Acta Cryst. (1964). **17**, 102

The Molecular and Crystal Structure of Trimethylamine Oxide, $(CH_3)_3NO$

By Aimery Caron, Gus J. Palenik,* Elihu Goldish† and Jerry Donohue

Department of Chemistry, University of Southern California, Los Angeles 7, California, U.S.A.

(*Received* 21 *November* 1962)

Crystals of $(CH_3)_3NO$ are monoclinic, space group $C2/m$, 4 molecules in a unit cell with lattice constants $a=10{\cdot}054$, $b=8{\cdot}793$, $c=5{\cdot}006$ Å and $\beta=91{\cdot}04°$. The required molecular symmetry is m. Fourier and least-squares refinement on 514 visually estimated intensities were used to obtain optimum values for 23 positional and 23 thermal parameters. The value of R is 7·4%. The bond distances found are (values including the libration correction are given in parentheses): N–O = $1{\cdot}388 \pm 0{\cdot}005$ (1·404), average C–N = $1{\cdot}477 \pm 0{\cdot}006$ (1·495), and average C–H = $1{\cdot}01 \pm 0{\cdot}07$ Å. The bond angles at the nitrogen atom are O–N–C = $110{\cdot}0 \pm 0{\cdot}6°$ and average C–N–C = $109{\cdot}0 \pm 0{\cdot}6°$.

The C–N and N–O bond distances are compared with those in other compounds.

Introduction

The molecular structure of trimethylamine oxide has been studied by the electron diffraction method in the gas phase (Lister & Sutton, 1939; Rundle, 1950) and by infrared spectroscopy in the crystalline state (Giguère & Chin, 1961). The N–O bond lengths reported are: $1{\cdot}36 \pm 0{\cdot}03$ Å (Lister & Sutton), $1{\cdot}44 \pm 0{\cdot}04$ Å (Rundle), and $1{\cdot}44 \pm 0{\cdot}03$ Å (Giguère & Chin) while the C–N bond lengths are $1{\cdot}54 \pm 0{\cdot}03$ Å (Lister & Sutton), $1{\cdot}49 \pm 0{\cdot}02$ Å (Rundle), and $1{\cdot}51 \pm 0{\cdot}01$ Å (Giguère & Chin). As may be seen, the agreement among these results is not entirely satisfactory.

Experimental

Crystals were prepared according to the procedure given by Hickinbottom (1957). They are colorless needles elongated along c. The constants for the monoclinic unit cell were determined from a few high order reflections on oscillation photographs calibrated with NaCl powder; the values thus obtained are

$$a=10{\cdot}154 \pm 0{\cdot}001,\ b=8{\cdot}793 \pm 0{\cdot}004,$$
$$c=5{\cdot}006 \pm 0{\cdot}001 \text{ Å};\ \beta=91{\cdot}04 \pm 0{\cdot}01°$$
$$[\lambda(\text{Cu } K\alpha_1)=1{\cdot}54051 \text{ and } \lambda(\text{Cu } K\alpha_2)=1{\cdot}54433 \text{ Å}]\,.$$

The deviations indicated are those resulting from comparison of the α_1 and α_2 results.

The calculated density for $Z=4$ is 1·116 g.cm^{-3}; the density as obtained by flotation in a mixture of carbon tetrachloride and benzene is 1·11 g.cm^{-3}.

The only systematic extinctions, hkl for $h+k$ odd, lead to a choice of three space groups: $C2$, Cm, and $C2/m$. The application of the centricity test (Howells, Phillips & Rogers, 1950) indicated that $C2/m$ is the correct space group. Thus, the molecules lie on mirror planes at $y=0$ and $\frac{1}{2}$ with two carbon atoms per molecule in the eightfold position $8(j)$, while the remaining heavy atoms are in special positions, $4(i)$.

Two crystals in sealed soft glass capillaries were used to collect Weissenberg intensity data. A needle measuring approximately $0{\cdot}15 \times 0{\cdot}15 \times 2$ mm was used to record data around c ($l=0$, 1, and 2). A second crystal with approximate measurements $0{\cdot}3 \times 0{\cdot}2 \times 0{\cdot}2$ mm provided intensity data both around a ($h=0$, 1, 2, 3, 4, 5, and 6) and b ($k=0$, 1, 2, 3, 4, and 5).

The intensities were estimated visually with the multiple film technique, corrected with Lorentz-polarization-Tunnell factors, and correlated. The range in recorded intensities was from 1 to 18,000. Of the 548 non-extinguished unique reflections in the Cu $K\alpha$ sphere, 34 were not in position to record, 106 were too weak to be observed, and 408 had measurable intensity. No absorption corrections were made.

Determination of the structure

A non-sharpened three-dimensional Patterson function was calculated* without removing the origin peak. The Patterson plane at $v=0$ was first investigated since it contains the interatomic vectors for the atoms in special positions. Fortunately, intramolecular and intermolecular vectors were easily separable so that the proper identification of the vector peaks in the $v=0$ plane was readily obtained.

It was then estimated that the carbon atoms in the general eightfold position, C(2), should lie at about $y=\frac{1}{8}$, $\frac{3}{8}$, $\frac{5}{8}$, and $\frac{7}{8}$. Thus, the Patterson layer at $v=\frac{1}{8}$ was found to contain all the vector peaks of the C(2) atoms with the heavy atoms in special positions. Only one peak remained to be located, namely, C(2) · · · C(2)′ (carbon atoms with two different *y* coordinates), and it was found, as expected, in the section at $v=\frac{1}{4}$. Thus, all peaks except those involving hydrogen atoms were identified and a consistent set of atomic coordinates was derived (see Table 1).

---

* Present address: Chemistry Division, U.S. Naval Ordnance Test Station, China Lake, California, U.S.A.

† Present address: Union Oil Company of California Research Center, Brea, California, U.S.A.

* The calculations for the Patterson function, the least-squares treatment, and the Fourier synthesis were carried out on an IBM 7090 with programs written by one of us (G. J. P.).

Table 1. *Refinement of positional parameters for the heavy atoms*

All values have been multiplied by 10^4

		Patterson	Least-squares	(σ)	Fourier	Final	(σ)
O	*x*	2062	2041	(2)	2041	2041	(2)
	z	3945	3987	(3)	3984	3985	(4)
N	*x*	2145	2094	(3)	2093	2094	(3)
	z	6945	6761	(4)	6754	6758	(8)
C(1)	*x*	3362	3472	(4)	3466	3469	(7)
	z	7612	7730	(7)	7727	7728	(8)
C(2)	*x*	1438	1418	(3)	1418	1418	(3)
	y	1333	1373	(3)	1374	1373	(3)
	z	7722	7775	(4)	7783	7779	(9)
R		41·3%	7·9%		7·4%		

Refinement of the structure

Least-squares

The refinement of the structure was carried out first by a full matrix least-squares treatment of the positional and anisotropic vibrational parameters of the heavy atoms. The quantity minimized was $\Sigma w^2(F_o-F_c)^2$. The weighting function used was that of Hughes (1941) with a value of 2·4 assigned to $4F_{\text{min}}$. Only those reflections of observable intensity were included in these calculations. The structure factors were computed with the scattering factors of Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) for C, N, and O and that of McWeeny (1951) for H.

