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The Crystal Structure of Alloxan

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The crystal structure of anhydrous alloxan, $C_4O_4N_2H_2$, has been determined because it was expected that the molecular packing would be such as to lead to a close intermolecular approach between a carbon atom and a carbonyl oxygen, similar to that previously observed in parabanic acid (Davies & Blum, 1955), chloranil (Chu, Jeffrey & Sakurai, 1962) and anhydrous barbituric acid (Bolton, 1963).

A complete analysis with three-dimensional photographic data has been carried out. Least-squares refinement of coordinate and anisotropic temperature parameters has reduced the R index to 9·3%.

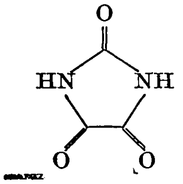
The molecule is in the 2,4,5,6-tetraoxo form; it has implied twofold symmetry and is planar within the limits of the analysis.

A remarkable feature of the intermolecular arrangement is the complete absence of hydrogen bonding. There is however a close carbon–oxygen interaction of length 2·79 Å in a similar orientation to those referred to. This links each molecule to four others in a closely packed array consistent with the comparatively high density of the crystals.

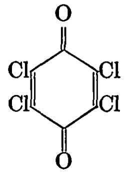
It is considered that this fourth example establishes the close $C=O\cdots C$ approach as a new structural feature in some way connected with the strong dipolar nature of the carbonyl group and only to be expected in certain compounds.

Introduction

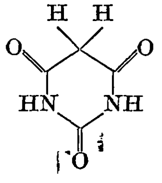
The results of some recent crystal structure determinations, *viz.* parabanic acid (I) (Davies & Blum, 1955), chloranil (II) (Chu, Jeffrey & Sakurai, 1962) and anhydrous barbituric acid (III) (Bolton, 1963) have revealed intermolecular contacts of as short as 2·77 Å between carbonyl oxygen atoms and ring carbon atoms. This is significantly less than the sum of the van der Walls radii (Pauling, 1960) of 3·1 Å. In all three structures the interaction is such that the σ bond direction of the C=O group is approximately collinear with the polar axis of the π bond of the carbon atom on the adjacent molecule.



(I)



(II)



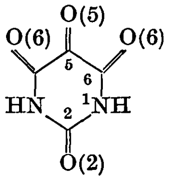
(III)

Although as a rule C=O groups are not generally associated with intermolecular separations less than the sum of the usual van der Waals radii, there are these three cases where it does occur. It is obviously desirable, therefore, to investigate this structural feature further if suitable examples can be discovered. By analogy with the molecules (I), (II) and (III), this would seem to be most likely in crystal structures with:

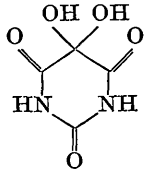
(*a*) Several carbonyl groups associated in a planar ring molecule.

(*b*) Insufficient protons for complete hydrogen bonding between the electronegative atoms in or attached to the ring.

Since alloxan (IV) satisfies these conditions its crystal structure was studied.



(IV)



(V)

Experimental

Anhydrous alloxan, 2,4,5,6-tetraoxopyrimidine (IV) is a comparatively rare substance. The common form is the (misnamed) alloxan monohydrate (V) which is really 5,5′-dihydroxybarbituric acid (Singh, 1960). Some of this was dried at 210 °C and 10 mmHg pressure and then sublimed slowly at 230 °C (Biltz, 1912) to give small lemon yellow crystals of anhydrous alloxan. These quickly decomposed to the monohydrate by reacting with water in the air, but it was possible to preserve them indefinitely with a thin coat of petrolatum. A notable property of these crystals was their very high relative density of 1·93 g.cm^{-3}.

