Crystal and Molecular Structure of *NN*-Dimethylacetamidoxime

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The crystal and molecular structure of the title compound, has been determined by a Fourier transform method from 665 unique *X*-ray diffraction intensities measured on a diffractometer, and refined by a least-squares procedure to *R* 4·5%. Crystals are triclinic, space group $P\bar{1}$, with cell parameters: a = 6·069(5), b = 7·582(5), c = 7·364(5) Å, α = 84·97(5)°, β = 79·66(5)°, γ = 114·16(5)°, Z = 2. The molecules are associated in pairs through a hydrogen bond between the hydroxy-group of one molecule and the oxime nitrogen of a neighbouring species. The hydroxy-moiety is *syn* (*i.e. cis*) to the methyl group.

In general, oximes (R^1R^2NOH) exhibit geometrical isomerism and two compounds can be isolated, one with OH *cis* and one with OH *trans* to R. However, it appears that when R is dialkylamino only one of the two isomers can be isolated. From dipole-moment studies, Exner[1] concluded that the isolable isomer of *NN*-diethylbenzamidoxime is the *syn*-form with OH *trans* to the benzo-group. However, consideration of the steric factors operating in such a system suggests that the *anti*-species should be considerably more stable than the *syn*-form. In order to obtain further data we have determined the structure of *NN*-dimethylacetamidoxime.

EXPERIMENTAL

Crystals from heptane were irregularly shaped. Cell dimensions were obtained from a least-squares fit to θ, $-\theta$ values measured for 30 reflections on a Nonius three-circle diffractometer.

Crystal Data.—$C_5H_{10}N_2O$, M = 114·08. Triclinic, a = 6·069(5), b = 7·582(5), c = 7·364(5) Å, α = 84·97(5), β = 79·66(5), γ = 114·16(5)°, U = 299 Å^3, Z = 2, D_c = 1·35 g cm^{-3}. Space group $P\bar{1}$. Mo-K_α radiation, λ = 0·7107 Å; μ(Mo-K_α) = 8·96 cm^{-1}.

An approximately cubic crystal (sides *ca.* 0·5 mm) was mounted on a Nonius automatic three-circle diffractometer, equipped with a scintillation counter and a pulse-height discriminator, with $[\bar{1}10]$ coincident with the ϕ axis of the diffractometer. Data were obtained with Zr-filtered Mo-K radiation using a θ—2θ scan. Zr Attenuation filters were used for strong reflections. The background on each side of the scan was measured for half the scan time. 665 Unique reflections had intensities significantly above background in the range $0 \leqslant \theta \leqslant 25°$ ($\sin\theta/\lambda \leqslant 0{\cdot}595$). After every 50 reflections a control reflection was measured as a check on crystal and electronic stability. No systematic variation of its intensity was observed.

The usual Lorentz and polarization factors were applied and structure amplitudes were obtained on a common arbitrary scale. The standard deviation, σ, of the net intensity observed, I, was derived from: $\sigma(I) = \{C + B_1 + B_2 + (0{\cdot}05 \times I^2)\}^{\frac{1}{2}}$, where C is the total integrated count, B_1 and B_2 are the backgrounds and $I = C - B_1 - B_2$. We further applied: $\sigma(I)/(2I) = \sigma(F_o)/F_o$, in which F_o is the structure amplitude.

Solution and Refinement of the Structure.—The three-dimensional Patterson function indicated that the structure contained more or less planar molecules lying roughly parallel with (110). The region around the Patterson origin showed a system of vector peaks (at *ca.* 1·5 Å) at 60° intervals. This is consistent with six possible orientations of each of the two possible stereoisomers. The location of the molecule within the cell was therefore determined by finding the minimum R as a function of molecular translation for all twelve possible models.

A program was written to calculate the structure factors for a molecular shift Δx with the aid of the expression:

$$F_c(h, \Delta x) = A_h \cos(2\pi\, h \cdot \Delta x) + B_h \sin(2\pi\, h \cdot \Delta x),$$

where $A_h = \sum_i f_i \cos 2\pi h x_i$, and $B_h = -\sum_i f_i \sin 2\pi h x_i$, x_i being the relative fractional co-ordinates of the atom i with respect to a common arbitrary origin. The coefficients A_h and B_h can be set up in a preliminary step, from whence R can be evaluated quite rapidly as a function of Δx.