The initial values of the atomic coordinates for the heavy atoms were those obtained from the Patterson function while those of the scale and temperature factors (isotropic *B* values of 3·0 Å^2) were arbitrary. These gave an *R* of 41·3%. After seven cycles it was apparent that convergence had been reached ($R=$ 15·5%), so the variables involving the hydrogen atoms were introduced. The hydrogen coordinates were derived by assuming C–H bond lengths of 1·0 Å, H–C–H angles of 110°, and staggered conformations of the methyl groups. This meant placing the C(2) hydrogen atoms — H(21), H(22) and H(23) — in three sets of positions 8(*j*), two C(1) hydrogen atoms – H(12) and H(12′) — in one set 8(*j*), and the third C(1) hydrogen atom, H(11), in 4(*i*). Constant isotropic temperature factor values of 6 Å^2 were assigned to the hydrogen atoms. Five more cycles were computed, *R* dropped to 8·8%, but good convergence could not be attained. The last four cycles were repeated with the application of one-third of the calculated shift values. The hydrogen isotropic temperature factors were then treated as parameters, and four more cycles were calculated. The final *R* value thus attained was 7·9%. The progress of the refinement of the atomic parameters together with the standard deviations obtained by the inversion of the full matrix at the last cycle may be followed and seen on Tables 1, 2 and 3. Table 4 is the list of observed and calculated (with the final least-squares parameter values) structure factors. The completeness of convergence may be judged from Table 5 which shows the maximum and average shifts of the last cycle expressed as a fraction of the estimated standard deviations.

Table 2. *Least-squares thermal parameters for the heavy atoms*

All values have been multiplied by 10^4

	ij	b_{ij}	(σ)
O	11	186	(4)
	22	242	(5)
	33	222	(8)
	13	20	(7)
N	11	134	(3)
	22	196	(4)
	33	234	(9)
	13	20	(7)
C(1)	11	137	(4)
	22	269	(8)
	33	439	(14)
	13	11	(12)
C(2)	11	185	(4)
	22	224	(5)
	33	340	(9)
	12	58	(6)
	13	21	(8)
	23	−37	(8)

Table 3. *Positional and thermal parameters for the hydrogen atoms*

		Assumed	Least-squares	Fourier	Final	σ
H(11)	*x*	0·353	0·344	0·351	0·348	0·009
	z	0·971	0·955	0·972	0·963	0·019
	B	6·0	4·6	—	4·6	0·9
H(12)	*x*	0·396	0·392	0·390	0·391	0·004
	y	0·093	0·076	0·091	0·083	0·016
	z	0·707	0·703	0·679	0·691	0·008
	B	6·0	4·5	—	4·5	0·6
H(21)	*x*	0·144	0·147	0·144	0·146	0·005
	y	0·136	0·128	0·138	0·133	0·010
	z	0·981	0·981	0·981	0·981	0·007
	B	6·0	4·9	—	4·9	0·7
H(22)	*x*	0·047	0·044	0·044	0·044	0·004
	y	0·136	0·132	0·129	0·131	0·005
	z	0·711	0·702	0·697	0·699	0·008
	B	6·0	4·6	—	4·6	0·6
H(23)	*x*	0·187	0·182	0·186	0·184	0·005
	y	0·229	0·227	0·233	0·230	0·007
	z	0·711	0·688	0·678	0·683	0·012
	B	6·0	4·5	—	4·5	0·6

