Crystal Structure of the Enol Form of 1-(4-Nitrophenyl)butane-1,3-dione

By **Raymond D. G. Jones**, Department of Inorganic Chemistry, The University of Sydney, Sydney, New South Wales, Australia 2006

The crystal structure of the title compound has been determined from three-dimensional, *X*-ray diffraction data collected by counter methods. The compound crystallizes in the orthorhombic space group $P2_12_12_1$ and has cell dimensions a = 3.864(2), b = 10.384(2), and c = 24.342(5) Å, Z = 4. The structure was solved by tangent refinement methods and refined by full-matrix least-squares to R 0.092 (0.049 for observed reflections) for 846 reflections. Interatomic distances and angles indicate that the enol tautomer is present. The two carbon–oxygen and the two carbon–carbon bond lengths in the enol ring are equivalent suggesting that the strong, intramolecular hydrogen bond [O · · · O 2.457(4) Å] is symmetric or statistically disordered. The dihedral angle between the phenyl and enol groups is 10.1°.

EXTENSIVE studies of 1,3-diketones (β-diketones) have been made by i.r. and n.m.r. techniques and suggest that a strong, intramolecular hydrogen bond is formed when the diketo-compound enolizes. *X*-Ray diffraction investigations have shown that the O · · · O contact is *ca.* 2.4—2.5 Å. For the simple β-diketones, *X*-ray analyses indicate that the enol hydrogen atom is asymmetrically placed with respect to the oxygen atoms in benzoylacetone [1] and dibenzoylmethane.[2] However, a recent analysis of dibenzoylmethane suggests that the hydrogen bond is symmetric.[3]

^{1}H N.m.r. studies of *para*-substituted benzoylacetones in deuteriochloroform show that the chemical shift of the enol hydrogen atom varies markedly with the nature of the *para*-substituent.[4] A structural study of some of the substituted compounds is being undertaken to determine if a relationship exists between the structural parameters and the nature of the *para*-substituent and to ascertain factors which contribute to symmetrical and asymmetrical hydrogen bonds.

EXPERIMENTAL

The compound was prepared by the method of Manyik *et al.*[4] and purified *via* the copper complex and subsequent sublimation. Pale yellow crystals were grown from acetone. Weissenberg and precession photographs showed the crystals were orthorhombic. The space group was uniquely determined as $P2_12_12_1$ from systematic absences.

Crystal Data.—$C_{10}H_9NO_4$, $M = 207.1$. Orthorhombic, $a = 3.864(2)$, $b = 10.384(2)$, $c = 24.342(5)$ Å, $U = 987.7$ Å^3, $D_m = 1.56$, $Z = 4$, $D_c = 1.41$ g cm^{-3}, $F(000) = 432$. Mo-$K_{\bar{\alpha}}$ radiation, $\lambda = 0.710\,69$ Å, μ(Mo-$K_{\bar{\alpha}}$) = 1.19 cm^{-1}.

A crystal measuring 0.18 × 0.12 × 0.38 mm was mounted such that the ***a****-axis was a few degrees off-set from the ϕ-axis of a Stoe four-circle goniometer and was used for determination of the cell dimensions and measurement of intensity data. Cell dimensions were obtained from the least-squares analysis of the 2θ values of 19 high-angle reflections which had been carefully centred in the detector aperture.

Intensity data were collected by the θ—2θ step-scan method by use of Mo-K_α radiation.[5] Each reflection was scanned 1.5° in 2θ in steps of 0.01° and the diffracted radiation counted for 0.5 s at each step. At the ends of the scan range, the background was counted for a time which allowed optimization of the counting statistics.[6] The intensity of a standard reflection measured every 50 reflections showed no fall off during data collection. Intensities for reflections $\{hkl\}$ and $\{h\bar{k}l\}$ with $2\theta \leqslant 45°$ were measured. Intensities were corrected for background, absorption and the Lorentz-polarization factor. For each reflection, σ_I^2 was determined.[6] Equivalent reflections were combined to yield 846 unique reflections. If the intensity was negative, it was set to a small positive value but the variance remained unchanged.

