4,4'-Dinitrobenzil

By Michio Kimura, Rebecca E. McCluney and William H. Watson*

FASTBIOS Laboratory, Department of Chemistry, Texas Christian University, Fort Worth, Texas 76129, *USA*

Abstract. $C_{14}H_8N_2O_6$, FW 276·22, triclinic, $P\bar{1}$, $a = 7·829$ (4), $b = 13·467$ (8), $c = 7·187$ (5) Å, $\alpha = 94·07$ (5), $\beta = 59·14$ (4), $\gamma = 87·35$ (5)°, $V = 645·8$ (6) Å^3, $Z = 2$, $D_c = 1·861$ Mg m^{-3}, $\mu = 1·326$ mm^{-1}, λ(Cu $K\alpha$) = 1·54178 Å. Full-matrix least-squares refinement (nonhydrogen atoms anisotropic, H atoms isotropic) based on 1381 reflections led to an R factor of 0·059. The two halves of the molecule are planar with an interplanar angle of 111·0° and a corresponding O—C—C—O torsion angle of 111·5°.

Introduction. α-Diketones such as benzil and biacetyl act as sensitizers in the photooxidation of olefins (Shimizu & Bartlett, 1976). In order to understand the mechanism of photooxidation the nature of the excited species of the sensitizer must be understood. It has been noted that bis-*para*-substituted benzils vary in their ability to sensitize the photooxidation reaction (Speth, 1978). Spectroscopic evidence indicates that the triplet states of benzil derivatives are planar and that variations in the absorption and fluorescence spectra may be related to variations in the interplanar angle of the ground state. Dipole-moment studies (Cumper & Thurston, 1972) and Kerr-constant measurements (Cureton, LeFevre & LeFevre, 1961) of benzil derivatives in solution indicate interplanar angles of 90 to 100°. A crystallographic investigation of benzil (Brown & Sadanaga, 1965) showed an interplanar angle of 104° in the solid state which may indicate that conformational changes as a result of packing interactions may be relatively small. We report the structure of 4,4'-dinitrobenzil in the solid state.

The title compound was synthesized by literature procedures (van Es & Backeberg, 1963*a,b*) and recrystallized from glacial acetic acid, m.p. 483–485 K. A crystal of dimensions 0·3 × 0·3 × 0·6 mm was used to collect all data. The unit cell was found to be triclinic and room-temperature cell dimensions were obtained by a least-squares fit to 15 medium-angle reflections using the computer routine furnished by Syntex. There were no systematic absences and statistics indicated space group $P\bar{1}$. Intensity data for $2\theta < 120°$ were collected on a Syntex $P2_1$ diffractometer by the $\theta:2\theta$

scan technique using graphite-monochromated radiation and a variable scan speed. A periodically-monitored reflection showed no significant crystal deterioration. Of the 1786 independent reflections measured, 1381 had intensities greater than $3\sigma(I)$ where $\sigma(I)$ was estimated from counting statistics. Reflections with negative measured intensities were assigned the value of zero. Lorentz and polarization corrections were applied but no absorption corrections were made.

The structure was solved by direct methods using *MULTAN* (Germain, Main & Woolfson, 1971) to calculate phases for the 400 $|E_h|$ values greater than 1·15. The E map computed from the phase set with the

Table 1. *Atomic positional parameters* ($\times 10^3$ *for* H *atoms and* $\times 10^4$ *for all others*)

|	x	y	z
O(1)	5672 (4)	7044 (2)	4344 (4)
C(1)	5815 (5)	7194 (3)	5940 (6)
C(2)	6432 (5)	6387 (2)	6851 (5)
C(3)	6903 (5)	5421 (3)	5796 (6)
C(4)	7565 (5)	4660 (3)	6531 (6)
C(5)	7719 (5)	4890 (3)	8330 (6)
C(6)	7263 (5)	5830 (3)	9414 (6)
C(7)	6613 (5)	6594 (3)	8649 (6)
N(1)	8459 (4)	4079 (2)	9127 (6)
O(2)	9151 (5)	3299 (2)	7961 (5)
O(3)	8292 (5)	4235 (2)	10899 (5)
O(4)	3754 (4)	8409 (2)	8879 (4)
C(8)	5249 (5)	8264 (3)	7082 (6)
C(9)	6456 (5)	9082 (2)	5918 (5)
C(10)	5839 (5)	10063 (3)	6918 (5)
C(11)	6910 (5)	10841 (2)	5914 (6)
C(12)	8619 (5)	10620 (2)	3886 (5)
C(13)	9295 (5)	9662 (3)	2859 (5)
C(14)	8193 (5)	8884 (2)	3878 (6)
N(2)	9798 (4)	11449 (2)	2797 (5)
O(5)	9185 (5)	12295 (2)	3690 (5)
O(6)	11368 (4)	11249 (2)	1059 (4)
H(3)	679 (4)	531 (2)	464 (5)
H(4)	785 (5)	400 (2)	579 (5)
H(6)	744 (5)	599 (3)	1065 (6)
H(7)	634 (4)	724 (2)	938 (4)
H(10)	473 (4)	1016 (2)	823 (5)
H(11)	655 (5)	1150 (2)	656 (5)
H(13)	1044 (5)	955 (2)	155 (5)
H(14)	857 (4)	822 (2)	315 (5)

