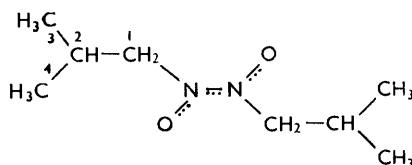


**716.** *The Crystal Structure of the trans-Dimer of Nitrosoisobutane.*

By HANS DIETRICH AND DOROTHY CROWFOOT HODGKIN.

The crystal structure of the *trans*-dimer of nitrosoisobutane has been determined by the calculation of the electron density in three projections. The molecule is centrosymmetric, the  $N_2O_2$  group is planar, with N-N,  $1.27 \pm 0.02$  Å, and N-O,  $1.30 \pm 0.02$  Å.

THE molecular structure of dimeric nitroso-compounds is of considerable theoretical interest, particularly in relation to the nature of the N-N bond connecting the two monomers. The discovery that the dimers of certain aliphatic nitroso-compounds can be obtained in *cis*- and *trans*-forms<sup>1</sup> shows that there is no free rotation around the N-N



bond and suggests this bond has considerable double-bond character. Evidence bearing on this view has been discussed recently by Gowenlock and Lüttke;<sup>2</sup> to this we now add X-ray data on the molecular structure of one of the aliphatic nitroso-compounds prepared by Gowenlock and Trotman,<sup>3</sup> the *trans*-dimer of nitrosoisobutane.

#### EXPERIMENTAL

The crystals of the *trans*-dimer of nitrosoisobutane are fragile, colourless, transparent monoclinic plates up to 1 mm. in length. The measured unit-cell dimensions are  $a = 8.84$ ,  $b = 9.93$ ,  $c = 6.14$  Å, and  $\beta = 96.17^\circ$ , the space group  $P2_1/c$ ;  $\rho$  (calc.) = 0.927, for  $M = 348$ ;  $F_{000} = 192$ . These figures correspond with the presence of two molecules of the dimer in the unit cell and imply that the dimer molecule itself is centrosymmetrical.

<sup>1</sup> Chilton, Gowenlock, and Trotman, *Chem. and Ind.*, 1955, 538; Gowenlock and Trotman, *J.*, 1955 4190.

<sup>2</sup> Gowenlock and Luttke, *Quart. Rev.*, 1958, **12**, 321.

<sup>3</sup> Gowenlock and Trotman, *J.*, 1956, 1670.

All the crystals examined were twinned, (100) being the twinning plane. The intensities of the X-ray reflections were recorded on Weissenberg photographs and measured by eye estimation, the multiple-film technique being used. Some overlapping of reflections from the twin components occurred for reflections other than the  $hk0$  series. This overlapping confused the intensity measurements of general reflections; it was allowed for in the zones studied by the examination of a few crystals where the twin components were noticeably unequal in weight; it led to the decision not to study this crystal structure by three-dimensional methods.

The measured intensities were corrected for the Lorentz and polarization effects but not for absorption or extinction; they were placed on an approximately absolute scale by Wilson's method and re-scaled later by comparison with the calculated values. The  $F$  values so derived for the different zones studied are recorded in Table 1. They are subject to rather different errors owing to the irregular shapes of the crystals used. The  $F^2$  values were sharpened to correspond approximately with those to be expected from atoms at rest before the calculation of the Patterson series.

TABLE 1. *Observed and calculated structure factors for trans-dimer of nitrosoisobutane (unobserved reflections omitted).*

