Acta Cryst. (1981). B**37**, 1381–1387

Neutron Diffraction at 16 K and *ab initio* Molecular-Orbital Studies of the Structure of Formamide Oxime

BY G. A. JEFFREY AND J. R. RUBLE

Department of Crystallography, University of Pittsburgh, Pittsburgh, PA 15260, *USA*

R. K. MCMULLAN

Chemistry Department, Brookhaven National Laboratory, Upton, New York 11973, *USA*

AND D. J. DEFREES AND J. A. POPLE

Department of Chemistry, Carnegie–Mellon University, Pittsburgh, PA 15213, *USA*

(*Received* 15 *October* 1980; *accepted* 9 *January* 1981)

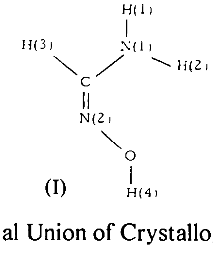
Abstract

The crystal structure of formamide oxime (*N*-hydroxymethaneimidamide), CH_4N_2O, has been refined using single-crystal neutron diffraction data measured at 16 K [$P2_12_12_1$, a = 8·187 (1), b = 7·111 (1), c = 4·7609 (7) Å; $R(F)$ = 0·017, $R(F^2)$ = 0·020, $wR(F)$ = 0·012, $wR(F^2)$ = 0·023 for 1230 reflections]. The non-hydrogen atoms are planar within 0·01 Å, but the C—NH_2 group is significantly non-planar. A segmented-body thermal-motion analysis gave a good fit with $\langle$r.m.s. $\Delta U_{ij}\rangle$ = 0·0003 Å^2 and $\sigma(U_{ij})$ = 0·0004 Å^2, for a model having two segments, CHNOH and NH_2. The r.m.s. torsion of the NH_2 group about the C—N bond was 5°. The observed and [corrected] bond lengths (Å) are: C—N 1·3447 (4) [1·351]; C=N 1·2959 (4) [1·299]; N—O 1·4283 (4) [1·435]; N—H 1·0120 (8) [1·026], 1·0162 (8) [1·032]; C—H 1·0899 (8) [1·101]; O—H 0·9906 (8) [1·002]. *Ab initio* molecular-orbital calculations were carried out for formamide oxime at the Hartree–Fock 3-21G level, and at 3-21G, 6-31G* and higher levels for the simpler related molecules methylamine, methanimine, hydroxylamine, and formaldehyde oxime. The observed *anti* isomer of formamide oxime was found to have the lowest theoretical energy with the 3-21G basis set, which predicted a completely planar molecule. The optimized bond lengths (Å) at the 3-21G level were C—N 1·353, C=N 1·269, N—O 1·469, N—H 0·993, 0·996, C—H 1·071, O—H 0·965. The most significant differences between experiment and theory are the non-planarity of the CNH_2 group and differences in the bond lengths of +0·030 (1) Å for C=N and −0·034 (1) Å for N—O, and in the *X*—H bonds which range from +0·030 (1) to +0·037 (1) Å. The higher-level calculations on hydroxylamine and formaldehyde oxime suggest that the N—O bond lengths in particular are very sensitive to choice of basis set and that there is some cancellation of errors at the 3-21G level. Inclusion of electron correlation increases the *X*—H bond lengths by about half the difference with the observed values.

Introduction

The crystal structure of formamide oxime, *N*-hydroxymethanimidamide, iso-uretin, $HON.CH.NH_2$, was determined by Hall & Llewellyn (1956) and refined by Hall (1965) using X-ray diffraction room-temperature data. This neutron diffraction refinement at 16 K has been carried out to provide more precise molecular structure data. These are compared with *ab initio* molecular-orbital calculations of the geometry, which refer to the isolated molecule at rest.

Formamide oxime is an inhibitor of DNA synthesis and an antitumor agent (Rosenkranz, Hjorth & Carr, 1971; Flora, Van't Reit & Wampler, 1978). In the crystals, the molecule is the *anti* isomer with respect to the C—N bond (*i.e.* HO and H *trans* in *R*HC=NOH), as shown in (I). The *anti–syn* isomerism found in more complex oximes (Kleinspehn, Jung & Studniarz, 1967; Hawkes, Herwig & Roberts, 1974) has never been observed for formamide oxime. Equilibrium between the tautomers $H_2N–CH=NOH \rightleftharpoons HN=CH–NH–OH$, in solution, has been considered (Brady, 1914).