Only the 50 strongest reflections with $\sin\theta/\lambda \leqslant 0{\cdot}287$ Å^{-1} were included in the calculation, and only one of the twelve models tested gave a reasonable R factor (22%). The next closest minimum R factor was 33%; the remaining ten models had $R \geq 45\%$.

The successful model was then refined by full-matrix least-squares techniques with isotropic temperature factors. The function minimized was $\Sigma w(F_o - F_c)^2$, R' being defined as: $[\Sigma w(|F_o| - |F_c|)^2/\Sigma w(|F_o|)^2]^{\frac{1}{2}}$ with $w = 1/\sigma(F_o)$. This refinement converged at R 19·6%, R' 26·5%, for all data. Refinement was continued with anisotropic vibration parameters. This reduced R to 9·1% and R' to 12·6%.

A difference-Fourier synthesis at this juncture using only data with $\sin\theta/\lambda \leqslant 0{\cdot}35$ Å^{-1} showed peaks of *ca.* 0·2 eÅ^{-3} in the regions where hydrogen atoms were expected. The hydroxy-hydrogen was clearly indicated, but the density at the methyl groups was rather confused. To clarify the methyl regions, we calculated a second difference-Fourier map with contributions from freely rotating methyl groups included in F_c. This map clearly showed the locations of all the methyl hydrogen atoms.

In the next two cycles the hydrogen atoms positions were refined, but their temperature factors were kept fixed; R was then 5·3% and R' 6·9%. In subsequent cycles the positional parameters and isotropic temperature factors for the hydrogen atoms were refined by using half shifts; the co-ordinates and an anisotropic temperature factor were refined for the non-hydrogen atoms. The refinement converged at a final R of 4·5%, with R' 5·5%.

Final atomic parameters are listed in Table 1 and the final calculated structure amplitudes together with the observed ones in Supplementary Publication No. SUP 20775 (2 pp.).*

For the refinement and the Fourier maps we used Ibers'

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index issue.

[1] O. Exner, *Coll. Czech. Chem. Comm.*, 1965, **30**, 652.

TABLE 1

Atomic co-ordinates and isotropic temperature factors, with estimated standard deviations in parentheses

Atom	*X*	*Y*	*Z*	*B*/Å^2
C(1)	0·2180(3)	0·2577(3)	0·1054(3)	*
C(2)	0·3253(6)	0·1621(4)	−0·0300(4)	*
C(3)	0·3992(8)	0·1578(7)	0·3436(7)	*
C(4)	0·1435(9)	0·3354(7)	0·4145(5)	*
N(1)	0·2288(4)	0·2282(3)	0·2888(3)	*
N(2)	0·1089(3)	0·3637(2)	0·0628(2)	*
O(ant)	0·0884(4)	0·3691(3)	−0·1278(2)	*
H(2A)	0·293(8)	0·184(6)	−0·146(7)	9·6(11)
H(2B)	0·261(6)	0·016(6)	0·019(4)	7·3(8)
H(2C)	0·505(6)	0·208(4)	−0·049(4)	5·8(7)
H(3A)	0·563(12)	0·261(8)	0·325(7)	13·6(17)
H(3B)	0·346(6)	0·114(6)	0·462(7)	7·7(10)
H(3C)	0·383(8)	0·047(7)	0·291(6)	9·5(13)
H(4A)	0·000(7)	0·332(5)	0·410(5)	7·4(10)
H(4B)	0·127(6)	0·288(5)	0·539(6)	8·1(9)
H(4C)	0·236(7)	0·470(7)	0·387(5)	8·1(11)
H(O)	0·019(5)	0·455(4)	−0·144(3)	4·6(6)

* These atoms were refined with anisotropic temperature factors. The form of the anisotropic thermal ellipsoid is given by: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$, with parameters ($\times 10^4$):

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	444(8)	254(5)	281(5)	187(5)	−101(5)	−54(4)
C(2)	647(14)	388(8)	370(8)	337(9)	−106(8)	−106(6)
C(3)	777(17)	549(13)	448(11)	411(13)	−254(11)	−21(10)
C(4)	961(19)	550(13)	271(7)	467(14)	−199(9)	−114(7)
N(1)	696(9)	431(6)	306(5)	380(6)	−197(5)	− 84(4)
N(2)	606(8)	304(5)	229(4)	280(5)	−130(4)	−67(3)
O(ant)	1004(10)	466(5)	264(4)	494(6)	−213(5)	−113(3)

version of ORFLS[2] and Zalkin's[3] Fourier program, respectively. Neutral atomic scattering factors from ref. 4 were employed throughout the refinement.