Table 4. *Observed and calculated structure factors*

hkl	F_o	F_c
0 0 2	49.0	-99.1
0 0 4	40.3	52.3
0 0 6	38.5	-44.9
0 0 8	15.4	17.6
2 0 0	13.6	-12.7
2 0 1	14.8	17.8
2 0 2	2.9	-3.6
2 0 3	28.5	38.3
2 0 4	0.7	0.8
2 0 5	2.7	-3.7
2 0 6	1.6	1.9
2 0 7	0.0	-1.4
2 0 8	0.0	1.3
2 0 9	5.8	-5.9
4 0 0	59.9	-79.0
4 0 1	33.0	-38.4
4 0 2	19.9	20.3
4 0 3	12.7	14.9
4 0 4	13.8	-16.0
4 0 5	14.7	-17.4
4 0 6	20.8	22.4
4 0 7	8.7	10.1
4 0 8	8.7	-8.7
4 0 9	1.0	-2.2
6 0 0	30.7	-27.2
6 0 1	31.9	34.1
6 0 2	33.7	41.4
6 0 3	30.4	-39.5
6 0 4	19.4	-24.5
6 0 5	14.0	15.0
6 0 6	7.3	7.9
6 0 7	5.8	-6.4
6 0 8	5.8	-7.4
6 0 9	3.9	6.4
8 0 0	28.6	26.0
8 0 1	31.4	29.0
8 0 2	12.9	-11.6
8 0 3	11.3	-12.0
8 0 4	10.7	10.1
8 0 5	17.8	17.7
8 0 6	9.9	-10.2
8 0 7	10.1	-12.1
8 0 8	0.0	3.8
10 0 0	6.6	5.4
10 0 1	5.3	4.4
10 0 2	15.7	-19.7
10 0 3	0.0	0.2
10 0 4	14.2	14.0
10 0 5	2.1	1.8
10 0 6	2.0	-2.4
10 0 7	0.0	-1.0
10 0 8	6.7	4.5
12 0 0	4.1	-3.5
12 0 1	44.7	-45.4
12 0 2	1.9	2.1
12 0 3	22.8	26.7
12 0 4	1.9	-2.1
12 0 5	24.9	-25.6
12 0 6	1.2	1.3
12 0 7	14.9	16.7
14 0 0	1.6	2.0
14 0 1	1.9	-2.9
14 0 2	6.1	8.6
14 0 3	3.1	4.7
14 0 4	6.5	-7.1
14 0 5	3.0	-2.4
14 0 6	0.0	-0.7
16 0 0	12.6	-13.0
16 0 1	14.2	16.3
16 0 2	8.8	8.5
16 0 3	8.1	-7.6
16 0 4	7.3	-6.1
18 0 0	7.7	8.3
18 0 1	7.2	8.9
0 1 1	21.2	-22.7
0 1 3	18.7	-18.7
0 1 5	11.2	-8.7
0 1 7	9.0	9.4
0 1 9	0.0	0.6
1 1 0	17.7	-13.8
1 1 1	49.8	-68.4
1 1 2	8.3	-10.1
1 1 3	28.3	29.1
1 1 4	4.5	4.0
1 1 5	22.7	-23.7
1 1 6	0.0	0.3
1 1 7	12.8	13.2
1 1 8	2.0	1.9
1 1 9	3.7	-4.0
2 1 0	28.5	-26.7
2 1 1	11.5	-12.1
2 1 2	57.8	60.5
2 1 3	19.7	20.6
2 1 4	39.8	-38.1
2 1 5	7.3	-6.7
2 1 6	7.8	8.6
2 1 7	2.1	2.2
2 1 8	8.6	-9.1
2 1 9	3.5	-2.5
3 1 0	32.0	30.0
3 1 1	30.2	-35.4
3 1 2	4.2	3.6
3 1 3	17.0	19.5
3 1 4	1.1	1.2
3 1 5	14.6	-15.9
3 1 6	5.2	-6.1
3 1 7	8.9	9.7
3 1 8	0.0	0.6
3 1 9	3.8	-4.0
4 1 0	42.9	-38.3
4 1 1	44.3	57.4
4 1 2	11.0	11.9
4 1 3	17.1	-18.5
4 1 4	5.8	-6.1
4 1 5	19.8	21.1
4 1 6	8.5	10.5
4 1 7	13.8	-13.7
4 1 8	2.6	-3.6
4 1 9	0.0	2.5
5 1 0	38.0	-29.3
5 1 1	10.5	11.2
5 1 2	25.0	27.7
5 1 3	4.1	5.8
5 1 4	17.5	-17.0
5 1 5	5.0	5.7
5 1 6	8.4	9.8
5 1 7	4.2	-4.8
5 1 8	6.1	-5.4
6 1 0	14.4	-12.3
6 1 1	0.0	-0.3
6 1 2	5.3	-6.0
6 1 3	11.9	-14.1
6 1 4	7.2	6.9
6 1 5	4.5	3.1
6 1 6	0.0	1.2
6 1 7	0.0	-1.1
6 1 8	2.4	2.4
7 1 0	21.7	-18.5
7 1 1	24.2	22.8
7 1 2	0.0	-1.7
7 1 3	15.9	-19.4
7 1 4	1.6	-1.3
7 1 5	11.4	11.8
7 1 6	5.6	6.5
7 1 7	7.3	-6.7
7 1 8	0.0	-1.6
8 1 0	50.0	42.1
8 1 1	24.6	-19.6
8 1 2	26.9	-25.3
8 1 3	7.7	7.5
8 1 4	15.6	17.3
8 1 5	9.5	-9.3
8 1 6	17.5	-16.1
8 1 7	6.6	6.6
8 1 8	7.6	5.8
9 1 0	20.8	18.8
9 1 1	5.1	-4.0
9 1 2	13.6	-13.0
9 1 3	6.1	-5.7
9 1 4	10.8	10.3
9 1 5	1.5	-1.7
9 1 6	8.1	-8.8
9 1 7	0.0	1.9
9 1 8	5.1	4.3
10 1 0	5.2	-5.0
10 1 1	22.3	-18.6
10 1 2	9.3	9.7
10 1 3	23.4	23.6
10 1 4	7.3	-7.3
10 1 5	11.3	-10.7
10 1 6	1.5	2.1
10 1 7	6.4	5.6
11 1 0	30.7	27.7
11 1 1	6.7	-5.1
11 1 2	19.8	-16.9
11 1 3	8.1	8.2
11 1 4	14.1	13.5
11 1 5	3.3	-2.9
11 1 6	14.5	-11.8
11 1 7	0.0	1.3
12 1 0	11.2	-12.3
12 1 1	4.6	-2.9
12 1 2	4.0	3.2
12 1 3	3.1	3.2
12 1 4	3.0	-2.7
12 1 5	1.4	-1.6
12 1 6	8.3	7.1
13 1 0	15.8	-18.4
13 1 1	0.0	-1.6
13 1 2	12.0	11.7
13 1 3	4.0	5.1
13 1 4	10.0	-9.2
13 1 5	0.0	-1.1
13 1 6	8.8	8.5
14 1 0	3.0	-3.9
14 1 1	17.1	16.6
14 1 2	3.8	5.0
14 1 3	21.2	-20.4
14 1 4	2.8	-4.0
14 1 5	10.7	10.0
14 1 6	1.6	1.6
15 1 0	11.9	-13.8
15 1 1	2.7	-3.1
15 1 2	10.9	10.3
15 1 3	2.5	-1.1
15 1 4	8.6	-8.5
15 1 5	1.1	-2.0
16 1 0	14.4	15.0
16 1 1	6.4	6.7
16 1 2	8.6	-8.6
16 1 3	3.2	-2.9
16 1 4	4.7	6.1
17 1 0	3.3	3.3
17 1 1	8.1	8.5
17 1 2	1.0	0.6
0 2 0	39.1	-20.7
0 2 2	4.1	1.9
0 2 4	9.3	7.6
