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The Enol Form of 1-(4-Bromophenyl)-1,3-butanedione

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Abstract. $C_{10}H_9BrO_2$, monoclinic, Cc, $a=23{\cdot}696$ (4), $b=7{\cdot}098$ (1), $c=5{\cdot}817$ (1) Å, $\beta=91{\cdot}51$ (1)°, $Z=4$, $d_m=1{\cdot}56$, $d_c=1{\cdot}63$ g cm^{-3}. The compound crystallizes as the enol tautomer. The intramolecular hydrogen bond is short with O···O being 2·481 (9) Å. The enol hydrogen atom could not be located but the bond lengths in the enol ring indicate a symmetrical bond. The dihedral angle between the phenyl ring and the enol ring is 17·3°.

Introduction. The compound was prepared by the method of Manyik, Frostick, Sanderson & Hauser (1953) and purified *via* the copper complex. Clear, colourless crystals were grown from an acetone–ethanol mixture and, after mounting, coated with shellac. Photographic methods showed that the crystals were monoclinic and spectra were absent for hkl when $h+k$ was odd and for $h0l$ when l was odd. The space group is either $C2/c$ or Cc but for an ordered structure the latter space group was suggested. Cell dimensions and intensity data were measured from a crystal of dimensions 0·26 × 0·16 × 0·20 mm and using Mo $K\alpha$ radiation. This crystal was mounted such that the c^* axis was a few degrees offset from the φ-axis of a computer-controlled, four-circle diffractometer. Intensity data were collected by the θ–2θ step-scan method (Elcombe, Cox, Pryor & Moore, 1971) and the scan range was 1·6°. The detector was a reverse-biased, surface barrier diode, kept at liquid nitrogen temperature, which allows discrimination of the Mo $K\alpha$ characteristic line (Beech & Eberhardt, 1973). Reflexions $\{hkl\}$ and $\{h\bar{k}l\}$, with $2\theta \leq 50°$, were measured. Beyond this range, few reflexions of significant intensity were available. Intensities were corrected for background, absorption $\{\mu(\text{Mo } K\alpha)=44{\cdot}1$ cm$^{-1}\}$ and the Lorentz-polarization factor. For each reflexion, $\sigma_I^2=\{\sigma_C^2+\sigma_A^2+(0{\cdot}035I)^2\}$ was calculated where σ_C is due to counting statistics, σ_A is due to absorption (Elcombe *et al.*, 1971) and I is the net intensity. The equivalent reflexions were averaged to yield 906 unique reflexions. When the variance due to the averaging was greater than $\sigma_C^2+\sigma_A^2$, the former value was included in the determination of σ_I^2.

The intensity of reflections with $h+l$ (and hence $k+l$) odd were very weak and the bromine atom position obtained from a Patterson map would give a

Table 1. *Final atomic coordinates (fractional coordinates) and thermal parameters* (Å^2), *all* × 10^4†

The form of the anisotropic temperature factor is

$$\exp\{-2\pi^2(h^2a^{*2}U_{11}+k^2b^{*2}U_{22}+l^2c^{*2}U_{33}+hka^*b^*U_{12}+2hla^*c^*U_{13}+2klb^*c^*U_{23})\}.$$

All hydrogen atoms have a fixed isotropic temperature factor.

In this table and all subsequent tables, the figure(s) in parentheses represent the estimated standard deviation in the least significant digit(s).