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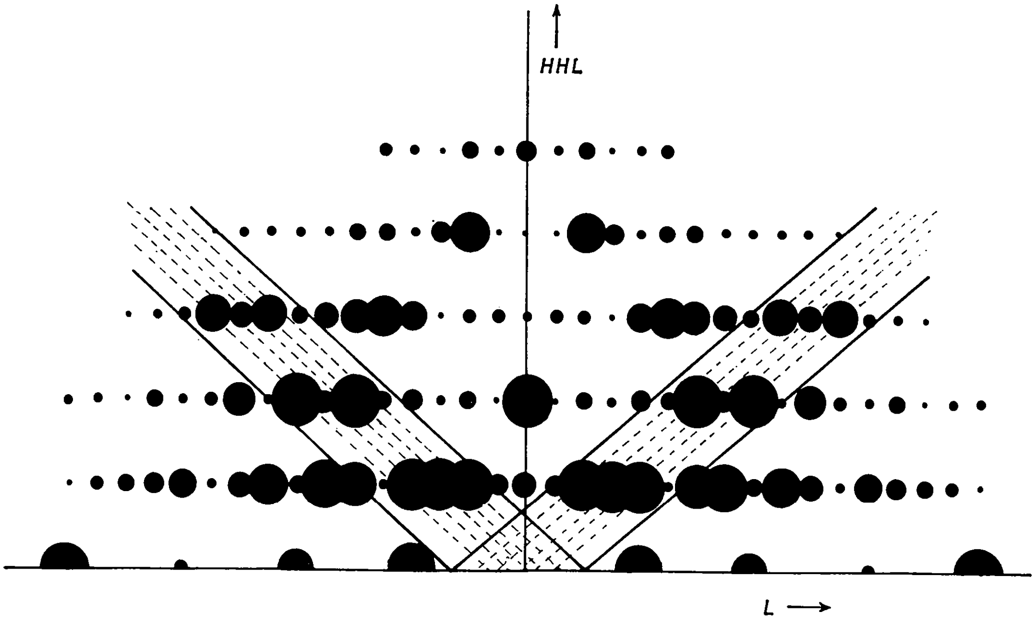

Fig. 1. A section of the weighted reciprocal lattice of alloxan through the points *hhl*. The molecular transform origin peak passes through the intense reflexions in the shaded area.

Preliminary X-ray photographs showed the crystals to be tetragonal with the non-centric space group $P4_12_12$ defined uniquely by the systematic absences $(00l)$ for $l \neq 4n$ and $(h00)$ for $h \neq 2n$. The unit cell dimensions measured from normal-beam Weissenberg photographs calibrated with sodium chloride are:

$a = 5{\cdot}886 \pm 0{\cdot}007$ Å $\quad D_x = 1{\cdot}934$ g.cm^{-3}
$c = 14{\cdot}100 \pm 0{\cdot}015 \quad Z = 4$.

The intensities were eye-estimated from multiple-film Weissenberg photographs taken with Cu $K\alpha$ radiation. These were reduced to relative structure amplitudes with an IBM 7070 program by Hall (1962), and then put on a common scale by internal correlation. No correction was made for the small absorption errors.

Out of a possible 360 independent reflexions, 346 were recorded and of these 23 were too weak to measure.

The structure determination

With four molecules in the unit cell the molecular symmetry is 2 and the O(2)C(2)C(5)O(5) axis of the molecule is at $x = y$; $z = 0$. Therefore, with a planar molecule of the expected configuration (IV), only the position of its centre along $x = y$; $z = 0$, and the angle between its plane and (001) were required in principle to solve the structure.

Preliminary attempts to find these two parameters by packing the molecules into a consistent hydrogen-bonded system, within the space group limitations, were unsuccessful. In fact it was soon realized that, unlike all related pyrimidine structures, the structure was not hydrogen bonded.

The inclination of the molecular plane was deduced from the orientation of the Fourier transform origin peak (Stadler, Bolton & Maitland, 1964), found by inspection, on the weighted reciprocal lattice. Fig. 1 shows a section containing the points *hhl*, through which the origin peak is constrained to pass by the space group symmetry. It is identifiable as the high scattering on a straight line through the origin.

