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The Crystal Structure of the Compound Formed by Benzene and Dinitrogen Tetroxide in the Mole Ratio One-to-One

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The crystal structure of the equi molecular complex formed by benzene and dinitrogen tetroxide has been determined from three-dimensional X-ray diffraction data obtained at −20°C. The trigonal unit cell with axes $a=10\cdot41$ Å and $c=6\cdot92$ Å contains three molecules of each kind. The space group is $R\bar{3}m$. As in the case of the benzene halogen complexes, the molecules form linear chains of infinite length consisting of donor and acceptor molecules alternately. The chain axes coincide with the trigonal axes of the lattice. The molecular planes are perpendicular to the chain axes, and the distance between neighbouring planes in a given chain is 3·46 Å, equal to half the length of the c axis. Both of the component molecules reorient cooperatively about the trigonal axis, and are distributed between two independent positional sets in the ratio 3:1 and 1:3 for benzene and dinitrogen tetroxide respectively. The statistical distribution has also been verified indirectly by considering the interpositional distances between chains relative to the accepted values for the van der Waals type. A model of the instantaneous molecular distribution in a crystalline domain is also proposed, according to which the nitrogen tetroxide molecules are placed with the nitrogen atoms equally close to two and two carbon atoms of the neighbouring benzene molecules in a common chain. This leads to the best possible contact between neighbouring component molecules.

Introduction

The present work was undertaken as part of an X-ray investigation of addition compounds formed (in particular) by benzene and various acceptor molecules in the solid state (see also Hassel & Strømme, 1958, 1959). As has been found in many addition compounds involving halogen and rather weak donors (Hassel & Strømme, 1958, 1959; Hassel & Rømming, 1962; Marstokk & Strømme, 1967) the present compounds form linear chains consisting of benzene and dinitrogen tetroxide molecules alternately. On a statistical basis, the organic molecule occupies two crystallographically independent, distinguishable orientations in the solid; whereas the inorganic component is distributed over six distinguishable mean molecular positions, divided into two crystallographically independent groups. Both of the component molecules reorient about the chain axes, as also do the benzene molecules in the solid complex containing benzene and bromine (or chlorine), even at temperatures considerably below −100°C.

Experimental

The melting point of the present compound has been reported to be −8°C (Addison & Sheldon, 1956). Dinitrogen tetroxide (m.p. −9°C) was prepared from lead nitrate (Vanino, 1943). Equimolecular amounts of benzene of reagent grade (m.p. 5°C) and dinitrogen tetroxide were mixed at 0°C and stored at the temperature of solid carbon dioxide (−78°C). A small amount of the yellow liquid mixture was transferred to a thin-walled boron-lithium capillary tube of 0·2 mm diameter and immediately frozen to produce a light yellow solid. The sample was kept in this form by means of a special cooling arrangement while the tube was sealed and transferred to a Weissenberg goniometer where it was held in a jet of cold dry air. By proper adjustment of the air speed, single crystals were grown having their hexagonal c axis along that of the tube, which was also the rotation axis.

Weissenberg oscillation and rotation photographs of single crystals together with powder diagrams were taken at −20°C with filtered Cu $K\alpha$ radiation ($\lambda=1\cdot5418$ Å). Multiple film integrated Weissenberg diagrams were taken of the first four layers with the equi-inclination technique. The specimen was rotated through 200°. The intensity of each reflexion on the five films of each layer was photometrically recorded, while the weakest intensities had to be measured visually by comparison with a standard scale. The intensity damping was considerable, so that even long time exposures could not record the outer reflexions on the film. As a result of this the intensities of not more than 60 symmetry independent reflexions were observed, although with Cu $K\alpha$ radiation 116 are theoretically possible.

Powder photographs taken at −100°C revealed the existence of a low symmetry, low temperature crystal form of the compound.

Determination of the structure

The crystals are rhombohedral with hexagonal unit cell dimensions $a=10\cdot42\pm0\cdot04$ Å, $c=6\cdot92\pm0\cdot02$ Å, values which were obtained by averaging over all measurements on Weissenberg rotation and powder photographs.

An approximate value of the density of the present compound was derived from the densities of crystalline benzene at $-3\,^\circ$C (Cox & Cruickshank, 1958) and crystalline dinitrogen tetroxide at about $-15\,^\circ$C (Groth, 1963). The result corresponds to 3·05 molecules of each kind per unit cell and it was therefore concluded that the unit cell contains three molecules of the 1:1 complex.

Of two possible space groups, the centrosymmetric $R\bar{3}m$ and the non-centrosymmetric $R3m$, the former was chosen since both component molecules are centrosymmetric (Kitaigorodskij, 1967).

By consideration of the space group properties, it was found that three benzene molecules per unit cell are able to satisfy the symmetry requirements of the lattice. Three molecules of dinitrogen tetroxide (or six units of nitrogen dioxide) of ordinary molecular symmetry cannot, however, occupy one distinct position each in one unit cell without violating the space group symmetry. This suggests that a statistical distribution of positions of the inorganic molecules occurs in the lattice.

Structure factor computations were performed for a variety of statistical models. It appeared that, in principle, the positions of one molecule of each kind had to be ascertained. For this purpose, the centres of gravity of all molecules were assumed to be at rest statistically, requiring that the benzene centre coincide with the origin *etc.* and that of dinitrogen tetroxide with the point $(0,0,\frac{1}{2})$ *etc.* (or *vice versa*). The molecular planes were assumed to be perpendicular to the c axis, whereby the dinitrogen tetroxide acquires a statistical hexagonal symmetry. The molecular dimensions of the free components have previously been determined with sufficient accuracy for the present purposes (Smith & Hedberg, 1956; Groth, 1963; Cartwright & Robertson, 1966). There is little reason to suppose that they will be significantly altered upon complexing. Thus, to keep the number of free parameters as small as possible, the molecular dimensions were kept fixed. In this compound the oscillating motion is probably much the same as in solid benzene, and it was therefore thought more appropriate to use the uncorrected molecular data for solid benzene (Cox & Cruickshank, 1958) and those obtained by linear extrapolation for dinitrogen tetroxide, rather than the gas phase values.

