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1-Benzyloxy-3-methyl-4-nitrobenzene, $C_{14}H_{13}NO_3$: Apparent Red and Yellow Forms

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Abstract. $M_r = 243.3$; lath (normally red) form (recrystallized from CH_2Cl_2–hexane): monoclinic, $P2_1/c$, $a = 7.274$ (2), $b = 18.379$ (4), $c = 9.446$ (2) Å, $\beta = 97.64$ (2)°, $U = 1251.7$ (5) Å^3, $D_x = 1.29$ g cm^{-3}, $Z = 4$, $R = 0.049$ for 812 diffractometer-measured reflections, λ (Mo $K\alpha$) = 0.71069 Å. A prism (normally yellow) form can be produced by recrystallization from *n*-hexane or methanol. It has the same crystal structure as the lath form, but occurs as twinned crystals. An apparent photochemical isomerism is shown to be due to impurity.

Introduction. The title compound was found to show what appeared to be polymorphism of a rather unusual kind. On crystallization from CH_2Cl_2–hexane, it formed red lath-shaped crystals. These were photosensitive, turning yellow under illumination by sunlight. What appeared to be the same yellow form was also produced as prismatic crystals by recrystallization (either before or after irradiation) from methanol or hexane. This study aimed to clarify what appeared to be isomerism.

Experimental. 3-Methyl-4-nitrophenol (11 g, 72 mmol) was dissolved in NaOH (4 g)/H_2O (80 cm^3) at room temperature. To this clear, dark liquid, benzyltri(*n*-butyl)ammonium bromide (0·55 g) was added and the solution was heated to 363K with vigorous stirring. Benzyl chloride (11·5 cm^3, 100 mmol) was added in a single portion and the mixture was stirred for 2 h, after which time TLC showed the absence of phenolic material. The liquid was cooled to room temperature, water (100 cm^3) and 2 *M* aqueous NaOH (20 cm^3) were added, and the two-phase mixture was steam-distilled until the distillate became clear. The remaining contents of the flask were cooled to room temperature and acidified (HCl). The crude 1-benzyloxy-3-methyl-4-nitrobenzene was extracted with dichloromethane (3 × 50 cm^3), filtered through a small pad of silica gel (to remove dark coloured impurities) and dried ($MgSO_4$). Evaporation of solvent yielded a light brown-yellow solid (17·2 g), which was recrystallized from hot methanol (40 cm^3). The resulting yellow solid was filtered off, washed with a little cold methanol and finally dried at reduced pressure over calcium chloride. Yield 15·7 g, 90%, m.p. 339–341K; ^{1}H NMR ($CDCl_3$); δ 2·61 (*s*, 3*H*), 5·11 (*s*, 2*H*), 6·86 (*m*, 2*H*), 7·40 (*m*, 5*H*), 9·07 (*m*, 1*H*) p.p.m.

A sample of this yellow material on recrystallization from dichloromethane–hexane (1:3 v/v) deposited a mass of red-orange crystals, m.p. 341–343K, with a ^{1}H NMR spectrum identical to that of the yellow form. TLC (silica gel, CH_2Cl_2) showed that the yellow and the red forms were indistinguishable chromatographically (R_F 0·7) (dibenzyl ether: R_F 0·45; 3-methyl-4-nitrophenol: R_F 0·15). UV–visible spectra of dilute solutions in methanol of both forms were identical, and dominated by a strong peak at 305 nm ($\varepsilon = 9\,200 \pm 200$ dm^3 mol^{-1} cm^{-1}). Concentrated solutions of both forms (0·165 mol dm^{-3}) showed considerable differences in the blue region of the spectrum with the 'orange' form absorbing 2–3 times as much as the 'yellow' form at 415–420 nm. A sample of the crystalline red form on standing in direct sunlight turned yellow. Repeated recrystallization from methanol yielded almost white material, while recrystallization from CH_2Cl_2–hexane always yielded orange-red material.

^{1}H NMR spectra were recorded on a Perkin Elmer *R*34 instrument (220 MHz) at ambient temperature (*ca* 296 K). Melting points were determined in capillary tubes using an electrothermal apparatus and are uncorrected. TLC plates were 0·2 mm thick precoated silica gel F_{254} (Merck) and spots were visualized using a low-power UV lamp. UV spectra were run on a Shimadzu 365 instrument.

Red form: Syntex $P2_1$ four-circle diffractometer, maximum $2\theta = 50°$, scan range $\pm 1.0°$ (2θ) around the $K\alpha_1$–$K\alpha_2$ angles, scan speed 2·5–29° min^{-1} (depending on the intensity of a 2 s pre-scan), backgrounds

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measured at each end of the scan for 0·25 of the scan time; three standard reflections monitored every 200 reflections showed slight changes during data collection and data were rescaled to correct for this; unit-cell dimensions and standard deviations obtained by least-squares fit to 15 high-angle reflections; of a total of 2406 reflections, 812 were considered observed $[I/\sigma(I) > 3{\cdot}0]$ and used in refinement and corrected for Lorentz and polarization effects; systematic absences $h0l$, $l \neq 2n$, $0k0$, $k \neq 2n$; structure solution by direct methods using *MULTAN*80 (Main, 1980), refinement by least-squares methods with anisotropic temperature factors (H atoms isotropic), unit weights used and shown to be satisfactory by a weight analysis; a final difference Fourier synthesis showed no peaks exceeding 0·2 e Å^{-3}; computing was with the XRAY 76 system (Stewart, 1976) on a Burroughs B6700 computer; scattering factors in the analytical form from *International Tables for X-ray Crystallography* (1974), $R = 0{\cdot}049$;[*] $F(000) = 512$.