(I)

0567-7408/81/071381-07$01.00

Experimental

Data collection and refinement

The data were collected at the Brookhaven High Flux Beam Reactor with a monochromated beam obtained by reflection from the (002) planes of beryllium. The neutron wavelength of 1·0442 (1) Å was determined by least-squares fit of diffractometer setting-angle data for 32 reflections of a standard KBr crystal [a_0 = 6·6000 (1) Å at room temperature]. Crystals of formamide oxime were obtained by slow evaporation of a methanol solution at room temperature. A specimen 3·0 × 1·7 × 1·5 mm, cut from a larger crystal, was mounted with [110] a few degrees off the φ axis of the diffractometer on an aluminum pin attached to the cold finger of a closed-cycle refrigerator* inside a helium-filled aluminum can. The crystal was cooled at approximately 1° $\min^{-1}$ to 15·0 ± 0·5 K. On preliminary cooling a small fragment cracked off the crystal. The remaining crystal weighed 0·00917 g and had a volume of 6·64 mm^3. It had nine natural faces [{110}, $\{1\underline{0}1\}$, {011}, $(1\bar{1}1)$] and two fracture faces [(100), $(00\bar{1})$]. Toward the end of data collection the temperature began to rise gradually to a final value of 15·75 K. Calibration of the platinum resistance thermometer was based on the observed magnetic transition of FeF_2 (78·4 K; Hutchings, Shulhof & Guggenheim, 1972).

The lattice parameters given in Table 1 were determined by least-squares fit to the $\sin^2\theta$ values for the 32 reflections with 47° < 2θ < 58°. Neutron integrated intensities were measured for two octants (h, k, $\pm l$) using a $\theta/2\theta$ step-scan method in which counts at each step were accumulated for a preset count of the direct beam (40 000; 2·25 s). Scans of $\Delta(2\theta)$ = 3·4° were used with $\sin\theta/\lambda \le 0{\cdot}44$ Å^{-1}; beyond this limit to 0·78 Å^{-1}, scans were computed from the expression $\Delta(2\theta) = (2{\cdot}859 + 2{\cdot}384\tan\theta)°$. The scattering from the aluminum pin and cryostat were examined over 5° ≤ 2θ ≤ 105° and found to be negligible. The integrated intensities and their standard deviations were evaluated from the scan profile data, as described by Craven & McMullan (1979). The intensities of two reflections, measured at intervals of 48 reflections throughout the data collection, showed no variation greater than 1%. Neutron absorption corrections were applied using an analytical procedure (de Meulenaer & Tompa, 1965; Templeton & Templeton, 1973). The linear absorption coefficient (μ = 228 m^{-1}) was calculated assuming the mean absorption coefficient for chemically bonded hydrogen to be 2·43 $\text{m}^2\ \text{kg}^{-1}$ at λ = 1·0442 Å (McMullan & Koetzle, 1980). The resulting transmission factors ranged from 0·68 to 0·74. The data for 553 symmetry-related reflections were averaged to give an agreement factor $\sum|\langle F^2\rangle - F^2|/\sum\langle F^2\rangle = 0{\cdot}011$. Of the 1249 reflections measured (675 independent), none had negative intensities.

Table 1. *Crystal data for formamide oxime*, CH_4N_2O

Space group $P2_12_12_1$; $Z = 4$.

	This work (16 K)	Hall & Llewellyn (1956) (298 K)
a	8·187 (1) Å	8·22 Å
b	7·111 (1)	7·36
c	4·7609 (7)	4·78
D_x	1·441 Mg m^{-3}	1·380 Mg m^{-3}
D_m		1·365

The atomic parameters reported by Hall (1965) were initially refined against the neutron data by differential synthesis. This refinement and an interatomic-distance calculation showed one hydrogen, H(4), to be incorrectly reported in the original paper. A subsequent structure factor calculation omitting H(4), followed by a difference Fourier synthesis, provided the correct hydrogen position.

Full-matrix least-squares refinement was carried out with a modified version of the computer program by Busing, Martin & Levy (1962). The quantity minimized was $\sum w\Delta^2$, where $w = 1/\sigma^2(F^2)$, with $\sigma(F^2) = [\sigma^2_{\text{counter}} + (0{\cdot}01F^2_{\text{obs}})^2 + (k/F^2_{\text{obs}})^2]^{1/2}$. The constant k = 17·56 was used to decrease the effect of weak reflections and was selected so that $F^2_{\text{obs}} = \sigma(F^2_{\text{obs}})$ for the space-group extinctions with the largest F^2_{obs} values. The neutron scattering lengths (fm) used were 6·6484 for C, 9·36 for N, 5·803 for O and −3·7409 for H (Koester, 1977). The final refinement using 1230 reflections included one scale factor, 24 positional parameters, 48 anisotropic temperature factors and 6 anisotropic extinction parameters for a type I crystal with Lorentzian distribution of mosaicity (Becker & Coppens, 1975). There were no changes greater than 0·01σ in any of the 79 parameters varied in the final refinement cycle. The agreement factors were $R(F)$ = 0·017, $R(F^2)$ = 0·020, $wR(F)$ = 0·012, $wR(F^2)$ = 0·023, and $S = [(\sum w\Delta^2)/(N_{\text{obs}} - N_{\text{param}})]^{1/2} = 1{\cdot}252$. The largest feature in the final difference map was 1·5 $\sigma(\rho)$, where $\sigma(\rho)$ = 0·06 fm Å^{-3} estimated from $\sigma(F^2)$ values. Extinction was significant; 34 reflections had correction factors between 0·80 and 0·58. The most severe correction ($0{\cdot}58F^2_{\text{calc}}$) was for the 210 reflection. The atomic parameters are given in Table 2.* The thermal-motion ellipsoids and atomic notation are shown in Fig. 1.

