

formation of the ester group. The analysis of ethyl benenate is being carried out three-dimensionally to place the structural evidence on a firm crystallographic basis.

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A Refinement of the Structure of Formamidoxime

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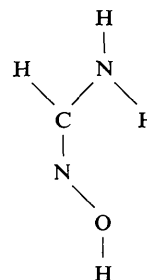
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The structure of formamidoxime has been further refined and hydrogen atoms located. The molecule has the amidoxime configuration predicted for it, but the bond lengths indicate a substantial contribution from the hydroxyamidine form.

Introduction

The crystal structure of the compound which might variously be described as formamidoxime, $\text{NH}_2\text{-CH}=\text{N-OH}$ (I), or hydroxyformamidine, $\text{NH}=\text{CH-NH-OH}$ (II), has previously been determined (Hall & Llewellyn, 1956), and the bond lengths shown to be intermediate between those expected for the two alternative formulae. Refinement was not, however, taken to the point where hydrogen atoms could be definitely located, and the detailed interpretation of the molecule and of the structure was equivocal. It has since been argued (Donohue, 1956) that the geometry of the intermolecular hydrogen bond system in the structure is such that the oxime nitrogen atom must be an acceptor in both of the bonds in which it is involved, and thus it cannot have a hydrogen attached to it. The infrared spectrum (Orville-Thomas & Parsons, 1958) demonstrates that in solution the molecule may be represented $\text{NH}_2\cdots\text{CH}\cdots\text{N-OH}$, or, in valence-bond terms, as a hybrid between (I) and $\text{N}^+\text{H}_2=\text{CH-N-OH}$ (III). The similarity of the appropriate region of the spectrum to that of formamide demonstrated that the atoms comprising $\text{NH}_2\text{-CH}=\text{N-}$ are coplanar, and it was further argued that the molecule is entirely planar with configuration



The infrared spectrum of crystalline formamidoxime supports the same general interpretation, although hydrogen bond shifts nullify the argument concerning planarity. It was apparent that the full potential of the X-ray data had not been realized because of insufficient computing facilities then available, and opportunity has recently been taken to complete the refinement. The results are described in this paper.

Refinement

Formamidoxime is orthorhombic, $a=8.22$, $b=7.36$, $c=4.78$ Å, four molecules per unit cell, space group $P2_12_12_1$. The intensity data used were those of the previous study, *viz.* 396 reflexions, visually estimated from equi-inclination Weissenberg photographs about the three principal axes. The heavy-atom coordinates reported previously were the starting point. Structure factors were calculated, with the use of the scattering

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Table 1. Atom coordinates and standard deviations

Atom	x/a	$\sigma_x(\text{\AA}^\circ)$	y/b	$\sigma_y(\text{\AA}^\circ)$	z/c	$\sigma_z(\text{\AA}^\circ)$	$q_{\max}(\text{e.\AA}^{-3})$
C	0.2930	0.003	0.2944	0.004	0.2432	0.003	7.1
N(1)	0.4243	0.004	0.4001	0.004	0.2223	0.004	7.8
N(2)	0.2554	0.003	0.1603	0.004	0.0828	0.003	8.5
O	0.3778	0.003	0.1360	0.003	-0.1221	0.002	10.7
H(1)	0.473		0.467		0.370		0.37
H(2)	0.506		0.380		0.086		0.50
H(3)	0.215		0.310		0.386		0.43
H(4)	0.341		0.60		-0.214		0.27

curves of Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955), and parameters refined by the differential synthesis procedure. Individual isotropic temperature factors were assumed for two cycles, and anisotropic temperature factors for a further three cycles. A three-dimensional difference Fourier synthesis then showed the four hydrogen atoms clearly, in positions corresponding to the formamidoxime molecule (I). The hydrogen atom coordinates were taken from the difference plot, using Booth's (1948) procedure. They were included in subsequent structure factor calculations, with an isotropic temperature factor of 1.0 \AA^2 , but were not refined. Several of the larger observed amplitudes were apparently affected by extinction, and had been excluded from the refinement. On inclusion of the hydrogen atoms it became apparent that extinction was more troublesome than had been realized, and in all 14 terms were omitted from the final cycles. Three further differential synthesis cycles completed the refinement, when the reliability index was 0.079.