Yellow form (recrystallized from MeOH or *n*-hexane): unit-cell determination gave a cell with *a, b* and β identical to those of the red form, within experimental error, but with a tripled *c* axis [28·324 (11) Å]; reflection data relating to this cell measured with scan range ± 1·3°, scan speed 1–29° min^{-1}, maximum $2\theta = 35°$, peak profiles rather broad and flat-topped. Inspection of the results revealed unusual intensity patterns, depending on the value of *h*. For $h = 3n$, only reflections with $l = 3n$ were present, for $h = 3n + 1$, reflections with $l = 3n$ and $l = 3n - 1$ occurred, and for $h = 3n + 2$, l could be $3n$ and $3n + 1$; this was eventually interpreted as a twinning phenomenon, from a true cell of the same dimensions as the red form. The two occurrences of a particular reflection were produced by the matrices

$$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 3 \end{pmatrix} \quad \text{and} \quad \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ -1 & 0 & -3 \end{pmatrix}$$

Consideration of the layers with $h \neq 3n$ enabled the intensity ratio (K) of the twin components to be estimated. For the intensities of reflections with $h = 3n$, pairs of observations have the form $I_{\text{tot}} = I_h + KI_{h'}$, $I'_{\text{tot}} = I_{h'} + KI_h$. Using the known value of K, individual intensities could be established and a complete unique data set built up, though this was not expected to be of high quality. Using the final coordinates of the red form as a starting point, isotropic refinements converged at $R = 0{\cdot}15$. Although, clearly, this data set was poor (probably caused by some reflections not having completely entered the counter aperture), this was sufficient to confirm the structural identity of the two forms. None of the temperature factors were very high, indicating the absence of substantial disorder and the maximum distance between corresponding atoms was 0·1 Å, *i.e.* within the expected error for the yellow-form positions.

Discussion. Final atomic coordinates for the red form are in Table 1, and bond lengths and angles in Table 2. The crystallographic study has shown no difference in the crystal between the red and yellow forms, apart from the propensity of the yellow form to occur as twinned crystals. This, with the identity of the two forms in solution (from UV and ^{1}H NMR spectra and TLC R_F values) indicates that we are dealing with a single compound. The origin of the colour difference probably lies in a trace impurity which co-crystallizes with the bulk material: this happens particularly in CH_2Cl_2–hexane. The impurity has not been identified chemically, but it may well be photosensitive. Photodecomposition would then be responsible for reduction of the colour intensity to give a yellow appearance.

Table 1. *Atomic coordinates* ($\times 10^4$, *for* H $\times 10^3$) *with e.s.d.'s in parentheses, and isotropic thermal parameters* (Å^2 $\times 10^3$)

For non-H atoms $U_{\text{eq}} = \frac{1}{3}(U_{11} + U_{22} + U_{33})$.

	x	y	z	U_{eq} or U
O(1)	2980 (8)	5404 (2)	1562 (4)	100
O(2)	3002 (9)	6413 (3)	2658 (4)	109
O(3)	2169 (6)	4103 (2)	7490 (3)	63
N(1)	2894 (8)	5759 (3)	2643 (5)	70
C(1)	2678 (9)	5363 (3)	3973 (5)	49
C(2)	2771 (9)	4610 (3)	3919 (5)	57
C(3)	2583 (9)	4200 (3)	5088 (5)	59
C(4)	2334 (9)	4551 (3)	6353 (5)	51
C(5)	2218 (9)	5298 (3)	6395 (5)	54
C(6)	2396 (9)	5724 (3)	5207 (5)	55
C(7)	2232 (12)	6544 (3)	5358 (6)	92
C(8)	2147 (10)	4430 (3)	8884 (6)	70
C(9)	2341 (10)	3820 (3)	9965 (5)	57
C(10)	4050 (10)	3521 (4)	10423 (6)	76
C(11)	4174 (13)	2963 (4)	11408 (7)	102
C(12)	2527 (19)	2739 (3)	11924 (6)	132
C(13)	847 (14)	3030 (4)	11468 (7)	112
C(14)	771 (10)	3571 (4)	10477 (6)	17
H(2)	306 (7)	440 (3)	312 (5)	58 (17)
H(3)	281 (7)	369 (3)	513 (5)	61 (16)
H(71)	355 (10)	676 (4)	527 (7)	119 (26)
H(72)	123 (10)	674 (4)	462 (7)	95 (25)
H(73)	187 (9)	668 (3)	610 (6)	90 (22)
H(81)	326 (7)	474 (3)	900 (5)	51 (16)
H(82)	88 (9)	470 (3)	888 (6)	105 (22)
H(10)	513 (9)	369 (3)	997 (6)	106 (23)
H(11)	533 (10)	277 (4)	1177 (7)	144 (26)
H(12)	283 (8)	245 (3)	1233 (5)	52 (19)
H(14)	−39 (7)	375 (2)	1012 (4)	47 (15)
H(5)	208 (8)	556 (3)	726 (5)	64 (17)
H(13)	−43 (8)	278 (3)	1192 (5)	225 (19)

