262. *The Crystal Structure of* s-*Bisnitroaminoethane* (*Ethylene Dinitroamine*).

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The crystal structure of *s*-bisnitroaminoethane has been completely determined by *X*-ray crystallographic methods utilising all the (*hkl*) diffracted beams obtainable with Cu-$K\alpha$ radiation. The molecular disposition is such that the atomic centres are confined to laminæ, parallel to (001), approximately 1·72 A. in thickness. Interatomic distances are C–C = 1·52, C–N = 1·41, N–N = 1·33, N–O = 1·21 A. There appears no doubt that the shortening of the N–N bond is attributable to the development of positive charges on both the nitrogen atoms; two possible resonance mechanisms, one of which violates Pauling's adjacent charge rule and is therefore considered the more improbable, provide a reasonable explanation of the bond lengths.

THERE is practically no information in the literature concerning the size and shape of the nitroamine grouping, and since various substances containing this group have achieved considerable importance in the last few years it was deemed worth while to initiate an investigation of some of the simpler organic nitroamine compounds. Moreover, Costain and Cox (*Nature*, 1947, **160**, 826) have examined the structure of dimethylnitroamine and their results reveal some striking anomalies in bond lengths; in particular, the N–N separation is considerably smaller than the sum of the single-bond covalent radii of the two nitrogen atoms. An investigation of the structure of *s*-bisnitroaminoethane is therefore desirable in order to determine, amongst other things, whether or not the anomalies observed in dimethylnitroamine are peculiar to that substance.

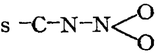
Preliminary Crystallographic Data.—*s*-Bisnitroaminoethane crystallises in the orthorhombic holohedral class with variable habit. Crystals exhibiting only {111} can be obtained readily by slow evaporation of an alcoholic solution. Optical measurements reveal (i) that (100) is the optic axial plane and (ii) that the refractive indices are $\alpha = 1{\cdot}427$, $\beta = 1{\cdot}686$, $\gamma = 1{\cdot}730$. The unit cell, determined by rotation photographs about the three principal axes, is defined by

$[a] = 10{\cdot}67$, $[b] = 8{\cdot}67$, $[c] = 6{\cdot}16$ A., the calculated density is $0{\cdot}439n$, and as that observed by flotation is 1·75 g./c.c., $n = 4$.

Series of oscillation photographs about the $[a]$, $[b]$, and $[c]$ axes exhibit the following systematic halvings: $(h0l)$ absent when $l \neq 2n$, $(0kl)$ absent when $k \neq 2n$, $(hk0)$ absent when $h \neq 2n$, whence the space-group is *Pbca*. This space-group accommodates 8 general positions, and since there are only four molecules in the unit cell it follows that the molecular symmetry is that of the four-fold special positions. There are two sets of four-fold special positions each of which is centrosymmetric; the choice between them is arbitrary, depending only upon a choice of the origin. The molecule is therefore located so that the centre of the carbon–carbon bond is coincident with the centre of symmetry [taken for convenience at (000)] and it is only necessary,