With a molecule in the inclination derived from this, the very weak 600 reflexion was found to lie in the middle of a very high peak (a benzene peak) of the transform. Consequently the fringe function at 600 was almost zero. By combination of Fourier transforms of the molecules in a unit cell (Taylor & Morley, 1959; Bolton, 1963), it was easily shown that this was $\cos 2\pi . 6X_c$; X_c being the x coordinate of the centre of the pyrimidine ring. Only one of the resulting values of X_c from $\cos 2\pi . 6X_c = 0$ gave reasonable packing.

A three-dimensional structure factor calculation with the molecule in this position gave an agreement index of 0·355 for the 250 lowest order reflexions. Slight movements of the whole molecule reduced this to 0·294. After refinement by differential syntheses with an IBM 7070 program by Shiono (1962) R was 0·139 for all observed reflexions. Further refinement was carried out by least squares, using the weighting scheme of Hughes (1941) and anisotropic tempera-

Table 1. *Observed and calculated structure factors*

	H	L	F_o	F_c
	0	4	285	342
	0	8	215	253
	0	12	70	71
	0	16	269	296
	1	1	217	233
	1	2	262	310
	1	3	226	222
	1	4	321	367
	1	5	309	336
	1	6	213	206
*	1	7	7	21
	1	8	110	125
	1	9	32	24
	1	10	156	153
	1	11	90	96
*	1	12	10	1
	1	13	100	80
	1	14	29	35
	1	15	69	53
	1	16	52	53
	1	17	72	68
	2	0	350	393
	2	1	314	304
	2	2	170	160
	2	3	235	248
	2	4	263	279
	2	5	182	190
	2	6	216	209
	2	7	266	306
	2	8	146	137
	2	9	124	110
	2	10	108	112
	2	11	65	63
	2	12	80	81
	2	13	82	82
	2	14	58	56
	2	15	46	49
	2	16	44	28
	2	17	45	43
	3	1	180	176
	3	2	77	60
	3	3	72	65
	3	4	94	88
	3	5	148	126
*	3	6	9	8
	3	7	120	121
	3	8	57	48
	3	9	56	49
	3	10	21	21
	3	11	18	12
	3	12	31	38
	3	13	28	31
	3	14	72	66
*	3	15	8	9
	3	16	55	50
	4	0	40	34
	4	1	44	40
	4	2	68	72
	4	3	25	17
	4	4	23	22
	4	5	61	53
	4	6	87	90
	4	7	114	104
	4	8	167	183
*	4	9	10	1
	4	10	62	42
	4	11	78	83
	4	12	33	32
*	4	13	8	9
*	4	14	8	9
*	5	1	10	13
	5	2	67	78
	5	3	108	103
*	5	4	10	8
	5	5	29	1
	5	6	120	121
	5	7	86	85
	5	8	37	25
	5	9	88	93
	5	10	41	47
	5	11	35	42
	5	12	22	22
	5	13	36	34
*	6	0	8	13
	6	1	188	213
	6	2	156	157
	6	3	82	85
*	6	4	8	17
	6	5	75	56
	6	6	41	41
	6	7	53	59
*	6	8	8	14
	6	9	37	25
	6	10	40	37
	7	1	49	34
*	7	2	8	13
	7	3	21	17
	7	4	88	94
	7	5	68	70
	7	6	43	43
	K = 1			
	1	0	120	105
	1	1	116	105
	1	2	505	434
	1	3	565	565
	1	4	838	749
	1	5	27	23
	1	6	242	242
	1	7	273	273
	1	8	76	67
	1	9	229	245
	1	10	120	126
	1	11	29	29
	1	12	157	150
	1	13	114	113
	1	14	92	95
	1	15	70	70
	1	16	23	22
	2	0	112	110
	2	1	267	266
	2	2	190	160
	2	3	303	272
	2	4	83	67
	2	5	150	148
	2	6	48	33
	2	7	54	56
	2	8	112	105
	2	9	334	38
	2	10	41	37
	2	11	100	84
	2	12	116	121
	2	13	64	59
	2	14	43	47
	2	15	52	53
