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GEOMETRICAL ISOMERS OF 2,4-DINITROPHENYLHYDRAZONES OF SOME BENZOPHENONES. ISOLATION AND THEIR CONFIGURATIONAL ASSIGNMENTS

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Geometrical isomers of 2,4-dinitrophenylhydrazones of asymmetrically substituted benzophenones were isolated in pure form by recrystallization. The configurational assignments to their E- and Z-isomers were made using electronic and NMR spectral data.

In spite of the fact that 2,4-dinitrophenylhydrazones have widely been used for identification of carbonyl compounds,$^{1)}$ there are only a few reports$^{2)}$ concerning the isolation of geometrical isomers which are considered theoretically possible to exist in such hydrazones of aldehydes and asymmetrical ketones. We wish to report here on the isolation and structural elucidation of geometrical isomers of 2,4-dinitrophenylhydrazones (hereafter referred to as 2,4-DNP) of seven asymmetrically substituted benzophenones.

The reaction of benzophenones with 2,4-dinitrophenylhydrazine by the usual procedure$^{3)}$ led to a mixture of E- and Z-isomers of the corresponding 2,4-DNP's (Fig.1), which were then separated by fractional crystallization using ethyl acetate as the solvent. Their melting points together with UV and NMR data are summarized in Table 1.

The configurational assignments were given based on the following arguments. According to the NMR spectra, azo structures were ruled out for two crystalline products separated by recrystallization. For instance, the two kinds of crystals which were separated from the mixture obtained by the reaction of 2-methylbenzophenone with the dinitrophenylhydrazine give resonance peaks, as shown in Fig. 2, at δ 2.46 (3H, s) and 2.17 (3H, s) for 2-CH_3 proton and at δ 11.51 (1H, s) and 10.90 (1H, s) for NH proton. No peaks due to methyl and methine protons expected in the azo structure were observed.

In the electronic spectra of 2,4-DNP's of benzophenones, there are principally

Table 1. Physical Properties of Some Substituted Benzophenone 2,4-Dinitrophenylhydrazones.

2,4- DNP	E-isomer							Z-isomer						
	mp, ^{o}C	UV, nm		NMR^{a}, δ				mp, ^{o}C	UV, nm		NMR^{a}, δ			
		$\lambda_{max}^{CHCl_3}$	$\varepsilon \times 10^4$	2-CH_3	3 or 5-CH_3	4-CH_3	NH		$\lambda_{max}^{CHCl_3}$	$\varepsilon \times 10^4$	2-CH_3	3 or 5-CH_3	4-CH_3	NH
a	207	382	2.69	2.46			11.51	193	387.5	2.86	2.17			10.90
b	216	387.5	2.78	2.43		2.33	11.42	218	390	2.94	2.10		2.46	11.03
c	199	386	2.77	2.38	2.29		11.42	164^{c}	389	2.94	2.10	2.38		10.88
d	235	394	2.99		2.31	2.31	11.17	205^{c}	392	2.94		2.37	2.41	11.31
e	235^{b}	394	2.93			2.41	11.08	222	391	2.86			2.50	11.18
f	225	399	2.95			3.85	11.06	196	392	2.88			3.91	11.23
g	235	439	3.00			3.04	11.11	220	399	2.95			3.08	11.42

[a] The NMR spectra were determined in $CDCl_3$ solution using a Varian A-60 spectrometer.

[b] See ref. 2a.

[c] A mixture which is composed of E- and Z-isomers with a ratio of 2:1. The ratio was determined by NMR.