---

* Air Products and Chemicals Inc. Displex® Model CS-202.

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35999 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Final atomic parameters for formamide oxime at* 16 K

The fractional coordinates are $\times 10^5$ for non-hydrogen atoms, $\times 10^4$ for hydrogen atoms. Anisotropic temperature factors ($\text{Å}^2 \times 10^5$ for non-hydrogen atoms, $\times 10^4$ for hydrogen atoms) are referred to the crystal axes and correspond to the temperature-factor expression $T = \exp(-2\pi^2 \sum_i^3 \sum_j^3 h_i h_j a_i^* a_j^* U_{ij})$. Estimated standard deviations given in parentheses refer to the least significant digit.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C	29272 (4)	30014 (4)	24211 (6)	574 (10)	598 (11)	546 (10)	−53 (9)	53 (10)	−87 (9)
N(1)	42744 (3)	40782 (3)	22678 (5)	732 (9)	754 (9)	764 (9)	−206 (7)	50 (7)	−198 (7)
N(2)	25413 (3)	16429 (3)	7326 (4)	535 (8)	619 (8)	620 (7)	−130 (8)	34 (7)	−66 (7)
O	37906 (5)	13951 (5)	−13287 (7)	609 (12)	650 (14)	525 (12)	−97 (12)	69 (10)	−98 (10)
H(1)	4562 (1)	4932 (1)	3895 (2)	243 (4)	243 (4)	194 (3)	−67 (3)	−8 (3)	−103 (3)
H(2)	5197 (1)	3691 (1)	963 (2)	163 (3)	236 (3)	221 (3)	−19 (3)	71 (3)	−52 (3)
H(3)	2043 (1)	3301 (1)	4073 (2)	192 (3)	260 (4)	191 (3)	−26 (3)	88 (3)	−66 (3)
H(4)	3350 (1)	365 (1)	−2507 (2)	190 (3)	175 (3)	170 (3)	−31 (2)	3 (3)	−70 (3)

Anisotropic extinction parameters (g_{ii} rad^2) ($\times 10^8$): g_{11} 11·6 (5), g_{22} 7·3 (3), g_{33} 11·5 (6), g_{12} 2·9 (2), g_{13} 1·2 (3), g_{23} 0·4 (3).

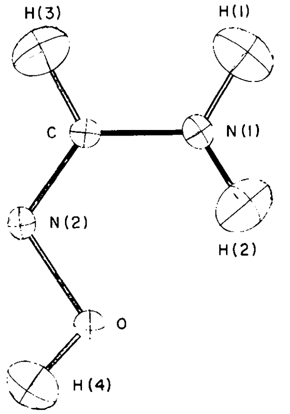


Fig. 1. Thermal ellipsoids at 90% probability (Johnson, 1976), and the atomic notation for formamide oxime at 16 K.

The thermal-motion analysis

With the four non-hydrogen atoms in a plane, the rigid-body analysis gives rise to a singularity. The segmented-body analysis method (Johnson, 1970) was therefore used. In this procedure, the non-torsional internal motions of the H atoms are first assumed or estimated from their thermal parameters. For this initial analysis, the eight atoms were grouped into four segments (the non-hydrogen atoms, the amide H atoms, the methylene H, and the hydroxyl H) with four flexible joints interconnecting the segments and the stationary lattice. The N—H r.m.s. stretch correction of 0·076 Å (Cyvin, 1968) was assumed. The NH_2 r.m.s. 'scissor' motion, in the molecular plane, was calculated to be 0·112 Å. For the methylene H, the C—H r.m.s. stretch correction (0·068 Å) and in-plane bending correction (0·115 Å) were the only significant terms. For the hydroxyl H, all three terms (r.m.s. stretch, 0·069 Å; in-plane bending, 0·103 Å; and out-of-plane bending, 0·090 Å) were significant. These internal motions were then subtracted from the r.m.s. displacements before fitting the segmented-body model.