	2	16	47	44
	3	0	138	131
	3	1	178	182
	3	2	154	142
	3	3	317	310
	3	4	187	187
	3	5	31	28
	3	6	39	42
	3	7	36	43
	3	8	68	70
	3	9	36	27
	3	10	37	33
	3	11	61	52
	3	12	78	75
	3	13	86	90
	3	14	30	30
	3	15	46	44
	4	0	31	20
	4	1	133	141
	4	2	27	22
	4	3	148	158
	4	4	75	65
	4	5	45	41
	4	6	87	80
	4	7	37	21
	4	8	54	50
	4	9	25	25
	4	10	82	76
	4	11	33	23
	4	12	93	78
	4	13	69	72
	4	14	27	28
	4	15	35	33
	5	0	58	55
	5	1	173	191
	5	2	113	112
	5	3	137	149
	5	4	61	59
	5	5	94	95
	5	6	39	40
	5	7	55	60
	5	8	45	40
	5	9	35	25
	5	10	38	42
	5	11	74	69
	5	12	21	32
	5	13	31	30
	6	0	51	52
	6	1	86	81
	6	2	64	52
	6	3	97	92
	6	4	69	65
	6	5	59	60
	6	6	56	58
*	6	7	10	14
*	6	8	10	15
	6	9	29	22
	6	10	21	23
	7	0	31	33
	7	1	27	21
	7	2	50	40
	7	3	86	87
	7	4	61	65
	7	5	44	49
	7	6	69	85
	K = 2			
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	2	2	73	52
	2	3	17	7
	2	4	97	90
	2	5	94	77
	2	6	306	307
	2	7	118	105
	2	8	329	338
	2	9	27	6
	2	10	191	198
	2	11	70	72
	2	12	45	41
	2	13	86	83
	2	14	23	8
	2	15	32	29
	2	16	35	42
	3	0	265	250
	3	1	164	137
	3	2	128	128
	3	3	100	99
	3	4	94	78
	3	5	130	138
	3	6	58	41
	3	7	165	164
	3	8	133	132
	3	9	146	145
	3	10	14	13
	3	11	48	46
	3	12	39	31
	3	13	14	15
	3	14	53	49
	3	15	33	35
	4	0	23	23
	4	1	182	175
	4	2	29	27
	4	3	134	120
	4	4	179	183
	4	5	133	134
	4	6	102	98
	4	7	153	156
	4	8	35	37
	4	9	107	91
	4	10	51	50
	4	11	27	24
	4	12	106	110
	4	13	68	76
	4	14	17	14
	5	0	53	42
	5	1	79	78
	5	2	102	100
	5	3	107	105
	5	4	70	67
	5	5	25	16
	5	6	56	43
	5	7	29	25
	5	8	45	46
	5	9	36	33
*	5	10	8	7
*	5	11	8	7
	5	12	31	38
*	6	0	10	14
	6	1	42	38
	6	2	82	76
	6	3	46	48
	6	4	57	49
	6	5	35	33
	6	6	104	103
*	6	7	7	7
	6	8	90	87
	6	9	23	20
	7	0	61	59
	7	1	36	41
	7	2	40	39
	7	3	15	18
	K = 3			
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	3	1	59	42
	3	2	64	76
	3	3	19	5
	3	4	154	169
	3	5	237	232
	3	6	169	159
	3	7	121	114
	3	8	91	101
	3	9	178	184
	3	10	138	148
	3	11	169	204
	3	12	61	81
	3	13	32	47
	3	14	19	16
	4	0	21	18
	4	1	84	91
	4	2	34	24
	4	3	83	66
	4	4	21	12
	4	5	94	94
	4	6	136	128
	4	7	124	120
	4	8	65	51
	4	9	94	94
	4	10	104	101
	4	11	56	63
	4	12	10	9
	4	13	32	35
	5	0	108	92
	5	1	23	28
	5	2	94	84
	5	3	18	17
	5	4	90	80
	5	5	97	110
	5	6	82	66
	5	7	55	53
	5	8	48	41
	5	9	31	33
	5	10	59	61
	5	11	66	81
	6	0	10	13
	6	1	31	27
	6	2	21	23
	6	3	27	35
	6	4	37	43
	6	5	19	23
	6	6	35	43
	6	7	30	41
	K = 4			
*	4	0	9	6
*	4	1	9	10
	4	2	219	243
	4	3	99	86
	4	4	26	9
	4	5	86	79
	4	6	79	73
	4	7	26	13
	4	8	21	2
	4	9	28	27
	4	10	36	31
	4	11	23	24
	5	0	79	87
	5	1	76	79
	5	2	55	42
	5	3	33	37
	5	4	27	18
	5	5	47	43
	5	6	39	32
	5	7	26	19
	5	8	31	22
	5	9	24	20
*	6	0	8	6
	6	1	33	27
	6	2	21	16
	6	3	36	25
	6	4	17	21
	6	5	27	33
	K = 5			
	5	0	98	130
	5	1	46	29
	5	2	73	89
*	5	3	8	6
	5	4	33	40
	5	5	49	49