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Br	0000	−2321 (1)	5000	534 (4)	984 (6)	832 (6)	67 (10)	56 (3)	24 (10)
O(1)	2588 (3)	−2819 (10)	246 (10)	660 (37)	1467 (50)	477 (31)	85 (36)	53 (27)	−122 (38)
O(2)	3616 (3)	−2741 (11)	1177 (13)	648 (40)	1604 (70)	730 (43)	112 (40)	175 (33)	42 (46)
C(1)	1892 (3)	−2546 (9)	3084 (13)	584 (42)	340 (30)	461 (36)	35 (27)	−12 (31)	1 (28)
C(2)	1478 (4)	−3228 (12)	1562 (17)	699 (57)	461 (42)	452 (46)	9 (43)	77 (40)	−84 (40)
C(3)	914 (4)	−3137 (12)	2089 (15)	671 (54)	626 (45)	450 (49)	−86 (35)	−96 (37)	30 (35)
C(4)	773 (3)	−2430 (10)	4174 (15)	504 (38)	518 (40)	617 (47)	19 (30)	−29 (32)	34 (37)
C(5)	1176 (3)	−1754 (10)	5767 (14)	584 (42)	515 (36)	383 (38)	86 (30)	−13 (30)	−64 (30)
C(6)	1736 (4)	−1853 (9)	5189 (14)	613 (42)	437 (33)	440 (40)	−32 (30)	−52 (31)	−21 (29)
C(7)	2488 (9)	−2632 (14)	2414 (35)	629 (40)	458 (33)	531 (40)	−3 (35)	49 (31)	34 (34)
C(8)	2942 (3)	−2443 (12)	3979 (14)	570 (45)	845 (56)	469 (45)	24 (38)	39 (35)	−70 (42)
C(9)	3502 (5)	−2526 (12)	3317 (22)	612 (57)	651 (56)	711 (65)	−4 (50)	18 (46)	11 (52)
C(10)	3976 (4)	−2323 (15)	5013 (22)	527 (53)	1464 (101)	1014 (81)	−106 (54)	−108 (52)	30 (72)
H(2)	154 (4)	−359 (12)	26 (16)	76					
H(3)	62 (4)	−355 (12)	83 (15)	76					
H(5)	107 (3)	−118 (11)	719 (16)	76					
H(6)	204 (4)	−137 (11)	638 (14)	76					
H(8)	290 (5)	−255 (10)	557 (21)	76					

† Except those for H, which are × 10^3.

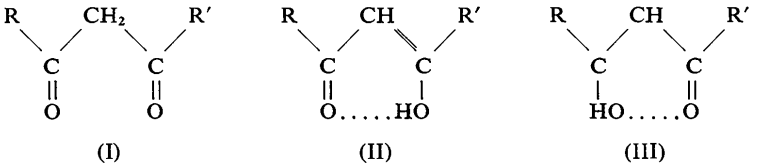
y coordinate of 0·25 and lead to spurious symmetry in the subsequent Fourier synthesis. E values, normalized so that $\langle E^2 \rangle$ for each parity group was unity, were determined and an E^2-1 Fourier synthesis calculated. The y coordinate of the bromine atom was 0·21 and the structure solution followed smoothly. The atomic parameters were refined by full-matrix least-squares methods, the function minimized being $\sum w(|F_o|-|F_c|)^2$. The non-hydrogen atoms were assigned anisotropic, and the hydrogen atoms isotropic, temperature factors. Statistical weights were used which were derived from σ_I^2. The final atomic parameters are shown in Table 1. All data were used in the refinement (Moore, 1972) and, at convergence, the R value was 0·048 (0·036 for reflexions with $I \geq 2{\cdot}3\sigma_I$) and wR was 0·048 (0·045). Scattering factors for the non-hydrogen atoms were taken from the tabulations of Cromer & Waber (1965) and for hydrogen from Stewart, Davidson & Simpson (1965). The anomolous scattering contributions for bromine were as listed by Cromer (1965). A diagram of the molecule is shown in Fig. 1.*

Discussion. Extensive studies of 1,3-diketones (β-diketones) have been made using infrared and p.m.r. spectral methods. These studies show that a strong, intramolecular hydrogen bond is formed when the diketoform (I) enolizes to either (II) or (III). For p-substituted benzoylacetones [R=CH_3, R′=XC_6H_4; X= Br, NO_2, H, CH_3, CH_3O, $(CH_3)_2N$], the chemical shift due to the enol proton varies markedly with the nature of X (Sardella, Heinert & Shapiro, 1969). Some X-ray diffraction studies have been undertaken to determine the nature of the hydrogen bond which may be symmetric (Hollander, Templeton & Zalkin, 1973) or asymmetric (Semmingsen, 1972: Williams, 1966). We have undertaken a study of some p-substituted benzoylacetones and simple β-diketones to determine factors which contribute to such hydrogen bonds.