The segmented model used had two segments CHNOH and NH_2 with two flexible joints, one between the two segments for determination of the NH_2 torsion, and one from the center of mass to the stationary lattice for determination of the rigid-body translation and libration of the CHNOH parent segment. The overall fit was good [$\langle \text{r.m.s. } U_{ij} - U_{ij_{SMB}} \rangle = 0{\cdot}0003$ Å^2 and $\sigma(U_{ij}) = 0{\cdot}0004$ Å^2]. The r.m.s. torsion of the NH_2 group about the C—N bond was 5°. With the internal torsion and H vibration motion subtracted, the rigid-body motion of the parent segment (NCHNOH) based on the inertial axes of the molecule was:

		I_1	I_2	I_3
T	0·071 Å	39·2°	51·4°	96·1°
	0·067	128·7	38·7	88·6
	0·007	84·3	87·3	6·3
ω	5·8°	0·9	89·3	90·6
	3·5	90·7	3·2	93·2
	1·6	89·5	86·8	3·2.

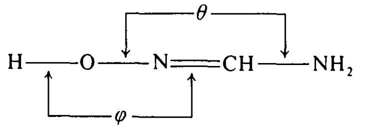
The translation motion is less than that measured in acetamide ($CH_3CO.NH_2$) by neutron diffraction at 23 K (Jeffrey, Ruble, McMullan, DeFrees, Binkley & Pople, 1980), but the libration amplitudes are larger.

The ab initio molecular-orbital calculations

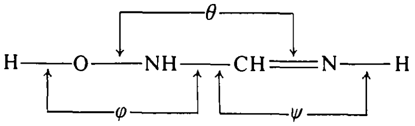
The potential-energy surface of formamide oxime was explored at the Hartree–Fock (HF) level of molecular-orbital theory using the STO-3G basis set (Hehre, Stewart & Pople, 1969) with subsequent refinement of the more stable structures with the 3-21G basis set (Binkley, Pople & Hehre, 1980). All calculations were performed with the *GAUSSIAN* 80 program on a VAX 11/780 computer (Binkley, Whiteside, Krishnan, Seeger, DeFrees, Schlegel, Topiol, Kahn & Pople, 1981). The HF/STO-3G energy was minimized with respect to all geometrical parameters for the four planar conformations of formamide oxime, (I)–(IV), and for one conformation of the proton tautomer (V). The resultant total and relative energies are shown in Table 3; the corresponding

Table 3. *Total theoretical energies (in hartrees) of some formamide oxime conformations with optimized geometry*

Relative energies in kJ mol^{-1} are given in parentheses. (1 hartree ≡ 4·35916 $\times 10^{-18}$ J.)

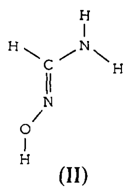


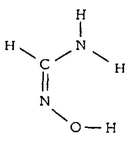
	θ (°)	φ (°)	HF/STO-3G	HF/3-21G
(I)	0	180	−220·97343 (0·0)	−222·63888 (0·0)
(II)	180	180	−220·97120 (5·9)	−222·63255 (16·8)
(III)	0	0	−220·95592 (46·2)	
(IV)	180	0	−220·96048 (34·0)	

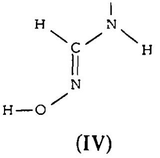


	θ (°)	φ (°)	ψ (°)	
(V)	0	0	180	−220·94599 (72·2)

geometrical parameters will be published elsewhere (Whiteside, Binkley, Krishnan, DeFrees, Schlegel & Pople, 1980). The optimized geometries of the two most stable conformers (at the HF/STO-3G level) were then obtained using the 3-21G basis set. The energies are given in Table 3; the molecular dimensions for the most stable conformer are given in Table 4. Computation of the complete second-derivative matrix (Pople, Krishnan, Schlegel & Binkley, 1979) of the HF/3-21G structure of (I) confirmed that it was a minimum on the full potential-energy surface.


(II)


(III)


(IV)

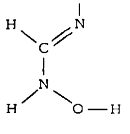

(V)

Table 4. *Experimental and theoretical molecular dimensions of formamide oxime*

Estimated standard deviations given in parentheses refer to the least significant figures. Thermal-motion corrections for the valence and torsion angles were insignificant.

