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# Hexamethylenetetramine–Hydroquinone (1:1)

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**Abstract.** $(CH_2)_6N_4.p\text{-}C_6H_4(OH)_2$, monoclinic, space group $P2_1/m$, $a = 6{\cdot}056$ (5), $b = 16{\cdot}70$ (1), $c = 6{\cdot}628$ (5) Å; $\beta = 110{\cdot}8$ (1)°; $Z = 2$, $D_m = 1{\cdot}334$ (5) by flotation in hexane/$CCl_4$, $D_x = 1{\cdot}327$ g cm$^{-3}$. The structure was determined from film data and refined to $R = 0{\cdot}099$. The site symmetries of the hexamethylenetetramine and hydroquinone molecules are $m$ and 1 respectively. The two types of molecules are linked by N···H—O hydrogen bonds to form infinite zigzag chains in the direction of $b$.

**Introduction.** Hexamethylenetetramine (hereinafter HMT) forms a variety of complexes with phenol (Moschatos & Tollens, 1892; Smith & Welch, 1934) and substituted phenols (Altpeter, 1931). The structure of the 1:3 adduct with phenol is known (Jordan & Mak, 1970), and crystal data for the 1:1 adduct and several other complexes of HMT with substituted phenols have been reported (Tse, Wong & Mak, 1977). The 1:1 adduct of HMT with hydroquinone (quinol) has an unusually high melting point, 201–202°C, which is indicative of extensive hydrogen bonding. Hydrogen bonds of the types N···O—H and O···H—O could conceivably be present, and to settle this point we have undertaken an X-ray analysis. It constitutes part of our investigation on hydrogen-bonded molecular compounds of HMT.

Colourless prisms of the adduct were prepared as described by Tse, Wong & Mak (1977). A roughly spherical crystal of diameter 0·4 mm was used for the X-ray measurements. Cell dimensions were determined from high-angle reflexions on all three zero-layer Weissenberg photographs calibrated with superimposed NaCl powder lines and refined by minimizing the sum of the residuals $|\sin^2\theta_m - \sin^2\theta_c|$. Intensities were collected about **a** for reflexions $0kl$–$5kl$ and about **c** for $hk0$–$hk6$ by the multiple-film equi-inclination Weissenberg method with Cu $K\alpha$ ($\lambda = 1{\cdot}5418$ Å) radiation. The intensities were estimated by comparison with a calibrated strip. They were corrected for Lorentz and polarization factors but not for absorption ($\mu = 7{\cdot}75$ cm$^{-1}$). A set of scaled structure amplitudes was derived by the least-squares procedure of Hamilton, Rollett & Sparks (1965). 1153 independent observed and 215 unobserved reflexions were obtained.

The structure was solved with *MULTAN* (Germain, Main & Woolfson, 1971). Full-matrix isotropic and anisotropic least-squares refinement yielded an $R$ of 0·165. Inspection of the low-order reflexions showed that they were subject to large extinction effects. Inclusion of a secondary extinction parameter $C$ (Zachariasen, 1967, 1968) as an additional variable

Table 1. *Fractional atomic coordinates with e.s.d.'s in parentheses*

| Atom | Bonded to | $x$ | $y$ | $z$ |
|---|---|---|---|---|
| C(1) | | 0·4315 (8) | $\frac{1}{4}$ | 0·4095 (8) |
| C(2) | | 0·9467 (10) | $\frac{1}{4}$ | 0·8328 (10) |
| C(3) | | 0·7950 (7) | 0·1783 (2) | 0·4974 (7) |
| C(4) | | 0·5823 (7) | 0·1788 (2) | 0·7422 (6) |
| N(1) | | 0·9290 (7) | $\frac{1}{4}$ | 0·6043 (9) |
| N(2) | | 0·7124 (8) | $\frac{1}{4}$ | 0·8541 (7) |
| N(3) | | 0·5564 (5) | 0·1769 (2) | 0·5138 (5) |
| C(5) | | 0·1133 (6) | 0·0321 (2) | 0·2057 (6) |
| C(6) | | 0·2195 (6) | 0·0353 (2) | 0·0528 (6) |
| C(7) | | −0·1099 (6) | −0·0040 (2) | 0·1510 (6) |
| O(1) | | 0·2181 (5) | 0·0601 (2) | 0·4124 (4) |
| H(1) | C(1) | 0·257 | $\frac{1}{4}$ | 0·421 |
| H(2) | C(1) | 0·420 | $\frac{1}{4}$ | 0·242 |
| H(3) | C(2) | 1·041 | 0·196 | 0·910 |
| H(4) | C(3) | 0·891 | 0·125 | 0·578 |
| H(5) | C(3) | 0·774 | 0·180 | 0·327 |
| H(6) | C(4) | 0·407 | 0·180 | 0·752 |
| H(7) | C(4) | 0·680 | 0·126 | 0·821 |
| H(8) | C(6) | 0·391 | 0·063 | 0·093 |
| H(9) | C(7) | −0·196 | −0·007 | 0·268 |
| H(10) | O(1) | 0·340 | 0·098 | 0·415 |