In principle, one was left with one azimuthal angle (running from 0 to 60°) of each component molecule about the c axis, in addition to the temperature and four scale factors, as free variables to be determined.

Starting with the $hk0$ reflexions, a series of sets of structure factors were computed for a number of values of the azimuthal angles. None of these were in reasonable agreement with the observations, however. The columns 7, 8, 9 and 10 of Table 1 therefore contain the possible sets of calculated structure factors based on combinations of either: carbon (and hydrogen) in positions termed $18(h)m$ ($z=0$, *etc.*), as in the aragonite structure, or the non-equivalent $18(f)2$, as in the calcite structure; and nitrogen in either of the positions $18(h)m$ ($z=\frac{1}{2}$, *etc.*) or $18(g)2$ [with oxygen in $36(i)$ ($z=\frac{1}{2}$ *etc.*)] of the space group $R\bar{3}m$, using the notation of *International Tables*. A common value of 6·0 Å^2 was used for the isotropic temperature factors. The atomic form factors (Hanson, Herman, Lea & Skillman, 1964) had to be properly weighted since the number of equivalent positions exceeds the number of atoms present. The agreement of the values of either of these sets with the observed data listed in column 4 is seen to be poor. A much better degree of agreement was obtained by taking a linear combination of these four sets. This corresponds to a statistical distribution of component molecules between the two non-equivalent positional sets defined above. The best fit was obtained with $\frac{3}{4}$ and $\frac{1}{4}$ of the benzene molecules in $18(f)2$ and $18(h)m$, respectively, and correspondingly, $\frac{1}{4}$ and $\frac{3}{4}$ respectively for dinitrogen tetroxide (see Table 1, column 6). Combinations of structures corresponding to intermediate values of the azimuthal angles were also considered. The R value varied only slowly with positional changes close to those introduced above. This is, however, to be expected owing to the effects of anisotropic motion. There appeared to be no reason to doubt that these positions correspond to the actual equilibrium orientations, bearing in mind that intermediate positions represent twice the number of statistical equilibrium positions at correspondingly smaller inter-minimum distances; a physically less probable situation.

Scale and temperature factors representing the heavy atoms were further refined by a least-squares technique, using a block-diagonal matrix computer program which was readily available. The values of the positional parameters were kept constant while the benzene molecules were assumed to be distributed between the positions $18(f)2$ and $18(h)m$ in the mole-ratio 3:1, and the dinitrogen tetroxide molecules between the positions $18(g)2$ and $18(h)m$ in the mole-ratio 1:3 as previously discussed. The values of the anisotropic temperature factor coefficients were computed from the expression

$$\exp\left[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{13}hl+\beta_{23}kl)\right].$$

The following symmetry relationships were imposed for atoms in special positions (Busing & Levy, 1958):

$(x,x,0;$ *etc.*$)$ $(18f2)$ or $(x,x,\frac{1}{2};$ *etc.*$)$ $(18g2)$: $\beta_{11}=\beta_{22}$, $\beta_{13}=-\beta_{23}$ $(x,\frac{1}{2}x,z;$ *etc.*$)$ $(18hm)$: $\beta_{11}=\beta_{12}$, $\beta_{13}=2\beta_{23}$.

These were obtained by assuming that one of the symmetry axes of the vibration ellipsoid of an atom at $(x,x,0)$ or $(x,x,\frac{1}{2})$ is parallel to the [110] direction *etc.* whereas the second case requires one of the principal axes to be normal to the mirror plane containing the corresponding atom at $(x,\frac{1}{2}x,z)$ or equivalent positions.

The benzene molecule was, in addition, assumed to be rigid. Since the c axis then became parallel to one of the main axes of the vibration ellipsoid of the carbon atoms, the corresponding values of β_{13} and β_{23} vanished for these atoms. No attempt was made to refine the thermal parameters of the hydrogen atoms and these were put equal to the corresponding values of the respective carbon atoms. Under these conditions the R value fell almost to 10%, excluding non-observable reflexions together with two reflexions which obviously suffered from extinction effects. Various sets of values of the distribution factors and position parameters were tried explicitly without significant deviation from the previous results being obtained.

At this stage in the refinement process a full-matrix least-squares program became available which required one to reset individual scale factor values by hand. In view of the relatively low electron density, it was not surprising to find that convergence could not be obtained when the parameters corresponding to the least populated nitrogen and oxygen positions were allowed to vary. Thus in the following refinement process, the values of individual scale factors and parameters of these atoms were reset by hand between cycles. In this connexion, a series of sets of structure factors were also calculated explicitly. The process was continued until the R value had fallen to an apparently steady figure of 7·4%. Excluded from this were the unobservable reflexions and two suffering from the effects of extinction. However, by omitting the third layer line reflexions, the intensities of which are small and less accurately determined, the R value fell from 6·1 to 5·6% upon further refinement. In addition to the above treatment, different sets of molecular distribution factor values were tried as fixed parameters in the least squares computations. At the same time, a number of alternative molecular orientations with respect to rotation about the c axis were attempted. The values of the weight-factors used in the least-squares refinement were determined from the standard weighting scheme $F_o \leq FB$, $WTG = A1(F_o)^{B1}$; $F_o > FB$, $WTG = A2(F_o)^{B2}$, with $A1 = 1{\cdot}0$, $B1 = 0{\cdot}5$, $FB = 2{\cdot}0$, $A2 = 2{\cdot}0$ and $B2 = -0{\cdot}5$. Finally, slightly modified values of the intrinsic molecular data were similarly tested. In none of these cases, however, could a significantly better agreement between observed and calculated quantities be obtained. The final set of structure factor values are listed in Table 1, column 5, while the normalized F_o values are shown in column 4. Table 2 presents the corresponding values of the position and thermal parameters. For the reasons given above, standard deviations in the thermal parameters have been evaluated only for the heavy atoms, apart from N(2) and O(2). The particularly high standard deviations for the β_{33} values are probably due to a dependence upon the individual scale factors. These could not be refined directly by using the actual full-matrix least-squares techniques as was pointed out previously. On the basis of the present results, a three-dimensional Fourier series analysis was performed using the calculated structure factor value of the 003 reflexion whose intensity cannot be measured with the technique actually used. As is to be expected, the resulting electron density map shows considerable overlap. The regions of highest density are, however, in accordance with expectation. Finally, a three-dimensional, total difference electron-density map was developed, excluding the 110, 012 and non-observable reflexions. From this it appears that the density has a maximum variation about zero of approixmately 0·1 electrons per Å^3, but is at most places close to zero.