ture factors, with Cruickshank's program for the Ferranti Pegasus computer.

The final residual for all 323 observed reflexions with C, O and N atoms was 0·102. With the imino hydrogen atoms, coplanar with the molecule at 1·0 Å from N, included in the calculation this was 0·092. Inclusion of the 23 reflexions too weak to measure at half the local threshold value gave $R=0{\cdot}093$. Results from the final structure factor calculation, multiplied by 10, are shown in Table 1. Reflexions too weak to measure are marked with an asterisk.

Table 2 shows the final atomic coordinates and anisotropic temperature parameters. The mean estimated standard deviations are $\sigma(x)=\sigma(y)=\sigma(z)=$

Table 2. *Atomic coordinates and anisotropic thermal parameters* (Å^2)

	x	y	z
C(2)	−0·0475	−0·0475	0
C(5)	0·2969	0·2969	0
C(6)	0·3153	0·0895	−0·0639
N	0·1430	−0·0646	−0·0576
O(2)	−0·1939	−0·1939	0
O(5)	0·4394	0·4394	0
O(6)	0·4793	0·0646	−0·1149
H	0·163	−0·199	−0·098

	B_{11}	B_{22}	B_{33}	B_{12}	B_{23}	B_{13}
C(2)	1·41	1·41	2·91	0·32	0·27	−0·27
C(5)	2·00	2·00	1·58	−0·79	0·18	−0·18
C(6)	1·92	2·29	1·11	−0·65	1·02	0·00
N	2·22	1·12	2·05	−0·08	−0·71	−1·04
O(2)	2·87	2·87	5·40	−0·54	−0·71	0·71
O(2)	3·65	3·65	3·37	−1·32	−0·57	0·57
O(6)	2·20	3·54	2·47	−0·65	−0·21	1·28

0·005 Å. The temperature parameters e.s.d.'s are $\sigma(B_{jj})=0{\cdot}18$ Å^2 and $\sigma(B_{ij})=0{\cdot}28$ Å^2.

Discussion of the structure

The alloxan molecule

The dimensions of the alloxan molecule are shown in Fig. 2. The bond length e.s.d.'s are 0·007 Å. The molecule has twofold rotational symmetry and is almost planar. The least-squares equation to the molecular plane is:

$$0{\cdot}4850x-0{\cdot}4850y+0{\cdot}7276z=0\,.$$

N(1), C(6) and O(6) are −0·002 Å, +0·011 Å and −0·005 Å from this, respectively.

