The Structure of *N,N*-Dimethylnitramine

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Abstract

$C_2H_6N_2O_2$, monoclinic, $P2_1/m$, $a = 6.129$ (1), $b = 6.501$ (1), $c = 6.060$ (1) Å, $\beta = 114.66$ (2)° at 293 K and $a = 6.088$ (1), $b = 6.266$ (1), $c = 5.995$ (1) Å, $\beta = 114.28$ (2)° at 143 K, $Z = 2$, $D_m = 1.36$ (2) (293 K), $D_x = 1.36$ (293 K), 1.44 (143 K) Mg m^{-3}. Separate determinations from counter-measured data at 293 (± 1) K ($R = 0.046$), 143 (± 3) K ($R = 0.036$) and 290 (± 3) K ($R = 0.059$). The molecule has exact *m* and almost *mm* symmetry (including H atoms). The mean bond distances (corrected for libration) are N–N 1.341 (4), N–O 1.232 (4) and C–N 1.459 (4) Å.

Introduction

An early report (Costain & Cox, 1947) on the structure of the title compound (DMN) gave cell dimensions and approximate bond distances, the molecule having symmetry *m* with the atoms (non-H) lying in that plane. Since then, several structures containing the nitramine group (C_2NNO_2) have been reported, the group being invariably non-planar but with the atoms NNO_2 in a plane. The present account is of two independent investigations of the structure of the title compound carried out simultaneously at the Universities of Münster and Lancaster. Whenever separate results are reported they will be indicated by (KM) or (CS) respectively.

Data were collected by (KM) at 293 ± 1 and 143 ± 3 K using graphite-monochromatized Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å) on a Syntex $P2_1$ diffractometer with an ω–2θ scan. The data of (CS) were obtained at 290 ± 3 K with Cu $K\alpha$ radiation ($\lambda = 1.542$ Å) using the manual diffractometer of Small & Travers (1962). The cell dimensions quoted are those of (KM) which differ from those of (CS) by no more than one standard deviation. The systematic absences 0*k*0, *k* odd, indicated space groups $P2_1$, $P2_1/m$. (KM) measured 522 (293 K) and 499 (143 K) independent reflexions of which 380 and 436 had $I > 2\sigma(I)$, (CS)

measured 520 reflexions of which 429 had $I > 2\sigma(I)$. Statistical intensity tests indicated the space group $P2_1/m$.

The structure was solved using both Patterson maps and an early version of *MULTAN* (Germain, Main & Woolfson, 1971). For the latter method, the space group $P2_1$ was used and the resulting E maps gave no indication of any deviation of the atoms from a plane parallel to (010); the centrosymmetric space group was therefore used for all subsequent work. After least-squares refinement of the non-H atom coordinates and anisotropic thermal parameters, difference Fourier maps gave well resolved positions for the H atoms which were refined with isotropic thermal parameters. Weights based on counting statistics were used by (KM), (CS) used unit weights. Final R values were (KM) 0.046 (293 K), 0.036 (143 K) and (CS) 0.059. Coordinates for all three determinations are given in Table 1.* For all calculations programs of the Syntex *XTL* system, and *ORTEP* (Johnson, 1970) were used by (KM); the XRAY 70 system (Stewart, Kundell & Baldwin, 1970) was used by (CS). There is agreement of not only the coordinates but also the U_{ij} and U values for the two room-temperature determinations.

Bond-length corrections for librational motion were applied using the program *MGTLS* of Gantzel & Trueblood (1970). Examination of the atomic vibrational ellipsoids showed that the molecular-thermal-motion pattern had approximate *mmm* symmetry. In order to obtain a determinate solution of the rigid-body motion it was necessary to make the screw tensor **S** of Schomaker & Trueblood (1968) equal to zero and further, to assume that one of the libration amplitudes L_{11} or L_{33} was zero (where L_{11} is parallel to N–N, L_{22} is normal to the molecular plane and L_{33} is normal to L_{11} and L_{22}). $L_{33} = 0$ involves the minimum correction to the N–N bond and $L_{11} = 0$ gives the maximum