The final atomic coordinates, with standard deviations (Cruickshank, 1949, 1950) are listed in Table 1,

thermal parameters in Table 2, observed and calculated structure factors in Table 3. The bond lengths and bond angles are shown in Fig. 1. The mean plane

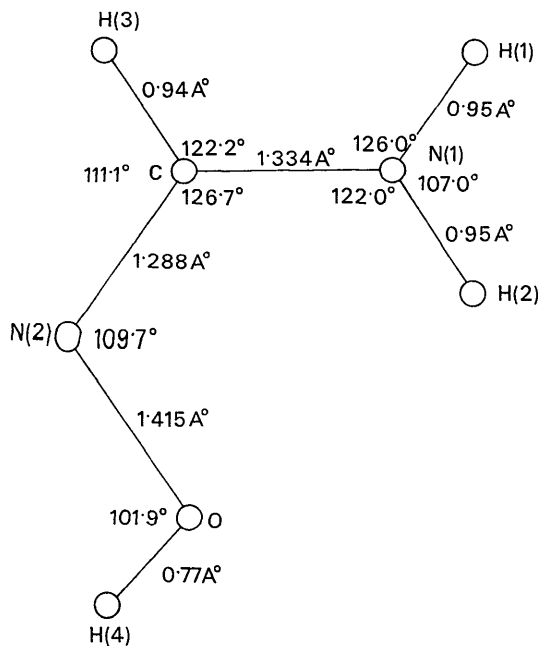


Fig. 1. Bond lengths and angles.

through the molecule, calculated by the procedure of Schomaker, Waser, Marsh & Bergman (1959), is $0.898X - 1.124Y + 1.112Z = 1$ with coordinates in \AA . Individual atom displacements from this plane are listed in Table 4.

Table 2. Anisotropic thermal parameters

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{23}	B_{31}
C	3.043	3.842	3.181	-0.436	0.119	0.322
N(2)	3.914	4.609	4.041	1.283	0.993	0.297
N(2)	2.940	4.830	3.333	-0.356	-0.082	0.196
O	3.055	4.381	2.835	-0.589	-0.629	0.235

The hydrogen atoms are situated in the molecule as for an amidoxime formula, as predicted by Donohue (1956) and in agreement with the interpretation of the infrared spectrum (Orville-Thomas & Parsons, 1958). The heavy-atom bond lengths differ slightly from those of the previous X-ray study, but still demonstrate considerable delocalization of the carbon-nitrogen bonds, again in conformity with the spectral evidence.

The results of various X-ray and neutron diffraction studies which have been made of oxime molecules have recently been summarized by Hamilton (1961). The observed lengths of the C=N bond (C-N(2) in this structure) vary from 1.225 to 1.29 \AA , and of the N-O bond from 1.32–1.39 \AA . The accuracy of these different studies varies somewhat, but in general the molecules may be described in terms of the structure $>C=N-OH$ with $>C-N=O^+H$ as a minor contributor. Such description would require a smaller value for the standard carbon-nitrogen double-bond length than has frequently been accepted (e.g. 1.265 \AA , Pauling (1940); 1.28 \AA , Cox & Jeffrey (1951)), and the value 1.24 \AA suggested by Vaughan & Donohue (1952) appears suitable. On the basis of this and the generally accepted 1.475 \AA for the single-bond length, the bond order-bond length relationship given by Pauling leads to the description of C-N(1) and C-N(2) as possessing 35 and 60% double-bond character respectively. The molecule may then be satisfactorily described in terms of the canonicals (I) and (III), with (I) predominating. The observed N-O bond is long for an oxime molecule, and the contribution of structures such as $NH_2-CH-N=O^+H$ must be small.

This description of the formamidoxime molecule is similar to that given for formamide (Ladell & Post, 1954); in both instances it is necessary to invoke a substantial contributor such as (III) to explain the observed value for the C-NH₂ bond. It is, however, more difficult to reconcile these results with those from

Table 3. Observed and calculated structure factors ($\times 10$)

Terms marked with * were assumed to be suffering from extinction. Terms marked ' unobserved, and the value listed as F_o is half the maximum value which would have escaped observation.