---

* To whom correspondence should be addressed.
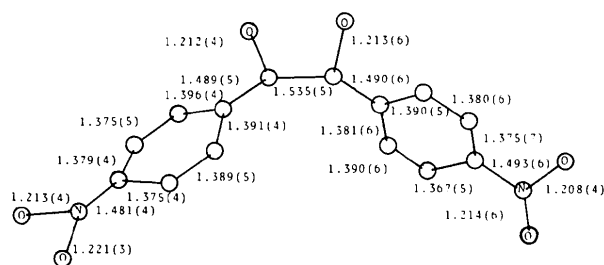
Fig. 1. Bond lengths (Å) for 4,4'-dinitrobenzil.

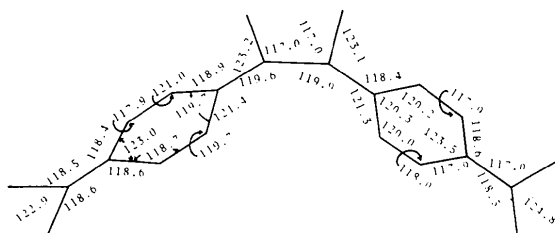
Fig. 2. Valence angles (°) for 4,4'-dinitrobenzil. Standard deviations are 0·4 or 0·5° for all angles.
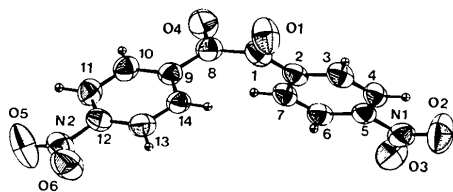

Fig. 3. ORTEP drawing of 4,4'-dinitrobenzil. Anisotropic thermal ellipsoids are drawn at the 50% probability level while isothermal spheres are of arbitrary size.

largest combined figure of merit revealed all 22 non-hydrogen atoms. Full-matrix least-squares refinement with anisotropic thermal parameters yielded an R value of 0·063 where $R = (\sum \Delta F_{meas} / \sum |F_{meas}|)$. A difference map computed with the phases from the least-squares refinement revealed the positions of all H atoms. Least-squares refinement with isotropic H-atom thermal parameters yielded a final R of 0·059 for the 1381 reflections with intensities greater than $3\sigma(I)$ and 0·069 for all 1786 observed reflections. The function minimized was $\sum w(\Delta F_{meas})^2$ where $w = 1/\sigma^2(F)$. The scattering factors for all atoms were taken from International Tables for X-ray Crystallography (1974).

All parameter shifts during the final cycle were less than 0·5σ, and a final difference map showed a largest peak of 0·34 e Å^{-3}. Atomic positional parameters are given in Table 1 while bond lengths and angles are indicated in Figs. 1 and 2.*

Discussion. Fig. 3 is an ORTEP drawing (Johnson, 1965) of the 4,4'-dinitrobenzil molecule. The two halves of the molecule are planar except for a small rotation of the N(1) nitro group. The interplanar angle is 111·0° while the O(1)C(1)C(8)O(4) torsion angle is 111·5° which reflects the planarity of the two halves of the molecule. The interplanar angle and torsion angle for benzil (Brown & Sadanaga, 1965) are 104 and 108°. The bond distances and angles for the two structures agree within 3σ. There are 12 intermolecular contacts between 3·25 and 3·40 Å with the shortest between O(2) and O(5) of adjacent molecules.

---

* Lists of structure factors, thermal parameters and torsion angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33953 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

BROWN, C. J. & SADANAGA, R. (1965). Acta Cryst. 18, 158–164.

CUMPER, C. W. N. & THURSTON, A. P. (1972). J. Chem. Soc. Perkin Trans. 2, pp. 106–111.

CURETON, P. H., LeFEVRE, C. G. & LeFEVRE, R. J. W. (1961). J. Chem. Soc. pp. 4447–4451.

Es, T. VAN & BACKEBERG, O. G. (1963a). J. Chem. Soc. pp. 1363–1370.

Es, T. VAN & BACKEBERG, O. G. (1963b). J. Chem. Soc. pp. 1371–1377.

GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). Acta Cryst. A27, 368–376.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

JOHNSON, C. K. (1965). ORTEP. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

SHIMIZU, N. & BARTLETT, P. D. (1976). J. Am. Chem. Soc. 98, 4193–4200.

SPETH, D. (1978). Private communication.