0 2 6	5.5	4.7
0 2 8	0.0	-0.2
1 2 0	34.0	-23.0
1 2 1	39.3	-39.4
1 2 2	7.2	-5.8
1 2 3	44.1	42.9
1 2 4	1.9	1.7
1 2 5	18.8	-17.7
1 2 6	10.0	9.4
1 2 7	9.3	9.1
1 2 8	0.0	-1.4
1 2 9	8.4	-7.7
2 2 0	2.6	-2.2
2 2 1	5.1	5.0
2 2 2	3.1	3.3
2 2 3	22.6	-20.6
2 2 4	2.7	-2.8
2 2 5	7.3	7.7
2 2 6	0.0	0.3
2 2 7	0.0	-1.8
2 2 8	0.0	-1.1
2 2 9	4.8	3.9
3 2 0	65.2	-51.3
3 2 1	7.4	6.5
3 2 2	22.6	32.7
3 2 3	25.2	-26.0
3 2 4	23.3	-22.1
3 2 5	5.5	4.3
3 2 6	12.5	16.8
3 2 7	0.0	-1.1
3 2 8	8.1	-7.0
3 2 9	6.0	5.2
4 2 0	4.6	-5.7
4 2 1	4.0	-3.6
4 2 2	10.2	9.2
4 2 3	4.5	5.1
4 2 4	10.5	-11.0
4 2 5	0.0	-1.3
4 2 6	0.0	1.0
4 2 7	0.0	0.7
4 2 8	0.0	-2.0
4 2 9	0.0	-1.6
5 2 0	45.4	40.9
5 2 1	24.1	24.8
5 2 2	12.0	-11.2
5 2 3	22.4	-21.9
5 2 4	6.8	6.7
5 2 5	13.9	14.0
5 2 6	12.4	-12.9
5 2 7	9.9	-8.8
5 2 8	4.3	2.0
6 2 0	19.3	17.2
6 2 1	24.7	-19.5
6 2 2	15.0	-14.6
6 2 3	19.8	17.9
6 2 4	12.1	11.2
6 2 5	9.7	-9.9
6 2 6	4.0	-4.7
6 2 7	3.8	4.8
6 2 8	7.9	3.8
7 2 0	29.1	23.9
7 2 1	30.5	27.5
7 2 2	22.0	-24.0
7 2 3	5.6	-5.4
7 2 4	18.0	18.5
7 2 5	12.2	12.7
7 2 6	11.4	-10.8
7 2 7	9.8	-8.2
7 2 8	0.0	6.6
8 2 0	8.7	6.3
8 2 1	8.3	7.5
8 2 2	6.0	-4.9
8 2 3	8.4	-7.1
8 2 4	4.7	4.7
8 2 5	3.7	3.3
8 2 6	0.0	-1.4
8 2 7	0.0	-1.6
9 2 0	1.6	-1.1
9 2 1	31.9	-28.6
9 2 2	12.0	-12.8
9 2 3	19.1	18.2
9 2 4	10.3	10.0
9 2 5	15.7	-15.2
9 2 6	0.0	0.5
9 2 7	11.4	9.4
10 2 0	6.2	-7.6
10 2 1	2.9	2.7
10 2 2	7.9	7.6
10 2 3	3.2	-3.1
10 2 4	8.4	-7.5
10 2 5	0.0	1.8
10 2 6	3.6	2.9
10 2 7	0.0	-1.2
11 2 0	12.5	-13.0
11 2 1	10.0	-8.5
11 2 2	17.6	18.5
11 2 3	0.0	-1.0
11 2 4	16.1	-14.7
11 2 5	5.5	-5.4
11 2 6	7.2	6.0
11 2 7	5.6	4.4
12 2 0	0.0	1.3
12 2 1	5.7	4.4
12 2 2	0.0	-1.3
12 2 3	0.0	-0.4
12 2 4	3.9	0.7
12 2 5	0.0	1.3
12 2 6	0.0	-0.7
13 2 0	17.6	-16.3
13 2 1	5.6	6.0
13 2 2	21.5	20.9
13 2 3	3.6	0.8
13 2 4	17.9	-16.3
13 2 5	4.6	3.9
13 2 6	6.8	7.3
14 2 0	0.0	1.6
14 2 1	0.0	0.3
14 2 2	3.7	-3.6
14 2 3	0.0	-0.8
14 2 4	4.7	4.5
14 2 5	0.0	0.6
15 2 0	0.0	2.4
15 2 1	16.0	14.3
15 2 2	7.7	-8.2
15 2 3	9.5	-9.2
15 2 4	5.5	6.5
16 2 0	1.2	0.6
16 2 1	0.0	0.1
16 2 2	0.0	0.4
16 2 3	2.9	-2.5
17 2 0	6.6	8.7
17 2 1	6.0	-5.8
0 3 1	12.1	-12.4
0 3 3	11.5	8.5
0 3 5	7.7	-9.1
0 3 7	5.7	3.9
1 3 0	14.3	-9.9
1 3 1	24.5	28.2
1 3 2	22.0	17.8
1 3 3	9.1	-7.7
1 3 4	19.4	-15.2
1 3 5	13.5	12.4
1 3 6	4.2	3.9
1 3 7	14.6	-7.9
1 3 8	8.1	-5.6
2 3 0	13.9	-10.7
2 3 1	7.2	-6.6
2 3 2	15.1	15.2
2 3 3	5.2	4.4
2 3 4	9.6	-8.2
2 3 5	2.4	-2.4
2 3 6	6.7	4.7
2 3 7	2.5	1.9
2 3 8	6.8	-4.5
3 3 0	3.4	3.6
3 3 1	18.0	16.4
3 3 2	19.4	-17.9
3 3 3	9.2	-8.9
3 3 4	17.9	16.7
3 3 5	11.2	10.2
3 3 6	0.0	-1.3
3 3 7	11.9	-6.6
3 3 8	7.6	5.4
4 3 0	8.4	-7.4
4 3 1	16.9	14.8
4 3 2	4.8	5.0
4 3 3	10.9	-8.5
4 3 4	6.4	-5.1
4 3 5	10.0	8.9
4 3 6	3.8	3.6
4 3 7	4.8	-4.0
4 3 8	0.0	-1.1
5 3 0	37.3	29.3
5 3 1	14.6	12.3
5 3 2	29.1	-26.3
5 3 3	25.1	-24.5
5 3 4	23.4	19.1
5 3 5	7.8	7.3
5 3 6	13.4	-11.0
5 3 7	2.2	-2.3
5 3 8	11.8	6.8
6 3 0	3.4	4.2
6 3 1	8.4	6.3
6 3 2	7.9	-6.7
6 3 3	8.4	-8.2
6 3 4	4.6	5.0
6 3 5	3.2	3.3
6 3 6	2.2	-2.2
6 3 7	3.7	-2.6
6 3 8	4.0	2.7
7 3 0	11.3	-9.1
7 3 1	25.2	-19.5
7 3 2	27.1	19.7
7 3 3	21.0	18.0
7 3 4	19.3	-17.2
7 3 5	12.4	-11.5
7 3 6	1.9	2.1
7 3 7	12.7	6.5
8 3 0	15.6	15.2
8 3 1	3.4	-3.0
8 3 2	8.2	-8.4
8 3 3	0.0	1.2
8 3 4	8.1	7.2
8 3 5	2.0	-2.6
8 3 6	7.2	-6.6
8 3 7	0.0	1.1
9 3 0	15.1	-14.3
9 3 1	12.4	-9.4
9 3 2	10.2	9.6
9 3 3	22.2	18.4
9 3 4	8.7	-7.1
9 3 5	8.6	-7.0
9 3 6	8.2	7.4
9 3 7	4.6	3.0
10 3 0	2.9	-2.5
10 3 1	10.4	-7.5
10 3 2	2.7	3.1
10 3 3	12.1	10.1
10 3 4	0.0	-1.7
10 3 5	6.0	-4.3
10 3 6	0.0	1.0
11 3 0	20.5	-17.8
11 3 1	14.3	9.4
11 3 2	9.9	9.3
11 3 3	16.5	-12.7
11 3 4	6.7	-4.9