Structure Determination.—*E*-Values were calculated and 168 reflections with $E \geqslant 1.2$ were used in the tangent refinement procedure.[7,8] 165 Reflections were phased and gave a satisfactory solution. The atomic parameters of the non-hydrogen atoms were refined by block-diagonal, and finally, full-matrix least-squares methods. The function minimized was $\Sigma w(|F_o| - k|F_c|)^2$ and each reflection was assigned unit weight. All hydrogen atoms except the enol hydrogen atom were located and their positional parameters were refined in subsequent cycles. Further refinement with all measured data [9] and experimental weights based on σ_I^2 led to convergence with a final R of 0.092 (0.049 for reflections having $I \geqslant 2.3\sigma_I$) and R' 0.055 (0.048) [$R' = \Sigma w(||F_o| - |F_c||)^2/\Sigma w(|F_o|)^2$]. The error-of-fit was 1.33. There was no dependence of $w\Delta^2$ on F_o or $(\sin\theta)\lambda^{-1}$. There were no significant peaks in a final electron-density difference map, not even where the enol hydrogen atom would be expected.

Scattering factors for non-hydrogen atoms were taken from ref. 10, that for hydrogen from ref. 11.

RESULTS

Final atomic parameters are listed in Table 1. Table 2 contains the interatomic distances and angles, the errors in which include contributions from the variance-covariance

---

[1] D. Semmingsen, *Acta Chem. Scand.*, 1972, **26**, 143.

[2] D. E. Williams, *Acta Cryst.*, 1966, **21**, 340.

[3] F. J. Hollander, D. H. Templeton, and A. Zalkin, *Acta Cryst.*, 1973, **B29**, 1552.

[4] R. M. Manyik, F. C. Frostick, J. J. Sanderson, and C. R. Hauser, *J. Amer. Chem. Soc.*, 1953, **75**, 5030.

[5] A. McG. Beech and J. E. Eberhardt, 'Semiconductor *X*-Ray Spectrometer System Type **454**,' 1973. Report AAEC E297, Australian Atomic Energy Commission.

[6] M. M. Elcombe, G. W. Cox, A. W. Pryor, and F. H. Moore, 'Programs for the Management and Processing of Neutron Diffraction Data,' 1971, Report AAEC TM578, Australian Atomic Energy Commission.

[7] J. Karle and I. L. Karle, *Acta Cryst.*, 1966, **21**, 849.

[8] H. A. Hauptman, 'Crystal Structure Determination.' The Role of Cosine Seminvariants,' 1972, Plenum Press, New York.

[9] F. H. Moore, IXth Congress Internat. Union Crystallography, Kyoto, 1972.

[10] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1964, **18**, 104.

[11] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

TABLE 1

Final positional (fractional co-ordinates) and thermal * parameters (Å² × 10⁴), with estimated standard deviations in parentheses

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
N(1)	−2 876(16)	327(5)	5 114(2)	897(44)	880(38)	528(30)	173(43)	14(32)	71(28)
O(1)	1 204(14)	−2 803(3)	2 973(1)	1 284(45)	560(22)	878(26)	−57(29)	215(30)	−90(20)
O(2)	3 581(14)	−2 625(4)	2 039(1)	1 225(45)	842(28)	832(26)	82(34)	106(30)	−301(23)
O(3)	−2 121(16)	1 422(4)	5 251(1)	1 745(60)	920(29)	708(25)	127(43)	207(38)	−143(24)
O(4)	−4 523(16)	−392(4)	5 412(2)	1 618(59)	1 402(39)	675(27)	−336(48)	405(35)	63(26)
C(1)	236(16)	−1 034(4)	3 558(2)	505(37)	511(30)	548(28)	10(32)	−63(30)	84(25)
C(2)	742(17)	248(5)	3 701(2)	816(48)	529(32)	493(29)	24(38)	14(34)	46(25)
C(3)	−227(17)	713(5)	4 208(2)	735(46)	550(31)	568(32)	67(40)	25(37)	27(28)
C(4)	−1 770(15)	−146(5)	4 569(2)	523(39)	653(35)	526(31)	42(35)	−17(30)	11(28)
C(5)	−2 360(16)	−1 431(5)	4 448(2)	595(45)	672(37)	651(35)	11(38)	−102(35)	128(28)
C(6)	−1 262(18)	−1 856(5)	3 937(2)	760(48)	584(35)	653(34)	11(43)	−38(36)	20(32)
C(7)	1 344(16)	−1 547(5)	3 020(2)	795(50)	573(32)	516(31)	60(37)	−59(34)	−47(28)
C(8)	2 519(17)	−832(5)	2 588(2)	583(38)	592(29)	506(30)	26(37)	45(31)	23(28)
C(9)	3 565(16)	−1 385(6)	2 091(2)	671(46)	771(39)	559(32)	95(41)	−80(35)	−68(31)
C(10)	4 719(27)	−600(7)	1 613(3)	1 113(70)	1 059(53)	563(37)	77(63)	137(45)	−221(38)
H(2) †	152(15)	90(4)	344(2)						
H(3)	−9(15)	179(4)	432(2)						
H(5)	−365(15)	−212(4)	471(2)						
H(6)	−166(17)	−262(5)	386(2)						
H(8)	271(16)	7(5)	262(2)						
H(101)	394(17)	−88(5)	120(2)						
H(102)	664(16)	−100(5)	147(2)						
H(103)	478(17)	631(4)	173(2)						

