

A Refinement of the Crystal Structure of *N,N'*-Dinitroethylenediamine

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The previously reported crystal structure of *N,N'*-dinitroethylenediamine ($\text{NO}_2\text{NHCH}_2\text{CH}_2\text{NHNO}_2$) has been refined from new three-dimensional data collected with an automatic diffractometer. The space group is *Pbca* with $a=10.793$ (7), $b=8.761$ (6), $c=6.169$ (2) Å, and 4 molecules per unit cell. The average N–O distance of 1.238 Å, the shortened N–N distance of 1.301 Å, the C–N distance of 1.463 Å, and the nearly planar CNHNO_2 group partially describe the molecular structure. Each molecule contains a center of symmetry. Net atomic charges and values for overlap populations taken from a molecular orbital calculation are reported. Packing in the crystal appears to be based predominantly on dipole–dipole interaction. The final reliability index is 4.7% and hydrogen atoms have been located.

Introduction

The crystal structure of *N,N'*-dinitroethylenediamine was reported almost twenty years ago by Llewellyn & Whitmore (1948) who were interested in establishing the size and shape of the nitramine group in response to a brief report by Costain & Cox (1947) indicating that the N–N bond length in dimethylnitramine is considerably shorter than the single-bond value. Llewellyn & Whitmore also found the N–N distance to be very much shortened and several resonance structures were proposed to explain this and other bond distances and angles in their crystal structure. Allentoff & Wright (1953) investigated the structure of the disodium salt of *N,N'*-dinitroethylenediamine to determine whether the metal is associated with the nitro group or with the amino nitrogen, and to characterize the nitramine ion which is presumably active in the alkylation of primary nitramines. Their results showed the Na^+ ions to be definitely associated with oxygen, but the methylation of the salt produces three times as much *N*-dimethyl as *O*-dimethyl derivative, leading to the conclusion that the structure determined is probably not significant for the methylation process, which proceeds in spite of the symmetry of the ethane-bisnitramine ion. In cyclotetramethylenetetranitramine (Eiland & Pepinsky, 1955; Cady, Larson & Cromer, 1963) and in nitramide (Beavers & Trotman-Dickenson, 1957) the N–N bond distance is only slightly shortened, while in tetramethylenedinitramine(diaquo)nickel(II) (Liebig, Robertson & Truter, 1966) the N–N distance closely approaches the value for a double bond.

Very recently, *N,N'*-dinitroethylenediamine has been shown to be a growth stimulant for several species of plants and animals (Holmsen, 1966; Lindsay & Mees, 1963), and accumulated evidence suggests that this small molecule, and not a derivative or metabolite, is the primary agent. In considering possible mechanisms for such activity, it may be helpful to know molecular dimensions and configuration accurately and to calculate the charge distribution on the molecule. The

present refinement was undertaken to provide the best possible values for such molecular measurements and to describe the nitramine group as accurately as possible.

Experimental

X-ray powder diffraction data were taken with crystal monochromatized $\text{Cu } K\alpha_1$ radiation ($\lambda=1.54050$ Å) with an AEG* Guinier camera using Seeman–Bohlin focusing (Hoffman & Jagodzinski, 1955). A 7.5μ Al foil used as the sample holder provided reference lines. Assuming space group *Pbca* as reported by Llewellyn & Whitmore (1948), the method of axial ratios (Frevel, 1964) was used with these data to refine the unit-cell dimensions. The refined values are

$$\begin{aligned} a &= 10.793 \pm 0.007 \text{ \AA} \\ b &= 8.761 \pm 0.006 \\ c &= 6.169 \pm 0.002 \end{aligned}$$

A single crystal of approximately 0.2 mm average diameter was selected from material recrystallized from water and showing a bipyramidal habit as reported by McCrone (1952). Intensities for all *hkl* and $\bar{h}k\bar{l}$ reflections were collected on a PAILRED† system using $\text{Cu } K\alpha$ radiation (1.54178 Å), a Si (111) monochromator, and a scintillation counter. After combining equivalent reflections, the original set of 1029 reflections reduced to 548, of which 75 are symmetry-extinct confirming the assumed *Pbca* space group, 138 are nonobserved, and 335 are nonequivalent observed reflections. All $F(\text{obs})$ having values less than 3σ of $F(\text{obs})$ were taken as nonobserved.