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Table 1. *Atomic coordinates* (*for* C, N, O *atoms* $\times 10^4$, H *atoms* $\times 10^3$; U *in* $\text{Å}^2 \times 10^3$)

For C, N and O atoms $y = 0.025$.

		x	z
C(1)	a	1222 (6)	3677 (7)
	b	1238 (7)	3674 (7)
	c	1155 (3)	3595 (3)
C(2)	a	2708 (8)	8295 (7)
	b	2710 (8)	8309 (8)
	c	2566 (4)	8270 (4)
N(1)	a	3118 (4)	6124 (4)
	b	3107 (5)	6117 (5)
	c	3020 (3)	6079 (3)
N(2)	a	5379 (4)	6364 (5)
	b	5375 (5)	6362 (6)
	c	5304 (3)	6357 (3)
O(1)	a	5721 (4)	4504 (4)
	b	5724 (5)	4498 (5)
	c	5694 (2)	4480 (2)
O(2)	a	6986 (4)	8426 (4)
	b	6997 (4)	8423 (5)
	c	6906 (2)	8460 (2)

		x	y	z	U
H(1)	a	131 (4)	133 (4)	276 (4)	89 (8)
	b	128 (5)	122 (5)	266 (5)	62 (10)
	c	125 (2)	126 (3)	268 (2)	34 (4)
H(2)	a	971 (7)	250	380 (6)	99 (13)
	b	979 (7)	250	317 (7)	40 (10)
	c	963 (4)	250	374 (4)	42 (6)
H(3)	a	327 (5)	116 (5)	912 (5)	144 (13)
	b	323 (7)	115 (7)	922 (7)	142 (15)
	c	317 (3)	116 (3)	919 (2)	63 (5)
H(4)	a	110 (7)	250	785 (6)	92 (13)
	b	107 (10)	250	793 (10)	93 (19)
	c	88 (4)	250	779 (4)	37 (6)

(*a*) Data of (KM) at 293 K. (*b*) Data of (CS). (*c*) Data of (KM) at 143 K.

correction. On the basis that the most likely interpretation lies somewhere between these extremes, the corrected bond distances given in Table 2 are the mean of the two librational models.

Description and discussion of the structure

The investigations have given no indication of non-planarity of the molecule. As Fig. 1 indicates, the major axis of the ellipsoids of vibration of all non-H atoms is perpendicular to the molecular plane. These large displacements could be interpreted as statistical positional disorder of a non-planar molecule about the symmetry plane. This possibility is discounted by a comparison of the mean-square displacements along the principal ellipsoid axes averaged over all six atoms for the ambient and low-temperature data; these are 0.0982, 0.0649, 0.0370 Å^2 and 0.0428, 0.0294, 0.0172 Å^2 respectively. The proportionate fall for all directions corresponding to a temperature change from 293 to 143 K indicates the true thermal character of the vibration parameters; this is in further agreement with the decrease of 0.235 Å in b with fall of temperature.

Fig. 1 shows how the disposition of the CH_3 groups gives molecular symmetry close to *mm*, with the nearest H atoms, H(2) and H(4) of opposite CH_3 groups, 2.34 Å apart in the symmetry plane. This distance is close to the expected van der Waals separation of 2.40 Å and is achieved by the C—N—C angle opening to almost 125°. The intramolecular H···O contacts of 2.69 and 2.61 Å involve the out-of-plane H atoms; if the CH_3 groups were rotated through 60° so that the H nearest the O was in the symmetry plane, the H···O separation would be only 2.10 Å. The shortest H···O intramolecular contacts found in nitramines are in the range 2.3–2.4 Å. It may be inferred that this