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[*] Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38097 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The dimensions of the compound (Table 2) show no abnormal values. The dihedral angle for the central C—O bond is 168·9 (5)°, giving an extended C—C—O—C chain, but the aromatic ring of the benzyl group is almost perpendicular to this plane, that of the other ring (Fig. 1) and of the nitro group. The packing (Fig. 2) is dominated by face-to-face π interactions involving the nitrobenzene ring. Remaining contacts are between C—H groups, the molecules having an overall herring-bone packing.

Table 2. *Bond lengths* (Å) *and angles* (°)

N(1)—O(1)	1·221 (6)	O(1)—N(1)—O(2)	122·2 (5)
N(1)—O(2)	1·204 (7)	O(1)—N(1)—C(1)	118·1 (5)
N(1)—C(1)	1·479 (7)	O(2)—N(1)—C(1)	119·7 (5)
C(1)—C(2)	1·387 (8)	N(1)—C(1)—C(2)	116·7 (5)
C(1)—C(6)	1·380 (8)	N(1)—C(1)—C(6)	121·7 (5)
C(2)—C(3)	1·358 (8)	C(2)—C(1)—C(6)	121·6 (5)
C(3)—C(4)	1·391 (7)	C(1)—C(2)—C(3)	120·8 (5)
C(4)—C(5)	1·376 (8)	C(2)—C(3)—C(4)	118·7 (5)
C(4)—O(3)	1·371 (6)	C(3)—C(4)—C(5)	120·2 (5)
C(5)—C(6)	1·389 (8)	C(3)—C(4)—O(3)	115·4 (5)
C(6)—C(7)	1·521 (8)	C(5)—C(4)—O(3)	124·4 (5)
		C(4)—C(5)—C(6)	121·7 (5)
		C(5)—C(6)—C(1)	116·9 (5)
		C(5)—C(6)—C(7)	117·8 (5)
		C(1)—C(6)—C(7)	125·4 (5)
O(3)—C(8)	1·448 (6)	C(4)—O(3)—C(8)	118·4 (4)
C(8)—C(9)	1·510 (7)	O(3)—C(8)—C(9)	107·2 (4)
C(9)—C(10)	1·375 (9)	C(8)—C(9)—C(10)	120·5 (6)
C(9)—C(14)	1·377 (10)	C(8)—C(9)—C(14)	118·5 (6)
		C(10)—C(9)—C(14)	121·0 (5)
C(10)—C(11)	1·379 (10)	C(9)—C(10)—C(11)	119·0 (7)
C(11)—C(12)	1·414 (16)	C(10)—C(11)—C(12)	117·8 (8)
C(12)—C(13)	1·351 (15)	C(11)—C(12)—C(13)	123·2 (6)
C(13)—C(14)	1·362 (10)	C(12)—C(13)—C(14)	117·4 (9)
		C(13)—C(14)—C(9)	121·6 (7)

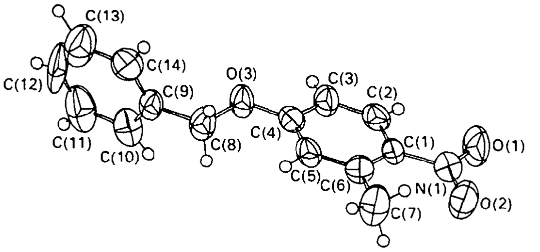

Fig. 1. The title compound, showing the atomic numbering.

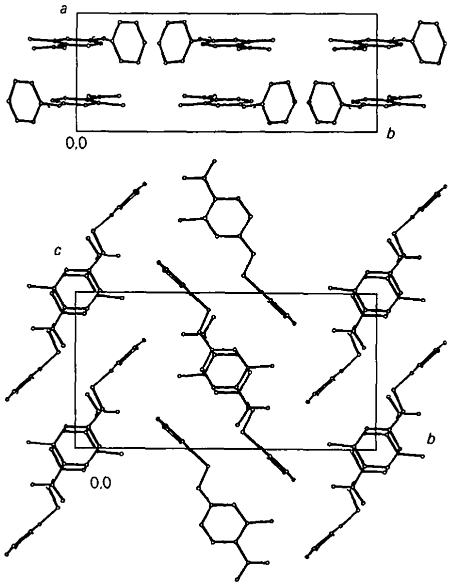

Fig. 2. The packing viewed down **c** (top) and **a** (bottom).

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