Punched paper tape output from PAILRED was converted to cards which were then processed on a

* Allgemeine Elektrizitäts-Gesellschaft.

† Philips Automatic Indexing Linear Reciprocal-space Exploring Diffractometer; the system at Philips Research Laboratories in Briarcliff Manor, New York, was made available through the courtesy of Dr Joshua Ladell and Mr Robert Smick.

Burroughs B5500 computer using a program written by the author. Counter statistics (Friedlander, Kenned- & Miller, 1964) were used to compute expected standard deviations, and the Lorentz-polarization correction was calculated from the following expression (Bond, 1959):

$$P_L = T \sin 2\theta \left\{ 1 + \left(\frac{q - \sin^2 \nu}{(1+q) \cos^2 \nu} \right) \times (1 + \cos 2\theta)^2 - \left(\frac{2q}{1+q} \right) (1 + \cos 2\theta) \right\}$$

where $q = \cos^2 2\theta_m$, θ_m is the Bragg angle for the monochromator, and

$$T = (\sin^2 \theta - \sin^2 \nu)^{1/2} / \sin \theta.$$

No absorption correction was made.

Structure refinement

The 200, 400, and 600 reflections were omitted from the observed data set because of poor agreement for equivalent crystal settings, leaving 332 nonequivalent structure factors to be used in refining 58 parameters. Calculations began with Llewellyn's atomic coordinates for carbon, nitrogen, and oxygen (Llewellyn & Whitmore, 1948) and with an overall thermal parameter $B = 3.0 \text{ \AA}^2$. Reflections were weighted by the reciprocals of their estimated standard deviations except for 67 reflections having $\sigma < 0.25$ ($w > 4.0$) for which a value

of $\sigma = 1.0$ was arbitrarily assigned. The final set of weights covered a range of values from 0.89 to 4.00. A full-matrix least-squares refinement minimizing $\sum w(F_o - F_c)^2$ was done on an IBM 7094 machine with the Oak Ridge FORTRAN least-squares computer program (Busing, Martin & Levy, 1962), and atomic scattering factors taken from *International Tables for X-ray Crystallography* (1962). Four cycles on xyz and B for C, N, O gave reliability indices of $R_1 = \sum |F(\text{obs}) - F(\text{calc})| / \sum |F(\text{obs})| = 0.099$ and $R_2 = \{ \sum [F(\text{obs}) - F(\text{calc})]^2 / \sum wF^2(\text{obs}) \}^{1/2} = 0.094$. Next, initial positions for the three hydrogen atoms were chosen from a model assuming tetrahedral carbon and trigonal nitrogen, and four cycles on $xyzB$ for H and on B for C, N, O gave $R_1 = 0.080$ and $R_2 = 0.079$. This was followed by four cycles on xyz and anisotropic β_{ij} for C, N, O with H included but not refined giving $R_1 = 0.051$ and $R_2 = 0.047$. Finally, three cycles on xyz for H, holding $B(H)$ and all C, N, O parameters constant, gave reliability indices of $R_1 = 0.049$ and $R_2 = 0.046$. At this point, a CDC 3800 computer became available and, using the Argonne National Laboratory least-squares program, ANL FLS 14E7043 (Gvildys, 1967), three more cycles of refinement were run varying all parameters, with thermal parameters anisotropic for C, N, and O, and isotropic for H. Final values for the reliability indices are $R_1 = 0.047$ and $R_2 = 0.046$. The average xyz parameter shift for C, N, O in the final cycle was 0.038σ and the maximum was 0.176σ . For hydrogen, the average shift was 0.075σ and the maximum was 0.214σ . Table 1 lists the atomic parameters and estimated standard

Table 1. *Final atomic parameters*

Numbers in parentheses are the estimated standard deviations from the least-squares refinement $\times 10^4$ for hydrogen and $\times 10^5$ for all other atoms.