hkl.	F (calc.).	F (obs.).	*hkl.*	F (calc.).	F (obs.).	*hkl.*	F (calc.).	F (obs.).	*hkl.*	F (calc.).	F (obs.).
200	−80·7	60·8	911	− 1·9	<6·5	271	− 9·3	10·4	232	10·9	11·1
400	−26·7	23·9	1011	− 1·9	<6·5	371	− 8·3	13·1	332	− 6·1	7·7
600	74·7	82·0	1111	− 5·4	4·6	471	0	< 6·5	432	0·3	< 4·9
800	−16·8	20·9	1211	− 1·4	6·4	571	5·3	7·0	532	− 7·1	7·0
1000	−15·6	14·3	021	−18·6	17·2	671	− 2·9	< 6·3	632	− 9·4	10·7
1200	2·3	12·4	121	−73·6	62·1	771	4·3	< 4·5	732	5·7	5·8
210	−41·2	38·2	221	10·8	11·9	871	− 4·9	4·2	823	3·8	< 5·8
410	13·1	13·6	321	32·6	29·4	081	−26·9	16·5	932	1·8	< 5·8
610	6·1	9·9	421	− 6·9	5·0	181	−29·7	36·5	1032	3·6	< 5·7
810	4·6	7·2	521	5·1	10·2	281	4·2	< 4·2	1132	4·2	< 5·2
1010	−18·3	19·0	621	− 2·8	< 5·3	381	0·2	4·2	042	13·6	19·4
1210	12·5	9·9	721	−20·6	21·7	481	2·2	3·9	142	−21·9	21·8
020	−19·6	23·6	821	3·3	11·9	581	13·0	16·1	242	10·1	8·7
220	64·4	58·6	921	9·9	11·5	681	− 5·0	6·2	342	−22·1	19·8
420	30·8	37·7	1021	1·1	< 6·6	781	−11·1	11·1	442	−16·2	14·6
620	− 2·9	< 4·0	1121	0·2	< 5·9	191	1·8	< 6·1	542	7·0	7·7
820	− 9·0	4·6	131	67·1	57·0	291	1·5	< 6·0	642	9·6	10·7
1020	− 1·8	< 4·2	231	−26·5	25·6	391	6·4	10·5	742	−15·2	13·8
1220	− 0·1	6·2	331	−43·1	39·5	491	− 4·4	4·6	842	4·1	< 4·5
230	15·8	23·6	431	− 3·3	< 4·7	591	1·3	< 4·7	942	−11·3	10·7
430	0·4	5·4	531	13·8	14·4	0101	12·0	12·4	1042	− 8·3	2·7
630	−16·1	20·2	631	− 1·8	< 5·6	1101	10·8	9·5	152	−14·5	15·8
830	2·4	< 4·1	731	31·9	36·6	002	158·4	84·4	252	−25·1	26·9
1030	6·1	7·7	831	−16·8	19·6	102	−91·6	68·8	352	14·2	15·2
040	53·8	59·5	931	−31·5	35·0	202	−70·7	62·4	452	13·0	11·5
240	26·3	22·9	1031	2·3	< 6·3	302	−15·3	11·6	552	− 0·2	< 4·8
440	−19·6	25·8	041	− 8·3	10·1	402	−24·1	24·4	652	7·9	13·7
640	21·1	25·4	141	22·6	19·1	502	15·3	14·5	752	−12·2	15·8
840	1·5	< 4·1	241	− 4·4	3·3	602	45·3	37·8	852	−16·9	18·4
1040	−14·2	13·0	341	−31·0	28·1	702	−30·2	29·3	952	9·0	10·0
250	−40·5	45·2	441	10·6	10·2	802	−11·4	14·5	1052	1·0	4·6
450	6·0	20·9	541	14·6	15·2	902	−11·5	11·6	062	30·1	34·5
650	13·5	23·5	641	− 7·4	9·1	1002	7·9	< 6·5	162	−13·8	14·0
850	−15·7	36·1	741	5·6	6·2	1102	4·0	< 5·9	262	−17·9	16·9
1050	12·0	15·0	841	− 1·2	< 6·0	112	−23·3	22·3	362	0·8	< 6·0
060	53·8	48·0	941	−13·1	13·5	212	−16·2	16·3	462	6·5	7·7
260	−15·4	22·1	1041	4·0	5·0	312	31·6	28·7	562	− 8·8	7·9
460	14·4	15·8	1141	5·6	5·8	412	3·5	< 4·3	662	7·7	9·3
660	10·6	14·9	151	4·1	5·3	512	− 5·5	6·4	762	−10·2	10·0
860	−13·4	17·6	251	− 4·2	< 5·3	612	4·0	3·9	862	− 9·4	9·3
270	0	< 4·1	351	24·0	25·4	712	−25·4	27·3	962	− 5·6	9·5
470	0·4	< 4·1	451	− 4·6	< 5·6	812	5·1	8·5	172	− 4·9	5·0
670	− 7·7	11·4	551	8·0	7·0	912	− 2·0	< 6·5	272	3·4	4·6
870	5·9	< 4·6	651	−10·4	12·5	1012	−14·3	13·6	372	4·5	4·6
080	− 1·8	< 3·9	751	−13·0	12·3	1112	6·7	6·4	472	− 1·6	5·4
280	14·2	17·8	851	−12·8	12·9	1212	10·0	5·8	572	− 6·6	7·1
480	1·5	< 4·3	951	4·5	< 6·3	022	−43·0	37·8	672	− 4·9	8·3
680	1·6	< 4·3	1051	− 1·5	3·0	122	3·4	3·3	772	2·5	< 5·9
290	− 9·2	12·6	061	− 3·3	< 5·7	222	32·0	23·1	872	7·8	< 4·6
490	6·1	8·7	161	− 3·2	< 5·7	322	−15·7	10·0	082	− 7·5	5·4
0100	3·2	9·7	261	0·2	< 5·9	422	13·1	13·4	182	0·1	5·0
111	41·8	41·0	361	4·8	4·3	522	−16·7	18·9	282	7·9	8·3
211	−28·4	24·9	461	− 2·2	< 6·3	622	− 8·8	9·1	382	− 6·3	6·4
311	2·9	2·7	561	− 1·5	< 6·5	722	−18·5	19·7	482	− 0·4	7·0
411	− 0·4	< 2·6	661	− 2·4	< 6·6	822	3·1	< 6·2	582	− 3·3	< 5·6
511	25·2	29·6	761	− 8·3	11·5	922	2·4	< 6·0	682	− 2·7	5·4
611	−17·1	18·3	861	3·0	< 6·1	1022	5·5	< 5·7	782	− 4·4	3·9
711	− 6·4	5·0	961	5·9	6·2	1122	0·6	< 3·9	192	− 4·4	4·3
811	−10·1	9·5	171	18·0	21·7	132	4·1	6·4	292	− 5·7	5·8