* The form of the anisotropic thermal parameter is $\exp[-2\pi(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})]$. † Hydrogen atoms were assigned a fixed isotropic thermal parameter, U, of 0.076 Å², and are numbered according to the carbon atom to which they are bonded. Hydrogen atom co-ordinates × 10³.

matrix and errors in cell dimensions. The equations of planes through selected atomic groupings are shown in Table 3. The Figure shows the molecule and indicates the labelling scheme. Observed and calculated structure

TABLE 2

Selected interatomic distances (Å) and angles (°)

(*a*) Interatomic distances

N(1)–O(3)	1.217(5)	N(1)–C(4)	1.476(5)
	1.261 *		1.495 *
N(1)–O(4)	1.219(5)	C(7)–O(1)	1.306(4)
	1.281 *	C(9)–O(2)	1.289(5)
C(1)–C(2)	1.385(5)	C(6)–C(1)	1.383(6)
C(2)–C(3)	1.376(6)	C(1)–C(7)	1.477(5)
C(3)–C(4)	1.386(6)	C(7)–C(8)	1.363(5)
C(4)–C(5)	1.381(6)	C(8)–C(9)	1.397(6)
C(5)–C(6)	1.385(6)	C(9)–C(10)	1.488(7)
O(1) · · · O(2)	2.457(5)	C(8)–H(8)	0.94(4)
C(2)–H(2)	0.97(4)	C(10)–H(101)	0.88(4)
C(3)–H(3)	1.15(4)	C(10)–H(102)	0.92(4)
C(6)–H(6)	0.83(4)	C(10)–H(103)	0.98(4)

(*b*) Interatomic angles

N(1)–C(4)–C(5)	117.6(4)	C(10)–C(9)–O(2)	117.7(4)
N(1)–C(4)–C(3)	118.8(4)	C(8)–C(9)–C(10)	122.7(5)
O(3)–N(1)–O(4)	121.9(4)	C(1)–C(2)–H(2)	123(2)
O(3)–N(1)–C(4)	119.1(4)	C(3)–C(2)–H(2)	115(2)
O(4)–N(1)–C(4)	119.0(4)	C(2)–C(3)–H(3)	123(2)
C(2)–C(1)–C(6)	118.7(4)	C(4)–C(3)–H(3)	119(2)
C(1)–C(2)–C(3)	121.5(4)	C(4)–C(5)–H(5)	126(2)
C(2)–C(3)–C(4)	117.5(4)	C(6)–C(5)–H(5)	118(2)
C(3)–C(4)–C(5)	123.6(4)	C(5)–C(6)–H(6)	117(2)
C(4)–C(5)–C(6)	116.6(4)	C(1)–C(6)–H(6)	121(2)
C(5)–C(6)–C(1)	122.2(4)	C(7)–C(8)–H(8)	120(3)
C(2)–C(1)–C(7)	121.8(4)	C(9)–C(8)–H(8)	117(3)
C(6)–C(1)–C(7)	119.5(4)	C(9)–C(10)–H(101)	114(3)
C(1)–C(7)–C(8)	125.9(4)	C(9)–C(10)–H(102)	107(3)
C(1)–C(7)–O(1)	115.0(4)	C(9)–C(10)–H(103)	108(3)
C(8)–C(7)–O(1)	119.1(4)	H(101)–C(10)–H(102)	78(3)
C(7)–C(8)–C(9)	122.8(4)	H(101)–C(10)–H(103)	125(3)
C(8)–C(9)–O(2)	119.6(5)	H(102)–C(10)–H(103)	122(3)

* Interatomic distance corrected for 'riding motion.'