Atomic coordinates						
	<i>x</i>	<i>y</i>	<i>z</i>			
C	0.03434 (27)	0.00199 (45)	0.10831 (48)			
N(1)	0.16651 (23)	0.02916 (38)	0.07271 (45)			
N(2)	0.21296 (18)	0.16500 (32)	0.04731 (38)			
O(1)	0.32610 (18)	0.17475 (30)	0.01496 (36)			
O(2)	0.14417 (18)	0.27755 (28)	0.05806 (35)			
H(1)	0.5310 (28)	0.5912 (49)	0.8089 (52)			
H(2)	0.5081 (30)	0.4047 (50)	0.8087 (59)			
H(3)	0.7112 (36)	0.5455 (54)	0.9463 (54)			
Anisotropic thermal displacements (\AA)†						
	$U_{11}^{1/2}$	$U_{22}^{1/2}$	$U_{33}^{1/2}$	$U_{12}^{1/2}$	$U_{13}^{1/2}$	$U_{23}^{1/2}$
C	0.165 (40)	0.208 (51)	0.184 (40)	-0.073 (37)	0.054 (35)	0.051 (41)
N(1)	0.161 (39)	0.173 (48)	0.231 (41)	0.048 (33)	0.018 (35)	0.036 (35)
N(2)	0.180 (37)	0.176 (42)	0.157 (33)	-0.069 (34)	-0.023 (31)	-0.040 (36)
O(1)	0.172 (32)	0.229 (42)	0.238 (38)	-0.095 (29)	0.076 (30)	-0.082 (34)
O(2)	0.214 (34)	0.178 (42)	0.212 (35)	0.054 (31)	0.027 (32)	-0.005 (33)
H(1)	0.118 (88)	} \ddagger	1.09 \pm 0.62	} isotropic <i>B</i> values		
H(2)	0.171 (101)		2.30 \pm 0.81			
H(3)	0.110 (99)		0.95 \pm 0.77			

† These values are the square roots of the mean-square amplitude tensors, U_{ij} , based on the expression $\exp(-h^2\beta_{11} - k^2\beta_{22} - l^2\beta_{33} - 2hk\beta_{12} - 2hl\beta_{13} - 2kl\beta_{23})$ and the relation $\beta_{12} = 2\pi^2 U_{12} a^* b^*$ (Cruickshank, 1965).

‡ These values are the square roots of the mean square displacements from the expression $B = 8\pi^2 \bar{u}^2$ and the temperature correction $\exp(-B \sin^2 \theta / \lambda^2)$. (Lipson & Cochran, 1953).

deviations for the refined structure. Table 2 compares observed structure factors with the final calculated values.

Discussion

Bond distances and angles and estimated standard deviations for the refined structure (Table 3) were calculated on the CDC 3800 computer with ANL FFE (Gvildys, 1964). The C—C distance has a normal single-bond value, the C—N distance agrees with the value for C bonded as C—N< and with the value in C—N=, the average N—O distance is just slightly longer than that found in other organic structures, and the N—N

distance is considerably shorter than a single bond (1.48 Å) but longer than a double bond (1.24 Å) (Sutton, 1958, 1965; Pauling, 1960). The N—N distance in other nitramine compounds ranges from 1.24 Å in tetramethylenedinitramine(diaquo)nickel(II) (Liebig, Robertson & Truter, 1966) to 1.37 Å and 1.41 Å in cyclotetramethylenetetranitramine (Cady, Larson & Cromer, 1963). The value of 1.301 Å in EDNA lies midway in this range. A least-squares fit to a plane was done for the —CNHNO₂ group (Schomaker, Waser, Marsh & Bergman, 1959) to give

