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MOLECULAR STRUCTURE DETERMINATION OF 4-METHYLBENZOPHENONE 2,4-DINITROPHENYLHYDRAZONE BY X-RAY ANALYSIS

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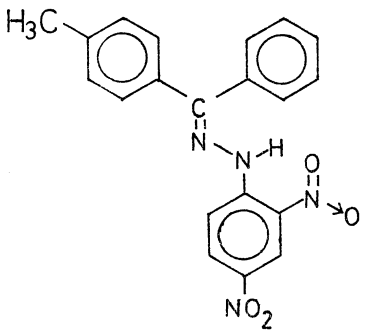
Three isomeric forms of the title compound; I, m.p. 235°C, II, m.p. 222°C and III, m.p. 200°C, were isolated by crystallization using dioxane-ethanol. The details of the molecular geometry of II was determined by X-ray analysis.

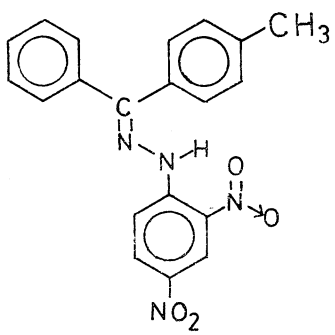
In a previous paper,[1] we reported that 2,4-dinitrophenylhydrazone (2,4-DNP) of 4-bromobenzophenone was obtained as a pair of geometrical isomers (E- and Z-isomer) which can be isolated by fractional crystallization from ethyl acetate and the unequivocal assignment of the geometrical isomers was determined by X-ray structure analysis.

In addition, we recently found that the crystallization of 4-methylbenzophenone 2,4-DNP using dioxane-ethanol as the solvent afforded three isomeric forms; orange crystal (I), m.p. 235°C,[2,3] red crystal (II), m.p. 222°C[2,3] and purple red crystal (III), m.p. 200°C.[4] We previously assigned I and II to be E- and Z-isomer, respectively,on the basis of conventional spectral data.[2,3] Tschetter[5] reported that as a result of solubility studies of 2,4-DNP's, the purple red crystal, m.p. 202.6°C, corresponded to the Z-isomer, but the melting point test and NMR spectral data[4] of the purple red crystal (III) suggested a complex composed of the orange and red crystals (1 : 1).

We wish to report here the unequivocal assignment of the red crystal (II) and the details of the geometry of the molecule by X-ray analysis.



E-isomer



Z-isomer

The red crystal (II) suitable for X-ray work was obtained by slow evaporation of the solvent in the dioxane-ethanol (1:1, v/v) solution.

The crystal is monoclinic, with four molecules in a unit cell with the dimensions of a = 15.128, b = 7.604, c = 15.962 Å, and β = 102.59°. The space group is $P2_1/c$. The intensity data were collected on an automatic four-circle diffractometer using Cu K_α radiation monochromatized with a LiF crystal. Out of the structure factors with 2θ values up to 140°, 3157 above σ(F) were selected for the structural study. The approximate positions of the non-hydrogen atoms were obtained by the symbolic-addition method, and refined by the block-diagonal-matrix least-squares method with anisotropic temperature factors. From a difference Fourier map, the locations of all 16 hydrogen atoms were also determined. Further least-squares refinement including these hydrogen atoms reduced the R factor to 5.0%. The final coordinates of the non-hydrogen atoms are listed in Table 1. All calculations necessary for the present analysis were performed on a FACOM 230-60 computer at the Computer Center of Hokkaido University using our programs. The molecular framework thus determined is shown in Fig. 2. The e.s.d.'s of the bond distances and angles given in Fig. 2 are less than 0.004 Å and 0.3°, respectively.

It was confirmed that the red crystal (II), m.p. 222°C, corresponds to the Z-isomer. The planes of the A, B, and C benzene rings make angles of about 19°, 56° and 12° respectively with the mean plane through the C(1), C(7), C(8), N(1), and N(2) atoms. The two nitro groups, O(1)-N(3)-O(2) and O(3)-N(4)-O(4), rotate by about 7°

