Mo atom. Another difference Fourier map where all reflections beyond $\sin\theta/\lambda = 0{\cdot}35$ were excluded provided densities less than 0·8 e Å^{-3}. In this map there were peaks at locations reasonable for hydrogen atoms, but attempts at refinement failed.

Atomic scattering factors for Mo, C and O were taken from Cromer (1974) and the anomalous dispersion corrections for Mo were obtained from Cromer & Liberman (1970).

The positional thermal parameters are reported in Table 1. Fig. 1 shows the structure and the atom numbering scheme. The bond distances (as well as the one important intermolecular contact) and the bond angles are listed in Table 2. The important least-squares planes are defined in Table 3. A table of structure factors is available.*

Discussion. The structure is in very close agreement with that of $Mo_2(O_2CCF_3)_4$. The two Mo–Mo distances, 2·093 (1) and 2·090 (4) Å are the same to within ±0·005 Å, despite the difference in the basicities of the CH_3COO^- and CF_3COO^- ligands. The average values of the other principal dimensions of this structure, *viz.* Mo–O, 2·12 ± 0·01; C–O, 1·280 ± 0·005; C–C, 1·501 ± 0·005 Å; Mo–Mo–O, 91·8 ± 0·8; O–C–O, 121·3 ± 0·5°, all agree closely with the corresponding dimensions of the $Mo_2(O_2CCF_3)_4$ structure. These dimensions would be suitable for use in molecular-orbital calculations or vibrational analyses.

The $Mo_2(O_2CCH_3)_4$ molecules are strung together in infinite chains in essentially the same way as the $Mo_2(O_2CCF_3)_4$ molecules. The oxygen atoms O(2) and O(2′) each make a contact that is essentially coaxial with the Mo–Mo bond to the closest Mo atom of the adjacent molecule. The O···Mo distance in this case, 2·645 (4) Å, is similar to those in $Mo_2(O_2CCF_3)_4$, 2·71 (1) Å, and $K_4[Mo_2(SO_4)_4].2H_2O$, 2·593 Å.

The fact that the Mo–Mo distance in the two carboxylato compounds (2·092 Å) is significantly (in a statistical sense) shorter than that [2·110 (3) Å] in the $[Mo_2(SO_4)_4]^{4-}$ ion may be due to the smaller 'bite' of the RCO_2^- ligand as compared to that of the SO_4^{2-} ligand. On the other hand, since Mo–Mo distances in various salts of the $Mo_2Cl_8^{4-}$ ion vary over a range of *ca.* 0·02 Å, (*cf.* Angell *et al.*, 1973), there may not be any such simple explanation.

We are grateful to the National Science Foundation (Grant No. GP33142X) for support and to The Robert A. Welch Foundation for funds used to purchase the diffractomerer.

* This table has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30598 (12 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

References

ANGELL, C. L., COTTON, F. A., FRENZ, B. A. & WEBB, T. R. (1973). *Chem. Commun.* pp. 399–400.

COTTON, F. A. & NORMAN, J. G. Jr (1971). *J. Coord. Chem.* **1**, 161–172.

CROMER, D. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV. Birmingham: Kynoch Press.

CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.

LAWTON, D. & MASON, R. (1965). *J. Amer. Chem. Soc.* **87**, 921–922.

Acta Cryst. (1974). B**30**, 2770

Benzidine–*s*-Trinitrobenzene Solvent-Free Molecular Complex

BY NOBORU TACHIKAWA,* KYUYA YAKUSHI AND HARUO KURODA

Department of Chemistry, Faculty of Science, The University of Tokyo, Tokyo, Japan

(*Received* 2 *May* 1974; *accepted* 11 *July* 1974)

Abstract. Orthorhombic, *Pbna*, $a = 14{\cdot}767$ (6), $b = 17{\cdot}574$ (7), $c = 7{\cdot}087$ (2) Å, $C_{12}H_{12}N_2.C_6H_3N_3O_6$, $Z = 4$, $D_x = 1{\cdot}44$, $D_m = 1{\cdot}44$ g cm^{-3}. Crystals were grown from a chloroform solution. Benzidine and *s*-trinitrobenzene are alternately stacked along **c** to form molecular columns. The two benzene rings in benzidine are twisted about the inter-ring bond. The nitro groups in *s*-trinitrobenzene are not in the plane of the benzene ring.

* Present address: Sumitomo Chemical Co., Ltd., Central Research Laboratory 2-40, Tsukahara, Takatsuki, Osaka, Japan.