$$1.76563x + 0.33234y + 6.08139z = 0.71520.$$

Table 2. Observed and calculated structure factors

H	L	FORS	FCALC	H	L	FORS	FCALC	H	L	FORS	FCALC	H	L	FORS	FCALC	H	L	FORS	FCALC	H	L	FORS	FCALC	H	L	FORS	FCALC	H	L	FORS	FCALC	
0	0	K = 0		3	6	8.13	7.86	1	2	4.14	3.47	10	3	3.59	3.09	9	1	30.79	30.50	7	1	6.17	6.85	7	1	10.16	10.05	6	8	0.00	0.57	
0	2	130.98	136.36	3	7	5.05	5.08	1	3	29.03	29.11	10	4	2.00	3.02	9	2	12.02	11.89	7	2	12.82	13.52	7	2	13.91	14.13	7	1	0.00	0.57	
0	4	11.19	11.03	4	1	0.00	0.66	4	1	11.36	11.13	11	1	0.00	0.05	9	3	12.06	11.89	7	3	7.65	8.31	7	3	4.44	4.91	7	2	11.13	10.51	
0	6	10.22	10.64	4	2	8.00	8.26	1	5	7.01	6.23	11	2	0.00	0.84	9	4	0.00	1.52	7	4	8.68	8.88	7	4	13.64	14.11	7	3	0.00	2.92	
1	2	86.36	85.93	4	3	8.34	8.48	1	6	9.86	9.49	11	3	0.00	0.25	10	0	7.16	7.32	7	5	0.73	0.73	7	5	2.51	1.02	7	4	6.80	6.62	
1	4	56.38	53.99	4	4	8.10	7.67	1	7	0.00	0.86	12	0	0.00	1.19	10	1	0.00	1.26	8	0	3.28	2.73	8	0	27.23	26.60	8	0	15.82	14.04	
1	6	18.13	18.87	4	5	9.25	9.16	2	2	10.25	10.82	12	1	0.00	0.21	10	2	5.11	4.93	8	1	0.00	2.80	8	1	0.00	2.80	8	1	3.63	2.94	
2	2	70.87	70.07	4	6	8.98	7.87	2	2	22.56	21.55	12	2	0.00	4.29	10	3	5.02	4.89	8	2	3.53	4.00	8	2	0.00	3.29	8	3	5.05	5.25	
2	4	25.97	25.33	4	7	8.88	8.82	2	3	17.85	17.61	12	3	0.00	0.77	10	4	0.00	0.77	8	3	0.00	3.29	8	3	0.00	3.29	8	3	0.00	3.29	
2	6	0.00	0.00	5	1	25.88	25.09	2	4	0.00	0.07	1	1	45.93	54.43	11	2	3.69	4.49	8	4	2.90	3.23	8	4	2.90	3.23	8	4	2.90	3.23	
3	2	11.31	10.69	5	2	5.95	6.27	2	5	11.37	11.34	1	2	6.08	6.01	11	3	6.19	6.81	9	1	13.08	13.51	9	1	10.01	9.79	9	1	0.00	1.60	
3	4	3.62	3.80	5	3	0.00	0.83	1	3	0.00	0.83	1	3	6.32	5.52	12	4	5.65	5.68	9	2	11.36	11.36	9	2	2.61	0.23	9	2	4.61	4.02	
3	6	7.92	7.95	5	4	5.66	5.75	2	7	5.65	5.50	1	4	5.26	5.84	12	1	0.00	1.47	9	3	6.29	6.87	9	3	4.83	10.83	10	0	2.68	0.91	
4	2	20.31	24.61	5	5	7.04	7.52	1	5	29.67	29.72	1	5	7.89	7.82	1	5	7.89	7.82	9	4	7.29	7.68	9	4	9.83	10.00	10	1	0.00	0.48	
4	4	7.33	7.41	5	6	3.93	3.78	3	2	9.67	9.20	1	6	3.29	3.10	1	6	12.96	13.40	10	5	0.00	1.51	10	1	0.00	1.51	10	2	0.00	2.73	
4	6	0.00	0.00	6	0	9.01	8.32	3	3	11.91	11.77	1	7	0.00	0.43	0	1	6.11	6.09	10	1	4.05	3.43	10	2	10.07	9.65					
4	8	16.58	14.36	6	1	17.09	16.56	3	4	0.00	0.79	2	0	17.36	17.08	0	1	16.00	16.09	10	2	5.98	6.21	10	3	0.00	2.15					
5	4	18.36	18.80	6	2	4.56	3.92	3	5	0.00	1.90	2	1	23.17	22.03	0	2	14.94	14.30	10	3	7.32	7.21	11	1	3.96	3.57	1	1	15.30	16.24	
5	6	8.98	9.91	6	3	18.05	17.77	3	6	0.00	2.39	2	2	10.10	9.72	0	3	3.02	3.42	11	1	4.01	6.48	11	1	4.01	6.48	1	2	3.62	3.06	
5	8	40.84	39.68	6	4	0.00	0.49	3	7	3	27.98	26.55	0	4	18.15	15.34	0	4	18.15	15.34	11	2	2.72	1.75	11	2	2.72	1.75	1	3	0.00	0.65
6	4	8.67	5.68	6	5	6.71	3.78	4	0	33.36	32.66	2	4	0.00	1.54	0	5	0.00	3.04	10	4	0.00	0.12	10	4	0.00	0.12	1	4	0.00	1.56	
6	6	0.00	3.18	6	6	0.00	0.33	4	1	5.41	5.16	2	5	7.07	6.94	0	6	9.46	9.75	0	6	0.00	0.12	10	5	0.00	0.12	1	5	5.41	6.11	