Table 2. *Selected interatomic distances* (Å) *and angles* (°)

Interatomic distances		Interatomic angles	
Br——C(4)	1·908 (7)	Br——C(4)–C(3)	120·1 (5)
	1·927*	Br——C(4)–C(5)	117·5 (5)
C(1)——C(2)	1·390 (10)	C(6)—C(1)–C(2)	119·3 (6)
C(1)——C(6)	1·381 (9)	C(1)—C(2)–C(3)	120·5 (6)
C(2)——C(3)	1·385 (10)	C(2)—C(3)–C(4)	118·9 (6)
C(3)——C(4)	1·353 (11)	C(3)—C(4)–C(5)	122·4 (7)
C(4)——C(5)	1·399 (9)	C(4)—C(5)–C(6)	117·8 (6)
C(5)——C(6)	1·380 (9)	C(5)—C(6)–C(1)	121·0 (6)
C(1)——C(7)	1·474 (17)	C(2)—C(1)–C(7)	118·8 (7)
C(7)——C(8)	1·398 (15)	C(6)—C(1)–C(7)	121·9 (7)
C(8)——C(9)	1·390 (12)	C(1)—C(7)–O(1)	117·5 (10)
C(9)——C(10)	1·484 (13)	C(1)—C(7)–C(8)	123·5 (10)
	1·520*	C(8)—C(7)–O(1)	118·9 (11)
C(7)——O(1)	1·297 (14)	C(7)—C(8)–C(9)	122·7 (9)
	1·338*	C(8)—C(9)–C(10)	121·5 (8)
C(9)——O(2)	1·290 (11)	C(8)—C(9)–O(2)	119·8 (8)
	1·330*	C(10)–C(9)–O(2)	118·7 (8)
O(1)···O(2)	2·481 (9)	C(7)—O(1)–O(2)	90·6 (9)
C(2)——H(2)	0·83 (8)	C(9)—O(2)–O(1)	90·9 (8)
C(3)——H(3)	0·79 (8)	C(1)—C(2)–H(2)	127 (6)
C(5)——H(5)	0·93 (8)	C(3)—C(3)–H(2)	112 (6)
C(6)——H(6)	1·13 (8)	C(2)—C(3)–H(3)	112 (6)
C(8)——H(8)	0·92 (10)	C(4)—C(3)–H(3)	129 (6)
		C(4)—C(5)–H(5)	119 (5)
		C(6)—C(5)–H(5)	123 (5)
		C(5)—C(6)–H(6)	123 (4)
		C(1)—C(6)–H(6)	116 (4)
		C(7)—C(8)–H(8)	123 (6)
		C(9)—C(8)–H(8)	113 (6)

* Interatomic distance has been corrected for 'riding' motion (Busing & Levy, 1964).



(R=CH_3, R′=BrC_6H_4 in this study)

The interatomic distances and angles in Table 2 confirm that the enol is the species in the solid state. This is consistent with the broad peak at ~ 1600 cm^{-1} in the infrared spectrum. The molecule is not planar, the dihedral angle between the phenyl and enol rings being 17·3°. In benzoylacetone, this angle is 6·3° (Semmingsen, 1972). No enol or methyl hydrogen atoms were located although $w\Delta^2$ for the very low angle data was slightly higher than for other regions. Hence, although these atoms were potentially locatable, disorder or excessive thermal motion has made this task impossible.

The O···O distance is 2·481 (9) Å, indicative of a strong, intramolecular hydrogen bond. The distance is similar to that in other β-diketones (Hollander *et al.*,

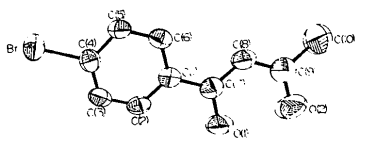


Fig. 1. A diagram of the molecule looking down the b axis. The atoms are represented as 50% thermal ellipsoids.

* A table of observed and calculated structure factor amplitudes has been deposited with the British Library Lending Division as Supplementary Publication No.SUP 31340 (7pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

1973; Williams, 1966; Engebretson & Rundle, 1964; Williams, Dumke & Rundle, 1962; Power & Jones, 1971; Schaefer & Wheatley, 1966; Semmingsen, 1972). C(7)–O(1) and C(9)–O(2) are equivalent, as are C(7)–C(8) and C(8)–C(9), which suggests that the enol hydrogen atom is either symmetrically located or disordered between two positions either side of the O···O centre. The latter description is more probable, arising from equal contributions from (II) and (III).