Results and discussion

According to the present observations, the benzene and dinitrogen tetroxide molecules are each distributed statistically between two crystallographically nonequivalent sets of positions in the solid complex at $-20\,^{\circ}$C, forming molecular chains of indefinite length along the threefold axes connecting benzene and dinitrogen tetroxide molecules alternately. The molecular planes are perpendicular to the chain axes, and the distance between neighbouring components in a chain is $c/2 = 3{\cdot}46$ Å. This value is only slightly larger than

Table 1. *Observed and calculated structure factors*

Reflexions suffering from effects due to secondary extinction are marked with an asterisk. The amplitudes of reflexions with small, non-observable intensities are put equal to zero in the F_o-table. The FI table is based on a linear combination of the structure factor sets FII, FIII, FIV and FV, which are obtained on the basis of the following molecular positions: C_6H_6 in 18(f)2 and N_2O_4 in 18(g)2 (FII), C_6H_6 in 18(f)2 and N_2O_4 in 18(h)m (FIII), C_6H_6 in 18(h)m and N_2O_4 in 18(h)m (FIV), and C_6H_6 in 18(h)m and N_2O_4 in 18(g)2 (FV). The F_c table lists the final set of calculated structure factors (see text).

H	K	L	Fo	Fc	FI	FII	FIII	FIV	FV
3	0	0	27.44	-27.12	-27.34	-28.46	-24.52	-31.86	-35.81
6	0	0	11.22	11.25	13.58	5.17	22.37	4.40	-12.81
9	0	0	.00	.98	-.61	4.34	.29	-7.37	-3.32
1	1	0	*62.54	73.75	75.56	75.60	75.31	76.02	76.31
4	1	0	10.84	-10.72	-11.75	-14.93	-8.39	-15.32	-21.86
7	1	0	4.34	4.85	5.33	6.02	9.34	-3.39	-6.71
10	1	0	.00	-.05	-.95	.87	-1.74	-1.17	1.44
2	2	0	36.90	-37.34	-39.64	-37.12	-44.12	-33.20	-26.20
5	2	0	3.43	3.12	3.77	4.62	2.79	4.87	6.70
8	2	0	.00	-.70	-1.20	.80	-1.00	-3.63	-1.83
0	3	0	27.44	-27.12	-27.34	-28.46	-24.52	-31.86	-35.81
3	3	0	10.46	-9.47	-11.95	-2.60	-20.92	-3.36	14.96
6	3	0	1.59	-1.55	-1.88	-3.06	-3.53	2.61	3.07
9	3	0	.00	-.50	-.14	.01	-.26	-.08	.19
1	4	0	10.84	-10.72	-11.75	-14.93	-8.39	-15.32	-21.86
4	4	0	2.75	-2.08	-2.98	.17	-10.01	7.93	18.11
7	4	0	.00	-.93	-.85	-3.28	-.68	1.22	-1.39
2	5	0	3.43	3.12	3.77	4.62	2.79	4.87	6.70
5	5	0	3.05	-2.12	-3.13	-7.99	-4.88	5.24	2.13
8	5	0	.00	.23	.82	.51	1.40	-.01	-.89
0	6	0	11.22	11.25	13.58	5.17	22.37	4.40	-12.81
3	6	0	1.59	-1.55	-1.88	-3.06	-3.53	2.61	3.07
6	6	0	.00	.21	.58	-1.88	1.45	1.31	-2.03
1	7	0	4.34	4.85	5.33	6.02	9.34	-3.39	-6.71
4	7	0	.00	-.93	-.85	-3.28	-.68	1.22	-1.39
2	8	0	.00	-.70	-1.20	.80	-1.00	-3.63	-1.83
5	8	0	.00	.23	.82	.51	1.40	-.01	-.89
0	9	0	.00	.98	-.61	4.34	.29	-7.37	-3.32
3	9	0	.00	-.50	-.14	-.01	-.26	-.08	.19
1	10	0	.00	-.05	-.95	.67	-1.74	-1.17	1.44
1	0	1	12.59	-12.61	-14.34	-14.34	-14.33	-14.37	-14.38
4	0	1	2.19	-.81	-2.93	8.27	-2.27	-15.44	-4.90
7	0	1	8.54	8.54	7.34	18.38	9.36	-7.74	1.28
10	0	1	.00	.35	.92	-1.63	2.24	.83	-3.04
2	1	1	1.20	.74	-.31	-1.42	-.53	1.22	.32
5	1	1	2.12	-2.77	-5.39	4.86	-5.50	-15.43	-5.06
8	1	1	4.61	4.81	6.16	6.77	8.82	.22	-1.83
11	1	1	.00	-.28	-.61	-1.75	-.81	.91	-.03
0	2	1	2.41	-3.24	-5.85	-5.15	-5.65	-6.95	-6.46
3	2	1	9.66	-8.63	-6.24	-16.70	-6.55	4.84	-5.32
6	2	1	5.29	4.35	5.18	6.27	5.46	3.54	4.34
9	2	1	.00	-1.04	-1.30	-2.61	-.77	-1.06	-2.90
1	3	1	.47	.38	-.67	.30	-.58	-1.84	-.96
4	3	1	4.68	-4.67	-1.28	-15.55	-1.55	13.52	-.47
7	3	1	.00	.24	.57	.72	-.02	1.62	2.37
2	4	1	8.25	-7.87	-6.73	-13.90	-6.64	.28	-6.98
5	4	1	.00	.41	3.06	-1.75	.06	13.63	12.00
0	5	1	3.22	-3.11	-7.61	8.99	-7.74	-23.95	-7.22
3	5	1	1.00	.52	3.43	-3.78	2.12	13.27	7.37
6	5	1	1.28	-1.23	-1.65	.54	-3.59	.06	4.19
1	6	1	3.31	4.42	3.20	12.94	4.00	-8.15	.80
4	6	1	.00	-.56	.27	.32	-2.12	5.02	7.46
7	6	1	.00	.34	-.36	1.14	-.31	-2.03	-.58
2	7	1	4.24	3.76	4.95	5.75	5.94	2.27	2.06
5	7	1	.00	-.69	-1.09	.20	-2.37	-2.08	-.11
0	8	1	7.45	7.71	9.15	13.05	12.46	-1.42	-.85