Introduction. From the systematic absences in preliminary Weissenberg and precession photographs ($k = 2n+1$ for $0kl$, $h+l = 2n+1$ for $h0l$ and $h = 2n+1$ for $hk0$) the space group was determined to be *Pbna*. Very weak diffuse streaks elongated along the a^* axis were observed around the 112, 212, 022, 122, 222, 024, 124, 134, 234, 044, 154, 136, 046, 146, 156 and 066 reflexions on the Weissenberg and precession photographs. These diffuse streaks were neglected in the structure analysis.

The precise cell constants and intensity data were measured on a Rigaku four-circle automatic diffractometer using Mo $K\alpha$ radiation. 700 independent

reflexions with reliable intensities [$F_o \geq 3\sigma(F_o)$] were obtained from 2128 reflexions with $2\theta < 55°$. Seven reflexions corresponding to systematic absences were observed in the intensity measurement but were neglected in the structure analysis because of their very weak intensities. No absorption correction was made since the linear absorption coefficient is small ($\mu = 1{\cdot}35$ cm^{-1}).

The structure was solved by the Patterson and R-index maps and was refined by the method of full-matrix least-squares. The final R value was 0·045.* The weighting scheme was: $w = 1/[\sigma^2(F_o) + (0{\cdot}06F_o)^2]$. Atomic scattering factors for carbon, nitrogen and oxygen were taken from *International Tables for X-ray Crystallography* (1962), and for hydrogen from Stewart Davidson & Simpson (1965).

Final parameters with their standard deviations are listed in Tables 1 and 2. Figs. 1 and 2 show the arrangement of the molecules viewed along **c** and **a** respectively. The dihedral angles between the nitro groups and the benzene ring are 7·3° and 2·3°; that between the benzene rings of the benzidine and the *s*-trinitrobenzene molecule is 14·0°. Interatomic distances shorter than van der Waals contacts between a benzidine molecule and its nearest-neighbour *s*-trinitrobenzene molecule are 3·290 (5) Å for C(1)–C(9) and 3·374 (7) Å for C(2)–C(8). The bond distances and the bond angles are given in Table 3.

Discussion. Benzidine and *s*-trinitrobenzene form a 1:1 solid molecular complex which contains benzene in the crystal lattice. X-ray powder diffraction patterns indicate that the benzene-containing complex crystals

* A table of observed and calculated structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30580 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Atomic parameters of hydrogen atoms*

Atomic coordinates as fractions of the cell edges and their standard deviations ($\times 10^3$). Thermal parameters and their standard deviations

BD	x	y	z	B
H(1)	311 (3)	300 (2)	84 (5)	4·1 (0·9)
H(2)	320 (3)	423 (2)	188 (6)	6·3 (1·0)
H(3)	48 (3)	431 (2)	115 (5)	4·2 (0·8)
H(4)	49 (3)	319 (2)	8 (6)	6·0 (1·2)
H(5)	133 (4)	534 (3)	262 (9)	9·8 (2·1)
H(6)	235 (4)	533 (3)	320 (10)	11·0 (2·0)
TNB				
H(7)	224 (3)	352 (2)	583 (5)	3·5 (1·0)
H(8)	4 (4)	250 (0)	500 (0)	2·8 (1·4)

Table 3. *Bond distances* (Å) *and bond angles* (°)

Benzidine			
N(1)–C(3)	1·406 (6)		
C(1)–C(2)	1·387 (7)	C(1)–C(2)–C(3)	122·1 (5)
C(2)–C(3)	1·378 (7)	C(2)–C(3)–C(4)	117·2 (4)
C(3)–C(4)	1·380 (7)	C(3)–C(4)–C(5)	120·7 (5)
C(4)–C(5)	1·366 (7)	C(4)–C(5)–C(6)	123·2 (4)
C(5)–C(6)	1·395 (6)	C(5)–C(6)–C(1)	115·8 (4)
C(6)–C(1)	1·384 (7)	C(6)–C(1)–C(2)	121·1 (5)
C(6)–C(6^i)	1·494 (5)	C(1)–C(6)–C(6^i)	122·4 (4)
C(1)–H(1)	0·87 (5)	C(5)–C(6)–C(6^i)	121·9 (4)
C(2)–H(2)	0·94 (4)	C(2)–C(3)–N(1)	122·4 (5)
C(4)–H(3)	0·97 (4)	C(4)–C(3)–N(1)	120·4 (5)
C(5)–H(4)	0·88 (4)		
N(1)–H(5)	0·88 (6)		
N(1)–H(6)	1·03 (6)		
s-Trinitrobenzene			
C(7)—C(8)	1·365 (6)	C(7)—C(10)–C(7^i)	117·6 (6)
C(8)—C(9)	1·369 (5)	C(8)—C(7)—C(10)	122·8 (4)
C(7)—C(10)	1·365 (5)	C(7)—C(8)—C(9)	116·5 (4)
C(7)—N(2)	1·484 (6)	C(8)—C(9)—C(8^i)	123·7 (4)
C(9)—N(3)	1·470 (8)	C(8)—C(7)—N(2)	118·9 (4)
N(2)—O(1)	1·206 (6)	C(10)–C(7)—N(2)	118·3 (4)
N(2)—O(2)	1·217 (5)	C(8)—C(9)—N(3)	118·2 (3)
N(3)—O(3)	1·199 (5)	C(7)—N(2)—O(1)	118·2 (4)
C(8)—H(7)	0·82 (4)	C(7)—N(2)—O(2)	118·8 (4)
C(10)–H(8)	0·73 (6)	C(9)—N(3)—O(3)	117·7 (3)
		O(1)—N(2)—O(2)	123·0 (4)
		O(3)—N(3)—O(3^i)	124·5 (6)