Indices	$F_{obs}$	$F_{calc}$	Indices	$F_{obs}$	$F_{calc}$	Indices	$F_{obs}$	$F_{calc}$	Indices	$F_{obs}$	$F_{calc}$	Indices	$F_{obs}$	$F_{calc}$	Indices	$F_{obs}$	$F_{calc}$
[001] zone			[001] zone			[001] zone			[010] zone			[101] zone			[101] zone		
020	60.8	69.8	3100	3.6	1.6	760	3.3	3.8	402	17.7	15.8	040	12.1	-11.9	343	1.5	-2.2
040	13.5	-13.0	400	4.9	-2.6	800	9.1	8.8	502	14.9	16.6	060	5.8	-5.9	353	5.2	4.7
060	6.2	-6.9	410	8.8	-8.0	820	4.7	4.5	602	20.4	20.4	080	3.8	5.2	363	1.0	-1.5
080	4.2	4.8	420	9.2	10.6	830	3.7	4.2	802	7.8	-7.2	0100	4.0	5.5	373	2.5	2.0
0100	4.2	4.8	430	10.1	-11.4				004	6.9	10.3	0120	2.1	2.7	383	1.6	1.6
100	36.7	45.0	440	17.5	17.7	[010] zone			104	3.9	-2.5	111	17.0	15.8	393	1.0	0.4
110	12.9	-14.9	450	4.8	-6.1	100	36.8	45.1	204	5.7	-8.2	121	9.1	-9.1	3103	1.6	1.5
120	31.4	36.1	460	15.1	13.9	200	5.7	-2.9	404	8.9	-8.0	131	18.7	-17.2	404	10.5	-9.6
130	24.6	-24.2	480	7.9	5.8	300	27.2	26.8	504	7.4	-8.2	141	2.9	-3.1	414	1.9	1.8
140	11.6	10.2	500	13.0	-11.9	400	5.8	-2.8	704	2.8	-3.0	151	7.3	-7.7	424	7.1	-5.8
150	17.0	-14.5	510	6.8	7.0	500	14.0	-12.6	804	3.2	-3.0	161	1.1	1.8	444	1.2	-0.8
200	4.6	-3.0	520	6.4	-5.6	600	9.0	-14.0	904	14.2	-11.2	171	0.9	0.9	454	1.5	-1.6
210	11.0	-9.1	530	4.8	5.1	700	5.0	5.0	104	12.9	-10.9	1101	0.7	-1.0	464	0.9	0.5
220	11.6	10.4	540	6.9	7.3	800	9.9	10.9	504	8.2	-7.8	1111	1.4	-1.6	474	0.7	0.7
230	22.7	-21.4	550	2.2	-4.3	900	1.8	2.2	604	13.2	-12.1	202	4.2	4.7	494	2.0	2.4
240	10.0	10.5	560	9.9	9.3	1000	2.8	4.0	704	4.8	-3.5	212	13.2	12.6	4101	0.8	-1.3
250	11.9	-10.7	580	5.1	4.3	1100	2.7	4.8	106	3.9	-4.6	222	8.2	8.4	515	8.0	7.1
290	5.8	6.1	600	8.3	-8.4	002	49.3	-66.2	206	4.6	2.5	232	24.1	24.4	525	3.8	2.8
300	25.9	-26.0	640	7.1	7.0	102	6.6	-5.4	306	3.3	-2.4	242	10.5	11.8	535	2.8	2.9
310	30.2	-30.8	650	5.7	5.5	202	13.1	15.5	106	2.8	-2.3	252	10.2	10.5	545	1.8	1.0
320	15.0	16.2	660	6.0	6.2	302	6.0	-4.6	206	5.6	-5.4	262	6.7	6.8	506	0.8	0.5
330	31.8	-32.6	700	4.3	4.3	402	14.0	13.4	306	1.3	0.9	272	1.0	-0.3	536	0.5	0.4
340	7.5	9.5	710	3.5	3.7	502	15.2	16.4	406	0.6	1.1	282	2.8	3.2	546	1.9	-2.0
360	9.2	10.2	720	6.8	5.4	602	5.2	7.6	506	1.5	-1.2	392	2.6	-2.6	556	0.4	-0.1
370	9.1	10.2	730	7.3	6.4	102	12.4	-9.6				513	5.4	6.1	566	1.6	-1.8
380	7.7	7.0	740	6.9	5.5	202	4.7	5.6	[101] zone			323	1.6	-1.6			
390	4.7	5.3	750	4.5	3.5	302	13.8	9.7	020	68.2	70.1	333	7.6	7.6			

The atomic scattering factors used were those of Berghuis, Haanappel, Potters, Loopstra, Macgillavry, and Veenendal, *Acta Cryst.*, 1955, **8**, 478.

*Structure Analysis.*—The  $x$  and  $y$  co-ordinates of the atomic positions were derived to a first approximation from a study of the sharpened Patterson projection along [001]. They were improved by the calculation of the corresponding electron-density projection and a difference map. The agreement factor between calculated and observed structure amplitudes was then  $R = 11.8\%$  and did not decrease substantially after two further rounds of calculation and difference maps; the latest value is  $11.1\%$ . The  $z$  parameters of the atoms were next estimated with the help of stereochemical and packing considerations and refined by the calculation of the sharpened Patterson projection along [010], two Fourier projections, three difference maps, and one round of least-squares refinement. The intensity estimations of the  $h0l$  reflections, on which these calculations were based, were subject to much larger experimental errors than the  $hk0$  reflections owing to the twinning and unfavourable shapes of the crystals. At this stage,  $R$  was quite large,  $26.5\%$ .