11 3 5	7.8	6.1
11 3 6	8.4	7.9
12 3 0	10.3	-9.8
12 3 1	0.0	-1.3
12 3 2	7.2	5.4
12 3 3	1.2	0.8
12 3 4	6.8	-4.9
12 3 5	7.6	-0.8
12 3 6	4.5	4.6
13 3 0	13.1	14.2
13 3 1	7.1	4.6
13 3 2	9.7	-9.1
13 3 3	11.8	-9.0
13 3 4	5.3	5.1
13 3 5	4.3	3.9
14 3 0	3.0	-3.4
14 3 1	7.6	5.4
14 3 2	4.5	3.6
14 3 3	7.0	-6.1
14 3 4	2.7	-2.6
15 3 0	12.5	10.3
15 3 1	3.1	-2.1
15 3 2	7.2	-7.2
15 3 3	5.9	6.7
16 3 0	6.6	5.5
16 3 1	3.6	3.6
0 4 0	41.1	-24.9
0 4 2	17.4	15.9
0 4 4	13.3	-11.6
0 4 6	13.0	11.8
1 4 0	0.0	0.7
1 4 1	7.2	8.7
1 4 2	4.0	4.4
1 4 3	11.7	-11.9
1 4 4	5.3	-5.2
1 4 5	5.1	5.7
1 4 6	1.4	-1.7
1 4 7	3.1	-2.1
2 4 0	2.0	-1.7
2 4 1	18.0	18.7
2 4 2	3.6	3.8
2 4 3	22.6	-22.6
2 4 4	4.1	-2.6
2 4 5	12.4	10.0
2 4 6	0.0	1.3
2 4 7	9.8	-7.3
3 4 0	10.0	8.1
3 4 1	0.0	-1.1
3 4 2	4.7	-5.3
3 4 3	8.9	8.0
3 4 4	7.9	2.8
3 4 5	0.0	-1.8
3 4 6	4.8	-3.6
3 4 7	0.0	-1.0
4 4 0	11.3	10.3
4 4 1	10.7	8.8
4 4 2	3.0	-2.7
4 4 3	3.8	-2.7
4 4 4	2.5	1.9
4 4 5	4.8	4.7
4 4 6	6.1	-6.1
4 4 7	4.0	-2.7
5 4 0	14.3	-13.2
5 4 1	3.7	-3.4
5 4 2	5.2	6.3
5 4 3	4.8	3.5
5 4 4	2.1	-1.9
5 4 5	2.5	-2.3
5 4 6	6.7	6.1
5 4 7	0.0	1.4
6 4 0	19.3	15.3
6 4 1	20.0	-17.6
6 4 2	19.8	-20.2
6 4 3	21.3	20.9
6 4 4	18.0	16.2
6 4 5	12.4	-10.2
6 4 6	8.3	-6.7
6 4 7	9.6	6.4
7 4 0	5.2	-5.2
7 4 1	12.3	-10.7
7 4 2	5.6	5.9
7 4 3	0.0	2.4
7 4 4	5.5	-5.0
7 4 5	6.0	-4.5
7 4 6	2.9	2.7
7 4 7	4.0	4.3
8 4 0	7.1	-6.5
8 4 1	9.8	-8.3
8 4 2	0.0	2.0
8 4 3	0.0	0.2
8 4 4	0.0	-0.8
8 4 5	5.8	-4.9
8 4 6	3.0	3.0
9 4 0	3.2	3.8
9 4 1	6.9	5.9
9 4 2	0.0	0.7
9 4 3	3.7	-2.7
9 4 4	2.6	-2.5
9 4 5	4.0	2.7
9 4 6	2.1	-2.2
10 4 0	15.8	-10.8
10 4 1	0.0	1.3
10 4 2	19.1	16.2
10 4 3	3.0	-3.1
10 4 4	15.0	-13.4
10 4 5	1.0	1.2
11 4 0	3.7	4.1
11 4 1	0.0	-0.3
11 4 2	6.1	-6.0
11 4 3	5.2	4.2
11 4 4	5.2	5.6
11 4 5	1.1	-0.8
12 4 0	2.5	-1.0
12 4 1	15.8	13.7
12 4 2	0.0	0.8
12 4 3	7.9	-6.5
12 4 4	0.0	-0.9
13 4 0	5.6	4.7
13 4 1	0.0	-0.6
13 4 2	8.7	-6.6
13 4 3	2.4	-2.1
14 4 0	10.7	6.9
14 4 1	3.4	1.8
14 4 2	11.2	-9.9
0 5 1	9.7	7.4
0 5 3	0.0	1.0
0 5 5	4.5	5.0
1 5 0	13.4	-9.2
1 5 1	2.9	-3.2
1 5 2	7.8	8.5
1 5 3	0.0	2.2
1 5 4	7.3	-6.3
1 5 5	0.0	-1.1
1 5 6	4.5	4.4
2 5 0	14.6	11.2
2 5 1	5.8	5.1
2 5 2	17.7	-17.0
2 5 3	6.3	-5.7
2 5 4	18.1	14.3
2 5 5	1.9	2.6
2 5 6	3.2	-4.0
3 5 0	8.8	6.5
3 5 1	0.0	1.7
3 5 2	4.8	-5.1
3 5 3	0.0	-0.8
3 5 4	3.3	3.1
3 5 5	0.0	0.9
3 5 6	2.6	-2.9
4 5 0	11.3	8.5
4 5 1	16.2	-16.3
4 5 2	4.7	-4.7
4 5 3	7.1	6.9
4 5 4	3.7	3.3
4 5 5	8.2	-9.4
4 5 6	3.8	-4.7
5 5 0	4.2	4.6
5 5 1	2.0	2.4
5 5 2	5.0	-4.8
5 5 3	0.0	-1.1
5 5 4	3.8	4.0
5 5 5	0.0	0.4
5 5 6	1.7	-2.4
6 5 0	0.0	1.2
6 5 1	0.0	-1.9
6 5 2	2.5	3.9
6 5 3	5.6	6.8
6 5 4	3.7	-4.1
6 5 5	1.6	-1.7
7 5 0	0.0	-0.5
7 5 1	4.5	-5.0
7 5 2	0.0	-0.3
7 5 3	4.8	3.8
7 5 4	0.0	1.0
7 5 5	2.2	-2.7
8 5 0	21.4	-16.7
8 5 1	7.4	8.1
8 5 2	8.7	9.7
8 5 3	3.6	-3.5
8 5 4	6.9	-6.4
8 5 5	3.6	4.9
9 5 0	0.0	-1.3
9 5 1	5.4	-4.8
9 5 2	0.0	1.2
9 5 3	3.5	3.2
9 5 4	1.6	-1.2
10 5 0	2.5	2.6
10 5 1	9.9	8.1
10 5 2	3.0	-3.6
10 5 3	10.5	-12.4
10 5 4	3.1	2.9
11 5 0	0.0	1.7
11 5 1	5.0	3.9
11 5 2	0.0	-0.9
12 5 0	8.4	6.5
12 5 1	0.0	0.6
0 6 0	26.1	16.5
0 6 2	10.9	-10.9
0 6 4	7.5	7.8
1 6 0	3.7	4.9
1 6 1	4.2	5.4
1 6 2	0.9	-2.5
1 6 3	7.0	-6.3
1 6 4	2.2	2.2
2 6 0	0.0	-1.4
2 6 1	3.4	3.4
2 6 2	0.9	0.2
2 6 3	0.0	1.2
2 6 4	0.0	0.2
3 6 0	11.8	9.2
3 6 1	2.4	-2.6
3 6 2	7.1	-7.2
3 6 3	4.7	4.4
3 6 4	5.3	5.5
4 6 0	10.5	-7.3
4 6 1	3.2	-3.2
4 6 2	2.4	2.9
4 6 3	0.0	0.6
4 6 4	1.6	-1.8
5 6 0	2.5	-2.5
5 6 1	7.1	-5.0
5 6 2	0.0	-0.1
5 6 3	5.7	5.8
6 6 0	1.6	-1.6
6 6 1	2.0	3.4
6 6 2	2.9	4.3
6 6 3	5.0	-5.9
7 6 0	7.6	-5.9
7 6 1	1.7	-2.3
7 6 2	5.0	5.6
8 6 0	2.5	3.4
8 6 1	4.0	3.8
9 6 0	1.2	-2.2