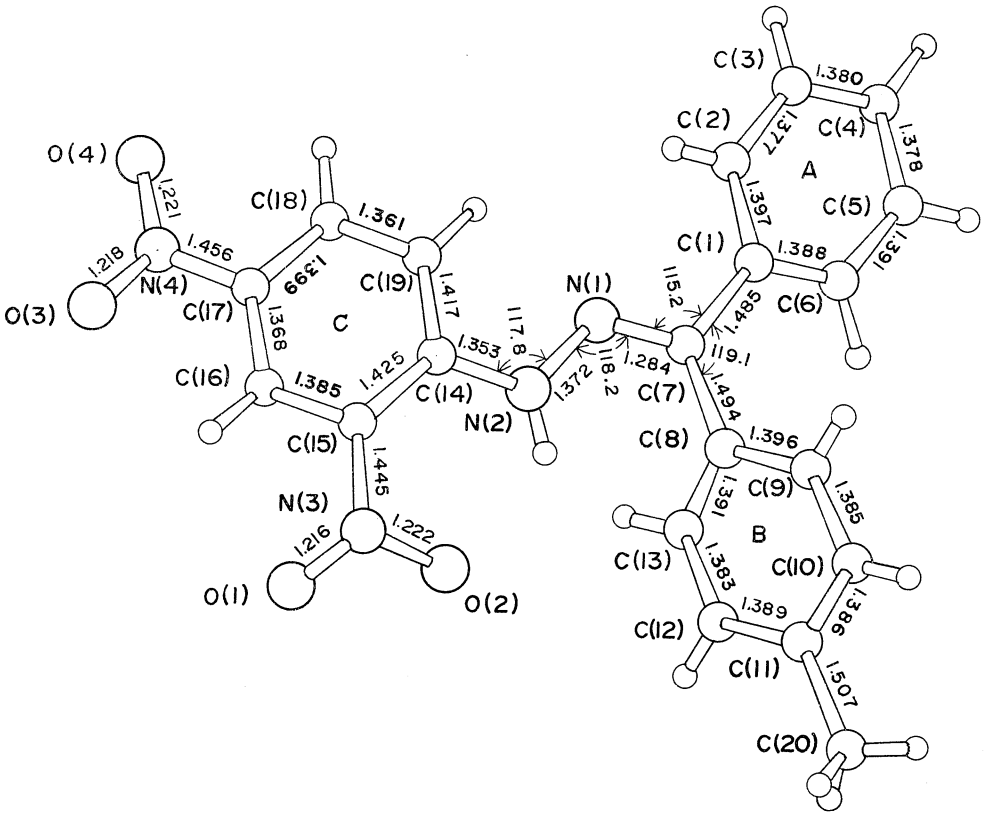


Fig. 2. Bond distances (Å) and bond angles (°) of the Z-isomer of 4-methylbenzophenone 2,4-DNP.

Table 1. Final Atomic Coordinates

Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c
O(1)	-0.0575	0.2758	0.2518	C(7)	0.2348	0.0900	0.0393
O(2)	0.0749	0.2127	0.2352	C(8)	0.2931	0.0967	0.1283
O(3)	-0.2894	0.4889	0.0209	C(9)	0.3717	0.1992	0.1443
O(4)	-0.2823	0.4195	-0.1077	C(10)	0.4267	0.2066	0.2262
N(1)	0.1501	0.1288	0.0182	C(11)	0.4059	0.1135	0.2939
N(2)	0.1073	0.1822	0.0811	C(12)	0.3278	0.0111	0.2775
N(3)	-0.0039	0.2554	0.2061	C(13)	0.2721	0.0027	0.1960
N(4)	-0.2489	0.4304	-0.0308	C(14)	0.0208	0.2399	0.0562
C(1)	0.2761	0.0377	-0.0330	C(15)	-0.0349	0.2822	0.1146
C(2)	0.2334	0.0802	-0.1175	C(16)	-0.1223	0.3458	0.0862
C(3)	0.2704	0.0280	-0.1848	C(17)	-0.1563	0.3672	-0.0002
C(4)	0.3504	-0.0659	-0.1699	C(18)	-0.1048	0.3257	-0.0601
C(5)	0.3936	-0.1080	-0.0869	C(19)	-0.0187	0.2643	-0.0322
C(6)	0.3567	-0.0566	-0.0184	C(20)	0.4649	0.1243	0.3834

and 11° around the C(15)-N(3) and C(17)-N(4) bonds respectively. The O(2) atom forms an intramolecular hydrogen bond with the N(2) atom, the O(2)···H(N) distance being about 2.02 ± 0.02 Å.

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