	Coordinates of molecule of second atom	r(H · · · O)	r(C · · · O)	∠ CH · · · O	∠ H · · · O · · · C	∠ O · · · C–H
O(2) and H(6)	$1-x, \frac{1}{2}+y, 1-z$	2·37 Å	3·31 Å	143·3°	11·4°	25·4°
O(1) H(7)	$1-x, \frac{1}{2}+y, -z$	2·56	3·63	160·4	5·9	13·7
O(2) H(7)	$1-x, \frac{1}{2}+y, -z$	2·83	3·59	124·6	14·8	40·6
O(3) H(3)	$-x, \frac{1}{2}+y, -z$	2·79	3·45	119·7	15·6	44·6
O(3) H(4)	$-x, \frac{1}{2}+y, -z$	2·69	3·40	122·7	15·7	41·6

cordingly $\Delta\nu/\nu_s$ would be about 0·0005, very much smaller than the observed value of 0·016 (Pinchas, 1955). Thus the force between the oxygen and the hydrogen is obviously insufficient to explain the observed frequency shift.

Sutor (1962) has recently described a number of short *inter*molecular H · · · O contacts as being hydrogen bonds. In *o*-nitrobenzaldehyde five similar intermolecular contacts are found (Table 5, Fig. 3). For the sample consisting of these five contacts and the five 'bonds' listed by Sutor we can calculate the correlation between H · · · O distance and C–H · · · O angle, as was done for O–H · · · O bonds by Hamilton (1962). We find the correlation coefficient to be −0·74, probably significantly different from zero. One should, however, be careful in interpreting this as evidence for the existence of C–H · · · O hydrogen bonds, since the values for the C–H · · · O angle are scattered between 102° and 173°, whereas the O–H · · · O angles listed by Hamilton tend to be close to 180°. When the C–H · · · O angle becomes small, shielding effects of other parts of the molecule become significant. They may prevent a close approach between the hydrogen and the oxygen atoms, thus producing a similar correlation.

It is also striking that most of the compounds listed by Sutor have a large number of hydrogen atoms, only a few of which participate in so-called hydrogen bonds. 1,3,7,9-Tetramethyluric acid, for example, has twelve hydrogen atoms and four oxygen atoms, all lying on the periphery of the molecule, while only one short C–H · · · O contact was observed. It is difficult to understand why these other atoms do not participate if such a hydrogen bond exists. We therefore prefer not to classify the intermolecular C–H · · · O contacts in *o*-nitrobenzaldehyde as hydrogen bonds.

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