DESCRIPTION OF THE STRUCTURE AND DISCUSSION

A view of the molecule, showing the atomic numbering scheme, is given in Figure 1.

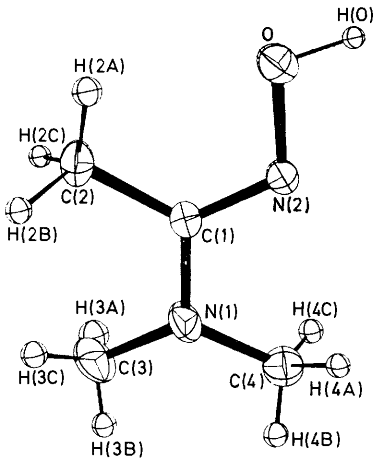

FIGURE 1 A drawing of the molecule showing the atom numbering scheme used. Non-hydrogen atom vibration ellipsoids are at 15, and hydrogen atom ones at 3% probability levels

A projection of the structure down [100] is shown in Figure 2. (Both were drawn with the aid of Johnson's ORTEP program[5]). The molecules are associated in centrosymmetric dimers *via* hydrogen bonds between the hydroxy-hydrogen of one molecule and the lone-electron-pair of the oxime nitrogen in the next.

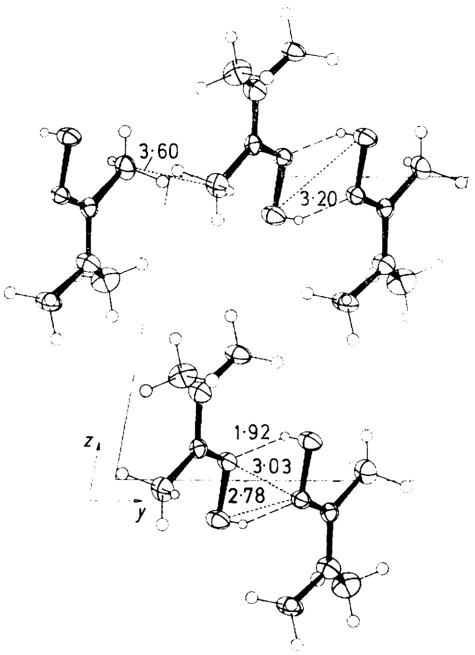

FIGURE 2 Unit cell contents projected down [100], showing the hydrogen bonding scheme and shortest intermolecular distances

TABLE 2

Bond lengths and angles, with estimated standard deviations in parentheses

(*a*) Bond lengths (Å)

C(1)–C(2)	1·491(3)	N(1)–C(3)	1·443(3)
C(1)–N(1)	1·367(3)	N(1)–C(4)	1·445(4)
C(1)–N(2)	1·284(2)	N(2)–O(ant)	1·430(2)
C(2)–H(2A)	0·92(5)	C(3)–H(3A)	0·96(6)
C(2)–H(2B)	1·01(4)	C(3)–H(3B)	0·86(5)
C(2)–H(2C)	0·98(3)	C(3)–H(3C)	0·93(5)
C(4)–H(4A)	0·87(4)	O–H(O)	0·92
C(4)–H(4B)	0·93(4)		
C(4)–H(4C)	0·92(4)	C–H (mean)	0·93

(*b*) Bond angles (°)