hkl.	F (calc.).	F (obs.).	*hkl.*	F (calc.).	F (obs.).	*hkl.*	F (calc.).	F (obs.).	*hkl.*	F (calc.).	F (obs.).
392	4·2	4·6	363	2·8	< 6·2	534	− 5·2	< 6·1	235	−10·6	6·4
492	5·0	4·6	463	3·9	< 6·3	634	0·6	< 5·5	335	− 8·5	6·4
113	−15·8	17·1	563	0·3	< 6·3	734	5·9	4·6	435	5·9	< 6·0
213	−30·7	23·1	663	2·6	< 6·1	834	1·9	< 4·6	535	− 0·1	< 5·2
313	0	4·6	763	1·5	< 5·9	934	1·1	< 4·1	635	9·8	12·1
413	6·0	7·7	863	6·0	< 5·1	044	−18·9	17·8	735	0·6	< 4·5
513	− 2·2	4·7	963	3·4	< 4·3	144	−11·5	10·1	835	−13·3	10·6
613	−17·7	17·1	173	− 0·3	< 6·1	244	− 8·7	8·7	045	1·2	< 5·0
713	5·8	5·0	273	−14·6	15·8	344	−12·2	12·1	145	15·2	10·7
813	−11·4	7·0	373	− 5·9	7·0	444	− 6·0	9·5	245	− 6·1	4·6
913	7·5	5·4	473	3·6	< 6·1	544	12·8	9·7	345	− 1·3	< 4·8
1013	1·4	< 5·5	573	0·6	< 5·8	644	− 4·3	< 4·8	445	9·7	7·9
1113	1·9	< 5·1	673	3·2	< 5·2	744	− 7·1	4·6	545	− 7·2	4·8
203	−25·7	28·1	773	0·8	< 4·6	844	4·1	< 4·0	645	4·8	< 4·8
123	−36·8	24·8	083	−22·2	26·6	944	1·1	< 3·5	745	4·5	< 4·3
223	19·5	18·1	183	−12·7	12·1	154	− 9·5	10·0	155	−10·2	9·3
323	16·5	11·8	283	8·3	9·1	254	2·5	< 5·1	255	4·4	< 6·1
423	−10·1	7·0	383	2·7	< 6·2	354	11·8	8·5	355	2·0	< 6·0
523	4·6	6·2	483	5·4	6·2	454	4·6	< 6·0	455	1·0	< 5·8
623	− 2·8	5·8	583	6·7	< 5·1	554	1·4	< 5·2	555	− 6·0	5·0
723	−10·9	10·2	193	− 2·0	< 5·1	654	3·1	< 4·6	065	1·8	< 5·9
823	6·1	5·0	293	4·6	5·0	754	2·9	< 4·2	165	1·4	< 5·5
923	6·7	5·0	393	− 2·2	3·3	854	4·2	< 3·6	265	1·0	< 5·1
1023	2·9	< 4·9	004	15·1	11·6	064	5·3	< 5·4	365	0·8	< 4·6
1123	0·8	< 4·5	104	−63·4	44·0	164	−11·7	14·4	465	3·1	< 4·1
133	5·5	6·8	204	−32·6	24·2	264	−14·0	14·0	175	− 6·9	5·8
233	−23·1	29·6	304	0	< 5·3	364	5·8	5·4	275	− 7·9	6·2
333	−26·2	24·2	404	− 8·5	5·4	464	3·0	< 5·4	006	− 8·8	8·5
433	1·2	< 4·9	504	20·5	17·4	564	4·4	< 5·3	106	−19·9	19·4
533	0·4	< 5·0	604	7·5	4·3	664	2·6	< 4·9	206	− 3·3	< 5·9
633	3·6	4·6	704	−16·6	12·8	174	−10·5	11·5	306	7·1	7·0
733	13·6	12·3	804	− 3·6	< 4·8	274	6·9	7·0	406	2·7	< 5·7
833	−25·0	23·7	904	− 7·0	4·7	374	3·7	4·2	506	11·6	8·0
933	−12·7	10·2	1004	3·4	< 4·1	474	− 6·7	3·3	606	3·2	< 4·2
1033	4·8	4·6	114	−16·5	14·7	574	4·9	< 4·0	116	− 4·9	5·8
043	− 9·2	5·4	214	8·8	7·7	084	−10·7	10·1	216	12·2	9·2
143	21·8	20·7	314	23·0	19·8	184	1·9	< 4·6	316	7·6	5·4
243	− 6·7	7·0	414	−10·5	7·1	284	0	< 3·5	416	− 8·4	7·0
343	−12·2	12·1	514	− 5·1	4·6	384	− 4·0	2·7	516	0·2	< 4·7
443	16·8	17·1	614	0·5	< 4·7	115	−17·0	12·7	026	−11·1	6·4
543	− 8·0	< 6·4	714	− 3·9	< 5·8	215	− 5·8	4·3	126	10·5	9·3
643	−11·7	9·7	814	7·3	5·8	315	4·4	< 5·1	226	10·2	9·7
743	9·1	6·4	914	− 3·1	< 5·9	415	8·5	7·9	326	2·3	5·4
843	− 3·1	6·2	1014	− 8·1	5·4	515	− 8·5	6·2	426	1·4	< 4·7
943	5·0	− 6·0	024	−35·3	30·8	615	2·7	< 5·8	526	3·7	< 4·3
1043	0·8	− 5·1	124	10·5	11·7	715	− 3·0	< 5·4	136	3·2	< 5·8
153	−13·3	10·4	224	1·0	< 5·3	815	1·8	< 4·9	236	1·3	< 5·7
253	− 2·3	< 5·5	324	− 4·6	6·4	915	9·0	6·4	336	3·4	< 5·5
353	7·6	7·5	424	− 1·6	< 5·5	025	−12·9	12·2	436	0·5	< 4·9
453	− 4·9	< 6·0	524	− 6·4	6·2	125	− 5·1	5·4	536	1·3	< 4·2
553	− 2·5	< 6·3	624	−10·8	8·1	225	11·6	11·7	046	−13·2	11·2
653	−14·7	15·0	724	− 7·0	6·4	325	10·5	11·1	146	0	< 5·3
753	6·9	< 5·9	824	6·0	5·0	425	− 6·6	5·0	117	3·9	< 3·9
853	0·2	< 5·7	924	2·5	< 4·2	525	4·3	< 5·2	217	3·9	< 3·7
953	7·0	< 4·9	134	5·0	5·0	625	0·9	< 4·9	027	− 5·9	4·3
063	2·2	< 5·9	234	3·2	4·6	725	3·2	< 4·3			
163	0·5	< 5·9	334	− 5·9	5·8	825	4·1	< 4·1			
263	1·3	< 6·0	434	0·3	< 6·1	135	− 8·3	7·7			