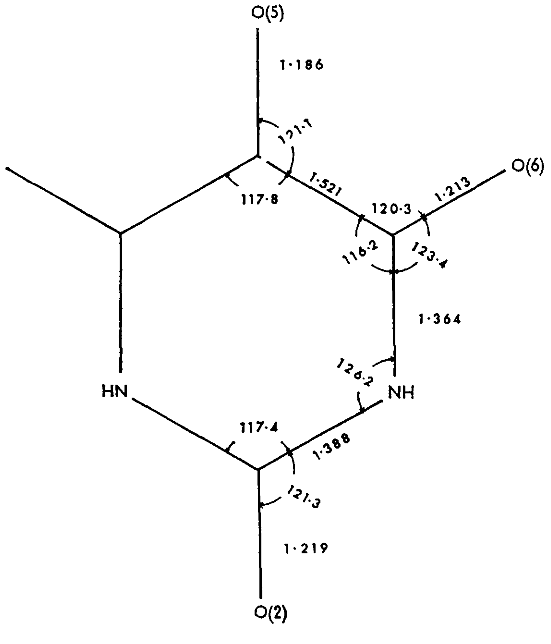

Fig. 2. Dimensions of the alloxan molecule.

The bond lengths are consistent with the 2,4,5,6-tetraoxopyrimidine formula (IV) and there are no significant differences between these and the mean dimensions of the barbituric acid (2,4,6-trioxopyrimidine) molecule (Jeffrey, Ghose & Warwicker, 1961; Bolton, 1963).

The intermolecular structure

The intermolecular distances less than 3·80 Å are shown in Table 3 and Fig. 3. The closest (N)H · · · O approaches are 2·38 Å and 2·47 Å to O(2) and O(6) with corresponding N(H) · · · O distances and NHO angles of 3·21 Å 3·22 Å and 144° and 131° respectively. Although the H · · · O(2) and H · · · O(6) distances are less than the sum of the van der Waals radii of about

Table 3. *Intermolecular approaches less than* 3·80 Å

Atoms				Distance
C(2)	III	O(5)	X	3·58 Å
C(2)	I	O(6)	IX	3·29
C(2)	III	O(6)	X	3·43
C(2)	III	O(6)	XII	3·60
C(2)	III	H	XII	3·12
C(5)	III	N	I	3·74
C(5)	III	O(6)	X	2·79
C(5)	I	H	VIII	3·37
C(6)	IV	O(2)	XIII	3·51
C(6)	IV	O(5)	XIV	3·44
C(6)	III	O(6)	X	2·97
C(6)	V	O(6)	XIV	3·01
C(6)	V	H	XIII	3·36
N	IV	O(2)	XIII	3·21
N	I	O(5)	X	3·45
N	IV	O(5)	XIV	3·06
N	II	O(6)	X	3·64
N	III	O(6)	X	3·22
N	V	O(6)	XIV	3·28
N	V	H	XII	3·62
N	V	H	XV	3·41
O(2)	I	O(5)	XII	3·05
O(2)	I	O(6)	IX	2·94
O(2)	III	O(6)	XII	3·07
O(2)	III	H	XII	2·38
O(5)	III	O(6)	I	3·70
O(5)	III	O(6)	X	3·31
O(5)	V	O(6)	XI	3·72
O(5)	I	H	VIII	3·01
O(5)	III	H	I	2·94
O(6)	III	O(6)	X	3·57
O(6)	V	O(6)	XI	3·68
O(6)	II	H	VII	3·60
O(6)	V	H	XIII	2·47
H	V	H	XIII	3·10

I	x, y, z
II	$y, x, \bar{z}$
III	$\frac{1}{2}-y,\ \frac{1}{2}+x,\ \frac{1}{4}+z$
IV	$\frac{1}{2}+y,\ \frac{1}{2}-x,\ \frac{3}{4}+z$
V	$\frac{1}{2}+x,\ \frac{1}{2}-y,\ \frac{3}{4}-z$
VII	$1+x, y, z$
VIII	$x, 1+y, z$
IX	$-1+x, y, z$
X	$x, -1+y, z$
XI	$x, y, -1+z$
XII	$-1+x, -1+y, z$
XIII	$x, -1+y, -1+z$
XIV	$-1+x, y, -1+z$
XV	$-1+x, -1+y, -1+z$