C(2)–C(1)–N(1)	118·8(2)	C(1)–N(1)–C(3)	121·3(3)
C(2)–C(1)–N(2)	124·3(2)	C(1)–N(1)–C(4)	118·1(2)
N(1)–C(1)–N(2)	116·8(2)	C(3)–N(1)–C(4)	116·5(3)
C(1)–N(2)–O(*anti*)	111·8(2)	N(2)–O(*anti*)–H(O)	104(2)
C(1)–C(2)–H(2A)	110(3)	N(1)–C(4)–H(4A)	115(2)
C(1)–C(2)–H(2B)	111(2)	N(1)–C(4)–H(4B)	112(2)
C(1)–C(2)–H(2C)	114(2)	N(1)–C(4)–H(4C)	114(2)
N(1)–C(3)–H(3A)	112(3)	H(2A)–C(2)–H(2B)	111(3)
N(1)–C(3)–H(3B)	106(3)	H(2A)–C(2)–H(2C)	108(3)
N(1)–C(3)–H(3C)	109(3)	H(2B)–C(2)–H(2C)	102(2)
H(3A)–C(3)–H(3B)	106(4)	H(4A)–C(4)–H(4B)	105(3)
H(3A)–C(3)–H(3C)	118(4)	H(4A)–C(4)–H(4C)	98(3)
H(3B)–C(3)–H(3C)	104(4)	H(4B)–C(4)–H(4C)	110(3)

The hydrogen bridge N · · · H–O distance is 2·778(2) Å, which compares well with the corresponding distances of 2·825(6) and of 2·784 Å in the structures

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[2] W. R. Busing, K. O. Martin, and H. A. Levy, ORFLS, Oak Ridge National Laboratory Report, ORNL TM 305.

[3] A. Zalkin, FORDAP, a Fortran Program for Crystallographic Fourier Synthesis, personal communication, 1962.

[4] 'International Tables for *X*-Ray Crystallography,' vol. III, 1962, Kynoch Press, Birmingham.

[5] C. K. Johnson, ORTEP, Oak Ridge National Laboratory, Report ORNL 3794.

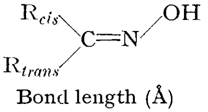
of *syn-p*-chlorobenzaldoxime[6,7] and of α-*p*-dimethylaminobenzaldoxime,[8] where a similar hydrogen bonding scheme occurs.

Bond distances and angles are listed in Table 2, together with their estimated standard deviations computed by ORFFE.[9] A comparison of selected bond lengths and angles in the title compound with those in some related compounds is given in Table 3.

It is evident from a study of previous reports on oximes that the molecular geometry of these compounds is largely governed by non-bonded interactions between the oxygen atom and the groups *cis* to oxygen. We find that *NN*-dimethylacetamidoxime occurs in the *syn*-configuration (*syn* and *anti* are conventionally used with respect to the least complex group attached to the oxime carbon), or, in other words, the hydroxy is *trans* to the *NN*-dimethyl group. In this configuration non-bonded interactions with the methyl groups are smallest and the molecular parameters compare well with those observed in other oximes where non-bonded interactions are also small (see Table 3). In particular we find the C(1)–N(2)–O angle [111·8(2)°] to be in good agreement with the corresponding angles in *syn-p*-chlorobenzaldoxime[6,7] [110·8(5)°], α-*p*-dimethylaminobenzaldoxime[8] [112·1(3)*], acetoxime[10] (111°), and formamidoxime[11] [109·5(6)°]. This contrasts with the values of 118 and 125·2(5)° found in *anti-p*-chlorobenzaldoxime[7] and in *anti-N*-methyl-*p*-chlorobenzaldoxime,[6] respectively, where non-bonded interactions force the oxygen atom away from the adjacent group, thus opening the C–N–O angle.

TABLE 3

C=N and N–O bond lengths and C=N–O and R–C=N angles in some related oximes



Compound	Bond length (Å)		Bond angles (°)		
	C=N	N–O	C=N–O	R_{cis}–C=N	R_{trans}–C=N
Acetoxime[a]	1·29(3)	1·36(3)	111	131	113
Formamidoxime[b]	1·301(10)	1·414(9)	109·5(6)	127·3(7)	
syn-p-Chlorobenzaldoxime[c,d]	1·260(8)	1·408(7)	110·8(4)		120·8(5)
anti-p-Chlorobenzaldoxime[d]	1·26	1·39	118	130	
N-Methyl-*p*-chlorobenzaldoxime[c]	1·309(7)	1·284(6)[e]	125·2(5)	124·7(5)	
α-*p*-Dimethylaminobenzaldoxime[f]	1·264(5)	1·420(4)	112·1(3)		121·5(4)
NN-Dimethylacetamidoxime[g]	1·284(2)	1·430(2)	111·8(2)	124·3(2)	116·8(2)

[a] Ref. 10. [b] Ref. 11. [c] Ref. 6. [d] Ref. 7. [e] Not comparable with other values since this is for $\overset{+}{N}=\overset{-}{O}$ double bond. Ref. 8. [g] Present work.