Table 5. *Maximum and average shifts of the last least-squares cycle expressed as a function of the e.s.d.'s*

	$\Delta x_i/\sigma_{x_i}$		$\Delta B_i/\sigma_{B_i}$	
	Maximum	Average	Maximum	Average
Heavy atoms	0·209	0·092	1·020	0·431
Hydrogens	0·375	0·182	0·240	0·185

Fourier syntheses

Three three-dimensional Fourier syntheses were prepared with the values of the atomic parameters as obtained from the least-squares refinement: F_o and F_c Fourier syntheses with the contribution of the hydrogen atoms, and a difference Fourier synthesis with no contribution from the hydrogen atoms. Only the observed structure factors were used in the summations. All three syntheses were evaluated at intervals of $a/60$, $b/40$, and $c/30$. The positions of the maxima (including those of the hydrogen atoms) were computed by the method of Shoemaker, Donohue, Schomaker & Corey (1950). Full back shift corrections were applied to the observed atomic coordinates, hydrogen coordinates excepted. No corrections were made to the final least-squares values of the temperature factors since the difference map was found to be fairly flat at the positions of the heavy atoms, as shown in Fig. 1.

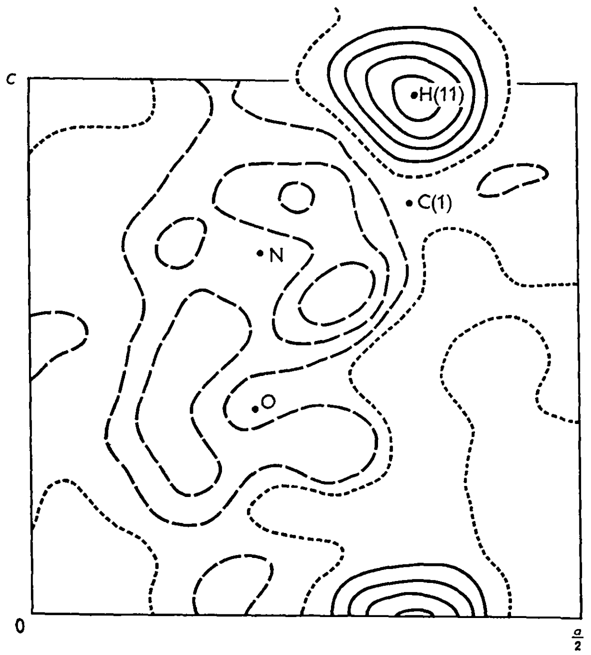

Fig. 1. Difference synthesis at $y=0$. Contour interval 0·1 e.Å^{-3}, zero level dotted, negative levels dashed.

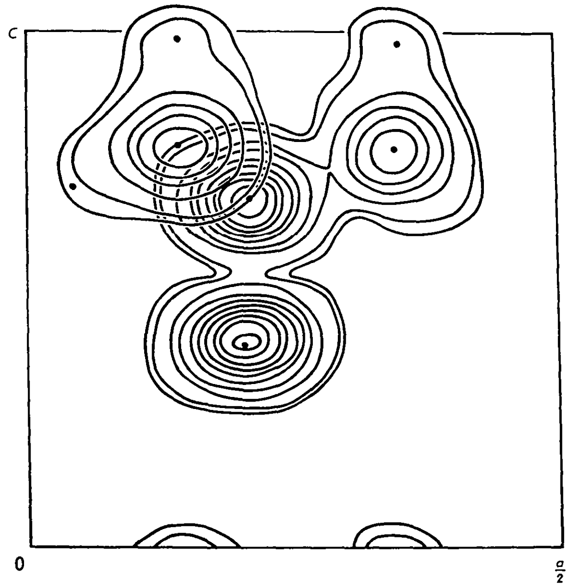

Fig. 2. Composite of two F_o Fourier sections at $y=0$ and 3/20. Contours at 0·5, 1, 2,. . . e.Å^{-3}.

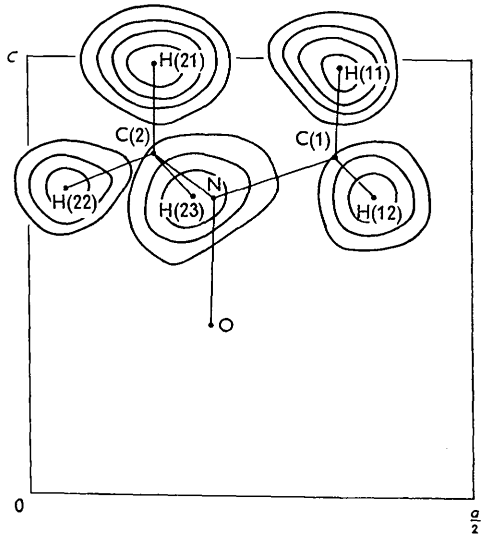

Fig. 3. Composite difference–Fourier synthesis. Contours at 0·5, 1, 2,. . . e.Å^{-3}.

A composite picture of the observed electron density at $y=0$ and 6/40 is shown in Fig. 2. The hydrogen atoms, with peak heights of 0·4 to 0·5 e.Å^{-3}, were easily located on the Fourier difference maps and no spurious peaks of comparable magnitude were found (Figs. 1 and 3).

The list of atomic coordinates as obtained from the Fourier syntheses is given in Tables 1 and 3. An R value of 7·4% was derived with these coordinates. This slight change in the value of R from that of the least-squares treatment is due mostly to a small change in the scale factor.

Final parameters

The final atomic coordinate values, listed in Table 1, were derived by averaging the least-squares and Fourier results. The two sets of results agree quite well. The results for only three coordinates differ by more than one least-squares standard deviation and none differs by more than two. The final standard deviations of the atomic coordinates (Table 1) were estimated by the usual method (Caron & Donohue, 1962; Shoemaker, Donohue, Schomaker & Corey, 1950).

Discussion

Thermal vibrations

The root mean square amplitudes and the direction cosines of the principal axes of the vibration ellipsoids are presented in Table 6. The atomic vibration ellipsoids are shown in Fig. 4. The amplitudes are of comparable magnitude but fairly large. The nitrogen atom coincides approximately with the center of gravity of the molecule; for this reason the nitrogen ellipsoid should essentially represent the translational motions of the whole molecule. This is substantiated by the following observations:

(*a*) The magnitude of the nitrogen amplitudes is smaller than or equal to the corresponding ones of the remaining atoms.

(*b*) The principal axes of the nitrogen ellipsoid are, within 2°, parallel to the crystallographic axes which correspond closely to the directions of the $O^- \cdots N^+$ and $N^+ \cdots O^-$ vectors in the lattice.

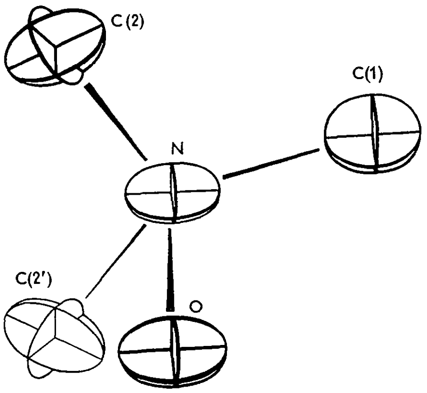

Fig. 4. View along [011] of the ellipsoids of vibration.

Table 6. *The ellipsoids of vibration*

Atom	i	$(\overline{r^2})^{\frac{1}{2}}$ (Å)	q_{ia}	q_{ib}	$q_{ic} \sin\beta$
O	1	0·3120	−0·9996	0	−0·0291
	2	0·3081	0	1	0
	3	0·1677	−0·0291	0	0·9996
N	1	0·2771	0	1	0
	2	0·2645	−0·9986	0	−0·0520
	3	0·1719	−0·0520	0	0·9986
C(1)	1	0·3248	0	1	0
	2	0·2676	−0·9996	0	−0·0284
	3	0·2359	−0·0284	0	0·9996
C(2)	1	0·3258	−0·8104	−0·5858	0·0142
	2	0·2806	−0·5827	0·8032	−0·1237
	3	0·2062	−0·0611	0·1085	0·9922

(*c*) The magnitudes of the amplitudes of the nitrogen atom appear to be proportional to the lengths of the $O \cdots N$ (or $N \cdots O$) vectors. Thus, the shortest $O \cdots N$ distances are 4·50 Å along y, 4·21 Å long x, and 3·62 Å along z. Correspondingly, the nitrogen amplitudes along the same directions are 0·278 Å, 0·265 Å, and 0·172 Å.