in order to define the structure, to determine the 15 parameters of the atoms  $-\mathrm{C}-\mathrm{N}-\mathrm{N}\langle{}^{\mathrm{O}}_{\mathrm{O}}$ (the positions of the hydrogen atoms on the carbon and the first nitrogen cannot be determined directly by means of *X*-rays).

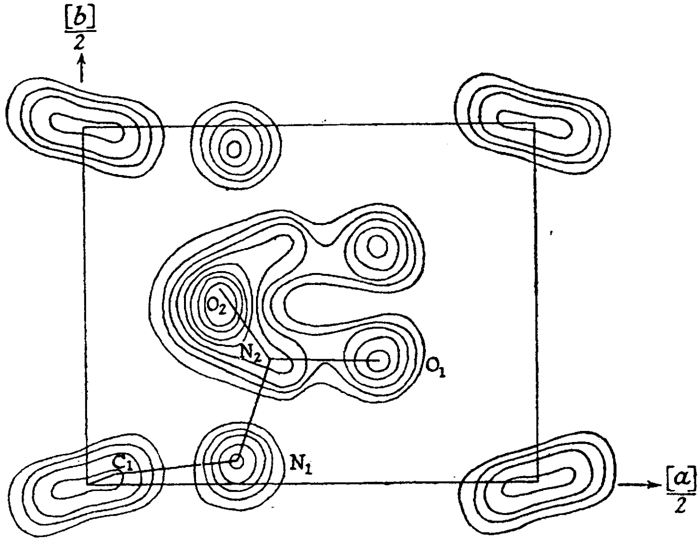
Measurement of Intensities.—The intensities of all the (*hkl*) diffracted beams observed with Cu-$K\alpha$ radiation were measured, on an arbitrary scale, by comparison of the photographic density produced by the beams, under standard development conditions, with photographic spots on a standard comparator. From these intensities structure amplitudes (F), still on an arbitrary scale, were calculated by means of the relation $F = IDp/L$, where I = intensity, D = Cox and Shaw's angular velocity correction, p = polarisation factor, and L = Lorentz factor.