The arrangement of the atoms in the crystal found through these calculations is shown by the projections along [001] and [010] in Figs. 1 and 2. In both of these projections the oxygen atom overlaps  $C_1$ ; as a consequence the N-O and C-N distances could not be precisely measured. It was observed, however, that no serious overlapping of atoms should occur in an electron-density projection along [101] and measurements were accordingly made of the intensities of  $hkl$  reflections. After one Fourier projection and one difference map the agreement between observed and calculated structure amplitudes for these reflections was  $R = 8.5\%$ ; it did not improve after one more difference map had been calculated.

FIG. 1. *Electron density projection along [001]. Here, and in Figs. 2 and 3, the contours are drawn at intervals of  $1 \text{ e}/\text{Å}^2$ .*

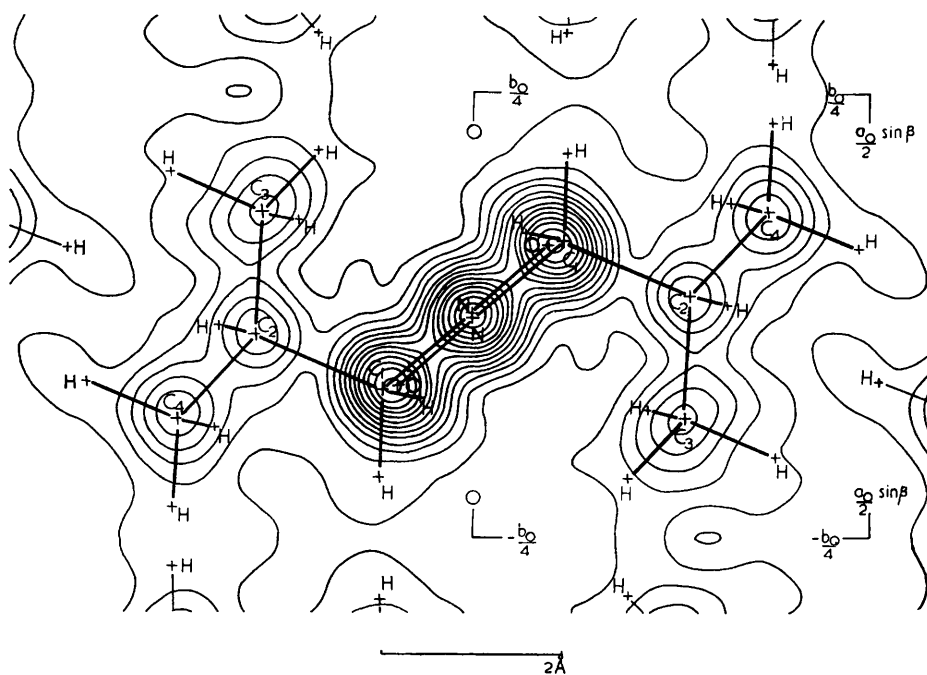
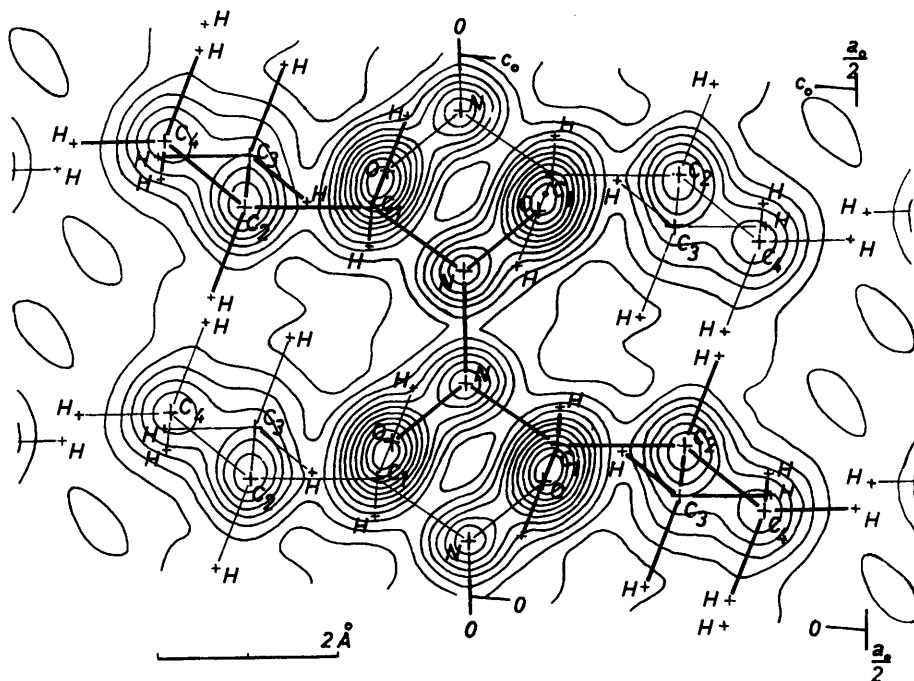