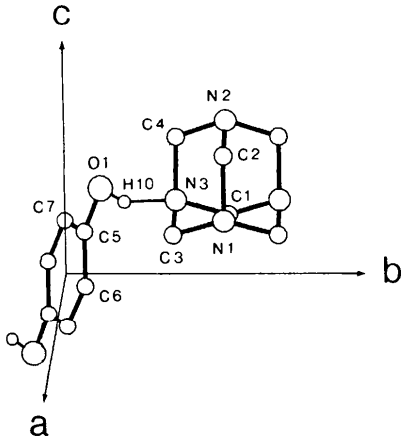


Fig. 1. Atom numbering in HMT–hydroquinone (1:1).

lowered $R$ to 0·114. Further refinement was attempted by the introduction of ring H atoms generated with a computer program based on an algorithm similar to that given for the $X_3CH$ group by Rollett (1965). Inclusion of nine methylene and aromatic H atoms with $B = 5{\cdot}5$ Å$^2$ gave a final $R$ of 0·099. The value obtained for $C$ was 0·000204 (9). A difference map calculated with reflexions with $\sin\theta/\lambda < 0{\cdot}50$ gave a well-resolved peak of 0·45 e Å$^{-3}$ in the expected position for the phenolic H(10); all other peaks in the map were < 0·28 e Å$^{-3}$.

Scattering factors for non-hydrogen atoms (numbering shown in Fig. 1) were taken from *International Tables for X-ray Crystallography* (1974), that for H from Stewart, Davidson & Simpson (1965). Structure factor calculation and least-squares refinement were carried out on an ICL 1904A computer with a modification of *ORFLS* (Busing, Martin & Levy, 1962). The function minimized was $\Sigma w(|F_o| - |F_c|/\mathrm{ZACH})^2$, with $\mathrm{ZACH} = \{C\beta I_o + [1 + (C\beta I_o)^2]^{1/2}\}^{1/2}$, where $I_o$ is the measured integrated intensity on approximately the right scale, and $\beta$ is an angular-dependent function (Zachariasen, 1963) evaluated for a crystal sphere of $\mu R = 1{\cdot}5$. The weighting scheme was that of Cruickshank (1961) with $\omega = (2F_{\min} + |F_o| + 2|F_o|^2/F_{\max})^{-1/2}$, where $F_{\min}$ and $F_{\max}$ were taken as 4·0 and 200·0 respectively.

The final atomic positional parameters are listed in Table 1.† A *PLUTO* (Motherwell, 1975) stereoplot of the structure is shown in Fig. 2. Bond lengths and angles are listed in Table 2.

Table 2. *Bond lengths* (Å) *and angles* (°) *with their e.s.d.'s*

| | | | |
|---|---|---|---|
| C(1)–N(3) | 1·473 (4) | C(5)–C(6) | 1·381 (5) |
| C(2)–N(1) | 1·480 (9) | C(5)–C(7) | 1·405 (5) |
| C(2)–N(2) | 1·475 (8) | C(6)–C(7)′ | 1·379 (5) |
| C(3)–N(1) | 1·479 (5) | C(5)–O(1) | 1·371 (5) |
| C(3)–N(3) | 1·487 (5) | O(1)–H(10) | 0·968 (14) |
| C(4)–N(2) | 1·473 (5) | O(1)···N(3) | 2·734 (4) |
| C(4)–N(3) | 1·466 (5) | H(10)···N(3) | 1·809 (15) |
| N(3)–C(1)–N(3)′ | 112·0 (4) | C(6)–C(5)–C(7) | 118·9 (3) |
| N(1)–C(2)–N(2) | 112·1 (5) | C(5)–C(6)–C(7)′ | 121·1 (3) |
| N(1)–C(3)–N(3) | 111·1 (3) | C(5)–C(7)–C(6)′ | 120·0 (3) |
| N(2)–C(4)–N(3) | 112·4 (3) | C(6)–C(5)–O(1) | 123·3 (3) |
| C(2)–N(1)–C(3) | 108·6 (3) | C(7)–C(5)–O(1) | 117·8 (3) |
| C(3)–N(1)–C(3)′ | 108·2 (4) | C(5)–O(1)–H(10) | 108·7 (8) |
| C(2)–N(2)–C(4) | 108·2 (3) | O(1)–H(10)···N(3) | 158·9 (11) |
| C(4)–N(2)–C(4)′ | 107·6 (4) | | |
| C(1)–N(3)–C(3) | 107·6 (3) | | |
| C(1)–N(3)–C(4) | 108·4 (3) | | |
| C(3)–N(3)–C(4) | 109·0 (3) | | |

**Discussion.** The site symmetries of the HMT and hydroquinone molecules are $m$ and $\bar{1}$ respectively. The structure is composed of alternate layers of the two kinds of molecules parallel to (010), the interlayer separation being $b/2$. Each molecule in a given layer is linked to two others in neighboring layers by N···H–O hydrogen bonds, resulting in zigzag chains extending along **b** (Fig. 2). Two of the four N lone pairs serve as acceptors in forming two hydrogen bonds. This mode of hydrogen bonding differs from that found for HMT.6$H_2O$ (Mak, 1965) and HMT.3$C_6H_5OH$ (Jordan & Mak, 1970), in each of which the HMT group forms three hydrogen bonds.