These structure amplitudes were rendered absolute by recording on the same film, and with equal exposure, a set of (*h*0*l*) diffractions from a small crystal of *s*-bisnitroaminoethane and a selected set of (*h*0*l*) diffractions from a similar crystal of pentaerythritol tetranitrate. As the crystals chosen were of the same size and almost equal density (density of pentaerythritol tetranitrate = 1·77 g./c.c.), direct comparison of the densities of the two sets of recorded spots made calculations of absolute structure factors for the bisnitroamine possible, since those for pentaerythritol tetranitrate had previously been obtained by comparison with rock-salt.

A list of the absolute structure amplitudes used in this determination, together with the values and phase angles calculated from the final co-ordinates, is shown in the table.

Determination of the Structure.—The structure amplitude of the plane (002) is large whilst that of (004) is very small; this observation, coupled with the observed cleavage parallel to (001), lends support to the view that the molecule is arranged approximately in the *c*-plane. Preliminary investigations were therefore confined to Fourier projections on to the *c*-plane using only the F_{hk0} structure amplitudes, and to Patterson sections, using all the F_{hkl} terms available, parallel to the *c*-plane. A Patterson three-dimensional section parallel to 001 at $z = \frac{1}{2}$ should produce maxima at $(2x_r2y_r)$ where (x_ry_r) represent the (xy) co-ordinates of an atom. Actually, such a section produced a contour map of considerable complexity which proved of no value in determining atomic co-ordinates.

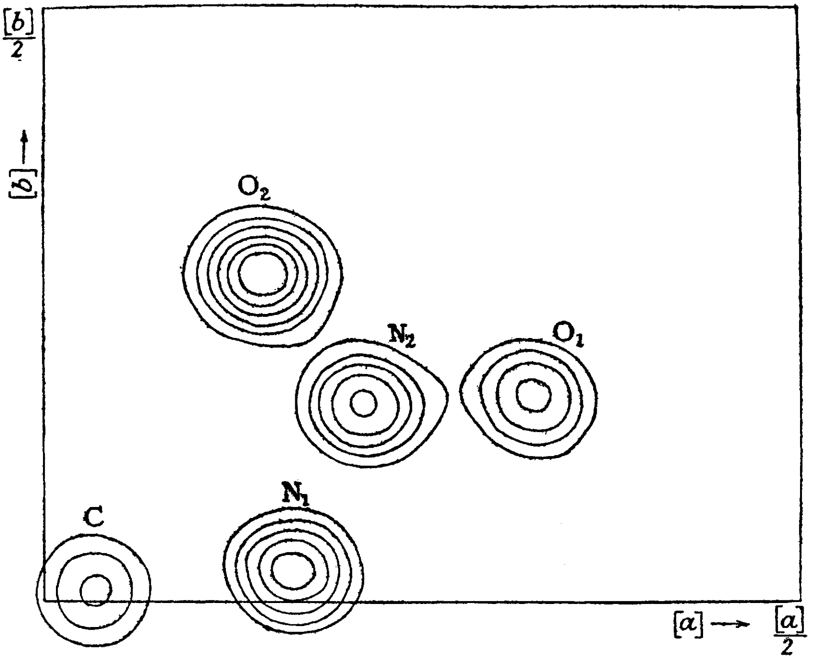
FIG. 1.



Projection on c-*face. The lowest contour represents* 1 *electron*/A.^{2}.

