MOLECULAR STRUCTURE DETERMINATION OF 4-BROMOBENZOPHENONE 2,4-DINITRO-PHENYLHYDRAZONE BY X-RAY ANALYSIS

Masayoshi TABATA, Yoshiyuki TAKADA, and Akira SUZUKI
Department of Chemical Process Engineering, Faculty of Engineering

and Akio FURUSAKI
Department of Chemistry, Faculty of Science
Hokkaido University, Sapporo, Japan

The molecular structure of 4-bromobenzophenone 2,4-dinitrophenyl-hydrazone was determined by X-ray analysis.

In spite of the theoretical possibility that 2,4-dinitrophenylhydrazones (2,4-DNP) of aldehydes and unsymmetrical ketones may exist in two geometrical isomers, the isomeric pairs of such hydrazones have only been reported in a few instances.[1]

In our previous paper,[2] it was reported that geometrical isomers of the 2,4-DNP's of six unsymmetrically substituted benzophenones were isolated in pure form by recrystallization and that the configurational assignments to their E- and Z-isomers were given on the basis of their NMR and UV spectral data (Fig. 1). On the other hand, Petrowitz[3] recently reported that as a result of his thin layer chromatographic studies in the 2,4-DNP's of the benzophenones with 4-F, 4-Cl, and 4-Br groups, the upper and lower side spots on the chromatoplate correspond to the E- and Z-isomers, respectively. We wish to report here the first unequivocal assignment to the geometrical isomers of 4-bromobenzophenone 2,4-DNP and the details of the geometry of the 2,4-DNP molecule determined by an X-ray structure analysis.

Fractional crystallization of the 4-bromobenzophenone 2,4-DNP using ethyl acetate as the solvent gave two isomeric forms; orange crystal, mp. 234°C, $\lambda_{max}^{CHCl_3}$ 385 nm (ε 29300) and red crystal, mp. 224°C, $\lambda_{max}^{CHCl_3}$ 388 nm (ε 31800). The latter crystal was found to be suitable for X-ray work.

Crystal data (red crystal): monoclinic, a = 15.192 $\overset{\circ}{A}$, b = 12.699 $\overset{\circ}{A}$, c = 9.622 $\overset{\circ}{A}$, β

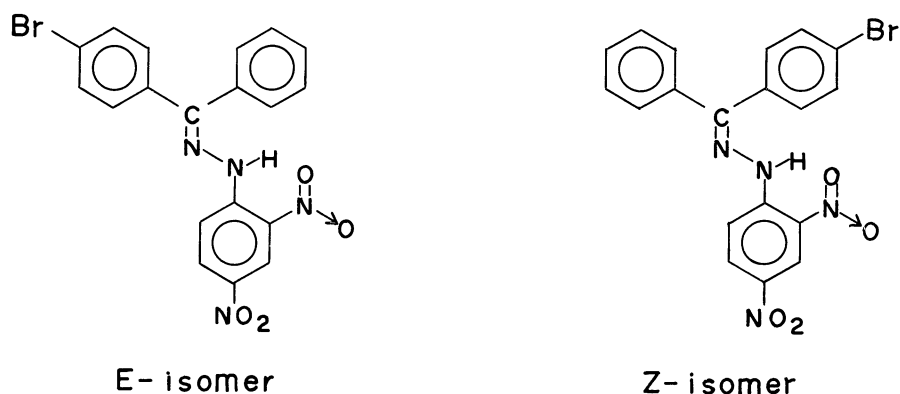= 97°.22', space group, P2₁/c with Z = 4.

Fig. 1   Geometrical isomers of 4-bromobenzophenone 2,4-DNP

Intensities of 2893 independent reflections with 2θ values up to 140° were

collected on a Rigaku automatic four-cycle diffractometer using monochromatized Cu

K_α radiation. The approximate coordinates of carbon, nitrogen, and oxygen atoms

were obtained by the heavy-atom method on the basis of the bromine position derived

from a sharpened Patterson function. After these coordinates were refined by the

least-squares method with anisotropic thermal parameters for all the atoms, a

difference synthesis was carried out. The resulting map revealed the locations of

13 hydrogen atoms. The atomic parameters thus obtained were further refined by the

block-diagonal least-squares method. The final R factor was 6.2 %. 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 bond distances and bond angles calculated with the final coordinates are

given in Fig. 2. The average standard deviation of the coordinates are about

0.0005, 0.003, and 0.004 $\overset{\circ}{A}$ for bromine, oxygen, and carbon atoms, respectively.