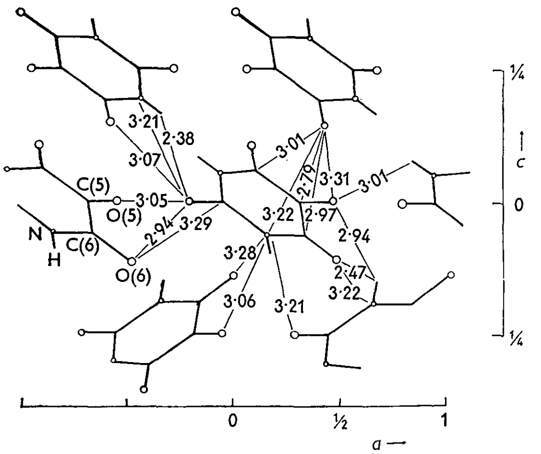

Fig. 3. Closest intermolecular approaches in the structure of anhydrous alloxan.

2·6 Å (Pauling, 1960), they are considerably longer than a (N)H · · · O hydrogen bond distance of about 1·7 Å (*i.e.* with N–H = 1·0 Å and N(H) · · · O = 2·80 Å (Pauling, 1960)). This, together with the non-collinearity of the nitrogen, hydrogen and oxygen atoms, excludes the possibility of hydrogen bonding between N and O(2) or O(6). The remaining oxygen atom, O(5), although it approaches within 3·06 Å of a nitrogen atom, is too far from the hydrogen at 2·94 Å to be hydrogen bonded. In this structure, therefore, although there are four carbonyl and two imino groups per molecule there is no hydrogen bonding. This is remarkable in view of the numerous crystal structures of compounds containing –NH.CO– groups, so far reported, in which hydrogen bonding appears to be the dominant factor in the molecular arrangement.

There are two intermolecular carbon-oxygen approaches less than the sum of the van der Waals radii of 3·10 (Pauling, 1960). These are C(6) · · · O(6) at 2·97 Å, and C(5) · · · O(6) at the very short distance of 2·79 Å. Both of these contacts involve carbonyl atoms only and are markedly similar in orientation to the ones mentioned in the introduction to this paper. Table 4 shows a comparison of the direction and length of C(6) · · · O(5) with these interactions.

One important difference in this structure is that C(5) is in close contact with two carbonyl oxygens* (Fig. 4.) whereas in the other structures there is one close approach per carbon atom. Each alloxan molecule takes part in C(5) · · · O(6) close approaches with four neighbours, forming a chain of interactions which links the molecules into a tightly packed three-dimensional array of interlocking spirals (Fig. 4).

Table 4. *Length and direction of intermolecular C · · · O interactions*

	Distance	e.s.d.	Angle C=O · · · C
Parabanic acid	2·77 Å	0·006 Å	157·4°
Chloranil	2·85	0·011	161·0
Barbituric acid	2·90	0·006	162·5
Alloxan	2·79	0·007	154·7

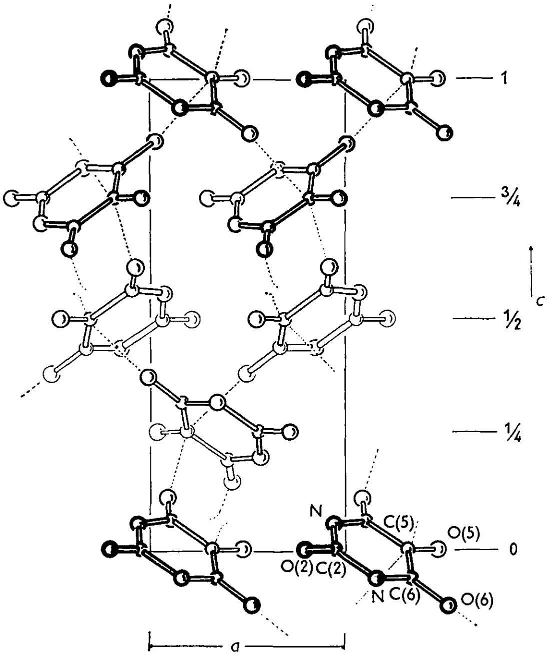

Fig. 4. The molecular arrangement in anhydrous alloxan. Dotted lines show how each C(5) has close approaches to two O(5) atoms in different molecules.