FIG. 2. *Electron density projection along [010].*



From the refined projections along [001] and [101] good values for the  $x$  and  $y$  parameters and much improved values for the  $z$  parameters of the atoms could be derived.  $R$  for the  $h0l$  reflections was reduced to 22.3% and, after a further difference map, to 19.8%. For each of the three zones studied, final Fourier projections were calculated, which are shown in Figs. 1—3. The latest calculated final structure amplitudes are recorded with the observed values in

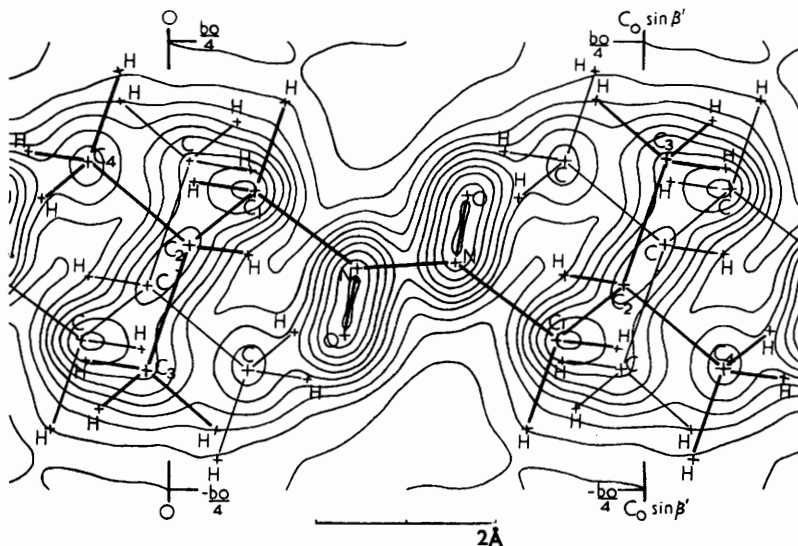
FIG. 3. *Electron density projection along [101].*

Table 1 while Table 2 gives the co-ordinates of the atoms and the individual isotropic thermal parameters on which these calculated values are based. As might be expected the individual atomic thermal parameters vary in the three projections studied; in all,  $C_3$  and  $C_4$  show much greater temperature vibrations than the other atoms, and their positions are correspondingly less well defined.

TABLE 2.

Atom	$x$	$y$	$z$	Atom	$x$	$y$	$z$	$B$		
								[001]	[010]	[101]
O	-0.095	-0.078	0.275	H <sub>2</sub>	0.067	0.093	0.122	5.48	4.25	6.28
N	0	-0.003	0.397	H <sub>3</sub>	0.320	0.012	0.487	5.48	4.25	4.19
C <sub>1</sub>	0.113	0.083	0.295	H <sub>4</sub>	0.195	-0.183	0.295	5.48	4.82	4.46
C <sub>2</sub>	0.273	0.023	0.333	H <sub>5</sub>	0.220	-0.107	0.048	5.48	4.25	6.33
C <sub>3</sub>	0.267	-0.117	0.220	H <sub>6</sub>	0.382	-0.160	0.237	6.67	6.38	7.74
C <sub>4</sub>	0.373	0.117	0.208	H <sub>7</sub>	0.378	0.217	0.330	6.67	5.60	7.30
H <sub>1</sub>	0.118	0.182	0.365	H <sub>8</sub>	0.327	0.127	0.035	6.67	6.38	7.74
				H <sub>9</sub>	0.488	0.075	0.230			

The parameters of the hydrogen atoms given in Table 2 were derived from stereochemical considerations, and their contributions were included in the latest structure-factor calculations. The first difference maps calculated during the analysis were based on structure factors derived for the heavier atoms only; in these, peaks occurred in the region of the hydrogen atoms but were not well enough defined to be used to place these atoms precisely.