6	8	28.52	28.24	7	1	5.56	5.94	4	2	12.86	12.30	2	6	0.00	1.92	1	1	16.00	16.49	1	1	0.00	0.19	0	7	0.00	2.16	1	6	8.19	8.30	
7	4	18.51	18.52	7	2	6.02	2.82	4	3	7.81	7.82	2	7	0.00	1.66	1	2	15.76	16.77	1	2	12.91	11.19	0	8	0.00	0.57	2	2	0.00	2.78	
7	6	0.00	0.06	7	3	6.05	6.15	4	4	0.00	2.78	3	1	41.86	39.32	1	3	16.54	16.09	1	2	8.95	8.84	0	9	0.00	3.60	3	3	13.67	13.67	
8	0	18.61	19.01	7	4	0.00	0.66	4	5	4.74	3.47	3	2	8.89	6.27	1	4	0.00	1.51	1	3	8.95	8.84	0	10	0.00	0.55	2	4	0.00	4.87	
8	2	13.61	13.68	7	5	0.00	0.33	4	6	0.00	2.32	3	3	22.92	21.69	1	5	10.88	10.84	1	4	0.00	1.51	1	1	1.87	0.89	2	5	6.14	6.28	
8	4	4.14	4.51	7	6	0.00	2.45	5	1	8.65	8.09	3	4	6.41	6.15	1	6	0.00	1.67	1	5	8.89	8.89	1	2	12.73	11.59	3	1	10.40	10.36	
8	6	0.00	1.64	8	0	7.29	6.93	5	2	17.09	15.92	3	5	0.00	1.71	2	1	21.62	20.83	2	6	0.00	1.51	1	3	0.00	0.40	1	7	0.00	0.40	
9	2	12.16	12.23	8	1	10.04	9.91	5	3	4.87	4.24	3	6	0.00	2.99	2	1	2.29	2.39	2	0	31.15	35.26	1	1	11.46	10.96	3	3	6.74	6.98	
9	4	4.92	4.33	8	2	6.83	7.15	5	4	6.01	6.76	4	0	4.56	4.40	2	2	9.58	8.34	2	1	0.00	1.57	1	5	0.00	0.23	3	4	5.68	5.25	
10	0	10.58	10.79	8	3	0.00	8.73	5	5	0.00	3.29	4	1	0.00	0.21	3	7	0.00	0.45	2	2	21.62	20.83	2	2	0.00	0.45	1	8	0.00	0.45	
10	2	4.99	4.57	8	4	6.47	6.68	5	6	0.00	1.37	4	2	0.00	0.81	2	4	0.00	3.57	2	3	0.00	0.75	2	3	0.00	0.75	4	0	3.90	3.82	
10	4	6.62	6.97	8	5	4.02	3.82	6	0	3.28	2.75	4	3	0.00	0.85	5	2	3.83	3.00	2	4	0.00	2.52	2	1	0.00	0.39	4	1	0.00	0.39	
11	2	0.00	0.00	9	1	0.00	1.07	6	1	3.06	3.44	4	4	0.00	2.10	3	1	22.32	25.39	2	5	0.00	1.45	2	2	13.08	13.02	4	2	0.00	0.39	
11	4	0.00	1.97	9	2	3.90	2.94	6	2	9.16	8.80	4	5	0.00	1.15	3	1	11.87	11.44	2	6	0.00	2.09	2	3	0.00	2.09	4	3	0.00	2.09	
12	0	0.00	1.84	9	3	7.50	6.65	6	3	3.02	3.60	5	1	13.21	11.28	3	2	18.68	17.50	3	1	20.05	19.83	2	4	11.97	12.15	4	4	0.00	2.94	
12	2	4.99	5.04	9	4	6.26	4.45	6	4	9.52	10.08	5	2	6.86	6.43	3	3	11.85	11.44	3	2	13.52	13.49	2	5	0.00	0.61	4	5	3.81	3.83	
		K = 1		9	5	6.88	6.93	6	5	0.00	1.26	5	3	0.00	0.51	3	4	11.67	11.30	3	3	6.80	6.83	2	6	2.78	2.47	4	5	1.59	1.54	
1	1	43.16	43.06	10	0	17.24	17.99	7	6	4.20	5.04	6	4	4.85	4.12	4	4	9.68	9.70	3	4	9.68	9.70	3	1	4.99	2.41	5	6	0.00	0.94	
1	2	23.44	20.91	10	1	0.00	2.68	7	2	18.27	18.11	5	5	0.00	0.93	4	5	21.65	20.78	3	6	0.00	2.05	3	6	0.00	2.05	5	7	0.00	2.41	
1	3	15.24	14.97	10	2	3.87	2.21	7	3	10.82	10.65	5	6	0.00	1.01	4	6	0.00	1.77	3	7	0.00	1.51	3	7	3.42	2.65	5	8	0.00	0.94	
1	5	14.50	13.89	10	3	7.07	7.07	7	4	6.32	6.74	6	1	3.17	0.74	4	7	13.97	13.29	4	1	2.96	2.61	3	8	0.00	0.09	6	1	3.59	2.61	
1	7	0.00	2.30	11	1	5.08	5.24	7	5	0.00	2.87	6	2	10.28	10.37	5	2	16.30	15.82	4	2	10.01	9.92	4	2	10.01	9.92	6	2	0.00	0.09	
2	0	39.99	36.31	11	2	5.02	3.27	7	6	3.43	4.21	6	3	6.08	6.73	5	3	6.28	5.33	4	3	3.66	3.28	4	3	0.00	1.83	6	3	3.78	3.24	
2	1	25.86	25.95	11	3	0.00	0.60	8	0	4.73	5.77	6	4	0.00	1.28	5	4	9.58	9.61	4	4	0.00	1.33	4	4	0.00</						