	Experimental at 16 K		Theoretical
	Observed	Corrected	3-21G
Bond lengths (Å)			
C–N(1)	1·3447 (4)	1·351	1·353
C–N(2)	1·2959 (4)	1·299	1·269
N(2)–O	1·4283 (4)	1·435	1·469
N(1)–H(1)	1·0120 (8)	1·026	0·993
N(1)–H(2)	1·0162 (8)	1·032	0·996
C–H(3)	1·0899 (8)	1·101	1·071
O–H(4)	0·9906 (8)	1·002	0·965
Bond angles (°)			
N(1)–C–N(2)	126·21 (3)	126·15	127·0
C–N(2)–O	110·10 (3)	110·01	108·2
H(1)–N(1)–C	119·39 (6)	119·30	121·8
H(2)–N(1)–C	119·25 (5)	119·41	118·1
H(1)–N(1)–H(2)	117·24 (8)	117·15	120·1
N(1)–C–H(3)	118·22 (5)	118·39	116·9
N(2)–C–H(3)	115·54 (5)	115·44	116·2
N(2)–O–H(4)	102·69 (5)	102·58	103·0
Torsion angles (°)			
N(1)–C–N(2)–O	1·63 (4)		0*
H(1)–N(1)–C–N(2)	−168·49 (7)		180*
H(2)–N(1)–C–N(2)	−11·91 (8)		0*
H(1)–N(1)–C–H(3)	13·32 (9)		0*
H(2)–N(1)–C–H(3)	169·89 (8)		180*
H(3)–C–N(2)–O	179·86 (6)		180*
C–N(2)–O–H(4)	−178·41 (6)		180*

Displacements (Å) from non-hydrogen-atom least-squares plane

$A = 3{\cdot}892,\ B = -4{\cdot}568,\ C = 2{\cdot}862,\ D = 0{\cdot}452$

C	0·0085 (3)	H(1)	0·1847 (9)
N(1)	−0·0028 (2)	H(2)	0·1600 (9)
N(2)	−0·0042 (2)	H(3)	0·0002 (9)
O	0·0054 (4)	H(4)	−0·0325 (8)

* Fixed values.

To calibrate the HF/3-21G results, the structures of some smaller related compounds, for which gas-phase structures are known, were computed. The results are given in Table 5, along with structural parameters obtained with more sophisticated theoretical models. These are HF/6-31G*, Hartree–Fock with a split-valence plus polarization (*d*-functions on C, O, and N) basis (Hariharan & Pople, 1974), and MP2/6-31G* and MP3/6-31G* which take partial account of electron correlation by the Møller–Plesset perturbation theory (Møller & Plesset, 1934; Pople, Binkley & Seeger, 1976).

Discussion of the crystal structure results

The crystal strucutre is as described by Hall (1965), except for one of the hydrogen atoms, H(4), where there may have been a typographical error in reporting the *y* coordinate. The molecule is in the *anti* conformation and, with the exception of H(1) and H(2), is

Table 5. *Comparison of optimized bond lengths* (Å) *for some simpler related molecules using various approximations with spectroscopic data*

Bond	Molecule	HF/3-21G[a]	HF/6-31G*[a]	MP2/6-31G*[b]	MP3/6-31G*[c]	Spectroscopic[d]
C–H	Formaldehyde	1·083	1·092	1·104	1·104	1·116 ± 0·010
	Formaldehyde oxime	1·071	1·075	–	–	1·086 ± 0·010
N–H	Methylamine	1·004	1·001	1·018	1·018	1·010 ± 0·020
	Formamide	0·997	0·995	–	–	1·002 ± 0·010
O–H	Methanol	0·966	0·946	0·970	0·967	0·963 ± 0·010
	Formaldehyde oxime	0·967	0·947	–	–	0·956 ± 0·005
N–O	Hydroxylamine	1·469	1·403	1·453	1·444	1·453 ± 0·005
	Formaldehyde oxime	1·447	1·369	–	–	1·408 ± 0·005
C–N	Methylamine	1·472	1·453	1·465	1·466	1·471 ± 0·010
	Methanimine	1·256	1·250	1·282	1·275	1·273 ± 0·010
	Formaldehyde oxime	1·255	1·249	–	–	1·276 ± 0·005

(*a*) Whiteside, Binkley, Krishnan, DeFrees, Schlegel & Pople (1980). (*b*) DeFrees, Levi, Pollack, Hehre, Binkley & Pople (1979). (*c*) DeFrees (1980). (*d*) Harmony, Laurie, Kuczkowski, Schwendeman, Ramsay, Lovas, Lafferty & Maki (1979).