Table 1 (*cont.*)*

3	8	1	.00	-1.15	-1.90	-1.83	-1.94	-1.89	-1.78
1	9	1	.00	1.36	1.77	-.17	3.50	.25	-3.43
2	10	1	.00	-.86	-1.65	-2.62	-1.68	-.60	-1.54
0	11	1	.00	.06	-.42	-2.27	-.31	1.21	-.76
2	0	2	31.12	30.62	29.74	29.67	30.07	29.14	28.75
5	0	2	2.01	1.22	1.88	-5.28	8.73	-4.65	-18.66
8	0	2	3.50	3.75	3.14	5.86	6.35	-6.00	-6.49
0	1	2	*86.42	130.25	125.94	125.95	125.95	125.92	125.92
3	1	2	23.22	-25.13	-25.51	-25.82	-25.09	-26.06	-26.78
6	1	2	6.00	7.27	8.62	5.53	13.20	2.52	-5.14
9	1	2	.00	.40	-1.11	2.07	-1.20	-4.11	-.84
1	2	2	14.24	-13.18	-11.80	-11.58	-12.30	-11.03	-10.31
4	2	2	4.11	-3.75	-4.37	-1.24	-7.34	-1.54	4.56
7	2	2	.00	.10	.09	1.03	.86	-2.40	-2.22
10	2	2	.00	.01	-.33	.06	-.78	.19	1.03
2	3	2	19.75	-19.33	-20.13	-16.08	-24.48	-15.45	-7.05
5	3	2	1.09	-1.15	-.84	.51	-4.59	5.30	10.39
8	3	2	.00	-.63	-.66	-.75	-.65	-.60	-.70
0	4	2	18.48	-18.60	-16.89	-20.83	-12.15	-22.41	-31.09
3	4	2	1.81	-1.71	-2.29	3.36	-8.55	4.58	16.50
6	4	2	2.29	-2.08	-2.26	-5.47	-3.31	3.05	.90
1	5	2	5.24	4.60	5.62	1.17	9.91	1.48	-7.27
4	5	2	3.35	-2.64	-3.04	-4.91	-6.49	5.72	7.31
7	5	2	.00	.07	.43	-1.22	1.07	.80	-1.49
2	6	2	2.50	2.60	2.65	2.55	3.25	1.53	.84
5	6	2	.00	-.74	-.93	-4.50	-.83	2.44	-1.23
0	7	2	7.30	8.98	8.93	6.89	14.67	-.50	-8.28
3	7	2	1.16	-1.43	-1.46	-2.33	-1.67	-.19	-.85
6	7	2	.00	.60	1.05	.46	1.76	.21	-1.10
1	8	2	.00	1.31	.38	3.65	1.84	-5.81	-4.00
4	8	2	.00	-.22	.20	-.45	.53	.19	-.79
2	9	2	.00	-.85	-.78	.51	-1.13	-1.39	.25
0	10	2	.00	-.28	-1.17	1.73	-1.72	-2.98	.46
0	0	3	-.00	12.74	-16.76	-16.76	-16.76	-16.76	-16.76
3	0	3	3.36	1.57	1.56	3.96	1.81	-1.32	.83
6	0	3	3.91	3.12	-.70	10.30	-.41	-12.27	-1.57
9	0	3	2.88	2.76	3.66	2.90	5.74	.25	-2.58
1	1	3	4.44	-3.86	-5.78	-5.96	-5.80	-5.54	-5.70
4	1	3	5.23	-4.44	-4.64	-.84	-4.66	-8.40	-4.58
7	1	3	5.90	6.92	5.93	9.80	7.62	-1.34	.84
10	1	3	.00	-.90	-.47	-1.98	-.11	.31	-1.57
2	2	3	3.89	-2.10	.02	-4.13	-.25	4.70	.81
5	2	3	.00	.00	-.05	-1.26	-.11	1.30	.15
8	2	3	.00	.51	1.02	.55	1.81	-.09	-1.35
0	3	3	3.43	3.45	1.56	3.96	1.81	-1.32	.83
3	3	3	6.95	-8.20	-4.36	-15.23	-4.22	6.24	-4.77
6	3	3	.00	1.98	2.50	1.19	1.49	5.81	5.51
9	3	3	.00	-1.80	-1.81	-1.99	-1.80	-1.67	-1.86
1	4	3	3.77	-3.19	-4.64	-.84	-4.66	-8.40	-4.58
4	4	3	.00	-.41	2.11	-5.96	.62	13.16	6.59
7	4	3	.00	-1.23	-1.44	-.41	-2.25	-.87	.97
2	5	3	.00	-.69	-.05	-1.26	-.11	1.30	.15
5	5	3	.00	-.48	.17	-.01	-2.17	5.02	7.18
0	6	3	2.40	2.42	-.70	10.30	-.41	-12.27	-1.57
3	6	3	.00	1.46	2.50	1.19	1.49	5.81	5.51
6	6	3	.00	-.61	-1.10	.72	-1.67	-1.77	.61
1	7	3	5.88	5.99	5.93	9.80	7.62	-1.34	.84
4	7	3	.00	-1.25	-1.44	-.41	-2.25	-.87	.97
2	8	3	.00	1.13	1.02	.55	1.81	-.09	-1.35
0	9	3	3.22	3.50	3.66	2.90	5.74	.25	-2.58
3	9	3	.00	-1.25	-1.81	-1.99	-1.80	-1.67	-1.86
1	10	3	.00	.21	-.47	-1.98	-.11	.31	-1.57