hkl	F_o	F_c	hkl	F_o	F_c	hkl	F_o	F_c	hkl	F_o	F_c
002	152*	183	190	23	22	380	19	22	631	18	16
004	18	25	191	19	20	381	17	17	632	39	35
006	46	46	200	166*	127	382	10	15	633	59	59
011	228*	325	201	181*	214	390	9	8	634	20	20
012	85	92	202	39	36	391	1	6	640	53	60
013	87	84	203	109	103	400	7	3	641	45	43
014	45	44	204	10	2	401	7	4	642	14	16
015	28	26	205	12	13	402	43	40	650	28	26
016	2	2	206	20	25	403	12	13	651	35	36
020	155*	176	210	255*	380	404	33	33	652	19	17
021	272*	357	211	223*	271	405	8	11	660	3	4
022	19	17	212	132	127	410	10	18	661	10	13
023	77	74	213	8	8	411	70	67	662	31	30
024	16	8	214	26	20	412	113	123	670	6	7
025	7	7	215	20	16	413	46	42	671	24	26
026	16	18	216	16	13	414	22	19	672	16	14
031	108	114	220	190*	227	415	3	3	701	103	110
032	28	35	221	100	101	420	85	79	702	5	2
033	55	53	222	160	167	421	121	128	703	28	27
034	39	37	223	61	64	422	33	32	704	13	11
035*	3	7	224	24	22	423	94	89	710	57	54
040	217	236	225	11	13	424	15	17	711	20	22
041*	3	3	230	150	169	425	9	11	712	50	44
042	12	3	231	117	129	430	109	113	713	32	27
043	40	41	232	100	96	431	40	37	714	28	22
044	42	42	233	22	18	432	136	133	720	74	78
045*	2	3	234	39	39	433	39	35	721	65	65
051	105	100	240	24	26	434	43	41	722	47	49
052	66	65	241	98	99	435	5	6	723	18	16
053	23	22	242	66	65	440	54	55	724	15	15
054*	3	4	243	77	79	441	10	9	730	80	78
055	31	33	244	29	30	450*	4	7	732	21	20
060	41	33	245	13	16	451	77	72	733	26	25
061	14	7	250	59	56	452	17	17	734	17	17
062	36	35	251	59	59	460	35	32	740	12	15
063	31	30	252	10	11	461	45	42	741	38	38
064	24	27	253	10	11	462	12	13	742	14	17
071*	4	3	254	31	33	470	32	29	750*	4	8
072	8	7	255	10	11	471	25	24	751*	4	7
073	12	10	260	67	61	472	36	36	752	16	18
074*	1	2	261	34	56	480	27	20	760*	3	1
080	11	7	262	38	35	481	12	13	761	15	17
081	32	30	263	20	21	482	4	4	762	7	9
082	15	8	264*	3	4	501	69	78	770	19	22
083	12	14	270	26	24	502	128	126	771	5	8
091	12	11	271	23	21	503	32	33	800	43	42
092*	1	13	272	16	15	504	18	12	801	20	21
101	109*	132	273	24	28	505*	2	1	802	49	52
102	10	5	274	4	8	510	61	62	803	14	14
103	122	124	280	21	25	511	124	127	804	45	48
104	24	22	281	17	17	512	86	80	810	49	45
105	37	39	282	10	12	513	45	36	811	56	52
106	23	27	283	8	8	514	11	10	812	28	25
110	98*	123	290*	2	3	515	21	19	813	18	17
111	183*	224	291	11	12	520	48	51	814	11	12
112	116	122	301	52	56	521	75	74	820	14	9
113	45	45	302	173	169	522	35	31	821	17	15*
114	64	65	303	77	77	523	52	53	822	17	16
115	60	61	304	58	58	524	29	26	823	17	18
116	19	19	305	28	31	525	19	19	830	12	10
120	28	35	310	92	91	530	8	10	831	21	20
121	206*	240	311	138	149	531	61	63	832	9	5
122	106	104	312	71	69	532	48	49	833	17	16
123	34	34	313	102	95	533	25	23	840	35	35
124	76	72	314	32	29	534	20	20	841	11	11
125	47	50	315	12	12	535	4	7	842	12	15
126	8	8	320	129	144	540	59	65	850*	3	1
130	112*	128	321	65	68	541	17	25	851	27	30
131	70	76	322	56	55	542	92	78	852	10	11
132	115	114	323	42	39	550	38	36	860	28	29
133	25	26	324	46	47	551	36	41	861	6	9
134	77	77	325	19	20	552	15	37	901*	3	5
135	15	15	330	7	5	560*	4	9	902	9	4
140	55	62	331	95	103	561	36	28	903	15	14
141	86	82	332	61	60	562	32	36	910	30	48
142	24	24	333	89	87	570*	3	2	911	12	14
143	51	56	334*	4	8	571	8	10	912	12	33
144	12	16	335	25	26	572	7	5	913	36	29
145	20	25	340	20	22	580*	2	1	920	33	32
150	32	37	341	75	76	581	9	8	921	36	35
151	12	14	342	79	75	600	117	127	922	10	9
152	45	44	343	25	25	601	43	44	923	12	16
153	21	17	344	40	40	602	11	8	930	50	52
154	9	9	345	20	22	603	24	15	931	20	18
160	25	22	350	42	45	604	8	2	932	1*	12
161	50	47	351	55	55	605	16	19	940*	2	4
162	16	13	352	84	79	610	12	9	941	21	25
163	16	16	353	56	53	611	56	55	942	7	10
164	32	30	354	40	40	612	54	49	950*	1	3
170	77	74	360	62	60	613	51	44	1000*	2	2
171	27	23	361	13	16	614	60	54	1001	20	21
172	13	16	362	53	46	615	16	16	1002	17	23
173	23	25	363	10	9	620	12	7	1010	23	22
174	8	9	364	6	3	621	20	21	1011	16	12
180	29	27	370	4	4	622	67	66	1012	8	12
181	27	22	371	36	36	623	51	49	1020*	1	2
182	21	21	372	9	9	624	12	14	1021	17	19
183	29	14	373	12	16	630	53	48	1030	4	4