From the above results it seems, if other aspects of packing are ignored, that the force of interaction between carbonyl atoms in different molecules (implied by close approach) determines the molecular arrangement rather than possible hydrogen bonding.

The discovery of the same type of close approach in the same orientation in four crystal structures establishes it as a definite structural feature. It appears to be different from the charge-transfer interactions discussed by Hassel & Romming (1962) where the bond linking the donor atom to, for instance, a halogen atom is roughly in the orientation of the non-bonding electron pairs in the donor atom before charge-transfer bond formation. This would make the C=O · · · C angle 'tetrahedral', not the observed value of about 160° (Table 4). Nor does it have an obvious link with the polarization complexes discussed by Wallwork (1961) in which the common factor is a plane-to-plane stacking of aromatic molecules with no abnormally close approaches.

As this interaction is observed only between atoms of carbonyl groups it is probably related in some way to the strongly dipolar nature of the C=O bond. This will be particularly strong in (I), (II), (III) and

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* An exactly analogous situation exists in triketoindane; this will be reported in the near future.

(IV) because of the inductive effects of the substituent electronegative atoms and hetero ring atoms. It is possible therefore that in these structures the stronger than usual attractive forces between $C^{\delta+}=O^{\delta-}$ dipoles are sufficiently powerful to influence the arrangement of molecules to bring carbonyl atoms closer together than London dispersion forces alone would allow. These forces would be dipole–dipole attraction (Keesom, 1921) and/or dipole-induced dipole attraction (Debye, 1920, 1921).

This suggestion agrees generally with the available observations. For instance the fact that the attraction of a $C^{\delta+}=O^{\delta-}$ dipole for a charge ($=C^{\delta+}$) is strongest along its axis will make the COC angle tend to 180 °C. This is about 160° in the reported cases. Also, on this basis the rather unusual arrangement in alloxan in which a ring carbon atom has close interactions with two oxygen atoms from opposite sides of the molecular plane (Fig. 4) is the expected result of the attraction of two $=O_6^{\delta-}$ for the same charge centre $=C_5^{\delta+}$. Perhaps the most puzzling thing about the close approach discussed here is that it has been observed in only four cases and not in compounds such as succinimide (Mason, 1956) and maleic anhydride (Marsh, Ubell & Wilcox, 1962) where there are non-hydrogen-bonded carbonyl groups. This is presumably because only in these four compounds is the $C^{\delta+}=O^{\delta-}$ dipole strong enough for interaction to occur.

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The Crystal Structure and Molecular Statics of Trindan, $C_{15}H_{18}$

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The crystal structure of trindan (tristrimethylenebenzene, $C_{15}H_{18}$) has been determined from three-dimensional X-ray data. The crystals are monoclinic, space group $P2_1/c$ (C_{2h}^5) with

$$a=12\cdot67,\ b=5\cdot87,\ c=16\cdot92\ \text{Å};\ \beta=111°\ 41'.$$

The principle conclusions are that there is no significant alternation of bond lengths in the benzene ring, and the molecule is not completely coplanar. The static configuration of the molecule was computed from two different sets of force constants. The results indicate a preference for one of two sets of force constants for benzene.

Introduction

Over thirty years ago Mills & Nixon (1930) reported an interesting phenomenon involving the benzene ring. They observed that, by fusing saturated hydrocarbon rings of different sizes onto a benzene ring, it was possible in some cases to produce chemical behavior indicative (in their interpretation) of the double bonds being fixed in one of the two Kekulé structures. In the case of 5-hydroxyhydrindene (I) for example, the

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