* The value of F_o for reflexion 003 should read 0·00.

that observed in the analogous chain complexes formed by equimolecular amounts of benzene and either bromine or chlorine.* Weak bonds are established through $\pi-\pi$ interactions between the donor and acceptor molecules thus causing small negative charges to be transferred from the benzene to regions closer to the acceptor molecules, with the effect of further electron delocalization (Andrews & Keefer, 1964; Briegleb, 1961). Since it is probable that the molecules reorient about the chain axis, these bonds are, however, likely to break and re-establish frequently. Table 3 lists the values of the molecular distribution coefficients together with basic molecular data, and Fig. 1 shows a schematical representation of the statistical atomic equilibrium positions.

Table 3. *R.m.s. amplitudes of vibration*

E.s.d. in parentheses.

	R.m.s. amplitude (Å)	$U(x)$ (Å)	$U(y)$ (Å)	$U(z)$ (Å)
C(1)	0·32 (0·009)	0·32	0·32	0·00
	0·26 (0·034)	−0·15	0·15	0·00
	0·14 (0·053)	0·00	0·00	0·14
C(2)	0·34 (0·050)	0·00	0·34	0·00
	0·28 (0·039)	0·32	0·16	0·00
	0·17 (0·126)	0·00	0·00	0·17
N(1)	0·19	0·00	0·00	0·19
	0·58	0·58	0·58	0·00
	0·38	0·22	−0·22	0·00
N(2)	0·39 (0·032)	0·38	0·19	−0·20
	0·37 (0·040)	0·00	0·37	0·00
	0·08 (0·36)	0·05	0·02	0·07
O(1)	0·02	0·00	−0·01	−0·02
	0·39	0·45	0·25	0·01
	0·21	0·01	−0·19	0·07
O(2)	0·44 (0·023)	0·40	0·39	0·18
	0·32 (0·176)	0·09	0·23	0·14
	0·18 (0·106)	0·11	0·01	0·14

The benzene molecule centres occupy the positions (0,0,0), $(\frac{1}{3},\frac{2}{3},\frac{2}{3})$ and $(\frac{2}{3},\frac{1}{3},\frac{1}{3})$ in the unit cell. The carbon and hydrogen atoms are distributed in the mole ratio 3:1 between 18(*f*)2 and 18(*h*)*m*, with molecular coordinates centred about the origin of:

$$(x,0,0),\ (x,x,0),\ (0,x,0),\ (\bar{x},0,0),\ (\bar{x},\bar{x},0),\ (0,\bar{x},0)$$

and

$$(2x,x,0),\ (x,2x,0),\ (\bar{x},x,0),\ (2\bar{x},\bar{x},0),\ (\bar{x},2\bar{x},0),\ (x,\bar{x},0)$$

respectively. One group is transformed into the other by means of a rotation of 30° about the *c* axis. The corresponding dinitrogen tetroxide molecules have

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* Hassel & Strømme (1958, 1959).

Table 2. *Position parameters (in fractions of the unit axes) and anisotropic temperature factors*

E.s.d. in parentheses. The thermal parameters of H(1) and H(2) were put equal to those of C(1) and C(2), respectively.

	C(1)	C(2)	N(1)	N(2)	O(1)	O(2)	H(1)	H(2)
x (ass.)	0·1324	0·1529	0·0830	0·0958	0·1465	0·1861	0·2349	0·2712
y (ass.)	0·1324	0·0756	0·0830	0·0479	0·9704	0·0673	0·2349	0·1356
z (ass.)	0·0	0·0	0·5	0·5	0·5	0·5	0·0	0·0
β_{11}	0·0229 (0·0010)	0·0191 (0·0051)	0·0476	0·0274 (0·0035)	0·0364	0·0331 (0·0032)		
β_{22}	0·0229	0·0252 (0·0057)	0·0476	0·0314 (0·0049)	0·0176	0·0379 (0·0024)		
β_{33}	0·0085 (0·0062)	0·0123 (0·0182)	0·0150	0·0183 (0·0107)	0·0025	0·0299 (0·0080)		
β_{12}	0·0290 (0·0026)	0·0191	0·0122	0·0274	0·0395	0·0497 (0·0057)		
β_{13}	0	0	0·0025	−0·0401 (0·0167)	−0·0017	0·0383 (0·0105)		
β_{23}	0	0	0·0025	−0·0201	−0·0069	0·0198 (0·0047)		

their centres at $(0,0,\frac{1}{2})$, $(\frac{1}{3},\frac{2}{3},\frac{1}{6})$ and $(\frac{2}{3},\frac{1}{3},\frac{5}{6})$; and are distributed in the mole ratio 1:3 between $18(g)2$ and $18(h)m$. For the molecule centred at $(0,0,\frac{1}{2})$, the statistical positions of the nitrogen atoms are obtained from the above sets by putting $z=\frac{1}{2}$. The corresponding oxygen atoms occupy general positions at $z=\frac{1}{2}$. In each of the two non-equivalent groups, the dinitrogen tetroxide molecule adopts statistically three distinct orientations.

A comparison of the two possible space groups may be appropriate at this point. The alternative noncentrosymmetric space group $R3m$ requires that the dinitrogen tetroxide molecule be situated closer to one of the two neighbouring benzene molecules to which it is bonded. For chemical reasons, the intermolecular distance can be only a little shorter than $\frac{1}{2}c$. Because of the equivalence of the benzene molecules and the high mobility of the system, it is to be expected that the acceptor molecule be distributed between two statistically equivalent equilibrium positions along the c axis, in which case the centre of mass is actually displaced from the midway position at equilibrium, providing a centre of symmetry. The present alternative, in which the dinitrogen tetroxide molecule is placed equally distant from the two benzene molecules therefore seems more likely from a chemical point of view. It is furthermore worth noting that the lattice will in any case be centrosymmetric with respect to each of the two component molecules viewed separately. It seems probable that the two sets of centres of symmetry coincide, corresponding to the space group $R\overline{3}m$. By way of comparison it may be mentioned that the space group of the disordered, rhombohedral phases of potassium nitrate, potassium nitrite and sodium nitrate is also $R\overline{3}m$. None of these phases are ferroelectric, and in all cases, the phases which are stable at temperatures below the transition points are centrosymmetric. Also in disordered cubic structures, the space group of highest symmetry within an observed Laue symmetry is generally chosen. The validity of this principle is in fact to be thermodynamic grounds for energy rich solids.