The dimensions of HMT are in good agreement with those in crystalline HMT (Becka & Cruickshank, 1963). The hydroquinone skeleton, including the phenolic H atoms, is planar within experimental error. The equation to the mean plane containing O(1), C(5)–C(7) and atoms related by the symmetry centre at the origin is $0{\cdot}3454X - 0{\cdot}8872Y + 0{\cdot}3057Z = 0$, where $X,Y,Z$ are Cartesian coordinates in Å referred to a set of axes directed along **a**, **b** and **c***. The estimated

† Tables of thermal parameters and structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32761 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

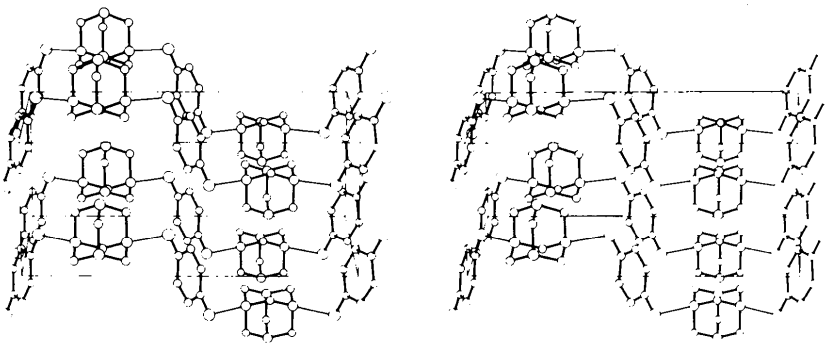

Fig. 2. A stereodrawing showing the molecular packing viewed approximately along **a** toward the origin of the unit cell at the lower left corner.

standard deviation of the non-hydrogen atoms from the least-squares plane is 0·014 Å. The dimensions of hydroquinone are also similar to those found in several other crystal structures (Mahmoud & Wallwork, 1975). The significant difference between C(6)–C(5)–O(1) and C(7)–C(5)–O(1) is in accord with the observation that, for many phenols, the C–C–OH angle is somewhat larger on the side of the H atom (Mahmoud & Wallwork, 1975).

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# 1-Methyl-2-naphthyl Acetate

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**Abstract.** $C_{13}H_{12}O_2$, monoclinic, $P2_1/c$, $Z = 4$, $M_r = 200$, $a = 6{\cdot}46$, $b = 8{\cdot}33$, $c = 20{\cdot}25$ Å, $\beta = 91{\cdot}90°$, $U = 1088$ Å$^3$, $D_m = 1{\cdot}41$, $D_x = 1{\cdot}22$ g cm$^{-3}$, $\lambda = 0{\cdot}7107$ Å, $\mu$(Mo $K\alpha$) $= 0{\cdot}88$ cm$^{-1}$, $F(000) = 424$, $R = 4{\cdot}6\%$. The molecular dimensions in the aromatic system are similar to those in naphthalene itself.

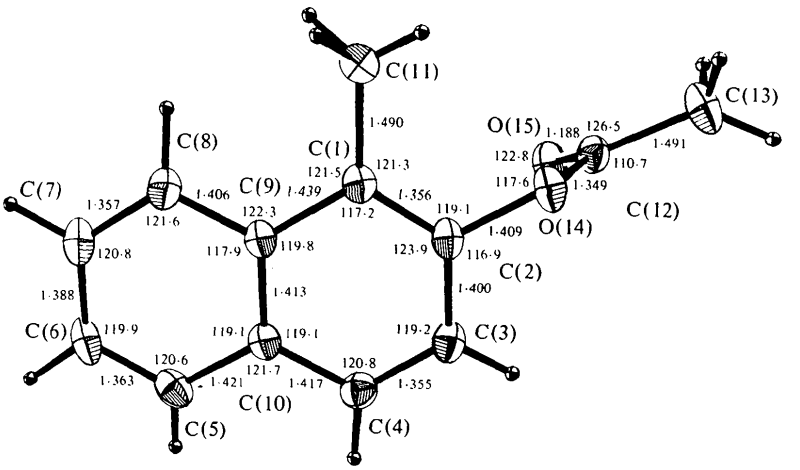


Fig. 1. A view of the molecule, showing bond lengths (Å) and bond angles (°).