It is clearly shown in Fig. 2 that the red crystal, mp. 224°C, corresponds to the

E-isomer. The A ring forms an angle of only about 5° with the C=N-N plane, while

the B ring forms an angle of no less than about 73° with the same plane. On the

other hand, the angle between the C ring and the plane is about 12°, the major part

of which arises from twisting around the N-N bond. The two nitro groups are both

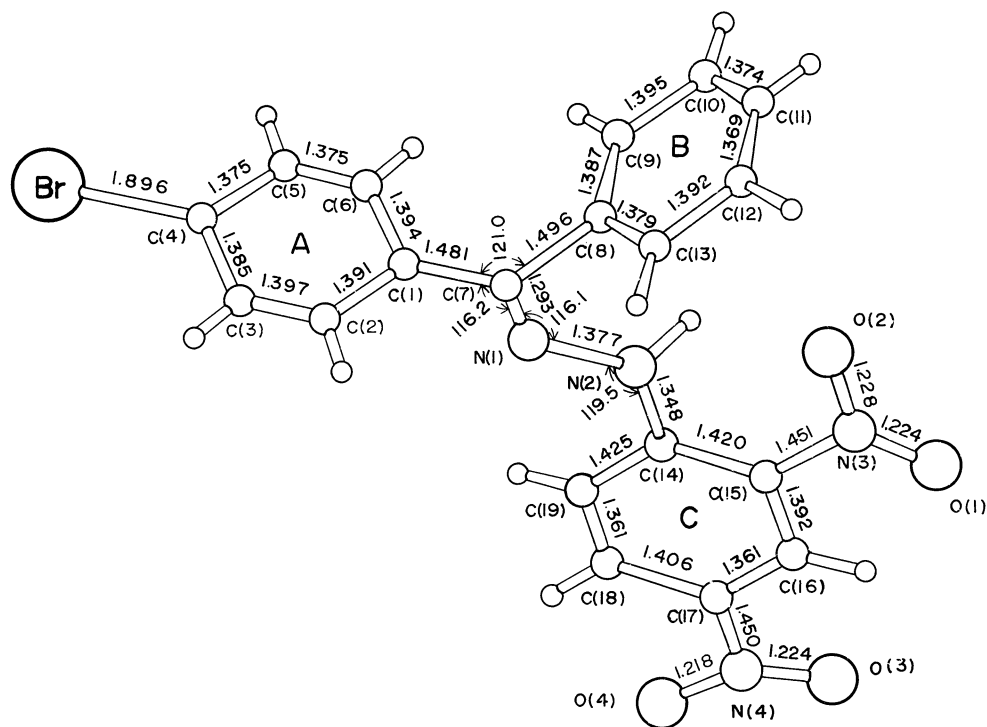twisted at an angle of only about 3° from the C ring. The nitro oxygen atom, O(2),

Fig. 2   Bond distances (Å) and bond angles of the E-isomer of
4-bromobenzophenone 2,4-DNP.

Table 1   Final atomic coordinates

Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c
Br	0.3550	1.0660	0.3751	C(6)	0.3542	0.7398	0.3801
O(1)	0.1171	0.1697	0.0128	C(7)	0.2705	0.6012	0.2361
O(2)	0.1891	0.2769	0.1581	C(8)	0.3244	0.5154	0.3120
O(3)	- 0.0687	0.2813	- 0.3865	C(9)	0.4101	0.4957	0.2837
O(4)	- 0.0857	0.4456	- 0.4361	C(10)	0.4583	0.4123	0.3500
N(1)	0.2057	0.5828	0.1381	C(11)	0.4216	0.3505	0.4447
N(2)	0.1869	0.4784	0.1093	C(12)	0.3379	0.3708	0.4764
N(3)	0.1386	0.2592	0.0504	C(13)	0.2896	0.4537	0.4096
N(4)	- 0.0532	0.3744	- 0.3617	C(14)	0.1285	0.4528	- 0.0032
C(1)	0.2898	0.7134	0.2692	C(15)	0.1033	0.3471	- 0.0357
C(2)	0.2439	0.7936	0.1926	C(16)	0.0428	0.3223	- 0.1522
C(3)	0.2622	0.8993	0.2245	C(17)	0.0081	0.4010	- 0.2384
C(4)	0.3281	0.9228	0.3336	C(18)	0.0314	0.5069	- 0.2117
C(5)	0.3738	0.8452	0.4122	C(19)	0.0899	0.5318	- 0.0972

and the imino atom, N(2), form an intramolecular hydrogen bond at a distance of about 2.60 Å. From this finding, we concluded that the orange crystal, mp. 234°C, corresponds to Z-isomer.

The re-examination of thin layer chromatographic separation indicated that the Z-isomer travels on the chromatoplate more slowly than the E-isomer, as reported by Petrowitz.[3]

Reference

1) (a) L. Tshetter, Proc. S. Dakota Akad. Sci., 43, 165 (1965). (b) E. M. Reiman, ibid., 43, 170 (1964). (c) F. Ramiretz and A. F. Kirby, J. Amer. Chem. Soc., 76, 1037 (1954). (d) H. M. Edwards, Jr., J. Chromatogr., 22, 29 (1966).

2) M. Tabata, K. Yokota, Y. Takada and A. Suzuki, Chemistry Letters, 659 (1972).

3) H.-J. Petrowitz, J. Chromatogr., 40, 458 (1969).