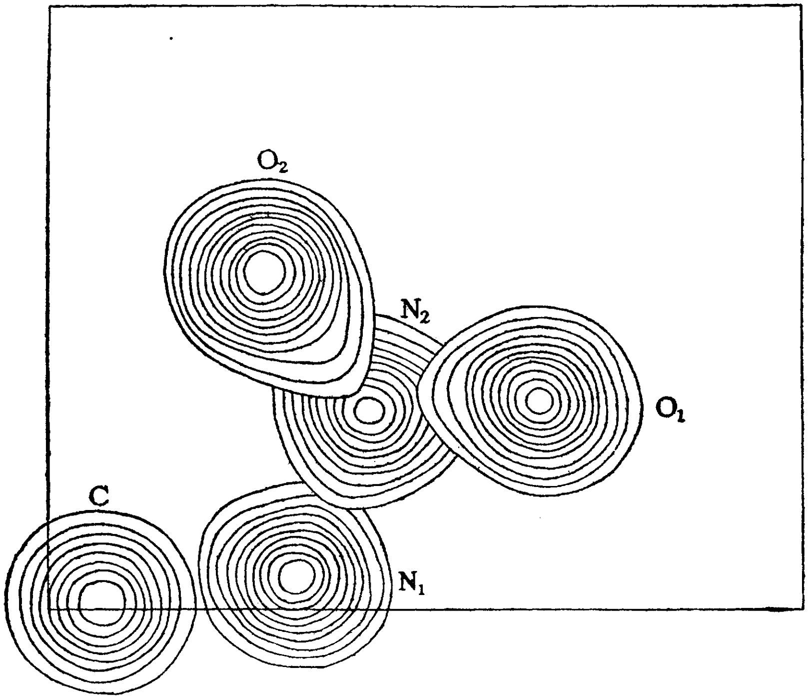
Use was then made of the method of trial and error using the Bragg structure amplitude charts which proved valuable in the case of pentaerythritol tetranitrate (Booth and Llewellyn, *J.*, 1947, 837), and after persistent application, a structure which gave calculated structure amplitudes in excellent agreement with the observed values of the *hk*0 planes was derived. The *xy* co-ordinates obtained in this manner were refined by successive two-dimensional Fourier projections on (001), using eventually all the *hk*0 structure amplitudes. The final projection is illustrated as a contour diagram in Fig. 1. On the basis of normal bond distances, *z* co-ordinates were calculated from these *xy* co-ordinates and refined by means of three-dimensional Fourier lines parallel to the *c*-axis, and passing through the *xy* co-ordinates of each atom. From these *z* co-ordinates the molecule spreads out very approximately in a plane parallel to (001), but it is not sufficiently flat to allow all the atoms to appear in a Fourier section at the mean *z* co-ordinate. Further refinement of the *xy* co-ordinates was effected therefore in the first instance by a three-dimensional Fourier section projection (Booth, *Trans. Faraday Soc.*, 1945, **41**, 434) between the limits $z_2 = 0{\cdot}12$ and $z_1 = -0{\cdot}02$. The final section projection is illustrated as a contour map (the contours are at arbitrary heights) in Fig. 2. The atoms C and O$_1$, both being near the limits of the section projection, give rise to peaks of smaller magnitudes than the other atoms. The final set of atomic co-ordinates was obtained, all the (*hkl*) structure

FIG. 2.



Section-projection between the limits $z = -0{\cdot}02$ *and* $z = 0{\cdot}12$.

FIG. 3.



Composite electron-density map of the three-dimensional sections parallel to the c-*face. The lowest contour represents* 1 *electron*/A.^{3}.

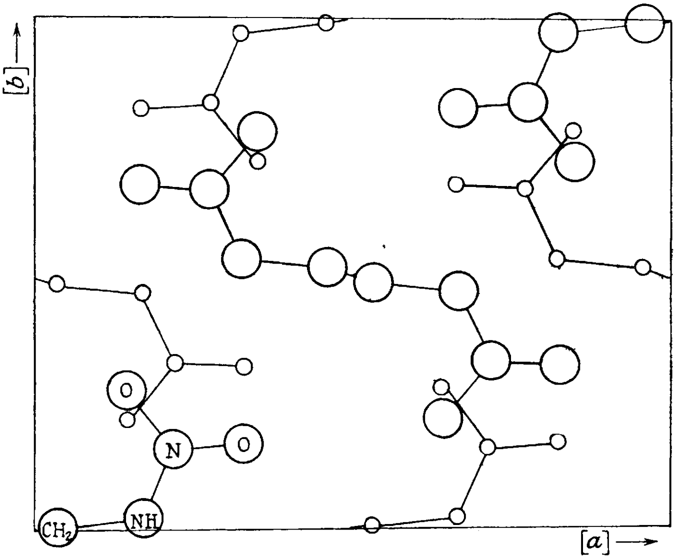
Final atomic co-ordinates.