Finally it may be mentioned that the chains or groupings formed by other charge-transfer complex molecules involving at least one centrosymmetric component, have all been observed to be centrosymmetric (see *e.g.* Hassel & Rømming, 1962). Thus the following discussion is based solely on the results obtained with the centrosymmetric space group.

It follows by inspection, that if the nitrogen atoms are situated equidistant from two and two neighbouring carbon atoms, the product of the ratio of the respective distribution factors must be equal to unity, as has been observed. Thus possible reorientations between non-equivalent positions can only occur simultaneously. On the basis of the observed magnitudes of the distribution factors, one finds, how-

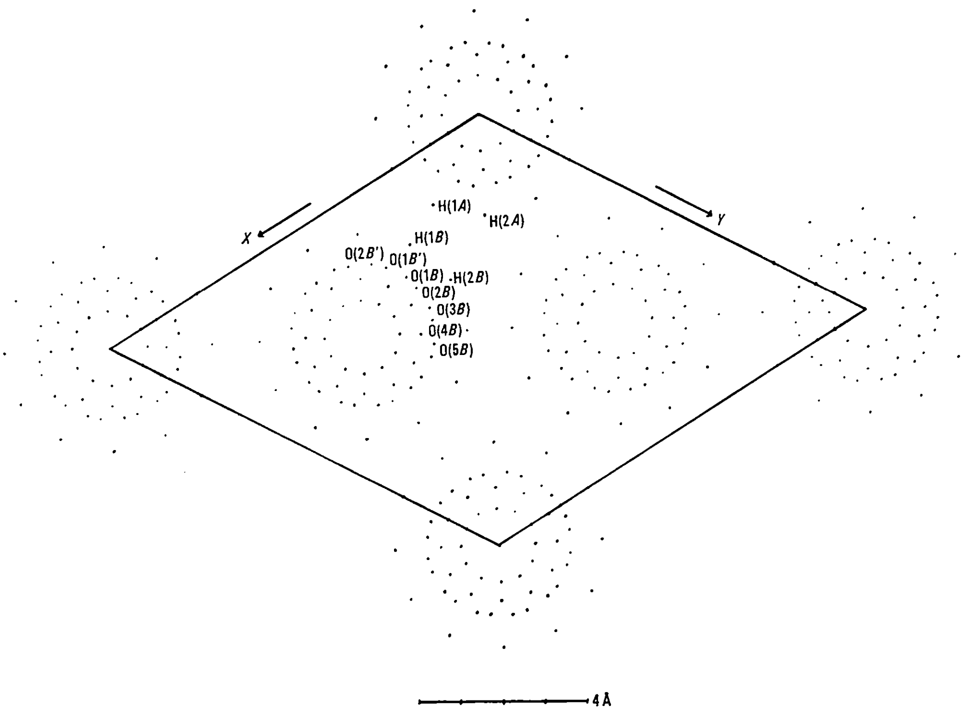

Fig. 1. Schematic representation of the statistical equilibrium positions of atoms. Points on circles of increasing diameter represent positions of nitrogen, carbon, oxygen and hydrogen atoms, respectively. Centres of the benzene molecules are at $(0,0,0)$, $(\frac{1}{3},\frac{2}{3},\frac{2}{3})$, $(\frac{2}{3},\frac{1}{3},\frac{1}{3})$ *etc.* Centres of the dinitrogen tetroxide molecules are at $(0,0,\frac{1}{2})$, $(\frac{1}{3},\frac{2}{3},\frac{1}{6})$, $(\frac{2}{3},\frac{1}{3},-\frac{1}{6})$ *etc.* The numbering of atoms is as in Table 4.

ever, that a certain fraction of the nitrogen atoms may alternatively be situated equidistant from two and two carbon atoms. The remainder will, of necessity, occupy positions above (or below) the carbon atoms. This may affect up to a maximum of one half of the nitrogen atoms. This is equivalent to saying that each dinitrogen molecule may spend up to as much as one half the its time in these latter positions if molecular reorientation occurs.

In the first case, equilibrium positions of the nitrogen atoms must be associated with positions equidistant from two and two carbon atoms, whereas additional equilibrium positions confined to regions above (or below) the carbon atoms are required in the second case. Chemically, the latter may seem unlikely unless determined by interactions from the neighbouring chains. In other charge transfer complexes the acceptor molecules have been observed to be situated equidistant from two and two bonded carbon atoms. See *e.g.* Andrews & Keefer (1964). Theoretical studies have shown that the nitrogen atoms in the free dinitrogen tetroxide molecule are electron deficient (See for example Harcourt, 1966). In the solid complex of dioxan and dinitrogen tetroxide the closest approach of the components is established in the π direction from nitrogen to oxygen (Groth & Hassel, 1962). Assuming the nitrogen atoms to be mainly responsible for the acceptor properties, it seems, from geometrical considerations, that the best contact between the molecules is established when the nitrogen atoms occupy positions which are equidistant from two and two carbon atoms. Thus, disregarding interactions between neighbouring chains, this relative positioning of the molecules is the more likely. The statistical distribution of the molecules as a whole must, however, be determined largely by interactions between the chains. Since the present complex is rather weakly bonded, lattice interactions may influence the choice of relative positions of donor and acceptor molecules. The values of the shortest statistical interatomic distances which were obtained between neighbouring chains are listed in Table 4. The numbering refers to Fig. 1. The shortest hydrogen–hydrogen distances are well above the van der Waals values, as are the oxygen–oxygen distances. Contact distances occur only between hydrogen and oxygen atoms. Two of the distances, both involving hydrogen positions in 18(*h*)*m* are significantly below the van der Waals value (Pauling, 1960). In the following discussion, these distances are treated as unacceptable at equilibrium.