## DISCUSSION

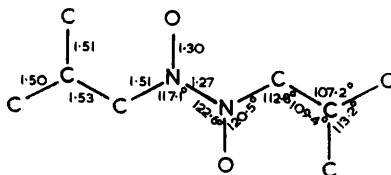
The interatomic distances and bond angles defined by the parameters of Table 1 for the *trans*-dimer of nitrosoisobutane are shown in Table 3 and Fig. 4. The positions of the atoms within the molecule appear to be closely determined by the usual conformational rules of preferred bond orientation. The central  $N_2O_2$  group, including the attached carbon atoms  $C_1$  and  $C_1'$ , is exactly planar, as can be seen clearly in Fig. 1.

TABLE 3.

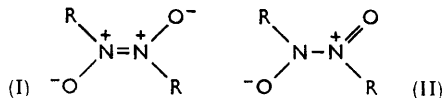
Bond lengths (Å)		Standard deviation	Bond angles	
N-N	1.27	0.02	O-N-N	122.4°
N-O	1.30	0.02	N-N-C <sub>1</sub>	117.1
N-C <sub>1</sub>	1.51	0.02	N-C <sub>1</sub> -C <sub>2</sub>	112.8
C <sub>1</sub> -C <sub>2</sub>	1.53	0.02	C <sub>1</sub> -C <sub>2</sub> -C <sub>3</sub>	109.2
C <sub>2</sub> -C <sub>3</sub>	1.51	0.04	C <sub>1</sub> -C <sub>2</sub> -C <sub>4</sub>	107.2
C <sub>2</sub> -C <sub>4</sub>	1.50	0.04	C <sub>3</sub> -C <sub>2</sub> -C <sub>4</sub>	113.2
			O-N-C <sub>1</sub>	120.5

Both the N-N and N-O distances have values intermediate between those expected for single and double bonds. The N-N bond length lies within the range 1.25–1.28 Å predicted by Gowenlock *et al.*<sup>4</sup> for the N-N bond in the *trans*-dimer of nitrosomethane by plotting the observed N-N bond lengths against the N-N bond order of 1.72–1.93, given by

FIG. 4.



J. W. Smith.<sup>5</sup> Correspondingly, if we use our bond length to estimate the bond order for the N-N bond observed in the *trans*-dimer of nitrosoisobutane we get the value 1.83. It would clearly be possible to account for this observation either in terms of resonance between structures (I) and (II) in the approximate proportions (I) 83%, (II) (two forms) 17%, or, as Gowenlock and Lüttke prefer, in terms of (I) only with an allowance for bond stretching on account of the adjacent formal positive charges on the nitrogen atoms. The C-N bond is, as might be expected, a little longer than the value 1.47 Å found for C-N (neutral)<sup>6</sup> bonds. It is close to the -C-N<sup>+</sup>H<sub>3</sub> distances of 1.50 Å and 1.49 Å found in alanine<sup>7</sup> and threonine.<sup>8</sup>



The distances also compare well with those recorded by Van Meersche and Germain for the *trans*-dimer of nitrosomethane itself, N-N 1.22, N-C 1.25, N-C 1.57.<sup>9</sup> This crystal structure, which we have also investigated, is disordered and the standard deviations of the bond lengths are so high that the differences between these distances and those found in the dimer of nitrosoisobutane are not significant.

For the crystals used in this study and valuable discussion we are indebted to Dr. B. G. Gowenlock, Birmingham. One of us (H. D.) thanks the Rockefeller Foundation for a stipend and support of this work.

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<sup>4</sup> Gowenlock, Trotman, and Bati, *Chem. Soc. Special Publ.*, No. 10, 1957, p. 78.

<sup>5</sup> Smith, *J.*, 1957, 1124.

<sup>6</sup> Sutton, "Interatomic Distances," *Chem. Soc. Special Publ.*, No. 11, 1958, p. S16.

<sup>7</sup> Donohue, *J. Amer. Chem. Soc.*, 1950, **72**, 949.

<sup>8</sup> Shoemaker, Donohue, Schomaker, and Corey, *J. Amer. Chem. Soc.*, 1950, **72**, 2328.

<sup>9</sup> Van Meersche and Germain, *Bull. Soc. chim. belges*, 1959, **68**, 244.