Table 2. *Bond distances* (Å) *and angles* (°) *uncorrected and corrected for libration*; (*a*) *data of* (*KM*) *at* 293 K; (*b*) *data of* (*CS*); (*c*) *data of* (*KM*) *at* 143 K

|	Uncorrected			Corrected for libration		
	a	b	c	a	b	c
C(1)—N(1)	1.453 (5)	1.447 (5)	1.455 (3)	1.463	1.457	1.458
C(2)—N(1)	1.438 (5)	1.447 (6)	1.449 (3)	1.450	1.458	1.455
N(1)—N(2)	1.332 (4)	1.335 (5)	1.331 (3)	1.342	1.349	1.334
N(2)—O(1)	1.230 (4)	1.235 (5)	1.242 (2)	1.242	1.246	1.246
N(2)—O(2)	1.226 (4)	1.231 (5)	1.237 (2)	1.236	1.240	1.240
C(1)—N(1)—C(2)	124.3 (3)	125.2 (3)	124.6 (2)	124.3	125.2	124.7
C(1)—N(1)—N(2)	117.6 (2)	117.3 (3)	117.7 (2)	117.6	117.6	117.6
C(2)—N(1)—N(2)	118.1 (2)	117.6 (3)	117.7 (2)	118.2	117.7	117.8
O(1)—N(2)—O(2)	124.2 (2)	123.7 (3)	124.0 (2)	124.3	123.8	124.0
O(1)—N(2)—N(1)	117.9 (2)	117.9 (3)	117.8 (2)	117.8	117.9	117.8
O(2)—N(2)—N(1)	117.9 (2)	118.5 (3)	118.2 (2)	117.8	118.3	118.1
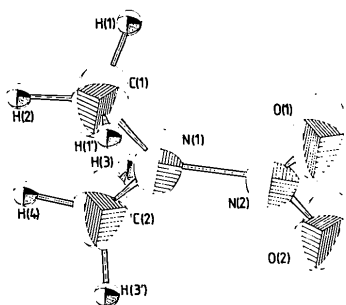
Fig. 1. Vibration ellipsoids (at 293 K) for N,N-dimethylnitramine scaled to 50% probability for non-H atoms. For clarity H atoms are scaled to $B = 0.7$ Å².

orientation of the CH_3 groups in DMN is excluded by H···O repulsion. The present compound may be compared with N-nitrosodimethylamine (Krebs & Mandt, 1975) which also has a symmetry plane passing through the C, N, O and two H atoms. It differs from DMN by having one O less, thus enabling the CH_3 furthest from the N—O bond to rotate through 60° since there is no H···O contact on this side of the molecule. The H···H distance with this arrangement is 2.57 Å in spite of a decrease of the C—N—C angle to 120°.

Although there is no simple explanation of the planarity of the molecule, *ab initio* MO calculations by Duke (1978) have shown that over a limited range of models with varying degrees of planarity, the one found in the present work has the lowest energy. The bond distances and angles within the molecule, apart from the C—N—C angle already mentioned, are similar to those in other nitramine structures. Two types of intermolecular interaction in nitramines have been pro-

posed, C—H···O hydrogen bonding (Choi & Boutin, 1970) and an interaction between a nitro N and an O (Cobbledick & Small, 1973). The closest intermolecular contacts found here are 2.64 Å for H···O, a value too large to be considered as an interaction. N···O contacts of 3.32 Å (for the 293 K results) of screw-axis-related N—O bonds are possible interactions in view of the expected thickness of a π-bonded system of 3.50 Å, and the highly polar nature of the N—O bonds; this N···O distance falls to 3.19 Å at 143 K.

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X-ray Diffraction Studies of 9-Methylanthracene and 5-Methylnaphthacene

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Abstract

The crystal structures of 9-methylanthracene (I) and 5-methylnaphthacene (II) have been elucidated by direct methods, with adjustment of pseudohomometric variants on E maps. Both compounds crystallize in the monoclinic space group $P2_1/c$, with $a = 8.920$ (3), $b = 14.641$ (4), $c = 8.078$ (4) Å, $\beta = 96.47$ (3)°, $Z = 4$ for (I), and $a = 10.794$ (2), $b = 14.697$ (4), $c = 7.980$ (2) Å, $\beta = 93.95$ (3)°, $Z = 4$ for (II). Least-squares adjustment of the atomic parameters resulted in $R = 0.079$ over 1166 reflexions for (I) and $R = 0.066$ over 1088