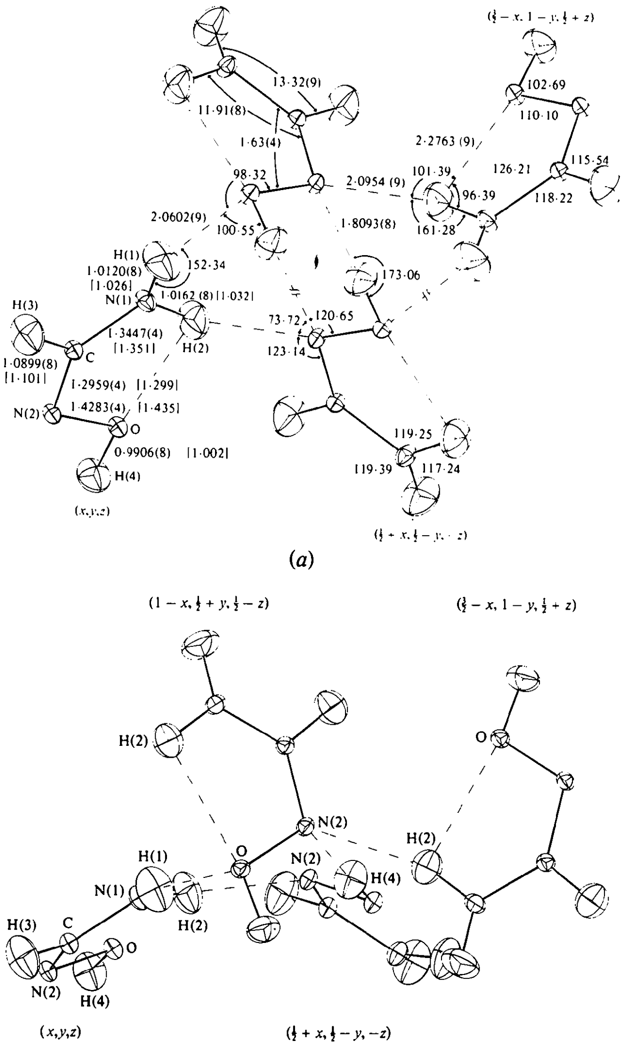


Fig. 2. Hydrogen bonding in the crystal structure of formamide oxime at 16 K. Thermal ellipsoids are at 70% probability. (*a*) View down **c**, (*b*) view approximately down [012].

close to planar, as shown in Table 4. The greatest deviation from the plane of the non-hydrogen atoms is +0·0085 (3) Å for the carbon. H(3) is exactly in the plane and H(4) is 0·033 (1) Å below the plane.

An interesting feature of the molecule is that the conformation of the C—NH_2 group is pyramidal. The angle between C—N(1) and the normal to the NH_2 plane is 109·86°, and H(1) and H(2) are +0·1847 (9) and +0·1603 (9) Å out of the non-hydrogen-atom plane. The N(1) atom is −0·1304 (2) Å out of the plane of C(1), H(1) and H(2). This was realized in the earlier X-ray analysis (Hall, 1965) but is contrary to the conclusions of Orville-Thomas & Parsons (1958) from the infrared spectra in solution.

The hydrogen-bond geometry is shown in Fig. 2. It consists of infinite chains which extend in the direction of one of the screw axes and involves all the NH_2 and OH hydrogen atoms. The shortest and most linear bonds are the O–H···N(2), 1·8093 (8) Å and 173·0 (5)°. As expected, the N—H···N bonds are longer, 2·0602 (9) and 2·0954 (9) Å. They are also less linear, 152·3 (5) and 161·3 (5)°. The intramolecular interaction NH(2)···O, which is a factor in the stabilization of the *anti* isomer in the isolated-molecule calculations, appears as the weaker component of a bifurcated interaction in the crystal structure.

In view of the non-planarity of the C—NH_2 group, it is notable that the atoms of the NH_2 group and those to which it is hydrogen bonded, *i.e.* O($1 - x, \frac{1}{2} + y, \frac{1}{2} - z$) and N(2) ($\frac{1}{2} + x, \frac{1}{2} - y, -z$), lie in one plane within 0·012 (1) Å and C is displaced 0·520 (1) Å out of that plane.

Comparison of experimental and theoretical results

The HF/3-21G calculations predict that the *anti* conformation of formamide oxime (I) is more stable than the *syn*, (II), by 16·8 kJ mol^{-1}. The other planar conformations (III) and (IV) are higher in energy, as shown in Table 3. This is consistent with the observation that only the *anti* conformation has been observed for this molecule. The additional stability must arise, at least in part, from the intramolecular N—H···O interaction, which persists as a weak bifurcated interaction in the crystal structure (see Fig. 2). This level of theory also predicts that the proton tautomer (V) lies 72·2 kJ mol^{-1} higher in energy than the preferred conformer (I), thereby making tautomerization very unlikely.

Theory does not reproduce the pyramidal conformation of the C—NH$_2$ group, but does predict that this degree of freedom is very flexible. Tilting the NH$_2$ plane by 20° with respect to the rest of the molecule results in an energy increase of only 3·4 kJ mol^{-1} at the HF/3-21G level. In view of the planarity of the NH$_2$ group and hydrogen-bond acceptor atoms described above, this difference between theory and experiment is possibly a crystal-field effect. However, it is known that this level of theory overemphasizes planar conformations of trivalent nitrogen. For example, the HF/3-21G H—N—H angle in ammonia is 112·4° (Binkley, Pople & Hehre, 1980), as compared with the experimental value of 106·7 ± 0·5° (Harmony, Laurie, Kuczkowski, Schwendeman, Ramsay, Lovas, Lafferty & Maki, 1979). We cannot therefore rule out the possibility that a higher-level calculation would result in a pyramidal C—NH$_2$ group for the isolated molecule.