C	0·035	0·005	0·107	O_1	0·327	0·173	0·014
N_1	0·165	0·028	0·074	O_2	0·146	0·278	0·057
N_2	0·215	0·167	0·043				

amplitudes being used, by computing successive sets of three-dimensional Fourier lines parallel to the [*c*] and three-dimensional Fourier sections parallel to (001) at the appropriate *z* co-ordinates until no further change in phase resulted. The various Fourier sections are plotted as a composite electron-density map in Fig. 3.

Discussion of the Structure.—The molecular orientation, viewed along the [*c*]-plane, is illustrated in Fig. 4; the larger atoms belong to molecules associated with symmetry centres in the plane of the paper, and the smaller atoms to molecules associated with centres halfway up the [*c*]. Fig. 5, which represents the view of the structure along the (*b*) axis, illustrates clearly the layer-like arrangement of the molecules. The atomic centres are all located in slabs lying parallel to the *c*-face, of thickness 1·32 A. It is also noteworthy that the form (001) develops largely in a number of the crystalline habits and that cleavage, admittedly poor, has been observed parallel to this direction.

FIG. 4.

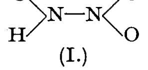


Molecular orientation viewed along the c-*axis. The atoms represented by the large circles refer to molecules having symmetry centres at* $z = 0$; *the small circles represent atoms of molecules having symmetry centres at* $z = \frac{1}{2}$.

The molecule itself is centrosymmetrical; the interatomic distances and bond angles calculated from the final atomic co-ordinates are :

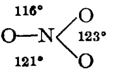
C–C	1·52 A.	N_2–O_1	1·21 A.	C–C–N_1	111° 26′	N_1–N_2–O_2	118° 9′
C–N_1	1·41 A.	N_2–O_2	1·21 A.	C–N_1–N_2	123° 9′	O_2–N_2–O_1	125° 21′
N_1–N_2	1·33 A.			N_1–N_2–O_1	117° 18′		

The sum of the three bond angles around N_2 is 360° 48′, in very close agreement with value, 360°, to be expected if the four atoms lie in a plane. The perpendicular distance of the carbon atom C_1 from the plane containing the nitroamine grouping is small and is within the probable experimental error (estimated at ± 0·02 A.; Booth, *Nature*, 1945, **51**, 156); the whole grouping (I) therefore is planar. This is in agreement with the results obtained by Cox in the dimethylnitroamine structure, where the molecule actually lies on a crystallographic plane of symmetry.

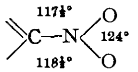


(I.)

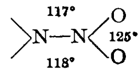
The two oxygen atoms of the nitroamine grouping are each separated from the nitrogen atom N_2 by a distance of 1·21 A.; this is somewhat shorter than the bond length observed in pentaerythritol tetranitrate (1·28 A.) and in *p*-dinitrobenzene (1·23 A.), but agrees with the value found in nitromethane. Despite these divergences in bond lengths and the different natures of the third bond to the nitrogen atom, the shape of the nitro-group remains remarkably similar in the three compounds :



Pentaerythritol tetranitrate.



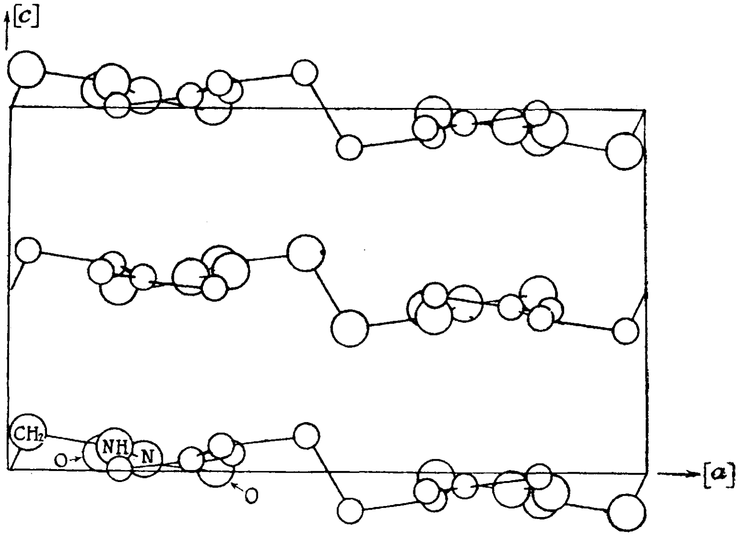
p-Dinitrobenzene.



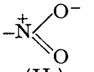
s-Bisnitroaminoethane.