(*d*) If the magnitudes of the nitrogen amplitudes are subtracted from the ellipsoids of the remaining atoms along the same directions, the resulting amplitudes are nearly zero along the bond axes, and of reasonable magnitude perpendicular to the bond axes, and thereby consistent with atomic bending motions and/or molecular librations. These motions correspond to bond length corrections (Cruickshank, 1956) of between 0·016 and 0·019 Å for the N–O and C–N bond lengths.

The molecular structure

Intramolecular distances and angles are presented in Table 7. The two C–N bond lengths, with an average value of 1·477 ± 0·006 Å, are in good agreement with the average value of 1·478 ± 0·011 Å observed in $(CH_3)_3NO.HCl$ (Caron & Donohue, 1962) and of 1·474 ± 0·005 for α-glycine (Marsh, 1958). Hahn (1957), from a literature survey, concluded that the C–N bond length for both atoms with ligancy four should have a value of about 1·50 Å; it would appear that this value is somewhat high. This conclusion is unexpected inasmuch as the average bond length for a different bond, $-\overset{|}{\underset{|}{C}}-\overset{..}{\underset{|}{N}}-$, is 1·472 ± 0·005 Å (Sutton, 1958), a value close to those given above. On the other hand, when the libration correction is applied, the apparent average C–N bond length in trimethylamine oxide becomes 1·495 Å,* a value now in agreement with the survey of Hahn, but significantly higher than the value found in α-glycine. There is thus a discrepancy either in one regard or another, depending upon the appropriateness of the libration correction.

Table 7. *Bond lengths, angles, and torsion angles*

(Values corrected for libration in parentheses)

Bond	Distance	σ
O–N	1·388 (1·404) Å	0·005 Å
N–C(1)	1·470 (1·489)	0·008
N–C(2)	1·484 (1·499)	0·004
C(1)–H(11)	0·95	0·10
C(1)–H(12)	0·95	0·11
C(2)–H(21)	1·02	0·03
C(2)–H(22)	1·06	0·04
C(2)–H(23)	1·04	0·06

Atoms	Angles	σ
O–N–C(1)	110·4°	0·6°
O–N–C(2)	109·6	0·4
C(1)–N–C(2)	109·2	0·7
C(2)–N–C(2′)	108·9	0·4
N–C(1)–H(11)	109	10
N–C(1)–H(12)	108	9
N–C(2)–H(21)	108	5
N–C(2)–H(22)	105	4
N–C(2)–H(23)	106	6
H(11)–C(1)–H(12)	116	22
H(12)–C(1)–H(12′)	100	18
H(21)–C(2)–H(22)	113	7
H(21)–C(2)–H(23)	119	8
H(22)–C(2)–H(23)	105	12
O–N–C(1)–H(12)	54	
O–N–C(2)–H(21)	179	
O–N–C(2)–H(22)	58	
O–N–C(2)–H(23)	53	
C(2)–N–C(1)–H(11)	59	
C(2)–N–C(1)–H(12)	67	
C(1)–N–C(2)–H(21)	60	
C(1)–N–C(2)–H(22)	179	
C(1)–N–C(2)–H(23)	68	

Application of the significance test shows that the

---

* In $(CH_3)_3NO.HCl$, the corrected values of the C(1)–N and C(2)–N bond lengths are 1·484 and 1·490 Å, respectively.

N–O bond lengths in trimethylamine oxide (1·388 ± 0·005 Å) and its hydrochloride (1·425 ± 0·011 Å) are significantly different ($P = 0·2\%$). The corresponding values after correction for libration are 1·404 and 1·438 Å, so that in this case the libration effect does not alter this observation. Although a difference Fourier synthesis did not show it, it is highly likely that in the hydrochloride the oxygen atom bears a proton and therefore no negative formal charge. On the other hand, the oxygen atom in trimethylamine oxide does carry a formal negative charge. Since the N–O bond in the latter compound is shorter than in the hydrochloride, it can only be concluded that a formal negative charge borne by an atom does not increase its covalent radius but that, as proposed by Sass, Vidale & Donohue (1957), opposite formal charges across the N–O bond do have a shortening effect. Pyridine-*N*-oxide hydrochloride has been found to be ionic in the crystalline state (Tsoucaris, 1961). The N–O bond length of 1·375 ± 0·03 Å in it may be compared to the value of 1·28 ± 0·02 Å for the same bond in 4,4′-*trans*-azopyridine-*N*-oxide (Eichhorn, 1959). Again, the same shortening effect appears to be a factor in this instance, although the difference of 0·095 Å is much larger than our findings and, if real, may possibly be connected with the fact that in the pyridine derivatives the nitrogen atoms are part of an aromatic system. The opposite formal charge effect would explain the fact that the experimental values found for N–O bond length in nitro compounds, average value of 1·22 Å (see Table 8), is about the same as the corresponding value of 1·218 ± 0·004 Å in the nitrate ion (Sass, Vidale & Donohue, 1957). The oxygen atoms carry $\frac{1}{2}$ and $\frac{2}{3}$ of a formal negative charge while the N–O bond numbers are 1·5 and 1·33, respectively. The N–O distance of 1·236 ± 0·004 Å in the nitrite ion is definitely longer than in the nitro group, although the bond numbers are both 1·5. The nitrogen atom in NO_2^- is formally neutral, however. Thus, it would appear that a difference in the formal charges is an important factor determining the N–O bond lengths in these compounds.

Table 8. *Selected* N–O *bond lengths*

(Values in parentheses are corrected for libration)

Compound	N–O Lengths	Reference
$(CH_3)_3N^+–OH.Cl^-$	1·425 ± 0·011 Å (1·438)	Caron & Donohue (1962) Rérat (1960)
$(CH_3)_3N^+–O^-$	1·388 ± 0·005 (1·404)	Present work
Pyridine-*N*-oxide hydrochloride	$1·37_5$ ± 0·03	Tsoucaris (1961)
4,4′-*trans*-Azopyridine-*N*-oxide	1·28 ± 0·02	Eichhorn (1959)
NO_3^-	1·218 ± 0·004	Sass, Vidale & Donohue (1957)
NO_2^-	1·236 ± 0·014	Carpenter (1955)
$R–NO_2$	1·22 ± 0·01	Sutton *et al.* (1958)

The O–N–C and C–N–C average bond angles in trimethylamine oxide are 110·0 ± 0·6° and 109·0 ± 0·6°, so that, within experimental error, the nitrogen atom has ideal valence angles of 109·5°. This structural feature was not found in the hydrochloride where the O–N–C(1) angle is small (103·9 ± 1·1°) and the two C–N–C angles fairly large (111·6 ± 1·5°). Rérat (1960) suggested that this was a consequence of methyl-methyl and methyl-chloride repulsions; however, no methyl-methyl repulsion seems to be at play in $(CH_3)_3NO$, and the $Cl^- \cdots H(21)$ distance in the hydrochloride is not shorter than 3·0 Å, the sum of the two van der Waals radii (likewise the $H(0) \cdots H(21)$ is not expected to be significantly shorter than 2·4 Å). There is thus no simple explanation to account for the non-ideal nitrogen valence angles in $(CH_3)_3NO.HCl$.