We can now suggest a reason why attempts to prepare the *anti*-isomer of *NN*-dimethylacetamidoxime have not been successful. If the relative positions of all other atoms are assumed to remain the same as for the *syn*-isomer, placing the oxygen in the *anti*-position with the angle C(1)–N(2)–O 112° would result in a C(4)–O distance of 1·95 Å. This very strong non-bonded interaction could be reduced not only by opening the N(1)–C(1)–N(2) and C(1)–N(2)–O angles, but also by rotating the NMe_2 group about the N(1)–C(1) bond. However, the stability of the molecule must be greatly influenced by the overlap between the orbital of the lone-electron-pair on N(1) and the π orbital of the double bond [C(1)–N(1)]. Rotation of the NMe_2 group by a considerable amount would reduce this interaction. Thus the *anti*-isomer would be expected to be far less stable than the *syn*.

Although we find that the NMe_2 group in the *syn*-form is not completely coplanar with the oxime group (see Table 4), the deviations from the plane through the oxime atoms do not suggest a significant rotation of the group about the N(1)–C(1) bond, but rather indicate that packing forces cause a slight bending of some of the bonds. This process requires far less energy than destroying the *N*-double-bond conjugation. Alternatively, there might be some sp^3 hybridization on N(1), as can be seen from the deviation [0·12(2) Å] of N(1) out of the plane of the carbon atoms surrounding it.

TABLE 4

Displacements (Å) of atoms from best least-squares plane through C(1), C(2), N(1), N(2), O

C(1) 0·02(2), C(2) 0·01(3), N(1) −0·03(2), N(2) 0·04(2), O −0·04(2), C(3) 0·29(2), C(4) 0·10(2)

In the similar case of *p*-chlorobenzaldoxime the *syn*-isomer[6,7] is almost planar, while the benzo-ring is reported to be inclined at 19° to the oxime plane in the *anti*-isomer.[7] So, in the *anti*-form the interaction between the π-electron system of the benzo-ring and that of the double bond should be fairly small. Nevertheless, in contrast to the *syn*- and *anti*-isomers of *NN*-dialkylketamidoximes, both isomers of *p*-chlorobenzaldoxime[6,7] are isolable and it may be concluded that decoupling of a benzo-ring from the double bond is far less serious, from the point of view of molecular

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* In ref. 8 the value for this angle is differently stated in the Table and in the Figure; the former is correct.

[6] K. Folting, W. N. Lipscomb, and B. Jerslev, *Acta Cryst.*, 1964, **17**, 1263.

[7] B. Jerslev, *Nature*, 1957, **180**, 1410.

[8] F. Bachechi and L. Zambonelli, *Acta Cryst.*, 1972, **B28**, 2489.

[9] W. R. Busing, K. O. Martin, and H. A. Levy, ORFFE, Oak Ridge National Laboratory, Report ORNL TM 306.

[10] T. K. Bierlein and E. C. Lingafelter, *Acta Cryst.*, 1951, **4**, 450.

[11] D. Hall and F. L. Llewellyn, *Acta Cryst.*, 1956, **9**, 108.

orbital energy, than the decoupling of an NR^1R^2 group.

This does not seem unreasonable considering that a decoupled benzo-group still retains a fully satisfied conjugated ring system, while decoupling of an NR^1R^2 group leaves an isolated lone-electron-pair on the nitrogen.

In this light, Exner's [1] conclusion that the isolable isomer of *NN*-diethylbenzamidoxime has its oxygen *cis* to the dialkylamino-group appears to be incorrect. This would allow the benzo-ring to remain in conjugation with the double bond at the expense of the amino-group. From the evidence we have presented, the reverse is to be expected.

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