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References

BEECH, A. McG. & EBERHARDT, J. E. (1973). *Semiconductor X-ray Spectrometer System Type* 454, Report AAEC/E297, Australian Atomic Energy Commission.
BUSING, W. R. & LEVY, H. A. (1964). *Acta Cryst.* **17**, 142–146.
CROMER, D. T. (1965). *Acta Cryst.* **18**, 17–23.
CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104–109.
ELCOMBE, M. M., COX, G. W., PRYOR, A. W. & MOORE, F. H. (1971). *Programs for the Management and Processing of Neutron Diffraction Data*, Report AAEC/TM578, Australian Atomic Energy Commission.
ENGEBRETSON, G. R. & RUNDLE, R. E. (1964). *J. Amer. Chem. Soc.* **86**, 574–581.
HOLLANDER, F. J., TEMPLETON, D. H. & ZALKIN, A. (1973). *Acta Cryst.* B**29**, 1552–1553.
MANYIK, R. M., FROSTICK, F. C., SANDERSON, J. J. & HAUSER, C. R. (1953). *J. Amer. Chem. Soc.* **75**, 5030–5032.
MOORE, F. H. (1972). IXth Congress of the International Union of Crystallography, Kyoto.
POWER, L. F. & JONES, R. D. G. (1971). *Acta Cryst.* B**27**, 181–184.
SARDELLA, D. J., HEINERT, D. H. & SHAPIRO, B. L. (1969). *J. Org. Chem.* **34**, 2817–2821.
SCHAEFER, J. P. & WHEATLEY, P. J. (1966). *J. Chem. Soc.* (*A*), pp. 528–532.
SEMMINGSEN, D. (1972). *Acta Chem. Scand.* **26**, 143–154.
STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3183.
WILLIAMS, D. E. (1966). *Acta Cryst.* **21**, 340–349.
WILLIAMS, D. E., DUMKE, W. L. & RUNDLE, R. E. (1962). *Acta Cryst.* **15**, 627–635.

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Die Kristallstruktur von Äthylammoniumtetrachloromanganat(II) bei Raumtemperatur

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Abstract. Orthorhombic, No. 64 *Abma* (=*Cmca* in standard setting), $a=7{\cdot}353$ (1), $b=7{\cdot}258$ (1), $c=22{\cdot}087$ (4) Å, $(C_2H_5NH_3)_2MnCl_4$, $M=288{\cdot}86$, $Z=4$, $D_x=1{\cdot}627$, $D_{pykn}=1{\cdot}67$ g cm^{-3}, μ(Mo $K\alpha$) = 19·7 cm^{-1}. The plate-like crystals were prepared by slow evaporation of a solution of $C_2H_5NH_3Cl$ and $MnCl_2$ in a mixture of water and ethanol. Bond length consideration resulted in a split-atom model with each carbon randomly occupying two symmetry-related positions. Least-squares refinement of a model with unusually large axes of thermal ellipsoids of the carbon atoms yielded a residual as good as the split-atom model.

Einführung. Rosafarbene, tafelige Kristalle von $(C_2H_5NH_3)_2MnCl_4$ (im folgenden C2MNRT genannt) wurden durch langsames Verdunsten einer Lösung von $C_2H_5NH_3Cl$ und $MnCl_2$ in einem Gemisch von Wasser und Äthanol erhalten. Eine mit Cr $K\alpha$ Strahlung hergestellte Guinieraufnahme wurde mit Hilfe des Programms *LATCON* (Schwarzenbach, 1971) ausgewertet und ergab die oben aufgeführten Gitterkonstanten. Präzessionsaufnahmen zeigten die Lauegruppe *mmm* und die Auslöschungsgesetze für *hkl*: $k+l=2n+1$, 0*kl*: $k=2n+1$ und *hk*0: $h=2n+1$. Daraus ergab sich als Raumgruppe Nr. 64 *Abma* (*Cmca* in der Standardaufstellung). Die ebenfalls mögliche azentrische Raumgruppe $Ab2_1n$ konnte wegen der Analogie zu $(C_3H_7NH_3)_2MnCl_4$ (Peterson & Willett, 1972) und wegen der Verteilung der *E*-Werte, die gut mit dem theoretischen zentrosymmetrischen Fall übereinstimmte, ausgeschlossen werden.

Die Sammlung der Intensitäten fand auf einem Nonius CAD4-Diffraktometer mit monochromatisierter Mo $K\alpha$-Strahlung im Bereich von $\sin\theta/\lambda \leq$ 0,8105 statt. Der verwendete Kristall war plättchenförmig mit den ungefähren Dimensionen 0,06 × 0,06 × 0,01 cm und befand sich in einer Glaskapillare. Die Rohdaten wurden wie üblich korrigiert, auf eine Absorptionskorrektur wurde verzichtet. Es standen insgesamt 1392 symmetrieunabhängige Reflexe zur Verfügung, von denen 713 signifikant von Null verschieden waren. Die totale Zahl möglicher symmetrieunab-