TABLE 3

Equations of planes, through selected atomic groupings, in the form $lX + mY + nZ + D = 0$, where l, m, and n are the direction cosines of the plane normal relative to orthogonal axes X, Y, and Z in Å. X is along the a axis, Y is in the ab plane, and Z is along c^*. Deviations (Å), of relevant atoms, from the planes are listed in square brackets

	l	m	n	D
Plane (1): C(1)—(6)	−0.8999	0.2294	−0.3710	3.546

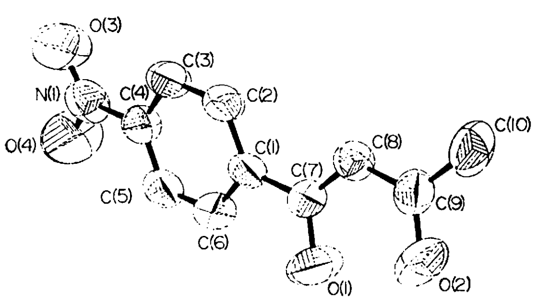
[C(1) 0.005, C(2) 0.004, C(3) −0.006, C(4) −0.001, C(5) 0.010, C(6) −0.012, N(1) 0.005, O(3) −0.122, O(4) 0.137]

	l	m	n	D
Plane (2): N(1), O(3), O(4)	−0.8522	0.3378	−0.3996	3.912
Plane (3): O(1), O(2), C(7)—(9)	−0.9310	0.0572	−0.3606	3.219

[O(1) 0.011, O(2) −0.015, C(7) −0.007, C(8) −0.008, C(9) 0.019, C(10) 0.068, C(1) 0.050, C(2) −0.282, C(6) 0.107]

Angles (°) between the planes

(1)–(2)	(1)–(3)	(2)–(3)
7.0	10.1	16.9



A diagram of the molecule showing the numbering used. The atoms are represented as 50% probability thermal ellipsoids. Hydrogen atoms are not shown factors are listed in Supplementary Publication No. SUP 21605 (8 pp., 1 microfiche).*

DISCUSSION

The structural analysis has confirmed the presence of the enol tautomer in the solid state and is consistent with the i.r. spectrum. The phenyl ring and the enol ring are both planar but the molecule as a whole is not. The dihedral angle between the phenyl and enol rings is 10.1°. It is unlikely that the molecule would be planar because of H · · · H and O · · · H interference between the individual planar groupings. In benzoylacetone,[1] the dihedral angle between phenyl and enol rings is 6.3° while for *p*-bromobenzoylacetone [12] it is 17.3°.

A strong intramolecular hydrogen bond is present with O · · · O 2.457(5) Å. This value is similar to that found in other β-diketones [1-3,12-16] and, in particular, can be compared with that in benzoylacetone [2.498(2) Å],[1] and *p*-bromobenzoylacetone [2.481(9) Å].[12] Although the O · · · O values for the benzoylacetones are different, there is no relationship between the phenyl–enol dihedral angle, the O · · · O contact, and the ^{1}H n.m.r. shift of the enol hydrogen atom.

No enol hydrogen atom could be located in this study. C(7)–C(8) and C(8)–C(9) are marginally different as are C(7)–O(1) and C(9)–O(2). Since the thermal motions are large, the errors in these bond lengths are probably greater than listed in Table 2, and the two sets of bond lengths can be considered equivalent. This suggests that the enol hydrogen bond is symmetric as was found in *p*-bromobenzoylacetone. For benzoylacetone, the pairs of carbon–carbon and carbon–oxygen bond lengths in the enol ring were different and the hydrogen bond was asymmetric. In a neutron diffraction study of benzoylacetone, the hydrogen bond was found to be asymmetric but the pairs of bond lengths in the enol ring were equivalent.[17] Neutron diffraction studies of the present compound are undoubtedly required to help resolve the problems.

This work was carried out during the tenure of a Research Fellowship from the Australian Institute of Nuclear Science and Engineering. The use of *X*-ray diffraction facilities at the Australian Atomic Energy Commission Research Establishment is gratefully acknowledged.

[5/1534 *Received, 4th August,* 1975]

---

* See Notice to Authors No. 7 in *J.C.S. Perkin II*, 1975, Index issue.

[12] R. D. G. Jones, *Acta Cryst.*, 1976, **B32**, in the press.

[13] D. E. Williams, W. L. Dumke, and R. E. Rundle, *Acta Cryst.*, 1962, **15**, 627.

[14] G. R. Engebretson and R. E. Rundle, *J. Amer. Chem. Soc.*, 1964, **86**, 574.

[15] J. P. Schaefer and P. J. Wheatley, *J. Chem. Soc.* (*A*), 1966, 528.

[16] L. F. Power and R. D. G. Jones, *Acta Cryst.*, 1971, **B27**, 181.

[17] R. D. G. Jones, submitted to *Acta Cryst.*