At the point *A*1 (Fig. 2), the benzene molecule ($z_C=0$) is assumed to be in a position representing 18(*h*)*m*. In accordance with the requirement stated above, the twofold axes of the dinitrogen tetroxide molecules ($z_N=\pm\frac{1}{6}$) at the six neighbouring *B* sites must either be directed towards the centre at *A*1 [18(*h*)*m*] or perpendicular to these directions in the (001) projection. This has been shown in particular at *B*1 where the molecule in the perpendicular direction has been represented by broken lines. The remaining four statistical orientations must be excluded. The benzene molecule at *B*1 ($z_C=\frac{1}{3}$), however, must be in 18(*f*)2 and not in 18(*h*)*m*, since the dinitrogen tetroxide molecules at *B*2 ($z_N=\frac{1}{6}$) and *B*4 ($z_N=\frac{1}{6}$) are directed neither towards the centre nor perpendicular to this direction. This must likewise be true for all the six neighbours ($z_C=\pm\frac{1}{3}$) of the benzene molecule at *A*1. Similarly, the benzene molecules at *B*5, *B*6 and *B*7 ($z_C=0$) *etc.* must also occupy the position 18(*f*)2. However, the benzene molecule at *A*2 ($z_C=-\frac{1}{3}$), whose centre lies on the line joining *A*1 and *B*1 in the (001) projection, may belong either to 18(*f*)2 or 18(*h*)*m*. The same applies to the molecules at *A*3, *A*4 *etc.* If the molecules at these sites are in 18(*h*)*m* positions, they become equivalent to that at *A*1, so that the same restrictions are imposed on the orientations of the neighbouring molecules. One then obtains a unit structure of four neighbouring benzene molecules, of which one belongs to 18(*h*)*m* and three to 18(*f*)2, in agreement with the observed statistical average. The relatively well-defined structure extends throughout the domain in three dimensions. This represents the maximum fraction of molecules to be found in 18(*h*)*m* positions (*A* sites), and corresponds, on the present basis to the most probable distribution of benzene molecules. However, the assumption that intermolecular distances between chains may not be much less than the accepted van der Waals values, does not in itself require a maximum density of *A* sites. Alternatively, long-range order is not necessarily implied by this requirement, although complete short-range order about the *A* sites is demanded. Since the value of the distribution factor is thought to be correct to within a few per cent, almost complete long-range order is however to be expected.

Table 4. *Interpositional distances between the chains*

The numbering of atoms refers to Fig. 1.

	Interpositional distance (Å)	Van der Waals distance (Å)
H(1*A*)–H(1*B*)	2·54	2·2–2·3
H(2*A*)–H(2*B*)	2·89	
H(1*A*)–O(1*B*)	2·21	
H(1*A*)–O(2*B*)	2·36	
H(1*A*)–O(3*B*)	2·72	
H(1*A*)–O(4*B*)	3·05	
H(1*A*)–O(5*B*)	3·24	
H(2*A*)–O(1*B*)	2·66	
H(2*A*)–O(2*B*)	2·65	2·5–2·6
H(2*A*)–O(3*B*)	2·81	
H(2*A*)–O(4*B*)	3·06	
H(2*A*)–O(1*B*′)	2·89	
H(2*A*)–O(2*B*′)	3·18	

In accordance with the model described above, only two orientations of the dinitrogen tetroxide molecule are possible at a *B* site (Fig. 2, *B*1). The molecule may be placed above (or below) two carbon atoms, or above (or below) two ‘double’ bonds. At an *A* site, on the other hand, any of the six statistically possible orientations are acceptable.

Thus, on the basis solely of the values given in Table 4, more detailed lattice-energetic considerations would not be expected to favour one type of relative orientation substantially more than the other. In deciding between these two alternatives, the charge transfer interaction probably becomes the determining factor.

According therefore to the above discussion, one would expect the acceptor molecules to occupy mean positions equally distant from two and two carbon atoms, rather than both such positions and positions of the second kind. The first alternative implies that an acceptor molecule at a *B* site can adopt one specific orientation belonging to 18(*h*)*m*, while at an *A* site it may choose from three possibilities offered by 18(*g*)2. One then obtains a statistical population ratio of 3:1, in agreement with observation. This model of the configuration of molecules in a coherent region of space (Fig. 2) appears to be the most reasonable one which can be constructed on the basis of present knowledge.

The structure forms a superlattice of analogous symmetry to that on the entirely statistical basis, provided that the acceptor molecules at *A* sites are considered to be completely delocalized among the three orientations offered by 18(*g*)2. The unit cell retains the original *c* axis, whereas the *a* and *b* axes have twice their original values. For this to be so, the intensities of the corresponding extra reflexions must be small. They are not, in fact, explicitly observable on the Weissenberg photographs where a marked diffuse scattering is revealed which is probably due largely to lattice motion.

The final values of the root-mean-square amplitudes of vibration are listed in Table 4. Although thought to be correct to an order of magnitude, the figures are not sufficiently accurate to justify an explicit rigid body motion analysis. They demonstrate nevertheless that vibrational-translational motion must be pronounced. It has been observed that the benzene molecules in solid benzene (Andrew & Eades, 1953) and in other benzene complexes (Gilson & McDowell, 1964; Strømme, 1967) rotate about the senary axis at sufficiently high temperatures. Values of the barriers to rotation are as low as 3–4 kcal/mole. Together with the evidence discussed above, this leaves no doubt that the molecules of the present compound also perform rather extensive motions across potential barriers as well as in intermediate regions, at a temperature of −20°C.

A structure of the present kind could hardly be stable in rigid form owing to the unfavourable packing of molecules of one chain relative to those of neighbouring chains. Thus a phase of low symmetry has been observed at a temperature lower than −100°C.