The largest deviation from the fitted plane is 0.031 Å for the hydrogen; the average deviation is 0.015 Å.

The bonding angles and the sum of the bonding angles for the amino nitrogen show approximately trigonal planar bonding symmetry about this atom, indicating that the orbitals are sp^2 hybridized. This, together with the shortening of the N–N bond and the planarity of the nitramine group, suggests considerable π -electron delocalization analogous to that in the nitrate ion. This view is further supported by a nonempirical molecular orbital calculation (Newton, Boer & Lipscomb, 1966a) based on the geometry of the refined structure which gives a larger value for the N–N reduced overlap population (Table 4) than that calculated for pyridazine (Newton, Boer & Lipscomb, 1966b) in which the N–N

distance is approximately 1.36 Å. Also, the matrix of Mulliken overlap populations for the 78 electrons in the molecule shows that 17.2% of the value for the N–N overlap integral is due to $2P_z-2P_z$ interaction. The relative net atomic charges as given by this calculation show the nitro group to be very polar. The center of symmetry in the molecule results in an overall zero dipole moment, but the internal dipoles play an important part in the molecular packing in the structure. The normal single-bond C–N and C–C distances, the approximately tetrahedral carbon bonding angles, and the location of the hydrogen atoms at the carbon atom confirm sp^3 hybridization for carbon which precludes the extension of the delocalization to include the whole molecule.

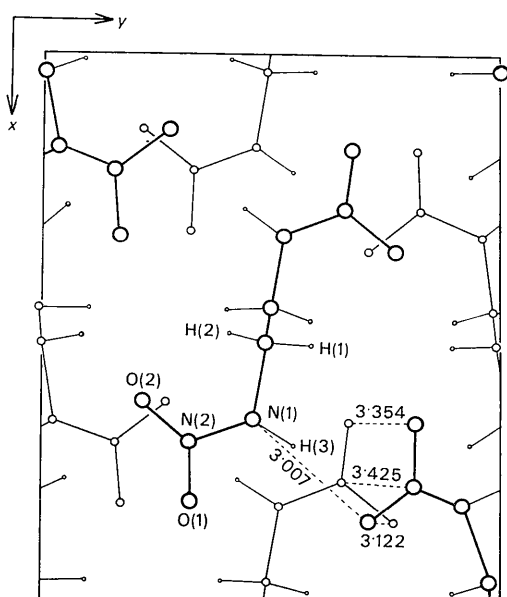


Fig. 1. Structure of N,N' -dinitroethylenediamine projected on (001). In the z direction, atoms represented by large circles lie above atoms represented by smaller circles. The smallest circles represent hydrogen atoms.