Although the standard deviations of the hydrogen coordinates are fairly high, the average C–H bond length, 1·01 ± 0·07 Å, agrees well with the accepted X-ray value of 1·05 Å. All the bond angles involving hydrogen atoms are, within experimental error, equal to 109·5° (average value: 112 ± 11°) and the torsion angles have values close to either 60° or 180°. Thus, in all respects, the conformation of this molecule (Fig. 5) conforms to general beliefs.

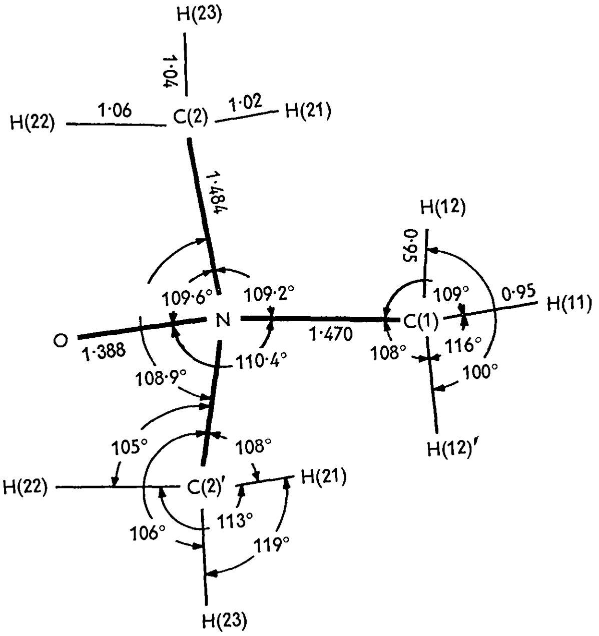

Fig. 5. The molecule with its bond lengths and bond angles.

Packing

The intermolecular distances are listed in Table 9 and the surroundings of a few molecules are shown on Fig. 6. The closest contacts are either of the H ⋯ H or H ⋯ O type. One H ⋯ H distance (2·17 Å) and one H ⋯ O distance (2.46 Å) are found to be shorter than the corresponding distances (2.4 and 2·6 Å) given by Pauling (1960); however, not significantly so.

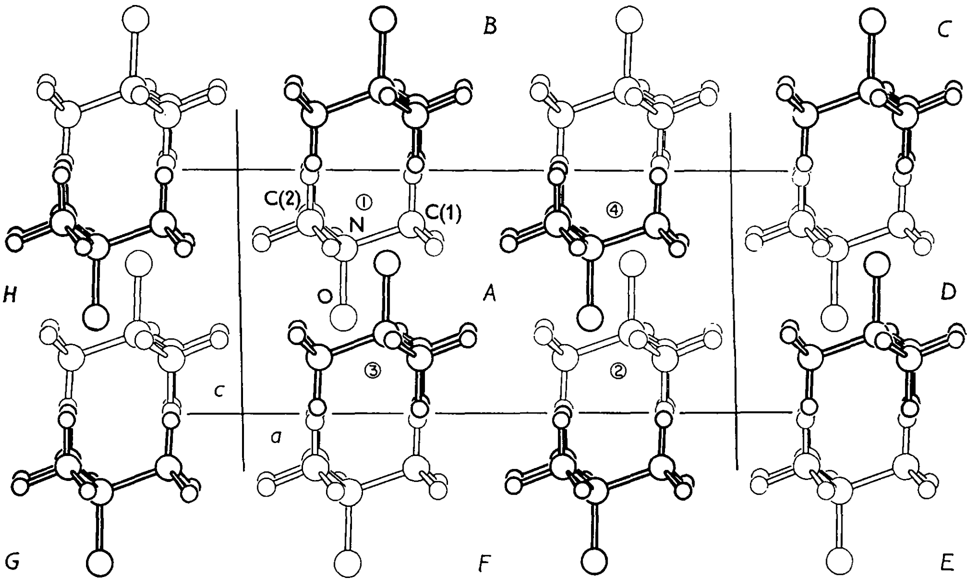

Fig. 6. The structure projected along the *b* axis.

Table 9. *Intermolecular distances*

	From atom in molecule *A*1	to atom	on molecule	Distance
Within $y=0$ layer	O	H(11)	*F*1	2·64 Å
	O	H(21)	*F*1	2·46
	H(22)	H(22)	*H*2	2·17
	H(22)	H(21)	*C*2	2·53
Between $y=0$ and $y=\frac{1}{2}$ layers	O	H(23)	*A*3	2·66
	H(23)	H(12)	*A*3	2·59

The dipole–dipole type forces seem to be the dominant packing forces even though there are no N · · · O contacts. This is evidenced by the fact that the nitrogen and oxygen atoms with their charges alternate along fairly straight lines which parallel the three crystallographic axes.

All calculations were done at the Western Data Processing Center. This work was supported by a grant from the U.S. Army Research Office (Durham). The figures were prepared by Mrs Maryellin Reinecke.

References

Berghuis, J., Haanappel, IJ. M., Potters, M., Loopstra, B. O., MacGillavry, C. H. & Veenendaal, A.L. (1955). *Acta Cryst.* 8, 478.

Caron, A. & Donohue, J. (1962). *Acta Cryst.* **15**, 1052.

Carpenter, G. B. (1955). *Acta Cryst.* **8**, 852.

Cruickshank, D. W. J. (1956). *Acta Cryst.* **9**, 757.

Eichhorn, E. L. (1959). *Acta Cryst.* **12**, 746.

Giguère, P. A. & Chin, D. (1961). *Canad. J. Chem.* **39**, 1214.

Hahn, T. (1957). *Z. Kristallogr.* **109**, 438.

Hickinbottom, W. J. (1957). *Reactions of Organic Compounds.* London, New York: Longmans, Green.

Howells, E. R., Phillips, D. C. & Rogers, D. (1950). *Acta Cryst.* **3**, 210.

Hughes, E. W. (1941). *J. Amer. Chem. Soc.* **63**, 1737.

Lister, M. W. & Sutton, L. E. (1939). *Trans. Faraday Soc.* **35**, 495.

McWeeny, R. (1951). *Acta Cryst.* **4**, 513.

Marsh, R. E. (1958). *Acta Cryst.* **11**, 654.

Pauling, L. (1960). *The Nature of tho Chemical Bond.* Ithaca: Cornell Univ. Press.

Rérat, C. (1960). *Acta Cryst.* **13**, 63.

Rundle, R. E., quoted by Allen, P. W. & Sutton, L. E. (1950). *Acta Cryst.* **3**, 46.

Sass, R. L., Vidale, R. & Donohue, J. (1957). *Acta Cryst.* **10**, 567.

Shoemaker, D. P., Donohue, J., Schomaker, V. & Corey, R. B. (1950). *J. Amer. Chem. Soc.* **72**, 2328.

Sutton, L. E. (1958). *Tables of Interatomic Distances and Configuration in Molecules and Ions.* Special Publication No. 11. London: The Chemical Society.

Tsoucaris, G. (1961). *Acta Cryst.* **14**, 914.