Table 1. *Atomic parameters of carbon, nitrogen and oxygen atoms*

Atomic coordinates ($\times 10^4$) as fractions of the cell edges and their standard deviations ($\times 10^4$). Thermal parameters and their standard deviations ($\times 10^4$). The B_{ij} values refer to the expression: $\exp[-(h^2B_{11} + k^2B_{22} + l^2B_{33} + 2hkB_{12} + 2hlB_{13} + 2klB_{23})]$.

BD	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C(1)	2613 (3)	3282 (3)	812 (7)	60 (3)	32 (2)	318 (14)	1 (2)	15 (5)	5 (4)
C(2)	2632 (4)	4018 (3)	1432 (8)	67 (3)	36 (2)	345 (14)	−12 (2)	21 (5)	−4 (4)
C(3)	1842 (4)	4432 (2)	1596 (6)	84 (3)	30 (2)	244 (12)	−1 (2)	32 (5)	6 (3)
C(4)	1048 (4)	4077 (3)	1086 (7)	70 (3)	40 (2)	287 (14)	12 (2)	11 (5)	1 (4)
C(5)	1029 (4)	3329 (3)	460 (6)	59 (3)	49 (2)	241 (12)	6 (2)	−8 (5)	7 (4)
C(6)	1816 (3)	2905 (2)	317 (5)	53 (2)	34 (1)	191 (10)	−2 (2)	5 (4)	7 (3)
N(1)	1869 (5)	5195 (2)	2191 (8)	109 (4)	32 (2)	390 (16)	4 (2)	50 (7)	−5 (4)
TNB									
C(7)	1015 (3)	3142 (2)	5421 (5)	49 (2)	31 (2)	233 (11)	−1 (2)	8 (4)	20 (3)
C(8)	1939 (3)	3163 (3)	5443 (6)	58 (3)	37 (2)	218 (12)	−6 (2)	−5 (4)	−1 (4)
C(9)	2377 (4)	2500 (0)	5000 (0)	38 (3)	36 (3)	272 (17)	0 (0)	0 (0)	−5 (5)
C(10)	536 (5)	2500 (0)	5000 (0)	41 (4)	35 (3)	299 (18)	0 (0)	0 (0)	22 (5)
N(2)	505 (3)	3847 (2)	5868 (5)	71 (3)	37 (2)	290 (11)	8 (2)	13 (4)	12 (3)
N(3)	3372 (4)	2500 (0)	5000 (0)	49 (4)	58 (3)	495 (21)	0 (0)	0 (0)	−33 (7)
O(1)	−311 (3)	3828 (2)	5785 (6)	61 (2)	48 (2)	715 (17)	13 (1)	27 (4)	−14 (4)
O(2)	925 (2)	4417 (2)	6300 (5)	93 (3)	36 (1)	456 (12)	7 (2)	14 (4)	−13 (3)
O(3)	3750 (3)	3028 (3)	5724 (8)	53 (2)	86 (3)	919 (23)	−14 (2)	−22 (5)	−116 (6)

lose benzene molecules in vacuum over a long period to form the solvent-free complex. The reverse process was also observed. Similar behaviour has been found for the benzidine–7,7,8,8-tetracyano-*p*-quinodimethane complex (Ohmasa, Kinoshita & Akamatu, 1969; Yakushi, Ikemoto & Kuroda, 1974). The relative orientation between benzidine and *s*-trinitrobenzene molecules determined in the present study almost agrees with the model proposed by Wallwork (1961). The benzidine molecule is not planar but twisted around the C–C bond connecting the two benzene rings, with a dihedral angle of 14·6°; a similar dihedral angle (30·8°) is found in the benzidine skeleton in the (2:1) molecular complex between *N,N,N′,N′*-tetramethylbenzidine and chloranil (Yakushi, Ikemoto & Kuroda, 1971). In the *s*-trinitrobenzene molecule the bond angles around the carbon atoms to which the nitro groups are connected are significantly larger than the others. This tendency is observed in the *s*-trinitrobenzene crystal (Choi & Abel, 1972), and the molecular complexes of *s*-trinitrobenzene (Pascard & Pascard-Billy, 1972; Prout & Tickle, 1973).