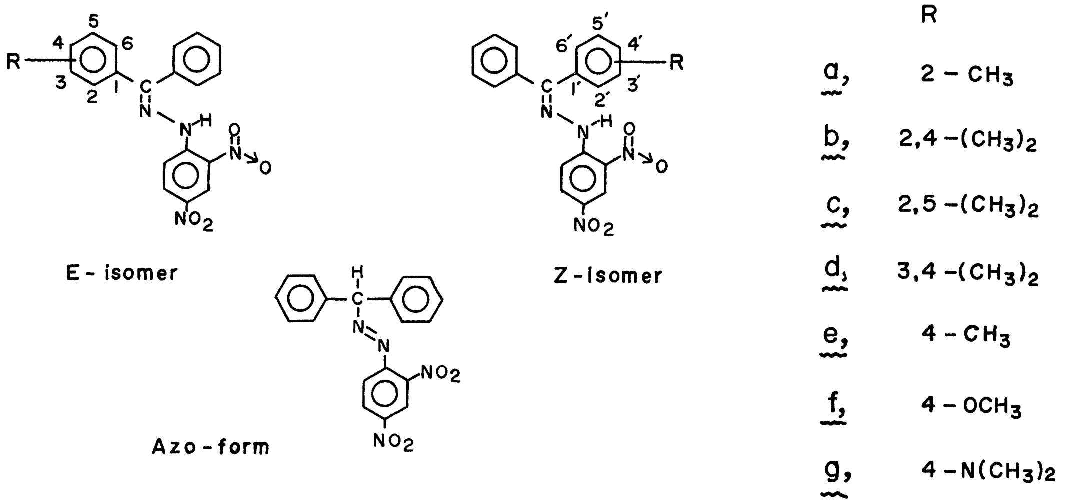

Fig. 1. 2,4-DNP's of benzophenones and azo-form.

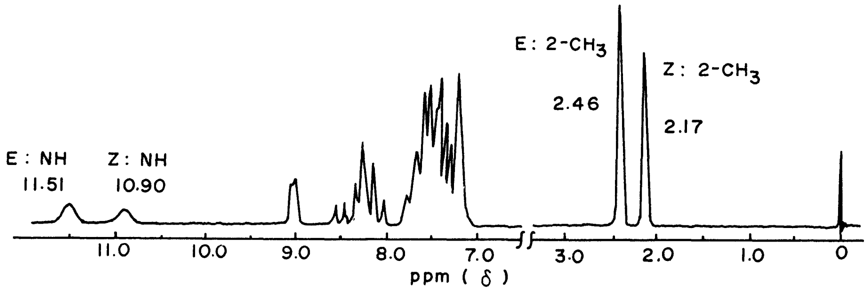

Fig. 2. The NMR spectrum of a mixture of 2-methylbenzophenone 2,4-DNP's.

three possibilities for conjugation, namely, a phenyl-phenyl interaction and two phenyl-2,4-DNP conjugations. The latter conjugation is well known to manifest itself in the 380 nm region.[4] Steric interference occurs not only between phenyl groups but also between the 2,4-dinitrophenyl and the cis-phenyl group. For this reason, it is considered that the cis-phenyl group is forced out of coplanarity with the C=N bond to a large extent, and the trans-phenyl group attains a greater degree of coplanarity. Actually, it has been recently shown by an X-ray study on the E-isomer of 4-bromobenzophenone 2,4-DNP that the unsubstituted phenyl group is located almost vertically to the C=N bond, and the bromophenyl, C=N, and dinitrophenylamino groups are all on the same plane.[5] The relationship of such stereochemical situations with electronic spectra should provide reliable structural information for the E- and Z-isomers, as employed in the cases of 1,1-diarylpropenes,[6] and triarylimines.[7] Based on the consideration concerning the conjugation effect by 4-substituents, spectra with their maxima at longer wavelengths should be assigned to the E-isomer in each set of 2,4-DNP's, d, e, f and g. This method of assignment is not applicable itself to the 2,4-DNP's with a 2-methyl group such as a, b and c, because the conjugation seems to be disturbed by steric hindrance exerted by the methyl group. In these 2,4-DNP's, the spectra with their maxima at shorter wavelengths were allotted to the E-isomers. The same kind of phenomena has been reported in the spectra of cis- and trans-1-(ortho-tolyl)-1-phenylpropene.$^{6)}$ The assignments to a, b and c on the basis of their electronic spectra are in agreement with those obtained from the NMR data as follows.

The benzene ring with 2-methyl group in the Z-isomer of 2-methylbenzophenone 2,4-DNP is more twisted than the unsubstituted phenyl group in the E-isomer. The NH proton might, therefore, be regarded to be more shielded in the Z-isomer than in the E-isomer due to the ring current of the phenyl group which is located at the same side of the dinitrophenyl group, as reported in some methyl substituted N-methylbenzophenoneimines.$^{8)}$ The NH proton signal at δ 11.51 is thus assigned to the E-isomer, and that at 10.90 to the Z-isomer. On the other hand, the 2'-methyl proton of the Z-isomer in 2,4-DNP's, a, b and c resonates, as listed in Table 1, at a considerably higher magnetic field than the 2-methyl of the corresponding E-isomer. This may be explained by the fact that such a 2'-methyl group is situated above the plane of the trigonal carbon atom of the C=N bond.

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