The comparison of the thermally corrected experimental and the theoretical bond lengths in Table 4 shows some interesting features. For the C—NH$_2$ group, the observed and calculated C—N bond lengths agree within the experimental uncertainty, but the theoretical N—H are shorter than the observed by 0·033 (1) Å. This is in contrast to the structure of acetamide (Jeffrey, Ruble, McMullan, DeFrees, Binkley & Pople, 1980), where a similar difference between the theoretical and experimental N—H bond lengths was accompanied by a significant difference of 0·021 (1) Å in the C—N distances. This was attributed to the hydrogen bonding in the crystal. However, this cannot be the sole explanation for the discrepancy between theoretical and crystal C—NH$_2$ lengths in the case of acetamide, since the —NH$_2$ groups form strong intermolecular hydrogen bonds in the formamide oxime structure also. The results for methylamine shown in Table 5 suggest that the good agreement for C—N single-bond lengths at the HF/3-21G level may be due to a fortuitous cancellation of basis set and correlation errors, since higher-order approximations result in poorer agreement with the microwave value. More sophisticated theoretical models also result in longer predicted NH bonds in methylamine, but this goes only part way to explaining the difference between the theoretical and crystal structure NH lengths of formamide oxime.

The HF/3-21G N—O bond length is 0·034 Å longer than the corrected neutron diffraction value. Much of this difference can be ascribed to deficiencies in the theoretical model, since a similar discrepancy is seen in the N—O separation for formaldehyde oxime, for which theory at the MP2/6-31G* level predicts a value in good agreement with the microwave value. The formally double carbon—nitrogen distance is 0·030 Å smaller at the HF/3-21G level than the crystal structure value. Again, this is due to deficiencies in the level of theory used, since similar differences observed in C=N bond lengths in methanimine and formaldehyde oxime are removed by more sophisticated calculations (see Table 5). We have, therefore, no definite evidence from these results on formamide oxime for perturbation of the lengths of C=N and N—O bonds due to crystal-field forces in the structure.

The inclusion of electron correlation with the 6-31G* basis consistently increases the C—H, N—H and O—H bond lengths in the simpler molecules, relative to the HF/3-21G level. This partially reduces the discrepancy with the thermal-motion-corrected formamide oxime values. For the N—H and O—H, the longer bonds observed in the crystal structure could be the result of intermolecular hydrogen bonding in the crystalline state, since there is good evidence from neutron structural data that N—H and O—H bond lengths converge to values of 1·00 and 0·95 Å with very long hydrogen-bond lengths (Olovsson & Jönsson, 1976).

The agreement in the valence angles is within 2°, except for the H—N(1)—H angle, which reflects the pyramidal *versus* planar conformation of the C—NH$_2$ group discussed above. The asymmetry of the C—NH$_2$ valence angles, C—N(1)—H(2) < C—N(1)—H(1), in the isolated molecule, is presumably due to the intramolecular H(2)···O interaction. This is not observed in the crystalline state, where much stronger intermolecular hydrogen bonds are present.

The neutron diffraction analysis in this research was carried out at Brookhaven National Laboratory under contract with the Department of Energy, and was supported in part by its Office of Basic Energy Sciences. We wish to thank Mr Joseph Henriques for his technical assistance. The theoretical calculations were supported by NSF Grant CHE79-01061 at Carnegie–Mellon University.

References

Becker, P. J. & Coppens, P. (1975). *Acta Cryst.* **A31**, 417–425.

Binkley, J. S., Pople, J. A. & Hehre, W. J. (1980). *J. Am. Chem. Soc.* **102**, 939–947.

Binkley, J. S., Whiteside, R. A., Krishnan, R., Seeger, R., DeFrees, D. J., Schlegel, H. B., Topiol, S., Kahn, L. R. & Pople, J. A. (1981). *Quantum Chemistry Program Exchange*, **13**, 406. Indiana Univ., Bloomington.

Brady, O. L. (1914). *J. Chem. Soc.* pp. 2104–2116.

Busing, W. R., Martin, K. O. & Levy, H. A. (1962). *ORFLS*. Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee.

Craven, B. M. & McMullan, R. K. (1979). *Acta Cryst.* B**35**, 934–945.

Cyvin, S. J. (1968). *Molecular Vibrations and Mean Square Amplitudes*. Amsterdam: Elsevier.

DeFrees, D. J. (1980). Unpublished data.

DeFrees, D. J., Levi, B. A., Pollack, S. K., Hehre, W. J., Binkley, J. S. & Pople, J. A. (1979). *J. Am. Chem. Soc.* **101**, 4085–4089.

Flora, K. P., Van't Reit, B. & Wampler, G. L. (1978). *Cancer Res.* **38**, 1291–1295.