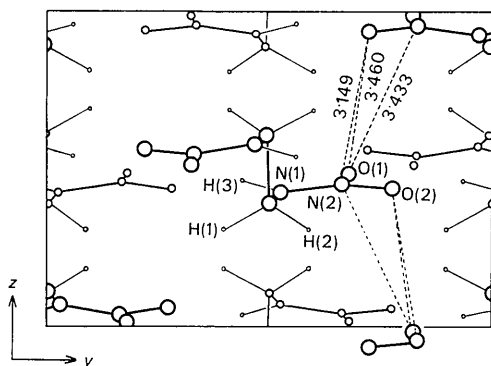


Fig. 2. Structure of N,N' -dinitroethylenediamine projected on (100). In the x direction, atoms represented by large circles lie above atoms represented by smaller circles. The smallest circles represent hydrogen atoms.

Table 4. *Reduced overlap populations and net atomic charges for EDNA*

Reduced overlap populations		Net atomic charges	
C—C	0.856	C	-0.050
C—H(1)	0.702	H(1)	+0.047
C—H(2)	0.710	H(2)	+0.058
C—N(1)	0.788	N(1)	+0.0007
N(1)—H(3)	0.607	H(3)	+0.106
N(1)—N(2)	0.904	N(2)	+1.557
N(2)—O(1)	0.771	O(1)	-0.865
N(2)—O(2)	0.782	O(2)	-0.852

Figs. 1 and 2 show the molecular packing projected on the (001) and (100) planes respectively, and the relevant intermolecular distances are given in Table 3. In Fig. 1 the molecule is seen to be extended approximately in the direction of the a axis and the packing is such that all but one of the close intermolecular distances in the structure are between nitro groups stacked in a direction parallel to the c axis. The N(2)–N(2), O(1)–O(1), and O(2)–O(2) distances are constant in this stack and have the values 3.425, 3.354, and 3.122 Å respectively. However, the planes of the stacked nitro groups are not parallel, with the result that the nitrogen in a given group is closer to the O(2) (3.149 Å) in the group above and to the O(1) (3.433 Å) in the group below than it is to the O(2) in the group below and the O(1) in the group above. Similarly, the O(1) is closer to the N(2) (3.433 Å) and the O(2) (3.460 Å) in the group above, and the O(2) is closer to the N(2) (3.149 Å) and the O(1) (3.460 Å) in the group below. These approaches are shown in Fig. 2. In this view of the packing it can be seen that the orientation of the molecules results in a general opposing of the $-\text{NO}_2$ dipoles, indicating strongly that the resultant dipole-dipole interaction is probably the predominant crystal-binding force in this structure. Fig. 2 also shows that the nitro group stacking produces alternating layers, parallel to the (010) plane, of nitro groups with high charge density and ethylene diamine groups with low charge density. One remaining short intermolecular distance in the structure is an $\text{NH}\cdots\text{O}(2)$ approach of 3.007 Å which may represent a very weak hydrogen bond, or alternatively may be only the result of the

dipole packing. Infrared and nuclear magnetic resonance spectra are inconclusive on this point. Such a hydrogen bond could conceivably play a part in determining the torsion angle about the C-N bond. This angle, as measured by the dihedral angle between planes defined by atoms C'-C-N(1) and by atoms C-N(1)-N(2), is $83.8 \pm 0.5^\circ$ and probably takes this value to allow the maximum packing density consistent with the required intermolecular spacing between nitro groups. In a biological system, the conformation of the molecule will be determined by the active site, and the torsion angle will take the corresponding required value.

Summary

The refinement of Llewellyn & Whitmore's structure for *N,N'*-dinitroethylenediamine has shown that their short C-N distance has a normal single-bond value and that their short N-N distance is even shorter in the refined structure. In preference to a discussion based on resonance structures, an interpretation of the molecular structure in terms of atomic orbitals has led to a satisfactory description of the nitramine group in which the overlapping of atomic orbitals is seen as contributing considerable double-bond character to the N-N bond. In addition, strong dipole-dipole interaction has been suggested as the predominant crystal-binding force in the crystal structure.

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