The proposed model implies that the coupling of molecular motion is more pronounced at *B* sites than at *A* sites, and a lower barrier to rotation is to be expected at the latter. From an energetic point of view however, simultaneous reorientation of all the molecules in an extended region of space is very unlikely. Instead, the reorientation process (and also the translational and librational motion) should be seen as fluctuations involving clusters of molecules (possibly in association with lattice faults). Interchange between *A* and *B* sites

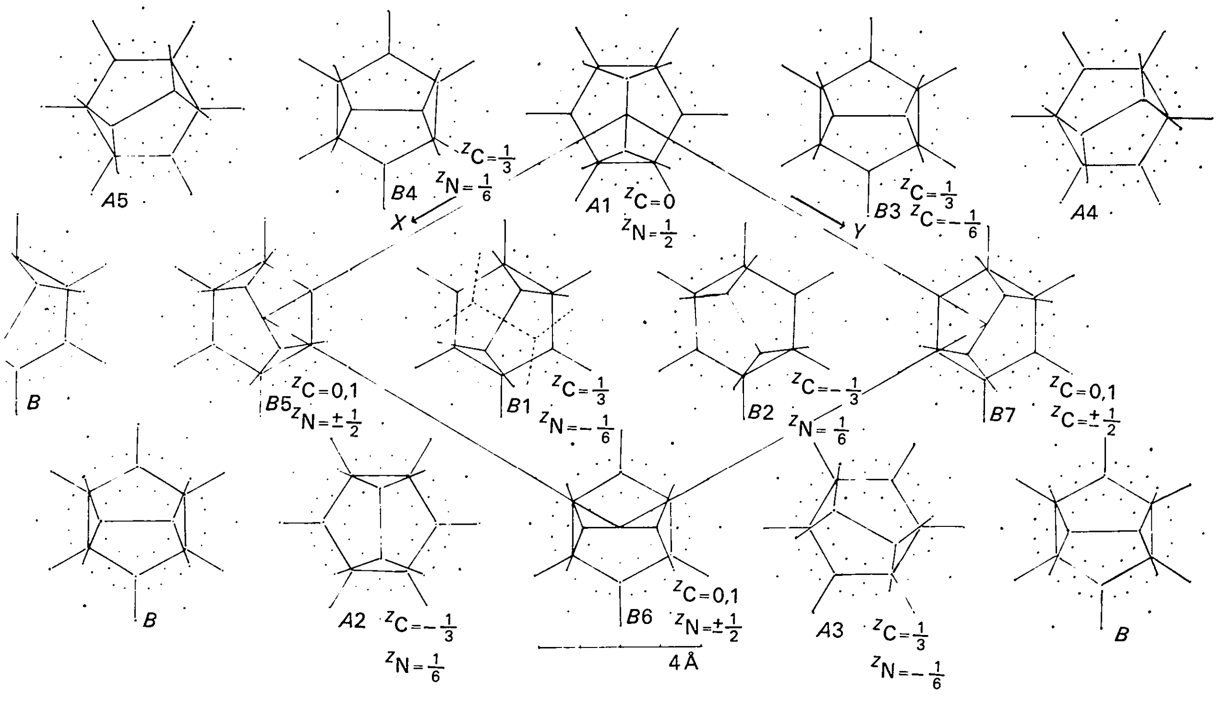

Fig. 2. Model of the instantaneous equilibrium distribution of molecules of a domain together with the statistical distribution of mean atomic positions.

is probably possible as a result of the motion, thus re-establishing the relative equilibrium configuration.

A study which is based solely on intensities of diffraction maxima, gives only restricted information about the average equilibrium properties, and it is clear that much additional information is latent in the diffuse part of the scattering. It may be concluded at the present, however, that the molecule spends considerably more time at points close to the indicated equilibrium positions than elsewhere. A similar conclusion applies to the integrated time spent in these regions. Although the energy spectrum of the lattice is complex, the above conclusion indicates that the majority of the system is in quantum states lying between the extreme cases approximated by the harmonic oscillator and the free rotator (Eyring, Walter & Kimball, 1949) respectively, at temperatures a little below the melting point. This situation pertains also in a number of other cases which will be discussed elsewhere.

Consideration of the configurational entropies implied by the distinctly different statistical models discussed above; and comparison with the experimental values of the entropy changes at the low temperature phase transformations, may further illuminate the structural problems considered here.

The full-matrix least-squares refinement program is a somewhat revised version of the original form written by Gantzel, Sparks & Trueblood (I.U.C. World List No 384). The Fourier program was written by Gantzel & Hope (Department of Chemistry, University of California, Los Angeles 24, California).

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Preparation, Structure and Properties of Triniobium Tetrasulphide, Nb_3S_4

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In the system niobium–sulphur a new phase, Nb_3S_4, has been prepared from the elements at 1000–1300°C. Fairly large needle-shaped crystals could be obtained by vapour transport with iodine. Nb_3S_4 is hexagonal ($a = 9{\cdot}5806$ Å; $c = 3{\cdot}3747$ Å; $c/a = 0{\cdot}35224$; space group $P6_3/m$) and isotypic with Nb_3Te_4 and Nb_3Se_4. The structure was refined from single-crystal diffractometer data obtained with Mo radiation. The structure is built up from NbS_6 octahedra which are linked together by shared faces and edges. Each metal atom is displaced by 0·306 Å from the octahedron centre towards one of the faces, In this way infinite zigzag metal chains are formed with Nb–Nb distances similar to those in Nb metal. Furthermore, the structure contains wide empty channels in the **c** direction. Nb_3S_4 is a metallic conductor with temperature-independent paramagnetism.

Introduction

The system Nb–S has been studied by Jellinek, Brauer & Müller (1960). The phases NbS_3, 2*s*-NbS_2, 3*s*-NbS_2, 2*s*-$Nb_{1+x}S_2$ and 3*s*-$Nb_{1+x}S_2$ were characterized, but the phase relationships in the more metal-rich range could not be disentangled. An investigation of this range has, therefore, been undertaken. The new phases