Table 4. Atom displacements from mean molecular plane

Atom	Displacement
C	0.006 Å
N(1)	-0.003
N(2)	-0.005
O	0.003
H(1)	0.322
H(2)	0.022
H(3)	0.036
H(4)	-0.070

a recent microwave study of formaldoxime (Levine, 1963) in which C=N and N-O bonds of length 1.276 and 1.408 Å respectively were reported. These are not greatly different from the corresponding bonds in formamidoxime, although no contributor such as (III) is here possible. It would appear that for carbon-nitrogen bonds possessing considerable double-bond character, the variation of bond length with bond order may be less than is often supposed.

A point of general similarity between formamidoxime, formaldoxime and other oximes previously studied (other than those involved in coordination compounds) is the value of the C=N-O bond angle, which varies between 109.7 and 112°. This is considerably smaller than the angle commonly observed about a carbon atom involved in a double bond (*e.g.* 126.7° for N(1)-C-N(2) in this structure), and these observations support the suggestion (Gillespie & Nyholm, 1957) that repulsions involving lone pair electrons are dominant factors controlling bond angles.

As previously discussed (Hall & Llewellyn, 1956) there are three close intermolecular approaches, which form spirals, parallel to *c*, of molecular interactions. These are the principal cohesive forces within the crystal and were assumed to be hydrogen bonds. They are detailed in Table 5, whence it may be seen that there is indeed a hydrogen atom associated with each and that the systems X-H...X' are not far from linear. The packing of molecules is such that for the shortest hydrogen bond [O-H...N(2)] the acceptor atom is coplanar with the molecule, but the two acceptors for the weaker hydrogen bonds from N(1) are substantially displaced, both in the same direction, from this plane. The displacement of atom H(1) from the molecular plane is presumably a consequence of this.

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Table 5. Intermolecular hydrogen bond dimensions (Å)

Bond X—H...X'	X—X'	X—H	H—X'	Displacement of H from line X—X'	Displacement of X' from molecular plane
O—H(4)...N(2)	2.82	0.77	2.05	0.07	-0.05
N(1)—H(1)...O	3.05	0.94	2.12	0.16	0.90
N(1)—H(2)...N(2)	3.12	0.95	2.23	0.26	0.73

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The Crystal and Molecular Structure of [3.3]Paracyclophane*

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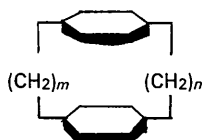
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[3.3]Paracyclophane ($C_{18}H_{20}$) forms monoclinic crystals with $a_0=9.715$, $b_0=8.138$, $c_0=8.524$ Å, $\beta=90.69^\circ$, and two molecules in the unit cell in space group $P2_1/n$. The structure has been refined by full-matrix least-squares methods, and the final parameters include small corrections for molecular libration. The aromatic rings are deformed slightly into a symmetrical boat form, the bending being about 6° at each end; the α -carbons are bent further, by an average of nearly 4° . The two rings do not lie directly above one another, being displaced about 0.5 Å from such an arrangement. The bond angles in the side chain are slightly larger than the normal values, and the dihedral angles are also slightly greater than those in n-butane. All bond distances are consistent with those found in other hydrocarbons. There are no short non-bonded intermolecular contacts, and the shortest intramolecular ones are only slightly less than the sum of the van der Waals radii, and thus are consistent with the comparatively small observed distortion of the molecule. The distribution of the strain energy in this and similar molecules is discussed.

Introduction

Cram, Allinger & Steinberg (1954) interpreted the ultraviolet absorption spectra of some paracyclophanes,



in terms of (1) trans-annular π -electron interactions between the two benzene rings, and (2) distortion of

the benzene rings from their normal planar configurations. Further evidence for the first of these effects was reported by Cram & Bauer (1959) in their study of the molecular complexes of the paracyclophanes with tetracyanoethylene (TCNE), and significant out-of-plane distortions of the aromatic rings have been found in [2.2]paracyclophane ($m=n=2$) (Brown, 1953a; Lonsdale, Milledge & Rao, 1960; Bekoe & Trueblood, 1964) and in the corresponding diolefin (Coulter & Trueblood, 1963). Similar distortions are observed in the related compounds [2.2]metacyclophane (Brown, 1953b) and 4,12-dimethyl[2.2]metacyclophane (Hanson, 1962). The molecule studied in the present analysis, [3.3]paracyclophane, is of interest not only because, among all the paracyclophanes, it forms the strongest molecular complex with TCNE, but also because it possesses most of the sorts of strains and distortions of the four above-mentioned hydrocarbons,

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