Hall, D. (1965). *Acta Cryst.* **18**, 955–958.

Hall, D. & Llewellyn, F. J. (1956). *Acta Cryst.* **9**, 108–112.

Hariharan, P. C. & Pople, J. A. (1974). *Mol. Phys.* **27**, 209–214.

Harmony, M. D., Laurie, V. W., Kuczkowski, R. L., Schwendeman, R. H., Ramsay, D. A., Lovas, F. J., Lafferty, W. J. & Maki, A. G. (1979). *J. Phys. Chem. Ref. Data*, **8**, 619–721.

Hawkes, G. E., Herwig, K. & Roberts, J. D. (1974). *J. Org. Chem.* **39**, 1017–1028.

Hehre, W. J., Stewart, R. F. & Pople, J. A. (1969). *J. Chem. Phys.* **51**, 2657–2664.

Hutchings, M. T., Shulhof, M. P. & Guggenheim, H. J. (1972). *Phys. Rev. B*, **25**, 154–168.

Jeffrey, G. A., Ruble, J. R., McMullan, R. K., DeFrees, D. J., Binkley, J. S. & Pople, J. A. (1980). *Acta Cryst.* B**36**, 2292–2299.

Johnson, C. K. (1970). *Thermal Neutron Diffraction*, edited by B. T. M. Willis, ch. 9, pp. 132–159. Oxford Univ. Press.

Johnson, C. K. (1976). *ORTEP* II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee.

Kleinspehn, G. G., Jung, J. A. & Studniarz, S. A. (1967). *J. Org. Chem.* **32**, 460–462.

Koester, L. (1977). *Springer Tracts in Modern Physics*. Vol. 80, edited by G. Hohler, p. 37. New York: Springer-Verlag.

McMullan, R. K. & Koetzle, T. (1980). Unpublished.

Meulenaer, J. de & Tompa, H. (1965). *Acta Cryst.* **19**, 1014–1018.

Møller, C. & Plesset, M. S. (1934). *Phys. Rev.* **46**, 618–622.

Olovsson, I. & Jönsson, P.-G. (1976). *The Hydrogen Bond – Recent Developments in Theory and Experiments*, edited by P. Schuster. Amsterdam: North-Holland.

Orville-Thomas, W. J. & Parsons, A. E. (1958). *Trans. Faraday Soc.* **54**, 460–468.

Pople, J. A., Binkley, J. S. & Seeger, R. (1976). *Int. J. Quantum Chem. Symp.* **10**, 1–19.

Pople, J. A., Krishnan, R., Schlegel, H. B. & Binkley, J. S. (1979). *Int. J. Quantum Chem. Symp.* **13**, 225–241.

Rosenkranz, H. S., Hjorth, R. & Carr, H. S. (1971). *Biochim. Biophys. Acta*, **232**, 48–60.

Templeton, L. K. & Templeton, D. H. (1973). Am. Crystallogr. Assoc. Meeting, Storrs, CT. Abstract E10.

Whiteside, R. A., Binkley, J. S., Krishnan, R., DeFrees, D. J., Schlegel, H. B. & Pople, J. A. (1980). *Carnegie–Mellon Quantum Chemistry Archive*. Chemistry Department, Carnegie–Mellon Univ., Pittsburgh, PA 15213.

Acta Cryst. (1981). B**37**, 1387–1390

cis-cisoid-cis-transoid-cis-cisoid-cis-Perhydro-*cis*-6,13-pentacenediyl Diacetate

By P. Van Nuffel, G. H. Petit, A. T. H. Lenstra and J. Van Loock

University of Antwerp (UIA), Department of Chemistry, Universiteitsplein 1, *B*-2610 *Wilrijk, Belgium*

and P. Vanhee

Department of Organic Chemistry, State University Gent, Krijgslaan 271 (*S*-4*bis*), *B*-9000 *Gent, Belgium*

(*Received* 16 *December* 1980; *accepted* 21 *January* 1981)

Abstract

$C_{26}H_{40}O_4$ is orthorhombic, *Pbca*, with $Z = 8$, $a = 9.972\,(4)$, $b = 21.285\,(4)$, $c = 21.825\,(9)$ Å, $D_c = 1.195$ Mg m^{-3}. $R_w = 0.035$ for 2160 reflections. Ring *B* occurs in a boat-like conformation, while the other four six-membered rings are in a distorted chair conformation.

Introduction

The title compound, shown in Fig. 1, is important in a study of the ring inversion in perhydropolycenes (De Pessenier, Anteunis & Tavernier, 1978; Vanhee, De Pessenier, Anteunis & Tavernier, 1979). It was first synthesized by Vanhee (1981). A determination of its configuration from spectroscopic data only was difficult

0567-7408/81/071387-04$01.00