The carbon–carbon separation of 1·52 A. is again shorter than in diamond (Bragg and Bragg, *Proc. Roy. Soc.*, 1913, *A*, **89**, 277) and in various hydrocarbons, but it falls into line with that found in a number of other organic molecules, *viz.*, 1·50—1·52 A. The carbon–nitrogen separation of 1·41 A. agrees exactly with that found in *p*-dinitrobenzene (Llewellyn, *J.*, 1947, 884), but it is considerably shorter than the calculated value (1·47 A.) obtained by summing the accepted covalent radii of nitrogen and carbon. If it is assumed that the covalent radius of carbon is 0·76 A., then the radius of the nitrogen atom of the nitro-group in *p*-dinitrobenzene and of the first nitrogen in the bisnitroamine is 0·65 A. In the first compound the resonance between the two structures (II) and (III) necessitates the development of a formal positive charge on the nitrogen atom and this would be expected to lead to a change in the covalent radius towards that of oxygen. Pauling (" The Nature of the Chemical Bond ", p. 169) suggests a decrease in the single-bond radii of N in these circumstances of 0·02 A.; Elliot (*J. Amer. Chem. Soc.*, 1937, **59**, 1380) has shown that the N–O bond in the nitrate ion is 0·03 A. shorter than the expected value and attributes this also to the development of a formal positive charge on the nitrogen atom. The conclusion to be drawn, then, from the observed length of the C–N bond in the bisnitroamine is that there is an electronic drift, involving the loan pair of electrons on this first nitrogen atom, presumably towards the electrophilic nitro-grouping, leaving the nitrogen positively charged. The nitrogen–nitrogen separation (1·33 A.) is also less than the sum of the single-bond covalent radii of two nitrogen atoms (1·40); this shortening may be due to the existence of a resonance hybrid (IV), in which each nitrogen atom carries a formal positive charge and the two are linked by a double bond. Alternatively, it may be postulated that the

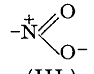
FIG. 5.



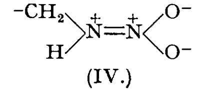
Molecular orientation viewed along the b-*axis. The atoms represented by the large circles refer to molecules having symmetry centres at y* = 0; *the small circles represent atoms of molecules having symmetry centres at y* = ½.



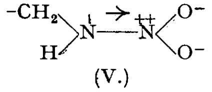
(II.)



(III.)

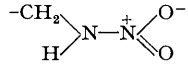


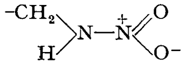
(IV.)

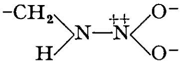


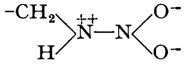
(V.)

tendency for the amine nitrogen to lose its electrons increases the polar nature of the nitro-group as in (V), and that the loan pair of electrons orginally on the amine nitrogen distribute themselves between the two nitrogens, leaving both with incomplete octets. In such a mechanism there is no need of a double bond between the two nitrogen atoms since the formal positive charge on each together with the incomplete octet would account for the observed bond length. The participating resonance forms of the molecule could then be written as in (*A*)—(*D*). The observed inter-bond angles do not favour either mechanism; the angles CN_1N_2 is 123° and both angles NNO approximate to 117°; since the whole grouping is planar, it appears that both nitrogens dispose three bonds at 120° intervals distorted in the instance of the second atom by the negative charges on the oxygens; alternatively, the approximate 120° disposition is also explained by the existence of the double bond between the two nitrogen atoms.

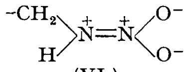

(*A*.)


(*B*.)


(*C*.)


(*D*.)

That the resonance hybrid (VI) does not contribute largely to the structure can be readily shown by calculating the extent of double-bond character of the N–N bond and neglecting any shortening effect attributable to the development of positive charges. The N–N single bond separation being taken as 1·40 A., and the double bond as 1·23 A., then the observed bond distance of 1·33 A. is compatible with *ca.* 15% double-bond character. This figure represents the maximum contribution of the double-bond resonance form; most probably its contribution is very much less.


(VI.)

On balance, then, it appears that the resonance mechanism involving doubly-charged nitrogen atoms is the more probable.

The results of this structure determination, whilst they demonstrate conclusively the planar nature of the nitroamine group and establish the existence of a short N–N bond, do not provide sufficient data to establish unequivocally the nature of the chemical bonds involved. Further work is to be undertaken on this point. In particular, it is hoped that an examination of a suitable substance, involving both a nitrate and a nitroamine grouping so disposed that the occurrence of the double bonds which have been suggested may form a conjugated system, will provide the additional information.

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THE UNIVERSITY, BIRMINGHAM, 15. [*Received, October* 20*th*, 1947.]