The authors wish to thank Professor Yoshihiko Saito for helpful suggestions and advice.

The HITAC 8700/8800 computer at the Computer Centre, University of Tokyo, was used with the UNICS (1967) programs.

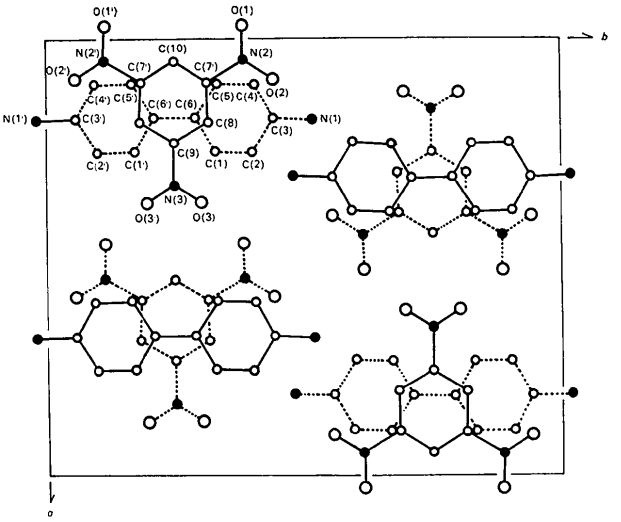

Fig. 1. Projection of the molecular arrangement onto the (001) plane.

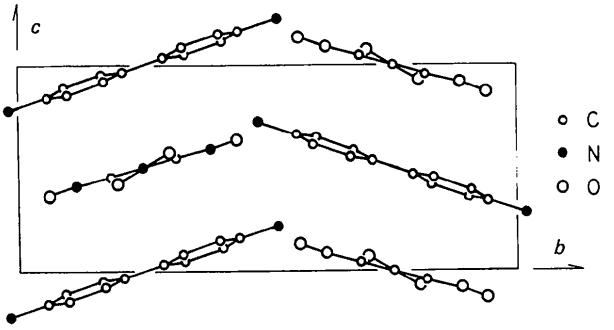

Fig. 2. Projection of the molecular arrangement onto the (100) plane.

References

CHOI, C. S. & ABEL, J. E. (1972). *Acta Cryst.* B**28**, 193–201.
International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.
OHMASA, M., KINOSHITA, M. & AKAMATU, H. (1968). *Bull. Chem. Soc. Japan*, **42**, 2402.
PASCARD, P. R. & PASCARD-BILLY, C. (1972). *Acta Cryst.* B**28**, 1926–1935.
PROUT, C. K. & TICKLE, I. J. (1973). *J. Chem. Soc. Perkin* II, pp. 734–737.
STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
UNICS (1967). *Universal Crystallographic Computation Program System.* Edited by T. SAKURAI. Tokyo: The Crystallographic Society of Japan.
YAKUSHI, K., IKEMOTO, I. & KURODA, H. (1971). *Acta Cryst.* B**27**, 1710–1718.
YAKUSHI, K., IKEMOTO, I. & KURODA, H. (1974). *Acta Cryst.* B**30**, 1738–1742.
WALLWORK, S. C. (1961). *J. Chem. Soc.* pp. 494–499.

Acta Cryst. (1974). B**30**, 2772

Tris(äthylen-1,2-dioxo)wolfram(VI)*

VON JOHANN SCHERLE UND F. A. SCHRÖDER†

Lehrstuhl I für Anorganische Chemie der Universität, D-7800 Freiburg in Breisgau, Albertstr. 21, Deutschland (BRD)

(*Eingegangen am* 31. *Mai* 1974; *angenommen am* 18. *Juli* 1974)

Abstract. Tris(ethylene-1,2-dioxo)tungsten(VI), $W(OC_2H_4O)_3$, orthorhombic, $P2_12_12_1$ (No. 19), $a=6{\cdot}905$ (2), $b=10{\cdot}418$ (4), $c=12{\cdot}669$ (4) Å, $Z=4$, $D_m=2{\cdot}66$, $D_x=2{\cdot}784$ g cm^{-3}. Each molecule is formed by a tungsten atom octahedrally coordinated by six oxygen atoms which belong in pairs to three five-membered W–O–C rings. The mean value of the W–O bond lengths is 1·908 (15) Å.

* Beiträge zur Chemie von Mo und W, 16. Mitteilung. 15. Mitt. s. Schröder, Scherle & Hazell (1974).

† Gegenwärtige Adresse: Gmelin Institut, D-6000 Frankfurt/Main 90, Varrentrappstr. 40/42, Deutschland (BRD).